CHROMIA CATALYSED HALOGEN EXCHANGE REACTIONS OF CHLOROFLUOROETHANES.

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To my mother and father.

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SUMMARY

The vapour phase catalytic fluorination of chlorofluoroethanes, in which hexachloroethane is converted to chloropentafluoroethane using hydrogen fluoride, has been studied using [^{18}F]-fluorine and [^{36}Cl]-chlorine radiotracers.

Uptake of [^{36}Cl]-chlorine labelled hydrogen chloride at 623 K on pre-fluorinated chromia was smaller than that determined for [^{18}F]-fluorine labelled hydrogen fluoride at the same temperature. On chromia which had not been pre-treated with HF, the uptake of [^{36}Cl]-chlorine from $H^{36}Cl$ was comparable with that determined for [^{18}F]-fluorine from $H^{18}F$ treatment. Two types of chlorine-containing species have been detected on the catalyst, compared with the three types of fluorine-containing species reported in a previous study. In the case of both catalyst-chloride and catalyst-fluoride species, one type of halide species was catalytically active towards the reactions of chlorofluoroethanes and a second type was permanently bound to the catalyst. The reaction of [^{36}Cl]-chlorine labelled 1,1-dichlorotetrafluoroethane at a temperature of 623 K and above, resulted in uptake of [^{36}Cl]-chlorine by the catalyst in the same range as that previously determined for $H^{36}Cl$. The behaviour of catalyst-[^{36}Cl]-chlorine originating from $H^{36}Cl$ and [^{36}Cl]-CCl_2FCF_3 was indistinguishable.

[^{36}Cl]-Chlorine was incorporated in the products from the reaction of 1,1,2-trichlorotrifluoroethane or 1,2-dichlorotetrafluoroethane with the chlorinated catalyst.

The results of a previous [^{18}F]-fluorine radiotracer study showed that catalyst-[^{18}F]-fluorine was also incorporated in the reaction products under similar conditions. A halogen exchange model involving Cl-for-F and F-for-Cl exchange between the catalyst and reacting chlorofluoroethanes is proposed. Experiments using mixed HF, HCl, $C_2Cl_3F_3$ gas flows indicate that HCl had a mild deactivating effect on the fluorination reactions.

The results of a diffuse reflectance spectroscopic study show that C-F and C-Cl bonds were affected by adsorption of CCl_2FCClF_2 on to pre-fluorinated chromia at room temperature. Kinetic data were consistent with the reactions to form chlorinated and fluorinated products occurring on the catalyst surface.

Experiments involving the reaction of isomer mixtures and radiochemical analysis of the catalyst provided no evidence for direct isomerisation in the case of $C_2Cl_2F_4$ or $C_2Cl_3F_3$. In common with the proposed dismutation reactions, isomerisation can be described by a series of halogen exchange reactions and this model alone can account for all the experimental observations in the vapour phase system.

CHAPTER ONE

INTRODUCTION

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1.1 The Chlorofluoroethanes

The chlorofluoroethane class of compounds is a range of completely halogenated ethanes of the general formula $C_2Cl_xF_{6-x}$. In common with other completely halogenated chlorofluoroethanes, the ethanes are stable at high temperature and are practically chemically inert, being neither corrosive nor toxic. These properties make chlorofluoroethanes attractive in a wide range of situations and their principal uses include[1] aerosol propellants, refrigerants for air conditioning and refrigeration systems, solvents for cleaning electronic components and fire extinguishants. A naming system based on a numerical code is used to define the chlorofluoroethanes. The code numbers comprise three digits, F.C. XYZ, where Z refers to the number of fluorine atoms, Y refers to the number of hydrogen atoms + 1 and X refers to the number of carbon atoms - 1. When positional isomers exist the letter 'a' is added to the code number to indicate the asymmetric isomer (Table 1.1).

The boiling and melting points of chlorofluoroethanes fall with increasing fluorine content (Table 1.2), and the boiling points, in common with other fluorine containing compounds, are low in view of their molecular weights. The results of electron diffraction studies show that the

Table 1.1 Ethane Series of Chlorofluorocarbons.

Formula	Code Number
CCl_3CCl_3	110
CCl_3CCl_2F	111
CCl_2FCCl_2F	112
CCl_3CClF_2	112a
CCl_2FCClF_2	113
CCl_3CF_3	113a
$CClF_2CClF_2$	114
CCl_2FCF_3	114a
$CClF_2CF_3$	115
CF_3CF_3	116

Table 1.2 Boiling Points and Melting Points of Chlorofluoroethanes.

Formula	Boiling Point (K)	Melting Point (K)
CCl_3CCl_3	sublimes	457.7
CCl_3CCl_2F	410.0	373.2
CCl_2FCCl_2F	366.0	297.8-299.2
CCl_3CClF_2	364.7	313.8
CCl_2FCClF_2	320.8	238.2
CCl_3CF_3	319.1	287.4
$CClF_2CClF_2$	277.0	179.2
CCl_2FCF_3	276.8	216.6
$CClF_2CF_3$	234.5	167.2

bond length in C-F, and to a lesser extent C-Cl, shortens as the number of fluorine atoms attached to a carbon atom increases (Table 1.3) and that two conformations, trans and gauche, can be adopted by chlorofluoroethane molecules. The gauche conformer is reported to be the least energetic for CCl_2FCCl_2F [2] and CCl_2FCClF_2 [3] and the author of a recent matrix isolation study of CCl_2FCClF_2 [6] estimated the enthalpy difference between the two conformers to be 1.06±0.11 kJ mol^{-1}. The high energy cis conformers receive no attention in the reported studies. In $CClF_2CClF_2$ the more stable conformer is the trans form [7], where interaction among the fluorine atoms will be at a minimum, but the gauche form is stabilised by adsorption on to erbium trifluoride or erbium trichloride. It seems reasonable to suggest that stabilisation of the more energetic conformers may also be found on other fluorinated or chlorinated surfaces.

1.2 The Ozone-Chlorofluorocarbon Problem.

During the 1960's and 1970's production of chlorofluoromethanes and ethanes rose sharply. This increase in production was largely in response to greater demand for aerosols as the general public became attracted by the convenience and labour saving aspects of these products. In 1974 Rowland and Molina [8] suggested that because chlorofluoroethanes are stable in the lower atmosphere they could migrate into the earth's stratosphere where they would decompose because of the action of ultraviolet radiation to produce atomic chlorine.

Table 1.3 C-F, C-Cl and C-C Bond Lengths in Chlorofluoroethanes.

Compound	Bond Length (Å)			Reference
	C-F	C-Cl	C-C	
$CCl_2F\ CCl_2F$	1.38±0.02	1.76±0.01	1.54±0.06	2
$\overset{1}{C}Cl_2F\ \overset{2}{C}ClF_2$	$\overset{1}{C}$-F, 1.38±0.02 $\overset{2}{C}$-F, 1.33±0.01	$\overset{1}{C}$-Cl, 1.76±0.01 $\overset{2}{C}$-Cl, 1.75±0.03	1.54±0.06	3
$CClF_2\ CClF_2$	1.33±0.01	1.74±0.01	1.54±0.06	4
$CF_3\ CF_3$	1.32±0.01	-	1.56±0.03	5

The basic chemical constituents of the stratosphere are dioxygen and dinitrogen with minor constituents, one of which is ozone, O_3. The source of ozone is the photochemical dissociation of dioxygen into two atoms of oxygen. The atomic oxygen then combines with dioxygen to form ozone, which absorbs a proportion of the radiation entering the earth's atmosphere. Any depletion in the concentration of ozone would be associated with an increase in solar ultraviolet radiation reaching the earth's surface which may lead to an increase in skin cancer and, eventually, to climatic changes.

Recent concern about ozone depletion has centred on the role of atomic chlorine, the source of which is chlorofluorocarbons. Reactions such as these shown in equations (1.1a) and (1.1b) are thought to account for the destruction of ozone.

$$Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2 \qquad (1.1a)$$

$$ClO\bullet + O\bullet \longrightarrow Cl\bullet + O_2 \qquad (1.1b)$$

$$\underline{\text{overall}} \quad O_3 + O\bullet \longrightarrow 2O_2$$

<u>Equation (1.1)</u>

However, other atmospheric pollutants participate in related reactions and Crutzen[9] has suggested a catalytic cycle for removal of ozone based on nitric oxide (Equation (1.2))

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (1.2a)$$

$$NO_2 + O\bullet \longrightarrow NO + O_2 \qquad (1.2b)$$

<u>Equation (1.2)</u>

Interest in nitric oxide centres on its emission by supersonic aircraft which fly in the stratosphere, thus releasing nitric oxide directly into a region where it cannot be "rained out". Further concern has been expressed at the increasing use of nitrogeneous fertilisers, which may decompose to nitric oxide and increase the concentration of nitric oxide available for transport to the stratosphere.

The models used to predict the rate of ozone depletion are generally agreed to be imperfect. Often only average concentrations for radical species can be obtained and these may be of little use when calculating a local rate of reaction for ozone depletion.[1] Experimental results from a microwave study at a height of 30 km[10] confirmed that the concentration of ClO• decreases towards sunset and falls substantially during the night, as is expected on the basis of the photochemical reaction in equation (1.1a), but the inconsistency of the various models relating ClO• concentration to ozone depletion make further analysis difficult.[10] The prediction which is regarded as the best founded[10] suggests that over a period of 70-100 years the global content of ozone will be depleted by 11-16%, although this prediction is based on the high releases of chlorofluorocarbons prevailing in the mid-1970's.

A downward revision of the estimated global loss of ozone may be appropriate with the reduction in chlorofluorocarbon release achieved since 1977.

Concern has been expressed about ozone depletion in the Antarctic atmosphere during the spring months. A recent study[11a] observed that the appearance of this 'ozone hole' was co-incident with an increase during spring in the vapour phase concentrations of the halogenated species HCl and $ClONO_2$. The authors concluded that a major fraction of the total chlorine-containing species must either be frozen out or present in some other chemical form during the winter months. The former possibility is supported by the observed correlation between increasing temperature and the increasing concentration of the halogenated species. The results of this study are consistent with a role for chlorofluorocarbons in ozone depletion.

The implications of the Antarctic ozone hole are unknown, but the intense political and environmental debate which has arisen from the discovery of the hole has affected the U.K. Government's attitude to restrictions in the use of chlorofluorocarbons.[11b] The U.K. now seems likely to accept a reduction of up to 50% in the use of chlorofluorocarbons worldwide. A move to reduce emissions of chlorofluorocarbons is a sensible precaution in advance of more conclusive evidence regarding the Antarctic 'ozone hole' and its relationship to global ozone depletion.

1.3 Preparation of Chlorofluoroethanes.

Substitution of chlorine atoms by fluorine atoms is the basis of the many catalytic processes known for the production of chlorofluoroethanes. A large number of inorganic fluorides, including potassium fluoride, mercurous fluoride and cobalt(111) fluoride, have been studied and used as halogen exchange agents but current industrial production centres on two processes. The first is a liquid phase process involving homogeneous catalysis using hydrogen fluoride in the presence of antimony halides. The second is a vapour phase process involving heterogeneous catalysis on chromia in the presence of gaseous HF. In both cases the starting material is the saturated chlorocarbon hexachloroethane which, in the vapour phase process, is generally formed from the reaction of dichlorine and tetrachloroethene (Equation (1.3)) immediately before admission to the catalyst.

$$Cl_2 + C_2Cl_4 \xrightarrow{623K} C_2Cl_6$$

Equation (1.3)

This pre-reaction avoids handling difficulties associated with hexachloroethane, which is a solid at room temperature.

1.3.1. The Liquid Phase Process.

The liquid phase fluorination of carbon tetrachloride using antimony trifluoride was first described by Swarts in 1895. This process involved refluorination of Sb(III) using hydrogen fluoride in a separate reaction vessel from that used for the fluorination of chlorofluoromethanes. Midgely and Henne obtained patents[12] for an industrial process in which fluorination of the organic component and refluorination of the antimony halide catalyst took place in the same vessel (Equation (1.4)).

for example:

$$SbCl_5 + 3HF \longrightarrow SbCl_2F_3 + 3HCl$$

$$SbCl_2F_3 + 2CCl_4 \longrightarrow SbCl_5 + CCl_3F + CCl_2F_2$$

Equation (1.4a)

Since the process is continuous the pentavalent antimony species is regarded as a fluorine carrier and the overall process is written as:

$$3HF+2CCl_4 \xrightarrow[373K,\ 10\text{-}30atm.]{SbCl_xF_y} CCl_3F+CCl_2F_2+3HCl$$

where $x+y = 5$

Equation (1.4b).

This process is one of the most important industrial fluorination processes currently in use and is used predominantly to produce chlorofluoromethanes.

Fluorination of hexachloroethane using $SbCl_2F_3$ has been studied by Henne and co-workers[13] and is found to give the symmetric isomers in high yield.

$$CCl_3CCl_3 \rightarrow CCl_3CCl_2F \longrightarrow CCl_2FCCl_2F \longrightarrow CCl_2FCClF_2 \longrightarrow CClF_2CClF_2$$

Scheme 1.1

Kolditz and Schultz[14] studied the mechanism of fluorination in the system $SbCl_4F/CCl_4$ and, on the basis of kinetic data, concluded that F-for-Cl exchange, with the antimony (V) halide as the source of fluorine, was involved with carbon as the centre of the transition species (Figure 1.1).

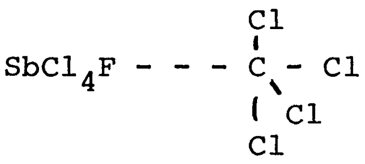
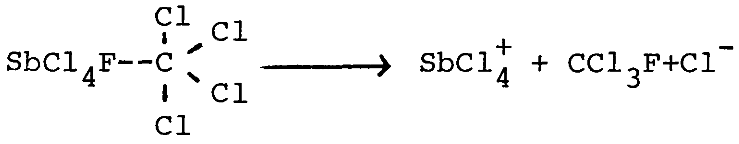


Figure 1.1.

The reaction to form CCl_3F from the transition species in Figure 1.1 is thought to follow a substitution mechanism (Equation (1.5)).



$$SbCl_4F\text{--}CCl_4 \longrightarrow SbCl_4^+ + CCl_3F + Cl^-$$

$$SbCl_4^+ + Cl^- \longrightarrow SbCl_5$$

Equation (1.5).

The results of earlier work by Booth and Swinehart[15] led them to suggest a transition species involving coordination of chlorine to antimony(V) (Figure 1.2).

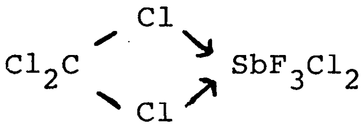


Figure 1.2.

However, there is no direct evidence for the species shown in Figure 1.2. The proposal for its involvement is based on the observation that the antimony halide catalyst undergoes F-for-Cl exchange. A transition species involving direct interaction between Cl_3C-Cl and Sb(V) is therefore attractive.

Interest in the antimony halide fluorination system continues and the nature of the species involved remains unclear. However, it is interesting to note that F-for-Cl exchange followed by regeneration of the antimony(V) fluorine containing species by the action of hydrogen fluoride forms the basis of the fluorination process.

The antimony(V) halide process works well at temperatures at or below 353K but, at higher temperatures, chlorine dissociation and the formation of reduced antimony halides reduce the yield of fluorinated products obtained.[16] This makes the application of the liquid phase process to the fluorination of the chlorofluoroethane series difficult, since these compounds require higher reaction temperatures to obtain economic yields of fluorinated compounds. For this reason, interest in the fluorination of hexachloroethane has focussed on the vapour phase process, where these temperature constraints do not apply.

1.3.2. The Vapour Phase Process.

The vapour phase fluorination of chlorofluoroethanes by anhydrous hydrogen fluoride has received widespread attention in the literature. The most common catalyst is based on amorphous chromia, but aluminium trifluoride has also been extensively studied in laboratory systems.

Fluorination of hexachloroethane using hydrogen fluoride is carried out readily in the temperature range 573-723K and the full range of fluorinated derivatives of C_2Cl_6 is obtained. Using aluminium trifluoride as the catalyst the reaction is found to give asymmetric isomers as the major products[17] (Scheme 1.2).

$$C_2Cl_6 \rightarrow CCl_3CCl_2F \longrightarrow CCl_3CClF_2 \longrightarrow CCl_3CF_3 \longrightarrow$$

$$CCl_2FCF_3 \longrightarrow CClF_2CF_3$$

Scheme 1.2.

Modification of the catalyst to include small amounts of the halides of iron, chromium and nickel alters the relative proportions of symmetric and asymmetric isomers and CCl_2FCClF_2 and $CClF_2CClF_2$ are the major products formed. Kolditz,[16] in a comparison of aluminium trifluoride and chromium oxide catalysts, observed that asymmetric isomers were formed in proportionally greater amounts on the aluminium trifluoride catalyst than on the chromium oxide catalyst. Increasing the contact time between chlorofluoroethane and the catalyst also increased the proportion of asymmetric isomers formed relative to symmetric isomers. Kolditz suggests that, by assuming the interaction between the substrate and aluminium trifluoride to be greater than that with chromia, the possibility of an "intramolecular transposition" of fluorine is greater in the case of aluminium trifluoride.

The mechanism by which isomerisation occurs on aluminium trichloride has been studied.[18] Using [^{36}Cl]-chlorine labelled $AlCl_3$ as catalyst and CCl_2FCCl_2F as reactant, unlabelled CCl_3CF_3 and [^{36}Cl]-CCl_3CClF_2 are the main products (Equation (1.6)).

$$CCl_2FCClF_2 \xrightarrow[327-333K]{[^{36}Cl]-AlCl_3} CCl_3CF_3\ (50\%)+[^{36}Cl]-$$

$$CCl_3CClF_2(40\%)+CCl_3CCl_2F(5\%)\ +recov.CCl_2FCCl_2F(5\%)$$

Equation (1.6).

The product distribution and the incorporation of [^{36}Cl]-chlorine in CCl_3CCl_2F suggests that, while replacement of Cl by F involves exchange between the catalyst and chlorofluoroethane, the isomerisation of CCl_2FCClF_2 to CCl_3CF_3 is an intramolecular process, since [^{36}Cl]-chlorine is not detected in this fraction. These results relate, however, to a suspension of $AlCl_3$ refluxing in CCl_2FCClF_2 and their relevance to the heterogeneous system is not known.

Kolditz and Schultz,[14] by analogy with the behaviour of the $CCl_2FCClF_2/AlCl_3$ system, suggest an intramolecular isomerisation mechanism for the isomerisation of chlorofluoroethanes on aluminium trifluoride or prefluorinated chromia (Figure 1.3).

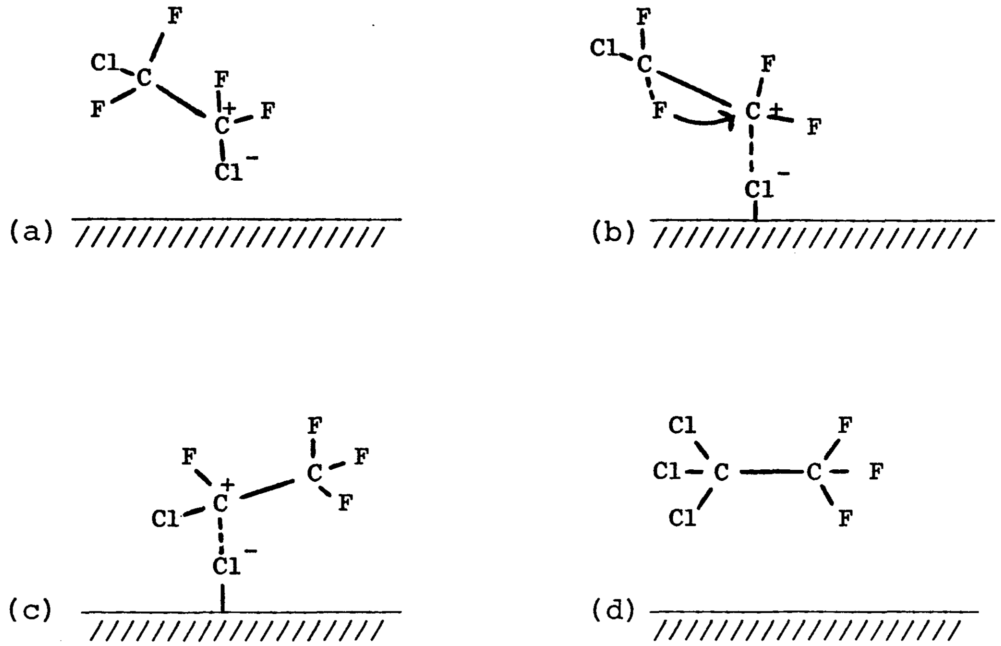


Figure 1.3. Isomerisation from symmetric to asymmetric isomer.

Isomerisation occurs from the symmetric to the asymmetric isomer. No experimental data relating to the equilibrium position of the isomerisation reaction are presented. The isomerisation model is, however, consistent with thermodynamic calculations[19] which show the asymmetric isomers to be thermodynamically more stable than the symmetric isomers.

1.4. Behaviour of Chlorofluoroethanes on Chromia.

1.4.1. Fluorination and chlorination reactions on chromia.

Detailed laboratory studies of the reactions of chlorofluoroethanes on chromia have used partially fluorinated chlorofluoroethanes as reactants, since this simplifies the product analysis (in terms of the number of products to be determined). Several different methods of preparing chromia are known and the patent literature contains many references to chromia catalysts containing chromia in the presence of other materials; for example, fluorides of metals other than Group I metals[20] and supports such as carbon.[21] Reference has already been made to the effect on the product composition of adding small quantities of transition metal halides (Section 1.3.2).

In all reports relating to fluorination of chlorofluoroethanes by hydrogen fluoride, the observed product composition indicates the occurrence of reactions leading to less highly fluorinated products, in addition to the expected reactions leading to more highly fluorinated products. For example, the results obtained by Kolditz and co-workers[16] illustrate these chlorination and fluorination processes in the reaction of CCl_2FCClF_2 and $CClF_2CClF_2$ on chromia (Table 1.4). Less highly fluorinated ("chlorinated") derivatives account for 18 mol % of the recovered material when $CClF_2CClF_2$ is reacted on prefluorinated chromia. Reacting CCl_2FCClF_2 on prefluorinated chromia leads to the formation of chlorinated products accounting for 26 mol % of the recovered material. Similar observations of significant chlorination are made when AlF_3 or AlF_3 containing the halides of Fe, Cr and Ni are used as catalysts in the vapour phase process.

Three basic types of catalytic reaction have been proposed to account for the chlorination and fluorination reactions:

Table 1.4 Reaction of CCl_2FCClF_2 or $CClF_2CClF_2$ on chromia. - (from Kolditz & co-workers[16]).

Reactant	Temperature (K)	Product Composition, mol %						
		C_2Cl_4	C_2Cl_6	C_2Cl_5F	$C_2Cl_4F_2$	$C_2Cl_3F_3$	$C_2Cl_2F_4$	C_2ClF_5
CCl_2FCClF_2	648	4	2	4	20	28	40	4
					(95)	(48)	(17)	
$CClF_2CClF_2$	693	trace	-	trace	4	14	46	30
						(45)	(12)	

Figures in parenthesis refer to the percentage of the asymmetric isomer in a particular isomeric mixture.

1. Cl-F exchange reaction, which leads to an increase in the degree of fluorination.

2. Dismutation to form one more highly fluorinated and one less highly fluorinated product.

3. Isomerisation as discussed above in Section 1.3.2.

The Cl-F exchange reaction is accepted as the principal route leading to more highly fluorinated products.[22,23] A halogen exchange mechanism involving polarisation of a reacting C-Cl bond has been suggested.[24] Adsorption of chlorofluoroethane via the C-Cl bond involves a Lewis acid site at which the chlorine is retained (Figure 1.4) with the carbocation migrating to an adjacent surface-fluoride species. Desorption of the fluorinated molecule leaves a surface vacancy which is occupied by HF. The cycle is completed by transfer of a proton from HF to the surface-chloride species and desorption of HCl

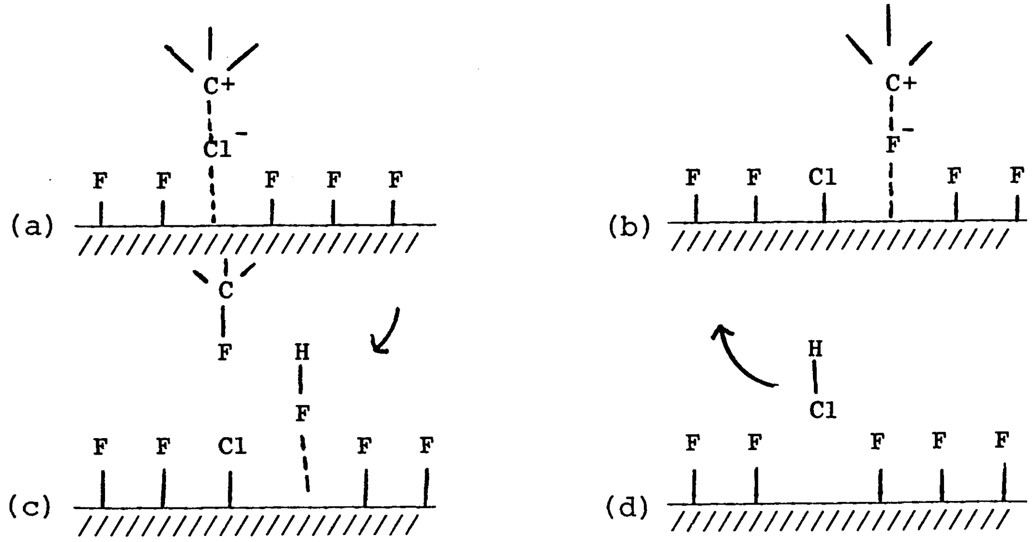


Figure 1.4 Mechanism of exchange reaction.

This model is consistent with the formation of HCl during the reaction of a chlorofluoroethane/HF gas flow on chromia observed by Marangoni and co-workers[22] and described by the general equation:

$$C_2F_xCl_{(6-x)} + \text{catalyst } F^- \longrightarrow C_2F_{(x-1)}Cl_{(5-x)} + HCl$$

Equation (1.7).

Presumably, although it is not stated in the literature, the "migration" of the cation involves a three centre transition state based on $Cl^{\delta-}(ads)---C^+---F^{\delta-}(ads)$. Fluorination by this mechanism, however, implies fission of a metal-fluorine bond and crystalline chromium trifluoride is known to exhibit practically no catalytic activity in the fluorination process.[16]

A parallel ionic, bimolecular reaction has been suggested to account for the production of less highly fluorinated derivatives of chlorofluoroethanes.[16] The initial adsorbed state of chlorofluoroethane is similar to that in Figure 1.4 but the source of fluorine is a second reacting chlorofluoroethane molecule (Figure 1.5). Simultaneous with the acceptance of a F^- ion a C-Cl bond is broken and the surface chloride ion is then incorporated into the molecule which donated the fluoride ion.

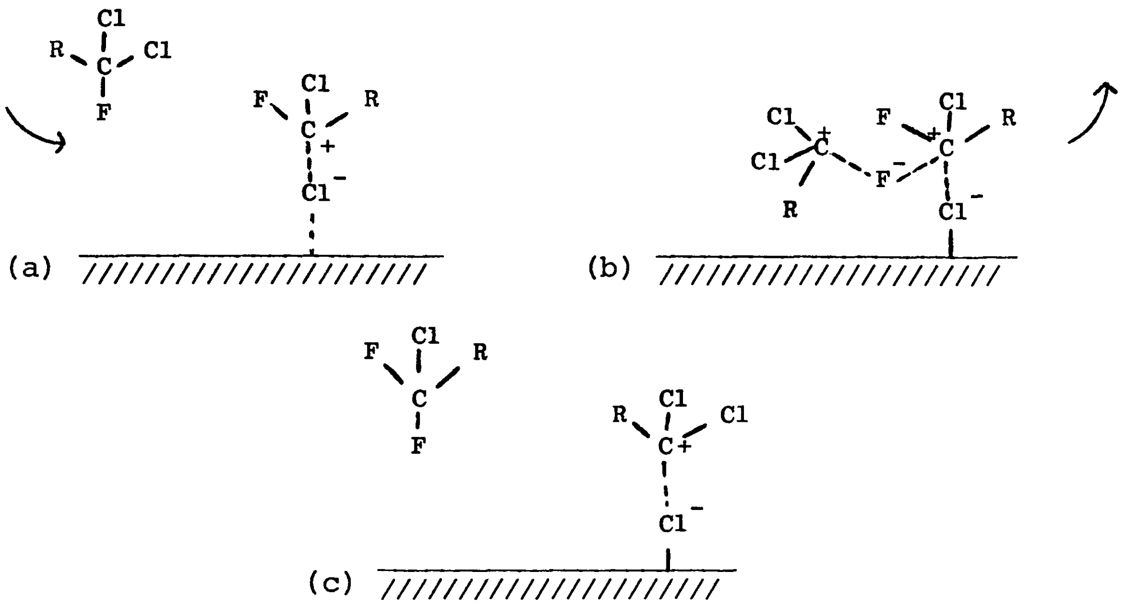


Figure 1.5 Ionic, bimolecular reaction mechanism.

The products from this reaction are one "fluorinated" and one "chlorinated" molecule (Equation 1.8)).

$$2\ CCl_2FCF_3 \longrightarrow CCl_3CF_3 + CClF_2CF_3$$

Equation (1.8)

Such dismutation reactions are not limited to reactions involving identical molecules, and dismutations involving two different reactants have been proposed.[16] Isomerisation reactions are formulated as a sequence of reactions as shown in equation (1.9).

$$2CClF_2CClF_2 \longrightarrow CCl_2FCClF_2 + CClF_2CF_3$$

$$CCl_2FCClF_2 + CClF_2CF_3 \longrightarrow CClF_2CClF_2 + CCl_2FCF_3$$

giving overall $CClF_2CClF_2 \longrightarrow CCl_2FCF_3$

Equation (1.9).

Recent work[25] based on [^{18}F]-fluorine tracer studies has shown the involvement of surface fluorine containing species in the fluorination of $C_2Cl_3F_3$ and $C_2Cl_2F_4$ on pre-fluorinated chromia. The source of fluorine in this study was [^{18}F]-fluorine labelled HF, which was admitted to chromia before reaction of chlorofluoroethane at 623K. Reaction of $C_2Cl_2F_4$ is zero order with respect to gaseous $C_2Cl_2F_4$ and surface adsorption of chlorofluoroethane during reaction is inferred.

The distribution of the [^{18}F]-fluorine label in the product fractions from reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ indicates higher [^{18}F]-fluorine count rates in fluorinated derivatives than in chlorinated derivatives and incorporation of [^{18}F]-fluorine activity in those product fractions corresponding to the starting material. Incorporation of [^{18}F]-fluorine activity in chlorinated products is highly significant, since it suggests that chlorination reactions can occur independently of fluorination reactions. It is not difficult to envisage dismutation reactions leading to [^{18}F]-fluorine labelled, chlorinated products, for example equation (1.10). Reaction of CCl_2FCClF_2 to form [^{18}F]-$CClF_2CClF_2$ would be followed by a dismutation reaction involving two molecules of [^{18}F]-$CClF_2CClF_2$ to form [^{18}F]-CCl_2FCClF_2 and [^{18}F]-$CClF_2CF_3$. However, in the dismutation reaction there is an equal probability that the [^{18}F]-fluorine label will be incorporated in CCl_2FCF_3 or $CClF_2CF_3$. A reaction pathway involving dismutation reactions would therefore be expected to produce chlorinated and fluorinated derivatives of similar specific [^{18}F]-fluorine count rates. The higher

$[^{18}F]$-fluorine count rates observed in the fluorinated derivatives of reacting chlorofluoroethane compared with the chlorinated derivatives would suggest that dismutation may not be an important process here.

$$CCl_2FCClF_2 \xrightarrow{[^{18}F]\text{-chromia}} [^{18}F]\text{-}CClF_2CClF_2$$

since $-CCl_2F$ fluorinates more readily than $-CClF_2$

$$2[^{18}F]\text{-}CClF_2CClF_2 \xrightarrow{\text{dismutation}} [^{18}F]\text{-}CCl_2FCClF_2 + [^{18}F]\text{-}CClF_2CF_3$$

Equation (1.10).

In those cases where $C_2Cl_2F_4$ is the reactant the most important $[^{18}F]$-fluorine labelled product is C_2ClF_5. Dismutation reactions involving $C_2Cl_2F_4$ would form significant quantities of C_2F_6, which is only observed in trace quantities under the conditions used by Kijowski and co-workers.[25]

A model based on stepwise F-for-Cl and Cl-for-F halogen exchange reactions is proposed by Kijowski et al[25] (Figure 1.6) Lower $[^{18}F]$-fluorine count rates in the chlorinated fractions are rationalised on the basis of fluorination reactions requiring fewer events at the surface than the corresponding chlorination reactions leading to $[^{18}F]$-labelled products.

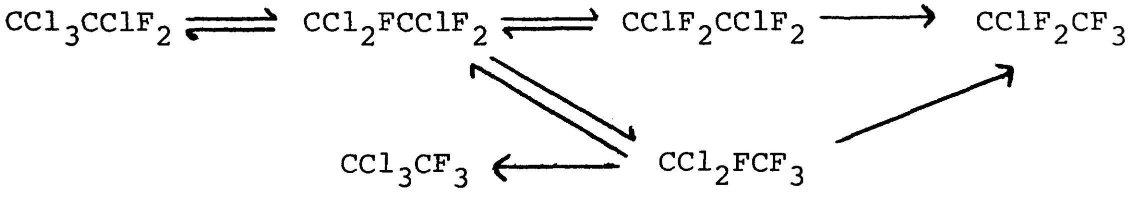


Figure 1.6 Halogen Exchange Mechanism.

The halogen exchange model is more attractive than the combination of Cl-F exchange and dismutation proposed by Kolditz[16], since it accounts for the observed product distribution without requiring the simultaneous arrival of two species at an active site. The active species for chlorination in this model involves chlorine retained by the catalyst, following F-for-Cl exchange with chlorofluoroethane. Although such species have yet to be investigated, circumstantial evidence for their existence comes from work on AlF_3 catalysts[17], where the chlorine content of the catalyst increases following passage of chlorofluoroethane/HF or chlorofluoroethane/N_2 gas flows at 673K. The chlorine retained by the catalyst must originate from the chlorofluoroethane, although it is not known whether the chlorine is present as part of an adsorbed organic molecule or some inorganic surface species.

Adsorption and retention of $H^{18}F$ during chromia pretreatment, observed by Kijowski and co-workers[26], favours a surface fluorinating species based on HF. Formation and desorption of hydrogen chloride would result from the interaction of a proton from HF with chlorine abstracted from the reacting chlorofluoroethane. Such a process can be represented as a series of equilibria involving halogen exchange between HX and the catalyst and between chlorofluoroethane and the catalyst (Equation (1.11)).

$$\text{HF} + \text{catalyst-Cl}^- \rightleftharpoons \text{HCl} + \text{catalyst-F}^-$$

$$C_2F_xCl_{(6-x)} + \text{catalyst-F}^- \rightleftharpoons C_2F_{(x+1)}Cl_{(5-x)} + \text{catalyst-Cl}^-$$

Equation (1.11).

However, no direct evidence for the existence of these surface chloride species has been reported in the literature.

1.4.2 Reactivity of the chlorofluoroethanes on chromia.

Investigations to determine the optimum conditions for the production of C_2ClF_5 have involved the reactivity of chlorofluoroethanes on chromia. The thermodynamics of the formal fluorination process:-

$$C_2F_xCl_{(6-x)} + HF \longrightarrow C_2F_{(x+1)}Cl_{(5-x)} + HCl$$

Equation (1.12).

show that formation of the asymmetric isomers is favoured over formation of symmetric isomers.[27] However, the observation that a decrease in the contact time favours formation of the symmetric isomer suggests that this is the kinetically favoured product.

The ease of substitution at saturated carbon atoms is known to decrease in the order[28] $R\text{-}CCl_3 > R\text{-}CCl_2F > R\text{-}CClF_2 > R\text{-}CF_3$. Where R is Cl the reactivity is substantially increased compared to R $= CCl_3 \rightarrow CF_3$, as shown by the relative ease with which chlorofluoromethanes are fluorinated compared with chlorofluoroethanes. Results from experiments to define the effects of contact time, temperature and isomeric ratio in the reaction of HF and $C_2Cl_2F_4$ on chromia[22] show that CCl_2FCF_3 is more reactive than $CClF_2CClF_2$. The same workers, in a study of CCl_2FCClF_2 reacting on an AlF_3/Ni, Cr, Fe catalyst,[22] report the reactivity of -CCl_2F towards replacement of Cl by F to be 24 times greater than that for -$CClF_2$. When the reactivities of -CCl_2F and -$CClF_2$ are compared in the two isomers CCl_2FCF_3 and $CClF_2CClF_2$, -CCl_2F is found to be more reactive than -$CClF_2$ but the difference in reactivity is less than that observed when the two groups were present in the same molecule. This effect is thought to be caused by the retarding of Cl-F exchange by the -CF_3 group adjacent to the -CCl_2F group. The greater electron withdrawing property of -CF_3 relative to -$CClF_2$ is presumably important in this respect.

