DYNAMIC STUDIES OF CHLOROFLUOROETHANES AT HALOGENATED SURFACES

BY

MARGARET M. McGEOUGH

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Department of Chemistry - University of Glasgow.

For Dad and Mum.

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Dynamic studies of haloethanes at halogenated surfaces.

Margaret M. McGeough

Summary

In 1950 William Miller and coworkers studied the isomerisation of CCl_2FCClF_2 in the presence of aluminium(III) chloride under reflux conditions. The products they obtained were CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2 and C_2Cl_6. When the reaction was repeated using [^{36}Cl]-chlorine labelled aluminium (III) chloride, only the chlorinated products CCl_3CClF_2 and C_2Cl_6 contained the [^{36}Cl]-chlorine isotope. There was no radiolabel observed in the isomeric product CCl_3CF_3. On the basis of these results an intramolecular mechanism was proposed to account for the isomerisation of CCl_2FCClF_2 in the presence of aluminium(III) chloride.

Recent work involving studies of the catalytic fluorination and chlorination of gaseous chlorofluoroethanes using HF-fluorinated chromia catalysts has cast doubt on the importance of an intramolecular isomerisation mechanism. Studies using [^{36}Cl]-chlorine and [^{18}F]-fluorine have indicated that isomerisation may occur as a result of a series of halogen exchange reactions.

The present work is aimed at resolving this problem and re-examines Miller's original work under a variety of conditions. The surfaces chosen for this study were aluminium(III) chloride, aluminium(III) chloride pretreated with CH_3CCl_3, aluminium(III) chloride supported on γ-alumina and [CCl_4]-chlorinated γ-alumina. All of these solids exhibit varying degrees of Lewis acidity.

Aluminium(III) chloride pretreated with CH_3CCl_3 and aluminium (III) chloride supported on γ-alumina were chosen for study to compare the results with untreated aluminium(III) chloride. [CCl_4]-Chlorinated γ-alumina was chosen for study because, like aluminium(III) chloride, it will dehydrochlorinate CH_3CCl_3 at room temperature but the reaction time for the alumina based catalyst is longer.

All reactions were carried out at room temperature. The products from the reaction between CCl_2FCClF_2 and aluminium (III) chloride were CCl_2FCClF_2, the isomer CCl_3CF_3, a fluorinated product CCl_2FCF_3 and the chlorinated products CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6. A quantity of material was also retained on the solid surface. This was always inversely proportional to the quantity of CCl_3CF_3 produced. Identical results were obtained from reactions between CCl_2FCClF_2 and aluminium(III) chloride pretreated with CCl_2FCClF_2. This suggested that either (i) the retained material did not affect the reaction sites on aluminium(III) chloride or (ii) the surface formed by the retained material was responsible for the observed reactions.

Information regarding the composition and reactivity of the retained material was obtained from [^{36}Cl]-chlorine radiolabelling experiments. Reaction of [^{36}Cl]-CCl_2FCClF_2 with aluminium(III) chloride resulted in the incorporation of the [^{36}Cl]-chlorine radiolabel on the surface. Further reaction of this solid, with gaseous CCl_2FCClF_2, resulted in a decrease of the surface count rate. This is believed to be due to chlorine self-absorption caused by the build-up of retained material on the solid surface. When aluminium(III) chloride pretreated with [^{36}Cl]-CCl_2FCClF_2 was left in a reaction vessel, after a series of reactions with CCl_2FCClF_2, the surface count rate increased and a build up of vapour was observed. The increase in surface count rate was due to the desorption of material from the solid surface thus reducing chlorine self absorption. The desorbed material gave rise to the increase in vapour pressure observed. The vapour was identified by i.r. spectroscopy as mainly CCl_2FCClF_2 but some CCl_3CF_3 was also present. Some radioactivity was detected in the gas phase but it was too small to be determined precisely. Reactions between CCl_2FCClF_2 and [^{36}Cl]-chlorine labelled aluminium(III) chloride were analysed by radio-g.c. The elutant fraction corresponding to CCl_3CF_3 did not contain any [^{36}Cl]-chlorine isotope which agreed with Miller's original observation.

Infrared studies of the vapour phase during the course of reaction between CCl_2FCClF_2 and aluminium(III) chloride showed that the presence of moisture inhibited the isomerisation mechanism. In a virtually moisture free environment the gaseous CCl_2FCClF_2 was consumed before the end of the 24 h reaction period. When moisture was present, CCl_2FCClF_2 remained in the vapour for the duration of the reaction. Kinetic data obtained from i.r. studies revealed that the production of CCl_3CF_3 did not occur via first or second order processes. Further information concerning the nature of the adsorbed species was obtained from ^{27}Al and ^{13}C MAS solid state n.m.r. studies. The ^{27}Al n.m.r. spectrum obtained from aluminium(III) chloride after reaction with CCl_2FCClF_2 was very similar to that for pure aluminium(III) chloride. This suggested that adsorption process does not result in a change in the surface structure. The adsorbed species was identified from ^{13}C MAS nmr studies as a chloro-carbon which was most probably C_2Cl_6.

The adsorbed species was chemically bound to the surface of aluminium(III) chloride as perfluorohexane, which has similar physical properties to CCl_2FCClF_2, did not interact with the solid. There was also no interaction between aluminium(III) chloride and $CClF_2CClF_2$. However, the reaction between CCl_3CClF_2 and aluminium(III) chloride produced CCl_2FCF_3, CCl_3CF_3, CCl_2FCClF_2 and CCl_3CClF_2 but the isomer CCl_2FCCl_2F was not observed. Aluminium(III) chloride pretreated with CCl_3CClF_2 also isomerised CCl_2FCClF_2 to CCl_3CF_3. The reaction between CCl_2FCClF_2 and aluminium(III) chloride pretreated with CH_3CCl_3 resulted in the production of CCl_2FCF_3. CCl_3CF_3, CCl_2FCClF_2, CCl_3CClF_2, CCl_3CCl_2F, C_2Cl_6 and the compound C_2Cl_4. The latter compound may have originated from the breakdown of the purple polymer on the surface of aluminium(III) chloride or from the dechlorination of C_2Cl_6. Mass balance studies indicated that a quantity of material was retained by the solid after reaction of CCl_2FCClF_2. This quantity was inversely proportional to the quantity of CCl_3CF_3 produced. Radiotracer experiments involving aluminium(III) chloride pretreated with $[^{36}Cl]$-chlorine labelled CH_3CCl_3 showed that the material retained by the solid after reaction with CCl_2FCClF_2 led to a reduction in the surface count rate. If the solid was left after a reaction for a period of time, vapour developed in the reaction vessel and the surface count rate increased. I.r. studies of the gas phase during the reaction between CCl_2FCClF_2 and aluminium(III) chloride pretreated with CH_3CCl_3 demonstrated the importance of a water free environment. Complete consumption of CCl_2FCClF_2 was observed during a reaction in water-free conditions, but CCl_2FCClF_2 remained when there was contamination by moisture. Kinetic data derived from the i.r. studies indicated that the production of CCl_3CF_3 did not follow a simple reaction process.

The ^{27}Al MAS solid state n.m.r. spectrum of aluminium(III) chloride pretreated with CH_3CCl_3, after reaction with CCl_2FCClF_2, provided evidence of both octahedral and tetrahedral aluminium environments. This suggested that the reaction of CH_3CCl_3 with aluminium(III) chloride involved some change in the surface structure.

Overall, the experimental work suggests that there is a similarity between the surface sites on aluminium(III) chloride responsible for the isomerisation of CCl_2FCClF_2 and for the dehydrochlorination of CH_3CCl_3.

Aluminium(III) chloride supported on γ-alumina facilitated the isomerisation of CCl_2FCClF_2. I.r. studies of the vapour during this reaction suggested that CCl_2FCClF_2 reacted on both aluminium(III) chloride and γ-alumina. The ^{27}Al MAS solid state n.m.r. spectrum of aluminium(III) chloride supported on γ-alumina, after reaction with CCl_2FCClF_2, indicated that there was a chemical interaction between aluminium(III) chloride and γ-alumina. This interaction may take the form of an $Al-O-AlCl_3$ linking group on which an aluminium(III) chloride network was formed.

For comparison with aluminium(III) chloride supported on γ-alumina, the reactions of CCl_2FCClF_2 in the presence of $[CCl_4]$-chlorinated γ-alumina were studied. Very little gaseous material was produced from these reactions but a large quantity of material was retained by the solid. The pretreatment of $[CCl_4]$-chlorinated γ-alumina with CH_3CCl_3 did not lead to an improved reaction with CCl_2FCClF_2, but pretreating $[CCl_4]$-chlorinated alumina with CCl_2FCClF_2 inhibited the dehydrochlorination of CH_3CCl_3. This indicated that the reactive sites responsible for dehydrochlorination of CH_3CCl_3 and isomerisation of CCl_2FCClF_2 on this material are the same.

In conclusion, only chlorofluoroethanes containing a $-CCl_xF_{3-x}$ group (x=3 or 2) will react with an aluminium(III) chloride based catalyst. Reaction involving a $-CClF_2$ group is possible providing it is bonded to a $-CCl_xF_{3-x}$ group (x = 3 or 2). The only chlorofluoroethane that is isomerised on an aluminium(III) chloride surface is CCl_2FCClF_2. Isomerisation requires the presence of a surface fluorine-containing species.

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Chapter 1

Introduction

1.1 Aluminium(III) Chloride

Aluminium(III) chloride is a colourless solid that sublimes at 177.8°C [1]. It is a very important Lewis acid and, for example, is used as a catalyst in many Friedel-Crafts reactions. It is very hygroscopic. On exposure to water vapour hydrogen chloride is produced and the surface of the solid is rapidly hydrated or hydroxylated. It is rapidly hydrolysed in water giving the hexaaquoaluminium(III) cation $[Al(H_2O)_6]^{3+}$, under some conditions [2]. A solid which has been claimed to be $[Al(H_2O]_6]Cl_3$ has been observed [3].

1.2 Preparation of Anhydrous Aluminium(III) Chloride

In order to prepare anhydrous aluminium(III) chloride great care must be taken to exclude even trace quantities of water. One method is to react highly pure aluminium metal with pure, dry dichlorine [4]. This route has been successfully used to prepare aluminium(III) chloride from aluminium scrap metal [5]. Alternatively, anhydrous hydrogen chloride is flowed over aluminium metal [6]. Since large scale production of aluminium(III) chloride is often carried out in plants fabricated from steel or its alloys, purification on a laboratory scale by sublimation is often carried out in the presence of aluminium metal. The latter acts as a reducing agent for any iron chloride inadvertently formed. This procedure has been used also for large scale purification [7].

Although other methods for the preparation of aluminium(III) chloride have been investigated [8,9] the yield and purity of the product are inferior to those obtained from dichlorine and hydrogen chloride routes.

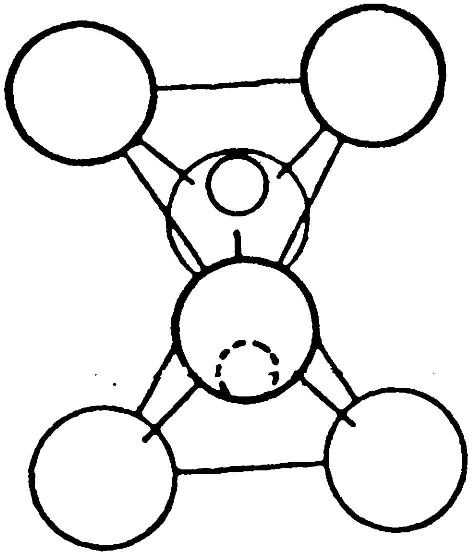
1.3 The Structure of Aluminium(III) Chloride

The structure of aluminium(III) chloride was first studied by Ketelaar in 1935 [10]. He concluded that the lattice was monoclinic and that the chloride atoms were arranged in a distorted cubic close packed structure. The aluminium atoms occupied a fraction of the octahedral holes, presumably one third, resulting in a layer lattice.

Doubt was cast on this structure by electron diffraction studies of aluminium(III) chloride vapour [11]. It was found that below 400°C aluminium(III) chloride, bromide and iodide, exist as dimers. The molecules can be described as edge sharing tetrahedra with an aluminium atom at the centre of each (Figure 1.1). Raman studies of aluminium(III) chloride, bromide and iodide in both the liquid and solid states have confirmed the presence of the edge sharing tetrahedra [12].

Ketelaar and coworkers resumed the investigation using monochromatic and single-crystal methods [13].

Figure 1.1 Structure of Aluminium (III) Chloride in the Vapour Phase



They found the cell constants to be a = 5.92±0.02Å b = 10.22±0.04Å, c = 6.16±0.02Å, β = 108°. There were four molecules of $AlCl_3$ per unit cell or two molecules of Al_2Cl_6. The chlorine atoms were found to be cubic close packed, confirming previous results [10].

The arrangement of the aluminium atoms was found to be in conflict with all previous conclusions [10,11,12]. In the revised structure aluminium occupies octahedral centres resulting in an ionic layered structure similar to that of $CrCl_3$ (Figure 1.2). The Raman spectra of both compounds are very similar [14]. In both structures corresponding positions between two layers are shifted over one third of the hexagonal axis. Unlike $CrCl_3$ the shift between layers of aluminium(III) chloride is in the same direction producing a monoclinic structure (Figure 1.3).

Near its sublimation temperature aluminium(III) chloride is almost completely dimeric [14]. The infrared spectrum of the vapour shows three bands at 625 cm^{-1}, 484 cm^{-1} and 420 cm^{-1}, attributed to vibrations of the dimer [14]. As the temperature is increased to 900°C the monomer, $AlCl_3$, is formed. This is planar with symmetry D_{3h}. The infrared spectrum of the vapour shows one band at 610 cm^{-1} in accordance with this symmetry. Two other bands relating to angle bending motions should exist but were not detected as they occur at very low frequencies. Calculation of bond-stretching force constants show that the terminal chlorines are bound to Al^{III} by 'normal' bonds. The Al-Cl stretching force constants involving the bridging

Figure 1.2 Structure of Solid Aluminium (III) Chloride

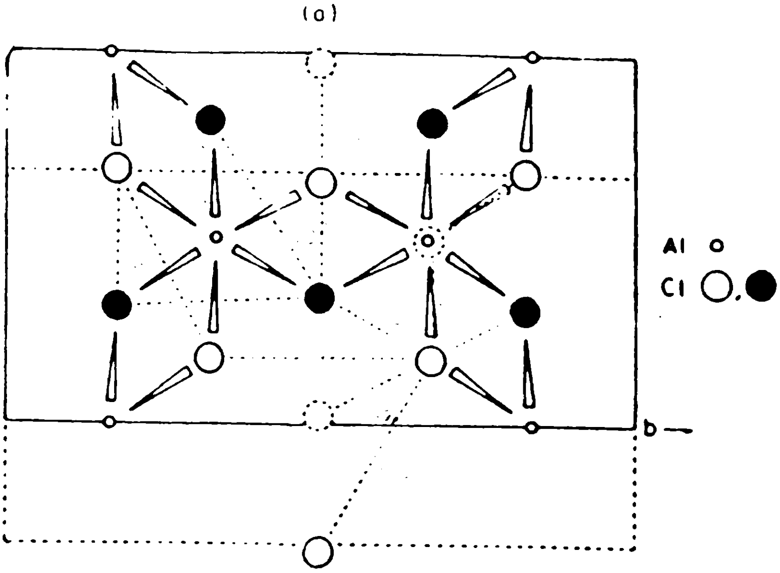
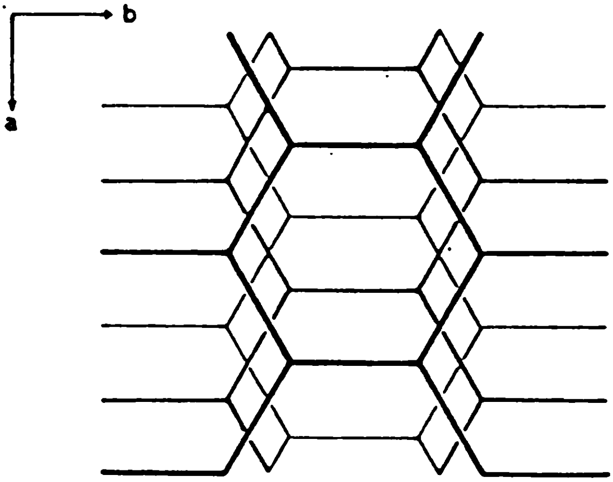


Figure 1.3 The Packing of Layers in Aluminium (III) Chloride



Cl atoms are half those determined for Al-Cl terminal bonds [15].

As aluminium(III) chloride reaches its melting point it undergoes a structural change from a layered monoclinic lattice to discreet Al_2Cl_6 dimers [16]. A study of the structure of liquid aluminium(III) chloride by Harris et al [16] has shown these dimers to be the same as those found by Palmer and Elliot in the vapour [11].

Conductivity measurements show that aluminium(III) chloride is covalent at room temperature but, on heating, the conductivity increases to 5 x 10^6 $\Omega^{-1} cm^{-1}$. On becoming liquid the conductivity falls to zero [17]. This phenomenon also accounts for the large decrease in density of aluminium(III) chloride as it melts [16].

The heavier aluminium halides of bromine and iodine in the solid state have the same type of bridging structure found for the chloride in the liquid and vapour states. Both are powerful Lewis acids and are covalent in both the solid and liquid states [17]. In contrast aluminium(III) fluoride is ionic in both states. Each aluminium is octahedrally coordinated and each fluorine is shared between two AlF_6 octahedra forming a continuous ionic network [18].

In solid aluminium(III) chloride the aluminium atoms are also octahedrally coordinated, suggesting an ionic solid, however it exhibits no conductivity at room temperature. It is therefore assumed that under the experimental conditions, used in this work, solid aluminium(III) chloride is covalent. However, the surface of the solid is unsaturated and therefore exhibits ionic phenomena.

1.4 Friedel-Crafts Chemistry

Friedel-Crafts reactions are those involving the alkylation and acylation of aromatic compounds by an electrophilic agent. The Lewis acid catalyst used serves to generate the carbocation $(RCO)^+$ or R^+ which acts as the electrophile.

1.4.1 Aluminium(III) Chloride as a Friedel-Crafts Catalyst

Aluminium(III) chloride is the most widely used catalyst for Friedel-Crafts reactions. However, the method of its preparation can affect its catalytic abilities [19]. For example, the sublimation of aluminium(III) chloride in the presence of aluminium metal is important [7]. The aluminium removes iron chloride impurities which inhibit reactions. However, the nature of the interaction between aluminium and iron chloride is unknown [20].

As it is difficult to obtain hygroscopic substances such as aluminium(III) chloride under completely water-free conditions, it was assumed in early work that the catalytic surface was $H^+[AlCl_3OH]^-$ or $H^+[AlCl_4]^-$ [21]. Formulation of a species such as $H^+[AlCl_3(OH)]^-$ implies the presence of a free H^+ ion.

A study by Brown and Pearsall of the catalyst couple between aluminium(III) chloride and hydrogen chloride concludes that $HAlCl_4$ does not exist [22].

Isotopic exchange between aluminium(III) chloride and $[^{36}Cl]$-HCl has been studied [23,24,25]. Each group of workers are of the opinion that, under completely anhydrous conditions, no exchange of chloride occurs between gaseous HCl and a solid aluminium(III) chloride surface. However if water is added to the system exchange occurs readily.

Surface species such as $[H_3O]^+$ $[AlCl_3(OH)]^-$ could be postulated. Hydrolysis of aluminium(III) chloride produces Al-OH_2 groups on the surface or Al-OH bound to the surface and HCl gas. These species can give rise to Brønsted acid sites:

$$\text{Al-OH} + AlCl_3(\text{bulk}) + HCl \longrightarrow AlOH_2^+ + AlCl_4^- \qquad \text{equation 1.1}$$

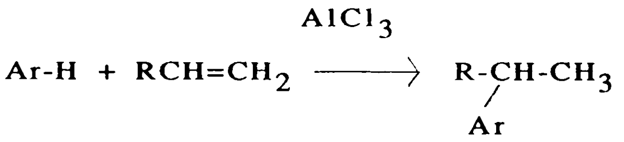
Brønsted acid sites can decrease the Lewis acidity of a catalyst, as the former are coordinatively saturated, and Lewis acids require an electron accepting centre such as Al^{III}.

1.4.2 Acylation and Alkylation

Typical alkylating agents used in Friedel-Crafts reactions are alkyl halides, ethers, alkenes, alkynes, alcohols, aldehydes, ketones and paraffins [26]. The overall reactions maybe written as:

$$\text{Ar-H} + \text{R-X} \xrightarrow{\text{AlCl}_3} \text{Ar-R} + \text{HX} \qquad \text{equation 1.2}$$

$$\text{Ar-H} + \text{R-OH} \xrightarrow{\text{AlCl}_3} \text{Ar-R} + \text{H}_2\text{O} \qquad \text{equation 1.3}$$



$$\text{Ar-H} + \text{RCH=CH}_2 \xrightarrow{\text{AlCl}_3} \underset{\text{Ar}}{\text{R-CH-CH}_3} \qquad \text{equation 1.4}$$

In the above and all following equations Ar refers to the aromatic centre to which a hydrogen atom is attached, R is any alkyl group, and X is the halogen eg. Cl. Aluminium(III) chloride is represented by AlCl_3; it does not imply that the catalyst is a monomeric species.

Friedel-Crafts acylation involves the introduction of an acyl group to an aromatic ring by reacting it with an acyl halide, acid anhydride, ester or an acid in the presence of a Friedel-Crafts catalyst. Typical reactions are shown below [27]:

$$\text{Ar-H} + \text{RCOX} \xrightarrow{\text{AlCl}_3} \text{ArCOR} + \text{HX} \qquad \text{equation 1.5}$$

$$\text{Ar-H} + (\text{RCO}_2)\text{O} \xrightarrow{\text{AlCl}_3} \text{ArCOR} + \text{RCO}_2\text{H} \qquad \text{equation 1.6}$$

$$\text{Ar-H} + \text{RCO}_2\text{H} \xrightarrow{\text{BF}_3} \text{ArCOR} + \text{H}_2\text{O} \qquad \text{equation 1.7}$$

$$\text{Ar-H} + \text{RCO}_2\text{R}' \longrightarrow \text{ArCOR} + \text{R}'\text{OH} \qquad \text{equation 1.8}$$

Acylating agents are more reactive than the corresponding alkylating agents for a given substitute. The complexes formed between aluminium(III) chloride and organic molecules were first observed in the late 1920s by Dougherty [28]. These were ionic complexes thought to be intermediates in Friedel-Crafts reactions. The reactions studied demonstrated halogen exchange between the two organic halides, the mechanism suggested being,

$$\text{RX} + \text{AlCl}_3 \longrightarrow \text{RXAlCl}_3 \longrightarrow \text{R}^+\text{-(XAlCl}_3)^- \qquad \text{equation 1.9}$$

$$\text{R}_1\text{X}_1 + \text{AlCl}_3 \longrightarrow \text{R}_1\text{X}_1\text{AlCl}_3 \longrightarrow \text{R}_1{}^+\text{-(X}_1\text{AlCl}_3)^- \qquad \text{equation 1.10}$$

$$\text{R}^+\text{-(XAlCl}_3)^- + \text{R}_1{}^+\text{-(X}_1\text{AlCl}_3)^- \longrightarrow \text{R}^+\text{-(X}_1\text{AlCl}_3)^- + \text{R}_1{}^+\text{-(XAlCl}_3)^- \qquad \text{equation 1.11}$$

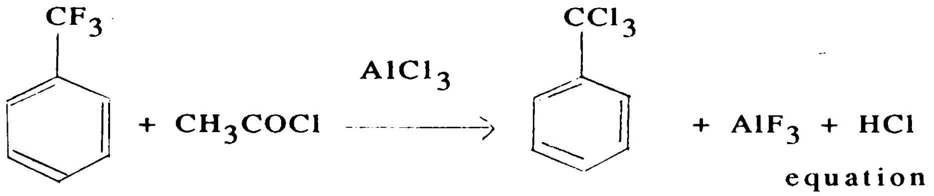
$$\text{R}^+\text{-(X}_1\text{AlCl}_3)^- \longrightarrow \text{RX}_1 + \text{AlCl}_3 \qquad \text{equation 1.12}$$

$$\text{R}_1{}^+\text{-(XAlCl}_3)^- \longrightarrow \text{R}_1\text{X} + \text{AlCl}_3 \qquad \text{equation 1.13.}$$

Friedel-Crafts reactions have been widely studied using NMR techniques to identify and obtain equilibrium constants for complex formation [29,30]. An investigation of the Friedel-Crafts acetylation of acetylene with acetyl chloride, using ^{1}H NMR spectroscopic techniques gives evidence for the 1:1 and 2:1 complexes of aluminium(III) chloride and acetyl chloride, and of the trans 1-chloro-1-buten-3-one aluminium(III) chloride complex [31].

1.5 Chlorine Exchange Reactions of Aluminium(III) Chloride

In 1938 Henne and Newman attempted a Friedel-Crafts acylation of trifluorotoluene with an acid chloride, in the presence of aluminium(III) chloride [32]. However, the reaction proceeded according to equation 1.14:



equation 1.14

No acylated products were obtained instead halogen exchange occurred between the trifluoromethyl group and the aluminium(III) chloride. This exchangeable chlorine has been investigated using [^{36}Cl]-chlorine radiotracer techniques [33,34]. Aluminium(III) chloride is readily exchangeable with liquid carbon tetrachloride at room temperature [33]. The mechanism of exchange is thought to involve a surface reaction rather than a homogeneous process involving CCl_3^+ and $AlCl_4^-$ ions. This system is catalytically active, as a Friedel-Crafts reaction between carbon tetrachloride vapour and benzene vapour occurs on an aluminium(III) chloride surface [35]. Carbon tetrachloride, in the presence of aluminium(III) chloride, is also known to catalyse the reactions of fluorinated alcohols [36].

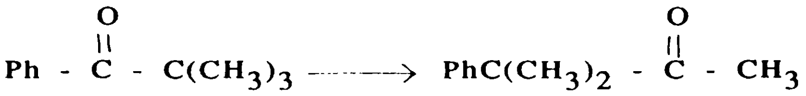
Chlorine exchange has been detected between [^{36}Cl]-chlorine labelled aluminium(III) chloride and

$(CH_3)_2CHCl$, CH_3CH_2Cl, $CHCl_3$ and CH_2ClCH_2Cl solvated in $MeNO_2$ or $PhNO_2$ (RNO_2) [34]. The ionic mechanism proposed involves the interaction of the alkyl chloride with the free cation $[AlCl_2.RNO_2]^+$. However it is not necessary to involve a solvent in these reactions as chlorine exchange between C_2H_5Cl, n-C_3H_7Cl, $CHCl_3$ and n-$C_5H_{11}Cl$ with [^{36}Cl]-chlorine labelled aluminium(III) chloride has been observed in the gas phase [35]. The amount of exchange observed is minimal and the results quoted are only qualitative as it is impossible to reproduce the surface of aluminium(III) chloride from one preparation to another.

1.6 Organic Rearrangements Catalysed by Aluminium(III) Chloride

Aluminium(III) chloride not only catalyses Friedel-Crafts acylation and alkylation reactions of organic molecules but can also induce rearrangement of the molecules. Many of these reactions have been patented [37,38,39]. The widespread interest in these reactions centres around the nature of the reactive intermediate.

In the study of the rearrangement of tert. butyl phenyl ketone equation 1.15:



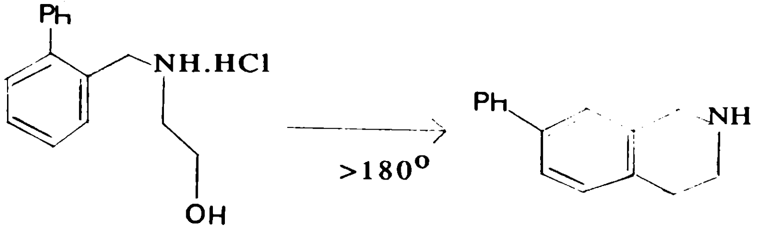
$$Ph - \overset{\overset{\displaystyle O}{\|}}{C} - C(CH_3)_3 \longrightarrow PhC(CH_3)_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$

equation 1.15

the proposed reactive intermediate is a 2:5 complex

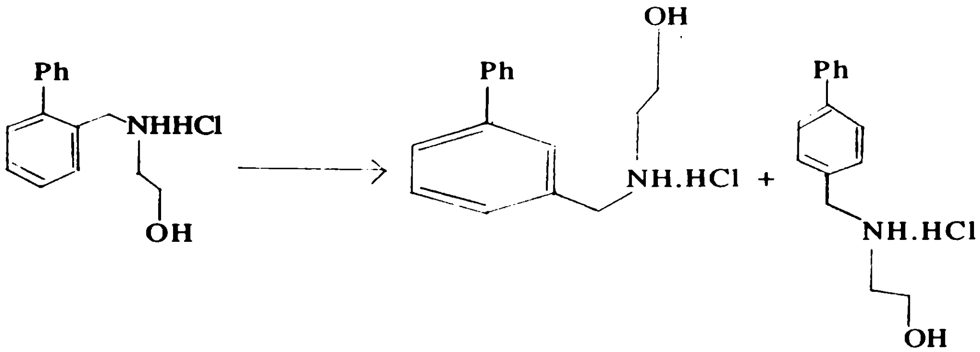
(Figure 1.4) which is developed from an initial 1:1 complex [40].

In contrast Kakiuchi et al propose a carbocation intermediate in the rearrangement of 5,6 disubstituted bicyclo[4.2.0]octan-2-ones with aluminium chloride [41]. The reaction scheme is shown in figure 1.5. The carbocation is formed by the coordination of aluminium to the oxygen of the ketone. In a recent paper by Mendelson et al aluminium(III) chloride induces cyclisation and isomerisation of N-(2-hydroxyethyl)-2-phenyl benzylamine hydrochloride (equation 1.16) [42].



equation 1.16

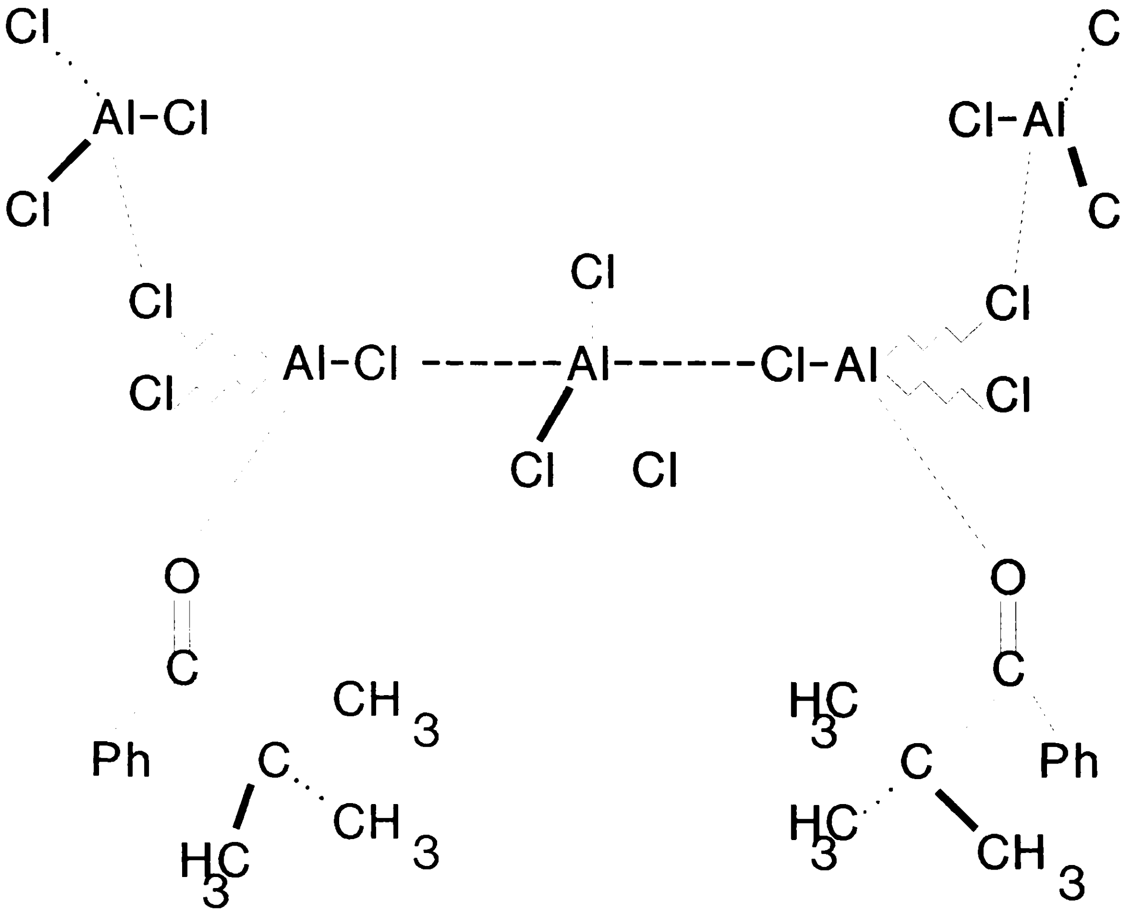
At 135°C no cyclisation occurs and the only reaction observed is shown in equation 1.17.



equation 1.17

It was concluded from ^{13}C NMR studies that the phenyl group is involved in the migration but the allyl group

Figure 1.4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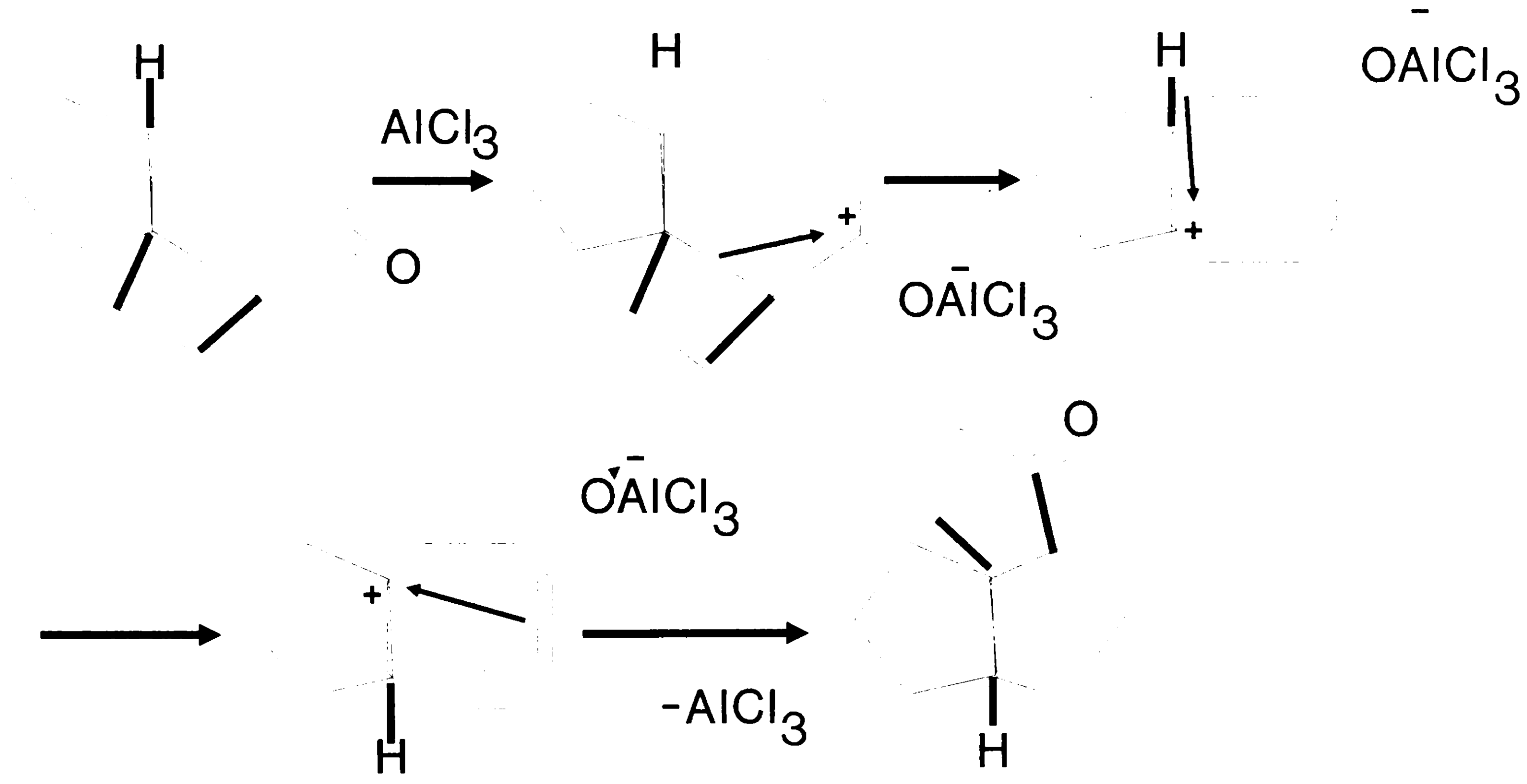
H3C
H3C
CH3

Figure 1.5



does not participate directly.

It is very important in these reactions, that the aluminium(III) chloride used should be kept as dry as possible. The isomerisation of 1,2 dichloropropane to 1,3 dichloropropane will occur only in the presence of anhydrous aluminium(III) chloride [43]. If water is allowed to enter the system no reaction occurs. This reaction is specific to aluminium(III) chloride as other Lewis acid catalysts used in this study including $SbCl_5$, $FeCl_3$, $TiCl_4$ and $AlCl_3.6H_2O$ were not successful.

However some reactions require the presence of moisture or hydrogen chloride in the presence of aluminium(III) chloride before they are initiated [44]. It is known that hydrogen chloride catalyses the intramolecular migration of alkyl groups in phenol homologues and aromatic ketones [45].

1.7 Chlorofluorocarbons

Chlorofluorocarbons were first introduced by Midgeley and Henne in 1930 in an attempt to find alternatives to NH_3 and SO_2 in refrigeration [46]. Being non-toxic and chemically inert made them the perfect solution to the problems posed by the toxic chemicals already used.

A three figure nomenclature system has been devised to identify chlorofluorocarbons. The first digit corresponds to the number of carbon atoms minus 1, the second to the number of hydrogens plus 1 and the third is equal to the number of fluorine atoms present. The fully halogenated methane series $CCl_{4-x}F_x$ is represented by a two-digit system as the first digit is zero. CCl_3F is CFC 11 and CF_4 is CFC 14. The nomenclature for the ethane series is listed in table 1.1.

1.7.1 Preparation of Chlorofluoroethanes

Chlorofluoroethanes are prepared by the fluorination of hexachloroethane using a variety of conditions and catalysts. Early work involved the use of antimony fluorides or molecular fluorine. An extensive study of this subject was made by Henne and coworkers in the late 1930s. They were able to fluorinate C_2Cl_6 with $SbCl_2F_3$ producing CCl_3CCl_2F, CCl_2FCCl_2F, CCl_2FCClF_2, $CClF_2CClF_2$ and $CClF_2CF_3$ by applying pressure to the system. The asymmetric isomers CCl_3CClF_2 and CCl_3CF_3 were produced by the photolysis of $CHCl_2CHF_2$ and CH_2ClCF_3 with molecular chlorine [47]. The fluorination of $CHCl_2CCl_3$ by $SbCl_2F_3$ favoured reaction at the $-CCl_3$ group. The presence of the hydrogen atom served to inhibit further fluorination of the CCl_3 group after two chlorine atoms were replaced [48], both chlorines on the $-CHCl_2$ group were also replaced by fluorine. However, if two hydrogen atoms were present on the same carbon, a $-CH_2Cl$ group became inert to fluorination [49].

These studies led to a reactivity series for the chlorofluoroethanes with respect to their ability to resist further fluorination [50]:

$$CF_3 > CClF_2 > CCl_2F > CCl_3.$$

Table 1.1
Nomenclature for Chlorofluoroethanes

Chlorofluoroethane	
CF3CF3	116
CClF2CF3	115
CClF2CClF2	114
CCl2FCF3	114a
CCl2FCClF2	113
CCl3CF3	113a
CCl2FCCl2F	112
CCl3CClF2	112a
CCl3CCl2F	111
CCl3CCl3	110

A CCl_3 group can be fluorinated rapidly to a CF_3 group whereas the presence of hydrogen in a molecule inhibits fluorination [51a]. However this problem can be overcome by introducing bromine to the molecule [51b]. Monofluorinated aliphatic molecules are unstable and liberate HF in concentrated acids but, if a CF_2X group is present the C-F bond is strengthened. The C-X bond of the third halogen is also strengthened making it difficult to replace. A $-CF_2X$ group also increases the stability of halogen atoms on adjacent carbon atoms [50].

The direction of fluorination is determined by the presence of hydrogen. The compounds CCl_3CCl_2F and CCl_2HCCl_2F are fluorinated producing the symmetric molecule CCl_2FCCl_2F and the unsymmetric molecule CCl_2HCClF_2 respectively [50]. The fluorination of chlorocarbons and chlorinated hydrocarbons by molecular fluorine produces symmetric molecules with at most two fluorine atoms [52,53]

1.7.2 <u>Chlorofluorocarbons and the Ozone Layer</u> [54]

Chlorofluorocarbons, due to their chemical inertness, are an environmental threat. Although excellent refrigerants, solvents and propellant gases, they are not decomposed in the lower atmosphere by photolysis nor are they soluble in water.

The ozone layer is contained in the stratosphere and is approximately 25 km above the earth's surface. Harmful u.v. radiation is absorbed by the ozone so that very little filters through.

Ozone is formed by the action of photolysing light on molecular oxygen. (equations 1.18 and 1.19)

$$O_2 \xrightarrow{hv} O\cdot + O\cdot \qquad \text{equation 1.18}$$

$$O_2 + O\cdot \longrightarrow O_3 \qquad \text{equation 1.19}$$

It enters a cycle through which ozone is completely destroyed and reformed. (equations 1.20 and 1.21)

$$O_3 \longrightarrow O_2 + O\cdot \qquad \text{equation 1.20}$$

$$O_2 + O\cdot \xrightarrow{hv} O_3 \qquad \text{equation 1.21}$$

This cycle can be disturbed by the inclusion of a radical other than oxygen. These radicals NO• , CH_3• and Cl• may arise from the breakdown of nitrous oxide methane and chlorofluorocarbons respectively. Most of these compounds are very inert in the lower atmosphere and breakdown naturally only when they have risen above the ozone layer.

As the CFC molecules rise high in the atmosphere the C-Cl bonds are broken producing chlorine radicals, Cl• , which enter the ozone cycle. For example using CF_3Cl the reactions would be as follows (equations 1.22-1.25)

$$CF_3Cl \longrightarrow CF_3\cdot + Cl\cdot \qquad \text{equation 1.22}$$

$$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2 \qquad \text{equation 1.23}$$

$$ClO\cdot + O\cdot \longrightarrow Cl\cdot + O_2 \qquad \text{equation 1.24}$$

The net result is the process

$$O\cdot + O_3 \longrightarrow 2O_2 \qquad \text{equation 1.25}$$

As chlorine radicals are not consumed by the reaction, many thousands of ozone molecules may be destroyed before a chlorine radical has filtered through the stratosphere [55].

The potential effects of ozone depletion on the earth's surface are great. Once the ozone layer is broken down, the temperature of the stratosphere will fall and possibly that of the troposphere also, affecting the earth's climate. As harmful U.V.B. radiation enters the earths atmosphere the incidence of skin cancer and cataracts will increase. Biological systems can also be affected for example many growing plants eg. rice are very susceptible to U.V.B.

1.7.3 Alternatives to Chlorofluorocarbons

The effects that CFCs have on the ozone layer were first realised by Rowland and Molina in 1973 [56] but it was not until 1987 that other scientists and governments accepted their findings. This resulted in the Montreal Protocol, an international agreement by governments to reduce and eventually cease the output of CFCs to the atmosphere.

The main CFCs targetted in 1987 were CCl_3F (CFC 11) and CCl_2F_2 (CFC 12); both are used as refrigerants and blowing agents. The need for the replacement of the industrial solvent CCl_2FCClF_2 (CFC 113) was also recognised. The requirements of the 1987 Protocol were:

(i) that there must be a 50% reduction in CFC consumption within 10 years and

(ii) a freeze on the use of halons (chlorofluoro bromocarbons CFBCs) within 4 years.

The Montreal Protocol was recently revised [55] and new targets have been set. All fully halogenated methanes ethanes and propanes are to be phased out by the end of the century together with the halons CF_2BrCl, CF_3Br and $C_2F_4Br_2$, carbon tetrachloride and CH_3CCl_3.

The search for alternatives to CFCs is already underway. The replacements are required to meet strict toxicological requirements and tests normally take up to 7 years. The substitutes for CFC 11 are hydrochlorofluorocarbons $CHCl_2CF_3$ (HCFC 123) and CH_3CFCl_2 (HCFC 141b); both have greatly reduced atmospheric lifetimes and ozone depletion potentials compared with CFC 11 [57]. The compound HCFC 123 is not as efficient a foam blowing agent as CFC 11, but it is a more powerful solvent. The drawback of HCFC 141b is that its vapour is flammable and for both alternatives it is not yet known whether the flammability of the foam will be affected by their use as foam blowing agents.

CFC 12 is to be replaced by CF_3CFH_2 (HCFC 134a). As this compound contains no chlorine its ozone depletion potential is nil. It has a very similar boiling point and melting point to CFC-12 and it is also non-flammable. Its biggest drawback as a replacement in the refrigeration industry is that it is not completely miscible with refrigeration lubricants and so new lubricants will have to be developed. Results of short term toxicity testing have shown that these replacements have as yet no harmful effects on humans or the environment.

There are still questions to be answered about these CFC replacements. They are known to decompose in the troposphere but the exact nature of their decomposition and indeed the products formed are as yet unknown. There is a fear that they may break up to form trifluoroacetic acid, which has unknown effects on the environment [58,59]. There is also a possibility of conversion to monofluoroacetic acid, a particularly dangerous chemical known for its toxicity to mammals. However it is likely this will be produced in infinitesimal amounts.

These HFC and HCFC alternatives are a short term solution to the ozone problem and, they will probably be replaced in the middle of the next century by compounds which are as yet unidentified.

1.8 Chlorofluoroethanes - Production in the Vapour Phase

The large scale production of chlorofluoroethanes in the vapour phase is based on the fluorination of hexachloroethane by HF in the presence of a fluorinated catalyst. This method of preparation has many advantages over the liquid phase process. The antimony halides used in the liquid phase process are prone to reduction and hydrolysis by SO_2 and H_2O respectively. These compounds are contaminants in commercial hydrogen fluoride [60]. The resulting decomposition products can react further with the starting material and with reactive products causing blockages in the reactor system. Reactions involving antimony halide based catalysts should not exceed a temperature of 80°C to avoid decomposition of the catalyst. This low temperature however determines the composition of the product mixture and highly fluorinated ethane derivatives are not obtained in economic yields [60].

These problems can be overcome by using a solid heterogeneous catalyst. The reactor temperature is normally 300-400°C allowing vapour to come into contact with the solid catalyst. The lifetime of the catalyst is longer and a more economic yield is obtained. Modification of the catalytic conditions can result in product selectivity.

The products obtained from the fluorination of CCl_2FCClF_2 with HF using aluminium(III) fluoride as the catalyst are mainly the unsymmetric isomers CCl_2FCF_3 and CCl_3CF_3, with small quantities of $CClF_2CF_3$ and the symmetric isomer $CClF_2CClF_2$. If the catalyst is mixed with a mixture of nickel, chromium and iron metal, the product distribution changes dramatically to give $CClF_2CClF_2$ in a 95% yield [61]. The symmetrical isomers are favoured as propellants and solvents, as they are less prone to hydrolysis. However they are thermodynamically less stable. Further studies on the aluminium(III) fluoride system by Tatlow and coworkers have suggested that the fluorination of hexachloroethane by HF, in the presence of aluminium(III) fluoride, involves three separate processes, dismutation, isomerisation and halogen exchange with the catalyst [62].

1.8.1 Dismutation and Isomerisation

Dismutation and isomerisation reactions have played important roles in the development of reaction mechanisms for chlorofluoroethanes on catalytic surfaces [60,63-66]. It is therefore important to review these reactions in some detail. Dismutation of a chlorofluoroethane results in the formation of one more highly fluorinated and one more highly chlorinated species [60]. For example the dismutation of CCl_2FCClF_2 is shown in equation 1.26.

$$2CCl_2FCClF_2 \rightarrow CCl_3CClF_2 + CClF_2CClF_2 \qquad \text{equation 1.26.}$$

In principle isomerisation can arise from a series of reactions some of which involve dismutation, (equations 1.27 - 1.30)

$$2CCl_2FCClF_2 \rightarrow CCl_3CClF_2 + CClF_2CClF_2 \qquad \text{eqn. 1.27}$$

$$2CClF_2CClF_2 \rightarrow CCl_2FCClF_2 + CClF_2CF_3 \qquad \text{eqn. 1.28}$$

$$CCl_3CClF_2 + CClF_2CF_3 \rightarrow CCl_2FCClF_2 + CCl_2FCF_3 \qquad \text{eqn. 1.29}$$

$$CCl_2FCClF_2 + CCl_2FCF_3 \rightarrow CClF_2CClF_2 + CCl_3CF_3 \qquad \text{eqn. 1.30}$$

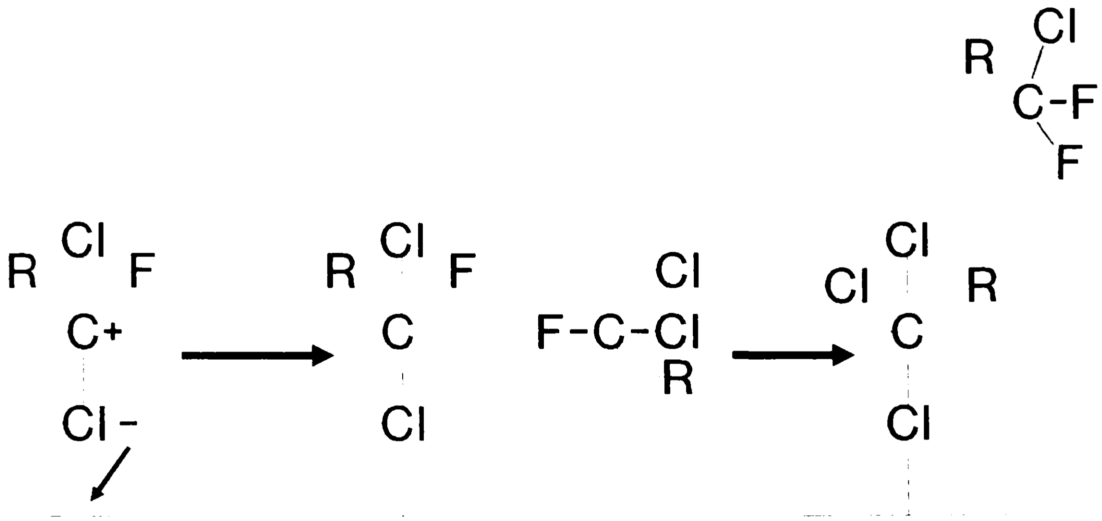
The overall result is the reaction (equation 1.31)

CCl_2FCClF_2 -> CCl_3CF_3 equation 1.31

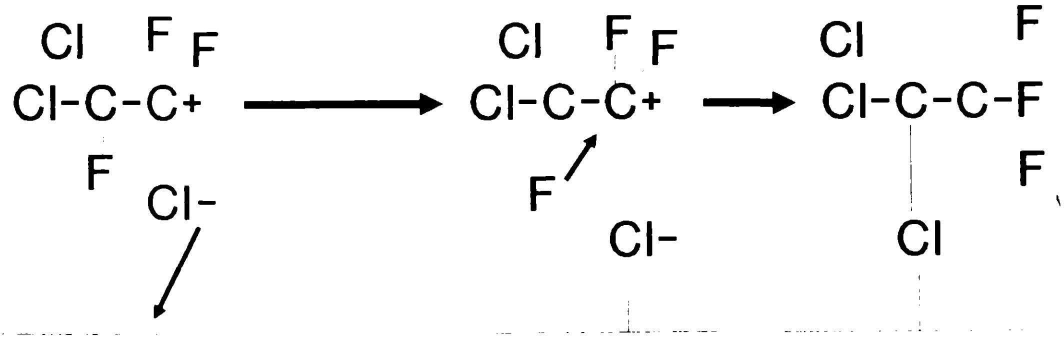
The proposed dismuation mechanism for these reactions is shown in Scheme 1.1. It is ionic in nature and involves the adsorption of the chlorofluoroethane at an active site on the surface via a carbon-chlorine bond. The fluorine source is another chlorofluoroethane molecule, thus a fluorinated molecule is formed leaving a chlorinated molecule adsorbed on the surface. This molecule subsequently desorbs leaving the site vacant for further reaction [60]. Isomerisation is envisaged as occurring via a series of such bimolecular reactions. It may also occur via an intramolecular process as shown in Scheme 1.2. Direct fluorination of the chlorofluoroethane by HF, adsorbed on the catalyst has also been proposed. The chlorofluoroethane is adsorbed to the surface via a carbon-chlorine bond. It obtains a fluorine from the catalyst surface and desorbs leaving an adsorbed chlorine. Hydrogen fluoride is adsorbed at the adjacent site and the hydrogen desorbs with the chlorine as hydrogen chloride, leaving the site vacant for further reaction [67] (Scheme 1.3). If the active fluorinating agent is a Cr-F species formed in the reaction, it follows that fluorination involves cleavage of a Cr-F bond. However chromium(III) fluoride is known to be quite inert with respect to substitution.

A kinetic study of the dismutation and isomerisation of trichlorotrifluoroethanes over chromia supported on activated charcoal has shown that an

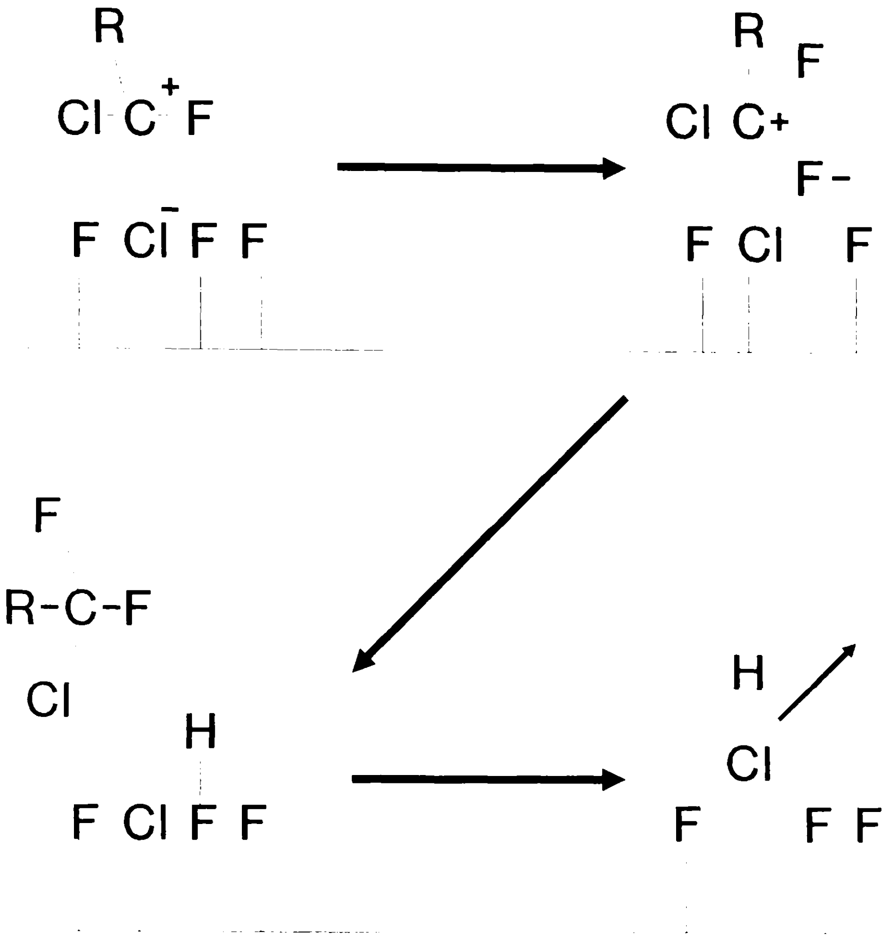
Scheme 1.1



Scheme 1.2



Scheme 1.3

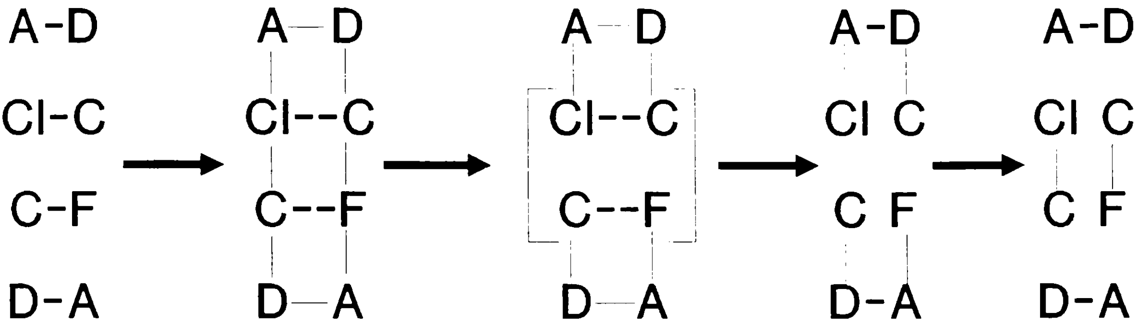


equilibrium stage is reached in the reactor, in which the isomerisation reaction CCl_2FCClF_2 -> CCl_3CF_3 is very slow [63]. The catalyst is deactivated by contact with pure CCl_3CF_3. This is due to the formation of a crystalline form of chromia, possibly α-chromia.

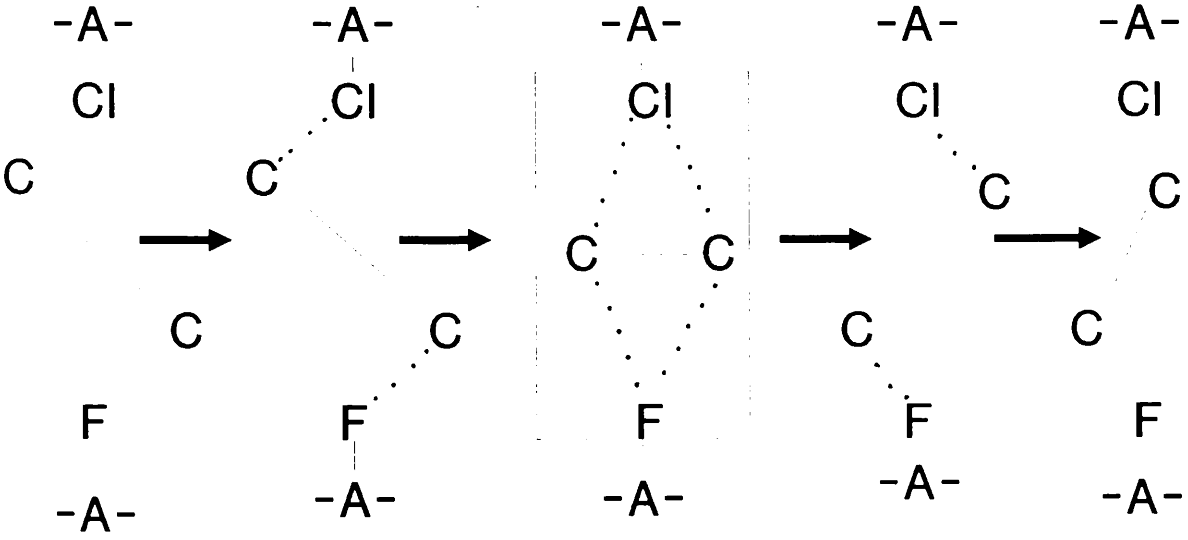
Chromia supported on alumina is more active catalytically than the charcoal based catalysts since a lower temperature is required to produce the same transformations [64]. The isomerisation of CCl_2FCClF_2 -> CCl_3CF_3 also occurs more readily on this catalyst. The nature of the site at which isomerisation occurs has been determined from poisoning experiments using pyridine [64]. This neutralises the strongest Lewis acid sites first and inhibits isomerisation without affecting dismutation. These stronger Lewis acid sites are attributed to isomerisation. The mechanisms for dismutation and isomerisation proposed by Canesson et al [64] differ from that of Kolditz [60,67]. Dismutation involves two adsorption sites per molecule, a donor site (D) to which the carbon atoms adsorbs and an acceptor site (A) to which the halogen atom adsorbs (Scheme 1.4). Isomerisation is an intramolecular process involving the adsorption of the chlorofluoroethane to two acceptor sites (A) via carbon-halogen bonds (Scheme 1.5).

Product selectivity is very important in these reactions and can be influenced by the acidity of the catalyst used [65]. Chromia based catalysts favour the formation of symmetric isomers, whereas, aluminium (III) fluoride favours asymmetric isomers.

