The Reactions of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride

A Thesis Presented to the University of Glasgow
for the Degree of
Doctor of Philosophy

by

David George McBeth

Dedicated to my Mother and Father

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ABSTRACT

Aluminium (III) chloride catalysed dehydrochlorination of 1,1,1-trichloroethane is industrially important, as it is considered to be one of the first steps in the degradation of 1,1,1-trichloroethane based solvents used in the large scale vapour degreasing of aluminium. The degradation and fouling observed has been attributed to aluminium (III) chloride catalysed dehydrochlorination of the solvent, followed by aluminium (III) chloride catalysed oligomerisation of the dehydrochlorinated product. There is evidence that heterogeneous phenomena are of importance in these reactions, and in this work the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride were studied.

The vapour phase in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride was studied using Fourier Transform infra-red spectroscopy to determine the stoichiometries and time dependences of the reactions. The latter system was also studied using pressure measurements. The reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride does not lead solely to the production of gaseous 1,1-dichloroethene and gaseous hydrogen chloride in a 1:1 molar ratio. Although dehydrochlorination of 1,1,1-trichloroethane appears to be the only important process in the early stages of reaction, the 1,1-dichloroethene produced reacts with the solid, and the main product of the overall reaction is a mixture of saturated and unsaturated involatile chlorohydrocarbons. Small quantities of gaseous carbon tetrachloride are also produced in the reaction. Gaseous 1,1-dichloroethene reacts with solid aluminium (III) chloride in the absence of any other species

to yield a mixture of involatile organic products, gaseous hydrogen chloride and small quantities of gaseous 1,1,1-trichloroethane and carbon tetrachloride. The gaseous 1,1-dichloroethene, and any 1,1,1-trichloroethane produced from it can be completely consumed in this reaction, and the amount of hydrogen chloride produced indicates that the involatile material produced is highly unsaturated. During the course of both reactions, the solid is progressively coated with a strongly purple coloured tar, which continues to evolve hydrogen chloride if the volatile material is removed. Autocatalytic effects are observed in both systems, and the time dependences of the reactions are consistent with a bimolecular surface reaction as the rate determining step in each case.

The interaction of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride with solid aluminium (III) chloride was studied using a direct monitoring Geiger-Müller radiochemical counting technique in the absence of a third component, and in the presence of water, 1,1,1-trichloroethane and 1,1-dichloroethene. Prior exposure of the solid to water vapour promotes adsorption of [^{36}Cl]-HCl on the solid and [^{36}Cl]-chlorine exchange between the species. When a mixture of gaseous [^{36}Cl]-HCl and 1,1,1-trichloroethane or 1,1-dichloroethene is exposed to solid aluminium (III) chloride, complete [^{36}Cl]-chlorine exchange occurs between the [^{36}Cl]-HCl and the chlorohydrocarbon. This observation is interpreted in terms of the involvement of [^{36}Cl]-HCl in the hydrochlorination/dehydrochlorination process.

The interactions of gaseous [^{14}C]-carbon-labelled carbon tetrachloride and [^{36}Cl]-chlorine-labelled carbon tetrachloride with solid aluminium (III) chloride were studied using the direct monitoring Geiger-Müller radiochemical counting technique. The results

are consistent with the occurrence of a small amount of adsorption of carbon tetrachloride on the solid and limited [^{36}Cl]-chlorine exchange between [^{36}Cl]-CCl_4 and aluminium (III) chloride. Prior exposure of the solid to water does not promote adsorption or [^{36}Cl]-chlorine exchange. Exposure of a mixture of gaseous [^{36}Cl]-CCl_4 and 1,1,1-trichloroethane or 1,1-dichloroethene to solid aluminium (III) chloride leads to the incorporation of the [^{36}Cl]-chlorine in the solid. In the latter system, [^{36}Cl]-chlorine activity is detected in the [^{36}Cl]-HCl recovered, indicating that chlorine atoms from carbon tetrachloride become involved in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride. This result is considered consistent with the occurrence of reversible aluminium (III) chloride catalysed alkylation of 1,1-dichloroethene derived oligomers and polymers by carbon tetrachloride.

The interaction of gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane with solid aluminium (III) chloride was studied using the direct monitoring Geiger-Müller radiochemical counting technique. Adsorption of [^{36}Cl]-CH_3CCl_3 on the solid occurs, and substantial [^{36}Cl]-chlorine activity is detected in [^{36}Cl]-HCl recovered from the reaction mixture; this indicates that intramolecular dehydrochlorination of 1,1,1-trichloroethane is an important process. Prior exposure of the solid to water vapour can completely inhibit the reaction, and no adsorption of [^{36}Cl]-CH_3CCl_3 on the solid is detected under these conditions. Exposure of a mixture of gaseous [^{36}Cl]-CH_3CCl_3 and carbon tetrachloride to solid aluminium (III) chloride leads to reaction, but to a reduced surface count rate compared to experiments in which carbon tetrachloride is not present; this is consistent with the occurrence of reversible aluminium (III) chloride

catalysed alkylation of 1,1-dichloroethene derived oligomers and polymers. There is no evidence for [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-CH_3CCl_3 and hydrogen chloride at room temperature.

Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFTS) and Surface Ionisation Mass Spectrometry (SIMS) were used to study the surface of solid aluminium (III) chloride. Strong evidence was obtained for hydration and hydrolysis of the samples studied. Spectra of the surfaces of solid aluminium (III) chloride samples which had been exposed to gaseous 1,1,1-trichloroethane contained peaks attributed to saturated long chain chlorohydrocarbons. The diffuse reflectance infra-red spectrum of a sample which had been exposed to gaseous 1,1-dichloroethene contained peaks attributed to saturated and unsaturated chlorohydrocarbons, and was very similar to the infra-red spectrum of a dehydrochlorinated poly-1,1-dichloroethene film. An infra-red spectrum was also obtained of the involatile organic material recovered from the "bleeding" reaction of liquid 1,1,1-trichloroethane with aluminium metal. The production of involatile materials in this system has been attributed to aluminium (III) chloride catalysed oligomerisation and polymerisation of 1,1-dichloroethene, and the spectrum obtained was very similar to the diffuse reflectance spectrum of the surface of aluminium (III) chloride which had been exposed to gaseous 1,1-dichloroethene.

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CHAPTER 1

CHAPTER 1

INTRODUCTION

Metal chloride catalysed hydrochlorinations and dehydrochlorinations are industrially important. Iron (III) chloride is, for example, used commercially to catalyse hydrochlorination of vinyl chloride (Equation 1.I), the first step in the industrial preparation

$$CHCl = CH_2 + HCl \xrightleftharpoons{FeCl_3} CHCl_2CH_3 \qquad \text{Equation 1.I}$$

of 1,1,1-trichloroethane. The main application of 1,1,1-trichloroethane is in the large scale vapour degreasing of metals, for example, aluminium in the engineering industry, and in this application inhibitors must be added to the solvent to prevent unwanted degradation and corrosion.

The degradation has been attributed to aluminium (III) chloride catalysed dehydrochlorination of the solvent, followed by aluminium (III) chloride catalysed oligomerisation of the dehydrochlorinated product.[1] However, the catalytic action of aluminium (III) chloride is not well understood, either in this application, or in the many other reactions which it catalyses. One of the reasons for this has been the inability to study the reactions or interactions of aluminium (III) chloride with organic compounds, such as chlorohydrocarbons, in the absence of trace quantities of water or hydrogen chloride, both of which are frequently reported to modify its catalytic properties. Another reason is that the solubility of aluminium (III) chloride in non-complexing solvents is low and this often leads to complicated multi-phase reaction systems.

The work which follows was undertaken to elucidate the role of aluminium (III) chloride as a catalyst with particular relevance to

its reaction with 1,1,1-trichloroethane.

1.1 Structure and Physical Properties of Aluminium (III) Chloride

Aluminium (III) chloride exists as a white solid at all temperatures below 183°C. At atmospheric pressure the solid sublimes at 183°C, and its melting point is 192.6°C at pressures > 1700 mm Hg. X-ray diffraction studies on a single crystal have shown that solid aluminium (III) chloride exists as an ionic layer lattice with each Al^{3+} ion surrounded by an octahedral arrangement of Cl^- ions[2] (Figures 1.I[3] and 1.II[4]). Recent results of Raman[5] and infra-red spectroscopic studies[4] on the solid are in agreement with this structure. The lattice can be considered a close packed array of Cl^- ions with Al^{3+} ions occupying $\frac{2}{3}$ of the octahedral holes. As can be seen from Figure 1.II, the solid surface is characterised by chloride ion vacancies.

Solid aluminium (III) bromide (and aluminium (III) iodide) exist as covalent dimers with the halogen bridged structure shown in Figure 1.III.[3] X-ray diffraction studies on a single crystal of aluminium (III) bromide indicated a molecular lattice of Al_2Br_6 units.[6] A ^{79}Br n.q.r. study on a single crystal of aluminium (III) bromide indicated that two types of terminal Al-Br bonds existed in addition to the bridging bonds.[7] Therefore, although the crystal is a molecular lattice of Al_2Br_6 units, there are apparently molecular forces greater than the normal dispersion forces acting between neighbouring molecules.

The specific conductivity of solid aluminium (III) chloride is zero at room temperature and increases very steeply just below the melting point to about $5 \times 10^6\ \Omega^{-1}cm^{-1}$. On melting, the conductivity falls almost to zero and rises slowly over the next 50° to about

FIGURE 1.I. Schematic Representation of the Solid Aluminium (III) Chloride Lattice

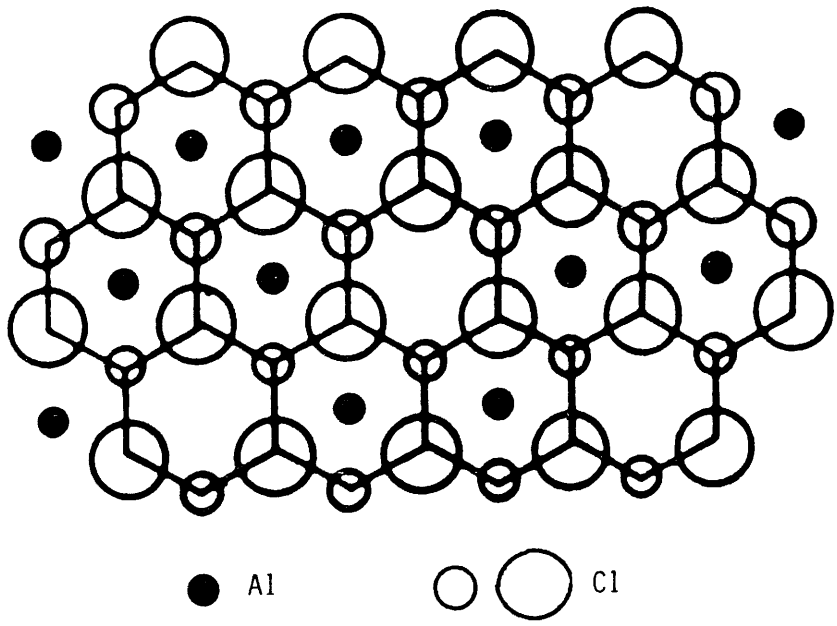


FIGURE 1.II. Diagram of the Solid Aluminium (III) Chloride Unit Cell

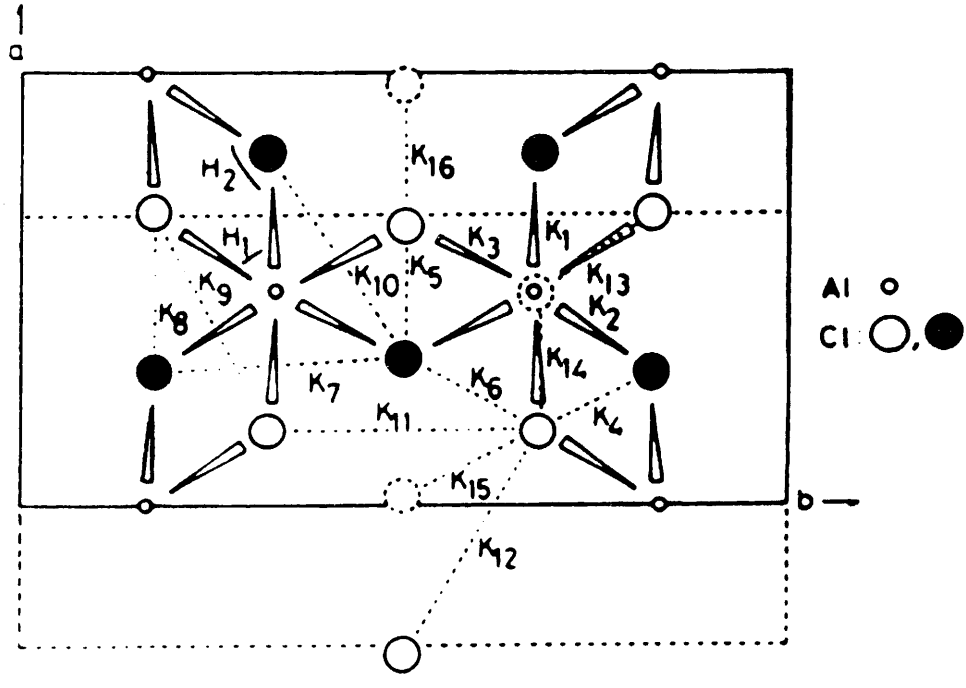


FIGURE 1.III. Chlorine Bridged Al_2Cl_6

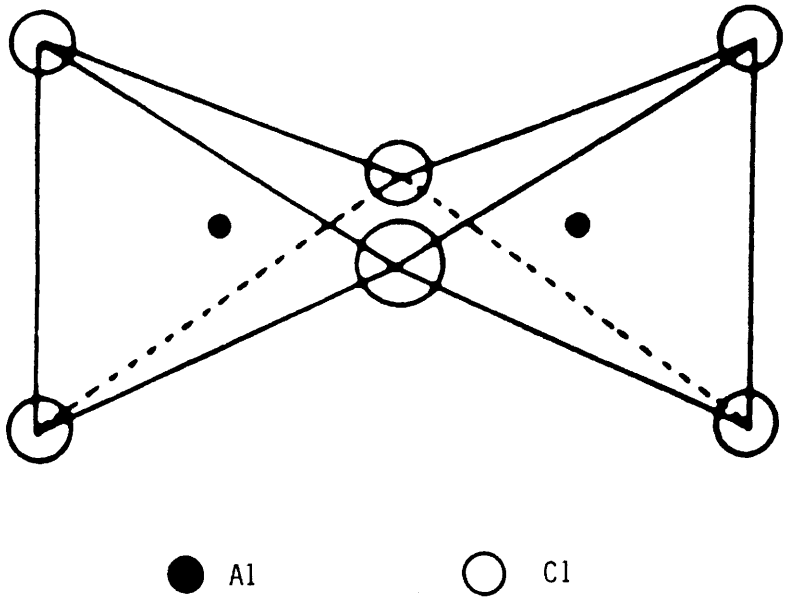
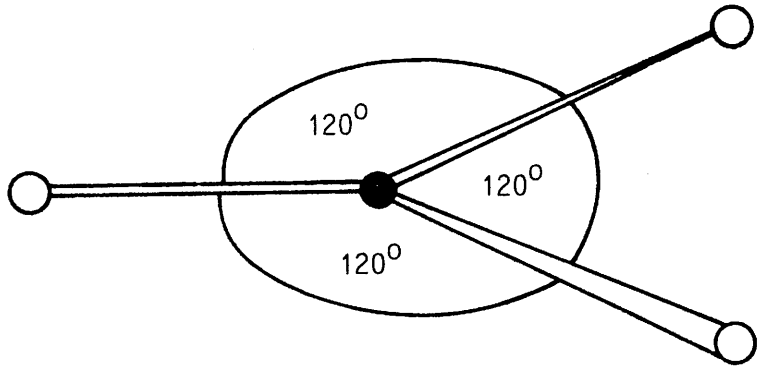


FIGURE 1.IV. Monomeric $AlCl_3$



$1 \times 10^6\ \Omega^{-1}cm^{-1}$.[8] No such effect is observed for aluminium (III) bromide and iodide which show no conductivity in the solid state and similar specific conductivity to aluminium (III) chloride when molten. The difference in behaviour has been attributed to a change from ionic to covalent properties of aluminium (III) chloride. Results from X-ray diffraction[9] and Raman[10,11] studies on molten aluminium (III) chloride are in agreement. The formula Al_2Cl_6 and the structure shown in Figure 1.III were suggested. Unlike aluminium (III) chloride, the bromide and iodide display the same Raman spectrum in the molten state as in the crystalline state,[10,12,13] both being indicative of Al_2X_6 structures.

In the gas phase the structures adopted by the aluminium (III) halides are temperature dependent. Molecular weight determinations from vapour pressure measurements on aluminium (III) halides (chloride, bromide, iodide) in the temperature range 350-600°C,[14] and electron diffraction studies in the range 225-440°C[15] indicated that the only species present up to 440°C was Al_2X_6 (X = Cl, Br, I) and that no higher polymer than the dimer was present up to 600°C. The Raman[16,17] and infra-red[18] spectra of gaseous aluminium (III) halides (chloride, bromide, iodide) in the range 225-440°C are in agreement with the Al_2X_6 formula and with D_{2h} symmetry (Figure 1.III). High resolution Raman and infra-red spectra of aluminium (III) chloride isolated in a solid argon matrix from temperatures within the range 225-440°C[19] also indicated the presence of the dimer and agree almost exactly with the frequencies reported for gaseous Al_2Cl_6.

Electron diffraction studies on aluminium (III) chloride at temperatures >800°C indicated the presence of monomeric $AlCl_3$ only.[20] Raman[16] and infra-red[18] spectra of gaseous aluminium (III) halides (chloride, bromide, iodide) in this range are in agreement with this

formula. High resolution Raman and infra-red spectra of aluminium (III) chloride isolated in a solid argon matrix from temperatures >800°C[19] indicated strongly that the species isolated was of D_{3h} symmetry (Figure 1.IV). Aluminium (III) fluoride was also reported, from electron diffraction studies, to adopt a monomeric structure at very high temperatures.[21]

Raman spectra of gaseous aluminium (III) halides (chloride, bromide, iodide) have shown that between 440-800°C the gas phase consists of an equilibrium mixture of dimer and monomer.[19]

1.2 Chemistry of Aluminium (III) Chloride

1.2.1 Lewis Acidity

The reactions of aluminium (III) chloride are predominantly due to the Lewis acidity of the species; that is its ability to accept electrons from other species. This can take the form of complexation or ionisation depending on the type of Lewis base (electron donor) involved.

For example, aluminium (III) chloride is often used in the preparation of mixed melts with alkali metal halides such as NaCl. In such media $AlCl_3$ accepts the Cl^- ion from NaCl to form $AlCl_4^-$ and $Al_2Cl_7^-$ anions.[11] Alkali chloroaluminate melts can be used to stabilise species with low oxidation states, and unusual cations. For example, aromatic amine radical cations were produced in a 50-50 mole % $AlCl_3$-NaCl melt at 175°C and were observed to remain as monomers in solution.[22] Such cations are known to dimerise rapidly in other solvents such as acetonitrile.

1.2.2 Hydration and Hydrolysis

Aluminium (III) chloride was reported to be very hygroscopic as early as 1827.[23] Exposure of the solid to air resulted in "rapid deliquescence, ultimately forming a clear liquid", and dissolution of the solid in water led to a "hissing noise and the development of much heat." Olah[24] suggested that the only suitable method of obtaining anhydrous aluminium halides was to react aluminium (99.99% pure) in a combustion tube attached to a vacuum system with the pure, dry halogen.[25] However, even this technique would be unlikely to produce anhydrous material as the release of small amounts of moisture from Pyrex glass which had been thoroughly flamed out has been reported.[26]

In his review of 1973[24] Olah included the report[27] that if the surface of aluminium (III) chloride was allowed to "glass" with a coating of aluminium chloride hexahydrate ($AlCl_3.6H_2O$) and the compound was then sealed, the water of the hydrate slowly diffused into the remaining anhydrous material and reacted by releasing hydrogen chloride, the build up of which could cause a pressure explosion. This interpretation had been questioned twenty years earlier by Fairbrother,[28] who stated that it was not obvious why a trace of moisture should immediately, without hydrolysis, form a hexahydrate which subsequently dissociates and the water molecules of which diffuse into the solid and lead to hydrolysis.

Fairbrother[28] studied the hydration and hydrolysis of anhydrous Al_2Br_6 in the vapour, solid and solution phases, with amounts of water ranging from trace up to that required for $AlBr_3.6H_2O$, using vapour pressure measurements. He postulated that the primary reaction was a hydration which may or may not be followed by hydrolysis depending on the temperature of reaction. The hydration was considered as a

three-step process with the successive formation of (a) tetrahedrally co-ordinate $AlBr_3.H_2O$, (b) octahedral $AlBr_3.3H_2O$ with Al-Br bonds still largely covalent and (c) progressive displacement of bromine atoms from the hydration sphere to give $[Al(OH_2)_6]^{3+}$ and $3Br^-$. Hydrolysis, yielding hydrogen bromide, was reported to be a slow process at room temperature.

Although no systematic study has been carried out, observations on the chloride suggest that similar processes occur. The hexaquo ion $[Al(OH_2)_6]^{3+}$ has been identified in solutions prepared by hydrolysis of aluminium (III) chloride,[30] and a study of concentrated solutions of AlX_3 (X = Br, Cl, I) has revealed that there is some replacement of one or more molecules in the co-ordination sphere by X to give e.g. $[Al(H_2O)_5X]^{2+}$ and $2X^-$.[31]

Waeschenbach and Lutz reported that crystals of material assumed to be $AlCl_3.6H_2O$ had been prepared by crystallisation from aqueous solutions containing excess hydrochloric acid and studied using polarised infra-red reflection spectroscopy.[32] The spectra suggested that a lattice structure with Al^{3+} surrounded by six water molecules existed, and that there was comparatively strong hydrogen bonding between individual water molecules and adjacent Cl^- ions. $AlCl_3.6H_2O$ was reported to undergo thermal decomposition to yield water, hydrogen chloride and γ-alumina.[33] Since hydration of aluminium (III) chloride is exothermic, it is possible that further decomposition could occur.

1.2.3 Dissociation of Aluminium (III) Chloride in Alkyl Halides

In solvents of low dielectric constant and weak Lewis basicity, aluminium (III) chloride is believed to dissolve as molecular Al_2Cl_6

and subsequently to dissociate into $AlCl_3$ which can be more strongly solvated. Conductimetric studies on $AlCl_3/CH_2Cl_2$[34] and $AlBr_3/CH_3Br$[35] have shown that when AlX_3 was added to the alkyl halide, two independent processes were observed. The more rapid process was attributed to the reaction of ion generating impurities, whereas the slower process appeared to be due to reaction in which n molecules of AlX_3 reacted to generate n ions. The solubilities of $AlBr_3$ in CH_3Br and $AlCl_3$ in CH_2Cl_2 agreed with solubilities estimated on a thermodynamic basis assuming that monomeric species were present. The equilibrium (Equation 1.II) was postulated.

$$Al_2X_{6(solution)} \rightleftharpoons 2AlX_{3(solution)} \rightleftharpoons [AlX_2^+][AlX_4^-] \quad \text{Equation 1.II}$$

Dissolution of aluminium (III) chloride in more basic and strongly solvating solvents is believed to lead to dissociation, ionisation and halide displacement leading to the formation of solvent-solute co-ordination complexes. For example, dissolution of aluminium (III) chloride in acetonitrile leads to the formation of $[Al(CH_3CN)_6]^{3+}$ and $3AlCl_4^-$ (Equation 1.III).[36]

$$4AlCl_3 + 6CH_3CN \longrightarrow [Al(CH_3CN)_6]^{3+} + 3AlCl_4^- \quad \text{Equation 1.III}$$

1.2.4 The Hydrogen Chloride/Aluminium (III) Chloride System

Olah[24] believed that $HCl/AlCl_3$ and $HBr/AlBr_3$ were superacids of strength approximately 10^2-10^5 times greater than concentrated H_2SO_4. In 1982, Farcasiu showed that in the protonation of benzene $HBr/AlBr_3$ was effectively a much stronger acid than HF/TaF_5[37] and in a review of the protonation of simple aromatics in superacid media he attempted to eliminate the widespread belief that HX/AlX_3 was in some

way a "weak" superacid.[38]

Nonetheless, there is no evidence for the combination of HCl and $AlCl_3$ or HBr and $AlBr_3$ under most conditions. Isotopic exchange studies using [^{36}Cl]-HCl and $AlCl_3$ showed no exchange at room temperature over 12 hours,[39] although complete exchange could be observed after 76 hours at 215^{o}C where both reactants were in the gas phase. A careful examination of the HCl/$AlCl_3$ system under a variety of conditions, including temperatures as low as -120^{o}C, using vapour pressure measurements yielded no evidence for combination, even in the presence of 2,2-dimethylbutane.[40] There was no evidence for combination of HCl and $AlCl_3$ in the presence of water, although it was observed that more than one mole of hydrogen chloride was generated for every mole of water introduced. This report was ambiguous because it is possible for hydrogen chloride to be formed but to undergo rapid subsequent reaction and not contribute to the overall pressure in the system.

1.2.5 Friedel-Crafts Reactions

A Friedel-Crafts reaction is the broad classification for any substitution, isomerisation, elimination, cracking, polymerisation or addition reaction catalysed by a Lewis acid type acidic halide or a proton acid.[24] Hence a huge body of published work is encompassed by the term "Friedel-Crafts". One feature which links much of this work is the use of aluminium (III) halides (particularly the chloride and bromide) as catalysts. Aluminium (III) chloride was the catalyst in the original reactions studied by Friedel and Crafts,[41,42] and, in the century since their discovery, no other inorganic compound has found such widespread application in effecting novel and useful trans-

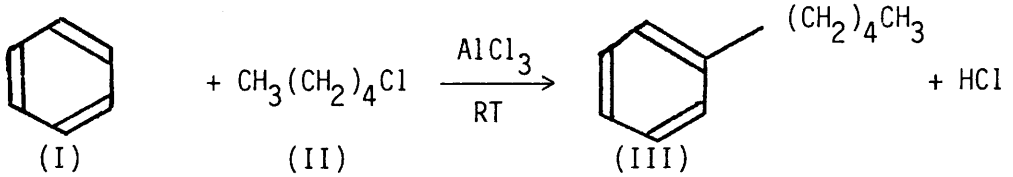
formations of organic compounds.

The scope of aluminium (III) halide catalysed Friedel-Crafts reactions has been extensively reviewed.[24] Published material on Friedel-Crafts reactions often consists of product analyses with little serious mechanistic investigation, and the aluminium (III) halide is often referred to as "anhydrous" when the reaction conditions described would lead to some hydration and/or hydrolysis.

Several examples have been chosen from the literature either to illustrate the continuing discovery and use of aluminium (III) halide catalysed Friedel-Crafts reactions or because of relevance to the work which follows. These examples have been split into three broad categories, although all Friedel-Crafts reactions involve side reactions which cover all three categories.

1.2.5.1 Alkylations, Allylations and Acylations

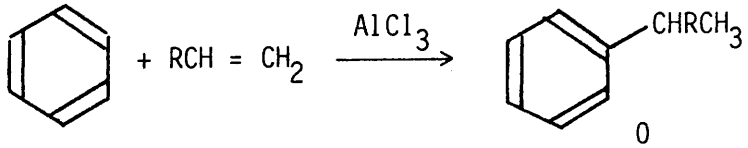
The early work of Friedel and Crafts concerned the aluminium (III) chloride catalysed alkylation of aromatic species;[41,42] for example, the alkylation of benzene (I) by 1-chloro-n-pentane (II) to give 1-phenyl-n-pentane (III) (Scheme 1.I). A mixture of unidentified high boiling organic products was also reported. Five weeks after



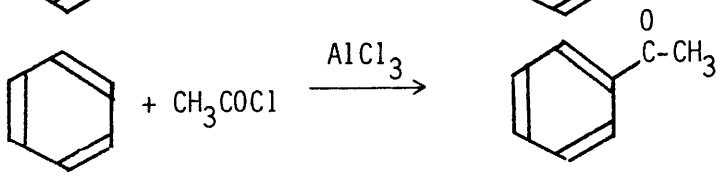
Scheme 1.I

the original publication, Friedel and Crafts reported that iron (III) chloride or zinc (II) chloride could be used as alternative catalysts and this observation has often been made subsequently.

Alkylations of aromatics by olefins (Scheme 1.II) and acylation of aromatics by acyl chlorides (Scheme 1.III) can be effected.

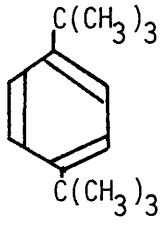


Scheme 1.II

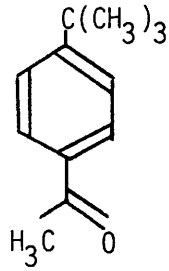


Scheme 1.III

Atoms other than hydrogen can be substituted; for example, acylation of p-di-t-butylbenzene (Formula 1.I) gave p-t-butylacetophenone (Formula 1.II) in 72% yield.[43] In almost every system studied, side



Formula 1.I



Formula 1.II

reactions such as isomerisation and polymerisation were reported.

Alkylation of olefins by alkylhalides[44] (Equation 1.IV) and alkylation of alkanes by olefins (Equation 1.V) are examples of the Friedel-Crafts alkylation of aliphatic species. In the former example

$$CHCl = CHCl + CHCl_3 \xrightarrow[50\text{-}55^{o}C]{AlCl_3} Cl_2HCCHClCHCl_2 \qquad \text{Equation 1.IV}$$

$$(CH_3)_2C = CH_2 + (CH_3)_3CH \xrightarrow{AlCl_3} (CH_3)_2CHCH_2C(CH_3)_3 \qquad \text{Equation 1.V}$$

the reaction did not go to completion and the reaction could be halted by the addition of an unidentified high boiling by-product from an identical reaction. This was attributed to removal or complexation of

aluminium (III) chloride with the by-product. In the latter category, all alkanes except methane and ethane can be alkylated.[45] Side reactions always occur and the more complex the reactants, the greater the variety of side reactions which occur. For example, the alkylation of isobutane by ethene is accompanied by at least seven types of side reaction,[24,45,46] namely (i) isomerisation of reactants and/or products; (ii) dealkylation of product alkane to give alkanes and alkenes with different carbon numbers which can react further by (i), (iii) and (iv); (iii) polyalkylation (reaction of the product alkane with the alkene); (iv) polymerisation of the alkene; (v) complexation of highly unsaturated hydrocarbons formed in (iv) with aluminium (III) chloride; (vi) hydrochlorination of the alkene and (vii) disproportionation.

Most reports of Friedel-Crafts alkylations are concerned with product identification, but in many instances mechanisms are proposed which, although rarely substantiated, have predictive value. Simple mechanisms postulated for most of the above reactions depend upon the ability of both alkyl and acyl halides (as well as reactants containing other heteroatoms such as O,N,S) to co-ordinate with aluminium (III) chloride by utilising their non-bonded electron pairs, forming Lewis acid-base complexes. Co-ordination could lead to ionisation and consequently the formation of a carbocation which could effect alkylation as shown in Scheme 1.IV for alkylation of an aromatic species.

$$R\text{-}Cl + AlCl_3 \rightleftharpoons R^{\delta+} - Cl \longrightarrow \overset{\delta-}{AlCl_3} \rightleftharpoons [R^+][AlCl_4^-]$$

$$R^+ + ArH \longrightarrow [ArRH^+] \longrightarrow ArR + H^+$$

$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Scheme 1.IV

Aluminium (III) chloride used in the above examples was always handled in air at some stage, hence water and hydrogen chloride would be present. For alkylation reactions performed with hydrocarbons the only route to carbocation formation is effective protonation, and Olah suggested that the hydrogen chloride present could take part, proposing Equations 1.VI, 1.VII and 1.VIII. However, there is no evidence for

$$RCH = CH_2 + H^+AlCl_4^- \rightleftharpoons R\overset{+}{C}HCH_3\ AlCl_4^- \qquad \text{Equation 1.VI}$$

$$RC \equiv CH + H^+AlCl_4^- \rightleftharpoons R\overset{+}{C}H = CH_2AlCl_4^- \qquad \text{Equation 1.VII}$$

$$R_2CH\text{-}CH_3 + H^+AlCl_4^- \rightleftharpoons R_2\overset{+}{C}H\,AlCl_4^- + CH_4 \qquad \text{Equation 1.VIII}$$

$H^+AlCl_4^-$ as a stable species (see 1.2.4) in the absence of a third species, or even in the presence of an alkane. For the alkenes and alkynes, aluminium (III) chloride catalysed hydrochlorination could yield alkyl and allyl chlorides (Equations 1.IX, 1.X) which could react

$$RCH = CH_2 + HCl + AlCl_3 \rightleftharpoons RCHClCH_3 + AlCl_3 \qquad \text{Equation 1.IX}$$

$$RC \equiv CH + HCl + AlCl_3 \rightleftharpoons RCCl = CH_2 + AlCl_3 \qquad \text{Equation 1.X}$$

as in Scheme 1.IV, but there is no direct evidence for this process.

The detection of carbocations in these systems is rare, though not unknown.[47] Halonium ions of the type $[R_2X^+]$ have been invoked in mechanistic interpretations of Friedel-Crafts reactions,[48] but although such ions have been identified in highly concentrated solutions of aluminium (III) halides in alkyl halides at low temperatures[24] there is no evidence for their existence under the conditions used in most Friedel-Crafts alkylations.

In a radiotracer study, Wallace and Willard showed that rapid

exchange of chloride occurred between solid aluminium (III) chloride and pure dry liquid carbon tetrachloride.[49] Gaseous carbon tetrachloride underwent exchange with solid anhydrous aluminium (III) chloride as did other alkyl halides,[50] but no exchange was observed with gaseous aluminium (III) chloride.[49] They suggested that the exchange did not take place via the formation of CCl_3^+ and $AlCl_4^-$, as may have been expected in view of the mechanistic interpretation of Friedel-Crafts reactions, but that an aluminium (III) chloride surface was required for exchange to take place. A Friedel-Crafts reaction occurred between gaseous carbon tetrachloride and gaseous benzene in the presence of solid aluminium (III) chloride[50] and the authors suggested that a surface mechanism might be general in Friedel-Crafts reactions where a mixture of dissolved and solid aluminium (III) chloride is often present.

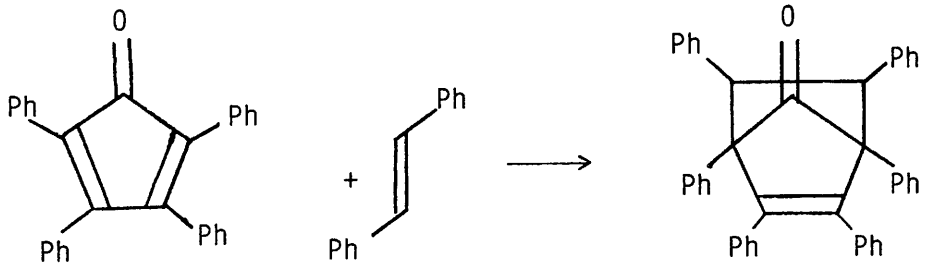
Another example of the importance of heterogeneous phenomena in aluminium (III) chloride catalysed reactions is the observed isomerisation and halogen replacement which occur when liquid 1,1,2-trichlorotrifluoroethane is refluxed with 15 mole % solid aluminium (III) chloride[51] (Equation 1.XI). Reaction rates decreased and induction times increased if the amount of aluminium (III) chloride present was less than a particular value which suggested that excess (solid) aluminium (III) chloride was required. Treatment of CCl_2FCClF_2 with $[^{36}Cl]$-$AlCl_3$ followed by product fractionation and counting indicated that the isomerisation was intramolecular since no chloride exchange was observed with the catalyst.

$$CCl_2FCClF_2 \xrightarrow{AlCl_3} \underset{50\%}{CCl_3CF_3} + \underset{40\%}{CCl_3CClF_2} + \underset{5\%}{CCl_3CCl_2F} + \underset{5\%}{\text{recov.}CCl_2FCClF_2}$$

Equation 1.XI

The continuing importance of aluminium (III) chloride in

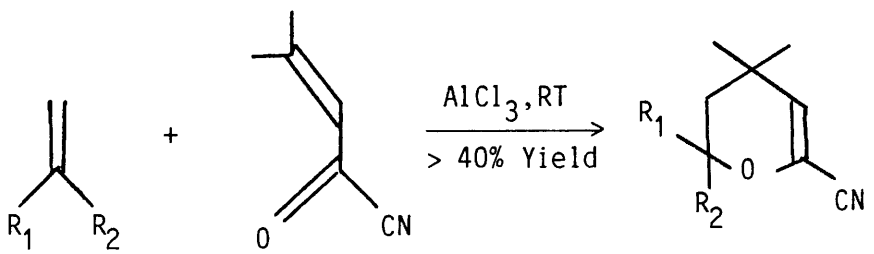
Friedel-Crafts chemistry is illustrated by the example which follows. Aluminium (III) chloride is known to catalyse conventional Diels-Alder cyclisation reactions and recent studies on the Diels-Alder reaction of tetraphenylcyclopentadienone (IV) with trans-stilbene (V) have shown that the stable complex of (IV) with $AlCl_3$ formed by σ-donation by the oxygen atom of (IV) is a precursor to (VI)[52] (Scheme 1.V)



(IV) (V) (VI)

Scheme 1.V

However, prior to 1982, intermolecular cycloadditions of simple alkenes to α,β-unsaturated carbonyl compounds to yield 3,4-dihydropyrans, which are classed as Diels-Alder reactions with inverse electron demand[53] were unknown. In 1982 it was reported that cyclisations of this type (Scheme 1.VI) could be carried out under the catalytic action of aluminium (III) chloride in benzene at room temperature over typically < 24 hours, occasionally with the normal Diels-Alder adduct as by product.[54] As is often the case, mechanistic detail was not discussed at length but the authors suggested that the

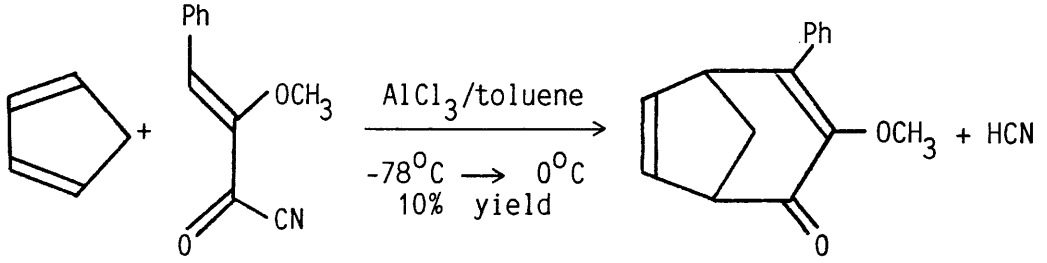


(VII)

Scheme 1.VI

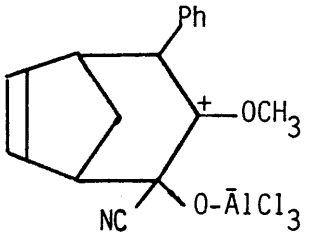
LUMO of the heterodiene (VII) was lowered by "Lewis acid complexation" presumably by analogy with the complexes formed in conventional Diels-Alder reactions.[52]

A further unexpected result was reported by the same authors in 1986.[54] In an attempt to carry out a reaction analogous to Scheme 1.VI using cyclopentadiene and (VIII), the 3,4-dihydropyran analogue was not formed but the novel bridged cycloadduct (IX) was produced (Scheme 1.VII). The precursor shown below (Formula 1.III) was postulated, but no direct evidence was presented for this species;



(VIII) (IX)

Scheme 1.VII



Formula 1.III

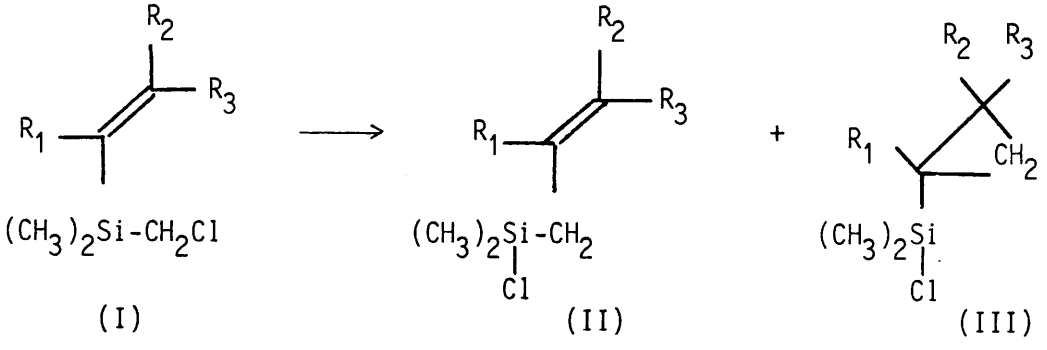
the proposal was made on the basis of the complexation expected between (VIII) and $AlCl_3$, and the expectation that the complex would behave in a manner analogous to that of an allyl cation.

These examples show the opening of a new area of the Friedel-Crafts reaction. They also unfortunately illustrate how novel product

formation tends to overshadow mechanistic investigation.

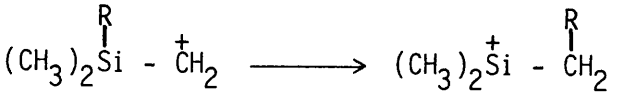
1.2.5.2 Isomerisations and Rearrangements

Friedel-Crafts catalysts such as aluminium (III) chloride find use in the field of organic synthesis because of their ability to bring about predictable isomerisation and rearrangement of various organic species. When a heteroatom is present in the organic species the rearrangement is often formulated in terms of σ-donor complexation of the heteroatom with aluminium (III) chloride, followed by ionisation and subsequent rearrangement of the cation formed. Recently, the aluminium (III) chloride catalysed rearrangement of alkenyl (chloromethyl) silanes (I) to allyl and cyclopropyl silanes (II, III) (Scheme 1.VIII) was reported,[55] and this was attributed to carbocation



Scheme 1.VIII

formation followed by a Wagner-Meerwein type rearrangement as shown in Scheme 1.IX.



Scheme 1.IX

However, alkanes also undergo aluminium (III) halide catalysed isomerisations and these reactions have been widely studied.

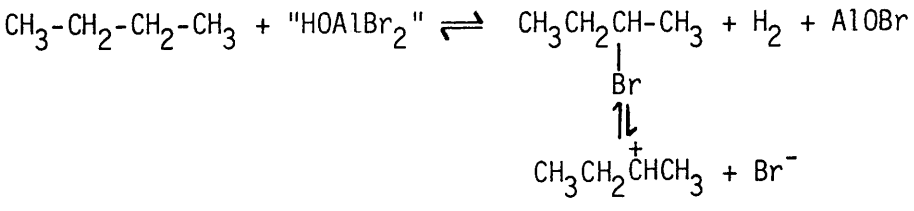
N-hexane and n-heptane react with aluminium (III) chloride to give the 2- and/or 3-methyl isomers.[56] For n-heptane, this isomerisation only accounted for 6% of the total reaction.[57] Dehydrogenation, condensation to form higher alkanes, hydrogenation and splitting of the chain to form lower alkanes accounted for the rest. The authors did not comment on the C-C bond fission.

However, n-pentane did not react with "anhydrous" aluminium (III) chloride or bromide.[58] Addition of small amounts of water, alkyl halides, hydrogen halides or hydrated aluminium (III) chloride to the mixture caused reaction to give isopentane, isomers of butane and unidentified high boiling substances soluble in the reaction mixture. The aluminium (III) chloride became coated with a brown tar consisting of a mixture of highly unsaturated halide containing compounds. Other authors have suggested that this mixture consists primarily of C_5 or C_6 rings.

When gaseous n-pentane carried by a stream of dry nitrogen was passed over "anhydrous" aluminium (III) chloride at 40-130^{o}C no reaction was observed. Addition of any of the initiators produced reaction. The proportion of butanes in the product mixture was larger than in the analogous solution reaction and hydrogen was also detected. Most of the higher boiling by-products remained on the aluminium (III) chloride and continued use led to the formation of a liquid. Under the same conditions aluminium (III) bromide produced reaction in the absence of initiators. No explanation was offered for this behaviour.

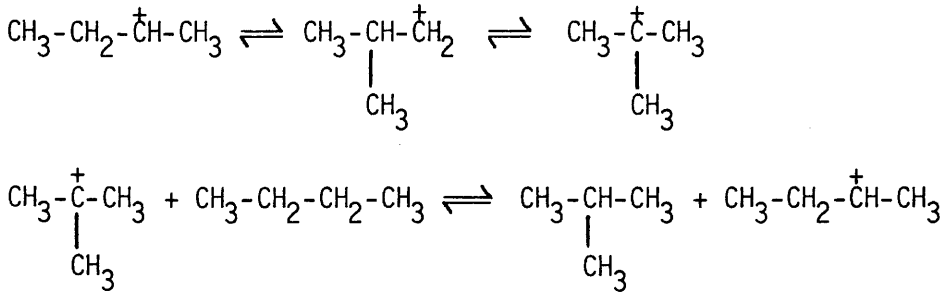
Rigorously purified n-butane did not isomerise in the presence

of $AlBr_3$/HBr at room temperature,[59,29,60] but addition of 0.03% by weight of n-butene or traces of oxygen, water or alkyl halide initiated the reaction. Hydrogen was a product. Further investigation showed that hydrated aluminium (III) chloride and bromide solids prepared by reacting water and aluminium (III) halides in ratios 1:1, 2:1 and 3:1 catalysed this isomerisation in the absence of a third component.[29] The authors acknowledged that such solids were mixtures. Deuteriation of the water used to prepare the 1:1 bromide solid produced the same % exchange between solid and butane irrespective of the amount of isomerisation, consistent with the involvement of carbon-bromine bonds in the isomerisation process as shown in Scheme 1.X. A chain



Scheme 1.X

mechanism of isomerisation via intra- and intermolecular methyl and hydrogen transfer was proposed (Scheme 1.XI) which could be considered general as all the initiators in the original study were considered "cation generating."



Scheme 1.XI

In a later study, Nenitzescu[61] proposed that the active species

present in the water treated aluminium (III) chloride solids was $H^+AlCl_3OH^-$. This is unrealistic, although a species of this stoichiometry is not impossible.

1.2.5.3 Olefin Polymerisation

Aluminium (III) chloride catalyses the polymerisation of most olefins to some degree and reactions of this type fall within the Friedel-Crafts classification. Alkyl aluminium compounds such as $(C_2H_5)_2AlCl$ find use in polymerisation reactions where they are added as complexing agents in the preparation of alternating co-polymers, and the cyclopolymerisation tendency of non-conjugated dienes was greatly increased when alkyl aluminium chlorides were present.[62] However, mechanistic investigation in this field has often been neglected.

As a result of the polymerisation of olefins in the presence of Friedel-Crafts catalysts, the solubility of aluminium (III) bromide in an olefin was of special interest. By careful purification of both reactants, Fairbrother prepared a solution of aluminium (III) bromide in pent-2-ene which was stable at room temperature.[26] The UV spectrum of this solution suggested solvent-solute complex formation and vapour pressure measurements were used as evidence to postulate a weak Al_2Br_6-pent-2-ene complex.[63] However, it is not clear how this complex should be formulated and it was not isolable.

Pure dry aluminium (III) chloride is inactive towards ethylene polymerisation[64] and styrene polymerisation.[65] The authors of the former paper did not recognise the ability of a third component to initiate reaction; in the latter, water was required to initiate polymerisation. In the 1950s, the presence of a third component or co-catalyst was believed to be necessary to initiate aluminium (III) chloride catalysed olefin polymerisation,[66] the function of the co-

catalyst being to act as a proton donor.

However, in the 1960s Cmelir et al. reported that a co-catalyst was not required in the system aluminium (III) chloride/isobutylene/methylene chloride.[67] Aluminium (III) bromide also polymerised isobutylene in heptane in the absence of a co-catalyst. Observations of this type became more general although the effort to exclude water from the systems varied.

The aluminium (III) chloride and bromide catalysed polymerisation of isobutylene in the corresponding isobutylhalide under high vacuum has been studied by Grattan and Plesch using conductimetric and radiotracer techniques.[35] They suggested that the initiating step was addition of AlX_2^+ to the double bond of the monomer with consequent formation of a carbocation. Experiments with other olefins and with saturated hydrocarbons appeared to confirm their conclusions.

Tertiary carbocation tetrachloroaluminates were stable electrolytes in air in very pure alkyl halide solvents. The very slow addition of isobutylene to solutions of aluminium halides in alkyl halides produced non-reacting mixtures from which the monomer but no polymer could be recovered. This indicated the complexing of isobutylene with aluminium (III) halides and appeared to rule out theories of initiation based on interaction of initiator molecules with the monomer.

This type of polymerisation was believed to lead to polymers in which the chain length was a multiple of the monomer chain length. However, Puskas and Meyerson reported in 1984 that polymerisation of propylene, 1-butene, cis-2-butene and isobutylene initiated by BF_3 and $AlCl_3$ led to non-multiple carbon numbers in the polymers formed, with the latter catalyst giving more non-multiple carbon number products than the former.[68] They suggested that the phenomenon was

more widespread than previous literature had indicated, and that chain transfers involving C-C bond cleavage were responsible for the formation of the non-multiple carbon numbered fragments.

1.3 Interactions of Aluminium and Aluminium (III) Chloride with Chlorohydrocarbons

Aluminium and aluminium (III) chloride, like many other metals and metal chlorides, exhibit several types of interaction with chlorohydrocarbons, from complexation to the catalysis of chlorination/dechlorination reactions, hydrochlorination/dehydrochlorination reactions and polymerisations. Water and hydrogen chloride often have important roles in the interactions. Since alkyl halides are often used in Friedel-Crafts reactions, some topics appropriate to this section have been covered in the preceding text.

1.3.1 Complexes of Chlorocarbons with Aluminium (III) Chloride

Aluminium (III) chloride can generate highly coloured solutions in chlorohydrocarbons and chlorocarbons. The species present in these solutions have been identified rarely, and most of those which have been isolated contain a third component such as hydrogen halide. However, some reasonably stable solid complexes have been isolated from solutions of aluminium (III) chloride in chlorocarbons.

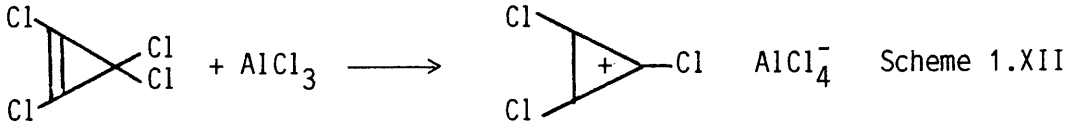
A bright yellow solid of stoichiometry $[C_3Cl_6.AlCl_3]$ was isolated on treatment of hexachloropropene with aluminium (III) chloride.[69] This species was assigned as pentachloropropenium tetrachloroaluminate ($[C_3Cl_5^+][AlCl_4^-]$) using infra-red spectroscopy,[70] mainly on the basis of the detection of the characteristic band for $AlCl_4^-$. The solid reacted with most solvents, but in methylene chloride an equilibrium was established (Equation 1.XII). A UV/visible

spectrophotometric investigation of this equilibrium suggested that

$$C_3Cl_5^+ AlCl_4^- \rightleftharpoons C_3Cl_6 + AlCl_3 \qquad \text{Equation 1.XII}$$

a hitherto unassigned band could be increased by the addition of water, and this was attributed to some ion association involving $C_3Cl_5^+$ and a partially hydrated aluminium (III) species.

Tetrachlorocyclopropene reacted with aluminium (III) chloride to yield a colourless crystalline solid[71] which was formulated as trichlorocyclopropenium tetrachloroaluminate (Scheme 1.XII) using infra-red spectroscopic evidence. Tetrachlorocyclopropene could be regenerated on the addition of water.



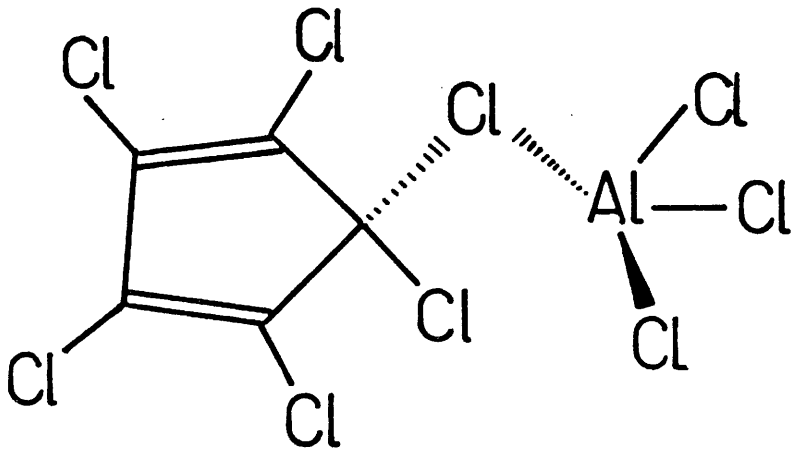
Scheme 1.XII

A red solid was isolated from the reaction of hexachlorocyclopentadiene and aluminium (III) chloride[72] which contained separable species of stoichiometry $C_{10}Cl_8$ and $[C_5Cl_6.AlCl_3]$. An infra-red study of the latter species did not show the $AlCl_4^-$ band, and was interpreted in terms of the chlorine bridged adduct (Formula 1.IV). However, an X-ray diffraction study of the red crystalline solid of stoichiometry $[C_4(CH_3)_4AlCl_3]$ obtained from the reaction of but-2-yne with aluminium (III) chloride (Equation 1.XIII)[73] showed that it had the structure shown in Formula 1.V. Analogous structures have been found for the products of reactions of other alkynes with aluminium

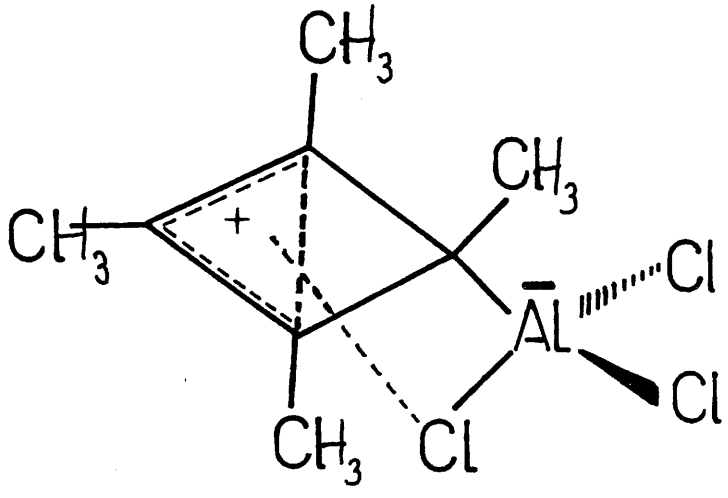
$$2\,MeC \equiv CMe + AlCl_3 \xrightarrow[CH_2Cl_2]{273K} [C_4Me_4AlCl_3] \qquad \text{Equation 1.XIII}$$

(III) chloride.[74] In his review of 1983, Winterton suggested that, by analogy with Formula 1.V, the species of stoichiometry $[C_5Cl_6AlCl_3]$

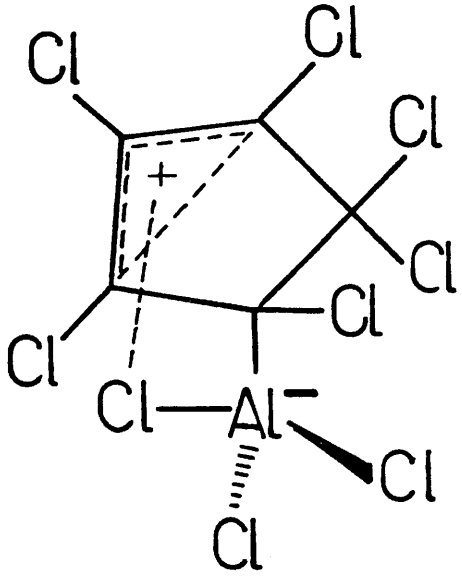
Formula 1.IV



Formula 1.V



Formula 1.VI



may adopt the structure shown in Formula 1.VI,[75] but no X-ray diffraction study has been carried out to confirm or refute this suggestion.

1.3.2 Metal Chloride Catalysed Hydrochlorination/Dehydrochlorination Reactions

Metal chloride catalysed hydrochlorinations of e.g. acetylene, 1,1-dichloroethene, chloroethene and 1,2-dichloroethene are commonly used industrially in the formation of chlorohydrocarbon products. For example, the iron (III) chloride catalysed hydrochlorination of 1,1-dichloroethene to form 1,1,1-trichloroethane is an important industrial process for the formation of the latter (Equation 1.XIV). Metal chloride catalysed dehydrochlorinations are often blamed for

$$CH_2{=}CCl_2 + HCl \xrightleftharpoons{FeCl_3} CH_3CCl_3 \qquad \text{Equation 1.XIV}$$

formation of by-products in industrial processes, and the ability of metal chlorides to catalyse dehydrochlorinations is well known; for example, caesium chloride supported on silica gel catalyses selective dehydrochlorination of 1,1,2-trichloroethane to give 1,1-dichloroethene[76] (Equation 1.XV).

$$CHCl_2CH_2Cl \xrightarrow{CsCl} CH_2{=}CCl_2 + HCl \qquad \text{Equation 1.XV}$$

Attempts to elucidate the mechanism of the hydrochlorination of gaseous acetylene by gaseous hydrogen chloride in the presence of main group and transition metal chlorides supported on carbon and silica have been reviewed.[77] The author proposed that the rate determining step for this reaction involved addition of hydrogen chloride to a surface metal chloride-acetylene Lewis acid/base complex.

The ability of a metal chloride to form complexes with acetylene and hydrogen chloride independently was considered to be a possible requirement for catalytic activity in this system. Solid aluminium (III) chloride displays no interaction with hydrogen chloride,[39,40] but the author reported 20% hydrochlorination of acetylene to give chloroethene in the presence of supported "solid aluminium (III) chloride" at 200°C. Insufficient detail was provided to determine the purity of the aluminium (III) chloride or the nature of its interaction with the support.

Attempts to elucidate the mechanism of the dehydrochlorination of gaseous t-butyl chloride on various metal chlorides were carried out using infra-red spectroscopy.[78] On the basis of the spectra obtained for nine metal chlorides, the structure shown in Figure 1.V was considered as a surface intermediate in this process. While

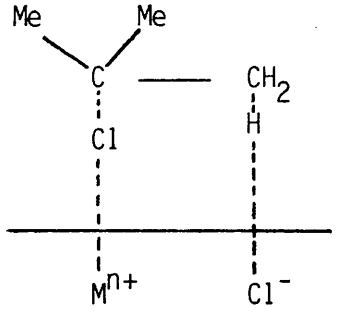


Figure 1.V

this model is reasonable in view of assignments made, at least two of the bands used as evidence to formulate its existence in the case of aluminium (III) chloride, at 3058 cm^{-1} and 809 cm^{-1}, are close to the frequencies associated with water molecules in the ionic compound $AlCl_3.6H_2O$ (3050 cm^{-1} and 820 cm^{-1}).[32] The spectra were apparently not background subtracted and it would be unusual if water were not present, but no assignments of H_2O bands were made. Hence, at least for the experiments involving aluminium (III) chloride, the

conclusions drawn are ambiguous.

The above examples demonstrate the importance of both supported and unsupported metal chlorides as catalysts in this field. However, there is ample scope for further work in this area, particularly with regard to identification of adsorbed species.

1.3.3 The Aluminium (III) Chloride/1,1,1-Trichloroethane System

1,1,1-trichloroethane is thermodynamically unstable with respect to dissociation into 1,1-dichloroethene and hydrogen chloride (Equation 1.XVI). Measurements[79] indicate that the equilibrium constant is 0.002 mol l^{-1}, leading to dissociation at equilibrium at room temperature of 1.5%. Kinetic studies on the thermolytic

$$CH_3CCl_3 \rightleftharpoons CH_2{=}CCl_2 + HCl \qquad \text{Equation 1.XVI}$$

elimination of HCl from 1,1,1-trichloroethane in a conditioned glass reactor[80] indicated that two dissociation mechanisms occurred simultaneously, but that the half-life of the fastest, even at the boiling point of 1,1,1-trichloroethane, was several hundred years.

Uninhibited 1,1,1-trichloroethane can react violently with aluminium metal. An example of this is the so-called "bleeding" reaction which occurs when aluminium metal is scratched under uninhibited liquid 1,1,1-trichloroethane. When scratched, the aluminium reacts immediately to give a dark red tarry material over the scratch. Gaseous hydrogen chloride is evolved at the scratch and this carries particles of the tar into the solvent, where they dissolve, giving rise to the "bleeding" phenomenon. The species responsible for the red colour is unidentified.

Aluminium can be completely corroded by this reaction and the

reported products include aluminium (III) chloride, 1,1-dichloroethene, 2,2,3,3-tetrachlorobutane and cis- and trans- dimers of the form $CH_3CCl = CClCH_3$,[1] although no description of the means of characterisation was given. The vigorous nature of the reaction was attributed to dehydrochlorination of 1,1,1-trichloroethane by aluminium (III) chloride produced in an early stage of the reaction. No evidence was given to support this proposal.

Kulikova[81] reported that 3 mole % hydrogen chloride was produced within 3 hours of treating 1,1,1-trichloroethane at 0^oC with 1% by weight aluminium (III) chloride, using a technique where the hydrogen chloride produced was continuously removed in a stream of nitrogen. One of the products of this reaction under more vigorous conditions was the polyene $\text{-}(CH = CCl)\text{-}_n$. Addition of this product at 1% by weight appeared to inhibit the dehydrochlorination, and polyenes of the type $\text{-}(CH = CH)\text{-}_m$ appeared to inhibit it still further. However, because of the technique used, it is unclear whether this effect was due to inhibition of dehydrochlorination or the more ready uptake of hydrogen chloride by the polyenes.

A bright violet colouration was reported for the mixture of 1,1-dichloroethene and aluminium (III) chloride at -50^oC to -80^oC after 30-60 hours.[82] No spectroscopic studies were carried out on the mixture and hydrogen chloride was not detected. The products isolated were the species of stoichiometry $C_4H_4Cl_4$, and which is claimed to be $CCl_2 = CHCCl_2CH_3$ (I), and 1,1,3,3,5,5-hexachlorocyclohexane (II). The formation of (I) and (II) was explained in terms of protonation. The source of H^+ was not specified, though dissolved water or very small amounts of hydrogen chloride from dehydrochlorination of 1,1-dichloroethene are possibilities.

When a mixture of aluminium (III) chloride and 1,1-dichloroethene was left at -23°C for 8 hours, 2,4,4,4-tetrachlorobut-1-ene (III) was produced.[83] Winterton[75] suggested that the formation of (III) could involve complexation between $AlCl_2^+$ and $CH_2 = CCl_2$ according to Scheme 1.XIII. Species (I) and (III) can be interconverted by

$$CH_2 = CCl_2 + AlCl_2^+ \rightleftharpoons Cl_2AlCH_2\overset{+}{C}Cl_2$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2 = CCl_2 \longrightarrow Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \longrightarrow CH_2 = CClCH_2CCl_3 + AlCl_3$$

(III)

Scheme 1.XIII

dehydrochlorination and rehydrochlorination although the position of the equilibrium (Equation 1.XVII) and its variance with temperature are not known.

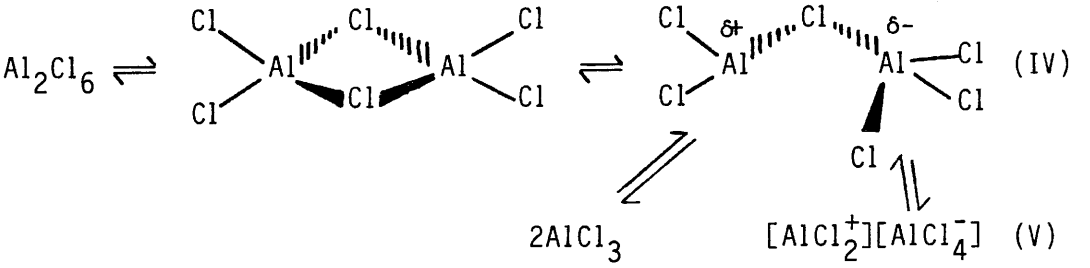
$$\underset{(III)}{CH_2 = CClCH_2CCl_3} \rightleftharpoons CH_2 = CClCH = CCl_2 + HCl \rightleftharpoons \underset{(I)}{CH_3CCl_2CH = CCl_2}$$

Equation 1.XVII

Kulikova reported that at higher temperatures > -60°C dehydrochlorination occurred so that, as well as (I) and (II), 1,1,3-trichloro,—1,3-butadiene and 1,3,5-trichlorobenzene were generated. Small quantities of a dehydrochlorinated acyclic trimer and a dehydrochlorinated polymer were also reported. Hydrochlorination of 1,1-dichloroethene and the dimer (I) to give 1,1,1-trichloroethane and 1,1,1,3,3 -pentachlorobutane were also reported. A scheme was presented

on the basis of products identified (Scheme 1.XIV). Without evidence to support the suggestion, Kulikova attributed the observed cessation of reaction at the dimer and cyclic trimer stage at lower temperatures to the formation of a purple complex between the dimer (I) and aluminium (III) chloride.

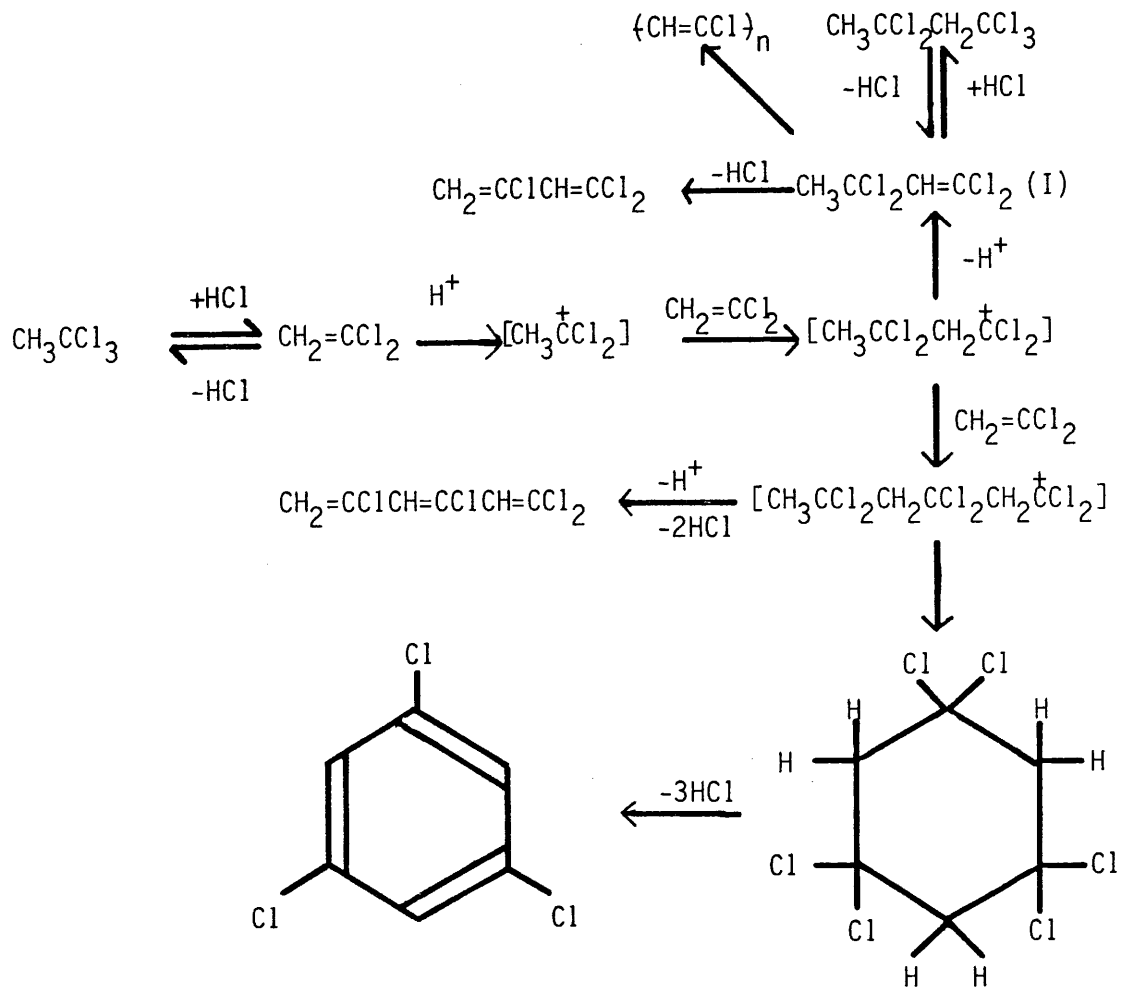
In his review of this field, Winterton[75] considered a mechanistic interpretation of Plesch's process for the dissociation of aluminium (III) chloride in an alkyl halide (Equation 1.II) and suggested that the dissociation of the dimer Al_2Cl_6 to the monomer $AlCl_3$ would take place by stepwise rather than simultaneous breaking of chlorine bridge bonds (Scheme 1.XV). Winterton suggested that the aluminium (III)



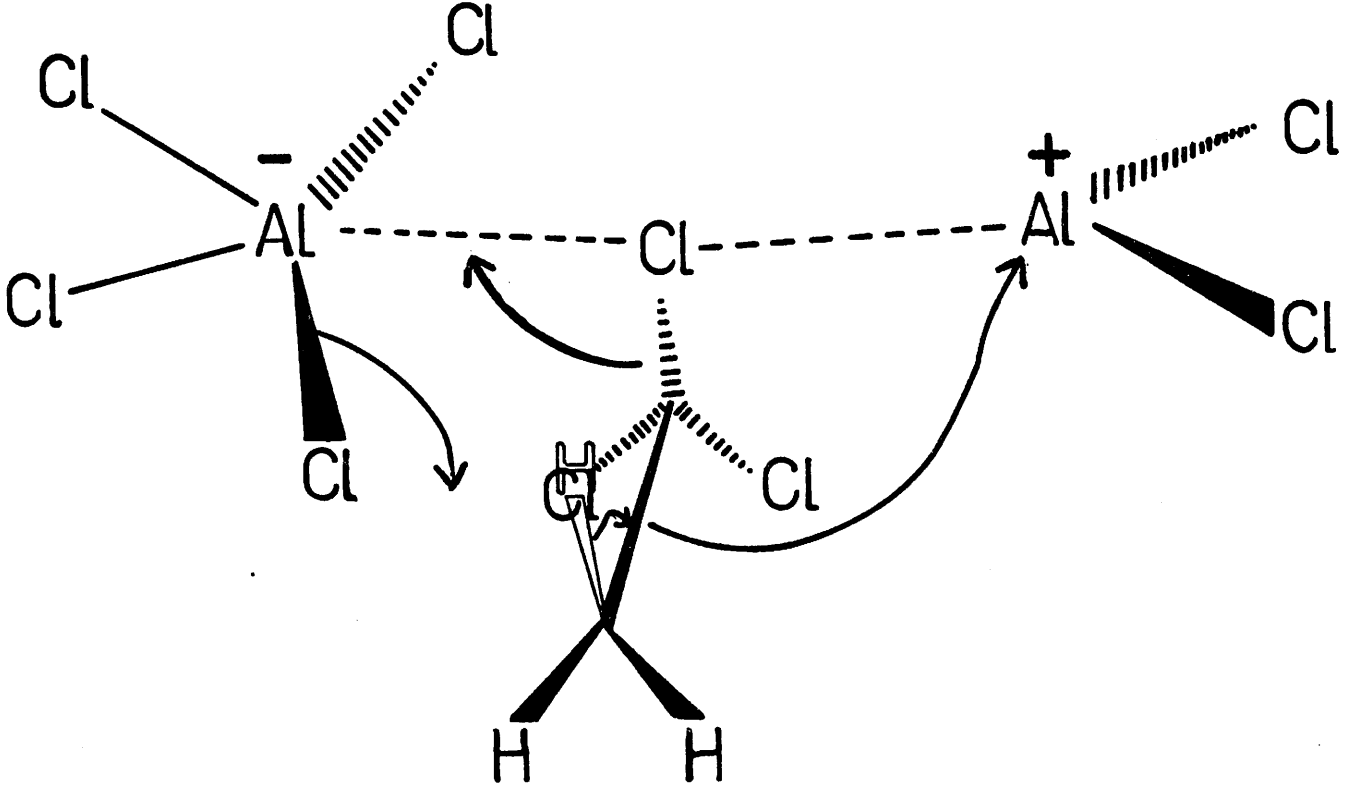
Scheme 1.XV

chloride catalysed dehydrochlorination of 1,1,1-trichloroethane could take place via the interaction of (V) or the species (IV) with a 1,1,1-trichloroethane molecule. He envisaged a solvent separated ion pair of geometry such that effective elimination of hydrogen chloride was facile (Formula 1.VII), by a process of chloride removal by co-ordination to Al^{3+} and H-Cl bond formation between a proton of the chlorohydrocarbon and a co-ordinated chloride. Loss of HCl from (Formula 1.VII) could lead to a 1,1-dichloroethene separated ion pair (Formula 1.VIII) or π-complex (Formula 1.IX).

SCHEME 1.XIV. Scheme Proposed by Kulikova to Account for the Reactions of 1,1,1-Trichloroethane and 1,1-Dichloroethene with Aluminium (III) Chloride.[82]

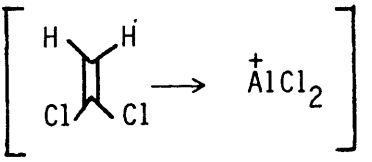


FORMULA 1.VII. 1,1,1-Trichloroethane Separated Ion Pair.[75]



$[Cl_2Al^+]CH_2 = CCl_2[AlCl_4^-]$

Formula 1.VIII

$[AlCl_4^-]$ 

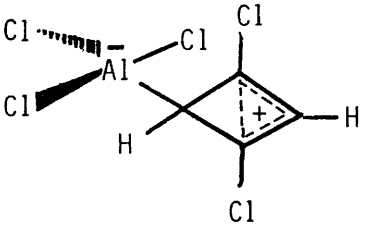
Formula 1.IX

Winterton also suggested that (IV) could be regarded as being analogous to the active sites of solid aluminium (III) chloride and comparison with the diagram of the unit cell shown in Figure 1.II shows that this is a reasonable and attractive model.

The formation of strong colours in this reaction system is often reported but the question of their origin is rarely addressed. The review of Winterton[75] contains the only serious attempt to narrow the range of possibilities using the circumstantial evidence available.

A Lewis acid/base complex in which one chlorine atom of 1,1,1-trichloroethane acted as a σ-donor to aluminium (III) chloride was considered unlikely as a source of colour formation, for although complexes of this type are quite common, the pure complexes are never coloured. The formation of a Lewis acid/base complex in which the double bond of a 1,1-dichloroethene molecule acted as a π-donor to aluminium (III) chloride was also considered unlikely as a source of colour formation, by comparison with known complexes of this type.[58] The formation of a π-complex between 1,1-dichloroethene and an $AlCl_2^+$ cation (Formula 1.IX) was considered unlikely as a source of colour formation, due to the very low concentrations of $AlCl_2^+$ expected (10^5-10^6 times less than the original "$AlCl_3$" concentration). The π-complex would therefore be required to have a huge extinction coefficient. Similarly, the formation of a 1,1,1-trichloroethane derived cation-tetrachloroaluminate complex was considered unlikely as a source of colour formation.

Although Grattan and Plesch discounted the importance of vinyl π-$AlCl_3$ complexes as intermediates in the aluminium (III) chloride catalysed polymerisation of isobutylene,[35] Winterton considered such complexes, with 1,1-dichloroethene as olefin, as possible precursors to Al-C σ-bond containing intermediates (IX) (Scheme 1.XVI). These intermediates could react with a further molecule of 1,1-dichloroethene to yield the C_4 analogue (X). Simple transformations of (X) such as loss of $AlCl_3$ after chlorine ion transfer could lead to most of the products reported by Kulikova. Furthermore, since 1,1-dichloroethene could be considered as a potential precursor to monochloroacetylene, (X) could be considered a potential precursor to the type of homocyclopropenium species discussed earlier (Formula 1.V) such as shown in Formula 1.X. Other compounds with similar structures have

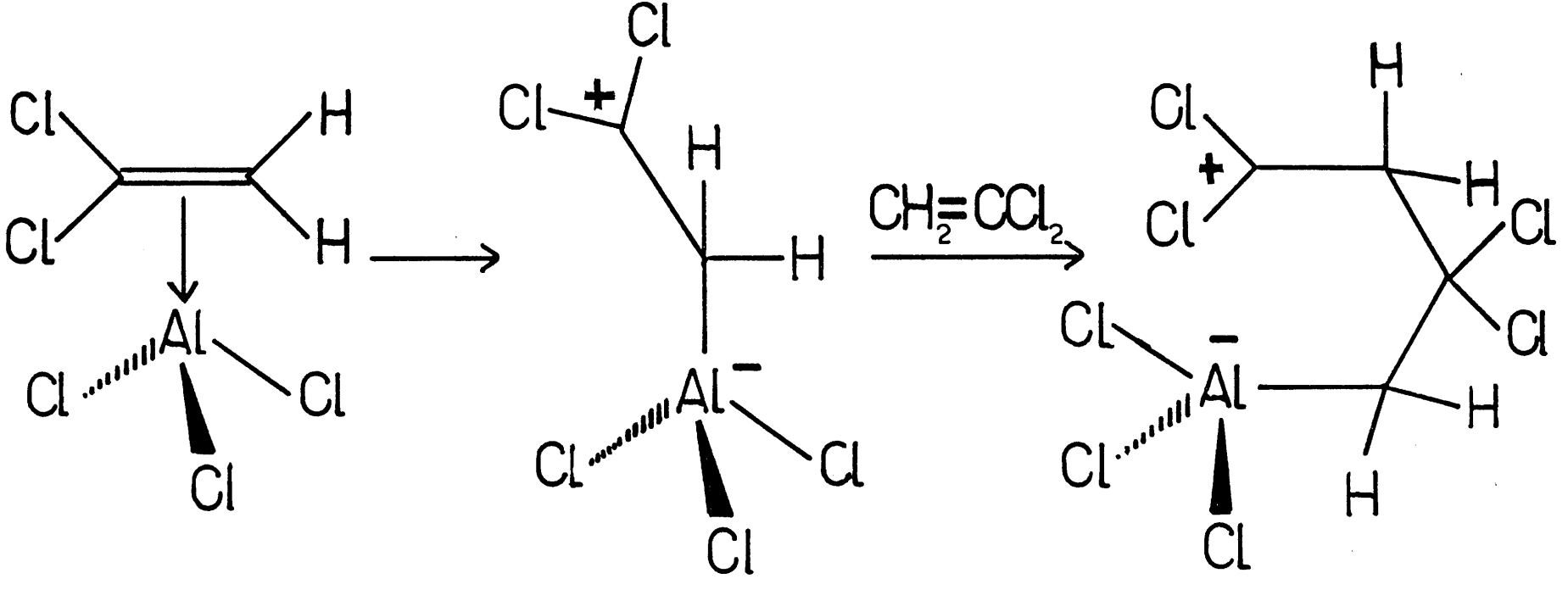


Formula 1.X

displayed strong colours, although the extinction coefficients have not been determined and no complexes of this type have been isolated from 1,1-dichloroethene solutions.

One possible explanation for the formation of strong colours in these systems which has been discussed by Winterton[75] is the protonation of highly unsaturated species formed by processes such as the polymerisation of 1,1-dichloroethene by the $HCl/AlCl_3$ superacid. Conjugated olefins can be protonated by strongly acidic media to give coloured species with very large extinction coefficients,[84] which could generate strongly coloured solutions when present in very small concentrations.

SCHEME 1.XVI. Proposed Formation of Al-C σ-bond Containing Intermediates in Aluminium (III) Chloride Catalysed Oligomerisation of 1,1-Dichloroethene.[75]



(IX) (X)

Spectral properties of conjugated olefins depend on the length of the conjugated system and can be modified by the introduction or removal of halo substituents.

If a polymer derived from 1,1-dichloroethene underwent dehydrochlorinations to yield a conjugated chloroolefin, then this could be protonated by $HCl/AlCl_3$ to yield strongly coloured species. Although there is evidence for highly unsaturated species in this system, there is no direct evidence to suggest that these are straight chain conjugated species.

The industrial importance of aluminium (III) chloride catalysed dehydrochlorinations and oligomerisations of chlorohydrocarbons has been illustrated. Although reactions between aluminium (III) chloride and 1,1,1-trichloroethane or related compounds have been well studied, the main emphasis has been on product isolation, either from homogeneous solution phase systems or from more complicated multi-phase systems. There is evidence that heterogeneous phenomena are of importance in these reactions, but no studies have been reported on the reactions of gaseous 1,1,1-trichloroethane or 1,1-dichloroethene with solid aluminium (III) chloride.