By analogy with the behaviour of the isomers of $C_2Cl_2F_4$, CCl_3CF_3 is expected to be more reactive than CCl_2FCClF_2. However, reaction of $CClF_2CClF_2$ with HF at 653K, 688K and 713K on chromia forms C_2ClF_5 and $C_2Cl_3F_3$, with the proportion of the asymmetric $C_2Cl_3F_3$ isomer increasing with increasing temperature[22] (Table 1.5). Dismutation or halogen exchange involving $CClF_2CClF_2$ will give CCl_2FCClF_2 as the most important chlorinated product and the direct formation of CCl_3CF_3 from $CClF_2CClF_2$ is not possible by any of the mechanisms previously discussed. There are two possible mechanisms to account for the increase in the proportion of CCl_3CF_3 in the eluant; direct isomerisation of $CCl_2FCClF_2 \rightarrow CCl_3CF_3$ and stepwise formation, for example $CClF_2CClF_2 \rightarrow CCl_2FCClF_2 \rightarrow CCl_2FCF_3 \rightarrow CCl_3CF_3$. The inference in either situation is that, once formed, CCl_3CF_3 exhibits less reactivity than CCl_2FCClF_2.

Canesson, in a study of the reactivity of $C_2Cl_2F_4$

Table 1.5 Isomeric Composition of $C_2Cl_3F_3$ obtained as a product in the reaction of HF and $CClF_2CClF_2$.

Temperature (K)	Mol % of eluant	Ratio $CCl_2FCClF_2:CCl_3CF_3$
653	2.9	81 : 19
688	7.6	43 : 57
713	3.8	32 : 68

(mole ratio CCl_2FCClF_2:CCl_3CF_3 = 3:1) on pre-fluorinated chromia[23], concludes that CCl_3CF_3 is more reactive than CCl_2FCClF_2 for the dismutation reaction, which occurs above 623K to form $C_2Cl_4F_2$ and $C_2Cl_2F_4$. This conclusion, based on extrapolation of the results to a contact time of zero seconds, appears to be in disagreement with the product distribution found in the eluant when higher contact times are used and the observed behaviour of pure CCl_3CF_3 on pre-fluorinated chromia, which forms part of the same study. At flow rates between 0.01 and 0.025 mol $C_2Cl_3F_3$ h^{-1} (g catalyst)$^{-1}$ values for the mole ratio (CCl_2FCClF_2:CCl_3CF_3) in the eluant are 2.7:1 and 3.6:1 respectively. At the lower flow rate the mole ratio CCl_2FCClF_2:CCl_3CF_3 in the eluant is in agreement with the results obtained by Marangoni[22], suggesting that the symmetric isomer reacts at a faster rate than the asymmetric isomer. At the higher flow rate this conclusion no longer seems to apply. The interpretation of these results is based on dismutation reactions of $C_2Cl_3F_3$. However, CCl_3CClF_2 determined in this investigation would be expected, on the basis of the halogen exchange model (Section 1.4.1). to undergo F-for-Cl exchange to form CCl_2FCClF_2 or CCl_3CF_3. Since the symmetric isomer is the kinetically favoured product, higher flow rates would be expected to increase the concentration of symmetric isomer relative to asymmetric isomer. This explanation of the apparent difference in the reactivity of the isomers at different flow rates is consistent with CCl_3CF_3 being the less reactive isomer. This order of reactivity accords with the catalyst deactivation observed when CCl_3CF_3 is admitted to the catalyst as the pure isomer.[23] No reaction is observed and subsequent admission of CCl_2FCClF_2 gives no reaction at temperatures up to 723K. Results obtained during the present work should clarify the position as regards the reactivities of CCl_2FCClF_2 and CCl_3CF_3.

1.5 The Chromia Catalyst.

The normal method for preparing chromia[29] is by slow addition of aqueous ammonia to a solution of $[Cr(H_2O)_6]^{3+}$. The resulting species, $[Cr(H_2O)_5OH]^{2+}$, undergoes condensation to form a high molecular weight polymer, which is thought to be, in effect, a condensation polymer of $Cr(H_2O)_3(OH)_3$.[29] Drying in air at 373K followed by heating in an inert atmosphere at 473-673K leads to water loss and at higher temperatures a vigorous exothermic change is observed.[30] This exothermic process, often termed the "glow phenomenum" yields crystalline α-Cr_2O_3.

The temperature at which the transition to crystalline α-Cr_2O_3 takes place is dependent on several factors. Uncalcined chromia shows a sharp exotherm at 673K, but calcined chromias heated at a rate of up to 5^o min^{-1} under atmospheres of air or nitrogen show no exotherm up to 1023K. Under inert atmospheres the exotherm occurs at a higher temperature for a given rate of heating.[31] Addition of sulphate to chromia also raises the temperature at which the exotherm is observed. This effect is attributed to the presence of tetrahedral sulphate groups inhibiting the formation of octahedral symmetry [32] round the chromium ion.

The formation of crystalline α-Cr_2O_3 in the vapour-phase fluorination of chlorofluoroethanes is undesirable since it exhibits little catalytic activity.[16] Amorphous chromias with an average oxidation of chromium between +3 and +4 are reported to exhibit the greatest catalytic activity towards vapour phase fluorination.

Many reactions have been studied over chromia, for example ethene polymerisation,[33] hydrogen-deuterium exchange,[34] dehydration of secondary alcohols,[35] cyclopropane isomerisations[36] and dechlorination of chloroethanes.[37] There has been much speculation as to the active catalytic sites and the effect of various pre-treatments on the density and nature of these sites. Several authors have described adsorption at coordinatively unsaturated sites on the chromia surface,[29,38] exposed Cr^{3+}-Cr^{3+} pair sites[33] or at strained sites formed by the elimination of H_2O from two adjacent surface hydroxyl groups.[39] The active site for metal oxide catalysts could be centred on either the metal or oxide ion, although evidence in the literature favours interaction between the metal ion and the reacting organic molecule.[40]

The results of infra-red studies on crystalline and amorphous chromia[41] suggest that dehydration of the catalyst creates coordinatively unsaturated Cr^{3+} ions with a coordination number of 4 or 5, as compared with the fully coordinated value of 6. Dehydration is an important factor in creating sites for the dehydrogenation of secondary alcohols on chromia[42]; increasing activity is observed as the water content of chromia decreases. Other factors, such as areas of microcrystallinity, are also important. Since passage of hydrogen fluoride over chromia dehydrates the catalyst,[26] an interaction between HF and coordinatively unsaturated Cr^{3+} is possible.

Other oxidation states of chromium are reported to be important in determining the activity of the catalyst. An average oxidation state of chromium between +3 and +4 is characteristic of the best chromia catalysts used in the vapour phase fluorination of chlorofluoroethanes. The difference in activity between crystalline and amorphous chromia may in part be attributable to the more open structure of the amorphous form, but this is unlikely to be the reason for the great differences reported. It has been established that the presence of Cr^{VI} is necessary to promote substantial catalytic activity towards secondary alcohol dehydrogenation,[35] n-butane dehydrogenation[43] and n-heptane dehydrocyclisation[43] on chromia. The results of a temperature programmed reduction of chromia[26] show that unfluorinated chromia contains both Cr^{IV} and Cr^{VI} in addition to Cr^{III}. Following hydrogen fluoride gas flow at 623K no Cr^{IV} is detected but Cr^{VI} is still present. An e.p.r. study of chromia[44] has been interpreted on the basis of an exchange interaction between Cr^{III} and higher oxidation states (Cr^{IV} to Cr^{VI}).

The observation that all active chromia catalysts contain chromium in oxidation states other than Cr^{III} and that their redox properties appear to be important is significant. Adsorption involving carbon-halogen or hydrogen-halogen bonds via the halogen atom will be favoured by a strong Lewis acid site, while desorption will be more facile if the Lewis acidity of the site is reduced. A rapid interchange of oxidation states promoted by electron exchange has been proposed[44] and this mechanism would create oscillating donor-acceptor functions on chromia.

1.6 Hydrogen Fluoride.

1.6.1 Hazards.

Exposure to hydrogen fluoride, whether aqueous (hydrofluoric acid) or anhydrous (AHF) causes damage to the skin and the underlying tissue while the effects of inhalation of HF vapours range from mild irritation to accute nausea and vomiting. The 'Threshold Limit Value' for exposure to HF vapour is 3 ppm.[45]

The recommended treatment for HF burns involves flushing with water for 15 minutes followed by application of a paste containing calcium gluconate.[46] Injection of a solution of calcium gluconate beneath the burn area is necessary in cases of severe burns.

1.6.2 Properties and Structure.

Anhydrous hydrogen fluoride is a colourless liquid at room temperature with a boiling point of 292.69K [47] and a density of 0.9576 g cm^{-3} [48] at 298K. The high boiling point compared with other hydrogen halides is a consequence of the association of HF molecules in the liquid state. The association of HF molecules is also observed in the gaseous state and there have been contradictory views on whether the species formed from the association of HF molecules are linear or cyclic.

Two different models have been proposed to account for the polymerisation of HF monomers in the gas phase; a continuous polymerisation model, first proposed by Strohmeier and Briegleb[49] and a "few species" model involving dimers, tetramers and hexamers. In the continuous polymerisation model a stepwise association of HF with $(HF)_n$ is proposed, as shown in equation (1.13).

$$HF + (HF)_n \rightleftharpoons (HF)_{n+1}$$

Equation (1.13)

The formation of a cyclic hexamer is also proposed with the decrease in entropy being offset by the additional stability introduced by the extra hydrogen bond. Results from a Raman study of HF dissolved in liquid SF_6[50] provide evidence for a cyclic hexamer in solution and the existence of a cyclic hexamer in the gaseous state has been established by electron diffraction.[51] A relatively recent vapour pressure analysis[52], where vapour density, heat capacity, excess entropy, excess enthalpy and infra-red data were combined to obtain a non-ideal associated vapour model, concludes that the cyclic hexamer is the most abundant in the temperature range 292.5 - 329K.

Higher cyclic $(HF)_n$ oligomers with $n < 12$ are proposed to enable experimental observations to fit the model.

Vibrational pre-dissociation spectra[53] obtained for gaseous $(HF)_n$, n = 3-6, show no evidence of terminal -H-F or -F-H groups and a cyclic structure is inferred. However, the authors of more recent work on matrix isolated species propose an open chain strcuture for $(HF)_3$. On the basis of a F.T.I.R. study[54] of $(HF)_n$ in solid neon at 5K, open chain structures for $(HF)_2$ and $(HF)_3$ are proposed, although broad bands in the region 3500-3100 cm^{-1} are tentatively assigned to cyclic $(HF)_3$. An F.T.I.R. study[55] of $(HF)_n$ in solid argon at 12K provides further evidence for the existence of the open trimer and the trans structure for the isolated species is suggested on the basis that the cis structure would probably collapse to give the more stable cyclic oligomer. The open tetramer is thought to exist in the argon matrix, but evidence for a cyclic tetramer in different structural conformations is present. Cyclic $(HF)_5$ and $(HF)_6$ are detected.

A more recent study by the same authors[56] presents further evidence for open trimers and tetramers and four cyclic $(HF)_n$ species, n = 3-6. In the opinion of the authors, oligomeric species with $n > 6$ seem unlikely, since no spectroscopic evidence for them could be obtained. Furthermore, they consider it unlikely that oligomers with $n > 6$ could be stable in the gas phase if they cannot be formed by association of HF in solid argon.

It seems reasonable to suggest, on the basis of published work, that gaseous HF adopts a chain structure for $(HF)_2$, chain or cyclic structures for $(HF)_3$ and $(HF)_4$ and cyclic structures for higher oligomers, notably $(HF)_5$ and $(HF)_6$. The interaction of HF with a surface, for example chromia, could involve stabilisation of HF chain structures at Lewis acid and Lewis base sites, forming a pseudo-cyclic oligomer and occupying the surface unsaturations round chromium and oxygen (Figure 1.7). Ab-initio studies[57] predict cyclic $(HF)_3$ and $(HF)_4$ oligomers to be more stable than the respective chain structures in the gas phase, but at the temperature of hydrogen fluoride pre-treatment of 623K, significant concentrations of the chain species might reasonably be expected. Stabilisation of these species through interaction with the surface to form pseudo-cyclic oligomers is therefore attractive.

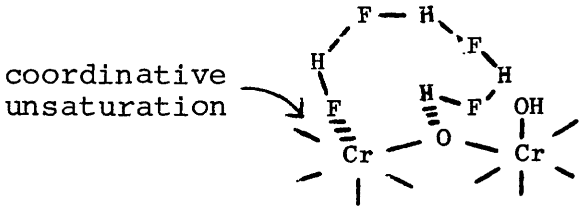


Figure 1.7 Pseudo-Cyclic Oligomer Based on $(HF)_4$

The solid state of hydrogen fluoride consists of a series of zig-zag chains of HF. Three possibilities for the arrangement of these chains were generally acknowledged; a completely parallel model where HF molecules in adjacent chains are parallel; a completely antiparallel model, where HF molecules in adjacent chains are antiparallel, and a disordered model, where the orientation of HF molecules varies in the chain. On the basis of Raman[58] and neutron diffraction[59] studies the arrangement of the zig-zag chains is assigned as being parallel.

1.6.3 The Hydrogen Difluoride Ion and Related Species.

Ions of the type $(HF)_nF^-$ are formed by hydrogen bonding of up to four HF molecules to a central fluoride ion. The ion HF_2^- is a linear species with the proton positioned symmetrically between the two fluorine atoms[60] and the ion $H_2F_3^-$, on the basis of an infra-red study[61], is assigned a bent structure of C_{2v} symmetry (Figure 1.8). Low temperature i.r. spectroscopy[62] suggests a planar D_{3h} configuration for the ion $H_3F_4^-$. No diffraction data are available to confirm this assignment, but ab-initio calculations[63] find the planar D_{3h} strcuture to be the least energetic for $H_3F_4^-$. The structure of the ion $H_4F_5^-$, obtained by X-ray crystallography[64] of crystalline $K[H_4F_5]$, is that of a slightly distorted tetrahedron.

In common with surface $(HF)_n$ oligomers, ions of the type $(HF)_nF^-$ could adsorb at Lewis acid and Lewis base sites, the proton associated with F^- interacting with the Lewis base site. Further consideration is given to these potential surface fluorine containing species in the discussion of hydrogen halide interactions with chromia. (Section 7.3)

1.6.4 Interaction between Hydrogen Fluoride and Chromia.

The literature contains only one extensive study of the interaction between hydrogen fluoride and chromia.[25] The results of this study, using $[^{18}F]$-fluorine labelled HF as

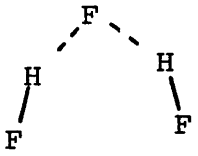
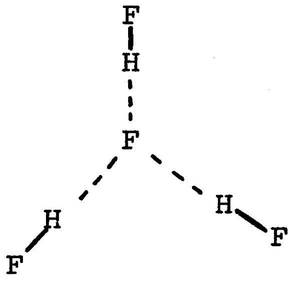
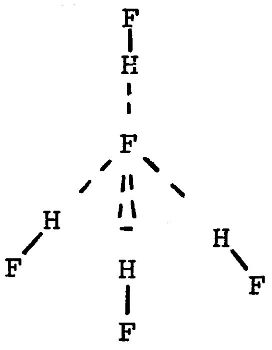
ION		SYMMETRY
$[HF_2]^-$	$[F - H - F]^-$	$D_{\infty h}$
$[H_2F_3]^-$		C_{2v}
$[H_3F_4]^-$		D_{3h}
$[H_4F_5]^-$		Td

Figure 1.8 Structures of Ions of General Type $(HF)_nF^-$

a radiotracer, show the existence of three types of surface fluoride at 623K. The three types of surface fluoride correspond to (i) weakly adsorbed fluoride, easily removed under conditions of inert gas flow, (ii) inert fluoride, which is not removed either by passage of dinitrogen at 623K or by incorporation into reacting chlorofluoroethanes, and (iii) catalytically active fluoride, which is incorporated into reacting chlorofluoroethanes. The results are interpreted on the basis of an equilibrium between the weakly adsorbed and catalytically active species, with the formation of an inert Cr^{III}-F species by gradual replacement of Cr^{III}-O by Cr^{III}-F (Equation (1.13)).

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

Equation (1.13)

Uptake of $[^{18}F]$-fluorine activity by the catalyst is in a range equivalent to 0.65 - 1.2 mmol $H^{18}F$ (g catalyst)$^{-1}$, of which ca. 15% is weakly adsorbed and ca. 65% remains on the catalyst following reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ at a temperature $\geqslant$ 623K.

No information is available, however, on the nature of these adsorbed species. Involvement of some form of oligomeric HF is inferred from the high uptake of $[^{18}F]$-fluorine activity and the known behaviour of HF. Whether one site is involved in the adsorption of all three types of fluorine or whether three distinct sites exist on the surface is still open to speculation.

1.7 Aims of the Present Work - A Possible Role for Surface Chloride in the Vapour Phase System.

Consideration of the proposed halogen exchange models whereby fluorine is incorporated in a reacting chlorofluoroethane molecule reacting at the catalyst surface[17,23,24,25] leads to the hypothesis that a similar mechanism may account for the chlorination reactions. The extent to which chlorination occurs is quite substantial in all the vapour phase systems, but the investigation by Kijowski and co-workers[25] is reviewed in detail here, because the same vapour phase system has been used in the present study.

Passage of CCl_2FCClF_2 at 623K over chromia, pre-treated with HF, results in a product mixture of CCl_3CClF_2, CCl_2FCClF_2, $C_2Cl_2F_4$ (both isomers) and C_2ClF_5. Formation of more highly fluorinated products accounts for ca. 25 mol % of the recovered material, while formation of more highly chlorinated products accounts for ca. 40 mol %. Reaction of $C_2Cl_2F_4$ at 698K results in a product mixture comprising CCl_3CClF_2, $C_2Cl_3F_3$ (both isomers), $C_2Cl_2F_4$ (both isomers) and C_2ClF_5. Fluorinated products account for ca. 35 mol % of the recovered material and chlorinated products ca. 7 mol %. In each case the fraction corresponding to reactant chlorofluoroethane contains [^{18}F]-fluorine activity, indicating that it has either exchanged fluorine with the surface or been formed by chlorination of a higher fluorinated species.

Three possible mechanisms may be proposed to account for chlorination processes:

1. Dismutation

2. Interaction between chlorofluoroethane and adsorbed chromia-chlorine species.

3. Interaction between chlorofluoroethane and adsorbed chromia-hydrogen chloride species.

The aim of the present work was to study the interaction between chlorine and chromia to investigate whether any evidence existed for the two latter mechanisms.

The possible sources of catalytic chloride in the vapour phase system are chlorine originating from chlorofluoroethane and hydrogen chloride, which is a product of the fluorination reaction. Formation of HCl could be either the step preceding desorption of any surface-chloride species, the precursor to such a species or the active chlorine containing species itself. The interaction between HF and HCl, when both are present on the catalyst, requires investigation, since their presence together would suggest that HCl is not a short lived surface species which desorbs immediately after formation. The pathway through the reactions of chlorine originating from chlorofluoroethane should establish the likely nature of any surface-chloride species on chromia. The nature of this investigation lends itself to radiotracer studies using [^{18}F]-fluorine and [^{36}Cl]-chlorine to probe surface interactions and deduce reaction pathways.

CHAPTER TWO

EXPERIMENTAL

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EXPERIMENTAL.

EQUIPMENT

2.1.1 The Vacuum Systems

Manipulation of volatile materials was carried out in evacuated systems. Two separate systems were used; a Pyrex glass line for handling chlorofluoroethanes and solvents, and a Monel metal line for handling anhydrous hydrogen fluoride. Monel is an alloy of nickel and copper and was selected for its chemical resistance to corrosive chemicals. Both systems were evacuated using rotary vane vacuum pumps. Volatile material was prevented from entering the pumps by glass waste traps cooled in liquid nitrogen. The vacuum was determined using a mercury Vacustat and was typically *ca*. 0.01 torr.

2.1.2 Pyrex Glass Line

The Pyrex glass vacuum system consisted of two manifolds arranged so that a sample could be divided into two identical aliquots, (Figure 2.1). This enabled two complementary analyses to be carried out on identical samples, for example, ^{19}F n.m.r. spectroscopic analyses of samples for scintillation counting. The manifolds were provided with points for the attachment of Rotaflow vessels. Pressure within the manifolds was determined using a mercury manometer.

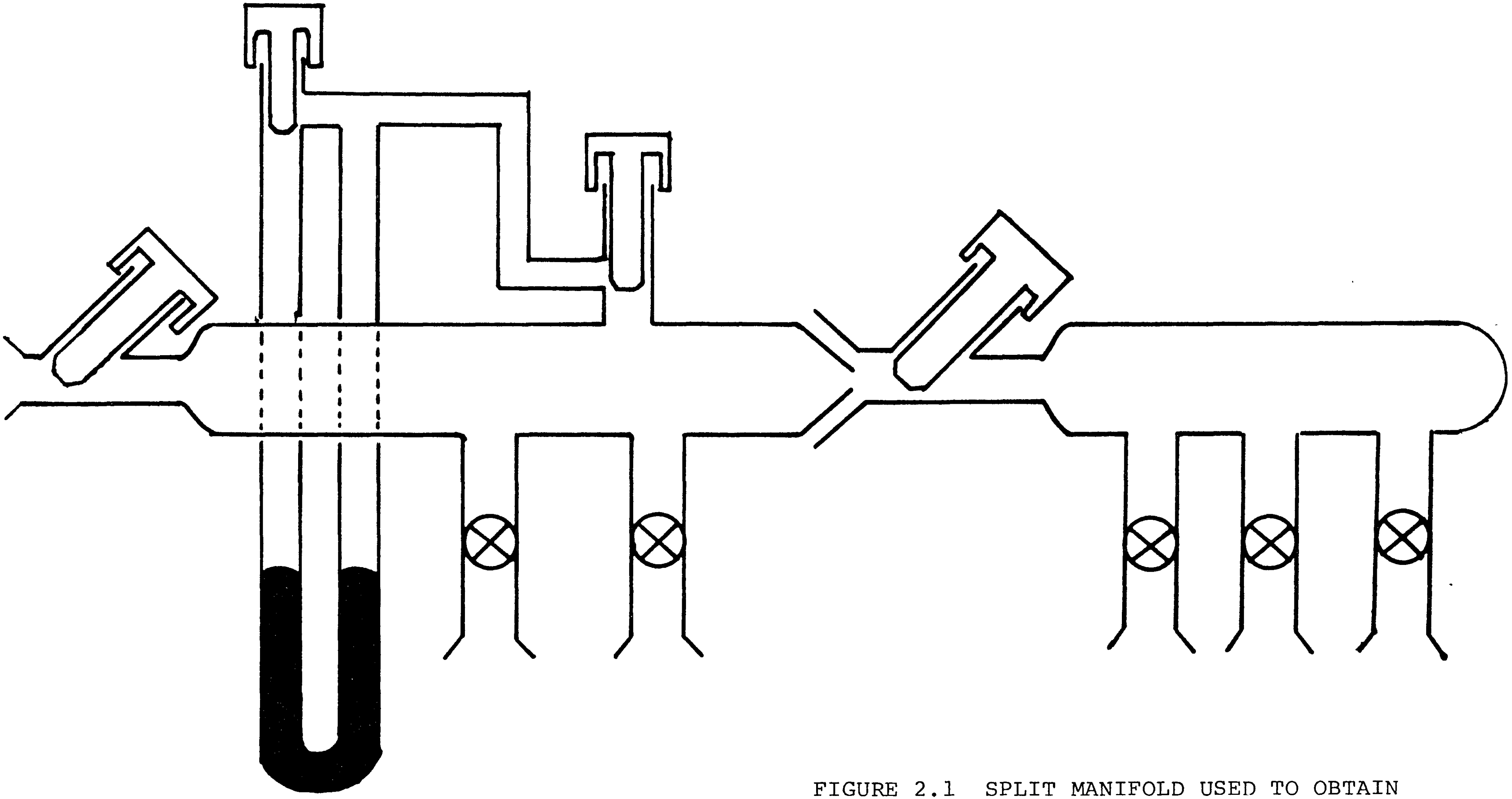


FIGURE 2.1 SPLIT MANIFOLD USED TO OBTAIN TWO IDENTICAL ALIQUOTS FOR ANALYSES.

2.1.3 Monel Metal Line

The Monel vacuum system was constructed using $^2/_5$ inch o.d. Monel tubing and Monel metal valves (Autoclave Engineers), (Figure 2.2). Stainless steel or Monel metal pressure bombs were connected to the line via nipple and collar screw couplings.(Autoclave Engineers, high pressure fittings 30VM). A lecture bottle of anhydrous HF, a Monel metal waste trap and a graduated Kel-F trap were also connected to the line. Pressure within the line was determined using a Budenberg gauge.

The Monel metal section of the line was connected to the vacuum pump through a 0.25 inch glass-metal joint and two cooled Pyrex solvent traps.

2.1.4 Transfer of Hydrogen Fluoride

Anhydrous hydrogen fluoride was distilled from a lecture bottle into the graduated Kel-F trap under vacuum. A measured volume was distilled into the evacuated stainless steel bomb and the bomb transferred to the reactor prior to admitting hydrogen fluoride to the catalyst.

2.2.1 The Reactor Systems

Two Monel metal flow systems were used in the catalytic studies. In both systems reactants passed through the reactor as a continuous flow of gas. Using reactor A (Section 2.2.2), pre-treatment of the catalyst with hydrogen fluoride was followed by chlorofluoroethane or hydrogen

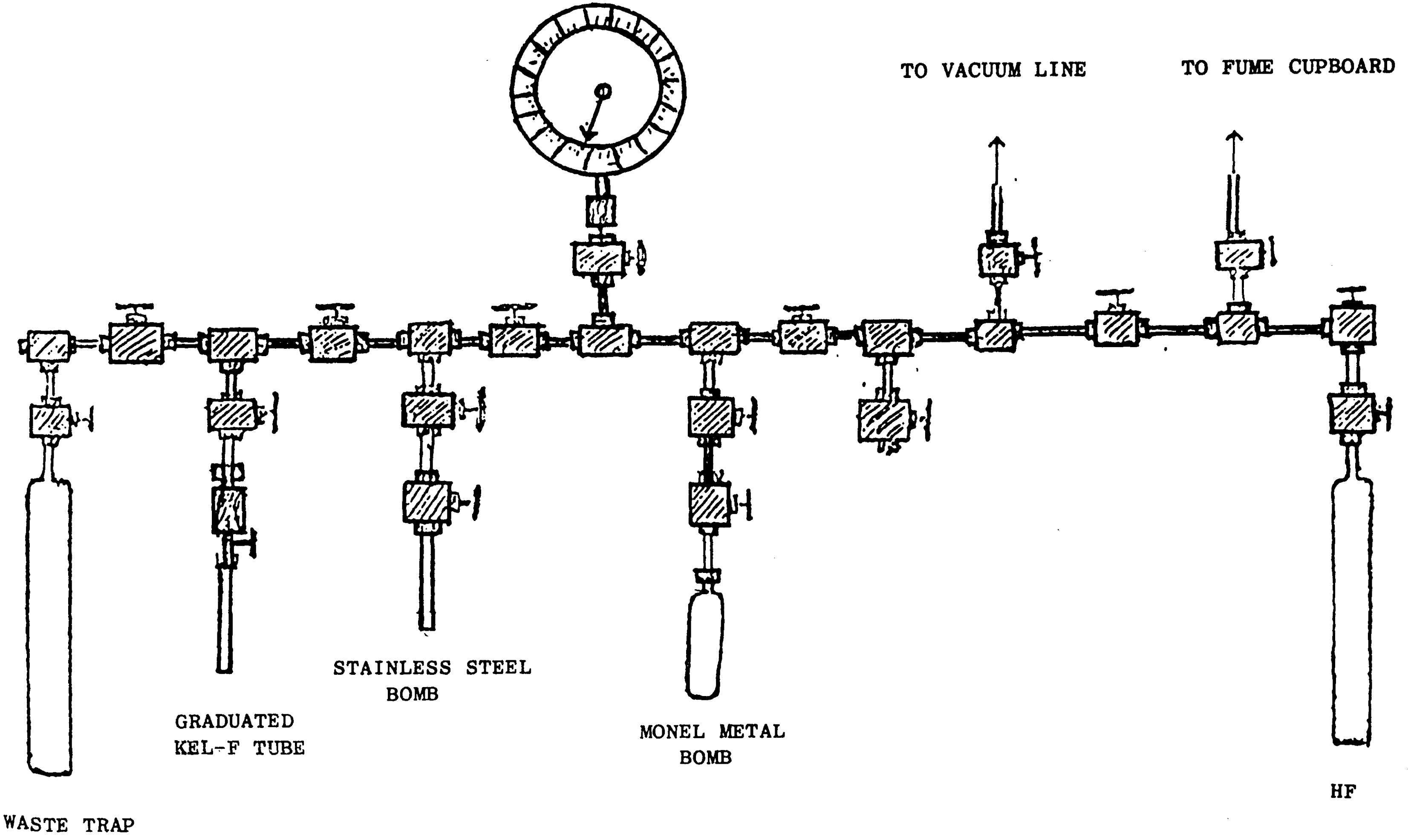


FIGURE 2.2 MONEL METAL LINE FOR STORAGE OF HF

chloride gas flow. Reactor B (Section 2.2.3) had the facility to admit HF, HCl and chlorofluoroethane to the catalyst simultaneously.

2.2.2 Reactor A (Figure 2.3)

The pelleted chromia catalyst was contained within a vertical Monel tube heated over a 18 cm. zone, the temperature being monitored by a centrally mounted thermocouple. Separate feed and exit lines for HF and chlorofluoroethane were provided and gas flow was from top to bottom. Reactions were carried out under atmospheric pressure. A smaller Monel metal tube (10 cm) modified with a F.E.P. side arm was used in [^{18}F]-fluorine labelling experiments, (Figure 2.4).

Before each experiment the catalyst was dried under dry nitrogen gas flow (623K, 4h). HF, dispensed from the stainless steel bomb heated to 333K, was then admitted to the catalyst. The flow of gaseous HF was controlled by a differential-pressure flowmeter and was typically 90 ml min^{-1}. During HF gas flow the catalyst temperature was maintained at 623K. Following the HF gas flow, the catalyst was purged with dry dinitrogen at 623K to remove weakly adsorbed HF.

The chlorofluoroethane or hydrogen chloride were stored in a cooled flow vessel and admitted to the catalyst in a stream of dry dinitrogen. The temperature of the flow vessel was maintained at 153K in the case of HCl and 253-258K in the case of the chlorofluorocarbon.

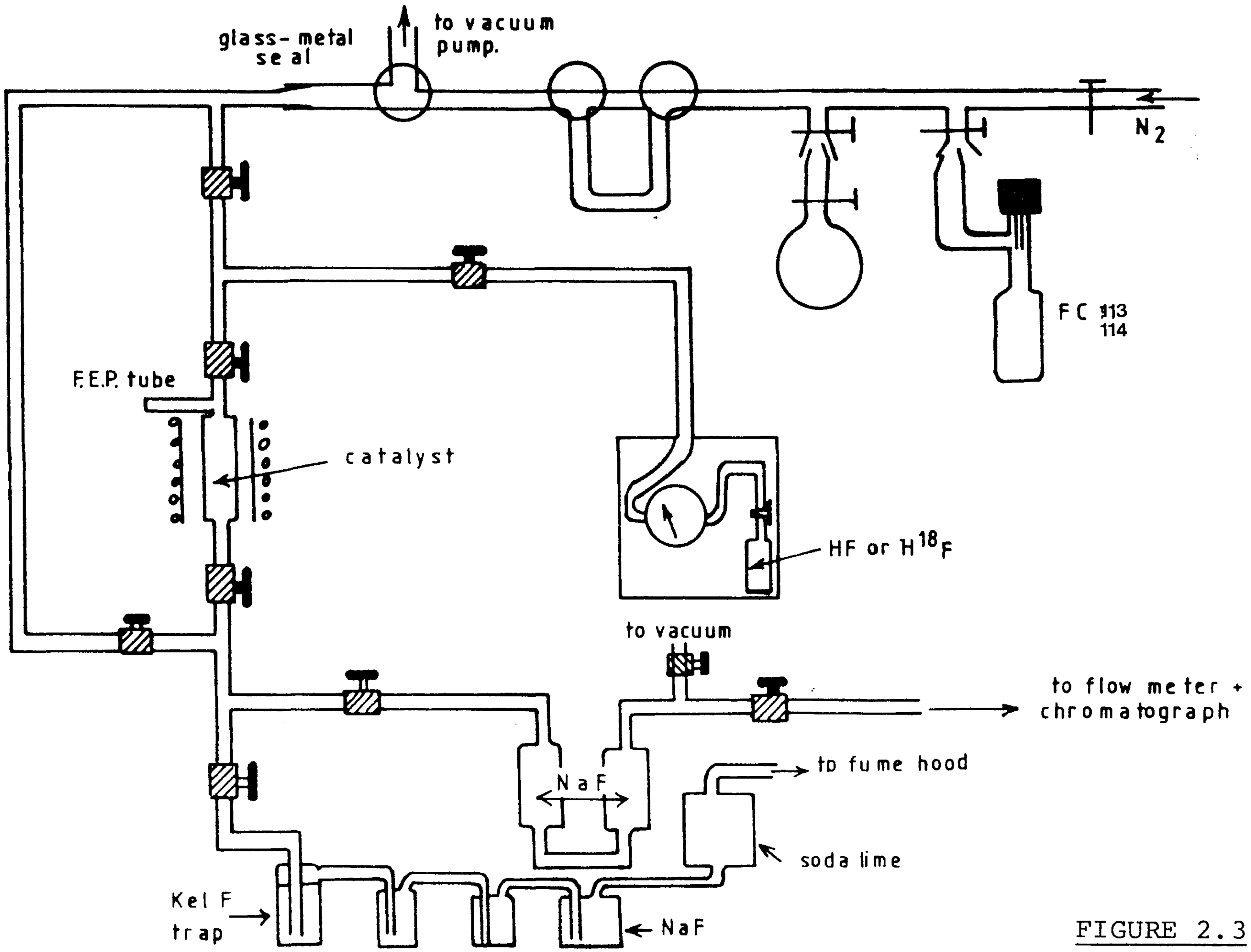


FIGURE 2.3 REACTOR A

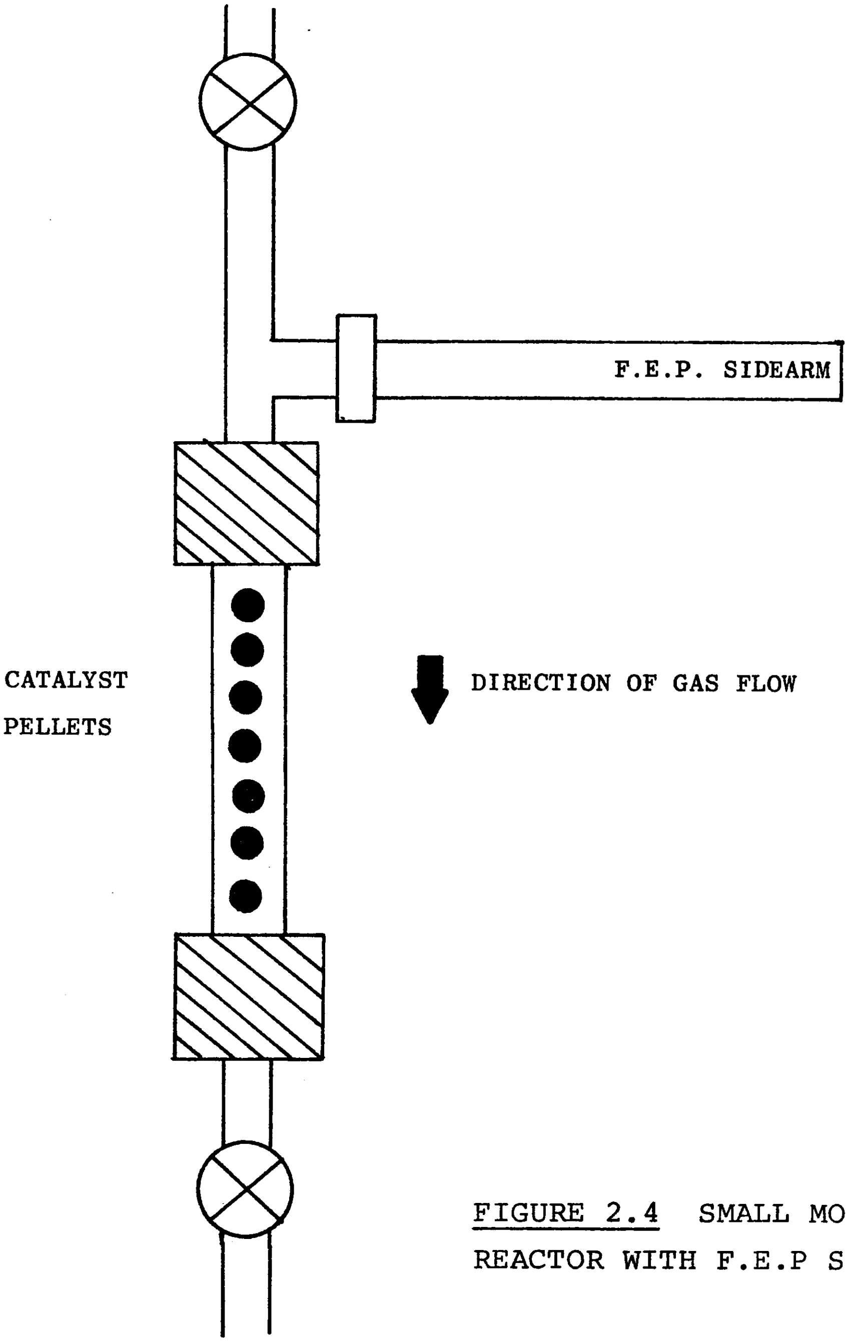


FIGURE 2.4 SMALL MONEL METAL REACTOR WITH F.E.P SIDEARM.