Scheme 1.4



Scheme 1.5

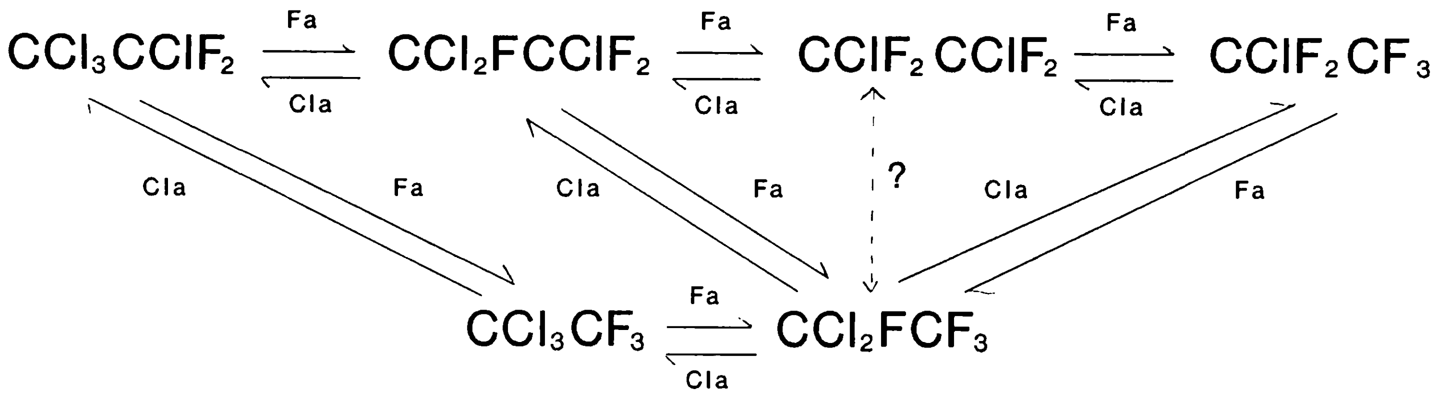


1.8.2 Halogen Exchange Mechanisms

Recent studies involving [^{18}F]-fluorine and [^{36}Cl]-chlorine radiotracers, have cast doubt upon the importance of dismutation and isomerisation mechanisms in the vapour phase fluorination of chlorofluoroethanes at fluorinated chromia surfaces. The mixtures of fluorinated and chlorinated products that are characteristically formed from such reactions are accounted for by a Cl-for-F and F-for-Cl exchange model [68-70]. A key feature of the work was that incorporation of the radiotracer, [^{18}F]-fluorine or [^{36}Cl]-chlorine was observed when feedstock was passed over catalysts previously labelled with $H^{18}F$, $H^{36}Cl$ or [^{36}Cl]-$CClF_2CClF_2$.

For example, an industrial chromia catalyst was treated with $H^{18}F$ at 300°C under flow conditions. This resulted in the uptake of $H^{18}F$ by the catalyst. The compound CCl_2FCClF_2 was then flowed over the labelled catalyst at 430°C and [^{18}F]-fluorine activity was observed in the product mixture [68]. Incorporation of the radiolabel in the products must have arisen from a halogen exchange mechanism involving the feedstock and the catalyst surface. By similar experiments direct evidence for catalytic fluorination and chlorination has been found for the transformations shown in Scheme 1.6.

Scheme 1.6 The Halogen Exchange Model



Further investigation of this catalytic surface using [^{18}F]-fluorine has shown that there are three types of fluorine species present on the surface [68]. The first can be described as hydrogen fluoride monomers or oligomers that are weakly adsorbed on the catalyst surface. They are easily removed by flow of an inert gas. The second type is irreversibly bound to the catalyst and does not take part in catalytic reactions. It is believed to be directly bonded to chromium(III) and is likened to chromium(III) fluoride. The third type is catalytically active and is involved in the halogen exchange reactions. It is possible that it is associated with the Cr^{IV} and Cr^{VI} sites. As reaction proceeds the amount of irreversibly bound fluorine increases [69] thus relating the three types of surface fluorine as follows:

HF(weakly adsorbed) $\longrightarrow$ catalytically active $F\text{->}Cr^{III}\text{-}F$

Studies using [^{36}Cl]-chlorine labelled chlorofluoro-ethanes and $H^{36}Cl$ have both substantiated the results on Scheme 1.6 and also provide an indication of the nature of the surface chlorine species present [70].

Two types were found; one that was irreversibly bound to the surface and inert to reactions, the other was catalytically labile. Both species are analogous to those formed by fluorine.

1.9 The Behaviour of Chlorofluorocarbons in the Presence of Aluminium(III) Chloride

The behaviour of chlorofluoroethanes in the presence of aluminium(III) chloride was studied extensively by Burton [71]. In most cases, using a variety of conditions he achieved isomerisation and chlorination of the starting material. For longer chain chlorofluorocarbons e.g. propanes and butanes the product mixture contained fully halogenated C_4, C_3, C_2, and C_1 molecules together with $CCl_2{=}CCl_2$. The exception was $CF_3CCl_2CCl_2CF_3$ which reacted with aluminium(III) chloride according to equation 1.32.

$$CF_3CCl_2CCl_2CF_3 \longrightarrow CCl_2{=}CCl_2 + CCl_3CCl_3 \qquad \text{eqn. 1.32}$$

The fate of the fluorine in this reaction was not determined. The reactions of the butanes $CClF_2CClFCClFCClF_2$ and $CClF_2CClFCF_2CCl_2F$ under similar conditions are shown in equations 1.33 and 1.34 respectively.

$$\begin{aligned} CClF_2CClFCClFCClF_2 \;\;->\;\; & CF_3CCl_2CCl_2CF_3 + CClF_3\text{ (trace)} \\ & + CF_3\ CCl_2F\text{(trace)} + CF_3CCl_3\text{(trace)} \\ \text{equation 1.33} \qquad & + CCl_2{=}CCl_2 + CCl_3CCl_3 \end{aligned}$$

$$\begin{aligned} CClF_2CClFCF_2CCl_2F \;->\; & CF_3CCl_2CF_2CCl_2F + \\ & CF_3CClFCF_2CCl_2F + CClF_3\text{ (trace)} \\ & + CF_3CCl_2F + CCl{=}CCl_2 \\ \text{equation 1.34} \qquad & + CCl_3CCl_3\text{(trace)} + C_6Cl_6\text{(trace)} \end{aligned}$$

From the results of these studies Burton proposed that the relevant order for reactivity towards the rearrangement reaction $RCXFCXF_2$ -> RCX_2CF_3 in the presence of aluminium(III) bromide or aluminium(III) chloride was terminal 1,2 dihalides > internal straight chain dihalides > cyclic dihalides.

In contrast to Burton's findings Hu and Lu showed, that on reaction with aluminium(III) chloride, $CCl_2FCClFCF_2CCl_2F$ produces entirely halogenated butanes [72] according to equation 1.35.

$$\begin{aligned} CClF_2CClFCF_2CCl_2F \rightarrow\ & CClF_2CClFCF_2CCl_3 \\ & + CCl_2FCClFCF_2CCl_3 \\ & + CCl_3CClFCF_2CCl_3 \\ & + CCl_3CCl_2CF_2CCl_3 \end{aligned}$$

equation 1.35

No isomeric products were obtained but the fluorines were systematically replaced by chlorine in the order.

$$-CCl_2F > -CClF_2 > -CClF- > -CF_2$$

Perhaloolefins with at least three carbon atoms rearrange in the presence of aluminium(III) chloride or bromide according to equation 1.36.

$$CF_2{=}CClCF_2CCl{=}CF_2 \rightarrow CF_2{=}CClCF{=}CClCF_3$$

equation 1.36

Reaction will only occur if the temperature is raised above the melting point of the olefin [73]. The action of aluminium(III) chloride on $CF_2{=}CFCF_3$ is shown in equation 1.37 [74].

$$\begin{aligned} CF_2{=}CFCF_3 \rightarrow\ & CF_3CF{=}CCl_2 + CF_3CF{=}CClF + CClF_2CF{=}CCl_2 \\ & \underbrace{CCl_3CF{=}CCl_2}_{\text{major products}} + \underbrace{CCl_2FCF{=}CCl_2 + CCl_3CCl{=}CCl_2}_{\text{minor products}} \end{aligned}$$

The presence of the double bond aids the replacement of fluorine by chlorine on the terminal $=CF_2$ group but the

-CF=group is inert to replacement. The mechanism proposed for this type of rearrangement is ionic and involves an intramolecular isomerisation (Scheme 1.7).

1.9.1 The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride

It was while studying the electrophilic reactions of CX- and CFX- compounds that Miller discovered the chlorinating ability of aluminium(III) chloride in the reaction (equation 1.38) [75].

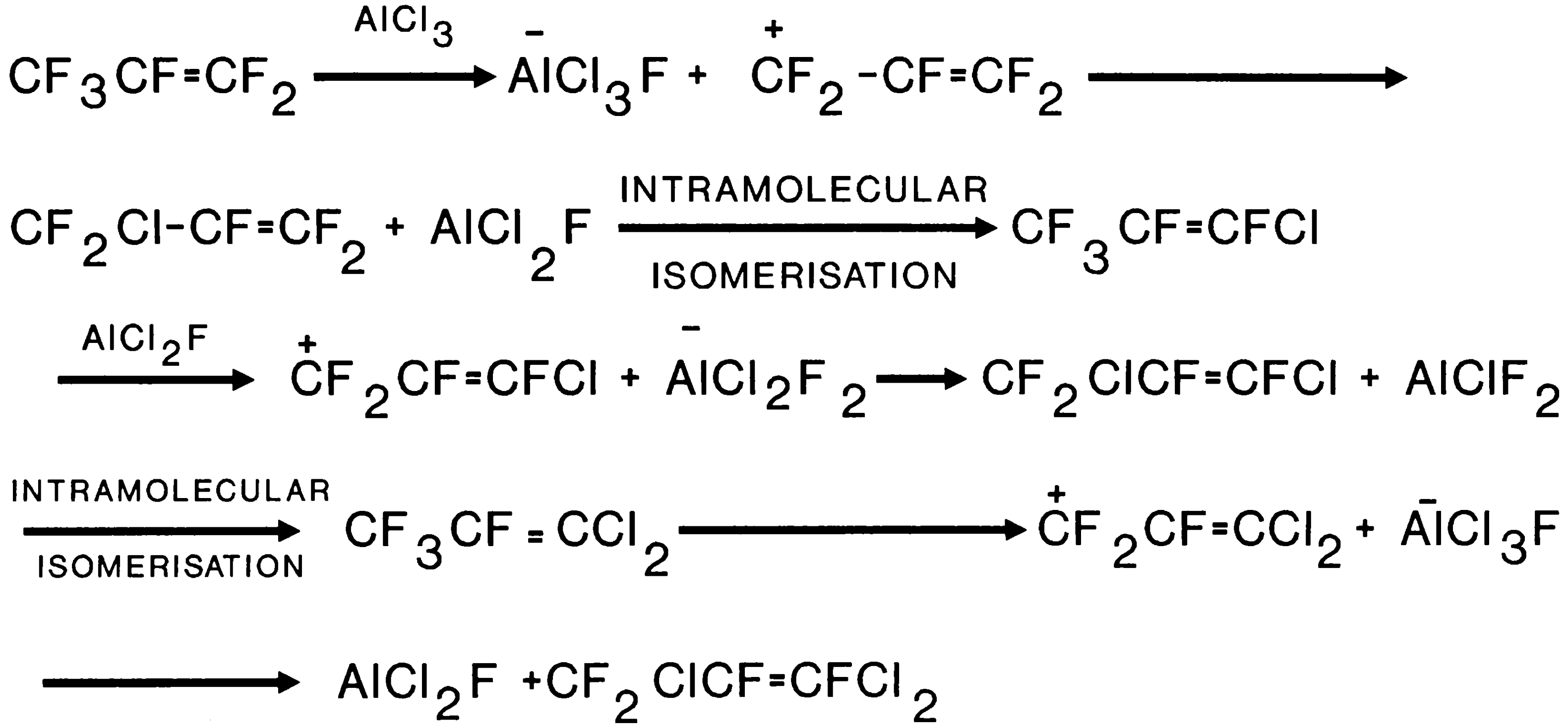
$$CCl_2FCClF_2 \rightarrow CCl_3CClF_2 \qquad \text{equation 1.38}$$

Further investigations of this work led to the discovery of the "Miller reaction" [76]. Miller refluxed CCl_2FCClF_2 with aluminium(III) chloride at 60°C for 5 h and obtained the product mixture shown in equation 1.39.

$$\begin{array}{lllllll} CCl_2FCClF_2 \rightarrow & CCl_3CF_3 & + & CCl_3CClF_2 & + & CCl_3CCl_3 & \\ & 50\% & & 40\% & & 5\% & \\ & + \; CCl_2FCClF_2 & & & & & \text{equation 1.39} \\ & 5\% & & & & & \end{array}$$

He repeated the reaction using [^{36}Cl]-chlorine labelled aluminium(III) chloride and discovered that radioactivity was found only in the chlorinated products CCl_3CClF_2 and CCl_3CCl_3. He therefore concluded that the isomerisation $CCl_2FCClF_2 \rightarrow CCl_3CF_3$ occurred via an intramolecular process. This was the first time that evidence had been obtained for intramolecular isomerisation. Studies of the isomerisation reaction

Scheme 1.7



$$CF_3CF{=}CF_2 \xrightarrow{AlCl_3} \overset{-}{Al}Cl_3F + \overset{+}{C}F_2{-}CF{=}CF_2 \longrightarrow$$

$$CF_2Cl{-}CF{=}CF_2 + AlCl_2F \xrightarrow[\text{ISOMERISATION}]{\text{INTRAMOLECULAR}} CF_3CF{=}CFCl$$

$$\xrightarrow{AlCl_2F} \overset{+}{C}F_2CF{=}CFCl + \overset{-}{Al}Cl_2F_2 \longrightarrow CF_2ClCF{=}CFCl + AlClF_2$$

$$\xrightarrow[\text{ISOMERISATION}]{\text{INTRAMOLECULAR}} CF_3CF{=}CCl_2 \longrightarrow \overset{+}{C}F_2CF{=}CCl_2 + \overset{-}{Al}Cl_3F$$

$$\longrightarrow AlCl_2F + CF_2ClCF{=}CFCl_2$$

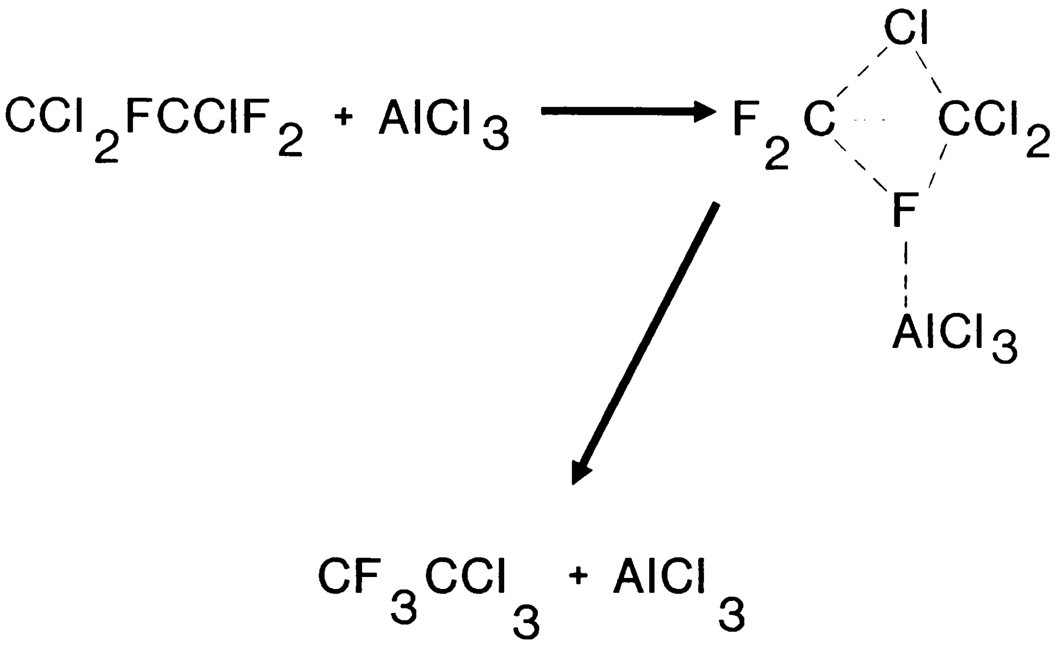
using various Lewis acid catalysts have shown that it is specific to aluminium(III) bromide and aluminium(III) chloride [71]. Both are very strong Lewis acids and it has already been shown that strong Lewis acid sites are required for the isomerisation of CCl_2FCClF_2 -> CCl_3CF_3 [64]. Aluminium(III) bromide is the stronger Lewis acid, and the isomerisation occurs at lower temperatures [71].

On the basis of these findings a reaction mechanism was proposed similar to the one used in later years by Canesson [64] and Kolditz [60]. It is shown in Scheme 1.8. An ionic mechanism was not favoured as it would allow exchange between the catalyst and the adsorbed species.

The relationship between the isomerisation and chlorination reactions in this system has been studied by Okuhara [77]. He observed that isomerisation did not always occur but that chlorination occurred in every case tried. After reaction analysis of the catalyst showed that its composition corresponded to AlF_xCl_{3-x}. This type of catalyst has already been used successfully in the isomerisation of CCl_2FCCl_2F [78], which is an easier transformation than CCl_2FCClF_2 -> CCl_3CF_3 [79].

When nitro benzene, tetrahydrofuran or triethylamine were added to the reaction mixture, both isomerisation and substitution reactions were inhibited. However solvents such as benzene, n-hexane and carbon disulphide selectively inhibit isomerisation.

Scheme 1.8



The chlorination reaction is believed to involve a carbocation intermediate the first step being the formation of the ion pair $[CF_2ClCCl_2]^+.[AlFCl_3]^-$. The active species for isomerisation is believed to be an aluminium chloride fluoride, formed from the substitution reaction between CCl_2FCClF_2, and aluminium (III) chloride. It was observed that vigorous stirring inhibited isomerisation [77], possibly as it prevents the formation of the active catalyst AlF_xCl_{3-x}. Once the active catalyst is formed, it is proposed that two types of species can occur on the solid surface as shown in equations 1.40 and 1.41.

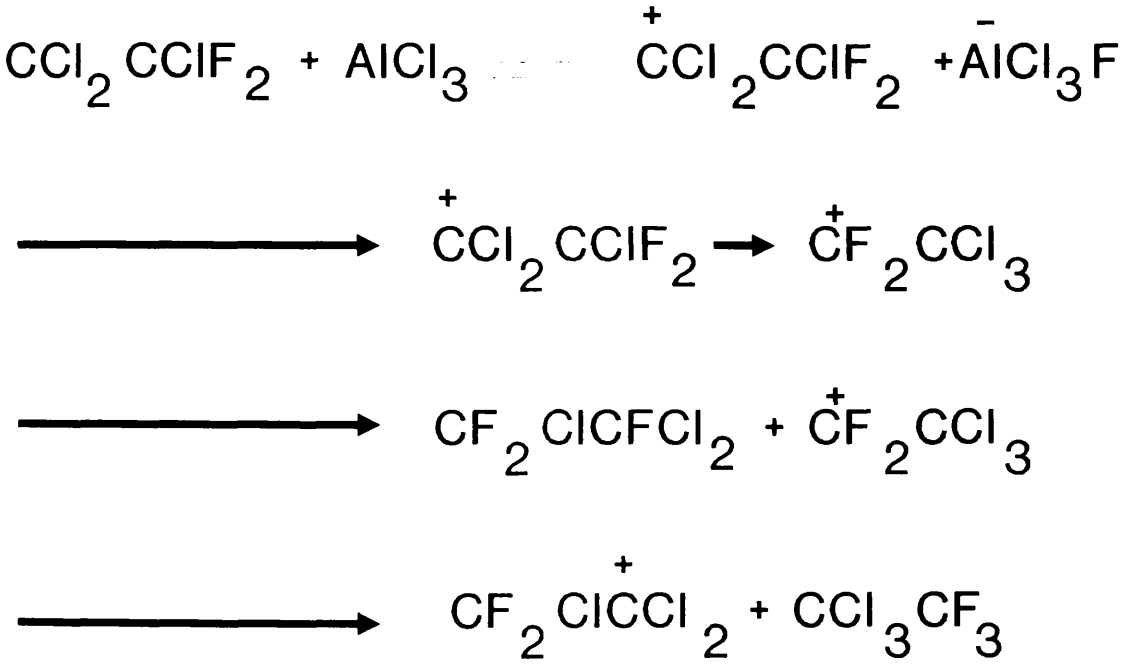
$$RF + AlCl_3 \longrightarrow R^+ + AlFCl_3^- \qquad \text{equation 1.40}$$

$$R^+AlFCl_3^- \longrightarrow R^+ + AlFCl_3^- \qquad \text{equation 1.41}$$

Catalytic activity ensues if the carbocation R^+ formed in equation 1.41 abstracts a halide from a CCl_2FCClF_2 molecule. For isomerisation to occur it is necessary for the carbocation intermediate to be more reactive and have a longer lifetime than that required for substitution. The mechanism thus proposed is shown in Scheme 1.9.

Electron spin resonance studies of halocarbon matrices reveal that the $CF_2ClCFCl$ radical can rearrange to form CF_3CCl_2 [80]. The isomerisation then proceeds via a chlorofluoroalkyl carbonionic species formed reversibly by electron transfer.

Scheme 1.9



$$CCl_2CClF_2 + AlCl_3 \longrightarrow \overset{+}{C}Cl_2CClF_2 + \overset{-}{Al}Cl_3F$$

$$\longrightarrow \overset{+}{C}Cl_2CClF_2 \rightarrow \overset{+}{C}F_2CCl_3$$

$$\longrightarrow CF_2ClCFCl_2 + \overset{+}{C}F_2CCl_3$$

$$\longrightarrow CF_2Cl\overset{+}{C}Cl_2 + CCl_3CF_3$$

Aims of the Present Work

In Miller's original paper [76] he concluded that the isomerisation CCl_2FCClF_2 -> CCl_3CF_3 occurred via an intramolecular process. This was assumed because aluminium(III) chloride containing [^{36}Cl]-chlorine reacted with CCl_2FCClF_2 producing [^{36}Cl]-chlorine labelled CCl_3CClF_2 and unlabelled CCl_3CF_3. The description of this experiment is very brief and provides insufficient detail, with which to judge the reliability of the observation.

[^{18}F]-Fluorine and [^{36}Cl]-chlorine radiotracer studies, of the vapour phase catalytic fluorination of chlorofluoroethanes, by hydrogen fluoride over chromia catalysts, provide evidence for the involvement of surface fluorine- and chlorine- containing species in the reactions [68-70]. The reactions observed can be described as a series of F-for-Cl and Cl-for-F halogen exchanges at the catalyst surface. These results put in doubt the importance of dismutation and isomerisation reactions in the vapour phase system. In all cases the products obtained can be explained by a series of Cl-for-F, F-for-Cl halogen exchange reactions, but there was no evidence to support a direct isomerisation reaction.

In the present work the Miller reaction [76] will be re-examined using [^{36}Cl]-chlorine and [^{18}F]-fluorine labelled CCl_2FCClF_2 and [^{36}Cl]-chlorine labelled aluminium(III) chloride. This will provide information on surface adsorbed species and determine the value of Miller's original observations. In conjunction with these experiments infra-red studies of the vapour phase, during the course of the reaction, will be carried out in order to obtain kinetic information.

It was also originally intended to study the reactions of CCl_2FCClF_2 over a fluorinated commercial chromia catalyst and aluminium(III) fluoride, but during the course of the present work it was discovered that aluminium(III) chloride pretreated with CH_3CCl_3 was also a catalyst for the isomerisation CCl_2FCClF_2 -> CCl_3CF_3. Aluminium catalyses the room temperature dehydrochlorination of CH_3CCl_3 producing a purple polymeric surface [81]. A line of enquiry was set up to study this system; the results will be discussed in chapter 4.

The last line of enquiry will involve the behaviour of CCl_2FCClF_2 over chlorinated γ-alumina. γ-Alumina chlorinated with carbon tetrachloride is known to be a Lewis acid capable of catalysing the dehydrochlorination of CH_3CCl_3 [82], a reaction also catalysed by aluminium (III) chloride. The isomerisation of CCl_2FCClF_2 over CCl_4 treated γ-alumina will be studied.

Work has been carried out on the superacid aluminium(III) chloride supported on γ-alumina by Drago and Getty [83]. Preliminary studies of the behaviour of CCl_2FCClF_2 in the presence of this catalyst have been conducted, and the results obtained, together with those obtained from the CCl_4 treated γ-alumina study will be presented in chapter 5.

CHAPTER 2

EXPERIMENTAL

Aluminium(III) chloride is a very hygroscopic substance and therefore should be handled under strictly water free conditions. To ensure this criterion all work was performed in vacuo (10^{-4} Torr) or in a dry atmosphere box (H_2O < 10 ppm).

2.1 Vacuum Apparatus

The vacuum line (Figure 2.1) was constructed from Pyrex glass and consisted of a Vacuostat, used to measure the vacuum in the line, a constant volume manometer and two manifolds, all of which could be individually isolated. The equipment was evacuated using an oil sealed rotary pump, and a mercury diffusion pump to a pressure of 10^{-4} Torr. All volatile materials were prevented from entering the pumps by means of three traps cooled with liquid N_2. The constant volume manometer was calibrated before use and measurements were made to a precision of ± 0.5 Torr. The manifolds consisted of high vacuum stopcocks (Rotaflo or J. Young) with ground B14 sockets. Vacuum vessels (Figure 2.2) equipped with stopcocks (Rotaflo or J. Young) and B14 cones were attached to the sockets using Kel-F grease.

All vessels attached to the line were flamed out with a gas/oxygen flame with the system under dynamic vacuum. This results in a substantial reduction of moisture adsorbed on the surface of the vessels [84].

Figure 2.1 The Vacuum Line

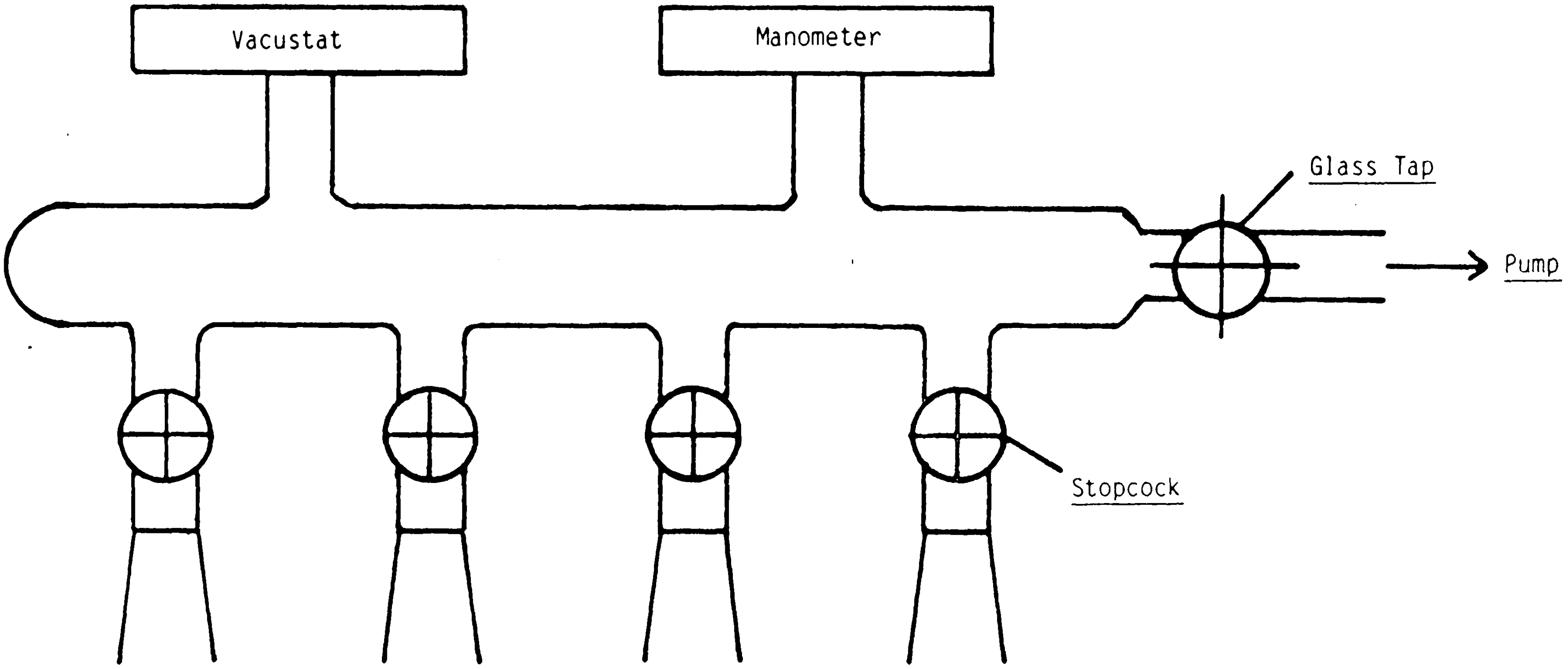
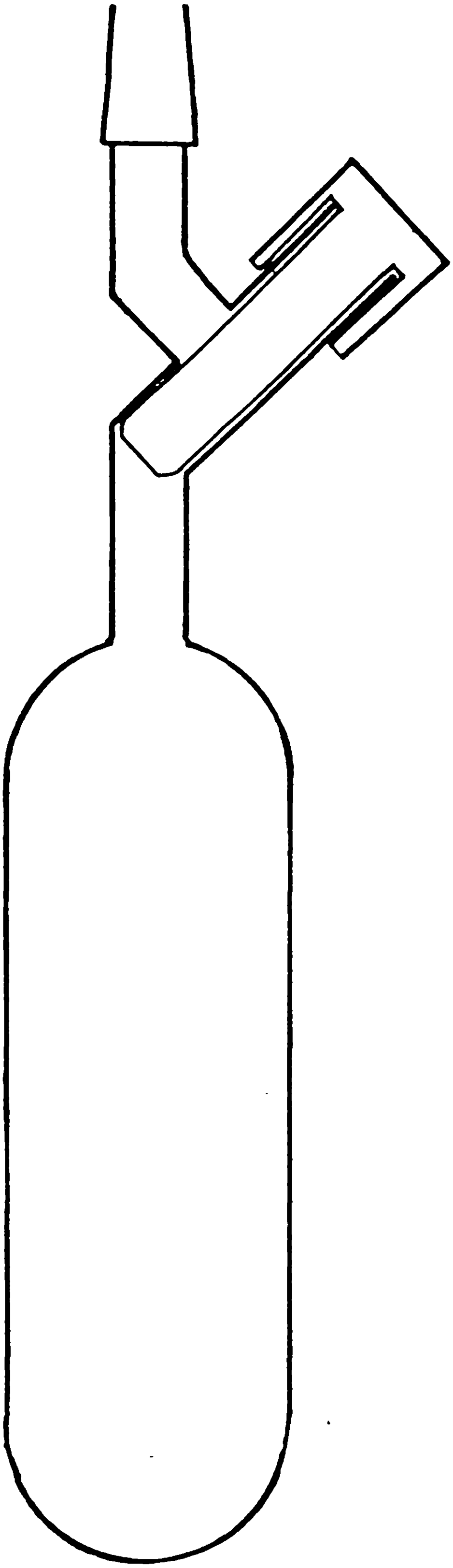


Figure 2.2 A Vacuum Vessel



2.2 The Dry Box

A glove box with nitrogen atmosphere was used for handling solid samples (H_2O < 10 ppm. Faircrest). All vessels were thoroughly flamed out before being placed in the box.

2.3 Purification of Reactants

2.3.1 Purification of 1,1,2-Trichlorotrifluoroethane

1,1,2-Trichlorotrifluoroethane (ICI C & P Ltd) was degassed by three freeze-thaw cycles before distillation onto activated 3A molecular sieves. Its composition was determined by G.C. and ^{19}F n.m.r. There were no detectable impurities.

2.3.2 Purification of 1,1,1-Trichlorotrifluoroethane

1,1,1-Trichlorotrifluoroethane (ICI C & P Ltd) was purified by the same method used in 2.3.1. Analysis by ^{19}F n.m.r of the solvent showed its composition to be 1.0% 112a, 3.8% 113, 95.2% 113a.

2.3.3 Purification of 1,1,1-Trichloroethane

1,1,1-Trichloroethane (99% BDH) was purified as in 2.3.1 but was stored in a darkened vessel.

2.3.4 Purification of 1,1-Dichloroethene

1,1-Dichloroethene (99% Aldrich Chemical Co) was vacuum distilled to remove stabiliser, which inhibits oxidation, then, was stored over activated 3A molecular sieves in a darkened vessel to avoid photopolymerisation. It was degassed before use.

2.3.5 Purification of Chloroform

Chloroform (99% May & Baker) was purified according to the method used in 2.3.4.

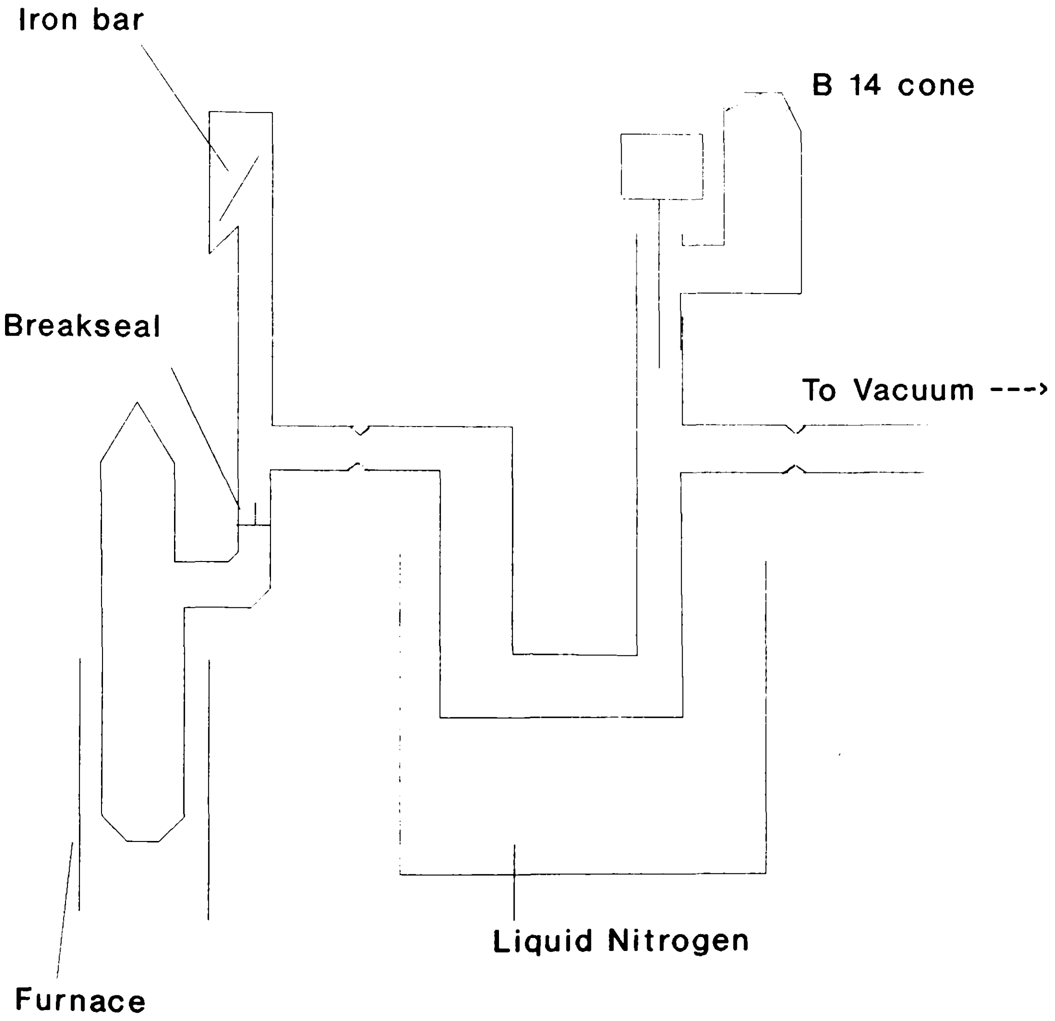
2.3.6 Purification of Perfluoro-n-hexane

Perfluoro-n-hexane (99% ICI C & P Ltd) was purified according to the method used in 2.3.4.

2.3.7 Purification of Aluminium(III) Chloride

An evacuated vessel was flamed out, under dynamic vacuum, three times before being placed in the dry box. Aluminium(III) chloride (anhydrous > 99% pure Fluka AG) was added together with a piece of aluminium wire (99.99% pure Fluka AG/Balzers). The function of the aluminium wire was to remove any iron chloride present. The aluminium(III) chloride was degassed before attachment via the breakseal to the sublimation apparatus (Figure 2.3). The apparatus was flamed out three times before the breakseal was opened and the aluminium(III) chloride heated to 120°C using a furnace. The sublimate was trapped in the Pyrex U-bend of the

Figure 2.3 Sublimation Apparatus



reaction vessel held at -196°C under vacuum (10^{-4} Torr). The apparatus was heated gently during this operation to prevent the sublimate sticking to the walls of the apparatus. Once the sublimation process was completed, the reaction vessel was sealed under vacuum, at the constrictions, using a gas/oxygen flame. The vessel was attached to the vacuum line and the freshly sublimed aluminium(III) chloride was used immediately.

2.4 Radiochemical Isotopes

2.4.1 The [^{36}Cl]-Chlorine Radioisotope

The [^{36}Cl]-chlorine radioisotope is a soft beta β^- emitter and has a half life of 3×10^5y [85]. An aqueous solution of Na^{36}Cl (Amersham International) was diluted with concentrated hydrochloric acid to give a [^{36}Cl]-chloride solution with a specific activity of 9.3 x 10^5 Bq cm^{-3}.

2.4.2 The [^{18}F]-Fluorine Radioisotope

The [^{18}F]-fluorine radioisotope is a positron β^+ emitter and the annihilation of β^+ by electrons causes the release of γ-radiation. The half life of [^{18}F]-fluorine is 109.8 min [85], therefore all experiments using this isotope must be completed within one working day. After six half lives (11 h) only 1.56% of the original activity remains.

2.5 Radiochemical Preparations

2.5.1 The Preparation and Purification of [^{36}Cl]-Chlorine labelled Dichlorine

The apparatus used in this preparation is shown in Figure 2.4. Anhydrous [^{36}Cl]-Cl_2 was generated from the reaction between aqueous [^{36}Cl]-HCl andaqueous potassium permanganate, $KMnO_4$, according to equation 2.1.

$$4H^{36}Cl + KMnO_4 \rightarrow K^{36}Cl + MnO_2 + 2H_2O + {}^{3}/_{2}[Cl^{36}Cl]$$

Equation 2.1.

A solution of potassium permanganate (0.101 mol) in water ($300 cm^3$) contained in a pressure equilibrated dropping funnel, was added dropwise, with stirring to a solution of $Na^{36}Cl$ ($2.4\ cm^3$, 60 μCi Amersham International) in concentrated HCl ($30cm^3$, 36% w/w May & Baker) contained in a round bottomed flask (Vessel A). This was heated to 100°C using a water bath. Vessel A was attached to the vacuum pump and was periodically opened to reduce pressure in the system. This procedure was repeated regularly to draw gaseous [^{36}Cl]-Cl_2 into the cooled traps. Traps B & C were held at -80°C using methylene chloride/solid CO_2 baths and contained solid $KMnO_4$ to remove excess HCl. Traps D & E were held at -80°C using methylene chloride/solid CO_2 and contained P_2O_5 to remove moisture. The collection vessel F, held at -196°C, was equipped with high vacuum stopcocks (J. Young) so that it could be isolated from the system. The [^{36}Cl]-Cl_2 collected in this vessel was transferred to the vacuum line where it was degassed and stored over P_2O_5 in a Monel metal bomb.

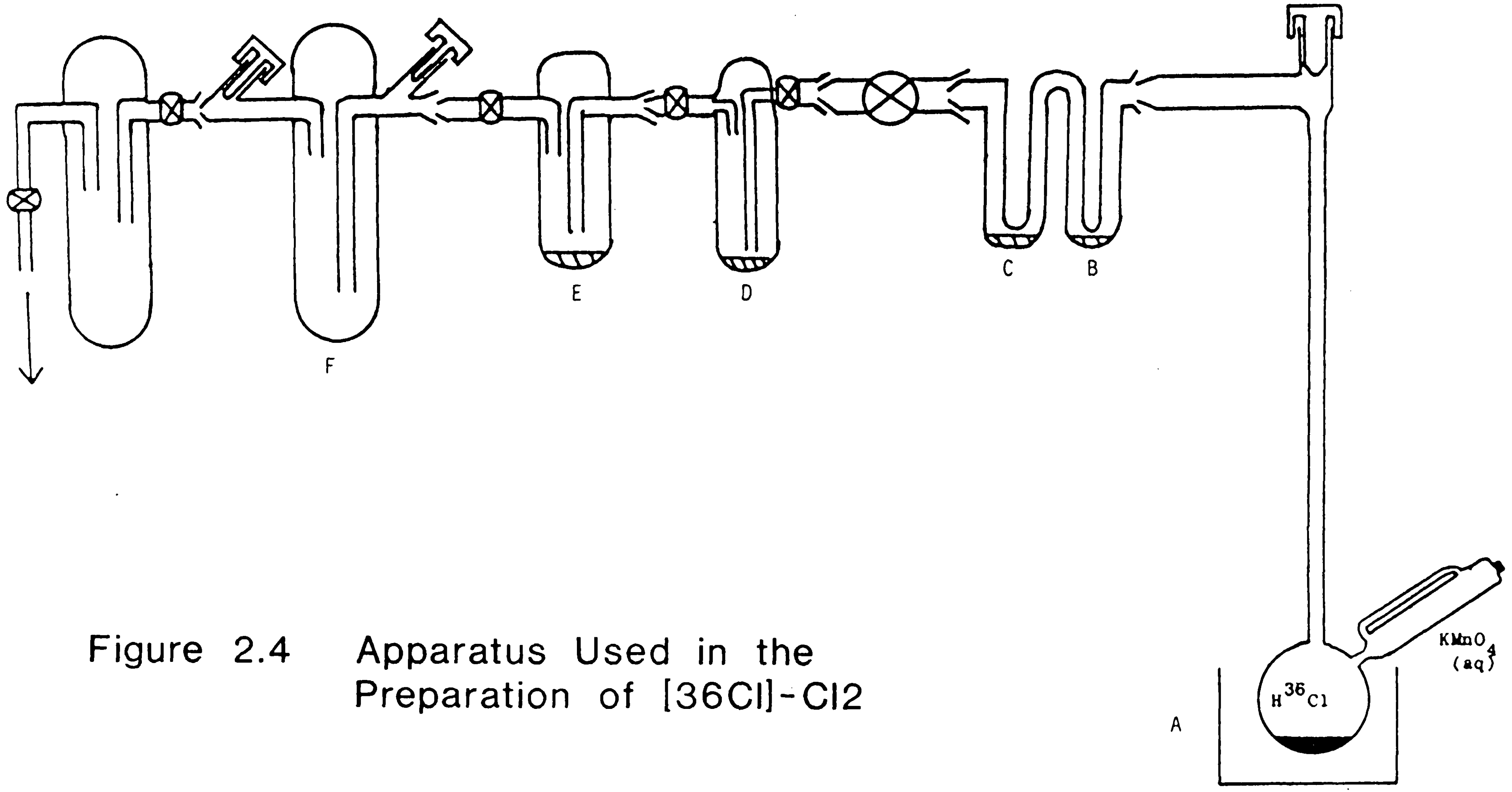


Figure 2.4 Apparatus Used in the Preparation of [36Cl]-Cl2

2.5.2 Preparation and Purification of [^{36}Cl]-Chlorine labelled 1,1,2-Trichlorotrifluoroethane

This method was derived from that used for the preparation of 1,1-dichlorotetrafluoroethane by L. Rowley [86]. [^{36}Cl]-Chlorine labelled CCl_2FCClF_2 was prepared by the vapour phase, mercury lamp photolysis of 1,1,2-trifluoroethane CH_2FCHF_2 and Cl_2 according to equation 2.2.

$$CH_2FCHF_2 + 3[^{36}Cl]\text{-}Cl_2 \xrightarrow{h\nu} [^{36}Cl]\text{-}CCl_2FCClF_2 + 3H^{36}Cl$$

Equation 2.2

[^{36}Cl]-Cl_2 as prepared in 2.5.1 (10.87 mmol) and CH_2FCHF_2 (3.53 mmol PCR Research Chemicals Inc.) were distilled into an evacuated Pyrex vessel (2*l*). The mixture was irradiated at room temperature for 24 h, after which the products were distilled onto moist NaOH pellets and left at room temperature for 24 h. This procedure removed $H^{36}Cl$ and excess [^{36}Cl]-Cl_2. The [^{36}Cl]-CCl_2FCClF_2 (count rate 616 min^{-1} $mmol^{-1}$) was distilled onto activated 3A molecular sieves. It was identified by gas chromatography and infrared spectroscopy.

2.5.3 Preparation and Purification of [^{36}Cl]-Chloride labelled Carbon Tetrachloride.

[^{36}Cl]-Chlorine labelled CCl_4 was prepared by the thermal chlorination of chloroform with [^{36}Cl]-Cl_2 [87] according to equation 2.3.

$$CHCl_3 + [^{36}Cl]\text{-}Cl_2 \longrightarrow [^{36}Cl]\text{-}CCl_4 + [^{36}Cl]\text{-}HCl$$

Equation 2.3.

Dry $CHCl_3$ (see 2.3.5) (28.2 mmol AnalaR May & Baker) and $[^{36}Cl]\text{-}Cl_2$ (34.7 mmol as prepared in 2.5.1) were distilled into a conditioned evacuated Monel metal bomb (i.e. one that had previously contained HCl or Cl_2) and heated to 330°C for 42 h. The most volatile products, mainly HCl but also some $OCCl_2$ were removed by cooling the bomb to -80°C using a methylene chloride/solid CO_2 both before opening it to the manifold. The vapour in the manifold above the product mixture was condensed into a bomb held at -196°C (liquid N_2). This process was repeated three times. The remaining fraction was distilled into a vacuum vessel containing mercury, and left at room temperature for 2 h to remove any unreacted Cl_2 by formation of the involatile $HgCl_2$. The presence of $OCCl_2$ in the product mixture was attributed to the reaction of $CHCl_3$ with metal oxides or H_2O in the walls of the Monel bomb. The $[^{36}Cl]\text{-}CCl_4$ was distilled into a darkened vessel containing activated 3A molecular sieves and degassed before use. It was identified by infrared spectroscopy.

2.5.4 The Preparation and Purification of $[^{36}Cl]$-Chlorine labelled Aluminium(III) Chloride.

$[^{36}Cl]$-Chlorine labelled aluminium(III) chloride was prepared by the thermally promoted isotope exchange between solid aluminium(III) chloride and $[^{36}Cl]\text{-}CCl_4$ as shown in equation 2.4.

$$AlCl_3 + [^{36}Cl]\text{-}CCl_4 \longrightarrow [^{36}Cl]\text{-}AlCl_3 + CCl_4$$

Equation 2.4.

This procedure was derived from a literature method [33]. [^{36}Cl]-Chlorine labelled CCl_4 (0.98 mmol as prepared in 2.5.3) was distilled onto freshly sublimed aluminium(III) chloride (see 2.3.7) cooled to -196°C in a Pyrex reaction vessel. The reactants were heated to 60°C for 23 h, then cooled to room temperature. The volatile products were removed by distillation into an evacuated ampoule at -196°C. The [^{36}Cl]-chlorine labelled solid had a specific count rate of the order of 10^4 min^{-1} $mmol^{-1}$.

2.5.5 The Preparation and Purification of [^{36}Cl]-Chlorine labelled Hydrogen Chloride [88].

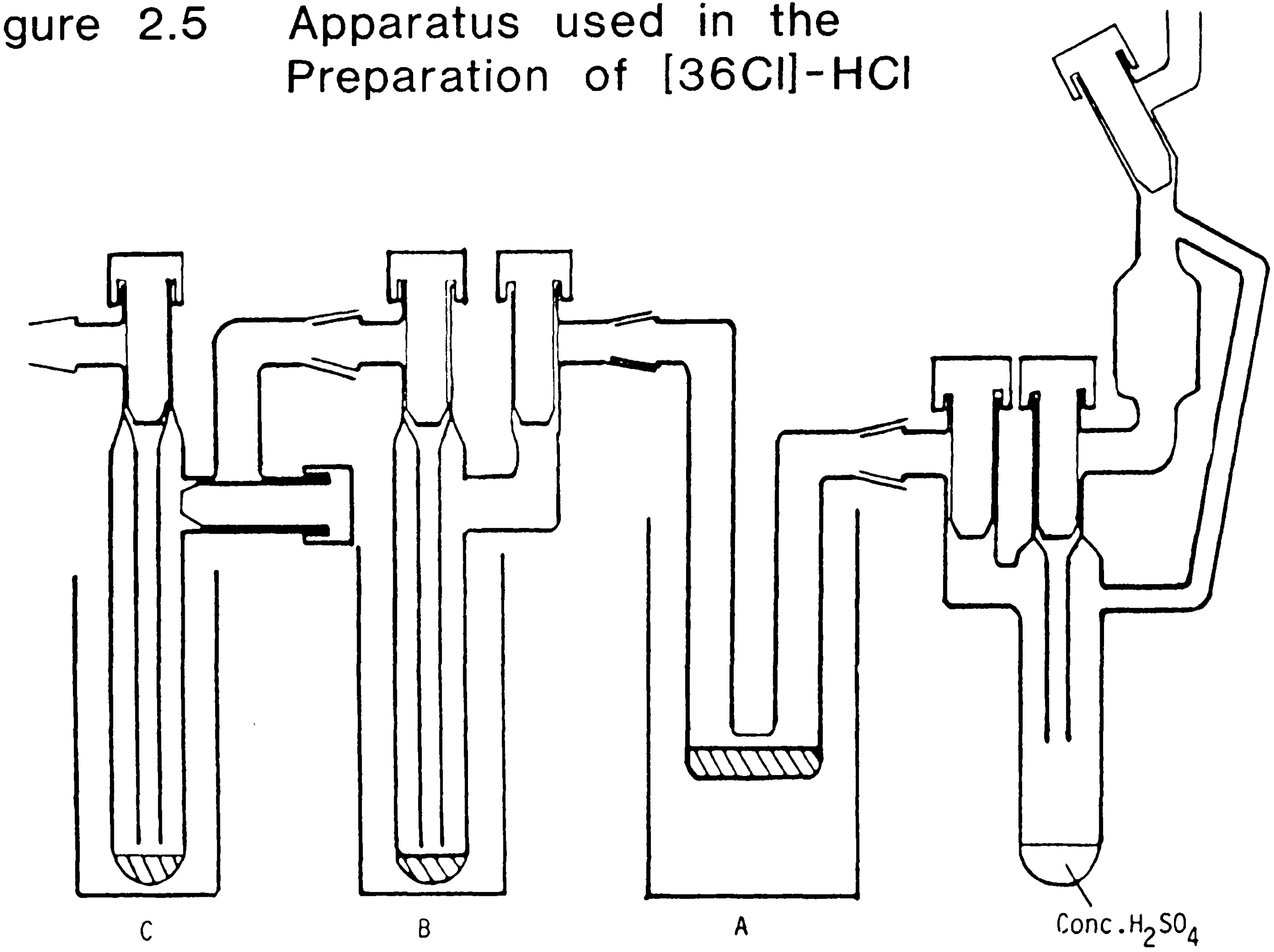
The apparatus for this preparation is shown in Figure 2.5. Anhydrous, gaseous [^{36}Cl]-HCl was evolved from the reaction between an aqueous solution of $H^{36}Cl$ and concentrated H_2SO_4 as shown in equation 2.5.

$$H^{36}Cl(aq) + H_2SO_4(aq) \longrightarrow H^{36}Cl(g) + H_2SO_4(aq)$$

Equation 2.5.

Aqueous [^{36}Cl]-NaCl (25 cm^3 62.5 µCi Amersham International) was diluted with HCl (10 cm^3, 35.4% w/v, May & Baker). This solution was added dropwise from a pressure equilibrated dropping funnel to concentrated sulphuric acid. A glass encased iron bar and magnet were used to agitate the mixture. The gaseous $H^{36}Cl$ generated was distilled using a series of two traps to remove moisture. Trap A contained P_2O_5 held at -80°C (methylene chloride/solid CO_2). Trap B contained P_2O_5 held at -90°C (methylene chloride/liquid N_2).

Figure 2.5 Apparatus used in the Preparation of [36Cl]-HCl



Collection vessel C contained two high vacuum stopcocks (J. Young) so that it could be isolated from the system. It contained P_2O_5 and was held at -120°C (isopentane/liquid N_2). The $H^{36}Cl$ collected in vessel C was transferred to the vacuum line, degassed and vacuum distilled from -90°C to -196°C and stored over P_2O_5 in a vacuum flask at -196°C.

2.5.6 The Preparation and Purification of [^{36}Cl]-Chlorine labelled 1,1,1-Trichloroethane.

[^{36}Cl]-Chlorine labelled 1,1,1-trichloroethane was produced by the room temperature hydrochlorination of $CH_2{=}CCl_2$ with $H^{36}Cl$ as shown in equation 2.6. The reaction is catalysed by anhydrous iron(III) chloride.

$$CH_2{=}CCl_2 + H^{36}Cl \xrightarrow{FeCl_3} [^{36}Cl]\text{-}CH_3CCl_3$$

Equation 2.6.

A conditioned Monel metal bomb was loaded with $FeCl_3$ (anhydrous 99.0% pure Fluka AG) in an inert atmosphere box and closed. The compound $CH_2{=}CCl_2$ (34 mmol 99% Aldrich Chemical Co) purified as described in (2.3.4) and $H^{36}Cl$ (35 mmol prepared as described in 2.5.5.) were vacuum distilled into the bomb which was then closed and held at room temperature for 48 h. Excess $H^{36}Cl$ was removed by cooling the bomb to -80°C (methylene chloride/solid CO_2) and then opening it to the manifold. The vapour in the manifold above the product mixture was isolated and condensed into a vessel held at -196°C (liquid N_2). This procedure was repeated three times.

The $[^{36}Cl]$-CH_3CCl_3 was identified by infrared spectroscopy. It was vacuum distilled from -80°C to -196°C into a darkened vessel containing activated 3A molecular sieves and diluted by the addition of inactive CH_3CCl_3 (1.5 ml AnalaR Hopkin & Williams). It was degassed before use.

2.5.7 Preparation of $[^{18}F]$-labelled Caesium Fluoride.

The $[^{18}F]$-fluorine isotope was prepared using the SURRC facilities at East Kilbride. Lithium carbonate pellets (20 x 0.1g) were irradiated in a neutron flux (3.6 x 10^{12} neutron cm^{-2} s^{-1}) for ca 40 min using the large rabbit system. $[^{18}F]$-Fluorine was produced from the sequence $^{6}Li(n,\alpha)^{3}H$, $^{16}O(^{3}H,n)$, ^{18}F [89]. The pellets were dissolved in 50% v/v H_2SO_4/H_2O and the $H^{18}F$ liberated was distilled into an aqueous solution of caesium hydroxide cooled to 0°C. This solution containing $Cs^{18}F$ was neutralised by the addition of aqueous HF and evaporated to dryness, producing a finely divided white powder.

2.5.8 Preparation of $[^{18}F]$-Fluorine labelled Uranium Hexafluoride

$[^{18}F]$-Fluorine labelled caesium fluoride was activated by treatment with $(CF_3)_2CO$ (23 mmol) for 30 min. The volatile material was distilled into an evacuated bomb held at -196°C and the $[^{18}F]$-CsF was heated to 110°C for 30 min. The compound UF_6 (11.7 mmol ^{235}U depleted BNFL) was distilled onto the $[^{18}F]$-CsF held at -196°C. The mixture was warmed to room temperature then heated to 110°C for 60 min. A sample of the product was removed and counted as a solution in MeCN. The specific count rate of the $[^{18}F]$-UF_6 prepared was of the order 10^5 COUNTS $MIN^{-1}MMOL^{-1}$.

2.6 Gas Chromatography

2.6.1 Equipment

The GC analysis of product mixtures was carried out using a Perkin-Elmer Sigma 3B dual Flame Ionisation detector gas chromatograph and a Perkin-Elmer 8410 gas chromatograph equipped with a hot wire detector. Flame ionisation is more sensitive than hot wire detection and can detect components in very small concentrations, though, the compounds are destroyed during the process. Hot wire detection does not destroy the sample components and once separated by G.C. they can be analysed for radioactivity using an Isoflo counter. It is therefore essential to obtain baseline separation, so that the radioactivity of each fraction could be calculated precisely.

2.6.2 Separation of 1,1,1-Trichlorotrifluoroethane and 1,1,2-Trichlorotrifluoroethane

The main reaction studied in this work was the isomerisation of CCl_2FCClF_2 to CCl_3CF_3, therefore it was necessary to determine their individual compositions in the product mixture. Separation by G.C. proved difficult as CCl_3CF_3 boils at 45.8°C and CCl_2FCClF_2 boils at 47.7°C. When using capillary columns the retention times for the isomers were less than 1 min however no separation was achieved. Packed columns proved successful but retention times very long ca 20 min. Any reduction of retention times by either increasing the oven temperature or increasing the flow rate caused the peaks to merge with baseline separation.

The most successful column used was made of stainless steel (2m x $^1/_8$"od). It was packed with 80/120 carbopack B/3% SP-1500 (Supelco), a graphitized carbon which has a surface area of ca $100 m^2 g^{-1}$.

The conditions used for the separation of the isomers and their retention times are shown in Table 2.1. Less volatile components of the product mixture had longer retention times under isothermal conditions. To reduce these it was necessary to ramp the temperature of the oven.

Table 2.1

The Separation of CCl_2FCClF_2 and CCl_3CF_3 by Gas Chromatography

Oven Conditions

Method of Detection	Oven Temp.1 (°C)	Time (min)	Ramp Rate °C min^{-1}	Oven Temp.2 (°C)	Time (min)
Flame ionisation (F.I.D)	60	22	10	200	10
Hot Wire (H.W)	60	90	-	-	-

CFC	Retention Time (min)	
	F.I.D	H.W.
CCl_2FCF_3	4.2	4.6
CCl_2FCClF_2	16.8	19.5
CCl_3CF_3	18.8	22.0
CCl_3CClF_2	32.1	56.8
CCl_3CCl_2F	36.9	-
CCl_3CCl_3	44.1	88.9

Injector temperature : 100°C

Detector temperature : 200°C

Carrier gas N_2, Flow rate 30 cm^3 min^{-1}

2.6.3 Calibration Chromatographs.

The response factor of a component on a column can affect its detection and the resulting chromatograph. If the response factors of a sample's components are different, then a correction must be made so that the component ratios analysed by G.C. correspond to the true ratios in the sample. Samples of mole ratios 1:1, $CCl_2FCClF_2:CCl_3CF_3$ and 1:100 $CCl_2FCClF_2:CCl_3CF_3$ were injected onto the column. The resulting chromatographs gave peak areas with the expected ratios, therefore no correction factor was required.

2.6.4 Gas Chromatography/Mass Spectrometry (G.C./M.S).

When unknown peaks were encountered, the optimum conditions for chromatography were established and the sample was identified by G.C/M.S. As the component molecules elute from the column to the inside of the mass spectrometer (V.G.7070-F analytical instrument), they are bombarded with a beam of electrons causing them to fragment and ionise. This process is reproducible providing the instrument conditions are constant. The recording of the masses of the ionised fragments represents a unique "finger print" by which components can be identified. These "finger prints" were very useful in helping distinguish between the isomers of $C_2Cl_4F_2$ and $C_2Cl_2F_4$ as their isomers had similar retention times on the packed column.

2.7 Infrared Spectroscopy

2.7.1 Equipment

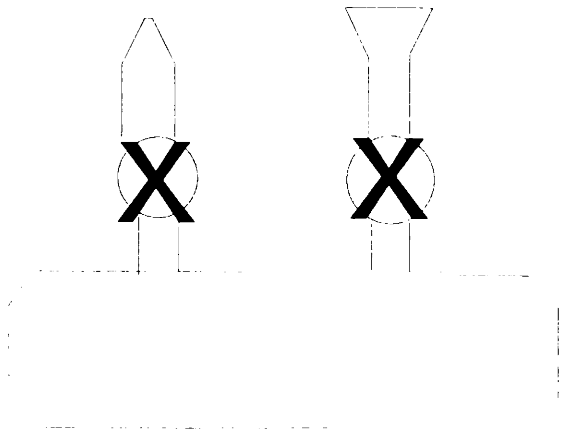
The infrared spectroscopic analyses of the vapour phase in gas/solid systems were carried out using a Perkin-Elmer 983 grating infrared spectrometer with data station. Kinetic infrared spectroscopic analyses of the vapour phase in gas/solid systems were also carried out using this instrument.