The work which follows was carried out in order to:-

i) determine whether the generally held belief that aluminium (III) chloride catalysed dehydrochlorination of 1,1,1-trichloroethane produces 1,1-dichloroethene and hydrogen chloride in a 1:1 molar ratio was correct.

ii) determine, as far as possible, the time dependences of the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride.

iii) obtain direct evidence for adsorbed species in these reactions in the presence and absence of a third component such as water

or hydrogen chloride.

iv) determine the [^{36}Cl]-chlorine exchange behaviour between components of the reaction systems studied in situations where no chemical change results and where reaction occurs.

v) determine, as far as possible, the identity of species giving rise to strong colours in these reactions.

CHAPTER 2

CHAPTER 2

EXPERIMENTAL

All operations were carried out under the most rigorously water-free conditions available, due to the hygroscopic properties of aluminium (III) chloride. The solid was handled in vacuo (10^{-4} Torr) or in an inert atmosphere box (H_2O < 10 ppm) at all times.

2.1 Vacuum and Inert Atmosphere Equipment

2.1.1 The Vacuum System

The vacuum line (Figure 2.I) was an enclosed Pyrex glass structure which consisted of a manifold, a constant volume manometer and a Vacustat, all of which were mutually isolable. The line was evacuated to a pressure of 10^{-4} Torr using a mercury diffusion pump and an oil-sealed rotary pump. The Vacustat was used to measure the pressure which the pumps achieved. The pumps were protected from volatile material in the line by a series of waste traps which were cooled in liquid nitrogen and which condensed any volatiles present. The pumps and waste traps could be isolated from the rest of the line using a glass tap.

The constant volume manometer was used to measure pressures of gases in the line to an accuracy of $\pm$ 0.5 Torr. The manifold had several B14 ground glass sockets which could be isolated from the line using high vacuum stopcocks (J. Young). Vacuum flasks (Figure 2.II) and ampoules (Figure 2.III), equipped with high vacuum stopcocks (J. Young) and B14 cones, were attached to the sockets of the manifold using Kel-F grease. All vessels and the line itself were flamed out, while the system was pumped, using a gas/oxygen flame. Although this process does not remove all moisture adsorbed on a glass surface,[26] a

FIGURE 2.I. The Vacuum System

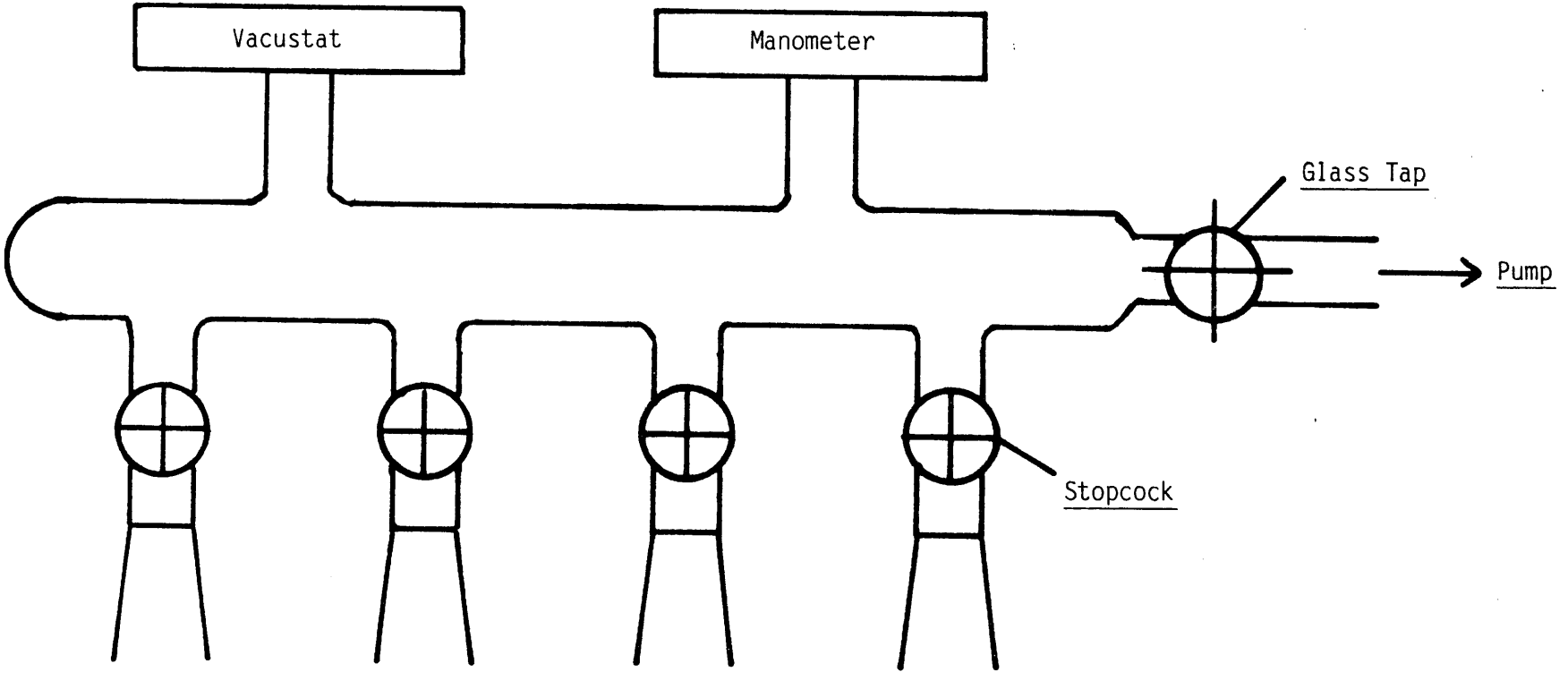


FIGURE 2.II. Vacuum Flask

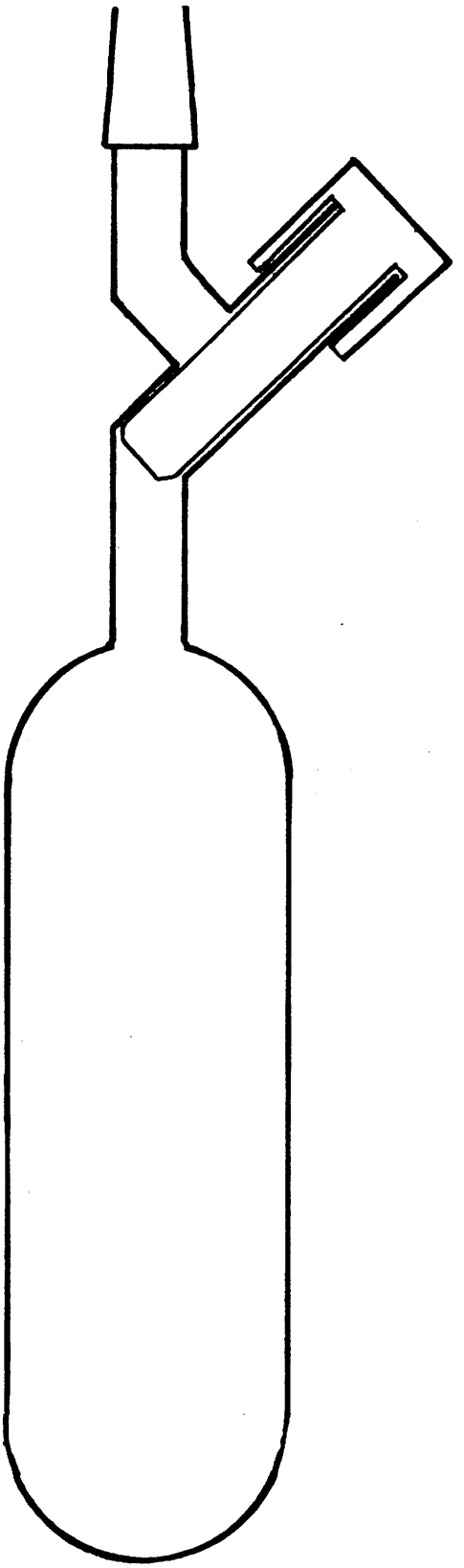
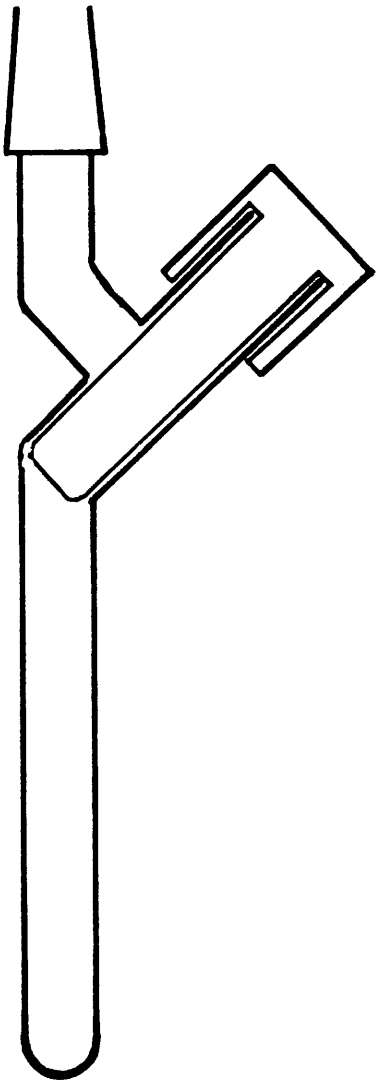


FIGURE 2.III. Vacuum Ampoule



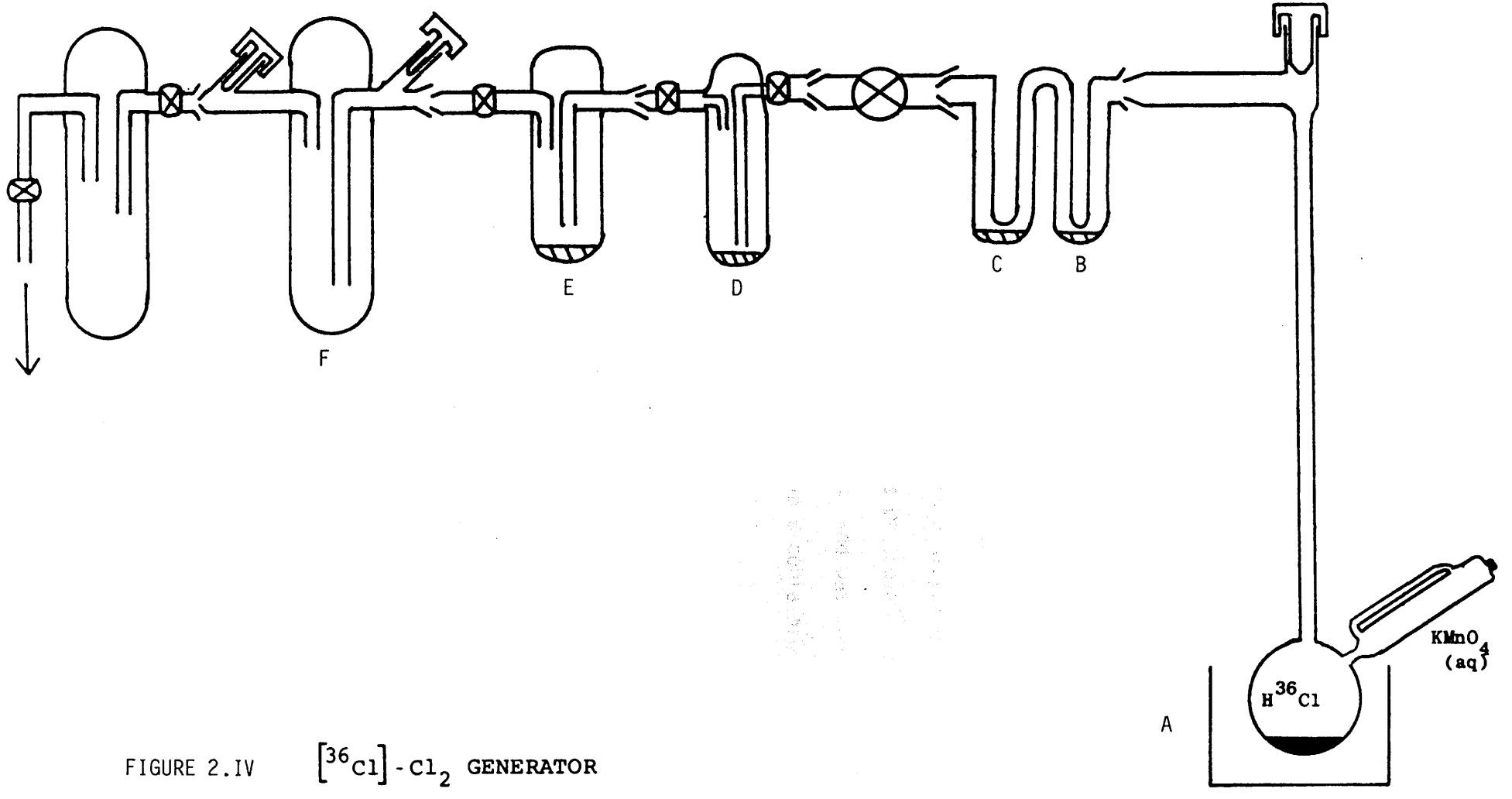


FIGURE 2.IV $[^{36}Cl]$-Cl_2 GENERATOR

substantial reduction in the amount of adsorbed moisture can be achieved.

2.1.2 The Inert Atmosphere Box

An argon atmosphere box (H_2O < 10 ppm, Lintott) was used. All Pyrex glass vessels used were evacuated and flamed out before being placed in the box.

2.2 Preparation and Purification of Reactants

2.2.1 Preparation and Purification of [^{36}Cl]-Chlorine-Labelled Dichlorine

[^{36}Cl]-Chlorine-labelled dichlorine was prepared by reaction of [^{36}Cl]-Chlorine-labelled hydrochloric acid with potassium permanganate solution, according to Equation 2.I.[85] [^{36}Cl]-Chlorine-labelled Cl_2 was generated in an apparatus consisting of a round-bottom

$$4[^{36}Cl]\text{-}HCl + KMnO_4 \longrightarrow [^{36}Cl]\text{-}KCl + MnO_2 + 2H_2O + {}^{3}/_{2}\,[^{36}Cl]\text{-}Cl_2$$

Equation 2.I

flask reaction vessel (A), to which a series of cooled traps were attached (Figure 2.IV). Traps B and C contained solid $KMnO_4$ to remove HCl, and were cooled to -78°C in methylene chloride/solid CO_2 baths. Traps D and E contained solid P_2O_5 to remove moisture, and were cooled to -78°C in methylene chloride/solid CO_2 baths. Collection vessel F was equipped with high vacuum stopcocks (J. Young) so that it could be isolated from the rest of the apparatus. The ground glass joints of the apparatus were sealed with Kel-F grease and the operations were carried out in dry air at reduced pressure.

Aqueous [^{36}Cl]-NaCl (2.4 ml, 60 μCi, Amersham International) was

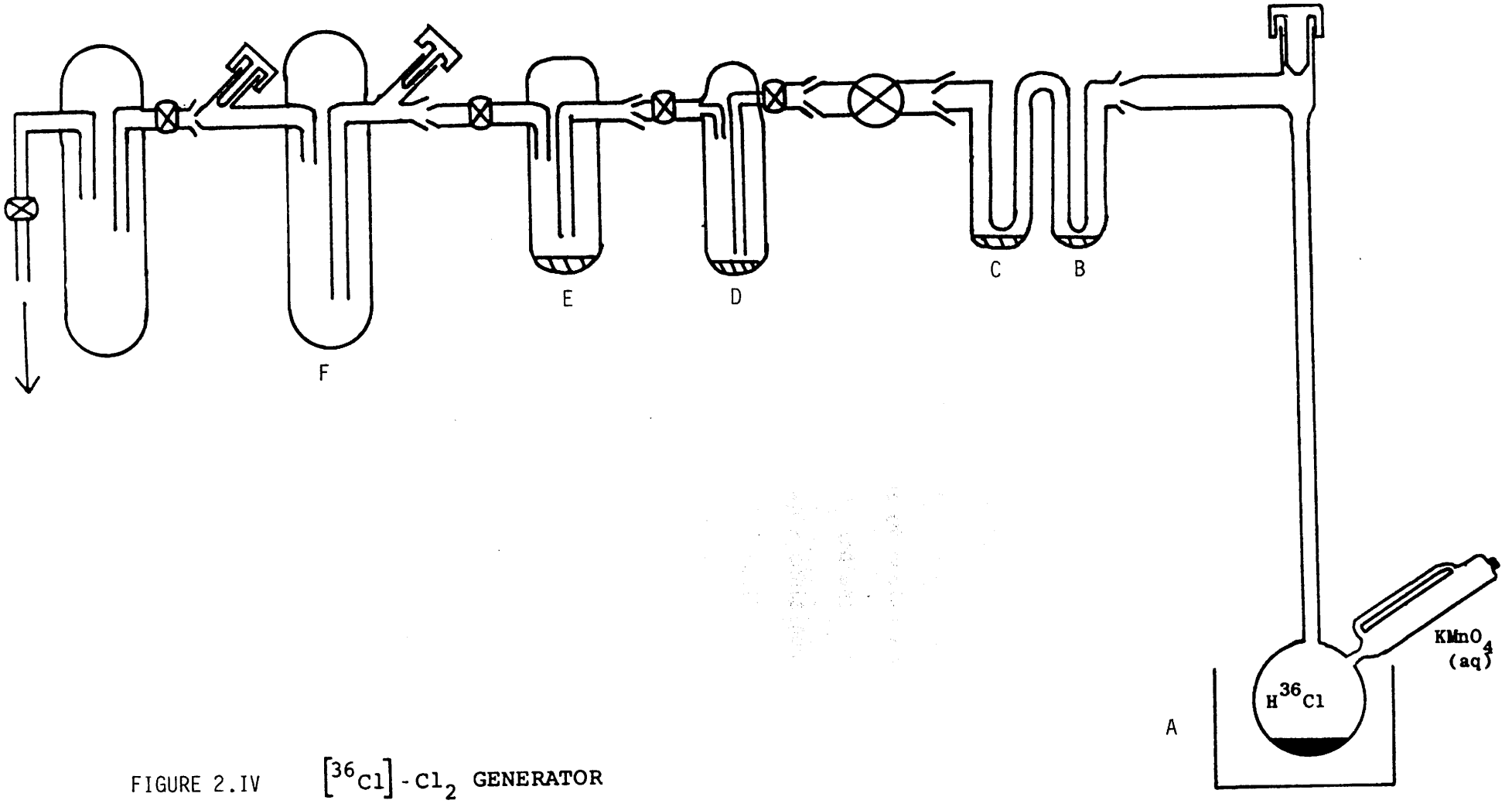


FIGURE 2.IV $[^{36}Cl]$-Cl_2 GENERATOR

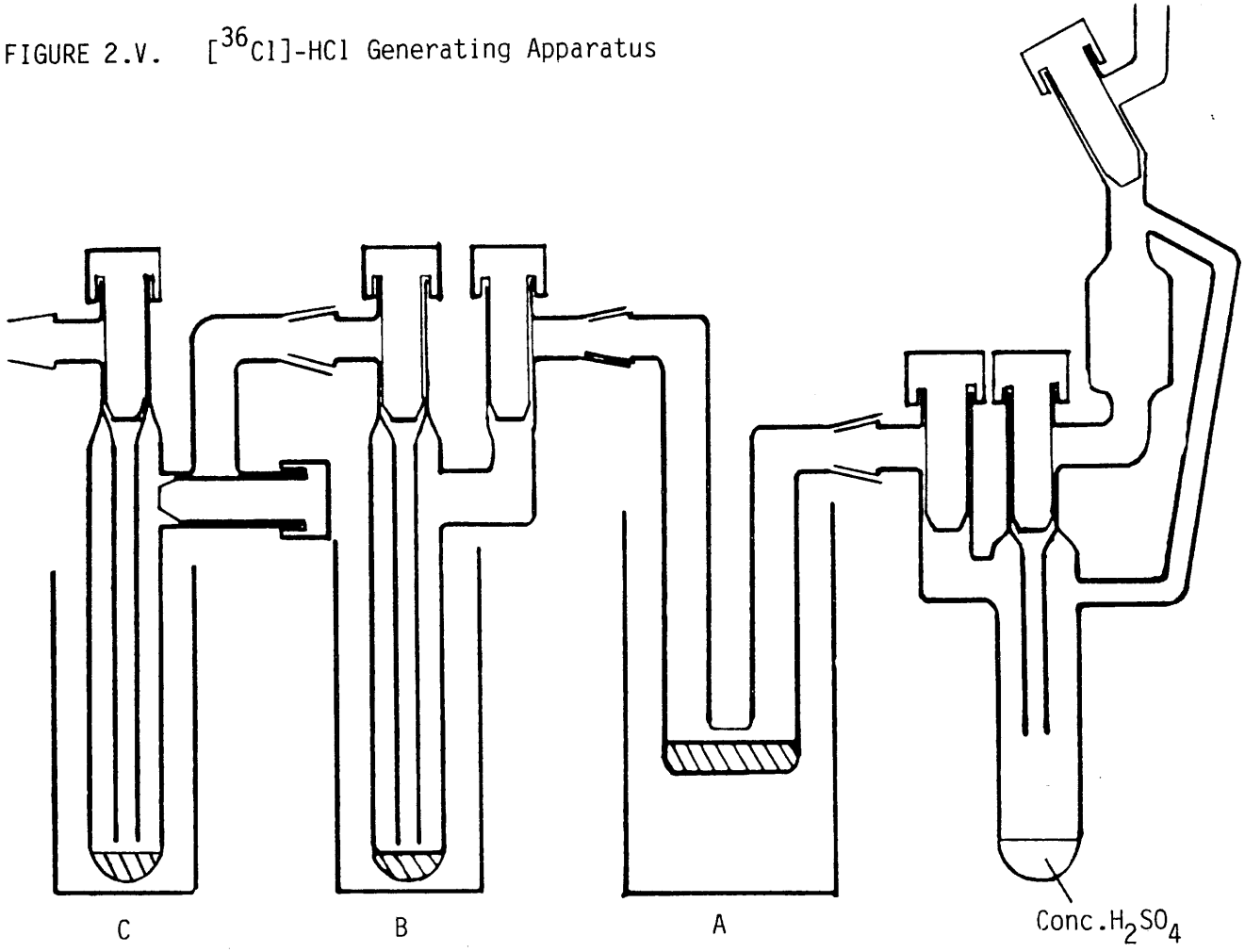
added to 35.4% w/v hydrochloric acid (30 ml, Hay's Chemicals) in A which was heated to 60°C in a water bath. A solution of 0.3mol l^{-1} $KMnO_4$ was added dropwise with stirring. The [^{36}Cl]-Cl_2 liberated was distilled through traps B to E and collected in F at -78°C. F was transferred to a vacuum line where the [^{36}Cl]-Cl_2 was degassed and stored over P_2O_5 in a Monel metal bomb.

2.2.2 Preparation and Purification of [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride[86]

[^{36}Cl]-Chlorine-labelled hydrogen chloride was generated in an apparatus consisting of a reaction vessel with a dropping funnel and pressure equilibrating arm, to which a series of cooled traps were attached (Figure 2.V). Trap A contained P_2O_5 and was cooled to -78°C in a methylene chloride/solid CO_2 bath. Trap B contained P_2O_5 and was cooled to -90°C in a methanol/liquid nitrogen bath. Collection vessel C contained P_2O_5 and was cooled to -120°C in an isopentane/liquid nitrogen bath. C was equipped with high vacuum stopcocks (J. Young) so that it could be isolated from the rest of the apparatus. The ground glass joints of the apparatus were sealed with Kel-F grease and the operations were carried out in dry air.

Aqueous [^{36}Cl]-NaCl (1.5 ml, 37.5 μCi, Amersham International) was diluted with 35.4% hydrochloric acid (5.5 ml, Hay's Chemicals) and this solution added dropwise to concentrated sulphuric acid. The [^{36}Cl]-HCl generated was distilled through traps A and B and collected in C at -120°C. C was transferred to a vacuum line where the [^{36}Cl]-HCl was degassed, vacuum distilled twice from -90°C to -196°C onto P_2O_5, and stored over P_2O_5 in a vacuum flask at -196°C.

FIGURE 2.V. [^{36}Cl]-HCl Generating Apparatus



2.2.3 Preparation and Purification of [^{14}C]-Carbon-Labelled Carbon Tetrachloride

[^{14}C]-Carbon-labelled carbon tetrachloride (250 μCi, Amersham International) was vacuum distilled from a breakseal storage vessel onto CCl_4 (20 ml, ANALAR, May & Baker) which had been previously degassed. The [^{14}C]-CCl_4 was stored over activated 3A molecular sieves and further degassed before use.

2.2.4 Preparation and Purification of [^{36}Cl]-Chlorine-Labelled Carbon Tetrachloride

[^{36}Cl]-Chlorine-labelled carbon tetrachloride was prepared by thermal chlorination of chloroform with [^{36}Cl]-Cl_2[87] according to Equation 2.II. A conditioned Monel metal bomb was loaded with

$$CHCl_3 + [^{36}Cl]\text{-}Cl_2 \longrightarrow [^{36}Cl]\text{-}CCl_4 + [^{36}Cl]\text{-}HCl \qquad \text{Equation 2.II}$$

$CHCl_3$ (10 mmol, ANALAR, May & Baker) and [^{36}Cl]-Cl_2 (20 mmol, prepared as described in 2.2.1) on a vacuum line. The bomb was closed and held at 350°C for 23h, at the end of which the contents of the bomb were distilled into a vacuum flask containing mercury. The product mixture was allowed to stand over mercury in the vacuum system for 2h at room temperature to remove any Cl_2 still present by direct reaction with the mercury to produce involatile $HgCl_2$.

The flask containing the product mixture was held at -78°C in a methylene chloride/solid CO_2 bath. The vapour in the manifold above the product mixture was isolated and condensed into a second flask held at -196°C in liquid nitrogen. This procedure was repeated three times to remove unwanted [^{36}Cl]-HCl and [^{36}Cl]-$COCl_2$; the latter was identified in the gaseous product mixture using infra-red spectros-

copy. The presence of $COCl_2$ in the product mixture was attributed to reaction of $CHCl_3$ with metal oxides or water on the walls of the bomb. This was supported by a decrease in the amount of $COCl_2$ detected, using infra-red spectroscopy, after successive preparations of $[^{36}Cl]$-CCl_4 using this technique.

The residual $[^{36}Cl]$-CCl_4 was identified using infra-red spectroscopy, vacuum distilled from $-80^{o}C$ to $-196^{o}C$ into a vessel containing activated 3A molecular sieves, and degassed before use.

2.2.5 Preparation and Purification of $[^{36}Cl]$-Chlorine-Labelled 1,1,1-Trichloroethane

$[^{36}Cl]$-Chlorine-labelled 1,1,1-trichloroethane was prepared by iron (III) chloride catalysed hydrochlorination of 1,1-dichloroethene (Equation 2.III).

$$CH_2{=}CCl_2 + [^{36}Cl]\text{-}HCl \xrightleftharpoons{FeCl_3} [^{36}Cl]\text{-}CH_3CCl_3 \qquad \text{Equation 2.III}$$

A conditioned Monel metal bomb was loaded with $FeCl_3$ ("anhydrous", >99.0% pure, Fluka AG) in the inert atmosphere box and closed. The bomb was subsequently attached to the vacuum line and loaded with $CH_2{=}CCl_2$ (34 mmol, 99%, Aldrich Chemical Co.) and $[^{36}Cl]$-HCl (35 mmol, prepared as described in 2.2.2). The bomb was closed and held at room temperature for 48h, after which it was held at $-78^{o}C$ in a methylene chloride/solid CO_2 bath and opened to the manifold. The vapour in the manifold above the product mixture was isolated and condensed into a vacuum flask held at $-196^{o}C$ in liquid nitrogen. This procedure was repeated three times to remove unwanted $[^{36}Cl]$-HCl.

The residual $[^{36}Cl]$-CH_3CCl_3 was identified using infra-red spectroscopy, and vacuum distilled from $-80^{o}C$ to $-196^{o}C$ into a vessel

containing activated 3A molecular sieves. Inactive CH_3CCl_3 (1.5 ml, ANALAR, Hopkin & Williams) was distilled onto the $[^{36}Cl]$-CH_3CCl_3 to dilute the label. $[^{36}Cl]$-CH_3CCl_3 was degassed before use.

2.2.6 Purification of Aluminium (III) Chloride

Aluminium (III) chloride ("anhydrous", >99% pure, Fluka AG) was purified by sublimation under vacuum (10^{-4} Torr) at 120°C in the presence of aluminium wire (99.99% pure, Fluka AG/Balzers) to reduce any iron chloride impurities. The sublimate was collected in a flamed-out Pyrex U-tube at -196°C. The U-tube was sealed and transferred to the inert atmosphere box where the sublimate was transferred to several vacuum ampoules. The samples in the ampoules were degassed and stored under vacuum.

2.2.7 Purification of 1,1-Dichloroethene

1,1-Dichloroethene (99%, Aldrich Chemical Co.) was stored over activated 3A molecular sieves in a vacuum flask, under subdued light to inhibit photopolymerisation. This material contained small quantities of stabiliser to inhibit oxidation and polymerisation. It was vacuum distilled, to remove the stabiliser, and degassed before use.

2.3 Infra-Red Spectroscopy

2.3.1 Equipment

Infra-red spectroscopic analyses of the vapour phase in gas/solid systems were carried out using a Perkin Elmer 983 grating infra-red spectrometer and a Nicolet 5DXC Fourier Transform infra-red spectrometer. Kinetic infra-red spectroscopic analyses of the vapour phase in gas/solid systems were carried out using a Nicolet 20SXB

Fourier Transform infra-red system.

Two gas infra-red cells were used. Each cell had a purpose built holder to ensure reproducible positioning in the spectrometer beam. Cell A (Photo 2.I) was of 10 cm path length with KBr windows. A B14 cone and tap arrangement facilitated attachment to the vacuum line. The cell also had a B14 socket for attachment of an ampoule loaded with solid, and a depression along the bottom to ensure that none of the solid impinged on the spectrometer beam. Cell A had a volume of 54.44 $\pm$ 0.06 ml.

Cell B (Photo 2.II) had two interconnected barrels. One barrel was of 10 cm path length with KBr windows and was positioned in the spectrometer beam. The other barrel was slightly shorter with Pyrex ends, and did not impinge on the spectrometer beam. Cell B possessed the same features as cell A except for the following. Solid could be allowed to fall into or near the beam only if this was required, because the socket for attachment of the solid-containing ampoule was positioned on the non-beam barrel. In addition Cell B had a socket for the addition of more solid, or attachment of a septum cap for syringe gas injection/sampling, and a cold finger for distilling in reactants.

2.3.2 Identification of Gaseous Compounds

In all infra-red spectroscopic analyses of the vapour phase in gas/solid systems, species were assigned by comparison with standard vapour phase spectra. When possible, the techniques of GCIR (Gas Chromatography Infra-Red) and GCMS (Gas Chromatography Mass Spectrometry) were used to confirm assignments. Each of these techniques involved separation of a gas mixture using a gas chromatograph. The components were detected using an infra-red spectrometer in the former

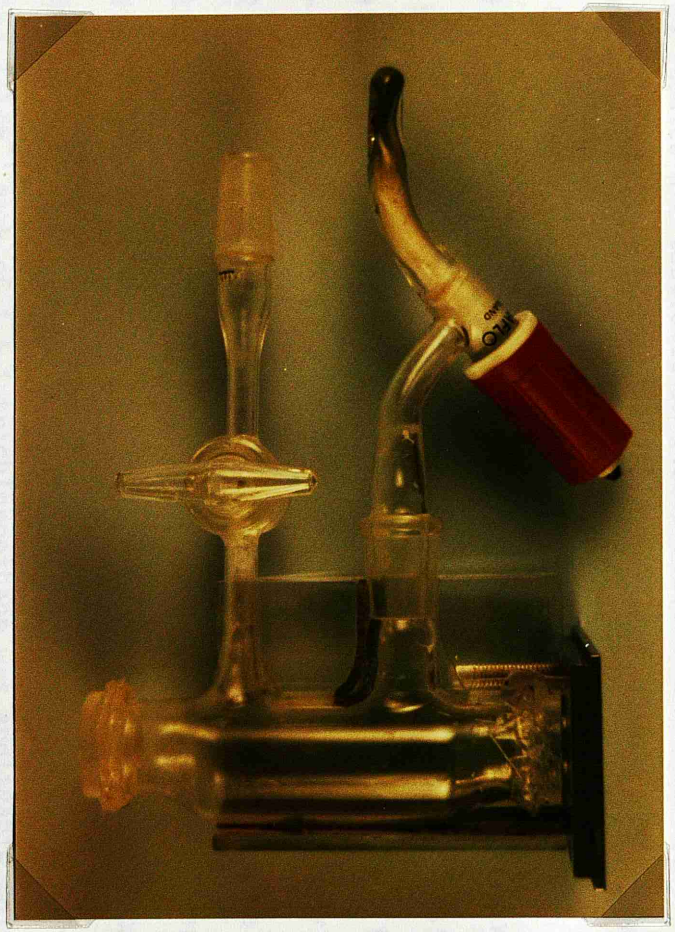


Photo 2.I

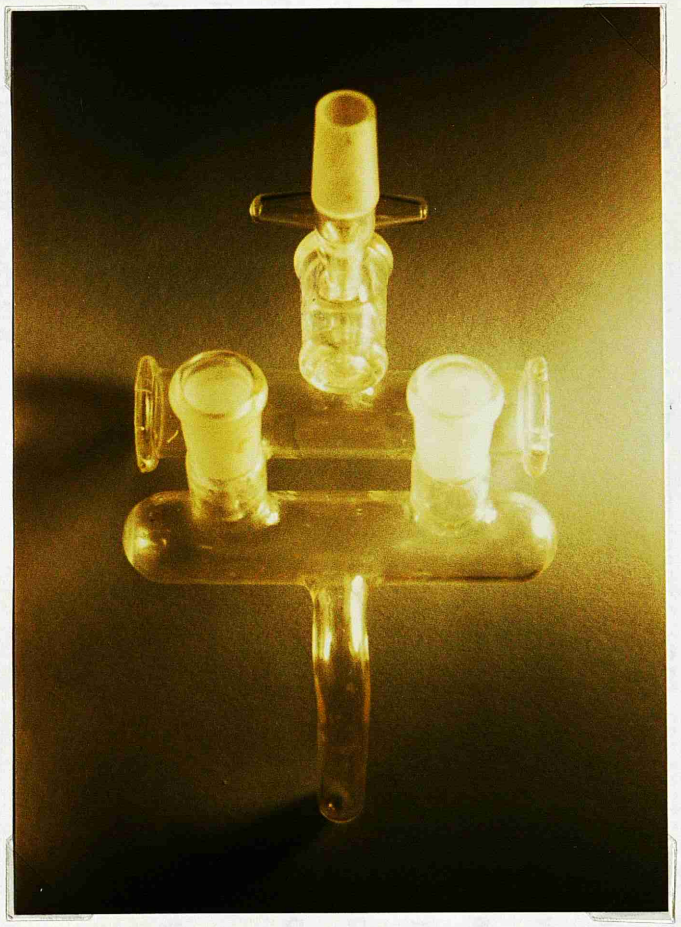


Photo 2.II

case and a mass spectrometer in the latter, in addition to a conventional flame detector.

In GCIR investigations the components were separated on a 530 μm internal diameter BPI(OVI) column in a Perkin-Elmer 8310 gas chromatograph, and a Nicolet 20SXB Fourier Transform infra-red system was used as detector. A program was used which compared spectra obtained with standard spectra from a database and printed the five closest literature spectra to that which was found, for visual comparison. In GCMS investigations the components were separated on a 50m CPSIL 5 column in a Hewlett Packard 5790A gas chromatograph and a VG Analytical 7070E double focussing magnetic sector mass spectrometer was used as detector.

2.3.3 Calibration Spectra

Analytically useful infra-red peak positions of gaseous species studied are tabulated in (Table 2.I). The 794 cm^{-1} peak of carbon tetrachloride is the only peak in the range 4000-600 cm^{-1} for this species, and the close proximity of a peak at 796 cm^{-1} for 1,1-dichloroethene can reduce its analytical utility in systems where both gases are present. Spectra were obtained for various pressures of gaseous 1,1,1-trichloroethane, 1,1-dichloroethene and carbon tetrachloride using cell A. Examples are shown in Figures 2.VI, 2.VII and 2.VIII. Plots of absorbance and peak area *vs.* pressure were constructed. Plots which had correlation coefficients >0.99 were obtained for the peaks in Table 2.II, and were considered acceptable calibrations. An example is shown in Figure 2.IX. The calibration for the 722 cm^{-1} peak of 1,1,1-trichloroethane was applicable only at pressures < 10 Torr in the cell. An absorbance *vs.* pressure calibration

TABLE 2.I

Analytically Useful Infra-Red Peak Positions

Species	Peak Position(s)
CH_3CCl_3 (g)	$1385cm^{-1}$, $722cm^{-1}$
$CH_2{=}CCl_2$ (g)	$1627cm^{-1}$, $1614cm^{-1}$, $870cm^{-1}$
CCl_4 (g)	$794cm^{-1}$
HCl (g)	$2900\text{-}2800cm^{-1}$

TABLE 2.II

Peaks with Acceptable Pressure vs Absorbance/Peak Area Calibrations

Species	Peak Monitored	Absorbance/Peak Area
CH_3CCl_3 (g)	$1385 \pm 5cm^{-1}$	Peak area
	$722 \quad cm^{-1}$	Absorbance
$CH_2{=}CCl_2$ (g)	$1627 \pm 5cm^{-1}$	Peak area
	$1627 \quad cm^{-1}$	Absorbance
	$1614 \pm 5cm^{-1}$	Peak area

FIGURE 2.VI. Infra-Red Spectrum of Gaseous 1,1,1-Trichloroethane

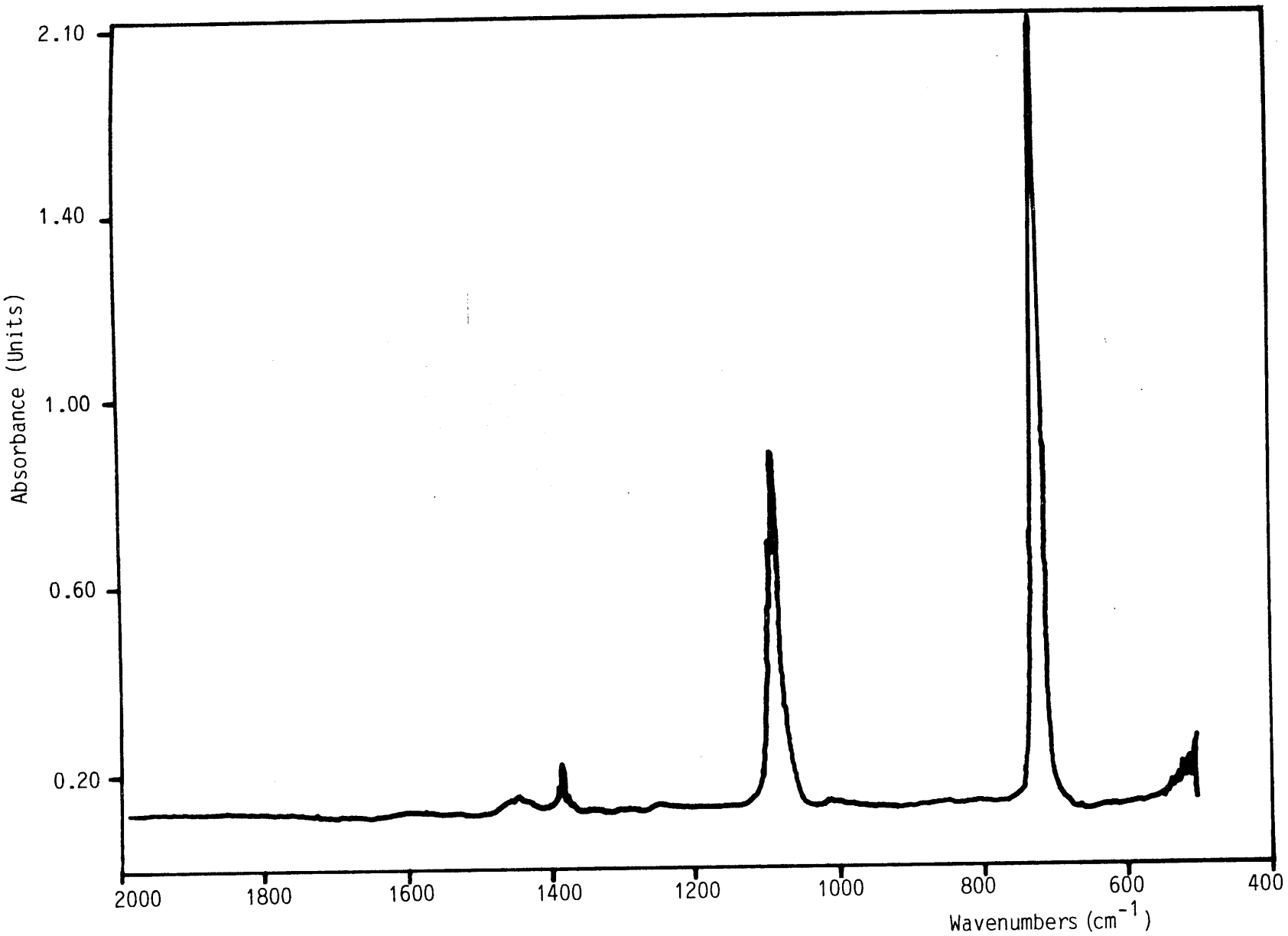


FIGURE 2.VII. Infra-Red Spectrum of Gaseous 1,1-Dichloroethene

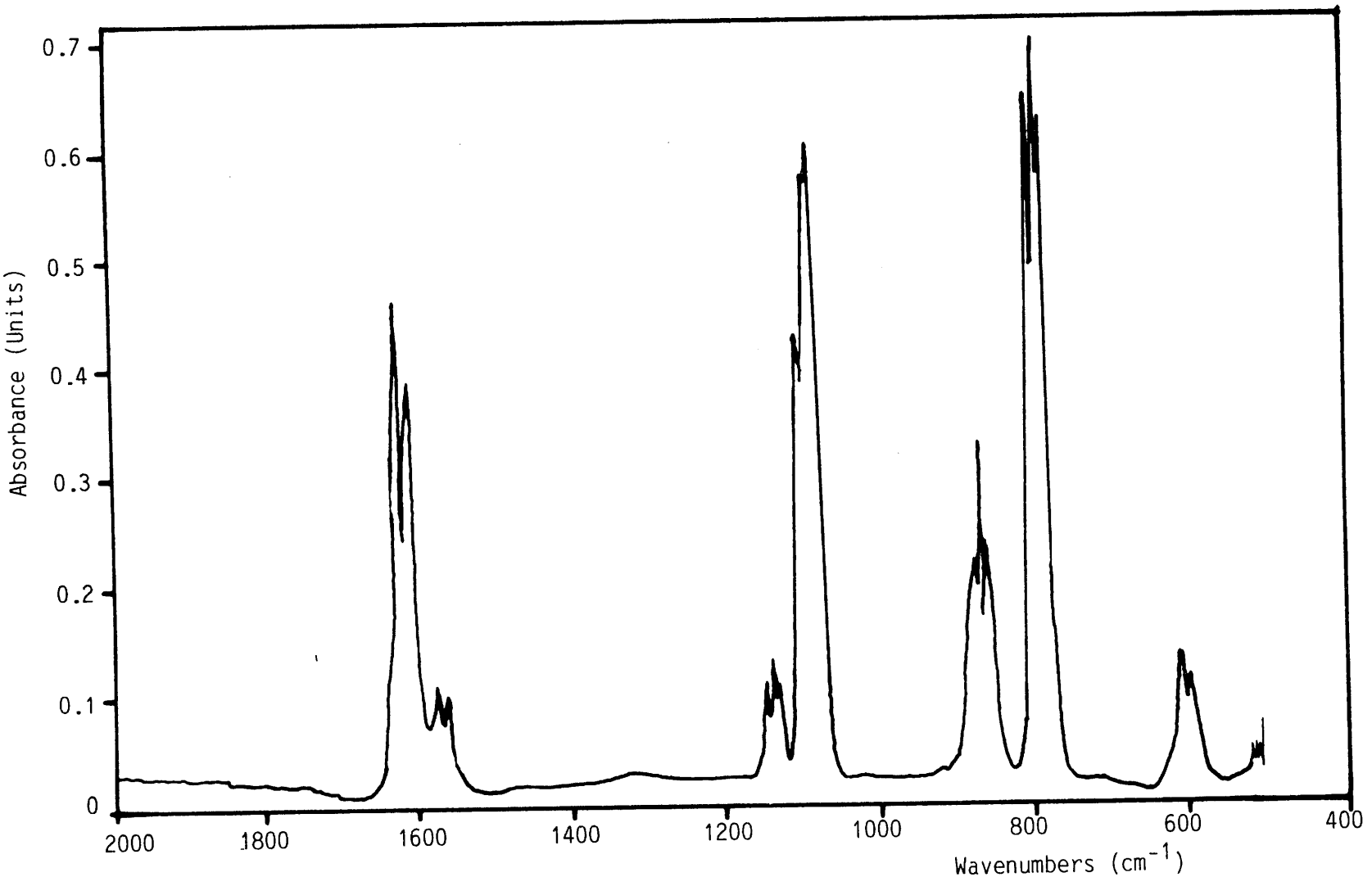


FIGURE 2.VIII. Infra-Red Spectrum of Gaseous Carbon Tetrachloride

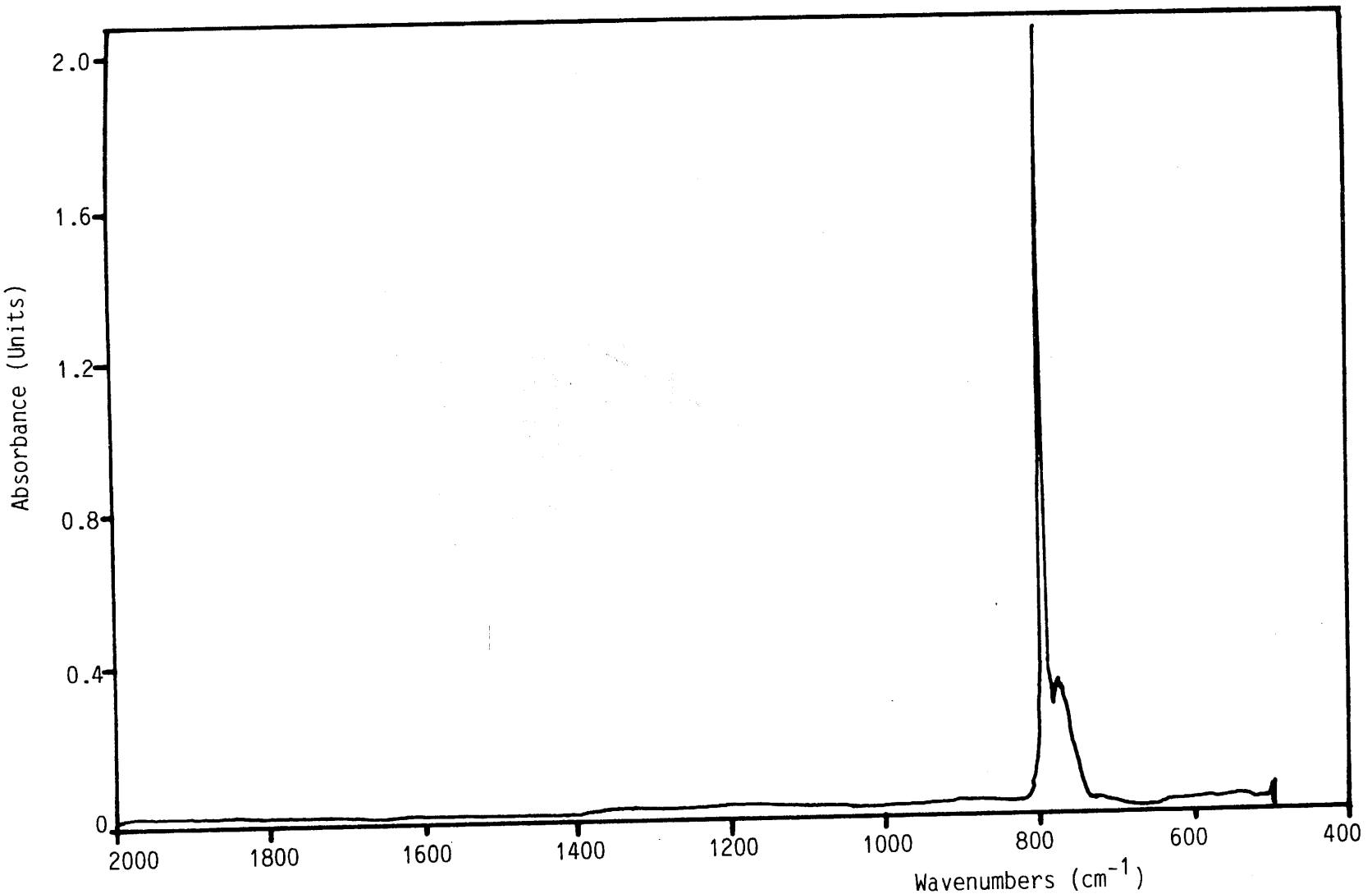
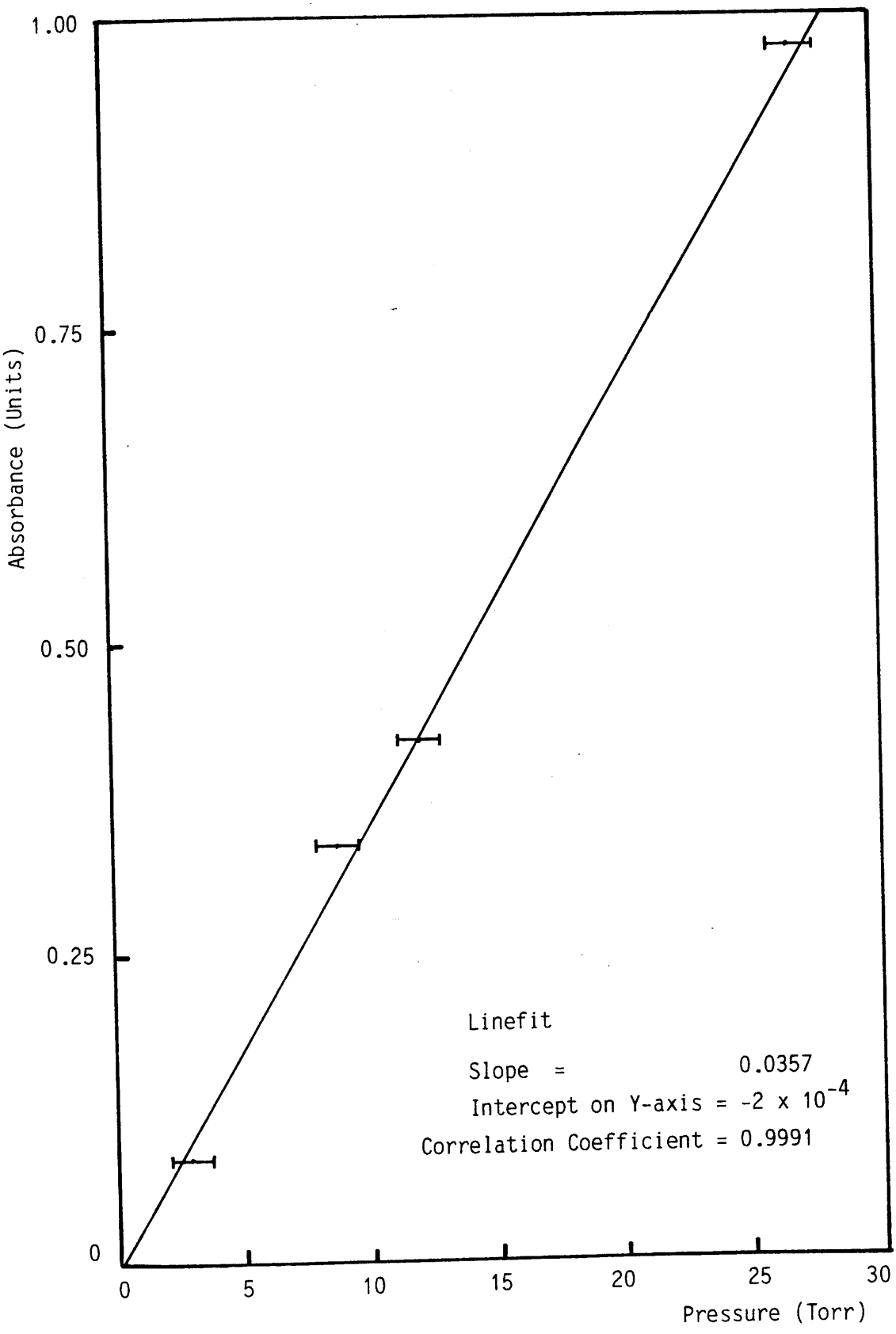


FIGURE 2.IX. Plot of Absorbance vs Pressure for the 1627 cm^{-1} Peak of Gaseous 1,1-Dichloroethene



for HCl under the same conditions was provided by the co-operating body.[88]

2.3.4 Vapour Phase Infra-Red Analysis in Gas/Solid Systems

In studies on the interaction of gases with solids, an ampoule containing a weighed sample of degassed solid was attached to the cell. The cell was evacuated and a desired pressure of gas was isolated in the cell. The cell was placed in the spectrometer beam and the stop-cock on the ampoule was opened. Spectra were collected as required.

2.3.5 Kinetic Analysis of Vapour Phase Infra-Red Data

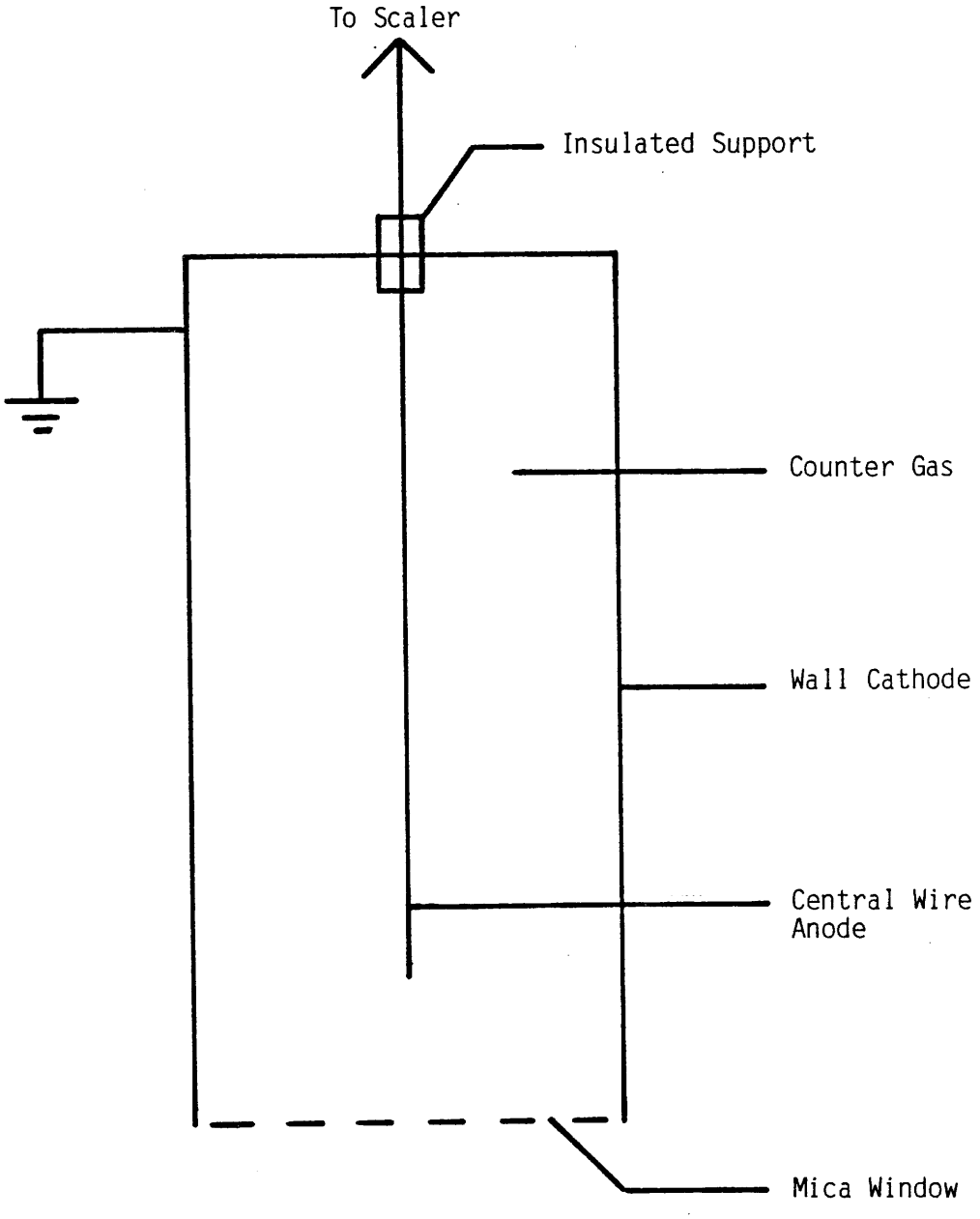
The procedure was identical to that described in 2.3.4. Reaction was initiated when the stopcock on the ampoule was opened, and spectra were collected and stored at one per 18s. for the first 30 min. of reaction (100 spectra) and subsequently one per min until 60 min had elapsed. A program was used to treat these data and to construct, for desired peaks, plots of absorbance/peak area vs time, followed by first and second order kinetic plots.

2.4 Radiochemical Counting Using Geiger-Müller Counters

A Geiger-Müller counter is an earthed metal tube with a thin, gas-tight, mica window at one end and a gas-tight insulated support for a thin central wire at the other (Figure 2.X). The inside wall of the tube forms an enclosed cylindrical cathode and the central wire is an anode. The tube is filled with a gas mixture such as 90% argon/10% methane, and is connected to a scaler.

Ionising radiation (α, β, or γ-radiation) entering the tube causes partial ionisation of the gas, producing positive ions and free

FIGURE 2.X. Geiger-Müller Counter



electrons. The central wire is held at a high positive potential with respect to the wall cathode; hence the electrons formed move rapidly towards the wire and the positive ions drift relatively slowly towards the wall. At high applied voltages, the electrons gain sufficient energy to cause further ionisation as they collide with gas molecules, and the number of electrons collected on the wire becomes greater than the number created by the passage of radiation through the detector gas. This phenomenon is known as ion multiplication and its effect is often called an "electron avalanche".

The Geiger region is reached when the number of electrons produced by ion multiplication per primary electron produced by radiation becomes so great that a given "avalanche" spreads along the entire tube. At this stage the number of electrons collected on the wire, and hence the magnitude of the resultant voltage pulse, is independent of the number of electrons created by the passage of radiation through the detector.

Methane (or alcohol, or ether vapour) is present in the tube to act as a "quench gas". When the positive ions formed by ion multiplication reach the cathode they can cause secondary electron emission from the surface of the wall which can in turn lead to a spurious discharge of the counter. This undesirable effect can be suppressed by the presence of a quench gas which reacts by electron transfer with the positive ions to yield ultimately stable products.

[^{36}Cl]-Chlorine decays by β-emission according to Equation 2.IV and has a half-life of 3×10^5y.

$$^{36}_{17}\mathrm{Cl} \longrightarrow {}^{36}_{18}\mathrm{Ar} + {}^{0}_{-1}\beta \qquad \text{Equation 2.IV}$$

[^{14}C]-Carbon decays by β-emission according to Equation 2.V and has a

half life of 5730y. As the half-lives of these isotopes are long, no decay correction was required. The maximum energies of β-particles

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}\beta \qquad \text{Equation 2.V}$$

(electrons) for these isotopes are 0.714 MeV and 0.155 MeV respectively. The efficiency of the counter is typically <5% for low energy β-emitters such as these, due to the absorption of much of the incident radiation by the mica window.

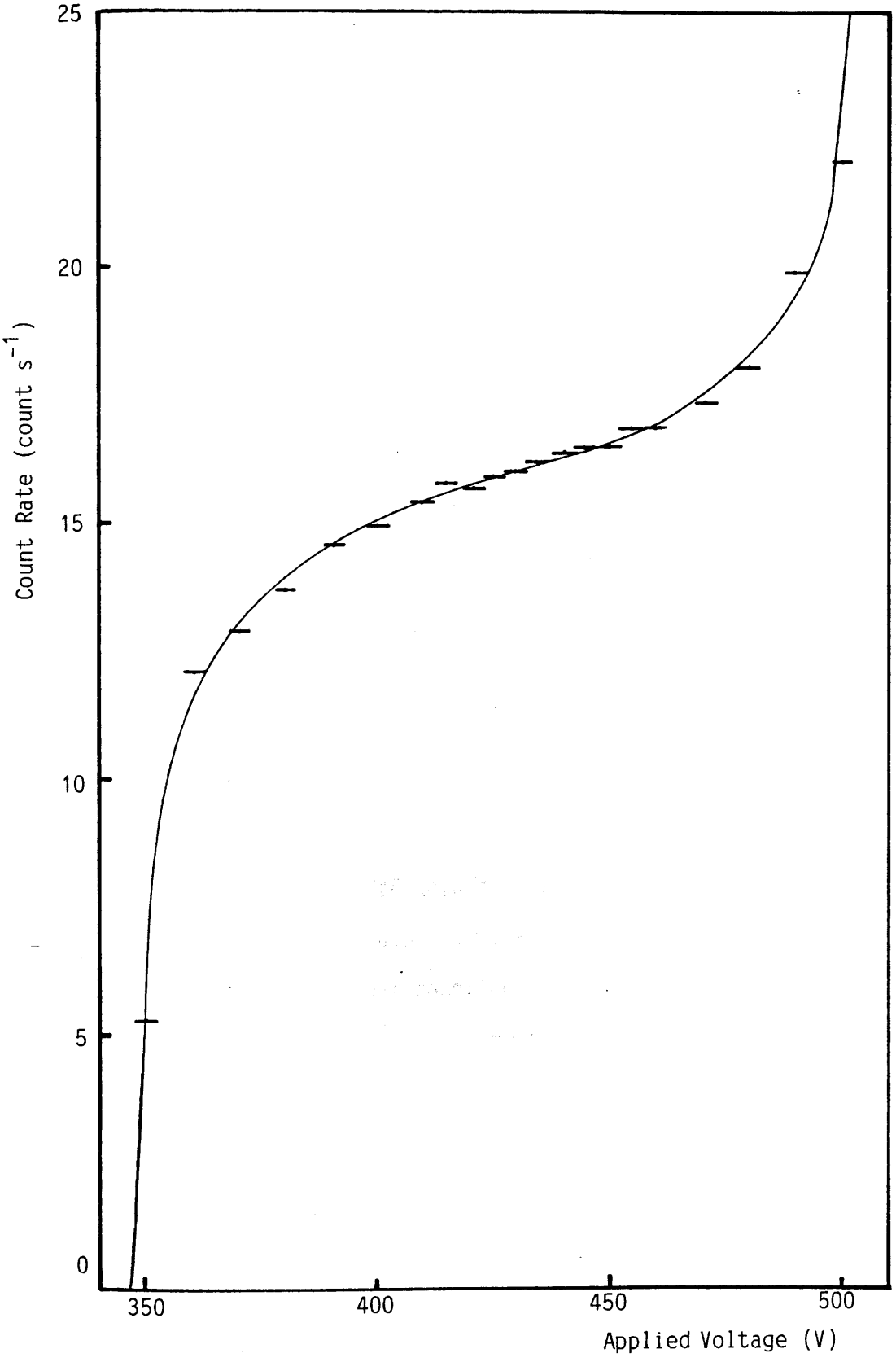
2.4.1 Plateau Curve

The voltage plateau of a Geiger-Müller counter is a region in which the counting rate caused by a given radiation source is approximately independent of applied voltage. It is desirable to work at a voltage which is in the middle of the plateau region. The plateau region was determined for each Geiger-Müller counter used by constructing a plot of counts obtained from a solid [^{14}C]-carbon source *vs* applied voltage. Figure 2.XI shows a typical plateau curve obtained. As the applied voltage was increased above the minimum voltage required to produce ion multiplication, V_o, the count rate increased until the plateau region was reached. As the applied voltage was increased towards the end of the plateau region the count rate began to increase and then increased very steeply. This effect is due to the counter beginning to discharge as the quench gas becomes unable to suppress secondary electron emission at the cathode wall.

2.4.2 Dead Time

The electrons formed in a Geiger-Müller tube reach the central wire very quickly, typically in about 5×10^{-7}s. However, the positive

FIGURE 2.XI. Plot of Counts Obtained from a Solid [^{14}C]-Carbon Source *vs* Applied Voltage



ions formed by ion multiplication remain in the vicinity of the wire for a short time. This sheath of positive ions reduces the voltage gradient below the value necessary for ion multiplication (V_o), and another event cannot be recorded until the positive ions reach the cathode, which typically takes about 3×10^{-4}s. The insensitive period is called the dead time and it is important that a correction is made for the counts lost during the dead time in counting experiments, particularly at high counting rates.

Dead times of Geiger-Müller tubes were determined by counting samples of [^{18}F]-CsF for > 330min [$t_{\frac{1}{2}}(^{18}F)$ = 110 min]. Equation 2.VI is general for radioisotopes. Thus a plot of $\ln A_t$ vs time should be

$$A_t = A_o e^{-\lambda t} \qquad \text{Equation 2.VI}$$

where

λ = decay constant in s^{-1}

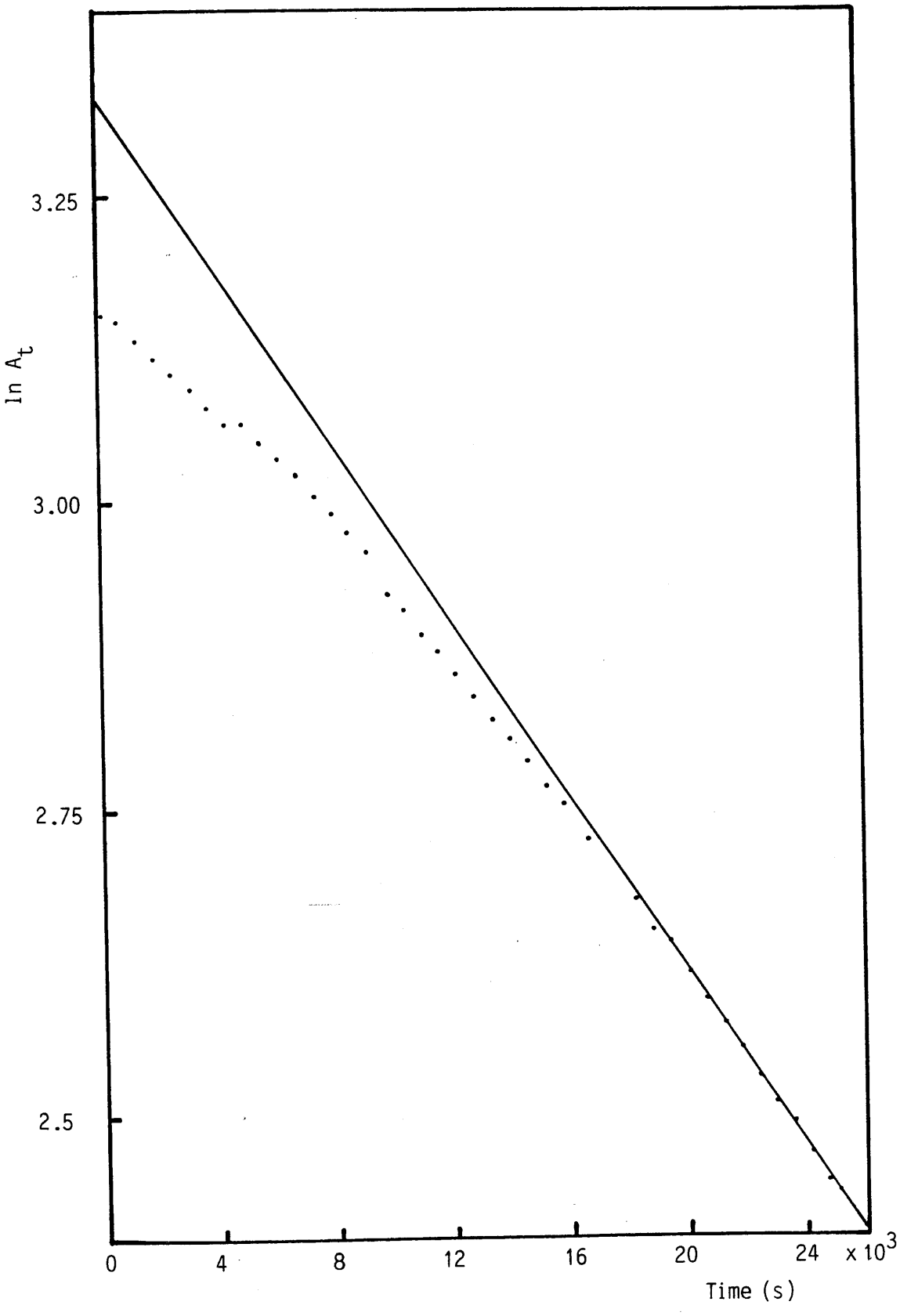
A_t = activity of sample at time t

A_o = activity of sample at time zero

linear with gradient $-\lambda$ and intercept $\ln A_o$. Plots of this type were constructed for the [^{18}F]-CsF counts. Plots obtained were linear at t > 300 min, but showed curvature at t < 300 min which was due to the effect of dead time at higher counting rates (Figure 2.XII). The linear portion of the plot was extrapolated to t = 0. This line gave N_t, the calculated true count rate at any time t, which is related to N_o, the observed count rate at time t, by Equation 2.VII, where τ is the dead time. A program was used to calculate τ from N_t and N_o for

$$N_t = \frac{N_o}{(1-N_o\tau)} \qquad \text{Equation 2.VII}$$

FIGURE 2.XII. Plot of ln A_t vs Time for a Sample of [^{18}F]-CsF (s).



the first twenty points after t = 0,[89] and the mean value of τ was taken to be the dead time of the Geiger-Müller counter.

2.4.3 Background

A Geiger-Müller counter will register some counts in the absence of a radioactive source. In laboratory environments these counts are due primarily to cosmic radiation and radiation from materials used in the construction of the laboratory. An average background count must be subtracted from all counts in radiochemical counting experiments to correct for this effect.

The background registered by a Geiger-Müller counter can be minimised by enclosing the tube and the sample to be counted in a lead walled container, often called a lead castle. The walls are several centimetres thick and the lead shields the tube from a significant fraction of the background radiation. Lead castles are used to count solid radioactive samples.

An important feature of lead castles is the use of a sample holder or tray. This means that the sample to tube distance is fixed, as is the relative geometry of sample and tube. These factors are important in the counting of solid β-emitters, where effects such as self-absorption (see 2.4.4) and self-scattering of β-particles depend not only on β-particle energy but also on the geometrical arrangement of sample and detector.

2.4.4 Self-Absorption

[^{36}Cl]-Chlorine was counted in the solid phase as [^{36}Cl]-AgCl. When counting a solid β-emitter such as [^{36}Cl]-AgCl a correction for the absorption of β-particles within the solid must be made unless all

samples counted are of identical weight. This was done by measuring count rates for different weights (≡ thicknesses) of samples with the same specific count rate. A self-absorption curve was constructed by plotting count rate per mg (counts $s^{-}mg^{-1}$) against weight of [^{36}Cl]-AgCl, and this curve (Figure 2.XIII) was used to standardise all counts obtained in radiochemical counting experiments to a sample weight of 30 mg.

2.4.5 Statistical Errors

Radioactive decay is a completely random process. This means that if a source of constant activity is measured in a way that excludes all other errors in measurement, the number of disintegrations observed in successive periods of fixed duration will not be constant. The probability $W_{(m)}$ of obtaining m disintegrations in time t from N_o original radioactive atoms is given by the binomial expression (Equation 2.VIII) where p is the probability of a disintegration

$$W_{(m)} = \frac{N_o!}{(N_o-m)!\,m!}\, pm\,(1-p)^{N_o-m} \qquad \text{Equation 2.VIII}$$

occurring within the time of observation. From this expression it can be shown that the expected standard deviation for radioactive disintegration, σ is given by Equation 2.IX.[91] In practice, observation time t is short compared with $t_{\frac{1}{2}}$, so λt is small and Equation

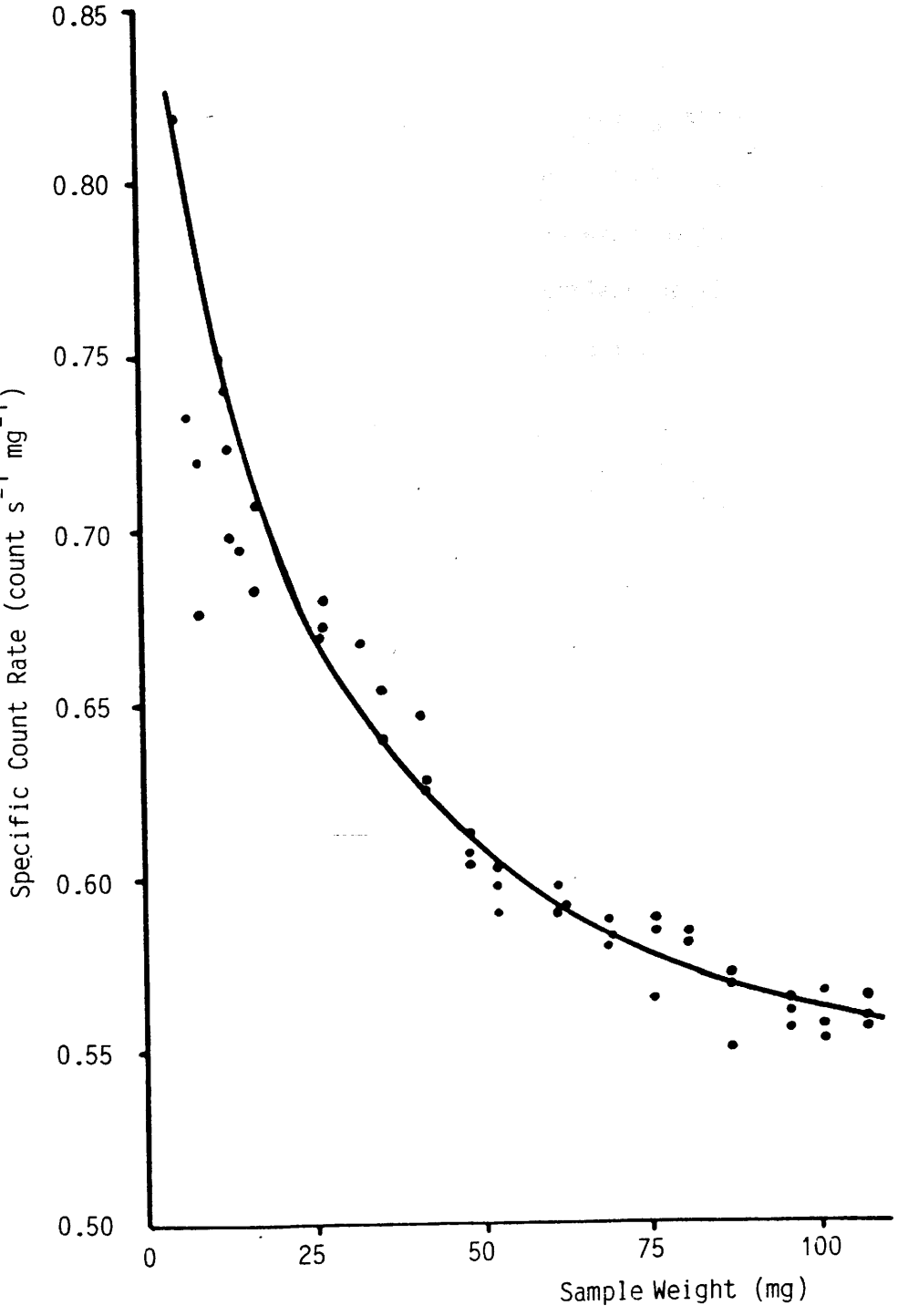
$$\sigma = \sqrt{me^{-\lambda t}} \qquad \text{Equation 2.IX}$$

2.X can be invoked. The error on a result is often quoted as $\pm 2\sigma$

$$\sigma = \sqrt{m} \qquad \text{Equation 2.X}$$

and this convention has been adopted throughout this work. All errors

FIGURE 2.XIII. Self-Absorption Curve for [^{36}Cl]-AgCl



quoted on radiochemical measurements are the combination of the radiochemical error and the uncertainty in physical measurements such as pressure of gas.

2.5 The Direct Monitoring Geiger-Müller Radiochemical Counting Technique

The direct monitoring Geiger-Müller radiochemical counting technique was developed by Thomson, and modified by Al-Ammar and Webb,[91] to determine surface radioactivity on solids exposed to radiolabelled gases. The technique has been successfully used to detect both weakly and strongly adsorbed species in a variety of situations[92] and has proved to be a powerful tool in the elucidation of mechanism in heterogeneous catalysis.

2.5.1 Equipment

The Pyrex reaction vessel (Figure 2.XIV) had two Geiger-Müller tubes, and was connected via a manifold to a constant volume manometer and gas handling facilities. The vessel had a B14 socket (a) for the attachment of an ampoule containing a solid. Inside the vessel was a Pyrex boat (b) which had two sections, each capable of being loaded with a solid, and which could be moved along the length of the vessel by means of a magnet. The whole apparatus was calibrated before use. The Geiger-Müller tubes were intercalibrated regularly. Various pressures of radioactive gas were counted and a plot of counts from Geiger-Müller 2 vs counts from Geiger-Müller 1 was constructed. A straight line was obtained (Figure 2.XV) whose gradient was equal to the counting ratio between the two tubes. This ratio should remain constant and was usually about 1.05.

FIGURE 2.XIV. Pyrex Reaction Vessel Used in Direct Monitoring GM Radiochemical Counting Technique.