The reactor eluant gas was monitored at 10 → 20 minute intervals using an on-line gas chromatograph (see Section 2.13). The eluant gas was collected in cooled traps downstream of the gas chromatograph and retained for further analyses.

2.2.3 Reactor B (Figure 2.5)

The ground catalyst (particle diameter 0.4mm - 0.7mm) was contained within a Monel tube heated over a 18 cm zone, the temperature being monitored by a centrally mounted thermocouple. Before each experiment the catalyst was dried under a dry dinitrogen flow (623K, for various times). Following this, HF was admitted from a reservoir (623K, ½h. at 700 ml min^{-1}). Chlorofluoroethane and HF were admitted to the catalyst through separate feed lines. The eluant gases exited to waste through a gas sampling port. Samples of the eluant were taken using a 1.0 cm^3 ground glass syringe and the sample was analysed by gas chromatography (see Section 2.13).

2.2.4 Temperature Programmed Fluorination

Temperature programmed fluorination was used to determine the energies of activation for the fluorination and chlorination processes of reacting $C_2Cl_2F_4$. In this technique the products of reaction were quantitatively determined by integrating the area under a characteristic infra-red absorption for each product. The apparatus (Figure 2.6) comprised an oven with a temperature control

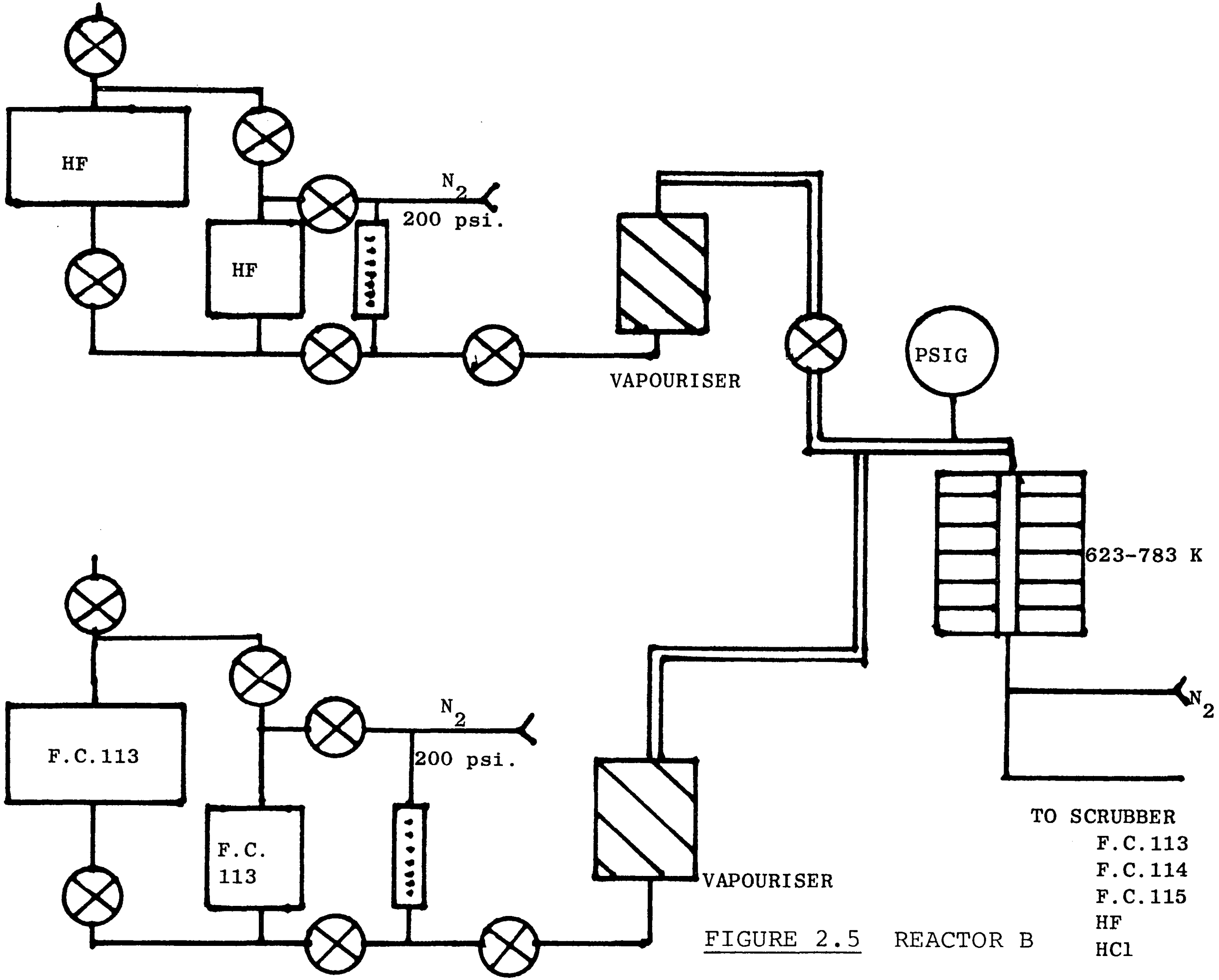


FIGURE 2.5 REACTOR B

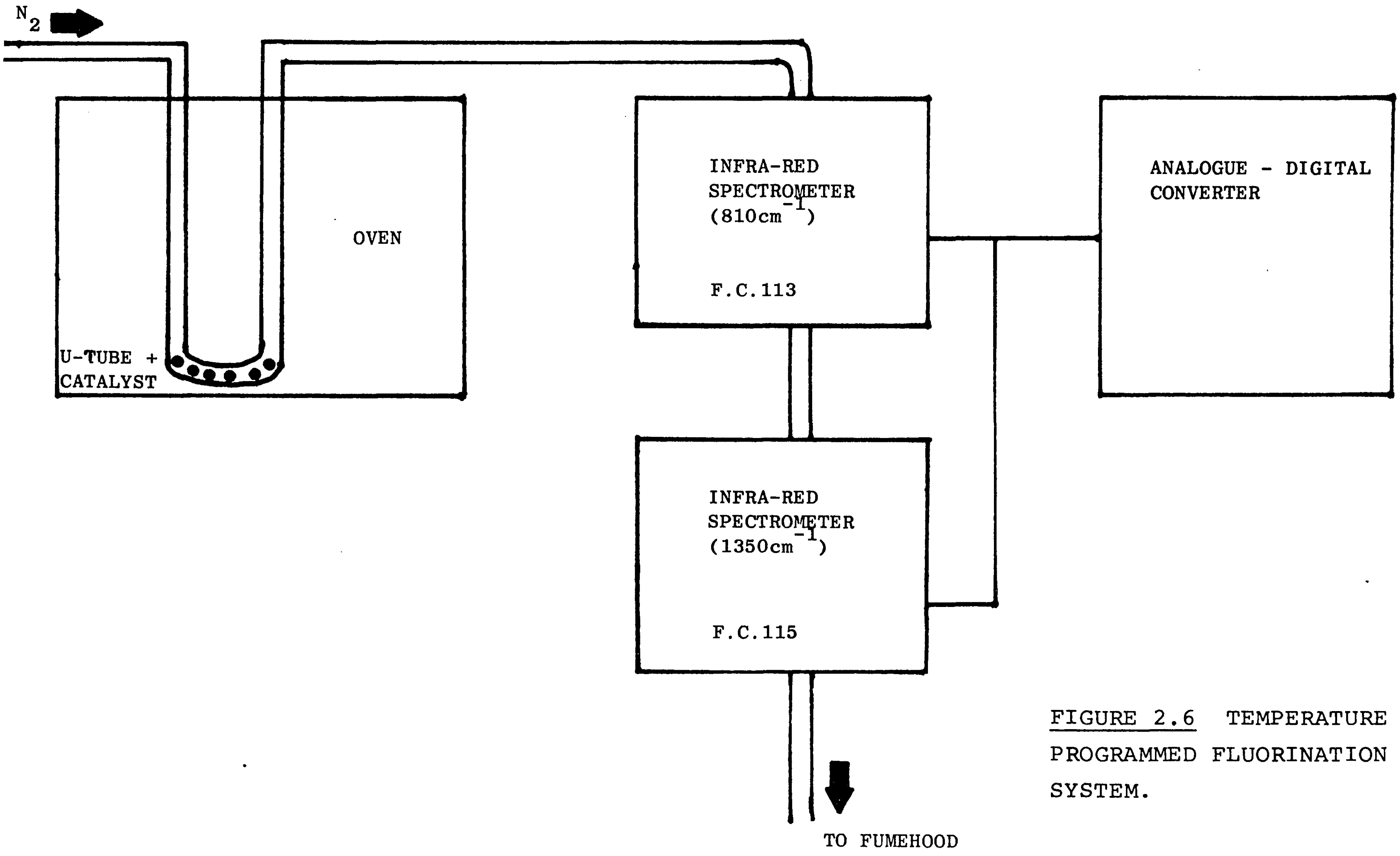


FIGURE 2.6 TEMPERATURE PROGRAMMED FLUORINATION SYSTEM.

to regulate the rate of temperature increase. A measured quantity of pre-fluorinated chromia catalyst (typically 0.4g - 1.0g) was placed in a glass U-tube inside the oven and a stream of $C_2Cl_2F_4$ vapour admitted.

The reaction products were monitored using infra-red absorption bands at 810 cm^{-1} (CCl_2FCClF_2) and 1350 cm^{-1} ($CClF_2CF_3$).

Each i.r. spectrometer was connected to an integrator which stored the accumulated signal area/time data. These time-based data were converted to temperature-based data using the measured ramp rate and the apparent activation energy calculated from the slope of a plot of log (reaction rate) versus reciprocal temperature.

The T.P.F. system was calibrated by admitting $CClF_2CF_3$ (100 ml gas) or CCl_2FCClF_2 (400 μl liquid) as appropriate to an evacuated glass bulb of known volume (2298 cm^3). Air was admitted to the bulb to return it to atmospheric pressure and the bulb shaken and allowed to equilibrate for 15 minutes. Several samples (1cm^3) were taken from the bulb and injected into the stream of dinitrogen diluent flowing through the i.r. cells. The i.r. signals were integrated and a calibration factor in μmol/unit area obtained. Care was taken to ensure that dinitrogen flow remained constant between calibration and experiment.

The $C_2Cl_2F_4$ reactant feed contained both isomers (mole ratio $CClF_2CClF_2$: CCl_2FCF_3 = 51.0 : 49.0 by ^{19}F n.m.r. spctroscopy). Consequently, the isomer CCl_3CF_3

would be expected as a major product from the chlorination of CCl_2FCF_3 (Equation (2.1))

$$CCl_2FCF_3 + \text{surface-}Cl^- \longrightarrow CCl_3CF_3 + \text{surface-}F^-$$

Equation (2.1)

However, only the symmetric isomer was determined.

RADIOCHEMICAL PREPARATIONS.

2.3 Radioisotopes

2.3.1 The radioisotope [^{18}F]-fluorine

The [^{18}F]-fluorine isotope is a β^+ emitter, and annihilation of β^+ particles with negative electrons releases energy in the form of γ-radiation. The maximum γ-emission energy is 0.51 MeV and the half-life of [^{18}F]-fluorine is 109.72±0.06 min.[65] Since the half-life of the isotope is relatively short experimental work must be completed in one working day. After six half-lives (11h) only 1.6% of the original activity remains.

2.3.2 The radioisotope [^{36}Cl]-chlorine

The [^{36}Cl]-chlorine isotope decays by β^- emission with a half-life of 3×10^5 years. The isotope was supplied as an aqueous solution of Na^{36}Cl (Amersham International p.l.c) and was diluted with concentrated hydrochloric acid to give a solution with a specific [^{36}Cl]-chlorine activity of *ca*. 9.3×10^5 Bq cm^{-3}.

2.4.1 Preparation of $Cs^{18}F$

$[^{18}F]$-Fluorine was prepared by irradiating lithium carbonate (ca.2 g) in the central core of the Scottish Universities Research Reactor at East Kilbride using the sequence $^{6}Li(n,\alpha)^{3}H$, $^{16}O(^{3}H,n)^{18}F$.[66] Typical irradiation conditions were 30 minutes at a flux of 3.6×10^{12} neutrons $cm^{-2}s^{-1}$. The sample of Li_2CO_3 was contained within an aluminium screw-top can (height, 8cm ; diameter, 3cm). A graphite rod (length, 7cm ; diameter 1.5 cm) inside the aluminium can acted as a neutron moderator, slowing the neutrons to improve the possibility of collision with lithium nuclei. The $Li^{18}F$ produced in the irradiation was converted to $H^{18}F$ by reaction with sulphuric acid, (conc. $H_2SO_4 : H_2O = 1:1$ by volume). The $H^{18}F$ was then distilled into a solution of caesium hydroxide at 273K. Neutralisation of the solution by addition of aqueous HF was followed by evaporation to dryness to give $Cs^{18}F$ as a finely divided white powder.

2.4.2 Preparation of $H^{18}F$

$H^{18}F$ was prepared by an exchange reaction between anhydrous HF (ca.3-5 cm^3 liquid) and $Cs^{18}F$ (typically 1.5×10^6 Bq) at 523K in a Monel metal pressure vessel connected to the Monel metal vacuum line. Following exchange, ca, 30 min; the resulting $H^{18}F$ was transferred to a stainless steel bomb and admitted to the catalyst.

2.5 Determination of [^{18}F]-Fluorine Count Rates

2.5.1 The Scintillation Counter

The γ-rays produced in the annihilation process of a positron interacting with a negative electron were counted using a Tl/NaI scintillation counter (Ekco electronics instruments) and scaler (Scaler Ratemeter SR7, Nuclear Enterprises). Before use the scaler and scintillation counter were calibrated using a standard caesium-137 γ-source and then a sodium-22 source, which emits γ-rays of the same energy as those emitted by [^{18}F]-fluorine (0.51 MeV). In each case a γ-ray spectrum was obtained by monitoring the counts from the source at various voltages. The γ-ray spectrum obtained from a Cs^{18}F source is shown in Figure 2.7. In normal use the scaler was set to count at the voltage corresponding to the maximum count rate from the ^{22}Na source ± 10%.

2.5.2 Decay Correction

The decay of activity from radioactive nuclei follows an exponential rate law.

$$At = Ao\ e^{-\lambda t}$$

where Ao = activity of sample in Bq at $t = o$

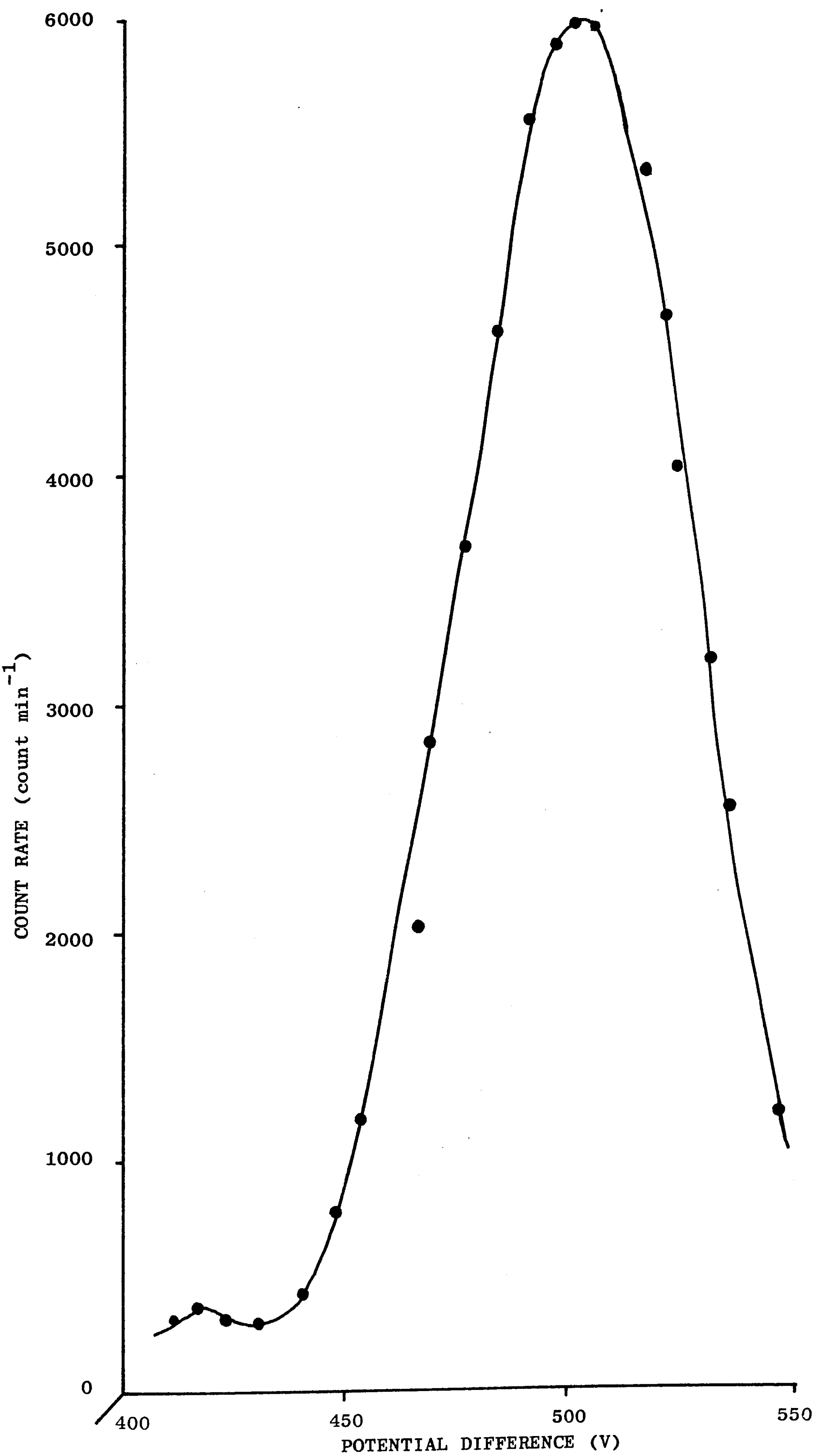
At = activity of sample in Bq at time, t.

λ = decay constant $= \frac{\ln 2}{t_{\frac{1}{2}}}$

$t_{\frac{1}{2}}$ = half life of isotope

Equation 2.2

FIGURE 2.7 γ-EMISSION SPECTRUM FOR [^{22}Na]-SODIUM



Since significant decay occurred in the time taken to carry out one experiment, all datawere corrected to the activity at time of the last count rate determination using equation (2.2).

2.5.3 Specific Count Rate of $H^{18}F$

A measured pressure of $H^{18}F$ in a known volume was condensed on to dried CsF (0.5g) in a fluorinated ethene/ propene (F.E.P) tube. The solid complex, $Cs^{+}HF_2^{-}$, was counted and the result expressed as specific count rate (mol $[^{18}F]$-fluorine)$^{-1}$.

2.5.4 Specific Count Rate of $[^{18}F]$-labelled chromia

Three or four chromia pellets were tipped into the reactor side arm (Figure 2.4), avoiding exposure to the atmosphere. The pellets were counted in the same manner as the $Cs^{+}HF_2^{-}$ complex. Since the specific count rate of a solid complex of $H^{18}F$ was known the count for the catalyst could be expressed as equivalent to a quantity of HF, assuming no difference in specific count rate between the two systems. This assumption is valid for $[^{18}F]$-fluorine since it is a γ-emitter and no self-absorption losses are expected (Section 2.8.3).

2.6

2.6.1 Preparation of $H^{36}Cl$

The reaction of concentrated hydrochloric acid with concentrated sulphuric acid was used to generate $H^{36}Cl$ using the apparatus shown in Figure 2.8.

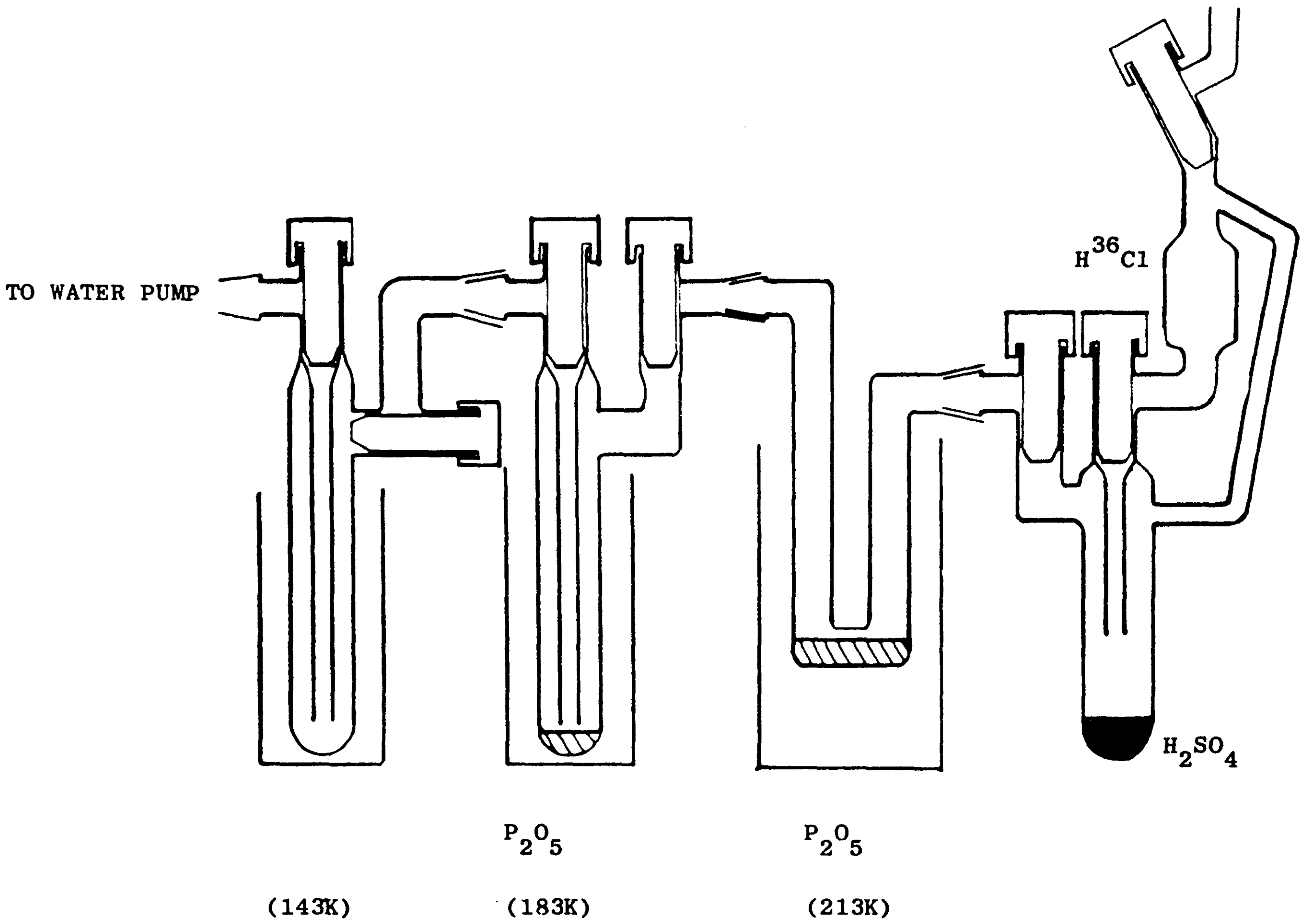


FIGURE 2.8 $H^{36}Cl$ GENERATOR

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

Equation 2.3

The $Na^{36}Cl/HCl$ solution was added dropwise from the upper chamber of the reaction vessel to concentrated sulphuric acid in the lower chamber. Pressure between the two chambers was balanced by a pressure equilibration arm. An iron bar sealed in glass was used to stir the solution. The gaseous $H^{36}Cl$ passed through a U-trap containing P_2O_5 at 213K and was liquified at 183K over P_2O_5. This treatment removed water from the $H^{36}Cl$. A further distillation of $H^{36}Cl$ from 183K to 143K was carried out and the product was degassed before transfer to the reactor flow vessel.

2.6.2 Preparation of $[^{36}Cl]-Cl_2$

Oxidation of Cl^- (aq) to Cl_2 was used to generate $[^{36}Cl]-Cl_2$. Potassium permanganate (300ml, 0.3 mol dm^{-3}) was added dropwise with stirring to a 500 ml round bottomed flask containing concentrated hydrochloric acid and $Na^{36}Cl$ (35 cm^3, 1.9 MBq) (Figure 2.9). This vessel was heated by a water bath at 333K and connected through a series of cooled traps containing $KMnO_4$, to react with HCl, or P_2O_5, to remove water, to a partially evacuated vessel (vessel G, Figure 2.9). Periodically vessel G was isolated from the vacuum pump and opened to reduce the pressure in the rest of the apparatus. This procedure was carried out every five minutes to draw gaseous $[^{36}Cl]-Cl_2$ into the cooled traps. After $[^{36}Cl]-Cl_2$ generation had ceased the traps

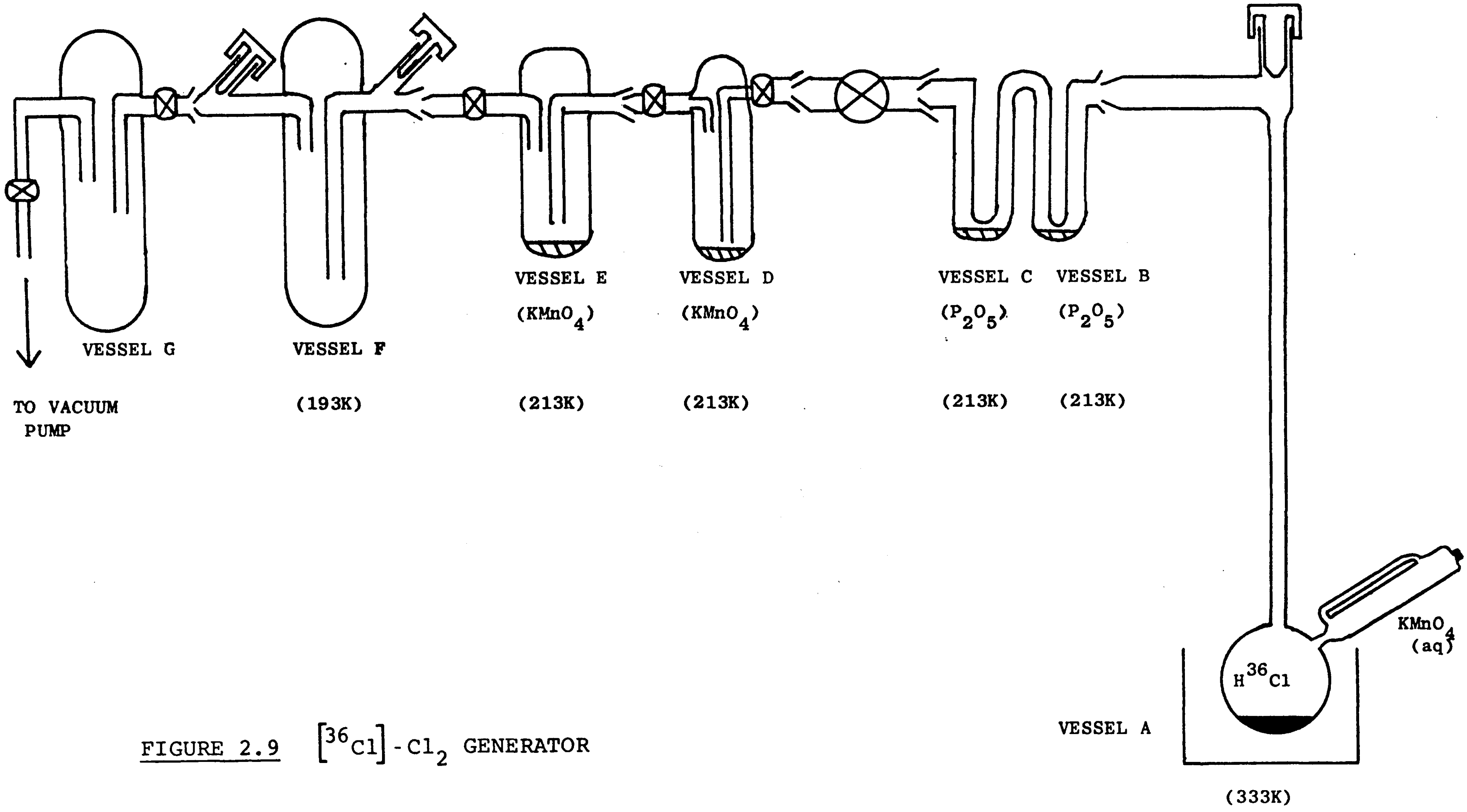


FIGURE 2.9 $[^{36}Cl]$-Cl_2 GENERATOR

were progressively removed and [^{36}Cl]-Cl_2 collected in vessel F at 193K. The [^{36}Cl]-Cl_2 was degassed in-vacuo and stored in a Monel pressure bomb.

2.6.3 Preparation of [^{36}Cl]-Chlorine labelled dichlorotetrafluoroethane.

[^{36}Cl]-Chlorine labelled CCl_2FCF_3 was prepared by vapour phase, mercury lamp photolysis according to equation (2.4):-

$$CHClFCF_3 + [^{36}Cl]\text{-}Cl_2 \xrightarrow{hv} [^{36}Cl]\text{-}CCl_2FCF_3 + H^{36}Cl$$

Equation (2.4)

Photolysis of $CHClFCF_3$, [^{36}Cl]-Cl_2 mixtures was performed in an evacuable Pyrex bulb (21) using various mole ratios and irradiation times (8-68h.) Optimum conditions were 36h. irradiation using 205 torr [^{36}Cl]-Cl_2 and 195 torr $CHClFCF_3$. The progress of the reaction was followed by monitoring infra-red spectral bands at 820 and 700 cm^{-1} ($CHClFCF_3$) and 735 cm^{-1} (CCl_2FCF_3). [^{36}Cl]-chlorine labelled HCl and unchanged Cl_2 were removed by treatment with moist NaOH pellets and the chlorofluoroethane was isolated in > 90% yield. The molecular weight, determined by vapour density measurements, was 171.3±1.6 anu (lit. 170.9 anu).

Products and reactants were easily differentiated by their ^{19}F n.m.r. spectra (Table 2.1). N.m.r. analysis of the product indicated that the mole ratio CCl_2FCF_3 : $CClF_2CClF_2$ was 19 : 1 which compares with the mole ratio

Table 2.1 ^{19}F n.m.r. Spectra [a] of C_2ClHF_4 and $C_2Cl_2F_4$.

	$\delta(CF_3)$ [ppm]	$\delta(CF_2)$ [ppm]	$\delta(CF)$ [ppm]	$^3J(FF)$ [Hz]	$^2J(HF)$ [Hz]	$^3J(HF)$ [Hz]
CCl_2FCF_3	-84.2		-76.9	8		
$CClF_2CClF_2$		-71.1				
$CHClFCF_3$	-82.2		-157.0	10	48	4
CHF_2CClF_2		-73.8 -133.7		7	55	2

[a] Chemical shift with respect to CCl_3F

$CHClCF_3$: CHF_2CClF_2 of 24 : 1 in the starting material.

The specific activity of $[^{36}Cl]$-CCl_2FCF_3 was determined by liquid scintillation counting (Section 2.11). Specific $[^{36}Cl]$-chlorine count rates were determined for $[^{36}Cl]$-Cl_2 and $H^{36}Cl$, produced in the irradiation, by precipitation of $[^{36}Cl]$-chlorine as $Ag^{36}Cl$ (Section 2.7). Specific $[^{36}Cl]$-chlorine activities of the eluant fractions from the reaction of $[^{36}Cl]$-CCl_2FCF_3 on chromia were compared with the initial specific activity of the reactant. Specific count rates derived from $[^{36}Cl]$-Cl_2 and $H^{36}Cl$ were used to calculate the specific count rate of $[^{36}Cl]$-CCl_2FCF_3 according to equation (2.5).

$$2(\text{s.c.r}[^{36}\text{Cl}]\text{-Cl}_2)=\text{s.c.r H}^{36}\text{Cl}+2(\text{s.c.r}[^{36}\text{Cl}]\text{-CCl}_2\text{FCF}_3)$$

<u>where</u> s.c.r is the specific count rate in count s^{-1} $(mol\ Ag^{36}Cl)^{-1}$

Equation (2.5)

Using this method, count rates from $[^{36}Cl]$-chlorine on chromia following reaction of $[^{36}Cl]$-CCl_2FCF_3 could be related indirectly to a $[^{36}Cl]$-chlorine count rate determined on $Ag^{36}Cl$. The count rate data were treated in the same manner as those for $[^{36}Cl]$-activity originating from $H^{36}Cl$ (Section 2.7).

Specific count rates obtained for $H^{36}Cl$ and $[^{36}Cl]$-Cl_2 after their conversion to $Ag^{36}Cl$ were $(6.5\pm0.2)\times 10^4$ and $(7.1\pm0.2)\times 10^4$ count s^{-1} $(mol\ AgCl)^{-1}$ after 36h. irradiation. Specific count rates obtained after 68h. irradiation, using a different batch of $[^{36}Cl]$-Cl_2, were $(3.2\pm0.1)\times10^4$ count s^{-1}

(mol AgCl)$^{-1}$ for $H^{36}Cl$ and (3.9±0.1)x10^{4} count s^{-1} (mol AgCl)$^{-1}$ for [^{36}Cl]-Cl_2. On the basis of these results Cl-for-Cl exchange between [^{36}Cl]-Cl_2 and C_2HClF_4 or $C_2Cl_2F_4$ does not appear to be an important route for [^{36}Cl]-chlorine incorporation during a 36h. photolysis.

ANALYTICAL TECHNIQUES

2.7 Determination of Chloride Ion by Gravimetry

Specific [^{36}Cl]-chlorine count rates of $H^{36}Cl$ and [^{36}Cl]-Cl_2 were determined by precipitating the chloride ion as $Ag^{36}Cl$ and counting the precipitate in a lead castle/ Geiger-Müller tube counting system (Section 2.8).

An aliquot of [^{36}Cl]-Cl_2 or $H^{36}Cl$ was distilled on to moist sodium hydroxide (Equation (2.6))

$$H^{36}Cl + NaOH \longrightarrow Na^{36}Cl + H_2O$$

$$[^{36}Cl]\text{-}Cl_2 + NaOH \longrightarrow Na^{36}Cl + NaO^{36}Cl + H_2O$$

$$NaO^{36}Cl + H_2O_2 \longrightarrow Na^{36}Cl + H_2O + O_2$$

Equation (2.6)

Conversion to NaCl, based on the initial aliquot of $H^{36}Cl$ or [^{36}Cl]-Cl_2, was > 95%.

The solution of chloride ion was acidified using concentrated nitric acid, to prevent precipitation of other silver salts, which might form in neutral solution (for example CO_3^{2-}), and transferred to a darkened beaker. Silver nitrate (0.2 mol l^{-1}) was added dropwise with stirring (Equation (2.7)) and the suspension heated near to boiling point until the precipitate coagulated.

$$AgNO_3 + Cl^-(aq) \longrightarrow AgCl(s) + NO_3^-(aq)$$

Equation (2.7)

The solution was allowed to cool. When cold, usually after standing for 2h. at room temperature, the precipitate of silver chloride was filtered through a dried, weighed number 4 Gooch crucible and washed with dilute HNO_3 to remove any metallic silver which might be present. The precipitate was then dried and weighed.

In order to achieve reproducible results yields of 95% or better were required. Several determinations of chloride precipitated from inactive solutions of known molarity were carried out. The yield, based on the known quantity of chloride ion present in the solution, was 98% ± 2% (Table 2.2).

Table 2.2 Precipitation of chloride ion as AgCl.