The infrared cell used in these experiments (Figure 2.6) was constructed of Pyrex glass. Its pathlength was 10 cm and it was equipped with KBr plates and a Pyrex stopcock (Springham) with a B14 cone, for attachment to a vacuum line. Joined to the body of the cell was a B14 socket to which vacuum ampoules containing solid samples could be attached and solid added in vacuo. A depression along the base of the cell ensured that solid did not mask the infrared beam. The volume of the cell was $46.99 \pm 0.5\ \text{cm}^3$. A purpose built holder for the cell enabled reproducible positioning in the infrared beam.

2.7.2 Identification of Compounds in the Vapour Phase

In all infrared spectroscopic analyses of the vapour phase in gas/solid systems, species were identified from the vapour phase spectra of pure samples, or by comparison with standard vapour phase spectra obtained from the Aldrich library of Infrared Spectra [90].

Figure 2.6 Infrared Cell



2.7.3 Calibration Spectra

The vapour phase studied in these infrared investigations consisted of 1,1,2-trichlorotrifluoroethane and its isomer 1,1,1-trichlorotrifluoroethane. The wavenumbers at which both these compounds absorb are listed in Table 2.2. The 859 cm^{-1} band of CF_3CCl_3 was very distinct and did not overlap with any bands of its isomer; it was therefore chosen to calibrate CCl_3CF_3. The nearest band of CCl_2FCClF_2 to the 859 cm^{-1} band of CCl_3CF_3 was at 816 cm^{-1} and therefore this was chosen to calibrate CCl_2FCClF_2. Both bands have strong absorbances, so only small pressures of vapour could be admitted to the cell for calibration. Calibration was achieved by admitting measured pressures of each gas to the cell and recording the spectrum from 1000 cm^{-1} to 700 cm^{-1}. The area of each band was related to a known pressure and thus the number of moles of gas present could be calculated. Plots of band area vs pressure were constructed for CCl_2FCClF_2 and CCl_3CF_3 (Figures 2.7 and 2.8 respectively).

2.7.4 Vapour Phase Infrared Analysis in Gas/Solid Systems

In these studies an evacuated ampoule containing a weighed solid sample was attached to the cell, which was then evacuated. A measured pressure of gas was admitted to the cell before it was placed in the spectrometer beam. A spectrum from $1000cm^{-1}$ to $700cm^{-1}$

Table 2.2
Infrared Band Positions CCl2FCClF2 [91]

Wavenumber cm-1	Assignment	Functional Group
1214 (s)	CF2 sym str	-CClF2
1130 (vs)	CF2 sym str	-CClF2
1118 (vvs)	CF2 asym str	-CClF2
1049 (vs)	CF str	-CClF2
1043 (vs)	CF str	-CClF2
909 (vs)	CC str	-C-C-
816 (vvs)	CCl str	
653 (w)	CCl str	-CCl2F
632 (vw)	CCl str	-CClF2
531 (vw)	CCl str	

Infrared Band Positions CCl3CF3 [92]

Wavenumber cm-1	Assignment	Functional Group
1255 (vvs)	CF3 str	-CF3
1225 (vvs)	CF3 str	-CF3
909 (vs)	CC str	-C-C-
859 (vvs)	CCl str	-CCl3
714 (vs)	CF3 bend	-CF3

Figure 2.7 CCl2FCClF2 Calibration Curve

Pressure vs Area

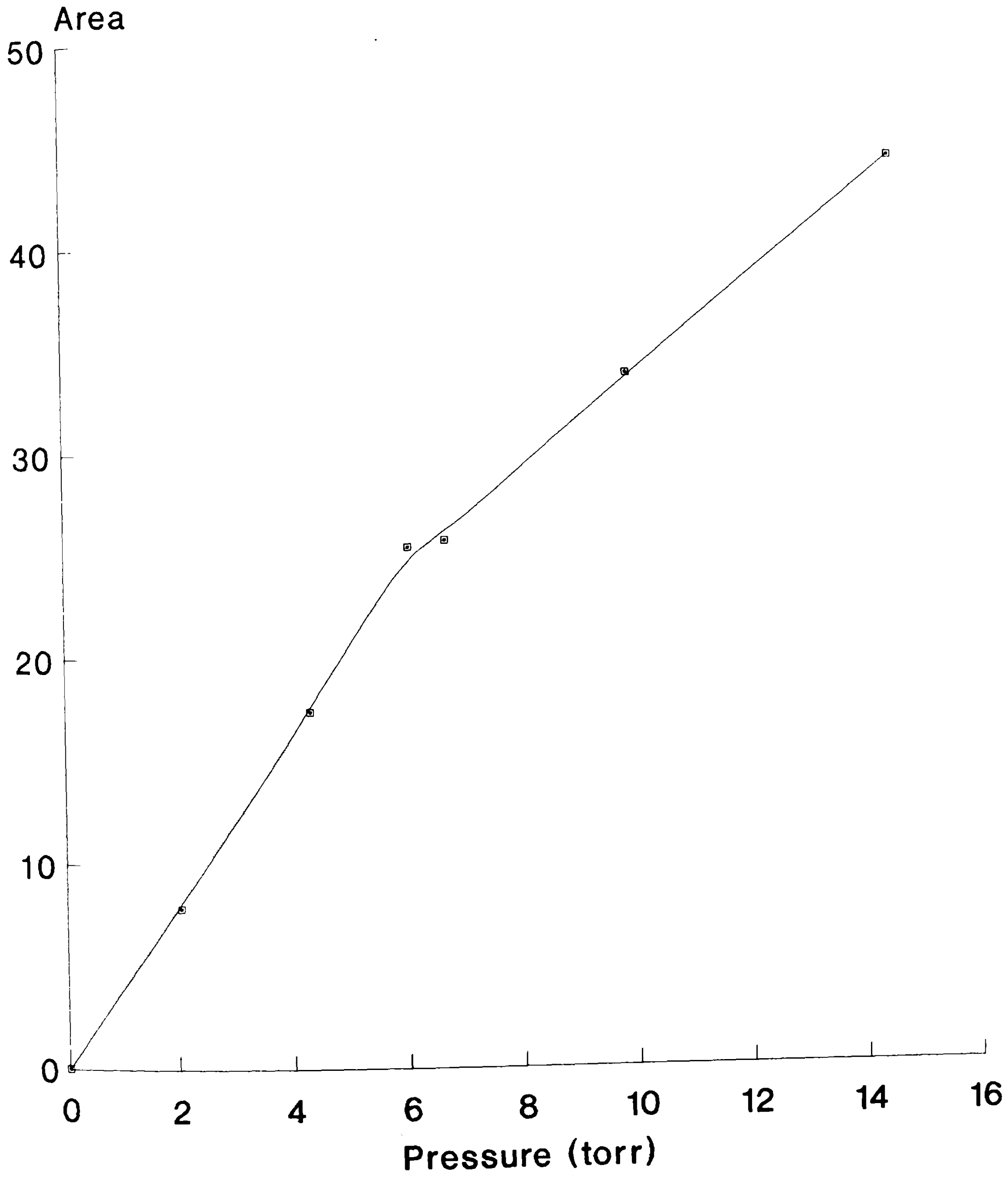
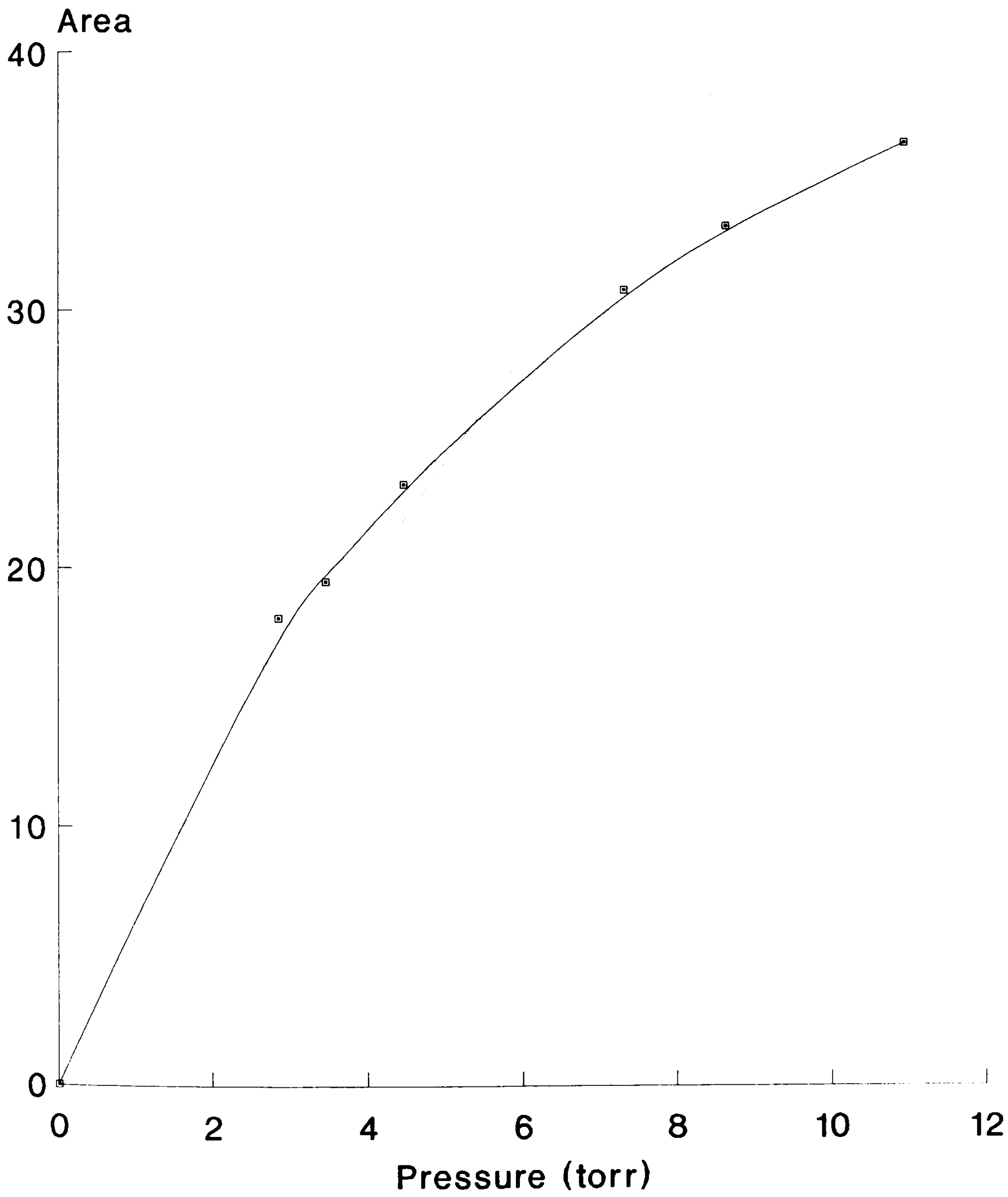


Figure 2.8 CCl3CF3 Calibration Curve

Pressure vs Area



was recorded before the stopcock of the ampoule was opened admitting solid to the system. Spectra were collected as required.

2.7.5 Kinetic Analysis of Vapour Phase Infrared Data.

The procedure was identical to that described in 2.7.4. The spectra were collected and stored on disk once every 15 min for a period of ca 16 h and subsequently once every 4 h for the last 8 h of reaction. A Perkin-Elmer program was used to treat these data and to construct for desired peaks plots of peak area vs. time. From this information kinetic plots were derived.

2.8 Nuclear Magnetic Resonance Spectroscopy

2.8.1 ^{19}F N.m.r Spectroscopy

^{19}F Nmr spectra were obtained using either Bruker WP 200 SY or AM 200 Fourier Transform nmr spectrometers at 188 MHz for ^{19}F. The magnet had a strength of 4.7 Tesla with a 5mm quadruple pole probe. The free induction decays obtained were Fourier transformed to give frequency spectra. The compound $CDCl_3$ was used as an internal lock and $CFCl_3$ as an external reference. The compounds present were identified by comparison with spectra of pure samples and by comparison with literature data [93]. Chemical shifts and coupling constants for the chlorofluoroethanes are shown in Table 2.3.

Table 2.3

^{19}F N.m.r Chemical Shifts and Coupling Constants for Chlorofluoroethanes

	δCF_3(ppm)	δCF_2(ppm)	δCF(ppm)	^{3}J(FF)(Hz)
CCl_2FCF_3	84(d)		77(q)	6
CCl_2FCClF_2		68(d)	73(t)	9
CCl_3CF_3	82(s)			
CCl_3CClF_2		65(s)		
CCl_3CCl_2F			63(s)	

q = quartet

t = triplet

d = doublet

s = singlet

2.8.2 ^{27}Al Magic Angle Spinning Solid State NMR Spectroscopy

The ^{27}Al MAS nmr spectroscopy investigation was carried out at the Industrial Research Laboratories of the University of Durham using a Varian UXR 300/89 nmr spectrometer. This is equipped with a 7.0 Tesla superconducting magnet with 89 mm vertical bore. The pulse width was 15 degrees and 1000 free induction decays were accumulated every 0.5 s. The probe was aluminium free so no background was obtained. A solution of aqueous aluminium(III) chloride was used as an external reference for all chemical shifts. The information obtained from magic angle spinning at 3kHz and 4kHz was combined with the information obtained from single pulse excitation to produce time domain data which were Fourier transformed producing frequency spectra.

2.9 Radiochemical Counting Using Geiger Müller Counters

A Geiger Müller counter is basically an earthed metal tube filled with gas, usually argon. At one end is a thin window made of mica that allows the penetration of α, β and γ radiation. The operation of a Geiger Müller counter is based on the ionisation of the argon gas by the radiation. In the centre of the tube is a thin metal wire that acts as an anode, while the metal cylinder acts as a cathode. When the gas is ionised the positive ions and electrons thus formed cause a current to flow between the wire and the tube. The electrons formed move rapidly towards the wire and the positive ions drift relatively slowly towards the wall.

When the voltage between the electrodes is high, the electrons collide with the gas molecules with such a force they cause further ionisation. Then the number of electrons collected on the wire is independent of that created by the initial irradiation. This cascade of electrons is termed as an "avalanche" and results from the phenomenon of ion multiplication. When the avalanche spreads along the entire length of the wire, the size of the voltage pulse becomes independent of the initial number of electrons created by the primary irradiation. The system now operates as a Geiger counter [94].

Secondary emission arises when the positive ions created reach the walls of the tube. This results in a spurious discharge from the counter and is normally suppressed by the addition of a "quench gas" to the system. Typical quench gases used are alcohol, ether or methane and comprise <u>ca</u> 10% of the gas in the tube. The positive ions react with these to form polyatomic organic ions and thus the energy is dissipated. The count obtained is recorded by the scaler attached to the system.

[^{36}Cl]-Chlorine has a long half life, 3 x 10^5 y, thus no decay correction was required. The maximum energy of a β particle from [^{36}Cl]-chlorine is 0.714 MeV [95]. The counter efficiency is <5% as much of the incident radiation is absorbed by the mica windows.

2.9.1 Plateau Region

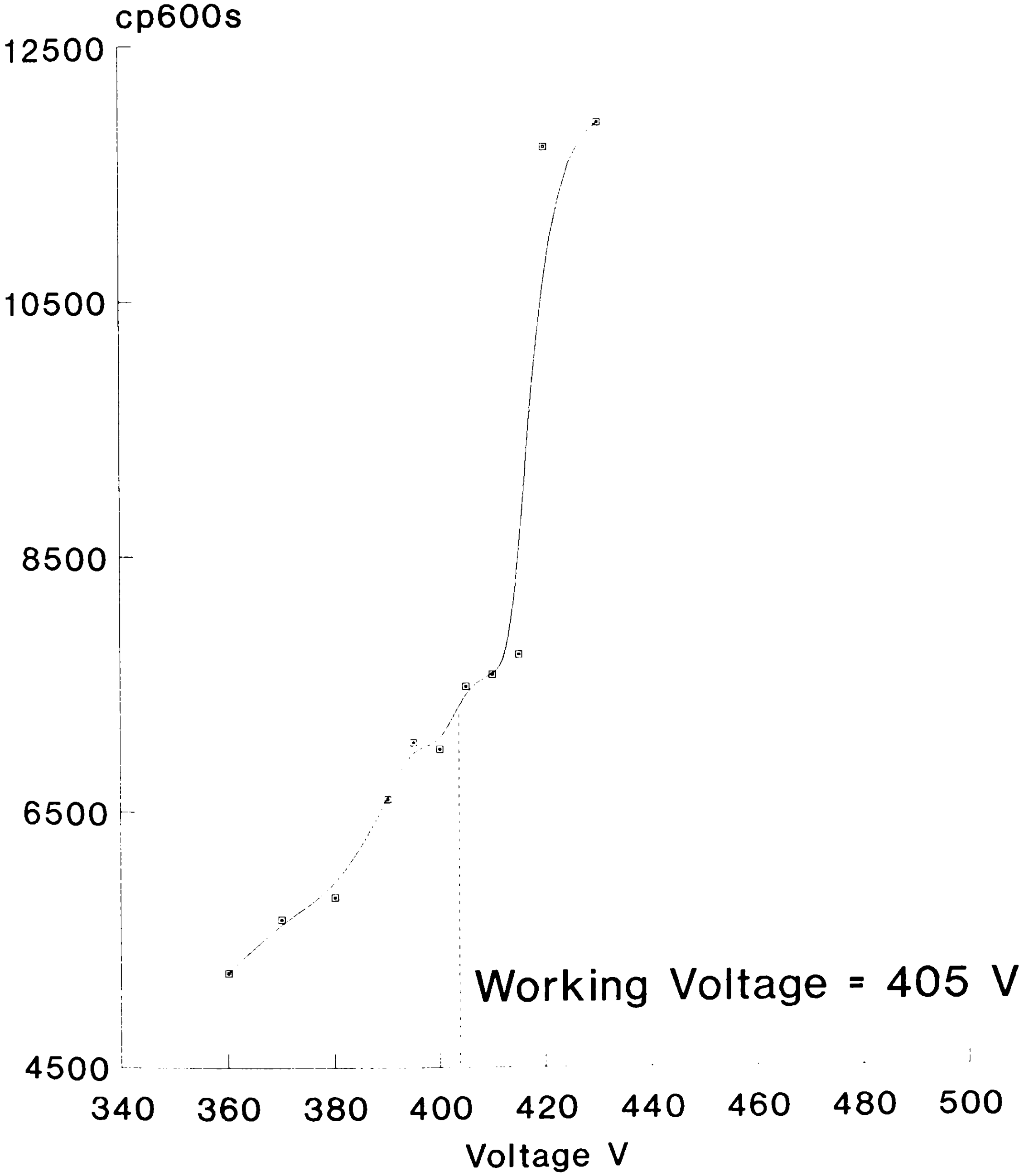
Geiger Müller counters are only operated when the applied voltage is large enough to attract electrons to the anode. Once the threshold is achieved, the count rate rises steadily until a plateau region is reached where the count rate has little or no dependence on the voltage. A slight rise in this region is due to secondary discharge. If the voltage is further increased the Geiger Muller counter goes into continuous discharge. It is desirable to work at a voltage in the middle of the plateau region.

The plateau region was determined by placing a solid ^{60}Co source underneath each Geiger Muller counter. A plot of counts obtained in 600 s vs applied voltage was constructed (Figure 2.9). The count rate increased dramatically with voltage after the threshold was reached then became fairly constant in the plateau region before rising sharply as the counter discharges. The working voltage was set in the middle of the plateau region.

2.9.2 Dead Time

The electrons reach the anode of a Geiger Müller tube very quickly ca 5 x 10^{-7} s [94]. However, positive ions still in the vicinity of the anode have to reach the cathode before another event can be recorded as their presence reduces the field near the centre wire

Figure 2.9 Plateau Region
Voltage vs Counts per 600 secs



and this prevents an avalanche forming. This period when no counts can be detected is known as the dead time. In experiments where the count rate is high it is necessary to correct for counts lost in this period in order to obtain accurate results.

The dead times of the Geiger Muller tubes were determined by counting samples of $[^{18}F]$-CsF for 330 min ($t.^1/_2$ ^{18}F = 110 min). The activity of a radioactive sample of time t can be calculated from equation 2.7.

$$A(t) = A(o)e^{-\lambda t} \qquad \text{Equation 2.7.}$$

λ - decay constant

A(t) - activity of sample at time t

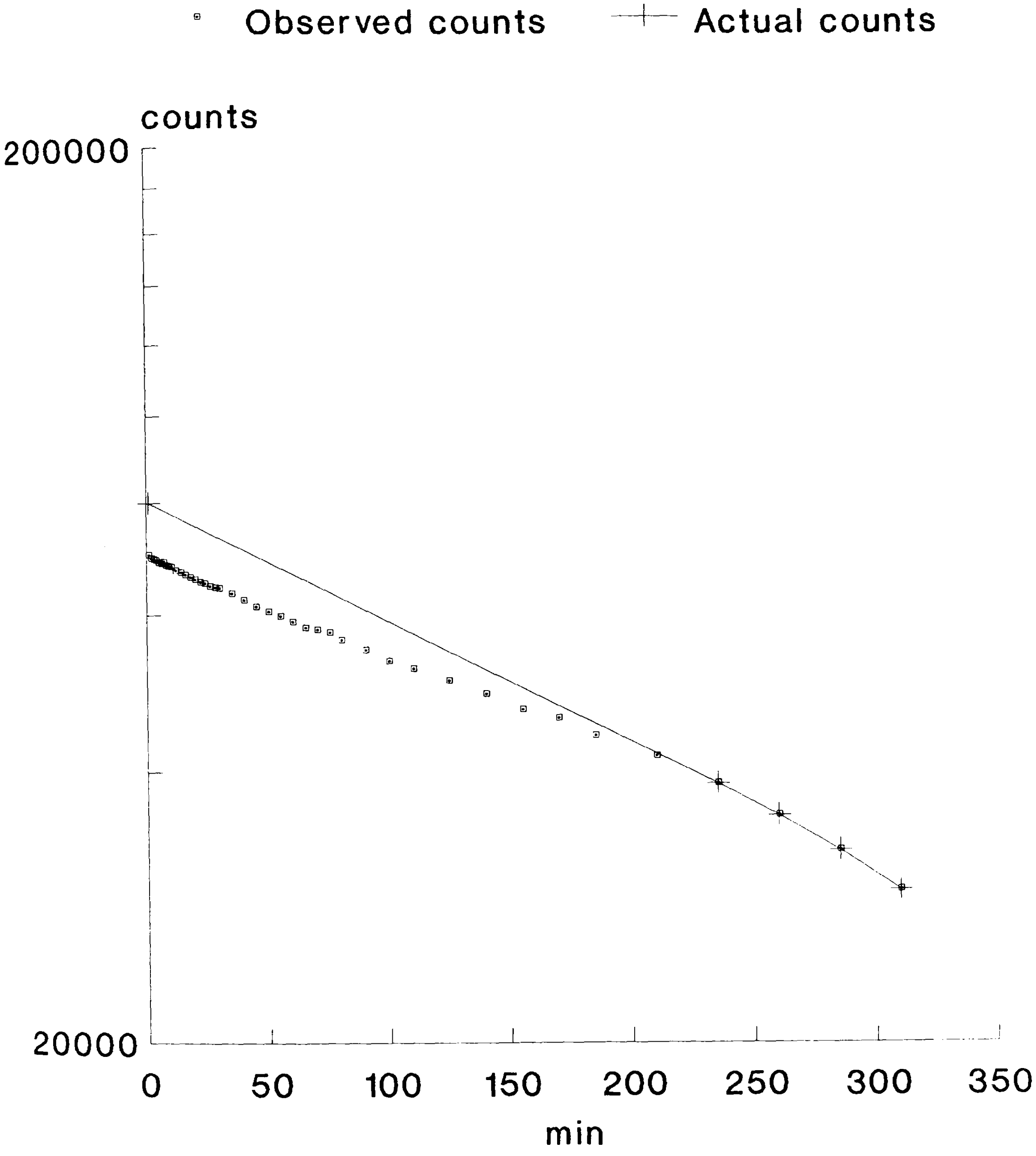
A(o) - activity of sample at time zero

Thus a plot of lnA(t) vs time should be linear with gradient $-\lambda$ and intercept lnA(o). When a plot of lnA(t) vs time was drawn a linear relationship was obtained for t>200 min. At t<200 min a curve was obtained because at these times the dead time had a noticeable effect. The linear part of the graph was extrapolated to t = 0 giving a true count, N(t) for the sample at time t. This was related to No the observed count and τ the dead time by equation 2.8.

$$N(t) = \frac{N(o)}{(1-N(o)\tau)} \qquad \text{Equation 2.8.}$$

A computer program was used to calculate the dead time τ from N(t) and N(o) for the first 20 points after t = 0. The mean value of τ was taken to be the dead time, for the Geiger Müller counter. Figure 2.10 shows both the experimentally observed line and the extrapolated line.

Figure 2.10 Dead Time
Time (min) vs counts



2.9.3 Background Count

Background radiation can be detected by Geiger Müller counters in the absence of any radioactive source. It can arise from radioactive species that occur naturally, however, the main source is cosmic radiation. Before any radiochemical experiments are begun, an average background count rate must be measured so that it may be subtracted from all sample count rates.

2.9.4. Statistical Errors [96].

All radioactive nuclei decay independently of each other, thus radioactive decay is a completely random process. The problem of finding a decay constant can be solved statistically by applying the binomial theorem. The probability W(m), of obtaining (m) disintegrations in time (t) from N(o) original radioactive atoms is expressed in equation 2.9.

$$W(m) = \frac{N(o)!}{(N(o)-m)!m!} \quad p^{m}(1-p)^{N(o)-m}$$

Equation 2.9.

P is the probability of a disintegration 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

$$\sigma = \sqrt{Me^{-\lambda t}}$$

Equation 2.10.

In practice the observation time, t, is short compared with the half life thus λt becomes negligible. The expression is reduced to

$$\sigma = \sqrt{m} \qquad \text{Equation 2.11.}$$

where m is the number of counts obtained. In order to minimise the radiochemical error, counts collected were of the order 10^4. The error is $\pm\ 10^2$ i.e. 1%.

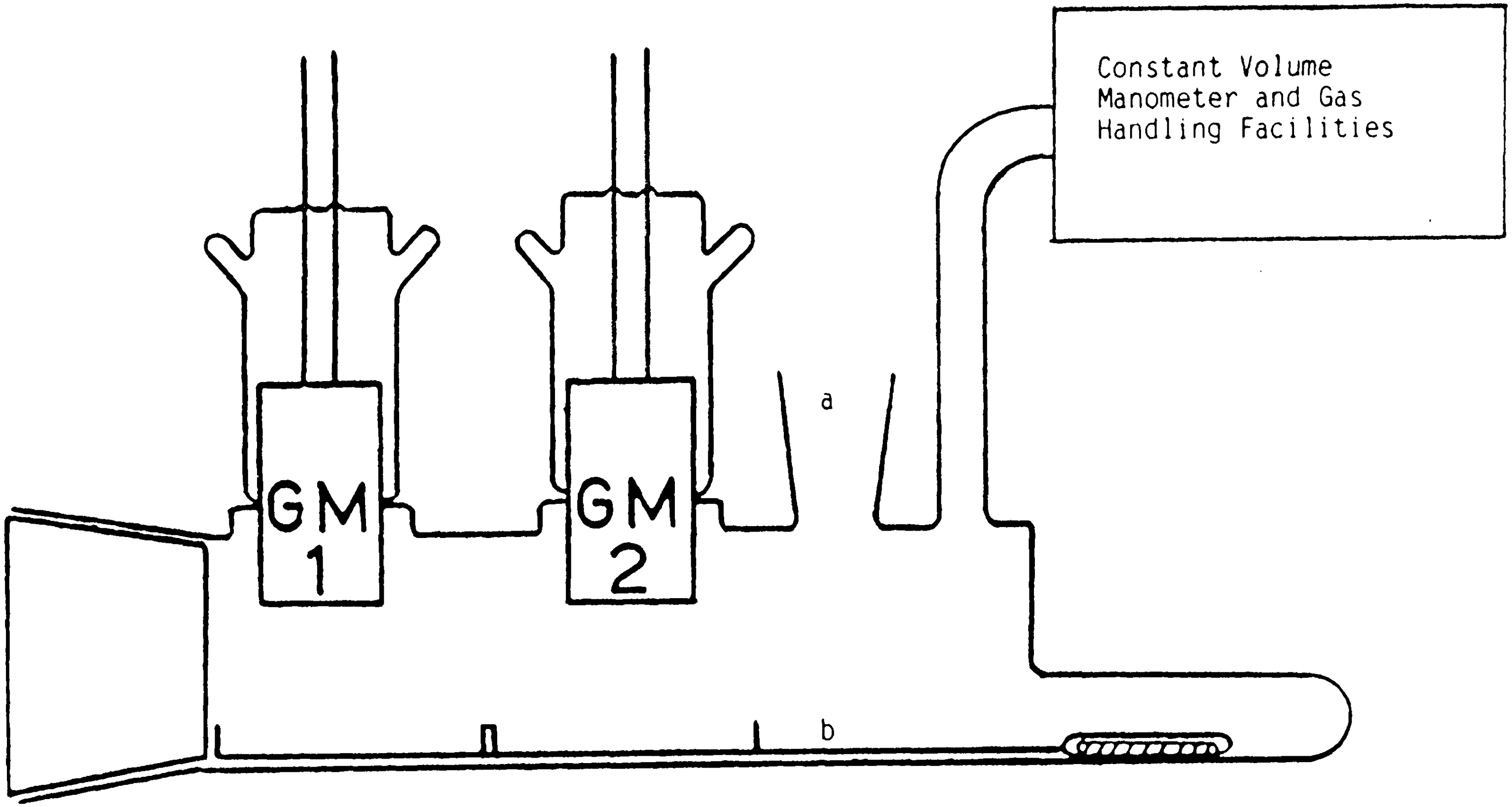
2.10 The Direct Monitoring Geiger Müller Radiochemical Counting Technique.

The direct monitoring Geiger Müller radiochemical technique was developed by Thomson and modified by Al-Ammar and Webb [97] to determine the surface activity of solids exposed to radiolabelled gases. The technique has been successful in detecting both strong and weakly adsorbed species on the surface of a catalyst [98].

2.10.1 Equipment

The Pyrex reaction vessel (Figure 2.11) consisted of two Geiger Müller tubes and a B14 socket to which ampoules containing solid samples could be attached. It was connected via a small manifold to gas handling facilities and a constant volume manometer. Inside the vessel was a glass boat with two compartments each capable of holding a solid sample. The boat was positioned under the Geiger Müller tubes by means of a magnet and iron bar. The whole apparatus was calibrated before use. The Geiger Müller tubes were

Figure 2.11 The Radiochemical Counting Vessel



intercalibrated by admitting pressures of a radioactive gas, eg. $H^{36}Cl$, and noting the counts obtained in 600 s. A plot of pressure vs count rate (Figure 2.12) gave a straight line through the origin, with the gradient, 0.964, equal to the ratio of the two counts.

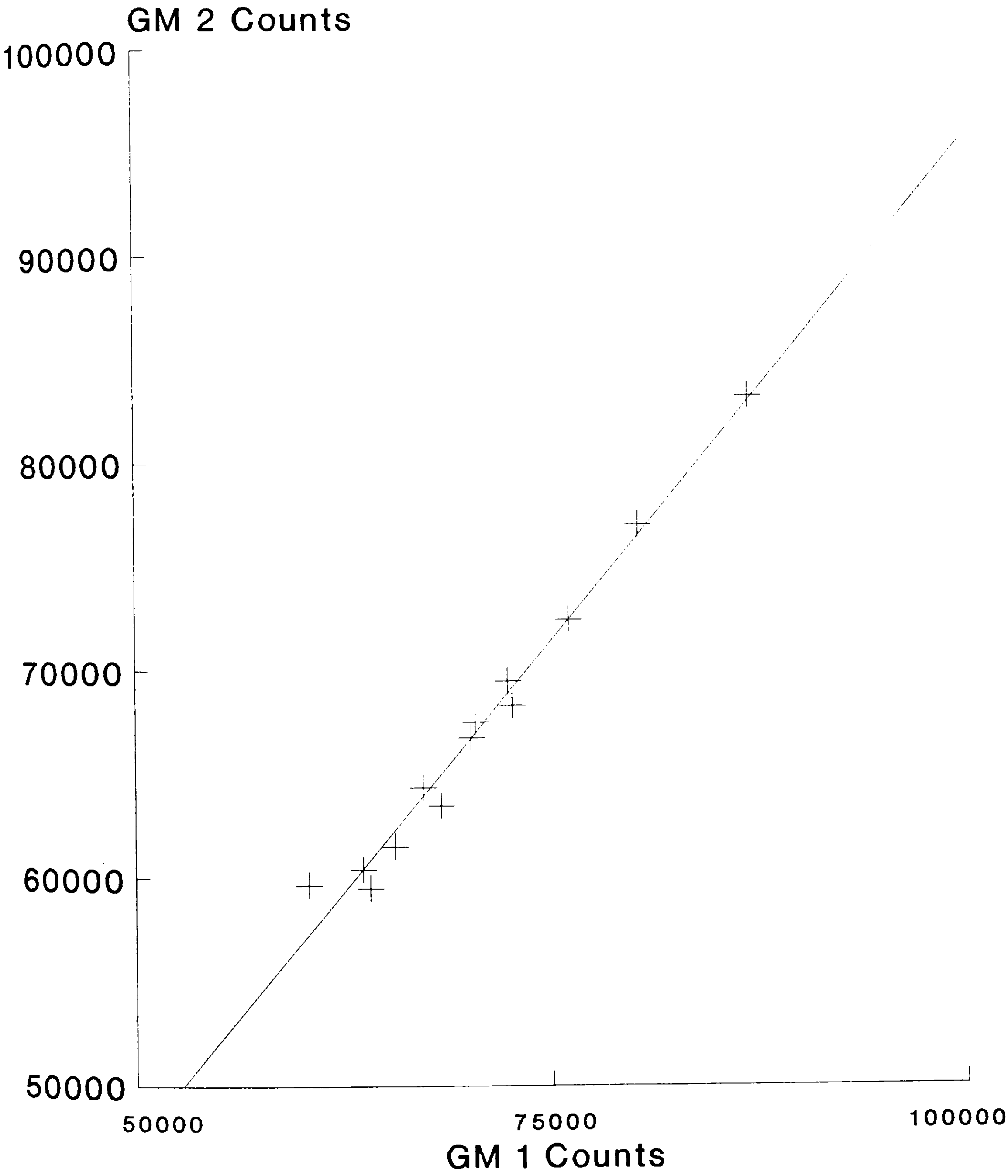
2.10.2 Application of the Technique to Gas/Solid Systems

The procedure for application of the technique to gas/solid systems was as follows. The vessel was flamed out under dynamic vacuum and a weighed solid sample was dropped into the right hand portion of the boat and positioned under Geiger Müller 2 with the left hand portion under Geiger Müller 1.

Radioactive gas of previously determined specific count rate was admitted to the cell and the reaction vessel was isolated from the rest of the system. Counts were recorded from both Geiger Müller tubes with time. Geiger Müller 1 monitored the radioactivity in the gas phase only whereas Geiger Müller 2 monitored the radioactivity on both the solid and in the gas phase. The counts from Geiger Müller 1 corrected for dead time, background and intercalibration were subtracted from Geiger Müller 2 corrected for background and dead time to give values for surface counts. From these values graphs in counts per minute were derived and plotted against time.

Figure 2.12 Intercalibration of GM Tubes

GM 1 Counts vs GM 2 Counts



2.11 Self Absorption

When monitoring the radioactivity of a β^- emitter one must be aware that a proportion of the emissions interact with the surrounding matter and are absorbed. This phenomenon is termed self absorption. For very soft β^- emitters eg. [^{35}S]-sulphur it can be assumed that all radioactivity originates from the surface as subsurface emissions are completely adsorbed. In the case of [^{36}Cl]-chlorine, not all subsurface emissions are self adsorbed and can be detected. Therefore, it is possible, that the total activity detected originates both from the surface and from the first few planes beneath the surface.

Chapter 3

3.1 Introduction

A Study of the Interaction Between Aluminium(III) Chloride and Chlorofluoroethanes

Previous studies of the interaction between aluminium(III) chloride and 1,1,2-trichlorotrifluoroethane have involved refluxing liquid 1,1,2-trichlorotrifluoroethane with solid aluminium(III) chloride at temperatures > 50°C [76,77]. There is no evidence to suggest that precautions were made to minimise the water content in the system. In the present study the experimental conditions were designed so that CCl_2FCClF_2 vapour would contact the aluminium(III) chloride surface. This heterogeneous system allowed surface/vapour interactions to be studied using radiolabelling techniques. Such interactions would not be observed under reflux conditions. All experiments were carried out at room temperature. Stringent attempts were made to remove all moisture from the system ensuring anhydrous conditions as far as possible.

Results

3.2 The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride

Sublimed aluminium(III) chloride was reacted with gaseous CCl_2FCClF_2 at room temperature. The aluminium(III) chloride used was either loaded into the reaction vessel in the dry box or sublimed directly into the reaction vessel. After 24h the volatile products were removed and a second aliquot of CCl_2FCClF_2 was admitted to the reaction vessel. This process was repeated. Mass balance data were used to determine the retention of organic material by the catalyst. This was calculated according to equation 3.1.

$$\% \text{ Retention} = \frac{CCl_2FCClF_2 \text{ added (g)} - \text{Products (g)} \times 100}{CCl_2FCClF_2 \text{ added (g)}} \qquad \text{equation 3.1}$$

The volatile product mixtures were analysed qualitatively by i.r. spectroscopy and mass spectrometry. Quantitative analyses were carried out using ^{19}F nmr spectroscopy and gas chromatography. The quantity of chlorofluorocarbon produced was calculated according to equation 3.2

$$\%\text{CFC produced} = \frac{\text{CFC in Product (g)} \times 100}{CCl_2FCClF_2 \text{ added (g)}} \qquad \text{equation 3.2}$$

All experiments carried out have been labelled MA, MB, MC and so on. Each experiment was composed of a series of reactions and these have been numbered. For example experiment MA comprised four reactions, MA1, MA2, MA3 and MA4.

3.2.1 Using Aluminium(III) Chloride Handled in the Dry Box

The results from the preliminary experiment MA indicated that CCl_2FCClF_2 was isomerised to CCl_3CF_3 in the presence of aluminium(III) chloride at room temperature. The volatile products were analysed qualitatively by ir spectroscopy, the results are shown in table 3.1. Mass balance data were consistent with retention of material on the solid surface. Experiment MB involved a more detailed investigation of this system. The products were analysed quantitatively using ^{19}F nmr spectroscopy. During the course of these reactions the solid developed a pale yellow colour. The colour lightened on removal of the gas phase but the solid never returned to its original shade. The mass balance data indicated that initially there was a substantial quantity of organic material retained on the solid surface (Figure 3.1). On addition of a second aliquot of CCl_2FCClF_2 to the reaction vessel the quantity of retained material fell, and after reaction MB3 the quantity of material retained was 12% of the original quantity of CCl_2FCClF_2 added. (Figure 3.1). After reaction MB4 the quantity of retained material had risen sharply to 84% of the original quantity of CCl_2FCClF_2 added.

Mass balance data were not obtained for reaction MB5 but after reaction MB6 the quantity of retained material was 68% of the original quantity of CCl_2FCClF_2 added.

Table 3.1

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Mass Balance data for Experiment MA.

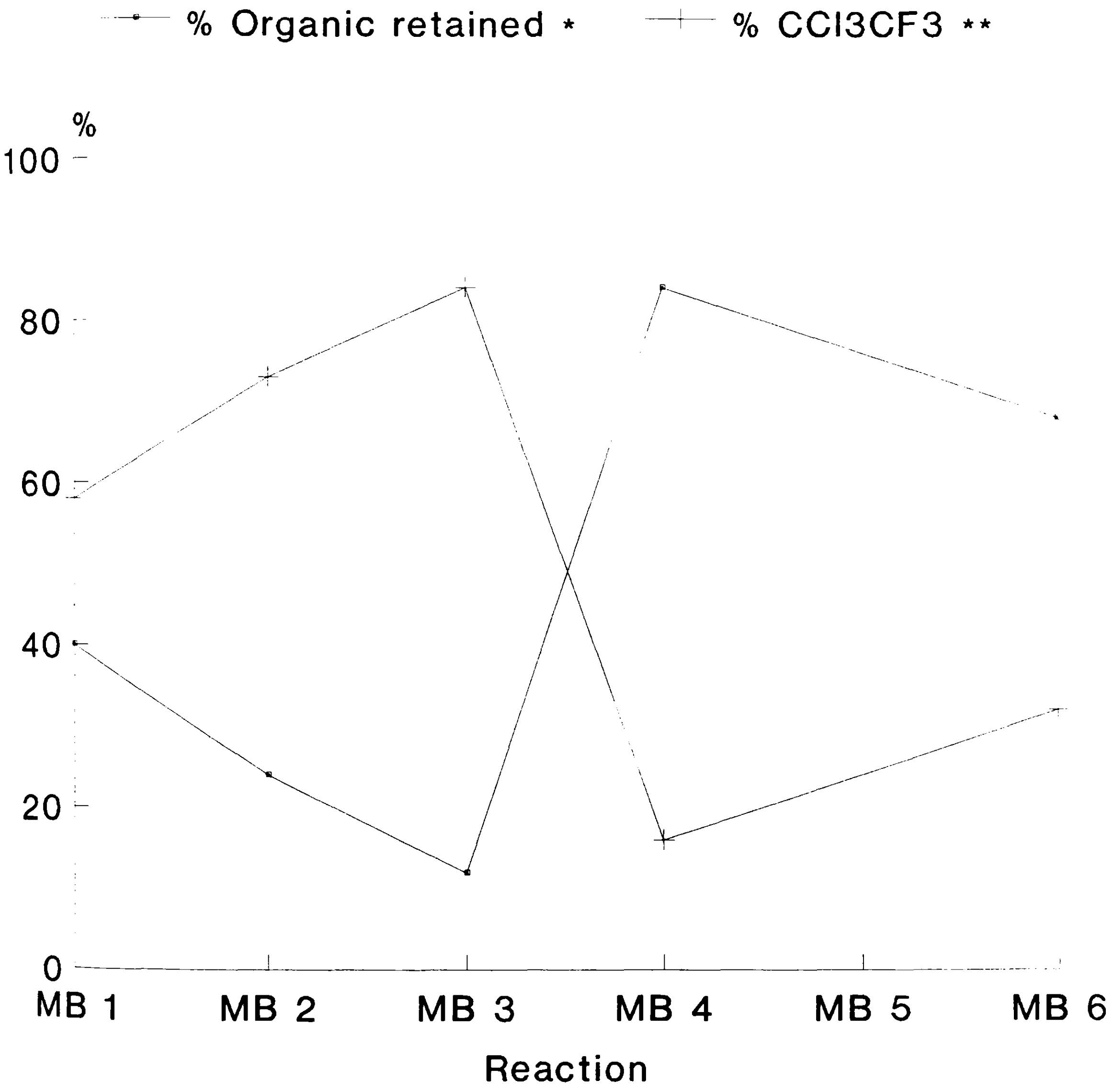
Weight of solid 0.83g (6.3 mmol)

Reaction	CCl_2FCClF_2 added (g)	Volatile Products (g)	Retention$^{\alpha}$ %	$CCl_3CF_3$$^{\beta}$ Present
MA1	-	0.02	-	Yes
MA2	0.69	0.42	38	Yes
MA3	0.25	0.22	8	Yes
MA4	0.68	0.38	44	Yes

α Calculated as described in equation 3.1.

β The volatile products were analysed qualitatively by i.r. spectroscopy. Each spectrum showed the presence of CCl_3CF_3.

Figure 3.1 Experiment MB
Reaction between CCl_2FCClF_2 and
Aluminium (III) Chloride



Wt of $AlCl_3$: 1.24g (9.29mmol)
*Calculated as shown in equation 3.1
**Calculated as shown in equation 3.2

The quantity of CCl_3CF_3 in the volatile product mixture was expressed as a % of the original CCl_2FCClF_2 added. The results are shown in figure 3.1. The quantity of CCl_3CF_3 produced rose after reactions MB1, MB2 and MB3 but fell after reaction MB4, before increasing in reaction MB6. It bore an inverse relationship to the percentage of material retained.

Analysis of the product mixtures of reactions MB1-MB6 by ^{19}F nmr spectroscopy showed the major product to be CCl_3CF_3. Traces of CCl_2FCF_3 and CCl_3CClF_2 were present also. The results are shown in table 3.2. Only the asymmetric isomers were observed, there was no indication that CCl_2FCCl_2F or $CClF_2CClF_2$ were present. The presence of CCl_2FCF_3 was interesting as it indicated that fluorination had occurred. This was not reported by Miller in his original paper[76]. The fluorine balance among the volatile products suggested that the retained material was highly chlorinated as there was more fluorinated product than chlorinated product in the volatile product mixture. During the series of reactions MB1-MB6 a build up of colourless crystalline material was observed on the surface of aluminium(III) chloride and on the walls of the reaction vessel. After six reactions were completed a sample of the crystalline material was separated manually and recrystallised from diethyl ether. The mass spectrum obtained from the solid had a fragmentation pattern identical to that of an authentic sample of hexachloroethane (Figure 3.2).

Table 3.2.

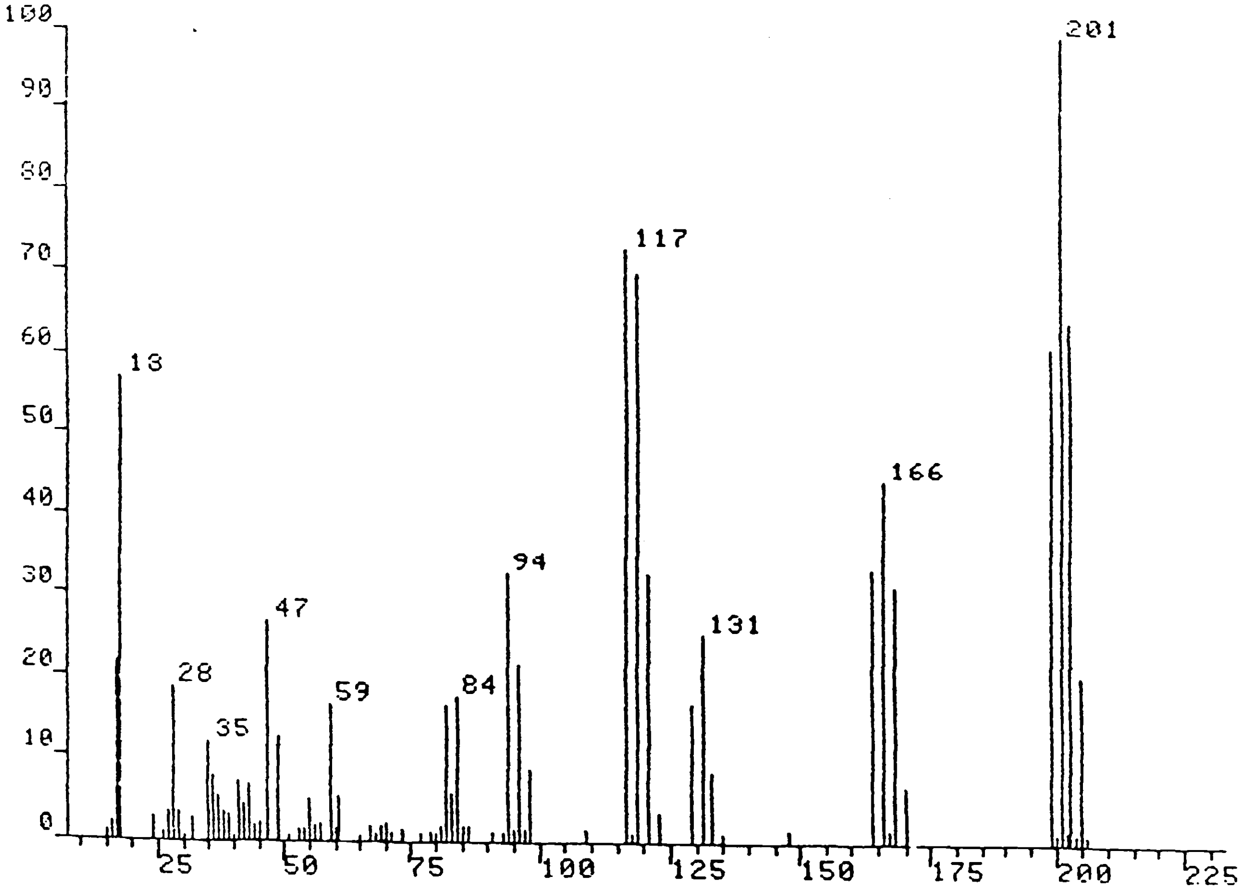
The Interaction Between Gaseous CCl_2FCClF_2 and Aluminium(III) Chloride handled in the Dry Box at room temperature.

Analyses of the Volatile Product Mixtures from Experiment MB by ^{19}F nmr Spectroscopy.

Reaction	Chlorofluoroethane Present %*		
	CCl_2FCF_3	CCl_3CF_3	CCl_3CClF_2
MB1	1	58	trace
MB2	2	73	1
MB3	3	84	trace
MB4	trace	16	-
MB5	trace	47	-
MB6	trace	32	-

*Calculated as shown in equation 3.2.

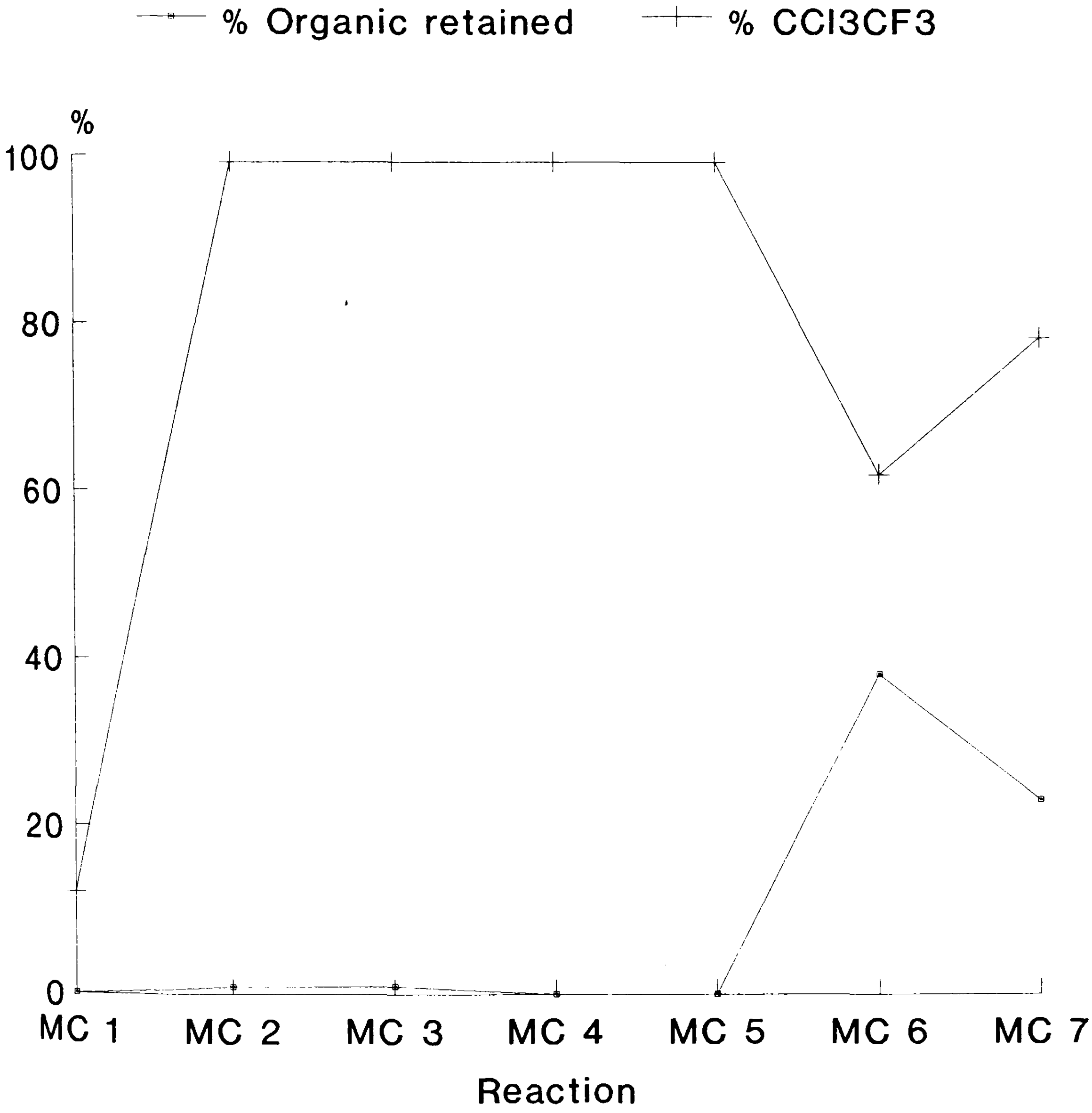
Figure 3.2 The Mass Spectrum of Hexachloroethane



A second sample of aluminium(III) chloride was sublimed and loaded into the reaction vessel in the dry box. An aliquot of CCl_2FCClF_2 was added and the vapour was allowed to interact with the solid surface for a period of 24 h. The volatile products were removed and weighed then analysed by gas chromatography. A second aliquot of CCl_2FCClF_2 was added to the reaction vessel and the process was repeated. This procedure was followed for a series of 7 reactions. The quantity of organic material retained on the solid surface and the quantity of CCl_3CF_3 produced, for each reaction MC1-MC6, are plotted in figure 3.3. After reaction MC1 very little organic was retained by the solid. Retention was observed after reaction MC6 but this fell after reaction MC7. There was little CCl_3CF_3 (<15%) produced after reaction MC1 but this rose to nearly 100% after reactions MC2, MC3, MC4 and MC5. The quantity of CCl_3CF_3 produced decreased after reaction MC6 then rose after reaction MC7. The composition of the product mixture was analysed by gas chromatography. The results are shown in table 3.3.

These results are not complete as the program for analysis was set to detect only CCl_2FCClF_2 and CCl_3CF_3. In later experiments the g.c. analysis program was altered so that all chlorofluoroethanes produced would be detected.

Figure 3.3 Experiment MC
Reactions between CCl2FCClF2 and
Aluminium (III) Chloride



Wt AlCl3 : 0.69g (5.17mmol)
Reacton time 24h

Table 3.3

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride, Handled in a Dry Box at Room Temperature

Analyses of the Volatile Product Mixtures from Experiment MC by Gas Chromatography.

Reaction	Chlorofluoroethane Present % *		
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3
MC1	trace	88	12
MC2	trace	-	100
MC3	-	-	-
MC4	1	-	99
MC5	1	-	99
MC6	-	-	-
MC7	1	-	77

* Calculated as shown in equation 3.2.

3.2.2 Using Freshly Sublimed Aluminium(III) Chloride

In section 3.2.1 experiments MA, MB and MC involved the transfer of sublimed aluminium(III) chloride to the reaction vessel in the dry box. The water vapour level in the dry box was <10 ppm. Due to the hygroscopic nature of aluminium(III) chloride this moisture could have been sufficient to cause hydration or hydroxylation of the surface. To avoid this possibility a series of experiments was carried out in which aluminium(III) chloride was sublimed directly into the reaction vessel. An aliquot of CCl_2FCClF_2 was added to the reaction vessel and the vapour was allowed to interact with the surface for a period usually of 24 h. The volatile products were removed and weighed before another aliquot of CCl_2FCClF_2 was admitted to the reaction vessel. This process was repeated. The product mixtures were analysed by g.c. or ^{19}F nmr spectroscopy.

In the first experiment MD, a large retention of material 66% (table 3.4) was observed after reaction MD1. This was attributed to the long reaction time of 42 h. The products obtained were solid at room temperature. The very low yield made analysis impossible.

Table 3.4

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride, directly sublimed into the Reaction Vessel, at room temperature.

Mass Balance Data for Experiment MD
Weight of Solid:- 0.90g (6.8 mmol)

Reaction	CCl_2FCClF_2 added g.	Volatile Products (g)	Retention * %
MD1	0.42	0.14	66
MD2	1.23	0.82	33

A second aliquot of CCl_2FCClF_2 (reaction MD2) was admitted to the reaction vessel. The volatile products were removed after 23 h. The quantity of material retained on the surface was 33% (table 3.4). The product mixture of reaction MD2 was analysed by g.c. and contained 6 components which were identified by g.c./m.s as described in section 2.6.4 (figure 3.4). The composition of the product mixture is tabulated in table 3.5.

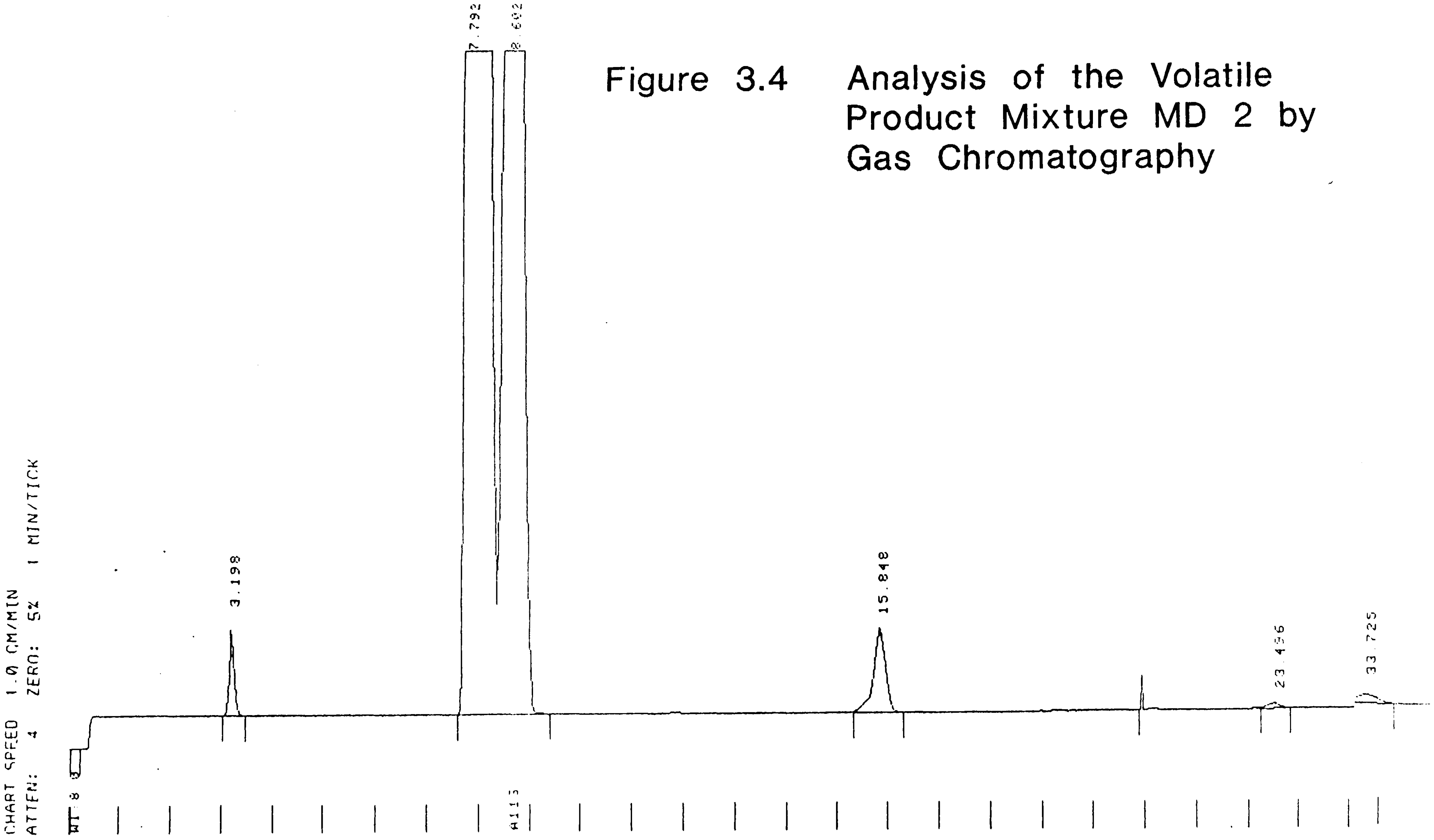


Figure 3.4 Analysis of the Volatile Product Mixture MD 2 by Gas Chromatography

Table 3.5

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride. Analysis of the Volatile Product Mixture from Reaction MD2 by GC/MS.

Chlorofluoroethane	% Present *
CCl_2FCF_3	0.2
CCl_2FCClF_2	46.8
CCl_3CF_3	18.2
CCl_3CClF_2	0.5
CCl_3CCl_2F	trace
C_2Cl_6	trace

* Calculated as described in equation 3.2.