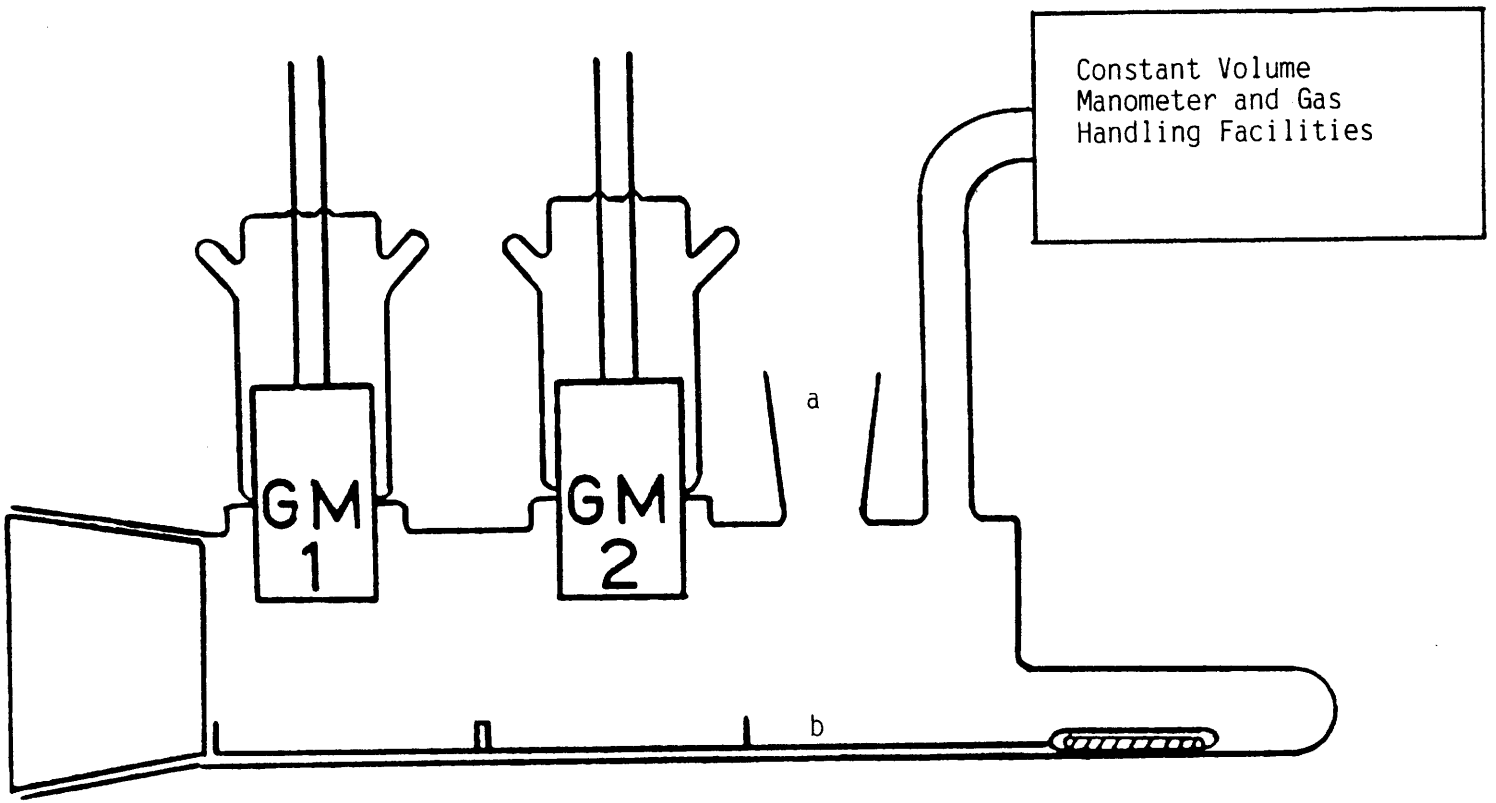
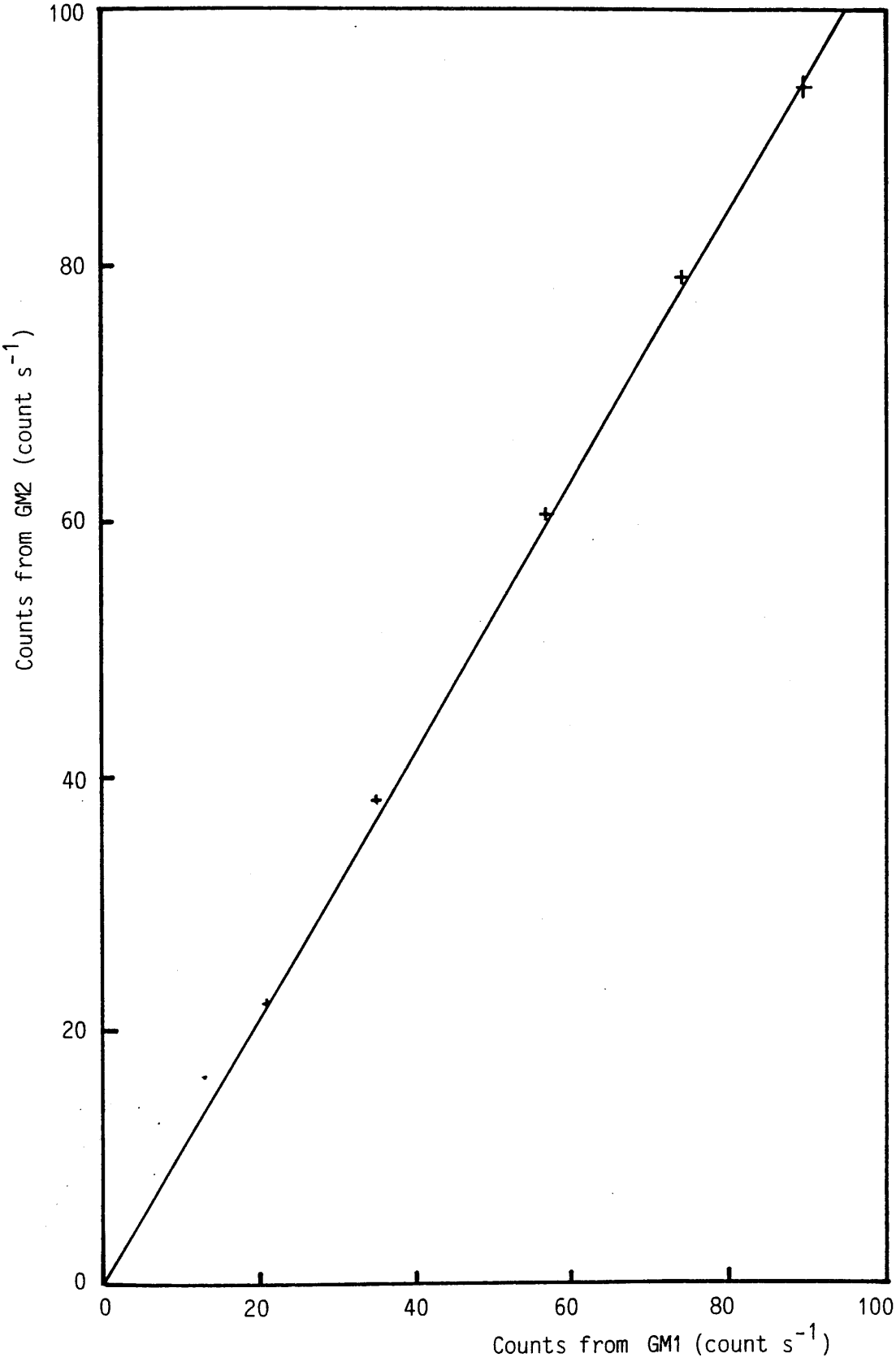


FIGURE 2.XV. Intercalibration of GM Tubes



2.5.2 Application of the Technique to Gas/Solid Systems

The procedure for application of the technique to gas/solid systems was as follows. The reaction vessel was evacuated, flamed out, and a weighed sample of solid was dropped into the left hand portion of the boat. The boat was moved so that the left-hand portion was directly under Geiger-Müller 1, and the empty right-hand portion was directly under Geiger-Müller 2.

An accurately measured amount of radioactive gas of measured specific count rate was admitted at a desired initial pressure to the reaction vessel, and the reaction vessel was isolated from the rest of the system. Counts were taken from both Geiger-Müller tubes with time so that the left hand side counts, from Geiger-Müller 1, were from the gas and solid, whereas the right hand side counts, from Geiger-Müller 2, were from the gas alone. The counts from Geiger-Müller 2, corrected for dead time background and intercalibration, were subtracted from the counts from Geiger-Müller 1, corrected for dead time and background to give values for surface counts. From these values, figures in counts per second were derived and plotted against time.

2.6 Determination of Specific Count Rates of [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride.[93]

[^{36}Cl]-HCl was vacuum distilled onto an excess of a frozen aqueous solution of sodium hydroxide (> 98% pure, Hopkin & Williams), and both were allowed to warm up and react in a closed vessel at room temperature for at least 3 hours. The resultant solution was decanted into a beaker. The vessel was washed out with distilled water and the washings added to the solution in the beaker. The solution was acidified with ten drops of concentrated nitric acid.

Under subdued light, a solution of silver nitrate ($0.22\,mol\,l^{-1}$, > 98% pure, Johnson Matthey Chemicals) was added with stirring until precipitation of AgCl was judged to be complete. The precipitate was allowed to settle and a few more drops of silver nitrate were added. The suspension was heated on a hotplate nearly to boiling point with occasional stirring and digested until the precipitate coagulated. The beaker was removed from the hotplate and the precipitate allowed to settle. The beaker was set aside in a dark cupboard for at least one hour.

A sintered glass crucible (porosity 4) was dried to constant weight at $150^{o}C$. The precipitate was filtered with very dilute nitric acid (approximately one part concentrated nitric acid to one thousand parts distilled water) and washed in the crucible with very dilute nitric acid until 3 ml of the washings gave no turbidity with dilute hydrochloric acid. The crucible and precipitate were dried to constant weight at $150^{o}C$. $[^{36}Cl]$-HCl was converted to $[^{36}Cl]$-AgCl with an efficiency >96%.

Accurately weighed portions of $[^{36}Cl]$-AgCl obtained were counted using a Gieger-Müller tube in a lead castle for periods of time sufficient to accumulate significant (10^{4}) counts.

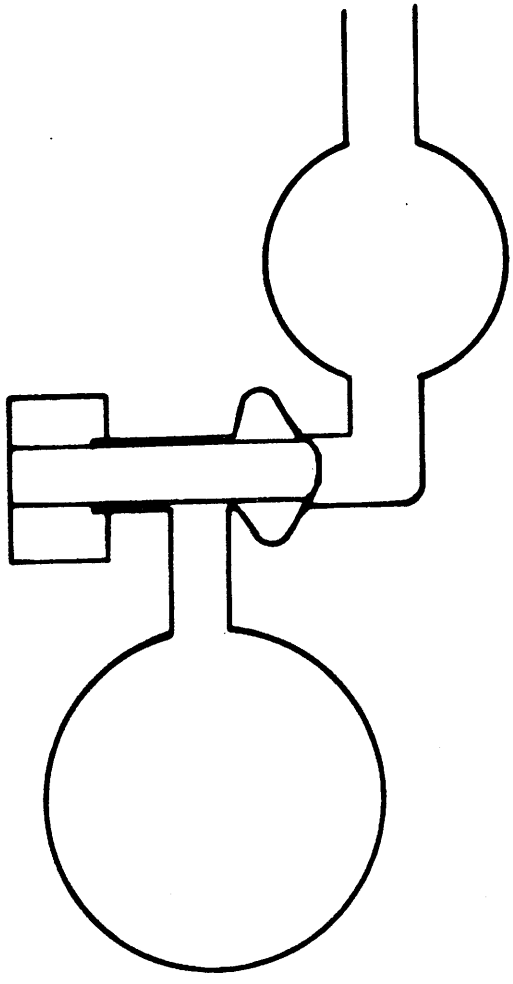
2.7 Pressure Measurement Studies

2.7.1 Equipment

The vacuum system used in these studies was an enclosed 316 stainless steel structure which consisted of a manifold and several pressure transducers. The line was evacuated to a pressure of 10^{-5} Torr using an identical pumping system to that described in 2.1.1.

A vessel was designed (Figure 2.XVI) so that, when connected

FIGURE 2.XVI. Vessel Used in Pressure Measurement Studies



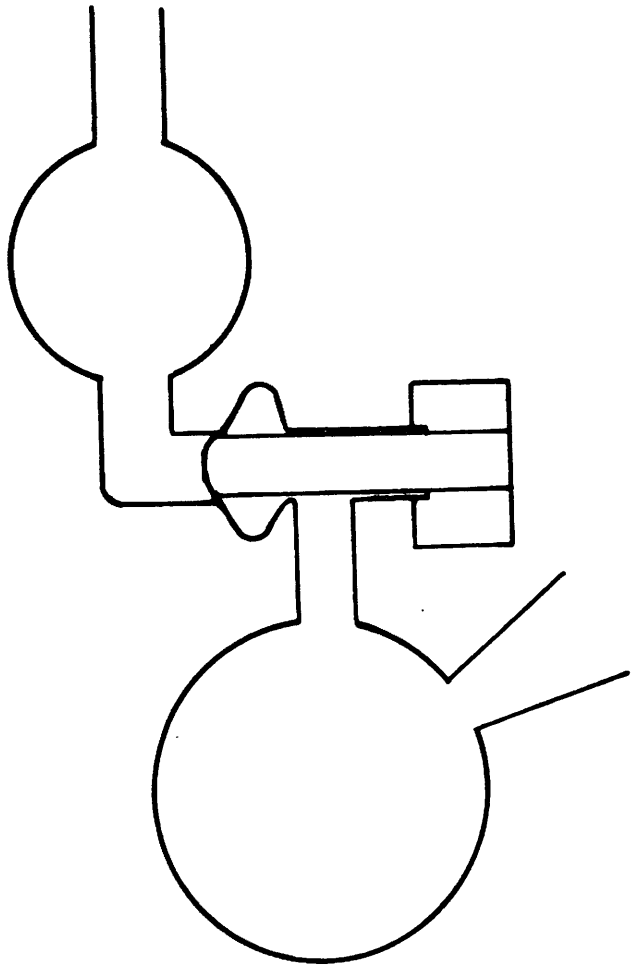
to the vacuum system, the dead space was of a very similar volume to the lower part of the vessel. Hence, when a gas was isolated in the dead space with the lower section evacuated, opening of the high vacuum stopcock (J. Young) would decrease the pressure by a factor of 2. The reaction vessel and dead space were volume calibrated before use. Temperature readings were obtained from a thermocouple attached to the outside of the vessel. Pressure readings (in Torr) were obtained from a pressure transducer inside the dead space. A modified reaction vessel (Figure 2.XVII) was designed, the only difference being the inclusion of a B14 socket to which a septum cap could be attached for syringe gas sampling.

Data collection was microprocessor controlled and hard copy was obtained in the form; Time, Temperature, Pressure and Pressure Increment. The maximum rate of data collection was one reading per 3s.

2.7.2 Application of the Technique to Gas/Solid Systems

The reaction vessel was weighed, loaded with a sample of solid, reweighed, attached to the vacuum system and pumped overnight. A desired pressure of gas was admitted to the dead space and data collection was initiated at the maximum rate. The stopcock on the vessel was opened and data were collected at the maximum rate for 10 min, then at one per min for a further 30 min and finally at one per 5 min until no further change in pressure was detectable. Normally a reaction was followed for 5h.

FIGURE 2.XVII. Modified Vessel Used in Pressure Measurement Studies.



CHAPTER 3

CHAPTER 3

Infra-Red Spectroscopic Studies of the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

3.1 Introduction

Aluminium (III) chloride is known to catalyse the dehydrochlorination of 1,1,1-trichloroethane to give 1,1-dichloroethene and hydrogen chloride (Equation 3.I). Although aluminium (III) chloride is not used industrially to effect transformations of 1,1,1-trichloroethane, the dehydrochlorination is relevant to the degradation of 1,1,1-trichloroethane based solvents used in the large scale vapour degreasing of aluminium. The conditions for the reaction are such that a mixture of solid and dissolved aluminium (III) chloride and liquid and gaseous 1,1,1-trichloroethane is present. Kulikova's product analyses of the reactions of 1,1,1-trichloroethane and 1,1-dichloroethene with aluminium (III) chloride were conducted under similar conditions.[81,82] However, Willard suggested that, in many reactions, an aluminium (III) chloride surface was required for catalytic activity to be observed.[49,50]

$$CH_3CCl_3 \overset{AlCl_3}{\rightleftharpoons} CH_2{=}CCl_2 + HCl \qquad \text{Equation 3.I}$$

The vapour phase in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride was studied in the present work using infra-red spectroscopy to determine the stoichiometry and time dependence of the reaction. Fourier Transform infra-red spectroscopy was a particularly useful tool, as the rates of collection and storage of spectra meant that kinetic treatments were possible,

and computed spectral subtraction techniques could be used. However, it was not normally possible to study the solid in this reaction using conventional infra-red spectroscopic techniques, and investigations of the solid are reported in Chapter 8.

3.2 Results

3.2.1 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride

When cell A (described in 2.3.1) was used, the results obtained were reproducible. A vapour phase infra-red spectrum collected before the stopcock of the ampoule was opened showed 1,1,1-trichloroethane only (Figure 3.I). A spectrum collected 5 min after the stopcock was opened showed 1,1,1-trichloroethane (absorbances of peaks greatly reduced compared to Figure 3.I), 1,1-dichloroethene and hydrogen chloride (Figure 3.II). GCIR, GCMS and computed subtraction of a standard 1,1-dichloroethene spectrum from Figure 3.II were used to show that carbon tetrachloride was present at this stage. A spectrum collected after 60 min showed that the absorbances of peaks due to 1,1,1-trichloroethane had decreased, the absorbances of peaks due to 1,1-dichloroethene had decreased, the absorbances of peaks due to hydrogen chloride had increased and carbon tetrachloride was present (Figure 3.III). A spectrum collected 90 min after the stopcock was opened was identical to Figure 3.III. Experiments carried out using cell B led to the detection of 1,1-dichloroethene only if the solid was allowed to fall near the beam.

The aluminium (III) chloride, which was initially a white, free-flowing powder (Photo 3.I), turned bright purple when the stopcock was opened (Photo 3.II). If the gaseous 1,1,1-trichloroethane was allowed to stand in contact with the solid, the colour deepened

FIGURE 3.I. Vapour Phase Infra-Red Spectrum Collected Before Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride was Initiated.

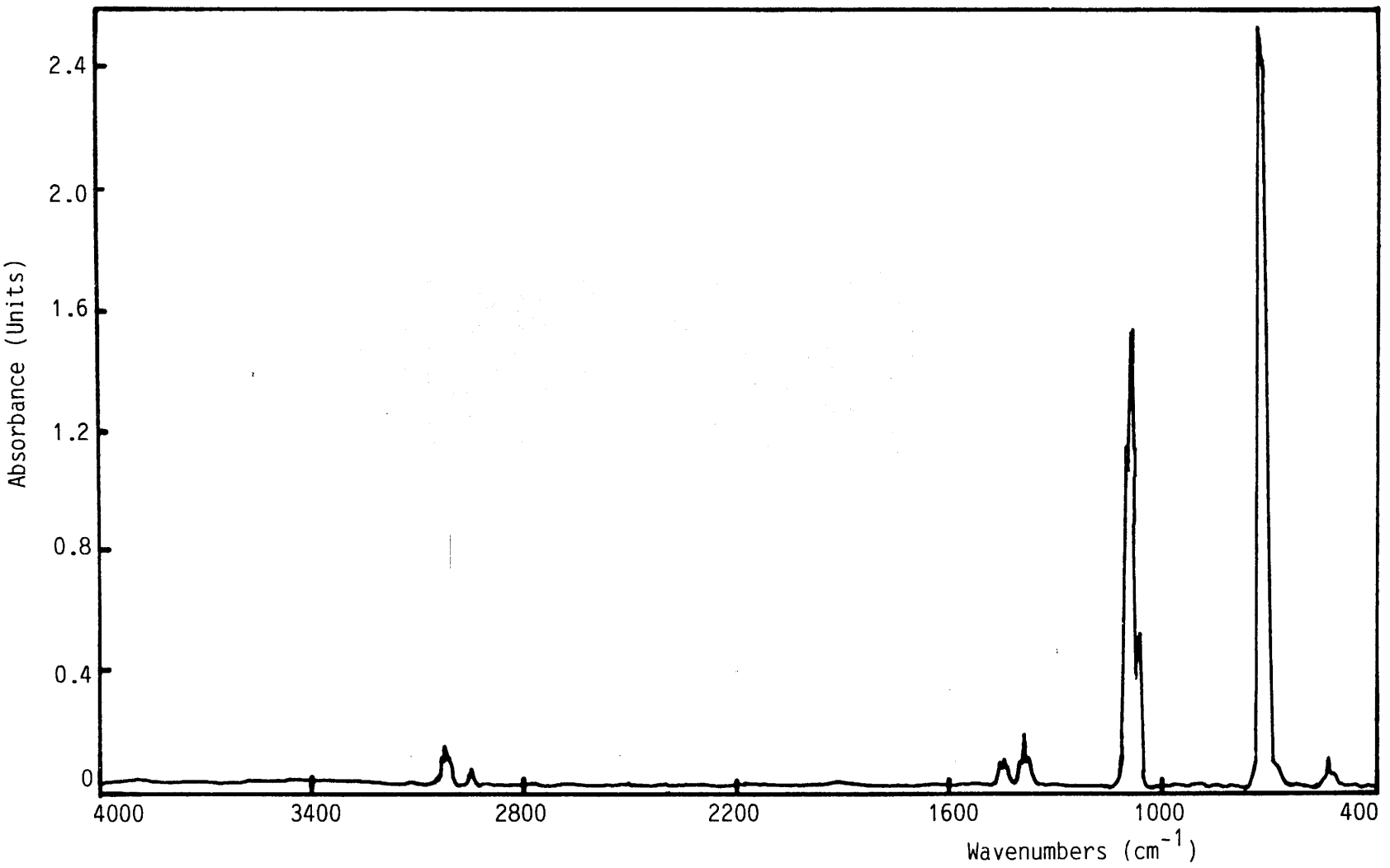
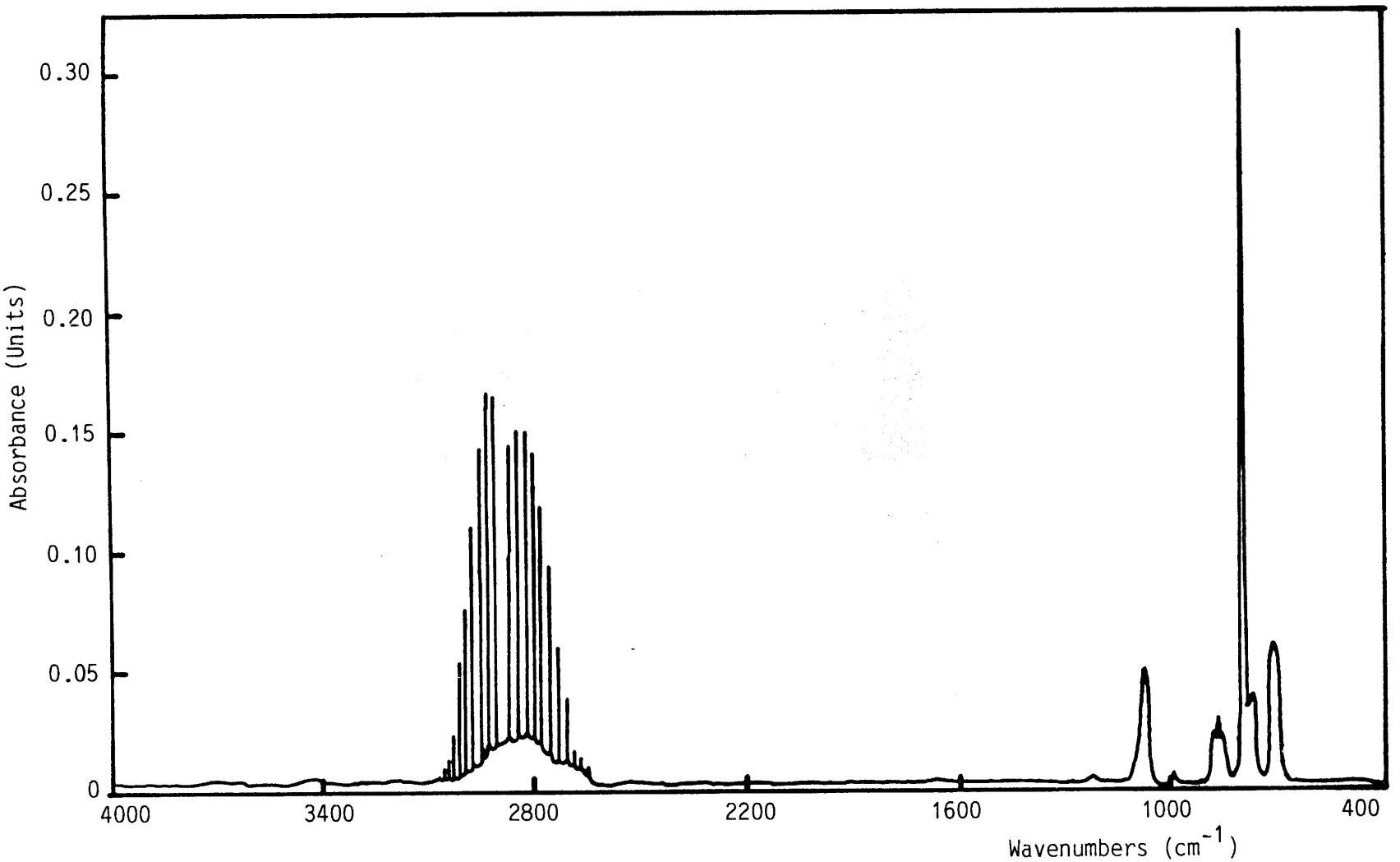


FIGURE 3.III. Vapour Phase Infra-Red Spectrum Collected at t = 60 min in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.



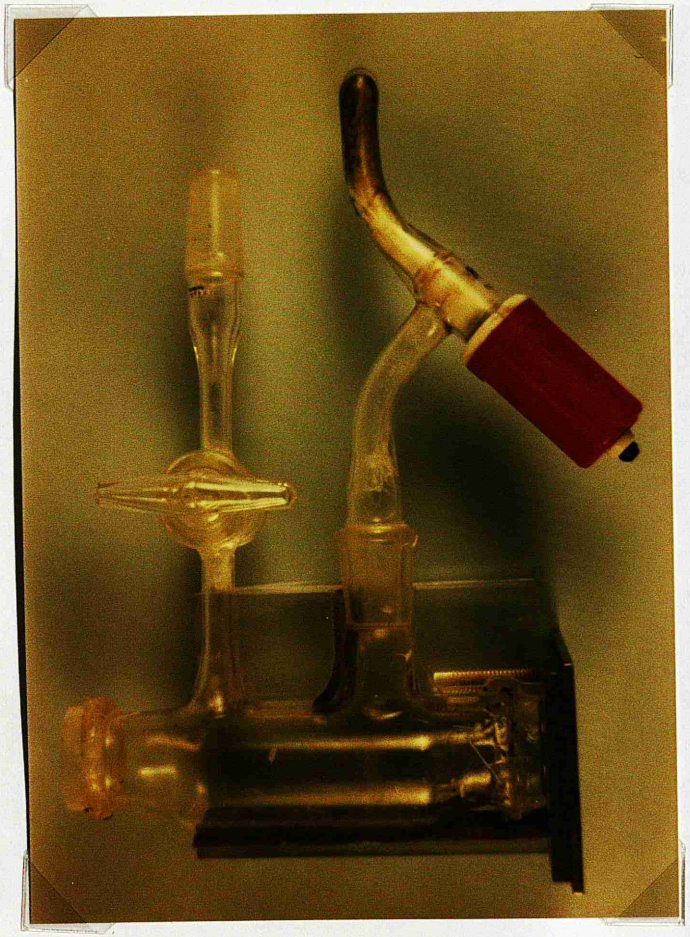


Photo 3.I

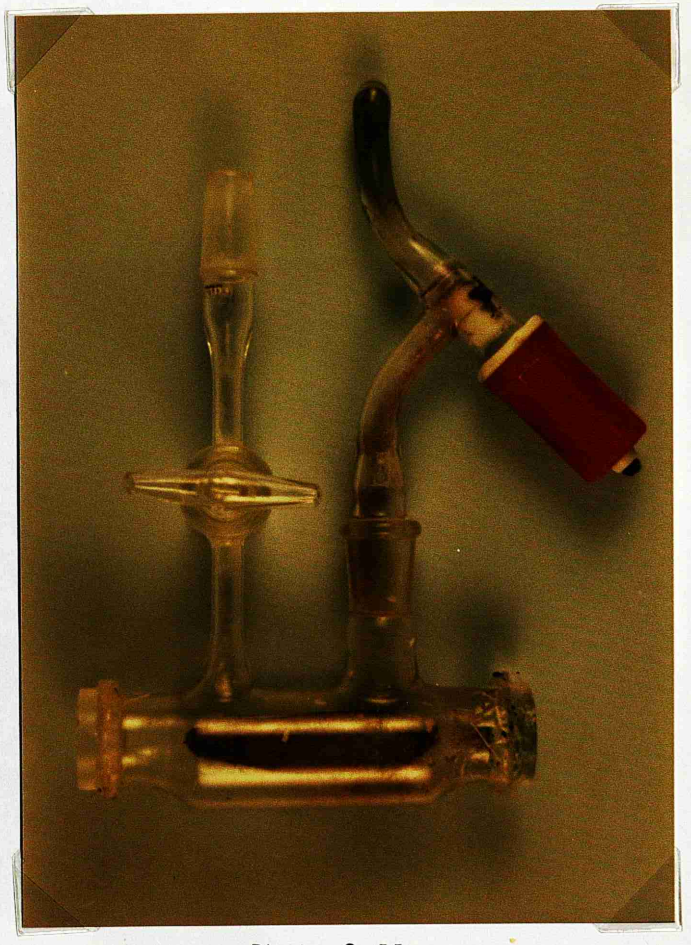


Photo 3.II

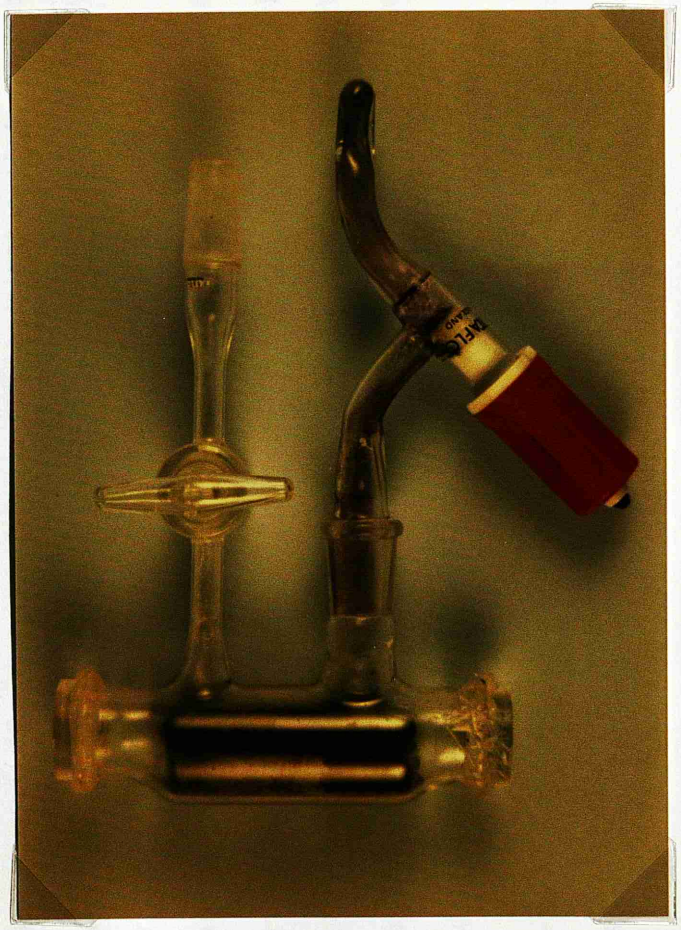


Photo 3.III

over 60 min until the solid had an almost black, lustrous, tarry appearance (Photo 3.III). If the gaseous 1,1,1-trichloroethane was removed by pumping within 5 min of the start of reaction, some of the colour was discharged.

If the cell windows became contaminated with the purple solid, several additional peaks were observed in the infra-red spectrum. These peaks did not vary in intensity with time and were not removed by evacuation of the cell, which suggested that they were due to the solid. The peak positions (in cm^{-1}) and relative intensities were:-

2965(w), 2900(w), 1400(m), 1268(s), 1082(s), 810 (shoulder 840,s), 690 (shoulder 680,m), 665(m), 640(m), 630(m), 580(m) and 480(m).

These results indicate strongly that reactions other than the expected dehydrochlorination occur when gaseous 1,1,1-trichloroethane reacts with solid aluminium (III) chloride. Although the pressure of 1,1,1-trichloroethane decreased during the course of the reaction and the expected dehydrochlorination products were detected, the pressure of 1,1-dichloroethene also decreased during the course of the reaction. This suggests that the 1,1-dichloroethene produced by dehydrochlorination of 1,1,1-trichloroethane reacts further. The observation that 1,1-dichloroethene was detected only when the solid was near the spectrometer beam indicates that the 1,1-dichloroethene produced does not diffuse from the vicinity of the solid in detectable quantities. This suggests that the 1,1-dichloroethene produced is rapidly consumed in a reaction occurring at the solid surface.

The detection of gaseous carbon tetrachloride indicates that C-C bond cleavage must take place. There have been no reports of the detection of carbon tetrachloride or other C-C bond fission products

in the solution reaction of 1,1,1-trichloroethane with aluminium (III) chloride. However, the aluminium (III) chloride catalysed alkylation of 1,1,2,3,4,5,5-heptachloropentene by CCl_4 (Equation 3.II) is reversible,[94] and C-C bond fission has been reported as a side reaction in

$$CCl_4 + CCl_2{=}CClCHClCHClCHCl_2 \rightleftharpoons[AlCl_3] CCl_3CCl_2CCl_2CHClCHClCHCl_2$$

Equation 3.II

alkane isomerisations[57] and olefin polymerisations[68] catalysed by aluminium (III) chloride. There was no evidence from the spectra obtained, or from GCIR or GCMS studies, for gaseous methane, methyl chloride or any other C-C fission product, which may mean that the species co-produced with carbon tetrachloride is not volatile.

The generation of tarry coatings on solid aluminium (III) chloride in heterogeneous reactions with organic compounds has often been reported,[50,58] and is usually attributed to polymerisation of the organic species. Also, 1,1-dichloroethene is known to polymerise in the presence of $ZnCl_2$[95] which is considered a poorer Lewis acid than aluminium (III) chloride. The strong purple colour of the solid obtained in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride may be analogous to the strong red and purple colours which were reported for solutions of aluminium (III) chloride in 1,1,1-trichloroethane and 1,1-dichloroethene.[82] The observation that some of the colour can be discharged from the solid by pumping away the reactant gas in the early stages of reaction suggests that the colour could arise in part from a weakly bound surface species.

The spectrum obtained if the cell windows became contaminated with the purple solid suggests that the solid contains organic species. The detection of two bands in the region 2980-2850 cm^{-1} is usually

attributed to the C-H stretching modes of a saturated organic species. Bands in the region 1400-1050cm^{-1} can be attributed to $\rangle$C-H deformation modes of saturated organic species, and bands in the region 800-600cm^{-1} can be attributed to C-Cl stretching modes. It would appear that at least some of the peaks observed are due to a saturated, chlorine containing, organic species, the identity of which is investigated further in Chapter 8.

3.2.2 Infra-Red Spectroscopic Analysis of Vapour Phase Over Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

When gaseous 1,1,1-trichloroethane was allowed to react with solid aluminium (III) chloride for 90 min and the volatile material was then removed from the cell by pumping, a spectrum collected 5 min after removing the volatile material showed 1,1,1-trichloroethane, carbon tetrachloride and hydrogen chloride (Figure 3.IV). A spectrum collected 5 min later showed the same species (Figure 3.V). The absorbances of the hydrogen chloride peaks had increased compared to Figure 3.IV. A spectrum collected after a further 10 min was identical to Figure 3.V. If the cell was subsequently evacuated and closed, a spectrum collected 5 min after the cell was closed showed hydrogen chloride only (Figure 3.VI). A spectrum collected after a further 5 min was identical to Figure 3.VI.

The results indicate that hydrogen chloride is emitted by the purple solid formed by the reaction of gaseous 1,1,1-trichloroethane with aluminium (III) chloride. This implies that a reaction which yields hydrogen chloride continues to take place after gaseous 1,1,1-trichloroethane is removed from the system. The production of gaseous 1,1,1-trichloroethane and carbon tetrachloride could have several explanations. Firstly, a reaction which yields these

FIGURE 3.IV. Vapour Phase Infra-Red Spectrum Collected 5 min After Removing the Volatile Material from the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

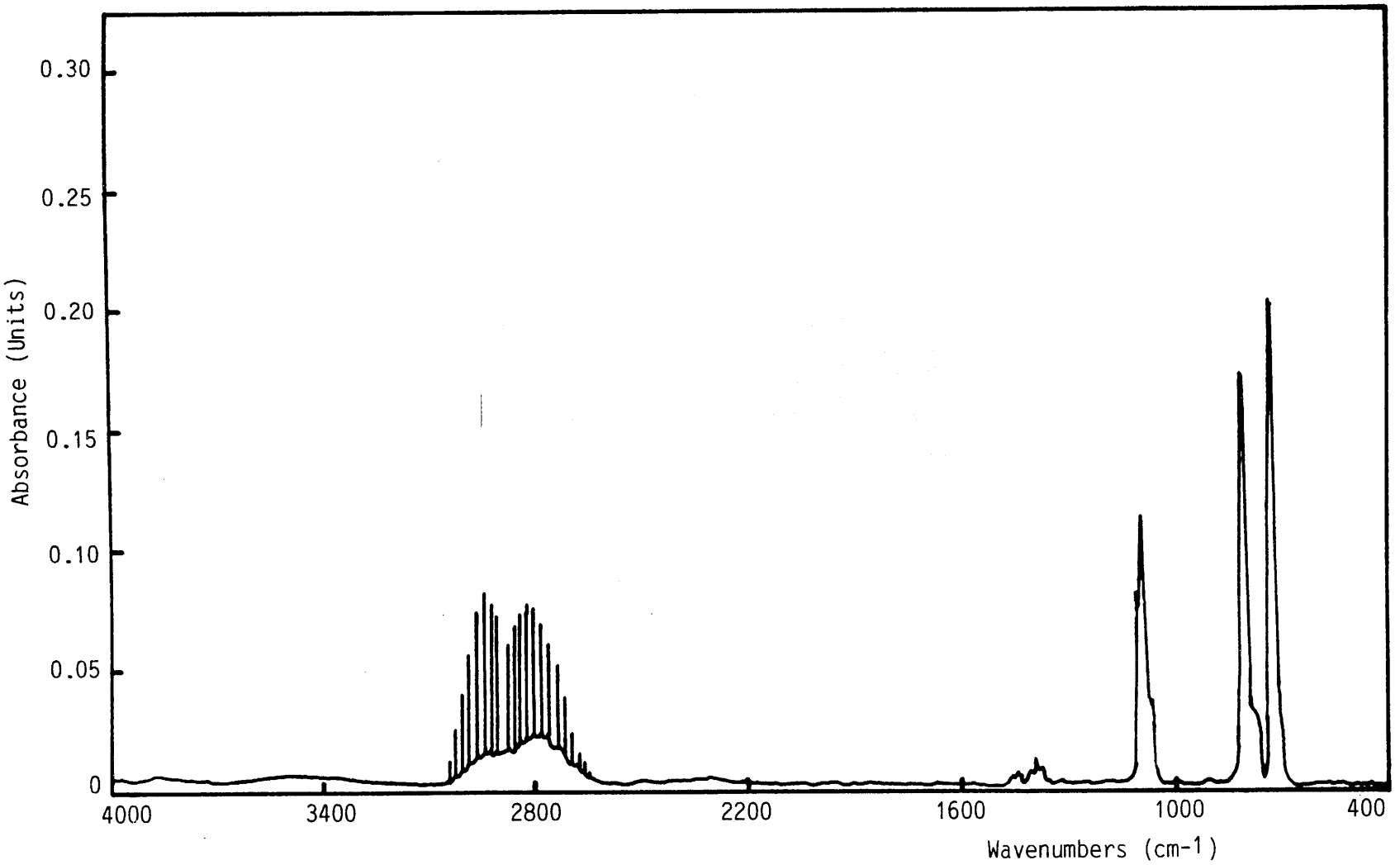


FIGURE 3.V. Vapour Phase Infra-Red Spectrum Collected 10 min After Removing the Volatile Material from the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

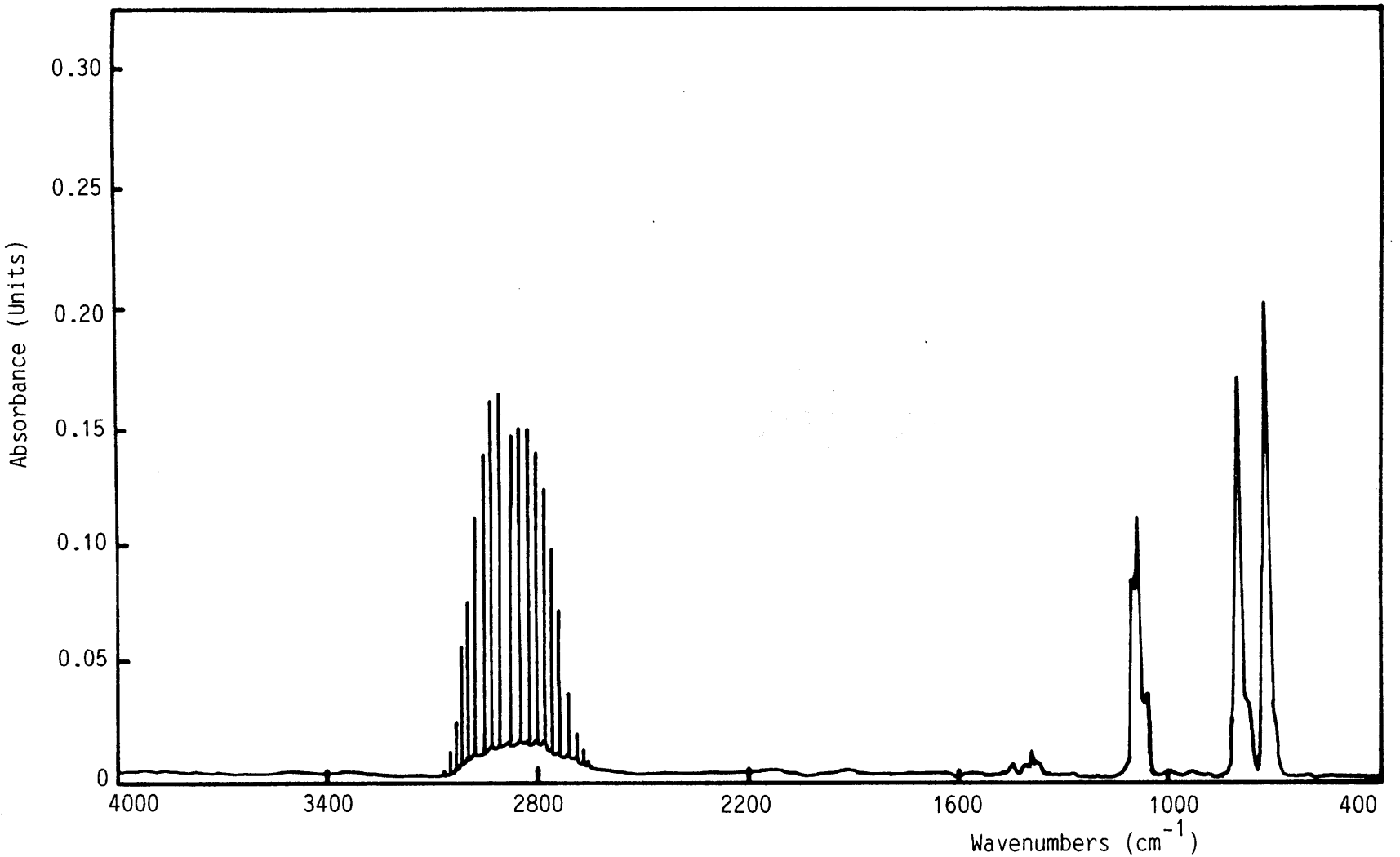
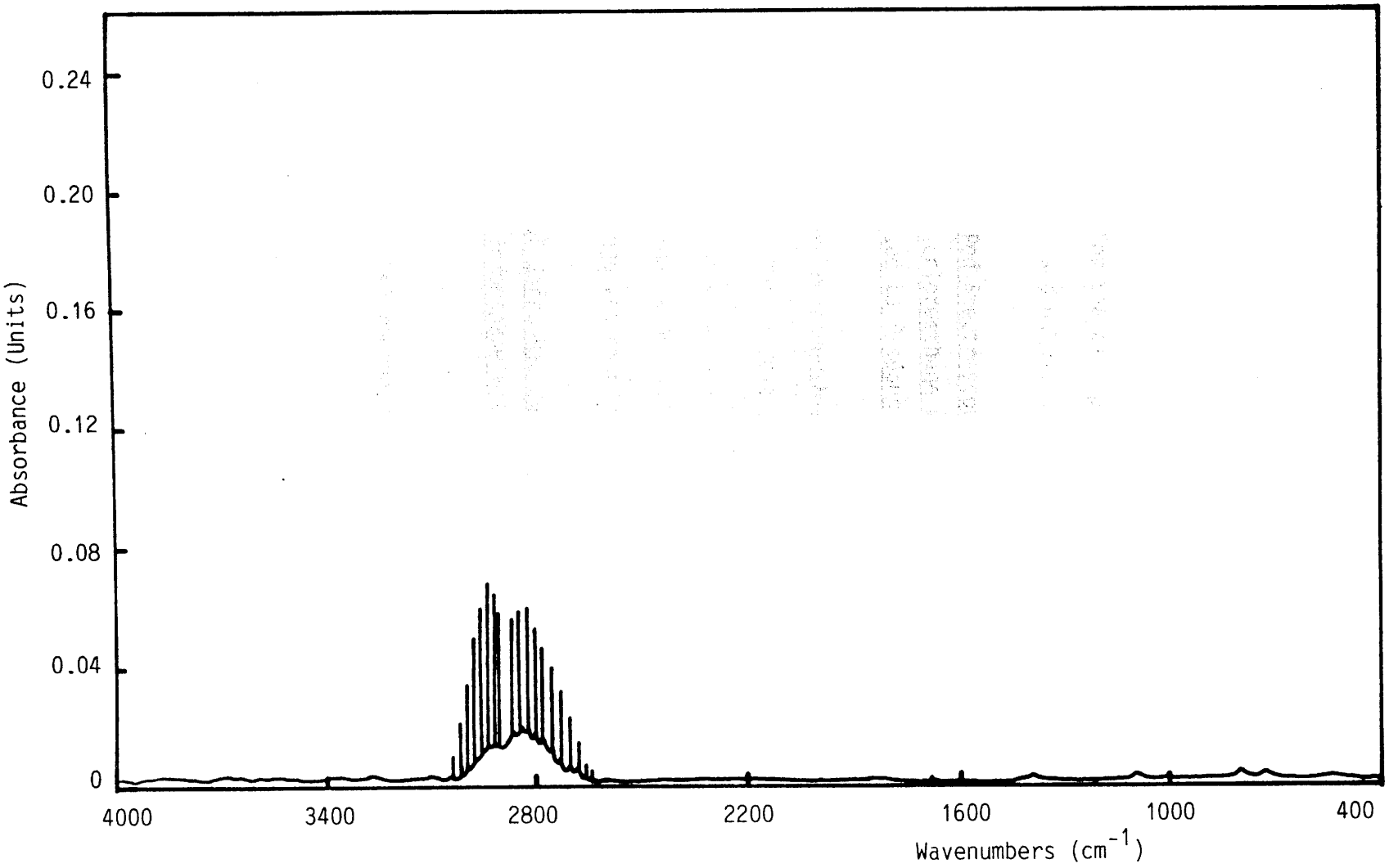


FIGURE 3.VI. Vapour Phase Infra-Red Spectrum Collected 5 min After Evacuation of Cell.



chlorohydrocarbons could continue to take place for a short time after the reactant gas is removed. Secondly, desorption of 1,1,1-trichloroethane and carbon tetrachloride from the solid could explain the observation. This may be an unlikely explanation, since the surface area of aluminium (III) chloride is expected to be small on the basis of geometric considerations. Thirdly, desorption of these species from the glass walls of the cell could account for the observation. Further evidence for the adsorption of these species on glass is described in 7.2.1 and 6.2.1.

3.2.3 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1,1-Trichloroethane with Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane

The observations were reproducible and qualitatively identical to those obtained in 3.2.1. This result suggests that a steady state is attained in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride, since 1,1,1-trichloroethane was still present when no further change was observed in 3.2.1.

3.2.4 Kinetic Treatment of Infra-Red Data from the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride

In even the simplest heterogeneous catalytic dehydrohalogenation of the type shown in Equation 3.III, the overall rate depends upon the relative rates of five distinct processes, any of which may

$$X - CH_2CH_3 \rightleftharpoons C_2H_4 + HX \qquad \text{Equation 3.III}$$

be rate determining. These are:

(i) mass transport of the reactant to the solid surface.

(ii) adsorption of the reactant at the surface.

(iii) reaction of adsorbed species at the surface, with the possibility of more than one bond breaking/forming step.

(iv) desorption of products.

(v) mass transport of products away from the surface.

Results reported in 3.2.1, 3.2.2 and 3.2.3 illustrate that the reaction of gaseous 1,1,1-trichloroethane with aluminium (III) chloride is not a simple dehydrochlorination. At least five factors must be considered. These are:

(a) 1,1-dichloroethene produced by dehydrochlorination appears to take part in further reaction with the solid. This may involve aluminium (III) chloride catalysed oligomerisation or polymerisation of 1,1-dichloroethene.

(b) An involatile organic product is formed, the nature of which appears to change during the course of the reaction. The presence of this product could alter the number and nature of reactive sites on the solid, or provide another phase in which reaction can occur. This product may also provide a barrier through which reactants or products must diffuse, and this may affect the rates of processes (i) and (v) above.

(c) Hydrogen chloride is produced in the reaction and may modify the reactive sites by adsorption leading to either blocking of active sites or formation of different active sites.

(d) A C-C bond fission reaction occurs, possibly as a result of a reaction at the surface.

(e) It would be unusual if water were not present in some form on the aluminium (III) chloride surface, and it may be involved in the reactions.

The interpretation of time dependences in this reaction would be expected to be difficult, particularly in a closed system where the volatile products were not removed and the potential for the attainment of a steady state existed. However, the results of these studies were reproducible. The plots used as examples relate to the same experiment (B6 in Table 3.VII).

When gaseous 1,1,1-trichloroethane reacted with solid aluminium (III) chloride, the pressure of 1,1,1-trichloroethane (as represented by the absorbance of the 1385 cm^{-1} peak in Figure 3.VII) showed a large decrease during the first 1000s. A small decrease towards an apparent constant pressure was observed over the ensuing 2500s.

Gaseous 1,1-dichloroethene was detected in the first spectrum collected. The pressure of 1,1-dichloroethene (represented by the absorbance of the 1627 cm^{-1} peak in Figure 3.VIII) increased to a maximum, typically in 500s, before decreasing over the ensuing 3000s towards an apparent constant pressure. Table 3.I shows the initial quantities of reactants and the time at which the maximum pressure of 1,1-dichloroethene was observed. There appears to be an inverse relationship between the initial quantity of gaseous 1,1,1-trichloroethane and the time at which the maximum pressure of 1,1-dichloroethene is observed.

Gaseous hydrogen chloride was detected in the first spectrum collected. The pressure of hydrogen chloride (as represented by the absorbance of the 2821cm^{-1} peak) increased during the course of the experiment as shown in Figure 3.IX.

An absorption at ca 795cm^{-1} was detected in the first spectrum collected. The absorbance of this peak increased during the course

FIGURE 3.VII. Plot of Absorbance vs Time for the 1385 cm^{-1} Peak of 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

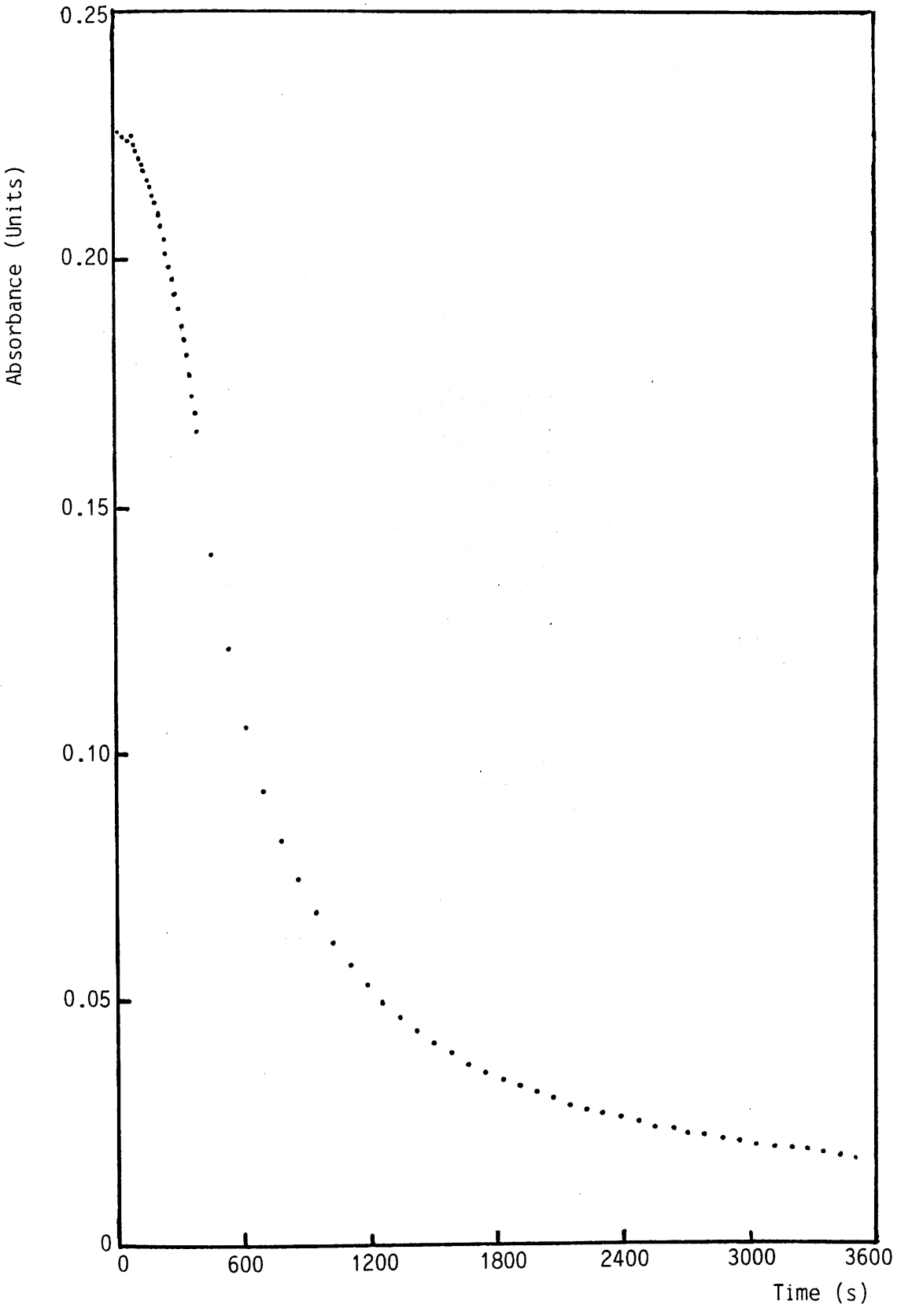


FIGURE 3.VIII. Plot of Absorbance vs Time for the 1627 cm^{-1} Peak of 1,1-Dichloroethene in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

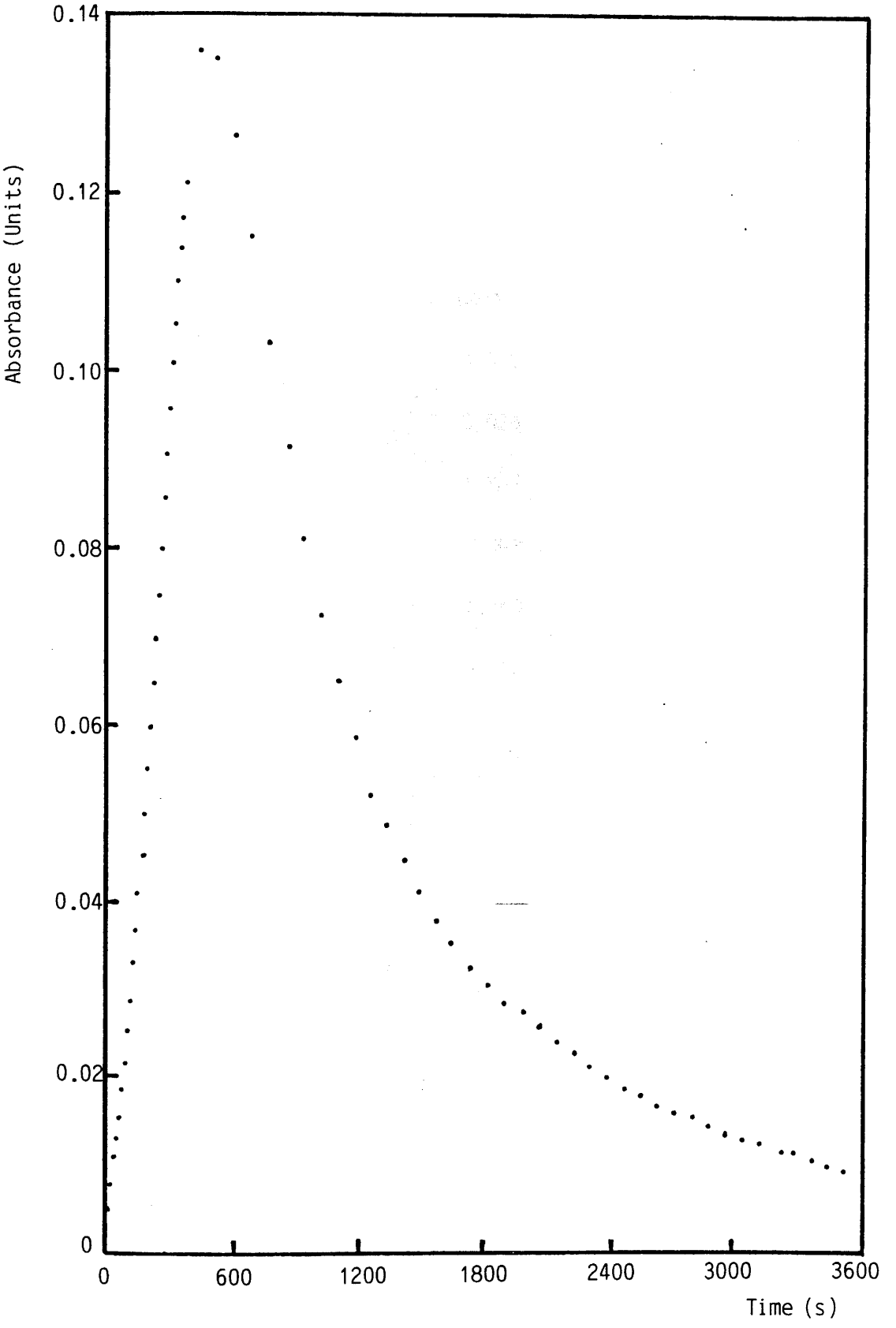
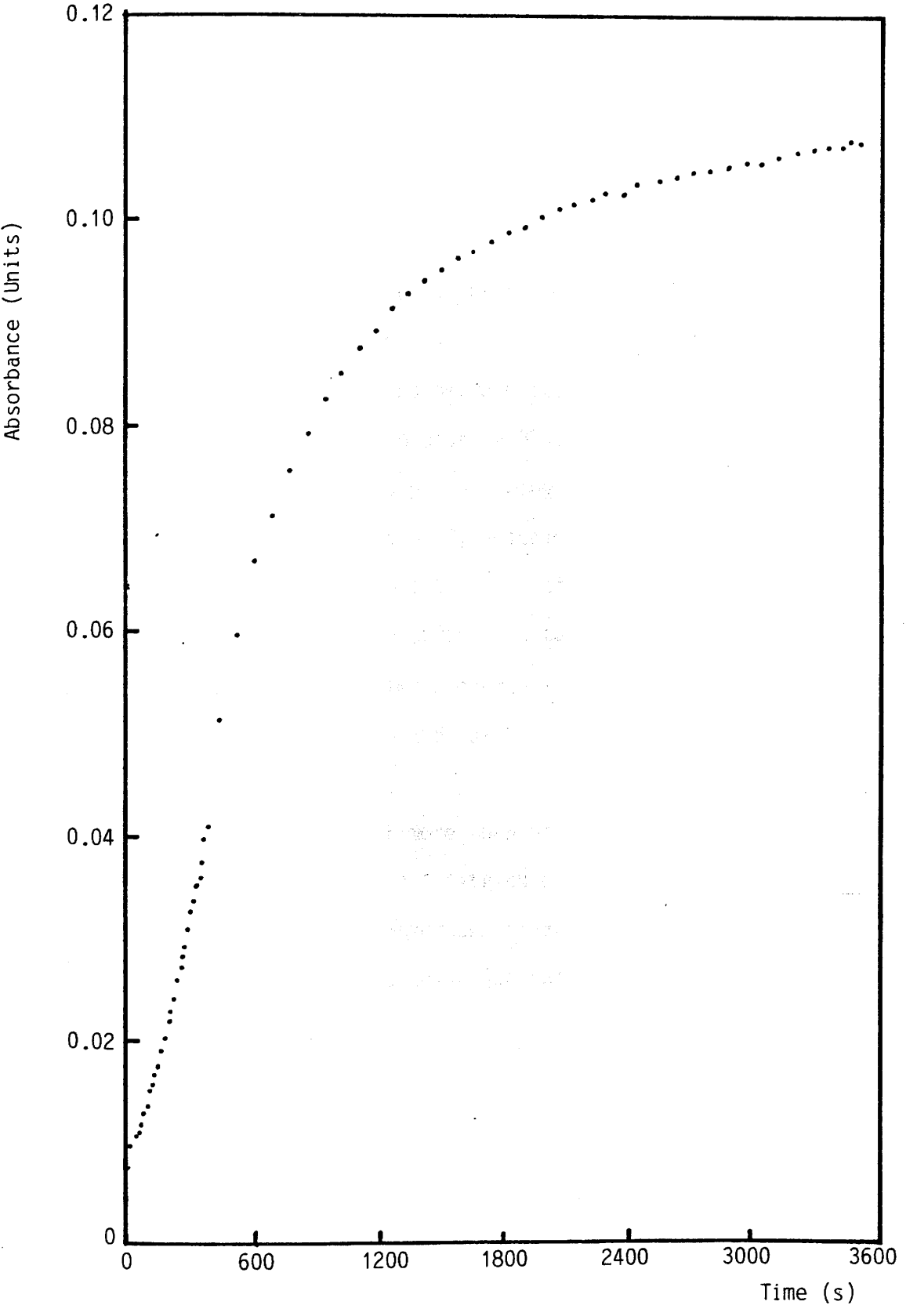


TABLE 3.I. Quantities of Reactants and Time of Maximum $CH_2=CCl_2$ (g) Pressure in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial CH_3CCl_3 (g) (mmol)	$AlCl_3$ (s) (mmol)	Time of Maximum $CH_2=CCl_2$ (g) Pressure (s)
B1	0.023 ± 0.002	4.079	1325 ± 100
B4	0.059 ± 0.002	3.028	1520 ± 100
B6	0.115 ± 0.002	1.837	455 ± 20
B7	0.152 ± 0.002	2.042	400 ± 20
B8	0.189 ± 0.002	1.340	500 ± 20
B9	0.232 ± 0.002	1.745	170 ± 20

FIGURE 3.IX. Plot of Absorbance vs Time for the 2821 cm^{-1} Peak of Hydrogen Chloride in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.



of the experiment as shown in Figure 3.X. The behaviour of this peak has been attributed to the dominance of the 796cm^{-1} peak of 1,1-dichloroethene in the first 500s and the dominance of the 794cm^{-1} peak of carbon tetrachloride thereafter.

Table 3.II contains the quantities of gaseous material involved in four of these experiments. Initial pressures of 1,1,1-trichloroethane were obtained using a constant volume manometer when the cell was loaded. Carbon tetrachloride pressures were estimated by comparison with standard spectra. All other pressures were calculated using determined relationships between absorbance or peak area and pressure. At least 70%, and usually 85%, of the 1,1,1-trichloroethane was lost from the gas phase during the course of the reaction. The maximum pressure of gaseous 1,1-dichloroethene detected ranged from 10 to 30% of the original 1,1,1-trichloroethane pressure. The maximum pressure of hydrogen chloride detected ranged from 70 to 150% of the original 1,1,1-trichloroethane pressure. The maximum pressure of carbon tetrachloride detected was 6% of the original 1,1,1-trichloroethane pressure.

The observation that more than one mole of hydrogen chloride can be produced per mole of 1,1,1-trichloroethane consumed indicates that a process other than dehydrochlorination of 1,1,1-trichloroethane must lead to the formation of hydrogen chloride. The amount of carbon tetrachloride detected indicates that it is a comparatively minor product of the reaction. The total amount of gaseous carbon containing material at the end of the reaction was greatly reduced; reductions of 46 to 93% in the amount of gaseous organic material were observed. This confirms that a non-volatile organic species is produced in the reaction.

FIGURE 3.X. Plot of Absorbance *vs* Time for the Peak at *ca.* 795 cm^{-1} in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

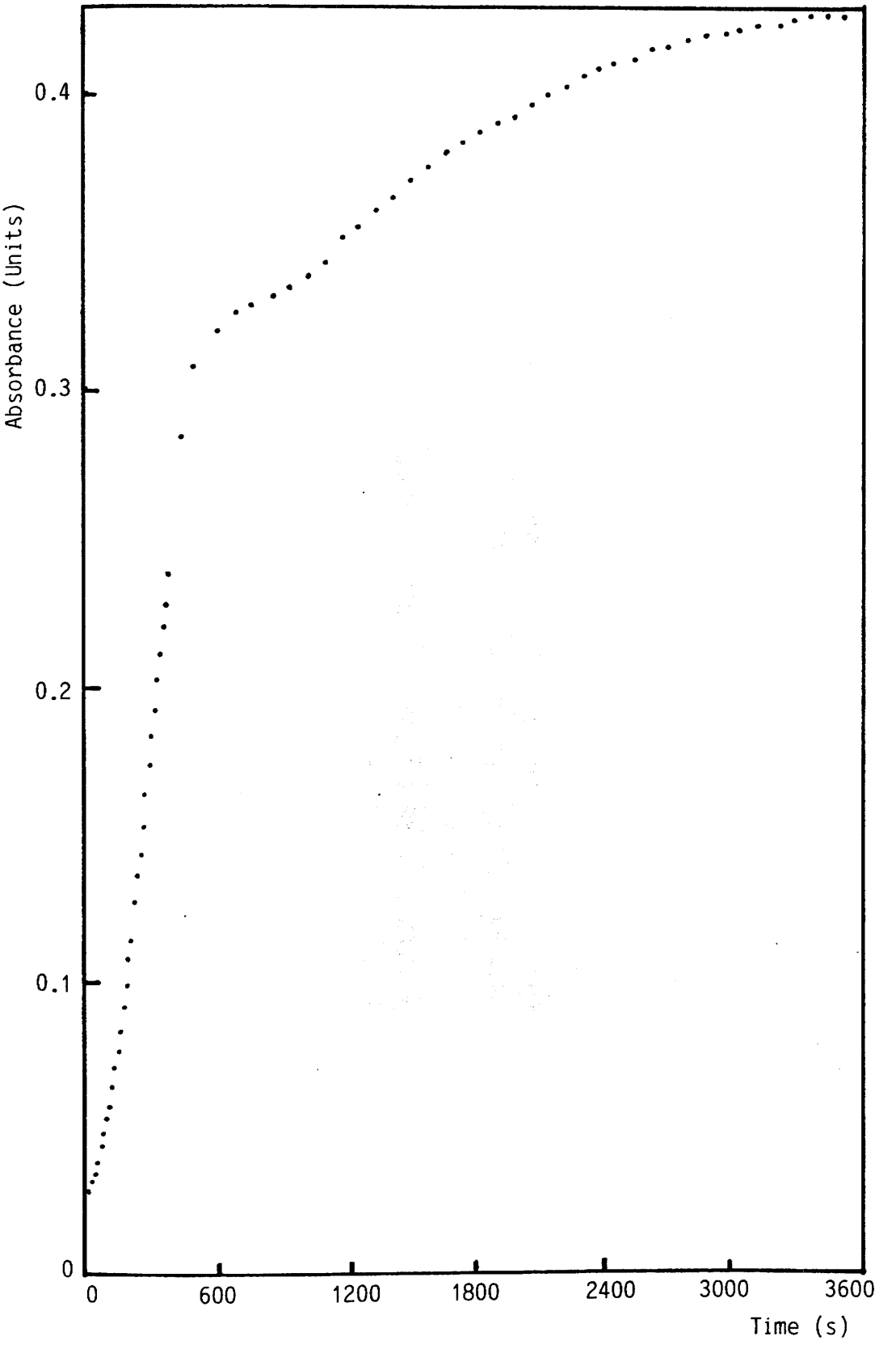


TABLE 3.II(a). Quantities of CH_3CCl_3 (g) and $CH_2=CCl_2$ (g) at Selected Times in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial CH_3CCl_3 (g)		CH_3CCl_3 (g) at time of maximum $CH_2=CCl_2$ (g) pressure		CH_3CCl_3 (g) at end of experiment	
	(Torr)	(mmol)	(Torr)	(mmol)	(Torr)	(mmol)
B1	8.0 ± 0.5	0.023 ± 0.002	1.7 ± 0.2	0.005 ± 0.0006	1.2 ± 0.2	0.003 ± 0.0005
B6	39.8 ± 0.5	0.115 ± 0.002	24.4 ± 1.9	0.071 ± 0.006	1.8 ± 0.2	0.005 ± 0.0006
B7	52.6 ± 0.5	0.152 ± 0.002	27.5 ± 2.6	0.080 ± 0.008	5.9 ± 0.5	0.017 ± 0.002
B8	65.3 ± 0.5	0.189 ± 0.002	28.2 ± 2.6	0.082 ± 0.008	17.8 ± 1.7	0.052 ± 0.005

Run No.	$CH_2=CCl_2$ (g) in first spectrum		Maximum $CH_2=CCl_2$ (g)		$CH_2=CCl_2$ (g) at end of experiment	
	(Torr)	(mmol)	(Torr)	(mmol)	(Torr)	(mmol)
B1	1.2 ± 0.3	0.003 ± 0.001	3.1 ± 0.3	0.009 ± 0.0009	2.9 ± 0.3	0.008 ± 0.0008
B6	0.14 ± 0.01	0.0004 ± 0.0003	3.8 ± 0.2	0.011 ± 0.0005	0.26 ± 0.01	0.0007 ± 0.00003
B7	6.9 ± 0.2	0.020 ± 0.0006	10.3 ± 0.3	0.030 ± 0.001	7.0 ± 0.2	0.020 ± 0.0006
B8	4.4 ± 0.2	0.013 ± 0.0006	6.6 ± 0.2	0.019 ± 0.0006	5.4 ± 0.2	0.016 ± 0.0006

TABLE 3.II(b). Quantities of HCl (g) and CCl_4 (g) at Selected Times in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	HCl (g) in First Spectrum		HCl (g) at time of maximum $CH_2=CCl_2$ (g) pressure		HCl (g) at end of experiment	
	(Torr)	(mmol)	(Torr)	(mmol)	(Torr)	(mmol)
B1	1.2 ± 0.3	0.003 ± 0.001	not obtained	not obtained	8.0 ± 0.2	0.023 ± 0.0006
B6	2.0 ± 0.5	0.006 ± 0.002	15.9 ± 0.5	0.046 ± 0.002	28.8 ± 0.5	0.084 ± 0.002
B7	6.3 ± 0.6	0.018 ± 0.002	42.2 ± 0.5	0.122 ± 0.002	83.3 ± 0.5	0.242 ± 0.002
B8	2.0 ± 0.5	0.006 ± 0.002	25.2 ± 0.6	0.073 ± 0.002	72.3 ± 0.5	0.210 ± 0.002

Run No.	CCl_4 (g) at end of experiment	
	(Torr)	(mmol)
B1	< 0.5	< 0.0015
B6	< 1.0	< 0.0029
B7	< 1.5	< 0.0043
B8	< 1.0	< 0.0029

Figure 3.XI shows the variation of pressure (≡ concentration) with time of the gaseous reactants and products in a typical experiment (B6 in Table 3.VII). Table 3.III shows the quantity of 1,1,1-trichloroethane consumed and the quantities of 1,1-dichloroethene and hydrogen chloride present at selected times in this experiment. Carbon tetrachloride is not included because the peak at ca 795 cm^{-1} is known to be due to two species with different absorbance vs time behaviour. The quantity of hydrogen chloride present is very close to the quantity of 1,1,1-trichloroethane consumed at times < 455s which suggests that one mole of hydrogen chloride is produced per mole of 1,1,1-trichloroethane consumed in the period before the maximum 1,1-dichloroethene pressure is detected. The quantity of 1,1-dichloroethene present is close to the quantity of 1,1,1-trichloroethane consumed only in the very early stages of the reaction, < 100s. This may indicate that the dehydrochlorination is the only important reaction taking place in the very early stages and that the reactions which consume 1,1-dichloroethene and produce carbon tetrachloride only become significant once a certain amount of 1,1-dichloroethene and/or hydrogen chloride is produced.

Under homogeneous conditions, the expected behaviour for series first-order reactions (Scheme 3.I) is shown schematically

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

Scheme 3.I

in Figure 3.XII where A_o is the initial concentration of A.[96] Comparison of Figure 3.XII with the plots of absorbance vs time for 1,1,1-trichloroethane (Figure 3.VII), 1,1-dichloroethene (Figure

FIGURE 3.XI. Variation of Pressure with Time for Gaseous Reactants and Products in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

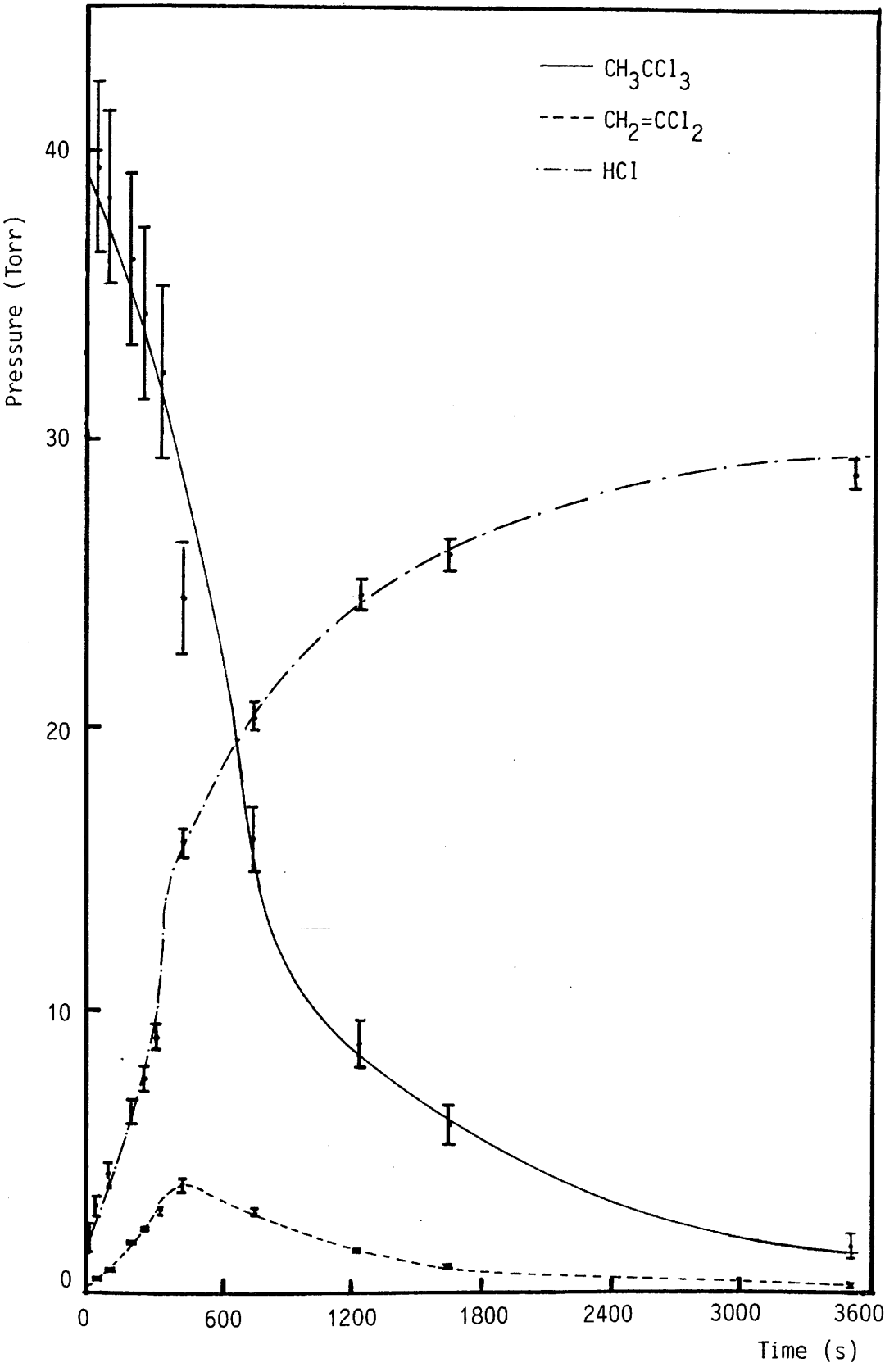
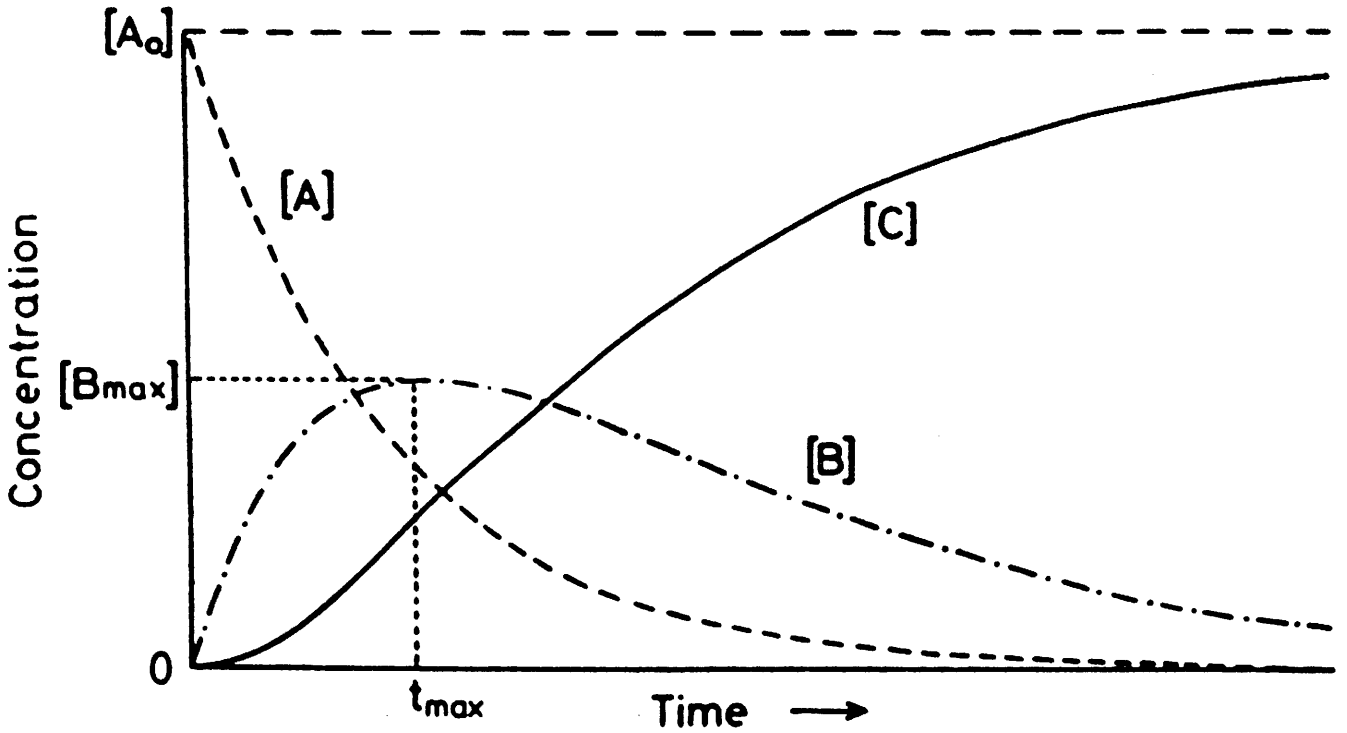


TABLE 3.III. Quantities of CH_3CCl_3 (g) Consumed and $CH_2=CCl_2$ (g) and HCl (g) Present at Selected Times in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Time (s)	CH_3CCl_3 (g) consumed (mmol)	$CH_2=CCl_2$ (g) (mmol)	HCl(g) (mmol)
11	0.000 ± 0.009	0.0004 ± 0.00003	0.006 ± 0.002
51	0.001 ± 0.009	0.0012 ± 0.00006	0.009 ± 0.002
115	0.004 ± 0.009	0.0023 ± 0.0001	0.012 ± 0.002
208	0.010 ± 0.009	0.0052 ± 0.0001	0.019 ± 0.002
259	0.016 ± 0.009	0.0064 ± 0.0002	0.022 ± 0.002
311	0.022 ± 0.009	0.0082 ± 0.0002	0.026 ± 0.002
455	0.045 ± 0.006	0.0110 ± 0.0005	0.046 ± 0.002
761	0.069 ± 0.003	0.0083 ± 0.0002	0.058 ± 0.002
1246	0.090 ± 0.003	0.0043 ± 0.0001	0.071 ± 0.002
1650	0.098 ± 0.002	0.0028 ± 0.0001	0.075 ± 0.002
3510	0.110 ± 0.002	0.0007 ± 0.00003	0.084 ± 0.002

FIGURE 3.XII. Concentration vs Time Behaviour for Series First Order Reactions.[96]



3.VIII) and hydrogen chloride (Figure 3.IX) shows that if 1,1,1-trichloroethane is A, 1,1-dichloroethene is B and hydrogen chloride is C, then there is at least a superficial similarity. However, in addition, hydrogen chloride must be co-produced with 1,1-dichloroethene.