Experiment	mmol NaCl in solution	mmol AgCl recovered.		chloride recovery (%)
		1st weighing	2nd weighing	
1	4.015	3.972	3.971	98.9 98.9
2	7.627	7.619	7.617	99.9 99.8
3	1.475	1.474	1.474	99.9 99.9
4	1.236	1.185	1.184	95.9 95.8
5	5.701	5.665	5.664	99.4 99.3
6	0.627	0.603	0.603	96.2 96.2

Average recovery = 98% ± 2%

2.8 Determination of [^{36}Cl]-Chlorine Count Rates

2.8.1 Plateau Curve

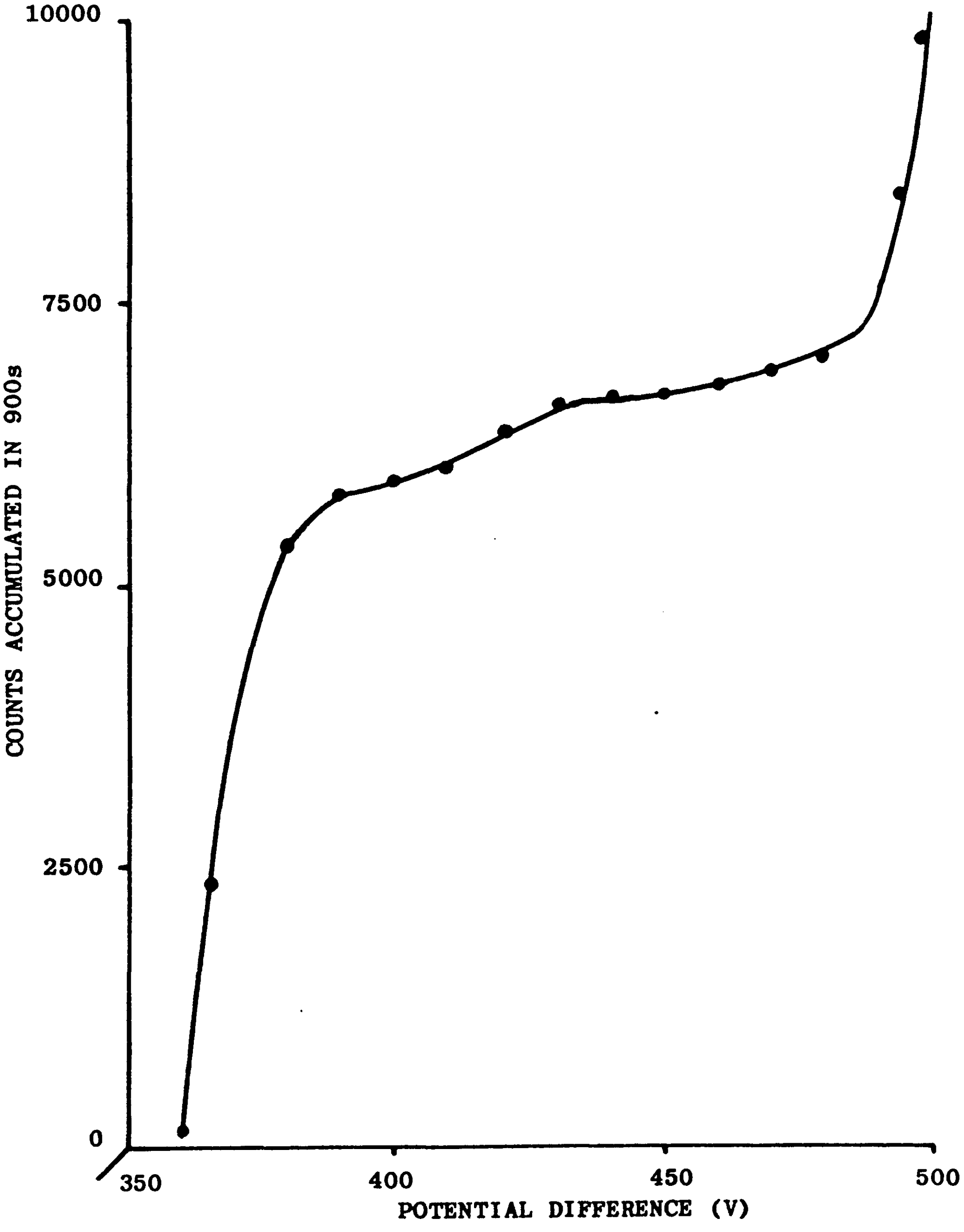
In a Geiger-Müller tube no discharge occurs until a sufficiently large potential difference is applied across the tube to enable movement of free electrons. The rate of discharge increases rapidly above this minimum potential (Vo) until a plateau is reached. The plateau is not infinite, however, and the rate of discharge increases at the end of the plateau region. The operating potential across the G-M tube is set in the centre of this plateau to ensure that the count rate is not affected by small variations in mains voltage across the power supply.

The plateau region was determined, for all G-M tubes used, by counting a sample of Ag^{36}Cl in the voltage range 350-500 V. The counting equipment consisted of a G-M tube, shielded in lead, connected to a scaler (Scaler Ratemeter SR7, Nuclear Enterprises). A typical plateau curve is shown in Figure 2.10.

2.8.2 Background Count.

Background counts arise from decay of naturally occurring radioisotopes present in the environment, cosmic radiation and decay processes resulting from nuclear weapon testing. These decay processes contribute to the counts accumulated while counting radio-labelled samples, even where the samples are contained within a lead shield, as here. The background count was determined before counting samples and was subtracted from the count recorded by the scaler before

FIGURE 2.10 PLATEAU CURVE FOR GEIGER-MÜLLER TUBE.



any treatment of data.

Desorption of weakly bound [^{36}Cl]-chlorine species from chromia, and adsorption of these species on the window of the G-M tube, caused the background count rate to increase. To obviate this problem G-M tubes were changed when the background count exceeded 0.8 count s^{-1}.

2.8.3 Self Absorption

The isotope [^{36}Cl]-chlorine is a β-emitter and a proportion of the emissions interact with surrounding matter and are absorbed. This effect, termed self absorption, is corrected for by constructing a self absorption curve. This curve is obtained by measuring the count rate per mg for different weights of [^{36}Cl]-chlorine labelled sample and plotting a graph of Specific Count Rate per mg versus Weight sample. The absorption correction necessary to relate observations at one weight to observations at any other weight is the quotient of the values of (count rate mg^{-1}) at the two weights.

Self absorption curves were obtained for Ag^{36}Cl and [^{36}Cl]-labelled chromia (Figures 2.11 and 2.12). All count rates were corrected to the lowest sample weight for which the self-absorption curve was considered reliable; 20mg for AgCl and 20mg for chromia. At lower sample weights weighing errors become significant, and the error on the specific count rate of the sample is too large for accurate self absorption corrections to be made.

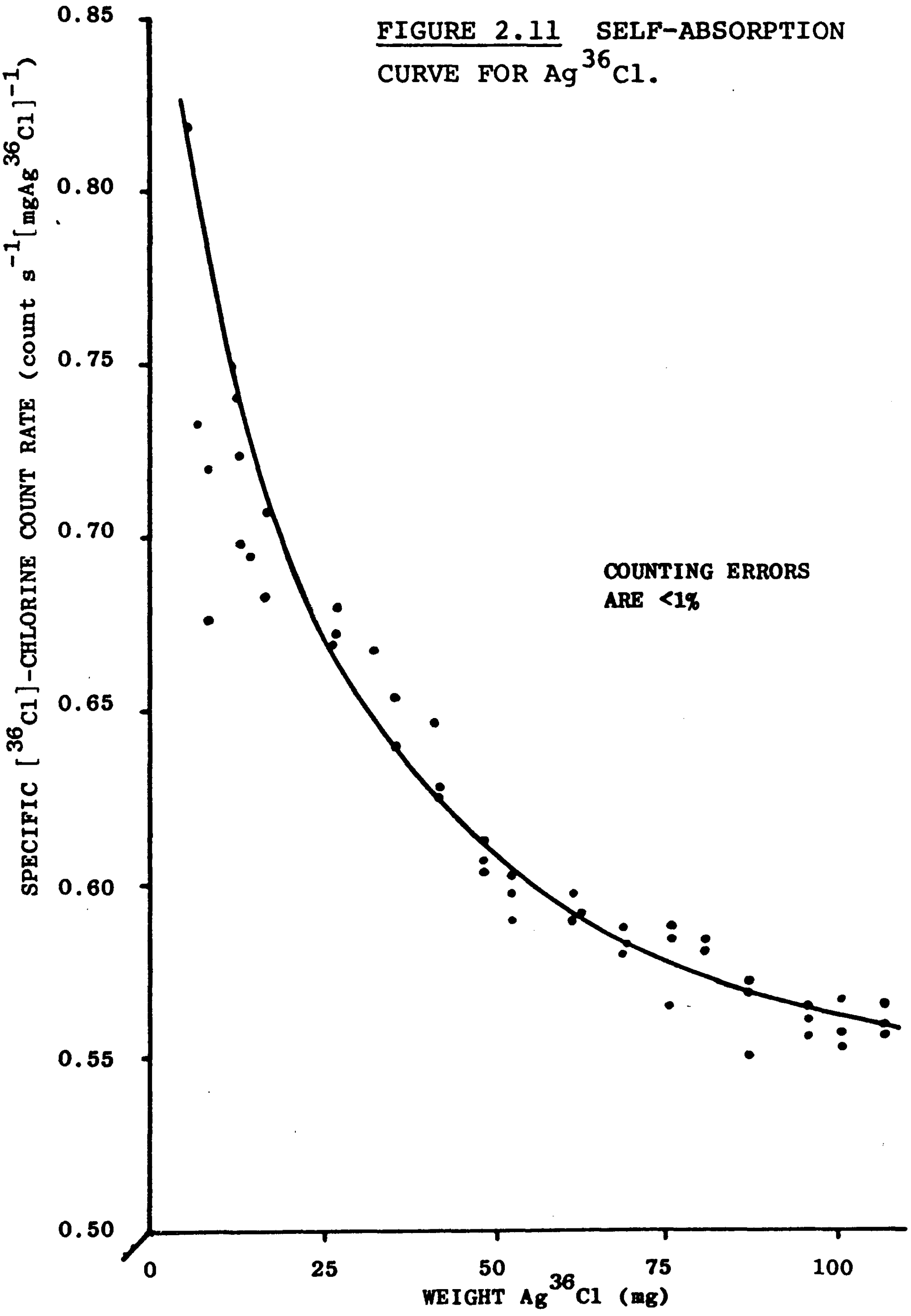


FIGURE 2.11 SELF-ABSORPTION CURVE FOR Ag^{36}Cl.

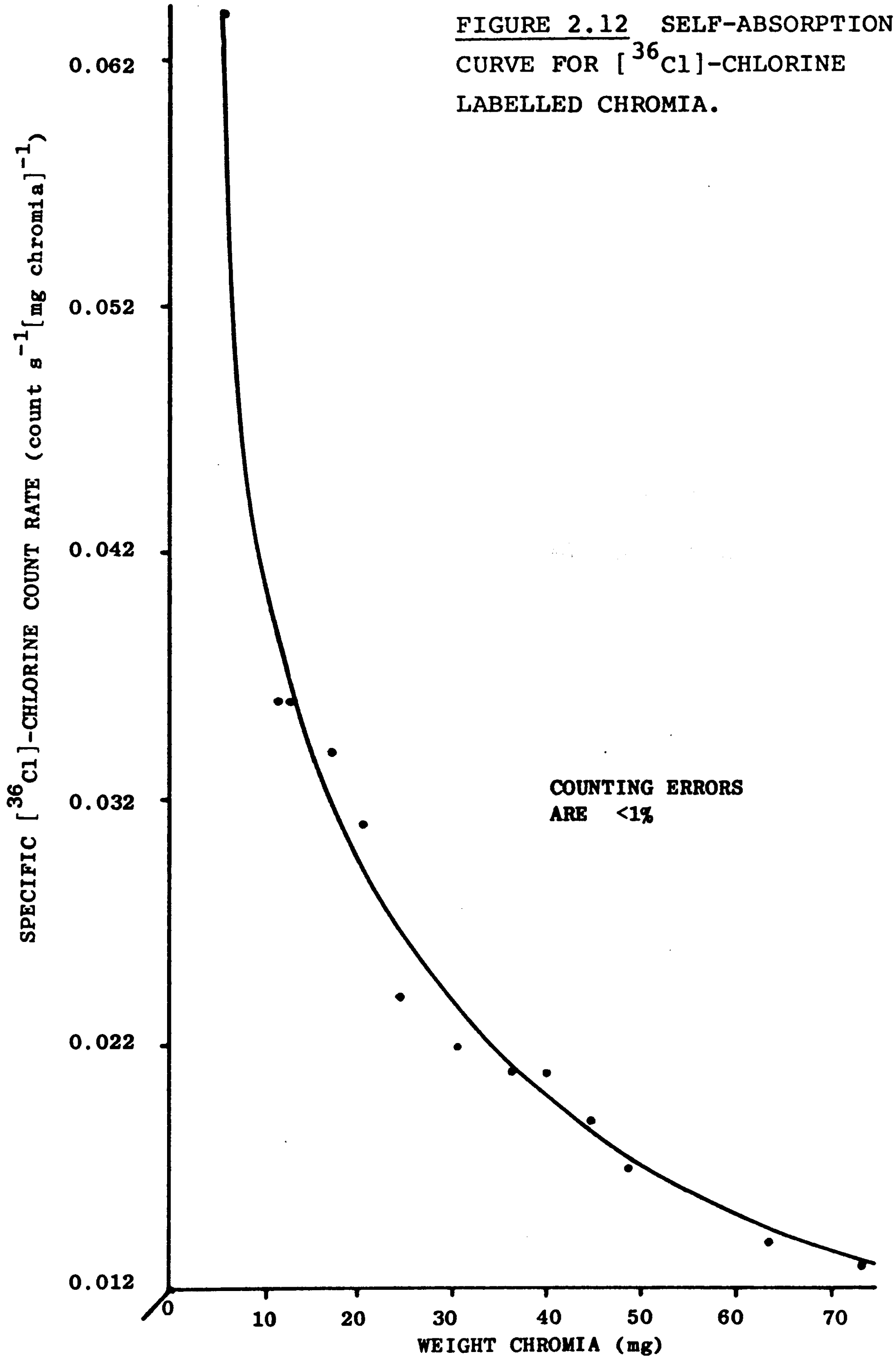


FIGURE 2.12 SELF-ABSORPTION CURVE FOR [^{36}Cl]-CHLORINE LABELLED CHROMIA.

2.9 Determination of Count Rates for [^{36}Cl]-Chlorine Adsorbed on Chromia

Unlike [^{18}F]-fluorine, [^{36}Cl]-chlorine is a β-emitter and the in-situ counting method adopted for [^{18}F]-fluorine labelled catalysts could not be used because β-particles were unable to penetrate the F.E.P side arm of the reactor. Instead, the catalyst was removed from the reactor and counted in the Geiger-Müller tube/lead castle system (Section 2.8). Since this involved exposing the catalyst to water vapour and oxygen the catalyst was not used in further experiments.

Two methods of determining [^{36}Cl]-chlorine count rates were attempted. The first involved precipitation of adsorbed [^{36}Cl]-chlorine as Ag^{36}Cl. The chromia pellets, to which H^{36}Cl or [^{36}Cl]-CCl_2FCF_3 had been admitted, were crushed and allowed to stand overnight in concentrated sodium hydroxide solution. Chloride ion was precipitated from the acidified solution as Ag^{36}Cl. However, co-precipitation of other Ag^+ salts, primarily Ag_2SO_4 from sulphate ion present in the catalyst, occurred. The varying purity of Ag^{36}Cl precipitate rendered comparison between different experiments impossible. This method of determining count rates of [^{36}Cl]-chlorine adsorbed on chromia was not, therefore, pursued.

The method adopted for obtaining [^{36}Cl]-chlorine count rates involved counting a known weight of crushed chromia pellets (ca. 50 mg). The count rates were corrected for self absorption (Section 2.8.3). Conversion of these count rates to uptakes of chlorine is discussed in detail in Section 5.2.

2.10 Determination of Chlorine Uptake on Chromia using Neutron Activation Analysis.

Chlorine uptakes on chromia were determined using neutron activation analysis, (N.A.A). N.A.A. is a non-destructive analytical technique based on activation of stable isotopes to radioactive isotopes in a beam of neutrons. The identity of isotopes is deduced from the energy of γ-rays emitted from the sample. By observing the intensity of the γ-emissions with time a count is obtained for the isotopes of interest. Since the γ-emission spectrum was observed self-absorption was not a problem and uptakes of chlorine on chromia were obtained directly from the count rate data.

The formation of a radioisotope is governed by the first order rate laws:-

rate of formation = $n\sigma\phi$

where n = number of nuclei of stable isotope.

σ = neutron capture cross section (barn)

ϕ = irradiation flux (neutrons cm^{-2} s^{-1})

rate of decay = $N\lambda$

where N = number of nuclei formed

λ = decay constant of product = $\frac{\ln 2}{t_{\frac{1}{2}}}$

$t_{\frac{1}{2}}$ = half life of isotope formed (s) overall $\frac{dN}{dt} = n\sigma\phi - N\lambda$

$$\Rightarrow N = \frac{n\sigma\phi}{\lambda}(1 - e^{-\lambda t})$$

similarly $A = n\sigma\phi\,(1 - e^{-\lambda t})$

where A = activity at end of irradiation (Bq)

Equation (2.8)

If unknown samples are irradiated with samples of known chlorine content using an identical flux, the quantity of chlorine in an unknown sample is obtained by proportion:-

$$\frac{\text{Cl in sample}}{\text{Cl in standard}} = \frac{\text{Counts from Cl in sample}}{\text{Counts from Cl in Standard}}$$

Equation (2.9)

Samples were irradiated in the Scottish Universities Research Reactor, East Kilbride using the "Rabbit Loop". Weighed samples were contained in sealed plastic vials (Figure 2.13) which were placed in the "Rabbit". The "Rabbit" (Figure 2.13) is a cylindrical plastic container which is transferred between the laboratory and the reactor by means of an evacuated loop. Care was taken to ensure that all samples were placed in similar positions in the "Rabbit" so that each were subject to an identical flux. Typical irradiation conditions were 45s at 300kw power (approximate flux 3.6×10^{12} neutrons $cm^{-2}s^{-1}$). During irradiation ^{38}Cl($t_{\frac{1}{2}}$=37.3min.) was produced by the process $^{37}Cl(n,\gamma)^{38}Cl$.

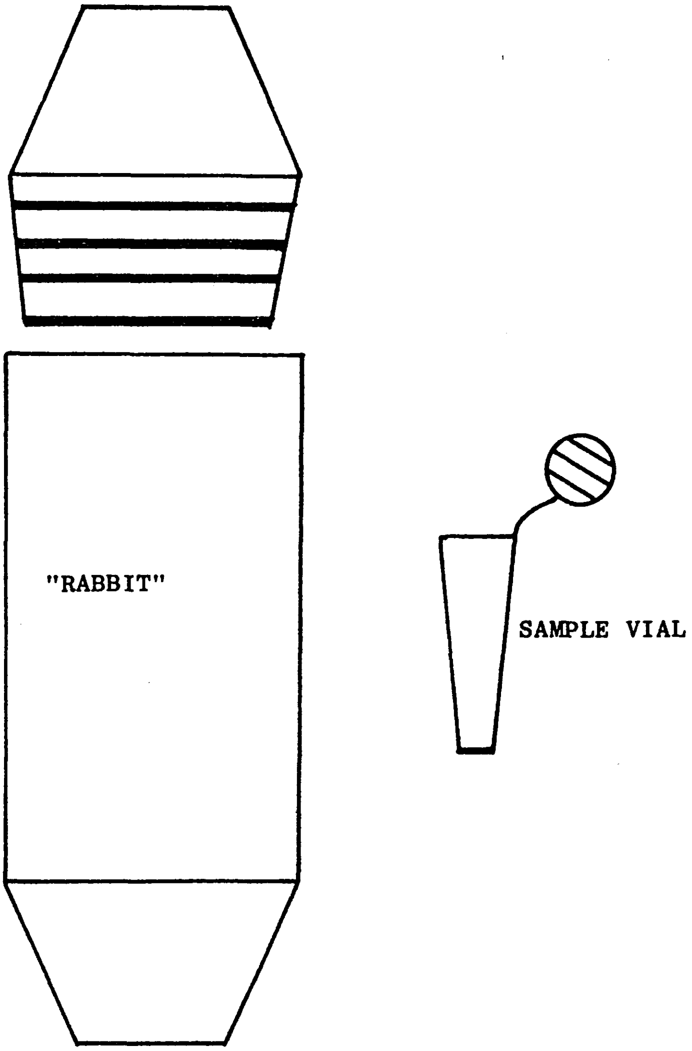
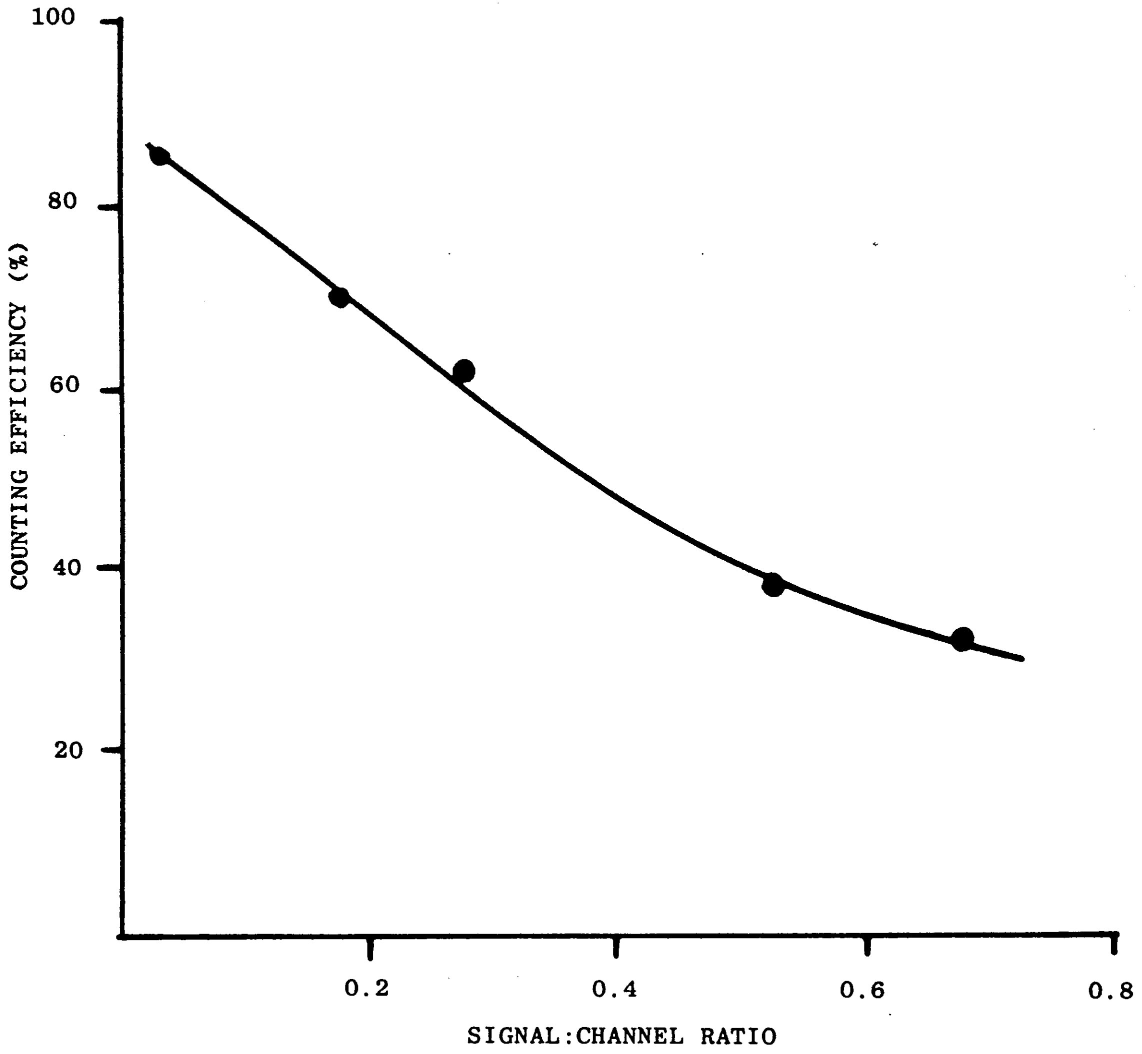


FIGURE 2.13 "RABBIT" AND SAMPLE VIAL USED IN NEUTRON ACTIVATION ANALYSIS.

The ^{38}Cl γ-emission peak (1642±0.7 keV)[67] of irradiated samples was counted on a germanium-lithium counting system (Ortec 7030) and compared with a known quantity of $MgCl_2.6H_2O$ (typically $2 \times 10^{-4} - 5 \times 10^{-5}$ mole) irradiated as a standard at the same time.

2.11 Determination of [^{36}Cl]-Chlorine Labelled Chlorofluoroethane Count Rates by Scintillation Counting

[^{36}Cl]-Chlorine in chlorofluoroethane mixtures, resulting from catalytic experiments using [^{36}Cl]-labelled chromia, was determined by liquid scintillation counting (Philips PW4700 liquid scintillation counter). The scintillation counting system was calibrated using solutions of scintillator ($2cm^3$, Packard Instagel) and [^{36}Cl]-chlorine labelled hydrochloric acid (3.7×10^3Bq), to which known quantities of $C_2Cl_3F_3$ had been added (Table 2.3). These solutions were counted and a plot of counting efficiency versus (signal : channel) ratio obtained (Figure 2.14). This "quenching curve", which is analogous to the $Ag^{36}Cl$ self absorption curve described in Section 2.8.3, was used to correct all scintillation count data to a counting efficiency of 100%. In this way specific [^{36}Cl]-chlorine activities of chlorofluoroethane fractions could be obtained.



<u>FIGURE 2.14</u> QUENCHING CURVE FOR $\left[{}^{36}Cl^{-}\right]/C_2Cl_3F_3$ MIXTURES

Table 2.3 Samples used in determination of [^{36}Cl]-chlorine/$C_2Cl_3F_3$ quenching curve

Sample.	Quantity $C_2Cl_3F_3$ added (mol)	Counts Accumulated	Efficiency %
1	0	616251	86.7
2	$3.4x10^{-4}$	500474	70.4
3	$8.2x10^{-4}$	442148	62.2
4	$1.19x10^{-3}$	269571	37.9
5	$1.71x10^{-3}$	227591	32.0

The chemical composition of samples counted by scintillation counting was determined by ^{19}F n.m.r spectroscopy (Section 2.12).

2.12 ^{19}F n.m.r. spectroscopy.

The chemical composition of samples counted by scintillation counting was determined by ^{19}F n.m.r. spectroscopy. ^{19}F n.m.r. spectra were obtained using a 100 MHz Fourier Transform n.m.r spectrometer (JEOL JNM - FX100) at 84.67 MHz. The internal reference was CCl_3F with $CDCl_3$ as an internal lock. Chemical shifts and coupling constants for chlorofluoroethanes are given in Table 2.4. All samples were volatile and the n.m.r tubes were sealed under vacuum before analysis.

Two identical samples of a given eluant fraction were obtained by distilling the fraction into one limb of an

Table 2.4 ^{19}F n.m.r spectra[a] of Chlorofluoroethanes

Compound	$\delta(CF_3)$ [ppm]	$\delta(CF_2)$ [ppm]	$\delta(CF)$ [ppm]	$^3J(FF)$ [Hz]
CCl_3CClF_2	-	64.9	-	-
CCl_2FCClF_2	-	68.0	72.0	10
CCl_3CF_3	82.2	-	-	-
$CClF_2CClF_2$	-	71.1	-	-
CCl_2FCF_3	84.2	-	76.9	8
$CClF_2CF_3$	86.3	74.7	-	<1

[a] Chemical shift with respect to CCl_3F

evacuated double limbed vessel (Figure 2.15) and admitting a portion of the sample to the second limb. One sample was then distilled into a scintillation counting vessel (Figure 2.15) containing a degassed scintillator (Packard Instagel, 2cm^3). The vessel was sealed below the crimp and the sample counted. The second sample was analysed by ^{19}F n.m.r spectroscopy.

2.13 Gas Chromatography.

On line gas chromatography was used to identify chlorofluoroethanes in the eluant gas stream of the reactor. A 3m, 0.125 inch column containing O.P.N. on Porasil C was used to separate the various product fractions. Both flame ionisation and hot wire detection were used. Hot wire detection combined with a temperature programmable oven enabled separation of the isomers of $C_2Cl_3F_3$ and $C_2Cl_2F_4$. Column conditions and retention times were as follows:-

Detection by Flame Ionisation (Perkin Elmer F11)

N_2 carrier gas
Flow rate 30 ml min^{-1}
Oven Temperature 80^oC

Fraction	Retention Time (min)
F.C.116	2.2
F.C.115	3.8
F.C.114/114a	4.8
F.C.113/113a	9.6
F.C.112/112a	18.4

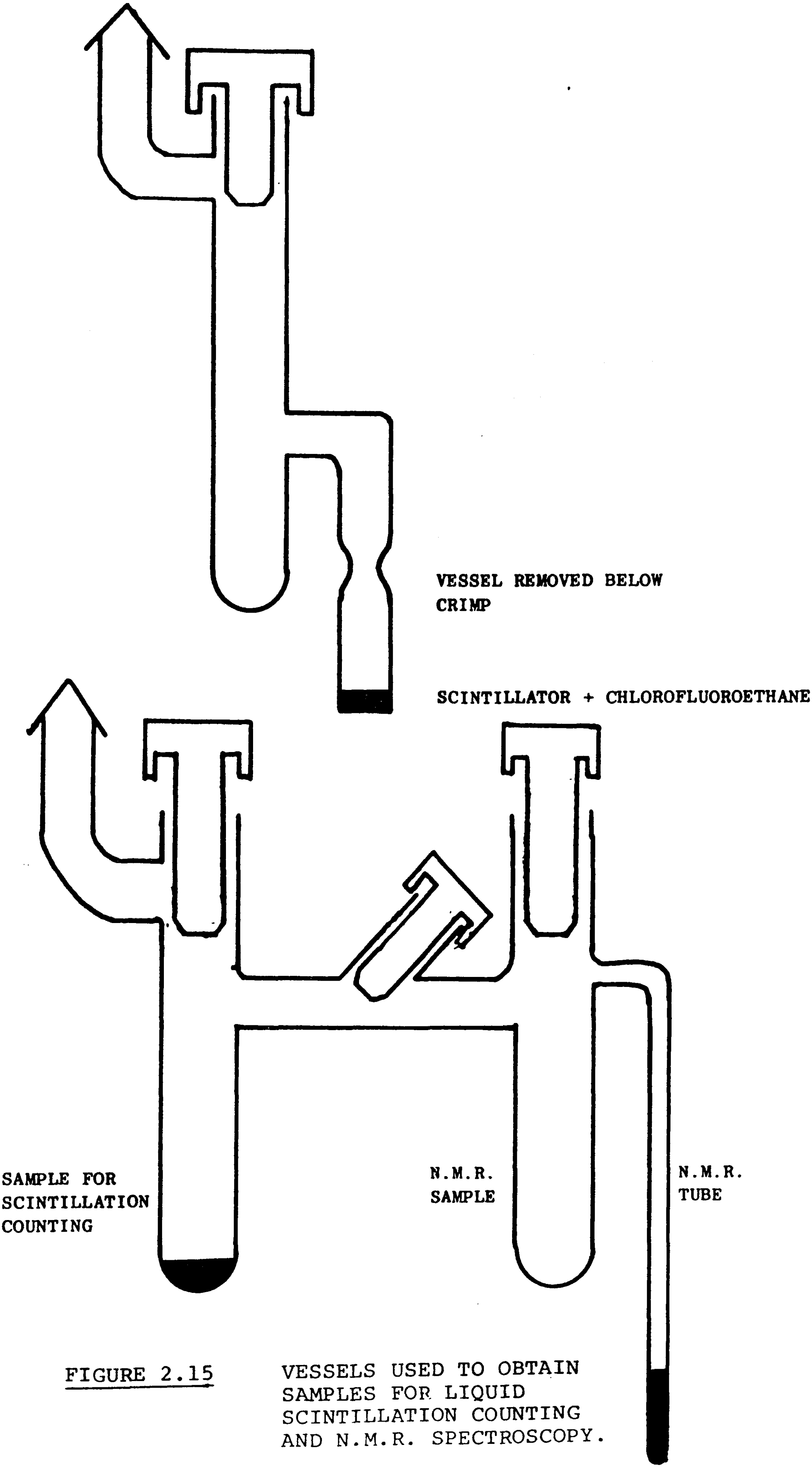


FIGURE 2.15 VESSELS USED TO OBTAIN SAMPLES FOR LIQUID SCINTILLATION COUNTING AND N.M.R. SPECTROSCOPY.

Detection by Hot Wire (Perkin Elmer 8410)

N_2 carrier gas

Flow rate 5 ml min^{-1}

Programme 1

Oven Temperature 1	30°C, 7 minutes
Oven Temperature 2	70°C, 8 minutes
Oven Temperature 3	90°C, 10 minutes

Total Analysis Time = 28 minutes

Programme 2

Oven Temperature 1	40°C, 15 minutes
Oven Temperature 2	70°C, 3.5 minutes

Total Analysis Time = 20 minutes

Separation of isomers was improved by longer residence times. However, a longer analysis increases the time required to perform a given experiment and the conditions selected are therefore a compromise.

Fraction	Retention Time (min)	
	Programme 1	Programme 2
F.C.115	8.9	6.2
F.C.114	15.0	14.2
F.C.114a	15.6	14.8
F.C.113	24.6	-
F.C.113a	24.9	-

2.14 Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy.

Diffuse Reflectance Infra-red Fourier Transform (D.R.I.F.T.S) spectra were obtained using a D.R.I.F.T.S. cell (Spectra-Tech. Inc.) attached to a Fourier Transform Infra-red Spectrometer (Nicolet 5DXC FTIR). The cell consisted of four flat and two aspherical mirrors to focus and collect infra-red energy on to or from the sample (Figure 2.16).

Before use the D.R.I.F.T.S. cell was aligned using a small mirror, M4, in place of a sample. Mirrors M1 - M3 and M5 - M7 were adjusted to achieve the maximum throughput of energy. (Following alignment no further adjustments of mirrors M1, M2, M6 and M7 were necessary). Fine adjustments of mirrors M3 and M5 were usually necessary when samples were changed since the height of the sample in the sample cup was not exactly reproducible between experiments. The D.R.I.F.T.S. cell was provided with an evacuable shroud fitted with KBr windows. When this shroud was fitted, chlorofluoroethane adsorbate could be expanded on to or evacuated from the sample. Samples of chromia were dispersed in diamond dust (1-5% w/w chromia) and finely ground before use.

Peak intensities in transmission spectra are expressed in either transmission or absorbance units, but for reflectance spectra Kubelka-Munk Units[67] are used. These units are a function of reflectance where

$$f(R) = \frac{(1-R)^2}{2R}$$

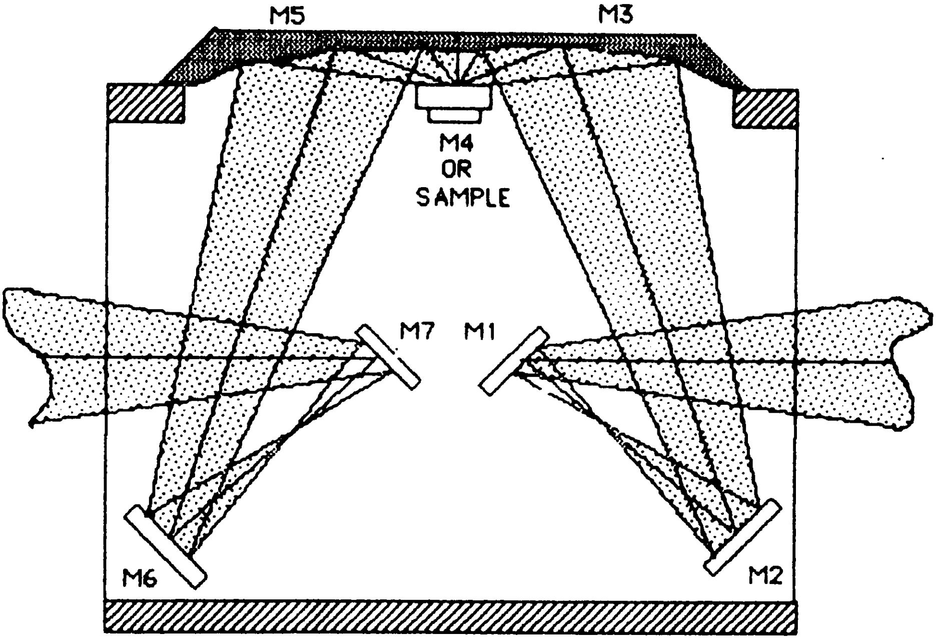


FIGURE 2.16 D.R.I.F.T.S. CELL

where R is the reflectance at infinite depth.

Equation (2.10)

However, the Nicolet 5DXC F.T.I.R. does not have the facility to plot spectra in Kebelka-Munk units. Instead, spectra are plotted using the absorbance plot made giving a y-scale of "absorbance units". The use of this arbitrary scale does not affect interpretation of the results since the work presented is not quantitative.

2.15 Surface Area Determinations.

Surface areas of chromia were determined using the Brunauer, Emmett and Teller (B.E.T) method[69] with dinitrogen as adsorbate. The quantity of nitrogen required to form a monolayer on the surface of a solid is determined using the B.E.T. equation

$$\frac{P}{x(p_o-p)} = \frac{1}{x_m c} + \frac{1}{x_m} \cdot \frac{P}{Po}$$

where x is the number of molecules adsorbed at pressure p

po is the saturated vapour pressure of the gas at the adsorption temperature

c is a constant for the particular gas/solid system under study.

x_m is the number of molecules required to form a monolayer on the solid surface.

Equation (2.11)

The apparatus used is shown in Figure 2.17.

The amount of dinitrogen adsorbed is determined by taking the difference between the measured volume of gas in the manometer and the volume expected on the basis of the gas laws if there had been no adsorption. For this reason the "dead volumes", sections A and B in Figure 2.17, were determined using helium, since it is not adsorbed to any appreciable extent, even at 77K.