The products amount to 65.7% of the original CCl_2FCClF_2 added. The remaining 34.3% is attributed to the organic material retained on the catalyst. A fluorine balance among the volatile products indicated that the quantity of CCl_2FCF_3 formed was less than that expected from a dismutation reaction. If dismutation of CCl_2FCClF_2 were the only reaction occurring then the quantity of CCl_2FCF_3 produced would equal that of CCl_3CClF_2 (equation 3.3)

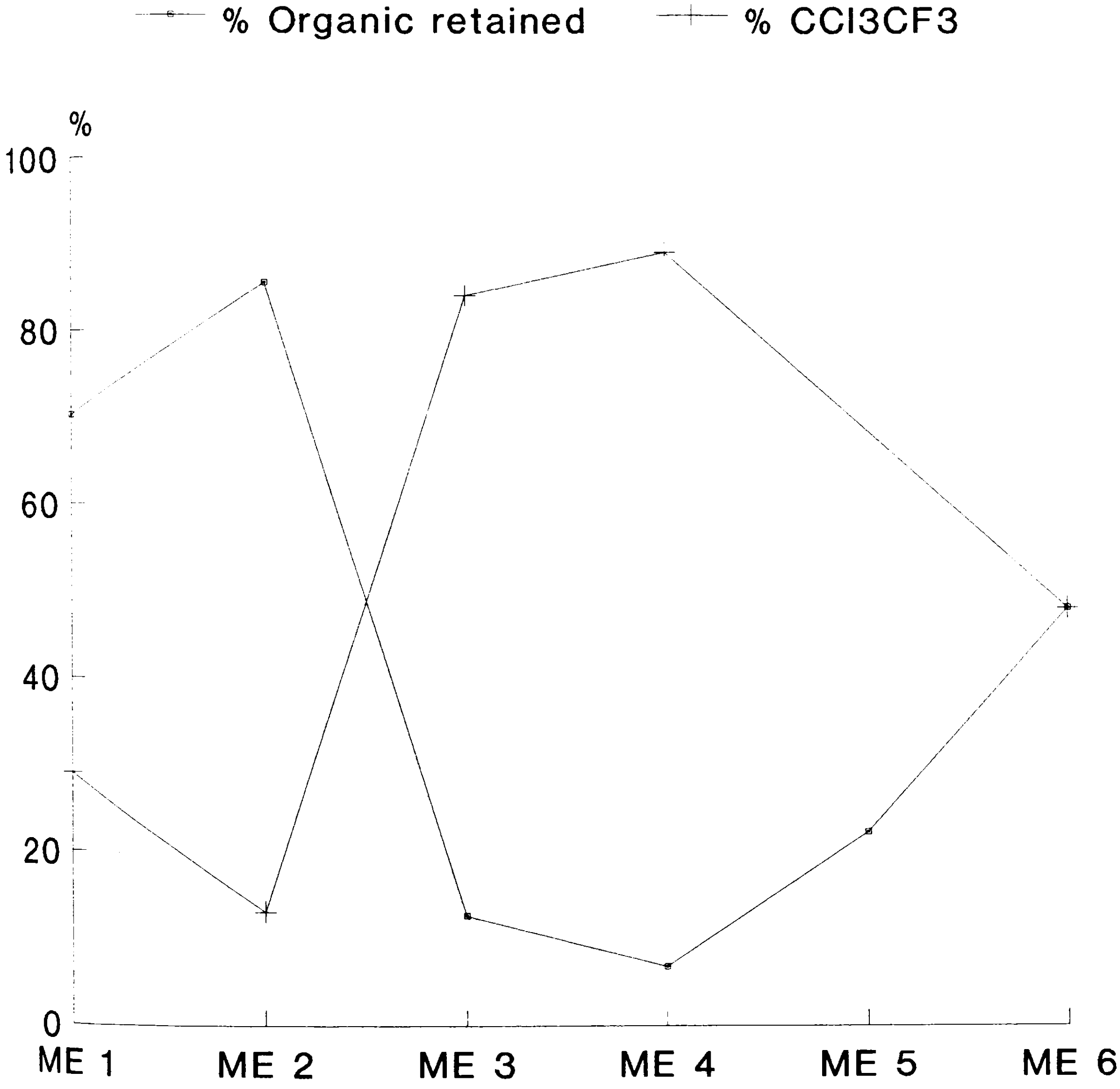
$$2CCl_2FCClF_2 \rightarrow CCl_3CClF_2 + CCl_2FCF_3$$

equation 3.3

Fluorine was lost from CCl_2FCClF_2 as a result of the formation of the chlorinated products CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6 but only a fraction of this pool of fluorine was used in the formation of CCl_2FCF_3.

The procedure outlined for experiment MD was repeated with a fresh sample of sublimed aluminium(III) chloride. In experiment ME, the large quantity of organic material retained after reaction ME1 increased to 85% of the original CCl_2FCClF_2 added after reaction ME2 (figure 3.5). The quantity of material retained at the surface dropped after this point to 6% after reaction ME4. An increase in the material retained was observed after reactions ME5 and ME6. As with all previous experiments an inverse relationship was observed between the quantity of material retained by the solid and the amount of CCl_3CF_3 produced in the vapour phase (figure 3.5). The largest conversion of CCl_2FCClF_2 to CCl_3CF_3 (89%) occurred when the least quantity of material was retained at the solid surface

Figure 3.5 Experiment ME Reactions between CCl2FCClF2 and Aluminium (III) Chloride



Wt of AlCl3 : 1.7096g (8.08mmol)
Reaction time 24h

(6%). The poorest production of CCl_3CF_3 (13%) was observed when the greatest quantity of material was retained at the solid surface (85%).

During this series of reactions the solid developed a yellow colour and the build up of crystalline hexachloroethane identified by m.s was observed. The quantity of hexachloroethane formed was not determined.

The volatile product mixtures were analysed by ^{19}F nmr spectroscopy. The results are shown in table 3.6. In reactions ME1, ME3, ME4 and ME6 the quantity of fluorinated product (CCl_2FCF_3) formed did not account for all the fluorine lost in the chlorination of CCl_2FCClF_2. However in reaction ME2 1% of the volatile products were fluorinated but there was only a trace of chlorinated volatile products. This suggested that fluorination was not due to a dismutation reaction since if this were the case chlorinated and fluorinated compounds would be in balance.

Table 3.6

The Interaction Between Gaseous CCl_2FCClF_2 and Aluminium(III) Chloride, directly sublimed into the Reaction Vessel at room temperature.

Analyses of the Volatile Product Mixtures from Experiment ME by ^{19}F nmr Spectroscopy.

React^n	Chlorofluoroethane Present % *				
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2	CCl_3CCl_2F
ME1	trace	-	29	1	-
ME2	1	trace	13	trace	-
ME3	1	-	84	2	trace
ME4	1	1	89	2	trace
ME6	1	2	48	2	-

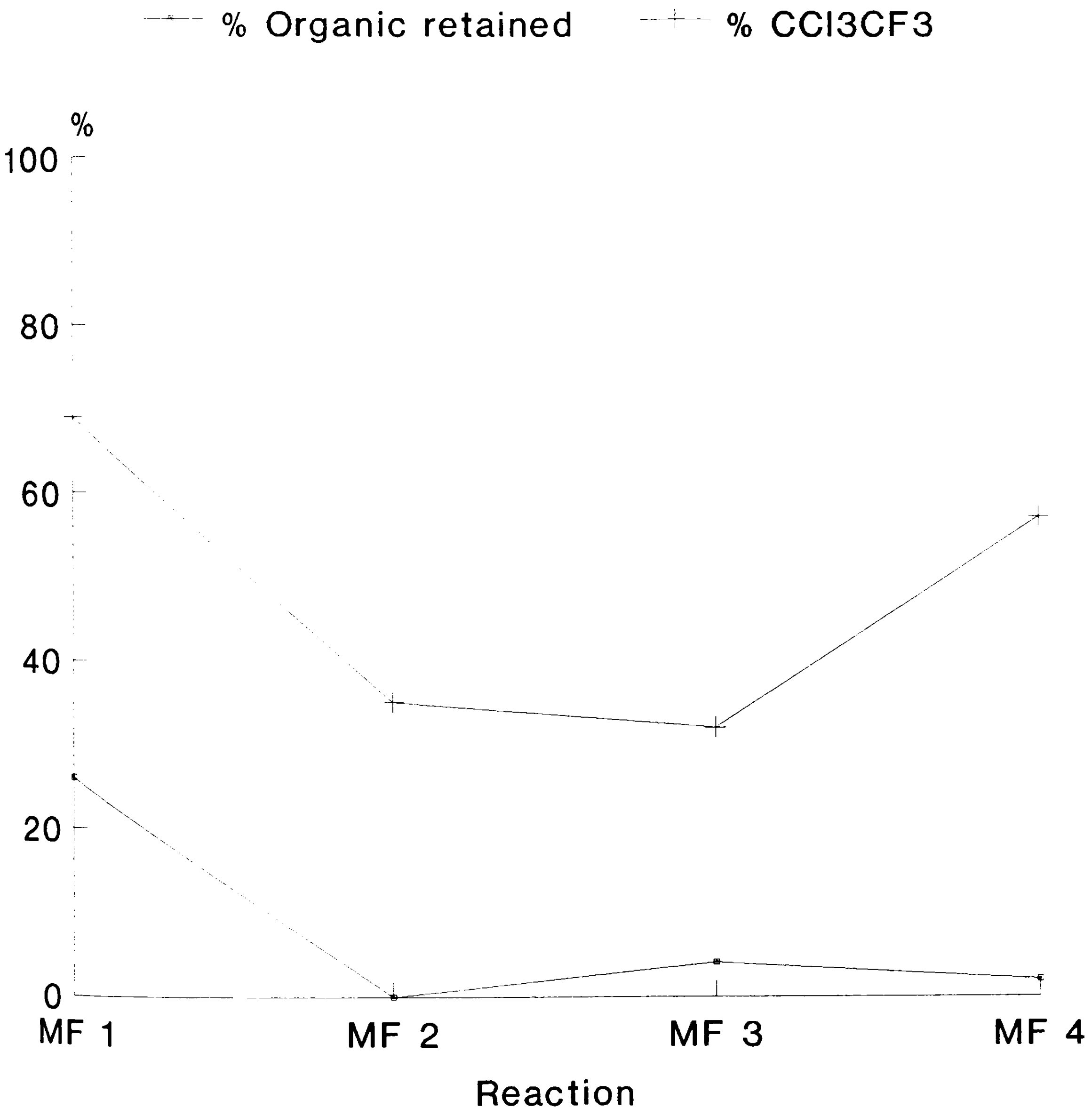
* Calculated as described in equation 3.2.

This series of reactions was repeated with a fresh sample of aluminium(III) chloride. The quantity of retained material on the solid after reaction MF1 was high at 26% but was not significant in subsequent runs (figure 3.6). During the course of reactions MF1-MF4 the solid developed a yellow colour similar to that observed in experiment ME and the build up of crystalline hexachloroethane was also noted.

The quantity of CCl_3CF_3 produced in reaction MF1 was 69% of the original quantity of CCl_2FCClF_2 added. Production of CCl_3CF_3 fell during reactions MF2 and MF3 but rose to 57% of the original CCl_2FCClF_2 added, during reaction MF4. In this experiment a direct relationship was observed between the quantity of organic material retained by the solid and the quantity of CCl_3CF_3 produced (figure 3.6). Previous experiments MD and ME resulted in an inverse relationship between the two phenomena.

Analyses of the volatile product mixtures for reactions MF1-MF4 (table 3.7) have shown that the quantity of CCl_2FCF_3 formed was less than or equal to the quantity of chlorinated products formed.

Figure 3.6 Experiment MF Reactions between CCl2FCClF2 and Aluminium (III) Chloride



Wt AlCl3 : 0.9755g (7.30mmol)
Reaction time 24h

Table 3.7

The Interaction Between Gaseous CCl_2FCClF_2 and Aluminium(III) Chloride, sublimed directly into the Reaction Vessel at Room Temperature.

Analyses of the Volatile Product Mixtures from Experiment MF by ^{19}F nmr Spectroscopy.

React^n	Chlorofluoroethane Present % *				
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2	CCl_3CCl_2F
MF1	1	trace	69	3	-
MF2	1	62	35	2	trace
MF3	1	62	32	1	-
MF4	1	37	57	1	-

* Calculated as described in equation 3.2.

There was no evidence to suggest a simple relationship but the data were not conclusive. Dismutation may occur but the results from experiments MD and ME have suggested that it is not the only process by which fluorination and chlorination occur.

There was no evidence to suggest the formation of the symmetric isomers CCl_2FCCl_2F and $CClF_2CClF_2$ in experiments MD, ME and MF.

3.3 [^{36}Cl]-Chlorine Radiolabelling Experiments

The isomerisaton of CCl_2FCClF_2 was observed to occur under reflux conditions in the presence of aluminium(III) chloride. Miller repeated this reaction using [^{36}Cl]-chlorine labelled aluminium(III) chloride [76]. This resulted in the incorporation of the [^{36}Cl]-chlorine radiolabel in the chlorinated product CCl_3CClF_2 but not in the isomer CCl_3CF_3. This observation prompted Miller to state that the isomerisation of CCl_2FCClF_2 over aluminium(III) chloride occurred via an intramolecular mechanism [76]. There is no indication that any material was retained on the solid surface. The main objective of the following experiments was to obtain independent evidence that organic material was deposited on the solid surface.

The nature of the organic layer could not be determined by the [^{36}Cl]-chlorine labelling experiments but merely that [^{36}Cl]-chlorine was present on the surface. The experiments undertaken involved:-

(i) The reaction between [^{36}Cl]-CCl_2FCClF_2 and aluminium(III) chloride. The vapour of [^{36}Cl]-CCl_2FCClF_2 was allowed to interact with solid aluminium(III) chloride for a period of 24 h. The vapour phase and solid count rates were monitored during this time and the count rate of the solid was measured once all the volatile products were removed.

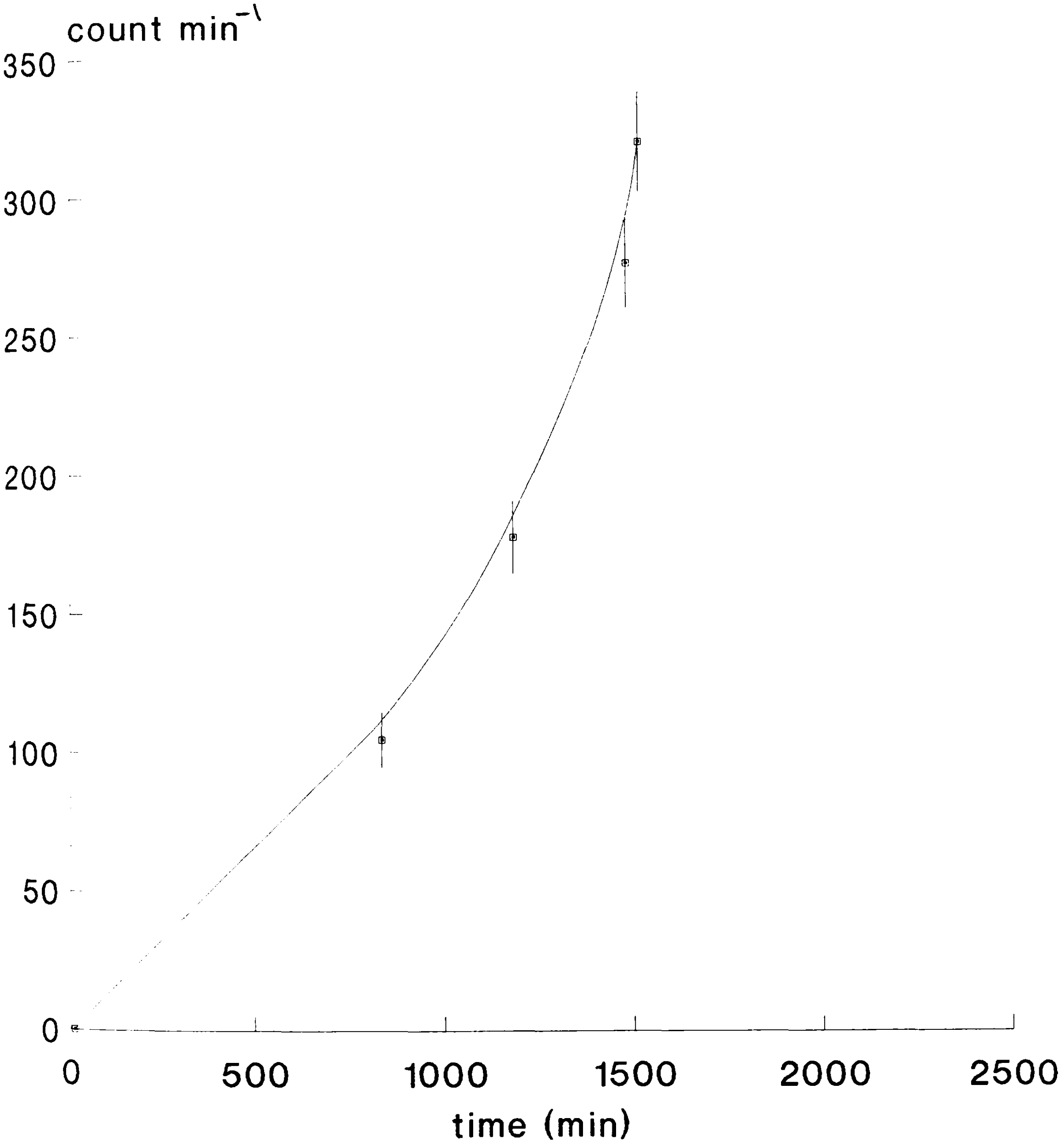
(ii) The reaction between CCl_2FCClF_2 and aluminium(III) chloride pretreated with [^{36}Cl]-CCl_2FCClF_2. Non radioactive CCl_2FCClF_2 was allowed to react with aluminium(III) chloride pretreated with [^{36}Cl]-CCl_2FCClF_2 for a period of 24 h. The count rates of the vapour phase and that of the solid were monitored during this time and once all vapour was removed.

(iii) The reaction between CCl_2FCClF_2 and [^{36}Cl]-chlorine labelled aluminium(III) chloride. This experiment repeated Miller's work [76] but the conditions were different. This reaction was carried out in vacuo at 25^{o}C for a period of 24 h.

3.3.1 The Reaction Between [^{36}Cl]-Chlorine labelled CCl_2FCClF_2 and Aluminium(III) Chloride.

Freshly sublimed aluminium(III) chloride was loaded into the counting vessel as described in section 2.10.1. Gaseous [^{36}Cl]-chlorine labelled CCl_2FCClF_2 was admitted to the vessel and allowed to react with the solid for a period of 24 h. The uptake of [^{36}Cl]-chlorine by the catalyst was monitored over this period. A plot of surface count rate vs time is shown in figure 3.7. The surface count rate after the volatile products were removed was 320 count min^{-1}. This did not decrease when the volatile material was pumped away

Figure 3.7 The Uptake of [36Cl]-CCl2FCClF2 by Aluminium (III) Chloride Solid count rate vs time



The last point corresponds to the reading taken once the gas was removed

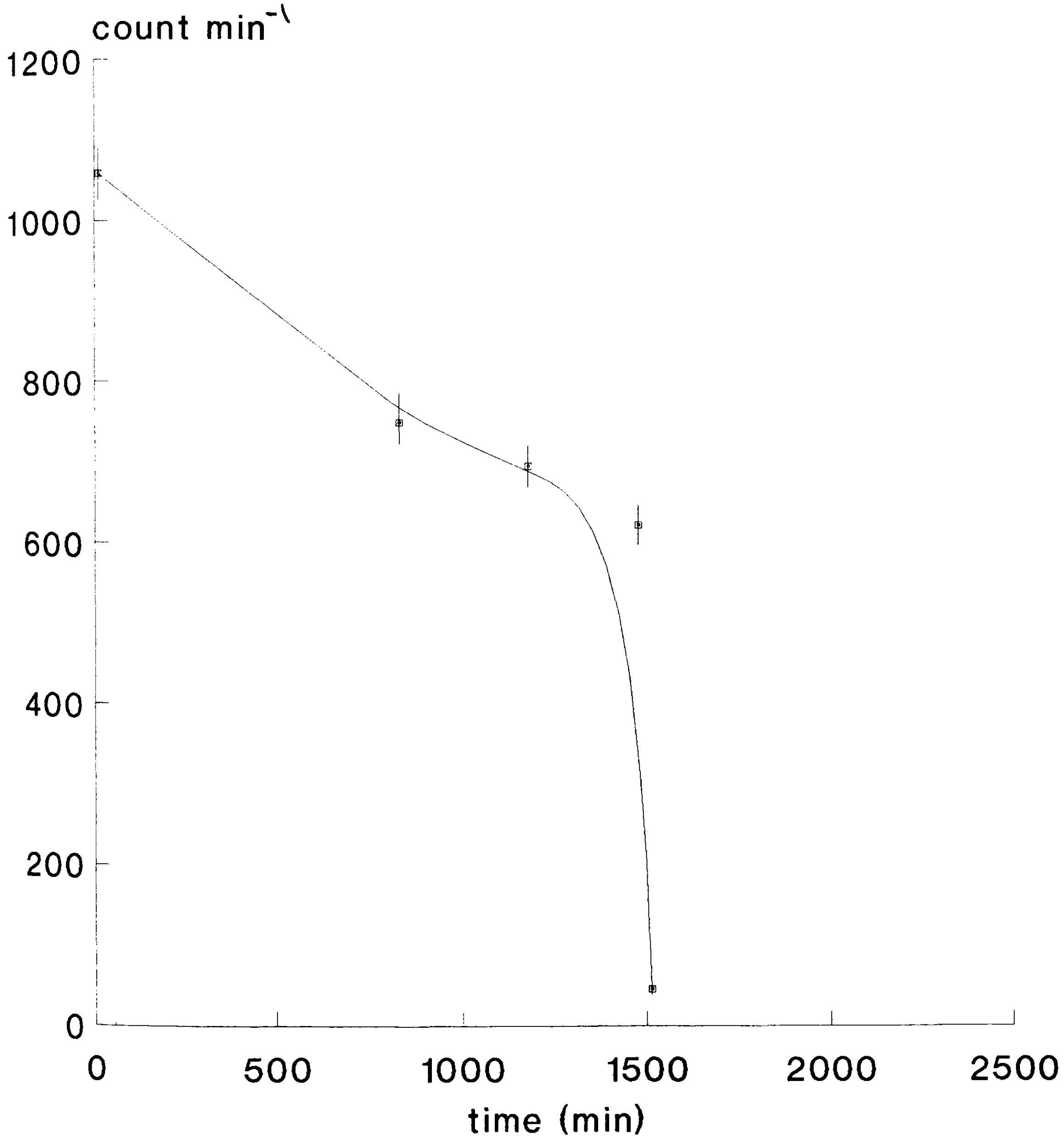
indicating that the organic layer was adsorbed to the solid surface.

A steady decrease in the vapour phase count rate was observed during the reaction (figure 3.8). This was consistent with the radioactivity taken up by the solid. Mass balance data showed that 42% of the original [^{36}Cl]-CCl_2FCClF_2 added was retained by the solid. This accounts for the 41.3% drop in the vapour phase count rate during the reaction. The composition of the product mixture was not determined but it was assumed to consist of CCl_2FCF_3, CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2 CCl_3CCl_2F and C_2Cl_6.

3.3.2 Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with [^{36}Cl]-CCl_2FCClF_2

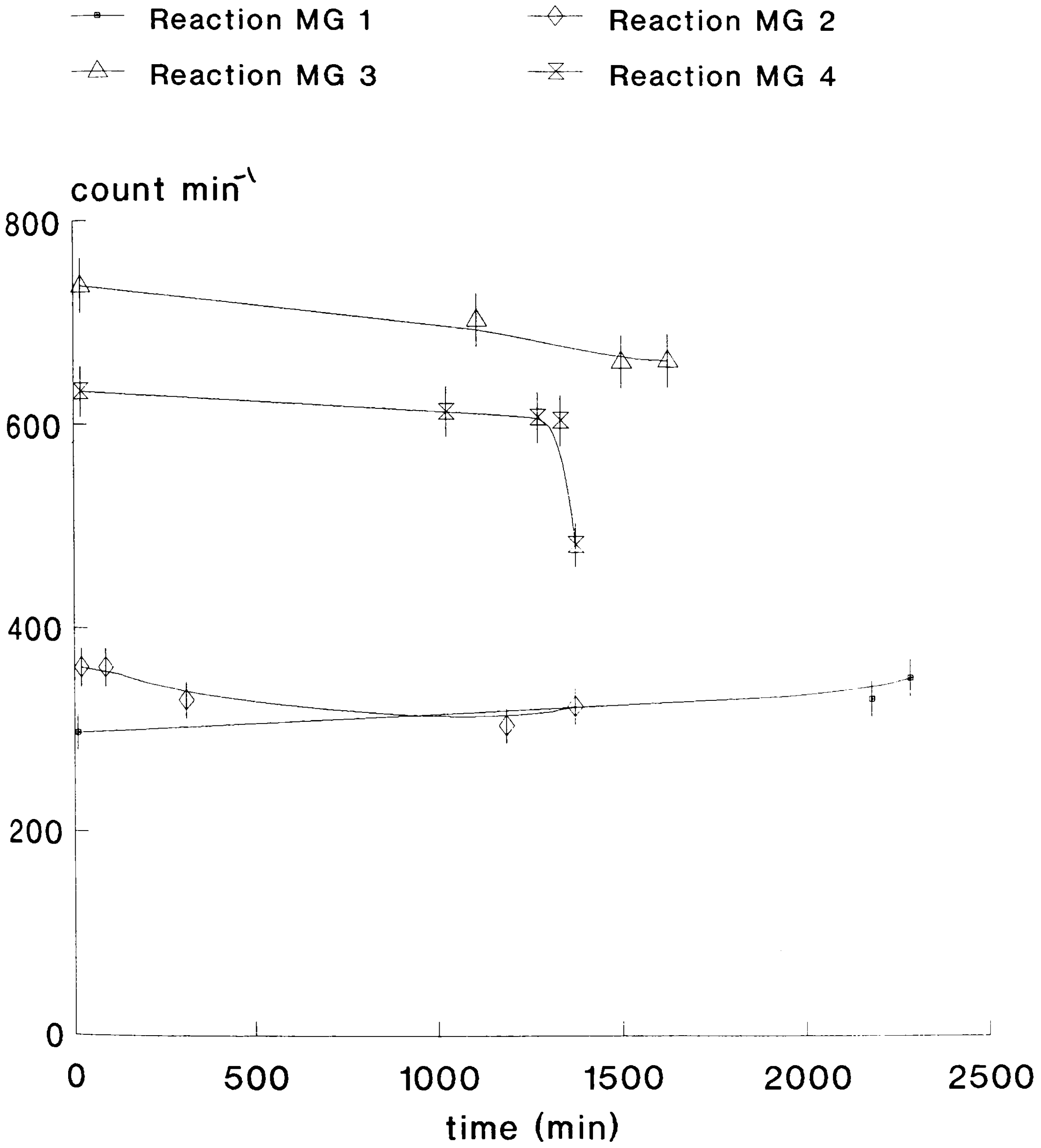
Aluminium(III) chloride was pretreated with [^{36}Cl]-CCl_2FCClF_2 as described in 3.3.1. Four aliquots of non-radioactive CCl_2FCClF_2 were each allowed to interact with this solid. In each reaction the solid count rate was monitored and the results are plotted in figure 3.9. For reactions MG1 and MG2 the surface count rate remained essentially constant at 350 and 320 count min^{-1} respectively, over the 24 h period. The gas admitted in reaction MG2 was left in contact with the surface for 4 weeks by which time the surface count rate had increased to 770 count min^{-1}. This new surface count rate remained constant when the next aliquot of gas was admitted. In reaction MG4 the surface count rate fell immediately the new aliquot of gas was admitted, but remained constant thereafter. The

Figure 3.8 The Uptake of [36Cl]-CCl2FCClF2 by Aluminium (III) Chloride Gas phase count rate vs time



The last point corresponds to the reading taken once the gas was removed

Figure 3.9 Experiment MG Reactions of CCl2FCClF2 with [36Cl]-CCl2FCClF2 treated Aluminium (III) Chloride Solid count rate vs time



The last point corresponds to the reading taken once the gas was removed
In run 2 it is the reading after 272mins

decrease in count rate observed after the removal of volatile material in MG4 was probably due to the inadvertent admission of air to the counting vessel. In each reaction radioactivity was detected in the vapour phase but it was too small to be measured precisely. Infrared spectra of the volatile products obtained after reactions MG1, MG2 and MG4 were consistent with CCl_3CF_3 being the predominant component in the vapour phase. Once all the volatile material had been removed from the counting vessel after reaction MG4, the solid was left in vacuo for a few weeks. During this period the surface count rate increased to 780 count min^{-1}, a similar value to the count rate after reaction MG2. A pressure developed in the counting vessel over this time equivalent to 7.68 mmol of CCl_2FCClF_2. Its infrared spectrum showed it to be predominantly CCl_2FCClF_2 with a little CCl_3CF_3. Mass balance data for these reactions are tabulated in table 3.8. In all cases a high percentage of organic material was retained by the solid. The maximum quantity retained occurred after reaction MG2.

3.3.3 The Reaction Between CCl_2FCClF_2 and [^{36}Cl]-Chlorine Labelled Aluminium(III) Chloride

Aluminium(III) chloride was heated with gaseous [^{36}Cl]-CCl_4 at 55°C. After 22 h the volatile material was removed. The quantity of material lost in this process was less than 0.1 mmol of [^{36}Cl]-CCl_4. The solid was loaded into the counting vessel as described in 2.10.1. Gaseous CCl_2FCClF_2 was admitted and left to react for a period of 12 h. The solid and vapour phase count rates were monitored during this time.

Table 3.8

The Interaction Between Gaseous CCl_2FCClF_2 and Aluminium(III) Chloride, pretreated with [^{36}Cl]-CCl_2FCClF_2, at Room Temperature.

Mass Balance Data for Experiment MG.

Reaction	CCl_2FCClF_2 added(mmol)	Volatile Product(mmol)	Retention * %
MG1	2.0	1.2	37
MG2	3.0	1.1	61
MG3	3.3	1.3	60
MG4	3.6	1.9^{α}	47

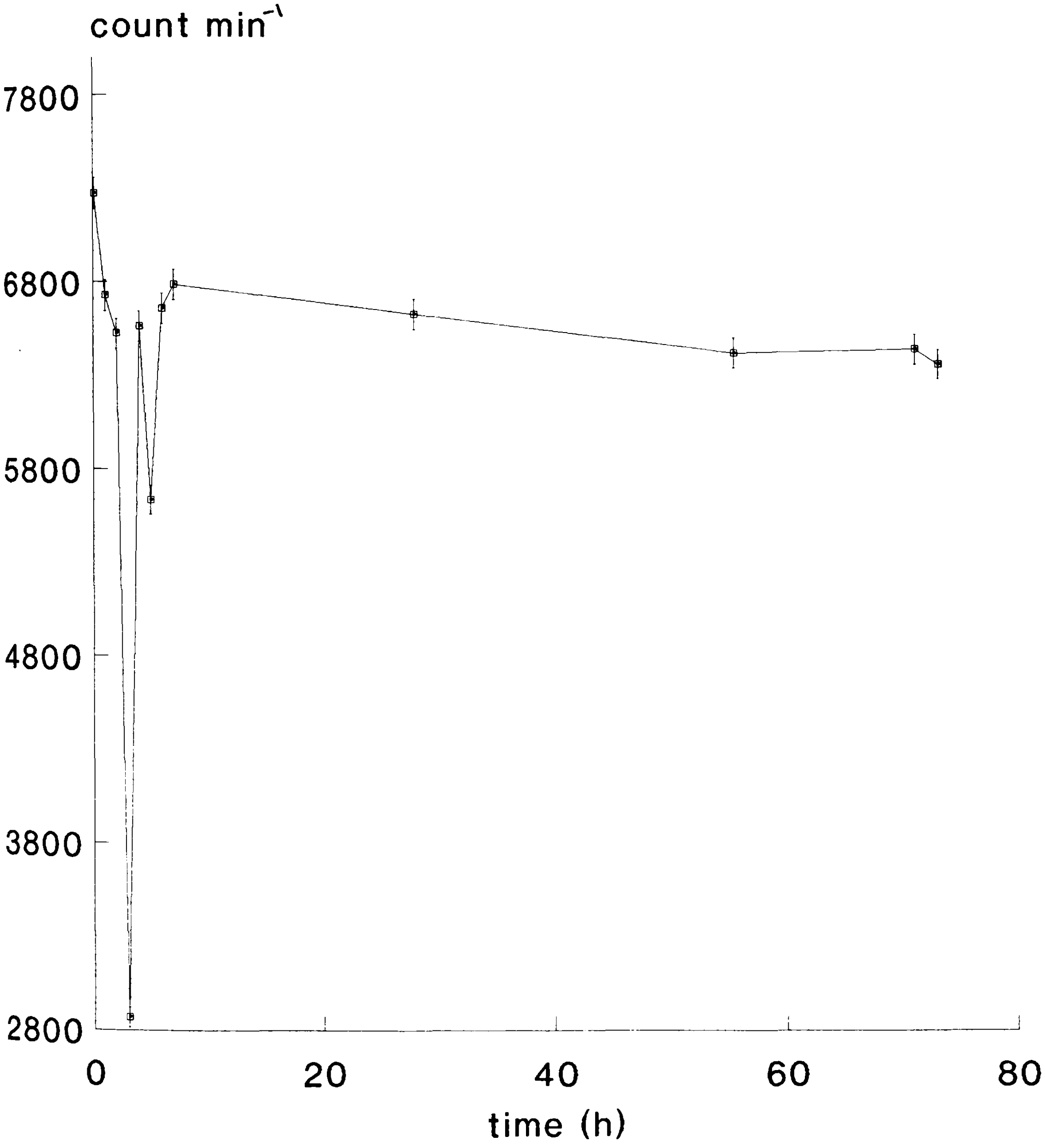
* Calculated as described in equation 3.1.

α Air admitted to the system.

A plot of solid count rate vs time is shown in figure 3.10. The drop in the solid count rate observed after 3 h was due to an electric fault. Ignoring this result the solid count rate remained constant. [^{36}Cl]-Chlorine activity was observed in the vapour phase but it was too small to be determined precisely. An infrared spectrum of the volatile products showed evidence for CCl_2FCClF_2. There were no peaks corresponding to CCl_3CF_3. Mass balance data for the reaction indicated that the retained material was equivalent to 95% of the original CCl_2FCClF_2 added.

A fresh sample of [^{36}Cl]-chlorine labelled aluminium(III) chloride was prepared, but was not transferred to the counting vessel. Gaseous CCl_2FCClF_2 was allowed to react with the solid. After 24 h the volatile products were removed. Mass balance data indicated that 37% of the original CCl_2FCClF_2 added was retained by the solid. The volatile products were analysed by radio G.C. and ^{19}F nmr spectroscopy. The results are shown in tables 3.9 and 3.10 respectively. These agree with Miller's original observation [76] as there was no [^{36}Cl]-chlorine activity observed in the CCl_3CF_3 fraction. The discrepency between the data shown in tables 3.9 and 3.10 is accounted for by the fact that the oven temperature for g.c. analysis was set at 60°C. This was not high enough to separate the highly chlorinated products CCl_2CClF_2, CCl_3CCl_2F and C_2Cl_6 completely; obviously C_2Cl_6 cannot be detected using ^{19}F nmr spectroscopy.

Figure 3.10 Reaction of CClF2CClF2 with [36Cl]-Aluminium (III) Chloride Solid count rate vs time



The last point corresponds to the reading taken once the gas was removed

Table 3.9

The Interaction Between Gaseous CCl_2FCClF_2 and [^{36}Cl]-Chlorine labelled Aluminium(III) Chloride at Room Temperature.

Analyses of the Product Mixture by Gas Chromatography.

Chlorofluorocarbon	% *	Count Rate count min^{-1}
CCl_2FCF_3	2	30
CCl_2FCClF_2	1	10
CCl_3CF_3	47	4
CCl_3CClF_2	4	not determined
CCl_3CCl_2F	6	not determined
C_2Cl_6	2	not determined

* Calculated as described in equation 3.2.

Table 3.10

The Interaction Between Gaseous CCl_2FCClF_2 and [^{36}Cl]-Chlorine labelled Aluminium(III) Chloride.

Analyses of the Product Mixture by ^{19}F nmr Spectroscopy

Chlorofluorocarbon	% *
CCl_2FCF_3	trace
CCl_2FCClF_2	trace
CCl_3CF_3	36
CCl_3CClF_2	26.2
CCl_3CCl_2F	trace

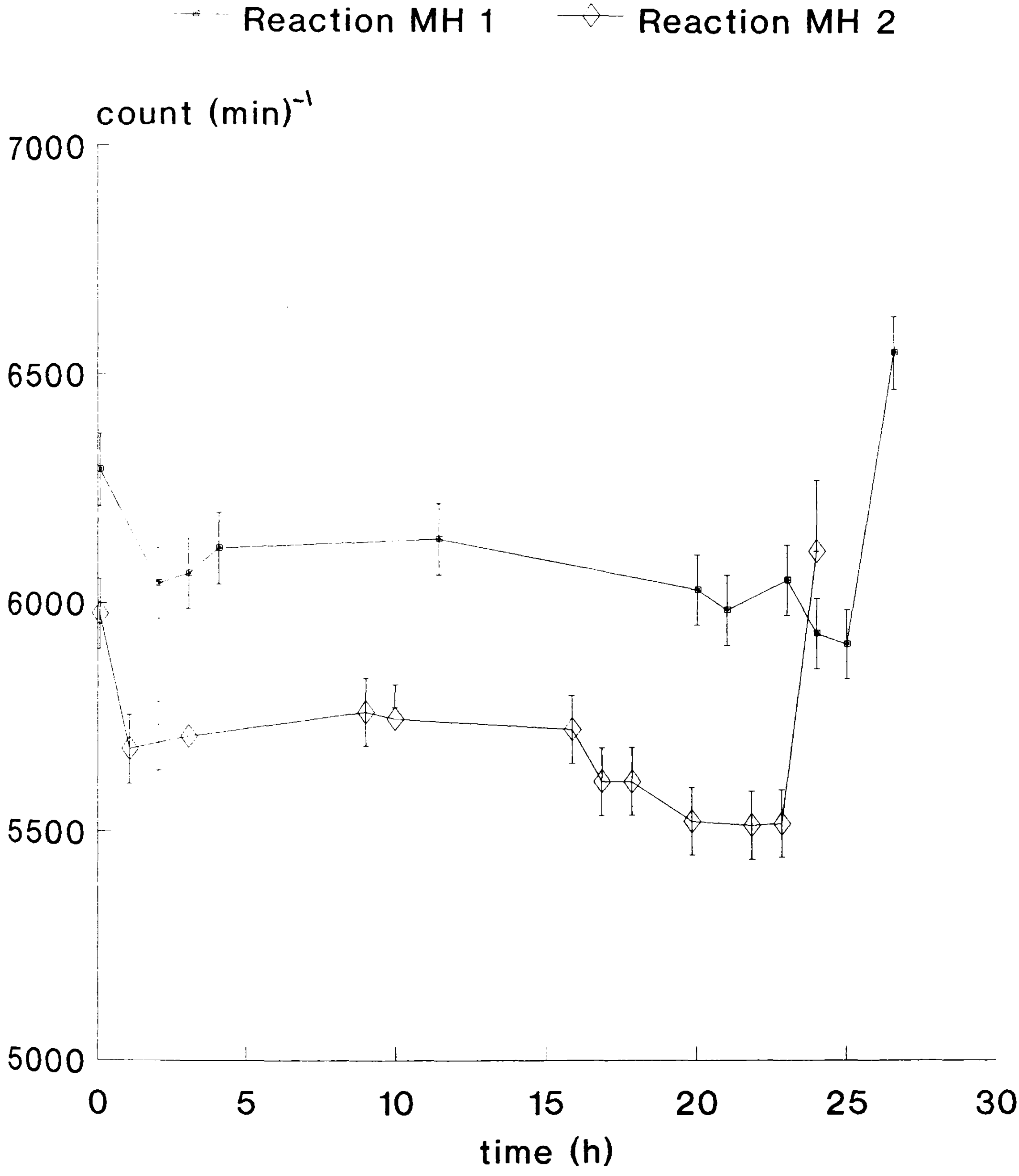
* Calculated as described in equation 3.2.

3.3.4 A Study of the Reaction Between CCl_2FCClF_2 and [^{36}Cl]-Chlorine labelled Aluminium(III) Chloride Pre-treated with CCl_2FCClF_2

[^{36}Cl]-Chlorine labelled aluminium(III) chloride pretreated with CCl_2FCClF_2 was prepared in the counting cell as described in 3.3.3. Two aliquots of CCl_2FCClF_2 were successively allowed to react with the solid for a period of 24 h. The solid and vapour phase count rates were monitored for the duration of the reaction. The results are shown in Figure 3.11. The solid count rate remained constant at 6 x 10^3 count min^{-1} during reaction MH1 but increased to 6500 count min^{-1} after the volatile products were removed.

The solid count rate fell gradually to 5500 count min^{-1} during reaction MH2 but increased to 6 x 10^3 count min^{-1} once the volatile products were removed. This was a significant decrease from the initial surface count rate of 8 x 10^3 count min^{-1}. After all gaseous material had been removed from the counting vessel the solid was left in vacuo for 36 h. During this time the surface count rate fell to 5.5 x 10^3 count min^{-1}. A vapour phase count rate was detected but it was too small to be determined precisely.

Figure 3.11 Experiment MH Reactions of CCl_2FCClF_2 with CCl_2FCClF_2/[^{36}Cl]-Aluminium Chloride Solid count rate vs time

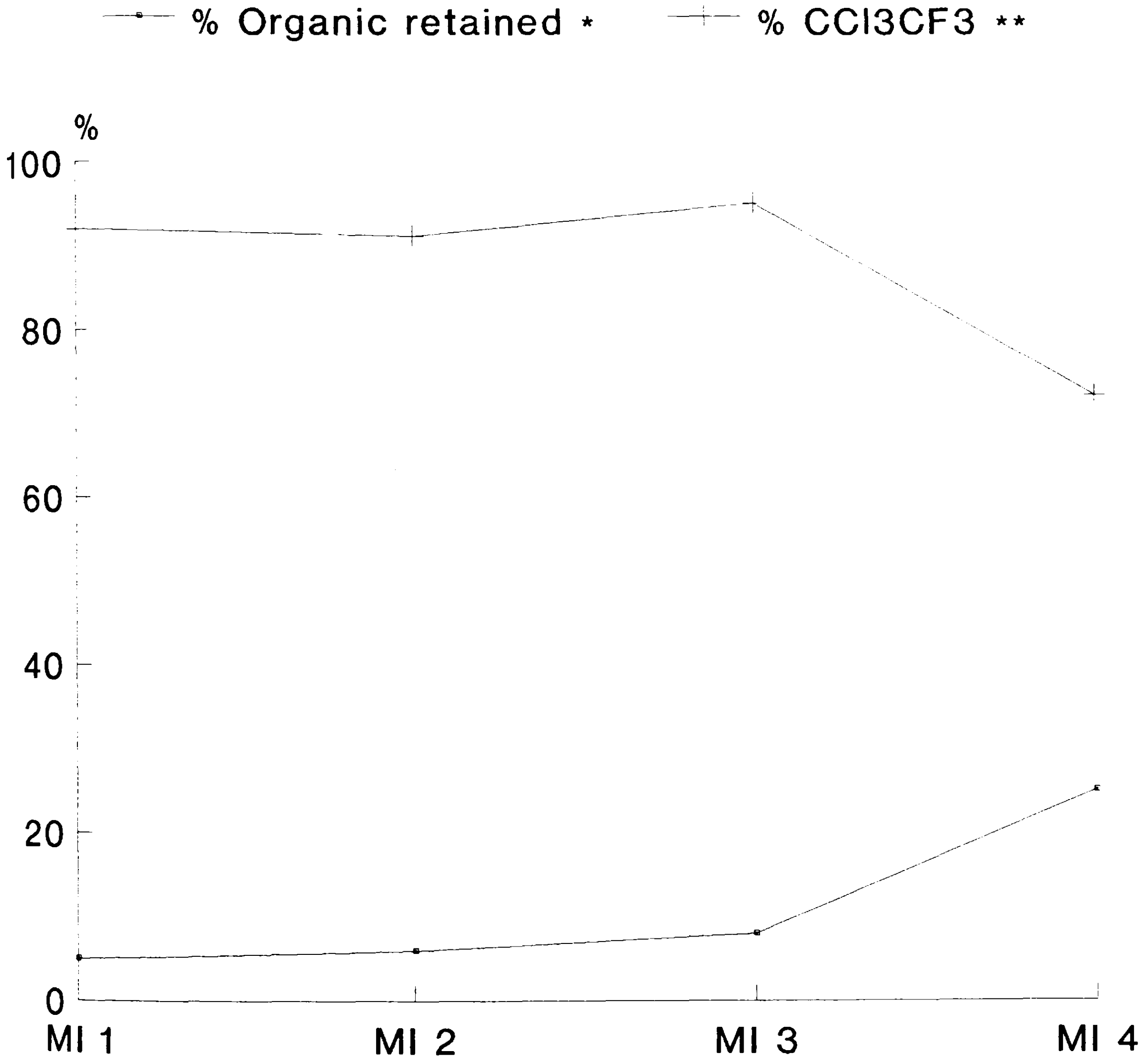


The last point corresponds to the reading taken once the gas was removed

The volatile products from reactions MH1 and MH2 were analysed qualitatively by i.r. spectroscopy. There was no evidence in either spectrum to support the formation of CCl_3CF_3. Mass balance data showed that the amount of organic material retained on the solid surface after reactions MH1 and MH2 was 15% and 25% respectively. These values are expressed as a percentage of the original aliquot of CCl_2FCClF_2 used in the reaction. A second experiment was conducted in an alternative reaction vessel, to ensure no moisture contaminated the solid. This vessel was not equipped with Geiger-Müller counters. The mass balance data and the amount of CCl_3CF_3 produced for each reaction studied in this experiment are shown in figure 3.12. After reactions MI1, MI2 and MI3 the quantity of material retained on the surface was less than 10% of the quantity of CCl_2FCClF_2 added at the start of the reaction. However, the quantity of CCl_3CF_3 produced was equivalent to 90% of the CCl_2FCClF_2 added. The quantity of material retained on the surface after reaction MI4 increased to 25% but the quantity of CCl_3CF_3 produced decreased.

The volatile product mixtures were analysed by ^{19}F nmr spectroscopy, the results are shown in table 3.11. In all reactions studied the quantity of CCl_2FCClF_2 produced was less than the total quantity of chlorinated products formed. This experiment was repeated using non radiolabelled CCl_4. The purpose of this experiment was to examine the interaction, if any, between solid aluminium(III) chloride and CCl_4 vapour. Gaseous CCl_4 was heated at 50^{o}C in the presence of solid

Figure 3.12 Experiment MI Reactions between CCl2FCClF2 and CCl2FCClF2 treated [36Cl]-Aluminium (III) Chloride



Wt AlCl3 : 1.24g (9.20mmol)
*Calculated as shown in equation 3.1
**Calculated as shown in equation 3.2

Table 3.11

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with $[^{36}Cl]$-CCl_2FCClF_2

Analyses of the Volatile Product Mixtures.
From Experiment MI by ^{19}F nmr Spectroscopy.

React^n	Chlorofluoroethane Product % *				
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2	CCl_3CCl_2F
MI1	1	trace	92	2	trace
MI2	1	trace	91	2	trace
MI3	1	trace	95	1	trace
MI4	1	trace	72	2	trace

* Calculated as described in equation 3.2.

aluminium(III) chloride for 20 h. During this time the solid developed a yellow colour that remained after the volatile products were removed. The infrared spectrum of the product mixture showed evidence of CCl_4. Peaks corresponding to the decomposition products $COCl_2$ and HCl were not detected. The quantity of material retained by the solid was less than 10% of the original quantity of CCl_4 added.

After treatment with CCl_4 gaseous CCl_2FCClF_2 was allowed to interact with the solid surface for 24 h. An infrared spectrum of the volatile products showed the presence of CCl_3CF_3. There was no evidence to support the formation of CCl_4 or HCl. The mass balance data for this reaction showed that the quantity of organic material retained by the solid was 14% of the initial aliquot of CCl_2FCClF_2 added.

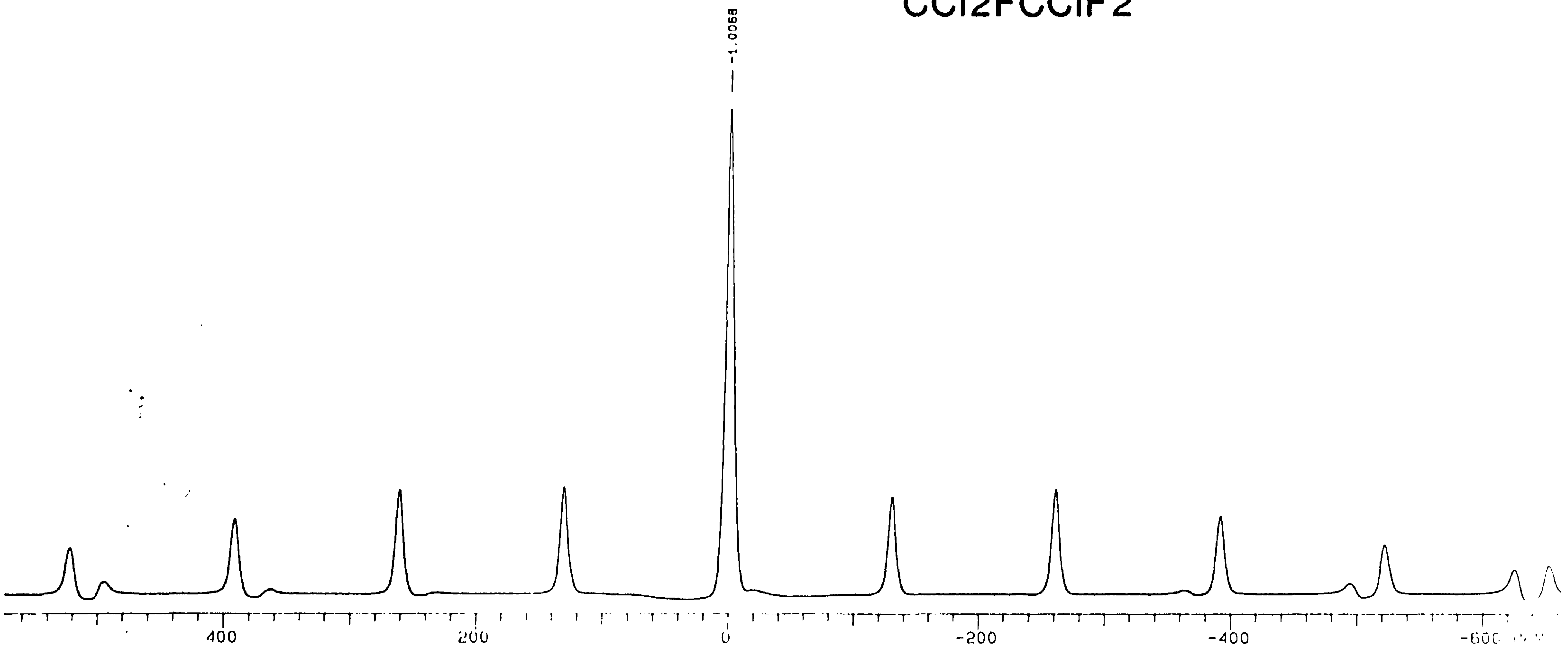
The solid was analysed by ^{27}Al and ^{13}C MAS solid state nmr spectroscopy. A signal at -1.00 ppm corresponded to octrahedrally coordinated aluminium atoms (figure 3.13). The other eight peaks in this spectrum were attributed to spinning side bands. The ^{13}C solid state nmr spectrum showed a peak at +105.7 ppm (figure 3.14). This was in the region of chloroflurocarbon signals and corresponded to hexachloroethane which has a signal at 105 ppm [99]. The signal was broad due to background signals from the probe rotor endcaps. The spectrum was proton decoupled but not ^{19}F decoupled so any carbon that was directly bonded to a fluorine would have given a signal too broad to be observed.

3.3.5 The Preparation of [^{18}F]-Fluorine Labelled CCl_2FCClF_2

Attempts were made to fluorinate CCl_3CClF_2 and CCl_2FCCl_2F with UF_6 but the reactions were not successful. The infrared spectra of the products obtained showed the presence of UF_6 and SiF_4.

An alternative method of production was to flow CCl_2FCClF_2 over a chromia catalyst labelled with [^{18}F]-fluorine. This was successful but such a small quantity of [^{18}F]-CCl_2FCClF_2 was formed that it could not be isolated. If the product were isolable the activity in the [^{18}F]-CCl_2FCClF_2 would be so low that it would be unsuitable for use in a radiolabelling experiment.

Figure 3.13 27Al MAS nmr Spectrum of Aluminium (III) Chloride Pretreated with CCl4 then CCl2FCClF2



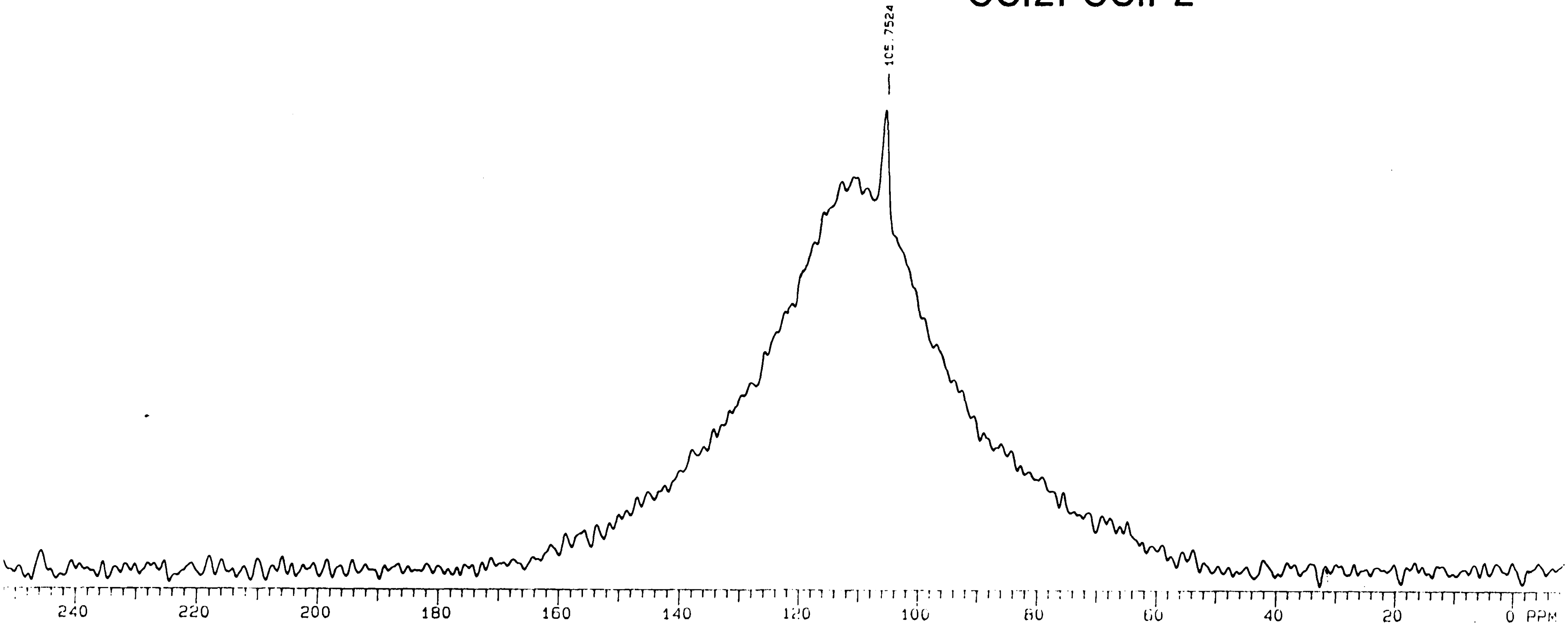


Figure 3.14 13C MAS nmr Spectrum of Aluminium (III) Chloride Pretreated with CCl4 then CCl2FCClF2

3.4 Studies of the Vapour Phase by Infrared Spectroscopy

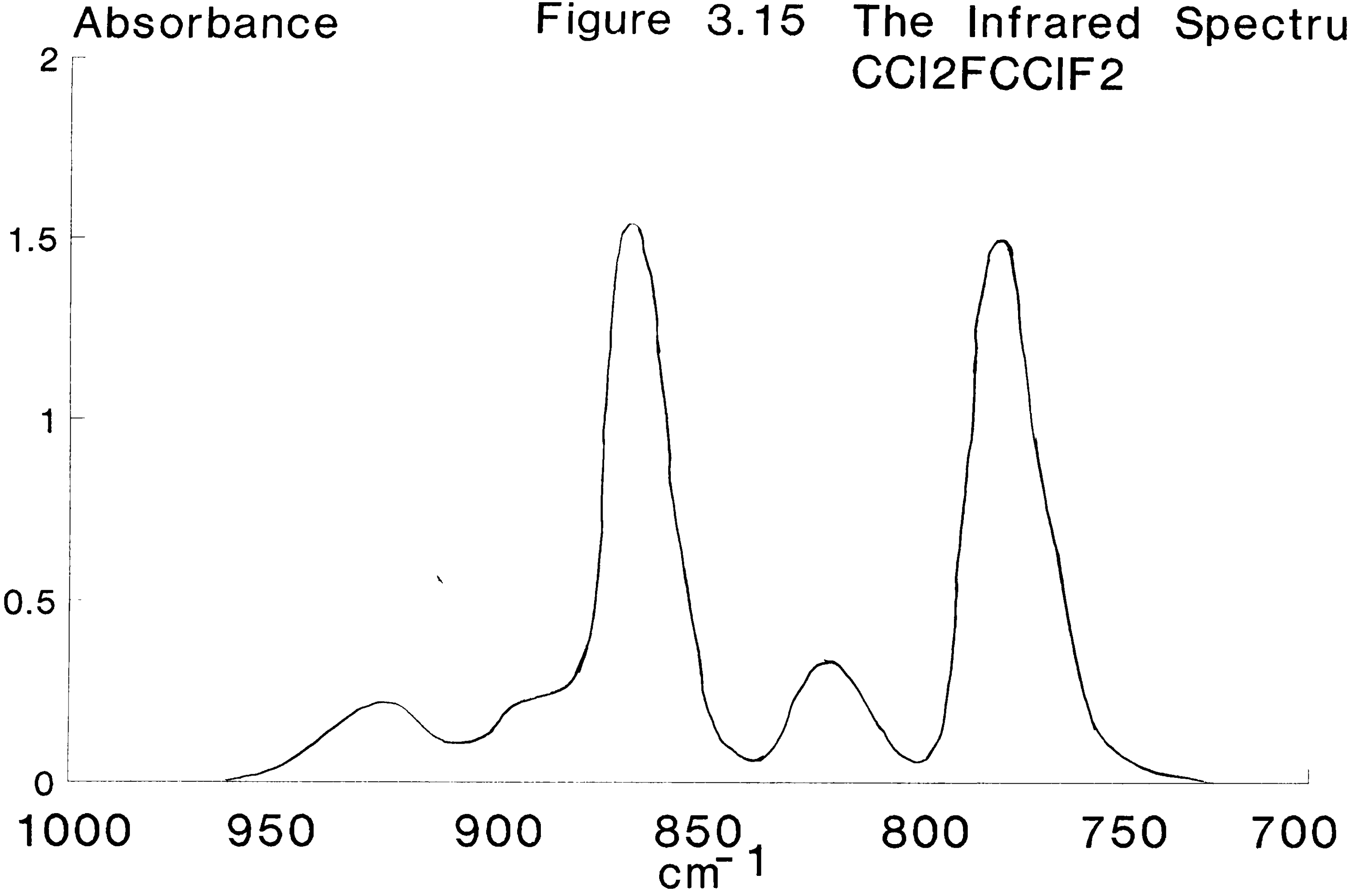
Infrared studies of the vapour phase during the course of the reaction were undertaken to obtain information on the kinetics of the isomerisation reaction $CCl_2FCClF_2 \rightarrow CCl_3CF_3$. These studies were successful and emphasised the importance of a moisture free environment.

3.4.1 Infrared Spectroscopic Studies of the Vapour Phase of the Reaction between Gaseous CCl_2FCClF_2 and Solid Aluminium(III) Chloride.

An experiment was conducted using the cell described in section 2.7.1. A spectrum of CCl_2FCClF_2 before solid was admitted to the cell is shown in figure 3.15. After a 24 h reaction period the two peaks corresponding to CCl_2FCClF_2 had diminished and those corresponding to CCl_3CF_3 had grown (figure 3.16). Infrared spectra obtained during a typical reaction are shown in figure 3.17. The 3 distinct isosbestic points indicated that CCl_3CF_3 was formed directly from CCl_2FCClF_2 without the build up of significant amounts of intermediate.