Without considering the order of the reaction, it is possible to construct a simple model which can account for many of the observed results (Scheme 3.II), where A is 1,1,1-trichloroethane, B is 1,1-

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$

$$B_{(g)} \rightleftharpoons D_{(s)} + C_{(g)} \qquad \text{Scheme 3.II}$$

dichloroethene, C is hydrogen chloride and D is unidentified. If the condition at the end of the experiments was close to the steady state of Scheme 3.II, then the amount of gaseous C at this time, c, should be given by Equation 3.IV, where a_o is the initial amount of

$$c = 2a_o - 2_a - b \qquad \text{Equation 3.IV}$$

A, a is the amount of A at the time of measurement and b is the amount of B at the time of measurement. For the four experiments in Table 3.II, where a_o, a and b are known, values of c were calculated and compared with the observed values in Table 3.IV. In three of the experiments the calculated values are close to those observed.

The absorbance vs time plot for hydrogen chloride (Figure 3.IX) is very similar to that expected for the product species in a second-order autocatalytic reaction.[97] Scheme 3.II could not account for this behaviour, nor would it be possible at this stage to rule out a reaction of the type shown in Scheme 3.III, where D and E are unidentified.

TABLE 3.IV. Calculated and Found Quantities of HCl (g) in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Calculated HCl (g) (mmol)	Found HCl (g) (mmol)
B1	0.032 ± 0.003	0.023 ± 0.0006
B6	0.219 ± 0.004	0.084 ± 0.002
B7	0.250 ± 0.004	0.242 ± 0.002
B8	0.258 ± 0.008	0.210 ± 0.002

$A_{(g)} \rightleftharpoons D_{(s)} + C_{(g)}$ Main Reaction

$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$ Side Reaction

$B_{(g)} \rightleftharpoons E_{(s)}$

Scheme 3.III

Time dependences must be examined in more detail before any further discussion. The first order plots were of the form $-\ln x/x_0$ vs time, where x_0 was the absorbance of the desired peak in the first spectrum collected, and x was the absorbance at time t. The second order plots were of the form $^1/x - ^1/x_0$ vs time. A linear plot in either case indicated a first/second order process.

The first order plot for 1,1,1-trichloroethane is a curve (Figure 3.XIII). The second order plot for 1,1,1-trichloroethane is linear at times >300s (Figure 3.XIV). This indicates that the loss of gaseous 1,1,1-trichloroethane is a second order process with an induction period of ca 250s. In homogeneous reactions, a 40 fold or greater excess of one reactant is usually required to be maintained during the course of the experiment for pseudo-first order conditions to apply. In a heterogeneous reaction such as this, reaction would be expected only on the solid surface. Neither the surface area nor the number of active sites on aluminium (III) chloride is known, hence it is impossible to determine whether pseudo-first order conditions applied. Therefore it is not valid to state that the loss of gaseous 1,1,1-trichloroethane is second order in 1,1,1-trichloroethane; only that the reaction is second order overall.

The first order plot for 1,1-dichloroethene is shown in Figure 3.XV). Although its curvature is small at times >2000s, close inspection reveals that the plot is non-linear. The second order plot for 1,1-dichloroethene is a curve (Figure 3.XVI). The

FIGURE 3.XIII. First Order Plot for 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

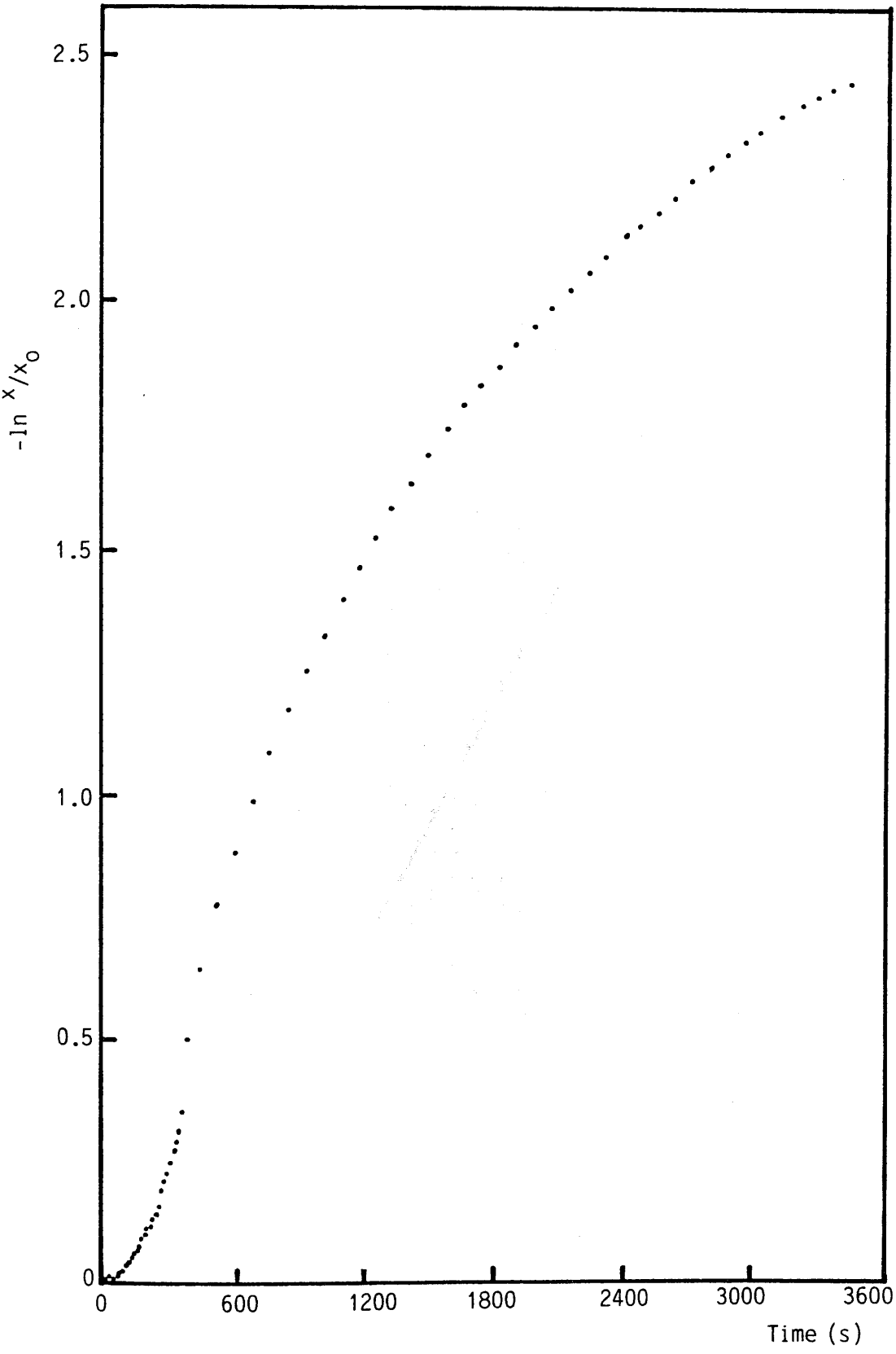


FIGURE 3.XIV. Second Order Plot for 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

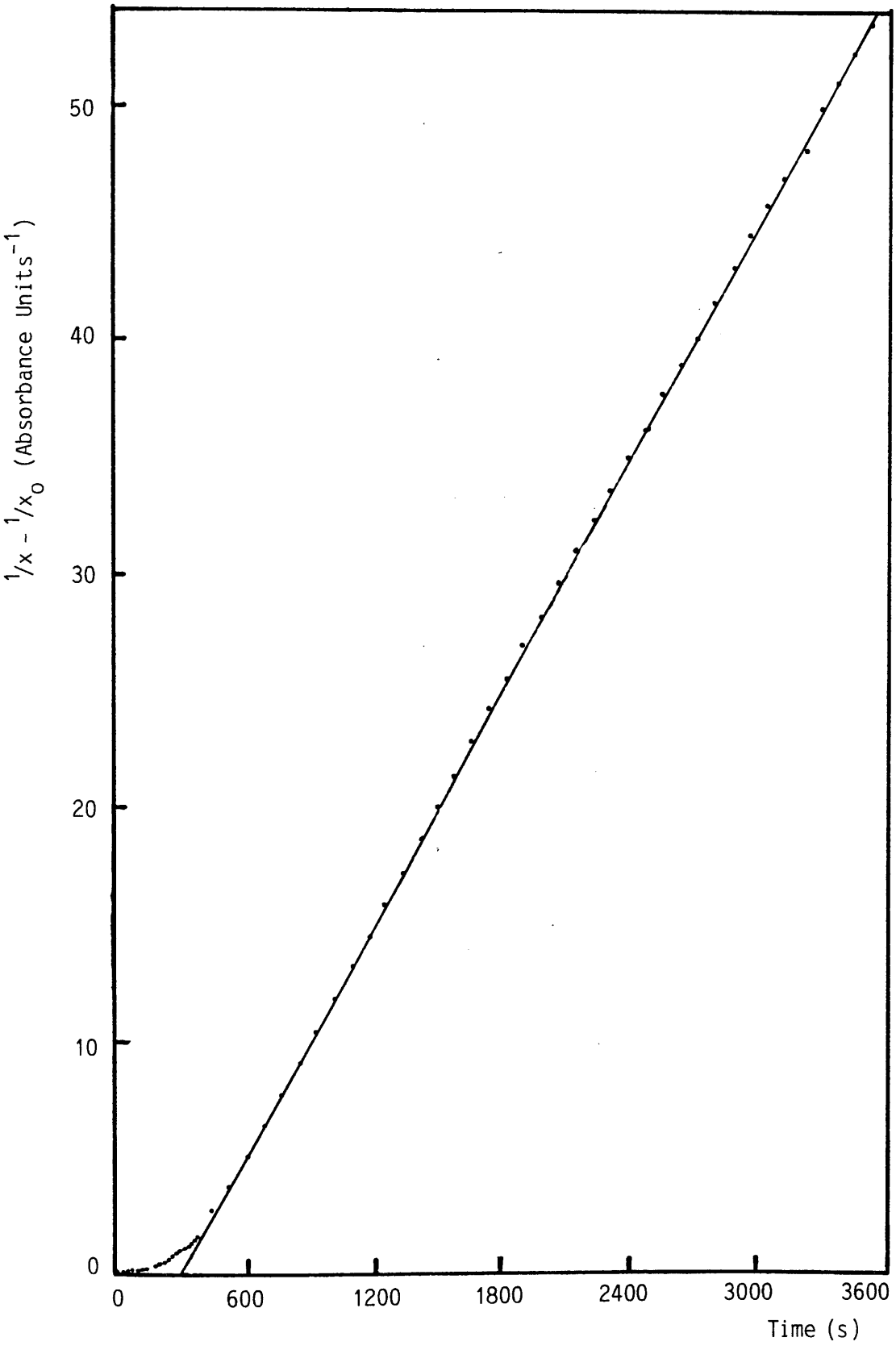


FIGURE 3.XV. First Order Plot for 1,1-Dichloroethene in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

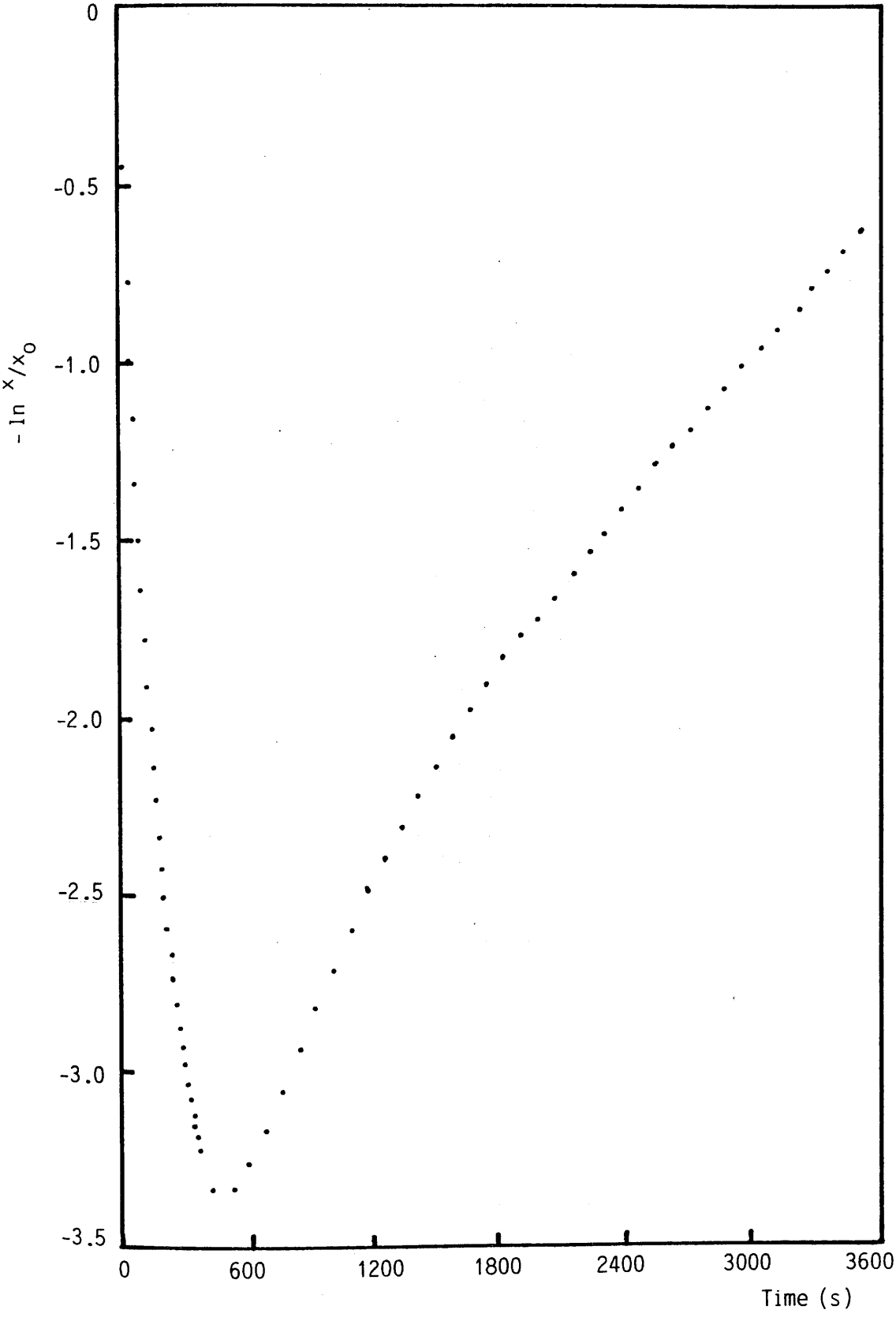
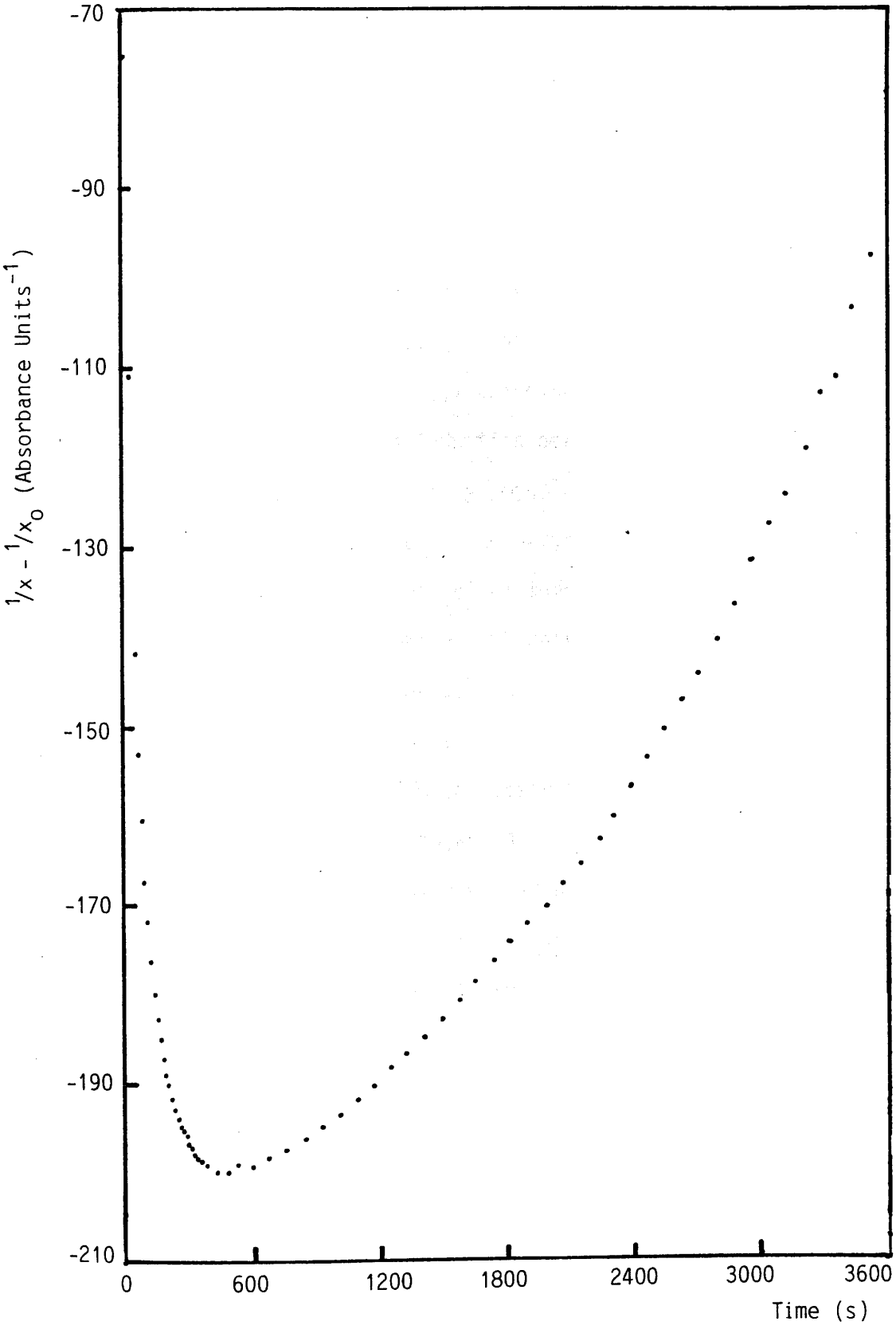


FIGURE 3.XVI. Second Order Plot for 1,1-Dichloroethene in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.



position of the minimum in Figure 3.XVI is very close to the end of the induction period observed in Figure 3.XIV.

The first order plot for hydrogen chloride is a curve (Figure 3.XVII). The second order plot is linear at times >1000s (Figure 3.XVIII). This indicates that hydrogen chloride is produced by a second order process at times >1000s.

The peak at 795cm^{-1} is known to be due to two species with different absorbance vs time behaviour and so the first and second order plots derived were of little analytical value.

The loss of gaseous 1,1,1-trichloroethane appears to be a second order process with an induction period and, as noted earlier, the absorbance vs time plot for hydrogen chloride has the shape expected for the product in a second order autocatalytic process,[97] which also implies the presence of an induction period. The second order plot for hydrogen chloride is linear only at times >1000s. It can be seen from Figures 3.VII and 3.IX that comparatively little 1,1,1-trichloroethane is consumed and little hydrogen chloride is produced at times >1000s. These observations are not contradictory, as there is evidence that hydrogen chloride is produced by at least two processes. The combination of two processes, one of which is the dehydrochlorination of 1,1,1-trichloroethane and which is not rate determining, and the other of which is the rate determining reaction, may account for the observed behaviour if the former reaction is significant only during the first 1000s.

Kinetic measurements alone are insufficient for the establishment of mechanism. In the simplest heterogeneous systems, reaction is confined to a single layer on the surface and the concentrations of adsorbed species are usually not directly observable.[98]

FIGURE 3.XVII. First Order Plot for Hydrogen Chloride in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

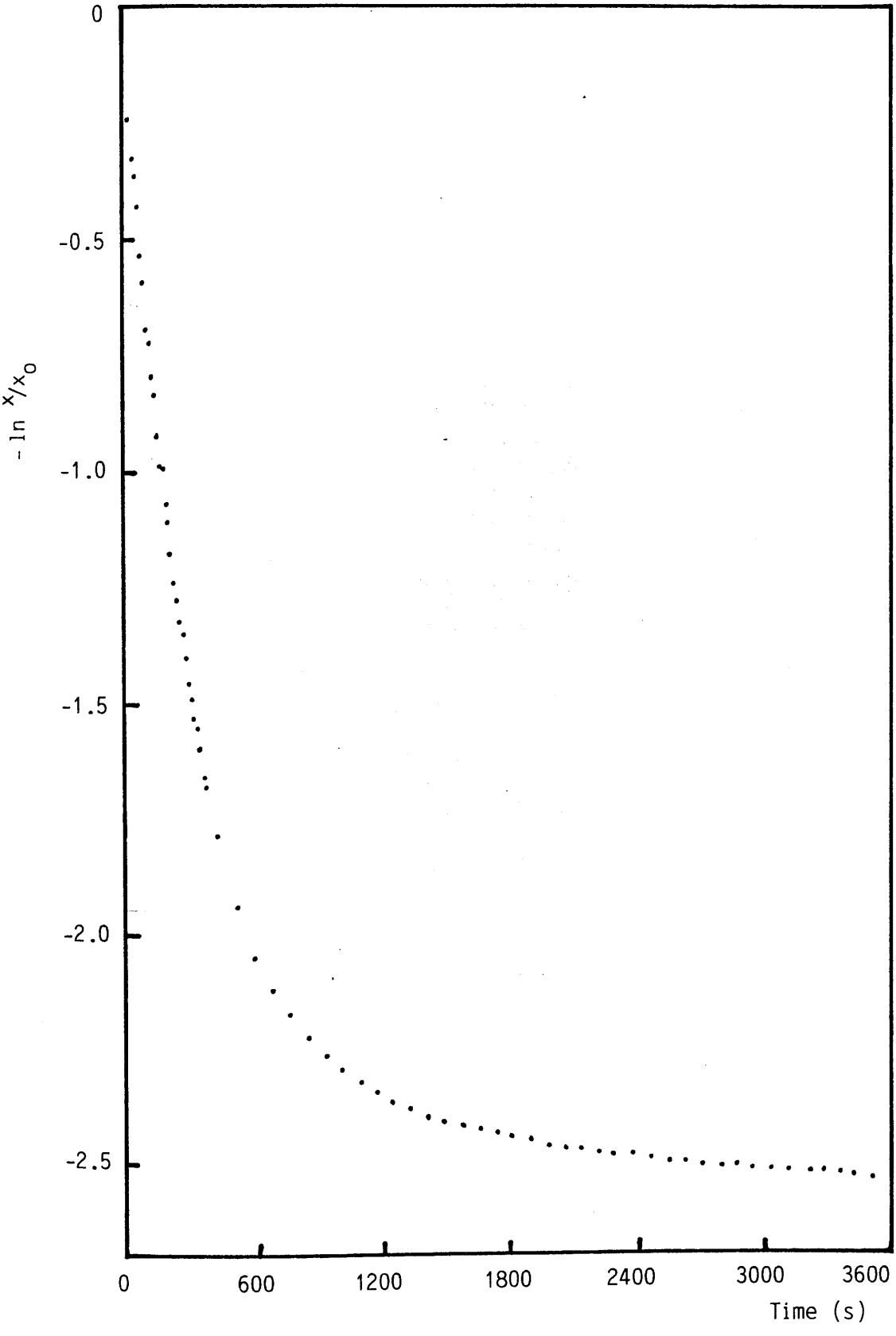
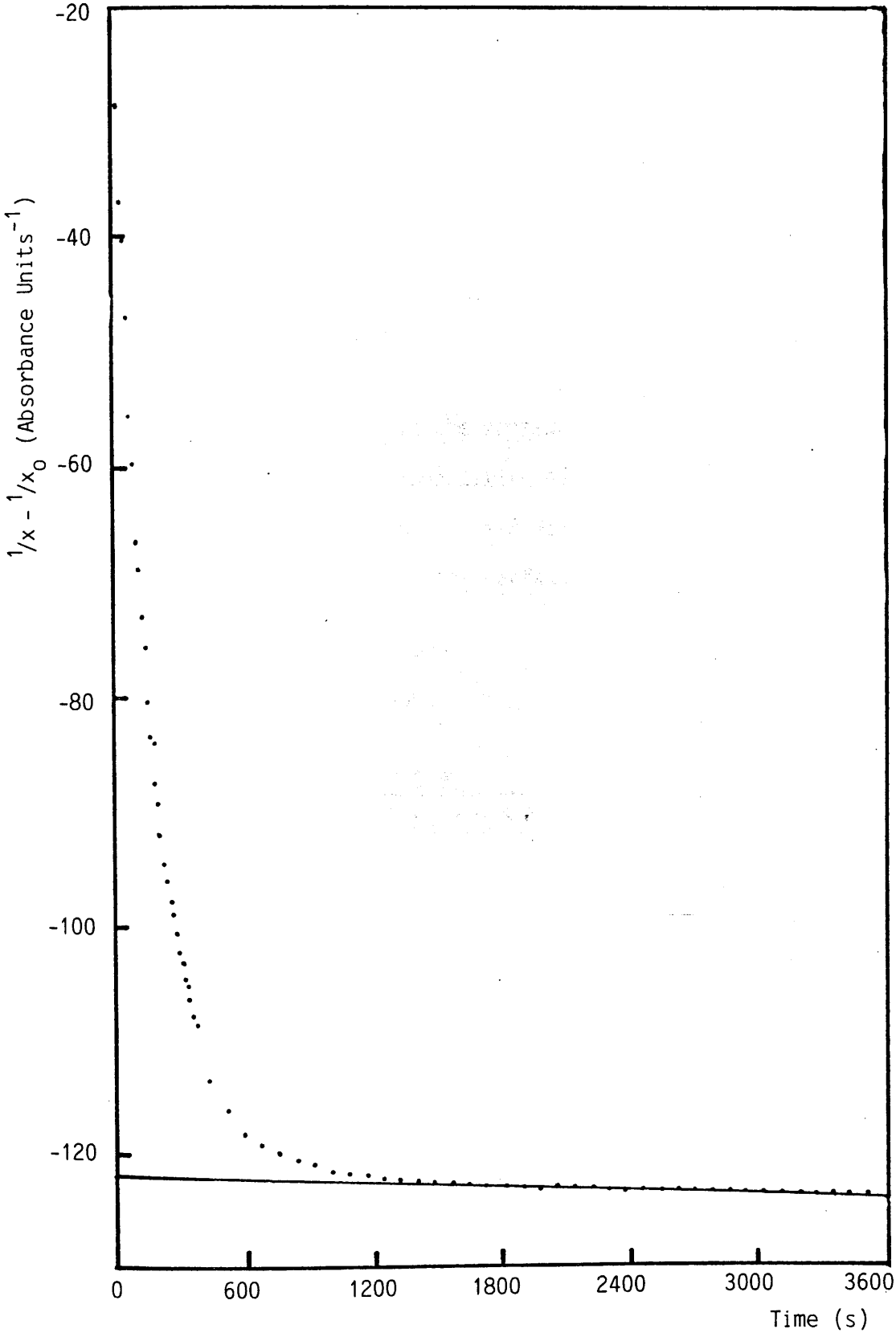


FIGURE 3.XVIII. Second Order Plot for Hydrogen Chloride in the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.



Kinetic interpretations of surface reactions often employ the Langmuir isotherm which relates gas phase concentrations (≡ pressures) to surface concentrations. For adsorption of a single species (Equation 3.V), the Langmuir isotherm is given by Equation 3.VI, where

$$A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A(ad) \qquad \text{Equation 3.V}$$

θ_A is the fractional surface coverage of A, b_A is the adsorption

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A} \qquad \text{Equation 3.VI}$$

coefficient ($= k_a/k_d$) and p_A is the pressure of gaseous A in equilibrium with the surface. For the competitive adsorption of two species on the same surface sites, Equations 3.VII and 3.VIII apply. The Langmuir isotherm assumes that the surface is homogeneous. This

$$\theta_A = \frac{b_A p_A}{(1 + b_A p_A + b_B p_B)} \qquad \text{Equation 3.VII}$$

$$\theta_B = \frac{b_B p_B}{(1 + b_A p_A + b_B p_B)} \qquad \text{Equation 3.VIII}$$

condition is unlikely to apply to the aluminium (III) chloride in these studies as the effect on the surface of water, hydrogen chloride and the involatile organic product must be considered.

The observed behaviour could be explained in several ways. The induction period indicates that a sufficient concentration of one of the products must be achieved, but in such a complex system it is impossible to say which. If the autocatalytic species is adsorbed 1,1-dichloroethene, then a model can be constructed which explains many of the observations. Adsorbed 1,1,1-trichloroethane is the

expected precursor to adsorbed 1,1-dichloroethene, and so it is likely that 1,1,1-trichloroethane and 1,1-dichloroethene compete for sites. A 1:1 reaction of adsorbed 1,1,1-trichloroethane with adsorbed 1,1-dichloroethene to yield the postulated species $C_4H_4Cl_4(ad)$, which can react further, and hydrogen chloride is represented by Equation 3.IX.

$$CH_3CCl_3(ad) + CH_2{=}CCl_2(ad) \rightleftharpoons C_4H_4Cl_4(ad) + HCl(g)$$

Equation 3.IX

The rate of this reaction is proportional to the probability that 1,1,1-trichloroethane and 1,1-dichloroethene are adsorbed on neighbouring sites, and thus it is proportional to the fractions of the surface covered by 1,1,1-trichloroethane and 1,1-dichloroethene as shown in Equation 3.X, where A is 1,1,1-trichloroethane, B is 1,1-dichloroethene

$$\text{Rate} = k\theta_A\theta_B \qquad \text{Equation 3.X}$$

and k is a constant. Thus, from Equations 3.VII and 3.VIII the rate is given by Equation 3.XI.

$$\text{Rate} = \frac{kb_Ap_Ab_Bp_B}{(1+b_Ap_A+b_Bp_B)^2} \qquad \text{Equation 3.XI}$$

At very low surface coverages, the rate of desorption will be very much greater than the rate of adsorption and b_Ap_A and b_Bp_B become very small. Thus the term "$1 + b_Ap_A + b_Bp_B$" tends to one, and, since b_A and b_B are constants, the rate expression can be simplified to Equation 3.XII, which would lead to a second order process.

$$\text{Rate} = k' p_Ap_B \qquad \text{Equation 3.XII}$$

However, most of the evidence points to the operation of an $A \longrightarrow B \longrightarrow C$ process which Equation 3.IX does not fulfil.

Dehydrochlorination of 1,1-dichloroethene derived oligomers has been reported in systems where the oligomerisation was catalysed by aluminium (III) chloride.[82] An adaptation of the scheme proposed by Winterton[75] (Scheme 1.XIII in 1.3.3) may provide an explanation which is more consistent with the evidence (Scheme 3.IV). At very

$$CH_3CCl_3(g) \overset{\text{fast}}{\rightleftharpoons} CH_3CCl_3(ad) \qquad \text{(i)}$$

$$CH_3CCl_3(ad) \overset{\text{fast}}{\rightleftharpoons} CH_2{=}CCl_2(ad) + HCl(g) \qquad \text{(ii)}$$

$$CH_2{=}CCl_2(ad) \rightleftharpoons CH_2{=}CCl_2(g) \qquad \text{(iii)}$$

$$CH_2{=}CCl_2(ad) + AlCl_2^+ \overset{\text{fast}}{\rightleftharpoons} Cl_2AlCH_2\overset{+}{C}Cl_2 \qquad \text{(iv)}$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_2(ad) \overset{\text{r.d.s}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 \qquad \text{(v)}$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \rightleftharpoons Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3 \qquad \text{(vi)}$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2 = CCl_2CH_2CCl_3 + AlCl_3 \qquad \text{(vii)}$$

$$CH_2 = CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} CH_2 = CClCH = CCl_2 + HCl(g) \qquad \text{(viii)}$$

Scheme 3.IV

low surface coverages such a scheme should give rise to a rate expression similar to Equation 3.XII and a reaction which is second order overall.

If a reaction scheme such as that shown in Scheme 3.IV operates, the calculated steady state amount of hydrogen chloride, c, (see Scheme 3.II and Equation 3.IV) is given by Equation 3.XIII, where a_o, a and b are as defined earlier, assuming that all the 1,1-dichloroethene

$$c = a_o - a + \left(\frac{a_o - a - b}{2}\right) \qquad \text{Equation 3.XIII}$$

produced at the surface is in mobile equilibrium with the gas phase. While such an assumption is unrealistic, the number of adsorbed 1,1-dichloroethene molecules at any instant once steady state is attained must be very small compared to the number of gaseous 1,1-dichloroethene molecules, and the latter quantity can be considered to be the amount of material produced by dehydrochlorination which has not reacted further (b). Values of c were calculated using Equation 3.XIII for the values of a_o, a and b in Table 3.II, and are compared with the observed values of c in Table 3.V. The calculated values of c are closer to the found values than those calculated using Equation 3.IV in three of the experiments.

The study of time dependences in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride has led to the suggestion that Scheme 3.IV may provide a reasonable explanation for most of the observations. Direct evidence for some of the species in Scheme 3.IV is presented later, principally in Chapters 7 and 8. Possible explanations for the C-C bond fission are discussed in Chapter 9.

3.3 Experimental

3.3.1 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride

Experiments were carried out using the procedure described in 2.3.4. Table 3.VI contains the quantities of material used. Spectra were collected before opening the stopcock, and typically after 5, 60 and 90 min of reaction. When no further change was observed in

TABLE 3.V. Calculated and Found Quantities of HCl (g) in the Reaction of CH_3CCl_3(g) with $AlCl_3$ (s)

Run No.	Calculated HCl(g) (mmol)	Found HCl(g) (mmol)
B1	0.026 ± 0.002	0.023 ± 0.0006
B6	0.165 ± 0.002	0.084 ± 0.002
B7	0.192 ± 0.003	0.242 ± 0.002
B8	0.198 ± 0.006	0.210 ± 0.002

TABLE 3.VI. Quantities of Reactants in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial Pressure of CH_3CCl_3 (g) (Torr)	Initial CH_3CCl_3 (g) (mmol)	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)
A1	8.9 ± 0.5	0.026 ± 0.002	0.6160	4.614
A2	21.6 ± 0.5	0.063 ± 0.002	0.4361	3.267
A3	21.9 ± 0.5	0.07 ± 0.02	0.3719	2.786
A4	58.8 ± 0.5	0.171 ± 0.002	0.2290	1.715

TABLE 3.VII. Quantities of Reactants in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3 (g)

Run No.	Initial Pressure of CH_3CCl_3 (g) (Torr)	Initial CH_3CCl_3 (g) (mmol)	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)
C1	15.1 ± 0.5	0.044 ± 0.002	0.6160	4.614
C2	15.1 ± 0.5	0.05 ± 0.01	0.5998	4.493
C3	60.0 ± 0.5	0.20 ± 0.05	0.3719	2.786

successive spectra collected, the cell was evacuated.

3.3.2 Infra-Red Spectroscopic Analysis of Vapour Phase Over Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane

An evacuated cell containing a sample of solid aluminium (III) chloride, which had been previously exposed to gaseous 1,1,1-trichloroethane for 90 min, was placed in the spectrometer beam and spectra were collected at 5 min intervals until no further change was observed. The samples from experiments A1 and A2 (Table 3.VI) were treated in this way.

3.3.3 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane

Experiments were carried out using the procedure described in 2.3.4. The solid aluminium (III) chloride used had been previously exposed to gaseous 1,1,1-trichloroethane for 90 min. Table 3.VII contains the quantities of material used.

3.3.4 Kinetic Treatment of Infra-Red Data from the Reaction of Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride

Experiments were carried out using the procedure described in 2.3.5. Table 3.VIII contains the quantities of material used.

TABLE 3.VIII. Quantities of Reactants in the Reaction of CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial Pressure of CH_3CCl_3 (g) (Torr)	Initial CH_3CCl_3 (g) (mmol)	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)
B1	8.0 ± 0.5	0.023 ± 0.002	0.5446	4.079
B2	8.9 ± 0.5	0.026 ± 0.002	0.7020	5.258
B3	11.5 ± 0.5	0.033 ± 0.002	0.3801	2.847
B4	20.5 ± 0.5	0.059 ± 0.002	0.4042	3.028
B5	37.3 ± 0.5	0.108 ± 0.002	0.2886	2.162
B6	39.8 ± 0.5	0.115 ± 0.002	0.2453	1.837
B7	52.6 ± 0.5	0.152 ± 0.002	0.2726	2.042
B8	65.3 ± 0.5	0.189 ± 0.002	0.1789	1.340
B9	79.7 ± 0.5	0.232 ± 0.002	0.2330	1.745

CHAPTER 4

CHAPTER 4

THE REACTION OF GASEOUS 1,1-DICHLOROETHENE WITH SOLID ALUMINIUM (III) CHLORIDE

4.1 INTRODUCTION

The solution reaction of 1,1-dichloroethene with aluminium (III) chloride at various temperatures has been studied by Kulikova.[82] Products detected varied with temperature, and included dimers, trimers and polymers of 1,1-dichloroethene (see 1.3.3). In Chapter 3, an adaptation of a scheme proposed by Winterton[75] to explain the formation of 2,4,4,4-tetrachlorobut-1-ene in a mixture of 1,1-dichloroethene and aluminium (III) chloride at $-23^{o}C$[83] (Scheme 1.XIII in 1.3.3) was presented as a reasonable explanation for most of the observations made in an infra-red spectroscopic study of the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (Scheme 3.IV in 3.2.4). The adapted scheme involves a bimolecular surface reaction of an adsorbed 1,1-dichloroethene molecule with a 1,1-dichloroethene/$AlCl_2^+$ complex as the rate determining step (Equation 4.I).

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_{2(ad)} \underset{\text{r.d.s.}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2$$

Equation 4.I

The composition of the vapour phase in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride was studied to determine whether the reaction was consistent with Scheme 3.IV, using:

(i) Fourier Transform infra-red spectroscopy to determine the gaseous products, stoichiometry and time dependence of the reaction.

(ii) Pressure measurements to determine whether an induction period, similar to that observed in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride, existed.

It was not possible to study the solid in this reaction using conventional infra-red spectroscopic techniques, and investigations of the solid are reported in Chapter 8.

4.2 Results

4.2.1 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride

The results obtained were reproducible. A vapour phase infra-red spectrum collected before the stopcock of the ampoule was opened showed 1,1-dichloroethene alone (Figure 4.I). A spectrum collected 5 min after the stopcock was opened showed 1,1-dichloroethene, 1,1,1-trichloroethane and hydrogen chloride (Figure 4.II). The absorbances of the peaks due to 1,1-dichloroethene were reduced compared to Figure 4.I. Computed subtraction of a standard 1,1-dichloroethene spectrum from Figure 4.II, GCIR and GCMS were all used to show that carbon tetrachloride was present at this stage. A spectrum collected 60 min after the stopcock was opened showed 1,1-dichloroethene, 1,1,1-trichloroethane, hydrogen chloride and carbon tetrachloride (Figure 4.III). The absorbances of the peaks due to 1,1-dichloroethene were greatly reduced compared to Figure 4.II; those due to 1,1,1-trichloroethane and hydrogen chloride had increased compared to Figure 4.II. A spectrum collected 90 min after the stopcock was opened was identical to Figure 4.III.

The aluminium (III) chloride, which was initially a white,

FIGURE 4.I. Vapour Phase Infra-Red Spectrum Collected Before Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride was Initiated.

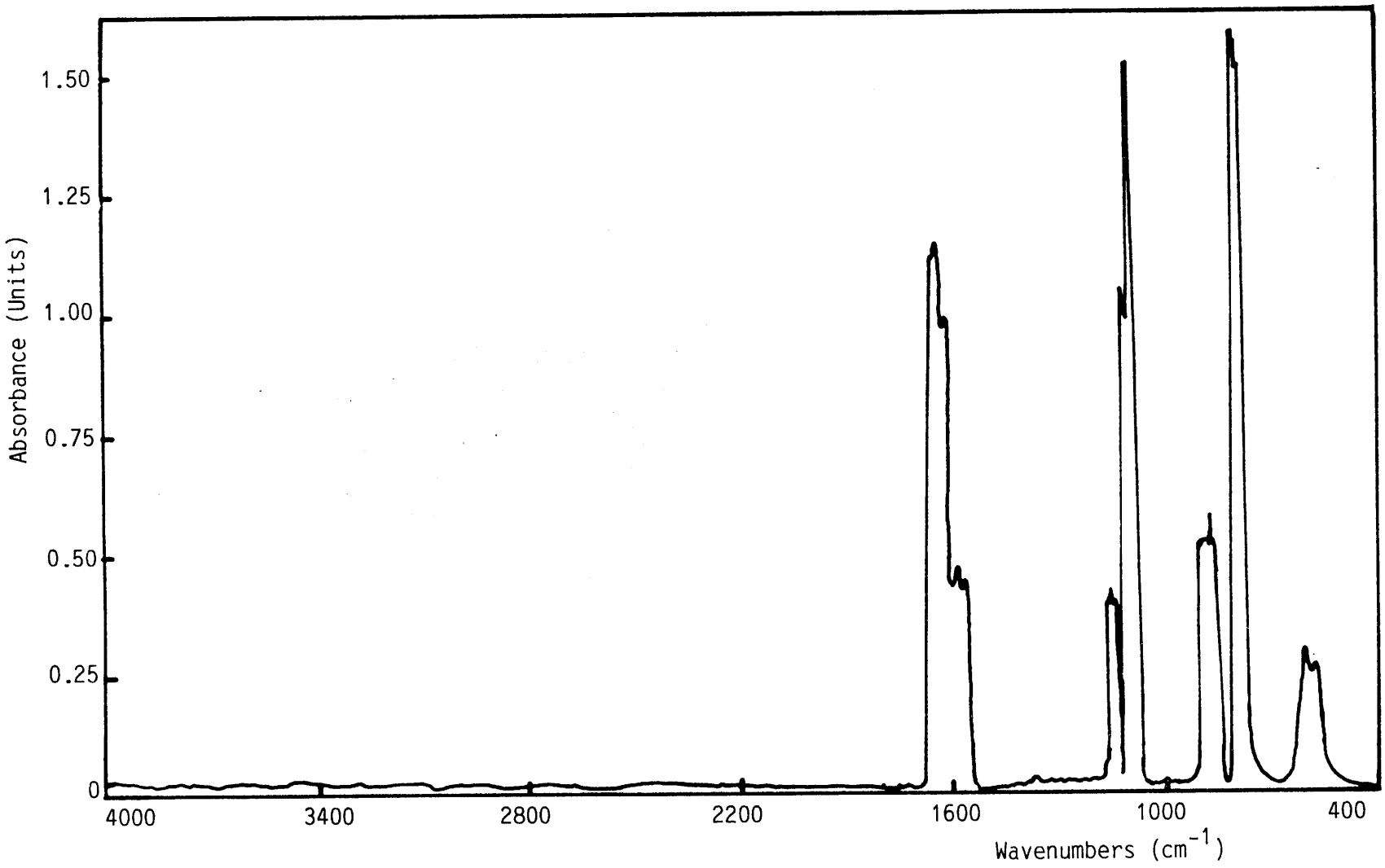


FIGURE 4.II. Vapour Phase Infra-Red Spectrum Collected at t = 5 min in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

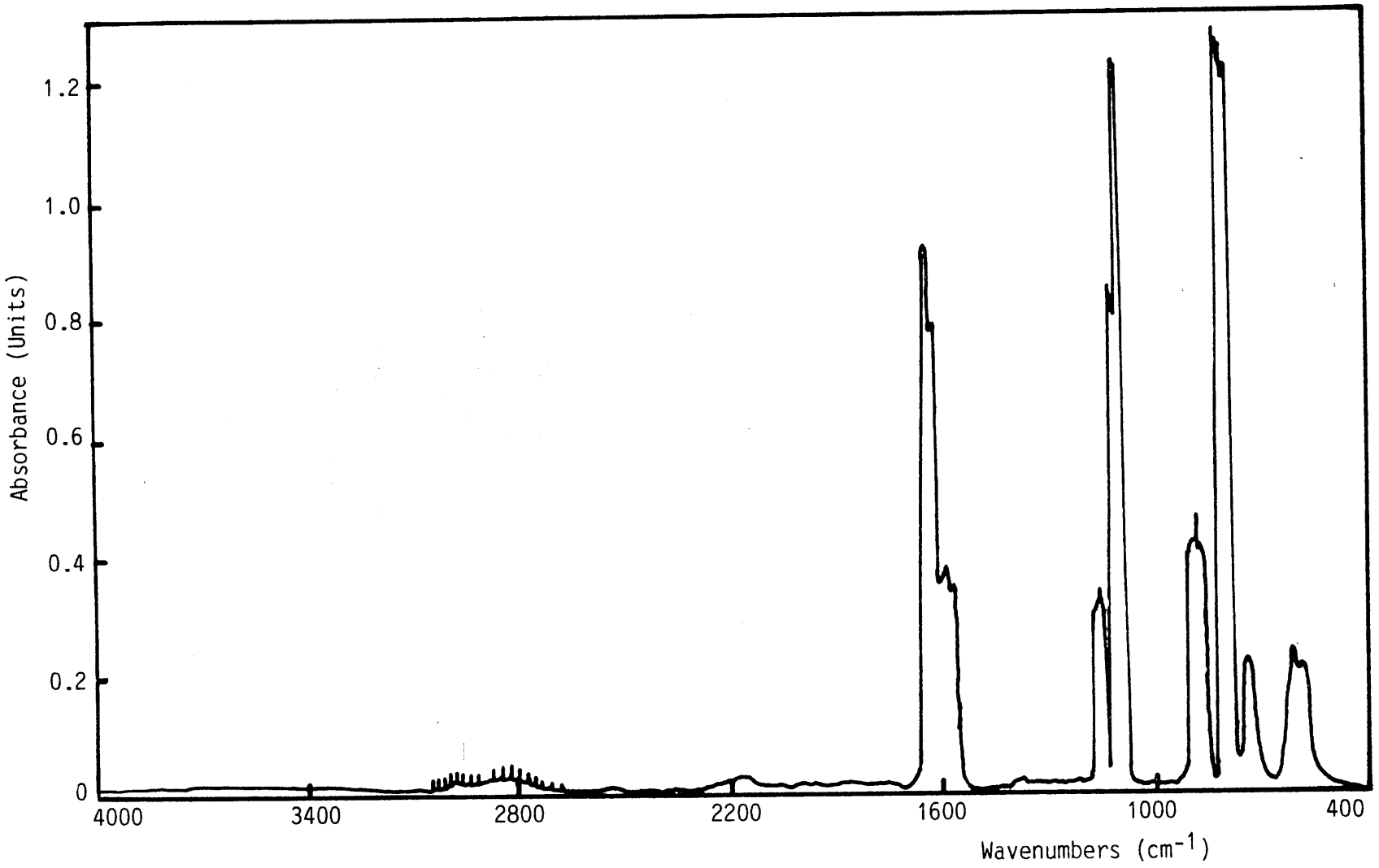
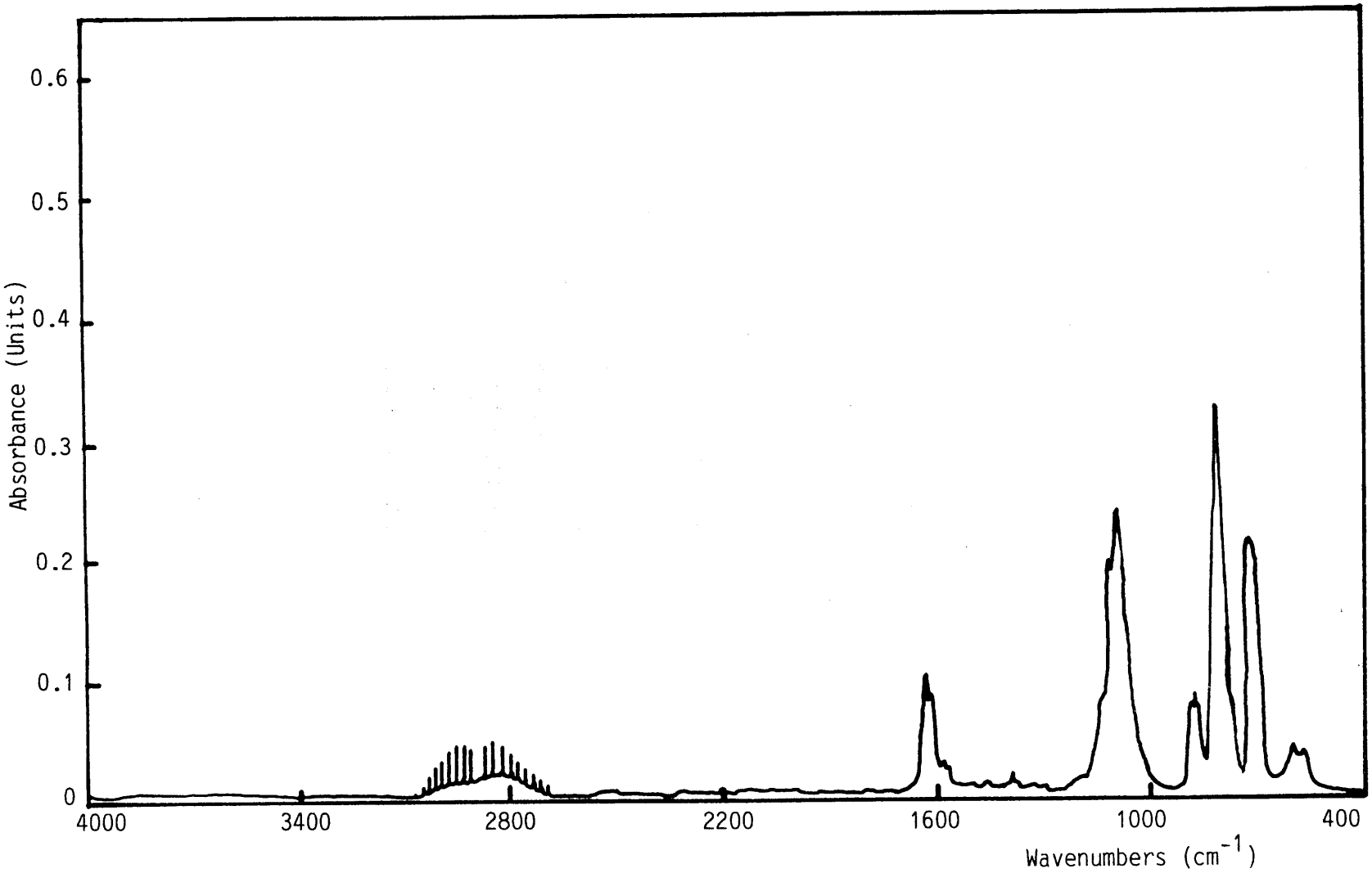


FIGURE 4.III. Vapour Phase Infra-Red Spectrum Collected at t = 60 min in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.



free flowing powder (Photo 4.I), turned purple when the stopcock was opened (Photo 4.II). If the gaseous 1,1-dichloroethene was allowed to stand in contact with the solid, the purple colour deepened over 60 min until the solid had an almost black, lustrous, tarry appearance (Photo 4.III). If the volatile material was removed by pumping within 5 min of the start of reaction, some of the colour was discharged.

These results indicate that gaseous 1,1-dichloroethene reacts with solid aluminium (III) chloride, in the absence of any other species, to yield hydrogen chloride. This observation is consistent with Scheme 3.IV. There was no evidence from the spectra, or from GCIR or GCMS, for monochloroacetylene which would be the expected product of the simple dehydrochlorination of 1,1-dichloroethene. This indicates either that the hydrogen chloride is produced by dehydrochlorination of an involatile species derived from 1,1-dichloroethene, such as poly-1,1-dichloroethene, or that monochloroacetylene is produced in the reaction, but is consumed rapidly at the surface. The production of gaseous 1,1,1-trichloroethane confirms that aluminium (III) chloride catalysed hydrochlorination of 1,1-dichloroethene is a significant process in this reaction; it also confirms the reversibility of steps (i) and (ii) in Scheme 3.IV.

The detection of gaseous carbon tetrachloride indicates that C-C bond cleavage must take place. There was no evidence from the spectra, or from GCIR or GCMS, for gaseous methane, methyl chloride or any other C-C bond fission product. This may mean that the species co-produced with carbon tetrachloride is not volatile. If the involatile organic species produced in this reaction is poly-

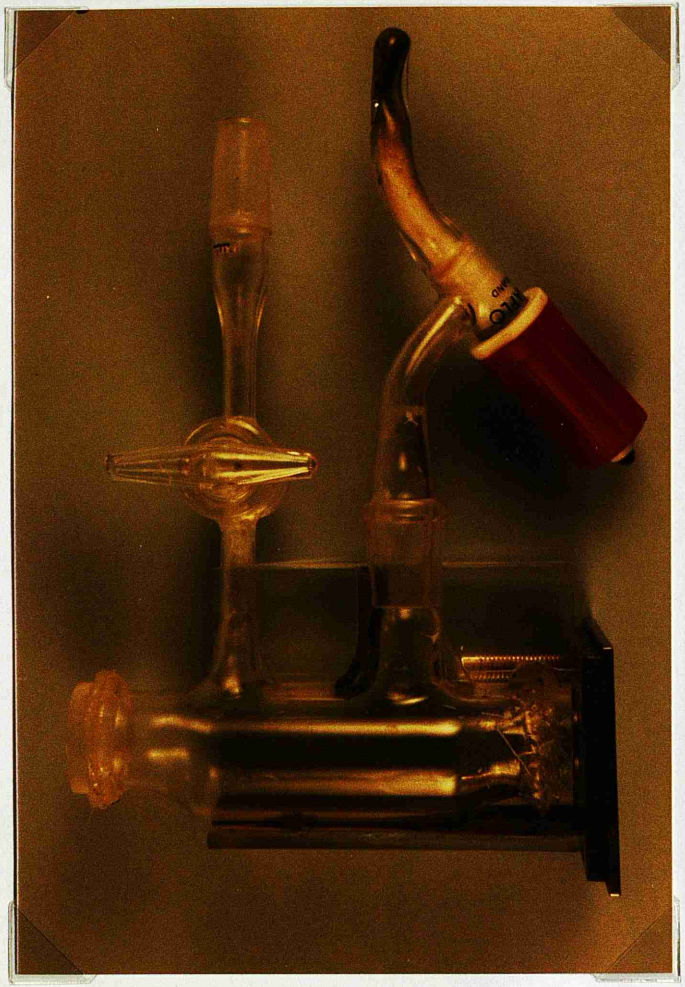


Photo 4.I

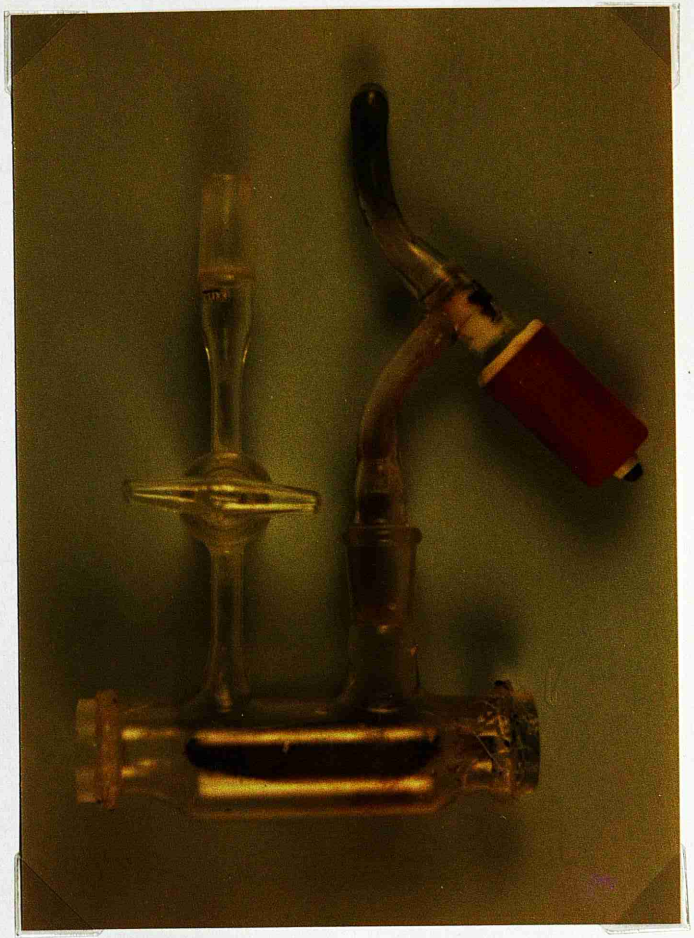


Photo 4.II

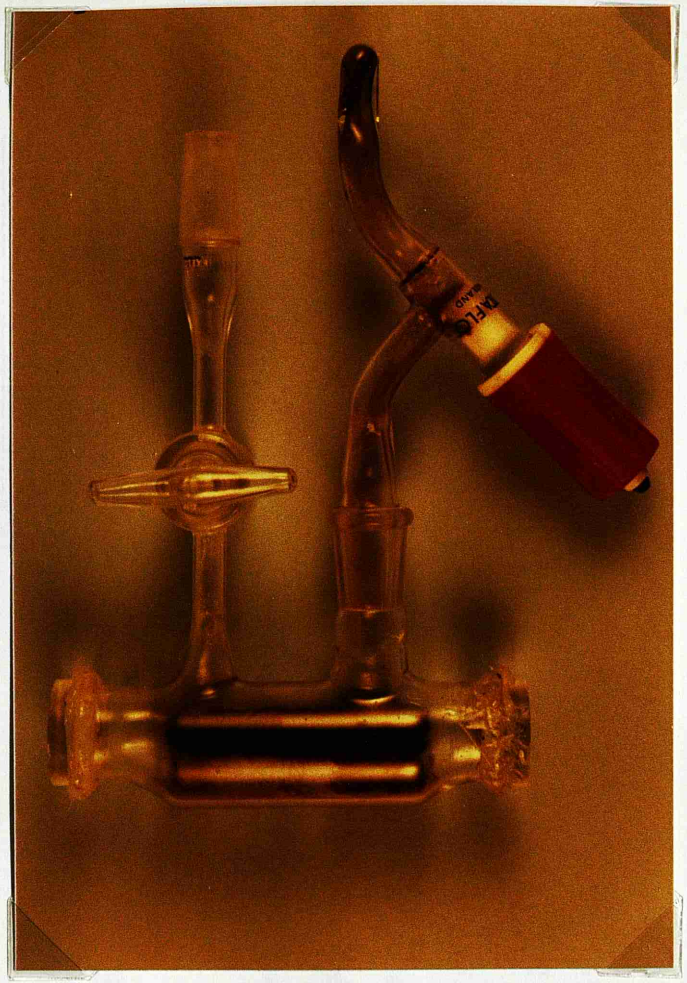


Photo 4.III

FIGURE 4.IV. *Vapour Phase Infra-Red Spectrum Collected 5 min After Removing the Volatile Material from the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.*

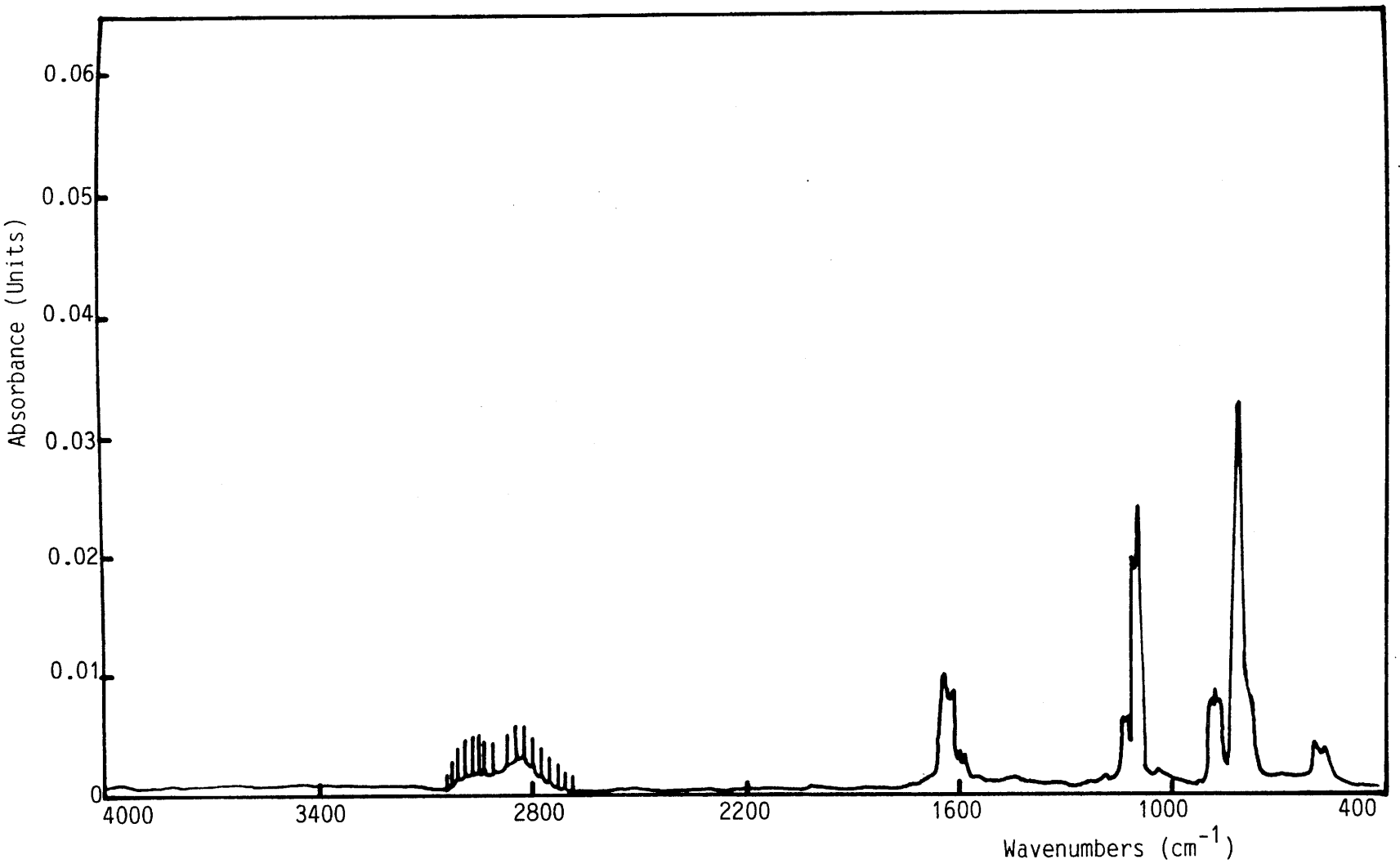


Figure 4.IV. A spectrum collected after a further 10 min was identical to Figure 4.V. If the cell was subsequently evacuated and closed, a spectrum collected 5 min after the cell was closed showed hydrogen chloride only (Figure 4.VI). A spectrum collected after a further 5 min was identical to Figure 4.VI.

The results indicate that hydrogen chloride is emitted by the purple solid formed by the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride. This suggests that a reaction which yields hydrogen chloride continues to take place after gaseous 1,1-dichloroethene is removed from the system; thus the dehydrochlorination of an involatile species derived from 1,1-dichloroethene, such as poly-1,1-dichloroethene (4.2.1), may be the most significant route to the formation of gaseous hydrogen chloride in this system. The production of gaseous 1,1-dichloroethene and carbon tetrachloride for a short time after the removal of volatile material has several possible interpretations, as discussed for 1,1,1-trichloroethane and carbon tetrachloride in 3.2.2. There is further evidence for the adsorption of carbon tetrachloride on glass (6.2.1).

4.2.3 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene

The results obtained were reproducible. The observations were qualitatively identical to those obtained in 4.2.1. This result suggests that a steady state is attained in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride, since 1,1-dichloroethene was still present when no further change was observed in 4.2.1 after 90 min.

4.2.4 Infra-Red Spectroscopic Analysis of the Interaction of Gaseous 1,1-Dichloroethene with Gaseous Hydrogen Chloride.

No gaseous 1,1,1-trichloroethane, or any other species, was detected in the infra-red spectrum within 90 min in a 1:1 molar mixture of gaseous 1,1-dichloroethene and hydrogen chloride. This indicates that the hydrochlorination of 1,1-dichloroethene does not lead to the production of a detectable quantity of 1,1,1-trichloroethane under the conditions used in 4.2.1 and 4.2.3 unless solid aluminium (III) chloride is present.

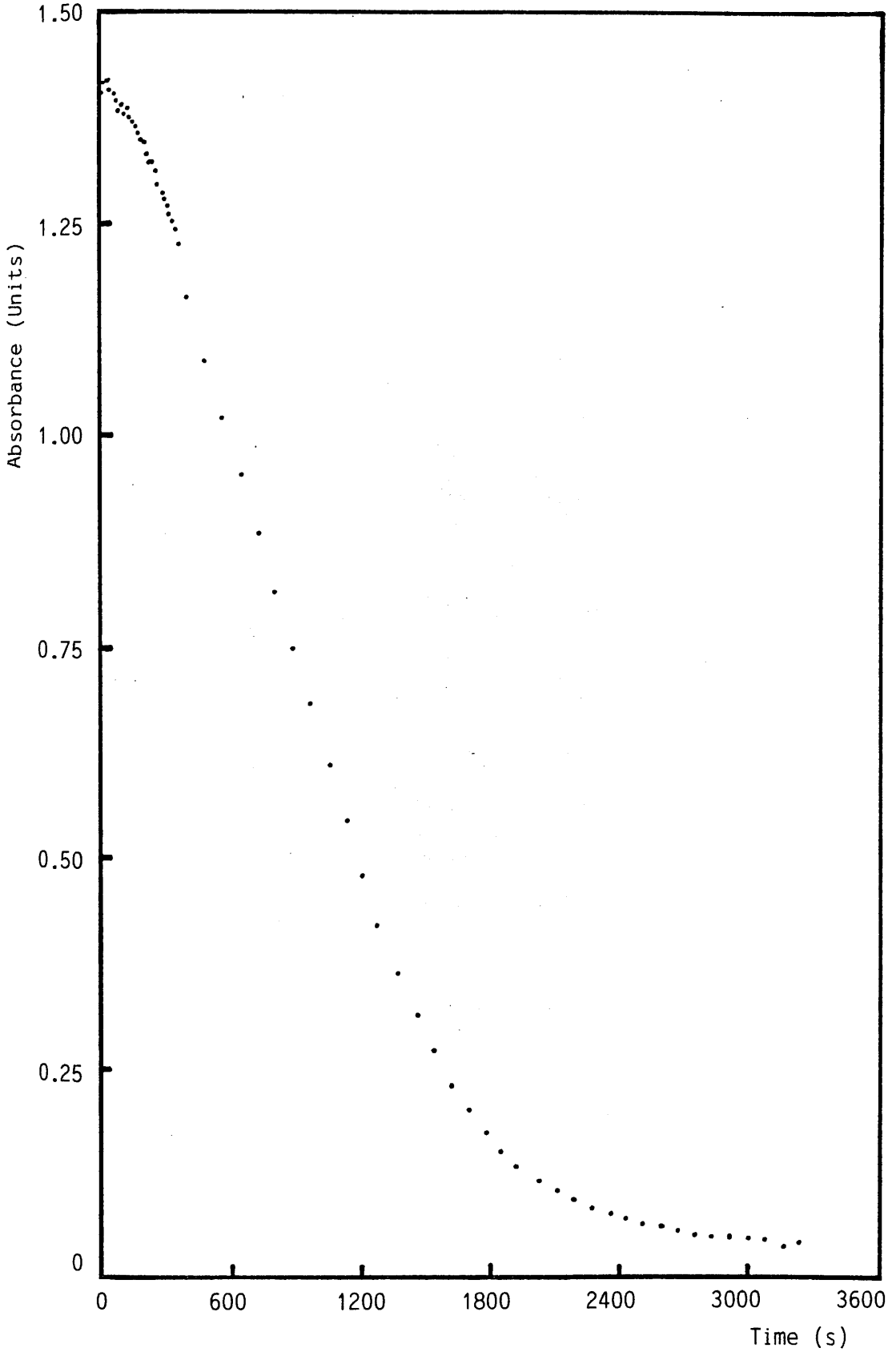
4.2.5 Kinetic Treatment of Infra-Red Data from the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

The interpretation of time dependences in this reaction is expected to be difficult, since 1,1-dichloroethene is consumed by at least two processes, namely (i) the reaction which ultimately yields hydrogen chloride, and which is believed to be aluminium (III) chloride catalysed oligomerisation or polymerisation of 1,1-dichloroethene, and (ii) the aluminium (III) chloride catalysed hydrochlorination of 1,1-dichloroethene. The results obtained were reproducible in five of the seven experiments. The plots used as examples relate to the same experiment (D6 in Table 4.XI).

When gaseous 1,1-dichloroethene reacted with solid aluminium (III) chloride, the pressure of 1,1-dichloroethene (represented by the absorbance of the $1627cm^{-1}$ peak in Figure 4.VII) showed a large decrease during the first 1300s. A small decrease was observed thereafter.

Gaseous 1,1,1-trichloroethane was detected within 30s, and the pressure (represented by the absorbance of the $722cm^{-1}$ peak

FIGURE 4.VII. Plot of Absorbance vs Time for the 1627 cm^{-1} Peak of 1,1-Dichloroethene in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.



in Figure 4.VIII) increased to a maximum, typically in 1000s, before decreasing over the ensuing period towards an apparent constant pressure. Table 4.I contains the initial quantities of reactants and the times at which the maximum pressures of 1,1,1-trichloroethane were observed. There does not appear to be any simple relationship between these quantities.

Gaseous hydrogen chloride was detected within 30s, and its pressure (represented by the absorbance of the 2821 cm^{-1} peak in Figure 4.IX) increased during the course of the experiment. The absorbance at ca. 795cm^{-1} displayed the same behaviour as the 1,1-dichloroethene peaks. This behaviour was attributed to the dominance of the 796cm^{-1} feature of 1,1-dichloroethene during most of the experiment.

Table 4.II contains the quantities of gaseous material involved in four of these experiments. Initial pressures of 1,1-dichloroethene were obtained using a constant volume manometer when the cell was loaded. Carbon tetrachloride pressures were estimated by comparison with standard spectra. All other pressures were calculated using calibrations (2.3.3). At least 80% of the 1,1-dichloroethene was lost from the gas phase during the course of the experiment. The maximum pressure of 1,1,1-trichlorethane detected was <22% of the original 1,1-dichloroethene pressure. The maximum pressure of hydrogen chloride detected at the end of the experiment ranged from 20 to 70% of the original 1,1-dichloroethene pressure. The maximum pressure of carbon tetrachloride detected was 1% of the original 1,1-dichloroethene.

The observation that gaseous 1,1,1-trichloroethane is produced and consumed in this reaction is expected in view of the

FIGURE 4.VIII. Plot of Absorbance vs Time for the 722 cm^{-1} Peak of 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

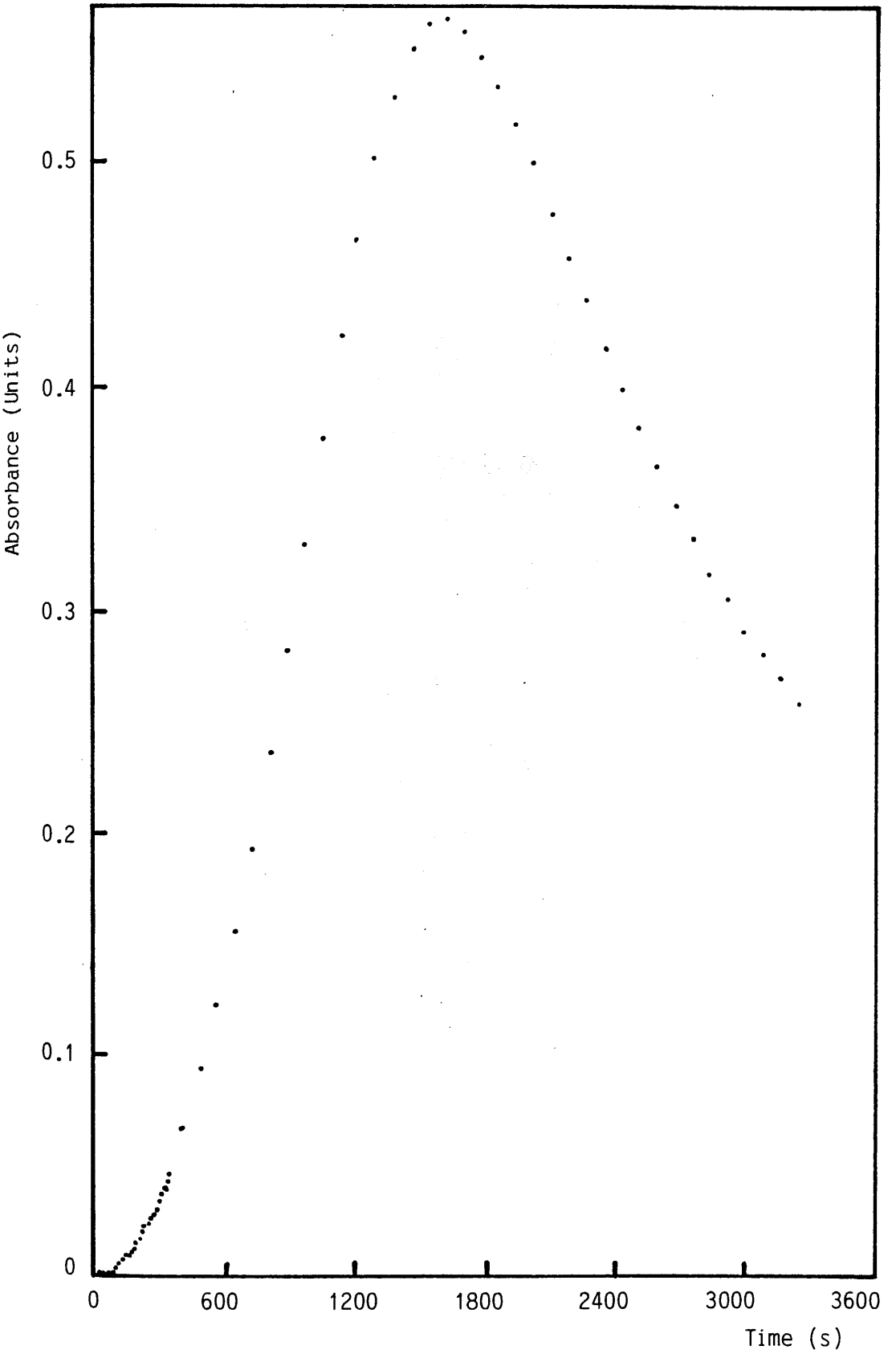


TABLE 4.I

Initial Quantities of Reactants and Times of Maximum 1,1,1-Trichloroethane Pressure in Reaction of Gaseous 1,1-Dichloroethene and $AlCl_3$(s)

Run No.	Initial $CH_2=CCl_2$(g) (mmol)	$AlCl_3$(s) (mmol)	Time of Maximum CH_3CCl_3(g) Pressure (s)
D1	0.024 ± 0.002	3.507 ± 0.003	1080 ± 50
D4	0.071 ± 0.002	5.508 ± 0.003	2820 ± 100
D5	0.144 ± 0.002	3.875 ± 0.003	830 ± 50
D6	0.150 ± 0.002	3.379 ± 0.003	1600 ± 100
D7	0.245 ± 0.002	2.953 ± 0.003	800 ± 50

FIGURE 4.IX. Plot of Absorbance vs Time for the 2821 cm^{-1} Peak of Hydrogen Chloride in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

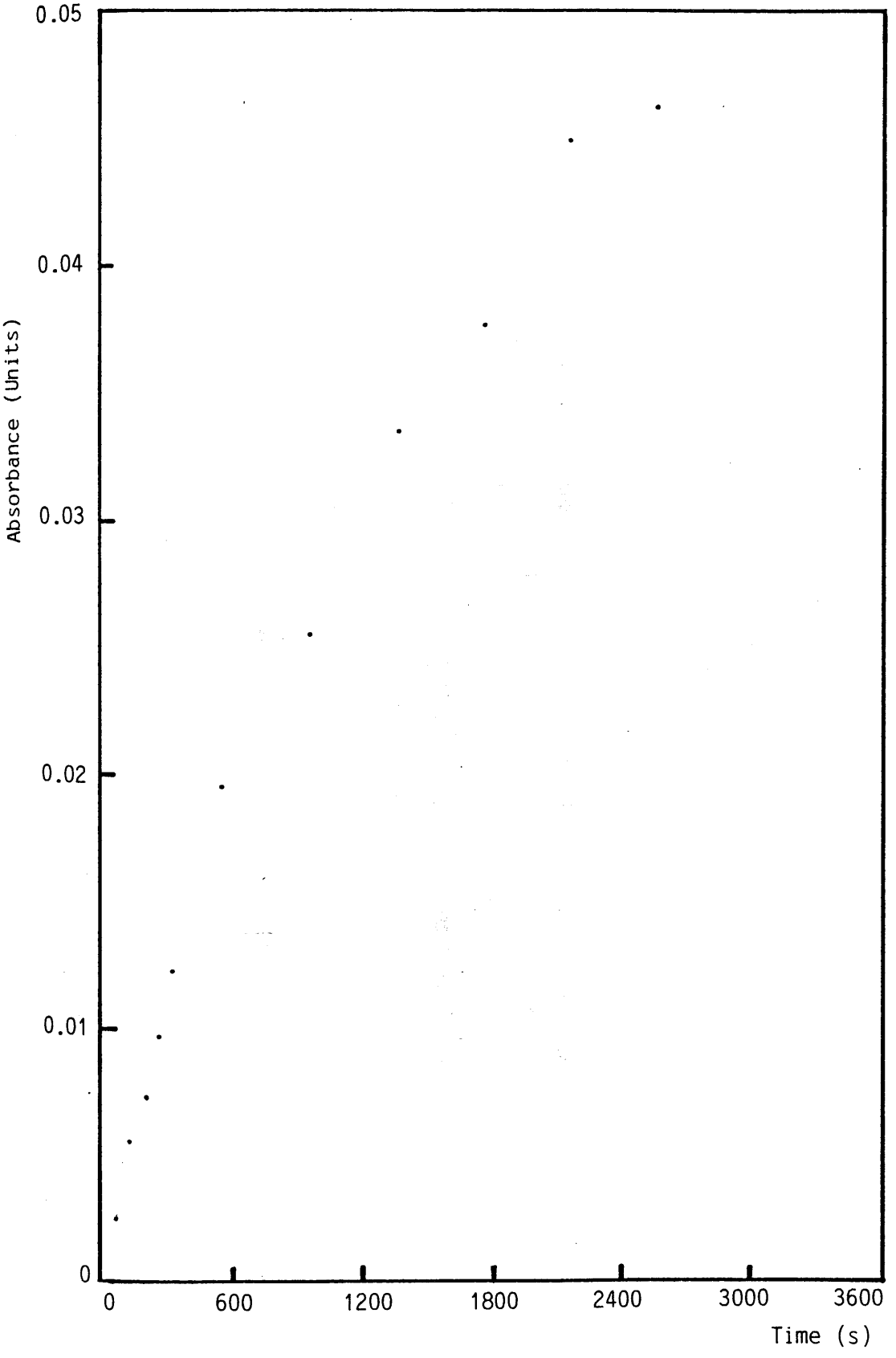


TABLE 4.II(a): Quantities of Reactant and Products at Selected Times in Reactions of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial $CH_2=CCl_2$ (g)		$CH_2=CCl_2$ (g) at time of maximum CH_3CCl_3 (g) pressure		$CH_2=CCl_2$ (g) at end of experiment	
	Torr	mmol	Torr	mmol	Torr	mmol
D1	8.3 ± 0.5	0.024 ± 0.002	2.2 ± 0.2	0.006 ± 0.0006	1.0 ± 0.2	0.003 ± 0.0006
D4	24.5 ± 0.5	0.071 ± 0.002	5.8 ± 0.2	0.017 ± 0.001	4.3 ± 0.2	0.012 ± 0.0006
D5	49.5 ± 0.5	0.144 ± 0.002	10.0 ± 1.0	0.029 ± 0.003	4.4 ± 0.2	0.013 ± 0.0006
D6	51.6 ± 0.5	0.150 ± 0.002	6.5 ± 0.2	0.019 ± 0.001	1.1 ± 0.04	0.012 ± 0.0001

Run No.	CH_3CCl_3 (g) in first spectrum		Maximum CH_3CCl_3 (g)		CH_3CCl_3 (g) at end of experiment	
	Torr	mmol	Torr	mmol	Torr	mmol
D1	0.05 ± 0.01	0.0001 ± 0.0002	1.9 ± 0.2	0.006 ± 0.0006	1.4 ± 0.2	0.004 ± 0.0005
D4	0.6 ± 0.05	0.002 ± 0.0002	1.8 ± 0.2	0.005 ± 0.0006	1.5 ± 0.2	0.004 ± 0.0005
D5	0.8 ± 0.07	0.002 ± 0.0002	2.6 ± 0.2	0.008 ± 0.0006	1.0 ± 0.1	0.003 ± 0.0003
D6	0 ± 0.01	0 ± 0.0002	2.3 ± 0.2	0.007 ± 0.0006	1.0 ± 0.1	0.003 ± 0.0003

TABLE 4.II(b): Quantities of Products at Selected Times in Reactions of $CH_2{=}CCl_2$ (g) With $AlCl_3$ (g)

Run No.	HCl (g) in first spectrum		HCl (g) at time of maximum CH_3CCl_3 (g) pressure		HCl (g) at end of experiment	
	Torr	mmol	Torr	mmol	Torr	mmol
D1	0 ± 0.2	0 ± 0.0006	1.8 ± 0.4	0.005 ± 0.001	3.6 ± 0.2	0.010 ± 0.0006
D4	2.8 ± 0.6	0.008 ± 0.001	8.5 ± 0.5	0.025 ± 0.001	10.1 ± 0.5	0.029 ± 0.001
D5	0 ± 0.5	0 ± 0.001	not recorded	not recorded	35.1 ± 0.5	0.102 ± 0.001
D6	0.6 ± 0.5	0.002 ± 0.001	11.0 ± 1.1	0.032 ± 0.003	12.3 ± 0.7	0.036 ± 0.001

Run No.	CCl_4 (g) at end of experiment	
	Torr	mmol
D1	< 0.25	< 0.0007
D4	< 0.25	< 0.0007
D5	< 0.25	< 0.0007
D6	< 0.25	< 0.0007

results obtained in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (3.2.1, 3.2.4). The amount of carbon tetrachloride detected indicates that it is a minor product of the reaction. The total amount of gaseous carbon containing material decreased substantially from the start to the end of the experiment; reductions of 71 to 96% in the amount of gaseous organic material were observed. This observation confirms that a non-volatile organic species is produced in the reaction.