Volume A was determined with Volume B evacuated and helium in A. The height of mercury in the U-tube was varied by varying the height of the mercury reservoir and a set of readings of V and P obtained. By the gas laws

$$(V+A) = \frac{kT}{P}$$

<u>where</u> k is a constant whose value depends on the size of the helium sample taken (cm^3 torr K^{-1})

A is the dead volume above the zero mark on the burette (cm^3)

T is the temperature (K)

P is the pressure (torr)

<u>Equation (2.12)</u>

A plot of V against $T/_P$ has slope k and intercept -A. Volume B was determined using the same sample of helium but with the sample cooled to 77K and volume B open to the apparatus (Equation (2.12))

$$(V+A+B) = kT/_P$$

<u>Equation (2.13)</u>

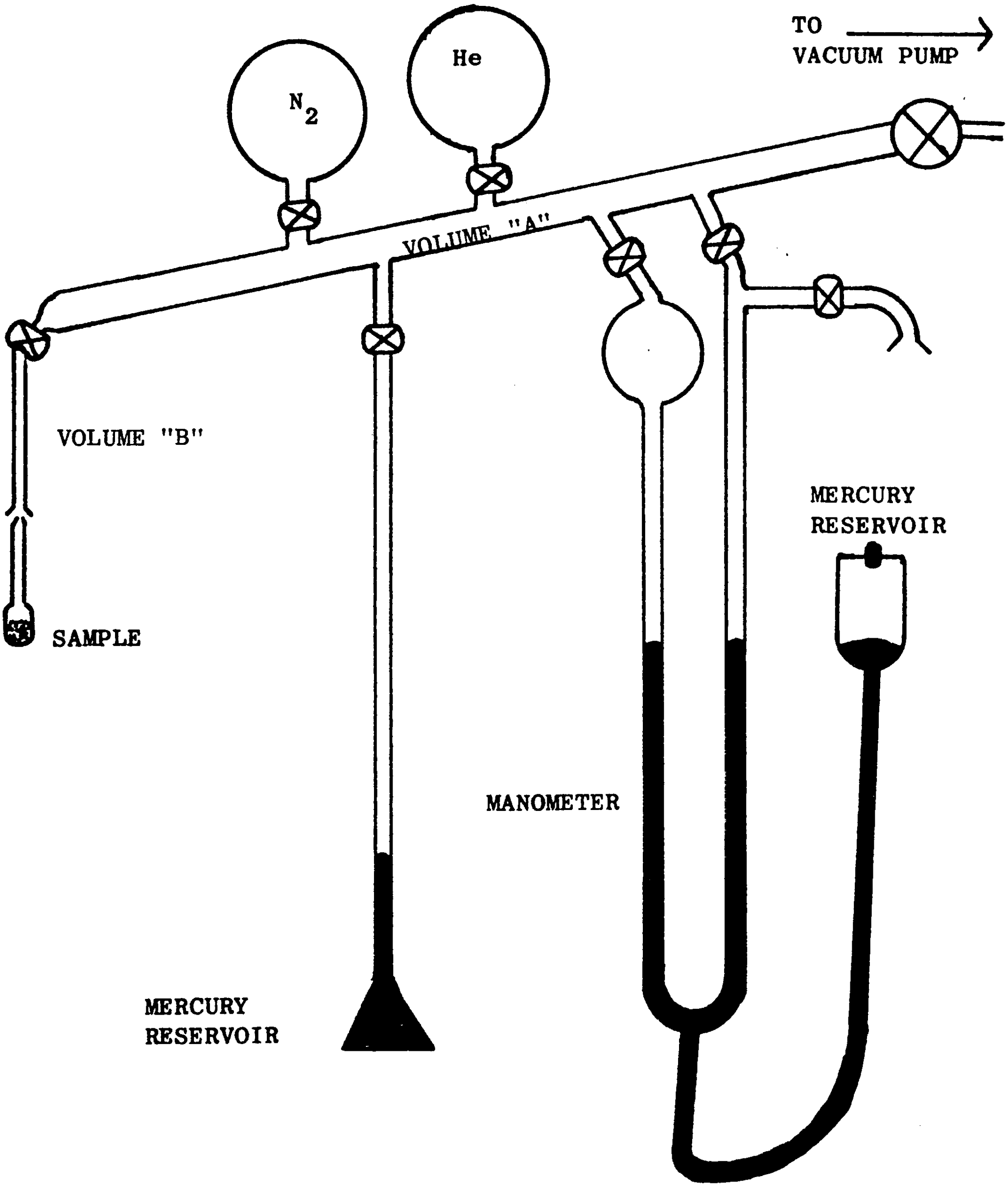


FIGURE 2.17 B.E.T. APPARATUS FOR DETERMINATION OF SURFACE AREAS.

A plot of V against $T/_{p}$ has slope k and intercept -(A+B).

This procedure was repeated for dinitrogen at room temperature and at 77K to give two further plots of V against $T/_{p}$ with different slopes but identical intercepts to the corresponding helium determinations. On the basis of no adsorption, the 77K data for dinitrogen should fit a line parallel to the room temperature isotherm for dinitrogen with an intercept -(A+B). At any pressure, the difference between the volume coordinate on this line and that on the experimental line is the volume adsorbed measured at the appropriate pressure. The number of molecules adsorbed, x, is given by

$$x = \frac{P\Delta V}{T} \quad x \quad \frac{N}{R}$$

<u>where</u>

P is in torr

ΔV is in cm^3

T is in K

N is Avogadro's Number

R is the gas constant in $cm^3 torrK^{-1} mol^{-1}$

<u>Equation (2.14)</u>

From the B.E.T. equation (Equation 2.11) a plot of $\frac{p}{x(po-p)}$ against $\frac{p}{po}$ is a straight line of slope $1/_{x_m}$. From this surface areas were calculated by assuming that each nitrogen molecule occupied 16.2 $Å^2$ of surface.

A surface area determination on chromia treated with hydrogen fluoride is tabulated in Table 2.5. Plots of V versus $T/_{p}$ under the various conditions used and $\frac{p}{x(po-p)}$

versus $^P/_{P_O}$ are shown in Figures 2.18 and 2.19 respectively. From Figure 2.19;

$$\text{Gradient} = (2.68 \pm 0.13) \times 10^{-20} (\text{molecules})^{-1}$$

$$= \quad x_m = (3.73 \pm 0.19) \times 10^{19} \text{ molecules}$$

For a sample mass of 0.1951g this is equivalent to a surface area of 30.9±1.5 $m^2 g^{-1}$.

Table 2.5 Surface Area Determination on a Prefluorinated Chromia Pellet.

	Volume(cm^3)	Pressure(torr)	$^T/_P$
Helium at 298.3 K	55.56	273.56	1.09
	64.32	255.09	1.17
	68.68	246.69	1.21
	74.80	237.02	1.26
	85.00	221.37	1.34
	92.94	209.94	1.42
Helium at 77 K	54.36	167.06	1.78
	62.40	160.32	1.86
	68.52	156.05	1.91
	73.72	152.33	1.95
	83.88	145.71	2.04
	90.96	141.04	2.11
Nitrogen at 296.9 K	68.36	361.39	0.82
	73.28	347.94	0.86
	77.24	339.25	0.88
	83.16	326.30	0.91
	86.64	317.58	0.94
	92.28	306.87	0.97
Nitrogen at 77 K	52.96	240.74	1.24
	61.20	230.60	1.29
	68.32	223.24	1.33
	73.80	217.85	1.37
	84.80	206.34	1.44
	90.76	202.32	1.47

Table 2.5 contd.

$^{T}/_{P}$ (Ktorr^{-1})	ΔV(cm^3)
1.00	9.0
1.05	9.5
1.10	10.0
1.15	10.5
1.20	11.0
1.25	11.5
1.30	12.0

$$x = \frac{P\Delta V}{T} \times 9.6\times10^{18} = 8.79\times10^{19} \text{ molecules}$$

P	x10^{22} $\frac{P}{x(po-p)}$	$^{P}/_{Po.}$
297.7	74.0	0.392
283.5	68.4	0.373
270.6	63.6	0.356
258.8	59.3	0.340
248.0	55.7	0.326
238.1	52.4	0.313
229.0	49.6	0.301

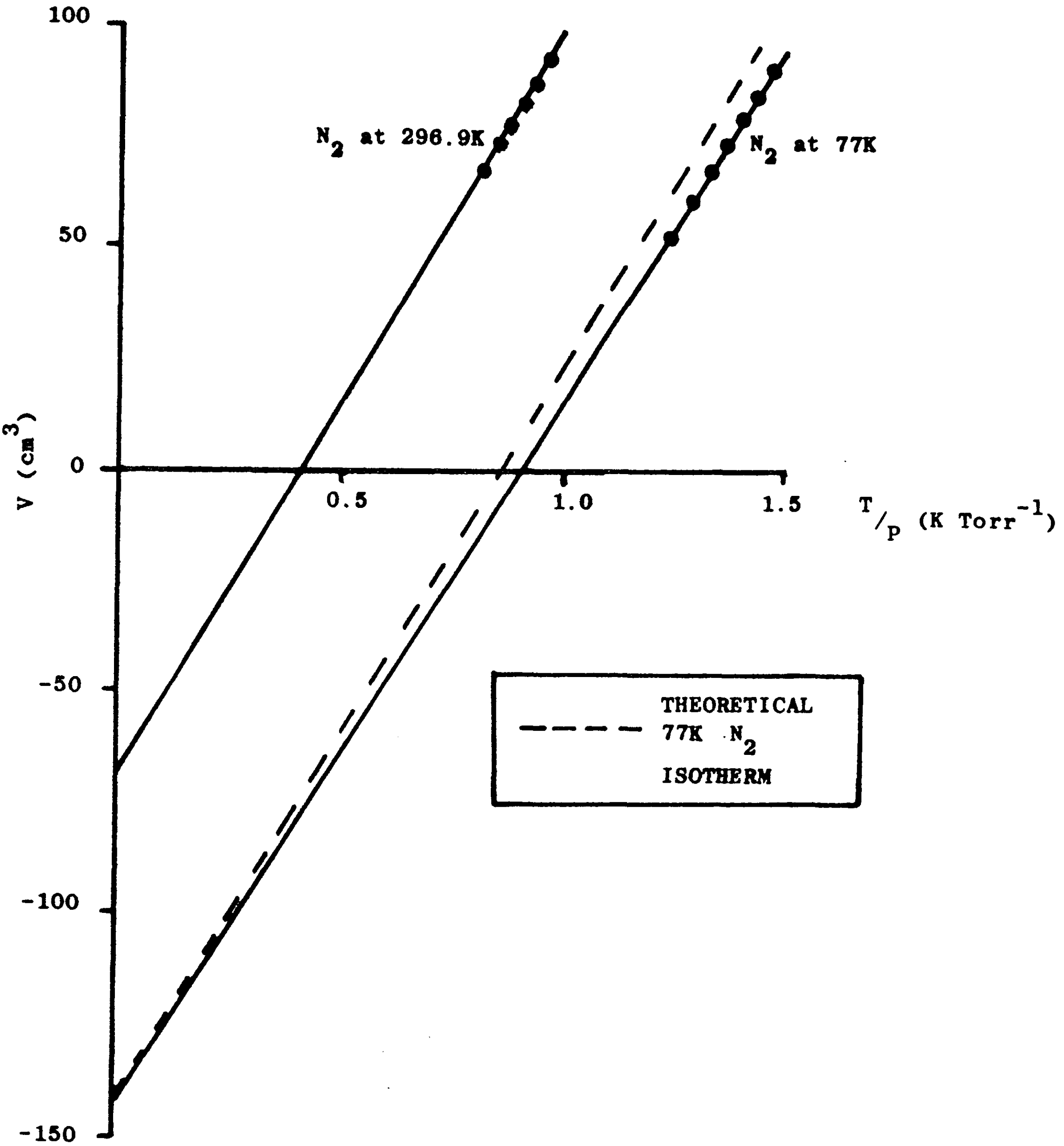
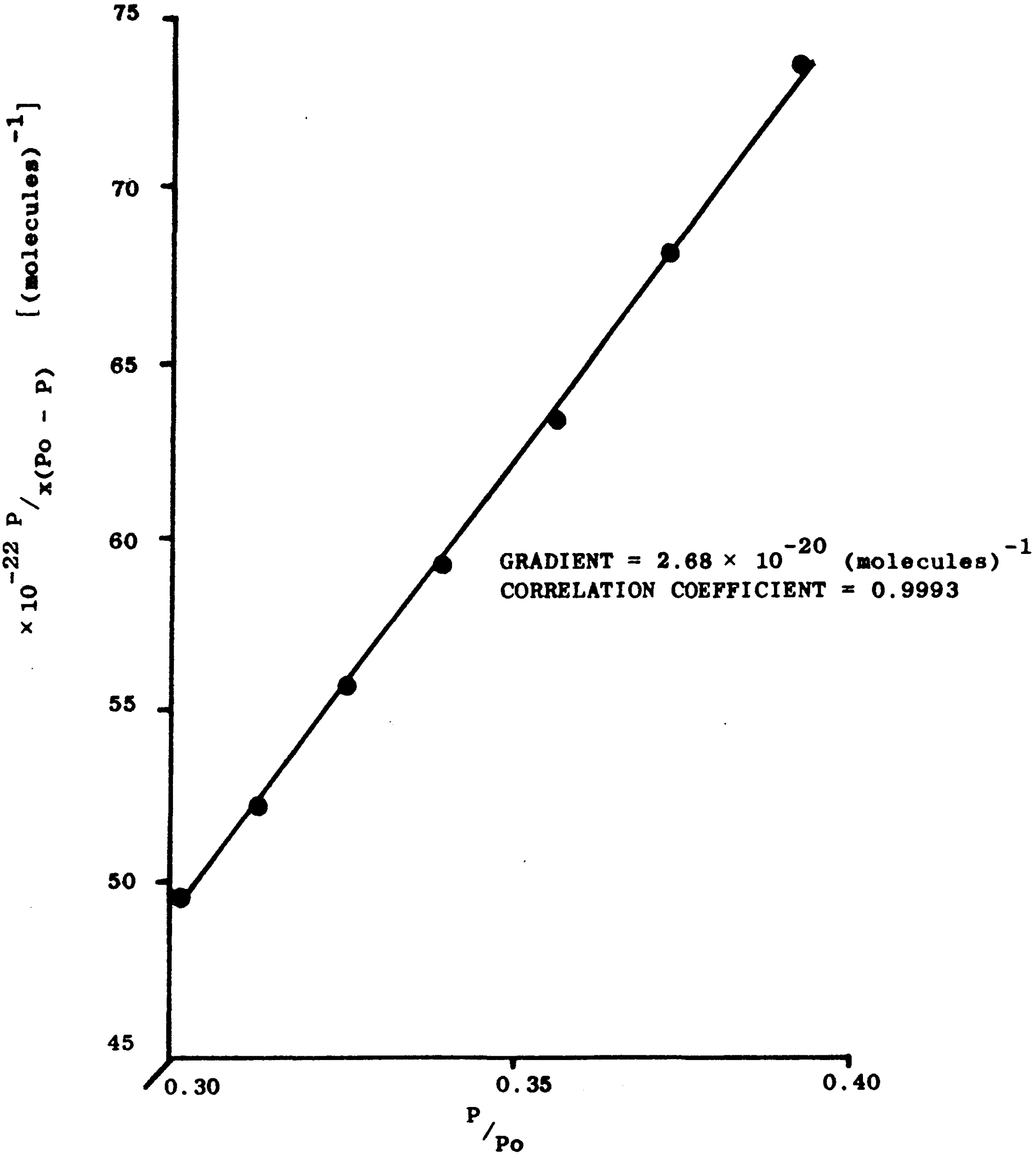


FIGURE 2.18 SURFACE AREA DETERMINATION ON CHROMIA CATALYST PREVIOUSLY TREATED USING HF.

FIGURE 2.19 $\frac{P}{x(Po - P)}$ versus $P/_{Po}$

DATA FROM FIGURE 2.18



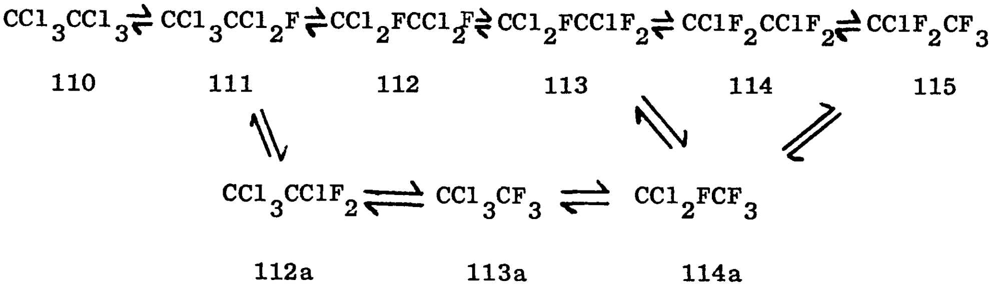
CHAPTER THREE

CHEMISTRY OF THE VAPOUR PHASE PROCESS

CHAPTER THREE.

Chemistry of the Vapour Phase Process.

The reaction of hexachloroethane with anhydrous hydrogen fluoride on chromia to form chloropentafluoroethane involves a series of reactions in which chlorine is replaced by fluorine (Scheme 3.1)



All reactions are shown as reversible
to illustrate the potential chemistry
involved.

Scheme 3.1

Experimentally, the formation of C_2ClF_5 is best studied using $C_2Cl_3F_3$ or $C_2Cl_2F_4$ as the reactant, since the number of different products to be determined is smaller than in the full reaction sequence starting from C_2Cl_6. Using $C_2Cl_3F_3$ as the reactant produces relatively more of the chlorinated products than is the case when $C_2Cl_2F_4$ is the reactant and ideally $C_2Cl_3F_3$ would be selected for a study of surface-chloride species and chlorination reactions. However, the principal chlorinated product from reaction of $C_2Cl_3F_3$ at 623 K on pre-fluorinated chromia is the involatile compound $C_2Cl_4F_2$, whereas using $C_2Cl_2F_4$ as the reactant gives the volatile compound $C_2Cl_3F_3$ as the main chlorinated product. Formation of involatile compounds leads to blockage of the reactor and to eliminate this problem $C_2Cl_2F_4$ was used as the reactant for most of the experiments described in this thesis.

3.1 Reaction of $C_2Cl_2F_4$ on Chromia at 703 K.

The reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia at 703 K was studied to establish a set of product distribution data to which subsequent experiments could be related. Product analysis was by on-line gas chromatography and ^{19}F n.m.r spectroscopy.

Reacting $C_2Cl_2F_4$ (mole ratio $CClF_2CClF_2:CCl_2FCF_3 = 17:1$ by ^{19}F n.m.r spectroscopy) at a $N_2/C_2Cl_2F_4$ flow rate of 23.5 ± 3.6 cm^3min^{-1} and a temperature of 703 K, produced fluorinated products (C_2ClF_5 and trace C_2F_6) comprising _ca_. 25 mol % of the reactor eluant gases. Chlorinated products ($C_2Cl_3F_3$ and trace $C_2Cl_4F_2$) comprised _ca_. 12 mol % and $C_2Cl_2F_4$ _ca_. 63 mol %. (Figure 3.1). At a lower $N_2/C_2Cl_2F_4$ gas flow rate (15 ± 1 cm^3 min^{-1}) production of fluorinated products increased substantially (Figure 3.2) and they comprised _ca_. 47 mol % of the eluant. Chlorinated products accounted for _ca_. 9 mol % and $C_2Cl_2F_4$, 44 mol %. C_2F_6 and CCl_3CClF_2 were present in trace quantities (<2 mol %). The isomer CCl_2FCCl_2F was not detected. A similar experiment with $N_2/C_2Cl_2F_4$ gas flow at a rate of 110 cm^3 min^{-1} gave only trace (<2 mol %) quantities of C_2ClF_5 with no detectable chlorinated products. The flow rate is related to the contact time between a reacting molecule and the catalyst so that, as the gas flow rate is increased, the

FIGURE 3.1 REACTION OF $C_2Cl_2F_4$ AT 703K TO FORM C_2ClF_5 AND $C_2Cl_3F_3$.

Mole Ratio F.C.114:114a = 17:1

Gas Flow Rate ($C_2Cl_2F_4$ + N_2) = 23.5±3.6 cm^3min^{-1}.

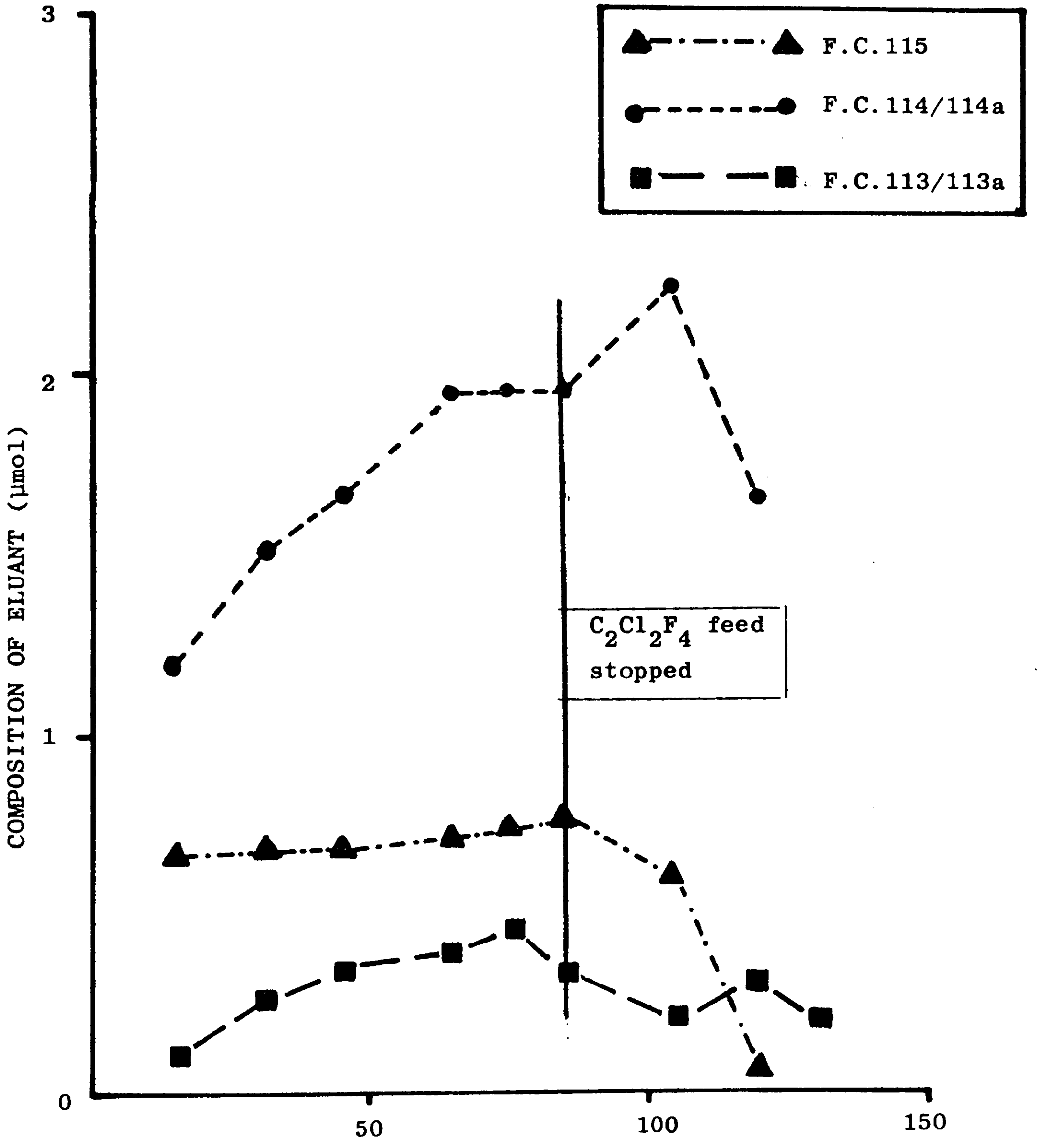
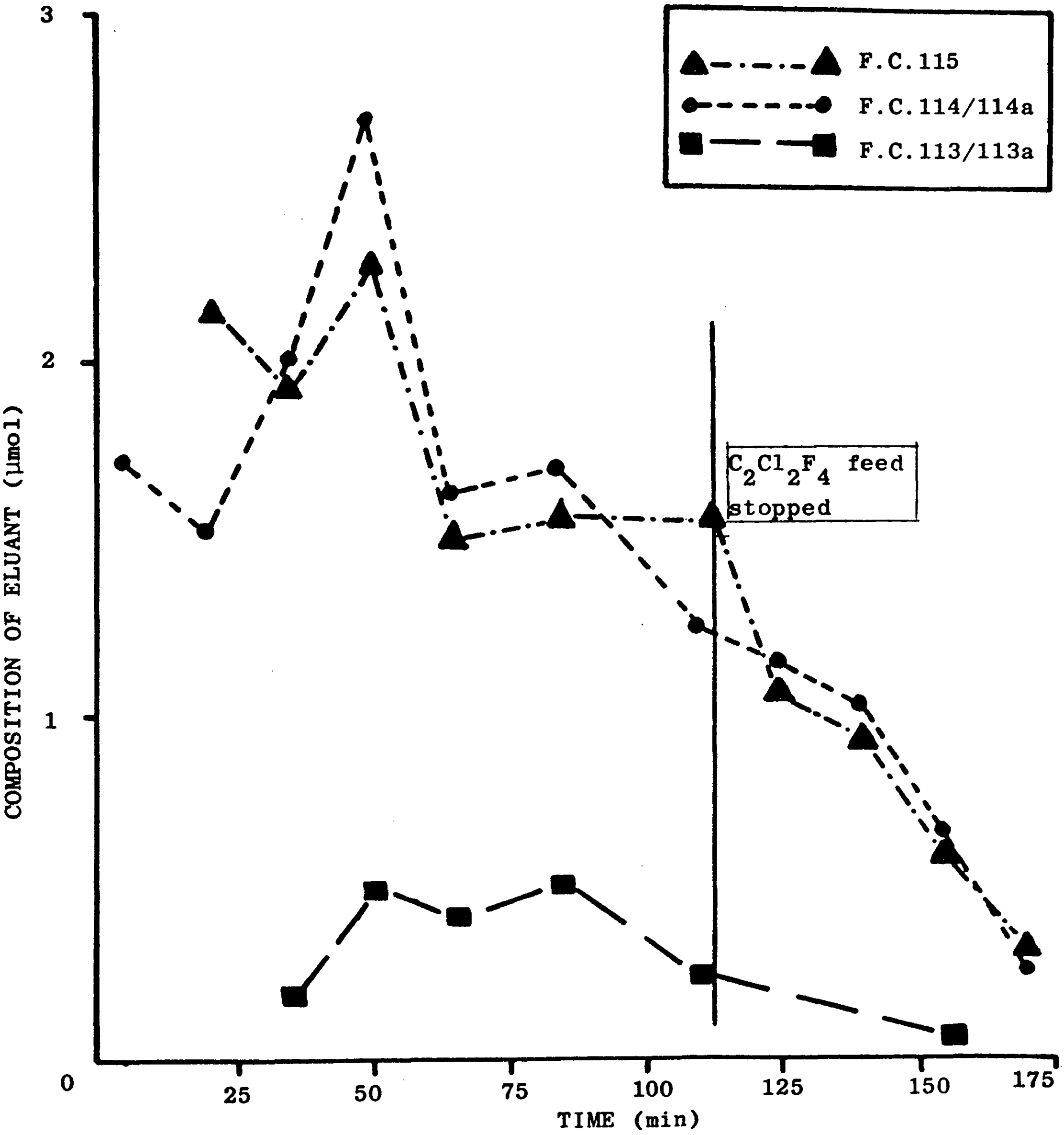


FIGURE 3.2 REACTION OF $C_2Cl_2F_4$ AT 703K TO FORM C_2ClF_5 AND $C_2Cl_3F_3$.
Mole Ratio F.C.114:114a = 17:1
Gas Flow Rate ($C_2Cl_2F_4$ + N_2) = 15±1 $cm^3 min^{-1}$



contact time decreases. The contact time between reacting molecules and chromia is an important factor in determining the extent to which reaction occurs.

The concentration of asymmetric isomers in the reactor eluant, determined by ^{19}F n.m.r spectroscopy, was much higher than might be expected on the basis of a symmetric:asymmetric isomer ratio of 17:1 in the reacting $C_2Cl_2F_4$. In Run 1 (Figure 3.1) the ratio of symmetric:asymmetric isomers in the reactor eluant was 2.1:1 for $C_2Cl_2F_4$ and 0.3:1 for $C_2Cl_3F_3$. The corresponding ratios for Run 2 (Figure 3.2) were 1.6:1 for $C_2Cl_2F_4$ and 3.9:1 for $C_2Cl_3F_3$. The relative increase in the concentration of asymmetric isomers can be interpreted as indicating either that the symmetric isomers of $C_2Cl_2F_4$ and $C_2Cl_3F_3$ react more readily than the asymmetric isomers, or that a reaction pathway leading to formation of asymmetric isomers from $CClF_2CClF_2$ is involved. However, $C_2Cl_2F_4$ comprising predominantly the asymmetric isomer (mole ratio $CClF_2CClF_2:CCl_2FCF_3 = 1:19$) reacted to form ca. 85 mol % C_2ClF_5 at a $N_2/C_2Cl_2F_4$ gas flow rate of 20 cm^3 min^{-1} and a temperature of 693 K. This observation is consistent with the greater ease of fluorination of CCl_2FCF_3 compared with $CClF_2CClF_2$ reported in other studies.[22]

3.2 Extended Reaction of $C_2Cl_2F_4$ on Pre-fluorinated Chromia.

In order to establish the quantity of C_2ClF_5 which can be produced for a given catalyst pre-treatment, a total of 0.16 mol $C_2Cl_2F_4$ (mole ratio $CClF_2CClF_2:CCl_2FCF_3 = 57:43$) was admitted over several experiments to chromia pre-treated with 0.6 mol HF at 623 K. Analysis of the reactor eluant was by gas chromatography.

During the first admission of $C_2Cl_2F_4$ to the catalyst at 693 K, C_2ClF_5 comprised ca. 23 mol % of the eluant. Chlorinated products comprised ca. 12 mol % , principally $C_2Cl_3F_3$, with $C_2Cl_4F_2$ in trace amounts. $C_2Cl_2F_4$ comprising ca. 65 mol % was also detected (Table 3.1). Reaction of further aliquots of $C_2Cl_2F_4$ formed slightly lower concentrations of C_2ClF_5 in the eluant, but 18.6 mol % was the lowest determined.

There are two sources of fluorine in the vapour-phase system; HF adsorbed on chromia and fluorine originating from the chlorination of $C_2Cl_2F_4$ to $C_2Cl_3F_3$. In any of the mechanisms proposed to account for the product distributions[17,23,24,25] formation of a chlorinated product is accompanied by the release of a fluorine atom which is then available for a fluorination reaction. The amount of fluorine which must have originated from HF can therefore be calculated by subtracting the number of moles of chlorinated product from the number of moles of fluorinated product. This assumes that no product differs from the reactant by more than one halogen atom, that is only $C_2Cl_3F_3$ and C_2ClF_5 are formed from reaction of $C_2Cl_2F_4$. Since $C_2Cl_4F_2$ and C_2F_6 were present in the eluant only at trace level, this is a reasonable assumption. Mass balances calculated from G.C. data were >92% in all cases. On this basis 25 mmol of fluorine originated from the HF pre-treatment which was equivalent to 4.4 mmol fluorine (g catalyst)$^{-1}$

adsorbed during pre-treatment (Table 3.1).

To check whether any reaction was occurring on the walls of the Monel metal reactor a similar experiment was undertaken with the catalyst contained within a glass U-tube. Since the catalyst had been pre-fluorinated using reactor A there was no opportunity for the U-tube to absorb HF during the catalyst pre-treatment. A stream of $C_2Cl_2F_4$ (mole ratio $CClF_2CClF_2:CCl_2FCF_3 = 57:43$) was admitted to the catalyst (0.59g, 683-693 K) over 345 min. The total gas flow rate (N_2+$C_2Cl_2F_4$) was 4-5 cm^3 min^{-1} with $C_2Cl_2F_4$ fed at ca. 0.02 mmol min^{-1}. Etching of the glass U-tube occurred during the reaction. This phenomenon is characteristic of the reaction of HF with silica to form silicon tetrafluoride. The source of HF for the etching process must have been the pre-fluorinated catalyst.

The composition of the eluant from reaction of $C_2Cl_2F_4$ was C_2ClF_5, ca. 30 mol %, and $C_2Cl_3F_3$, ca. 5 mol % (Figure 3.3). Fluorine not accounted for by chlorination reactions was 1.7 mmol, or 2.9 mmol fluorine (g catalyst)$^{-1}$ adsorbed during the HF pre-treatment. The chlorofluoroethane mass balance for this reaction is not available and therefore a fluorine mass balance cannot be inferred in this case. Nevertheless, chromia pre-treated with hydrogen fluoride is clearly a substantial and long term source of fluorine for the reactions of $C_2Cl_2F_4$.

Table 3.1 Extensive Reaction of $C_2Cl_2F_4$ on Pre-fluorinated Chromia at 698 K.

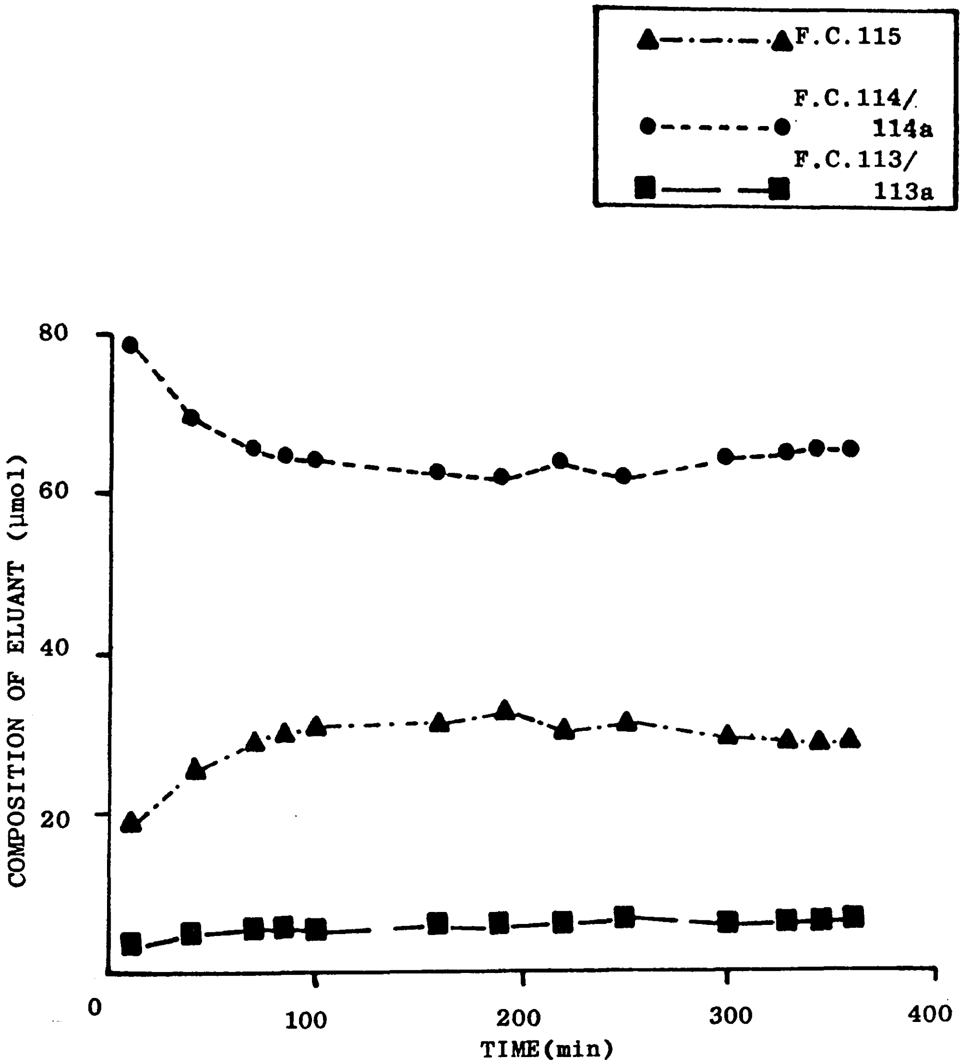
Run	Pre-treatment	$C_2Cl_2F_4$ Admitted (mol)	Products (mol %)(1)	
			Fluorinated	Chlorinated
1	N_2 gas, 4h, 623 K HF, 0.6 mol, 623 K	0.020	23.1	12.1
2	none	0.040	18.6	7.9
3	none	0.020	n/d	n/d
4	none	0.053	19.2	10.2
5	none	0.031	19.6	9.5

Note: (1) Fluorinated products, C_2ClF_5 and C_2F_6 (trace)
Chlorinated products, $C_2Cl_3F_3$ and $C_2Cl_4F_2$ (trace)
Products determined by gas chromatography.

n/d = not determined.

FIGURE 3.3 EXTENDED REACTION OF $C_2Cl_2F_4$ AT 683-693K.

Mole Ratio F.C.114:114a = 57:43



3.3 Reaction of Chlorofluoroethane and Hydrogen Chloride on Extensively Fluorinated Chromia.

The reactions of $C_2Cl_3F_3$ and $C_2Cl_2F_4$ on chromia subjected to extensive HF pre-treatment were studied. Pre-treatment of the catalyst using HF followed by HCl might be expected to increase the proportion of chlorinated products formed. Hydrogen chloride was admitted to the catalyst following HF pre-treatment in certain of the experiments described here.