It was impossible to obtain mass balance data for these experiments because insufficient volatile material was produced. Only the quantity of CCl_2FCClF_2 vapour admitted to the cell, could be measured with any precision. The percentage of CCl_2FCClF_2 and CCl_3CF_3 in the vapour phase during the course of a reaction with respect to the original amount of CCl_2FCClF_2 added was

Figure 3.15 The Infrared Spectrum of CCl2FCClF2



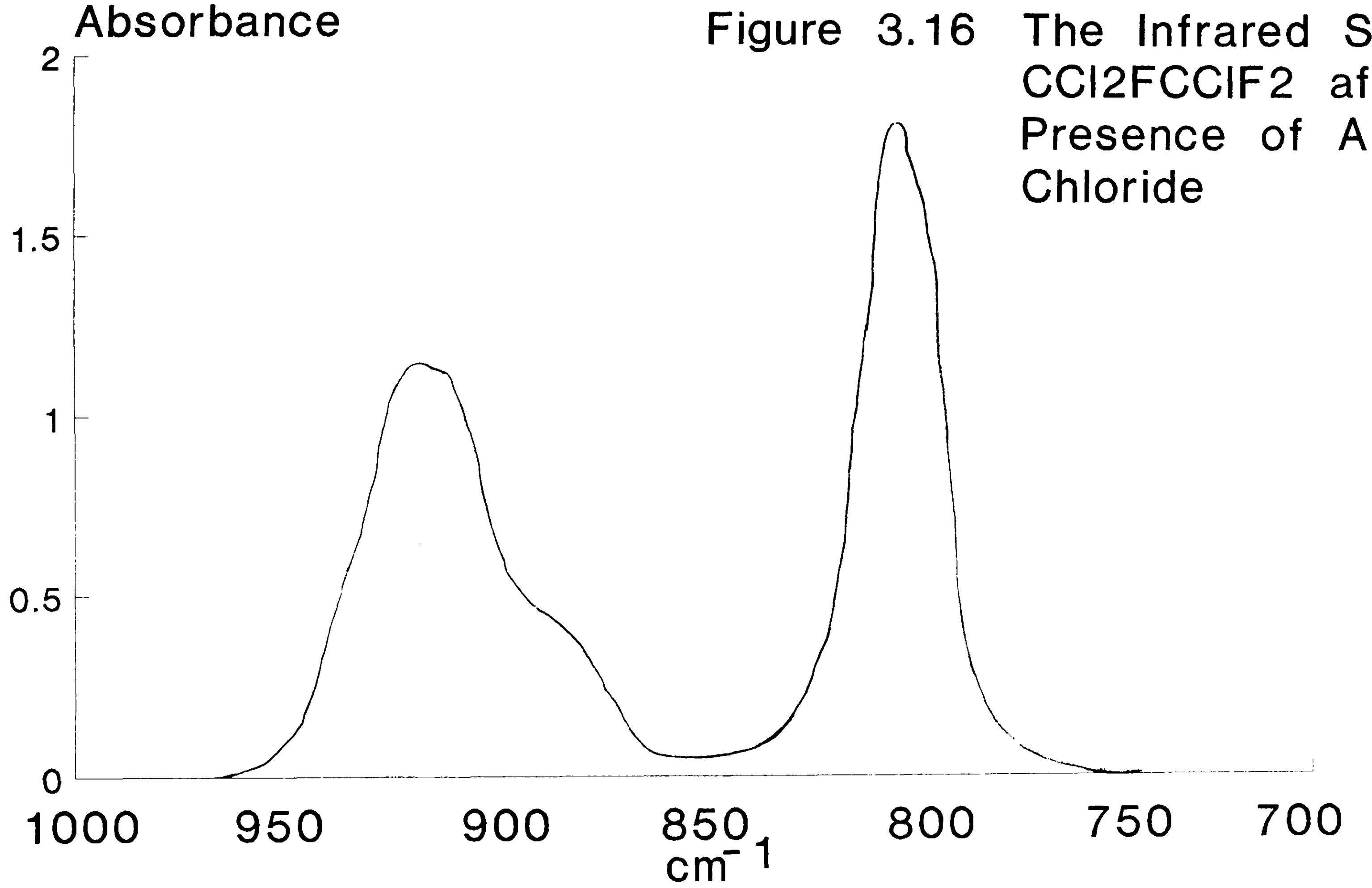
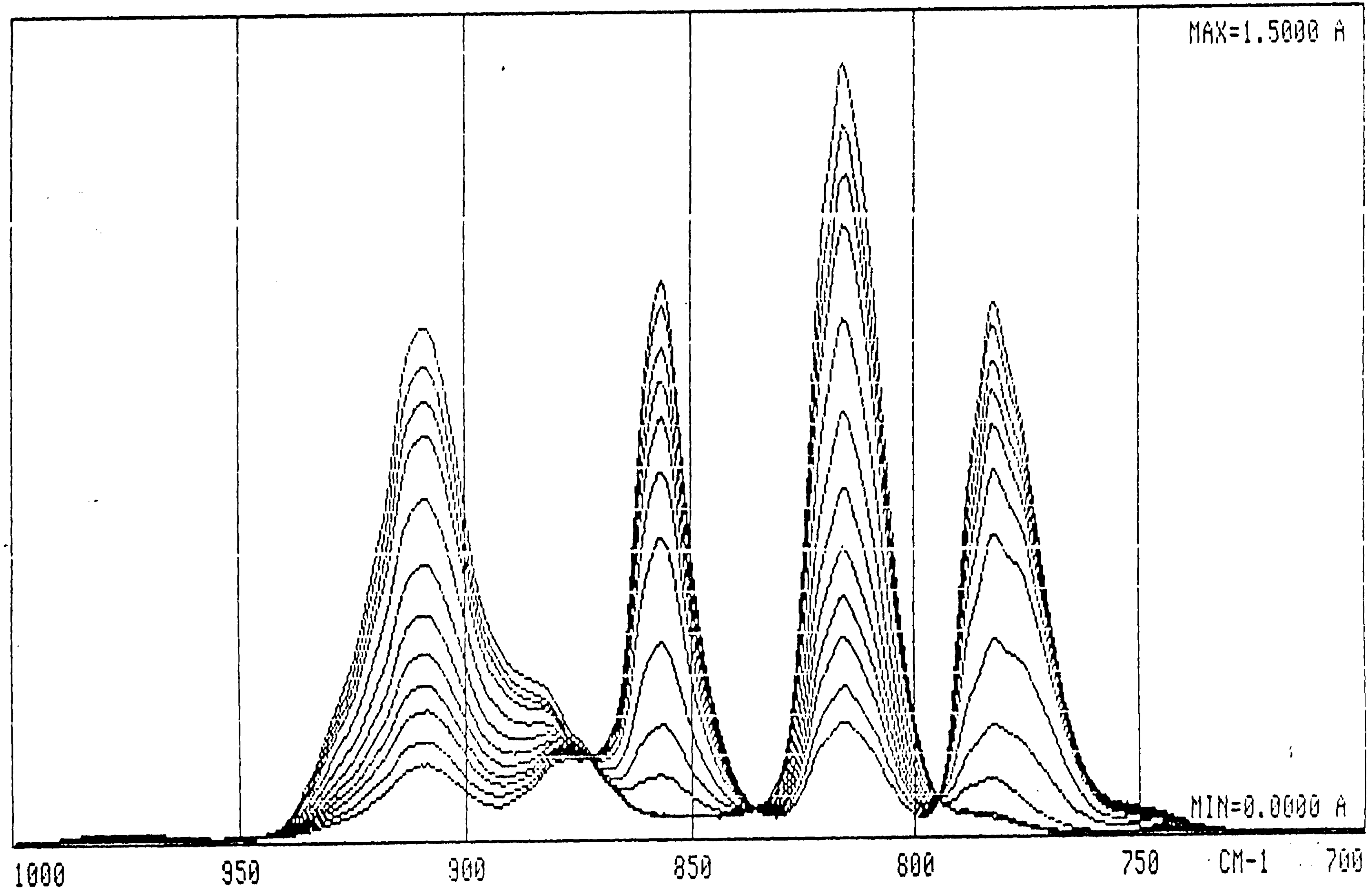


Figure 3.16 The Infrared Spectrum of CCl2FCClF2 after 24h in the Presence of Aluminium (III) Chloride

Figure 3.17 The Spectra Accumulated During a 24h Reaction Between CCl2FCClF2 and Aluminium (III) Chloride



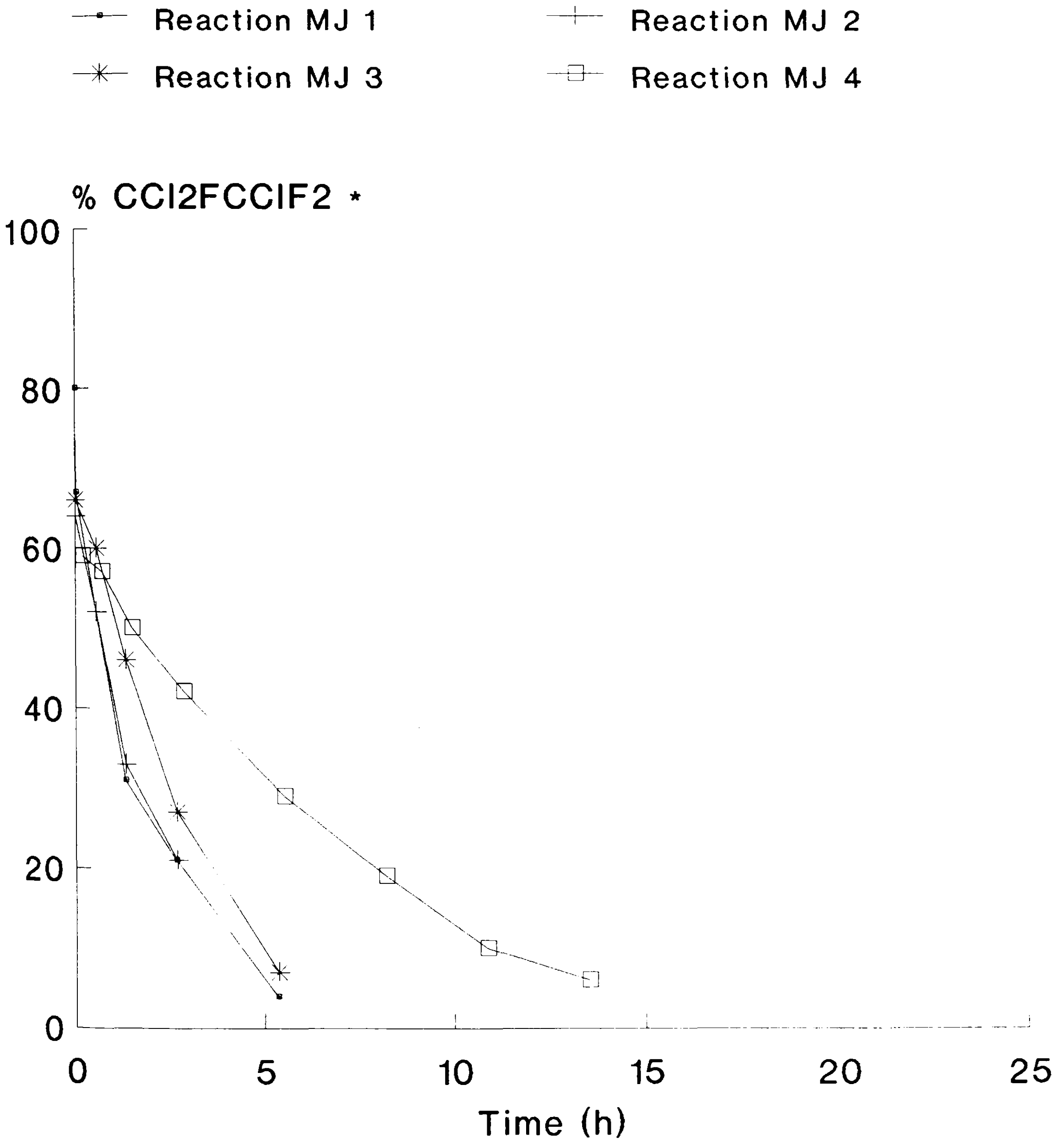
calculated. The results are shown in figures 3.18 and 3.19 respectively.

In experiment MJ the maximum amount of CCl_3CF_3 produced in each reaction always occurred immediately after all the CCl_2FCClF_2 was consumed by the reaction (figures 3.18 and 3.19). In reactions MJ1, MJ2 and MJ3 the quantity of CCl_3CF_3 in the vapour phase decreased after the maximum was reached. However in reaction MJ4 the quantity of CCl_3CF_3 produced increased over the 24 h reaction period but the maximum quantity of CCl_3CF_3 produced in reaction MJ1 was not exceeded (figure 3.19).

This experiment was repeated using a fresh sample of aluminium(III) chloride. The quantities of CCl_2FCClF_2 and CCl_3CF_3 produced in each reaction expressed as percentages of the original aliquot of CCl_2FCClF_2 added, are plotted in figures 3.20 and 3.21 respectively. Reaction MK was the only reaction in which all the CCl_2FCClF_2 was consumed before the end of the reaction period (figure 3.20). The quantity of CCl_3CF_3 produced in reactions MK1 - MK4 increased steadily throughout the 24 h period (figure 3.21) but the maximum quantity of CCl_3CF_3 produced in reaction MK1 was not exceeded.

This experiment was repeated but owing to a leak in the infrared cell anhydrous conditions were not maintained throughout. The quantity of CCl_3CF_3 produced in each reaction as a percentage of the original amounts of moles of CCl_2FCClF_2 added is shown in figure 3.22. Data were not obtained to calculate a

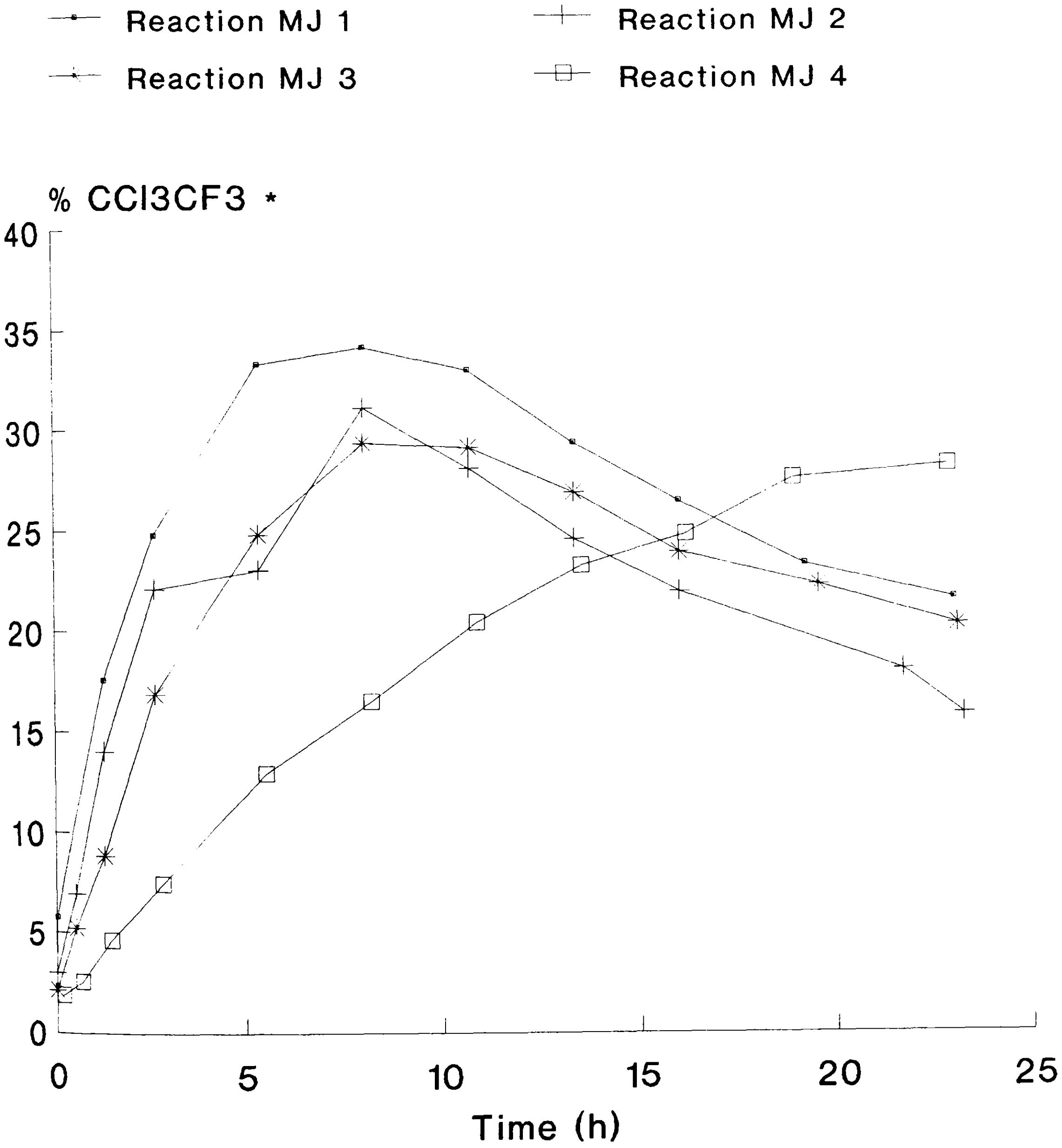
Figure 3.18 Experiment MJ IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride %CCl2FCClF2 vs time



* Calculated as shown in equation 3.2

Figure 3.19 Experiment MJ IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride

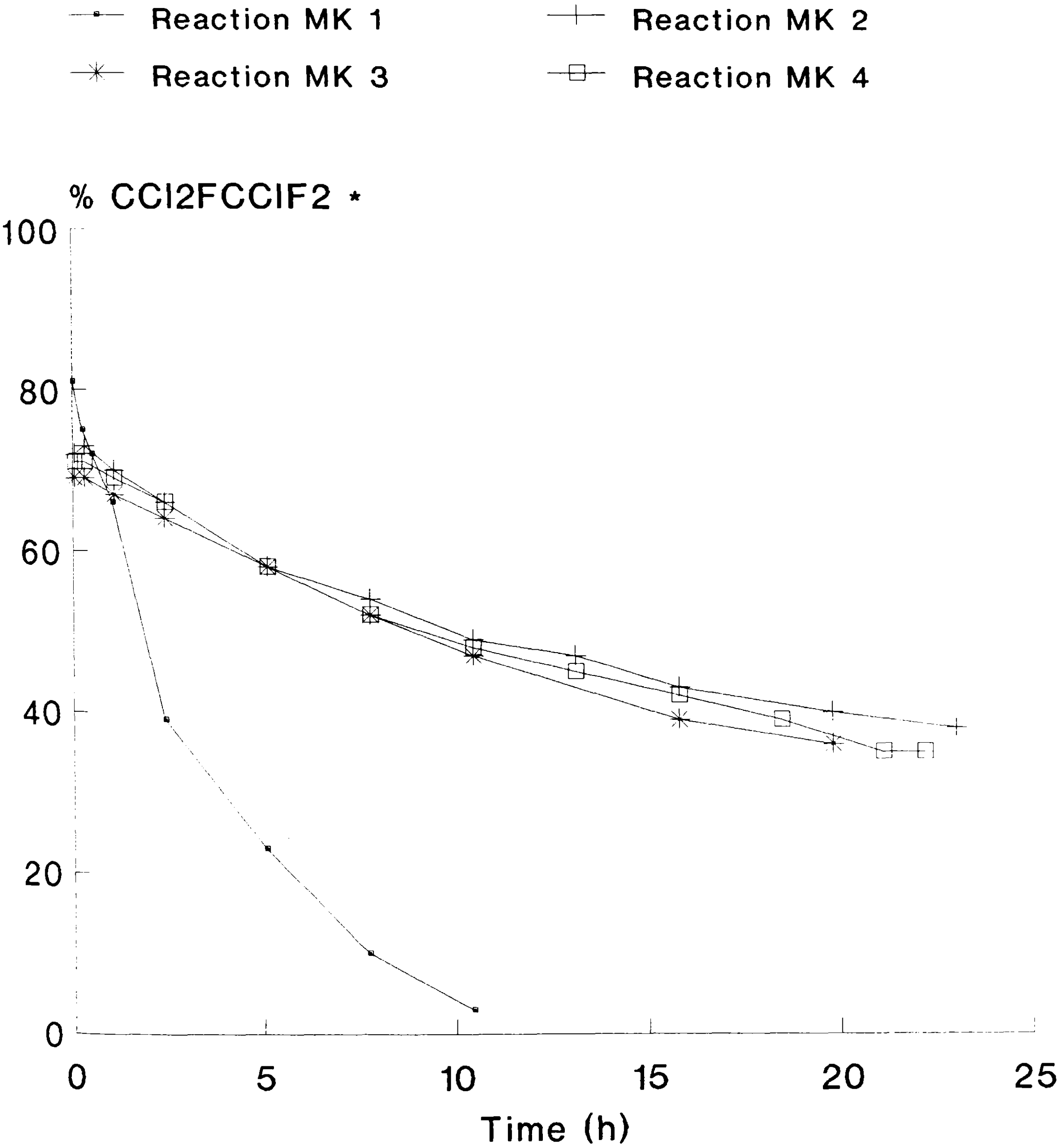
% CCl3CF3 vs time



* Calculated as shown in equation 3.2

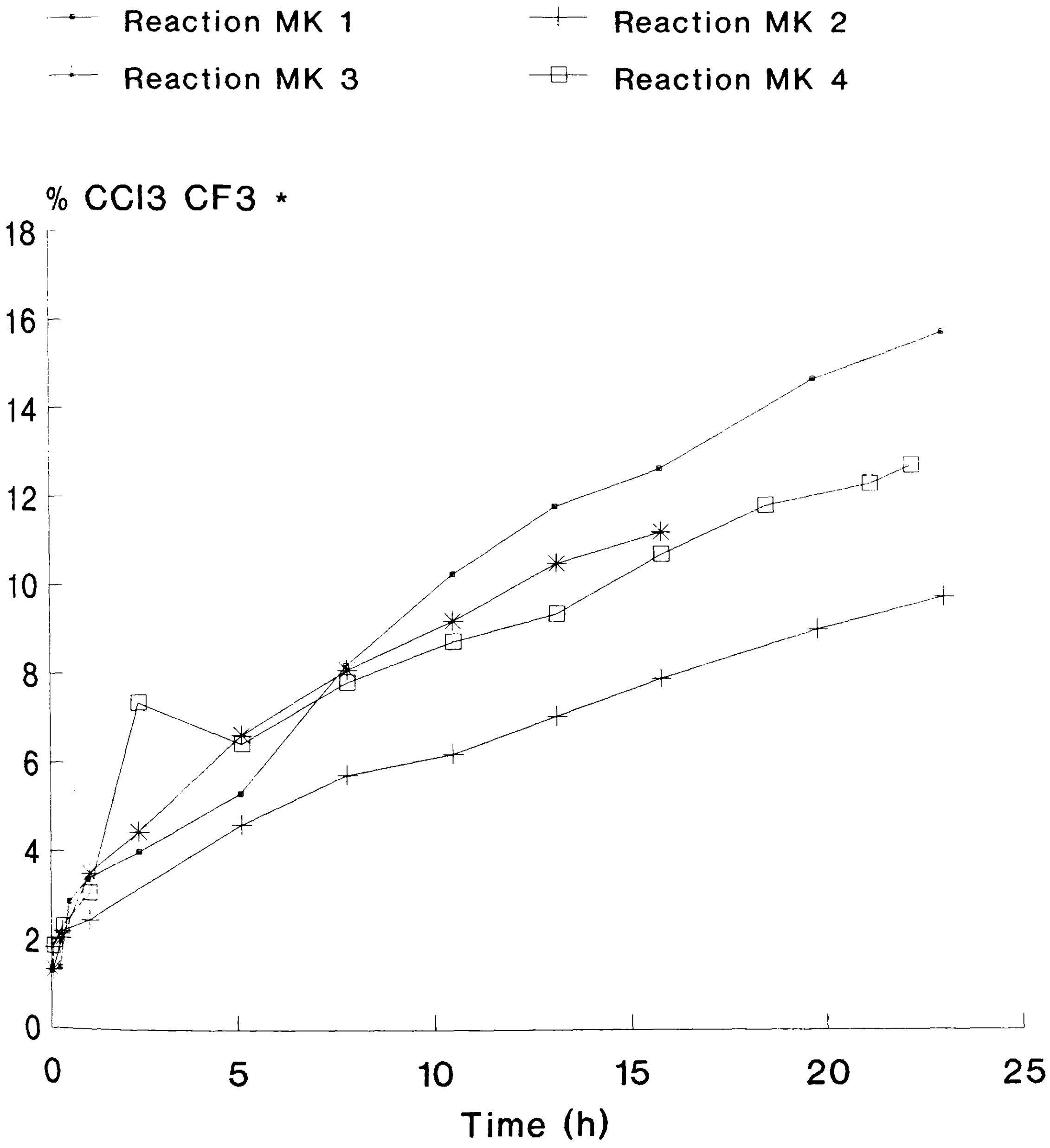
Figure 3.20 Experiment MK IR Studies of Reactions between CCl2FCClF2 and Aluminium (III) Chloride

%CCl2FCClF2 vs time



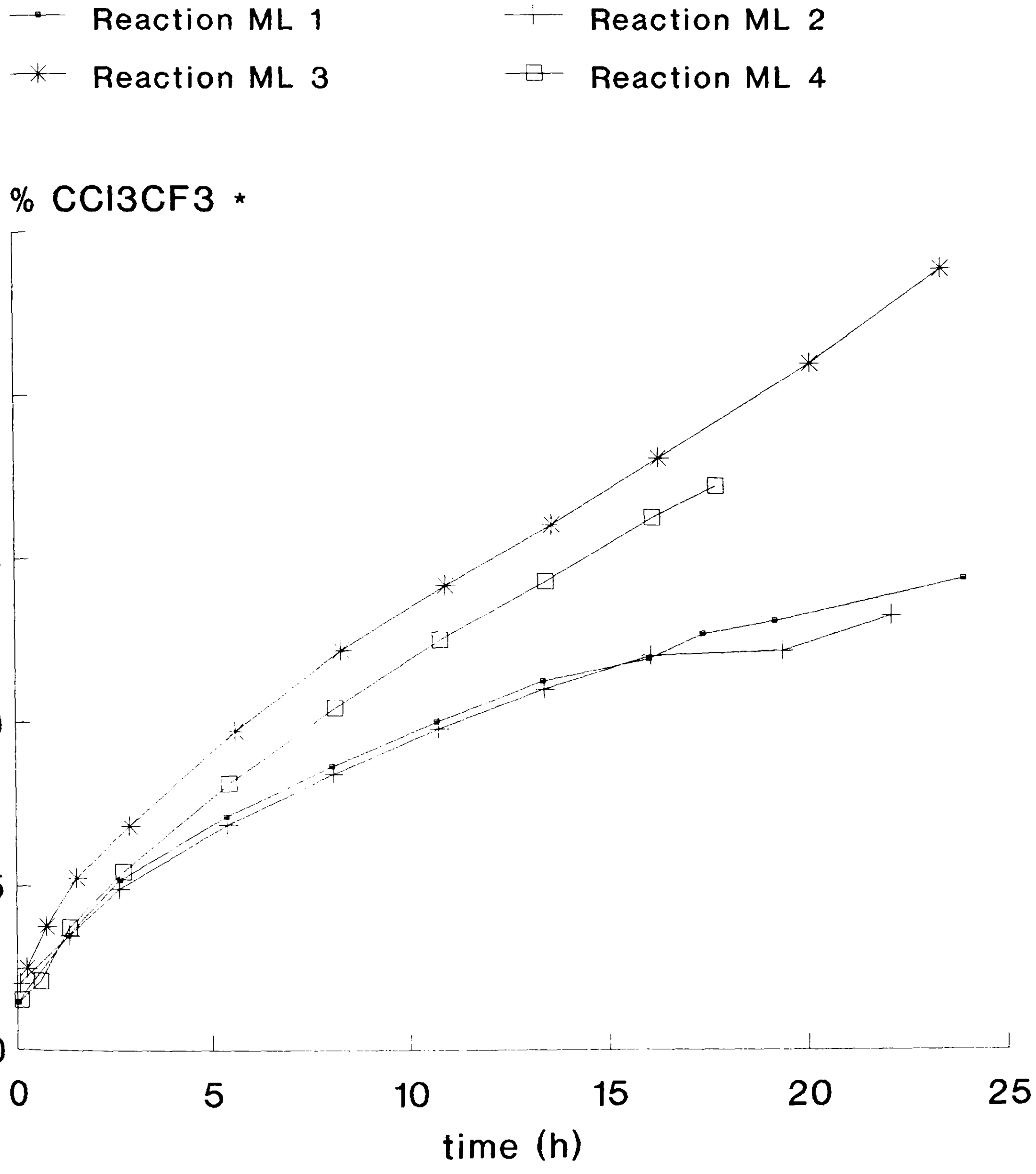
* Calculated as shown in equation 3.2

Figure 3.21 Experiment MK IR Studies of Reactions between CCl2FCClF2 and Aluminium (III) Chloride
% CCl3CF3 vs time



* Calculated as shown in equation 3.2

Figure 3.22 Experiment ML IR Studies of Reactions Between CCl2FCClF2 and Aluminium (III) Chloride
% CCl3CF3 vs time



* Calculated as shown in equation 3.2

similar plot for CCl_2FCClF_2. The maximum amount of CCl_3CF_3 produced in this experiment occurred in reaction ML3 and not in reaction ML1, as found for previous experiments. Evidently the presence of moisture inhibited the isomerisation of CCl_2FCClF_2. Experiment MJ was essentially moisture free and the maximum amount of CCl_3CF_3 produced was 34% of the original CCl_2FCClF_2 added. The maximum quantities of CCl_3CF_3 produced in experiments MK and ML were 16% and 24% in reactions MK1 and ML3 respectively.

3.4.2 Kinetic Studies of the Reaction Between Gaseous CCl_2FCClF_2 and Solid Aluminium(III) Chloride.

The experiments described thus far indicate that the reaction of gaseous CCl_2FCClF_2 with solid aluminium(III) chloride does not simply result in the isomerisation reaction $CCl_2FCClF_2 \rightarrow CCl_3CF_3$. Fluorination and chlorination reactions are also involved. The loss of material to the surface is also an important feature as this changes the catalyst surface and may also affect reaction sites.

The reaction of interest is the isomerisation $CCl_2FCClF_2 \rightarrow CCl_3CF_3$. Plots of the first and second order kinetics for the production of CCl_3CF_3 in experiments MJ, MK and ML were calculated. Linear relationships were not obtained therefore the production of CCl_3CF_3 does not follow a simple kinetic process.

3.5 Reaction of Aluminium(III) Chloride with other Fluorocarbons and Chlorofluorocarbons.

The reaction of CCl_2FCClF_2 with aluminium(III) chloride produced CCl_2FCF_3, CCl_3CF_3, CCl_3CClF_2 CCl_3CCl_2F and C_2Cl_6. In this section, a study made of the interaction of other chlorofluorocarbons with solid aluminium(III) chloride is described. The reactions studied were:

(i) the reaction of CCl_3CClF_2 with aluminium(III) chloride

(ii) the reaction of CCl_2FCClF_2 with aluminium(III) chloride pretreated with CCl_3CClF_2

(iii) the reaction of perfluorohexane with aluminium(III) chloride, and

(iv) the reaction of $CClF_2CClF_2$ with aluminium(III) chloride.

3.5.1.1 Reaction of Aluminium(III) Chloride with CCl_3CClF_2.

The compound CCl_3CClF_2 is a solid at room temperature but melts at 40°C [100]. The solid was allowed to interact with an aluminium(III) chloride surface for a period of 24 h. Analysis of the volatile product mixture by ^{19}F nmr spectroscopy showed it to contain CCl_3CF_3 3.7%, CCl_3CClF_2 91.8% and CCl_3CCl_2F 4.4%. The product mass was not determined, therefore the percentage of each product with respect to the original aliquot of CCl_2FCClF_2 added could not be calculated.This experiment was repeated using a fresh sample of aluminium(III) chloride. The volatile products were removed after 24 h and the mass balance data indicated that 89% of the original aliquot of CCl_3CClF_2 added was retained on the surface. The volatile product mixture was analysed by ^{19}F nmr spectroscopy. The quantity of each product was expressed as a percentage of the original amount of CCl_3CClF_2 added. The results are shown in table 3.12

Table 3.12
Reaction Between CCl_3CClF_2 and Aluminium(III) Chloride at room temperature.
Analyses of the Product Mixture by ^{19}F nmr Spectroscopy.

Chlorofluoroethane	% *
CCl_2FCF_3	trace
CCl_2FCClF_2	0.3
CCl_3CClF_2	5.73
CCl_3CF_3	5.07

*** Calculated as described in equation 3.2.**

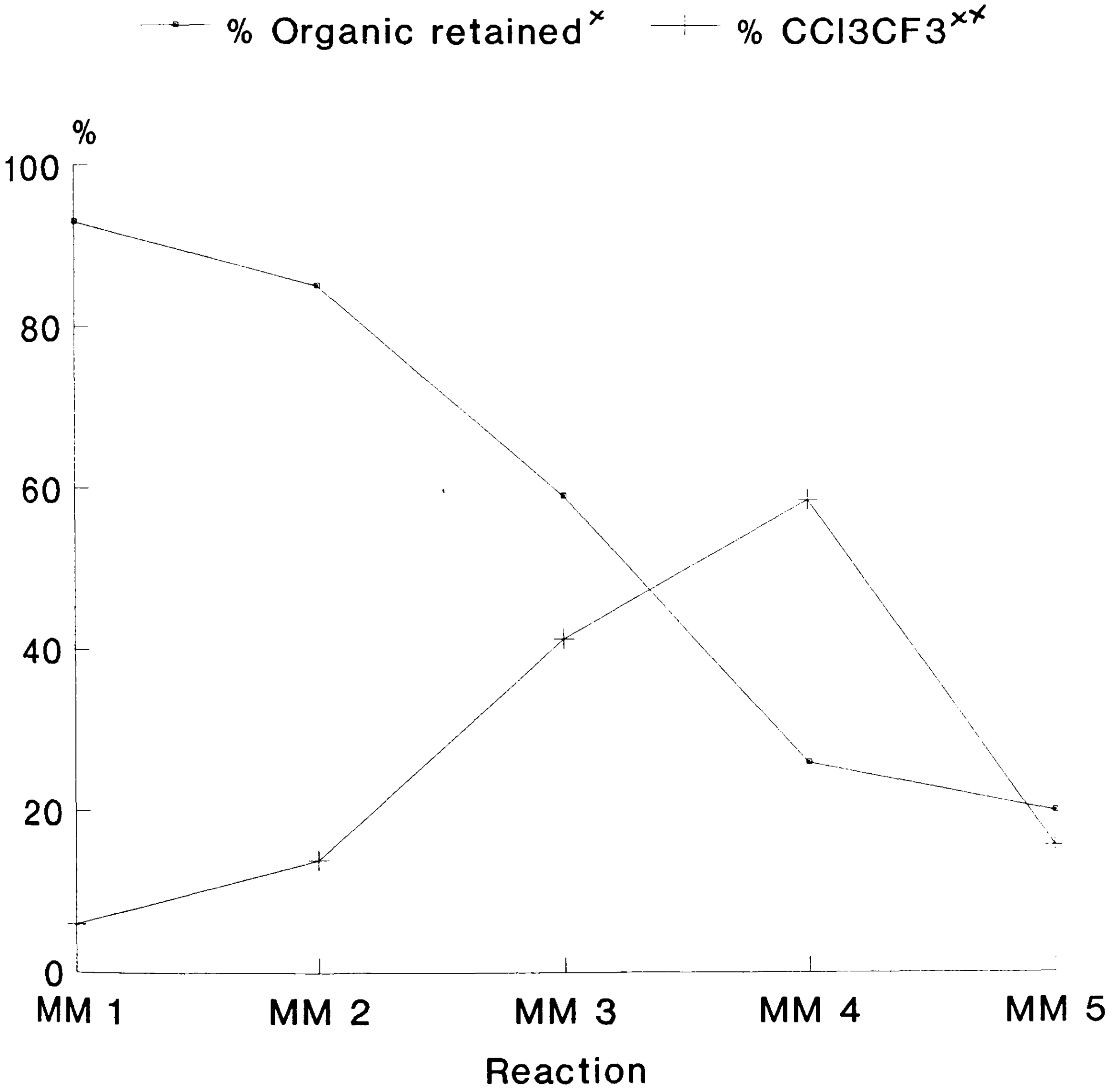
These results showed that at room temperature CCl_3CClF_2 was fluorinated in the presence of aluminium (III) chloride but it was not isomerised.

3.5.1.2 Reaction of Gaseous CCl_2FCClF_2 with Aluminium(III) Chloride Pretreated with CCl_3CClF_2.

Aluminium(III) chloride was pretreated with CCl_3CClF_2. Gaseous CCl_2FCClF_2 was allowed to interact with the solid. After 24 h the volatile products were removed. Mass balance data showed that >90% of the CCl_2FCClF_2 added was retained by the solid (figures 3.23). The quantity of CCl_3CF_3 produced was equivalent to 6% of the amount of CCl_2FCClF_2 added (figure 3.23). Quantitative analyses of the volatile product mixtures were carried out by ^{19}F nmr spectroscopy. The results are shown in table 3.13. Isomerisation occurred in each reaction but in reactions MM4 and MM5 a significant quantity of CCl_2FCClF_2 remained unreacted. It was also interesting to note that with the exception of reaction MM4 the quantity of CCl_2FCF_3 produced in each reaction exceeded the amount of chlorinated products.

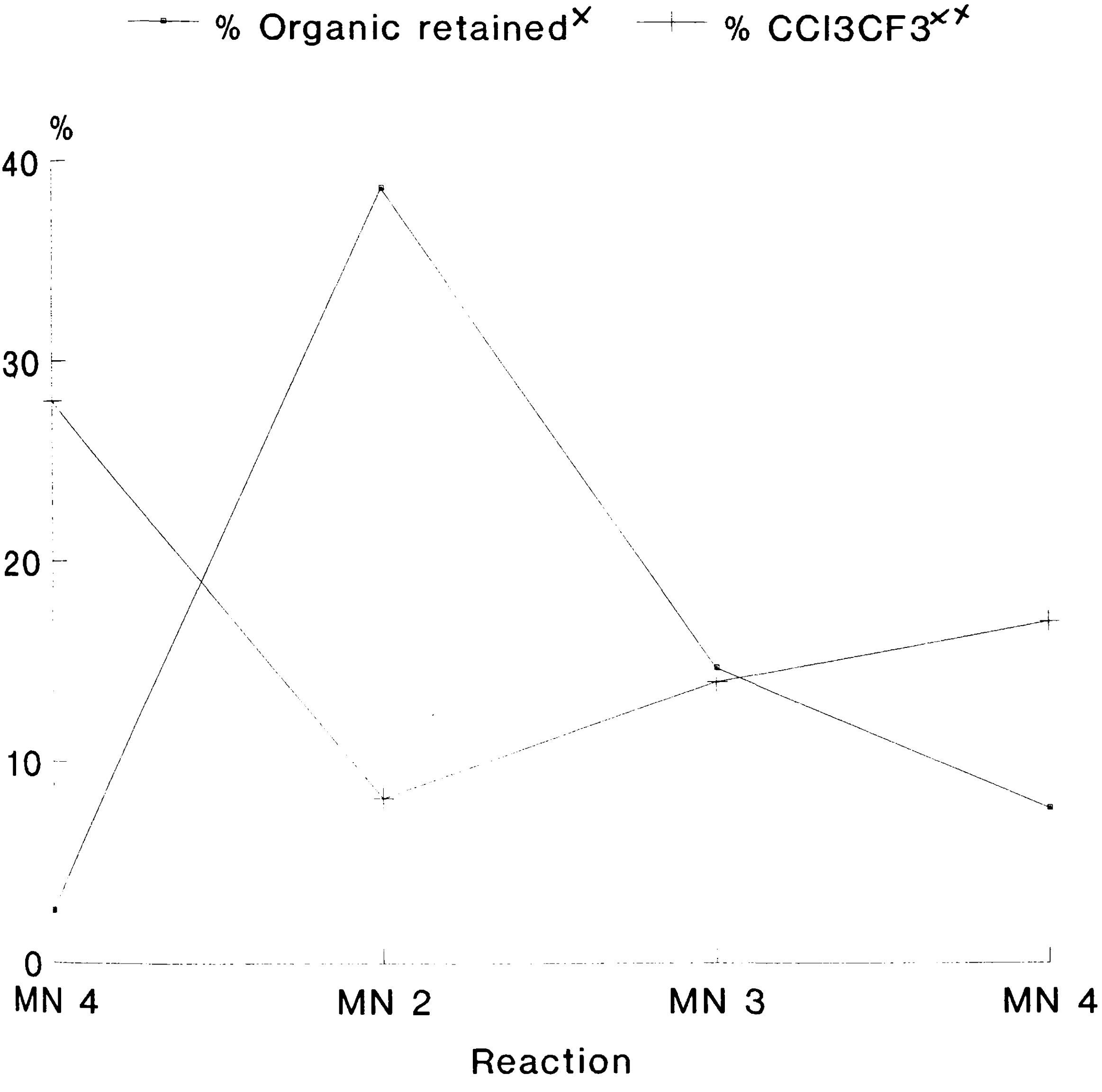
This experiment was repeated with a fresh sample of solid. After reaction MN1 the mass balance data showed the quantity of material retained at the surface was >5% of the CCl_2FCClF_2 added (cf. MM1 >90%). The quantity of CCl_3CF_3 produced was >30% of the CCl_2FCClF_2 added (figure 3.24). The maximum quantity of CCl_3CF_3 produced occurred after reaction MN2. The lowest quantity of material retained by the surface > 10g% of the original CCl_2FCClF_2 added was also observed after this reaction.

Figure 3.23 Experiment MM Reactions between CCl2FCClF2 and CCl3CClF2/Aluminium (III) Chloride



Wt AlCl : 2.8365g (11.51mmol)
*Calculated as shown in equation 3.1
**Calculated as shown in Equation 3.2

Figure 3.24 Experiment MN Reactions between CCl2FCClF2 and CCl3CClF2/Aluminium (III) Chloride



Wt AlCl3 : 0.6812g (5.10mmol)
* Calculated as shown in equation 3.1
** Calculated as shown in equation 3.2

Table 3.13
The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CCl_3CClF_2 at Room Temperature. Analyses of the Volatile Product Mixtures from Experiment MM by ^{19}F nmr Spectroscopy.

React^n	Chlorofluoroethane Present % *			
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2
MM1	trace	trace	6	trace
MM2	trace	trace	14	trace
MM3	1	trace	41	-
MM4	1	14	58	1
MM5	trace	63	16	-

* Calculated as described in equation 3.2.

Quantitative analyses of the volatile product mixtures were carried out by ^{19}F nmr spectroscopy. The results are shown in table 3.14. In all reactions a high proportion of CCl_2FCClF_2 remained unreacted and the quantity of CCl_2FCF_3 produced was always less than the amount of chlorinated products.

3.5.2 Reaction of Aluminium(III) Chloride with Perfluorohexane.

Gaseous perfluorohexane (C_6F_{14}) was allowed to interact with aluminium(III) chloride. After 36 h the volatile products were removed. The mass balance data showed that a negligible quantity of organic material was retained by the solid. The volatile products were analysed qualitatively by i.r. spectroscopy.

Table 3.14

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride at Room Temperature

Analyses of the Volatile Product Mixtures from Experiment MN by ^{19}F nmr Spectroscopy.

Reaction	Chlorofluoroethane Present % *			
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2
MN1	1	66	28	2
MN2	trace	52	9	1
MN3	trace	70	14	1
MN4	trace	74	17	1

* Calculated as described in equation 3.2.

The infrared spectrum obtained was identical to that of C_6F_{14}. Gaseous CCl_2FCClF_2 was then exposed to the solid. After 24 h the products were removed and analysed qualitatively by i.r spectroscopy. The infrared spectrum obtained showed the presence of CCl_2FCClF_2 and CCl_3CF_3.

The purpose of this experiment was to determine whether or not the retained layer was chemisorbed to the solid. Perfluorohexane has a similar boiling point and vapour pressure to CCl_2FCClF_2. If there were simply a physical attraction between the organic layer and aluminium(III) chloride then uptake of C_6F_{14} by the solid should have been observed. No such uptake was observed and further reaction of the solid with gaseous CCl_2FCClF_2 yielded products typical of those produced by reaction of CCl_2FCClF_2 and untreated aluminium(III) chloride. There was no spectroscopic evidence to suggest the presence of highly fluorinated compounds.

3.5.3 Reaction of Gaseous $CClF_2CClF_2$ with Solid Aluminium(II) Chloride.

Gaseous $CClF_2CClF_2$ was allowed to interact with aluminium(III) chloride. After 24 h the volatile products were removed. Mass balance data showed negligible loss of material. The volatile products were analysed qualitatively by i.r spectroscopy. There was no spectroscopic evidence to suggest the presence of the isomer CCl_2FCF_3. Only $CClF_2CClF_2$ was observed. Further analysis of the product mixture by gas chromatography confirmed these results.

The solid was then exposed to gaseous CCl_2FCClF_2. After 24 h the volatile products were removed. The mass balance data showed that 61% of the original CCl_2FCClF_2 added was retained by the solid. Gaseous $CClF_2CClF_2$ was allowed to interact with this modified surface. After 24 h the volatile products were removed but there was still no spectroscopic evidence to support the presence of CCl_2FCF_3. The purpose of this experiment was to determine the reaction by which CCl_2FCF_3 was formed. As $CClF_2CClF_2$ would not react with either aluminium(III) chloride or aluminium(III) chloride pretreated with CCl_2FCClF_2 then the presence of CCl_2FCF_3 in the product mixture must have arisen from the fluorination of CCl_3CF_3. This experiment also showed that a chlorofluoroethane will react with aluminium(III) chloride only if it contains a $-CCl_xF_{3-x}$ group where $x = 2$ or 3.

Experimental

3.6.1 The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride.

3.6.1.1 Using Aluminium(III) Chloride Handled in the Dry Box.

Aluminium(III) chloride (~ 0.2g) was sublimed as described in section 2.3.7. The sublimate was transferred to the dry box where it was loaded into a reaction vessel equipped with a side arm. The vessel was attached to the vacuum line and degassed. A weighed quantity of CCl_2FCClF_2, purified as described in 2.3.1, was distilled into the side arm and the vapour allowed to react with the solid surface for a period of

24 h. The volatile products were removed and weighed, before another aliquot of CCl_2FCClF_2 was added. This procedure was repeated a number of times. The products were analysed by g.c. and g.c/m.s as described in sections 2.6.1 and 2.6.4 respectively or by ^{19}F nmr spectroscopy as described in section 2.8.1.

3.6.1.2 Using Freshly Sublimed Aluminium(III) Chloride

The procedure was identical to that described in section 3.6.1.1. but the aluminium(III) chloride was sublimed directly into a reaction vessel equipped with a side arm.

3.6.2 The Reaction Between [^{36}Cl]-Chlorine labelled CCl_2FCClF_2 and Aluminium(III) Chloride

Aluminium(III) chloride (8.15 mmol) was sublimed and loaded into the counting vessel (described in 2.10.1). [^{36}Cl]-Chlorine labelled CCl_2FCCF_2 (2.45 mmol) (prepared in 2.5.2) specific count rate 540 count min^{-1} $mmol^{-1}$ was admitted and left to react for 24 h. The radioactivity on the solid and in the vapour phase was monitored over this period. After the reaction the volatile products were removed and the [^{36}Cl]-chlorine activity on the solid was counted.

3.6.3 Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride pretreated with $[^{36}Cl]$-CCl_2FCClF_2

Gaseous CCl_2FCClF_2 (1.95 mmol) was admitted to the counting cell and allowed to react with the $[^{36}Cl]$-chlorine labelled surface for 24 h. The count rates on the solid and in the vapour phase were monitored during this period. After 24 h the volatile products were removed and the $[^{36}Cl]$-chlorine activity on the solid was counted. A further three aliquots of CCl_2FCClF_2 were admitted to the vessel and each allowed to react with the solid for approximately 24 h.

3.6.4 The Reaction Between CCl_2FCClF_2 and $[^{36}Cl]$-Chlorine labelled Aluminium(III) Chloride.

$[^{36}Cl]$-Chlorine labelled aluminium(III) chloride was prepared as described in 2.5.4. The solid was loaded into the counting cell and gaseous CCl_2FCClF_2 was admitted. The $[^{36}Cl]$-chlorine activity was monitored throughout the 24 h reaction period and the $[^{36}Cl]$-chlorine activity was noted when the vapour phase was removed. This series of reactions was repeated in a Pyrex reaction vessel, not equipped with Geiger-Müller tubes.

3.6.5 The Reaction Between CCl_2FCClF_2 and $[^{36}Cl]$-Chlorine labelled Aluminium(III) Chloride pretreated with CCl_2FCClF_2.

The catalyst prepared in section 3.6.4 was reacted with further aliquots of gaseous CCl_2FCClF_2 the procedure followed is outlined in section 3.6.3.

3.6.6 The Preparation of [^{18}F]-Fluorine labelled CCl_2FCClF_2.

3.6.6.1 Reaction Between UF_6 and CCl_2FCClF_2.

The compound UF_6 was heated with either CCl_2FCClF_2 or CCl_3CClF_2 (4.97 mmol) at 60-100°C for 1 h. The products were removed and analysed by i.r spectroscopy.

3.6.6.2 Fluorination of CCl_2FCClF_2 by a Fluorinated Commercial Chromia Catalyst.

A pelleted commercial chromia catalyst was activated by heating to 425°C in a stream of N_2 for 6 h. The catalyst was then fluorinated with $H^{18}F$ at 50°C. Gaseous CCl_2FCClF_2 was passed over this catalyst in a nirogen flow at 23 ml min^{-1} for 4 h. The reactor temperature was held at 425°C. The volatile products were collected in a series of traps cooled to -197°C.

3.6.7 Infrared Spectroscopic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride.

The infrared cell described in 2.7.1 was loaded with CCl_2FCClF_2 (0.05 mmol). This was allowed to interact with aluminium(III) chloride (2.46 mmol) and spectra were obtained every 15 min over a period of 24 h. The gas was removed and a further aliquot of CCl_2FCClF_2 admitted. This procedure was repeated for a total of four aliquots. The same series of experiments was repeated twice with aluminium(III) chloride (4.68 mmol and 3.57 mmol).

3.6.8 Kinetic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride.

The experiments outlined in 3.6.7 were analysed using the procedure described in 2.7.5.

3.6.9 Reaction of Aluminium(III) Chloride with CCl_3CClF_2.

The compound CCl_3CClF_2 (5.10 mmol) was distilled onto freshly sublimed aluminium(III) chloride and left to react for 24 h. At the end of this period all volatile products were removed. This process was repeated using CCl_3CClF_2 (4.44 mmol) and aluminium(III) chloride (5.10 mmol).

3.6.10 Reaction of CCl_2FCClF_2 with Aluminium(III) Chloride Pretreated with CCl_3CClF_2.

Aluminium(III) chloride pretreated with CCl_3CClF_2 was allowed to react with CCl_2FCClF_2 (6.42 mmol) for a period of 24 h. The products were removed and another aliquot of CCl_2FCClF_2 was added. This process was repeated 3 times.

3.6.11 Reaction of Aluminium(III) Chloride with Perfluorohexane.

Freshly sublimed aluminium(III) chloride (0.54 mmol) was exposed to perfluorohexane vapour for 36 h.

The gaseous products were removed and CCl_2FCClF_2 (3.14 mmol) was allowed to interact with the surface. After 24 h the volatile products were removed.

3.6.12 Reaction of Aluminium(III) Chloride with $CClF_2CClF_2$.

The compound $CClF_2CClF_2$ (0.48 mmol) was allowed to react with freshly sublimed aluminium(III) chloride (0.68 mmol) for 24 h. Gaseous products were removed and CCl_2FCClF_2 (0.97 mmol) was admitted. After 24 h the products were removed and another aliquot of $CClF_2CClF_2$ was admitted. The volatile products were removed after 40 h.

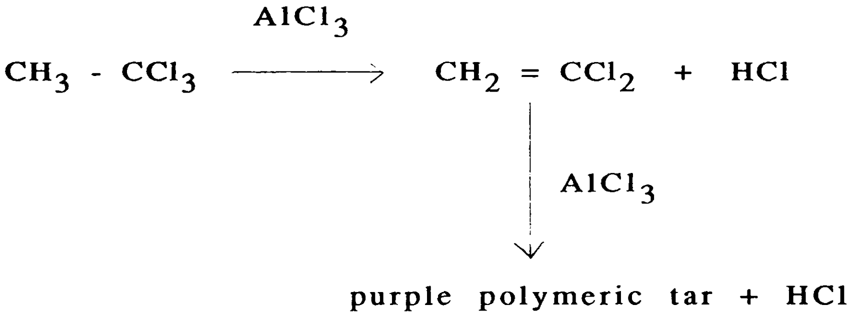
Chapter 4

The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with CH_3CCl_3.

4.1 Introduction

The polymerisation of most olefins occurs in the presence of aluminium(III) chloride. The active catalyst is usually in the form of an alkyl aluminium compound such as $(C_2H_5)AlCl_2$ [101].

The reaction between CH_3CCl_3 and aluminium(III) chloride results in the dehydrochlorination of CH_3CCl_3 forming $CH_2{=}CCl_2$ and HCl. The $CH_2{=}CCl_2$ produced reacts further with aluminium(III) chloride producing a purple polymer on the catalyst surface and gaseous HCl is evolved as shown in Scheme 4.1.



$$\begin{tikzcd}
CH_3 - CCl_3 \arrow[r, "AlCl_3"] & CH_2 = CCl_2 + HCl \arrow[d, "AlCl_3"] \\
 & \text{purple polymeric tar} + HCl
\end{tikzcd}$$

Scheme 4.1

An extensive study was made of this system by McBeth [25]. He concluded that the polymeric material was unlikely to be due to a single species and was probably a mixture of unsaturated oligomers [81]. The polymeric species may have the structure shown in figure 4.1, but the possibility that an aromatic species was

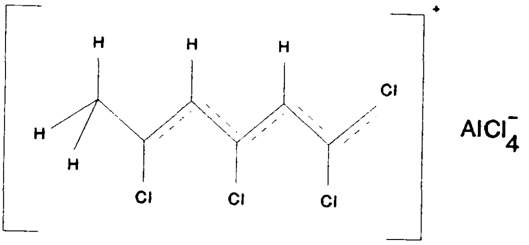


Fig. 4.1

responsible for the purple colour has not been ruled out. A red liquid with the stoichiometry

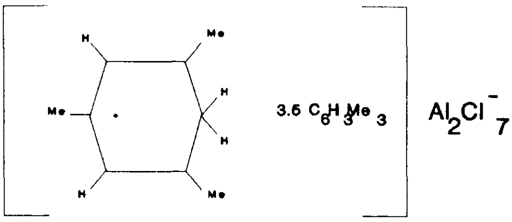


Fig. 4.2

$HCl.Al_2Cl_6.4.5C_6H_3Me_3$ (figure 4.2) has been obtained [102]. In this preparation the aluminium(III) chloride was sublimed into a reaction vessel containing aromatic hydrocarbon held at 2°C.

Other highly coloured complexes of aluminium(III) chloride with chlorocarbons have been observed. A bright yellow solid formed in the reaction of aluminium(III) chloride and hexachloropropene has been reported. The authors thought this to be due to the complex $[C_3Cl_5]^+[AlCl_4]^-$ [103]. More recently the formation of strongly coloured polymer-aluminium(III) chloride-solvent complexes have been observed [104,105]. The colours ranging from orange-brown to violet-green are thought to be due to the formation of charge transfer complexes.

When CCl_2FCClF_2 is adsorbed onto aluminium(III) chloride the solid undergoes a colour change from colourless to yellow. This may also be due to the formation of a charge transfer complex in the form of a polymeric species but the evidence is not conclusive.

Aluminium(III) chloride pretreated with CCl_2FCClF_2 will isomerise CCl_2FCClF_2 at room temperature. The reactive surface is thought to be organic in nature. Similarly aluminium(III) chloride pretreated with CH_3CCl_3 will catalyse the dehydrochlorination of CH_3CCl_3 at room temperature. The following work was undertaken to compare the behaviour of CH_3CCl_3 treated aluminium(III) chloride with that of untreated aluminium(III) chloride, and aluminium(III) chloride pretreated with CCl_2FCClF_2.

Results

4.2.1 The Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3.

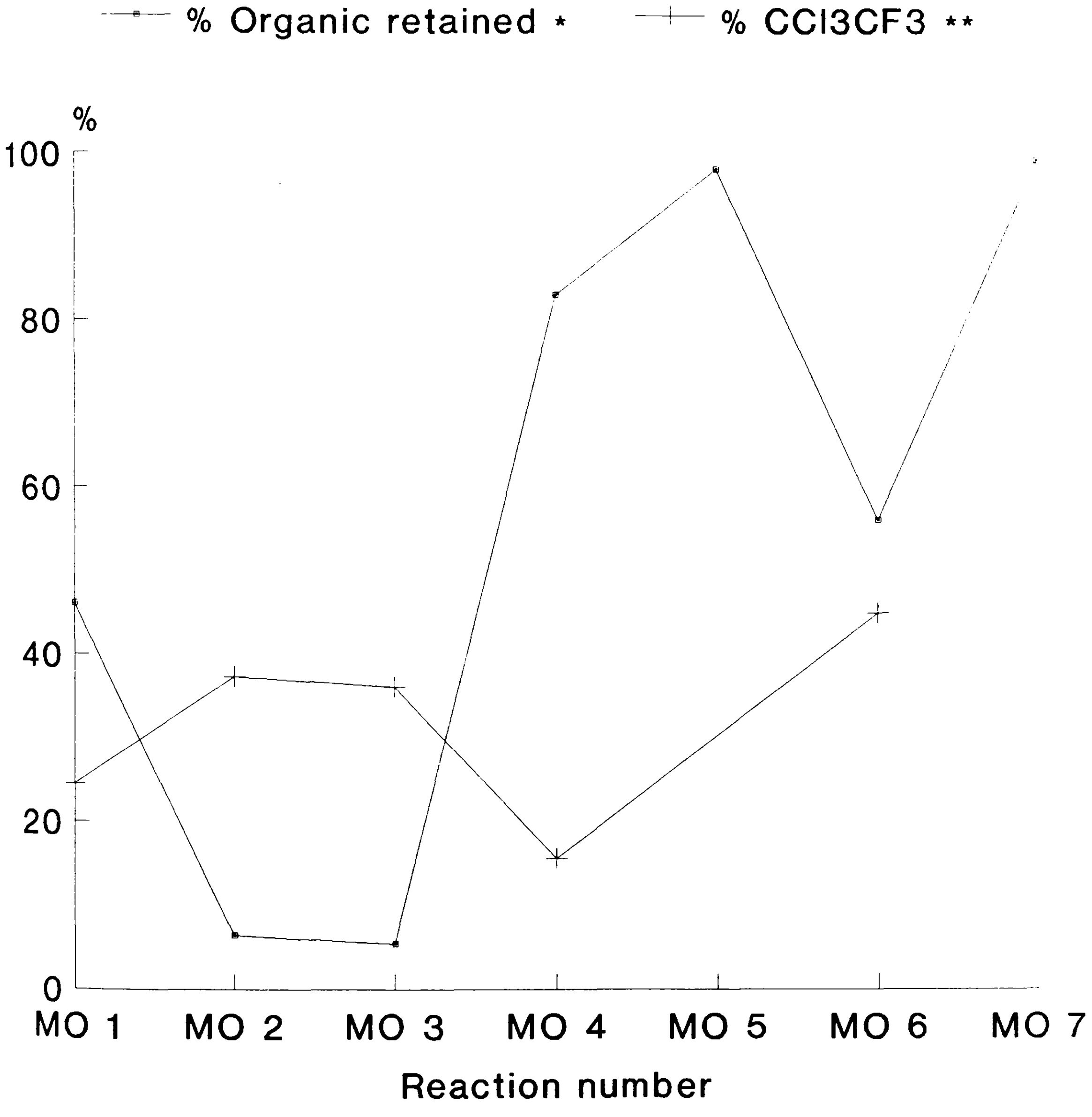
A series of three experiments was conducted. In all cases there was evidence that the isomerisation CCl_2FCClF_2 -> CCl_3CF_3 occurred over aluminium(III) chloride pretreated with CH_3CCl_3 at room temperature.

In experiment MO, CH_3CCl_3 vapour (0.034 mmol) was exposed to aluminium(III) chloride (0.011 mol). After 1 h the volatile products were removed leaving a purple polymeric material on the catalyst surface. An aliquot of gaseous CCl_2FCClF_2 was allowed to react with the solid. After 24 h the volatile products were removed.