Figure 4.X shows the variation of pressure with time of the gaseous reactants and products in a typical experiment (D6 in Table 4.XI). Table 4.III contains the quantity of 1,1-dichloroethene consumed and the quantities of 1,1,1-trichloroethane and hydrogen chloride present at selected times in this experiment. Carbon tetrachloride is not included because the peak at ca. 795cm^{-1} is known to be due to two species which have different absorbance vs time behaviour. The quantity of 1,1-dichloroethene consumed at time t was calculated by subtraction of the pressure at time t (obtained from a pressure vs absorbance calibration (2.3.3)) from the initial pressure. The calibration was only applicable at pressures <35 Torr; at times <250s the 1,1-dichloroethene pressure was >35 Torr and it was not possible to calculate the quantity consumed.

At any time t (>250s), the total amount of 1,1-dichloroethene consumed and the amount of gaseous 1,1,1-trichloroethane present are known (Table 4.III). Neglecting carbon tetrachloride, subtraction of the amount of 1,1,1-trichloroethane present from the total amount of 1,1-dichloroethene consumed gives the amount of involatile material formed at time t, in mmol of C2 units.

Some of the hydrogen chloride produced in the reaction takes part in the aluminium (III) chloride catalysed hydrochlorination of 1,1-dichloroethene to yield 1,1,1-trichloroethane. However, 1,1,1-trichloroethane undergoes reaction itself, and from 3.2.4, that process is expected to yield at least one mole of hydrogen chloride per mole of 1,1,1-trichloroethane consumed. Assuming that each mole of 1,1,1-trichloroethane consumed leads to the regeneration of one mole of gaseous hydrogen chloride, then, at any time t, summation of the amount of hydrogen chloride present and the amount of 1,1,1-trichloroethane present gives the net amount of hydrogen chloride formed at time t.

Table 4.IV contains amounts of involatile material formed and hydrogen chloride formed, calculated as described above. The net amount of hydrogen chloride produced is always 20-30 mol % of the amount of involatile material formed (expressed in terms of mmol C2). If Scheme 3.IV was accurate, the expected quantity of hydrogen chloride produced would be ca. 50 mol % of the amount of involatile material formed. Thus Scheme 3.IV is not accurate.

Another possibility which must be considered is the aluminium (III) chloride catalysed hydrochlorination of 1,1-dichloroethene derived oligomers and/or polymers. Such reactions have been reported for the solution reaction of aluminium (III) chloride with 1,1-dichloroethene[82] and were discussed by Winterton[75] as a possible source of the apparent "inhibition" of aluminium (III) chloride catalysed dehydrochlorination of 1,1,1-trichloroethane by the addition of -(CH=CCl-)_n polyenes.[81] This possibility is discussed further in Chapter 5.

FIGURE 4.X. Variation of Pressure with Time for Gaseous Reactants and Products in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

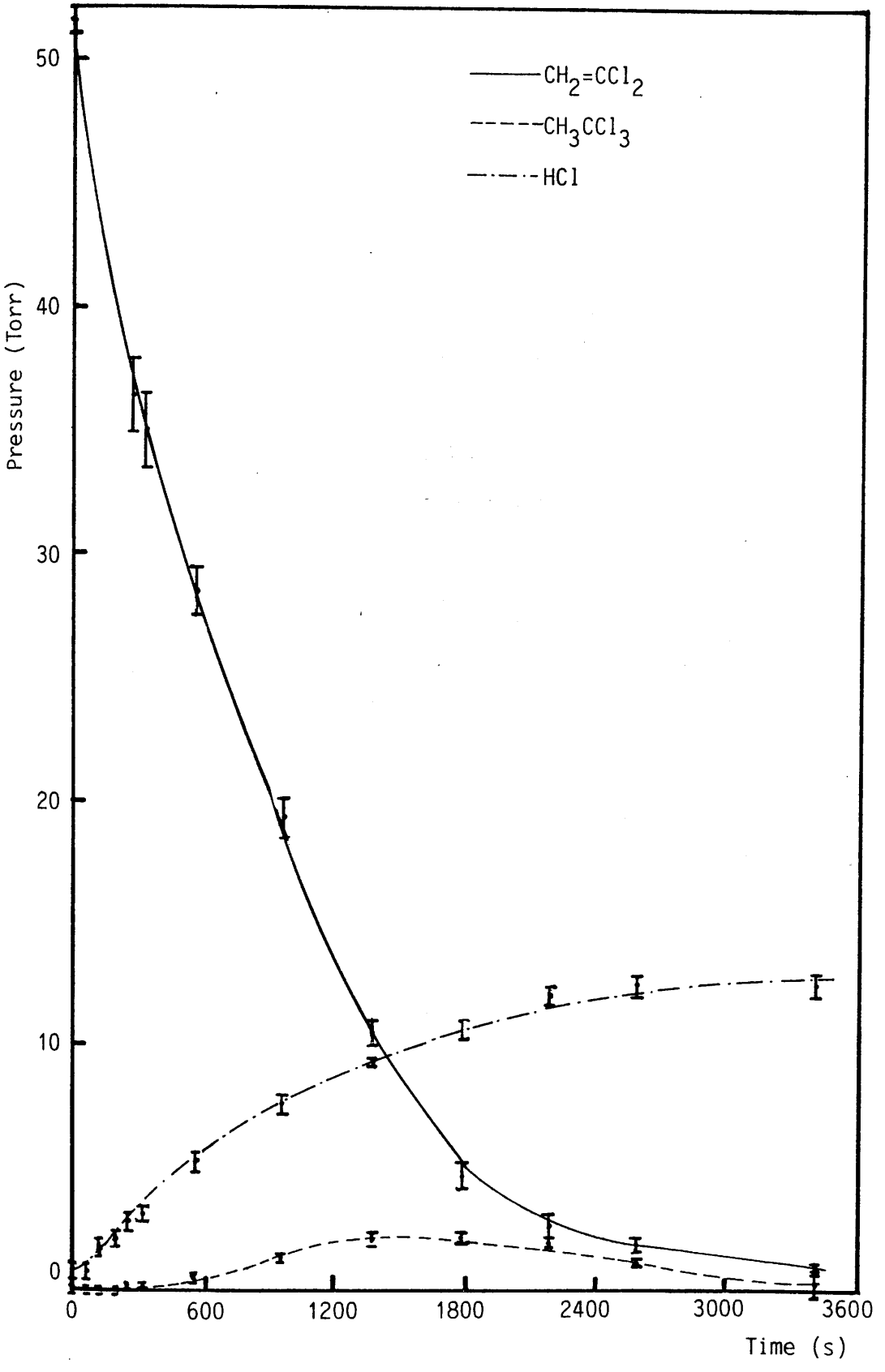


TABLE 4.III: Quantities of Reactant Consumed and Products Detected at Selected Times in a Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Time (s)	$CH_2=CCl_2$ (g) consumed (mmol)	CH_3CCl_3 (g) detected (mmol)	HCl (g) detected (mmol)
5		0 ± 0.0003	0.002 ± 0.001
70		0 ± 0.0003	0.002 ± 0.001
135		0.0001 ± 0.0003	0.004 ± 0.001
201		0.0002 ± 0.0003	0.006 ± 0.001
267	0.044 ± 0.004	0.0003 ± 0.0003	0.008 ± 0.001
332	0.048 ± 0.004	0.0004 ± 0.0003	0.009 ± 0.001
562	0.067 ± 0.003	0.0014 ± 0.0003	0.015 ± 0.001
965	0.094 ± 0.002	0.0039 ± 0.0003	0.022 ± 0.001
1369	0.120 ± 0.002	0.0062 ± 0.0005	0.028 ± 0.001
1773	0.136 ± 0.001	0.0064 ± 0.0005	0.031 ± 0.001
2178	0.142 ± 0.001	0.0054 ± 0.0005	0.035 ± 0.001
2582	0.145 ± 0.001	0.0043 ± 0.0004	0.036 ± 0.001
3304	0.149 ± 0.001	0.0029 ± 0.0003	0.036 ± 0.001

TABLE 4.IV: Quantities of Involatile Material and Gaseous Hydrogen Chloride Formed in a Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Time (s)	Involatile Material Formed (mmol C2)	Net HCl (g) Formed (mmol)
267	0.044 ± 0.004	0.008 ± 0.001
332	0.048 ± 0.004	0.009 ± 0.001
562	0.066 ± 0.003	0.016 ± 0.001
965	0.090 ± 0.002	0.026 ± 0.001
1369	0.114 ± 0.002	0.034 ± 0.001
1773	0.130 ± 0.001	0.037 ± 0.001
2178	0.137 ± 0.001	0.040 ± 0.001
2582	0.141 ± 0.001	0.040 ± 0.001
3304	0.146 ± 0.001	0.039 ± 0.001

None of the possibilities discussed above invalidates Scheme 3.IV although they indicate that the scheme is not complete as written. Time dependences must be examined in more detail before further discussion. The first and second order plots were constructed as described in 3.2.4.

The first and second order plots for the disappearance of gaseous 1,1-dichloroethene are curves as shown in Figures 4.XI and 4.XII. This suggests that the loss of gaseous 1,1-dichloroethene is a process which does not have a simple time dependence.

The first order plot for 1,1,1-trichloroethane is a curve (Figure 4.XIII). The second order plot is linear at times >1600s (Figure 4.XIV). However, the apparent linear second order plot in this instance is a consequence of the very small value of x_o, the absorbance of the $722cm^{-1}$ peak in the first spectrum in which it was detected; at higher absorbances $^1/x$, where x is the absorbance of the peak at time t, becomes very small compared with $^1/x_o$ and a limiting condition is reached where $^1/x - ^1/x_o \longrightarrow - ^1/x_o$ and a straight line with zero gradient is obtained.

The first and second order plots for hydrogen chloride are curves (Figures 4.XV and 4.XVI). The first and second order plots for the peak at ca. $795cm^{-1}$ displayed the same behaviour as those obtained for the 1,1-dichloroethene peaks.

For adsorption of a single species (Equation 4.II), the

$$B_{(g)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} B_{(ad)} \qquad \text{Equation 4.II}$$

Langmuir isotherm is given by Equation 4.III, where θ_B is the fractional surface coverage of B, b_B is the adsorption coefficient

$$\theta_B = \frac{b_B p_B}{1 + b_B p_B} \qquad \text{Equation 4.III}$$

FIGURE 4.XI. First Order Plot for 1,1-Dichloroethene in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

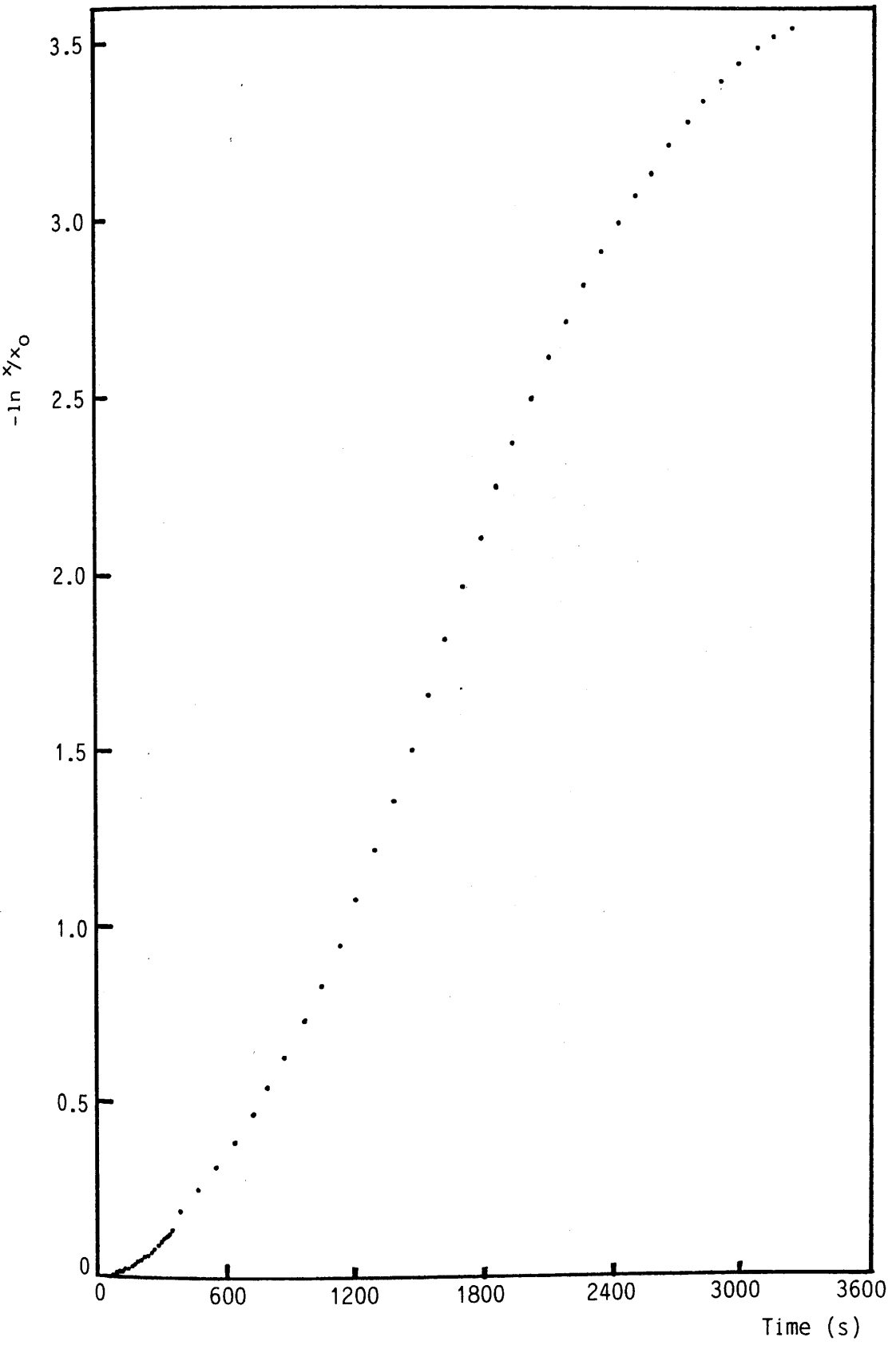


FIGURE 4.XII. Second Order Plot for 1,1-Dichloroethene in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

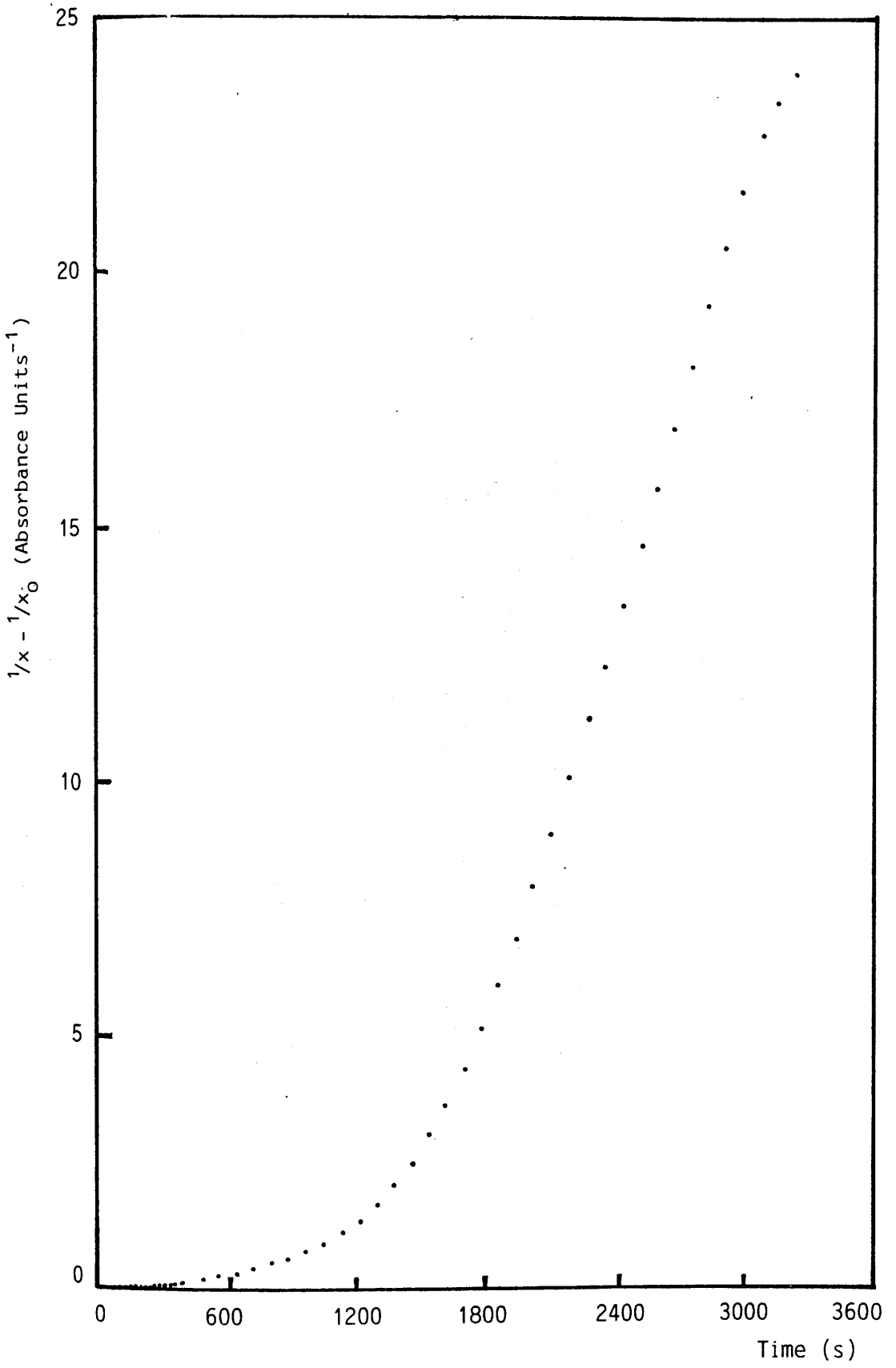


FIGURE 4.XIII. First Order Plot for 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

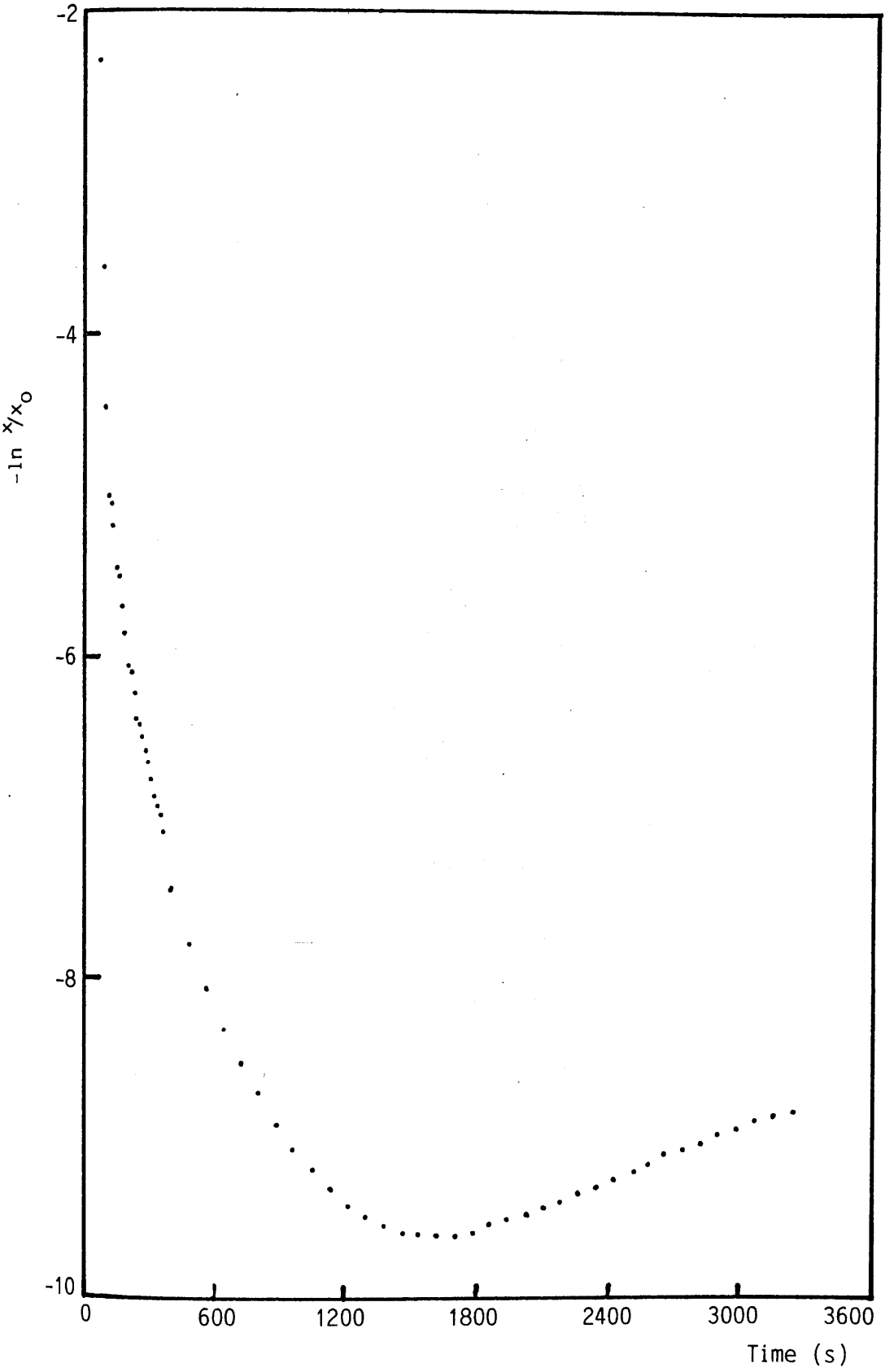


FIGURE 4.XIV. Second Order Plot for 1,1,1-Trichloroethane in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

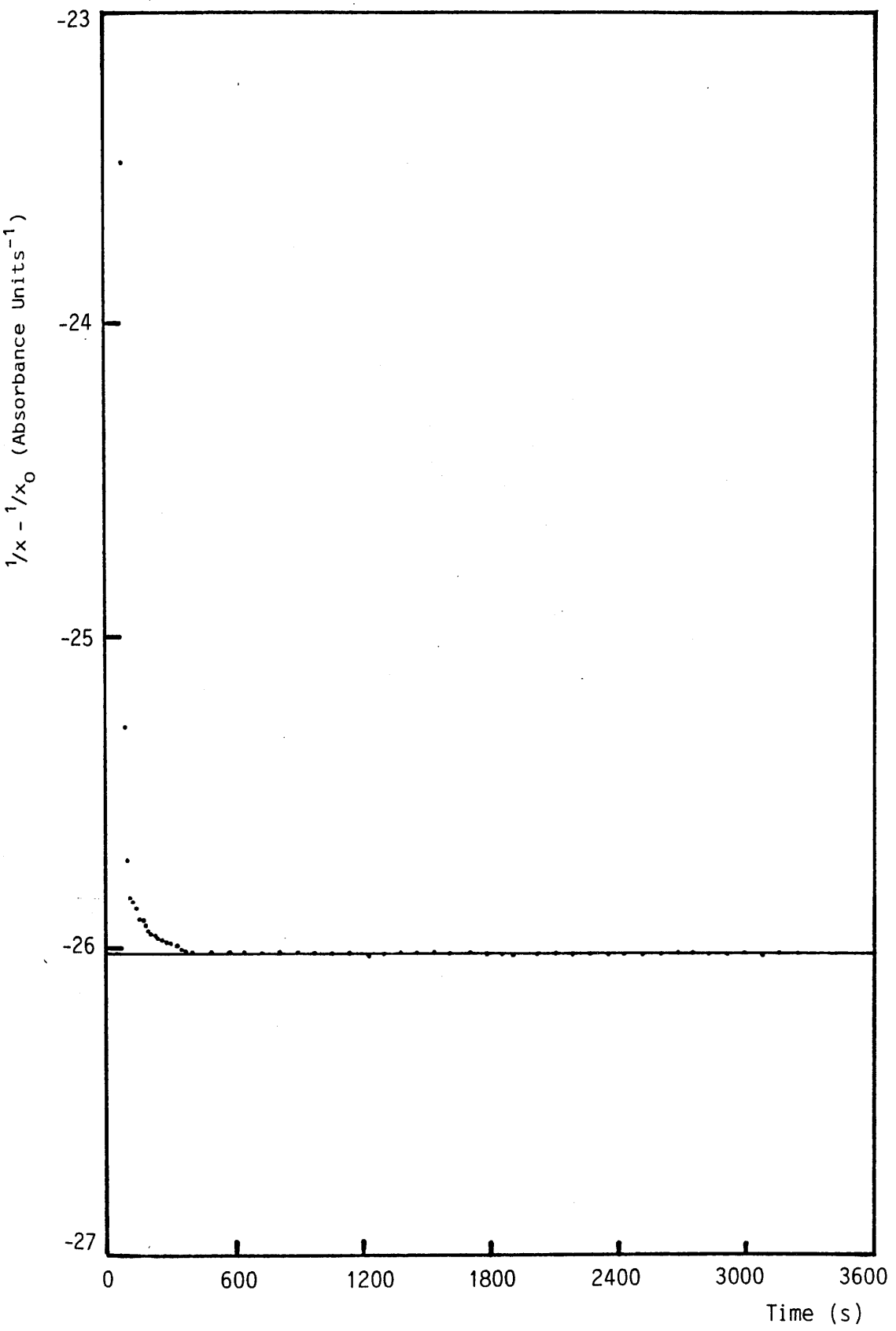


FIGURE 4.XV. First Order Plot for Hydrogen Chloride in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

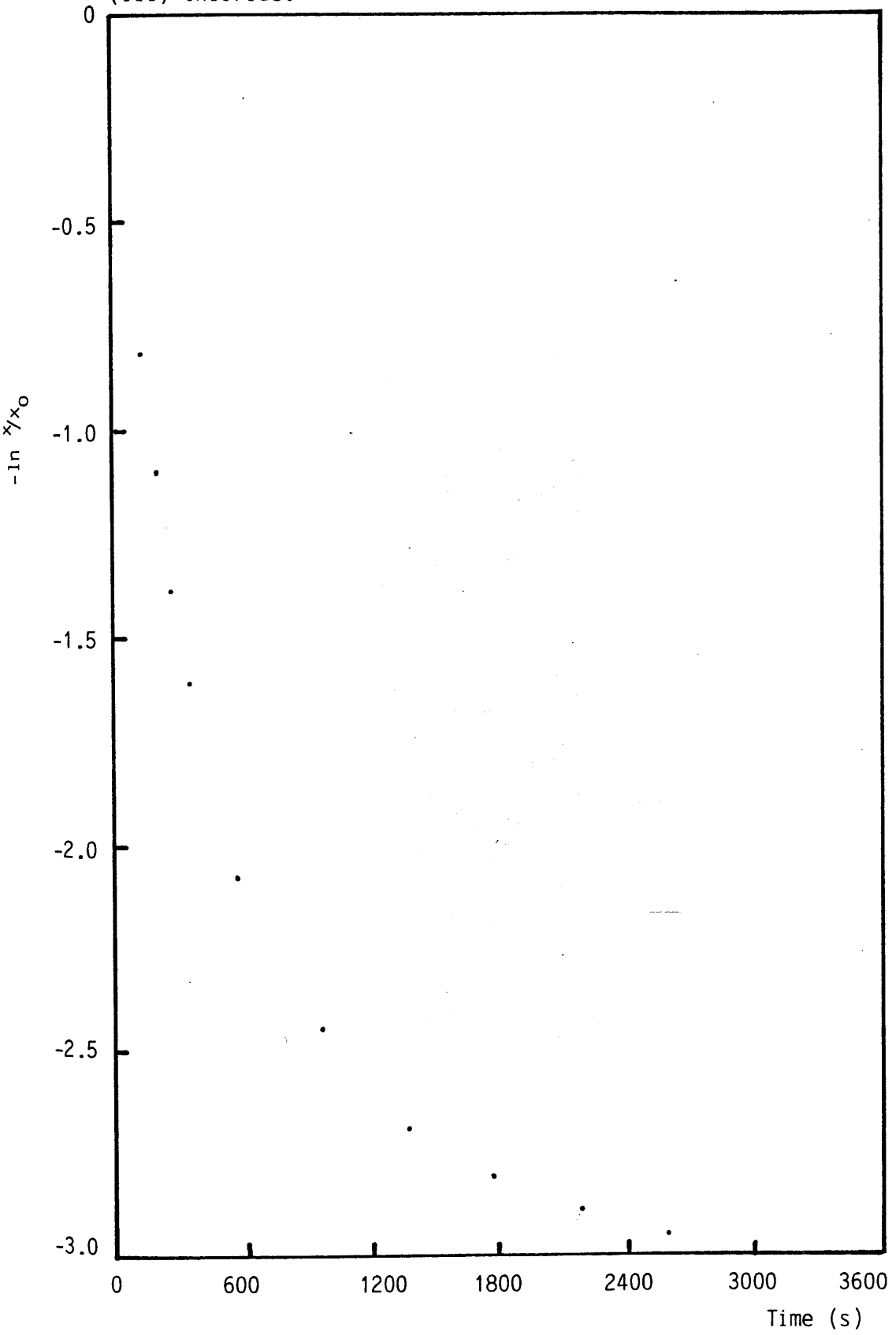
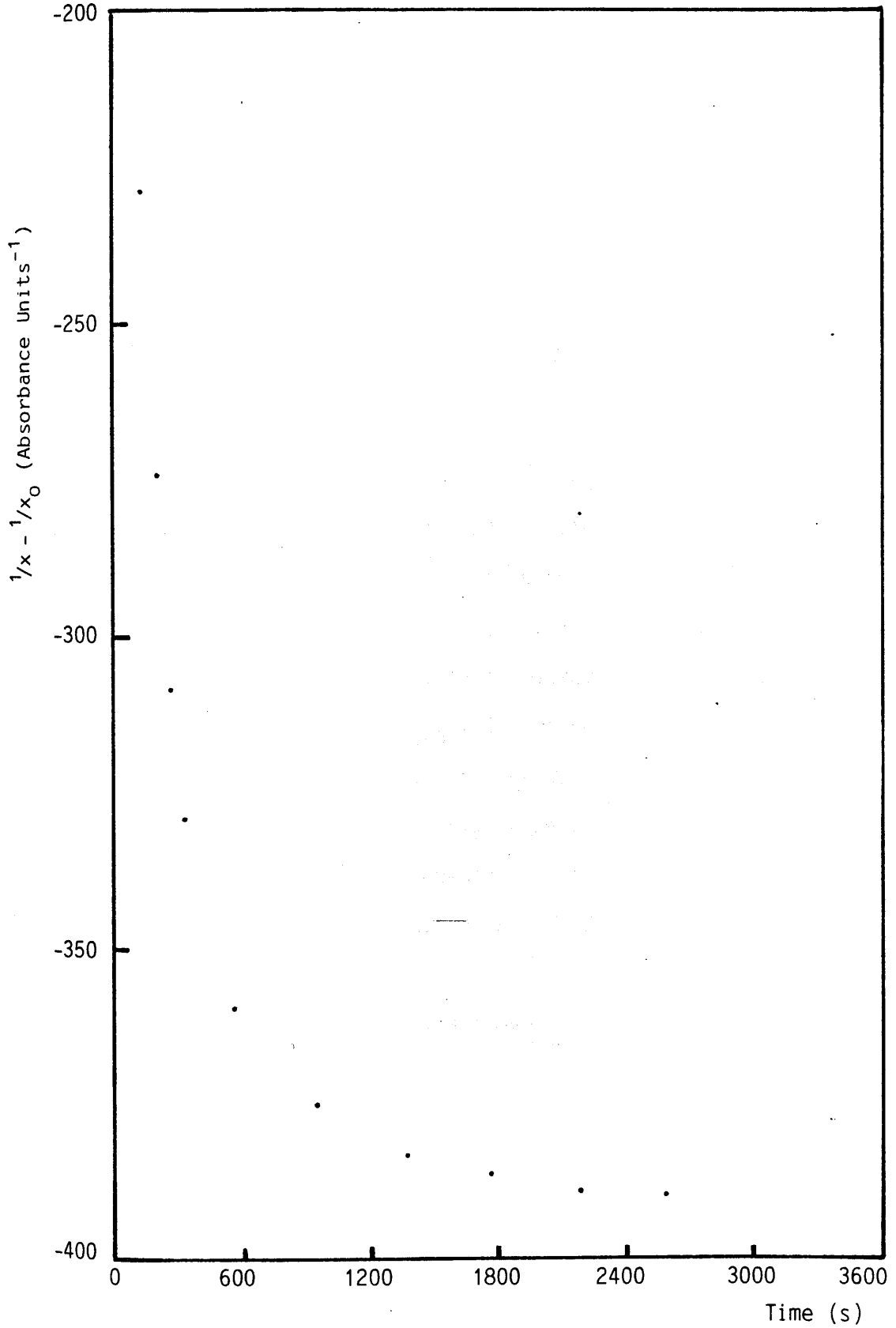


FIGURE 4.XVI. Second Order Plot for Hydrogen Chloride in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.



($= {}^{k_a}/_{k_d}$) and p_B is the pressure of gaseous B in equilibrium with the surface. If 1,1-dichloroethene is B, and the rate determining step in the main reaction with aluminium (III) chloride is a bimolecular surface of an adsorbed molecule of 1,1-dichloroethene with a 1,1-dichloroethene/$AlCl_2^+$ complex (Scheme 3.IV and Equation 4.I), then the rate of reaction is given by Equation 4.IV, which, from Equation 4.III, can be rewritten as Equation 4.V.

$$\text{Rate} = k\theta_B^2 \qquad \text{Equation 4.IV}$$

$$\text{Rate} = \frac{kb_B^2 p_B^2}{(1 + b_B p_B)^2} \qquad \text{Equation 4.V}$$

In the early stages of the reaction 1,1-dichloroethene is the only gaseous species present; there are no competitors for adsorption at this stage, and hydrochlorination of 1,1-dichloroethene is unimportant. If a partial surface coverage of 1,1-dichloroethene is achieved, then the term $b_B p_B$ will not be negligibly small compared to unity, since the rate of desorption will not be very much greater than the rate of adsorption. From Equation 4.V, the rate of reaction will therefore be a complex function of the 1,1-dichloroethene pressure, and the reaction can, in principle, have an order of anything between 0 and 2.

While the model outlined above can account for the observed behaviour in the early stages of the reaction, the hydrochlorination of 1,1-dichloroethene is known to be a significant process leading to the loss of gaseous 1,1-dichloroethene in the later stages (Table 4.III). Thus the observed first and second order plots for the loss of 1,1-dichloroethene are likely to reflect the combined

effect of at least two processes with comparable rates and possibly different orders of reaction.

Hydrogen chloride is known to be produced by at least two processes during the reaction, namely (i) the reaction of 1,1-dichloroethene alone with solid aluminium (III) chloride and (ii) the reaction of the 1,1,1-trichloroethane produced with aluminium (III) chloride (3.2.1); it is also consumed in the aluminium (III) chloride catalysed hydrochlorination of 1,1-dichloroethene. The first and second order plots for the ingrowth of hydrogen chloride are therefore likely to reflect the combined effect of these processes.

The principal difference between the five experiments of the type discussed above and the two which did not display this behaviour was that, in the latter, the pressure of 1,1,1-trichloroethane increased steadily during the course of the experiments. Table 4.V contains the quantities of gaseous material involved in both of these experiments. The normal gaseous products were detected. The only notable differences from Table 4.II were the comparatively small amounts of 1,1-dichloroethene consumed in both experiments (38 and 47% respectively) and the very large amount of hydrogen chloride detected in experiment D2 (167 mol % of the original 1,1-dichloroethene pressure).

Gaseous 1,1,1-trichloroethane is known to be produced and consumed in the reaction and the relative rates and relative importances of these two processes will control the shape of the pressure vs time plot obtained. The observed behaviour could be accounted for if the rate of production of gaseous 1,1,1-trichloroethane by aluminium (III) chloride catalysed hydrochlorination of

TABLE 4.V: Quantities of Reactant and Products at Selected Times in Reactions of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial $CH_2=CCl_2$ (g)		$CH_2=CCl_2$ (g) at end of experiment	
	Torr	mmol	Torr	mmol
D2	9.1 ± 0.5	0.026 ± 0.002	5.6 ± 0.2	0.016 ± 0.0006
D3	15.1 ± 0.5	0.044 ± 0.002	8.0 ± 0.2	0.023 ± 0.0006

Run No.	CH_3CCl_3 (g) in first spectrum		CH_3CCl_3 (g) at end of experiment	
	Torr	mmol	Torr	mmol
D2	0.7 ± 0.06	0.002 ± 0.0002	0.9 ± 0.1	0.003 ± 0.0003
D3	0 ± 0.06	0 ± 0.0002	0.2 ± 0.04	0.0005± 0.0001

Run No.	HCl (g) in first spectrum		HCl (g) at end of experiment	
	Torr	mmol	Torr	mmol
D2	0 ± 0.2	0 ± 0.0005	15.2 ± 0.3	0.044 ± 0.001
D3	0.7 ± 0.2	0.002 ± 0.0006	2.9 ± 0.2	0.008 ± 0.0006

Run No.	CCl_4 (g) at end of experiment	
	Torr	mmol
D2	<0.25	<0.0007
D3	<0.25	<0.0007

1,1-dichloroethene was greater than the rate of removal of gaseous 1,1,1-trichloroethane by the reactions discussed in Chapter 3 throughout the entirety of the experiment.

4.2.6 Pressure Measurement Studies of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride

Two types of behaviour were observed. At initial pressures of 1,1-dichloroethene >10 Torr the results obtained were reproducible. Figure 4.XVII shows the results of a typical experiment (E5 in Table 4.XII). Initially a small decrease in pressure was observed (A $\longrightarrow$ B). This was followed by a relatively large pressure decrease (B $\longrightarrow$ C) to the minimum pressure (C), and then by a pressure increase (C $\longrightarrow$ D). The only difference between experiments was the length of the period A $\longrightarrow$ B. There is no direct relationship between the length of the period A $\longrightarrow$ B and the initial pressure of 1,1-dichloroethene, although an increase in the latter does appear to result in a decrease in the former. The pressure variation observed during an experiment was usually about 7 Torr (Table 4.VI). There is no direct relationship between the magnitude of pressure variation observed and the initial pressure of 1,1-dichloroethene, although an increase in the latter does appear to result in an increase in the former. The pressure at the end of an experiment was usually close to the initial pressure of 1,1-dichloroethene (Table 4.VI).

A plot of pressure increment vs time for experiment E5 is shown in Figure 4.XVIII. Initially the pressure increments remained negative and constant (A' $\longrightarrow$ B'). This was followed by a period in which the pressure increments decreased to a minimum value

FIGURE 4.XVII. Plot of Pressure vs Time in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

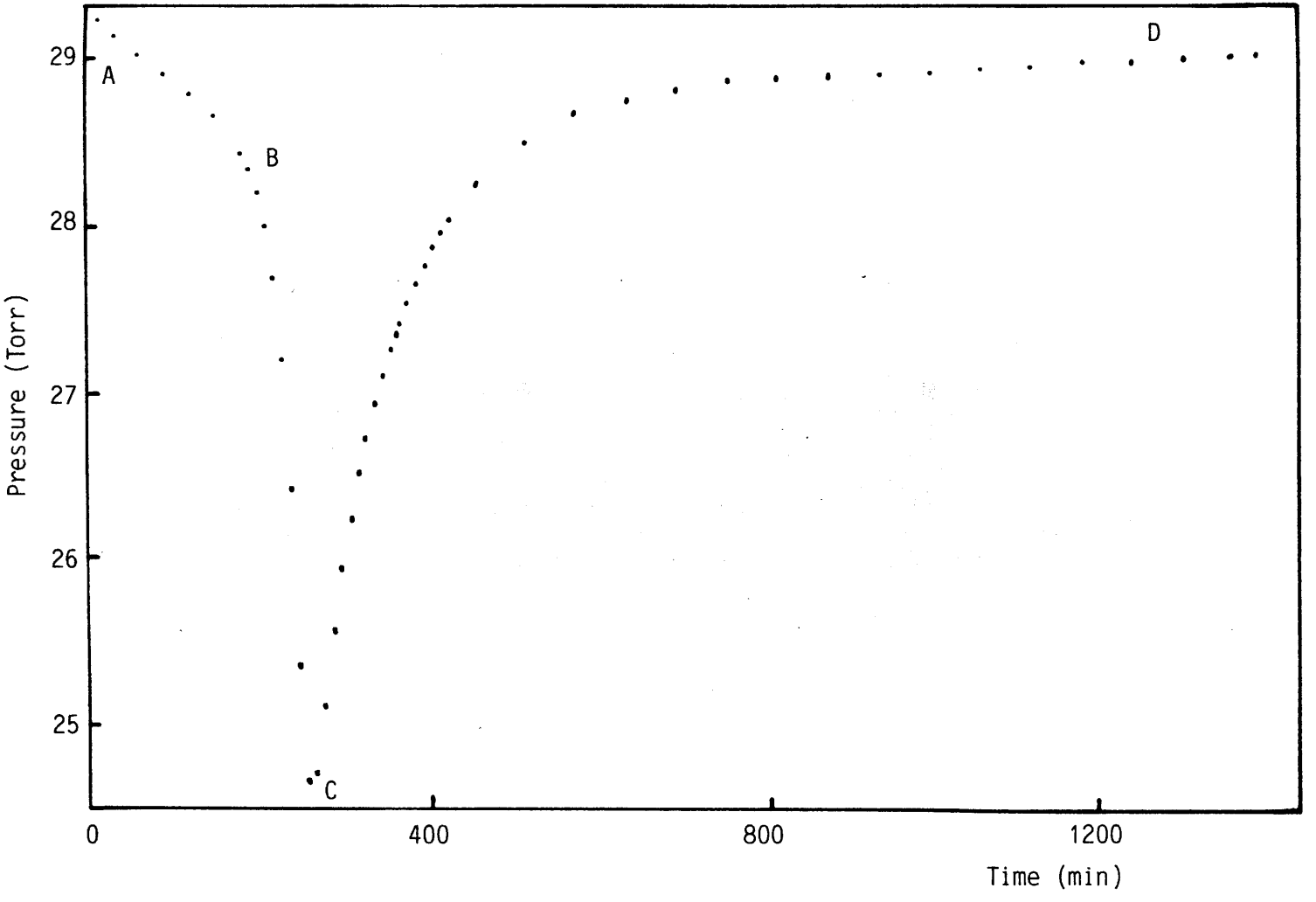
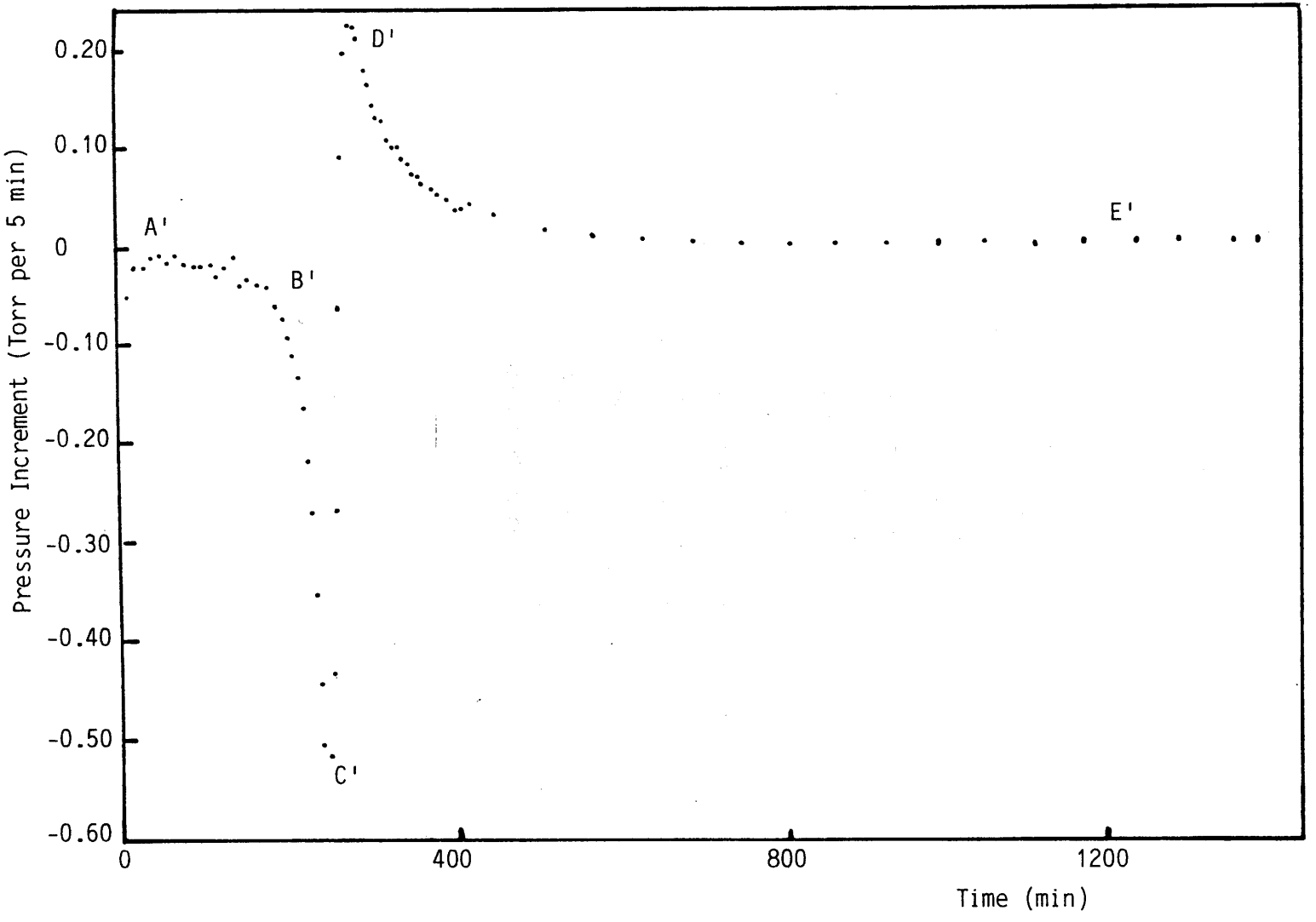


TABLE 4.VI: Pressure Measurements at Selected Times in the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (mmol)	Initial Pressure of $CH_2=CCl_2$ (Torr)	Minimum Pressure Observed (Torr)	Difference from (a) (Torr)	Final Pressure Observed (Torr)	Difference from (a) (Torr)	Time of Minimum (min)	Duration of Experiment (min)
E4	3.354 ± 0.003	18.45	16.74	-1.71	19.68	+1.23	350	1130
E5	2.043 ± 0.008	29.29	24.60	-4.69	28.94	-0.34	265	1390
E6	5.632 ± 0.003	33.11	25.76	-7.35	27.78	-5.33	45	295
E7	not recorded	35.95	29.94	-6.01	36.31	+0.31	90	335
E8	not recorded	37.64	30.32	-7.32	37.30	-0.34	105	280
E9	1.441 ± 0.003	47.18	36.99	-10.19	44.26	-2.92	90	185
E10	1.612 ± 0.003	53.38	44.63	-8.75	51.86	-1.58	13	180

FIGURE 4.XVIII. Plot of Pressure Increment vs Time in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.



(B' ⟶ C'), and then by a period in which the pressure increased to a maximum positive value (C' ⟶ D'). Finally, the pressure increments decreased towards zero (D' ⟶ E').

As the experiment proceeded, the surface of the solid underwent a colour change from white to light purple over period A ⟶ B (Figure 4.XVI), after which the solid darkened uniformly until it had an almost black, lustrous, tarry appearance. GCIR and GCMS investigations of a sample of the vapour removed from experiment E6 after 295 min showed the presence of hydrogen chloride and carbon tetrachloride only. This observation indicates that 1,1-dichloroethene, and any 1,1,1-trichloroethane derived from it, is completely consumed in the reaction.

As noted earlier, the total pressure at the end of the experiment is close to that at the start, and infra-red studies on the same system (4.2.5) indicated that carbon tetrachloride is a comparatively minor product. Thus close to one mole of hydrogen chloride must eventually be produced per mole of 1,1-dichloroethene consumed in forming the involatile product. Detection of such a large amount of hydrogen chloride is in contrast to the observations in the infra-red studies and suggests strongly that the involatile species produced in the reaction is highly unsaturated and/or highly cyclised.

The pressure variation observed suggests that the main reaction leading to the removal of gaseous 1,1-dichloroethene is autocatalytic. Initially a slow surface reaction which leads to the removal of gaseous 1,1-dichloroethene occurs. This period depends on the sample and may be dependent on the initial 1,1-dichloroethene pressure. When a sufficient concentration of a

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product of this reaction is present the loss of gaseous material accelerates; this observation has been attributed to the rapid removal of gaseous 1,1-dichloroethene, by analogy with infra-red studies on the same system (4.2.5). No vapour was removed from the experiment during the period when the rapid loss of gaseous material was observed, so the composition of the gas phase in this period is not known. The 1,1-dichloroethene, and any 1,1,1-trichloroethane derived from it, are completely consumed by the end of the experiment, thus the increase in pressure after the minimum pressure is observed must be due to the evolution of gaseous hydrogen chloride and carbon tetrachloride.

The identity of the species responsible for autocatalysis is not known. However, if the species is simply adsorbed 1,1-dichloroethene as postulated in 3.2.4, then only a negligibly short induction period would be expected since initially 1,1-dichloroethene has no competitors for adsorption. If the species responsible for autocatalysis is a product of the reaction of 1,1-dichloroethene with solid aluminium (III) chloride, such as the involatile organic species or hydrogen chloride, then the time at which a sufficient concentration of the species is attained will be governed by the rate of the reaction leading to its formation. From Equation 4.V, the rate of this reaction is ultimately a function of the 1,1-dichloroethene pressure, albeit a complex one; thus the time required to attain a sufficient concentration of the species responsible for autocatalysis, which corresponds to the length of period A $\longrightarrow$ B in Figure 4.XVII, will be a function of the initial 1,1-dichloroethene pressure. Although there is no direct relationship between the length of period A $\longrightarrow$ B and the initial pressure of 1,1-dichloroethene,

an increase in the latter does appear to result in a decrease in the former, which suggests that the autocatalytic species is either the involatile organic species or hydrogen chloride.

The results outlined above differ in two ways from those obtained in infra-red spectroscopic experiments carried out using comparable reaction stoichiometry in a similar volume. The amount of gaseous material present at the end of pressure measurement experiments was close to the amount present at the start, and the mixture contained only hydrogen chloride and carbon tetrachloride. In the infra-red experiments the amount of gaseous material present at the end was substantially reduced compared to the initial amount of gaseous 1,1-dichloroethene, and the mixture contained 1,1-dichloroethene, 1,1,1-trichloroethane, hydrogen chloride and carbon tetrachloride. However, the infra-red experiments were studied for a maximum of 90 min, a considerably shorter time than the average duration of a pressure measurement experiment, and the difference in the observations could be accounted for if all the 1,1-dichloroethene and any 1,1,1-trichloroethane derived from it are eventually consumed in the reaction.

Secondly, the autocatalytic effect observed in the pressure measurement experiments was not observed in the infra-red experiments. In the latter, reaction appeared to start uniformly throughout the solid as soon as it was exposed to gaseous 1,1-dichloroethene and a substantial pressure decrease was observed in the early stages.

This difference in behaviour is attributed to different treatments of the solid. The affinity of solid aluminium (III) chloride for water was noted in 1.2.2. If the glass walls of the vessel used in pressure measurement experiments had adsorbed water

molecules, then pumping the solid in the vessel overnight would lead to some hydration of the solid surface. Hydration of the surface could lead to a reduction in the number of sites available for adsorption and reaction of 1,1-dichloroethene molecules. In pressure measurement studies the solid is not disturbed before exposure to gaseous 1,1-dichloroethene; thus, if the surface is extensively hydrated, adsorption and reaction can initially take place only at a few sites and this, in turn, may mean that some time elapses before a sufficient concentration of the species responsible for autocatalysis is reached. It is significant that experiment E10, which is the only experiment using an initial 1,1-dichloroethene pressure >10 Torr not to exhibit the autocatalytic effect was the only experiment in which the solid was pumped for 1h before use.

In infra-red experiments the solid is disturbed immediately prior to exposure to gaseous 1,1-dichloroethene. Even if the surface of the solid is extensively hydrated, this disturbance will expose new reactive sites, and hence it may be possible to attain a sufficient concentration of the species responsible for autocatalysis more quickly.

At initial pressures of 1,1-dichloroethene <10 Torr, the result was of the form shown in Figure 4.XIX for experiment E1. A uniform increase in pressure was observed over the course of the experiment, occasionally preceded by a short period (<5 min) in which a small decrease in pressure was observed. Pressure variation observed during the experiment was <1 Torr (Table 4.VII). The solid underwent a uniform colour change from white to dark purple during the course of the reaction.

This behaviour indicates that an autocatalytic effect is

FIGURE 4.XIX. Plot of Pressure vs Time in the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

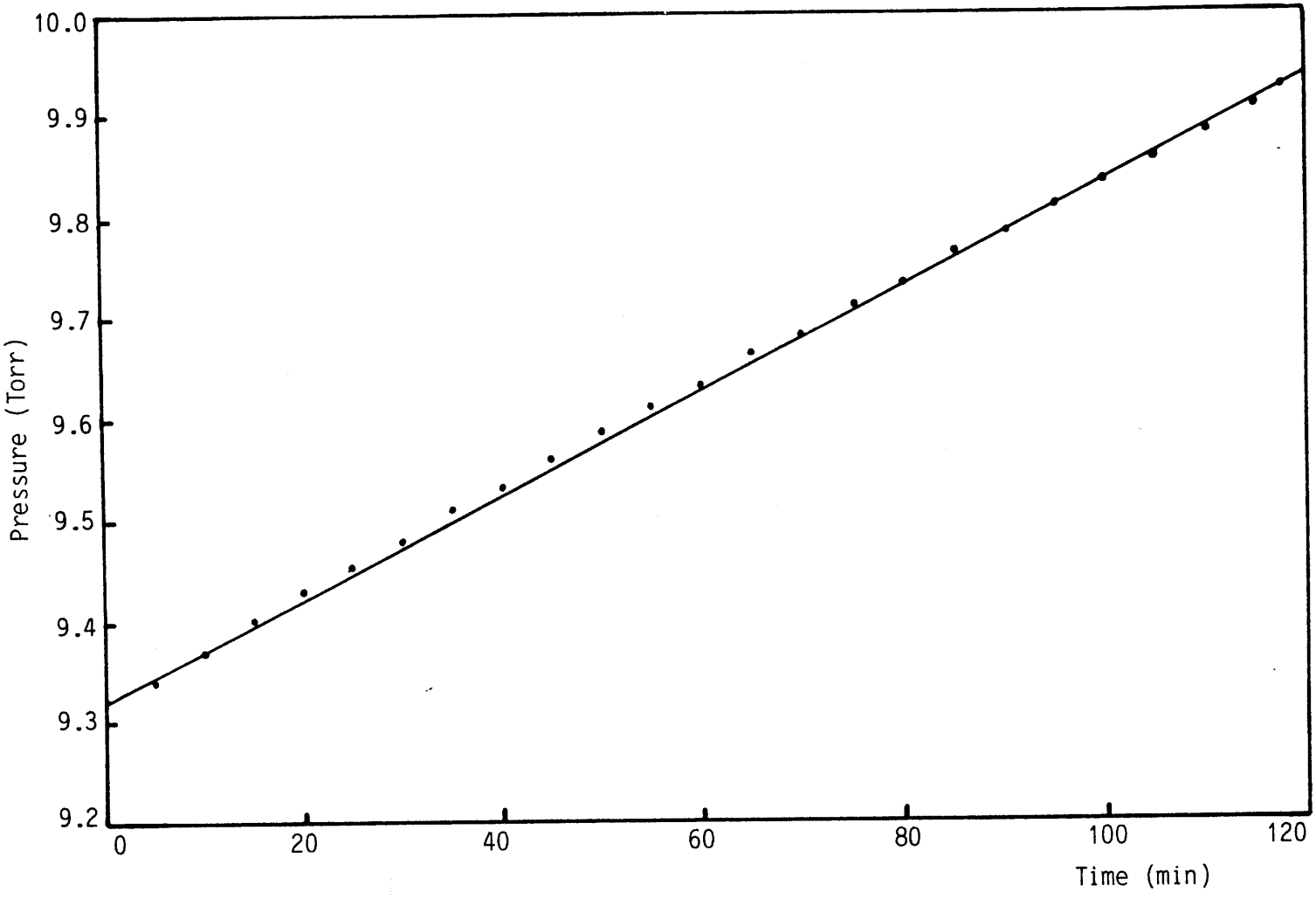


TABLE 4.VII: Pressure Measurements at Selected Times in the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (mmol)	Initial Pressure $CH_2=CCl_2$ (Torr)	Minimum Pressure Observed (Torr)	Difference from (a) (Torr)	Final Pressure Observed (Torr)	Difference from (a) (Torr)	Time of Minimum (min)	Total Time of Experiment (min)
E1	0.836	9.32	9.32	0	9.90	+0.58	0	110
E2	1.744	9.39	9.36	-0.03	9.64	+0.25	5	70
E3	2.999	10.07	10.07	0	11.19	+1.12	0	965

not observed in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride under the conditions described. This may be because the combination of the effects of a very small number of active sites and a comparatively small amount of reactant gas leads to a situation in which a sufficient concentration of the species responsible for autocatalysis is not attained during the timescale of experiments studied.

The results reported in the preceding sections have led to the ammendment of the Scheme proposed in Chapter 3 to describe the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (Scheme 3.IV).

The amended scheme is shown below (Scheme 4.I).

$$CH_3CCl_{3(g)} \overset{\text{fast}}{\rightleftharpoons} CH_3CCl_{3(ad)} \qquad \text{(i)}$$

$$CH_3CCl_{3(ad)} \overset{\text{fast}}{\rightleftharpoons} CH_2{=}CCl_{2(ad)} + HCl_{(g)} \qquad \text{(ii)}$$

$$CH_2{=}CCl_{2(ad)} \rightleftharpoons CH_2{=}CCl_{2(g)} \qquad \text{(iii)}$$

$$CH_2{=}CCl_{2(ad)} + AlCl_2^+ \overset{\text{fast}}{\rightleftharpoons} Cl_2AlCH_2\overset{+}{C}Cl_2 \qquad \text{(iv)}$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_{2(ad)} \overset{\text{r.d.s.}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 \qquad \text{(v)}$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3 \qquad \text{(vi)}$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2{=}CClCH_2CCl_3 + AlCl_3 \qquad \text{(vii)}$$

$$\tfrac{n}{2}CH_2{=}CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} \{CH{=}CCl\}_n + \tfrac{n}{2}HCl(g) \qquad \text{(viii)}$$

Processes leading to the formation of CCl_4 (g) (ix)

The reversibility of steps (i) and (ii) is verified by the results obtained in infra-red spectroscopic investigations of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (4.2.1, 4.2.3, 4.2.5), since gaseous 1,1,1-trichloroethane was detected in those experiments. These experiments also confirm

that gaseous 1,1-dichloroethene reacts with solid aluminium (III) chloride to yield an involatile product.

The pressure measurement experiments show that 1,1-dichloroethene and any 1,1,1-trichloroethane derived from it are completely consumed in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride. This indicates that step (vi), or one of those which follows it, is effectively irreversible. Secondly, the pressure vs time behaviour observed indicates that adsorbed 1,1-dichloroethene is not the species responsible for autocatalysis.

Step (ix) has been included to account for the production of carbon tetrachloride; the mechanism for its formation is not known and there is still no direct evidence for any of the 1,1-dichloroethene derived oligomers postulated in steps (vi), (vii) and (viii), although this aspect is discussed further in Chapters 8 and 9.

4.3 Experimental

4.3.1 Vapour Phase Infra-Red Analysis of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.3.4. Table 4.VIII contains the quantities of material used. Spectra were collected before opening the stopcock, and typically after 5, 60 and 90 min of reaction. When no further change was observed in successive spectra the cell was evacuated and collection of spectra terminated.

4.3.2 Infra-Red Spectroscopic Analysis of the Vapour Phase over Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene.

An evacuated cell containing a sample of solid aluminium (III) chloride which had been previously exposed to gaseous 1,1-dichloroethene for 90 min was placed in the spectrometer beam and spectra were collected at 5 min intervals until no further change was observed. The samples from experiments A1 and A2 (Table 4.VIII) were treated in this way.

4.3.3 Vapour Phase Infra-Red Spectroscopic Analysis of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene.

Experiments were carried out using the procedure described in 2.3.4. The solid aluminium (III) chloride used had been previously exposed to gaseous 1,1-dichloroethene for 90 min. Table 4.IX contains the quantities of material used.

TABLE 4.VIII: Initial Quantities of Reactants in Infra-Red Studies of the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial Pressure of $CH_2=CCl_2$ (g) (Torr)	Initial $CH_2=CCl_2$(g) (mmol)	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)
A1	10.0 ± 0.5	0.029 ± 0.002	0.4278 ± 0.0004	3.204 ± 0.003
A2	27.8 ± 0.5	0.081 ± 0.002	0.5281 ± 0.0004	3.956 ± 0.003

TABLE 4.IX: Initial Quantities of Reactants in Infra-Red Studies of the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s) which has been previously Exposed to $CH_2=CCl_2$ (g)

Run No.	Initial Pressure of $CH_2=CCl_2$ (g) (Torr)	Initial $CH_2=CCl_2$(g) (mmol)	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)
B1	15.8 ± 0.5	0.046 ± 0.002	0.6199 ± 0.0004	4.643 ± 0.003
B2	15.3 ± 0.5	0.044 ± 0.002	0.4278 ± 0.0004	3.204 ± 0.003
B3	21.6 ± 0.5	0.063 ± 0.002	0.5281 ± 0.0004	3.956 ± 0.003

TABLE 4.X: Initial Quantities of Reactants in Infra-Red Study of the Interaction of $CH_2=CCl_2$ (g) and HCl (g)

Run	Pressure $CH_2=CCl_2$(g) (Torr)	$CH_2=CCl_2$(g) (mmol)	Pressure HCl(g) (Torr)	HCl(g) (mmol)
C1	22.0 ± 0.5	0.064 ± 0.002	23.4 ± 0.5	0.068 ± 0.002

4.3.4 Infra-Red Spectroscopic Analysis of the Interaction of Gaseous 1,1-Dichloroethene and Gaseous Hydrogen Chloride.

An approximately 1:1 molar ratio of gaseous 1,1-dichloroethene and gaseous hydrogen chloride (Table 4.X) was allowed to stand in cell A (2.3.1) for 90 min and spectra were collected at regular intervals.

4.3.5 Kinetic Treatment of Infra-Red Data from the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.3.5. Table 4.XI contains the quantities of material used.

4.3.6 Pressure Measurement Studies of the Reaction of Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride

Experiments were carried out using the procedure described in 2.7.2. Table 4.XII contains the quantities of material used.

Samples of the gaseous mixture were removed from the reaction vessel at the end of experiment E7 and investigated using GCIR and GCMS. The total volume of the reaction vessel and dead space was calculated in each experiment and was always approximately 50ml.

TABLE 4.XI: Initial Quantities of Reactants in Kinetic Infra-Red Studies of the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial Pressure of $CH_2=CCl_2$(g) (Torr)	Initial $CH_2=CCl_2$ (g) (mmol)	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)
D1	8.3 ± 0.5	0.024 ± 0.002	0.4682 ± 0.0004	3.507 ± 0.003
D2	9.1 ± 0.5	0.026 ± 0.002	0.6432 ± 0.0004	4.818 ± 0.003
D3	15.1 ± 0.5	0.044 ± 0.002	0.5012 ± 0.0004	3.754 ± 0.003
D4	24.5 ± 0.5	0.071 ± 0.002	0.7353 ± 0.0004	5.508 ± 0.003
D5	49.5 ± 0.5	0.144 ± 0.002	0.5173 ± 0.0004	3.875 ± 0.003
D6	51.6 ± 0.5	0.150 ± 0.002	0.4511 ± 0.0004	3.379 ± 0.003
D7	84.4 ± 0.5	0.245 ± 0.002	0.3942 ± 0.0004	2.953 ± 0.003

TABLE 4.XII: Initial Quantities of Reactants and Durations of Experiments in Pressure Measurement Studies of the Reaction of $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)	Initial Pressure of $CH_2=CCl_2$ (g) (Torr)	CH_2CCl_2(g) (mmol)	Duration of experiment (min)
E1	0.1116 ± 0.0004	0.836 ± 0.003	9.32	0.03	110
E2	0.2328 ± 0.0004	1.744 ± 0.003	9.39	0.03	70
E3	0.4004 ± 0.0004	2.999 ± 0.003	10.07	0.03	965
E4	0.4478 ± 0.0004	3.354 ± 0.003	18.45	0.05	1130
E5	0.2728 ± 0.0004	2.043 ± 0.003	29.20	0.09	970
E6	0.7519 ± 0.0004	5.632 ± 0.003	33.11	0.09	295
E7	not recorded	not recorded	35.95	0.11	335
E8	not recorded	not recorded	37.64	0.11	280
E9	0.1924 ± 0.0004	1.441 ± 0.003	47.18	0.14	185
E10	0.2152 ± 0.0004	1.612 ± 0.003	53.38	0.14	180

CHAPTER 5

CHAPTER 5

THE INTERACTION OF GASEOUS [^{36}Cl]-CHLORINE-LABELLED HYDROGEN CHLORIDE WITH SOLID ALUMINIUM (III) CHLORIDE

5.1 INTRODUCTION

The interaction of hydrogen chloride with aluminium (III) chloride has been the subject of considerable interest, due primarily to the importance of the combined action of hydrogen chloride and aluminium (III) chloride in catalysing Friedel-Crafts reactions.[24] However, there is no evidence for the direct combination of hydrogen chloride and aluminium (III) chloride under most conditions (1.2.4). An isotopic exchange study using gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride and solid aluminium (III) chloride showed no exchange at room temperature over 12h,[39] although complete exchange was observed when both reactants were in the gas phase. Circumstantial evidence for weak physical adsorption of hydrogen chloride on solid aluminium (III) chloride was reported, but the surface of the solid was not studied directly. Furthermore, the study was not extended to ternary systems such as $H_2O/HCl/AlCl_3$.

Exchange behaviour can be radically altered in the presence of a third component. The interaction of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride with solid iron (III) chloride has been studied using the direct monitoring Geiger-Müller radiochemical counting technique described in 2.5 in an attempt to develop a better understanding of the mechanism of iron (III) chloride catalysed hydrochlorinations of organic species.[98] [^{36}Cl]-Chlorine exchange was not observed between the anhydrous components at room temperature and

[^{36}Cl]-HCl was not adsorbed on iron (III) chloride under these conditions. However, [^{36}Cl]-chlorine exchange and adsorption of [^{36}Cl]-HCl on the solid both occurred in the presence of small quantities of water. It is possible that exchange is facilitated in this system by the formation of $H_3O^+Cl^-$ at the surface.

The interaction of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride with solid aluminium (III) chloride was studied in this work using the direct monitoring Geiger-Müller radiochemical counting technique in an attempt to develop a better understanding of the mechanism of aluminium (III) chloride catalysed transformations of chlorohydrocarbons. The system was studied in the absence of a third component to determine whether any exchange or surface interaction occurred, and in the presence of water, 1,1,1-trichloroethane and 1,1-dichloroethene to determine the effect of these species on adsorption and exchange processes.

5.2 Results

5.2.1 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with the Pyrex Reaction Vessel

When gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride was admitted to the reaction vessel at room temperature, the count rates from both Geiger-Müller tubes were identical and remained constant over 3h. The initial and final background count rates were identical. This result was reproducible and indicates that the adsorption of [^{36}Cl]-HCl on the Pyrex glass of the reaction vessel is not a significant process over times $\lesssim$ 3h.

5.2.2 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride

In experiments in which the [^{36}Cl]-chlorine-labelled hydrogen chloride was distilled from -90°C to -196°C onto P_2O_5 immediately prior to use, a barely detectable surface count rate was observed as soon as the [^{36}Cl]-HCl was admitted, which did not increase significantly over 70 min. Accurate determinations of surface count rates were not made during the course of the exposure to gaseous [^{36}Cl]-HCl, as very long counting times would have been required. Pumping the solid for up to 5 days did not lead to a decrease in the surface count rate; surface count rates were determined for experiments A4, A7 and A10 after pumping the solid for 1 day, 3 days and 5 days respectively, and are tabulated (Table 5.I). The surface count rates in these experiments did not depend on the quantity of aluminium (III) chloride used or the initial pressure of gaseous [^{36}Cl]-HCl (Table 5.I). Figure 5.I is a plot of surface count rate vs time for experiment A7.

Specific count rates were determined for solid [^{36}Cl]-AgCl samples derived from the [^{36}Cl]-HCl recovered from three experiments of this type. The fraction of the [^{36}Cl]-chlorine label exchanged, f, was calculated using Equation 5.I.

$$f = \frac{S_o - S_t}{S_o - S_\infty} \qquad \text{Equation 5.I}$$

Where S_o is the specific count rate in count $s^{-1}mg^{-1}$ determined for a solid [^{36}Cl]-AgCl sample derived from [^{36}Cl]-HCl which had not been exposed to aluminium (III) chloride.

S_t is the specific count rate in count $s^{-1}mg^{-1}$ determined for a solid [^{36}Cl]-AgCl sample derived from [^{36}Cl]-HCl which had been exposed to aluminium (III) chloride.

FIGURE 5.I. Plot of Surface Count Rate vs Time in Interaction of [^{36}Cl]-HCl (g) with $AlCl_3$ (s).

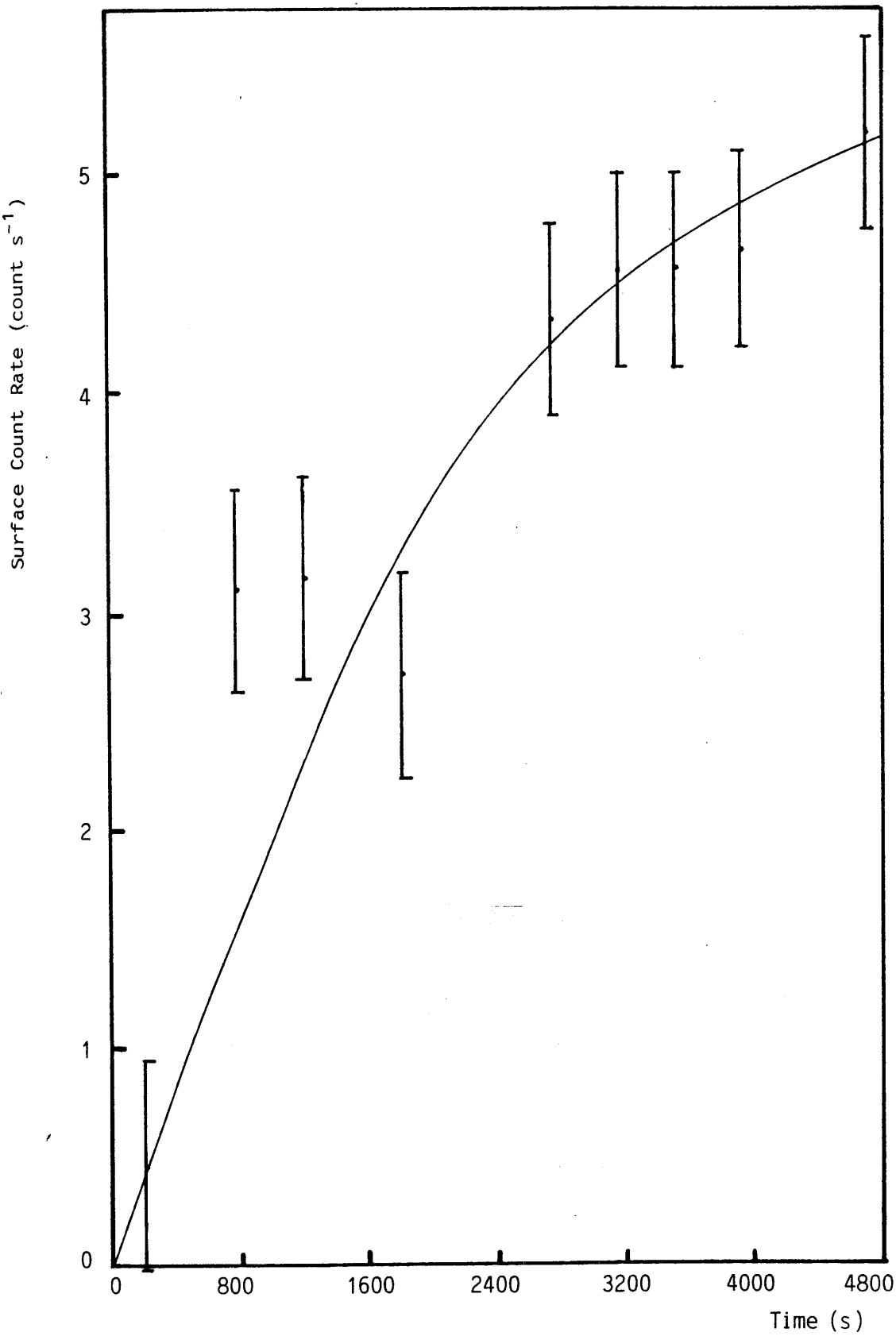


TABLE 5.I. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$(s)

Run No.	$AlCl_3$(s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Observed Surface Count Rate (count s^{-1})
A1	3.28	11.0 ± 1.0	not determined
A2	4.56	12.8 ± 0.4	not determined
A4	3.17	35.1 ± 3.0	7.5 ± 0.2
A7	5.53	39.6 ± 1.2	5.7 ± 0.1
A10	1.56	84.3 ± 2.5	not determined
A10a	1.56	83.6 ± 2.5	6.8 ± 0.1

TABLE 5.II. Specific Count Rates of $[^{36}Cl]$-AgCl and Fractional Exchanges in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s)

Run No.	S_o (count $s^{-1} mg^{-1}$)	S_t (count $s^{-1} mg^{-1}$)	S_∞ (count $s^{-1} mg^{-1}$)	f
A12	1.111 ± 0.030	0.825 ± 0.016	0.040 ± 0.003	0.27
A13	1.111 ± 0.030	0.866 ± 0.017	0.092 ± 0.006	0.24
A14	1.111 ± 0.030	1.134 ± 0.023	0.070 ± 0.005	0

S_∞ is the expected specific count rate of [^{36}Cl]-AgCl in count $s^{-1} mg^{-1}$ calculated on the basis that complete exchange of chlorine atoms occurred between the [^{36}Cl]-HCl and the aluminium (III) chloride sample.

Values of S_0, S_t, S_∞ and f are tabulated (Table 5.II). Exchange occurred to a small extent in experiments A12 and A13. Only experiment A14 agrees with the report of Richardson[39] that there is no [^{36}Cl]-chlorine exchange between [^{36}Cl]-HCl and solid aluminium (III) chloride at room temperature.

In experiments in which the [^{36}Cl]-HCl was not distilled from -90°C to -196°C onto P_2O_5 immediately prior to use and had been manipulated at least once in the vacuum system, a significant surface count rate was detected as soon as the gaseous [^{36}Cl]-HCl was admitted, and the surface count rate increased to a saturation value, as shown in Figure 5.II for experiment A6 (Table 5.III). The surface count rates observed did not depend on the quantity of aluminium (III) chloride used or on the initial pressure of [^{36}Cl]-HCl (Table 5.III). Pumping the solid for 24h did not lead to a decrease in the surface count rate. In experiments A3, A9 and A11a the surface count rates after pumping for 24h were 31.0 $\pm$ 0.6, 85 $\pm$ 1 and 36.4 $\pm$ 0.9 count s^{-1} respectively.

Specific count rates were determined for solid [^{36}Cl]-AgCl samples derived from the [^{36}Cl]-HCl recovered from four of these experiments. Values of S_0, S_t, S_∞ and f (Equation 5.I) are tabulated (Table 5.IV). In all four experiments [^{36}Cl]-chlorine exchange occurred; in three of these the extent of exchange was substantially greater than that noted in Table 5.II. There does not appear to be any relationship between the observed surface count rate at saturation

FIGURE 5.II. Plot of Surface Count Rate vs Time in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s).

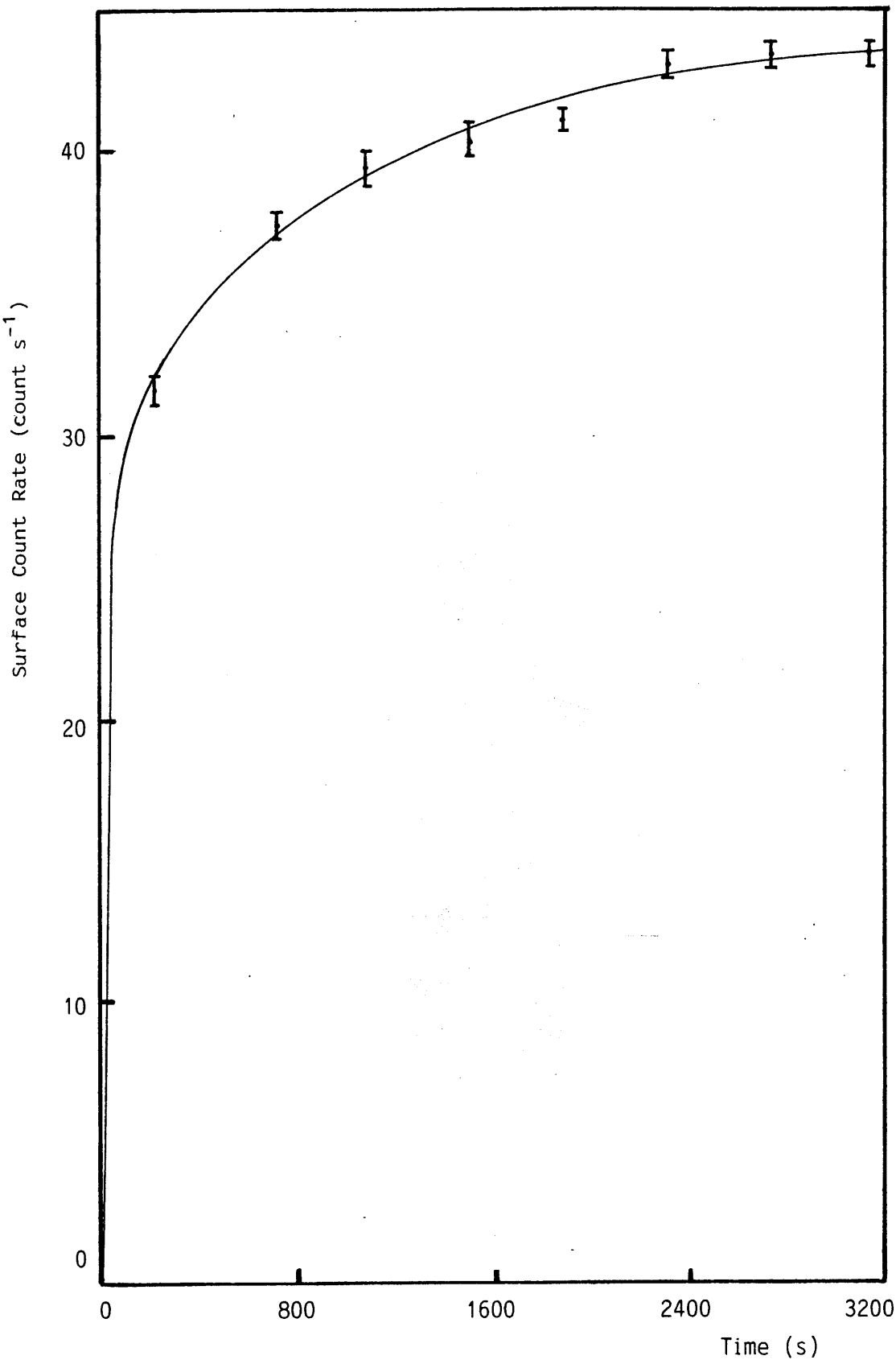


TABLE 5.III. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Observed Surface Count Rate at "Saturation" (count s^{-1})
A3	3.57	33.4 ± 1.0	20 ± 3
A5	11.00	36.6 ± 1.1	13 ± 3
A6	3.46	36.9 ± 1.2	42 ± 5
A8	2.69	69.2 ± 2.1	17 ± 3
A9	3.52	83.9 ± 2.6	82 ± 5
A11	4.21	90.2 ± 2.7	28 ± 3
A11a	4.21	85.6 ± 2.5	46 ± 5

TABLE 5.IV. Specific Count Rates of $[^{36}Cl]$-AgCl and Fractional Exchanges in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s)

Run No.	S_o (count $s^{-1} mg^{-1}$)	S_t (count $s^{-1} mg^{-1}$	S_∞ (count $s^{-1} mg^{-1}$)	f
A5	0.200 ± 0.005	0.130 ± 0.003	0.005 ± 0.0003	0.36
A6	0.234 ± 0.005	0.116 ± 0.003	0.019 ± 0.001	0.55
A8	0.200 ± 0.005	0.178 ± 0.003	0.036 ± 0.002	0.13
A9	0.234 ± 0.005	0.118 ± 0.002	0.039 ± 0.002	0.59

(Table 5.III) and the extent of [^{36}Cl]-chlorine exchange observed (Table 5.IV).