As shown in Table 3.2, Run 1, $C_2Cl_2F_4$ did not react on chromia which had not been pre-treated with HF, even when the catalyst was dried at 623 K in a stream of dinitrogen for 4h. Following admission of HF at 623 K, $C_2Cl_3F_3$ reacted to form $C_2Cl_2F_4$ and $C_2Cl_4F_2$ as the major products. Further HF treatments, some of which were followed by admission of HCl (Table 3.2), appear to have reduced the activity of the catalyst towards fluorination and chlorination of $C_2Cl_2F_4$ (Table 3.2, Runs 3 and 4). In Run 3, reaction of $C_2Cl_2F_4$ at 703 K formed _ca_. 1.3 mol % C_2ClF_5 and _ca_. 1.0 mol % $C_2Cl_3F_3$ + $C_2Cl_4F_2$. $C_2Cl_2F_4$ comprised _ca_. 97.7 mol % of the reactor eluant. The extent of reaction was found to increase following further catalyst treatment with HF (Table 3.2, Run 4) but the concentrations of fluorinated and chlorinated products remained significantly smaller than those observed during Run 2. No reaction was observed when $C_2Cl_2F_4$ was admitted to the catalyst at 703 K following further HF and HCl treatment (Table 3.2, Runs 5 and 6). Raising the temperature of the catalyst to 783 K during the

Table 3.2 Product Distributions for Reaction of Chlorofluoroethanes on Extensively Fluorinated Chromia - Calculated from ^{19}F n.m.r. Data

Run	Reactant (1)	HF admitted in Pre-treat ment. (cm3 liquid)	Temperature (K)	Flow Rate ($cm^3 min^{-1}$)	Mass Balance (from n.m.r) (%)	Product Distribution (mol % from nmr samples)						Isomer Ratios	
						112a	113	113a	114	114a	115	114:114a	113:113a
1	$C_2Cl_2F_4$	0	693	27±4	-	0	0	0	94	6	0	16:1	-
2	$C_2Cl_3F_3$	9	623	30±12	66.3	5.20	70.96	1.31	17.31	4.33	-	4:1	51.6:1
3	$C_2Cl_2F_4$	19+4cm^{3}HCl	693	8.6±4.6	85.1	0.06	0.75	0.23	89.97	8.99	1.28	10:1	3.25:1
4	$C_2Cl_2F_4$	44.5	703	17.7±3.6	77.6	0.09	1.68	0.43	81.88	7.31	8.61	11.2:1	3.9:1
5	$C_2Cl_2F_4$	19+5cm^{3}HCl	703	31.5±10.3	81.8	-	-	-	92.30	7.70	-	12:1	-
6	$C_2Cl_2F_4$	14	703	31.7±2.3	94.6	-	-	-	93.41	6.59	-	14.2:1	-
7	$C_2Cl_2F_4$	11	783	32.9±0.9	97.1	0.12	0.62	0.31	89.51	6.28	3.45	14.3:1	2.0:1

NOTE: (1) Mole Ratio 114:114a in $C_2Cl_2F_4$ = 17:1

Reactant $C_2Cl_3F_3$ contains 113a at trace level (<2 mol %)

admission of $C_2Cl_2F_4$ resulted in the formation of small quantities of C_2ClF_5 and $C_2Cl_3F_3$ (Table 3.2, Run 7).

During Runs 3 - 7 the activity of the catalyst towards fluorination and chlorination of $C_2Cl_2F_4$ was small in comparison with the activity achieved previously. However, the ratios of symmetric:asymmetric isomers in eluant $C_2Cl_3F_3$ were very different from those expected on the basis of the isomer ratio in the reactant $C_2Cl_2F_4$ (mole ratio symmetric: asymmetric = 17:1), especially when so little reaction to form C_2ClF_5 and $C_2Cl_3F_3$ had occurred. Symmetric: asymmetric isomer ratios in eluant $C_2Cl_2F_4$ were in the range 10.0:1 - 14.3:1 but those for eluant $C_2Cl_3F_3$ were in the range 2.0:1 - 3.3:1 (Table 3.2). There was no relationship between the flow rate of $N_2/C_2Cl_2F_4$ vapour over chromia and the isomer ratio in eluant $C_2Cl_3F_3$.

The fluorine content of the inactive catalyst, determined by microanalysis, was 5.5% w/w, considerably less than extensively fluorinated catalysts, which were still active towards fluorination and chlorination at 703 K (Table 3.3). The surface area of the inactive catalyst was $30.9 \pm 1.5\ m^2g^{-1}$, which was typical for active pre-fluorinated chromias and above that of active, extensively fluorinated chromias which had surface areas ca. 13 m^2g^{-1}. Extensive treatment of chromia in the manner described seems, therefore, to deactivate the catalyst towards the fluorination and chlorination of $C_2Cl_2F_4$ while the surface area and fluorine content remain within the ranges determined on other chromias which operate satisfactorily in this respect.

Table 3.3 Microanalysis of Inactive Catalyst.

Sample	Element (% w/w)			
	C	H	F	Cl
Fresh, untreated	4.29	0.37	0	0
Used,extensively fluorinated	n/d	n/d	28.4	0.2
Inactive	4.40	0.40	5.52	0.55 0.51

Note: n/d = not determined.

It seems unlikely that HCl treatment caused deactivation of the catalyst since further experiments involving HCl pre-treatment of pre-fluorinated chromias showed no catalyst deactivation (Chapter 5). This suggests that the HF treatment caused deactivation, but the mechanism by which this occurs is not clear.

There are two possible interpretations of the high proportion of CCl_3CF_3 observed in eluant $C_2Cl_3F_3$. Either the route to formation of CCl_3CF_3 is favoured over that to CCl_2FCClF_2, or CCl_3CF_3, once formed, takes little part in further reactions.

3.4 Formation of Hydrogen Chloride During Reaction of $C_2Cl_2F_4$ on Chromia

The infra-red spectrum of the eluant gases from reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia contained a band centred on 2880 cm^{-1} due to HCl. The reactor exit line was modified to include a Dreschel bottle containing 4 molar sodium hydroxide solution, _ca_. 150 cm^3 liquid, and HCl, originating from reaction of $C_2Cl_2F_4$, was collected as chloride ion. The efficiency with which chloride ion could be collected, determined by bubbling a known quantity of HCl through the NaOH solution in a stream of N_2 gas, was found to be _ca_. 13% based on conversion of Cl^- to AgCl.

Two experiments were carried out using $C_2Cl_2F_4$ (mole ratio $CClF_2CClF_2$:CCl_2FCF_3 = 58.7:41.3 by ^{19}F n.m.r spectroscopy) reacting in the temperature range 673 - 703 K. Chloride ion collected in the NaOH solution corresponded to 0.34 mmol (Table 3.4) and 0.36 mmol (Table 3.5) HCl, based on conversion of Cl^- to AgCl.

The amount of chlorine surplus to the requirements of fluorination reactions, estimated from the G.C. analyses (Section 3.2), was 18 mmol (Table 3.4) and 12 mmol (Table 3.5). Therefore, most of the HCl expected on the basis of equation (3.1) was either not formed, or was retained by the catalyst.

$$C_2Cl_2F_4 + HF \longrightarrow C_2ClF_5 + HCl$$

<u>Equation (3.1)</u>

The chlorine contents of two pellets from the experiment in Table 3.4, determined by neutron activation analysis, were 320 and 350 μmol Cl(g catalyst)$^{-1}$. Assuming the chlorine content was homogeneous along the catalyst bed, this suggests that a total of 2.5 - 2.8 mmol chlorine was retained by the catalyst. Taking into account the efficiency with which Cl^- was collected in the NaOH solution this leaves over 50% of the HCl expected on the basis of equation (3.1) unaccounted for. The absence of a chlorine mass balance could arise either because the principal reaction from $C_2Cl_2F_4$ to C_2ClF_5 and $C_2Cl_3F_3$ is dismutation, which does not involve production of HCl, or because HCl formed during the reaction is adsorbed by the Monel metal reactor. The latter route is certainly important, since very high [^{36}Cl]-chlorine count rates were detected on the reactor walls following passage of $H^{36}Cl$ at 623 K.

Tables 3.4 and 3.5

HCl Originating from Reaction of $C_2Cl_2F_4$ on Pre-fluorinated Chromia.

Table 3.4 $C_2Cl_2F_4$ at 703 K.

Time (min)	Product Distribution by G.C.(1) (μ mol)			
	112a	113/113a	114/114a	115
20	-	0.4	8.8	16.3
40	0.4	4.5	11.2	16.9
60	-	6.0	12.4	17.4
80	-	6.5	12.9	17.6

Flow rate $N_2/C_2Cl_2F_4$ = 13.2±5.1 cm^3 min^{-1}

AgCl recovered from basic solution = 0.34 mmol.

NOTE: (1) Isomers not resolved
Mole Ratio 114:114a in reactant = 58.7:41.3 by ^{19}F n.m.r.
Volume G.C. sample loop = 0.48 cm^3

Table 3.5 $C_2Cl_2F_4$ at 673 K.

Time (min)	Product Distribution by G.C.(1) (mol % of eluant)			
	112	113/113a	114/114a	115
25	-	12.5	62.4	29.6
80	-	10.7	56.5	32.8
140	-	11.7	57.3	30.9
175	-	11.5	58.3	30.2
210	-	11.5	58.3	30.2
245	-	11.5	58.4	30.1

Flow rate $N_2/C_2Cl_2F_4$ = 26.9±0.5 cm^3 min^{-1}

Flow rate $C_2Cl_2F_4$ = 0.25 mmol min^{-1}

AgCl recovered from basic solution = 0.36 mmol

NOTE: (1) Isomers not resolved
Mole Ratio 114:114a in reactant = 58.7:41.3 by ^{19}F n.m.r.

3.5 Reactions involving $CClF_2CClF_2/CCl_2FCF_3$ Isomer Mixtures.

The reaction of $C_2Cl_2F_4$ containing various mole ratios of $CClF_2CClF_2:CCl_2FCF_3$ was studied on pre-fluorinated chromia to establish the effect of temperature on the eluant $C_2Cl_2F_4$ isomer ratio. A stream of $N_2/C_2Cl_2F_4$ vapour was admitted to the catalyst at 620-650 K and the temperature increased in increments. Temperature control was difficult and the increments were therefore irregular. Before sampling the eluant, using gas chromatography, at any given reaction temperature, 30 minutes were allowed for the temperature to stabilise and for products from reaction at this temperature to be eluted from the reactor. Seven isomeric mixtures were used, covering the range from $CClF_2CClF_2$ containing 6 mol % CCl_2FCF_3 to CCl_2FCF_3 containing 5 mol % $CClF_2CClF_2$ (Table 3.6). Isomer mixtures were prepared by adding weighed aliquots of the individual isomers together. The isomeric compositions of the individual aliquots were determined by ^{19}F n.m.r spectroscopy.

Table 3.6 Isomer Mixtures

Experiment	Isomer Mixture	Mole Ratio $CClF_2CClF_2$	$:CCl_2FCF_3$
1	A	58	42
2	B	94	6
3	C	78	22
4	D	70	30
5	A	58	42
6	E	28	72
7	F	5	95

Isomer mixture A reacted to form ca. 30 mol % C_2ClF_5 and 11.5 mol % $C_2Cl_3F_3$ at a $N_2/C_2Cl_2F_4$ gas flow rate of 27 cm^3 min^{-1} and a constant temperature of 673 K (Table 3.7). $C_2Cl_2F_4$ comprised ca. 58.5 mol % of the eluant. The ratio of symmetric:asymmetric isomers of $C_2Cl_2F_4$ changed from 1.4:1 to 1.1:1 during the first 80 min. of reaction. Thereafter the isomer ratio was maintained at 1.1:1. The proportion of CCl_2FCF_3 in the eluant had increased at the expense of $CClF_2CClF_2$. Reacting isomer mixture A in the temperature ranges 622 - 833 K and 639 - 813 K resulted in the eluant ratio of $CClF_2CClF_2$:CCl_2FCF_3 changing from 1.64:1 at the lowest reaction temperature to 0.88:1 and 0.85:1 respectively at the highest reaction temperature (Tables 3.8 and 3.9). A similar pattern of increasing concentration of CCl_2FCF_3 relative to $CClF_2CClF_2$ was obtained when isomer mixtures B,C and D were admitted to the catalyst under similar temperature conditions (Tables 3.10-3.12) although, in the temperature region below 673 K, small increases in the mole ratio $CClF_2CClF_2$:CCl_2FCF_3 suggest that the asymmetric isomer might have been reacting faster than the symmetric isomer at lower temperatures. The observations at temperatures below 673 K are consistent with data obtained by Marangoni and co-workers[22] which show that below 673 K fluorination of CCl_2FCF_3 proceeds more quickly than fluorination of $CClF_2CClF_2$.

Isomer mixtures E and F, which unlike mixtures A-D contained a higher proportion of asymmetric isomer, did not react to give enhanced concentrations of CCl_2FCF_3 relative

Table 3.7 Isomer Mixture A at Constant Temperature.

Mole Ratio 114:114a in reactant = 1.38:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C.(1) (mol % of eluant)					Mole Ratio 114:114a in eluant
			113	113a	114	114a	115	
25	676	26.5		12.5	35.6	26.8	29.6	1.33:1
80	676	n/d		10.7	29.1	27.4	32.8	1.06:1
140	672	n/d	1.7	10.0	30.4	26.9	30.9	1.13:1
175	673	n/d		11.5	30.3	28.0	30.2	1.08:1
210	673	n/d		11.5	30.3	28.0	30.2	1.08:1
245	675	27.2		11.5	30.5	27.9	30.1	1.09:1

NOTE: n/d not determined.

Table 3.7 Isomer Mixture A at Constant Temperature.

Mole Ratio 114:114a in reactant = 1.38:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C.$^{(1)}$ (mol % of eluant)					Mole Ratio 114:114a in eluant
			113	113a	114	114a	115	
25	676	26.5		12.5	35.6	26.8	29.6	1.33:1
80	676	n/d		10.7	29.1	27.4	32.8	1.06:1
140	672	n/d	1.7	10.0	30.4	26.9	30.9	1.13:1
175	673	n/d		11.5	30.3	28.0	30.2	1.08:1
210	673	n/d		11.5	30.3	28.0	30.2	1.08:1
245	675	27.2		11.5	30.5	27.9	30.1	1.09:1

NOTE: n/d not determined.

Table 3.8 <u>Isomer Mixture A Between 622 K and 833 K.</u>

Mole Ratio 114:114a in reactant = 1.38:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C. (mol % of eluant)				Mole Ratio 114:114a
			113 113a	114	114a	115	in eluant
35	622	14.4	t	62.2	37.7	t	1.64:1
175	659	n/d	9.7	38.9	30.3	21.1	1.78:1
210	681	n/d	9.4	36.7	27.0	26.9	1.36:1
245	684	n/d	8.7	35.1	31.7	24.5	1.11:1
280	733	n/d	8.2	30.0	31.9	29.9	0.92:1
315	739	n/d	8.5	25.7	23.2	27.7	1.09:1
350	820	n/d	5.5	20.6	30.0	44.0	0.69:1
385	833	n/d	7.6	23.9	25.1	43.4	0.95:1
420	829	n/d	7.9	24.7	28.1	39.2	0.88:1

NOTE: n/d : not determined; t : trace

Table 3.9 <u>Isomer Mixture A Between 642 K and 813 K.</u>

Mole Ratio 114:114a in reactant = 1.38:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C. (mol % of eluant)					Mole Ratio 114:114a in eluant.
			113	113a	114	114a	115	
35	642	30.0	-	-	58.4	41.6	-	1.40:1
70	639	26.6	-	-	58.4	41.6	t	1.40:1
105	635	29.2	3.9		50.8	45.2	t	1.12:1
140	663	33.3	5.9		43.8	31.9	18.5	1.37:1
175	663	29.4	6.2		43.6	30.6	19.9	1.27:1
210	679	30.0	6.8		42.4	32.5	18.3	1.30:1
245	683	29.1	8.2		41.5	27.7	22.6	1.49:1
280	683	27.9	6.5		40.4	33.7	19.4	1.20:1
315	711	29.4	7.8		37.8	32.8	21.6	1.15:1
350	727	29.4	9.2		36.8	31.6	22.4	1.16:1
385	747	28.1	9.3		31.7	33.0	26.0	0.96:1
420	775	28.8	8.2		30.5	28.8	32.6	1.06:1
455	796	29.2	9.3		27.9	27.6	35.3	1.01:1
490	813	28.8	5.8		25.8	30.2	38.2	0.85:1

Table 3.10 Isomer Mixture B Between 637 K and 849 K.

Mole Ratio 114:114a in reactant = 16.0:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C.(1) (mol % of eluant) 114	114a	115	Mole Ratio 114:114a in eluant
25	637	36.3	100	-	t	-
75	659	35.2	93.0	-	7.0	-
100	668	34.8	81.2	t	18.8	-
125	691	34.8	73.6	t	26.4	-
150	708	43.4	71.2	t	28.8	-
175	720	41.6	66.1	t	33.9	-
200	733	60.0	75.9	t	24.1	-
225	738	60.0	71.4	~5	23.6	14.3:1
250	755	56.6	63.8	9.4	26.8	6.8:1
275	757	57.6	64.3	9.7	26.0	6.6:1
300	774	57.6	61.6	10.6	27.8	5.8:1
325	791	57.6	58.8	11.8	29.4	5.0:1
350	819	58.8	52.7	12.3	35.0	4.3:1
375	834	58.8	53.2	13.3	33.5	4.0:1
400	849	58.8	57.6	12.3	30.1	4.7:1

Note: (1) $C_2Cl_3F_3$ not determined; signal due to $C_2Cl_3F_3$ appears during G.C. cooldown (Section 2.13, Programme 2).

t = trace, <5%

Table 3.11 Isomer Mixture C Between 643 K and 829 K.

Mole Ratio 114:114a in reactant = 3.5:1

Time (min)	Temp (K)	Flow Rate $cm^3 min^{-1}$	Product Distribution by G.C.(1) (mol % of eluant) 114	114a	115	Mole Ratio 114:114a in eluant
50	643	57.6	72.0	19.5	8.5	3.7:1
75	655	55.5	70.2	20.1	9.7	3.5:1
100	675	56.6	64.4	20.8	14.8	3.1:1
125	679	56.6		n/d		-
150	699	61.2	59.5	19.8	20.7	3.0:1
175	701	61.2	60.3	19.4	20.3	3.1:1
200	717	58.8	59.3	20.4	20.3	2.9:1
225	726	57.6	58.7	20.9	20.4	2.8:1
250	743	56.6	56.8	21.1	22.1	2.7:1
275	766	56.6	51.8	20.7	27.5	2.5:1
300	785	60.0	47.9	20.8	31.3	2.3:1
325	805	60.0	45.9	21.9	32.2	2.1:1
350	829	57.6	40.6	21.3	38.1	1.9:1
355	806	56.6	47.7	21.7	30.6	2.2:1
400	726	54.5	62.3	20.8	16.9	3.0:1

NOTE: (1) $C_2Cl_3F_3$ not determined; signal due to $C_2Cl_3F_3$ appears during G.C. cooldown (Section 2.13, Programme 2)

n/d = not determined.

Table 3.12 Isomer Mixture D Between 637 K and 853 K.

Mole Ratio 114:114a in reactant = 2.3:1

Time (min)	Temp (K)	Flow Rate ($cm^3 min^{-1}$)	Product Distribution by G.C.(1) (mol % of eluant) 114	114a	115	Mole Ratio 114:114a in eluant
25	637	63.1	70.0	30.0	t	2.3:1
175	666	60.6	65.5	16.4	18.1	4.0:1
200	688	71.4	67.5	21.1	11.4	3.2:1
250	736	38.4	54.2	20.8	25.0	2.6:1
275	768	38.9	43.4	20.7	35.9	2.1:1
300	805	38.9	39.6	22.0	38.4	1.8:1
325	839	37.9	33.6	21.0	45.4	1.6:1

Note: (1) $C_2Cl_3F_3$ not determined; signal due to $C_2Cl_3F_3$ appears during G.C. cooldown (Section 2.13, Programme 2).

Table 3.13 Isomer Mixture E Between 624K and 768K.

Mole Ratio 114:114a in reactant = 1:2.57

Time (min)	Temp (K)	Flow Rate ($cm^3 min^{-1}$)	Product Distribution in G.C.$^{(1)}$ (mol % of eluant) 114	114a	115	Mole Ratio 114:114a in eluant
50	624	50.0	29.6	70.5	t	0.42:1
75	643	50.8	26.5	60.2	13.4	0.44:1
100	669	53.5	24.9	55.3	19.8	0.45:1
125	690	50.8	24.6	53.4	22.0	0.46:1
150	710	50.0	24.3	52.7	23.0	0.46:1
175	727	51.7	22.7	49.4	27.9	0.46:1
200	743	50.0	22.5	48.0	29.5	0.47:1
225	768	50.8	21.7	44.3	34.0	0.49:1

Note: (1) $C_2Cl_3F_3$ not determined; signal due to $C_2Cl_3F_3$ appears during G.C. cooldown (Section 2.13, Programme 2).

Table 3.14 Isomer Mixture F Between 638 K and 713 K.

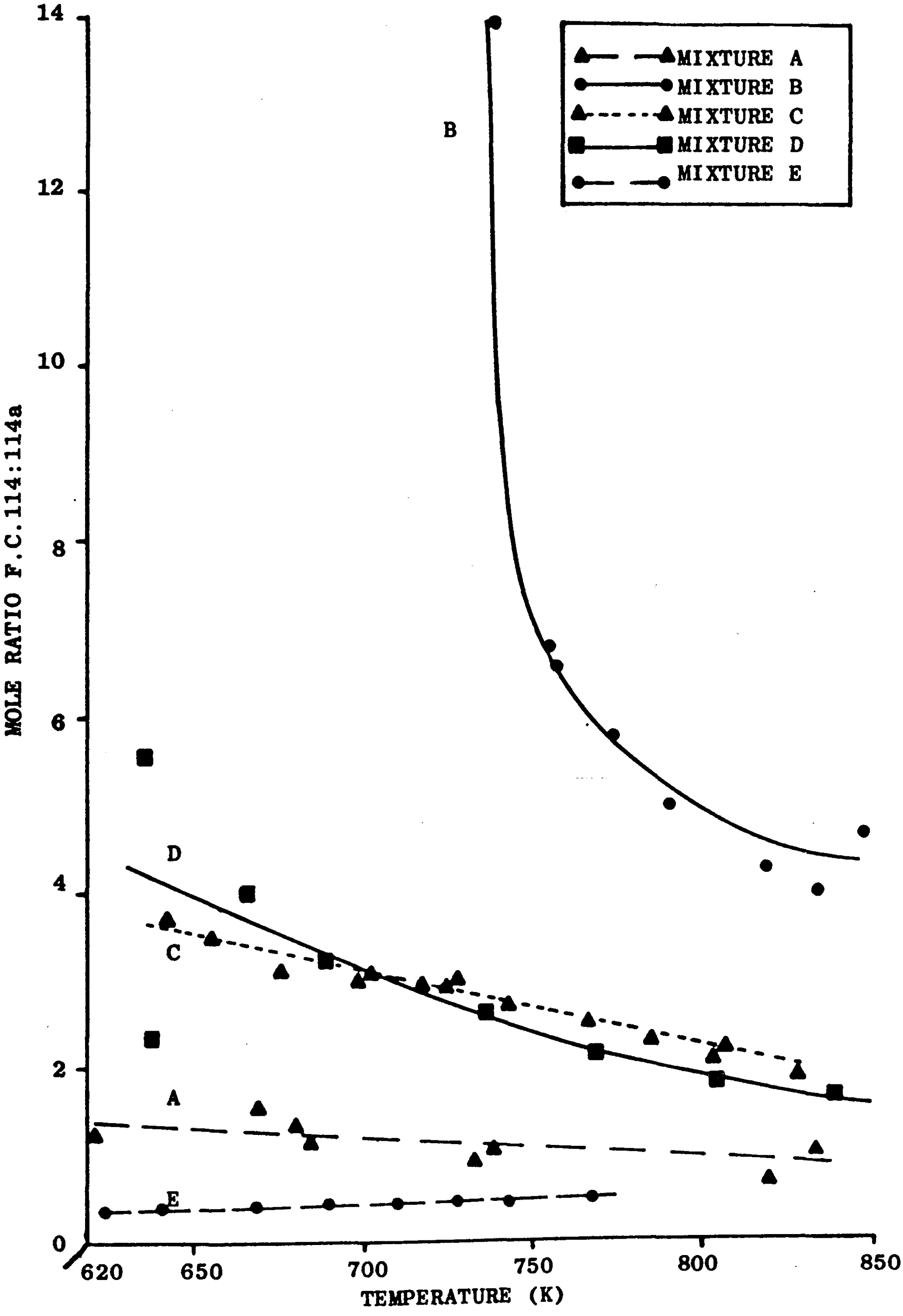
Mole Ratio 114:114a in reactant = 1:19

Time (min)	Temp (K)	Flow Rate ($cm^3 min^{-1}$)	Product Distribution by G.C.(1) (mol % of eluant)			Mole Ratio 114:114a in eluant
			114	114a	115	
25	638	50.8	t	84.0	16.0	-
50	653	53.5	t	75.6	24.4	-
75	673	51.7	t	67.8	32.2	-
100	699	50.8	t	59.5	40.5	-
125	703	26.5	t	46.1	53.9	-
150	713	24.0	t	56.0	44.0	-

NOTE: (1) $C_2Cl_3F_3$ not determined; signal due to $C_2Cl_3F_3$ appears during G.C. cooldown (Section 2.13, Programme 2).

t = trace, < 5%

FIGURE 3.4 REACTION OF $CClF_2CClF_2/CCl_2FCF_3$ ISOMER MIXTURES.



to $CClF_2CClF_2$. In a temperature range 623 - 768 K the ratio of symmetric:asymmetric isomers in eluant $C_2Cl_2F_4$ from the reaction of isomer mixture E rose from 0.42:1 to 0.49:1 with increasing temperature (Table 3.13). Mixture F, which contained 5 mol % $CClF_2CClF_2$, produced trace quantities (< 5 mol %) of $CClF_2CClF_2$ at all temperatures in a range 638 - 757 K (Table 3.14).

The results of the isomeric mixture experiments provide evidence for equilibria between the symmetric and asymmetric isomers of $C_2Cl_2F_4$, the equilibria moving towards a 1:1 symmetric:asymmetric isomer ratio with increasing temperature (Figure 3.4).

3.6 Kinetics of the Reactions to form $C_2Cl_3F_3$ and C_2ClF_5 from $C_2Cl_2F_4$ on pre-fluorinated chromia.

The kinetics of the reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia to form $C_2Cl_3F_3$ and C_2ClF_5 can be calculated from the gas chromatograph traces by calculating the number of substrate molecules reacting at any given time. The feed rate of reactant to the catalyst is given by the number of $C_2Cl_2F_4$ molecules divided by the flow time, and the number of molecules contacting the catalyst (Z) at any given time is the product of the feed rate (F molecule min^{-1}) and the catalyst volume (Vcm^3) divided by the flow rate (xcm^3min^{-1}) of $N_2/C_2Cl_2F_4$ vapour minus the number of molecules in the eluant, corrected to allow for the difference between the catalyst volume and gas chromatograph sampling loop volume, (Equation 3.2).

$$Z = F\ Vx^{-1} - (\text{Number of molecules in eluant})$$

Equation (3.2)

Plots of ΣZ versus time were obtained for three different $C_2Cl_2F_4$/chromia catalyst systems; (i) reaction of $C_2Cl_2F_4$ on active prefluorinated chromia to give C_2ClF_5, *ca*. 25 mol %, $C_2Cl_3F_3$, *ca*. 12 mol %, and $C_2Cl_2F_4$, *ca*. 63 mol %. (Figure 3.5), (ii) reaction of $C_2Cl_2F_4$ on inactive extensively fluorinated chromia to give C_2ClF_5, *ca*. 9 mol %, $C_2Cl_3F_3$, *ca* 2 mol %, and $C_2Cl_2F_4$ *ca*. 89 mol % (Figure 3.6), (iii) reaction of $C_2Cl_2F_4$ on active prefluorinated chromia treated with hydrogen chloride to give C_2ClF_5, *ca*. 27 mol %, $C_2Cl_3F_3$ *ca* 7 mol %. and $C_2Cl_2F_4$, *ca*. 66 mol % (Figure 3.7). Summation of gas chromatographic data for the three experiments indicated mass balances were >95%. The plot of ΣZ versus time for reaction of $C_2Cl_2F_4$ on inactive chromia (Figure 3.6) is linear, whereas those for reaction of $C_2Cl_2F_4$ on active chromias (Figures 3.5 and 3.7) are linear in the later stages of the reaction, but deviate initially. The observed behaviour indicates that in each of the three systems the reactions are zero-order with respect to gaseous $C_2Cl_2F_4$, at least in their later stages. The approximation to zero-order kinetics provides circumstantial evidence for the adsorption of $C_2Cl_2F_4$ on the catalyst before fluorination or chlorination.

FIGURE 3.5 ΣZ versus TIME FOR $C_2Cl_2F_4$ REACTING ON ACTIVE, PREFLUORINATED CHROMIA

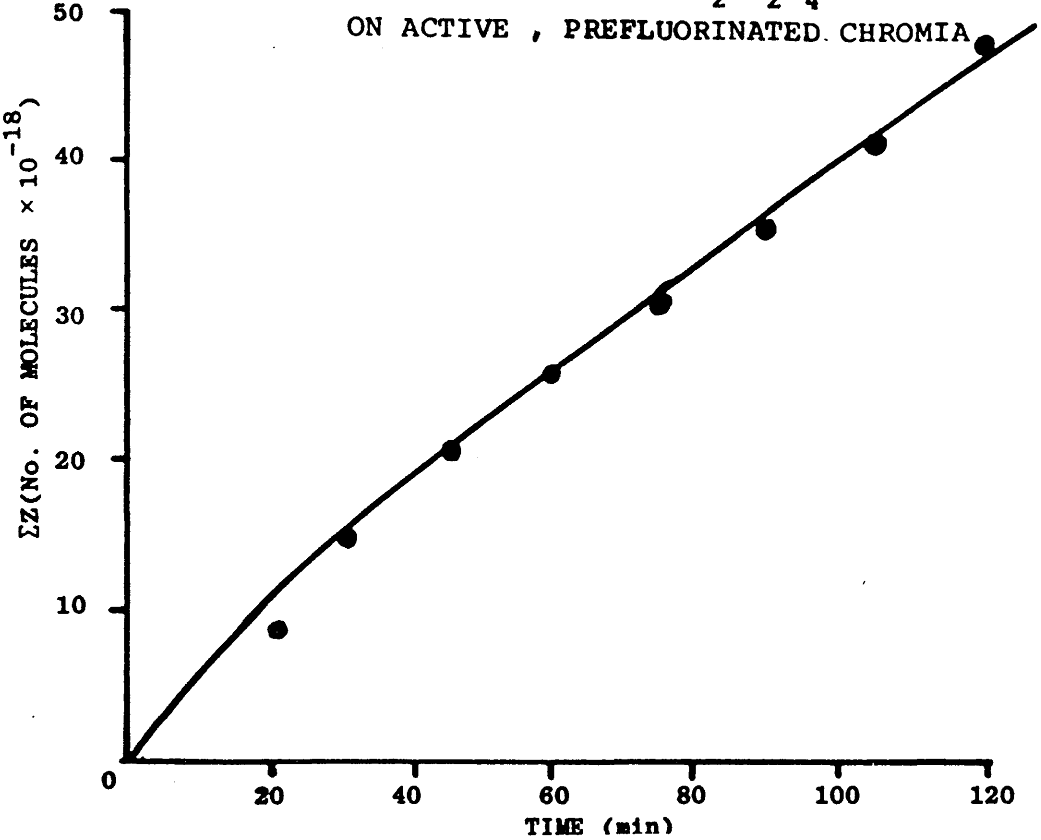


FIGURE 3.6 ΣZ versus TIME FOR $C_2Cl_2F_4$ REACTING ON INACTIVE CHROMIA

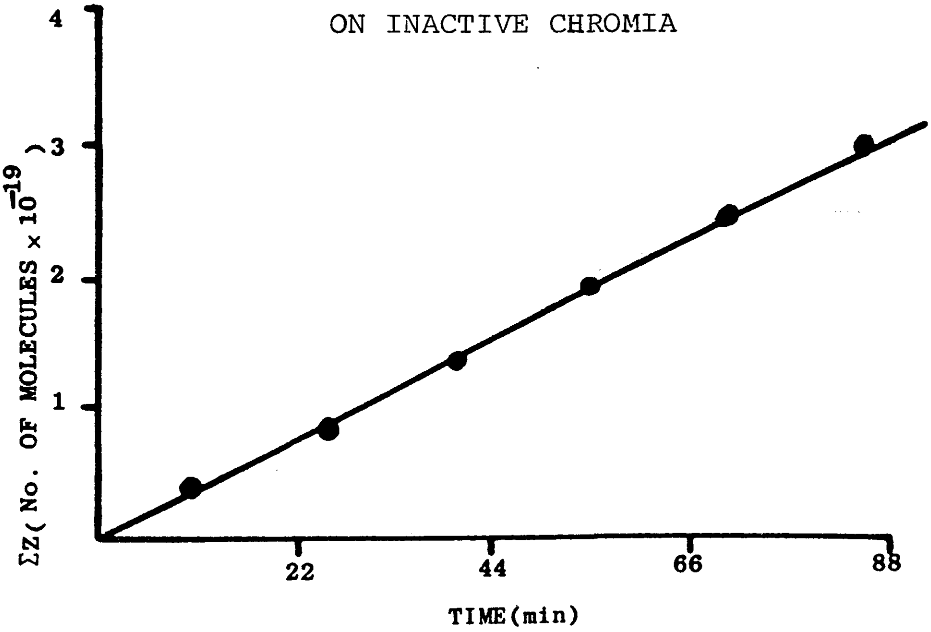
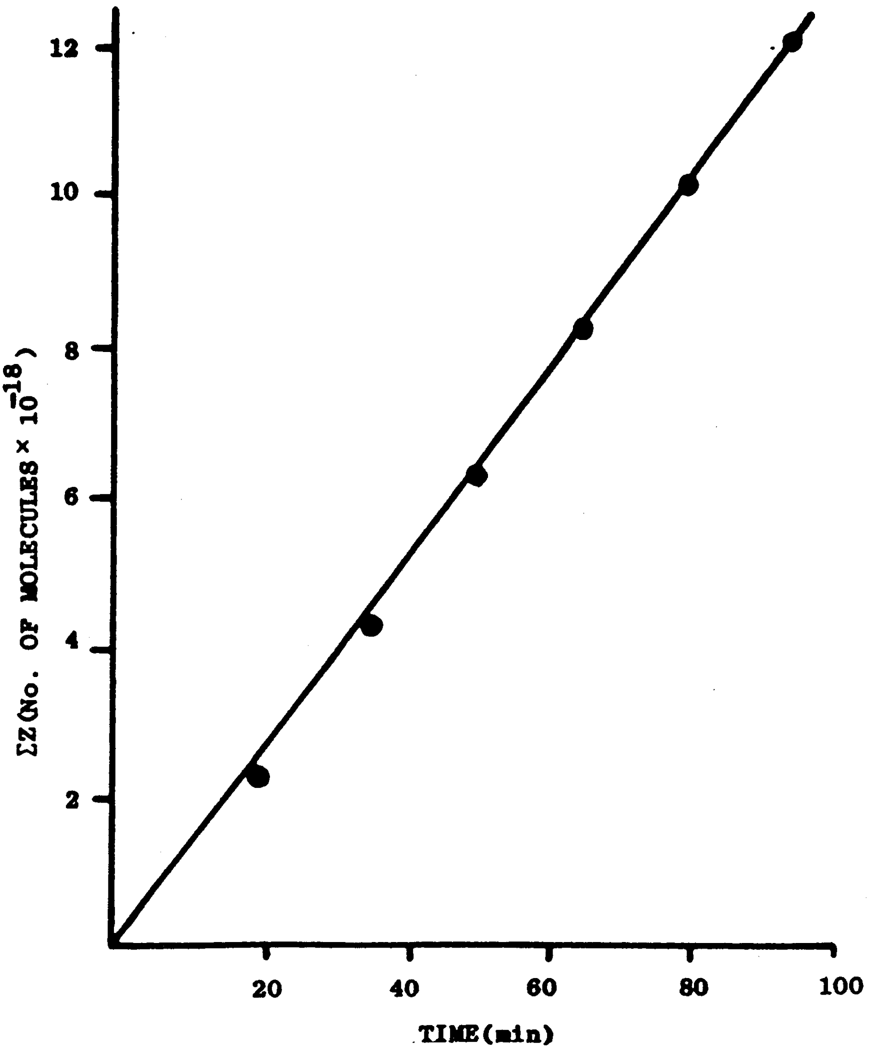


FIGURE 3.7 ΣZ versus TIME FOR $C_2Cl_2F_4$ REACTING ON ACTIVE , PREFLUORINATED CHROMIA TREATED USING $H^{36}Cl$



3.7. Reaction of $C_2Cl_2F_4$ Studied Using Temperature Programmed Fluorination.

The reactions $C_2Cl_2F_4 \longrightarrow C_2ClF_5$ and $C_2Cl_2F_4 \longrightarrow C_2Cl_3F_3$ were studied using temperature programmed fluorination (Section 2.2.4). Two chromia samples were used; a fresh, pre-fluorinated chromia containing ca. 5% w/w fluorine and a used, extensively fluorinated chromia containing ca. 30% w/w fluorine.