Six further aliquots of CCl_2FCClF_2 were admitted to the reaction vessel in succession. Each was allowed to react with the solid for a period of 24 h before the volatile products were removed and the next aliquot added. The mass balance data and the quantity of CCl_3CF_3 produced for each reaction are plotted in figure 4.3. An inverse relationship was observed between the two phenomena. The maximum quantity of CCl_3CF_3 (43%) was obtained when the quantity of retained material was 56% of the original aliquot of CCl_2FCClF_2 added. The volatile product mixtures were analysed quantitatively by ^{19}F nmr spectroscopy. The results are shown in table 4.1. Gaseous CCl_3CF_3 was the main product in reactions MO1, MO4 and MO6. The quantity of organic retained in these reactions was > 40% of the original CCl_2FCClF_2 added and < 6% of the CCl_2FCClF_2 added was left unreacted at the end of the reaction. In runs MO2 and MO3 very little material was retained < 7% but the quantities of CCl_3CF_3 produced were 37% and 36% respectively. However more than half the original CCl_2FCClF_2 added remained unchanged. The quantity of CCl_2FCClF_2 added in each of these reactions was double that added in reactions MO1, MO4 and MO6. A fluorine balance of the product mixtures indicated that more fluorine was lost in the production of the chlorinated products, CCl_3CClF_2 and CCl_3CCl_2F, than was used in the formation of CCl_2FCF_3. In run MO6 no chlorinated products were detected but CCl_2FCF_3 was obtained.

After run MO1 the purple-pink colour of the surface had become a grey-green colour. A white solid formed in the vessel during this experiment. It was

Figure 4.3 Experiment MO Reactions between CCl2FCClF2 and CH3CCl3 treated Aluminium(III) Chloride



*Calculated as shown in equation 3.1
**Calculated as shown in equation 3.2

Table 4.1

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride, pretreated with CH_3CCl_3, at room temperature.

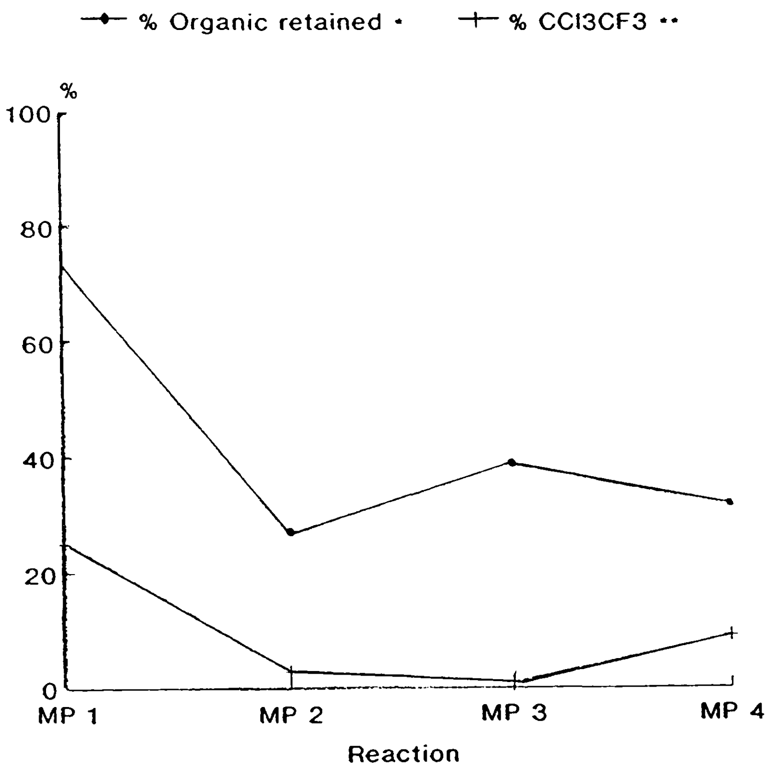
Analyses of the Volatile Product Mixtures from Experiment MO by ^{19}F nmr Spectroscopy.

Reaction	Chlorofluoroethane Present %				
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2	CCl_3CCl_2F
MO1	trace	6	24	6	1
MO2	1	53	37	1	trace
MO3	trace	54	36	3	1
MO4	trace	trace	15	trace	trace
MO5	-	-	-	-	-
MO6	1	-	43	-	-
MO7	-	-	-	-	-

identified using mass spectrometry and found to be C_2Cl_6.

In the second experiment MP aluminium(III) chloride (0.490 mmol) was pretreated with CH_3CCl_3 vapour (0.056 mmol). An inverse relationship between percentage retention of material and the amount of CCl_3CF_3 produced was observed (figure 4.4). This relationship was similar to that found in experiment MO. Analysis of the volatile product mixtures by g.c. showed the presence of seven components. Six of those were identified as CCl_2FCF_3, CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6. The seventh peak had a retention time of 35.5 min and was identified by g.c./m.s as being C_2Cl_4. The presence of this compound could have arisen from the dechlorination of C_2Cl_6 or from the breakdown

Figure 4.4 Experiment MP
Reactions between CCl2FCClF2 and CH3CCl3
treated Aluminium (III) Chloride



•Calculated as shown in equation 3.1
••Calculated as shown in equation 3.2

of the purple tar on the surface of the aluminium(III) chloride. The products produced in each reaction are listed in table 4.2. Very little isomerisation occurred during reaction MP1 but there was significant retention (73%) and chlorination (25%). The latter three reactions produced CCl_3CF_3 as the main product. In all runs the quantity of chlorinated products exceeded the quantity of CCl_2FCF_3 produced.

In experiment MQ aluminium(III) chloride (8.7 mmol) was pretreated with CH_3CCl_3 vapour (3.87 mmol). After 1 h the volatile products were removed. An aliquot of gaseous CCl_2FCClF_2 was added. After 24 h the volatile products were removed. This procedure was repeated 3 times. Mass balance data and the quantity of CCl_3CF_3 produced for each reaction are plotted in figure 4.5. An inverse relationship was established between these two phenomena similar to that found in experiments MO and MP, figures 4.3 and 4.4 respectively. The volatile product mixtures from experiment MQ were analysed by ^{19}F nmr therefore no information was obtained for C_2Cl_4 or C_2Cl_6. The results are listed in table 4.3. In reaction MQ1 all CCl_2FCClF_2 was consumed during the reaction. Only 25% of the material was retained. The bulk of the product mixture was the isomer CCl_3CF_3 (72%). In the next 3 reactions the quantity of material retained on the surface increased and the quantity of CCl_3CF_3 produced decreased The fluorine balance showed that there was more chlorinated than fluorinated products. This suggested that the fluorine retained by the surface exceeded the quantity expected from the adsorption of CCl_2FCClF_2.

Table 4.2

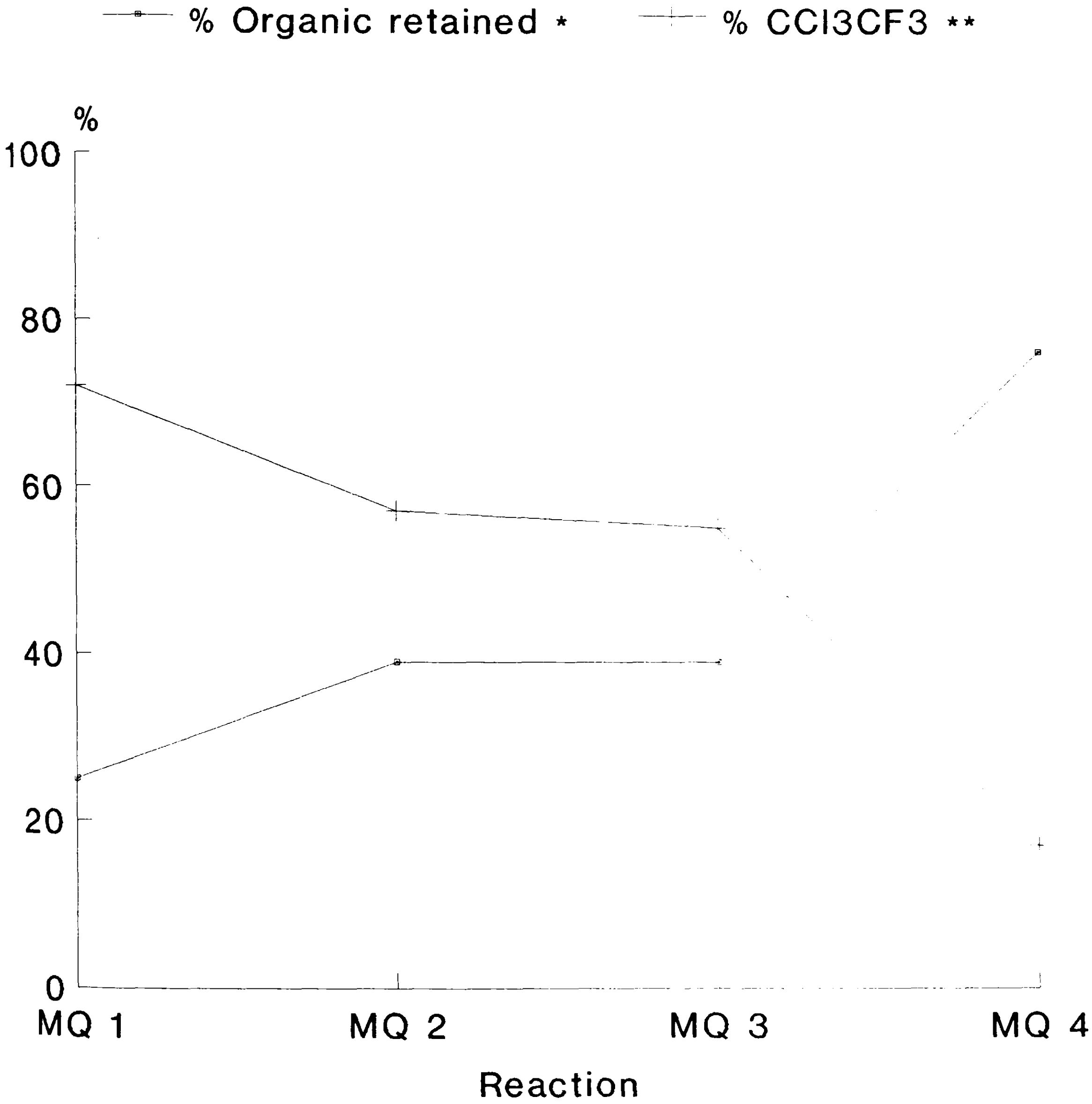
The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride, pretreated with CH_3CCl_3, at Room Temperature.

Analyses of the Volatile Products Mixtures From Experiment MP by Gas Chromatography.

Reaction	Chlorofluoroethane Present % *					
	CCl_2FCF_3	CCl_3CF_3	CCl_2FCClF_2	CCl_3CClF_2	C_2Cl_6	C_2Cl_4
MP1	-	1	-	25	trace	-
MP2	trace	67	trace	3	trace	trace
MP3	trace	59	trace	1	trace	trace
MP4	2	55	-	9	1	trace

*Calculated as described in Equation 3.1.

Figure 4.5 Experiment MQ
Reactions between CCl2FCClF2 and CH3CCl
treated Aluminium (III) Chloride



*Calculated as shown in equation 3.1
**Calculated as shown in eauation 3.2

Table 4.3

The Interaction Between CCl_2FCClF_2 and Aluminium(III) Chloride, Pretreated with CH_3CCl_3, at Room Temperature.

Analyses of the Volatile Product Mixtures From Experiment MQ by ^{19}F nmr Spectroscopy.

Reaction	Chlorofluoroethane Present % *				
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2	CCl_3CCl_2F
MQ1	trace	-	72	trace	trace
MQ2	1	trace	57	3	1
MQ3	2	1	55	2	trace
MQ4	1	trace	17	5	trace

Calculated as described in equation 3.2

Samples of aluminium(III) chloride pretreated with CH_3CCl_3, after reaction with CCl_2FCClF_2 from experiment MQ were analysed by magic angle spinning solid state nmr. Two peaks were observed in the ^{27}Al spectrum at +77.8 ppm and -19.9 ppm (figure 4.6). The latter peak had a shoulder at ~ 1 ppm corresponding to aluminium(III) chloride (cf figure 3.13). The signal at -19.9 ppm has not yet been assigned but a signal at -18.59 ppm has been obtained for AlF_4^- and another at -16.63 ppm has been obtained for aluminium(III) fluoride. There is no evidence to suggest these species were responsible for the observed shift at -19.9 ppm. The peak obtained at +77.8 ppm was consistent with an aluminium in a tetrahedral environment [106]. DRIFTS experiments have shown the existence of the $AlCl_4^-$ ion in aluminium(III) chloride pretreated with CH_3CCl_3 [25]. It was, therefore, possible that the shift at +77.8 ppm was due to the $AlCl_4^-$ ion.

The ^{13}C MAS solid state nmr spectrum is shown in figure 4.7. It contains a very strong signal at +106.1 ppm consistent with hexachloroethane [99]. The signal was not as broad as that shown in figure 3.14 suggesting that in this sample the organic species was more tightly bound to the surface of the solid. No signals were obtained that might correspond to a $(CH_2 = CCl_2)_n$ polymer.

Figure 4.6 27Al MAS nmr Spectrum of Aluminium (III) Chloride Pretreated with CH3CCl3 after reaction with CCl2FCClF2

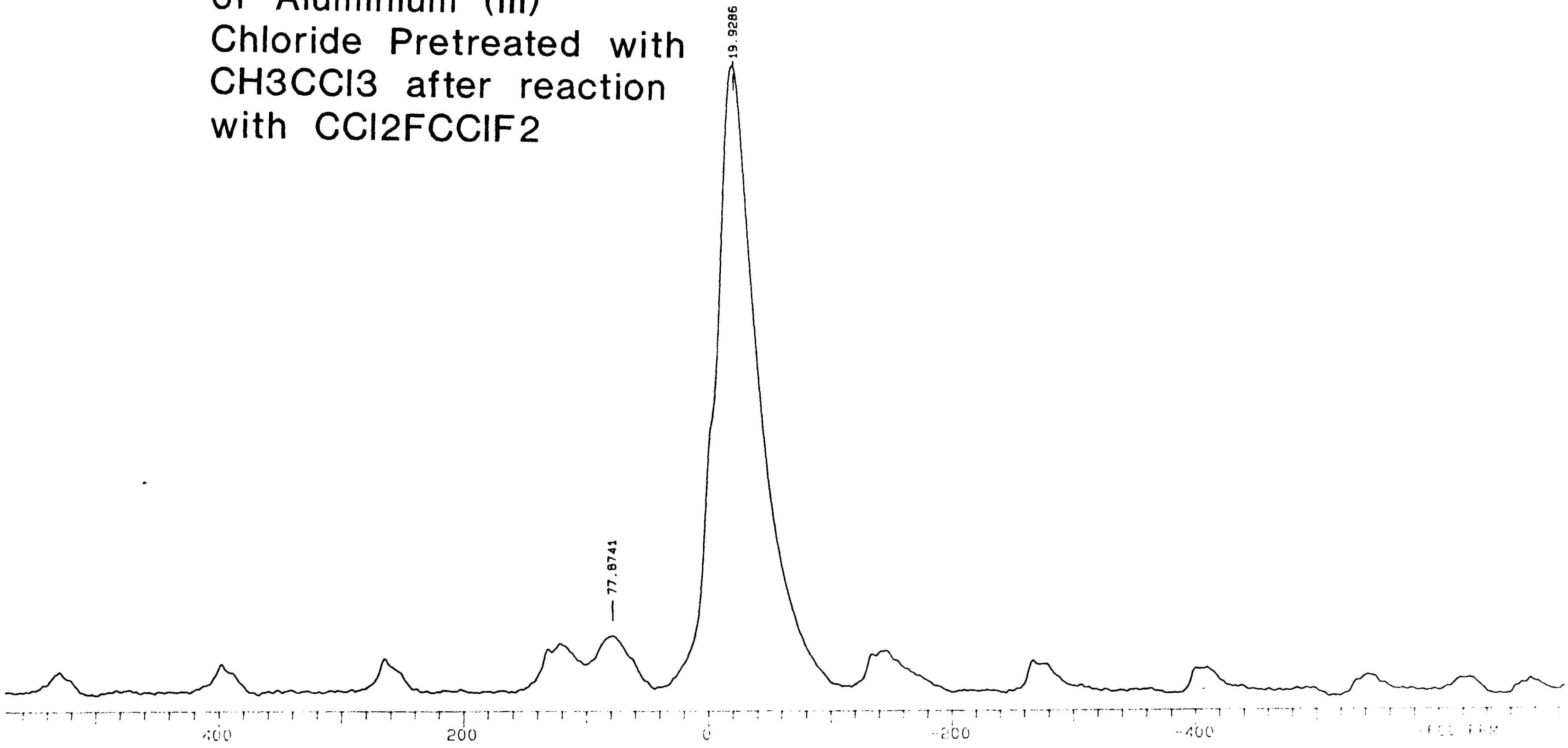
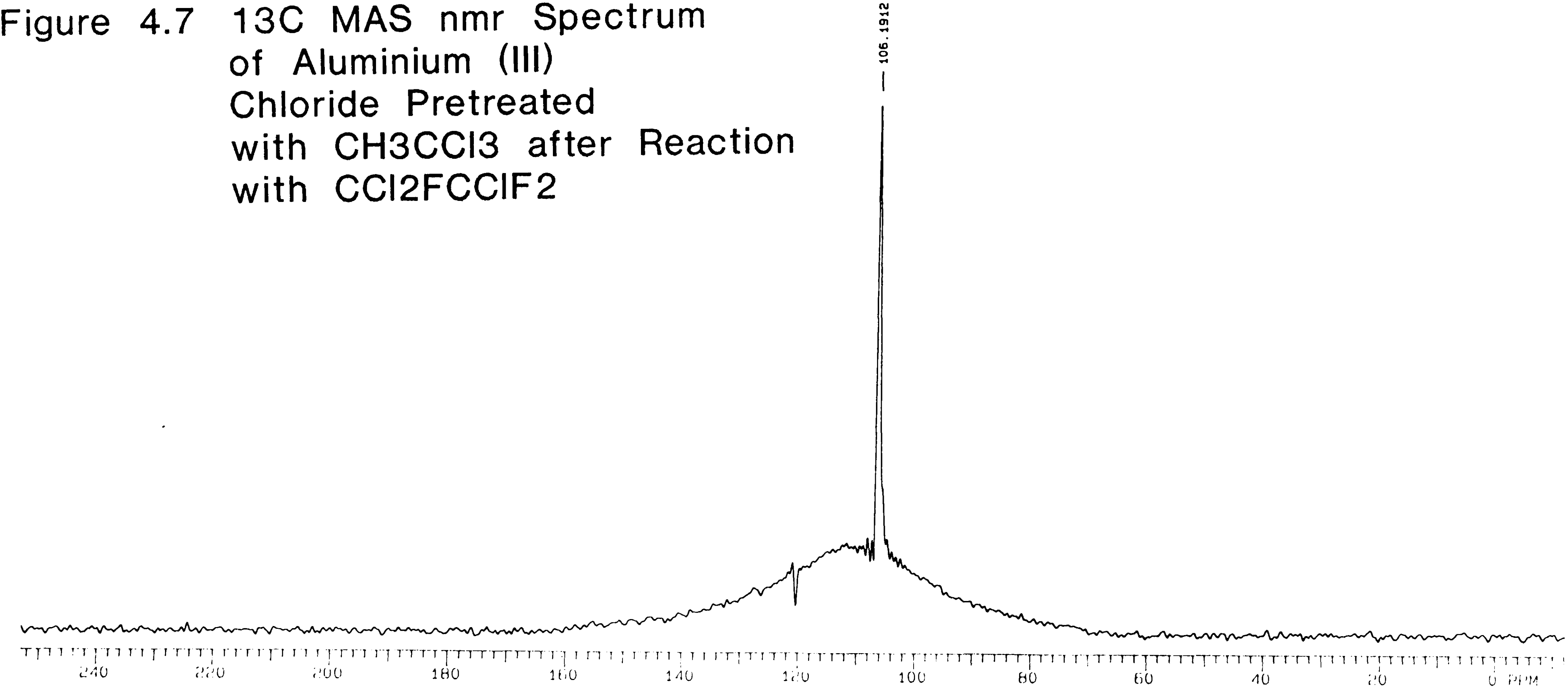


Figure 4.7 13C MAS nmr Spectrum of Aluminium (III) Chloride Pretreated with CH3CCl3 after Reaction with CCl2FCClF2



4.2.2 The Behaviour of CH_3CCl_3 in the Presence of Aluminium(III) Chloride pretreated with CCl_2FCClF_2

The experiments conducted in section 4.2.1 showed that the isomerisation CCl_2FCClF_2 -> CCl_3CF_3 occurred over aluminium(III) chloride pretreated with CH_3CCl_3. In this section the situation is described whereby aluminium(III) chloride was pretreated with CCl_2FCClF_2 then reacted with CH_3CCl_3.

Aluminium(III) chloride (6.8 mmol) was allowed to interact with CCl_2FCClF_2 vapour (2.27 mmol). The volatile products were removed after 42 h and 93% of the original material was found to be retained on the surface. A second aliquot of CCl_2FCClF_2 (6.7 mmol) was added and the product mixture was analysed after 24 h. It consisted of CCl_2FCF_3, CCl_3CF_3, CCl_2FCClF_2, CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6. The quantity of material retained was 33% of the original quantity of CCl_2FCClF_2 added. The compound CH_3CCl_3 (0.38 mmol) was then added to the system. After 30 min an infrared spectrum of the volatile products was obtained. This contained absorbances corresponding to the dehydrochlorination products HCl and $CH_2=CCl_2$. Gaseous CH_3CCl_3 was also present. A fourth component in the vapour phase was found to be CCl_3CF_3. This experiment was repeated and the observations described above were confirmed.

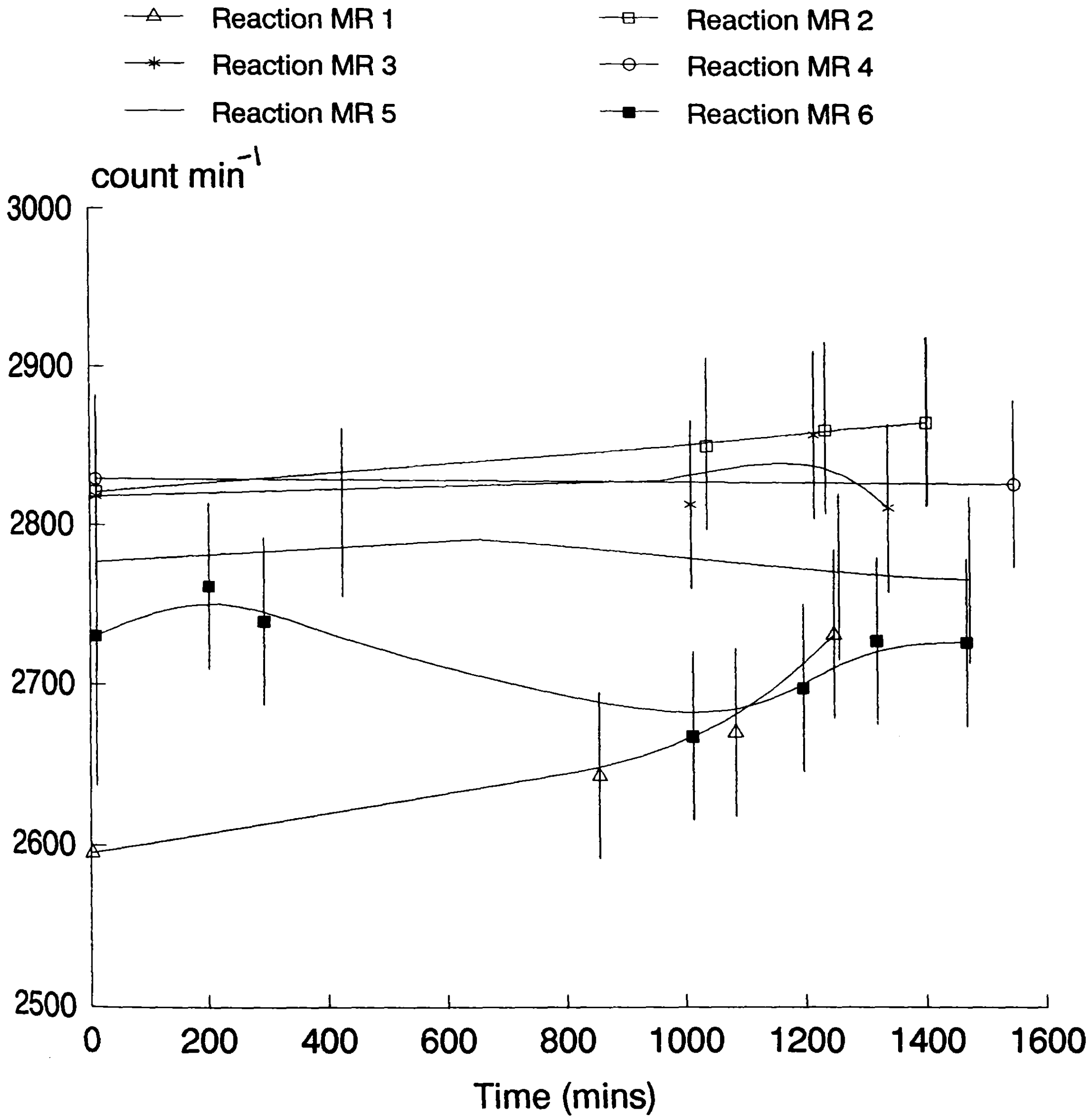
This result was interesting as it showed that the catalytic sites on aluminium(III) chloride responsible for the dehydrochlorination of CH_3CCl_3 and the isomerisation of CCl_2FCClF_2 are related in some way. A detailed discussion will be presented in Chapter 6.

4.3 The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with [^{36}Cl]-CH_3CCl_3

Two experiments were conducted. In experiment MR, aluminium(III) chloride (8.48 mmol) was pretreated with [^{36}Cl]-CH_3CCl_3 (0.97 mmol), specific count rate 577 count min^{-1} $mmol^{-1}$, prepared as described in 2.5.6. After 1 h all gaseous products were removed and the surface count rate was 42,379 count min^{-1}. Six aliquots of CCl_2FCClF_2 were then allowed to react successively with the catalyst and in each case the change to the surface count rate was monitored over a 24 h period. After each reaction the volatile products were removed and the surface count rate noted. The results obtained are plotted in figure 4.8.

In reaction MR1 the surface count rate fell immediately to 2600 count min^{-1} after the addition of CCl_2FCClF_2 but remained constant thereafter. In general the surface count rate remained constant for the duraction of a particular reaction but varied between reactions. [^{36}Cl]-Chlorine activity was observed in the vapour phase but it was too small to be determined precisely. The volatile products from reactions MR1-MR3, MR5 and MR6 were analysed qualitatively by i.r spectroscopy. Each spectrum showed CCl_2FCClF_2 to be dominant in the vapour phase. The isomer CCl_3CF_3 was produced but was not present in a substantial amount.

Figure 4.8 Experiment MR Reactions of [36Cl]-CH3CCl 3/Aluminium (III) Chloride with CCl2FCClF2 Solid count rate vs time



The last point corresponds to the last reading before the gas was removed

After all volatile products were removed the catalyst was left in the counting cell for a few days. A sample of the vapour phase was analysed by ^{19}F nmr spectroscopy. The results are shown in table 4.4. The mass balance data obtained for reactions MR1-MR6 are tabulated in table 4.5. In the light of previous results reaction MR1 should have produced the least amount of CCl_3CF_3 and run MR2 the maximum.

In experiment MS the catalyst was prepared by treating aluminium(III) chloride (9.46 mmol) with [^{36}Cl]-CH_3CCl_3 (1.36 mmol) for 1 h. After the volatile products were removed, the surface count rate was 7830 count min^{-1}. On addition of the first aliquot of CCl_2FCClF_2 (2.04 mmol) (reaction MS1) the surface count rate fell immediately to 6600 count min^{-1}. After 65 h the volatile products were removed and the surface count rate was 6000 count min^{-1}. Three further aliquots of CCl_2FCClF_2 were allowed to react successively with the solid and the surface count rate was monitored over a 24 h period. The results are plotted in figure 4.9. The surface count rate remained constant for the duration of a reaction but decreased from reaction MS2-MS4.

The volatile products of reactions MS1-MS4 were analysed qualitatively by ir spectroscopy. In each reaction the main product was CCl_2FCClF_2 with little CCl_3CF_3 present. The lack of isomerisation in experiments MR and MS may have been due to the presence of moisture as it was difficult to flame out the counting cell to the same degree as the sublimation apparatus.

Table 4.4

The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with $[^{36}Cl]$-CH_3CCl_3.

Analyses of the Volatile Product Mixture from Reaction MR2 by ^{19}F nmr Spectroscopy.

Chlorofluoroethane	% Present *
CCl_2FCF_3	trace
CCl_2FCClF_2	75
CCl_3CF_3	14
CCl_3CClF_2	11

* Calculated as described in equation 3.2.

Table 4.5

The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with $[^{36}Cl]$-CH_3CCl_3.

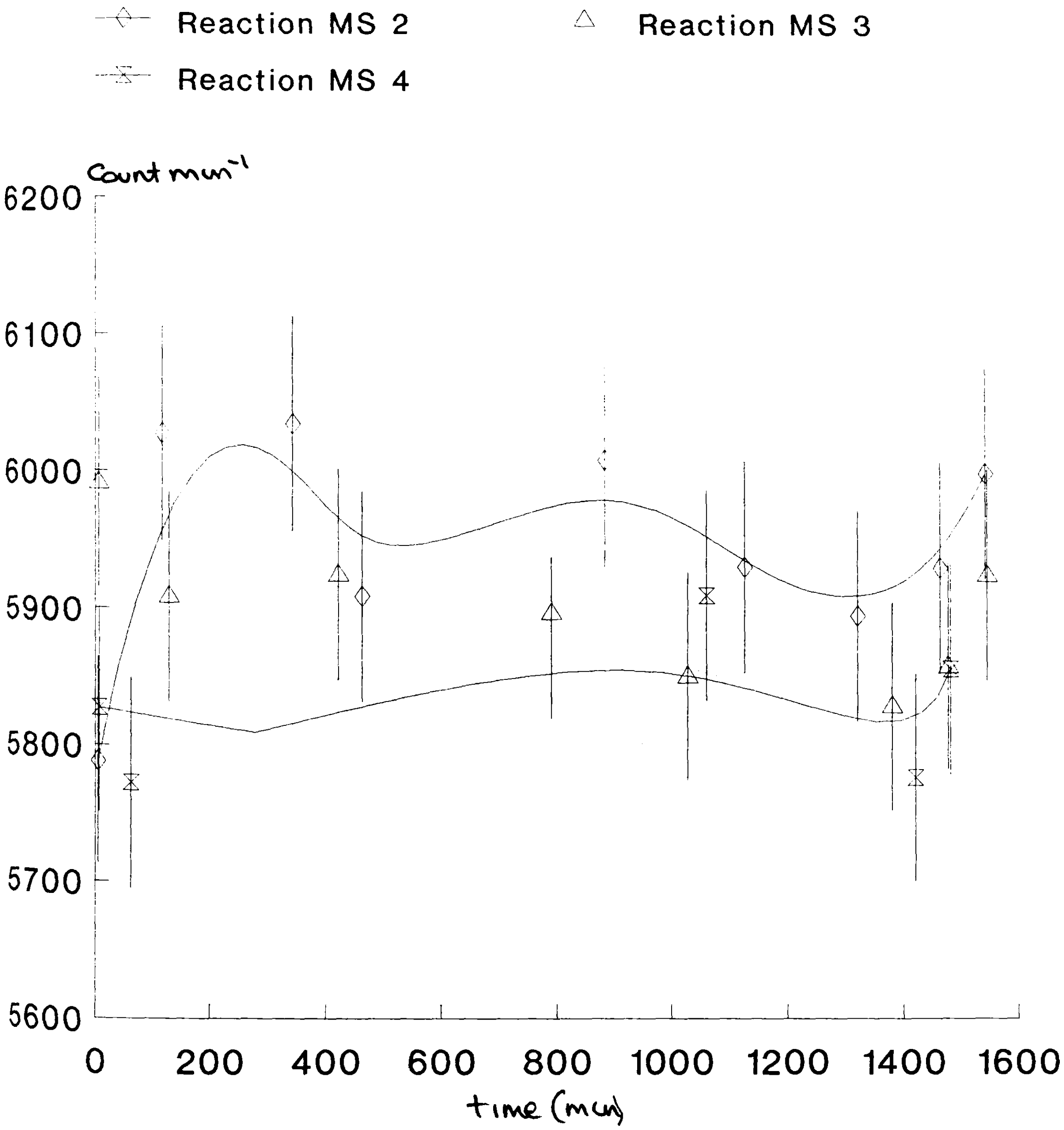
Mass Balance Data for Experiment MR.

Reaction	CCl_2FCClF_2 added(mmol)	Volatile β Products(mmol)	Retention α %
MR1	1.9	1.4	29
MR2	1.4	1.3	11
MR3	2.0	1.6	19
MR4	1.6	1.3	15
MR5	2.4	1.8	23
MR6	2.4	2.0	16

α - Calculated as described in equation 3.1

β - Treated as CCl_3CF_3 for ease of calculation.

Figure 4.9 Experiment MS Reactions of [36Cl]-CH3CCl3/Aluminium (III) Chloride with CCl2FCClF2 Solid count rate vs time



The last point corresponds to the reading taken once the gas was removed

The mass balance data obtained (table 4.6) showed that retention occurred after reaction MS1 but did not occur thereafter.

4.4 An Infrared Spectroscopic Study of the Vapour Phase During the Reaction between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3.

Two experiments MT and MU were undertaken using the cell described in 2.7.1. At the start of each experiment a spectrum of CCl_2FCClF_2 vapour was obtained before any solid was admitted to the cell. Once the solid was admitted, spectra in the range 1000-700 cm^{-1} were obtained every 15 min. The spectra accumulated from a typical reaction are shown in figure 4.10. During the course of the reaction the 810 cm^{-1} peak of CCl_2FCClF_2 diminished as the 849 cm^{-1} peak of CCl_3CF_3 increased. Mass balance data for both experiments were not determined as the quantities of materials used were so small.

The change in composition of CCl_2FCClF_2 and CCl_3CF_3 in the vapour phase during the course of a reaction in experiment MT was calculated using the calibration curves shown in figures 2.7 and 2.8. The results obtained are shown in figures 4.11 and 4.12 respectively. The quantity of CCl_2FCClF_2 in the volatile products increased with each reaction. This indicated that with the addition of each new aliquot of CCl_2FCClF_2 a greater percentage was remaining unreacted. In reaction MT1 the gaseous products were removed after 4 days and showed no evidence of CCl_2FCClF_2.

Table 4.6

The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with $[^{36}Cl]$-CH_3CCl_3

Mass Balance Data for Experiment MS.

Reaction	CCl_2FCClF_2 added(mmol)	Volatile β Products(mmol)	Retention α %
MS1	2.0	1.3	36
MS2	1.0	1.0	0
MS3	0.8	0.8	0
MS4	0.8	-	-

α - Calculated as described in equation 3.1.

β - Assumed to be CCl_3CF_3 for ease of calculation.

Figure 4.10 The Spectra Accumulated During a 24h Reaction Between CCl2FCClF2 and Aluminium (III) Chloride Pretreated with CH3CCl3

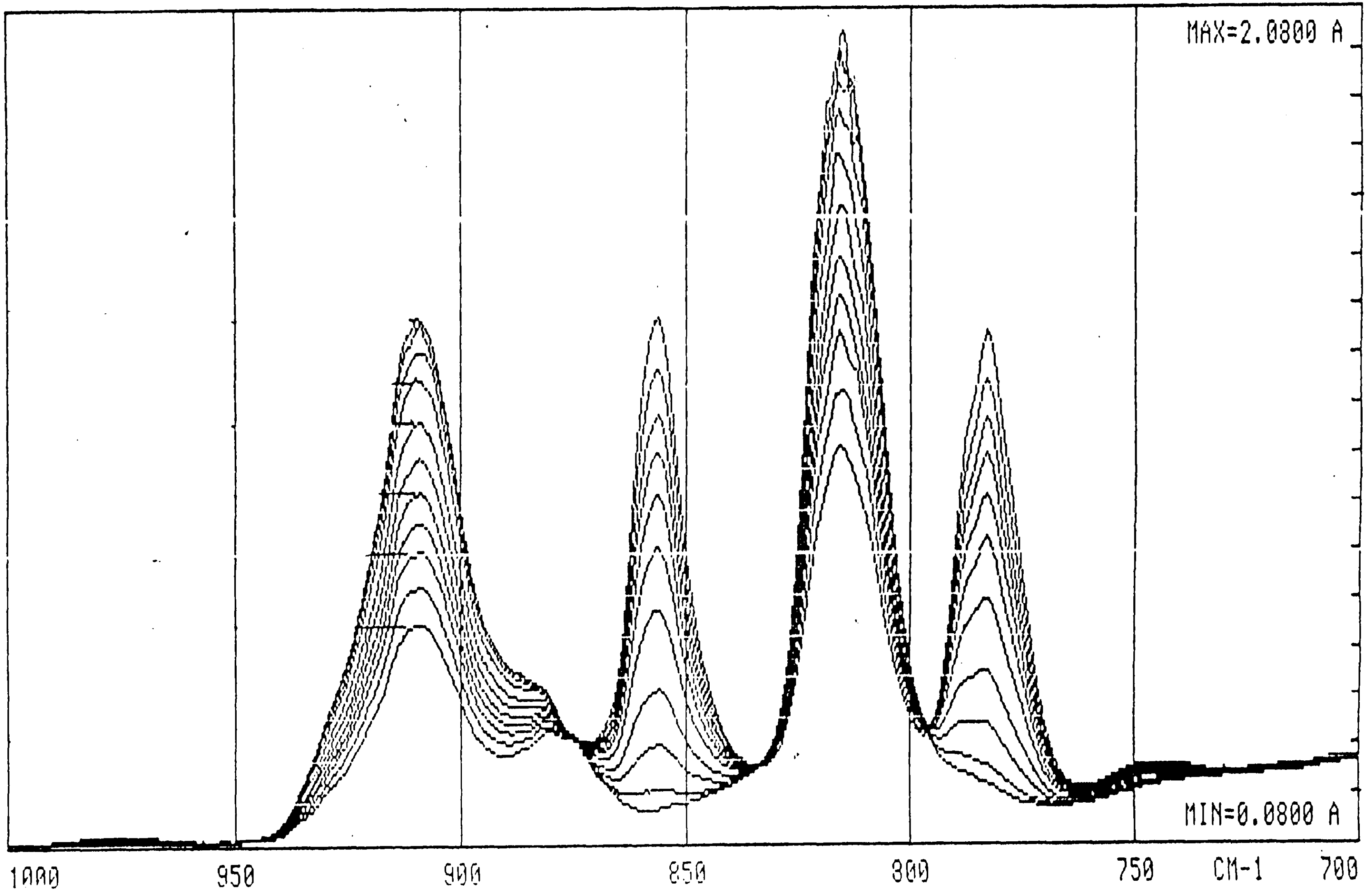
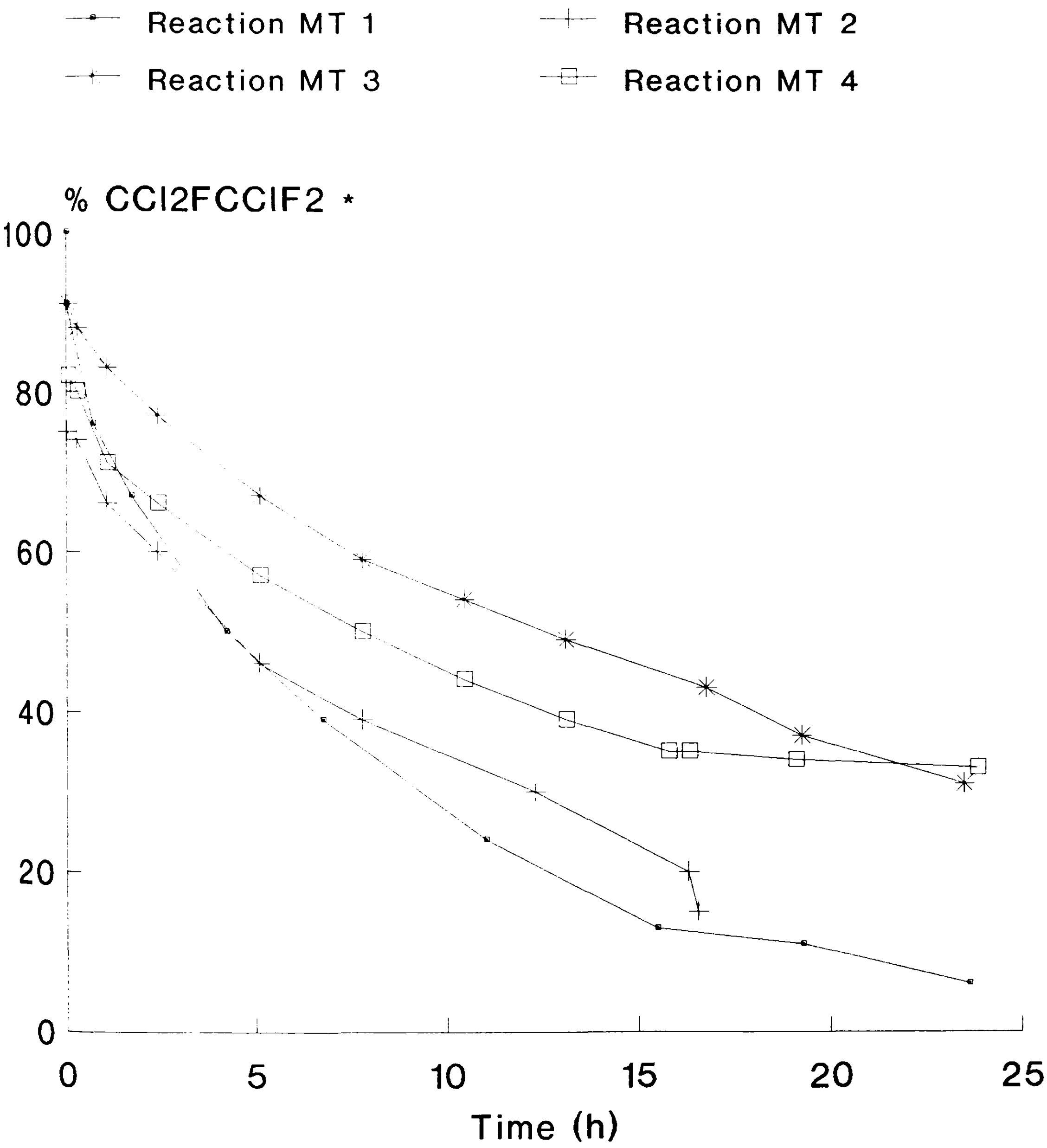


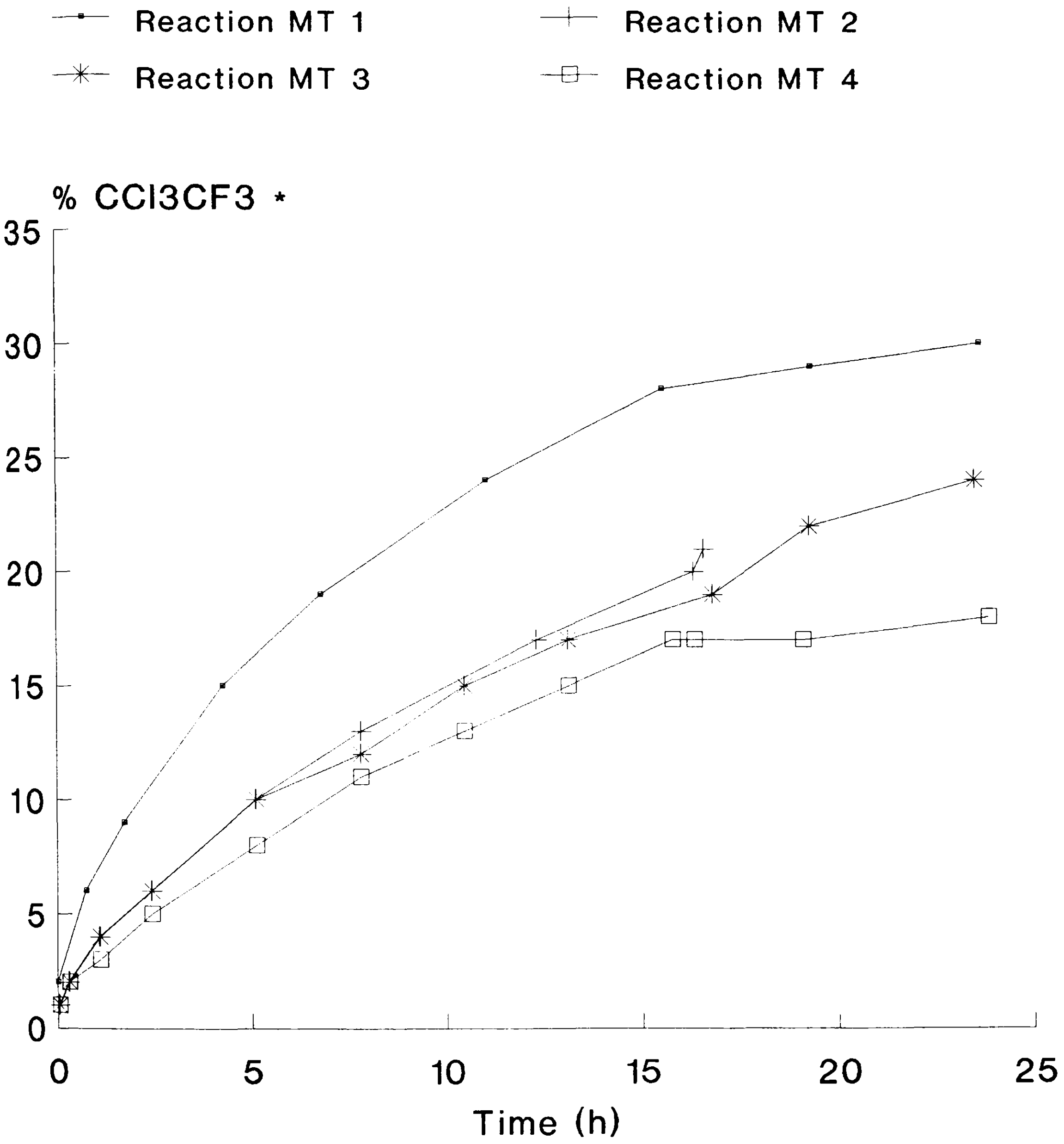
Figure 4.11 Experiment MT IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride

%CCl2FCClF2 vs time



* Calculated as shown in equation 3.2

Figure 4.12 Experiment MT IR Studies of reactions between CCl_2FCClF_2 and Aluminium (III) Chloride % CCl_3CF_3 vs time



* Calculated as shown in equation 3.2

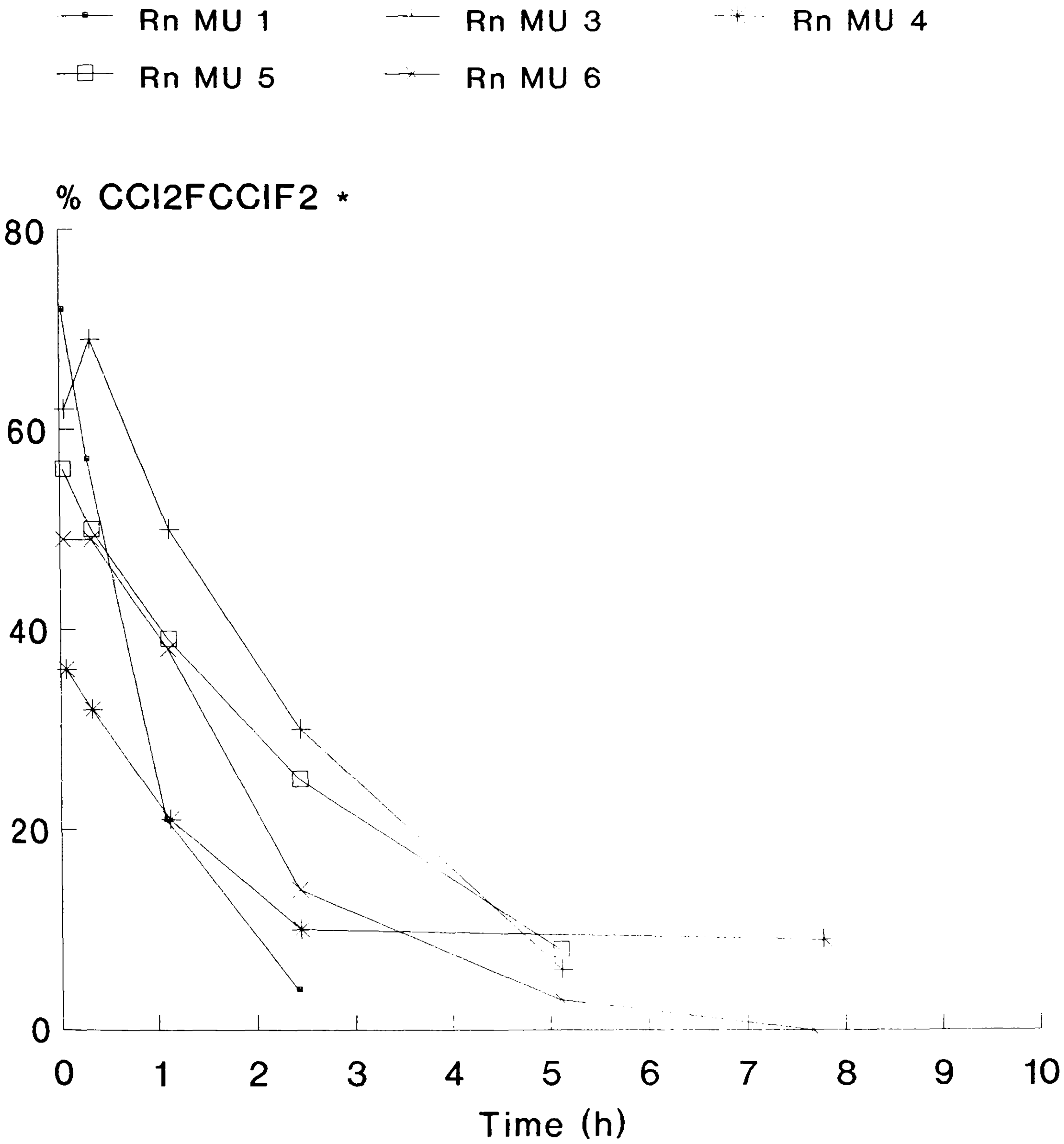
Experiment MU consisted of six reactions. In each reaction all CCl_2FCClF_2 was consumed before the end of the 24 h period (figure 4.13). As the experiment proceeded the time taken to completely consume all CCl_2FCClF_2 vapour increased with each reaction. The maximum quantity of CCl_3CF_3 was produced when all the CCl_2FCClF_2 was consumed, and decreased thereafter (figure 4.14). In both experiments the extent of the isomerisation never exceeded 30%. The decrease in the quantity of gaseous CCl_3CF_3 is interesting as CCl_3CF_3 does not react with the solid. An experiment to confirm this was conducted. The resulting spectra are shown in figure 4.15. Over the 24 h period there was a decrease of 1 mol %. There was no spectroscopic evidence for any other volatile products. A subsequent experiment indicated that CCl_3CF_3 did not react with Pyrex glass.

4.5 Kinetic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3.

In the presence of aluminium(III) chloride pretreated with CH_3CCl_3 the compound CCl_2FCClF_2 undergoes isomerisation, fluorination, chlorination and also produces C_2Cl_4. This latter compound may have arisen from the dechlorination of C_2Cl_6 or the breakdown of the purple polymeric surface. First and second order kinetic plots for the production of CCl_3CF_3 were calculated for experiments MT and MU. A linear relationship was not observed suggesting that reaction kinetics are more complicated.

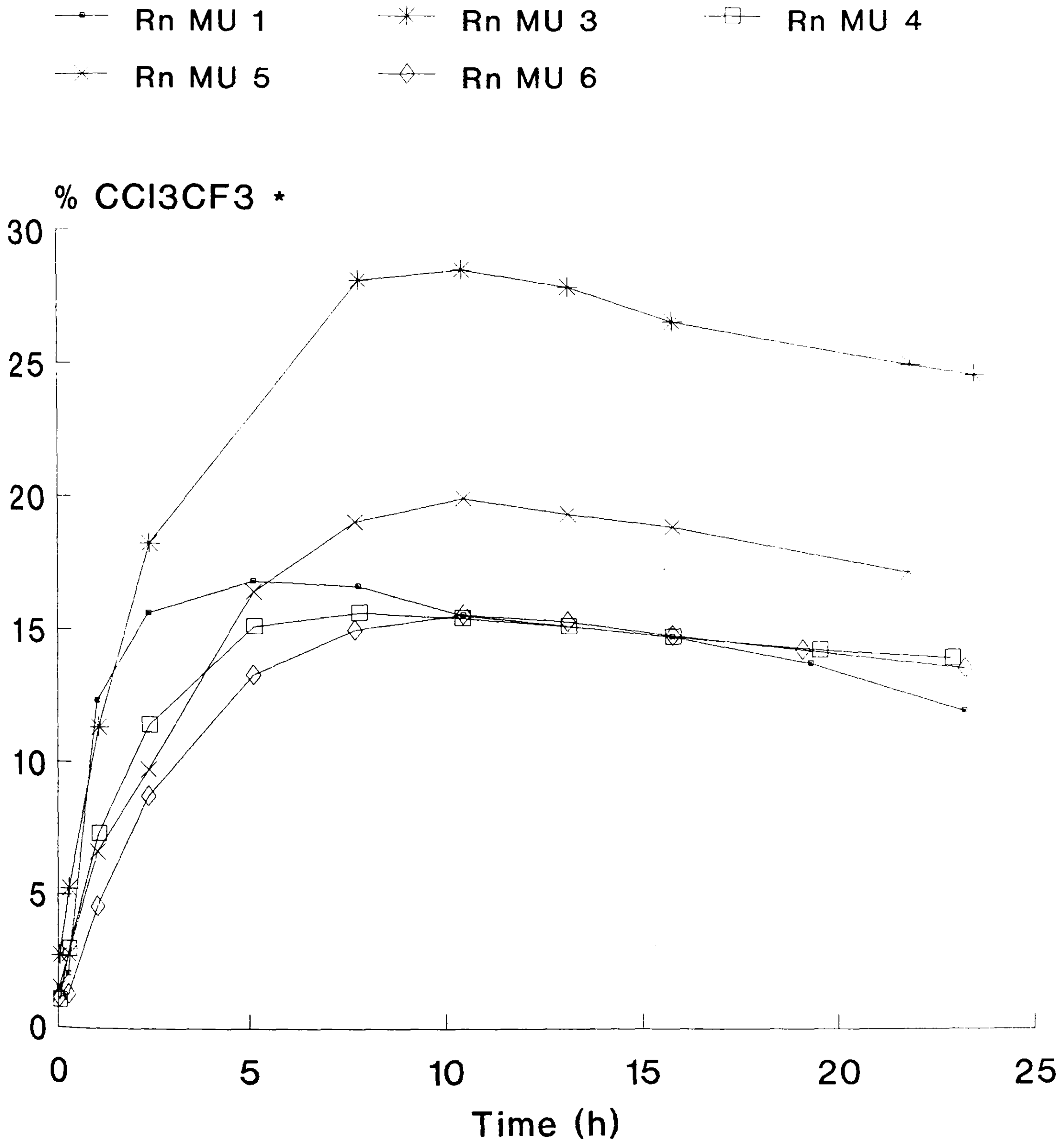
Figure 4.13 Experiment MU IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride

%CCl2FCClF2 vs time



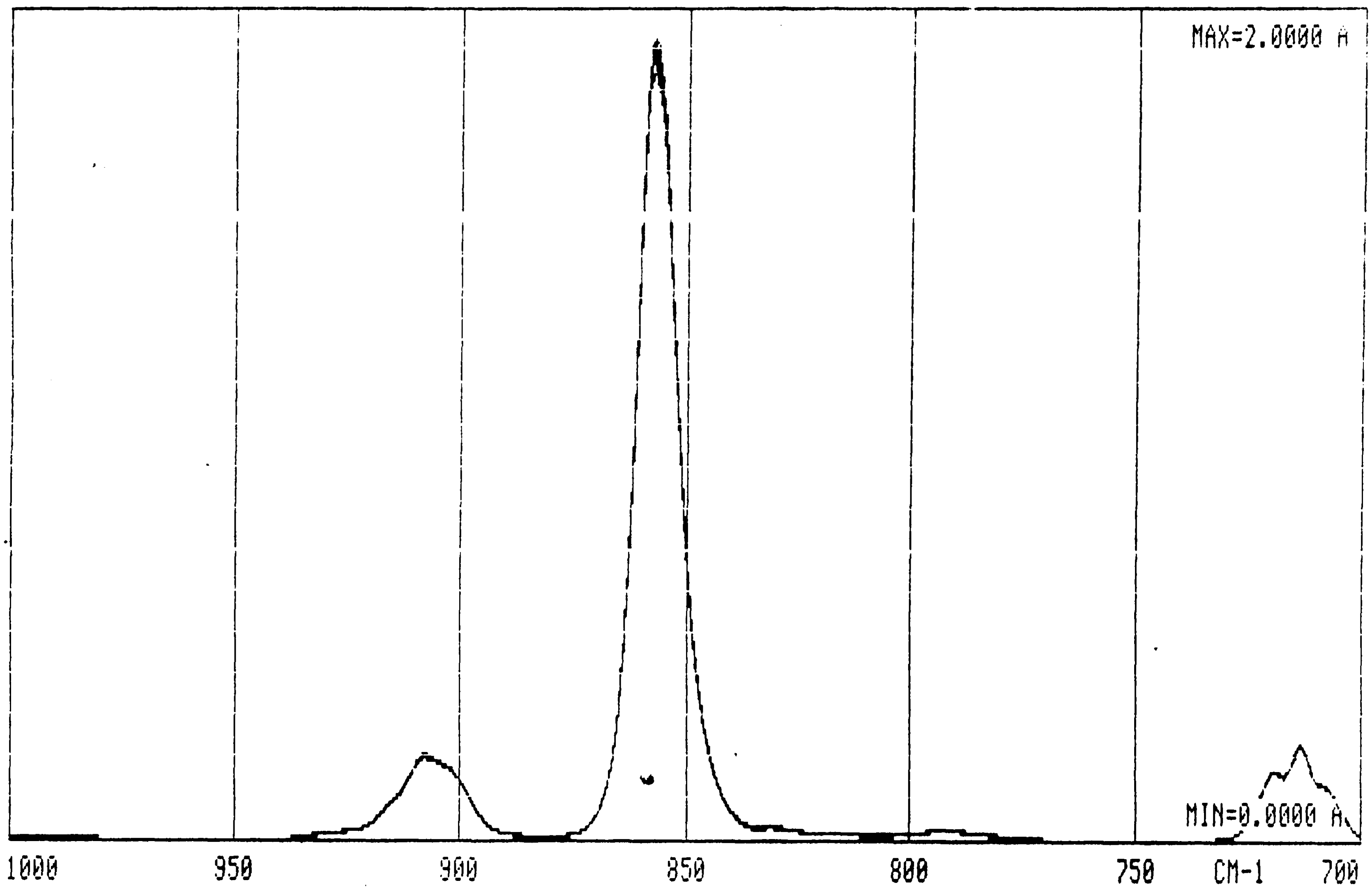
* Calculated as shown in equation 3.2

Figure 4.14 Experiment MU IR Studies of the Reactions between CCl2FCClF2 and Alminium (III) Chloride % CCl3CF3 vs time



*Calculated as shown in equation 3.2

Figure 4.15 The Spectra Accumulated During 24h Reaction Between CCl3CF3 a Aluminium (III) Chloride Pretreated with CH3CCl3



Experimental

4.6.1 The Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3

Aluminium(III) chloride (0.011 mol) was sublimed directly into a reaction vessel as described in 2.3.7. Gaseous CH_3CCl_3 (0.034 mmol) as purified in 2.3.3 was admitted. All volatile products were removed after 1 h. The compound CCl_2FCClF_2 purified as in 2.3.1, was distilled into the side arm of the vessel. The vapour was allowed to react with the solid surface for 24 h. The volatile products were removed and weighed before quantitative analysis by ^{19}F nmr spectroscopy or gas chromatography. This process was repeated for a series of aliquots of CCl_2FCClF_2.

4.6.2 The Behaviour of CH_3CCl_3 in the Presence of Aluminium(III) Chloride Pretreated with CCl_2FCClF_2

Aluminium(III) chloride (6.8 mmol) was sublimed as described in 2.3.7. Gaseous CCl_2FCClF_2 (2.27 mmol) purified as before was admitted. All volatiles were removed after 24 h. Gaseous CH_3CCl_3 as purified in 2.3.3 was reacted with the solid for 1 h. The products were removed and analysed qualitatively by i.r. spectroscopy.

4.7 The Behaviour of CCl_2FCClF_2 in the Presence of Aluminium(III) Chloride Pretreated with [^{36}Cl]-CH_3CCl_3

Aluminium(III) chloride (8.48 mmol) was sublimed as before and loaded into the counting cell described in 2.10.1. Gaseous CH_3CCl_3 (0.97 mmol) specific count rate 577 count min^{-1} $mmol^{-1}$ was admitted and allowed to react. After 1 h the volatile products were removed. The solid count rate was obtained before CCl_2FCClF_2 was admitted. The gaseous products were removed after 24 h and weighed. The ^{36}Cl radioactivity on the solid and in the gas phase were monitored during this time. This process was repeated for a further 5 aliquots of CCl_2FCClF_2.