The results obtained when the [^{36}Cl]-HCl was distilled from -90^{o}C to -196^{o}C onto P_2O_5 immediately prior to use indicate that a small surface interaction occurs, and that the very small amount of [^{36}Cl]-chlorine present on the solid surface as soon as the [^{36}Cl]-HCl is admitted is irreversibly bound there. The extent of [^{36}Cl]-chlorine exchange was small ($f \leqslant 0.3$) in two of the experiments studied; only one of the results is in agreement with the report of Richardson[39] that there is no [^{36}Cl]-chlorine exchange between [^{36}Cl]-HCl and solid aluminium (III) chloride at room temperature.

Richardson[39] purified aluminium (III) chloride by fractionation in a dry nitrogen atmosphere and sublimed it under vacuum directly onto the walls of the flamed out Pyrex reaction vessel. The [^{36}Cl]-HCl was counted as a vapour in situ using a Geiger-Müller counter. Although the release of small amounts of moisture by Pyrex glass which had been previously flamed out has been reported,[26] Richardson's work involved much less manipulation of solid and gas than the work reported here and it is possible that the quantity of water present was smaller as a result of this. The small uptake of activity and [^{36}Cl]-chlorine exchange observed in the work reported here has been attributed to the presence of small quantities of water.

The results obtained when the [^{36}Cl]-HCl was not dried immediately prior to use indicate that a surface interaction occurs and that the [^{36}Cl]-chlorine present on the solid surface at the end of the experiment is irreversibly bound there. Substantial, though incomplete, exchange of the [^{36}Cl]-chlorine label ($0.13 \leqslant f \leqslant 0.59$) occurred. Since the principal difference between these experiments

and those reported earlier is the treatment of the [^{36}Cl]-HCl prior to use, the difference in behaviour has been attributed to the presence of water in the [^{36}Cl]-HCl, caused by its exposure to the glass of the vacuum system.

The action of water in promoting [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride is discussed in 5.2.3. Direct evidence for the presence of water in aluminium (III) chloride samples prepared as described in 2.2.6 is presented in Chapter 8.

5.2.3 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous Water.

A solid aluminium (III) chloride sample was exposed to water vapour in the reaction vessel for 1h, at the end of which the solid was pumped in situ for 1h. When the solid was then exposed to gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride a significant surface count rate was detected on the solid (Table 5.V).

Specific count rates were determined for solid [^{36}Cl]-AgCl samples derived from the [^{36}Cl]-HCl recovered from three experiments of this type. Values of S_o S_t, S_∞ and f (Equation 5.I) are tabulated (Table 5.VI). In all three experiments [^{36}Cl]-chlorine exchange occurred; the extent of exchange, though not complete, was greater than that noted in Table 5.IV (5.2.2).

The histories of the solid samples used in experiments B1 and B2 (Table 5.V) are shown in Figures 5.III and 5.IV. The differences in behaviour between experiments A10/A10a/B1 (Figure 5.III) and A11/A11a/B2 (Figure 5.IV) can be attributed to differences in the

TABLE 5.V. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g).

Run No.	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Observed Surface Count Rate at "Saturation" (count s^{-1})
B1	1.56	79.7 ± 2.4	20 ± 4
B2	4.21	130.0 ± 5.0	38 ± 5

TABLE 5.VI. Specific Count Rates of $[^{36}Cl]$-AgCl and Fractional Exchanges in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	S_o (count $s^{-1}mg^{-1}$)	S_t (count $s^{-1}mg^{-1}$)	S_∞ (count $s^{-1}mg^{-1}$)	f
B3	1.111 ± 0.030	0.492 ± 0.012	0.314 ± 0.028	0.78
B4	1.111 ± 0.030	0.510 ± 0.011	0.106 ± 0.009	0.60
B5	1.111 ± 0.030	0.241 ± 0.006	0.059 ± 0.005	0.83

FIGURE 5.III : History of $AlCl_3$ (s) Used in Experiment B1

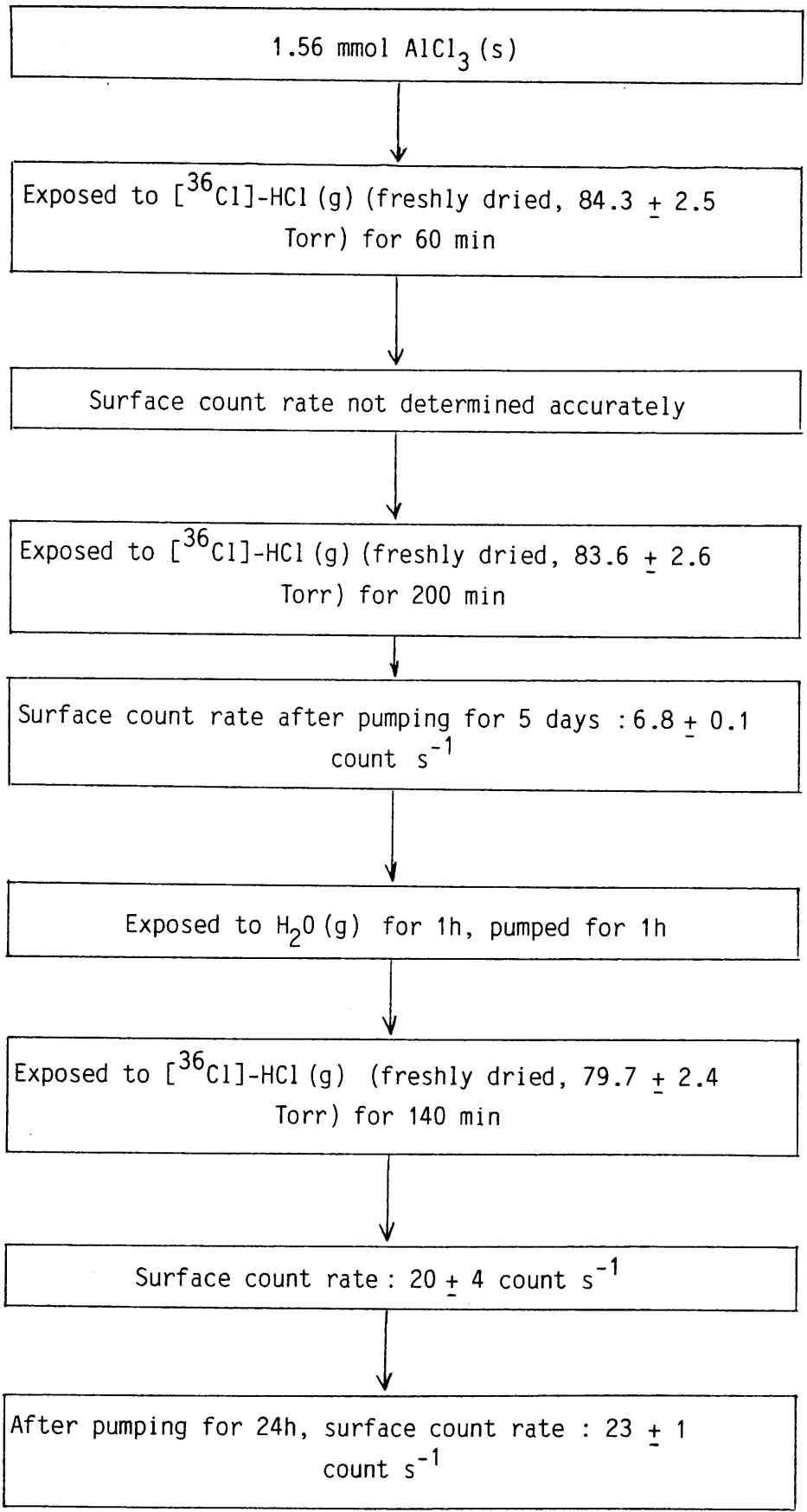
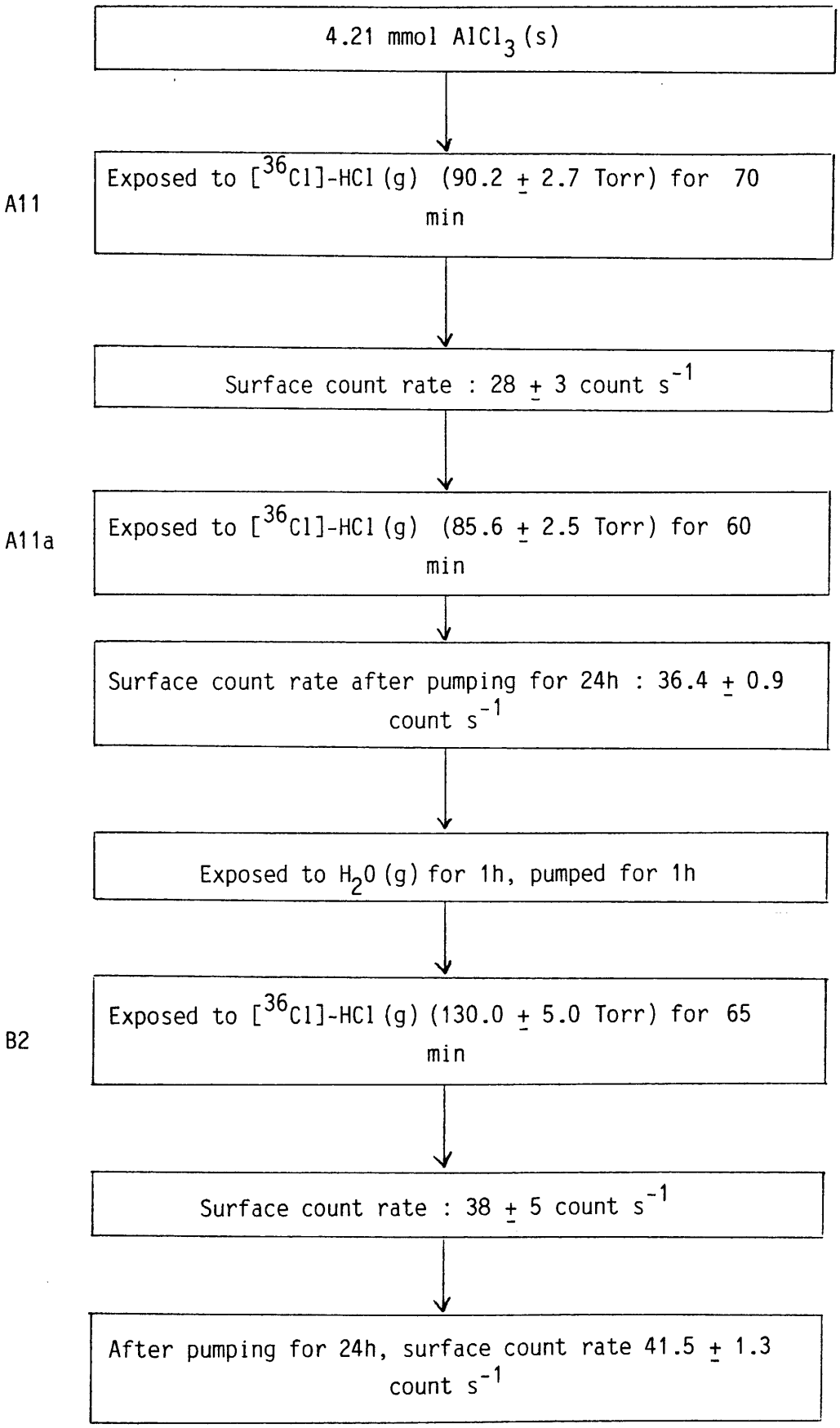


FIGURE 5.IV : History of $AlCl_3$ (s) Used in Experiment B2



amount of water to which the solid had been exposed at each stage. The solid used in experiment B1 had previously been exposed to gaseous [^{36}Cl]-HCl on two occasions and a barely detectable surface count rate was observed. However, exposure of the solid to water vapour followed by exposure to a comparable quantity of gaseous [^{36}Cl]-HCl, treated in an identical manner to the [^{36}Cl]-HCl used in previous exposures, led to a substantial increase in the surface count rate. This observation suggests that the interpretation of the exchange observed in 5.2.2 is correct; that is, that small quantities of water promote [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride.

The solid used in experiment B2 had previously been exposed to [^{36}Cl]-HCl, which had not been dried immediately prior to use, and a significant surface count rate was detected. Exposure of the solid to water vapour, followed by exposure to a comparable quantity of gaseous [^{36}Cl]-HCl did not lead to a significant increase in the surface count rate. Also, in all experiments in which a significant surface count rate is produced (5.2.2, 5.2.3), the surface count rate rises to an apparent saturation value during the course of the experiment. However, even in experiments in which solid aluminium (III) chloride is exposed to water vapour prior to exposure to gaseous [^{36}Cl]-HCl, complete exchange of the [^{36}Cl]-chlorine label is never observed. Willard investigated the exchange of [^{36}Cl]-chlorine between solid [^{36}Cl]-$AlCl_3$ and gaseous carbon tetrachloride.[50] One of the characteristics of the process was that the extent of exchange observed in successive exposures of the solid to gaseous carbon tetrachloride decreased substantially. This was attributed to [^{36}Cl]-chlorine depletion of the surface layers of the solid; resublimation

of the solid and exposure to further gaseous carbon tetrachloride allowed exchange to continue. The operation of a similar process in this work, in which the surface layers of the aluminium (III) chloride become comparatively enriched in [^{36}Cl]-chlorine, can account for the behaviour observed.

The promotion of [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride by water is analogous to the observation in the H_2O/[^{36}Cl]-HCl(g)/$FeCl_3$(s) system.[98] The action of water in the latter system was interpreted in terms of the surface interaction of [^{36}Cl]-HCl and the species $[Fe(H_2O)_4Cl_2]^+$, which has been identified in X-Ray diffraction studies of the crystalline hydrates $FeCl_3.6H_2O$[99] and $FeCl_3.2\frac{1}{2}H_2O$.[100] Hydration of aluminium (III) chloride is generally believed to be an analogous process to the hydration of aluminium (III) bromide proposed by Fairbrother.[28] Such a process could lead to the formation of an aluminium analogue of $[Fe(H_2O)_4Cl_2]^+$. However, none of the species postulated by Fairbrother have been identified in the solid state, and the structure of aluminium (III) chloride hexahydrate ($AlCl_3.6H_2O$) has not been unequivocally established, although a study using polarised infra-red reflection spectroscopy of a material with stoichiometry $AlCl_3.6H_2O$ indicated that a lattice structure with Al^{3+} surrounded by six water molecules existed.[32]

A mechanism of [^{36}Cl]-chlorine exchange in this system involving aluminium (III) hydrates cannot be postulated at this stage, since the structures of these species have not been determined and there is no direct evidence for their presence. The simplest possible surface mechanism which can be considered involves the co-ordinatively unsaturated aluminium (III) on the surface of aluminium (III) chloride

(1.1). Physical adsorption of a water molecule at a co-ordinatively unsaturated aluminium (III) site can be considered as a precursor to chemisorption and ultimately to the formation of a surface hydroxyl group. Interaction of a [^{36}Cl]-HCl molecule with a chemisorbed water molecule may lead to the production of a surface $H_3O^+ {}^{36}Cl^-$ ion pair which can facilitate exchange. Another possibility is that the interaction of a second water molecule with a chemisorbed water molecule and an adjacent surface chloride ion may lead to the formation of a surface hydroxyl group and a surface $H_3O^+Cl^-$ ion pair which can facilitate [^{36}Cl]-chlorine exchange when [^{36}Cl]-HCl is introduced.

5.2.4 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

A solid aluminium (III) chloride sample was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 2h, at the end of which the purple solid formed was pumped in situ for 24h. When the solid was exposed to gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride, which had been distilled from -90^{o}C to -196^{o}C onto P_2O_5 immediately prior to use, a barely detectable surface count rate was observed as soon as the [^{36}Cl]-HCl was admitted, which did not increase significantly in 100 min. Accurate determinations of surface count rates were not made during the course of the exposure to gaseous [^{36}Cl]-HCl, as very long counting times would have been required. Pumping the solid for up to 12h did not lead to a decrease in the surface count rate; surface count rates were determined for experiments C2, C3, C4 and C5 after pumping the solid for 2h, 3.5h, 12h and 12h respectively, and are tabulated (Table 5.VII). The surface count rates in these experiments did not depend on the quantity of aluminium

TABLE 5.VII. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3 (g)

Run No.	$AlCl_3$(s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl(g) (Torr)	Observed Surface Count Rate (count s^{-1})
C1	1.12	15.3 ± 0.5	not determined
C2	1.48	23.7 ± 2.0	7.3 ± 0.3
C3	1.43	24.8 ± 2.1	9.1 ± 0.1
C4	4.11	27.3 ± 0.5	4.69 ± 0.07
C5	4.21	53.8 ± 0.5	1.88 ± 0.06

TABLE 5.VIII. Specific Count Rates of $[^{36}Cl]$-AgCl and Fractional Exchanges in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3 (g)

Run No.	S_o (count s^{-1} mg^{-1})	S_t (count s^{-1} mg^{-1})	S_∞ (count s^{-1} mg^{-1})	f
C5a	0.217 ± 0.005	0.194 ± 0.007	0.022 ± 0.003	0.12
C6	1.111 ± 0.030	0.423 ± 0.008	0.141 ± 0.012	0.71
C7	1.111 ± 0.030	0.431 ± 0.008	0.059 ± 0.005	0.65
C8	1.111 ± 0.030	0.512 ± 0.012	0.087 ± 0.007	0.58

(III) chloride used or the initial pressure of [^{36}Cl]-HCl (Table 5.VII).

Specific count rates were determined for solid [^{36}Cl]-AgCl samples derived from the [^{36}Cl]-HCl recovered from four experiments of this type. Values of S_o, S_t, S_∞ and f (Equation 5.I) are tabulated (Table 5.VIII). The combined [^{36}Cl]-HCl recovered from experiments C1, C4 and C5 (Table 5.VII) was used in experiment C5a (Table 5.VIII). In all four experiments [^{36}Cl]-chlorine exchange occurred. However, exposure of solid aluminium (III) chloride to gaseous 1,1,1-trichloroethane is known to lead to the formation of an involatile, chlorine containing organic material (Chapters 3 and 4); the quantity of this material formed in these experiments is not known, and the possibility of [^{36}Cl]-chlorine exchange between [^{36}Cl]-HCl and the involatile material cannot be dismissed.

These observations have several possible interpretations. The [^{36}Cl]-chlorine exchange observed may be due to hydration or hydrolysis of the solid surface, as in 5.2.2 and 5.2.3. The effect of very small quantities of water was discussed in 5.2.2 and 5.2.3 and although the 1,1,1-trichloroethane used was stored over activated 3A molecular sieves it may have become contaminated by small quantities of moisture from the glass walls of the vacuum system during manipulation. The very low surface count rates observed for the amount of exchange observed (5.2.2, 5.2.3) can be accounted for if the production of the involatile organic material reduces the number of sites at which adsorption and exchange can take place, compared with aluminium (III) chloride which had not been exposed to gaseous 1,1,1-trichloroethane.

Another possible interpretation of the results is that the involatile organic material produced on exposure of solid aluminium (III) chloride to gaseous 1,1,1-trichloroethane is a partially

chlorinated unsaturated material, such as poly-1,1-dichloroethene, which can undergo aluminium (III) chloride catalysed hydrochlorination and dehydrochlorination in the presence of hydrogen chloride. If the organic material consists of a film several layers deep, then such processes could account for the [^{36}Cl]-chlorine exchange and comparatively low surface count rates observed.

The involatile organic material produced in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride is known to produce gaseous hydrogen chloride after the gaseous product mixture is removed (3.2.2). A third possible interpretation of the observations is that the involatile material continues to produce gaseous hydrogen chloride, even after pumping for 24h, and that this leads to dilution of the [^{36}Cl]-chlorine label of [^{36}Cl]-HCl, and hence to a reduction in the specific count rate of the [^{36}Cl]-AgCl derived from it. This proposal cannot account for the detection of a surface count rate, but the possibility that this process contributes to the results observed cannot be excluded.

The validity of the second and third possibilities discussed above could be investigated by exposing a sample of solid aluminium (III) chloride to gaseous [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane for 2h, pumping the purple solid formed for 24h, exposing it to inactive hydrogen chloride for 100min and investigating the specific count rate of solid [^{36}Cl]-AgCl derived from the hydrogen chloride.

5.2.5 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride and Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

Exposure of a mixture of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride and gaseous 1,1,1-trichloroethane to solid aluminium

(III) chloride resulted in the detection of a significant surface count rate on the solid, and a decrease in the count rate from the gas. Figure 5.V shows the variation in the counts from the gas alone, and from the gas and solid with time in a typical experiment (D2 in Table 5.IX). Figure 5.VI is a plot of surface count rate vs time for the same experiment. The surface count rate increases steadily for approximately 1h, and is constant thereafter. The values of the surface count rate at saturation are directly related to the initial pressure of [^{36}Cl]-HCl (Table 5.IX) and a plot of the former against the latter is linear (Figure 5.VII). The surface count rates observed were much greater than those observed when a comparable quantity of [^{36}Cl]-HCl was exposed to solid aluminium (III) chloride which had been previously exposed to gaseous 1,1,1-trichloroethane (5.2.4). Pumping the solid in situ for up to 24h after removal of the gas mixture did not lead to a decrease in the surface count rate. Surface count rates were determined for experiments D1, D2 and D4 after pumping the solid for 2h, 2h and 24h respectively. The surface count rate in experiment D1 was 18.8 $\pm$ 0.4 count s^{-1}, in D2 it was 40.4 $\pm$ 0.6 count s^{-1} and in D3 it was 43.0 $\pm$ 0.8 count s^{-1}.

During the experiments the solid darkened uniformly, the colour change being white to purple. Prolonged exposure (>1h) to the gaseous mixture led to little change in the surface count rate but the physical appearance of the solid changed from a free-flowing powder to a tarry mass.

The specific count rate was determined for a solid [^{36}Cl]-AgCl sample derived from the combined [^{36}Cl]-HCl recovered from experiments D1 and D2 (Table 5.IX). The specific count rate of this [^{36}Cl]-AgCl was 0.142 $\pm$ 0.003 count s^{-1} mg^{-1} compared with 0.593 $\pm$ 0.014 count

FIGURE 5.V. Variation in Counts from Gas Phase Alone and from Gas and Solid Combined in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s).

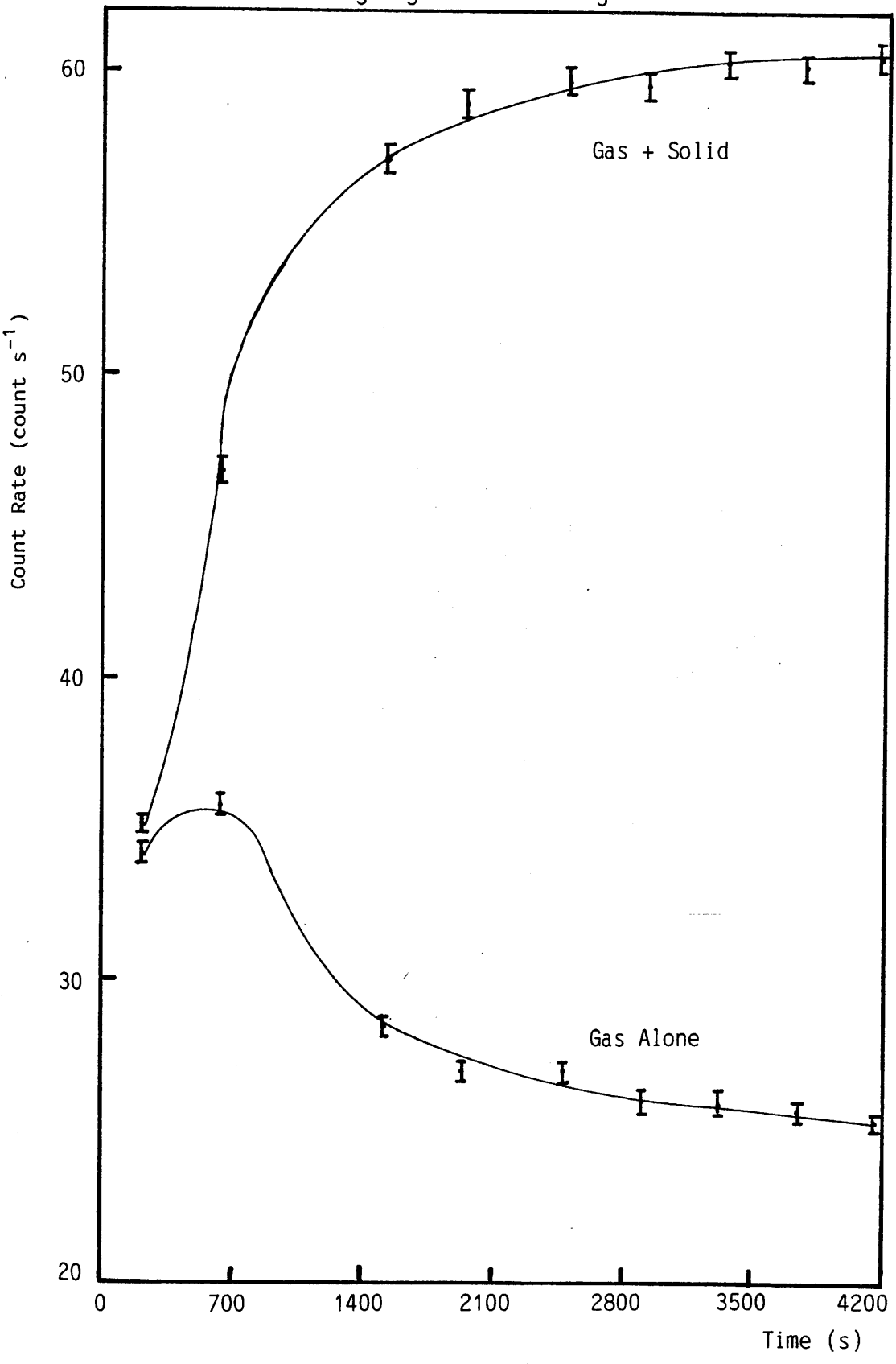


FIGURE 5.VI. Plot of Surface Count Rate vs Time in the Interaction of a Mixture of [^{36}Cl]-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s).

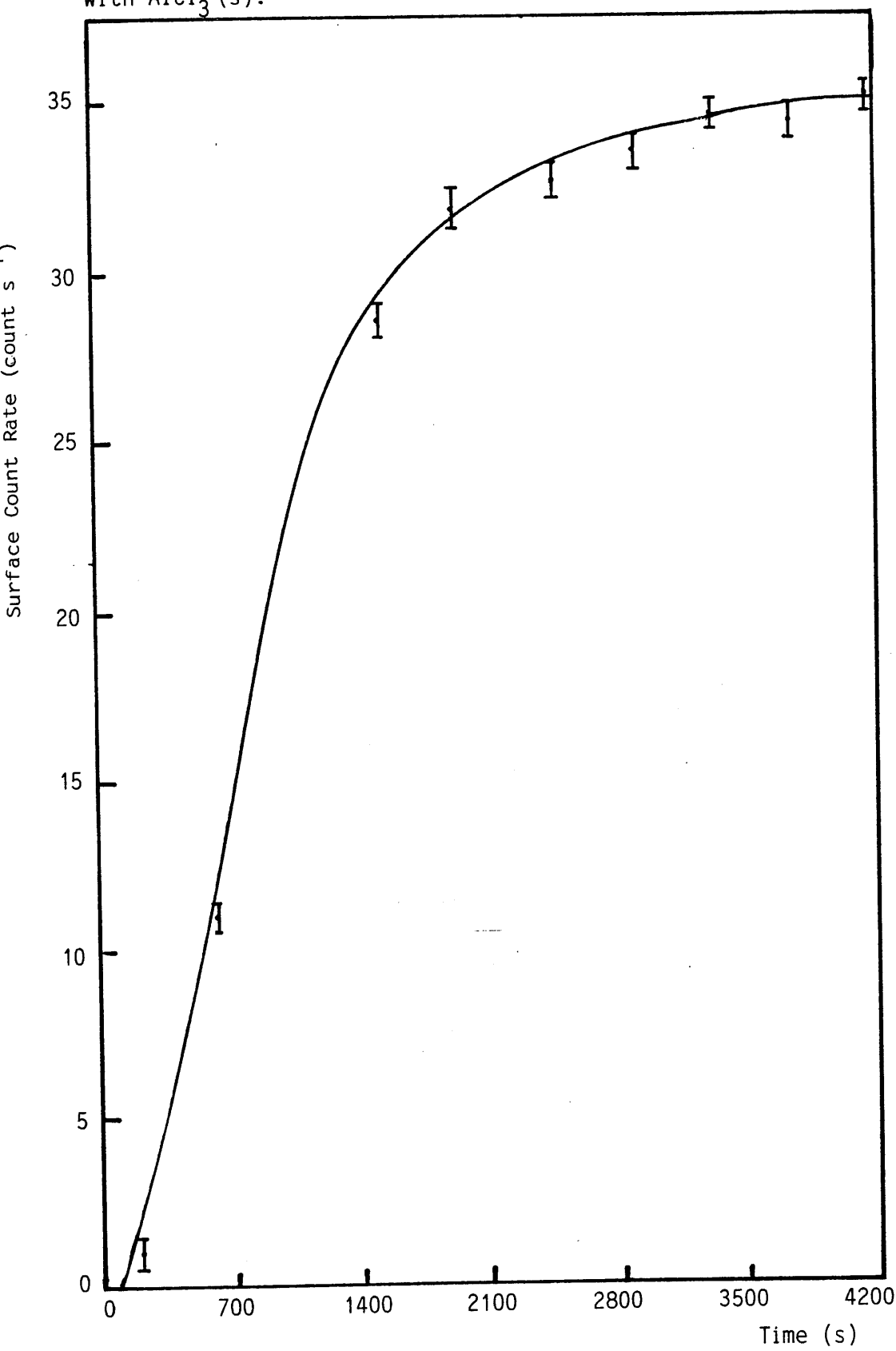


TABLE 5.IX. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Initial Pressure of CH_3CCl_3 (g) (Torr)	Observed Surface Count Rate at "Saturation" (count s^{-1})
D1	1.40	40 ± 2	33 ± 2	25 ± 1
D2	3.91	51 ± 3	57 ± 4	35 ± 1
D4	3.07	70 ± 4	53 ± 3	49 ± 2

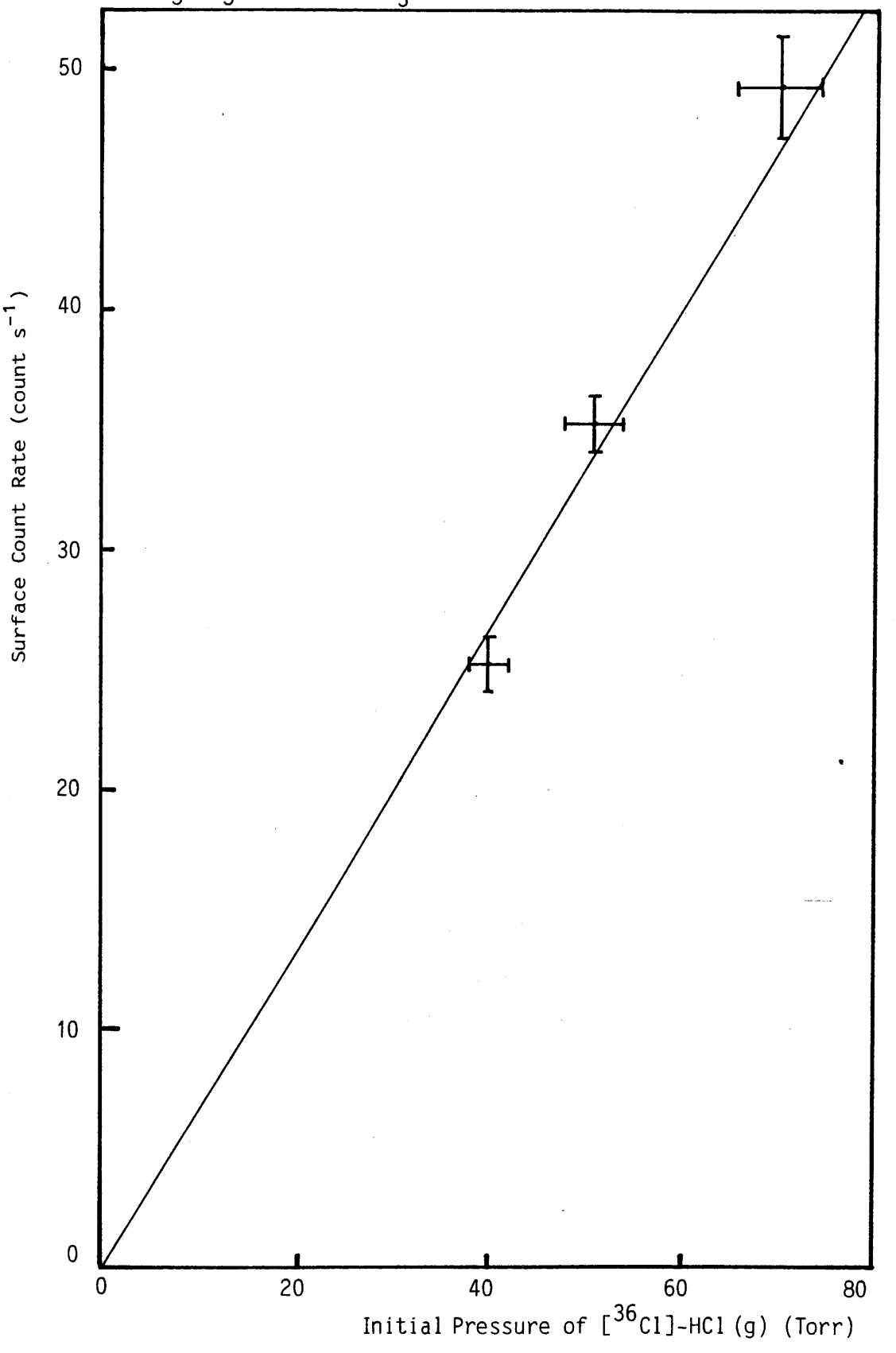
TABLE 5.X. Specific Count Rates of $[^{36}Cl]$-AgCl and Fractional Exchanges in the Interaction of $[^{36}Cl]$-HCl (g) and CH_3CCl_3 (g)

Run No.	S_o (count s^{-1} mg^{-1})	S_t (count s^{-1} mg^{-1})	S_∞ (count s^{-1} mg^{-1})	f
D5	1.111 ± 0.030	0.976 ± 0.020	0.290 ± 0.044	0.16
D6	1.111 ± 0.030	0.892 ± 0.017	0.316 ± 0.049	0.28
D7	1.111 ± 0.030	1.084 ± 0.024	0.302 ± 0.049	0.03

TABLE 5.XI. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s), which had been Exposed to H_2O (g)

Run No.	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Initial Pressure of CH_3CCl_3 (g) (Torr)	Observed Surface Count Rate (count s^{-1})
D3	5.30	55 ± 3	55 ± 3	9.7 ± 0.1

FIGURE 5.VII. Plot of Surface Count Rate vs Initial Pressure of [^{36}Cl]-HCl (g) in the Interaction of a Mixture of [^{36}Cl]-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s).



$s^{-1}mg^{-1}$ for [^{36}Cl]-AgCl derived from [^{36}Cl]-HCl which had not been exposed to aluminium (III) chloride.

Three experiments were carried out in which approximately equimolar quantities of gaseous [^{36}Cl]-HCl and gaseous 1,1,1-trichloroethane were allowed to interact at room temperature for up to 60h. Specific count rates were determined for [^{36}Cl]-AgCl samples derived from [^{36}Cl]-HCl recovered from these experiments. Values of S_o, S_t, S_∞ and f (Equation 5.I) are tabulated (Table 5.X). The values of S_∞ were calculated on the basis of complete exchange of the [^{36}Cl]-chlorine label between the [^{36}Cl]-HCl and the 1,1,1-trichloroethane. These results indicate that some [^{36}Cl]-chlorine exchange takes place. However, there are other interpretations of this observation and these are discussed later in this section.

The chlorohydrocarbon product mixture from experiments D1 and D2 was identified using infra-red spectroscopy as a mixture of 1,1,1-trichloroethane and carbon tetrachloride, the former being the major component. This mixture was counted in the gas phase, the count rate being 1.25 $\pm$ 0.02 counts s^{-1} at 29 Torr. Under identical conditions the count rate for [^{36}Cl]-HCl before the reaction was 24.3 $\pm$ 0.3 counts s^{-1}.

When a mixture of gaseous [^{36}Cl]-chlorine labelled hydrogen chloride and gaseous 1,1,1-trichloroethane was exposed to a solid aluminium (III) chloride sample, which had been previously exposed to water vapour, a barely significant surface count rate was detected as soon as the gas mixture was admitted, and the surface count rate did not increase significantly in 90 min. Accurate determinations of surface count rate were not made during the course of the exposure to the mixture, as very long counting times would have been required.

Pumping the solid for 6h did not lead to a decrease in the surface count rate, which was determined at the end of this period and is tabulated (Table 5.XI). The gas phase [^{36}Cl]-chlorine count rate decreased by 15 count s^{-1} during the course of the experiment. As the experiment proceeded the surface of the solid underwent a colour change from white to grey, while the solid beneath the surface underwent a colour change from white to dark purple.

The principal differences between the observations noted above and the observations when a comparable quantity of gaseous [^{36}Cl]-HCl was exposed to solid aluminium (III) chloride, which had been previously exposed to a comparable amount of gaseous 1,1,1-trichloroethane (5.2.4) are:

(i) a much larger surface count rate is produced when the mixture is exposed to solid aluminium (III) chloride

(ii) the value of the surface count rate produced when the mixture is exposed to solid aluminium (III) chloride is directly proportional to the initial pressure of gaseous [^{36}Cl]-HCl in the mixture.

The detection of [^{36}Cl]-chlorine activity in the gaseous mixture of 1,1,1-trichloroethane and carbon tetrachloride at the end of the experiment indicates that the observed surface count rates and apparent exchange are not due solely to the action of trace water in promoting [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride. It also excludes the interpretation that the observed reduction in the specific count rate of [^{36}Cl]-AgCl derived from [^{36}Cl]-HCl recovered from the experiment, compared to that derived from unused [^{36}Cl]-HCl, is simply due to dilution of the [^{36}Cl]-chlorine label of the [^{36}Cl]-HCl by inactive gaseous hydrogen

chloride, which is known to be a product of the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (3.2.1).

The detection of [^{36}Cl]-chlorine activity in the gaseous chlorohydrocarbon mixture indicates that gaseous [^{36}Cl]-HCl becomes directly involved in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride. A scheme for this reaction was presented in Chapter 4 (Scheme 4.I, 4.2.6), and is reproduced below (Scheme 5.I). There are at least three possible routes by which the

$$CH_3CCl_3(g) \overset{\text{fast}}{\rightleftharpoons} CH_3CCl_3(ad) \qquad \text{(i)}$$

$$CH_3CCl_3(ad) \overset{\text{fast}}{\rightleftharpoons} CH_2{=}CCl_2(ad) + HCl(g) \qquad \text{(ii)}$$

$$CH_2{=}CCl_2(ad) \rightleftharpoons CH_2{=}CCl_2(g) \qquad \text{(iii)}$$

$$CH_2{=}CCl_2(ad) + AlCl_2^+ \overset{\text{fast}}{\rightleftharpoons} Cl_2AlCH_2\overset{+}{C}Cl_2 \qquad \text{(iv)}$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_2(ad) \overset{\text{r.d.s.}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 \qquad \text{(v)}$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3 \qquad \text{(vi)}$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2{=}CCl\,CH_2CCl_3 + AlCl_3 \qquad \text{(vii)}$$

$$\tfrac{n}{2}CH_2{=}CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} \{CH{=}CCl\}_n + \tfrac{n}{2}HCl(g) \qquad \text{(viii)}$$

$$\text{Process(es) leading to the formation of } CCl_4\ (g) \qquad \text{(ix)}$$

Scheme 5.I

[^{36}Cl]-chlorine from [^{36}Cl]-HCl can become involved in the reaction Scheme. These are:

(a) aluminium (III) chloride catalysed hydrochlorination of the 1,1-dichloroethene produced; that is, at step (ii) in Scheme 5.I

(b) hydrochlorination of the proposed 1,1-dichloroethene oligomers and polymers formed in steps (vii) and (viii)

(c) prior [^{36}Cl]-chlorine exchange with solid aluminium (III) chloride which then takes part in step (vi).

The decrease in the count rate from the gas phase during the course of the experiments (Figure 5.V), and the direct relationship between the initial [^{36}Cl]-HCl pressure and the surface count rate observed suggest that (c) is unlikely, since the surface count rate is expected to be a function of the amount of water present rather than the amount of [^{36}Cl]-HCl present.

Detection of [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and gaseous 1,1,1-trichloroethane was unexpected in view of reported thermodynamic and kinetic studies of the dissociation of 1,1,1-trichloroethane[79,80] to yield 1,1-dichloroethene and hydrogen chloride. The observed reduction in specific count rate of the [^{36}Cl]-HCl may be due to the presence of trace quantities of aluminium (III) chloride on the Pyrex glass walls of the reaction bulb. The presence of trace aluminium (III) chloride would lead to the dehydrochlorination of gaseous 1,1,1-trichloroethane to yield gaseous 1,1-dichloroethene and hydrogen chloride, and such a process would lead to a reduction in the specific activity of the [^{36}Cl]-HCl present. However, because reaction was not expected, the gaseous mixture at the end of the experiments was not studied using, for example, infra-red spectroscopy to determine whether gaseous 1,1-dichloroethene was present.

If complete exchange of the [^{36}Cl]-chlorine label between gaseous [^{36}Cl]-HCl and gaseous 1,1,1-trichloroethane occurs in the reaction of the mixture with solid aluminium (III) chloride, then, neglecting the possible involvement of the chlorine atoms of aluminium (III) chloride in the process, the specific count rate of [^{36}Cl]-AgCl derived from [^{36}Cl]-HCl recovered from experiments D1 and D2 (S_t') should

be approximately 25% of that derived from unused [^{36}Cl]-HCl (S_o'), since the quantities of [^{36}Cl]-HCl and 1,1,1-trichloroethane used were approximately equimolar. The observed value of S_t' was $0.24\,S_o'$, which is consistent with complete exchange of the [^{36}Cl]-chlorine label between the two species.

Step (vi) or one of the subsequent steps in Scheme 5.I is irreversible (4.2.6). Gaseous 1,1,1-trichloroethane was the major component of the chlorohydrocarbon mixture at the end of experiments D1 and D2, although there is evidence that it can be completely consumed in the reaction over longer periods (4.2.6). The complete exchange of [^{36}Cl]-chlorine label between [^{36}Cl]-HCl and 1,1,1-trichloroethane noted above therefore indicates that the [^{36}Cl]-HCl becomes involved in the reaction scheme at step (ii) (Scheme 5.I), although it is not incompatible with the involvement of [^{36}Cl]-HCl in the hydrochlorination of the proposed oligomers and polymers formed in steps (vii) and (viii).

The behaviour observed when the solid aluminium (III) chloride had been previously exposed to water vapour suggests that hydration of the solid surface inhibits the reaction of the surface with gaseous 1,1,1-trichloroethane. The decrease in gas phase counts and colour change of the solid beneath the surface indicate that the reaction proceeds throughout the bulk. This effect is discussed further in Chapter 7.

5.2.6 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride and Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

Exposure of a mixture of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride and gaseous 1,1-dichloroethene to solid aluminium (III)

chloride resulted in the appearance of a significant surface count rate on the solid, and a decrease in the count rate from the gas. Figure 5.VIII shows the variation in the counts from the gas alone, and from the gas and solid with time in a typical experiment (E4 in Table 5.XII). Figure 5.IX is a plot of surface count rate vs time for the same experiment. The surface count rate increases steadily for approximately 1h and is constant thereafter. The values of the surface count rate at saturation are not directly related to the initial pressure of [^{36}Cl]-HCl, although an increase in the latter does lead to an increase in the former (Table 5.XII). The surface count rates observed are comparable to those observed when a mixture of gaseous [^{36}Cl]-HCl and 1,1,1-trichloroethane was exposed to solid aluminium (III) chloride (5.2.5). Pumping the solid in situ for up to 24h after removal of the gas mixture did not lead to a decrease in the surface count rate. Surface count rates were determined after pumping for 24h and are tabulated (Table 5.XIII).

During the experiments the solid darkened uniformly, the colour change being white to purple. Prolonged exposure (>1h) to the gaseous mixture led to little change in the surface count rate, but the physical appearance of the solid changed from a free-flowing powder to a tarry mass.

The specific count rate was determined for a solid [^{36}Cl]-AgCl sample derived from the combined [^{36}Cl]-HCl recovered from experiments E3 and E4 (Table 5.XII). The specific count rate of this [^{36}Cl]-AgCl was 0.199 $\pm$ 0.004 count $s^{-1}mg^{-1}$ compared with 0.593 $\pm$ 0.014 count s^{-1} mg^{-1} for [^{36}Cl]-AgCl derived from [^{36}Cl]-HCl which had not been used. No experiments were carried out in which equimolar quantities of gaseous [^{36}Cl]-HCl and gaseous 1,1-dichloroethene were allowed to

TABLE 5.XII. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and $CH_2{=}CCl_2$ (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$(s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	Initial Pressure of $CH_2{=}CCl_2$ (g) (Torr)	Observed Surface Count Rate at "Saturation" (count s^{-1})
E1	1.28	29 ± 2	30 ± 2	11 ± 2
E2	0.85	31 ± 2	31 ± 2	25 ± 2
E3	2.63	54 ± 3	56 ± 4	56 ± 2
E4	3.97	55 ± 4	58 ± 4	42 ± 2
E5	1.44	56 ± 4	57 ± 4	45 ± 2

TABLE 5.XIII. Surface Count Rates of $AlCl_3$ (s) which had been Exposed to a Mixture of $[^{36}Cl]$-HCl (g) and $CH_2{=}CCl_2$ (g) and Pumped In Situ for 24h.

Run No.	Surface Count Rate (count s^{-1})
E1	12.0 ± 0.2
E2	21.1 ± 0.5
E3	49.4 ± 0.9
E4	44.1 ± 0.5
E5	42.9 ± 0.6

interact in the absence of aluminium (III) chloride, but these species are known to yield no detectable 1,1,1-trichloroethane over 1h from infra-red spectroscopic experiments (4.2.4).

The chlorohydrocarbon product mixture from experiments E3 and E4 was identified using infra-red spectroscopy as a mixture of 1,1-dichloroethene and 1,1,1-trichloroethane, the former being the major component. Carbon tetrachloride was not detected because of the strong 796cm^{-1} peak of 1,1-dichloroethene (2.3.3). The mixture was counted in the gas phase, the count rate being 2.94 $\pm$ 0.04 count s^{-1} at 21 Torr. Under identical conditions the count rate for [^{36}Cl]-HCl before the reaction was 16.4 $\pm$ 0.3 count s^{-1}.

The behaviour noted above is closely analogous to that observed in 5.2.5. The detection of [^{36}Cl]-chlorine activity in the gaseous mixture of 1,1-dichloroethene and 1,1,1-trichloroethane indicates that the observed surface count rate and apparent exchange cannot be attributed solely to the action of trace water in promoting [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride. It also excludes the interpretation that the observed reduction in the specific count rate of [^{36}Cl]-AgCl derived from [^{36}Cl]-HCl recovered from the experiment, compared to that derived from unused [^{36}Cl]-HCl, is simply due to dilution of the [^{36}Cl]-chlorine label of the [^{36}Cl]-HCl by inactive gaseous HCl which is known to be a product of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (4.2.1).

The detection of [^{36}Cl]-chlorine activity in the gaseous chlorohydrocarbon mixture indicates that gaseous [^{36}Cl]-HCl becomes directly involved in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride. Scheme 5.I describes this reaction

and the possible routes by which the [^{36}Cl]-chlorine from [^{36}Cl]-HCl can become involved in the reaction scheme are the same as in 5.2.5. The existence of a relationship, albeit a non-linear one, between the initial [^{36}Cl]-HCl pressure and the surface count rate observed suggests that possibility (c) is unlikely.

If complete exchange of the [^{36}Cl]-chlorine label between gaseous [^{36}Cl]-HCl and gaseous 1,1-dichloroethene occurs in the reaction of the mixture with solid aluminium (III) chloride, then, neglecting the possible involvement of the chlorine atoms of aluminium (III) chloride in the process, the specific count rate of [^{36}Cl]-AgCl derived from experiments E3 and E4 (S_t') should be approximately 33% of that derived from unused [^{36}Cl]-HCl (S_o'), since the quantities of [^{36}Cl]-HCl and 1,1-dichloroethene used were approximately equimolar. The observed value of S_t' was $0.34S_o'$, which is consistent with complete exchange of the [^{36}Cl]-chlorine label between the two species.

Step (vi) or one of the subsequent steps in Scheme 5.I is irreversible (4.2.6). Gaseous 1,1-dichloroethene was the major component of the chlorohydrocarbon mixture at the end of experiments E3 and E4, although there is evidence that it is completely consumed in the reaction over longer periods (4.2.6). The complete exchange of [^{36}Cl]-chlorine between [^{36}Cl]-HCl and 1,1-dichloroethene noted above therefore indicates that the [^{36}Cl]-HCl becomes involved in the reaction scheme at step (ii) (Scheme 5.I), although it is not incompatible with the involvement of [^{36}Cl]-HCl in the hydrochlorination of the proposed oligomers and polymers formed in steps (vii) and (viii).

5.3 Experimental

5.3.1 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with the Pyrex Reaction Vessel.

The reaction vessel (2.5.1) was evacuated and flamed out. Gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride (83.9 $\pm$ 2.6 Torr, 2.14 $\pm$ 0.12 mmol) was admitted and the reaction vessel was isolated from the rest of the vacuum system. Counts were taken from both Geiger-Müller tubes for 3h, at the end of which the gaseous [^{36}Cl]-HCl was removed. The procedure was repeated using [^{36}Cl]-HCl (41.1 $\pm$ 1.2 Torr, 1.33 $\pm$ 0.06 mmol).

5.3.2 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride.

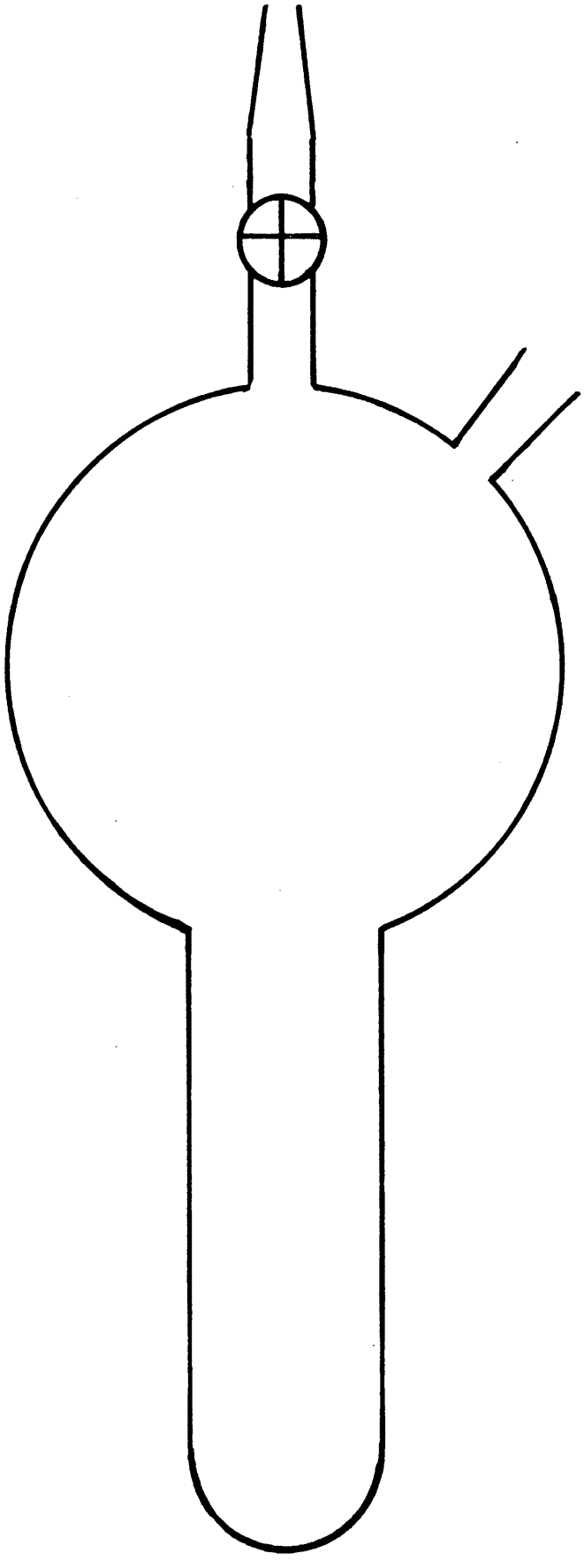
Experiments were carried out using the procedure described in 2.5.2. Table 5.XIV contains the quantities of material used and the durations of the experiments. The [^{36}Cl]-chlorine-labelled hydrogen chloride used was distilled from -90^{o}C to -196^{o}C onto P_2O_5 immediately prior to use in experiments A1, A2, A4, A7, A10 and A10a. The [^{36}Cl]-HCl recovered at the end of experiments A5, A6, A8 and A9 was treated as described in 2.6 to yield [^{36}Cl]-AgCl. The solid was pumped in situ for at least 24h after the [^{36}Cl]-HCl was removed.

A further three experiments were carried out according to the following procedure. The reaction bulb (Figure 5.X) was evacuated, flamed out and a weighed sample of solid aluminium (III) chloride, purified as described in 2.2.6, was dropped into the bottom of the bulb. A measured quantity of gaseous [^{36}Cl]-HCl, which had been distilled from -90^{o}C to -196^{o}C onto P_2O_5 immediately prior to use, was vacuum distilled into the bulb. The bulb was then closed and allowed

TABLE 5.XIV. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl (g) (mmol)	Duration (min)
A1	0.4375 ± 0.0004	3.28	11.0 ± 1.0	0.38 ± 0.03	65
A2	0.6093 ± 0.0004	4.56	12.8 ± 0.4	0.33 ± 0.02	80
A3	0.4766 ± 0.0004	3.57	33.4 ± 1.0	0.85 ± 0.04	65
A4	0.4233 ± 0.0004	3.17	35.1 ± 3.0	1.22 ± 0.08	60
A5	0.8598 ± 0.0004	11.00	36.6 ± 1.1	0.93 ± 0.05	70
A6	0.4620 ± 0.0004	3.46	36.9 ± 1.2	0.94 ± 0.05	50
A7	0.7384 ± 0.0004	5.53	39.6 ± 1.2	1.28 ± 0.06	75
A8	0.3590 ± 0.0004	2.69	69.2 ± 2.1	1.76 ± 0.10	70
A9	0.4697 ± 0.0004	3.52	83.9 ± 2.6	2.14 ± 0.12	60
A10	0.2076 ± 0.0004	1.56	84.3 ± 2.5	2.73 ± 0.13	60
A10a	0.2076 ± 0.0004	1.56	83.6 ± 2.5	2.72 ± 0.14	200
A11	0.5619 ± 0.0004	4.21	90.2 ± 2.7	2.92 ± 0.14	70
A11a	0.5619 ± 0.0004	4.21	85.6 ± 2.5	2.79 ± 0.15	60

FIGURE 5.X. Reaction Bulb



to stand at room temperature for typically 2h, at the end of which the [^{36}Cl]-HCl was treated as described in 2.6 to yield [^{36}Cl]-AgCl. Table 5.XV contains the quantities of material used and the durations of the experiments.

5.3.3 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous Water.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. The solid aluminium (III) chloride was exposed to water vapour in the reaction vessel for 1h, at the end of which the solid was pumped in situ for 1h, before the gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride was admitted to the reaction vessel. The solid was pumped in situ for at least 24h after the [^{36}Cl]-HCl was removed. Table 5.XVI contains the quantities of material involved and the durations of the experiments.

A further three experiments were carried out using the procedure described in 5.3.2 with the modification noted above. Table 5.XVII contains the quantities of material used and the durations of the experiments.

5.3.4 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. The solid aluminium (III) chloride was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 2h, at the end of which the solid was pumped in situ for 24h, before the gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride was

TABLE 5.XV. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s).

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl(g) (mmol)	Duration (min)
A12	0.9801 ± 0.0004	7.342 ± 0.003	58.3 ± 0.5	0.83 ± 0.06	120
A13	0.3641 ± 0.0004	2.727 ± 0.003	58.8 ± 0.5	0.83 ± 0.06	120
A14	0.6084 ± 0.0004	4.557 ± 0.003	65.0 ± 0.5	0.92 ± 0.06	150

TABLE 5.XVI. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl(g) (mmol)	Duration (min)
B1	0.2076 ± 0.0004	1.56	79.7 ± 2.4	2.58 ± 0.13	140
B2	0.5619 ± 0.0004	4.21	130.0 ± 5.0	4.20 ± 0.23	65

TABLE 5.XVII. Quantities of Reactants and Durations of Experiments in the Interaction of [^{36}Cl]-HCl (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of [^{36}Cl]-HCl (g) (Torr)	[^{36}Cl]-HCl (g) (mmol)	Duration (min)
B3	0.0928 ± 0.0004	0.695 ± 0.003	57.9 ± 0.5	0.82 ± 0.06	120
B4	0.3492 ± 0.0004	2.616 ± 0.003	58.8 ± 0.5	0.83 ± 0.06	120
B5	0.6876 ± 0.0004	5.151 ± 0.003	61.0 ± 0.5	0.87 ± 0.06	120

TABLE 5.XVIII. Quantities of Reactants and Durations of Experiments in the Interaction of [^{36}Cl]-HCl (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3 (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of [^{36}Cl]-HCl (g) (Torr)	[^{36}Cl]-HCl (g) (mmol)	Duration (min)
C1	0.1492 ± 0.0004	1.12	15.3 ± 0.5	0.38 ± 0.05	90
C2	0.1981 ± 0.0004	1.48	23.7 ± 2.0	0.83 ± 0.06	110
C3	0.1914 ± 0.0004	1.43	24.8 ± 2.1	0.86 ± 0.06	120
C4	0.5488 ± 0.0004	4.11	27.3 ± 0.5	0.95 ± 0.05	90
C5	0.5623 ± 0.0004	4.21	53.8 ± 0.5	1.87 ± 0.10	100

admitted to the reaction vessel. The combined [^{36}Cl]-HCl recovered at the end of experiments C1, C4 and C5 was treated as described in 2.6 to yield [^{36}Cl]-AgCl. The solid was pumped in situ for at least 24h after the [^{36}Cl]-HCl was removed. Table 5.XVIII contains the quantities of material involved and the durations of the experiments.

A further three experiments were carried out using the procedure described in 5.3.2 with the modification noted above. Table 5.XIX contains the quantities of material used and the durations of the experiments.

5.3.5 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride and Gaseous 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. Approximately equimolar quantities of gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride and gaseous 1,1,1-trichloroethane were condensed into an ampoule attached to the manifold of the vacuum system (2.1.1). The contents of the ampoule were allowed to warm up to room temperature in a measured volume of the vacuum system, and only when this had been achieved were they allowed to expand further into the counting vessel. Table 5.XX contains the quantities of material involved and the durations of the experiments.

The gaseous product mixture from experiments D1 and D2 was vacuum distilled into a vessel held at -196^{o}C in a liquid nitrogen bath. The mixture was allowed to expand into the manifold by raising the temperature of the vessel to -78^{o}C in a methylene chloride/solid CO_2 bath. When there was no further increase in pressure the non-volatile material held at -78^{o}C was isolated from the vapour and the

TABLE 5.XIX. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-HCl (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3 (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl (g) (mmol)	Duration (min.)
C6	0.2604 ± 0.0004	1.950 ± 0.003	60.1 ± 0.5	0.85 ± 0.06	120
C7	0.6797 ± 0.0004	5.091 ± 0.003	60.2 ± 0.5	0.85 ± 0.06	120
C8	0.4475 ± 0.0004	3.352 ± 0.003	60.6 ± 0.5	0.86 ± 0.06	120

TABLE 5.XX. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl (g) (mmol)	Initial Pressure of CH_3CCl_3 (g) (Torr)	CH_3CCl_3 (g) (mmol)	Duration (min)
D1	0.1869 ± 0.0004	1.40	40 ± 2	1.4 ± 0.1	33 ± 2	1.1 ± 0.1	180
D2	0.5224 ± 0.0004	3.91	51 ± 3	1.8 ± 0.1	57 ± 4	2.0 ± 0.2	70
D3	0.7069 ± 0.0004	5.30	55 ± 3	1.9 ± 0.1	55 ± 3	1.9 ± 0.1	90
D4	0.4104 ± 0.0004	3.07	70 ± 4	2.4 ± 0.2	53 ± 3	1.8 ± 0.1	60

latter condensed in an ampoule held at -196°C. The procedure was repeated four times. The infra-red spectrum of the more volatile material thus separated showed only hydrogen chloride. This [^{36}Cl]-HCl was treated as described in 2.6 to yield [^{36}Cl]-AgCl. The infra-red spectrum of the less volatile material thus separated was collected, and this material was counted in the vapour phase.

A further three experiments were carried out according to the following procedure. The reaction bulb (Figure 5.X) was evacuated and flamed out. Approximately equimolar quantities of gaseous [^{36}Cl]-HCl and gaseous 1,1,1-trichloroethane were condensed into the bulb, which was then closed. The bulb was allowed to stand at room temperature for typically 24h, at the end of which the bulb was cooled to -196°C in a liquid nitrogen bath. The [^{36}Cl]-HCl was separated from the mixture using the procedure described above, and was treated as described in 2.6 to yield [^{36}Cl]-AgCl. Table 5.XXI contains the quantities of material involved and the durations of the experiments.

5.3.6 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled Hydrogen Chloride and Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.5.2 with the modifications described in 5.3.5. Table 5.XXII contains the quantities of material involved and the durations of the experiments.

TABLE 5.XXI. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-HCl (g) with CH_3CCl_3 (g).

Run No.	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl (g) (mmol)	Initial Pressure of CH_3CCl_3 (g) (Torr)	CH_3CCl_3 (g) (mmol)	Duration (h)
D5	87.9 ± 0.5	1.25 ± 0.08	83.2 ± 0.5	1.18 ± 0.08	20
D6	96.5 ± 0.5	1.37 ± 0.09	81.2 ± 0.5	1.15 ± 0.08	20
D7	100.3 ± 0.5	1.42 ± 0.09	89.4 ± 0.5	1.27 ± 0.08	60

TABLE 5.XXII. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{36}Cl]$-HCl (g) and $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (g) (mmol)	Initial Pressure of $[^{36}Cl]$-HCl (g) (Torr)	$[^{36}Cl]$-HCl (g) (mmol)	Initial Pressure of $CH_2=CCl_2$ (g) (Torr)	$CH_2=CCl_2$ (g) (mmol)	Duration (min)
E1	0.1708 ± 0.0004	1.28	29 ± 2	1.0 ± 0.09	30 ± 2	1.0 ± 0.09	155
E2	0.1138 ± 0.0004	0.85	31 ± 2	1.1 ± 0.09	31 ± 2	1.1 ± 0.09	140
E3	0.3514 ± 0.0004	2.63	54 ± 3	1.9 ± 0.1	56 ± 4	1.9 ± 0.2	90
E4	0.5298 ± 0.0004	3.97	55 ± 4	1.9 ± 0.2	58 ± 4	2.0 ± 0.2	75
E5	0.1920 ± 0.0004	1.44	56 ± 4	1.9 ± 0.2	57 ± 4	2.0 ± 0.2	160

CHAPTER 6

CHAPTER 6

THE INTERACTION OF GASEOUS [^{14}C]-CARBON-LABELLED CARBON TETRACHLORIDE AND GASEOUS [^{36}Cl]-CHLORINE-LABELLED CARBON TETRACHLORIDE WITH SOLID ALUMINIUM (III) CHLORIDE

6.1 INTRODUCTION

Blau, Wallace and Willard studied the interaction of carbon tetrachloride and other organic chlorides with [^{36}Cl]-chlorine-labelled aluminium (III) chloride in order to develop an understanding of the mechanism of chlorine exchange between the species and, ultimately, of the mechanism of Friedel-Crafts reactions.[49,50] They found that the [^{36}Cl]-chlorine label in solid [^{36}Cl]-$AlCl_3$ exchanged readily with the chlorine in liquid carbon tetrachloride, even at the melting point of the latter.[49] Exposure of the solid to moisture inhibited exchange completely at temperatures <30^{o}C, and substantially reduced the extent of exchange at higher temperatures. The [^{36}Cl]-chlorine label of solid [^{36}Cl]-$AlCl_3$ also exchanged readily with the chlorine in gaseous carbon tetrachloride,[50] but when both reactants were in the gas phase no exchange was observed.[49] The authors suggested that an aluminium (III) chloride surface was required for exchange to take place. In experiments in which [^{36}Cl]-chlorine exchange was observed the exchange was incomplete, except at temperatures >100^{o}C; also, the extent of exchange in successive exposures of solid [^{36}Cl]-$AlCl_3$ to carbon tetrachloride decreased, but resublimation of the solid before further exposure to carbon tetrachloride led to an increase in the extent of exchange. These observations indicate that reorganisation of the solid aluminium (III) chloride lattice is a very slow process at temperatures <100^{o}C.

Wallace and Willard considered an exchange process involving ionisation of carbon tetrachloride (Equation 6.I).[49] They estimated that the activation energy of the reaction was ca. 800 kJ mol^{-1}, minus

$$CCl_4 + AlCl_2{}^{36}Cl \rightleftharpoons CCl_3^+ [AlCl_3{}^{36}Cl]^- \rightleftharpoons CCl_3{}^{36}Cl + AlCl_3$$

Equation 6.I

the energy of binding Cl^- to $AlCl_3$, and concluded that this process could not account for the observed exchange. The authors suggested that the observations were consistent with a mechanism involving adsorption of carbon tetrachloride on the surface of aluminium (III) chloride (1.1). However, the work reported consisted solely of product analyses and no direct evidence for an adsorbed species was obtained.

Gaseous carbon tetrachloride is a product of the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride (3.2.1, 4.2.1). The mechanism for its formation is not known, although it is possible that chain transfer reactions involving C-C bond cleavage in the polymerisation of 1,1-dichloroethene are involved. Another possibility is that carbon tetrachloride is formed by aluminium (III) chloride catalysed dealkylation of a hydrochlorinated 1,1-dichloroethene derived oligomer. Such reactions have been reported in Friedel-Crafts alkylations[24] and isomerisations,[57] and the reversible aluminium (III) chloride catalysed alkylation of 1,1,2,3,4,5,5-heptachloropentene by carbon tetrachloride, reported by Prins,[94] may be directly analogous (Equation 6.II).

$$CCl_4 + CCl_2{=}CClCHClCHClCHCl_2 \overset{AlCl_3}{\rightleftharpoons} CCl_3CCl_2CCl_2CHClCHClCHCl_2$$

Equation 6.II

The interactions of gaseous [^{14}C]-carbon-labelled carbon tetrachloride and [^{36}Cl]-chlorine-labelled carbon tetrachloride with solid aluminium (III) chloride were studied in this work using the direct monitoring Geiger-Müller radiochemical counting technique (2.5). The $CCl_{4(g)}/AlCl_{3(s)}$ system was studied in the absence of a third component to obtain evidence for the adsorption of carbon tetrachloride on the solid, and in the presence of moisture to determine what, if any, effect water had on the observed behaviour. The $CCl_{4(g)}/CH_3CCl_{3(g)}/AlCl_{3(s)}$ and $CCl_{4(g)}/CH_2{=}CCl_{2(g)}/AlCl_{3(s)}$ systems were studied to gain information on the mechanism of carbon tetrachloride production in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride.

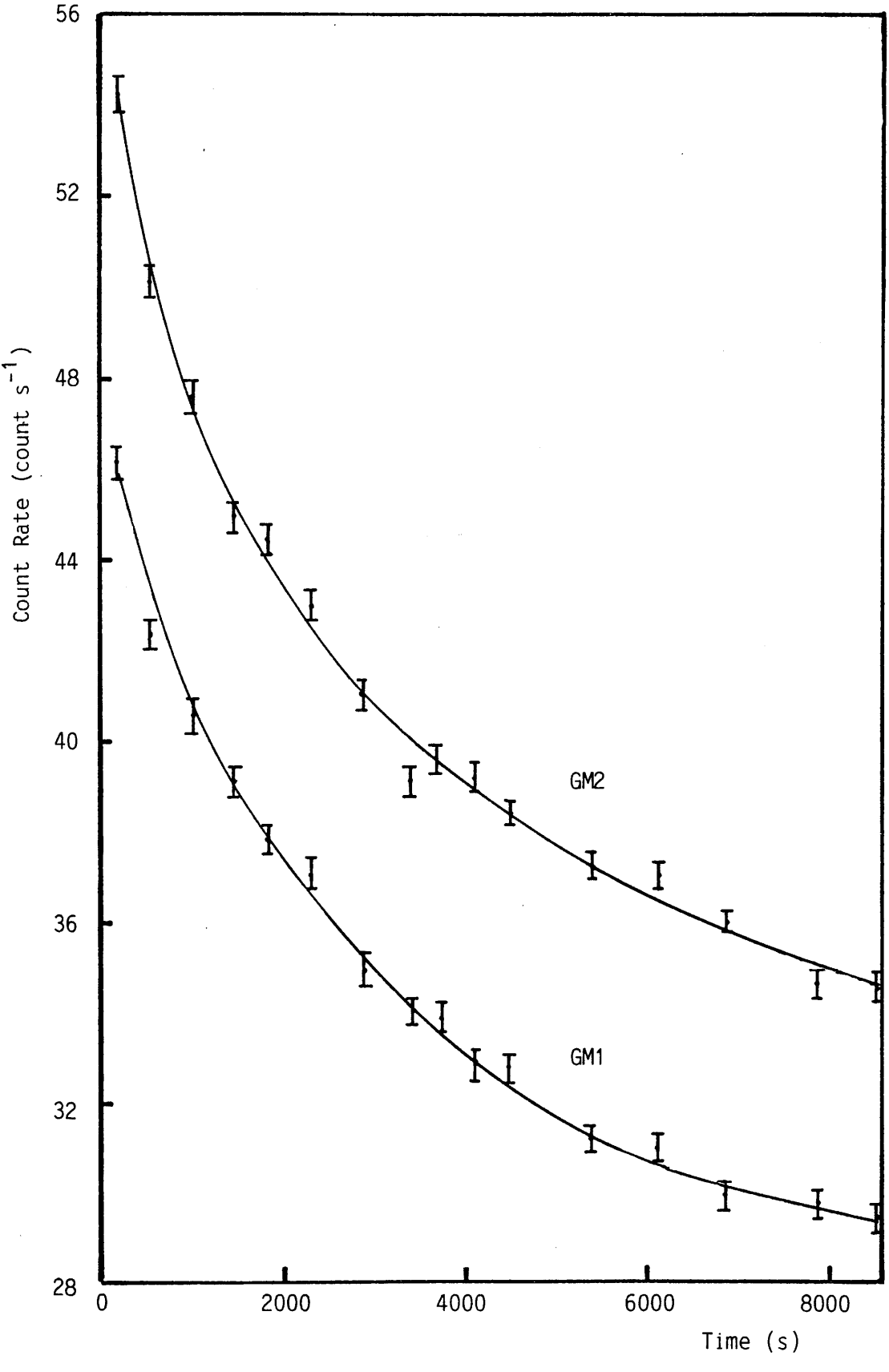
6.2 Results

6.2.1. The Interaction of Gaseous Radiolabelled Carbon Tetrachloride with the Pyrex Reaction Vessel.

When gaseous [^{14}C]-carbon-labelled carbon tetrachloride was admitted to the reaction vessel, the count rates from both Geiger-Müller tubes decreased during the first 6000s and remained constant thereafter, as shown in Figure 6.I for experiment A3. The background count rates from both tubes after the gaseous [^{14}C]-CCl_4 had been removed were usually greater than those obtained prior to admitting the [^{14}C]-CCl_4 by <1 count s^{-1}. Flaming out the reaction vessel and pumping for 12h resulted in a return to the original background count rates.

The observed behaviour was identical when the reaction vessel had been exposed to water vapour for 2h prior to admitting gaseous [^{14}C]-CCl_4, and when gaseous [^{36}Cl]-chlorine-labelled carbon tetrachloride

FIGURE 6.I. Count Rates from Both G.M. Tubes in the Interaction of [^{14}C]-CCl_4 (g) with the Pyrex Reaction Vessel.



was used; it indicates that carbon tetrachloride is adsorbed on the Pyrex glass of the reaction vessel. This effect is taken into account in 6.2.2 and subsequent sections.

6.2.2 The Interaction of Gaseous Radiolabelled Carbon Tetrachloride with Solid Aluminium (III) Chloride.

When gaseous [^{14}C]-carbon-labelled carbon tetrachloride was exposed to solid aluminium (III) chloride, the observed behaviour was identical to that described in 6.2.1 in all six experiments studied (Table 6.VII). No significant surface count rate was detected on the solid, and the observed count rates from both tubes were identical after the gaseous [^{14}C]-CCl_4 was removed. There was no change in the physical appearance of the solid during the course of an experiment. Solid aluminium (III) chloride, which had been exposed to water vapour in the reaction vessel for 1h and subsequently pumped in situ for 1h, was exposed to gaseous [^{14}C]-CCl_4. The observed behaviour was identical to that described above in all four experiments studied (Table 6.VIII).

When gaseous [^{36}Cl]-chlorine-labelled carbon tetrachloride was exposed to solid aluminium (III) chloride the behaviour was identical to that described above in five of the experiments studied (Table 6.VIII). However, in four of the experiments the count rate from the gas and solid decreased by less than that from the gas alone, (shown in Figure 6.II for experiment B102), and a barely detectable surface count rate was observed. Pumping the solid in situ for 24h did not lead to a decrease in the surface count rate, and surface count rates were determined after 24h pumping in all four experiments (Table 6.I). The physical appearance of the solid did not change during the course

FIGURE 6.II. Variation in Count Rates from the Gas and Solid Combined and from the Gas Alone in the Interaction of [^{36}Cl]-CCl_4(g) with $AlCl_3$(s)

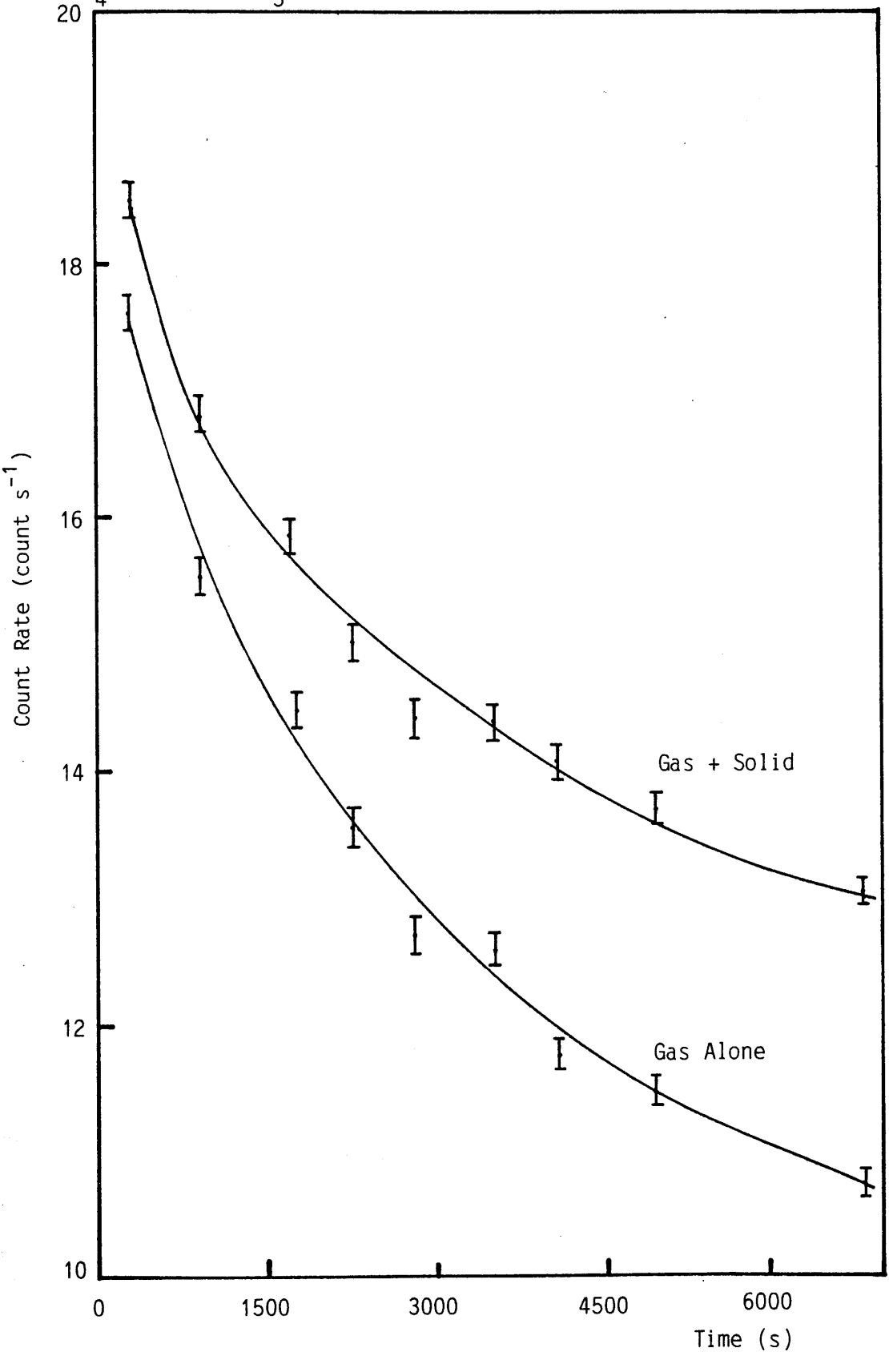


TABLE 6.I. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-CCl_4 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g) (Torr)	$AlCl_3$ (s) (mmol)	Observed Surface Count Rate (count s^{-1})
B102	32.7 ± 2.8	3.17	1.58 ± 0.03
B103	33.5 ± 2.8	5.24	10.9 ± 0.2
B104	36.7 ± 3.1	1.24	1.06 ± 0.02
B105	40.2 ± 3.4	4.40	1.65 ± 0.03

TABLE 6.II. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-CCl_4 (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g) (Torr)	$AlCl_3$ (s) (mmol)	Observed Surface Count Rate (count s^{-1})
B304	70.8 ± 6.0	14.65	1.04 ± 0.02

of the experiments, except in B103 in which the solid changed colour from white to dark brown as soon as it was exposed to gaseous $[^{36}Cl]$-CCl_4. This observation, and the comparatively high surface count rate observed in B103 suggest that the sample of $[^{36}Cl]$-CCl_4 was contaminated with an unidentified organic species which reacted with aluminium (III) chloride and facilitated adsorption of carbon tetrachloride and/or $[^{36}Cl]$-chlorine exchange on the brown material.