Admission of $N_2/C_2Cl_2F_4$ vapour (mole ratio $CClF_2CClF_2$: CCl_2FCF_3 = 51:49) to the used catalyst resulted in the production of C_2ClF_5, and $C_2Cl_3F_3$ at trace levels (<2 mol%), at temperatures above 583 K. At temperatures above 643 K a rapid increase in the concentrations of C_2ClF_5 and $C_2Cl_3F_3$ was observed. The exact temperature at which this rapid increase in product concentration occurred varied among experiments. During the first admission of $C_2Cl_2F_4/N_2$ vapour to the used catalyst the rapid increase in reaction to form C_2ClF_5 occurred above 658 K (Figure 3.8). After cooling of the catalyst to 523 K in a flow of dinitrogen a second aliquot of $C_2Cl_2F_4/N_2$ vapour was admitted. In this experiment, the rapid increase in reaction to form C_2ClF_5 was observed above 643 K (Figure 3.10). Reaction to form $C_2Cl_3F_3$ from $C_2Cl_2F_4$ increased rapidly at the same temperatures as reaction to form C_2ClF_5 (Figures 3.9 and 3.11). The T.P.F. plots of (Number of moles C_2ClF_5 or $C_2Cl_3F_3$) versus temperature over the temperature range 613 - 723 K for the reaction of $C_2Cl_2F_4$ on used chromia can be divided into three regions:-

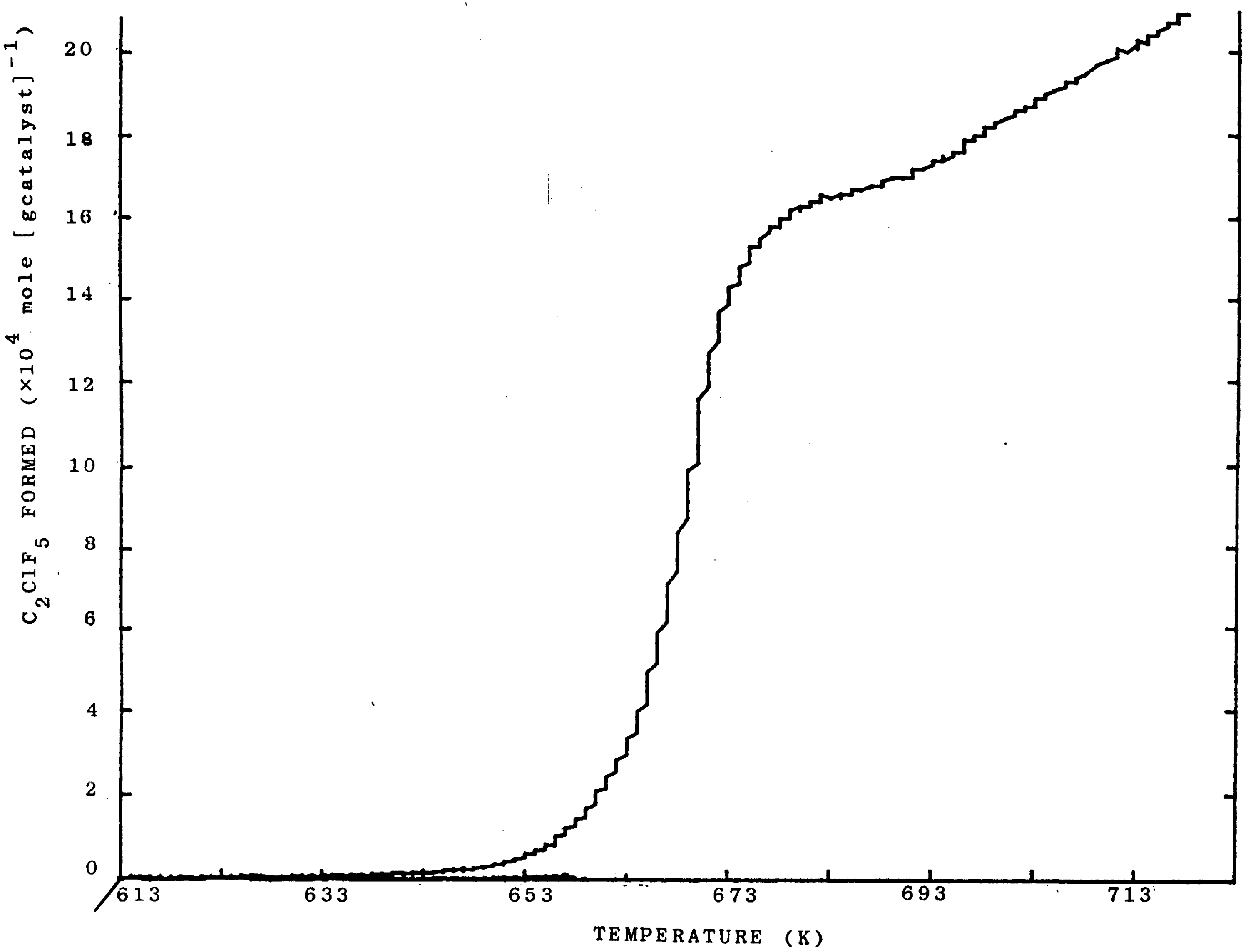


FIGURE 3.8

REACTION OF $C_2Cl_2F_4$ TO FORM C_2ClF_5 ;FIRST ADMISSION TO USED CATALYST.

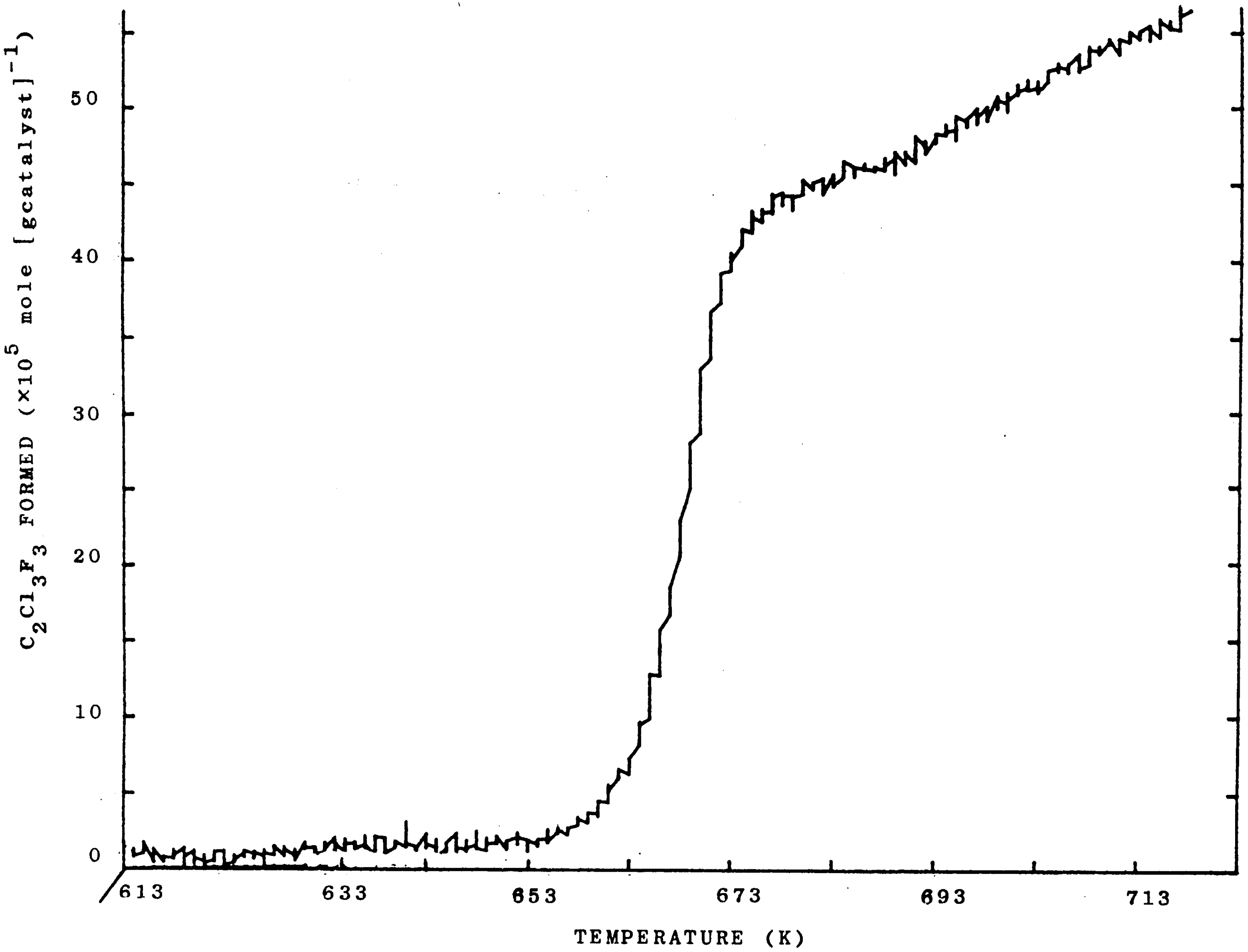


FIGURE 3.9

REACTION OF $C_2Cl_2F_4$ TO FORM $C_2Cl_3F_3$;FIRST ADMISSION TO USED CATALYST.

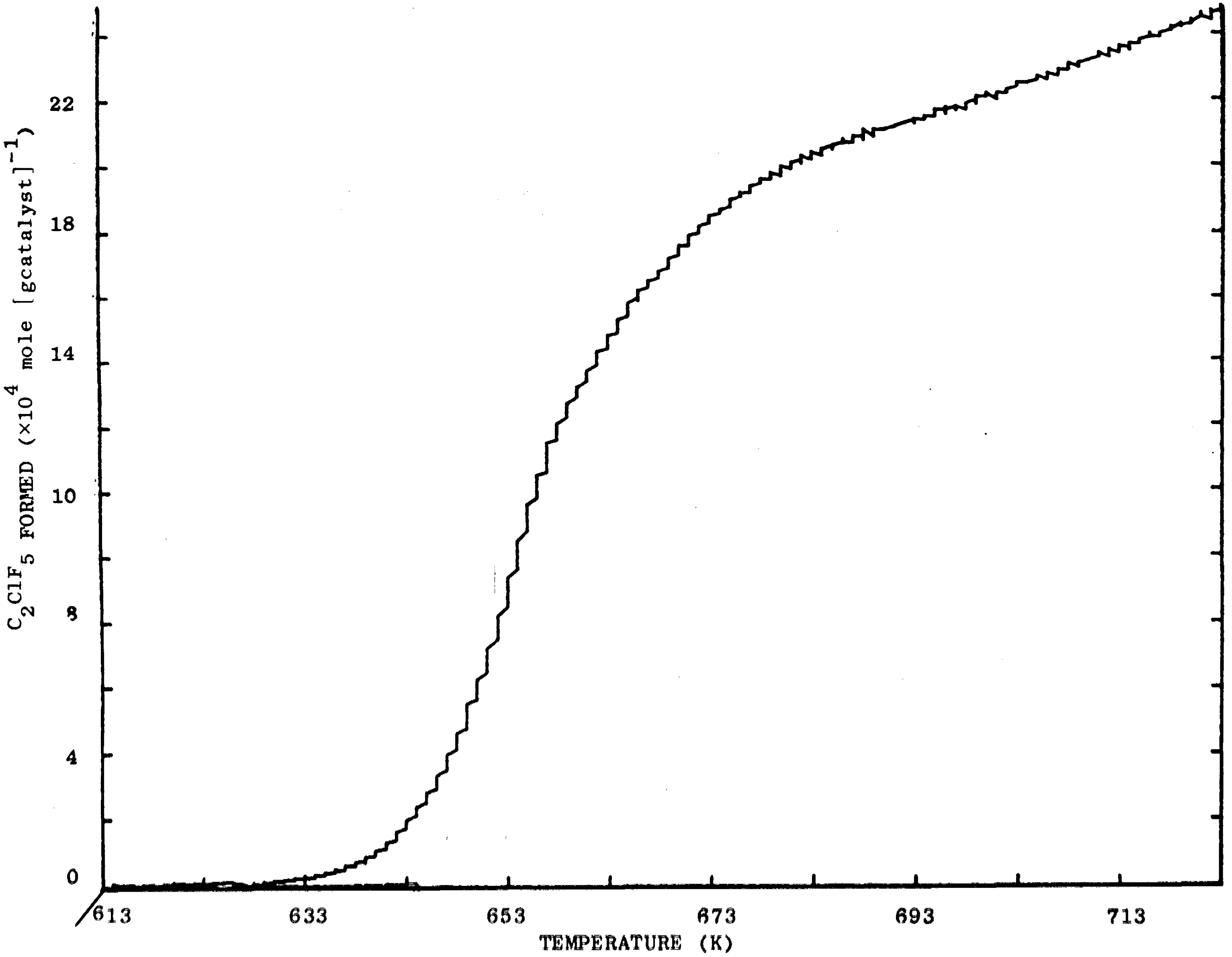


FIGURE 3.10

REACTION OF $C_2Cl_2F_4$ TO FORM C_2ClF_5 ; SECOND ADMISSION TO USED CATALYST.

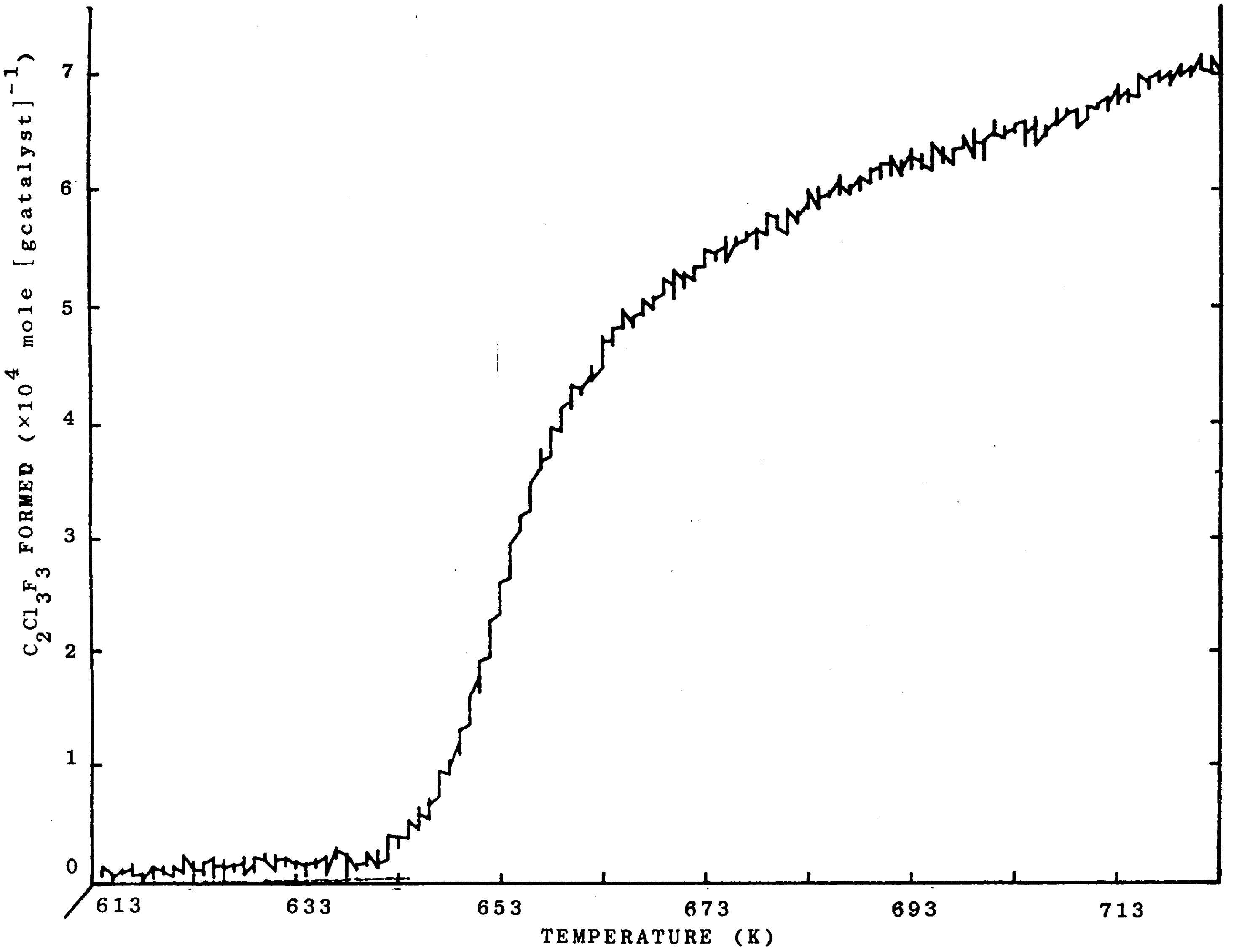


FIGURE 3.11

REACTION OF $C_2Cl_2F_4$ TO FORM $C_2Cl_3F_3$;SECOND ADMISSION TO USED CATALYST.

(a) a low temperature region below 633 K involving very little reaction.

(b) an intermediate temperature region between 633 and 673 K within which reaction increases rapidly with increasing temperature.

(c) a high temperature region above 673 K where the extent of reaction increases relatively slowly with temperature, compared with the intermediate temperature region.

During reaction of $C_2Cl_2F_4$ on fresh, pre-fluorinated chromia a rapid increase in reaction to form C_2ClF_5 was observed above 663 K (Figure 3.12). During subsequent admissions of $C_2Cl_2F_4$ to the same catalyst sample, the rapid increases in reaction to form C_2ClF_5 occurred above 633 K and 673 K, for the second and third admissions respectively (Figures 3.13 and 3.14). Data were not obtained for the reactions to form $C_2Cl_3F_3$ on the fresh, prefluorinated catalyst. The T.P.F. plots for the reaction of $C_2Cl_2F_4$ on fresh, prefluorinated chromia contain only two regions, corresponding to the low and intermediate temperature regions observed for the reaction on used chromia. Although data were not collected at temperatures above 693 K in these experiments, there is no indication from the T.P.F. plots (Figures 3.12 - 3.14) that the rapid increase in C_2ClF_5 concentration was beginning to level off.

The low and intermediate temperature sections of the T.P.F. plots, for reaction of $C_2Cl_2F_4$ on both used and fresh catalyst, are interpreted on the basis that at temperatures

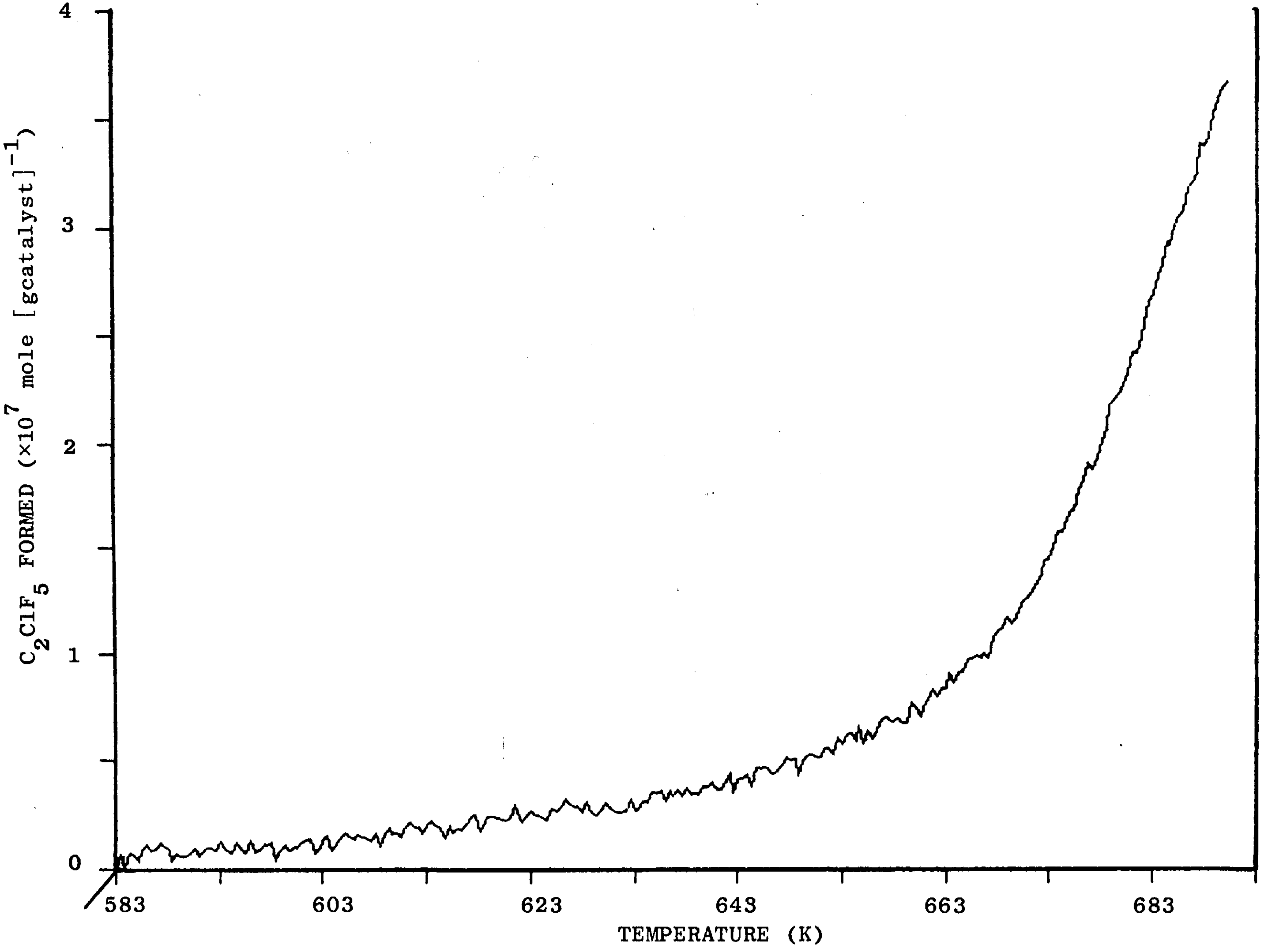


FIGURE 3.12

REACTION OF $C_2Cl_2F_4$ TO FORM C_2ClF_5 ;FIRST ADMISSION TO FRESH PRE-FLUORINATED CATALYST.

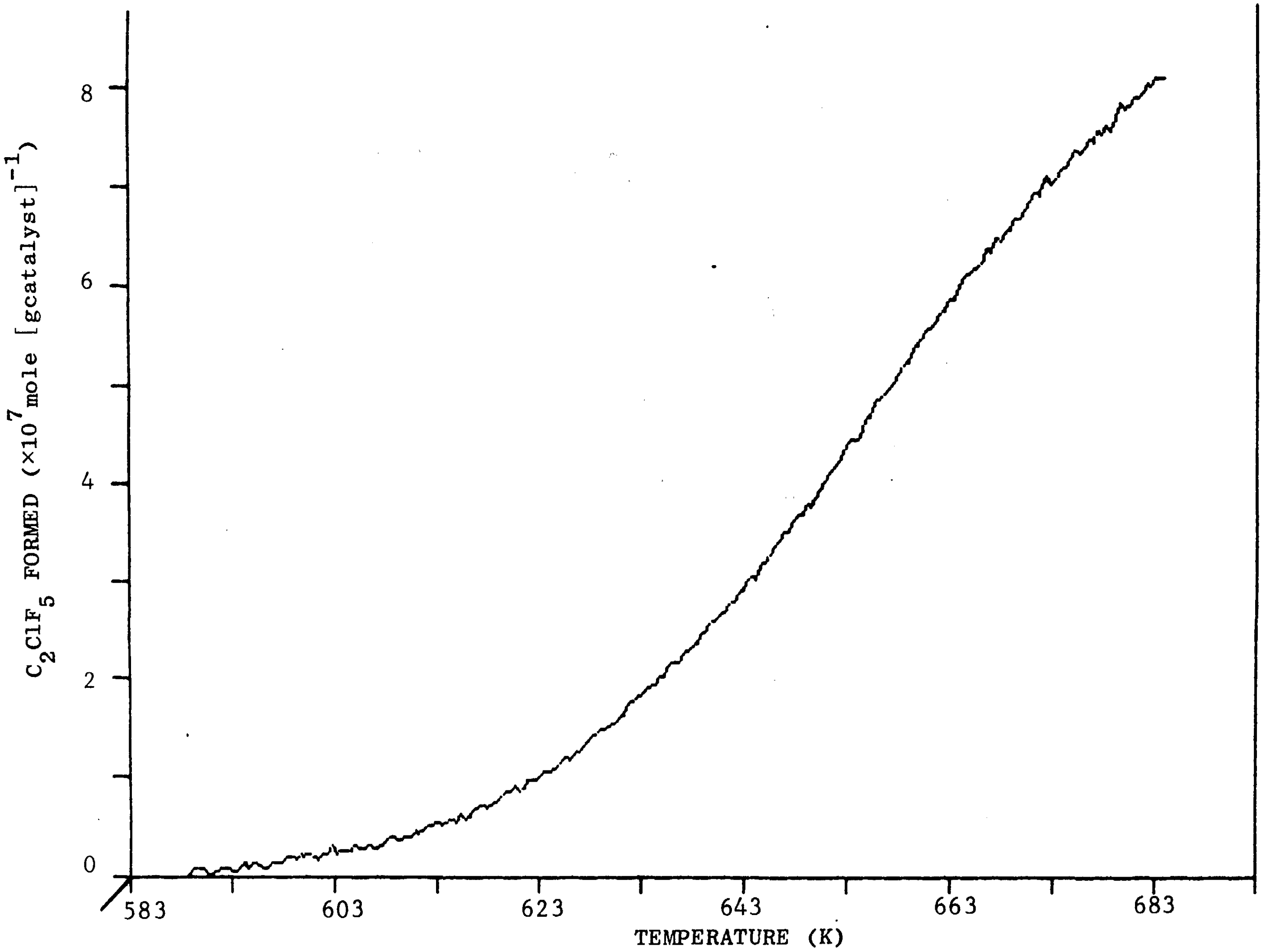


FIGURE 3.13

REACTION OF $C_2Cl_2F_4$ TO FORM C_2ClF_5 ;SECOND ADMISSION TO FRESH PRE-FLUORINATED CATALYST.

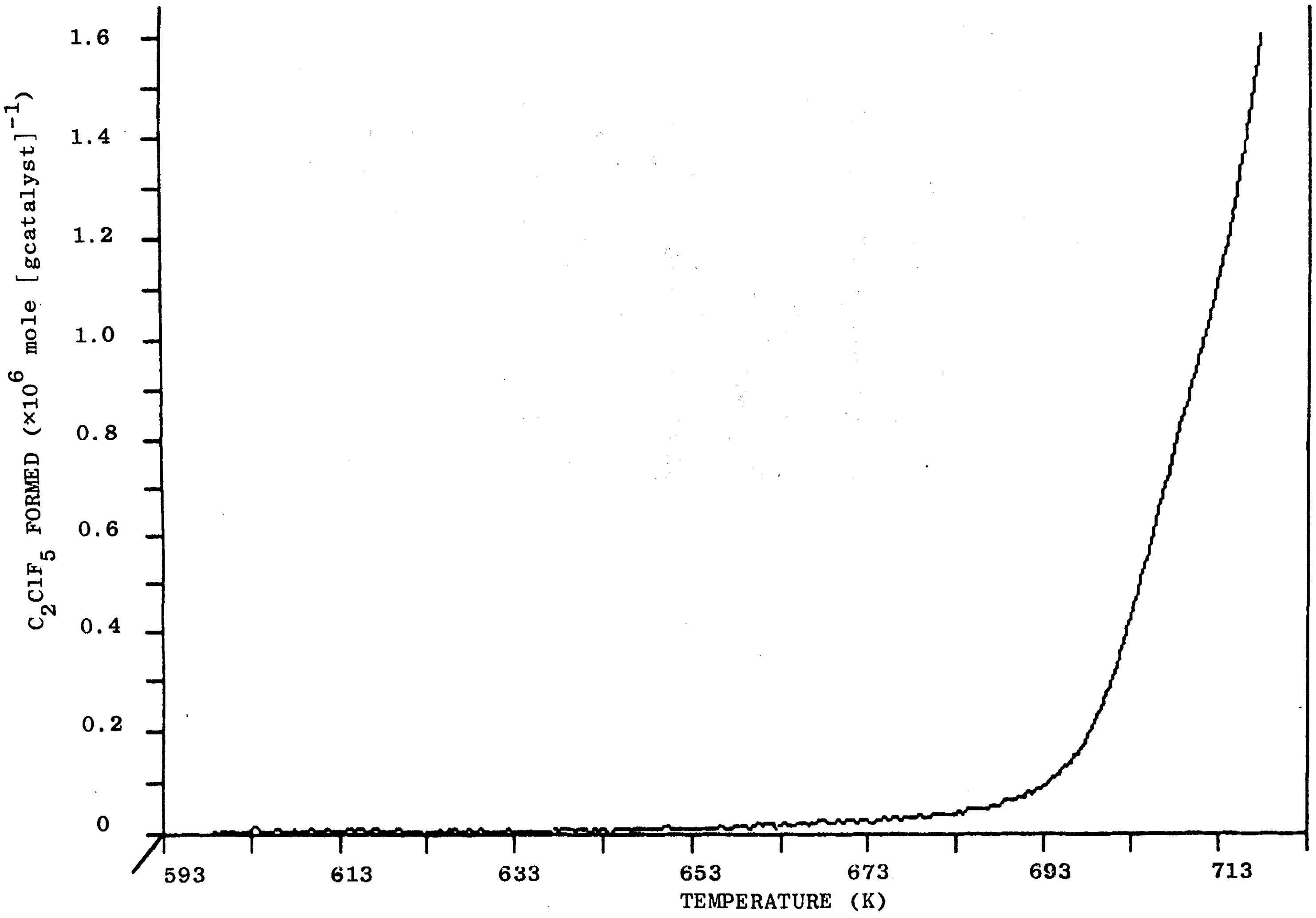
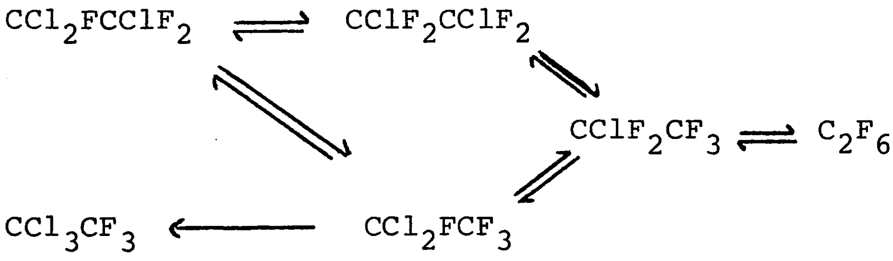


FIGURE 3.14

REACTION OF $C_2Cl_2F_4$ TO FORM C_2ClF_5 ; THIRD ADMISSION TO FRESH PRE-FLUORINATED CATALYST.

below ca. 343 K the extent of the reactions to form either $C_2Cl_3F_3$ or C_2ClF_5 from $C_2Cl_2F_5$ is very small. Variations in the position of the intermediate temperature region are probably accounted for by experimental error. Small differences in the flow rate through the reactor may have caused variations in the time taken for the molecules to travel from the reactor to the infra-red gas cells.

Further interpretation of the data is difficult for three reasons. First, the temperature differences are relatively small to obtain accurate activation energies. Second, it is not certain that the reactions are at equilibrium. Third, the reaction pathway is a complicated series of reactions (Scheme 3.2)



Scheme 3.2.

and the extent to which reactions such as $C_2F_6 \rightarrow C_2ClF_5 \rightarrow C_2Cl_2F_4$ occur is unknown. However, activation energies calculated from the high temperature sections of the plots for the formation of $C_2Cl_3F_3$ (Figure 3.10) and C_2ClF_5 (Figure 3.11) on used catalyst are 18±5 kJ mol^{-1} and 19±4 kJ mol^{-1} respectively. These values, calculated for the temperature range 673 - 723 K, are typical for a reaction limited by the diffusion of reactant to the surface. Within the temperature range studied on fresh catalyst, this diffusion limitation does not seem to apply.

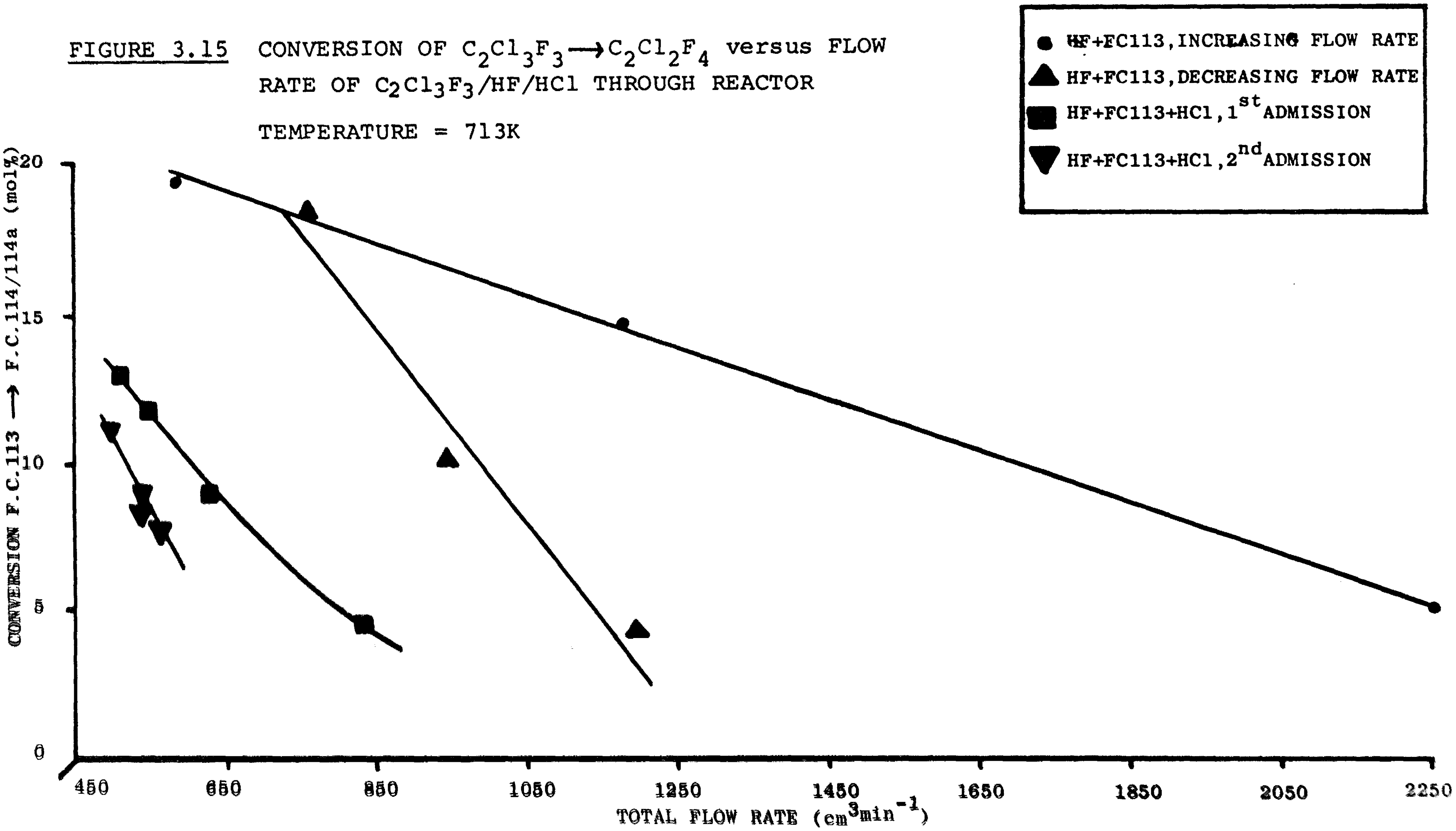
3.8 Effect of Hydrogen Chloride Flow During Simultaneous Admission of $C_2Cl_3F_3$ and Hydrogen Fluorine to Chromia.

The effect on the formation of $C_2Cl_2F_4$ of adding small quantities of HCl to a HF/$C_2Cl_3F_3$ gas flow was studied using Reactor B,(Section 2.2.3). Simultaneous admission of HF and $C_2Cl_3F_3$ (mole ratio HF:$C_2Cl_3F_3$ = 3:1, total gas flow [HF + $C_2Cl_3F_3$] = 584 $cm^3 min^{-1}$) to used chromia at 713 K resulted in a reactor eluant comprising ca. 20 mol % $C_2Cl_2F_4$, 2 mol % $C_2Cl_4F_2$, 1 mol % C_2ClF_5 and 77 mol % $C_2Cl_3F_3$, based on gas chromatographic analysis of the organic fractions. The concentration of $C_2Cl_2F_4$ in the eluant fell linearly with increasing gas flow due to the reduction in contact time and increased at higher pressures with the increase in contact time. However, the concentration of $C_2Cl_2F_4$ in the eluant returned to ca. 20 mol % when the initial conditions were re-established (Figure 3.1^5).

Introducing hydrogen chloride to the reactor feed (various mole fractions of the total feed) caused a significant reduction in the concentration of $C_2Cl_2F_4$ in the eluant; 20 mol % at 0 mol % HCl, 13 mol % at 7.8 mol % HCl (Figure 3.15). Switching off the HCl feed resulted in a partial recovery of $C_2Cl_2F_4$ concentration but never to the levels previously obtained. After two runs with HCl fed to the reactor the maximum achievable concentration of

FIGURE 3.15 CONVERSION OF $C_2Cl_3F_3 \longrightarrow C_2Cl_2F_4$ versus FLOW RATE OF $C_2Cl_3F_3$/HF/HCl THROUGH REACTOR

TEMPERATURE = 713K



$C_2Cl_2F_4$ during a normal $HF/C_2Cl_3F_3$ run was ca. 11 mol %. This corresponded to a 45% drop in catalytic activity towards fluorination of $C_2Cl_3F_3$. Determination of the chlorine and fluorine contents of the catalyst by microanalysis showed no significant change in composition. Surface area and pore volume density determinations gave identical results for samples before and after the experiments (Table 3.15).