This experiment was repeated with a fresh sample of sublimed aluminium(III) chloride (9.46 mmol) pretreated with [^{36}Cl]-CH_3CCl_3 (1.36 mmol) 577 count min^{-1} $mmol^{-1}$.

4.8 An Infrared Study of the Vapour Phase During the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3.

The compound CCl_2FCClF_2 was admitted to the infrared cell described in 2.7.1. and a spectrum obtained. Aluminium(III) chloride pretreated with CH_3CCl_3 was admitted to the cell and spectra were obtained over a 24 h period. The volatile products were removed and a further aliquot of CCl_2FCClF_2 admitted. This procedure was repeated for a total of

4 aliquots. The experiment was repeated with a fresh solid sample.

4.9 Kinetic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Pretreated with CH_3CCl_3

These experiments were carried out using the procedure described in 2.7.5.

Chapter 5

The Behaviour of CCl_2FCClF_2 in the Presence of Chlorinated γ-Alumina

5.1 Introduction

The advantage of using chlorinated aluminas in reactions in preference to aluminium(III) chloride is that the former are product selective and do not form strongly acidic by-products [107]. Aluminas can be chlorinated using a variety of substances including HCl, Cl_2, CCl_4 and aluminium(III) chloride. Thomson has made an extensive study of the dehydrochlorination of CH_3CCl_3 in the presence of [CCl_4]-chlorinated γ-alumina [82]. He proposed that both Brønsted and Lewis acid sites were formed in the chlorination reaction but only the Lewis acid sites (figure 5.1) took part in the dehydrochlorination reaction.

Melcher and co-workers reported that aluminium(III) chloride/alumina was a good catalyst for n-butane isomerisation [108]. The surface species they postulated is shown in figure 5.2.

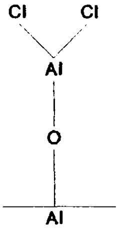


figure 5.2

A similar study was conducted by Marczowski [109]. The surface species he proposed is shown in figure 5.3

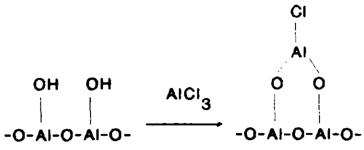
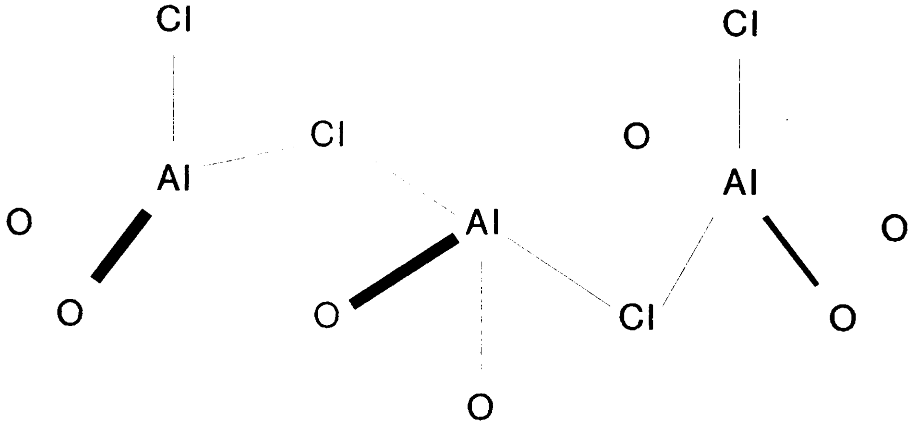


figure 5.3

Figure 5.1 A Lewis Acid Site



He also proposed that the superacid properties of this catalyst were linked with the Al^{III} electron acceptor sites on the surface [110]. These sites were caused by the adsorption of $AlCl_3$ on an adjacent oxygen anion. Drago and Getty refluxed aluminium(III) chloride with various inorganic oxides in the presence of CCl_4. The catalysts were characterised using infrared spectroscopy. When pyridine was adsorbed on the surface infrared shifts indicative of both Brønsted and Lewis acid sites were observed . From solid state MAS nmr spectroscopy they suggested that the catalytically active sites are -O-$AlCl_2$ species [83]. The following work was undertaken to determine whether CCl_2FCClF_2 would be isomerised in the presence of a γ-alumina based catalyst. The two catalysts chosen for this study were [CCl_4]-chlorinated γ-alumina and aluminium(III) chloride supported on γ-alumina.

Results

5.2 The Behaviour of CCl_2FCClF_2 in the Presence of [CCl_4]-Chlorinated γ-Alumina

In experiment MV seven aliquots of CCl_2FCClF_2 were allowed to react with the same solid sample. [CCl_4]-chlorinated γ-alumina is blue in colour but lightened on reaction with CCl_2FCClF_2. The colour darkened as the volatile products were removed. Each product mixture was weighed and analysed qualitatively by ir spectroscopy. There was no evidence to suggest the formation of CCl_3CF_3. However the mass balance data (table 5.1) indicated that material was being retained by the surface. The large percentage retentions after reactions MV6 and MV7 are attributed to the extended reaction times of 116 h and 1 week respectively but

Table 5.1

The Behaviour of CCl_2FCClF_2 in the Presence of $[CCl_4]$-Chlorinated γ-Alumina.

Mass Balance Data for Experimemt MV.

Reaction	CCl_2FCClF_2 added (g)	Volatile Products (g)	Retention $^{\alpha}$ %
MV1	1.02	0.97	4.1
MV2	2.13	2.12	0.7
MV3	1.19	0.94	21.1
MV4	1.39	1.32	5.3
MV5	1.37	1.22	10.8
MV6 $^{\beta}$	0.99	0.18	81.5
MV7 $^{\beta}$	0.96	0.54	43.9

Weight of $[CCl_4]$-chlorinated γ-alumina - 0.58 g.

α - Calculated as described in equation 3.1.

β - The reaction time was increased from 24 h to 116 h and 1 week for reactions MV6 and MV7 respectively.

even after these long periods there was no spectroscopic evidence for CCl_3CF_3. This experiment was repeated to obtain quantitative results for the volatile product mixtures. Six reactions were carried out in experiment MW. The volatile products were analysed by ^{19}F nmr spectroscopy. In all reactions there was evidence for CCl_3CF_3, CCl_2FCF_3 and CCl_3CClF_2 but the major component of the product mixture was CCl_2FCClF_2 (table 5.2). A fluorine balance of the volatile product mixtures showed that the quantity of fluorinated product did not exceed the quantity of chlorinated product. Although there was very little isomerisation in this experiment an inverse relationship between retention and isomerisation was observed (figure 5.4).

Figure 5.4 Experiment MW
Reactions between CCl2FCClF2 and
[CCl4]-Chlorinated γ-Alumina

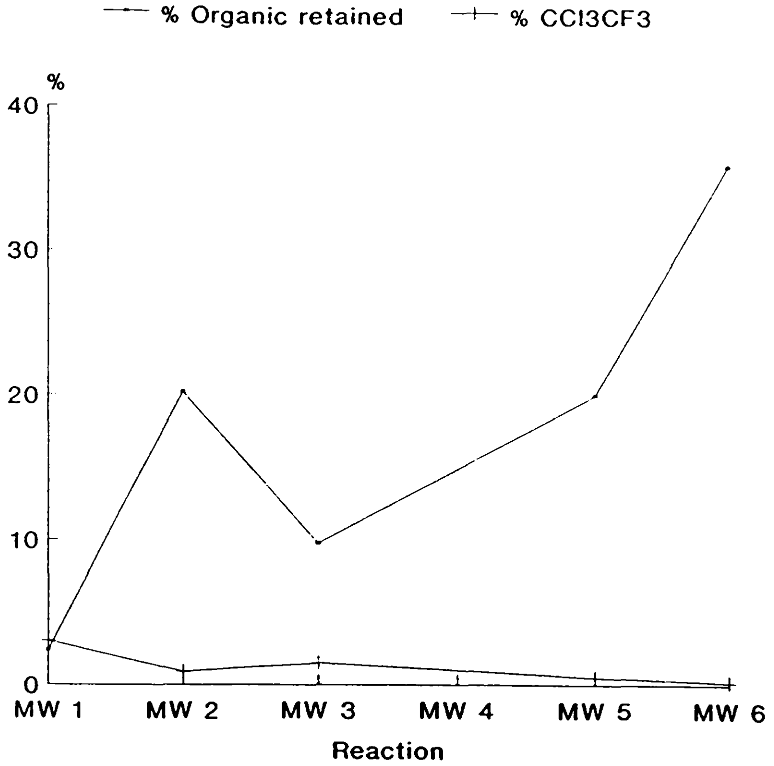


Table 5.2.

The Behaviour of CCl_2FCClF_2 in the Presence of $[CCl_4]$-Chlorinated γ-Alumina.

Analyses of the Volatile Product Mixtures for Experiment MW by ^{19}F nmr Spectroscopy.

Reaction	Chlorofluoroethane % $^{\alpha}$			
	CCl_2FCF_3	CCl_2FCClF_2	CCl_3CF_3	CCl_3CClF_2
MW1	0.6	90.7	3.0	3.0
MW2	0.2	77.8	0.9	0.4
MW3	0.5	87.5	1.5	0.5
MW4	-	-	-	-
MW5	0.1	76.9	0.5	0.3
MW6	trace	62.8	0.2	0.1

α - Calculated as described in equation 3.2.

5.3 The CH_3CCl_3, CCl_2FCClF_2 and [CCl_4]-Chlorinated γ-Alumina System

In the preceding section it was observed that very little isomerisation occurred during the reaction between CCl_2FCClF_2 and [CCl_4]-chlorinated γ-alumina at room temperature. Another reaction catalysed by this solid is the room temperature dehydrochlorination of CH_3CCl_3, but the rate is slower than that observed when aluminium(III) chloride is the catalyst [25]. It has been observed that aluminium(III) chloride pretreated with CH_3CCl_3 will catalyse the isomerisation of CCl_2FCClF_2 and that CCl_3CF_3 is produced when CH_3CCl_3 is reacted with aluminium(III) chloride pretreated with CCl_2FCClF_2. A similar study was conducted for [CCl_4]-chlorinated γ-alumina.

5.3.1 The Reaction Between CH_3CCl_3 and [CCl_4]-Chlorinated γ-Alumina Pretreated with CCl_2FCClF_2.

Calcined γ-alumina was chlorinated with CCl_4 then pretreated with CCl_2FCClF_2 vapour. After 24 h all volatile material was removed and 27% of material was retained on the solid. Gaseous CH_3CCl_3 was admitted to the reaction vessel. Samples of the vapour phase were examined by infrared spectroscopy after 30 min and 90 min. There was no evidence to support the presence of CH_2CCl_2 or HCl in either spectrum.

5.3.2 The Reaction Between CCl_2FCClF_2 and $[CCl_4]$-Chlorinated γ-Alumina Pretreated with CH_3CCl_3.

Calcined γ-alumina was chlorinated with CCl_4, then pretreated with CH_3CCl_3. After 4 h the gaseous products were removed. An infrared spectrum of the products showed evidence for CH_2CCl_2, HCl, CCl_4 and CH_3CCl_3. Gaseous CCl_2FCClF_2 was admitted to the reaction vessel. After 18 h the solid developed a white colouration. The material responsible for this was volatile as the colour disappeared when the sidearm was frozen with liquid N_2. There was no infrared spectroscopic evidence to support the presence of CCl_3CF_3 but it is possible it was present in minute quantities. However after 3-5 days there was still no evidence of CCl_3CF_3. On removal of the gaseous products it was observed that 8% of material was retained by the solid. A second aliquot of CCl_2FCClF_2 was admitted but after 24 h there was still no evidence of CCl_3CF_3.

5.4 An Infrared Study of the Vapour Phase During the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Supported on γ-Alumina

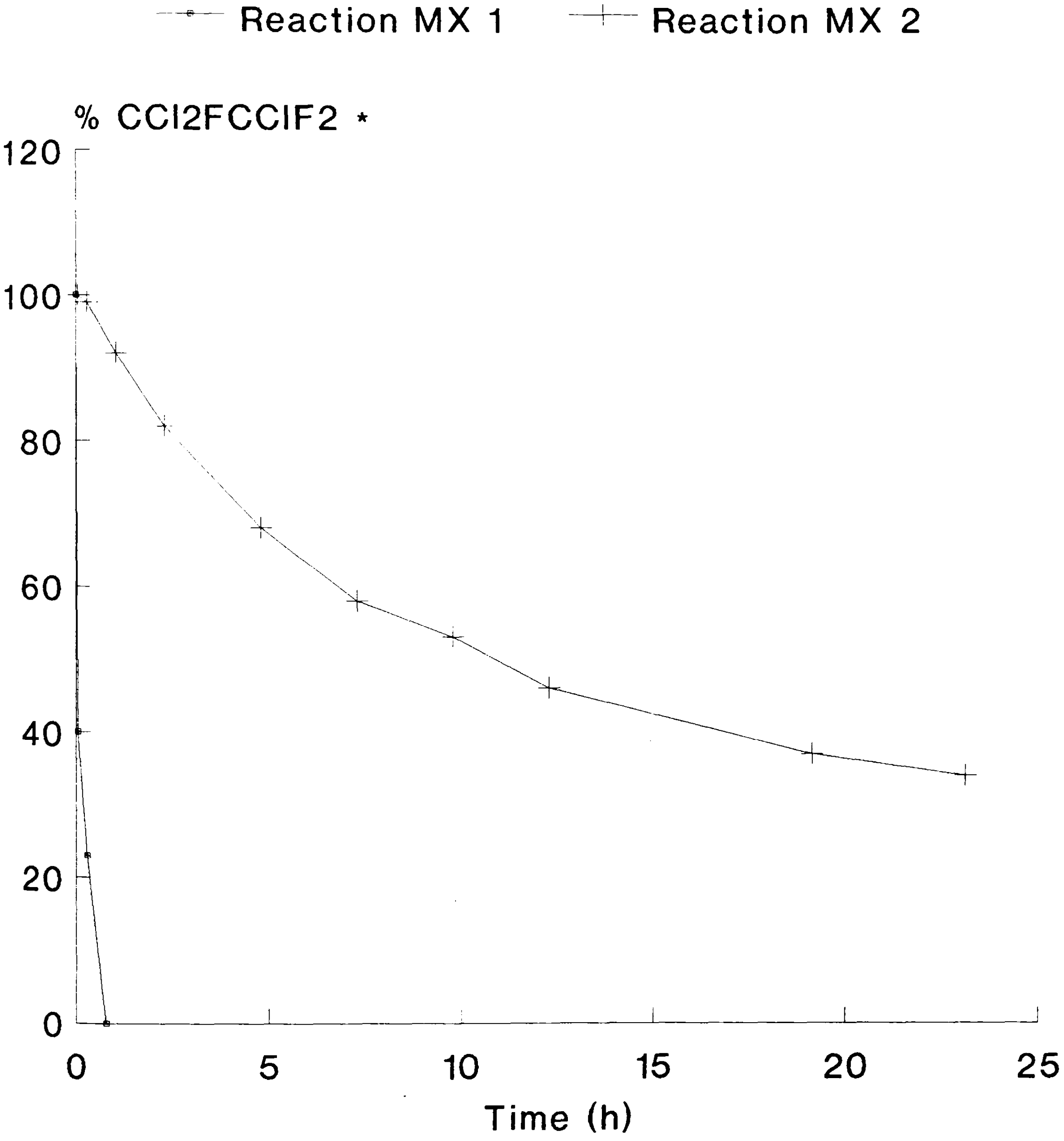
Experiment MX was undertaken using the infrared cell described in 2.7.1. At the start of the first reaction, MX1, a spectrum of pure CCl_2FCClF_2 was obtained before the solid sample of aluminium(III) chloride supported on γ-alumina was added. Thereafter, spectra were obtained every 15 min. Mass balance data for the experiment were not determined as the quantities of materials used were so small. The change in the quantities of CCl_2FCClF_2 and CCl_3CF_3, in the vapour phase, during the course of a reaction are shown in figures 5.5 and 5.6 respectively. During reaction MX1 CCl_2FCClF_2 was reacting with a clean surface. There was no gaseous CCl_2FCClF_2 present after 50 min (figure 5.5). The maximum quantity of CCl_3CF_3 was produced immediately after this point. The quantity of gaseous CCl_3CF_3 then decreased but remained constant after 4.8 h (figure 5.6). The i.r. spectra for this reaction, figure 5.7, did not exhibit isosbestic points. This suggested that in reaction MX1 the conversion of CCl_2FCClF_2 to CCl_3CF_3 involved the formation of an intermediate state.

In reaction MX2 CCl_2FCClF_2 reacted with aluminium(III) chloride supported on γ-alumina pretreated with CCl_2FCClF_2. The quantity of CCl_2FCClF_2 (figure 5.5) decreased during the reaction but was still present at the end of the 24 h period. The isomer CCl_3CF_3 was also present and the quantity of this increased during the reaction (figure 5.6). Three isosbestic points were observed in the spectra obtained during this reaction (figure 5.8). This indicated that the conversion of CCl_2FCClF_2 to CCl_3CF_3 occurred via a very short lived intermediate. Similar spectra were observed during the reactions between CCl_2FCClF_2 with aluminium(III) chloride or aluminium(III) chloride pretreated with CH_3CCl_3.

Experiment MY consisted of two reactions. During reaction MY1 the quantity of CCl_2FCClF_2 in the vapour phase fell steadily and the quantity of CCl_3CF_3 rose

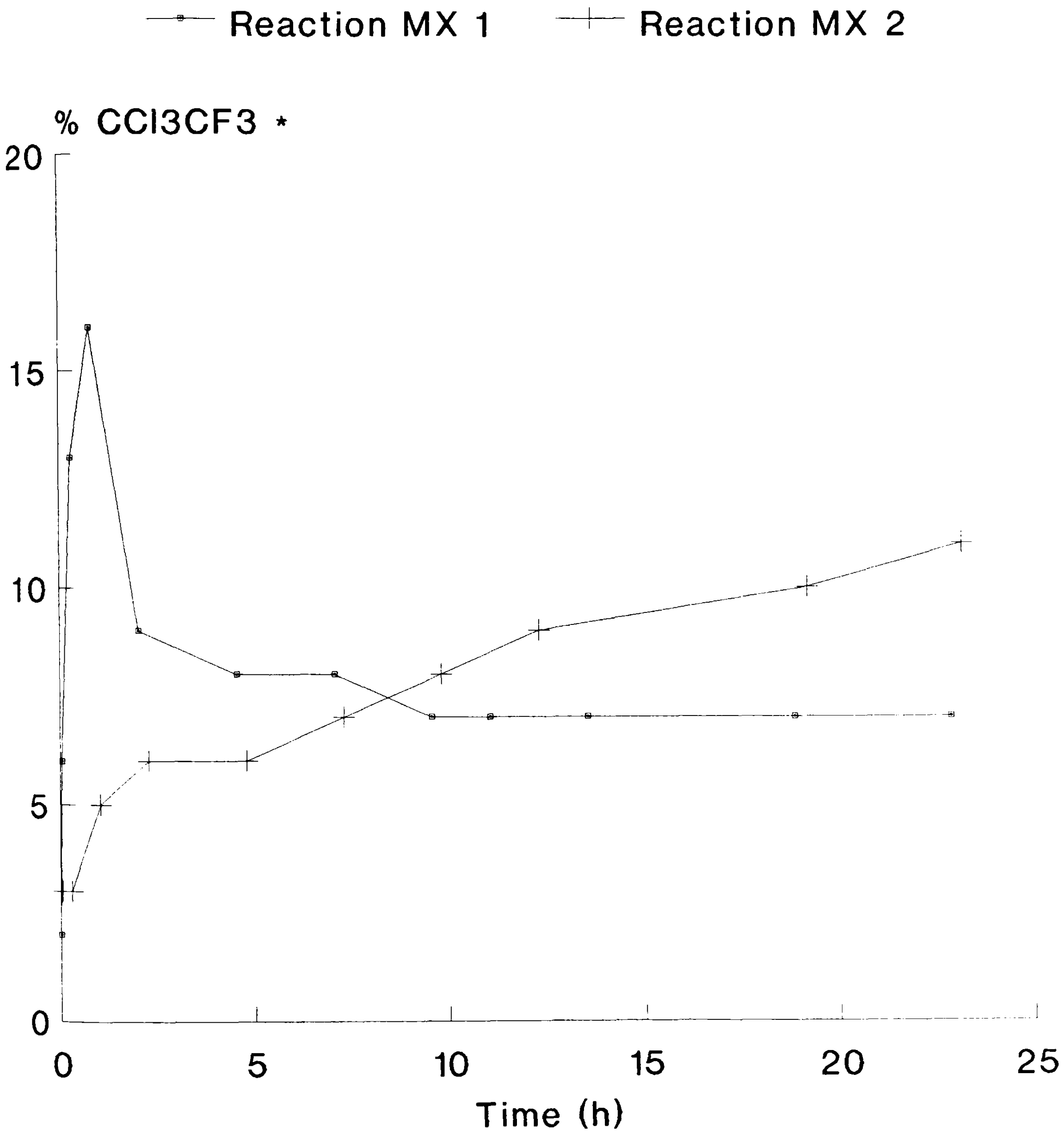
Figure 5.5 Experiment MX IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride

%CCl2FCClF2 vs time



* Calculated as shown in equation 3.2

Figure 5.6 Experiment MX IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride
% CCl3CF3 vs time



* Calculated as shown in equation 3.2

Figure 5.7 The Spectra Accumulated During 24h Reaction Between CCl2FCClF2 and Aluminium (III) Chloride Supported on γ-Alumina

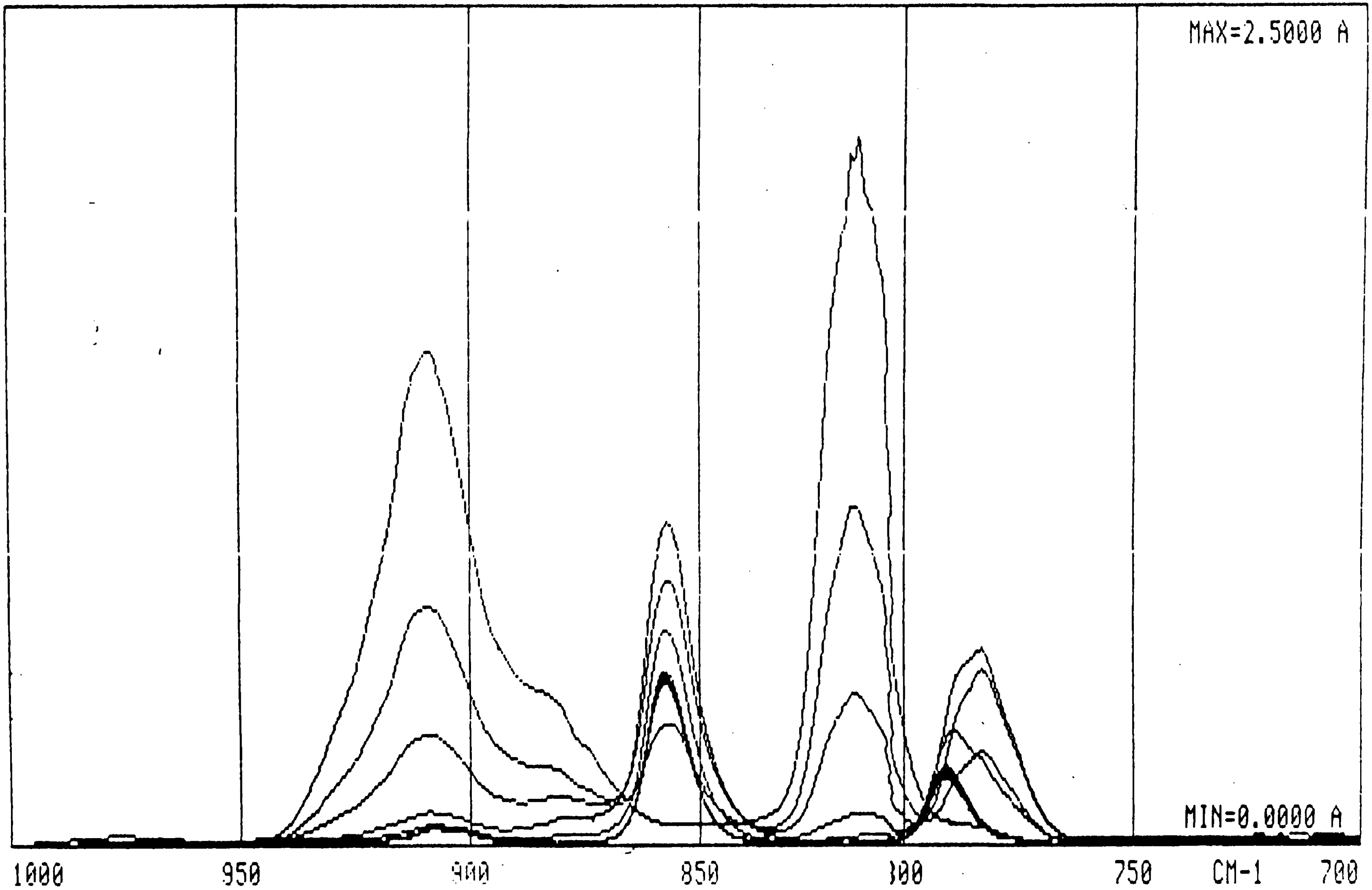
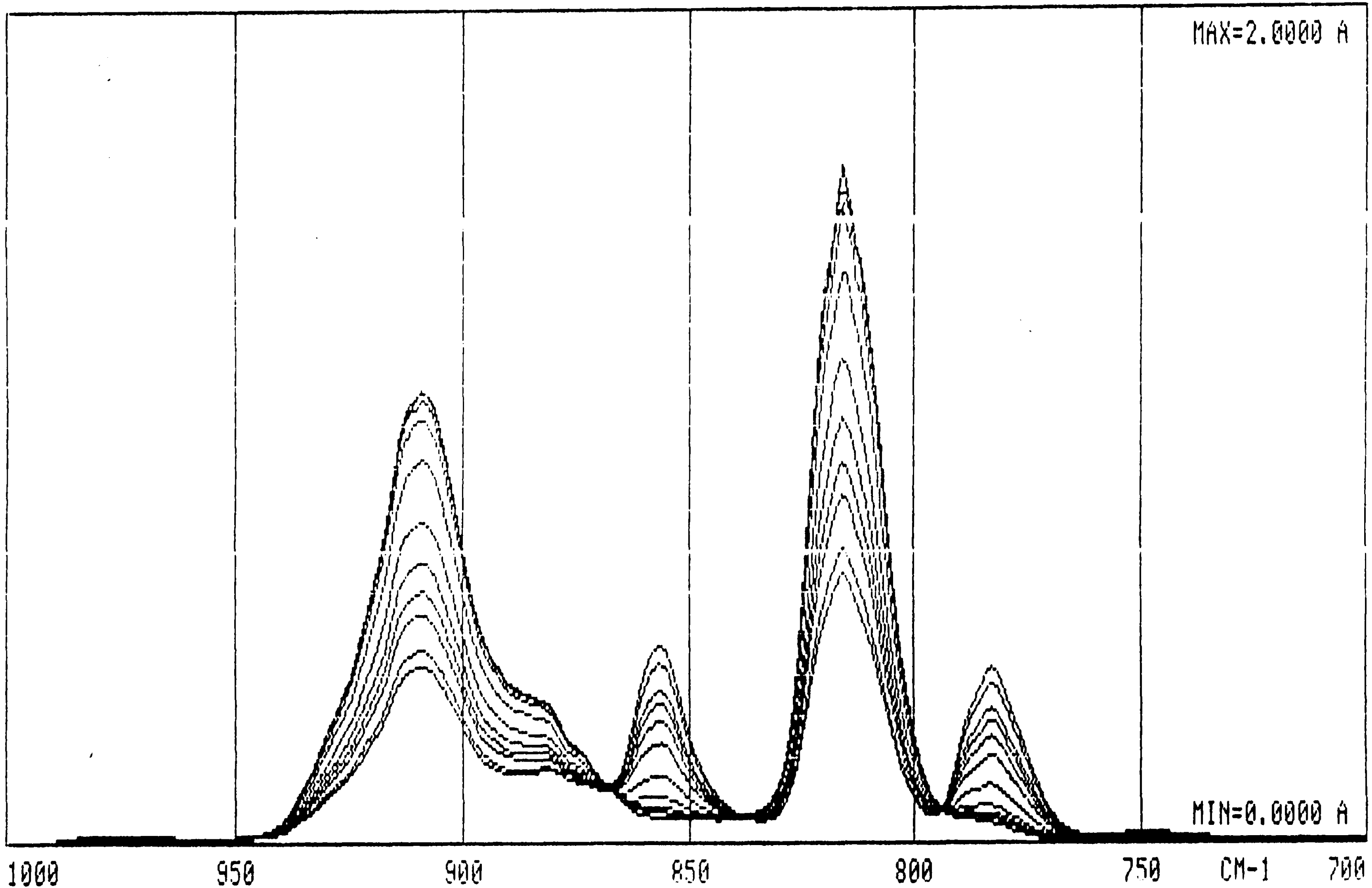


Figure 5.8 The Spectra Accumulated During Reaction MX2



steadily. There was still CCl_2FCClF_2 present in the vapour at the end of the reaction (figure 5.9), unlike reaction MX1. The isosbestic points were also observed during this reaction indicating that CCl_3CF_3 was being formed as quickly as CCl_2FCClF_2 was consumed. No data were obtained for reaction MX2, and no CCl_3CF_3 was observed in the vapour after 3 days.

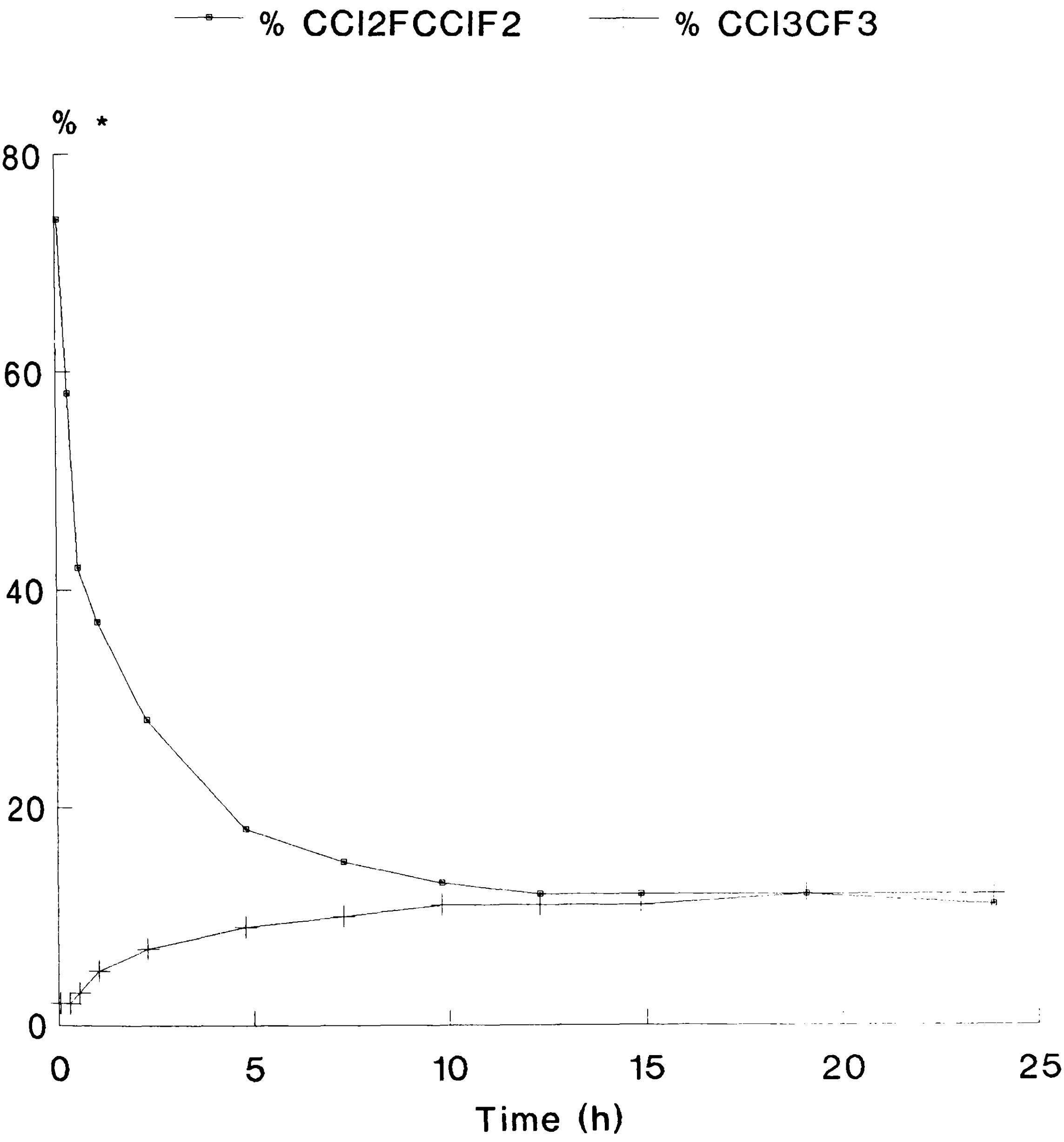
Samples of aluminium(III) chloride supported on calcined γ-alumina were analysed using ^{27}Al MAS nmr spectroscopy. The spectrum obtained (figure 5.10) showed a signal at -1.18ppm, corresponding to octahedral aluminium in γ-alumina and aluminium(III) chloride [82]. A second signal at 58.05 and 56.49 ppm was also observed. This is attributed to tetrahedral aluminium environments. The tetrahedral aluminium environments of calcined γ-alumina observed by Thomson occurred at 73.05 ppm [82]. Adsorption of HCl caused an upfield shift to 69.75 ppm [82]. Therefore it is possible that the signals at 58.05 ppm and 56.49 ppm were due to upfield shift of the tetrahedral aluminium environments of γ-alumina caused by the adsorption of aluminium(III) chloride. Drago has reported aluminium-27 signals at 85 and 65 ppm for aluminium(III) chloride adsorbed on SiO_2 [83]. He claimed this was due to the formation of Si-O-$AlCl_2$ groups. Hence the signals observed in figure 5.10 may be due to the formation of Al-O-$AlCl_x$ groups.

5.5 Kinetic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Supported on γ-Alumina

From ^{19}F nmr spectroscopic analysis (Table 5.2) it has been observed that the interaction between

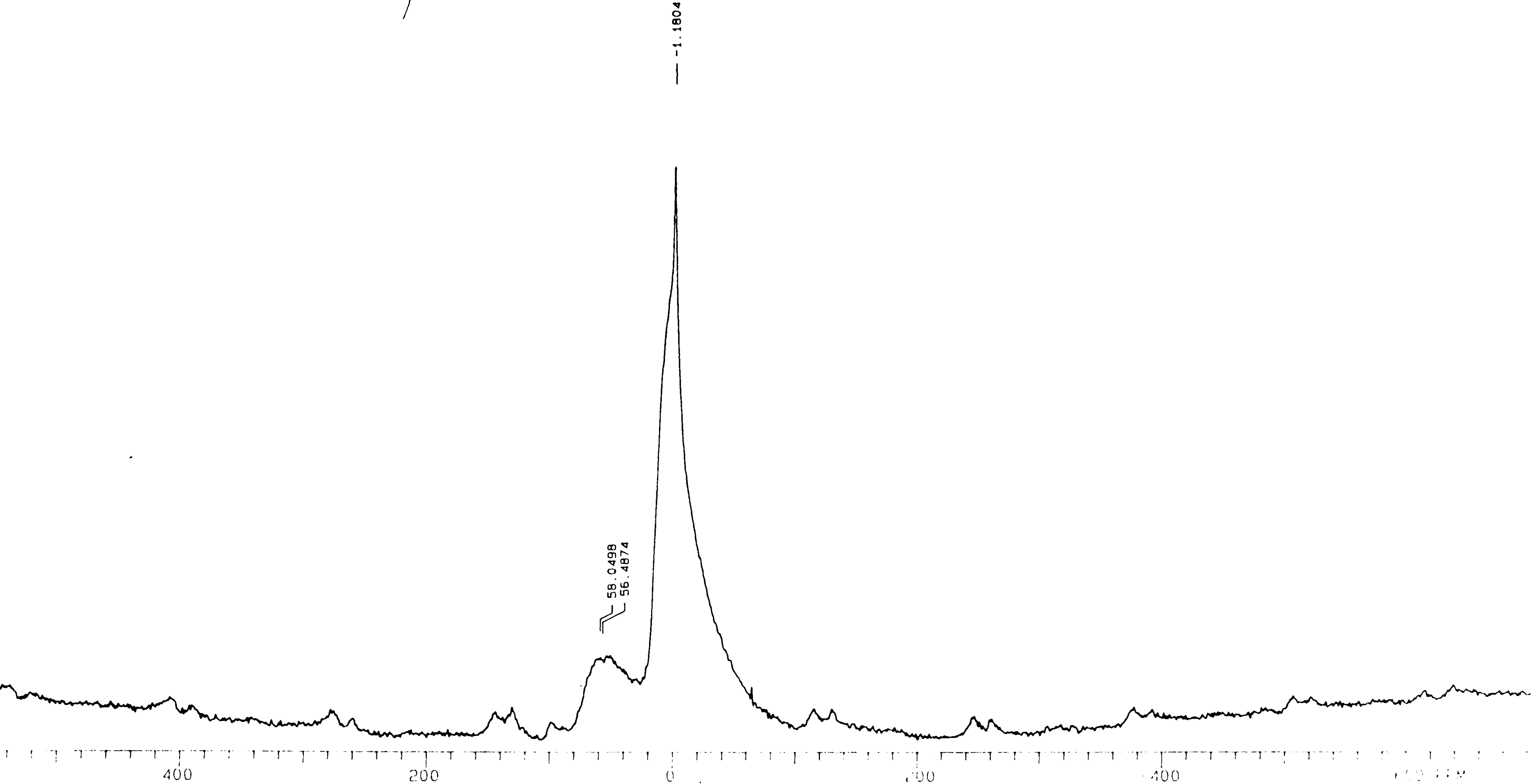
Figure 5.9 Experiment MY IR Studies of reactions between CCl2FCClF2 and Aluminium (III) Chloride with time

Reaction MY1



* Calculated as shown in equation 3.2

Figure 5.10 27Al MAS nmr Spectrum of Aluminium (III) Chloride Supported on γ-Alumina



CCl_2FCClF_2 and aluminium(III) chloride supported on γ-alumina results in the chlorination, fluorination and isomerisation of CCl_2FCClF_2. However the quantity of CCl_3CF_3 produced was less when compared to unsupported aluminium(III) chloride. The rate at which isomerisation occurred also was greatly reduced. For reactions MX1 and MX2 first and second order plots for the production of CCl_3CF_3 were not linear. This suggests a more complicated reaction process. The consumption of CCl_2FCClF_2 during the course of these reactions was also observed, but a simple reaction order was not observed for either reaction. This could be due to the fact that isomerisation is not the only reaction that CCl_2FCClF_2 undergoes on the surface of the solid.

First and second order kinetic plots for the production of CCl_3CF_3 were also made for reaction MY1 but no linear relationship was observed. Similar results were also obtained from 1st and 2nd order kinetic plots for the consumption of CCl_2FClF_2.

Experimental

5.6 The Behaviour of CCl_2FCClF_2 in the Presence of [CCl_4]-Chlorinated γ-Alumina.

5.6.1 Preparation of [CCl_4]-Chlorinated γ-Alumina

Commercially available Degussa 'C' γ-alumina was loaded into a Pyrex vessel in the dry box. The vessel was attached to a vacuum line and degassed, before calcination at 250°C. After 8 h, 0.5g was loaded into a conditioned Monel metal bomb in the dry box. The bomb was transferred to the vacuum line and the solid was degassed. Carbon tetrachloride (AnalaR May and Baker) (2 mmol) was distilled into the bomb. The mixture was heated overnight at 250°C to ensure the centre of the bomb was 227°C. The gaseous products were removed. Infrared analysis of the product mixture showed it to contain HCl, CO_2, $COCl_2$ and CCl_4.

5.6.2 The Behaviour of CCl_2FCClF_2 in the Presence of $[CCl_4]$-Chlorinated γ-Alumina

$[CCl_4]$-Chlorinated γ-alumina was loaded into a round bottomed flask, equipped with a side arm, in the dry box. The solid was transferred to the vacuum line and degassed. Seven aliquots of CCl_2FCClF_2 vapour were individually allowed to react with the solid sample for a period of 24 h. The products were removed and weighed before they were analysed either qualitatively by infrared spectroscopy or quantitatively by ^{19}F nmr spectroscopy. The experiment was repeated with a fresh solid sample and a further six aliquots of CCl_2FCClF_2.

5.7.1 The Reaction Between CH_3CCl_3 and $[CCl_4]$-Chlorinated γ-Alumina Pretreated with CCl_2FCClF_2

$[CCl_4]$-Chlorinated γ-alumina was treated with CCl_2FCClF_2 (483 mmol) for 24 h. The volatile products were removed and CH_3CCl_3 (0.6 mmol) was distilled into the reaction vessel. Samples of the gas phase were taken after 30 and 90 min and analysed qualitatively by infrared spectroscopy.

5.7.2 The Reaction Between CCl_2FCClF_2 and $[CCl_4]$-Chlorinated γ-Alumina Pretreated with CH_3CCl_3

$[CCl_4]$-Chlorinated γ-alumina was pretreated with CH_3CCl_3 (1.08 mmol). The volatile products were removed after 4 h and analysed by ir spectroscopy. The compound CCl_2FCClF_2 (4.52 mmol) was distilled into the reaction vessel. Samples of the gas phase were analysed by ir spectroscopy after 18 h and 3.5 days. The volatile products were removed and a second aliquot of CCl_2FCClF_2 (4.22 mmol) was admitted to the vessel. An ir spectrum of the products was obtained after 24 h.

5.8 The Preparation of Aluminium(III) Chloride supported on γ-Alumina.

Aluminium(III) chloride was loaded into a break seal vessel in the dry box, then degassed before attachment to the sublimation apparatus. γ-Alumina was calcined in situ at 250°C overnight and allowed to cool. Aluminium(III) chloride was sublimed onto the calcined alumina. Any excess aluminium(III) chloride was removed by a second sublimation of the alumina.

5.8.1 An Infrared Study of the Vapour Phase During the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride Supported on γ-Alumina.

The infrared cell described in 2.7.1. was filled with gaseous CCl_2FCClF_2 and a spectrum obtained.

Aluminium(III) chloride supported on γ-alumina was admitted to the cell. Infrared spectra were obtained every 15 min and stored on a disk. After 24 h all gaseous products were removed and a second aliquot of CCl_2FCClF_2 was admitted. This experiment was repeated with a fresh solid sample on a further two aliquots of CCl_2FCClF_2.

5.9 Kinetic Studies of the Reaction Between CCl_2FCClF_2 and Aluminium(III) Chloride supported on γ-alumina

The procedure followed was that outlined in 2.7.5 using the data obtained in 5.8.1.

Chapter 6 - Discussion

From the results presented in Chapter 3 it has been established that the compound CCl_2FCClF_2 is isomerised to CCl_3CF_3 at room temperature in the presence of aluminium(III) chloride. Similar results were obtained when aluminium(III) chloride was pretreated with CH_3CCl_3 or supported on calcined γ-alumina.

All of these solids have different surface morphologies. Aluminium(III) chloride possesses 6-coordinate aluminium atoms throughout the bulk structure. At the surface of the solid the aluminium atoms remain in an octahedral environment but they are coordinatively unsaturated. These uncoordinated atoms are reactive sites and are Lewis acidic. Aluminium(III) chloride pretreated with CH_3CCl_3 is also a Lewis acid. The compound CH_3CCl_3 is polymerised on the surface of this solid. The exact nature of the polymeric species is unknown but it is thought to be attached to surface aluminium atoms [25]. Solid state nmr results (figure 4.6) suggest the surface of aluminium(III) chloride has been modified as there is evidence of tetrahedral aluminium possibly in the form of $AlCl_4^-$ ions.

Aluminium(III) chloride adsorbed on calcined γ-alumina is classed as a superacid. The aluminium-27 solid state MAS nmr (figure 5.10) suggested that the surface of this solid consisted purely of aluminium(III) chloride but the adsorption of aluminium(III) chloride on γ-alumina resulted in the formation of tetrahedral Al-O-$AlCl_x$ links between the two aluminium compounds. The value of x is unknown, Drago has suggested x=2 [83] but in this study it was assumed x = 3.

For comparison, reactions of CCl_2FCClF_2 with $[CCl_4]$-chlorinated γ-alumina were also studied. Although this solid is not based on aluminium(III) chloride it is also a Lewis acid and possesses tetrahedral aluminium sites [82].

From mass balance studies it was observed that for all the reaction systems studied the weight of the gaseous products was less than that of the CCl_2FCClF_2 added. This phenomenon was not observed by Miller and co-workers [76]. This deficit, which varied from reaction to reaction is believed to be due to the formation of an organic layer on the surface of the solid. This is thought to have caused the colour change of the solid observed during a reaction. Aluminium(III) chloride was a colourless solid but on reaction with CCl_2FCClF_2 it developed a pale yellow colour. The colour lightened on removal of the gaseous products but the solid never returned to its original shade. Aluminium(III) chloride pretreated with CH_3CCl_3 which was originally a deep purple colour became grey-white under the same reaction conditions and $[CCl_4]$-chlorinated γ-alumina changed from dark-blue to pale blue.

Identical experimental methods were followed for each solid. A sample of CCl_2FCClF_2 was allowed to interact with the solid surface at room temperature for 24 h. All gaseous products were removed before a second aliquot of CCl_2FCClF_2 was added. This procedure was repeated for at least 4 reactions before the solid sample was changed. When aluminium(III) chloride was exposed to repeated aliquots of CCl_2FCClF_2 the quantity of material retained by the solid increased but the quantity of CCl_3CF_3 decreased, with each subsequent reaction. This trend was not observed in all cases but the quantity of material retained always bore an inverse relationship to the quantity of CCl_3CF_3 produced. Similar results were also observed when aluminium(III) chloride pretreated with CH_3CCl_3 was the solid studied. Reactions of CCl_2FCClF_2 with $[CCl_4]$-chlorinated γ-alumina resulted in very little CCl_3CF_3 being produced ($<10\%$ of the original quantity of CCl_2FCClF_2 added) but there was a large quantity of material retained.

Information regarding the composition and catalytic activity of the organic layer was obtained from radiolabelling experiments.

The purpose of these experiments was to confirm the presence of chlorine on the surface of the solid, they gave no indication as to the nature of the surface species. This study followed the same experimental procedure as outlined for the non radioactive experiments. The systems studied were:

(i) $[^{36}Cl]$-CCl_2FCClF_2 and aluminium(III) chloride
(ii) $[^{36}Cl]$-CCl_2FCClF_2 labelled aluminium(III) chloride and CCl_2FCClF_2

(iii) [^{36}Cl]-CH_3CCl_3 labelled aluminium(III) chloride and CCl_2FCClF_2

(iv) [^{36}Cl]-aluminium(III) chloride and CCl_2FCClF_2

The reaction between gaseous [^{36}Cl]-CCl_2FCClF_2 and aluminium(III) chloride resulted in the uptake of the [^{36}Cl]-chlorine label by the solid (section 3.3.1). The initial reaction of gaseous CCl_2FCClF_2 with [^{36}Cl]-CCl_2FCClF_2 labelled aluminium(III) chloride (section 3.3.2 experiment MG) resulted in an immediate decrease of the surface count rate on admission of CCl_2FCClF_2 to the reaction vessel. Thereafter the surface count rate remained constant for the duration of the reaction. During subsequent reactions of CCl_2FCClF_2 with the same sample of [^{36}Cl]-CCl_2FCClF_2 labelled aluminium(III) chloride the surface count rate remained constant.

When gaseous CCl_2FCClF_2 was left in contact with the [^{36}Cl]-CCl_2FCClF_2 labelled surface for a long period of time (> 1 week) the surface count rate increased. This was probably due to the organic layer desorbing from the solid. After each reaction of CCl_2FCClF_2 with [^{36}Cl]-CCl_2FCClF_2 labelled aluminium(III) chloride a quantity of material was observed to be retained by the solid. At the end of a series of reactions a build up of C_2Cl_6 was observed on the walls of the reaction vessel. The C_2Cl_6 resulted as a product from the chlorination of CCl_2FCClF_2 by the solid surface. It is not a very volatile compound therefore desorption would have been a very slow process. Over a period of time desorption would have occurred resulting in the formation of C_2Cl_6 on the walls of the reaction vessel. The desorption process led to a reduction in the chlorine content on the surface of the solid. This resulted in a decrease in chlorine self absorption and therefore the surface count rate increased. A similar observation was made when the solid was left in vacuo for 4 weeks once all the vapour was removed. A pressure of gas built up in the reaction vessel during this time. It was identified by i.r. spectroscopy to be mainly CCl_2FCClF_2 but there was evidence that small quantities of CCl_3CF_3 were also present. The opposite effect was observed during the reaction between CCl_2FCClF_2 and $[^{36}Cl]$-CCl_2FCClF_2 labelled aluminium(III) chloride. Adsorption of CCl_2FCClF_2 by the solid led to an increase of the surface chlorine content, thus chlorine self absorption increased therefore the surface count rate decreased.

Radioactivity was detected in the gas phase but it was too small to be determined precisely. However the possibility that $[^{36}Cl]$-CCl_3CF_3 was formed cannot be ruled out.

The results obtained from the reactions between CCl_2FCClF_2 and $[^{36}Cl]$-CCl_2FCClF_2 labelled aluminium(III) chloride were similar to those found when CCl_2FCClF_2 was allowed to react with aluminium(III) chloride which had been pretreated with $[^{36}Cl]$-CH_3CCl_3 (section 4.3). The disappointing feature of these reactions was the lack of isomerisation. This was probably due to the hydration and hydroxylation of aluminium(III) chloride caused by the desorption of water vapour from the Geiger-Müller tubes and the walls of the counting vessel. When the reactions between CCl_2FCClF_2 and $[^{36}Cl]$-chlorine labelled aluminium(III) chloride were studied using the counting vessel (sections 3.3.3 and 3.3.4), it was observed that after the initial reaction 95% of the quantity of CCl_2FCClF_2 added was retained by the solid and no CCl_3CF_3 was observed in the product mixture. However when the reactions were studied in an alternative reaction vessel, initially 37% of the original quantity of CCl_2FCClF_2 added was retained by the solid and 47% of the original quantity of CCl_2FCClF_2 added produced CCl_3CF_3 (experiment MI section 3.3.4). Analysis of the product mixture MI1 by radio g.c. showed that there was no [^{36}Cl]-chlorine label present in CCl_3CF_3 fraction. The result was consistent with Miller's original observation [76]

Attempts were made to conduct a similar investigation using [^{18}F]-fluorine, but the short half life of [^{18}F]-fluorine (110 min) and the lengthy preparation of [^{18}F]-CCl_2FCClF_2 made this study impracticable.

Further information about the nature of the solids studied was obtained from solid state MAS nmr spectroscopy. The purposes of these analyses were two-fold. Firstly to identify the nature of the retained organic substrate and secondly to discover if the surface structure had changed.

The solids studied were:

i. Aluminium(III) chloride after reaction with CCl_2FCClF_2.

ii. Aluminium(III) chloride pretreated with CH_3CCl_3 after reaction with CCl_2FCClF_2.

and iii. Aluminium(III) chloride supported on γ-alumina

^{27}Al MAS nmr spectra were obtained for all three solids and ^{13}C MAS nmr spectra were also obtained for samples i and ii. The ^{27}Al MAS nmr spectrum for sample(i) aluminium(III) chloride after reaction with CCl_2FCClF_2 (figure 3.13) showed a sharp signal at -1.01 ppm. This was consistent with octahedrally coordinated aluminium environments. No other aluminium signals were observed. The ^{13}C MAS nmr spectrum (figure 3.14) of the same sample showed a broad signal with a peak at 105.7 ppm. This was identified as C_2Cl_6. There was a long delay in obtaining these spectra and it is possible that all the organic material retained by the solid was fully chlorinated during this time to produce C_2Cl_6. Since the ^{27}Al MAS spectrum showed only one signal, corresponding to that of an octahedrally coordinated aluminium atom, it was assumed that adsorption of the organic material by aluminium(III) chloride did not alter the structure of the aluminium(III) chloride. However the new surface formed contained some organic material.

The ^{27}Al MAS nmr spectrum of aluminium(III) chloride pretreated with CH_3CCl_3, after reaction with CCl_2FCClF_2 (figure 4.6) showed two signals one at 77.9 ppm and the other at -19.9 ppm. This latter signal was not identified but it contained a shoulder at -1 ppm corresponding to octahedral aluminium environments. The signal at 77.9 ppm was attributed to tetrahedral aluminium atoms, and was most probably due to the presence of the $AlCl_4^-$ ion, also observed in the infrared studies of the reaction between aluminium(III) chloride and gaseous CH_3CCl_3 [25]. The signals observed in this spectrum are thought to result from the interaction between aluminium(III) chloride and CH_3CCl_3. The adsorption of CCl_2FCClF_2 by aluminium(III) chloride did not affect the inorganic structure therefore it was thought unlikely that the adsorption of CCl_2FCClF_2 by aluminium(III) chloride pretreated with CH_3CCl_3 resulted in any further structural change of the solid but the possibility was not ruled out. The ^{13}C MAS nmr spectrum of aluminium(III) chloride pretreated with CH_3CCl_3, after reaction with CCl_2FCClF_2 (figure 4.7) also showed evidence for the presence of C_2Cl_6. The third ^{27}Al MAS nmr spectrum obtained was of aluminium(III) chloride supported on calcined γ-alumina.

This showed three signals (figure 5.10). The signal at -1.2 ppm corresponded to octahedral aluminium environments and was attributed to aluminium(III) chloride. However calcined γ-alumina also contains octahedral aluminium atoms therefore this observed signal may have been due to both octahedral aluminium(III) chloride atoms and octahedral γ-alumina atoms. The signals at 56 ppm and 58 ppm for aluminium(III) chloride adsorbed on γ-alumina may have arisen from the combination of two factors:

(i) The chlorination of the tetrahedral aluminium environment of γ-alumina by aluminium(III) chloride and (ii) The formation of new tetrahedral environments from the reaction between aluminium(III) chloride and γ-alumina. These new sites may have the form Al-O-AlCl$_3$.

It is not suggested that the Al-O-AlCl$_3$ groups were the surface of the solid but rather they formed the basis on which an aluminium(III) chloride network was built. Thus the solid surface appeared to be that of aluminium(III) chloride. The presence of Al-O-AlCl$_3$ surface species was not ruled out but its ability to isomerise CCl$_2$FCClF$_2$ was uncertain.

Infrared studies of the vapour phase during the reaction between CCl$_2$FCClF$_2$ and aluminium(III) chloride, aluminium(III) chloride pretreated with CH$_3$CCl$_3$ or aluminium(III) chloride supported on γ-alumina have been conducted. The experimental procedure followed was identical to that followed for the non-radioactive experiments. The spectra obtained for these experiments contained three isosbestic points with the exception of reaction of MX1 (section 5.4). In this reaction the lack of isosbestic points was attributed to retention of CCl$_2$FCClF$_2$ by γ-alumina rather than by reaction of CCl$_2$FCClF$_2$ with aluminium(III) chloride. The isosbestic points indicated that CCl$_3$CF$_3$ was being formed directly from CCl$_2$FCClF$_2$ without the build up of an intermediate species. The presence of moisture affected these experiments as it did with the radiolabelling experiments. When there was little or no moisture present all the CCl$_2$FCClF$_2$ was consumed during the course of the reaction (sections 3.4.1 and 4.4, experiments MJ and MO respectively). Immediately after the total consumption of CCl_2FCClF_2 the maximum quantity of CCl_3CF_3 was produced but at the termination of the reaction the quantity of the CCl_3CF_3 present had decreased. The presence of moisture appeared to inhibit the reaction between CCl_2FCClF_2 and the solid. Under these conditions the quantity of CCl_2FCClF_2 in the gas phase was observed to decrease during the course of a reaction but it was not completely consumed. As a result, the quantity of CCl_3CF_3 produced during the reaction increased steadily reaching a maximum only at the end of the reaction.

Kinetic studies revealed that the production of CCl_3CF_3 did not follow a simple reaction order. The reaction of CCl_2FCClF_2 with any one of the solids studied, involved the adsorption of CCl_2FCClF_2 by the solid. This resulted in an immediate change of the surface. Once the adsorbed species was formed it could undergo isomerisation, fluorination or chlorination. This latter process resulted in material being retained by the surface of the solid thus changing its structure. Therefore during the course of a reaction the surface was constantly changing and this gave rise to the observed complex reaction order. The product mixture consisted of CCl_2FCF_3, CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6. Only the asymmetric isomers were identified, there was no evidence to suggest the presence of the symmetric isomers $CClF_2CClF_2$ and CCl_2FCCl_2F. The presence of CCl_2FCF_3 was interesting as it was not observed by Miller [76] and indicated that fluorination had occurred. The possibility that CCl_2FCF_3 could have been formed from the dismutation of

CCl_2FCClF_2 is not likely as the dismutation of CCl_2FCClF_2 would have given rise to equal quantities of CCl_2FCF_3 and CCl_3CClF_2 in the product mixture. However the quantity of chlorinated products exceeded that of fluorinated products. The compound $CClF_2CClF_2$ was not isomerised in the presence of aluminium(III) chloride or aluminium(III) chloride pretreated with CCl_2FCClF_2. Therefore the production of CCl_2FCF_3 may have arisen from the fluorination of CCl_3CF_3. This would explain decrease in the quantity of CCl_3CF_3, towards the end of a reaction, observed in the infrared experiments. When CCl_2FCClF_2 was chlorinated it deposited a fluorine on the solid surface. This fluorine source reacted with CCl_3CF_3 to form CCl_2FCF_3.

Miller conducted his original study under reflux conditions at 60°C [76]. At this temperature the compound CCl_3CClF_2 (mpt. 40°C) has a higher vapour pressure than it does at room temperature. This would account for the difference in results between this study and Miller's. Miller observed almost a 1:1 ratio between CCl_3CF_3 and CCl_3CCl_2F in the product mixture and there is no mention of material being retained by the solid. In this study the volatile products were mainly CCl_3CF_3 but often large quantities of material were retained by the solid. This retained layer was identified by ^{13}C MAS nmr to be C_2Cl_6 but initially CCl_2FCClF_2 would have been chlorinated to CCl_3CClF_2. As this latter product has a very low vapour pressure at room temperature, it was retained by the solid and underwent further chlorination to produce C_2Cl_6.

The reaction between CCl_3CClF_2 and aluminium(III) chloride (section 3.5.1.1) resulted in the production of CCl_3CF_3, CCl_3CClF_2 and CCl_3CCl_2F. The compound C_2Cl_6 was not detected by ^{19}F nmr spectroscopy but it was thought to be present as CCl_3CCl_2F is readily chlorinated. The isomerisation of CCl_3CClF_2 to CCl_2FCCl_2F did not occur but a large quantity of material was retained by the solid. When CCl_2FCClF_2 was allowed to react with aluminium(III) chloride pretreated with CCl_3CClF_2 (section 3.5.1.2) the products obtained were CCl_2FCF_3, CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2 and probably some C_2Cl_6. As the experiment proceeded the quantity of CCl_2FCClF_2 in the product mixtures increased, suggesting that the reaction was being inhibited. This was possibly due to the build up of C_2Cl_6 on the solid surface as it is formed more readily from CCl_3CClF_2 than CCl_2FCClF_2.

The possibility that the retained organic layer was simply physically adsorbed to the surface of the solid was ruled out by reacting perfluorohexane with aluminium(III) chloride. Perfluorohexane C_6F_{14} which has a similar boiling point (57.11°C cf. 47.7°C, CCl_2FCClF_2) and vapour pressure (29.05 cf 48.5KPa CCl_2FCClF_2) to CCl_2FCClF_2 did not interact with the aluminium(III) chloride surface. This indicated that chemical reactions must have taken place if organic material were to be retained by aluminium(III) chloride.

When aluminium(III) chloride was pretreated with CH_3CCl_3, the product mixture, after reaction with CCl_2FCClF_2 consisted of CCl_2FCF_3, CCl_2FCClF_2, CCl_3CF_3,

CCl_3CClF_2, CCl_3CCl_2F, C_2Cl_6 and C_2Cl_4. The presence of C_2Cl_4 was interesting as it was only observed when aluminium(III) chloride was pretreated with CH_3CCl_3. The other products were observed in all the systems studied. The reaction between CH_3CCl_3 led to the formation of CH_2CCl_2 and HCl. The CH_2CCl_2 is polymerised by aluminium(III) chloride and forms a purple tar on the surface of the solid. A full study of this system was carried out by McBeth [25]. The exact nature of the purple tar is unknown but it is possible it may have the structure $(CH_2\text{-}CCl_2\text{-}CH_2\text{-}CCl_2\text{-}CH_2\text{-}CCl_2)^+{}_n$ $AlCl_4^-$. The production of C_2Cl_4 therefore, may have arisen from the breakdown of this polymer chain or by the dechlorination of C_2Cl_6.