When the solid aluminium (III) chloride had been exposed to water vapour in the reaction vessel for 1h and subsequently pumped in situ for 1h, prior to admission of gaseous $[^{36}Cl]$-CCl_4, the behaviour was identical to that described in 6.2.1 in three of the four experiments studied (Table 6.X). In the fourth experiment a barely detectable surface count rate was observed, which did not decrease after 24h pumping (Table 6.II). There was no change in the physical appearance of the solid during the course of any of the experiments.

The apparent lack of interaction between gaseous $[^{14}C]$-CCl_4 and solid aluminium (III) chloride suggests either that gaseous carbon tetrachloride is not strongly adsorbed on aluminium (III) chloride, or that very few sites are available at which adsorption can take place. The lack of interaction in experiments in which the solid had been previously exposed to water vapour indicates that water does not promote adsorption of carbon tetrachloride on solid aluminium (III) chloride.

The result obtained when gaseous $[^{36}Cl]$-CCl_4 is exposed to solid aluminium (III) chloride indicates that some of the $[^{36}Cl]$-chlorine label can become irreversibly bound on the solid surface. Exposure of the solid to water vapour prior to admittance of gaseous $[^{36}Cl]$-CCl_4 had no effect on the observed behaviour. This indicates that water does not promote $[^{36}Cl]$-chlorine exchange between gaseous

$[^{36}Cl]$-CCl_4 and solid aluminium (III) chloride and is consistent with Wallace and Willard's observation that water inhibits $[^{36}Cl]$-chlorine exchange between liquid carbon tetrachloride and solid $[^{36}Cl]$-$AlCl_3$.[49] The detection of $[^{36}Cl]$-chlorine activity on the solid surface in these experiments can be accounted for as follows.

The $[^{36}Cl]$-chlorine exchange expected on the basis of the report of Blau and Willard[50] can take place only at sites at which carbon tetrachloride can adsorb. The number of sites available, which will be a characteristic of the sample and will depend upon the amount of surface hydration and hydrolysis, will govern the amount of carbon tetrachloride adsorbed at any time of measurement, for a given pressure of the gas. If the number of sites is small, and if reorganisation of the solid aluminium (III) chloride lattice is a very slow process at room temperature, as suggested by Wallace and Willard,[49] then adsorption of a $[^{36}Cl]$-CCl_4 molecule followed by $[^{36}Cl]$-chlorine exchange and desorption may lead to the formation of regions on the surface which are comparatively enriched in $[^{36}Cl]$-chlorine. However, at any time of measurement only very few carbon tetrachloride molecules will be adsorbed, and this may explain the differences between the results obtained using $[^{36}Cl]$-CCl_4 and $[^{14}C]$-CCl_4. The lack of interaction in some of the $[^{36}Cl]$-CCl_4 experiments can be accounted for if $[^{36}Cl]$-chlorine exchange was completely inhibited by water in those experiments.

Another possible interpretation of the apparent interaction between $[^{36}Cl]$-CCl_4 and some aluminium (III) chloride samples is that trace quantities of phosgene, which is known to undergo chlorine exchange in the solution phase with aluminium (III) chloride,[101] are responsible for the interaction. Phosgene is a by-product of the preparation of $[^{36}Cl]$-CCl_4 by the method described in 2.2.4, and although

measures were taken to remove it from the product mixture (2.2.4), it is possible that a trace amount of phosgene remained in the $[^{36}Cl]$-CCl_4 used; also, phosgene can be generated in liquid carbon tetrachloride on prolonged exposure to light if trace quantities of water are present,[102] and, although the $[^{14}C]$-CCl_4 used was stored under subdued light, the $[^{36}Cl]$-CCl_4 used was not.

6.2.3 The Interaction of Gaseous $[^{14}C]$-Carbon-Labelled Carbon Tetrachloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane

Solid aluminium (III) chloride was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 2h, and the purple solid produced was pumped in situ for 24h prior to admission of gaseous $[^{14}C]$-carbon-labelled carbon tetrachloride. The observed behaviour was identical to that described in 6.2.1. No significant surface count rate was detected in any of the experiments (Table 6.XI), and there was no change in the physical appearance of the solid during the course of an experiment.

This result is identical to that observed when gaseous $[^{14}C]$-CCl_4 is exposed to solid aluminium (III) chloride. It indicates that there is no detectable adsorption of $[^{14}C]$-CCl_4 on the purple solid formed by the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride.

6.2.4 The Interaction between Solid Aluminium (III) Chloride and a Mixture of Gaseous Radiolabelled Carbon Tetrachloride and Gaseous 1,1,1-Trichloroethane or a Mixture of Gaseous Radiolabelled Carbon Tetrachloride and Gaseous 1,1 - Dichloroethene.

When a mixture of gaseous $[^{14}C]$-carbon-labelled carbon tetrachloride and gaseous 1,1,1-trichloroethane was exposed to solid

aluminium (III) chloride, the count rates from both Geiger-Müller tubes behaved as described in 6.2.1. No significant surface count rate was detected in any of the experiments and the observed count rates from both tubes were identical after the volatile material was removed. During the course of an experiment the solid underwent a colour change from white to dark purple. Solid aluminium (III) chloride was exposed to a mixture of gaseous $[^{14}C]$-CCl_4 and gaseous 1,1-dichloroethene and the behaviour was identical to that described above in all three experiments studied (Table 6.XIV).

When a mixture of gaseous $[^{36}Cl]$-chlorine-labelled carbon tetrachloride and gaseous 1,1,1-trichloroethane was exposed to solid aluminium (III) chloride, the count rate from the gas and solid decreased by less than that from the gas alone (shown in Figure 6.III for experiment D101) and a barely detectable surface count rate was observed. Accurate determinations of surface count rates were not made during the course of the experiment due to the very long counting times required. Pumping the solid in situ for 24h did not lead to a decrease in the surface count rate, and surface count rates were determined after 24h pumping in both experiments studied (Table 6.III). During the course of an experiment the solid underwent a colour change from white to dark purple. Solid aluminium (III) chloride was exposed to a mixture of gaseous $[^{36}Cl]$-CCl_4 and gaseous 1,1-dichloroethene and the behaviour was identical to that described above in all three experiments studied (Table 6.XV). Surface count rates were determined after 24h pumping in all three experiments (Table 6.IV). The specific count rate was also determined for a sample of solid $[^{36}Cl]$-AgCl derived from the gaseous hydrogen chloride recovered from experiment D302 (Table 6.IV), and was 0.0095 ± 0.0002 count $s^{-1} mg^{-1}$. Although

FIGURE 6.III. Variation in Count Rates from the Gas and Solid Combined and from the Gas Alone in the Interaction of a Mixture of $[^{36}Cl]$-CCl_4(g) and CH_3CCl_3(g) with $AlCl_3$(s)

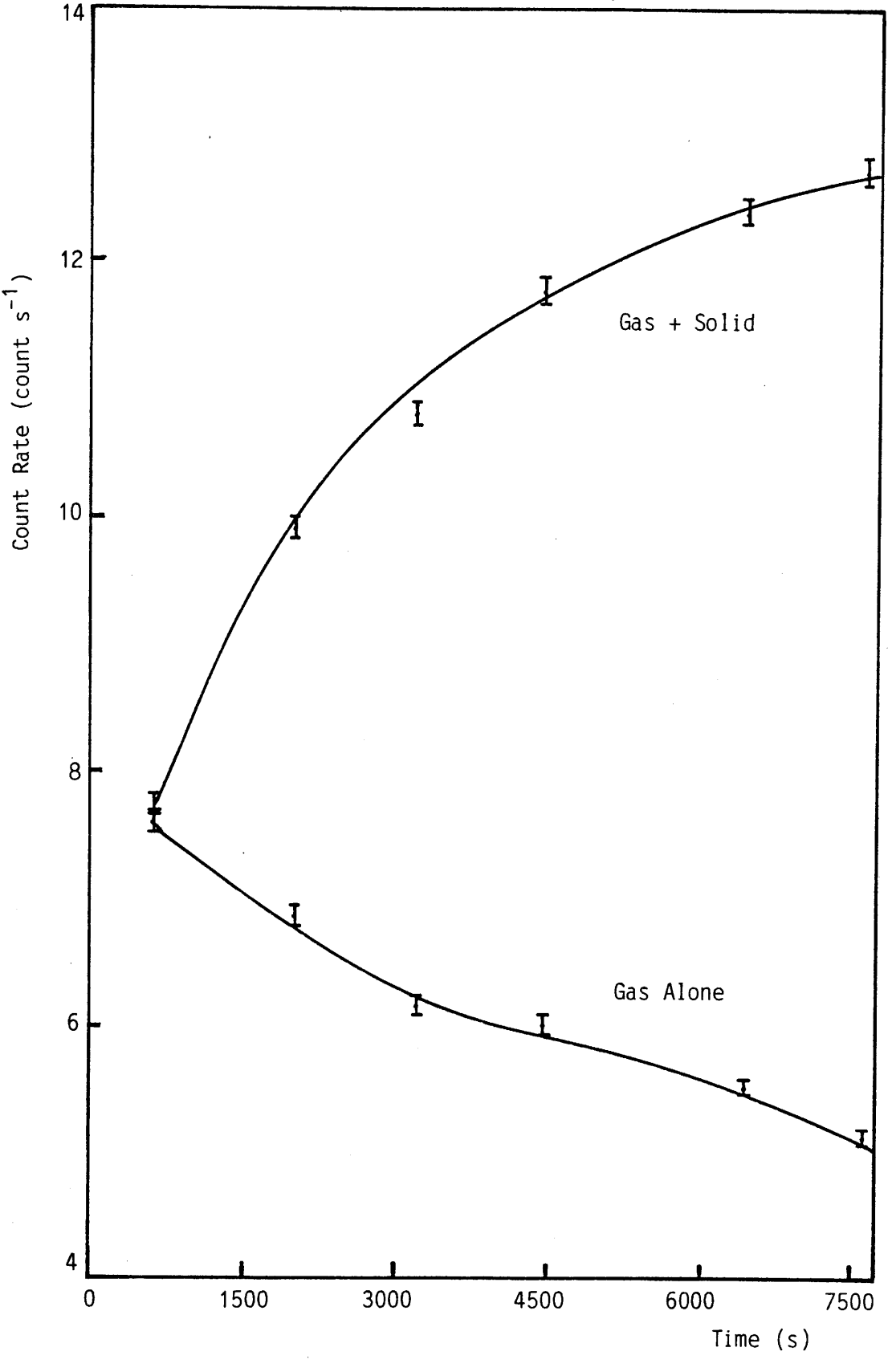


TABLE 6.III. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-CCl_4 (g) and CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g) (Torr)	Initial CH_3CCl_3 (g) (Torr)	$AlCl_3$ (s) (mmol)	Observed Surface Count Rate (count s^{-1})
D101	29.9 ± 2.5	39.5 ± 3.3	2.85	6.0 ± 0.2
D102	36.8 ± 3.1	38.3 ± 3.2	5.09	2.38 ± 0.04

TABLE 6.IV. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-CCl_4 (g) and $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g) (Torr)	Initial $CH_2=CCl_2$ (g) (Torr)	$AlCl_3$ (s) (mmol)	Observed Surface Count Rate (count s^{-1})
D301	20.0 ± 1.7	38.4 ± 3.2	7.98	7.2 ± 0.1
D302	31.7 ± 2.7	36.3 ± 3.1	3.55	2.67 ± 0.04
D303	47.4 ± 4.0	49.9 ± 4.2	3.20	1.97 ± 0.04

the specific count rate of the sample was very low, the presence of a count rate above background indicates that the hydrogen chloride recovered did contain some [^{36}Cl]-chlorine activity.

These results suggest either that gaseous [^{14}C]-CCl_4 is not adsorbed on the purple solids formed by the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride, or that very few sites are available at which adsorption can take place. The results obtained when mixtures of [^{36}Cl]-CCl_4 and gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene were exposed to solid aluminium (III) chloride indicate that some of the [^{36}Cl]-chlorine label can become irreversibly bound on the solid surface. The detection of [^{36}Cl]-chlorine activity in the gaseous hydrogen chloride recovered from experiment D302 indicates that the behaviour observed when a mixture of gaseous [^{36}Cl]-CCl_4 and gaseous 1,1-dichloroethene is exposed to solid aluminium (III) chloride is not due solely to the interaction of [^{36}Cl]-CCl_4 with solid aluminium (III) chloride, since that process does not lead to the formation of hydrogen chloride. Furthermore, a vapour phase infra-red spectrum of the [^{36}Cl]-CCl_4 from which the samples used in experiments D301, D302 and D303 were drawn showed carbon tetrachloride only. This indicates that the [^{36}Cl]-chlorine activity detected in the hydrogen chloride recovered from experiment D302 was not due to the presence of [^{36}Cl]-HCl as a contaminant in the [^{36}Cl]-CCl_4 used.

The detection of [^{36}Cl]-chlorine activity in the hydrogen chloride recovered from experiment D302 indicates that [^{36}Cl]-chlorine derived from gaseous [^{36}Cl]-CCl_4 becomes directly involved in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride. This is consistent with the detection of [^{36}Cl]-chlorine

activity on the surface of solid aluminium (III) chloride which had been exposed to a mixture of gaseous [^{36}Cl]-CCl_4 and gaseous 1,1,1-trichloroethane or to a mixture of gaseous [^{36}Cl]-CCl_4 and gaseous 1,1-dichloroethene. The observed behaviour has several possible interpretations. These are as follows:

(a) [^{36}Cl]-Chlorine exchange takes place between gaseous [^{36}Cl]-CCl_4 and gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene in the presence of aluminium (III) chloride, and the [^{36}Cl]-chlorine label is incorporated in the involatile organic product of the reaction of gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene with solid aluminium (III) chloride (3.2.4, 4.2.5). Evidence presented in 7.2.5 is consistent with this interpretation.

(b) [^{36}Cl]-Chlorine exchange takes place between gaseous [^{36}Cl]-CCl_4 and gaseous hydrogen chloride in the presence of solid aluminium (III) chloride. Complete exchange of [^{36}Cl]-chlorine between gaseous [^{36}Cl]-HCl at 1,1,1-trichloroethane or 1,1-dichloroethene is known to occur in the reactions of these gaseous chlorohydrocarbons with solid aluminium (III) chloride (5.2.5, 5.2.6), and incorporation of the [^{36}Cl]-chlorine label of gaseous [^{36}Cl]-CCl_4 in gaseous hydrogen chloride in this work would lead to incorporation of the label in the involatile product. However, it has been reported that there is no exchange of chlorine between gaseous hydrogen chloride and carbon tetrachloride at 20°C over 900 min.[103]

(c) Carbon tetrachloride interacts directly with the involatile organic material formed in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid

aluminium (III) chloride, by the reversible aluminium (III) chloride catalysed alkylation of a 1,1-dichloroethene derived oligomer such as 1,1,3,3-tetrachlorobut-1-ene (Equation 6.II) or 2,2,4,4-tetrachlorobut-1-ene (Equation 6.III). This could provide a plausible route for the formation of carbon tetra-

$$CCl_4 + CCl_2{=}CHCCl_2CH_3 \overset{AlCl_3}{\rightleftharpoons} \underset{(I)}{CCl_3CCl_2CHClCCl_2CH_3} \qquad \text{Equation 6.II}$$

$$CCl_4 + CH_2{=}CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} CCl_3CH_2CCl_2CH_2CCl_3 \qquad \text{Equation 6.III}$$

chloride in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride, by the aluminium (III) chloride catalysed dealkylation of a hydrochlorinated 1,1-dichloroethene derived oligomer such as 1,1,1,3,3-pentachlorobutane (Equation 6.IV). However, the dealkylation of species (I) in Equation 6.II might be expected

$$CCl_3CH_2CCl_2CH_3 \overset{AlCl_3}{\rightleftharpoons} CCl_4 + CH_2{=}CClCH_3 \qquad \text{Equation 6.IV}$$

to yield chloroform in addition to carbon tetrachloride, and processes such as Equations 6.II and 6.III are expected to lead to [^{14}C]-carbon incorporation as well as [^{36}Cl]-chlorine incorporation in the involatile material.

If the involatile organic product of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride is a mixture of 1,1-dichloroethene derived oligomers and polymers which undergo the reactions described in Scheme 5.I, and, as side reactions, those described in Equations 6.II, 6.III and 6.IV, and if the involatile organic product is progressively deposited on the solid during the course of the reaction, then the observed behaviour can be interpreted in terms of

process (c) as follows. When a mixture of gaseous [^{14}C]-CCl_4 and gaseous 1,1,1-trichloroethane or 1,1-dichloroethene is exposed to solid aluminium (III) chloride, the [^{14}C]-CCl_4 may take part in a reaction such as Equation 6.III. The [^{14}C]-carbon label can then either be liberated into the gas phase as carbon tetrachloride in the reverse process, or be covered by the deposition of further involatile organic material. Thus the amount of [^{14}C]-carbon bound at the surface at any time of measurement will not be a function of the total amount of [^{14}C]-carbon which has been incorporated in the involatile material. When a mixture of gaseous [^{36}Cl]-CCl_4 and gaseous 1,1,1-trichloroethane or 1,1-dichloroethene is exposed to solid aluminium (III) chloride, the [^{36}Cl]-CCl_4 may take part in a reaction such as Equation 6.III. The [^{36}Cl]-chlorine label can then undergo exchange with the chlorine atoms of the organic species (5.2.5, 5.2.6), and hence the amount of [^{36}Cl]-chlorine label present at the surface at any time of measurement will be a function of the total amount of [^{36}Cl]-chlorine incorporated into the involatile material.

6.3 EXPERIMENTAL

6.3.1 The Interaction of Gaseous Radiolabelled Carbon Tetrachloride with the Pyrex Reaction Vessel.

The reaction vessel (2.5.1) was evacuated, flamed out and an accurately measured quantity of gaseous radiolabelled carbon tetrachloride was admitted. The reaction vessel was isolated from the rest of the vacuum system and counts were taken from both Geiger-Müller tubes with time for typically 2.5h, at the end of which the radiolabelled carbon tetrachloride was vacuum distilled into the storage vessel.

This procedure was carried out at regular intervals during the course of the work using [^{14}C]-carbon-labelled carbon tetrachloride. The quantities of [^{14}C]-CCl_4 used and durations of experiments are contained in Table 6.V. In experiment A10 the reaction vessel was exposed to water vapour for 2h and was not flamed out prior to admission of the [^{14}C]-CCl_4. The procedure was carried out once using [^{36}Cl]-chlorine-labelled tetrachloride; the quantity used and duration of the experiment are contained in Table 6.VI.

6.3.2 The Interaction of Gaseous Radiolabelled Carbon Tetrachloride with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.5.2. The quantities of reactants and durations of experiments in which [^{14}C]-carbon-labelled carbon tetrachloride was used are contained in Table 6.VII. The quantities of reactants and durations of experiments in which [^{36}Cl]-chlorine-labelled carbon tetrachloride was used are contained in Table 6.VIII.

Further experiments were carried out using the procedure described in 2.5.2 with the following modification. The solid was

TABLE 6.V. Quantities of [^{14}C]-CCl_4 (g) and Durations of Experiments in Interactions of [^{14}C]-CCl_4 (g) with Pyrex Reaction Vessel.

Run No.	Initial [^{14}C]-CCl_4 (g) (Torr)	(mmol)	Duration of Experiment (min)
A1	24.4 ± 1.1	0.78 ± 0.06	130
A2	24.7 ± 1.1	0.79 ± 0.06	145
A3	26.0 ± 1.1	0.84 ± 0.06	135
A4	26.2 ± 1.2	0.84 ± 0.06	150
A5	26.9 ± 1.2	0.87 ± 0.06	150
A6	27.8 ± 1.2	0.89 ± 0.06	150
A7	28.4 ± 1.2	0.91 ± 0.07	200
A8	29.5 ± 1.3	0.95 ± 0.07	140
A9	30.8 ± 1.4	0.99 ± 0.07	140
A10	30.8 ± 1.4	0.99 ± 0.07	150
A11	40.1 ± 3.4	1.39 ± 0.09	70
A12	89.8 ± 0.5	2.90 ± 0.17	135

TABLE 6.VI. Quantities of $[^{36}Cl]$-CCl_4(g) and Durations of Experiment in Interaction of $[^{36}Cl]$-CCl_4(g) with Pyrex Reaction Vessel.

Run No.	Initial $[^{36}Cl]$-CCl_4(g)		Duration of Experiment
	(Torr)	(mmol)	(min)
A101	51.8 ± 0.5	1.80 ± 0.10	80

TABLE 6.VII. Initial Quantities of Reactants and Durations of Experiments in the Interaction of $[^{14}C]$-CCl_4 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{14}C]$-CCl_4 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(g)	(mmol)	(min)
B1	24.2 ± 1.1	0.78 ± 0.06	0.3041	2.28	135
B2	25.6 ± 1.1	0.82 ± 0.06	0.1657	1.24	135
B3	28.2 ± 1.2	0.91 ± 0.07	1.3283	9.95	180
B4	28.5 ± 1.3	0.92 ± 0.07	0.6638	4.97	135
B5	28.7 ± 2.4	0.99 ± 0.06	0.1812	1.36	70
B6	93.5 ± 0.5	3.01 ± 0.17	0.7387	5.53	150

TABLE 6.VIII. Initial Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-CCl_4 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(g)	(mmol)	(min)
B101	29.6 ± 2.5	1.03 ± 0.07	0.2726	2.04	90
B102	32.7 ± 2.8	1.13 ± 0.07	0.4231	3.17	110
B103	33.5 ± 2.8	1.16 ± 0.08	0.6993	5.24	105
B104	36.7 ± 3.1	1.27 ± 0.08	0.1657	1.24	85
B105	40.2 ± 3.4	1.39 ± 0.09	0.5877	4.40	200
B106	58.4 ± 4.9	2.02 ± 0.13	0.4966	3.72	150
B107	63.7 ± 5.4	2.20 ± 0.14	0.5233	3.92	110
B108	65.0 ± 5.5	2.25 ± 0.15	0.4022	3.01	125
B109	70.1 ± 5.9	2.43 ± 0.16	0.5462	4.09	165

exposed to water vapour in the reaction vessel for 1h, at the end of which the solid was pumped in situ for 1h, before the gaseous radiolabelled carbon tetrachloride was admitted. The quantities of reactants and durations of experiments in which $[^{14}C]$-CCl_4 was used are contained in Table 6.IX. The quantities of reactants and durations of experiments in which $[^{36}Cl]$-CCl_4 was used are contained in Table 6.X.

6.3.3 The Interaction of Gaseous $[^{14}C]$-Carbon-Labelled Carbon Tetrachloride with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. The solid was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 2h, at the end of which the solid was pumped in situ for 24h, before the gaseous $[^{14}C]$-carbon-labelled carbon tetrachloride was admitted. The quantities of reactants and durations of experiments are contained in Table 6.XI.

6.3.4 The Interaction Between Solid Aluminium (III) Chloride and a Mixture of Gaseous Radiolabelled Carbon Tetrachloride and Gaseous 1,1,1-Trichloroethane or a Mixture of Gaseous Radiolabelled Carbon Tetrachloride and Gaseous 1,1-Dichloroethene.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. Approximately equimolar quantities of gaseous radiolabelled carbon tetrachloride and gaseous 1,1,1-trichloroethane were condensed into a vacuum flask. The contents of the flask were then allowed to warm up to room temperature in a measured volume of the vacuum system, and only when this had been achieved was the mixture allowed to expand further into the reaction

TABLE 6.IX. Initial Quantities of Reactants and Durations of Experiments in the Interaction of $[^{14}C]$-CCl_4 (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	Initial $[^{14}C]$-CCl_4 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(g)	(mmol)	(min)
B201	26.9 ± 1.2	0.87 ± 0.06	0.3041	2.28	135
B202	28.1 ± 1.2	0.90 ± 0.06	0.7907	5.92	135
B203	29.5 ± 1.3	0.95 ± 0.07	0.1657	1.24	120
B204	38.6 ± 3.3	1.34 ± 0.09	0.2592	1.94	60

TABLE 6.X. Initial Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-CCl_4 (g) with $AlCl_3$ (s) which had been Exposed to H_2O (g)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(g)	(mmol)	(min)
B301	26.5 ± 2.2	0.92 ± 0.06	0.6807	5.10	45
B302	34.1 ± 2.9	1.18 ± 0.08	0.5489	4.11	95
B303	67.9 ± 5.7	2.35 ± 0.15	0.5180	3.88	180
B304	70.8 ± 6.0	2.45 ± 0.16	1.9557	14.65	130

TABLE 6.XI. Initial Quantities of Reactants and Durations of Experiments in the Interaction of $[^{14}C]$-CCl_4 (g) with $AlCl_3$ (s) which has been Exposed to CH_3CCl_3 (g)

Run No.	Initial $[^{14}C]$-CCl_4 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(g)	(mmol)	(min)
C1	24.5 ± 1.1	0.79 ± 0.06	0.2550	1.91	150
C2	24.9 ± 1.2	0.80 ± 0.06	0.5368	4.02	125
C3	27.3 ± 1.2	0.88 ± 0.06	0.4098	3.07	140
C4	32.1 ± 1.4	1.03 ± 0.07	0.2936	2.20	140

vessel. The quantities of reactants and durations of experiments in which gaseous [^{14}C]-carbon-labelled carbon tetrachloride was used are contained in Table 6.XII. The quantities of reactants and durations of experiments in which gaseous [^{36}Cl]-chlorine-labelled carbon tetrachloride was used are contained in Table 6.XIII.

The procedure described above was repeated using gaseous radiolabelled carbon tetrachloride and gaseous 1,1-dichloroethene. The quantities of reactants and durations of experiments in which gaseous [^{14}C]-CCl_4 was used are contained in Table 6.XIV. The quantities of reactants and durations of experiments in which gaseous [^{36}Cl]-CCl_4 was used are contained in Table 6.XV. The gaseous mixture recovered from experiment D302 (Table 6.XV) was collected in a vacuum flask cooled to -196^{o}C in a liquid nitrogen bath. The flask containing the product mixture was then warmed to -78^{o}C in a methylene chloride/solid CO_2 bath. The vapour in the manifold above the product mixture was isolated and condensed on to an excess of a frozen aqueous solution of sodium hydroxide (>98% pure, Hopkin & Williams). This procedure was repeated three times to recover most of the hydrogen chloride from the product mixture. The sodium hydroxide/hydrogen chloride mixture was allowed to warm up and react in a closed vessel at room temperature for 3h, and the resultant solution was treated as described in 2.6 to yield solid AgCl.

TABLE 6.XII. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{14}C]$-CCl_4 (g) and CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{14}C]$-CCl_4 (g)		Initial CH_3CCl_3 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(Torr)	(mmol)	(g)	(mmol)	(min)
D1	28.0 ± 2.4	0.97 ± 0.06	29.0 ± 2.4	1.00 ± 0.07	0.2368	1.77	60
D2	29.8 ± 2.5	1.03 ± 0.07	34.1 ± 2.9	1.18 ± 0.08	0.2319	1.74	45
D3	31.4 ± 2.6	1.08 ± 0.07	33.9 ± 2.9	1.17 ± 0.08	0.3734	2.80	60
D4	33.3 ± 2.8	1.16 ± 0.08	32.3 ± 2.7	1.12 ± 0.07	0.3378	2.53	65

TABLE 6.XIII. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{36}Cl]$-CCl_4 (g) and CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g)		Initial CH_3CCl_3 (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(Torr)	(mmol)	(g)	(mmol)	(min)
D101	29.9 ± 2.5	1.03 ± 0.07	39.5 ± 3.3	1.36 ± 0.09	0.3801	2.85	120
D102	36.8 ± 3.1	1.27 ± 0.08	38.3 ± 3.2	1.32 ± 0.09	0.6793	5.09	110

TABLE 6.XIV. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{14}C]$-CCl_4 (g) and $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial $[^{14}C]$-CCl_4 (g)		Initial $CH_2=CCl_2$ (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(Torr)	(mmol)	(g)	(mmol)	(min)
D201	30.5 ± 2.6	1.05 ± 0.07	70.3 ± 5.9	2.43 ± 0.16	0.3705	2.78	60
D202	31.4 ± 2.6	1.08 ± 0.07	61.9 ± 5.2	2.14 ± 0.14	0.2085	1.56	80
D203	33.4 ± 2.8	1.16 ± 0.08	31.9 ± 2.7	1.10 ± 0.07	0.3936	2.95	60

TABLE 6.XV. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{36}Cl]$-CCl_4 (g) and $CH_2=CCl_2$ (g) with $AlCl_3$ (s)

Run No.	Initial $[^{36}Cl]$-CCl_4 (g)		Initial $CH_2=CCl_2$ (g)		$AlCl_3$ (s)		Duration of Experiment
	(Torr)	(mmol)	(Torr)	(mmol)	(g)	(mmol)	(min)
D301	20.0 ± 1.7	0.69 ± 0.05	38.4 ± 3.2	1.33 ± 0.09	1.0647	7.98	165
D302	31.7 ± 2.7	1.10 ± 0.07	36.3 ± 3.1	1.25 ± 0.08	0.4741	3.55	140
D303	47.4 ± 4.0	1.64 ± 0.11	49.9 ± 4.2	1.72 ± 0.11	0.4278	3.20	130

CHAPTER 7

CHAPTER 7

THE INTERACTION OF GASEOUS [^{36}Cl]-CHLORINE-LABELLED 1,1,1-TRICHLOROETHANE WITH SOLID ALUMINIUM (III) CHLORIDE

7.1 INTRODUCTION

The importance of the reaction of 1,1,1-trichloroethane with solid aluminium (III) chloride was noted in 1.3.3 and 3.1. The vapour phase in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride was studied using infra-red spectroscopy (Chapter 3). The results indicated that, as well as the expected dehydrochlorination of 1,1,1-trichloroethane to yield gaseous 1,1-dichloroethene and hydrogen chloride, processes which led to the formation of gaseous carbon tetrachloride and an involatile organic product occurred. Scheme 3.IV was presented to account for most of the observations (3.2.4), and the scheme was modified as a consequence of the results reported in Chapters 4, 5 and 6. The modified scheme is shown below (Scheme 7.I).

$$CH_3CCl_{3(g)} \overset{\text{fast}}{\rightleftharpoons} CH_3CCl_{3(ad)} \qquad \text{(i)}$$

$$CH_3CCl_{3(ad)} \overset{\text{fast}}{\rightleftharpoons} CH_2{=}CCl_{2(ad)} + HCl_{(g)} \qquad \text{(ii)}$$

$$CH_2{=}CCl_{2(ad)} \rightleftharpoons CH_2{=}CCl_{2(g)} \qquad \text{(iii)}$$

$$CH_2{=}CCl_{2(ad)} + AlCl_2^+ \overset{\text{fast}}{\rightleftharpoons} Cl_2AlCH_2\overset{+}{C}Cl_2 \qquad \text{(iv)}$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_{2(ad)} \overset{\text{r.d.s}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 \qquad \text{(v)}$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3 \qquad \text{(vi)}$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2{=}CClCH_2CCl_3 + AlCl_3 \qquad \text{(vii)}$$

$$\frac{n}{2}CH_2{=}CClCH_2CCl_3 \rightleftharpoons \{CH{=}CCl\}_n + \frac{n}{2}HCl_{(g)} \qquad \text{(viii)}$$

Process(es) leading to the formation of $CCl_{4(g)}$ (ix)

Scheme 7.I

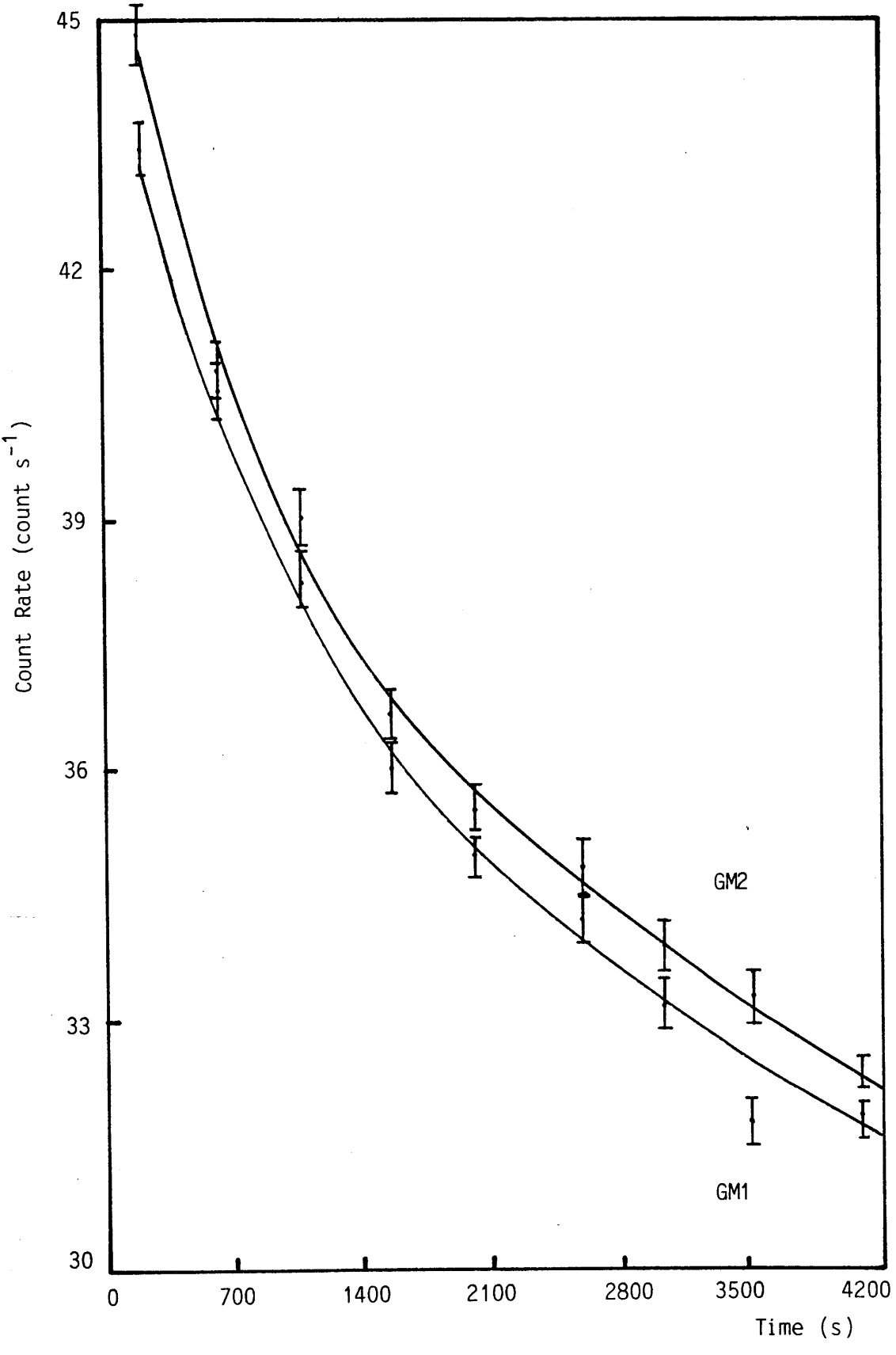
The interaction of gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane with solid aluminium (III) chloride was studied in this work using the direct monitoring Geiger-Müller counting technique in an attempt to obtain direct evidence for adsorbed 1,1,1-trichloroethane and to determine the fate of the [^{36}Cl]-chlorine label in subsequent reactions. The system was studied in the presence of water to determine whether the inhibition of the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride by water, reported in 5.2.5, was observed, and to develop an understanding of this inhibition. The system was also studied in the presence of gaseous carbon tetrachloride to determine the effect of this species on the observed behaviour, and to obtain information about the process leading to the formation of carbon tetrachloride in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride.

7.2 Results

7.2.1 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with the Pyrex Reaction Vessel.

When gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane (20.0 $\pm$ 1.7 Torr, 0.69 $\pm$ 0.04 mmol) was admitted to the reaction vessel at room temperature, the count rates from both Geiger-Müller tubes were identical and decreased over 3000s (Figure 7.I). The background count rates from both tubes after the gaseous [^{36}Cl]-CH_3CCl_3 had been removed were greater than those obtained before the gas was

FIGURE 7.I. Variation in Count Rates from Both GM Tubes in the Interaction of $[^{36}Cl]$-CH_3CCl_3(g) with the Pyrex Reaction Vessel



admitted by <1 count s^{-1}. Pumping the vessel for 1h resulted in a return to the original background count rates.

This result indicates that gaseous [^{36}Cl]-CH_3CCl_3 is adsorbed on the Pyrex glass walls of the reaction vessel. This effect is taken into account in 7.2.2 and subsequent sections.

7.2.2 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

When gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane was exposed to solid aluminium (III) chloride, the count rate from the gas and solid increased to an apparent saturation value over ca. 4000s, and the count rate from the gas alone decreased over the same period as shown in Figure 7.II for experiment A2 (Table 7.I). A significant surface count rate was detected as soon as the [^{36}Cl]-CH_3CCl_3 was admitted, and it increased to an apparent saturation value over ca. 4000s as shown in Figure 7.III for experiment A2. The surface count rates obtained were not related to the initial pressure of gaseous [^{36}Cl]-CH_3CCl_3 or to the quantity of aluminium (III) chloride used (Table 7.I). Pumping the solid in situ for several hours did not lead to a significant decrease in the count rate from the solid; in experiment A1 the surface count rate was 37.3 $\pm$ 0.5 count s^{-1} after 60h, in A2 and A3 the surface count rates were 47.6 $\pm$ 0.9 count s^{-1} and 31.8 $\pm$ 0.4 count s^{-1} respectively after 24h, and in A4 the surface count rate was 30.3 $\pm$ 0.6 count s^{-1} after 6h. During the course of an experiment the solid underwent a colour change from white to dark purple.

Specific count rates were determined for solid [^{36}Cl]-AgCl samples derived from the hydrogen chloride recovered from experiments

FIGURE 7.II. Variation in Count Rates from the Gas and Solid Combined and from the Gas Alone in the Interaction of $[^{36}Cl]$-$CH_3CCl_3(g)$ with $AlCl_3(s)$

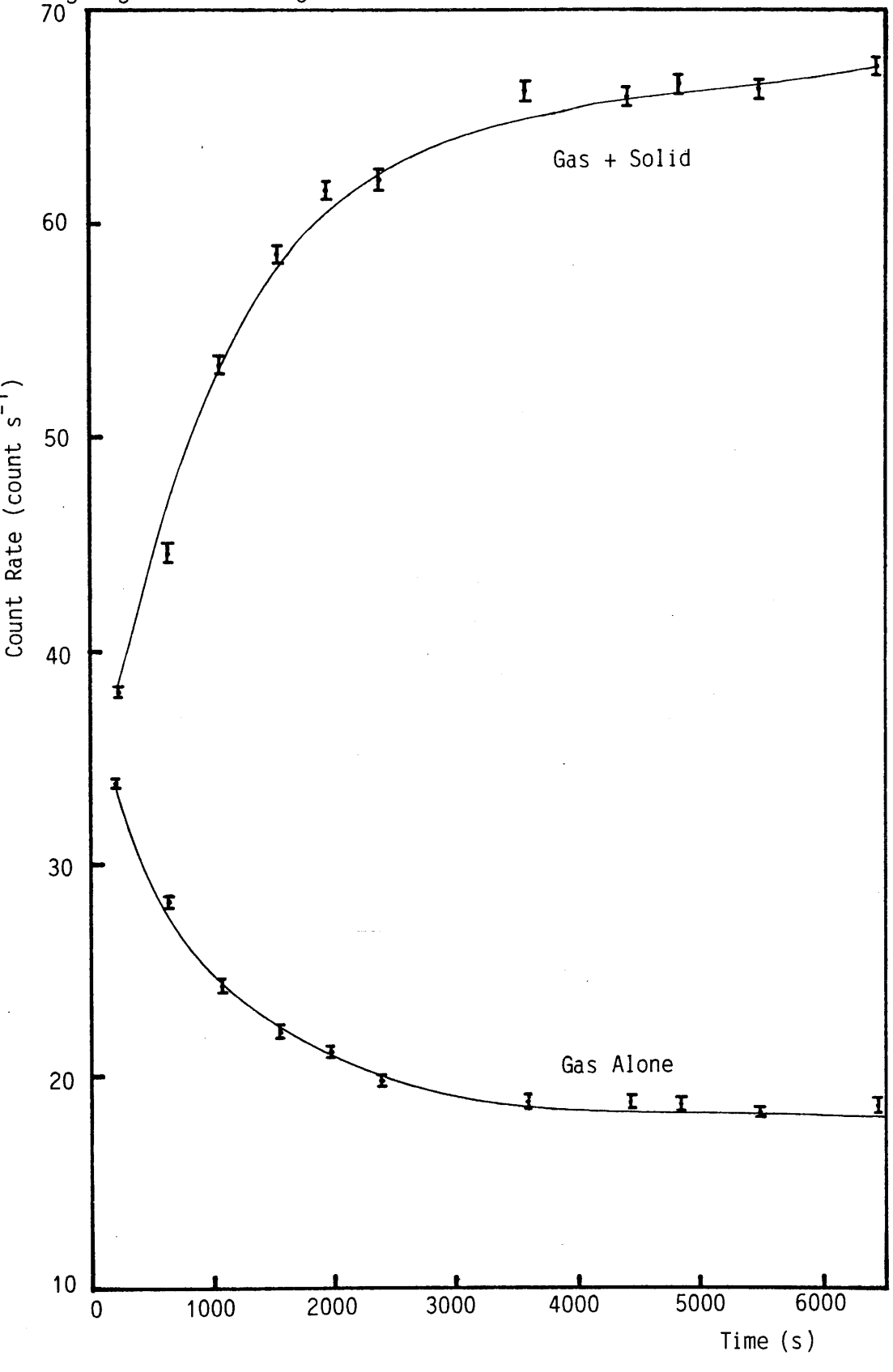


FIGURE 7.III. Plot of Surface Count Rate vs Time in the Interaction of $[^{36}Cl]$-CH_3CCl_3(g) with $AlCl_3$(s)

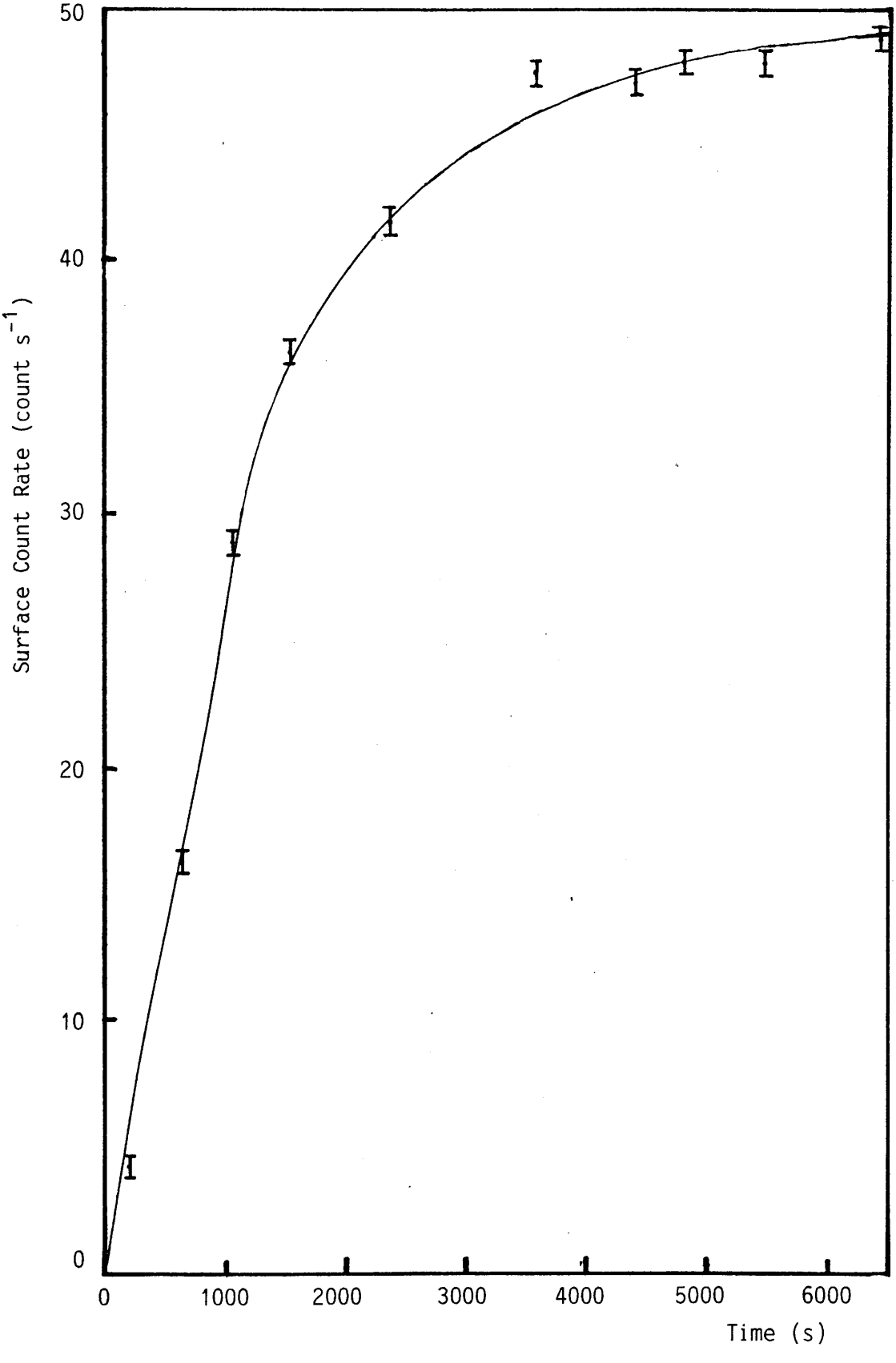


TABLE 7.I. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (mmol)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Observed Surface Count Rate at Saturation (count s^{-1})
A1	5.88	38.2 ± 3.2	40 ± 2
A2	2.83	38.3 ± 3.2	48 ± 2
A3	2.83	38.6 ± 3.2	38 ± 2
A4	5.93	38.6 ± 3.2	28 ± 1

TABLE 7.II. Quantities of Reactants and Observed Surface Count Rates in the Interaction of $[^{36}Cl]$-CH_3CCl_3 (g) with $AlCl_3$ (s) which had been Exposed to CH_3CCl_3(g)

Run No.	$AlCl_3$(s) (mmol)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Observed Surface Count Rate (count s^{-1})
B1	1.74	35.9 ± 3.0	3.2 ± 0.1
B2	3.20	37.8 ± 3.2	6.1 ± 0.2

A1, A3 and A4. These were 0.091 ± 0.002, 0.092 ± 0.002 and 0.073 ± 0.002 count $s^{-1}mg^{-1}$ respectively.

These results confirm that gaseous [^{36}Cl]-CH_3CCl_3 is adsorbed on solid aluminium (III) chloride (step (i), Scheme 7.I) and that the [^{36}Cl]-chlorine label is incorporated in the involatile product of the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride. The detection of [^{36}Cl]-chlorine activity in solid AgCl samples derived from gaseous hydrogen chloride recovered from these experiments confirms that the hydrogen chloride produced in the reaction is derived from 1,1,1-trichloroethane. If all the chlorine atoms of the hydrogen chloride produced in the reaction are derived solely from the [^{36}Cl]-CH_3CCl_3 admitted, then the specific count rates of [^{36}Cl]-AgCl samples derived from the hydrogen chloride recovered should be identical, since the [^{36}Cl]-CH_3CCl_3 samples used were of identical specific activity. Although the specific count rates of two of the [^{36}Cl]-AgCl samples obtained were identical, the other sample had a significantly different specific count rate. This behaviour may indicate the involvement of some of the chlorine atoms of aluminium (III) chloride in the process, as proposed in steps (iv) to (vi) of Scheme 7.I.

7.2.3 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

A solid aluminium (III) chloride sample was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 2h, at the end of which the purple solid formed was pumped in situ for 24h. When the solid was exposed to gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane, a barely detectable surface count rate was observed

on the solid as soon as the gas was admitted, and the surface count rate remained constant for 90 min. Accurate determinations of surface count rates were not made during the course of the experiments, as very long counting times would have been required. Pumping the solid in situ for 24h led to no observable decrease in the surface count rate, and surface count rates were determined after 24h pumping for each experiment (Table 7.II). The surface count rates observed were much smaller than those obtained when a comparable amount of gaseous $[^{36}Cl]$-CH_3CCl_3 was exposed to a comparable quantity of solid aluminium (III) chloride, which had not been previously exposed to gaseous 1,1,1-trichloroethane.

A solid aluminium (III) chloride sample was exposed to gaseous $[^{36}Cl]$-chlorine-labelled 1,1,1-trichloroethane in the reaction vessel for 2h, at the end of which the purple solid formed was pumped in situ for 24h. When the solid was exposed to gaseous unlabelled 1,1,1-trichloroethane the count rate from the gas and solid remained constant over 2h and was identical to the surface count rate of the solid prior to introduction of gaseous unlabelled 1,1,1-trichloroethane. The count rate from the gas alone remained constant over 2h and was approximately 1 count s^{-1} above background. This behaviour was reproducible.

The behaviour observed is consistent with Scheme 7.I. Exposure of gaseous 1,1,1-trichloroethane to the purple solid formed by the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride leads to the same vapour phase products as that reaction (3.2.1). Step (vi), or one of the subsequent steps in Scheme 7.I, is effectively irreversible (4.2.6); thus exposure of solid aluminium (III) chloride to gaseous 1,1,1-trichloroethane samples leads to

reaction, and the extent of reaction in successive exposures is expected to decrease as the involatile material progressively coats the solid and reduces the number of reactive sites available. Such a process can account for the behaviour in both sets of experiments noted above if the extent of exchange of chlorine atoms between the involatile organic species present in the purple solid and the gaseous 1,1,1-trichloroethane introduced is negligibly small.

The absence of a decrease in the surface count rate when gaseous unlabelled 1,1,1-trichloroethane was exposed to the purple solid formed by the reaction of gaseous $[^{36}Cl]$-CH_3CCl_3 with solid aluminium (III) chloride can be accounted for if the deposition of unlabelled involatile organic material does not lead to significant thickening of the surface coating, and hence does not lead to a substantial increase in the amount of $[^{36}Cl]$-chlorine self-adsorption in the material. The detection of a small amount of $[^{36}Cl]$-chlorine activity in the gas phase in these experiments is attributed to the production of small quantities of gaseous $[^{36}Cl]$-chlorine-labelled hydrogen chloride by the involatile organic material formed in the original exposure of the solid to gaseous $[^{36}Cl]$-CH_3CCl_3 (3.2.2).

7.2.4 The Interaction of Gaseous $[^{36}Cl]$-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride which had been Exposed to Gaseous Water.

A solid aluminium (III) chloride sample was exposed to water vapour in the reaction vessel for 2h, at the end of which the solid was pumped in situ for 1h. When the solid was exposed to gaseous $[^{36}Cl]$-chlorine-labelled 1,1,1-trichloroethane, the behaviour was identical to that described in 7.2.1 in experiments C2 and C3 (Table 7.VIII), and no significant surface count rate was detected. During

the course of these experiments the solid remained white. In experiment C1 (Table 7.VIII) the count rate from the gas and solid decreased by less than that from the gas alone and a barely significant surface count rate was detected. Pumping the solid in situ for 24h did not lead to a reduction in the surface count rate, which was 4.0 ± 0.1 count s^{-1}. During the course of experiment C1 the solid surface underwent a colour change from white to grey, while the solid underneath the surface underwent a colour change from white to dark purple.

When a mixture of gaseous $[^{36}Cl]$-CH_3CCl_3 and water vapour was exposed to solid aluminium (III) chloride, the count rate from the gas and solid increased to an apparent saturation value over ca. 1000s, and the count rate from the gas alone decreased during 7000s as shown in Figure 7.IV. A significant surface count rate was detected on the solid (Table 7.III), and Figure 7.V is a plot of surface count rate vs time. Pumping the solid in situ for 24h did not lead to a decrease in the surface count rate. During the course of the experiment the solid underwent a colour change from white to dark purple.

When the purple solid from experiment C4 (Table 7.III) was exposed to water vapour in the reaction vessel, the count rate from the gas and solid decreased steadily over 3h. The count rate from the gas alone remained constant over 3h and was approximately 2 count s^{-1} above background. During the course of this experiment the solid underwent a colour change from purple, through brown, to off-white. Pumping the solid in situ for 24h after the water vapour was removed did not lead to a decrease in the surface count rate, which was 30.0 ± 0.5 count s^{-1}.

FIGURE 7.IV. Variation in Count Rates from Gas and Solid Combined and from Gas Alone in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3(g) and H_2O(g) with $AlCl_3$(s)

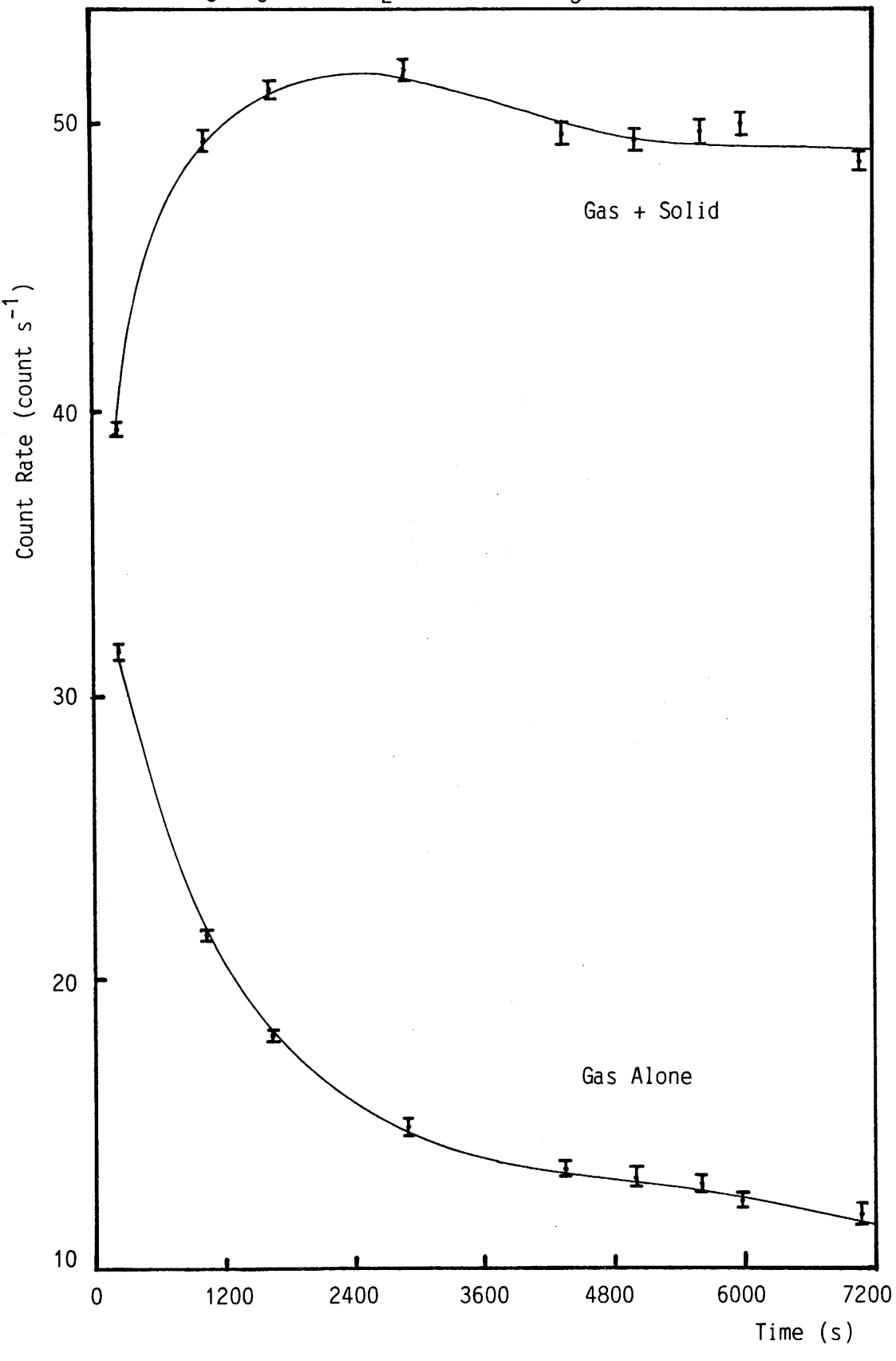


FIGURE 7.V. Plot of Surface Count Rate vs Time in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3(g) and H_2O(g) with $AlCl_3$(s)

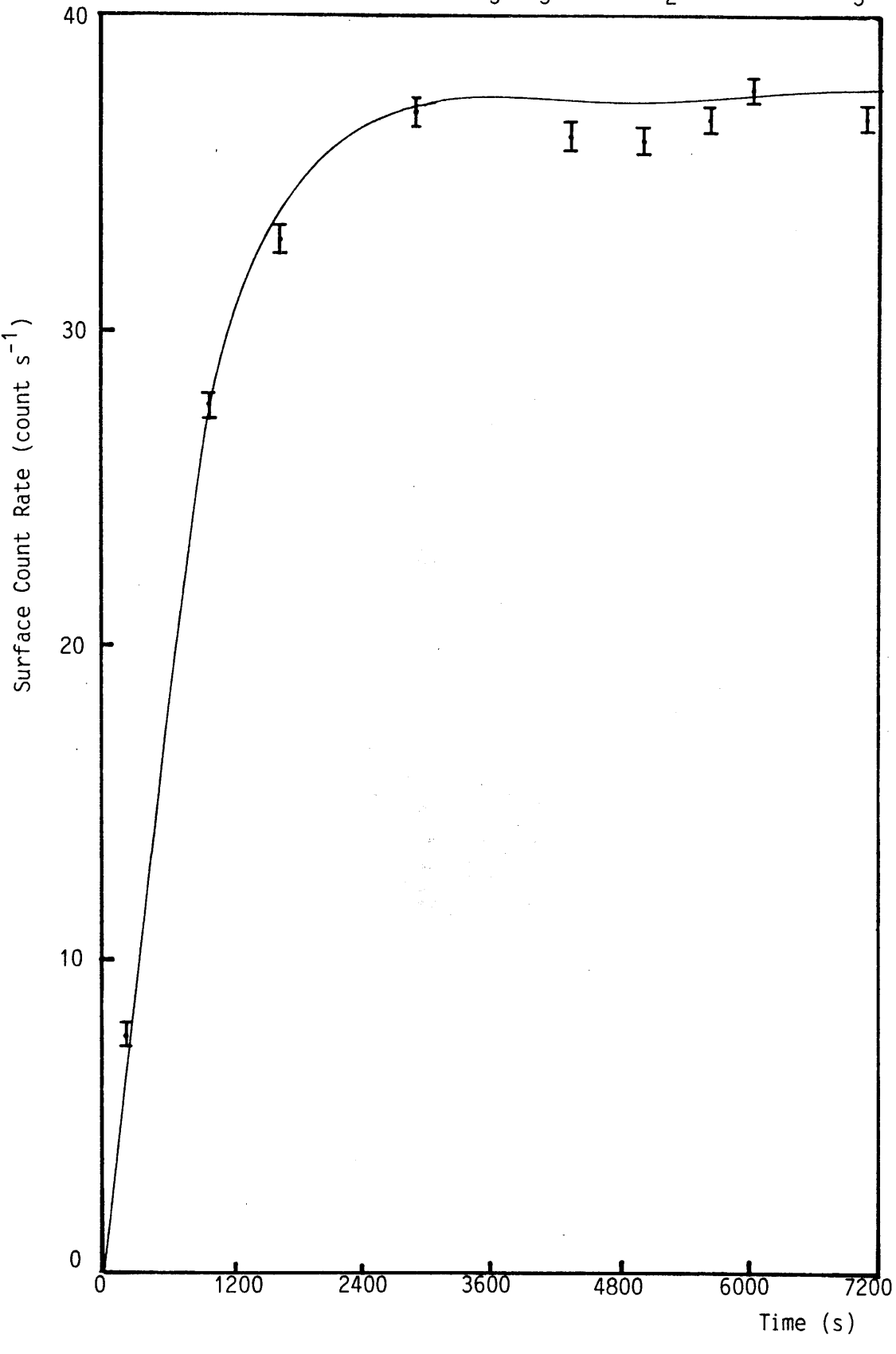


TABLE 7.III. Quantities of Reactants and Observed Surface Count Rate in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3 (g) and H_2O (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Initial Pressure of H_2O (g) (Torr)	Observed Surface Count Rate at Saturation (count s^{-1})
C4	3.54	37.4 ± 3.1	9.9 ± 0.7	37 ± 1

These results indicate that exposure of solid aluminium (III) chloride to water vapour prior to exposure to gaseous 1,1,1-trichloroethane can completely inhibit the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride. This confirms the observation noted in 5.2.5. The inhibition of this reaction by water can be accounted for if exposure of solid aluminium (III) chloride to water vapour blocks or removes the sites on the surface at which 1,1,1-trichloroethane molecules can adsorb and react. Physical adsorption of a water molecule at a co-ordinatively unsaturated aluminium (III) ion on the surface, followed by chemisorption and further reaction, as described in 5.2.3, can lead to the effective destruction of the site. If the site at which 1,1,1-trichloroethane adsorbs and reacts is the co-ordinatively unsaturated aluminium (III) ion on the surface, then widespread destruction of these sites can lead to non-attainment of the critical concentration of the product responsible for autocatalysis (3.2.4, 4.2.5, 4.2.6), and hence to the observed behaviour. These results also confirm that the sites created on the surface of aluminium (III) chloride by exposure of the solid to water vapour, which facilitate [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride and the solid (5.2.2, 5.2.3), are different from those which facilitate adsorption and reaction of gaseous 1,1,1-trichloroethane.

The observed behaviour when a mixture of gaseous [^{36}Cl]-CH_3CCl_3 and water vapour was exposed to solid aluminium (III) chloride indicates that water does not significantly inhibit the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride under these conditions. This indicates that the surface sites at which water can adsorb and react, and those at which 1,1,1-trichloro-

ethane can adsorb and react are the same, and that, in the presence of a 4-fold excess of chlorohydrocarbon, water does not compete efficiently for these sites. The observed behaviour when the purple solid formed by the reaction of a mixture of gaseous [^{36}Cl]-CH_3CCl_3 and water vapour with solid aluminium (III) chloride was exposed to water vapour indicates that [^{36}Cl]-chlorine activity can be transferred from the solid surface to the gas phase by water. This observation has several interpretations. The most plausible interpretation is that the water present in the gaseous mixture facilitated some [^{36}Cl]-chlorine exchange between [^{36}Cl]-HCl, formed in the reaction of gaseous [^{36}Cl]-CH_3CCl_3 with solid aluminium (III) chloride, and the solid itself; introduction of water vapour 24h after the gaseous mixture had been removed led to hydrolysis, and the evolution of gaseous [^{36}Cl]-HCl. The observation that most of the surface activity remained after the purple colour was discharged suggests that the colour is not due solely to the involatile organic material produced in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride.

7.2.5 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane and Gaseous Carbon Tetrachloride with Solid Aluminium (III) Chloride.

When a mixture of gaseous [^{36}Cl]-chlorine-labelled and gaseous carbon tetrachloride was exposed to solid aluminium (III) chloride, the behaviour was identical to that described in 7.2.2. The surface count rates obtained (Table 7.IV) were lower than those obtained when comparable amounts of gaseous [^{36}Cl]-CH_3CCl_3 alone were exposed to solid aluminium (III) chloride (Table 7.I). Pumping the solid in situ for 24h did not lead to a decrease in the surface count rate, and

TABLE 7.IV. Quantities of Reactants and Observed Surface Count Rates in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3 (g) and CCl_4 (g) with $AlCl_3$ (s)

Run No.	$AlCl_3$ (s) (mmol)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Initial CCl_4 (g) (Torr)	Observed Surface Count Rate at Saturation (count s^{-1})	Observed Surface Count Rate after 24h (count s^{-1})
E1	4.50	33.4 ± 2.8	85 ± 2	10 ± 1	8.9 ± 0.2
E2	1.72	33.8 ± 2.8	82 ± 2	22 ± 2	19.9 ± 0.4
E3	1.58	34.8 ± 2.4	37.8 ± 3.2	23 ± 2	24.4 ± 0.5

surface count rates were determined after 24h pumping (Table 7.IV). During the course of an experiment the solid underwent a colour change from white to purple.

This result is consistent with Scheme 7.I, and with the observation that [^{36}Cl]-chlorine activity is detected in AgCl derived from gaseous hydrogen chloride recovered from the interaction of a mixture of gaseous [^{36}Cl]-chlorine-labelled carbon tetrachloride and gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (6.2.4). However, the result noted above does not allow any additional information to be gained, principally because the hydrogen chloride recovered at the end of the experiments was not treated to yield AgCl. The observed behaviour has at least two interpretations. These are:

(a) that gaseous carbon tetrachloride competes efficiently with gaseous [^{36}Cl]-CH_3CCl_3 for the same surface sites. This possibility seems unlikely in view of the apparent lack of interaction between gaseous radiolabelled carbon tetrachloride and solid aluminium (III) chloride under most conditions (Chapter 6).

(b) that there is some exchange of chlorine atoms between carbon tetrachloride and 1,1,1-trichloroethane in the presence of solid aluminium (III) chloride; for example, by the reversible aluminium (III) chloride catalysed alkylation of a 1,1-dichloroethene derived oligomer such as 2,2,4,4-tetrachlorobut-1-ene (Equation 7.I).

$$CCl_4 + CH_2{=}CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} CCl_3CH_2CCl_2CH_2CCl_3 \quad \text{Equation 7.I}$$

7.2.6 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Gaseous Hydrogen Chloride.

Equimolar quantities of gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane were allowed to interact at room temperature for 24h. The count rates of AgCl samples derived from the hydrogen chloride recovered in all three experiments studied were identical to the background count rate.

This result indicates that there is no [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-CH_3CCl_3 and gaseous hydrogen chloride at room temperature over 24h. It suggests strongly that the exchange observed between gaseous [^{36}Cl]-chlorine labelled hydrogen chloride and gaseous 1,1,1-trichloroethane under identical conditions was due to contamination of the reaction vessel with a species such as aluminium (III) chloride, which catalysed the dehydrochlorination of 1,1,1-trichloroethane.

7.3 Experimental

7.3.1 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with the Pyrex Reaction Vessel.

The reaction vessel (2.5.1) was evacuated and flamed out. Gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane (20.0 $\pm$ 1.7 Torr, 0.69 $\pm$ 0.04 mmol) was admitted and the reaction vessel was isolated from the rest of the vacuum system. Counts were taken from both Geiger-Müller tubes for 1h, at the end of which the gaseous [^{36}Cl]-CH_3CCl_3 was removed.

7.3.2 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.5.2. Table 7.V contains the quantities of material used and the durations of the experiments. The solid was pumped in situ for at least 24h after the gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane was removed. Hydrogen chloride was separated from the gaseous product mixture as described in 5.3.5 in experiments A1, A3 and A4; the hydrogen chloride thus separated was treated as described in 2.6 to yield solid AgCl.

7.3.3 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. Solid aluminium (III) chloride was exposed to gaseous 1,1,1-trichloroethane in the reaction vessel for 1h, at the end of which the solid was pumped in situ for 24h, before gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane was admitted to the reaction vessel. The solid was pumped in situ for at least 24h after the volatile material was removed. Table 7.VI contains the quantities of material involved and the durations of the experiments.

A further three experiments were carried out as follows. Samples of solid aluminium (III) chloride which had been exposed to gaseous [^{36}Cl]-CH_3CCl_3 in experiments A1, A2 and A3 (Table 7.V) were exposed to gaseous 1,1,1-trichloroethane according to the procedure described in 2.5.2. The solid was pumped in situ for at least 24h

TABLE 7.V. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-CH_3CCl_3 (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Duration of Experiment (min)
A1	0.7846 ± 0.0004	5.88	38.2 ± 3.2	1.32 ± 0.09	165
A2	0.3782 ± 0.0004	2.83	38.3 ± 3.2	1.32 ± 0.09	105
A3	0.3777 ± 0.0004	2.83	38.6 ± 3.2	1.33 ± 0.09	80
A4	0.7917 ± 0.0004	5.93	38.6 ± 3.2	1.34 ± 0.09	95

TABLE 7.VI. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-CH_3CCl_3 (g) with $AlCl_3$ which had been Exposed to CH_3CCl_3 (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Duration of Experiment (min)
B1	0.2322 ± 0.0004	1.74	35.9 ± 3.0	1.24 ± 0.08	75
B2	0.4273 ± 0.0004	3.20	37.8 ± 3.2	1.31 ± 0.09	95

TABLE 7.VII. Quantities of Reactants and Durations of Experiments in the Interaction of CH_3CCl_3 (g) with $AlCl_3$ (s) which had been Exposed to $[^{36}Cl]$-CH_3CCl_3 (g)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of CH_3CCl_3 (g) (Torr)	Initial CH_3CCl_3 (g) (mmol)	Duration of Experiment (min)
B3	0.3782 ± 0.0004	2.83	33.4 ± 2.8	1.16 ± 0.08	135
B4	0.7846 ± 0.0004	5.88	35.8 ± 3.0	1.24 ± 0.08	105
B5	0.3777 ± 0.0004	2.83	40.3 ± 3.4	1.39 ± 0.09	110

after the volatile material was removed. Table 7.VII contains the quantities of material involved and the durations of the experiments.

7.3.4 The Interaction of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane with Solid Aluminium (III) Chloride which had been Exposed to Gaseous Water.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. The solid aluminium (III) chloride was exposed to water vapour in the reaction vessel for 2h, at the end of which the solid was pumped in situ for 1h, before gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane was admitted to the reaction vessel. The solid was pumped in situ for at least 24h after the gaseous [^{36}Cl]-CH_3CCl_3 was removed. Table 7.VIII contains the quantities of material involved and the durations of the experiments.

A further experiment was carried out using the procedure described in 2.5.2 with the following modification. Gaseous [^{36}Cl]-CH_3CCl_3 and water vapour were condensed into an ampoule attached to the manifold of the vacuum system (2.1.1). The contents of the ampoule were allowed to warm up to room temperature in a measured volume of the vacuum system, and stand therein for 15 min prior to expansion into the counting vessel. The solid was pumped in situ for 24h after the volatile material was removed, at the end of which the solid was exposed to water vapour and counts collected with time from both Geiger-Müller tubes over a period of 195 min. Table 7.IX contains the quantities of material used and the duration of the experiment.

TABLE 7.VIII. Quantities of Reactants and Durations of Experiments in the Interaction of $[^{36}Cl]$-CH_3CCl_3(g) with $AlCl_3$(s) which had been Exposed to H_2O(g)

Run No.	Weight $AlCl_3$(s) (g)	$AlCl_3$(s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	Initial $[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Duration of Experiment (min)
C1	0.5749 ± 0.0004	4.31	38.5 ± 3.2	1.33 ± 0.09	105
C2	0.2975 ± 0.0004	2.23	42.1 ± 3.5	1.46 ± 0.09	90
C3	0.2688 ± 0.0004	2.01	42.6 ± 3.6	1.47 ± 0.10	120

TABLE 7.IX. Quantities of Reactants and Duration of Experiment in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3 (g) and H_2O (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$ (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	$[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Initial Pressure H_2O (g) (Torr)	H_2O (g) (mmol)	Duration of Experiment (min)
C4	0.4725 ± 0.0004	3.54	37.4 ± 3.1	1.29 ± 0.08	9.9 ± 0.7	0.35 ± 0.03	115

TABLE 7.X. Quantities of Reactants and Durations of Experiments in the Interaction of a Mixture of $[^{36}Cl]$-CH_3CCl_3 (g) and CCl_4 (g) with $AlCl_3$ (s)

Run No.	Weight $AlCl_3$ (s) (g)	$AlCl_3$ (s) (mmol)	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	$[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Initial Pressure of CCl_4 (g) (Torr)	CCl_4 (g) (mmol)	Duration of Experiment (min)
D1	0.6010 ± 0.0004	4.50	33.4 ± 2.8	1.15 ± 0.08	85 ± 7	3.0 ± 0.2	195
D2	0.2302 ± 0.0004	1.72	33.8 ± 2.8	1.17 ± 0.08	82 ± 7	2.9 ± 0.2	175
D3	0.2104 ± 0.0004	1.58	34.8 ± 2.9	1.20 ± 0.08	37.8 ± 3.2	1.31± 0.09	95

7.3.5 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane and Gaseous Carbon Tetrachloride with Solid Aluminium (III) Chloride.

Experiments were carried out using the procedure described in 2.5.2 with the following modification. Gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane and gaseous carbon tetrachloride were condensed into an ampoule attached to the manifold of the vacuum system (2.1.1). The contents of the ampoule were allowed to warm up to room temperature in a measured volume of the vacuum system, and to stand therein for 15 min prior to expansion into the reaction vessel. The solid was pumped in situ for at least 24h after the gaseous mixture was removed. Table 7.X contains the quantities of material used and durations of the experiments.

7.3.6 The Interaction of a Mixture of Gaseous [^{36}Cl]-Chlorine-Labelled 1,1,1-Trichloroethane and Gaseous Hydrogen Chloride.

Three experiments were carried out using the following procedure. The reaction bulb (5.3.2) was evacuated and flamed out. Measured quantities of gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane and gaseous hydrogen chloride were condensed into the bulb, which was then closed. The bulb was allowed to stand at room temperature for 24h, at the end of which it was cooled to -196^{o}C in a liquid nitrogen bath. The bulb was opened to the manifold and the temperature was raised to -78^{o}C by replacing the liquid nitrogen bath with a methylene chloride/solid CO_2 bath. When there was no further increase in pressure, the non-volatile material held at -78^{o}C was isolated from the vapour and the latter condensed in an ampoule held at -196^{o}C. The procedure was repeated four times. The infra-red

spectrum of the more volatile material thus separated showed only hydrogen chloride. This hydrogen chloride was treated as described in 2.6 to yield AgCl. Table 7.XI contains the quantities of material used.

TABLE 7.XI. Quantities of Materials in the Interaction of $[^{36}Cl]$-CH_3CCl_3(g) with HCl(g)

Run No.	Initial Pressure of $[^{36}Cl]$-CH_3CCl_3 (g) (Torr)	$[^{36}Cl]$-CH_3CCl_3 (g) (mmol)	Initial Pressure of HCl (g) (Torr)	HCl (g) (mmol)
E1	32.2 ± 2.7	1.11 ± 0.07	40.8 ± 3.4	1.41 ± 0.09
E2	34.5 ± 2.9	1.19 ± 0.08	34.3 ± 2.9	1.19 ± 0.08
E3	40.1 ± 3.4	1.38 ± 0.09	39.8 ± 3.3	1.38 ± 0.09

CHAPTER 8

CHAPTER 8

SPECTROSCOPIC INVESTIGATIONS OF THE INVOLATILE ORGANIC MATERIALS PRODUCED IN THE REACTIONS OF GASEOUS 1,1,1-TRICHLOROETHANE AND GASEOUS 1,1-DICHLOROETHENE WITH SOLID ALUMINIUM (III) CHLORIDE AND IN THE REACTION OF LIQUID 1,1,1-TRICHLOROETHANE WITH ALUMINIUM METAL

8.1 INTRODUCTION

The reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride lead to the formation of an involatile organic material (3.2.4, 4.2.5). Involatile materials can be produced in the analogous solution reactions; for example, Kulikova reported that the polyene +CH=CCl+_n was produced in the solution reaction of 1,1,1-trichloroethane with aluminium (III) chloride.[81] Kulikova also investigated the solution reaction of 1,1-dichloroethene with aluminium (III) chloride and reported products included dimers, trimers and polymers of 1,1-dichloroethene, as well as hydrochlorinated and dehydrochlorinated derivatives thereof.[82] Aluminium (III) chloride catalysed oligomerisation of 1,1-dichloroethene is also thought to be an important process in the "bleeding" reaction of aluminium metal with liquid 1,1,1-trichloroethane,[1] and, although 1,1-dichloroethene derived dimers have been identified in the product mixture,[1] the dark red tar produced has not been identified.

Attempts to separate the involatile organic material from the product mixture in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride led to the isolation of a brown solid which was soluble in 1,1,1-trichloroethane and carbon tetrachloride. This material was studied using mass spectrometry and GCMS, but no assignments could be made and the

results from both techniques were consistent with the presence of a mixture of several organic species. In an attempt to obtain information about the identities of the involatile organic products of the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride, the surface of the solid was studied, before and after exposure to these gases, using Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFTS) and Surface Ionisation Mass Spectrometry (SIMS). The former was used for three reasons, these being:-

(i) the solid is handled at all times under vacuum or in the inert atmosphere box.

(ii) the surface of the solid is directly investigated.

(iii) computed spectral subtraction techniques can be used.

SIMS was used because it allows analysis of the surface, but this technique may also produce surface reactions and hence can be used in complex systems only when combined with other forms of analysis.

Aluminium (III) chloride was studied using DRIFTS and SIMS to obtain evidence for the presence of water on the surface of the solid and to determine, as far as possible, the nature of the surface water. The surface of the solid was studied using DRIFTS after exposure to gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene to obtain evidence for the presence of organic species, and in particular to determine whether there was any evidence for C=C stretching modes in the region 1650-1600 cm^{-1} or for features indicating the presence of cyclic compounds (4.2.6). The surface was studied using SIMS after exposure to gaseous 1,1,1-trichloroethane to obtain direct evidence for surface organic species.

As noted earlier, the involatile organic material formed in the

reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride is comparatively difficult to isolate because it coats the surface of the solid. It is easier to investigate the involatile organic material produced in the "bleeding" reaction, and this was considered useful because the involatile material is thought to be produced by aluminium (III) chloride catalysed oligomerisation of 1,1-dichloroethene.[1] The involatile material recovered from the "bleeding" reaction was studied using infra-red spectroscopy to obtain information about the functional groups present.

8.2 Results

8.2.1 DRIFTS Investigation of Solid Aluminium (III) Chloride.

Spectra obtained as described in 8.3.1 were reproducible. Figure 8.I shows the background subtracted spectrum over the range 4000-800 cm^{-1} of solid aluminium (III) chloride prepared as described in 2.2.6. The positions of the peaks (in cm^{-1}) and relative intensities were: 3400 (broad, vs), 2260 (broad, m), 1613 (s), 1116 (vs, sharp shoulder 994). Subsequent exposure of the sample to gaseous D_2O led to the detection of strong bands at 2480 cm^{-1} (a broad band which may mask the feature at 2260 cm^{-1}) and 1441 cm^{-1}; the peaks at 1613, 1116 and 994 cm^{-1} were unchanged. The spectrum of a sample of solid aluminium (III) chloride, prepared as described in 2.2.6, which had been exposed to gaseous D_2O prior to manipulation in the inert atmosphere box as described in 8.3.1, is shown in Figure 8.II. The positions of the peaks (in cm^{-1}) and relative intensities were:- 3350 (broad, m), 2480 (broad, s), 1441 (m), 1063 (s, sharp shoulder 988).

The bands observed in these spectra are not due to Al-Cl stretching modes, which occur at <435 cm^{-1} for solid aluminium (III)

FIGURE 8.I. Spectrum of the Surface of Solid Aluminium (III) Chloride

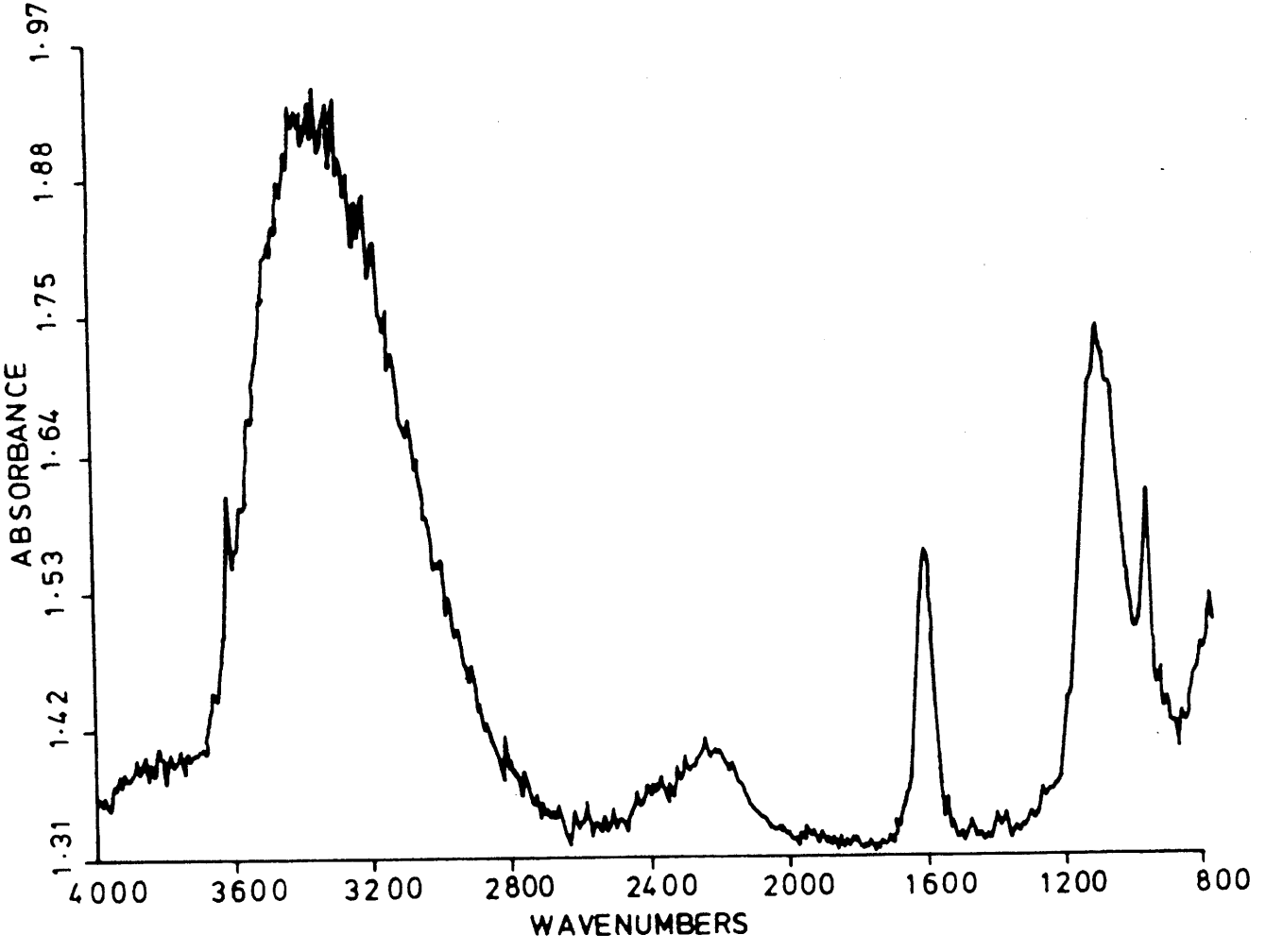
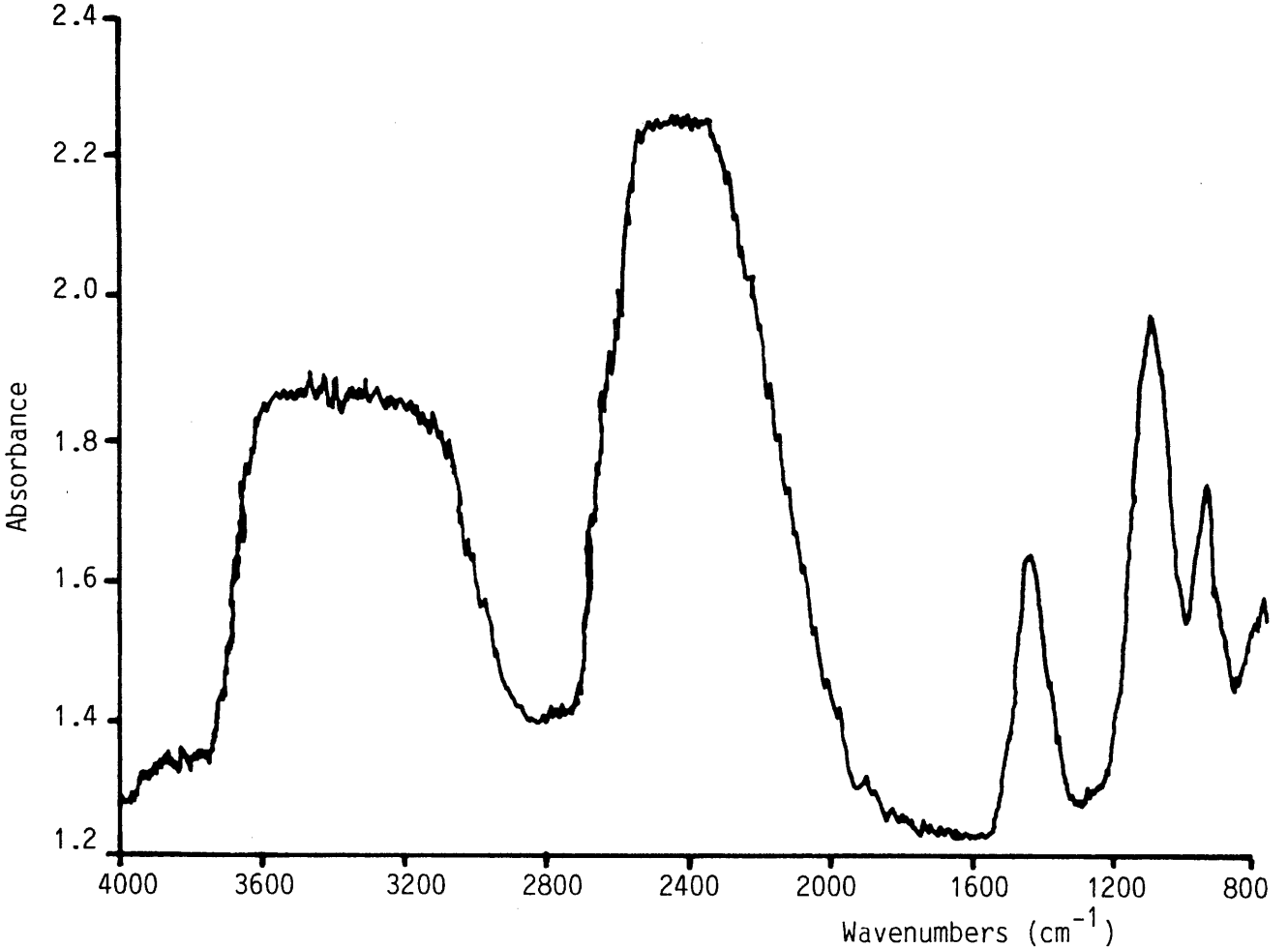


FIGURE 8.II. Spectrum of the Surface of Solid Aluminium (III) Chloride which had been Exposed to Gaseous D_2O.



chloride.[4] Those observed in the spectrum of solid aluminium (III) chloride prepared as described in 2.2.6 and handled as described in 8.3.1 (Figure 8.I) can be attributed to the presence of water on the surface of the solid. The peak at ca. 3400 cm^{-1} is attributed to the O-H stretching mode of a weakly hydrogen-bonded water molecule or a hydroxyl group. The band at 2260 cm^{-1} is attributed to the O-H stretching mode of a very strongly hydrogen-bonded water molecule or hydroxyl group. The peak at 1613 cm^{-1} is assigned to the H-O-H bending mode of a water molecule, and its position is consistent with the presence of hydrogen-bonded water.[32] Ginsberg et al. studied solids prepared by treating one mole of aluminium (III) chloride with 3 moles of sodium hydroxide under various conditions, and assigned bands in the infra-red spectra of these solids at 1100-900 cm^{-1} to Al-O-H deformations.[104] However, only one band in the region 1100-900 cm^{-1} was observed in each spectrum.[104] In an infra-red study of solids with stoichiometry corresponding to $Al(OH)_3$, Rouquerol reported that the position of the Al-O-H deformation band in the region 1100-900 cm^{-1} shifted towards higher wavenumber as the extent of hydrogen-bonding increased.[105] The bands observed in Figure 8.I at 1116 cm^{-1} and 994 cm^{-1} can be accounted for if two types of surface Al-O-H groups exist, one of which is very strongly hydrogen-bonded. This is also consistent with the observation of the band at 2260 cm^{-1}. There was no evidence in any of the spectra obtained for the peaks at ca. 3760, 2470 or 1740 cm^{-1} associated with surface H_3O^+ ions in hydrated single crystals of metals.[106]

The bands observed in the spectrum of solid aluminium (III) chloride which had been exposed to gaseous D_2O prior to manipulation in the inert atmosphere box (Figure 8.II) can be assigned as follows.

The peak observed at ca. 3350 cm^{-1} is assigned to an O-H stretching mode. This may be due to a weakly hydrogen-bonded water or HDO molecule or to a hydroxyl group. The band at 2480 cm^{-1} is attributed to an O-D stretching mode. The position of an O-D stretch corresponding to the 3400 cm^{-1} O-H stretch in Figure 8.I is expected to be 2405 cm^{-1} if the molecules are in identical environments. However, deviations will occur as the strength of hydrogen-bonding to D_2O and HDO molecules is less than that to an H_2O molecule in an identical environment. The band at 1441 cm^{-1} is attributed to the H-O-D bending mode of an HDO molecule, and its position is consistent with hydrogen-bonded HDO. The bands at 1063 cm^{-1} and 988 cm^{-1} are close to those assigned to Al-O-H deformations in Figure 8.I. The presence of the band at 3350 cm^{-1} in Figure 8.II confirms that O-H bonds are present, and Al-O-H deformations may be responsible for the bands observed at 1063 and 988 cm^{-1}. The extent of hydrogen-bonding will be reduced if these are principally HDO molecules, and this can account for the shift to lower wavenumber compared to Figure 8.I.[105] The presence of Al-O-D on the surface is likely and Al-O-D deformation modes may contribute to the bands observed in the region 1100-900 cm^{-1}.

When a sample of solid aluminium (III) chloride, whose spectrum had been recorded (Figure 8.I), was subsequently exposed to D_2O and a second spectrum collected, the bands at 2480 cm^{-1}, attributed to an O-D stretch, and at 1441 cm^{-1} attributed to an H-O-D bend were observed. However, there was no evidence for the reduction or disappearance of any of the bands associated with O-H vibrations.

A SIMS investigation of a solid aluminium (III) chloride sample which had been handled in a nitrogen atmosphere for 60s and handled under vacuum or in the inert atmosphere box at all other times

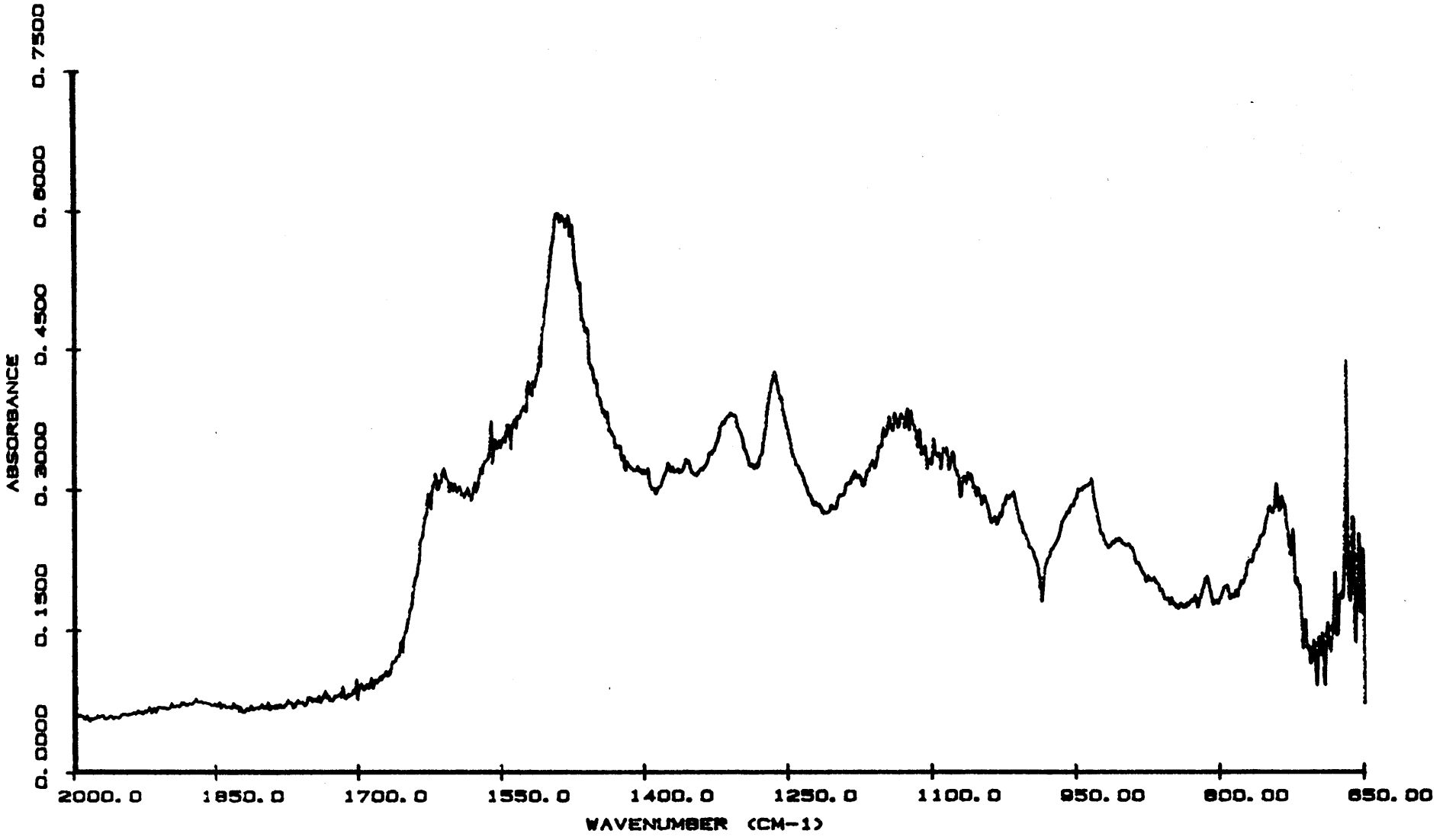
indicated that there was substantial contamination of the solid surface by water. Fragment ions detected were $AlOH^+$, Al_2O^+, $Al_2O_2H^+$, Al_2OCl^+ and $Al_2OCl_2^+$.

The observations noted above indicate that solid aluminium (III) chloride, prepared as described in 2.2.6, becomes contaminated with water if it is manipulated in the inert atmosphere box. The behaviour observed when a sample of solid aluminium (III) chloride which had been handled in the inert atmosphere box was subsequently exposed to D_2O vapour indicates that the surface was not completely hydrated or hydrolysed. There appear to be at least two species present on the solid surface, namely hydroxyl groups bound to aluminium atoms and strongly hydrogen-bonded water molecules; detection of the former provides strong evidence for some hydrolysis at the surface. These results provide evidence for the proposal that small quantities of water present in solid aluminium (III) chloride samples prepared as described in 2.2.6 promoted [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and the solid (5.2.2) and inhibited surface reaction between gaseous 1,1-dichloroethene and the solid (4.2.6).

8.2.2 DRIFTS Investigation of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.

Spectra obtained as described in 8.3.2 were reproducible. Figure 8.III shows a spectrum over the range 2000-650 cm^{-1} of the surface of the purple solid formed by exposure of solid aluminium (III) chloride to gaseous 1,1,1-trichloroethane, from which a background spectrum of aluminium (III) chloride has been subtracted. No analysis was possible in the region 1200-950 cm^{-1} due to over-subtraction of the bands attributed to Al-O-H deformation modes (8.2.1). The

FIGURE 8.III. Spectrum of the Surface of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane.



positions of the principal peaks (in cm^{-1}) and their relative intensities were:- ca. 1490 (m), 1318 (w), 1265 (w) and 750 (w). Exposure of the solid to further gaseous 1,1,1-trichloroethane led to increases in the intensities of the peaks at ca. 1490, 1318 and 1265 cm^{-1}, relative to the water and hydroxyl bands.

The peaks observed can be attributed to the stretching and bending modes of a chloro-organic species. The peak at ca. 1490 cm^{-1} can be assigned to the asymmetric deformation mode of a $-CH_3$ group. The peak at 1318 cm^{-1} can be attributed to the symmetric deformation mode of a $-CH_3$ group. The peak at 1265 cm^{-1} may be attributed to a $-CH_3$ rocking mode or a $-CH_2-$ wagging or twisting mode. The feature at 750 cm^{-1} is assigned to the asymmetric stretching mode of a $-CCl_3$ of $-CCl_2$ group.

In the vapour phase infra-red spectrum of 1,1,1-trichloroethane (Figure 2.VI, 2.3.3) the $-CH_3$ asymmetric deformation is a broad feature centred on 1440 cm^{-1}. The $-CH_3$ symmetric deformation is a sharp, weak peak at 1385 cm^{-1} and the $-CH_3$ rocking mode appears as a strong sharp band at 1086 cm^{-1}. The asymmetric stretching mode of the $-CCl_3$ group is a very strong, sharp peak at 722 cm^{-1}.[107]

If the assignments of the bands in Figure 8.III are correct, then the organic species present on the surface of the solid has several features in common with 1,1,1-trichloroethane. Chemisorption of a 1,1,1-trichloroethane molecule at a coordinatively unsaturated aluminium atom, similar to that proposed by Ng and Chan[78] for the adsorption of t-butyl chloride on metal chlorides (Figure 1.V, 1.3.2), would lead to an increase in the rigidity of the molecule and hence to the observed shifts towards higher wavenumber for the bands due to asymmetric deformation modes. However, SIMS investigation of a

solid aluminium (III) chloride sample which had been exposed to gaseous 1,1,1-trichloroethane led to the detection of the following fragment ions: CCl^+, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, $C_4H_3^+$, $C_6H_2^+$ and $C_6H_3^+$. This is consistent with the presence of an organic species on the surface of the solid, but suggests that the species is a long chain hydrocarbon.

No bands indicating the presence of unsaturated or cyclic species were observed in the spectrum. It appears that the involatile organic species produced on the surface of the solid in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride is a long chain, chlorine containing hydrocarbon, or a mixture of long chain, chlorine containing hydrocarbons, with structural features similar to 1,1,1-trichloroethane.

The differences between the peaks shown in Figure 8.III and the peaks observed when the purple solid produced by the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride contaminated the cell windows during analysis of the vapour phase in the reaction (3.2.1) can be accounted for by the differences in the techniques; DRIFTS investigations yield spectra of the surface only. The bands reported in 3.2.1 at $<700\ cm^{-1}$ are consistent with the presence of species containing Al-C bonds. The bands at 690, 665 and $580\ cm^{-1}$ are close to those attributed to Al-C stretching modes in the spectrum of solid triethylaluminium at -123^oC, while those at 640 and $630\ cm^{-1}$ are very close to those assigned to the $-CH_2-$ modes in that species.[108] The band at $480\ cm^{-1}$ (3.2.1) is characteristic of $AlCl_4^-$.[109] No analysis was possible using DRIFTS at $<590\ cm^{-1}$, but it is possible that although species containing Al-C bands and $AlCl_4^-$ ions are constituents of the purple tar, they are not

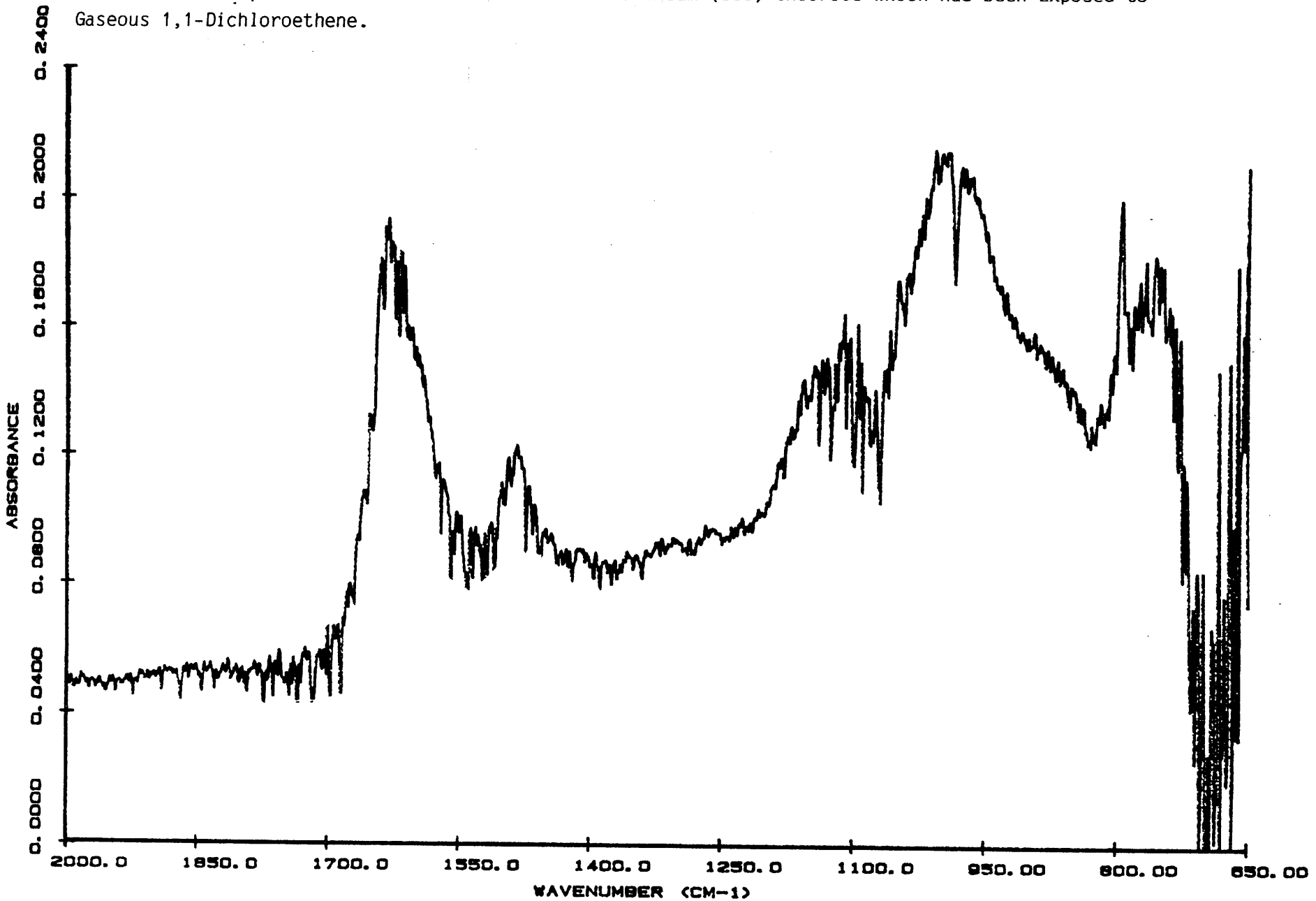
abundant surface species.

8.2.3 DRIFTS Investigation of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene.

Figure 8.IV shows the spectrum over the range 2000-650 cm^{-1} of the surface of the purple solid formed by exposure of solid aluminium (III) chloride to gaseous 1,1-dichloroethene, from which a background spectrum of aluminium (III) chloride has been subtracted. No analysis was possible in the region 1200-950 cm^{-1} due to over-subtraction of the bands attributed to Al-O-H deformation modes (8.2.1). The positions of the principal peaks (in cm^{-1}) and their relative intensities were :- ca. 1630 (s), 1490 (w) and 800 (s). When the purple surface was removed to reveal a black layer (8.3.4), the spectrum of the surface of that layer, from which a background spectrum of aluminium (III) chloride had been subtracted, contained both positive and negative absorbances. The negative absorbances were the peaks attributed to water in the spectrum of solid aluminium (III) chloride (8.2.1). The positive absorbances (in cm^{-1}) and their relative intensities were:- 2940 (vs), 2430 (m), 1648 (vs), 1483 (w) and 816 (s).

The peaks observed in Figure 8.IV can be attributed to the stretching and bending modes of a chloro-organic species. The peak at 1630 cm^{-1} is assigned to a C=C stretching vibration. The peak at 1490 cm^{-1} is attributed to the asymmetric deformation mode of a $-CH_3$ group, although the corresponding symmetric deformation and rocking modes were not detected. The feature at 800 cm^{-1} is assigned to the asymmetric stretch of a $-CCl_2$ group. The bands at 1630 cm^{-1} and 800 cm^{-1} are close in position to the corresponding features in the spectrum of gaseous 1,1-dichloroethene (Figure 2.VII, 2.3.3).[110]

FIGURE 8.IV. Spectrum of the Surface of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene.



The peaks at 1648, 1483 and 816 cm^{-1} in the spectrum of the black layer can be assigned as above. The peak at 2940 cm^{-1} is attributed to the C-H stretch of a saturated organic species. However, the peak at 2430 cm^{-1} is not easily assigned. Bands in this region are usually associated with the O-H stretching modes of very strongly hydrogen-bonded species such as carboxylic acids, or with highly unsaturated straight chain species such as alkynes or cumulated double bonds; bands in this region can also be assigned to overtone frequencies of aromatic species, although, if an aromatic species is present, at least one strong band in the region 1600-1500 cm^{-1} is expected. A band at 2175 cm^{-1} in the infra-red spectrum of a black dehydrochlorinated poly-1,1-dichloroethene film was attributed to a C≡C stretching mode, indicating that elimination of two hydrogen chloride molecules from a single 1,1-dichloroethene monomeric unit was possible.[111] Thus, the band at 2430 cm^{-1} may be accounted for by the presence of C≡C bonds. However, another possibility which must be considered is that one of the products of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride is a polyene such as $\{CH=CCl\}_n$ which is hydrolysed when the sample is handled in the inert atmosphere box to remove the surface layer. Such a process could lead to the formation of strongly hydrogen-bonded hydroxyl groups which could give rise to the observed peak.

Thus it appears that the involatile organic species produced in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride is a mixture of species, including saturated and unsaturated chlorohydrocarbons, one of which may be a dehydrochlorinated form of poly-1,1-dichloroethene.

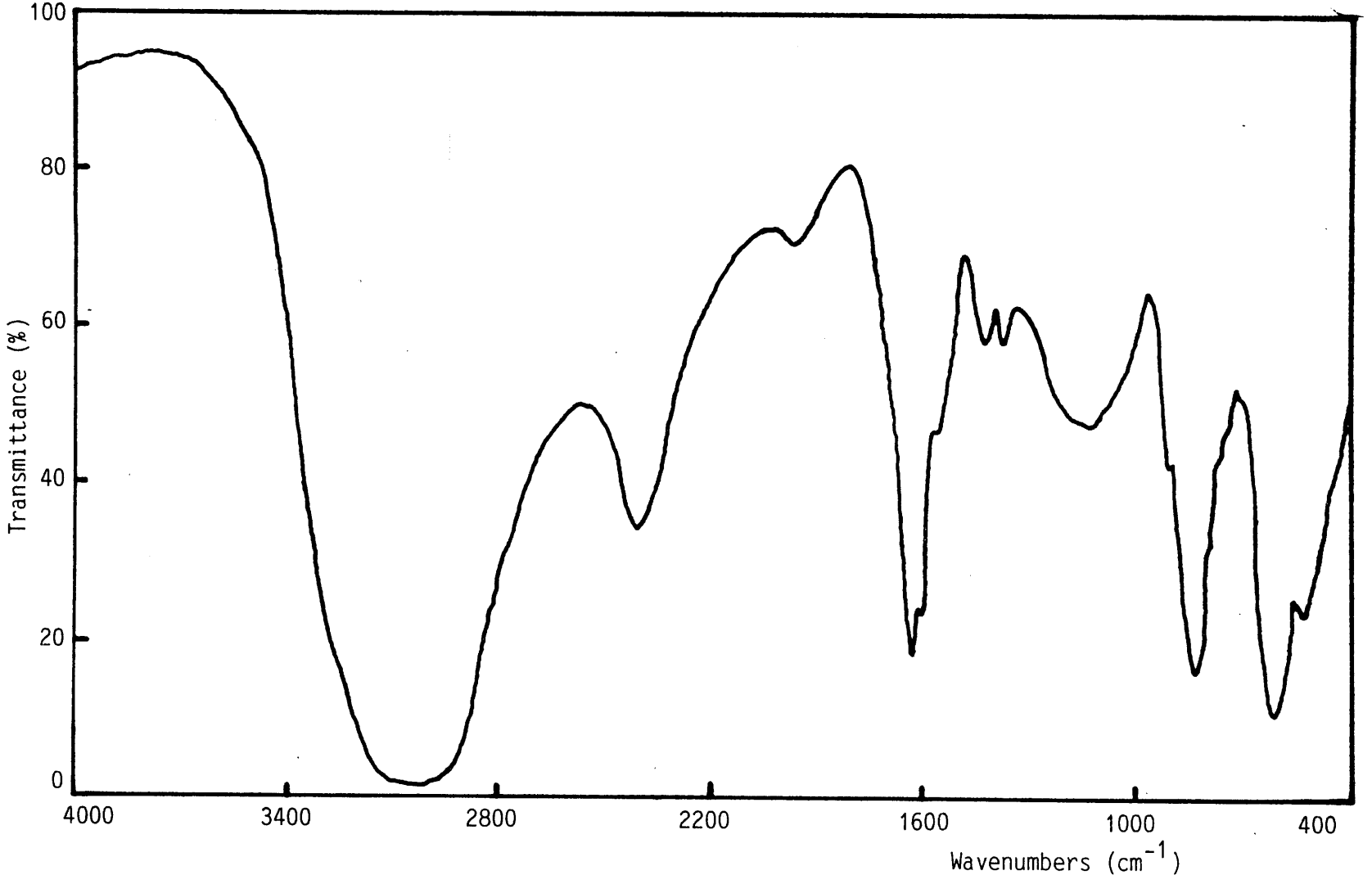
8.2.4 Infra-Red Spectrum of Involatile Organic Material Produced in the Reaction of Liquid 1,1,1-Trichloroethane with Aluminium Metal.

The infra-red spectrum over the range 4000-400 cm^{-1} of a KBr disc prepared using the brown solid recovered as described in 8.3.5 is shown in Figure 8.V. The positions of the principal peaks (in cm^{-1}) and their relative intensitives are: 3050 (broad, vs), 2410 (m), 1970 (w), 1636 (s, sh 1615, 1575), 1436 (w), 1378 (w), 845 (s, sh 910) and 607 (s, sh 542). The infra-red spectrum of a solution of the brown solid in carbon tetrachloride was collected. No analysis was possible in the region 850-700 cm^{-1} due to the absorption of carbon tetrachloride, but the spectrum obtained was very similar to Figure 8.V. The band at 2410 cm^{-1} was much weaker, that at 1970 cm^{-1} was not detected and a sharp, intense band was present at 1100 cm^{-1} (shoulder 1180 cm^{-1}).

The positions of the bands observed in these spectra are very close to those observed in the spectrum of the surface of the black tar produced by the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (8.2.3). However, the spectra obtained were not background subtracted and the contributions of water, either as a contaminant of the KBr itself or present due to handling the solid in air, to the peaks at 3050, 2410 and 1636 cm^{-1} cannot be neglected.

The peak at 3050 cm^{-1} can be assigned to the C-H stretching mode of a hydrocarbon species. The position of the band indicates that the hydrocarbon is unsaturated. The band at 2410 cm^{-1} may be attributed to a C≡C stretching mode as discussed in 8.2.3. However, the presence of another weak band at 1970 cm^{-1} may indicate that both

FIGURE 8.V. Infra-Red Spectrum of KBr Disc Prepared Using Brown Material Recovered from the Reaction of Liquid 1,1,1-Trichloroethane with Aluminium.



bands are overtone bands of an aromatic species. The band at 1636 cm^{-1} is assigned to a C=C stretching mode. The presence of other bands in this region at 1615 and 1575 cm^{-1} may indicate the presence of an aromatic species, since the presence of three bands in this region is characteristic of aromatic and polycyclic systems. An alternative explanation is that the three bands in this region are due to straight chain C=C bonds in different environments, and this interpretation is consistent with the spectrum of a dehydrochlorinated poly-1,1-dichloroethene film reported by He and Kise.[111] The peak at 1436 cm^{-1} is assigned to the asymmetric deformation of a $-CH_3$ group, while that at 1378 cm^{-1} is assigned to the symmetric deformation of such a group; the strong band at 1100 cm^{-1} in the solution spectrum can be attributed to a $-CH_3$ rocking mode. The positions of these three bands are close to the corresponding bands of 1,1,1-trichloroethane.[107] The peaks at 845 and 910 cm^{-1} can be assigned either to the out of plane vibrations of olefinic or aromatic C-H bonds, or to the asymetric stretch of a $-CCl_2$ group, although the position of the peaks is at a very high wavenumber to be attributed to the latter. The features at 607 cm^{-1} and 542 cm^{-1} are attributed to C-Cl stretching modes; the former is very close to the symmetric stretch of the $-CCl_2$ group in 1,1-dichloroethene.[110]

These results indicate that the involatile organic material produced in the reaction of liquid 1,1,1-trichloroethane with aluminium metal is an unsaturated chlorohydrocarbon, or a mixture of unsaturated chlorohydrocarbons, which may include aromatic species. Kulikova has reported that 1,3,5-trichlorobenzene is a product of the solution reaction of 1,1-dichloroethene with aluminium (III) chloride.[82] The detection of bands attributed to the vibrations of

$-CH_3$ groups and $-CCl_2$ groups indicates that such species may be present as end groups in the latter case, and as substituents in the former.

Attempts were made to study the brown solid using mass spectrometry. Evidence for fragments containing C, H and Cl was obtained, but attempts to carry out high resolution mass measurement on the sample did not lead to the unambiguous assignment of any of these fragments. It appears that the involatile organic material produced by the reaction of 1,1,1-trichloroethane with aluminium is a mixture of unsaturated chlorohydrocarbons, which may include a dehydrochlorinated form of poly-1,1-dichloroethene and aromatic species.

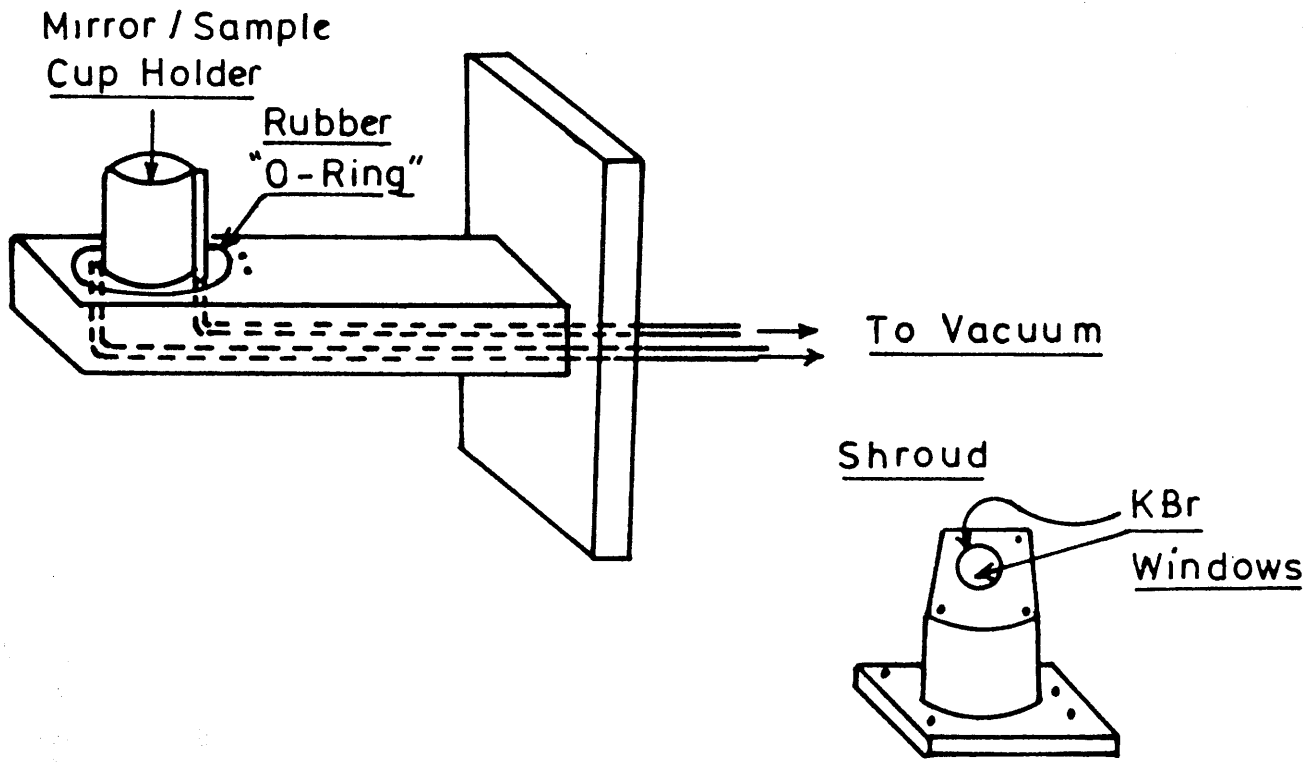
8.3 Experimental

8.3.1 DRIFTS Investigation of Solid Aluminium (III) Chloride

A DRIFTS cell ("Collector", Spectra-Tech Inc.) with evacuable stage was used in conjunction with Nicolet MX1 and 5DXC Fourier Transform infra-red spectrometers. The evacuable stage consisted of a backplate and stainless steel platform with a raised cylindrical holder into which the stainless steel sample cup or alignment mirror was inserted (Figure 8.VI). The shroud was a stainless steel structure with KBr windows (Figure 8.VI); a rubber "O-ring" provided an airtight seal when the shroud was fastened in position by means of four screws. Two pipes, equipped with valves, which passed through the platform, facilitated attachment of the stage to a vacuum system, and the sample compartment could be evacuated to a pressure of 0.05 Torr. The valves on the pipes isolated the sample compartment from the atmosphere when closed.

The following procedure was carried out to obtain a DRIFTS spectrum of solid aluminium (III) chloride. The alignment mirror was placed in the cup holder, the shroud was fastened and the sample compartment was evacuated to 0.05 Torr. The stage was placed in the DRIFTS cell, which had been fastened in the spectrometer beam, and a background spectrum was collected. The background spectrum contained peaks attributed to water and carbon dioxide. The stage was removed from the cell and placed in the inert atmosphere box, where the shroud and alignment mirror were removed. The sample cup was loaded in the inert atmosphere box with solid aluminium (III) chloride (ca. 0.2g, prepared as described in 2.2.6), and placed in the cup holder. The shroud was replaced, and the sample compartment

FIGURE 8.VI. Evacuable Stage and Shroud



evacuated to 0.05 Torr on the vacuum system, and closed by means of the valves. The stage was placed in the DRIFTS cell and a spectrum collected, from which the background was subtracted. In practice, the cut-off point was ca. 590 cm^{-1}. Also, because of the variable nature of the aluminium (III) chloride samples with respect to such factors as surface hydration and hydrolysis, it was not possible to compare the absorbance values of peaks obtained from sample to sample.

In one experiment the stage was removed from the cell and reattached to the vacuum system. The sample was then exposed to gaseous D_2O in situ for 1h, at the end of which the compartment was pumped for 30 min, closed, and replaced in the spectrometer. A spectrum was collected, from which the background spectrum was subtracted.

A further experiment was carried out using the procedure described above with the following modification. The solid aluminium (III) chloride sample, prepared as described in 2.2.6, was exposed to gaseous D_2O in the storage ampoule for 1h, at the end of which it was pumped for 30 min, closed and transferred to the inert atmosphere box, prior to use in the DRIFTS experiment.

8.3.2 DRIFTS Investigation of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1,1-Trichloroethane

The following procedure was carried out to determine whether gaseous 1,1,1-trichloroethane adsorbed on the KBr windows of the shroud. A background spectrum was collected with the alignment mirror in the cup holder as described in 8.3.1. The stage was removed from the cell and attached to the vacuum system. Gaseous 1,1,1-

trichloroethane (ca. 80 Torr) was admitted to the sample compartment for 30 min, at the end of which the sample compartment was pumped for 30 min, and closed. The stage was replaced in the DRIFTS cell and a spectrum was collected. The spectrum obtained was identical to the original background spectrum. This indicates that there is no detectable adsorption of gaseous 1,1,1-trichloroethane on the KBr windows of the shroud.

Three experiments were carried out according to the following procedure. The sample cup was loaded in the inert atmosphere box with solid aluminium (III) chloride (ca. 0.2g, prepared as described in 2.2.6) and placed in the cup holder. The shroud was fastened, the sample compartment was closed, and the stage was transferred to the vacuum system, where the sample compartment was evacuated to 0.05 Torr and closed. The stage was then placed in the DRIFTS cell and a background spectrum was collected. The background spectrum was identical to the spectrum of aluminium (III) chloride (8.2.1, 8.3.1). The stage was removed from the DRIFTS cell and reattached to the vacuum system. The sample was exposed to gaseous 1,1,1-trichloroethane (ca. 80 Torr) for 30 min, during the course of which the surface of the solid underwent a colour change from white to light purple. The 1,1,1-trichloroethane was removed, the sample compartment was pumped for 30 min and closed. The stage was replaced in the DRIFTS cell and a spectrum collected, from which the background spectrum was subtracted. In one of the experiments the procedure outlined above was repeated three times using the same solid sample.

8.3.3 SIMS Investigation of Solid Aluminium (III) Chloride Before and After Exposure to Gaseous 1,1,1-Trichloroethane

A surface ionisation mass spectrometer (Riber Instruments) was used. The sample cup was loaded in the inert atmosphere box with solid aluminium (III) chloride (ca. 0.2g, prepared as described in 2.2.6). The sample was transferred to the sample compartment of the instrument in a nitrogen atmosphere, the sample compartment was evacuated to 10^{-6} Torr and a spectrum was collected. The sample was then exposed to gaseous 1,1,1-trichloroethane (ca. 80 Torr) in situ for 1h, at the end of which the vapour was removed. A second spectrum was collected of the light purple solid formed.

8.3.4 DRIFTS Investigation of Solid Aluminium (III) Chloride which had been Exposed to Gaseous 1,1-Dichloroethene

The procedure described in 8.3.2 was carried out to determine whether gaseous 1,1-dichloroethene adsorbed on the KBr windows of the shroud. The spectrum obtained was identical to the original background spectrum, and indicates that there is no detectable adsorption of gaseous 1,1-dichloroethene on the KBr windows of the shroud.

An experiment was carried out according to the procedure described in 8.3.2 to obtain a spectrum of solid aluminium (III) chloride which had been exposed to gaseous 1,1-dichloroethene (ca. 100 Torr) in the sample compartment for 30 min. After the spectrum was collected, the stage was transferred to the inert atmosphere box, where the shroud was removed. The light purple surface layer of the solid in the sample cup was removed, using a spatula, to reveal a black, tarry material. The shroud was replaced, the sample

compartment was closed, and the stage was transferred to the vacuum system, where the sample compartment was evacuated to 0.05 Torr and closed. The stage was then placed in the DRIFTS cell and a further spectrum collected, from which the background spectrum was subtracted.

8.3.5 Infra-Red Spectrum of the Involatile Organic Material Produced in the Reaction of Liquid 1,1,1-Trichloroethane with Aluminium Metal

The operations which follow were carried out in air. A piece of aluminium wire (ca. 0.5g, 99.99% pure, Fluka AG/Balzers) was submerged in liquid 1,1,1-trichloroethane (ca. 40ml), and scratched using a stainless steel razor blade to initiate the "bleeding" reaction (1.3.3). When the reaction had proceeded to a stage at which the solution was brown throughout, the aluminium wire was removed and the solution allowed to evaporate to dryness. The brown solid which remained was dissolved in the minimum quantity of 1,1,1-trichloroethane and filtered. The cream coloured residue was discarded; the reddish brown filtrate was allowed to evaporate to dryness. A portion of the brown solid obtained was used to prepare a KBr disc and an infra-red spectrum was collected in the range 4000-400 cm^{-1}. A second portion of the solid was dissolved in carbon tetrachloride (ANALAR, May & Baker), and an infra-red spectrum of the solution was collected over the same range.

CHAPTER 9

CHAPTER 9

DISCUSSION

As a result of the work reported in Chapters 3 to 8, it has been shown that the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride does not lead simply to the production of gaseous 1,1-dichloroethene and gaseous hydrogen chloride in a 1:1 molar ratio. The 1,1-dichloroethene produced by dehydrochlorination of 1,1,1-trichloroethane reacts with the solid (3.2.1), and this was confirmed by exposing gaseous 1,1-dichloroethene to solid aluminium (III) chloride in the absence of other species (4.2.1); in the latter system, 1,1-dichloroethene, and any 1,1,1-trichloroethane produced as a result of its reaction with aluminium (III) chloride, can be completely consumed (4.2.6). Gaseous carbon tetrachloride is a product of the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride, although the main organic product is a mixture of saturated and unsaturated involatile chlorohydrocarbons, of which a dehydrochlorinated form of poly-1,1-dichloroethene may be a constituent (8.2.2, 8.2.3). A strongly purple coloured tar is deposited on the solid during the course of these reactions.

A scheme has been constructed on the basis of infra-red spectroscopic evidence (Scheme 3.IV, 3.2.4), and modified as a result of the observations reported in Chapters 4 to 8. The modified scheme (Scheme 9.I) has been reproduced overleaf. Direct evidence has been obtained for steps (i), (ii) and (iii). Direct evidence for the forward reaction of step (i) is provided by the detection of a surface count rate as soon as gaseous [^{36}Cl]-chlorine-labelled

$$CH_3CCl_3\,(g) \overset{\text{fast}}{\rightleftharpoons} CH_3CCl_3\,(ad) \qquad (i)$$

$$CH_3CCl_3\,(g) \overset{\text{fast}}{\rightleftharpoons} CH_2{=}CCl_2\,(ad) + HCl\,(g) \qquad (ii)$$

$$CH_2{=}CCl_2\,(ad) \rightleftharpoons CH_2{=}CCl_2\,(g) \qquad (iii)$$

$$CH_2{=}CCl_2\,(ad) + AlCl_2^+ \overset{\text{fast}}{\rightleftharpoons} Cl_2AlCH_2\overset{+}{C}Cl_2 \qquad (iv)$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_2\,(ad) \overset{\text{r.d.s.}}{\rightleftharpoons} Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 \qquad (v)$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3 \qquad (vi)$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2{=}CClCH_2CCl_3 + AlCl_3 \qquad (vii)$$

$$\tfrac{n}{2}CH_2{=}CClCH_2CCl_3 \overset{AlCl_3}{\rightleftharpoons} \{CH{=}CCl\}_n + \tfrac{n}{2}HCl\,(g) \qquad (viii)$$

Process(es) leading to the formation of $CCl_4\,(g)$ (ix)

Scheme 9.I

1,1,1-trichloroethane is exposed to solid aluminium (III) chloride (7.2.2), and observations from infra-red spectroscopic studies on the system are consistent with this behaviour (3.2.1, 3.2.4, 4.2.1). The detection of gaseous 1,1,1-trichloroethane in infra-red studies of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (4.2.1, 4.2.5) provides direct evidence for the reverse reactions of steps (i) and (ii). Gaseous 1,1-dichloroethene and gaseous hydrogen chloride are produced in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (3.2.1), and this confirms that the forward reaction of step (ii) and the reverse reaction of step (iii) occur. Infra-red spectroscopic studies on the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene provide direct evidence for the forward reaction of step (iii) (3.2.1, 3.2.4, 4.2.5).

Infra-red studies of the vapour phase in the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid

aluminium (III) chloride indicate that an involatile organic material is produced in these reactions (3.2.4, 4.2.5). A GCIR investigation of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride revealed that gaseous 1,1-dichloroethene, and any gaseous 1,1,1-trichloroethane derived from it, can be completely consumed in the reaction (4.2.6) to yield the involatile material. This indicates that one of the steps leading to the formation of the involatile material is effectively irreversible. Steps (iv) to (vii) are included to account for the production of the involatile material by comparison with Winterton's scheme[75] (Scheme 1.XII, 1.3.3) to account for some of the products isolated from the analogous solution reaction. Although the only direct evidence obtained for the involatile species postulated in steps (iv) to (vii) is the observation of bands attributed to Al-C stretching modes in the infra-red spectrum of the purple solid which contaminated the cell windows in a study of the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride, the observed time dependences of that reaction, and of the reaction of 1,1-dichloroethene with the solid, are consistent with a bimolecular surface reaction, step (v), being the rate determining step (3.2.4, 4.2.5).

The production of more than one mole of gaseous hydrogen chloride per mole of gaseous 1,1,1-trichloroethane consumed in the reaction of the latter with solid aluminium (III) chloride indicates that dehydrochlorination of 1,1,1-trichloroethane is not the only process leading to the formation of gaseous hydrogen chloride (3.2.4). The production of gaseous hydrogen chloride by the purple solid formed in the reaction, after removal of the volatile material, indicates that such processes may occur at the surface of the purple solid (3.2.2).

Similar phenomena are observed in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (4.2.2, 4.2.5); a DRIFTS study of the surface of the purple solid produced in this reaction suggests that one constituent of the involatile material is a dehydrochlorinated form of poly-1,1-dichloroethene (8.2.3). Step (viii) is proposed to account for these observations.

Step (ix) is included to account for the small quantities of gaseous carbon tetrachloride produced in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride (3.2.4, 4.2.5, 4.2.6). Possible reactions leading to the formation of carbon tetrachloride in these systems are discussed later in this Chapter. However, before the reactions detailed in Scheme 9.I are discussed further, it is important to consider the involvement of water in the reaction scheme.

DRIFTS investigation of the surface of solid aluminium (III) chloride samples prepared as described in 2.2.6 shows that the surface is contaminated with water; the spectra obtained indicate that hydroxyl groups bound to aluminium, and hydrogen-bonded water molecules are present (8.2.1). Although the preparation of samples for DRIFTS experiments (8.3.1) does involve additional manipulation of the solid in the inert atmosphere box compared to the experiments described in Chapters 3 to 7, the evidence obtained from DRIFTS studies indicates that any manipulation of the solid may result in surface hydrolysis.

Some authors have attributed the catalytic action of aluminium (III) chloride in effecting alkane isomerisations and olefin polymerisations to the presence of small quantities of water. Pines *et al.* demonstrated that solids prepared by treating solid aluminium (III) chloride with water were active in the isomerisation of n-butane.[29]

Draper reported that gaseous [^{36}Cl]-chlorine-labelled hydrogen chloride did not undergo exchange with solid iron (III) chloride in the absence of water, and used that evidence to suggest that the catalytically active species in the "iron (III) chloride" catalysed hydrochlorination of 1,1-dichloroethene was $[Fe(H_2O)_4Cl_2]^+$.[98] However, the same author suggested that the catalytically active species in the solution phase dehydrochlorination of 1,1,1-trichloroethane was molecular $FeCl_3$.

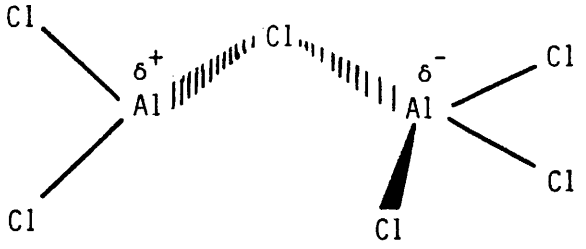
Evidence presented in Chapters 4, 5 and 7 indicates that, although the [^{36}Cl]-chlorine exchange between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride can be attributed to the hydration and hydrolysis of the solid surface (5.2.2, 5.2.3), prior exposure of solid aluminium (III) chloride to water can inhibit the reactions of the solid with gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene (5.2.5, 7.2.4, 4.2.6). For example, exposure of gaseous [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane to solid aluminium (III) chloride, which had been previously exposed to water vapour, led to no detectable adsorption and no reaction (7.2.4). The DRIFTS results reported above indicate that some degree of hydration and hydrolysis is likely in all the aluminium (III) chloride samples studied in this work. Thus the involvement of small quantities of water in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with the solid cannot be ruled out. However, there is strong evidence that exposure of the solid to larger quantities of water can completely inhibit these reactions.

The observation that prior exposure of the solid to water inhibits the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride (7.2.4, 5.2.1, 4.2.6) provides strong circumstantial evidence about the reactive sites

on the surface in the reactions of these chlorohydrocarbons with the solid. It suggests that water reacts with the surface, blocking or removing the sites at which 1,1,1-trichloroethane or 1,1-dichloroethene can adsorb and react. Physical adsorption of a water molecule at a co-ordinatively unsaturated aluminium (III) site on the surface, followed by chemisorption and, ultimately, the formation of a surface hydroxyl group, can lead to effective removal of the original site. Direct evidence from DRIFTS studies for the presence of Al-O-H groups on the surface of the solid is consistent with this model (8.2.1). There is also strong evidence from infra-red studies that, in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride, dehydrochlorination of the former is the only important reaction giving rise to gaseous products in the first 100s of reaction, and that reactions which consume 1,1-dichloroethene and produce carbon tetrachloride become significant only once sufficient 1,1-dichloroethene and/or hydrogen chloride are/is present. If the site at which the 1,1,1-trichloroethane adsorbs prior to reaction is the co-ordinatively unsaturated aluminium (III) on the surface, then widespread removal of these sites can lead to non-attainment of the critical concentration of the product responsible for autocatalysis (3.2.4, 4.2.5). The same argument can be applied to the inhibition of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride (4.2.6). In summary, it appears that the first step in the reaction of gaseous 1,1,1-trichloroethane or 1,1-dichloroethene with solid aluminium (III) chloride is adsorption of the chlorohydrocarbon molecule at the co-ordinatively unsaturated aluminium (III) sites on the surface of the solid.

There is no evidence for the adsorption of gaseous [^{36}Cl]-HCl

on solid aluminium (III) chloride in the absence of a third component (5.2.2). However, exposure of a mixture of gaseous [^{36}Cl]-HCl and gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene to solid aluminium (III) chloride leads to the detection of a significant surface count rate and complete exchange of [^{36}Cl]-chlorine between the [^{36}Cl]-HCl and the organic species (5.2.5, 5.2.6). Evidence which suggests that the [^{36}Cl]-chlorine becomes involved in the reaction scheme at the hydrochlorination/dehydrochlorination step (Step (ii), Scheme 9.I) was discussed (5.2.5, 5.2.6) and such a process was considered likely, though the involvement of [^{36}Cl]-HCl in other reactions was not excluded. One possible explanation of this effect is that the dehydrochlorination of 1,1,1-trichloroethane and hydrochlorination of 1,1-dichloroethene take place via a transition state similar to that suggested by Winterton[75] to account for the solution phase dehydrochlorination of 1,1,1-trichloroethane by aluminium (III) chloride (Formula 1.VII, 1.3.3). A co-ordinatively unsaturated aluminium (III) ion and an adjacent, co-ordinatively saturated aluminium (III) ion on the surface of aluminium (III) chloride may provide a surface environment analogous to the molecular species shown in Formula 9.I. Approach of a 1,1,1-trichloroethane molecule to such a

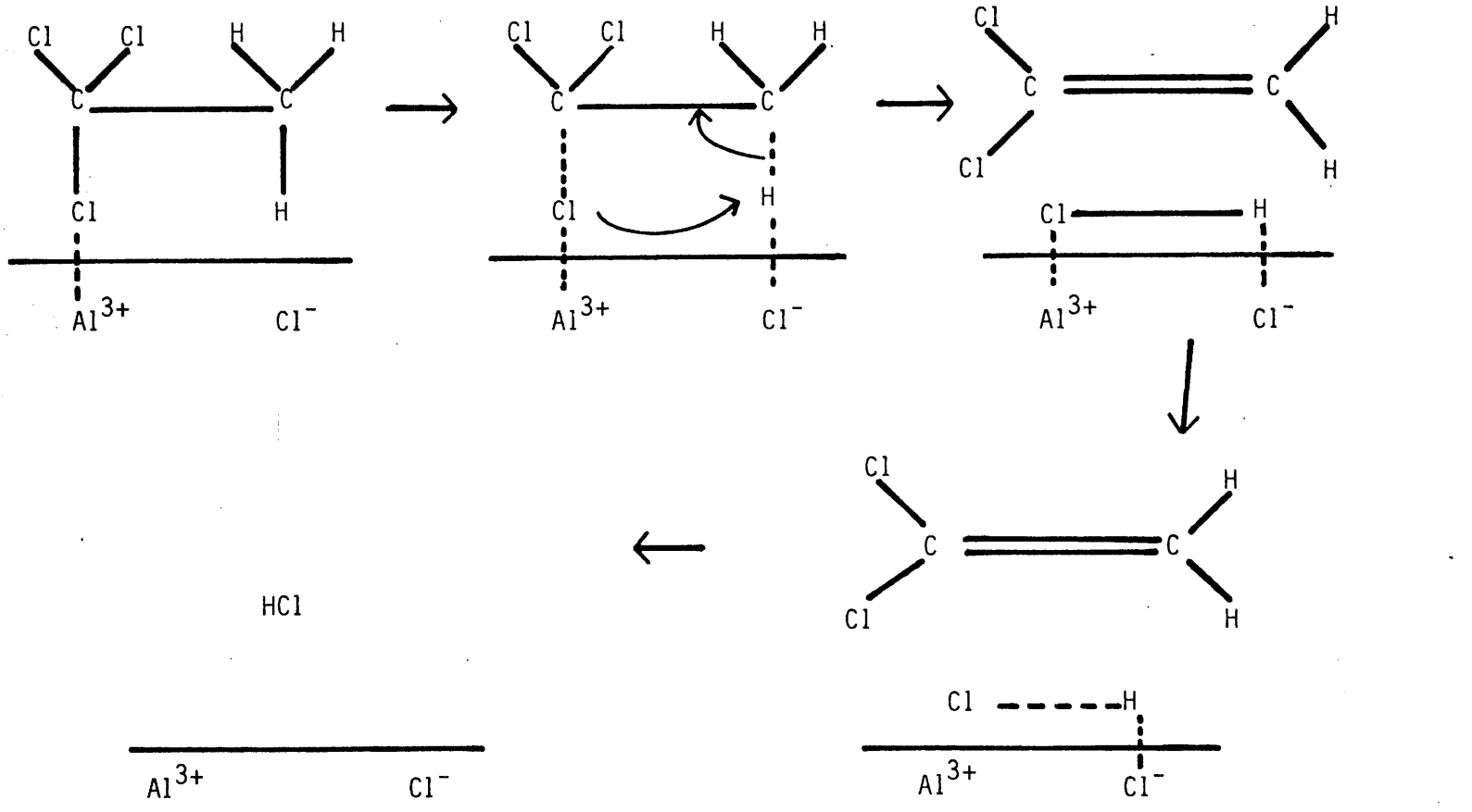


Formula 9.I

region of the surface may lead to the physisorption of the molecule, via a chlorine atom of the $-CCl_3$ group, at the co-ordinatively unsaturated aluminium (III) ion. Reorientation of the molecule can then lead to an intermediate complex of similar geometry to the 1,1,1-trichloroethane separated ion pair proposed by Winterton[75] (Formula 1.VII, 1.3.3), which can lose hydrogen chloride to yield an adsorbed 1,1-dichloroethene molecule.

However, were such an intermediate species to exist, the hydrogen chloride produced would contain inactive chlorine derived from the aluminium (III) chloride when gaseous $[^{36}Cl]$-CH_3CCl_3 was exposed to the solid. Although investigations of the specific count rates of $[^{36}Cl]$-AgCl samples derived from $[^{36}Cl]$-HCl recovered from the reaction of $[^{36}Cl]$-CH_3CCl_3 with solid aluminium (III) chloride indicate that some of the chlorine atoms of aluminium (III) chloride may be involved in the overall reaction (7.2.2), they suggest more strongly that intramolecular dehydrochlorination is an important process. The simplest way in which intramolecular dehydrochlorination of an adsorbed 1,1,1-trichloroethane molecule can occur is as follows. Physical adsorption of a 1,1,1-trichloroethane molecule at a co-ordinatively unsaturated aluminium (III) ion via a chlorine atom of the $-CCl_3$ group may lead to chemisorption and the formation of a species such as that proposed by Ng and Chan as an intermediate in the heterogeneous metal chloride catalysed dehydrochlorination of t-butyl chloride (Figure 1.V, 1.3.2).[78] The formation of such a species can provide a route to dehydrochlorination which is effectively concerted and intramolecular (Scheme 9.II). However, there is no direct evidence for the adsorbed species postulated in Scheme 9.II, and the operation of such a process might be expected to lead to an

SCHEME 9.II. Concerted Intramolecular Dehydrochlorination of 1,1,1-Trichloroethane Catalysed by Solid Aluminium (III) Chloride.



interaction, albeit weak, between gaseous [^{36}Cl]-HCl and solid aluminium (III) chloride. It is not possible to distinguish unambigously between the two models presented above, but the evidence presented suggests that the latter is more likely.

Before discussing possible mechanisms for the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride, the nature of the reaction medium must be addressed. In the discussion of results reported in Chapters 3 to 8, the purple tar which progressively coats the surface of the solid in the reactions studied has generally been treated as a "passive" medium, whose only effect is to block reactive sites. However, the purple material is not inert as it is known to evolve gaseous hydrogen chloride (3.2.2, 4.2.2), and this indicates that reactions take place on or in the coating or film.

The involatile organic material produced in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride is soluble in 1,1,1-trichloroethane (8.1). Similarly, aluminium (III) chloride is sparingly soluble in 1,1,1-trichloroethane and 1,1-dichloroethene. Thus the coating or film consists of a mixture of involatile organic products and aluminium (III) chloride, possibly with the reactant chlorohydrocarbon as solvent. The presence of the film and the possibility that reactions take place within it complicates the system considerably; as well as affecting the comparatively simple processes at the gas/solid interface by altering the number of reactive sites, the presence of the film means that heterogeneous processes at the gas/liquid and liquid/solid interfaces and homogeneous processes within the film itself must be considered. Furthermore, pumping the purple film will

change its composition, since not all of its constituents will have the same vapour pressure. This accounts for the differences in observed behaviour between experiments in which gaseous [^{36}Cl]-HCl was exposed to solid aluminium (III) chloride in the presence of gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene (5.2.5, 5.2.6), and those in which [^{36}Cl]-HCl was exposed to the purple solid produced by the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride (5.2.4).

The techniques used to examine the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride did not allow a distinction to be made between gas/solid and gas/liquid phenomena, and did not allow direct investigation of liquid/solid phenomena or homogeneous reaction in the film itself. Hence the physical states of reactants and products in the discussion of possible reaction pathways which follows are indicated only when there is evidence to support the suggestions made.

It is reasonable to assume that, in the early stages of the reactions of gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene with solid aluminium (III) chloride, the latter is the only catalytic species present. The reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride which yields hydrogen chloride must be the only process operating in the early stages when the solid is exposed to 1,1-dichloroethene (4.2.1). No evidence was obtained from a vapour phase infra-red study of this reaction for monochloroacetylene, which would be the expected product of the simple dehydrochlorination (4.2.1). This indicates either that the hydrogen chloride is produced by dehydrochlorination of an involatile species derived from 1,1-dichloroethene, or that monochloroacetylene

is produced in the reaction, but is consumed rapidly at the surface. No induction period is observed in the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride, unless the surface of the solid is partially hydrolysed, whereas an induction period is always observed in the reaction of gaseous 1,1,1-trichloroethane with the solid (4.2.5, 4.2.6, 3.2.4). These observations were discussed in 4.2.6 and it was postulated that the species responsible for autocatalysis in both reactions is a product of the reaction of adsorbed 1,1-dichloroethene with solid aluminium (III) chloride.

There is no evidence for the combination of hydrogen chloride and aluminium (III) chloride under most conditions (1.2.4), but the $HCl/AlCl_3$ mixture is capable of protonating very weak bases such as benzene.[37,38] Protonation of olefinic products, leading to rapid polymerisation, in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride can account for the autocatalysis observed in these systems. The detection of a band attributed to the $AlCl_4^-$ ion in the infra-red spectrum of the purple solid which contaminated the cell windows in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride is consistent with this proposal (3.2.1, 8.3.2). The species responsible for autocatalysis will be the protonated species "BH^+", and the induction period will be the time which elapses before the critical concentration of this species is attained. In the reaction of gaseous 1,1,1-trichloroethane with the solid, hydrogen chloride is produced in the very early stages (3.2.4), and in this reaction the induction period can be attributed to the time required for the attainment of a critical concentration of B, the species to be protonated. In the reaction of gaseous 1,1-dichloroethene with solid aluminium (III)

chloride, the initial products of the reaction include involatile species, and in this instance the induction period can be attributed to the time required for the attainment of a critical concentration of hydrogen chloride.

The detection of infra-red bands attributed to Al-C stretching modes (3.2.1, 8.2.2) is consistent with the formation of species containing Al-C bonds as intermediates in steps (iv) to (vii) of Scheme 9.I, and a precedent for the formation of Al-C bonds in the reactions of organics with aluminium (III) chloride is the production of a stable homocyclopropenium species in the reaction of but-2-yne with aluminium (III) chloride (Formula 1.V, 1.3.1).[73] In the early stages of the reaction of gaseous 1,1-dichloroethene with solid aluminium (III) chloride, the process which produces the involatile material must occur at the surface. A co-ordinatively unsaturated aluminium (III) ion on the surface of the solid can be considered analogous to the species $AlCl_2^+$; similarly, a co-ordinatively saturated aluminium (III) ion can be considered analogous to $AlCl_4^-$. A surface process involving both types of site which yields an oligomer such as 2,4,4,4-tetrachlorobut-1-ene may be the most likely route from adsorbed 1,1-dichloroethene to involatile oligomers. Surface intermediates containing Al-C bonds and $-\overset{+}{C}Cl_2$ groups may facilitate reaction with further adsorbed 1,1-dichloroethene molecules to yield higher oligomers. Formation of C4 and higher oligomers may be the step which creates the surface film. Aluminium (III) chloride catalysed dehydrochlorination of such oligomers can then allow the $HCl/AlCl_3$ catalysed polymerisation of the oligomers, or 1,1-dichloroethene itself, in the surface film.

The production of gaseous carbon tetrachloride in the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with

solid aluminium (III) chloride indicates that C-C bond fission occurs in these reactions (3.2.1, 4.2.1). In both instances carbon tetrachloride is a relatively minor product, accounting for <5 mol % of the reaction products (3.2.4, 4.2.5). No evidence was obtained for any other gaseous C-C bond fission product in either system (3.2.1, 4.2.1), and this observation indicates that the species co-produced with carbon tetrachloride is/are not volatile. As a result of these observations the interactions of mixtures of gaseous radiolabelled carbon tetrachloride and gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene with solid aluminium (III) chloride were studied (Chapter 6). The system $[^{36}Cl]$-$CH_3CCl_3(g)/CCl_4(g)/AlCl_3(s)$ was also studied, and the results of these radiochemical studies indicate that chlorine derived from carbon tetrachloride becomes incorporated in the products of the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride (6.2.4, 7.2.5).

These observations are consistent with the occurrence of aluminium (III) chloride catalysed alkylations and dealkylations of oligomers and polymers of 1,1-dichloroethene in this system. Reactions of this type have been reported in Friedel-Crafts alkylations[24] and isomerisations,[57] and the reversible aluminium (III) chloride catalysed alkylation of 1,1,2,3,4,5,5-heptachloropentene by carbon tetrachloride (Equation 9.I), reported by Prins,[94] may be directly analogous.

$$CCl_4 + CCl_2{=}CClCHClCHClCHCl_2 \overset{AlCl_3}{\rightleftharpoons} CCl_3CCl_2CCl_2CHClCHClCHCl_2$$

Equation 9.I

Furthermore, addition of carbon tetrachloride to 1,2-polybutadienes catalysed by tris(triphenylphosphine)ruthenium (II) chloride has been reported,[112] and this indicates that it is possible to alkylate long chain, highly unsaturated polymers, which is important in view of the

evidence for similar species in this system.

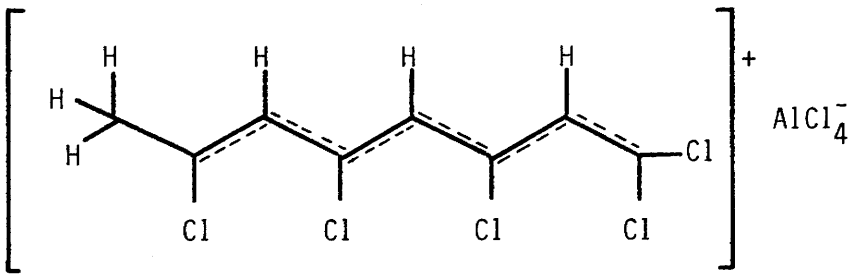
Whether protonation[82] or $AlCl_2^+/AlCl_4^-$ catalysis is invoked to account for the oligomerisation of 1,1-dichloroethene, the hydrochlorinated form of the oligomer will have alternating CH_x and CCl_x groups and a $-CCl_3$ end group. If the process which yields carbon tetrachloride in these reactions is aluminium (III) chloride catalysed dealkylation of a hydrochlorinated 1,1-dichloroethene derived oligomer or polymer, for example Equation 9.II, then it is not expected to yield any chloroform. Furthermore, in the absence of $-CHCl_2$ end

$$CCl_3CH_2CCl_2CH_3 \overset{AlCl_3}{\rightleftharpoons} CCl_4 + CH_2{=}CClCH_3 \qquad \text{Equation 9.II}$$

groups, or other mixed $-CH_xCl_{3-x}$ end groups, there is no scope for aluminium (III) chloride catalysed dealkylation leading to any product other than carbon tetrachloride.

The identity of the species which gives rise to the purple colour in the reactions of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride has not been unequivocally established. The involatile organic product is a mixture of saturated and unsaturated chlorohydrocarbons, containing a dehydrochlorinated form of poly-1,1-dichloroethene and, possibly, an aromatic species (8.2.2, 8.2.3). Although the spectroscopic evidence suggests that, during the course of the reaction, the purple material contains $AlCl_4^-$ and also species with Al-C bonds (3.2.1, 8.2.3), there is no evidence for such species from DRIFTS or SIMS studies of the surface of the purple material after pumping away the volatile material. However, investigation of the region $<600\,cm^{-1}$ was not possible using DRIFTS (8.3.1), and the possibility that either of these species was still present after pumping cannot be ruled out.

As noted in 1.3.3, conjugated olefins can be protonated in strongly acidic media to give coloured species,[84] and Winterton has postulated that the most likely source of strong colours in solutions of aluminium (III) chloride in 1,1,1-trichloroethane and 1,1-dichloroethene is the protonation of dehydrochlorinated polymers and oligomers derived from 1,1-dichloroethene by $HCl/AlCl_3$ to yield species such as Formula 9.II.[75] Evidence for the presence of a dehydrochlorinated



Formula 9.II

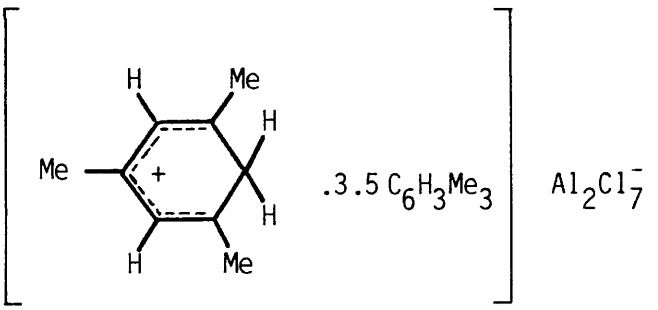
form of poly-1,1-dichloroethene has been obtained in this work (8.2.3), and this may be protonated in a similar manner to the species shown in Formula 9.II. If the protonation is reversible (Equation 9.III), this can account for the observed discharge of the purple colour when

$$\text{olefin} + HCl + AlCl_3 \rightleftharpoons [\text{olefin H}]^+ + AlCl_4^- \qquad \text{Equation 9.III}$$

the solid is exposed to controlled amounts of water vapour (7.2.3). Water is a stronger Brønsted base, and so will be more readily protonated than the olefin, and aluminium (III) chloride forms a Lewis acid /Lewis base complex with water, leading ultimately to hydrolysis and inability to act as a chloride ion acceptor. The intensity of the purple colour decreases if the solid is pumped in the early stages of the reaction, and this is attributed to the removal of hydrogen chloride from the system.

An additional possibility which cannot be excluded, and which

is not incompatible with the above proposal, is that a protonated aromatic species gives rise to the purple colour. Okami et al. have reported that a red viscous liquid of stoichiometry $HCl.Al_2Cl_6.4.5C_6H_3Me_3$ is stable at room temperature.[113] Nambu et al. proposed the structure shown in Formula 9.III for this species on the basis of ^1H and ^{13}C NMR studies.[114] The presence of such a



Formula 9.III

solvated carbenium ion, in which the proton exchanges rapidly between the aryl groups, in the liquid film produced in the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride is possible, particularly in view of the reported identification of 1,3,5-trichlorobenzene in the solution reaction of 1,1-dichloroethene with aluminium (III) chloride.[82]

Scheme 9.III contains a summary of the known and postulated reactions which occur when gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene reacts with solid aluminium (III) chloride. The scheme is split into two sections to illustrate the processes which are considered to occur at the gas/solid interface and those which may take place in the deposited film.

SCHEME 9.III. Reactions of Gaseous 1,1,1-Trichloroethane and Gaseous 1,1-Dichloroethene with Solid Aluminium (III) Chloride

Reactions at Gas/Solid Interface

$$CH_3CCl_3(g) \rightleftharpoons CH_3CCl_3(ad)$$

$$CH_3CCl_3(ad) \rightleftharpoons CH_2{=}CCl_2(ad) + HCl(g)$$

$$CH_2{=}CCl_2(ad) \rightleftharpoons CH_2{=}CCl_2(g)$$

$$CH_2{=}CCl_2(ad) + AlCl_2^+ \rightleftharpoons Cl_2AlCH_2\overset{+}{C}Cl_2$$

$$Cl_2AlCH_2\overset{+}{C}Cl_2 + CH_2{=}CCl_2(ad) \rightleftharpoons Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2$$

$$Cl_2AlCH_2CCl_2CH_2\overset{+}{C}Cl_2 + AlCl_4^- \rightleftharpoons Cl_2AlCH_2CCl_2CH_2CCl_3 + AlCl_3$$

$$Cl_2AlCH_2CCl_2CH_2CCl_3 \rightleftharpoons CH_2{=}CClCH_2CCl_3 + AlCl_3$$

Proposed Reactions in Deposited Film

$$CH_2{=}CClCH_2CCl_3 \overset{HCl/AlCl_3}{\rightleftharpoons} \left(CH_2\text{-}C(CH_2CCl_3)(Cl)\right)_n$$

$$CH_2{=}CCl_2 \overset{HCl/AlCl_3}{\rightleftharpoons} \{CH_2\text{-}CCl_2\}_n$$

$$\{CH_2\text{-}CCl_2\}_n \overset{AlCl_3}{\rightleftharpoons} \{CH{=}CCl\}_n + \tfrac{n}{2}HCl\ (g)$$

$$CCl_3CH_2CCl_2CH_3 \overset{AlCl_3}{\rightleftharpoons} CCl_4(g) + CH_2{=}CClCH_3$$

$$\{CH{=}CCl\}_n + HCl + AlCl_3 \rightleftharpoons [\{CH\cdots\cdots CCl\}_nH]^+ + AlCl_4^-$$

CHAPTER 10

CONCLUSIONS

The reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride does not lead solely to the production of gaseous 1,1-dichloroethene and gaseous hydrogen chloride in a 1:1 molar ratio. Although dehydrochlorination occurs, the 1,1-dichloroethene formed reacts further, leading to the formation of a mixture of involatile organic materials and small quantities of gaseous carbon tetrachloride. The involatile mixture contains saturated and unsaturated species, one of which may be a dehydrochlorinated form of poly-1,1-dichloroethene; aromatic and/or polycyclic species may also be present. Gaseous 1,1-dichloroethene reacts with solid aluminium (III) chloride in the absence of other species to yield the same products, and in this system the 1,1-dichloroethene, and any 1,1,1-trichloroethane produced in the reaction, can be completely consumed. A strongly purple coloured film is deposited on the solid during the course of both reactions, which provides a medium for homogeneous reactions to take place between aluminium (III) chloride, hydrogen chloride, and the organic constituents of the film.

The first step in the reaction of gaseous 1,1,1-trichloroethane with solid aluminium (III) chloride is adsorption of 1,1,1-trichloroethane, a process which is thought to occur via a chlorine atom of the $-CCl_3$ group at a co-ordinatively unsaturated aluminium (III) site on the surface. Adsorption is followed by dehydrochlorination, and evidence from studies using [^{36}Cl]-chlorine-labelled 1,1,1-trichloroethane and hydrogen chloride suggests that this is an intramolecular process. The subsequent reaction is considered to be aluminium (III) chloride catalysed oligomerisation of 1,1-dichloroethene at the surface.

Time dependences of the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with the solid are consistent with a bimolecular surface reaction as the rate-determining step, and this has been interpreted in terms of a reaction between an adsorbed 1,1-dichloroethene molecule and a surface $AlCl_2^+$/1,1-dichloroethene complex containing an Al-C bond. The reaction of adsorbed 1,1-dichloroethene to produce involatile material may be the step which creates the surface film, while the liberation of hydrogen chloride in this reaction has been attributed to aluminium (III) chloride catalysed dehydrochlorination of the oligomers formed.

Autocatalytic effects are observed in the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid aluminium (III) chloride. The most likely interpretation of these phenomena is that protonation of unsaturated, 1,1-dichloroethene derived oligomers by the $HCl/AlCl_3$ mixture, leading to rapid polymerisation, occurs once critical concentrations of all three constituents are present. This reaction is envisaged as taking place in the deposited film.

Small quantities of gaseous carbon tetrachloride are produced in these reactions, but no evidence was obtained for the presence of any other gaseous C-C bond fission product. This suggests that the species co-produced with carbon tetrachloride is not volatile. The results of studies in which mixtures of [^{36}Cl]-chlorine or [^{14}C]-carbon-labelled carbon tetrachloride and 1,1,1-trichloroethane were exposed to solid aluminium (III) chloride, and in which a mixture of [^{36}Cl]-CH_3CCl_3 and inactive carbon tetrachloride was exposed to the solid, are consistent with the occurrence of reversible aluminium (III) chloride catalysed dealkylations of hydrochlorinated 1,1-dichloroethene derived oligomers and/or polymers.

The identity of the species which gives rise to the purple colour of the deposited film has not been unequivocally established. The most plausible proposal, in view of the evidence available, is that the colour is due to protonation of a conjugated polyene, such as dehydrochlorinated poly-1,1-dichloroethene, by the $HCl/AlCl_3$ mixture. Another possibility, considered less likely, is that the colour is due to protonation of an aromatic species, such as 1,3,5-trichlorobenzene, by the $HCl/AlCl_3$ mixture to yield a solvated carbenium ion in the deposited film.

Aluminium (III) chloride is highly susceptible to hydration and hydrolysis and, despite stringent attempts to exclude water, some hydration and hydrolysis occurred when samples were manipulated in this work. Deliberate prior exposure of the solid to water vapour promotes $[^{36}Cl]$-chlorine exchange between gaseous $[^{36}Cl]$-HCl and the solid, but can completely inhibit the reactions of gaseous 1,1,1-trichloroethane and gaseous 1,1-dichloroethene with solid aluminium (III) chloride. Both effects have been attributed to the adsorption and reaction of water molecules at co-ordinatively unsaturated aluminium (III) sites; in the former instance this facilitates $[^{36}Cl]$-chlorine exchange by creating labile surface Cl^- ions, but in the latter it effectively removes the site at which the chlorohydrocarbons can adsorb. However, the presence of small quantities of water is likely in all the experiments reported, and the involvement of this water in the reactions of gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene with solid aluminium (III) chloride, for example, as a source of small quantities of hydrogen chloride, cannot be ruled out.

A complete understanding of the surface reactions which

occur in the early stages of the reactions of gaseous 1,1,1-trichloroethane and 1,1-dichloroethene with solid $AlCl_3$ is essential and so the most important area for further investigation in this field is the nature of the adsorbed species in the early stages of the reaction. DRIFTS and SIMS may prove to be very useful if sample handling facilities can be improved. Investigation of the purple film produced in these reactions may be extremely difficult, but flow experiments using DRIFTS could yield valuable information about the processes which take place at the gas/liquid interface. Removal of the volatile material from the reaction of gaseous 1,1,1-trichloroethane or gaseous 1,1-dichloroethene with solid aluminium (III) chloride in the very early stages of reaction <60s, followed by recovery of the involatile organic material may allow analysis of that material using, for example, GCMS at a stage when the variety of species present is low. Finally, a radiotracer study using solid $[^{36}Cl]$-$AlCl_3$ and gaseous, inactive 1,1,1-trichloroethane could allow the extent to which the chlorine atoms of the solid are involved in the reaction scheme to be determined.

In a wider context, the ubiquitous presence of some hydration and hydrolysis in solid aluminium (III) chloride samples used in this work may have important implications for mechanistic interpretations of organic transformations catalysed by aluminium (III) chloride. The role of water in metal halide/chlorohydrocarbon interactions is an important area which requires further clarification, and studies on the transformations of gaseous chlorohydrocarbons over chlorinated alumina may yield valuable information in this field.

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