Experiments were carried out to find a relationship, if any, between the reactive sites on aluminium(III) chloride responsible for the dehydrochlorination of CH_3CCl_3 and those responsible for the isomerisation of CCl_2FCClF_2. It was observed that aluminium(III) chloride pretreated with CH_3CCl_3 isomerised CCl_2FCClF_2 at room temperature. This suggested that either (i) the surface sites responsible for the dehydrochlorination of CH_3CCl_3 were completely separate from the sites responsible for the isomerisation of CCl_2FCClF_2 or (ii) the new surface formed from the purple tar was similar to the organic layer formed from the reaction of CCl_2FCClF_2 with aluminium(III) chloride, and that the purple tar promoted the isomerisation of CCl_2FCClF_2.

When CH_3CCl_3 was allowed to react with aluminium(III) chloride pretreated with CCl_2FCClF_2 the observed products were CH_2CCl_2, HCl, CH_3CCl_3 and CCl_3CF_3. The presence of CCl_3CF_3 was very interesting as it suggested that the surface sites of aluminium(III) chloride responsible for the isomerisation of CCl_2FCClF_2 were in close proximity or identical to the surface sites responsible for the dehydrochlorination of CH_3CCl_3. The fact that reaction of CH_3CCl_3 with aluminium(III) chloride pretreated with CCl_2FCClF_2 produced CCl_3CF_3 also implied that the retained organic species resulting from the reaction of CCl_2FCClF_2 with aluminium(III) chloride was also structurally similar to CCl_3CF_3.

A similar phenomenon was also observed when $[CCl_4]$-chlorinated γ-alumina was used. The reaction of CCl_2FCClF_2 with this solid resulted in the retention of large quantities of material on the solid surface. The product mixture obtained consisted mainly of CCl_2FCClF_2 but minute quantities of CCl_3CF_3, CCl_2FCF_3 and CCl_3CClF_2 were also detected. $[CCl_4]$-chlorinated γ-alumina will also facilitate the room temperature dehydrochlorination of CH_3CCl_3 producing a purple tar on the surface of the solid [82]. However the reaction of CCl_2FCClF_2 with $[CCl_4]$-chlorinated γ-alumina pretreated with CH_3CCl_3 did not result in the isomerisation of CCl_2FCClF_2 but a large quantity of organic material was retained by the solid (section 5.4.2). When $[CCl_4]$-chlorinated γ-alumina was pretreated with CCl_2FCClF_2 it did not catalyse the room temperature dehydrochlorination of CH_3CCl_3 (section 5.4.1). The results obtained from the experiments carried out in sections 5.4.1 and 5.4.2 indicated that the surface sites responsible for the dehydrochlorination of CH_3CCl_3 were blocked by the adsorption of CCl_2FCClF_2 and those responsible for the isomerisation of CCl_2FCClF_2 were blocked by the adsorption of the purple tar. This suggested that on $[{}^{36}Cl]$-CCl_4...

Proposed Mechanisms

In all the reactions studied the isomerisation of CCl_2FCClF_2 was always accompanied by the chlorination of CCl_2FCClF_2 and the retention of organic material on the solid surface. From kinetic studies it was shown that the production of CCl_3CF_3 followed neither a first nor second order reaction process. No kinetic information was obtained for the consumption of CCl_2FCClF_2 as it was involved in three different reaction processes namely fluorination, chlorination and isomerisation. Fluorination obviously could not have occurred first therefore the initial process must have been either chlorination or isomerisation.

The mechanistic details will be based on an aluminium(III) chloride surface. If isomerisation were completely separate from chlorination, as Miller implied, then possible intramolecular mechanisms could be:

(i) a twisting mechanism involving a 5-centre transition state (figure 6.1)

or (ii) intramolecular halogen exchange (figure 6.2).

Figure 6.1

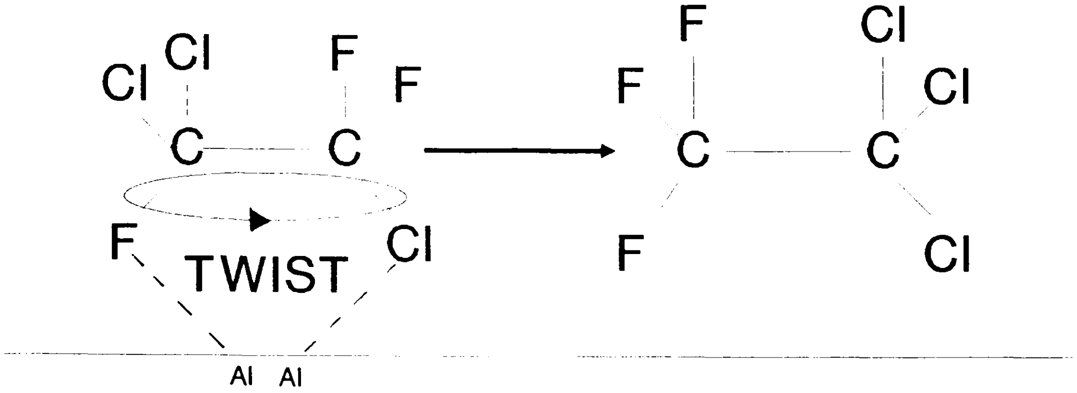
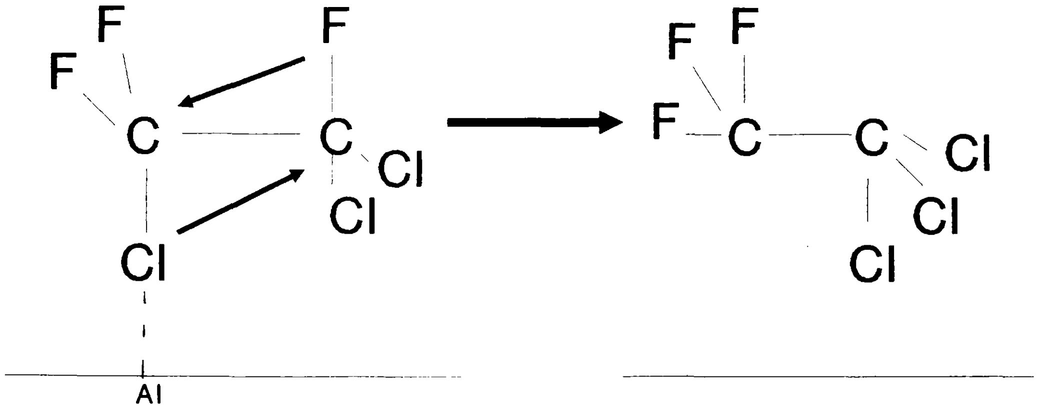


Figure 6.2



Both of these mechanisms are unlikely as they involve highly strained intermediates. If isomerisation were to occur before chlorination then the formation of CCl_3CClF_2 would arise from the chlorination of CCl_3CF_3. However the $-CF_3$ group is very difficult to chlorinate, therefore it is unlikely that CCl_3CClF_2 would be produced by the chlorination of CCl_3CF_3. Alternatively isomerisation may occur after chlorination. The chlorination of CCl_2FCClF_2, by aluminium(III) chloride results in the production of CCl_3CClF_2 and presumably the formation of an Al-F bond. The dissociative adsorption of CCl_2FCClF_2 by aluminium(III) chloride must occur via the $-CCl_2F$ group, as this is the group that is chlorinated.

The surface species presumed to be formed is shown in figure 6.3. This is prerequisite for the isomerisation of CCl_2FCClF_2. At room temperature CCl_3CClF_2 will remain bound to the surface and isomerisation may take place as shown in figure 6.4. The aluminium bound fluorine F^* attacks C_1 (6.4a), this results in the displacement of Cl^* to C_2 (6.4b). The CCl_3CF_3 molecule formed immediately desorbs from the surface (6.4c) leaving the site vacant for further reaction (6.4d). This mechanism may account for the production of CCl_3CF_3 observed when CCl_2FCClF_2 treated aluminium(III) chloride is left standing in a reaction vessel for 3 weeks but, it is not thought to be the dominant reaction. Infrared studies have shown the presence of isosbestic points, these suggest that CCl_3CF_3 is being formed directly from CCl_2FCClF_2 without the build up of an intermediate species. The

Figure 6.3

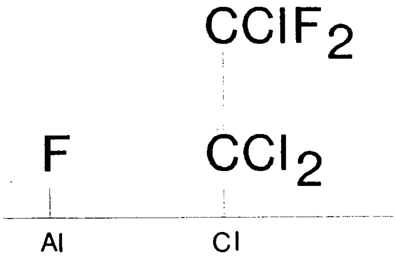
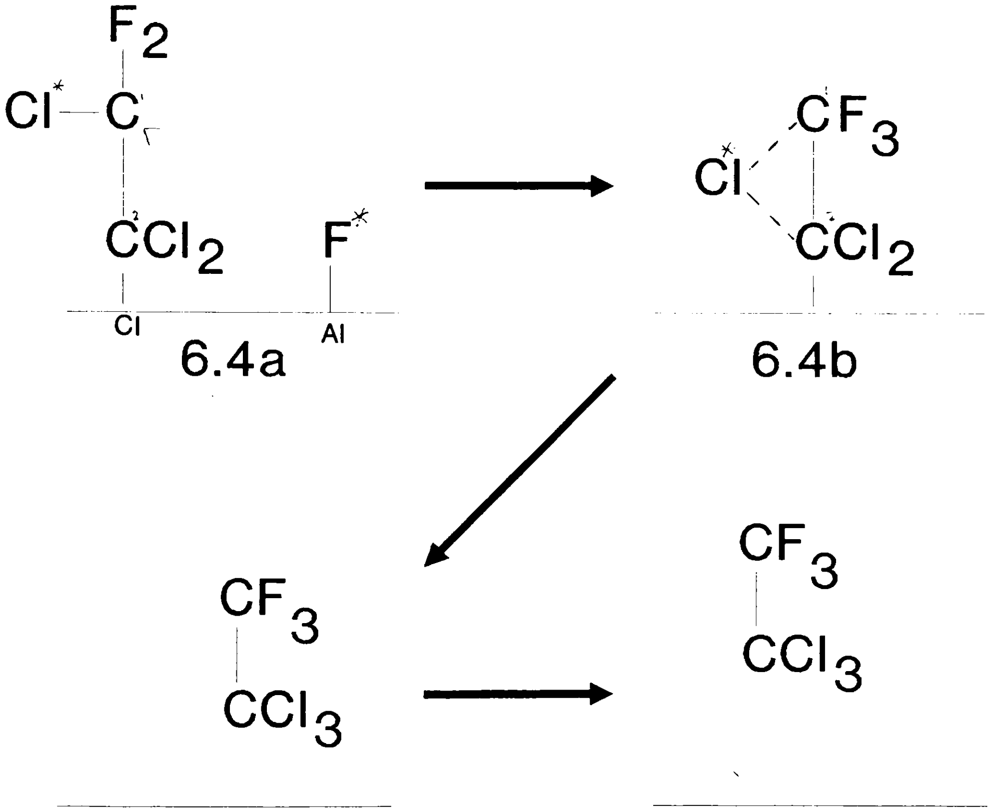


Figure 6.4



6.4a

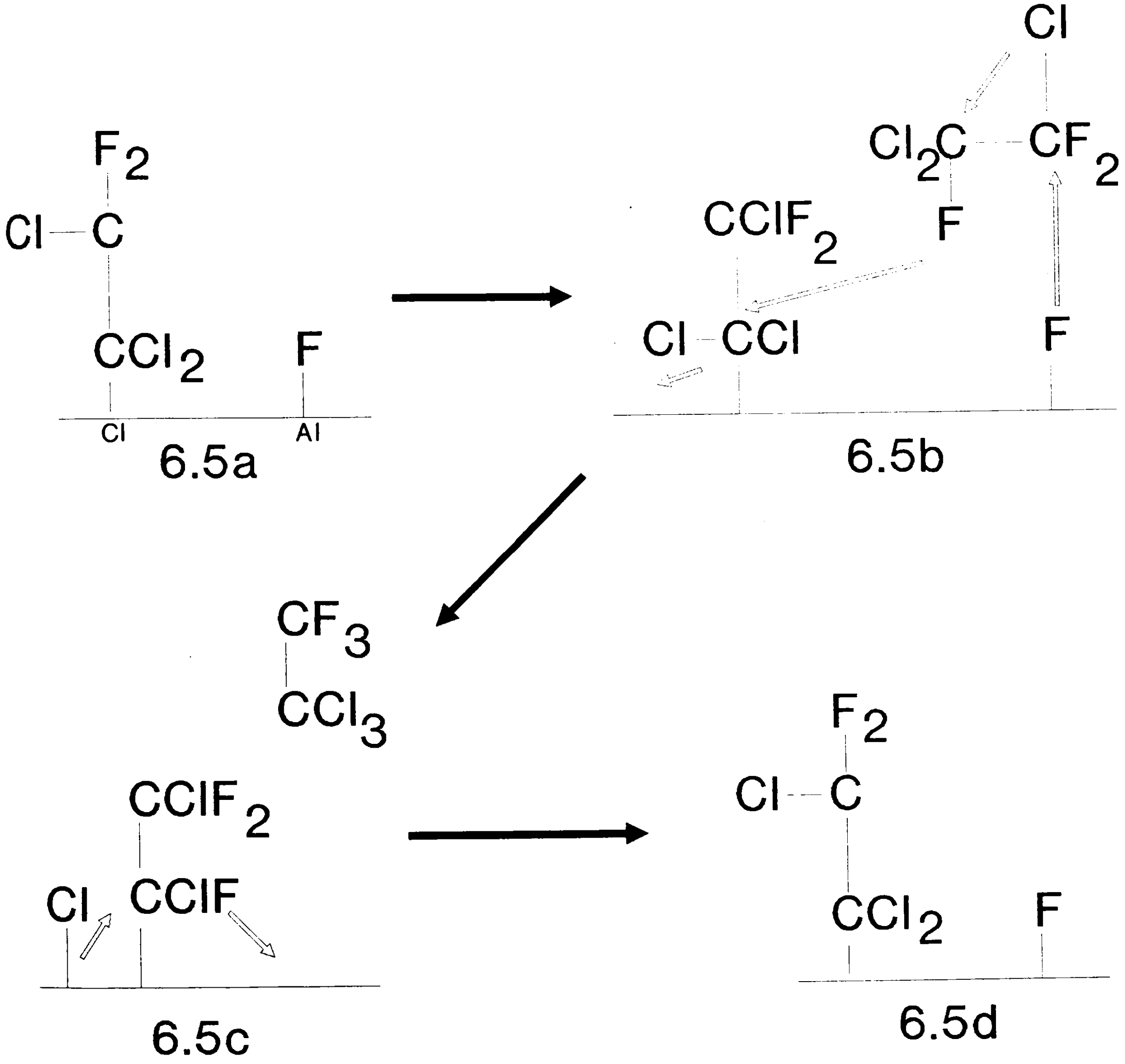
6.4b

6.4c

mechanism proposed in figure 6.4 suggests the intermediate species formed are adsorbed CCl_3CClF_2 and Al-F. An alternative mechanism for isomerisation is shown in figure 6.5. The compound CCl_2FCClF_2 dissociatively adsorbs on aluminium(III) chloride forming an Al-F bond and adsorbed CCl_3CClF_2 (6.5a). A second molecule of CCl_2FCClF_2 then reacts with these adsorbed species, via a series of halogen exchange mechanisms (6.5b) to form CCl_3CF_3, adsorbed CCl_2FCClF_2 and an Al-Cl bond (6.5c). The adsorbed CCl_2FCClF_2 dissociates forming adsorbed CCl_3CClF_2 and an Al-F bond (6.5d). This mechanism is the mirror image of the Michael reaction [111]. A typical example of the Michael reaction is shown in figure 6.6. The base NH_3, abstracts a proton from the α-carbon C^* of malonic acid (6.6a), thus generating a carbanion (6.6b). The carbanion produced attacks the conjugated carbonyl at C^* (6.6c). This produces a new C-C bond between the acid and the olefin and a delocalised negative charge at the end of the molecule (6.6d). The negative charge is neutralised by the abstraction of the H^+ ion from the base (6.6e) forming the new addition molecule (6.6f).

For the isomerisation of CCl_2FCClF_2 over aluminium(III) chloride the proposed mechanism (figure 6.5) begins with the generation of a carbocation via the loss of F^- to a Lewis acid site. There is a difference between the mechanism shown in figure 6.5 and those in figures 6.4, 6.2 and 6.1. In figure 6.5 the reactive sites for isomerisation occur not on pure aluminium(III) chloride but as a result of the surface species formed from the chlorination of CCl_2FCClF_2. Isomerisation

Figure 6.5



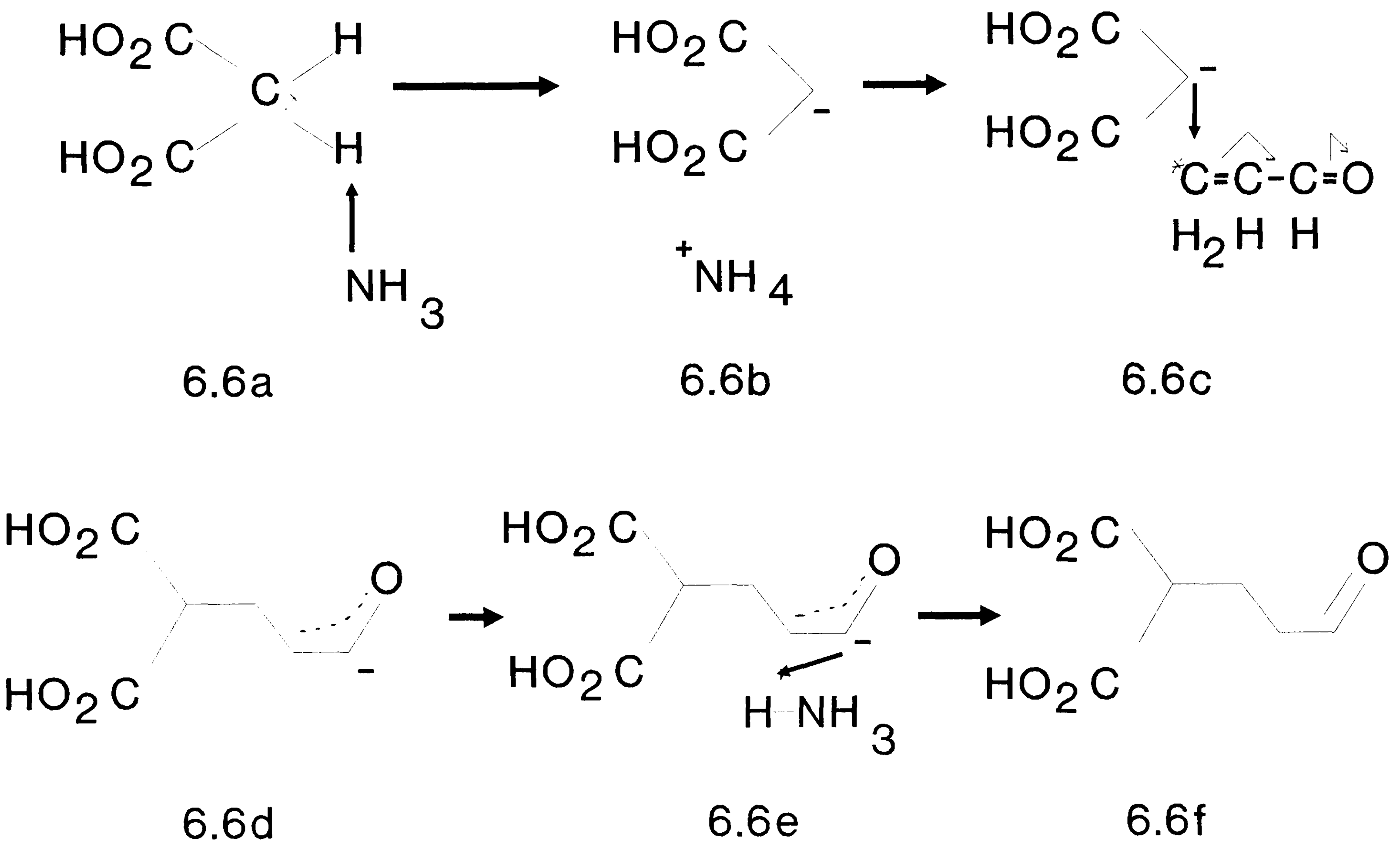
6.5a

6.5b

6.5c

6.5d

Figure 6.6 The Michael Reaction

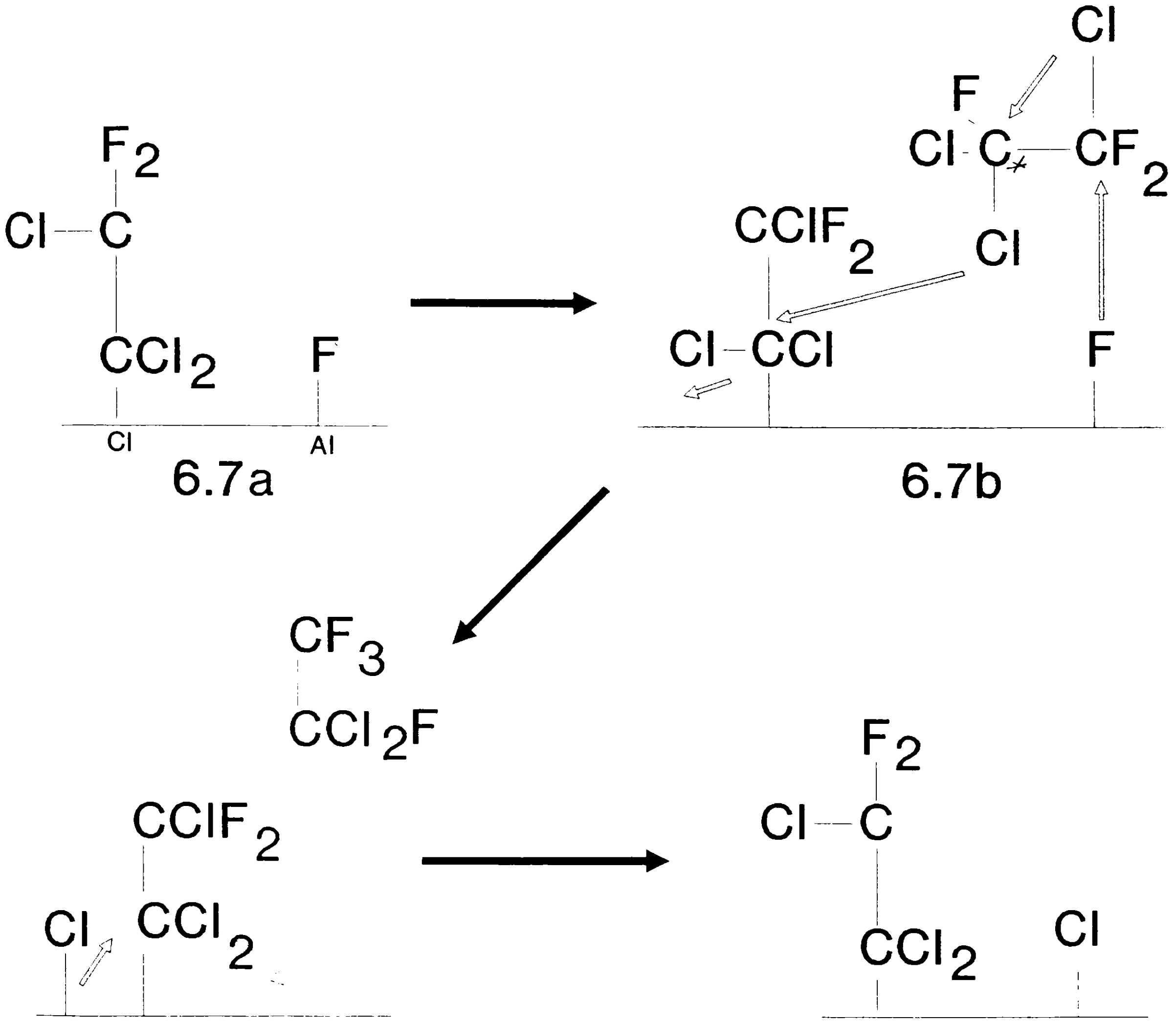


will only occur where surface Al-F bonds and surface bound organic species are present. The mechanism proposed is based on the formation of surface bound CCl_3CClF_2. However it need not be specific to CCl_3CClF_2, the organic species may or may not be fully chlorinated. It has been shown that the isomerisation of CCl_2FCClF_2 will occur over aluminium(III) chloride pretreated with CCl_3CClF_2. The organic species formed in this reaction will be CCl_3CCl_2F. Aluminium(III) chloride that has not been pretreated with an organic species is not as efficient at isomerising CCl_2FCClF_2 as pretreated aluminium(III) chloride [77].

A competing reaction for surface fluorine is the formation of CCl_2FCF_3. As stated in 3.5.3 this may arise from the fluorination of CCl_3CF_3. Once the fluorine is removed from the surface the site becomes inactive towards fluorination but chlorination may still occur. It is also possible that CCl_2FCF_3 may arise from the fluorination of CCl_2FCClF_2 (figure 6.7). This is a similar mechanism to that shown in figure 6.5 but the difference is a Cl leaves C^* to form CCl_2FCF_3 (6.7c) instead of F to form CCl_3CF_3 (6.5c).

When moisture is present in the system it inhibits the reaction between CCl_2FCClF_2 and aluminium(III) chloride. A possible explanation could be the formation of $Al-OH_2$ or Al-OH surface species which block the adsorption of CCl_2FCClF_2. Moisture is adsorbed onto strong Lewis acid sites therefore the proposed mechanisms must centre around the dissociative adsorption of CCl_2FCClF_2 by a similar Lewis acid site.

Figure 6.7



6.7a

6.7b

6.7c

6.7d

Aluminium(III) chloride pretreated with CH_3CCl_3 also isomerises CCl_2FCClF_2 at room temperature. The dehydrochlorination of CH_3CCl_3 over aluminium(III) chloride results in the formation of a purple polymeric material [25]. It is this material that is thought to catalyse the isomerisation of CCl_2FCClF_2 and not aluminium(III) chloride. The exact nature of the surface species formed from the interaction between the polymeric material and aluminium(III) chloride is not known but it is possible that it has the form shown in figure 6.8. Isomerisation could occur in a similar manner to that shown in figure 6.5. Dissociative adsorption of CCl_2FCClF_2 results in the formation of surface bound CCl_3CClF_2 and adsorbed C-F (6.9a). A second molecule of CCl_2FCClF_2 reacts with the newly adsorbed species (6.9b), producing CCl_3CF_3 and a carbocation. Rearrangement of the surface atoms (6.9c) produces an active site for further reaction (6.9a).

This mechanism (figure 6.9) involves the initial formation of a reactive site (6.9a) and the isomerisation of CCl_2FCClF_2 occurs without the formation of an intermediate species. An alternative mechanism is shown in figure 6.10. The adsorbed species are the same as before (6.10a). The adsorbed F^- attacks the adsorbed CCl_3CClF_2 (6.10b) producing CCl_3CF_3 which desorbs from the surface (6.10c). This mechanism involves the formation of an intermediate and is therefore not considered to be the main mechanism for the isomerisation of CCl_2FCClF_2. However this mechanism may be responsible for the production of CCl_3CF_3 when, aluminium(III) chloride pretreated with

Figure 6.8

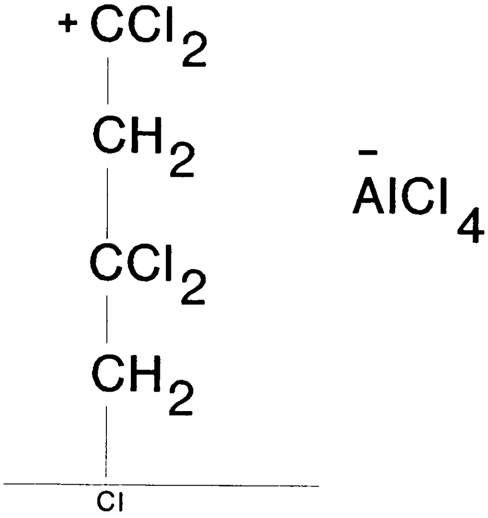
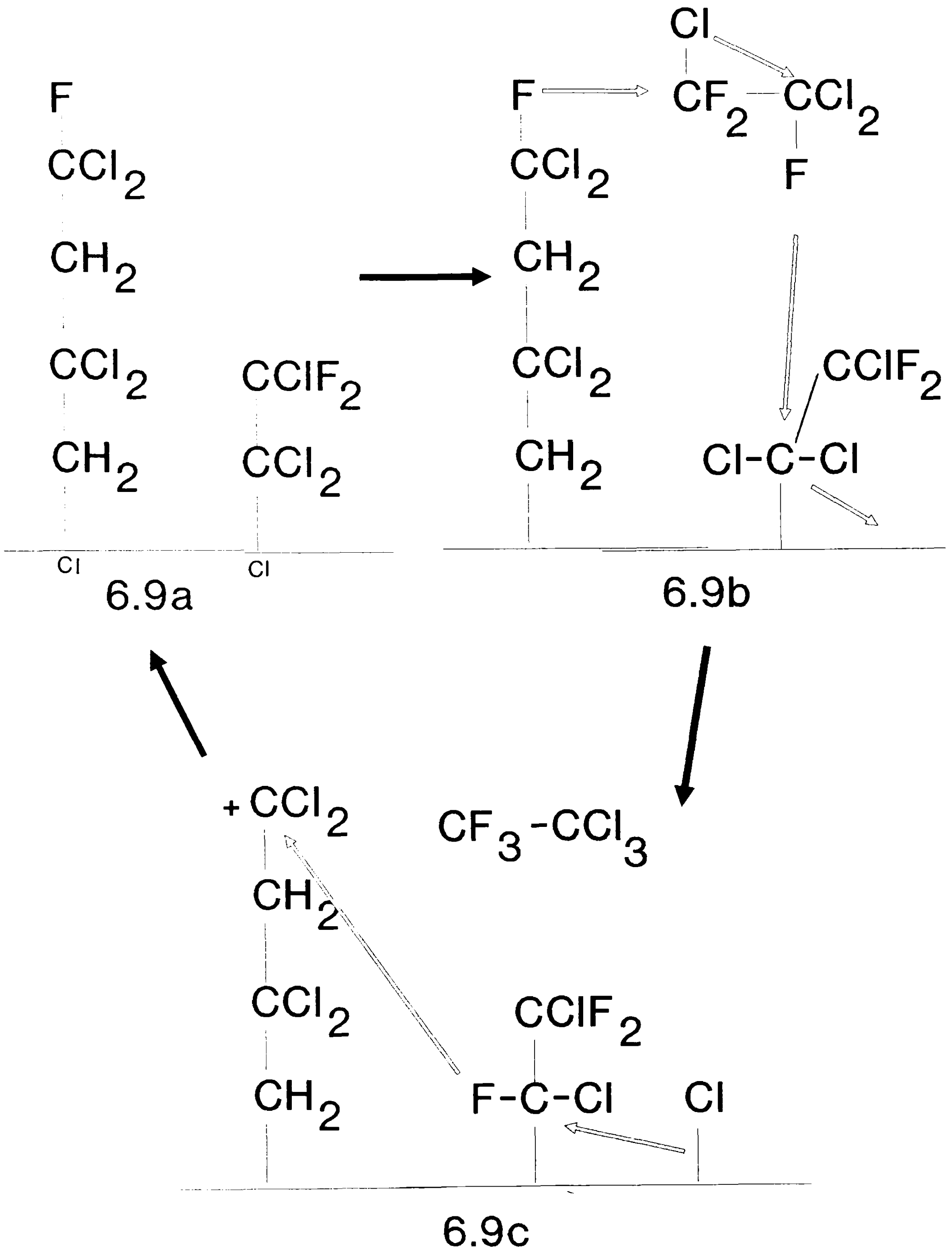


Figure 6.9

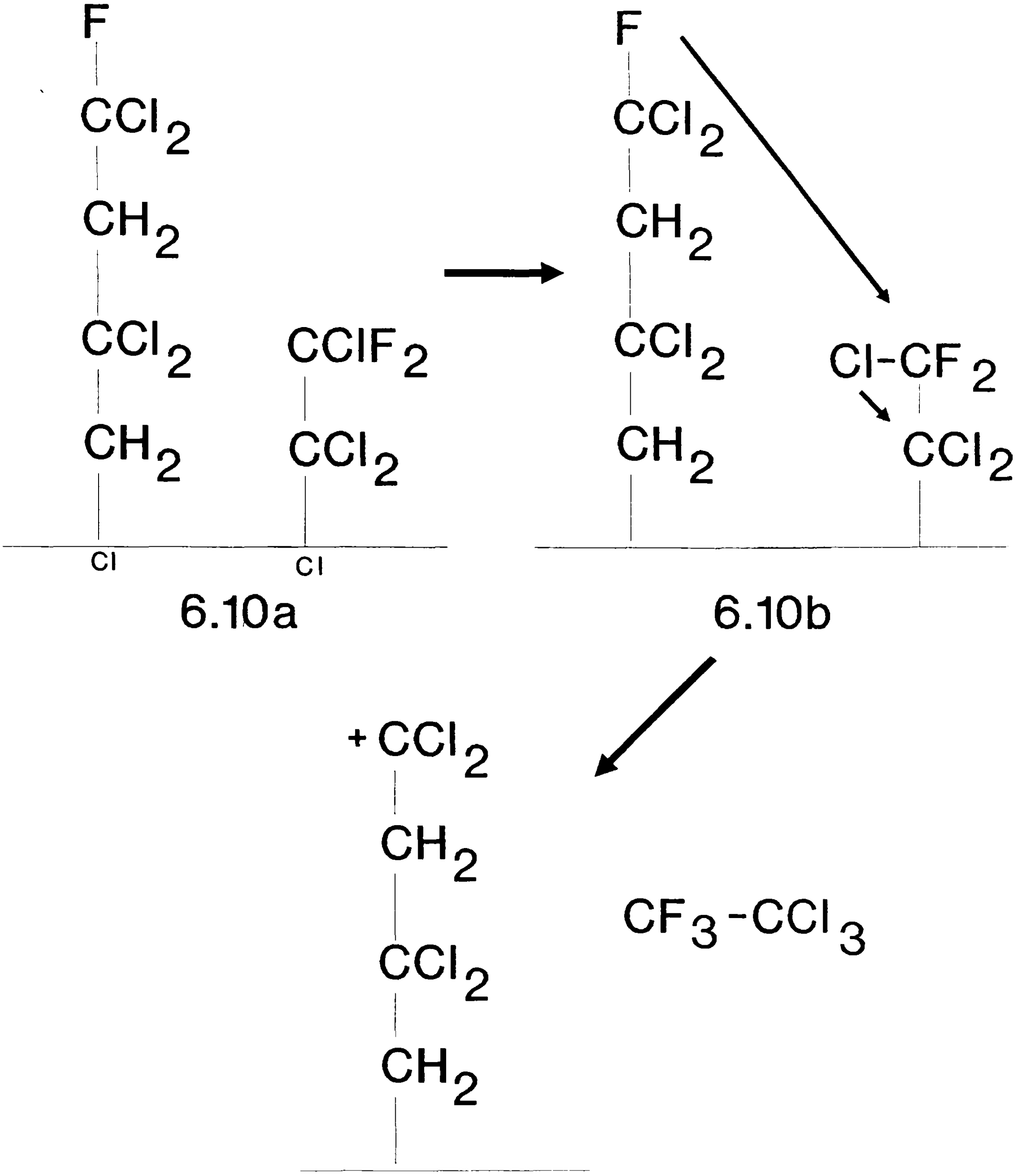


6.9a

6.9b

6.9c

Figure 6.10



6.10a

6.10b

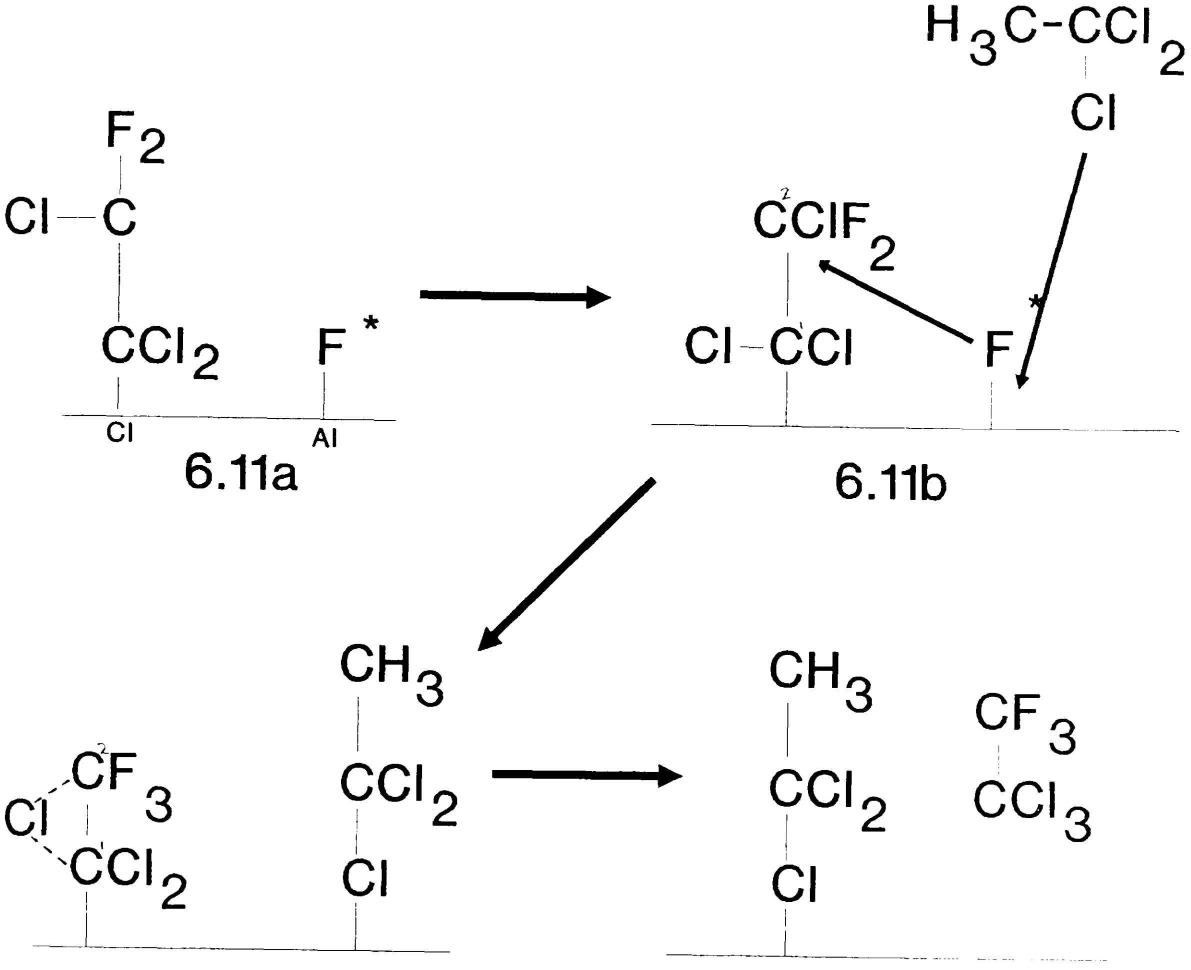
6.10c

CH_3CCl_3 after reaction with CCl_2FCClF_2, is left for long periods of time.

Aluminium(III) chloride pretreated with CCl_2FCClF_2 will dehydrochlorinate CH_3CCl_3. The products are $CH_2=CCl_2$, HCl, CH_3CCl_3 and CCl_3CF_3. This suggests that the surface sites of aluminium(III) chloride responsible for the dissociative adsorption of CCl_2FCClF_2 and the dehydrochlorination of CH_3CCl_3 are the same. A possible mechanism to explain these observations is shown in figure 6.11. The compound CCl_2FCClF_2 is dissociatively adsorbed onto aluminium(III) chloride (6.11a). The compound CH_3CCl_3 is adsorbed via an Al-Cl bond (6.11b). Displacement of F^* occurs as a result of the formation of the Al-Cl bond and it attacks C_2 of the adsorbed CCl_3CClF_2 (6.11b). This results in the displacement of Cl from C_2 to C_1 (6.11c). The CCl_3CF_3 formed then desorbs from the surface (6.11d).

Aluminium(III) chloride supported on γ-alumina will also isomerise CCl_2FCClF_2. Evidence from ^{27}Al MAS n.m.r of the solid suggests that there is an interaction between γ-alumina and aluminium(III) chloride, in the formation of an Al-O-$AlCl_3$ bridging species. This allows the build up of an aluminium(III) chloride network on the surface of the γ-alumina. If the aluminium(III) chloride network is the surface species, then isomerisation of CCl_2FCClF_2 will proceed by the mechanism shown in figure 6.5. However infrared studies of the vapour phase during the course of reaction between CCl_2FCClF_2 and aluminium(III) chloride

Figure 6.11



6.11a

6.11b

6.11c

6.11d

supported on γ-alumina do not show any isosbestic points (figure 5.11). This is probably due to the secondary reaction of CCl_2FCClF_2 with γ-alumina.

The last solid studied was $[CCl_4]$-chlorinated γ-alumina. Although this is not based on aluminium(III) chloride it is also Lewis acidic and will also dehydrochlorinate CH_3CCl_3 at room temperature [82]. The active sites of the solid responsible for the dehydrochlorination of CH_3CCl_3 are thought to have the structure shown in figure 6.12. However the isomerisation of CCl_2FCClF_2 does not occur readily over this surface, but the adsorption of CCl_2FCClF_2 by the surface is observed. The adsorbed species may have the form shown in figure 6.13. If isomerisation were to occur, via the mechanism shown in figure 6.5 then an intermediate species would be formed (figure 6.14). The aluminium atom Al^* originally 4 coordinated becomes five coordinated resulting in a distortion of the atoms. This may be unfavourable and the preferred mechanism for isomerisation of CCl_2CClF_2 over $[CCl_4]$-chlorinated γ-alumina could be a simpler rearrangement (figure 6.15). This mechanism is thought to result in the production of CCl_3CF_3 over long periods of time when using aluminium(III) chloride based solids. It may also explain why the isomerisation of CCl_2FCClF_2 over $[CCl_4]$-chlorinated γ-alumina is very slow and why a large quantity of material is retained by the solid.

Pretreating the surface with CH_3CCl_3 does not result in the production of greater quantities of CCl_3CF_3. This suggests that the purple polymer formed

Figure 6.12

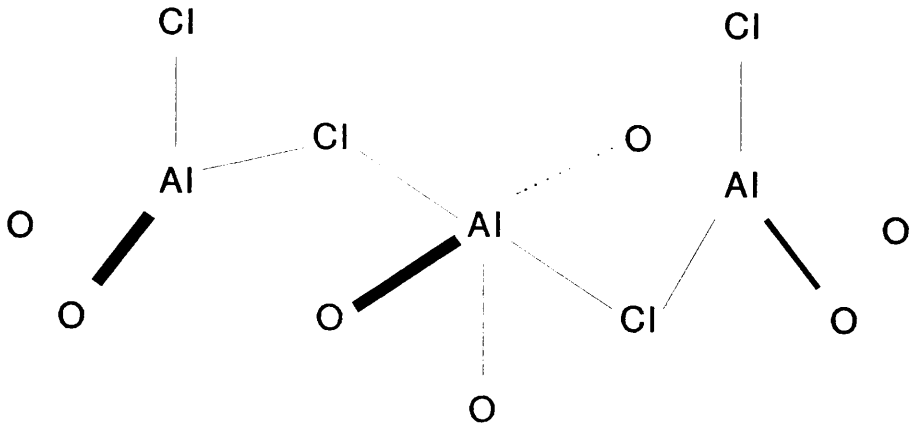


Figure 6.13

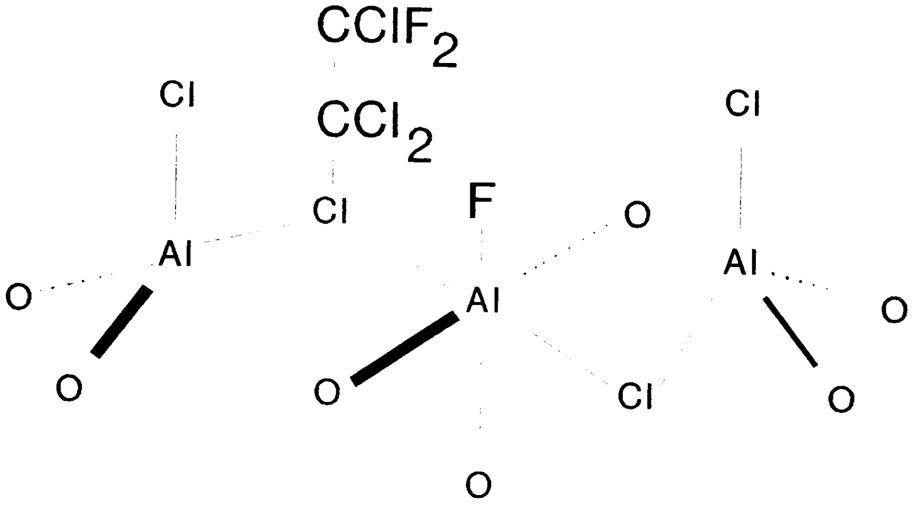


Figure 6.14

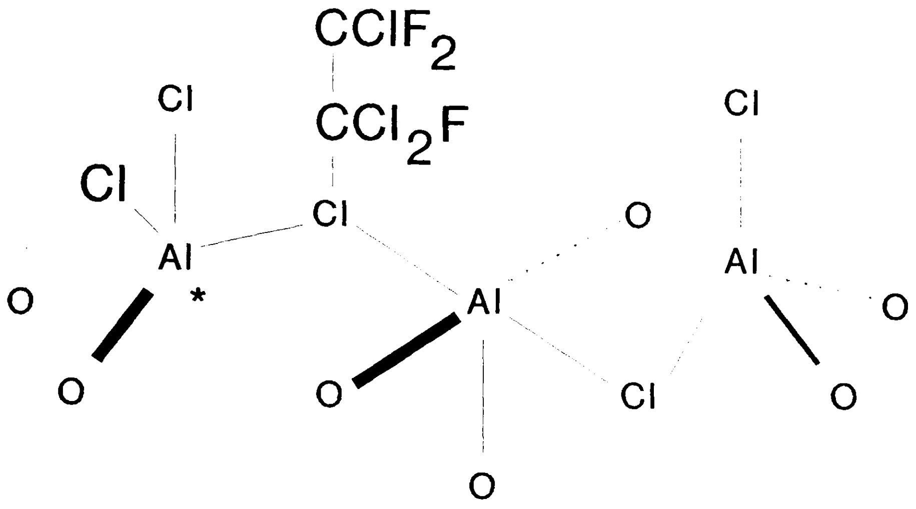
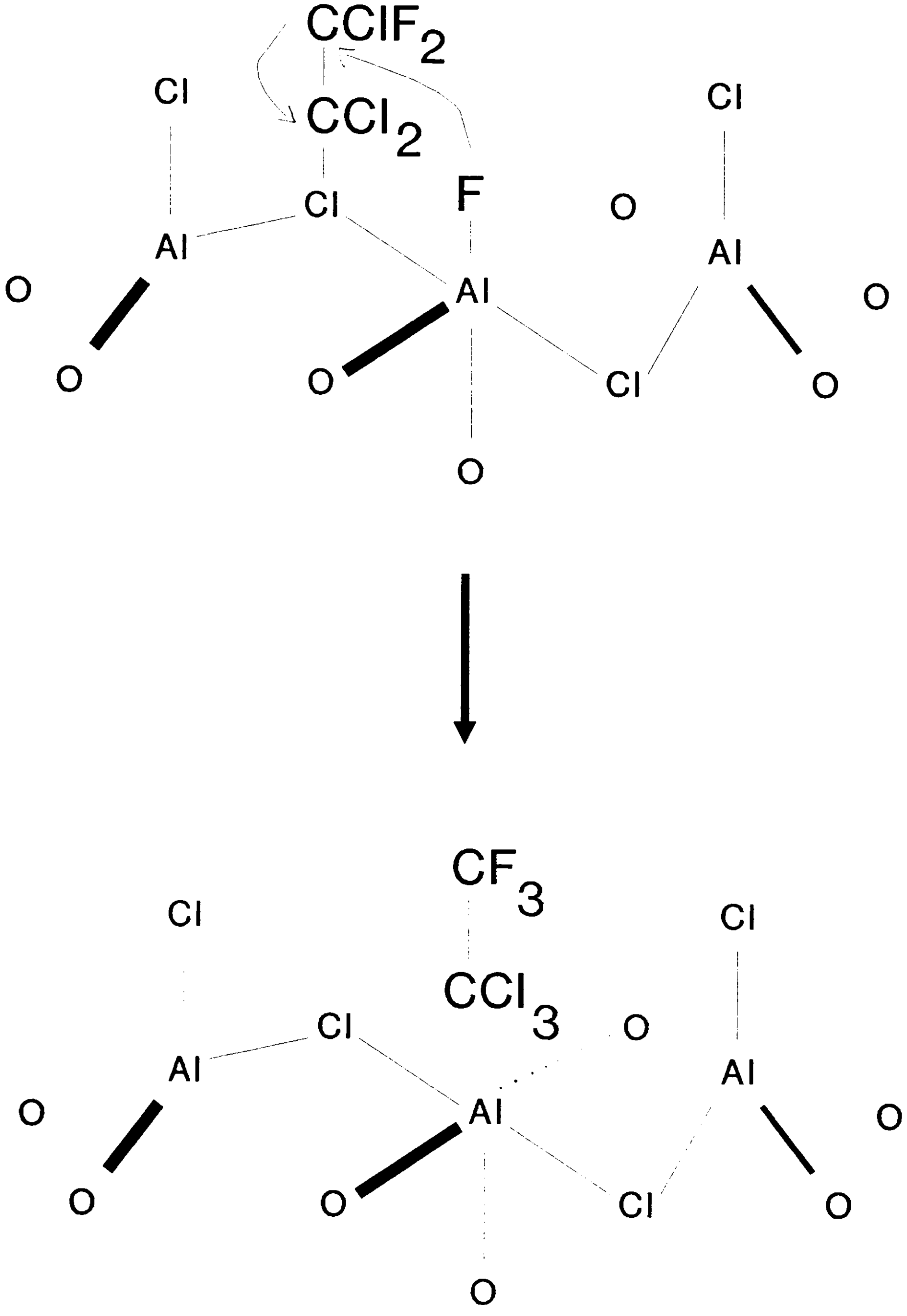


Figure 6.15



$CClF_2$
CCl_2
Cl
Cl
F
Cl
Al
Al
Al
O
O
O
O
O
O
O
Cl
O
CF_3
CCl_3
Cl
Cl
Cl
Al
Al
Al
O
O
O
O
O
O
O
Cl
O

on the surface of [CCl_4]-chlorinated γ-alumina does affect the reaction sites for CCl_2FCClF_2 isomerisation. However [CCl_4]-chlorinated γ-alumina pretreated with CCl_2FCClF_2 did not dehydrochlorinate CH_3CCl_3. Therefore the adsorbed species formed when CCl_2FCClF_2 reacted with [CCl_4]-chlorinated γ-alumina blocked the reactive sites responsible for the dehydrochlorination of CH_3CCl_3.

Reactions of CCl_2FCClF_2 with other Solids.

The isomerisation of CCl_2FCClF_2 is not confined to aluminium(III) chloride based catalysts. Burton noted that the isomerisation of CCl_2FCClF_2 was observed to occur at 0^oC, in the presence of aluminium(III) bromide. After 3 h the reaction products obtained were CCl_3CF_3 66% and CCl_2BrCCl_2Br 4% [71]. This accounted for 70% of the products, no reason was given to explain the missing 30%. It is interesting to note that the chlorobromocarbon produced CCl_2BrCCl_2Br is the analogue of CCl_2FCCl_2F. The latter symmetric isomer is not observed in the aluminium(III) chloride system only CCl_3CClF_2 is produced.

The reaction between CCl_2FCClF_2 and aluminium(III) fluoride pretreated with HF has been studied by Vecchio and co-workers [61]. These reactions were carried out at 400^oC. The products obtained were CCl_2FCF_3, CCl_3CF_3, $CClF_2CF_3$ and $CClF_2CClF_2$. Due to the high fluorine content of the system $CClF_2CF_3$ was observed together with the symmetric isomer $CClF_2CClF_2$. Both of these compounds were not observed in the aluminium(III) chloride system.

The reactions of chlorofluoroethanes in the presence of chromia based catalysts have also been widely studied, but at higher temperatures (>300°C). Dismutation has been used to account for the apparent chlorination and fluorination reactions by a number of workers [63,67]. In the presence of a charcoal supported chromia catalyst CCl_2FCClF_2 underwent chlorination and fluorination rapidly but isomerised slowly. It was shown that the reaction of CCl_3CF_3 with this catalyst resulted in irreversible deactivation. Changing the support had a major effect on the catalytic activity. Chromia supported on alumina isomerised CCl_2FCClF_2 at lower temperatures than those required for charcoal based catalysts [64]. The major difference between charcoal based catalysts and aluminium halide catalysts was that the former favoured the formation of symmetric isomers and the latter favoured the formation of asymmetric isomers.

Radiotracer studies using [^{18}F]-fluorine and [^{36}Cl]-chlorine have put in doubt the importance of dismutation reactions in the vapour phase fluorination of chlorofluoroethanes on fluorinated chromia surfaces. Direct evidence has been obtained for catalytic chlorination and fluorination of a chlorofluoroethane. The mechanisms proposed followed a series of halogen exchange reactions (scheme 1.6) [68,70]. No conclusive evidence was obtained to support a direct isomerisation mechanism but in the light of the present work the possibility cannot be ruled out.

More recent studies of this system were conducted by Thomson [112]. These indicated that the direct isomerisation of CCl_2FCClF_2 -> CCl_3CF_3 is an intramolecular process in the sense that it does not involve the surface halogen containing species that are involved in catalytic chlorinations and fluorinations. It was proposed that the isomerisation of CCl_2FCClF_2 on fluorinated chromia required the adsorption of CCl_2FCClF_2 in a 1,2 fashion (figure 6.16) or dissociative adsorption (figure 6.17). This latter proposal agrees favourably with the results presented in the present work.

Conclusions.

Miller's original work was carried out at 60°C. The products identified were CCl_2FCClF_2, CCl_3CF_3, CCl_3CClF_2 and C_2Cl_6 [76]. There is no mention of any material being retained at the surface or of the presence of fluorinated products. In the present work all reactions were conducted at room temperature. The compounds CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6 are far less volatile under these conditions. Therefore the carbonaceous layer may be a combination of CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6. For the chlorofluoroethanes $C_2Cl_xF_{6-x}$ ($x = 0$-6) the isomerisation reaction appears to be specific for CCl_2FCClF_2. This compound possesses a $-CCl_2F$ group which appears to be the prerequisite for reaction as this may be easily chlorinated forming

Figure 6.16

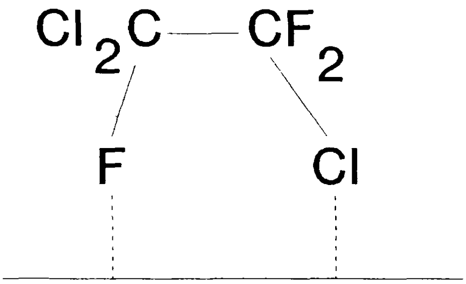
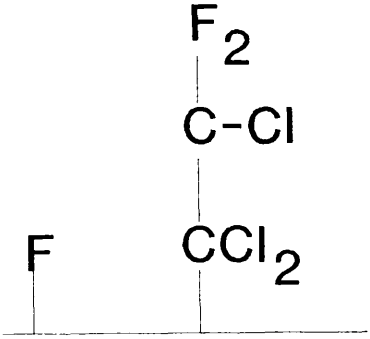


Figure 6.17



CCl_3CClF_2 (cf $CClF_2CClF_2$ section 3.5.3). Once the reactive surface is formed reactions may take place readily. A summary of these reactions is shown in figure 6.18 .

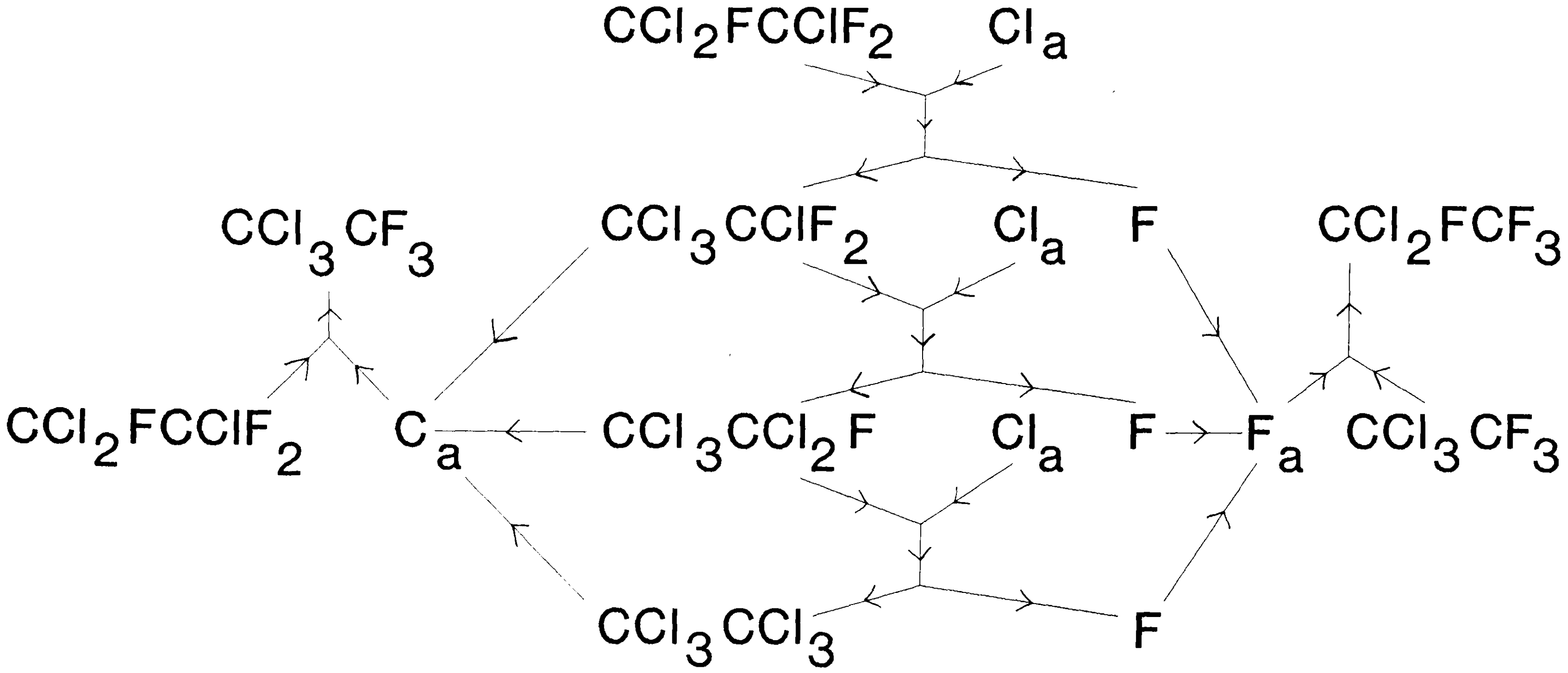
The organic surface is volatile and over a period of time will evolve CCl_3CF_3. This is thought to be due to reaction of adsorbed CCl_3CClF_2 with a surface fluorine species (figure 6.4).

The pretreatment of aluminium(III) chloride with CH_3CCl_3 does not affect the ability of the solid to isomerise CCl_2FCClF_2, but there is a relationship between the active sites responsible for the dehydrochlorination of CH_3CCl_3 and isomerisation of CCl_2FCClF_2. It is thought that both sites are the same.

Sublimation of aluminium(III) chloride onto γ-alumina results in the formation of Al-O-$AlCl_3$ linkages between γ-alumina and aluminium(III) chloride. These are believed to form the basis for an aluminium(III) chloride network which allows isomerisation of CCl_2FCClF_2 to occur.

Isomerisation of CCl_2FCClF_2 occurs more readily over supported aluminium(III) chloride than it does over [CCl_4]-chlorinated γ-alumina. This is presumably due to steric restrictions encountered during the isomerisation process (figure 6.1 4). Organic material is readily retained by [CCl_4]-chlorinated γ-alumina and the adsorption of CCl_2FCClF_2 on this solid inhibits the

Figure 6.18



Cl_a denotes surface active chlorine from Al-Cl
F_a denotes surface active fluorine from Al-F
C_a denotes active carbonaceous surface

dehydrochlorination of CH_3CCl_3 indicating that on this solid also, the reaction sites for isomerisation and dehydrochlorination are the same.

In summary the isomerisation of CCl_2FCClF_2 will occur in the presence of an aluminium(III) chloride based catalyst at room temperature. Other reactions involved are fluorination and chlorination. Retention of organic material by the surface is also observed and the quantity retained is inversely proportional to the quantity of CCl_3CF_3 produced. When $[CCl_4]$-chlorinated γ-alumina is the catalyst very little isomerisation occurs but there is substantial retention. The difference in behaviour of the two types of solid is due to the differences in their surface structures.

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