Table 3.15 Analysis of Used Catalyst Before and After $HF/HCl/C_2Cl_3F_3$ Experiments.

	Elemental Analysis (% w/w)		Surface Area $m^2 g^{-1}$	Pore Volume Density $cm^3 g^{-1}$
	F	Cl		
Before Experiments	28.4	0.2	13	0.13
After Experiments	29.4	0.3	13	0.13

Using fresh, prefluorinated chromia as catalyst, HF and $C_2Cl_3F_3$ (mole ratio $HF:C_2Cl_3F_3 = 3:1$, total flow rate $[HF + C_2Cl_3F_3] = 925\ cm^3 min^{-1}$) reacted at 623 K to form ca. 65 mol % $C_2Cl_2F_4$, 2 mol % $C_2Cl_4F_2$, 0.5 mol % C_2ClF_5 and 32.5 mol % $C_2Cl_3F_3$ (Figure 3.16). Feeding HCl (2 mol % of the total feed) resulted in the concentration of $C_2Cl_2F_4$ in the eluant falling to ca. 40 mol %. No increase in the formation of $C_2Cl_4F_2$ was observed. The concentration of $C_2Cl_2F_4$ in the eluant returned to ca. 65 mol % on stopping the flow of HCl. Restarting the HCl feed resulted in the concentration of $C_2Cl_2F_4$ falling over a period of 50 min to ca. 3-5 mol %. The concentration of $C_2Cl_2F_4$ did not increase when the HCl flow was stopped. Increasing the temperature from 623 to 676 K increased the concentration of $C_2Cl_2F_4$ in the eluant to ca. 50 mol %.

The concentration of $C_2Cl_2F_4$ observed during reaction of $C_2Cl_3F_3$ on a second sample of fresh, prefluorinated catalyst (mole ratio HF:$C_2Cl_3F_3$ = 3:1, total flow rate [HF + $C_2Cl_3F_3$] = 925 $cm^3 min^{-1}$) was ca. 42 mol % at a temperature of 676 K, 50^o higher than the temperature used in the previous reaction on fresh, prefluorinated chromia. $C_2Cl_3F_3$ comprised ca. 66 mol % of the eluant and traces of $C_2Cl_4F_2$ and C_2ClF_5, comprising ca. 1.5 and 0.5 mol % of the eluant were also observed. The reason for the difference in activity between the two fresh catalyst samples is not known, but is possibly explained by 'cold' HF, retained in the reactor feed lines during the catalyst change, being admitted to the catalyst and sintering the second sample. The response of the new catalyst sample to HCl feed (2 mol % of the total feed) was similar to that of the used catalyst. During each period of HCl feed the eluant concentration of $C_2Cl_2F_4$ fell, recovering partially after the HCl feed was stopped (Figure 3.17). Restarting the HF/$C_2Cl_3F_3$ feed after leaving the catalyst in a nitrogen gas atmosphere for 48 h. resulted in concentrations of $C_2Cl_2F_4$ eluant of ca. 30 mol %. However, on admission of HCl (ca. 2 mol % of the total feed) the concentration of $C_2Cl_2F_4$ in the eluant fell sharply to < 20 mol %.

The experiments on the HF/$C_2Cl_3F_3$/HCl systems demonstrate

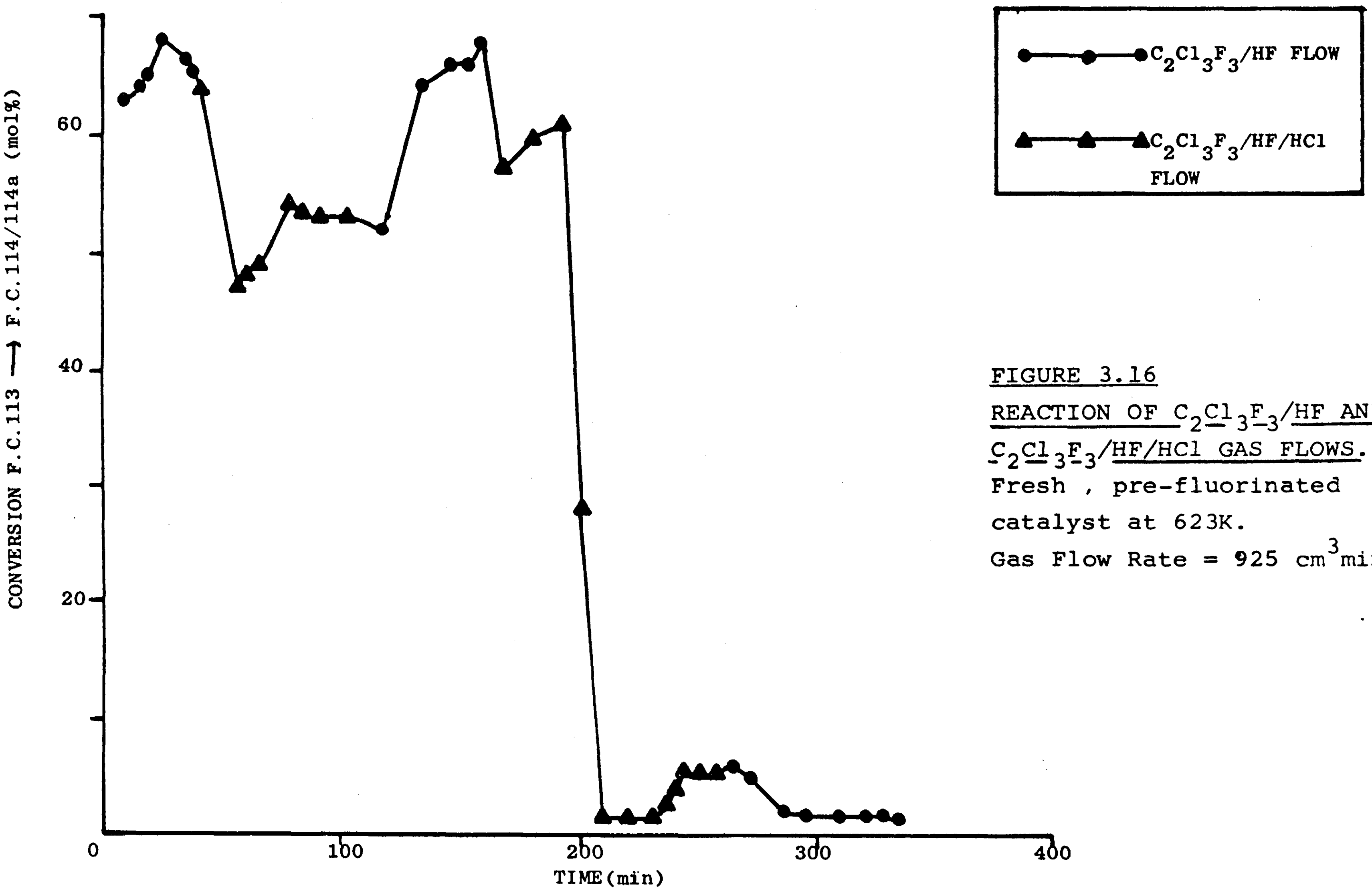


FIGURE 3.16

REACTION OF $C_2Cl_3F_3$/HF AND $C_2Cl_3F_3$/HF/HCl GAS FLOWS.
Fresh , pre-fluorinated catalyst at 623K.
Gas Flow Rate = 925 $cm^3 min^{-1}$

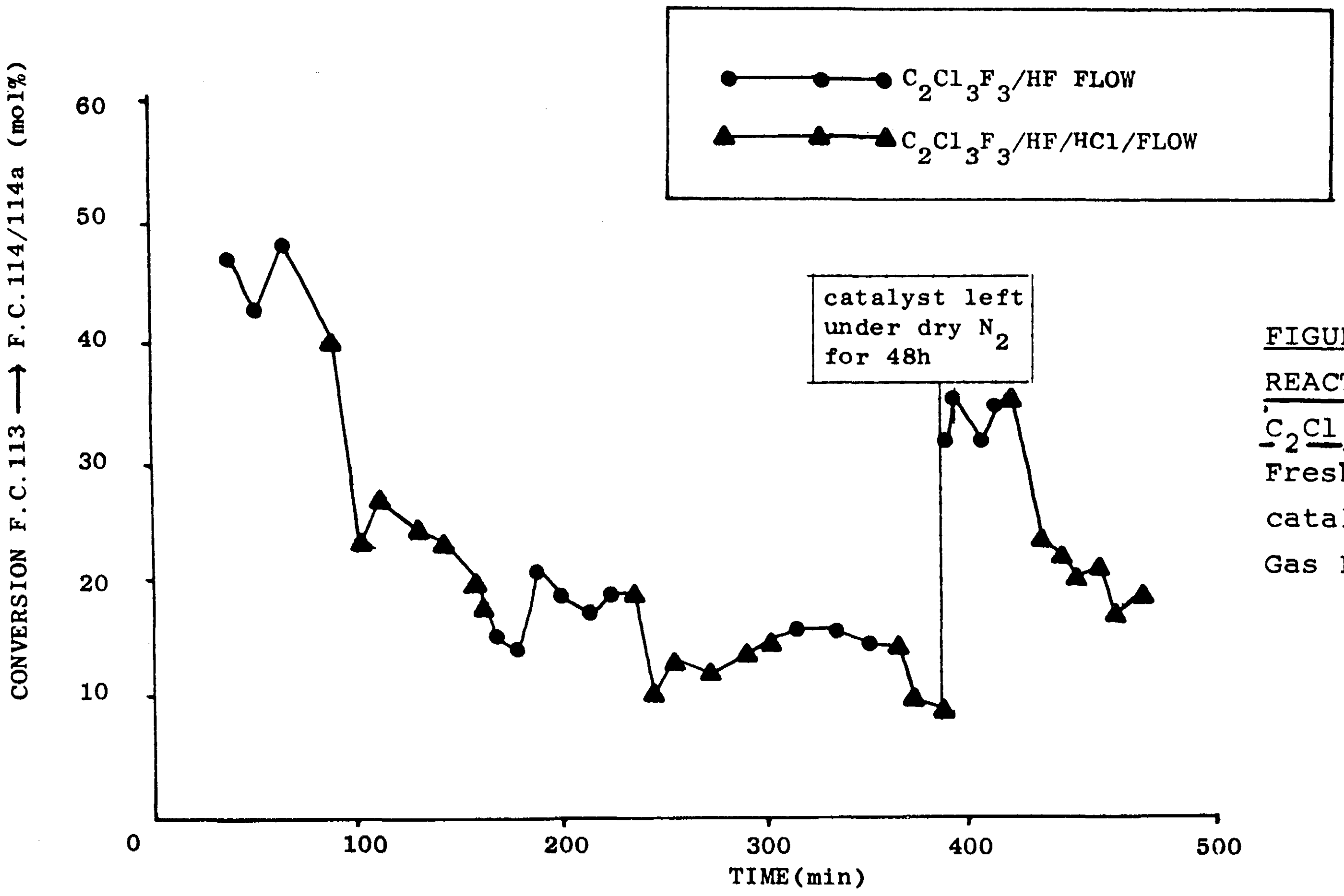


FIGURE 3.17

REACTION OF $C_2Cl_3F_3$/HF AND $C_2Cl_3F_3$/HF/HCl GAS FLOWS. Fresh , pre-fluorinated catalyst at 676K.

Gas Flow Rate = 925 cm^3min^{-1}

that addition of HCl to the feed has an effect on the activity of the catalyst towards fluorination of $C_2Cl_3F_3$. The concentration of HCl in the reactor feed was small, and concentration effects in the gas phase and changes in contact time resulting from the slightly higher flow rate when HCl was admitted (HF + $C_2Cl_3F_3$, flow rate = 925 cm^3min^{-1}, HF + $C_2Cl_3F_3$ + HCl, flow rate = 938 cm^3min^{-1}) can be ignored. On the basis of a $C_2Cl_3F_3$ flow rate of 10 mmol min^{-1} and a conversion to $C_2Cl_2F_4$ of 42 mol % of the reactant (Figure 3.17), the quantity of HCl expected to be formed by the reaction:-

$$C_2Cl_3F_3 + HF \longrightarrow C_2Cl_2F_4 + HCl$$

can be estimated to be 4.3 mmol HCl min^{-1}. The effect of admitting HCl to the reactor in a flow of 0.6 mmol min^{-1}, or ca. 14% of the total expected to be formed by fluorination of $C_2Cl_3F_3$, is therefore dramatic. Possible explanations for the effect of HCl on the fluorination of $C_2Cl_3F_3$ are the blocking of HF or $C_2Cl_3F_3$ adsorption sites or a change in a surface equilibrium involving fluorination of $C_2Cl_3F_3$ and desorption of HCl. A possible role for HCl in increasing the production of chlorinated derivatives is ruled out on the basis of the results.

3.9 Adsorption of CCl_2FCClF_2 on Chromia Studied by Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy.

Diffuse reflectance spectra were obtained for the compound CCl_2FCClF_2 admitted to a substrate of diamond dust or pre-fluorinated chromia dispersed in diamond dust (1-5% w/w chromia). Diamond dust was used as the dispersent to increase the throughput of infra-red energy. The spectra were compared with an authentic gas-phase infra-red spectrum of CCl_2FCClF_2 (Figure 3.18). Diamond and diamond/chromia samples were evacuated to a pressure of ca. 0.05 torr and background spectra obtained. Following this, CCl_2FCClF_2 was admitted to the sample and allowed to equilibrate for 30 min at a pressure of 250 torr. Spectra were then obtained and the background spectrum subtracted.

The spectra for CCl_2FCClF_2 on diamond (Figure 3.19) and diamond/chromia (Figure 3.20) were more complex than the gas-phase spectrum of CCl_2FCClF_2 (Figure 3.18). Adsorption of CCl_2FCClF_2 on diamond gave rise to a spectrum containing fewer doublets and multiplets than that for diamond/chromia. The spectral data, with the principal absorption bands, are shown in Table 3.16. The data indicate that adsorption of CCl_2FCClF_2 occurs on both diamond and chromia. Observed frequencies on diamond were compared with literature spectra[6] obtained from N_2 and Ar matrix isolation studies on CCl_2FCClF_2 and band assignments, based on a normal co-ordinate analysis from the same study, were possible (Table 3.17). There are two possible conformations which CCl_2FCClF_2 can adopt, C_s and C_1 (Figure 3.22). Since only physical adsorption should occur on diamond, the spectrum can be interpreted on the basis of physical adsorption involving both the C_s and C_1 conformers.

FIGURE 3.18 INFRA-RED SPECTRUM OF GASEOUS CCl_2FCClF_2.

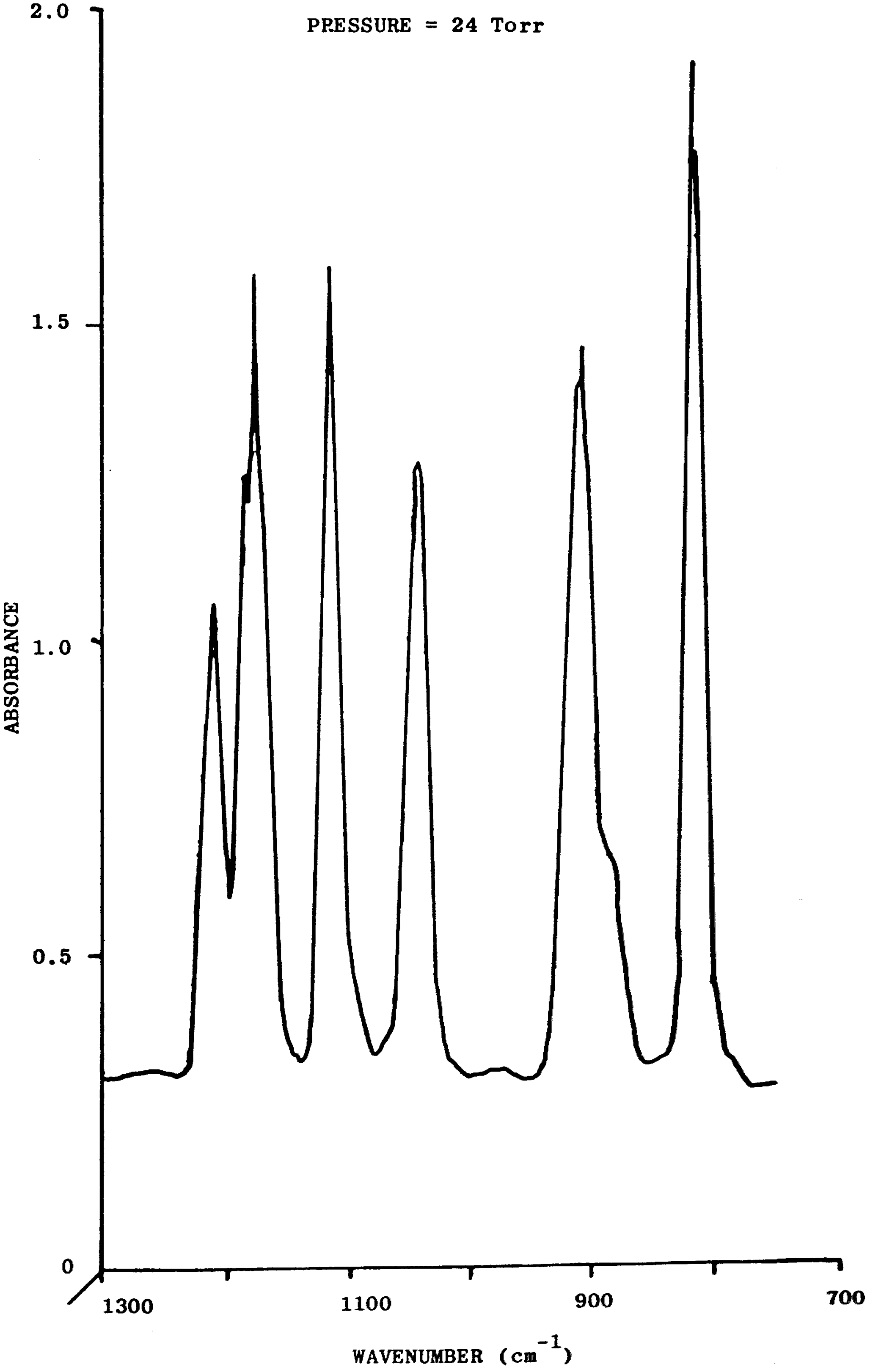


FIGURE 3.19 D.R.I.F.T.S. SPECTRUM OF $C_2Cl_3F_3$ ON DIAMOND

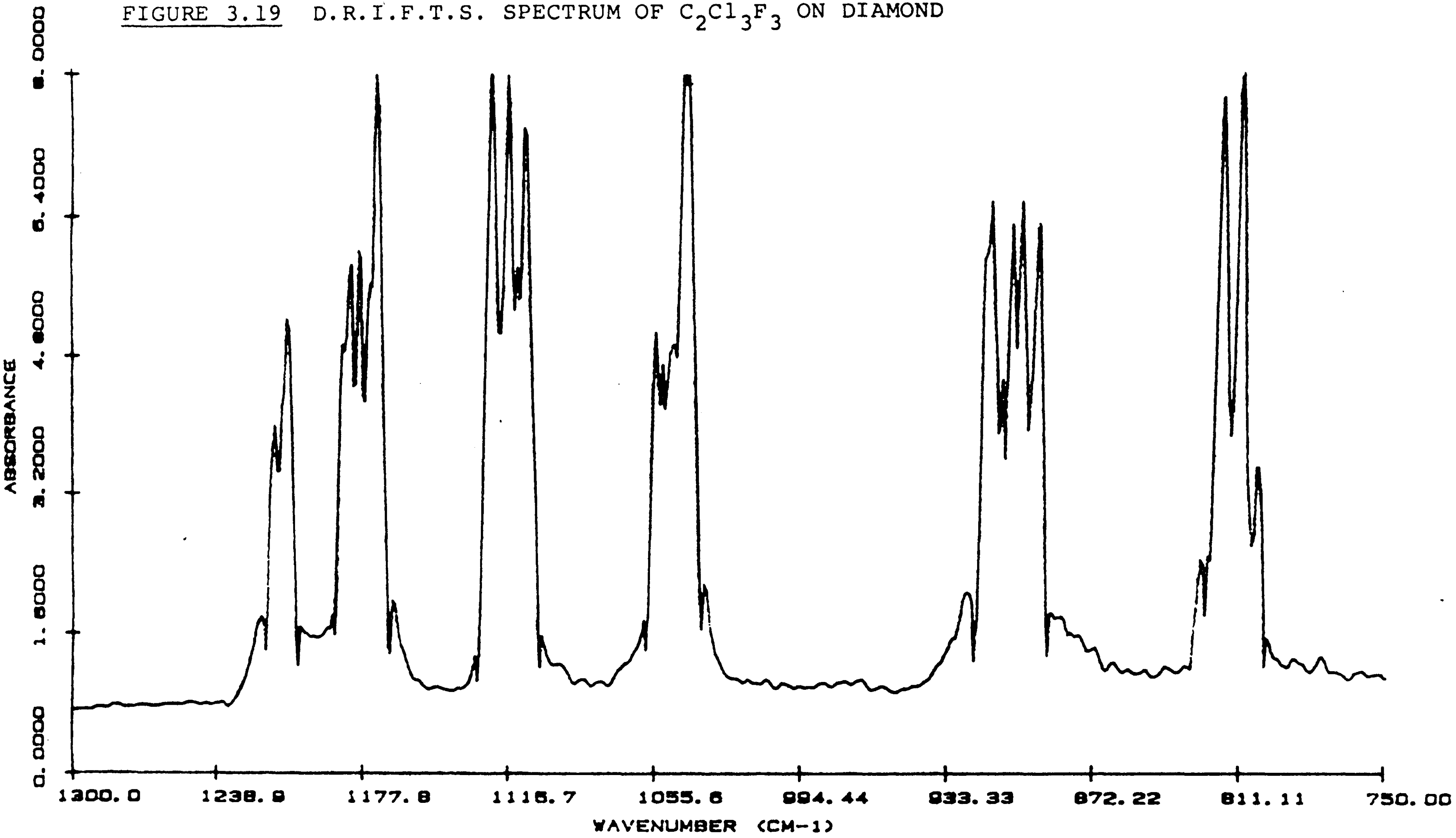


FIGURE 3.20 D.R.I.F.T.S. SPECTRUM OF $C_2Cl_3F_3$ ON CHROMIA/DIAMOND

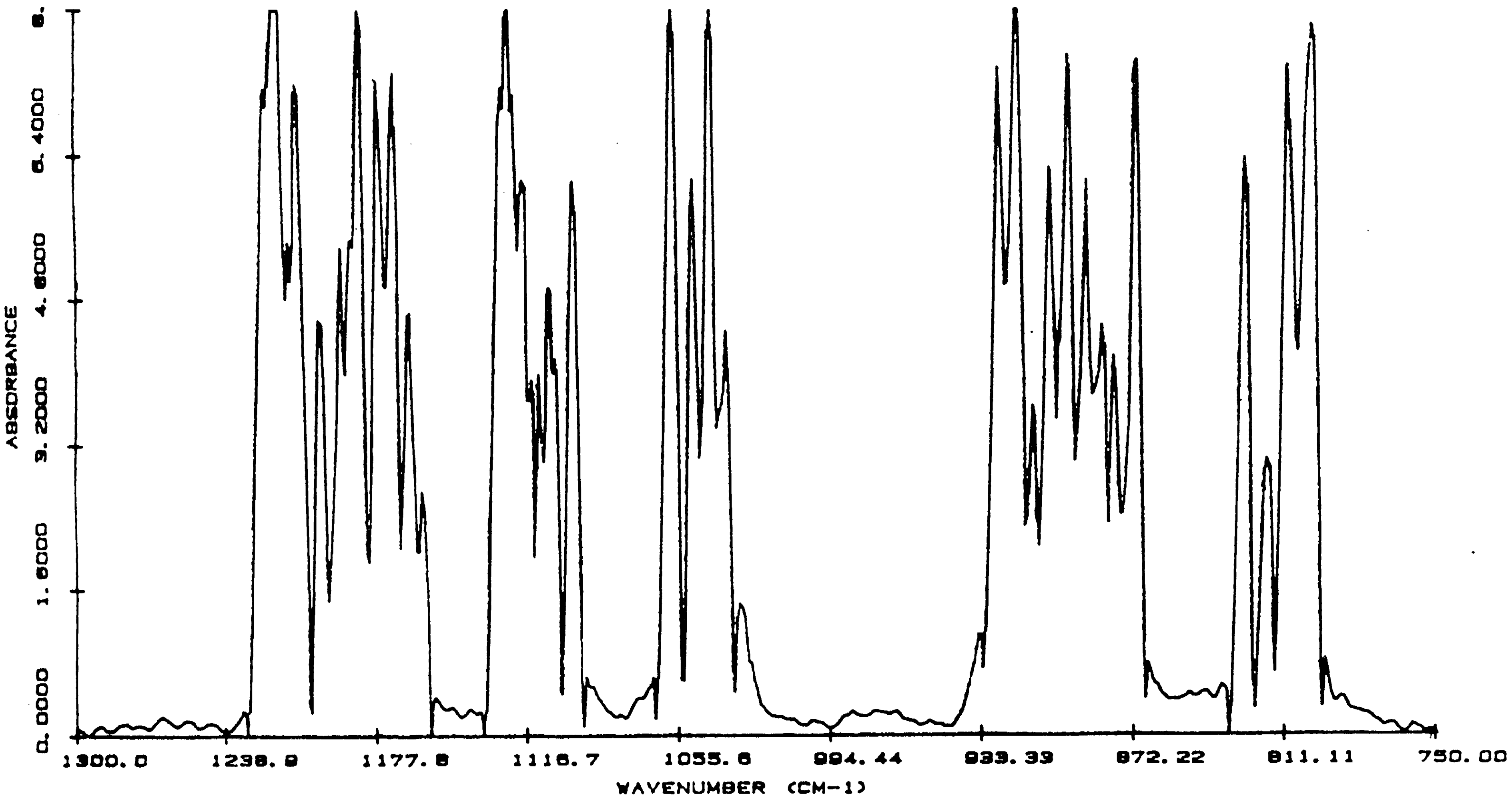


FIGURE 3.21 COMPUTED SUBTRACTION SPECTRUM OF $C_2Cl_3F_3$ ON CHROMIA

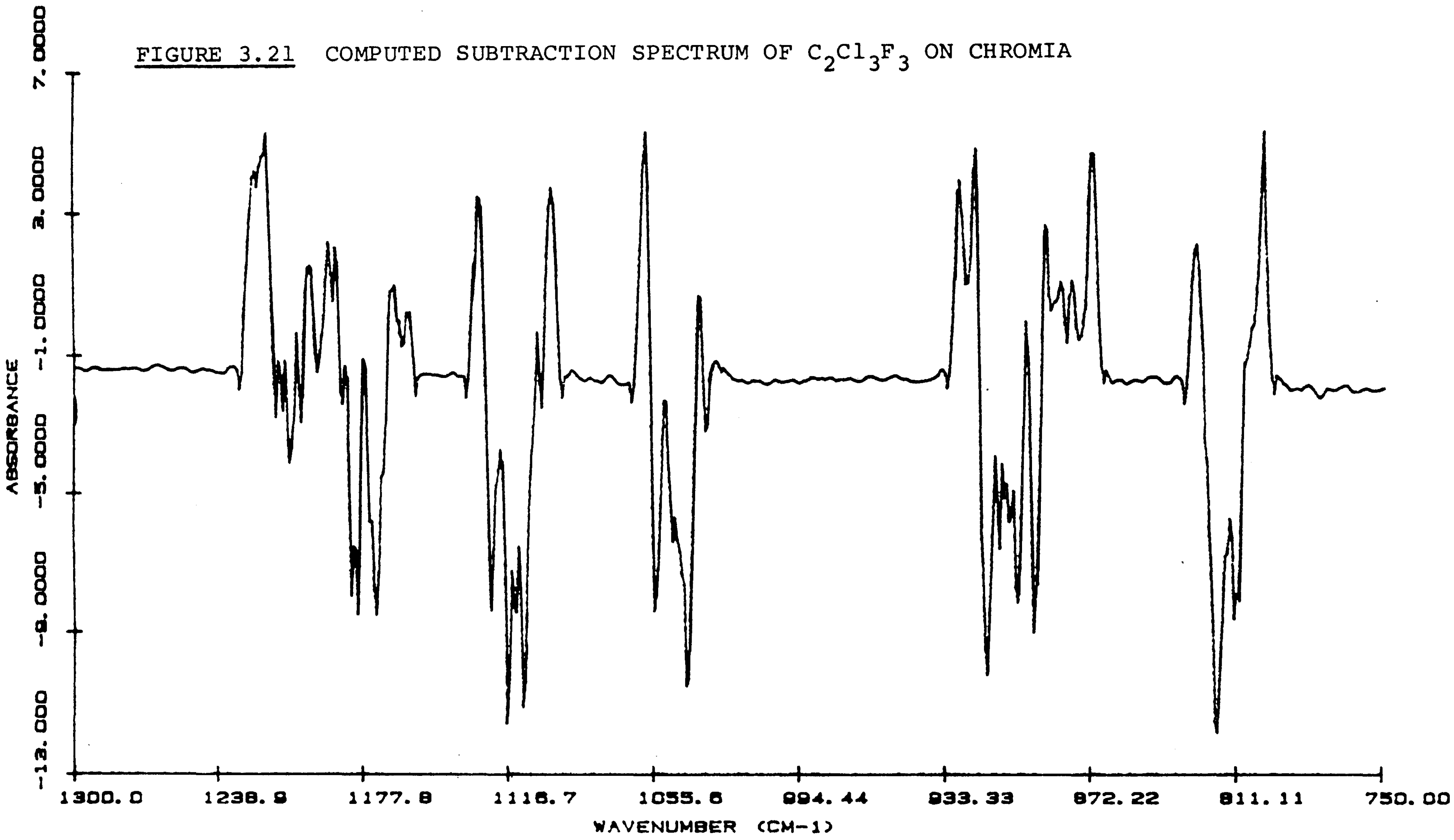


Table 3.16 Infra-Red Spectral Data for CCl_2FCClF_2

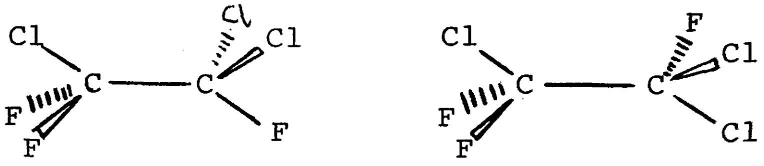
Vapour		Adsorbed		
Observed at 24 torr.	Literature[6]	Diamond	Chromia/Diamond	Computed Subtraction
1257 w	1251 w	-	-	-
			1221 vs	1223 vs
		1214 s	1217 vs	1218 vs
1213 s	1211 vs		1214 vs	1210 m
		1209 vs	1206 vs	1200 m
			1196 s	1192 m
		1186 s	1187 vs	1189 m
1189 vs	1186 vs			
		1183 vs	1181 vs	1184 m
1179 vs	1178 vs, Q	1179 vs		
		1174 vs	1174 vs	
1170 sh	1170 vs, Q	1172 vs		1164 m
			1160 s	1160 w
			1126 vs	1129 s
		1124 vs	1123 vs	
	1123 R	1117 vs	1111 vs	
1117 vs	1118 Q vs	1113 vs	1108 vs	
	1111 P	1110 vs	1101 s	1100 s
			1097 s	
		1055 vs	1060 vs	1060 s
1049 s	1047 vs, Q	1052 vs	1056 vs	
		1047 vs	1047 vs	
1042 s		1042 vs	1041 vs	1036 m
			1032 m	
979 w	976 m	-	-	-
			923 vs	928 s
		915 vs	918 vs	921 vs
		910 vs	909 vs	
909 vs	908 vs, Q	907 vs	906 vs	
		903 vs	902 vs	
		895 vs	895 vs	892 s
			891 vs	
			888 vs	885 m
			882 vs	881 m
			873 vs	
			870 vs	872 vs
817	818 R	819 vs	828 s	829 m
815 vs	813 Q vs	811 vs	812 s	
811	808 P	804 s	806 vs	800 vs

NOTE: Relative intensities; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table 3.17 Observed Frequencies of CCl_2FCClF_2 Adsorbed on Diamond Compared with Literature Values on N_2 or Ar Matrices.

Literature[6]	Observed	Conformer	Assignment 1)
1214	1214	C_s	$CCl{<}^{F}_{F}$
1210	1209	C_1	$CCl{<}^{F}_{F}$
1186	1186 1183	no assignment in literature	
1178	1179	C_1	$CCl{<}^{F}_{F}$ stretch
	1174		
1170	1172	C_s	$CCl{<}^{F}_{F}$ stretch
1118	1124 1117 1113 1110	C_s and C_1	CCl_2-F
	1055		
1047	1052	C_1	CF_2 - Cl
	1047		
1041	1042	C_s	C-Cl and C-F stretches
	915		
907	910	C_s	C - Cl
	907		
903	903	C_1	CF_2 - Cl
	895		

NOTE: Except where indicated, terms are combinations of stretching and bending modes.



C_s C_1

Figure 3.22 C_s and C_1 conformers of CCl_2FCClF_2.

Interpretation of the more complex spectrum for CCl_2FCClF_2 on a diamond/chromia substrate is more difficult. Compared with CCl_2FCClF_2 on diamond, the spectrum obtained using a chromia/diamond substrate showed further splitting of the vapour phase bands at 1211 cm^{-1}, 1123, 1118, 1111cm^{-1}, 1047cm^{-1} and 908cm^{-1}. The complexity of the spectrum on the chromia/diamond substrate indicates that physical adsorption is not the only interaction between the substrate and CCl_2FCClF_2. Chemical adsorption of CCl_2FCClF_2 on chromia can be inferred from the additional absorptions observed on the diamond/chromia substrate compared with the diamond substrate. The shifts occurred for both C-Cl and C-F absorbance bands. Computed subtraction of the spectrum of CCl_2FCClF_2 on diamond from that on diamond/chromia gave a spectrum containing both positive and negative absorbances (Figure 3.21). The positive absorbance bands represent the spectrum of CCl_2FCClF_2 on chromia alone and are tabulated in Table 3.16.

No conformational assignments can be made on the basis of the data in Table 3.16. However, by analogy with the interaction between $CClF_2CClF_2$ and erbium trifluoride or erbium trichloride[7], both C_s and C_1 forms would be expected.

The adsorbed species were completely removed from both diamond and chromia/diamond substrates by evacuating the samples to ca. 0.05 torr. This indicates that the interaction between CCl_2FCClF_2 and chromia is not strong compared with, for example, water, which cannot be completely removed by evacuation to ca. 0.05 torr for ½h. There was no evidence for chlorofluoroethanes adsorbed on fresh or used chromias following use of these catalysts in the reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$. However, removal of any adsorbed chlorofluoroethane was expected to occur under the conditions of dinitrogen flow in the reactor, by comparison with the observed behaviour of CCl_2FCClF_2 when chromia samples were evacuated.

CHAPTER FOUR

THE BEHAVIOUR OF ANHYDROUS HYDROGEN FLUORIDE ON CHROMIA

CHAPTER FOUR.

The Behaviour of Anhydrous Hydrogen Fluoride on Chromia.

4.1 Introduction

Chlorofluoroethanes did not react on chromia pre-treated with dinitrogen flow at 623 K (Section 3.3). Neither fluorinated nor chlorinated products were produced when $C_2Cl_3F_3$ or $C_2Cl_2F_4$ were admitted to the catalyst at 623 and 693 K respectively. Treatment of the catalyst with anhydrous hydrogen fluoride at 623 K followed by admission of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ (623 and 693 K respectively) resulted in the formation of fluorinated and chlorinated products. Anhydrous HF, whether present in a mixed chlorofluoroethane/HF feed (Section 3.8) or admitted to the catalyst as a pre-fluorinating agent (Section 3.1), is therefore important in promoting the fluorination and chlorination of chlorofluoroethanes.

The interaction between HF and chromia has been the subject of a detailed [^{18}F]-fluorine tracer study[26] (Section 1.6.4). However, an investigation into the nature of the adsorbed fluorine-containing species and any interactio between these species and the species responsible for the chlorination reactions was necessary to obtain a more complete understanding of the chemistry of the vapour phase fluorination process.

4.2 Removal of Surface Hydroxyl Groups by Pre-treatment of Chromia with Hydrogen Fluoride.

It has been shown previously[26] from [^{1}H]-hydrogen, [^{2}H]-hydrogen exchange reactions between [^{2}H]-dihydrogen and chromia on prefluorinated chromia that ca. 95% of the surface hydroxyl groups on chromia are lost during the first treatment of the catalyst with HF. Pre-treatment of chromia involving dinitrogen flow at 623 K followed by admission of HF at this temperature reduced the catalyst weight by 2.9%. The reduction in catalyst weight was probably accounted for by loss of water. Aqueous hydrofluoric acid was collected in the reactor eluant line and the solution was pale green in colour, a characteristic of aqueous Cr^{3+}. Reference has already been made (Section 1.5) to the importance of catalyst dehydration in promoting other catalytic processes on chromia, for example dehydrogenation of secondary alcohols[35]. Loss of water from the coordination sphere of chromium ions will create coordinativel unsaturated sites at which HF or the chlorofluoroethane could adsorb.

4.3 Effect of Hydrogen Fluoride Treatment on the Surface Area of Chromia.

Surface areas of unused and used chromia catalysts were determined by the B.E.T. method (Section 2.15) using dinitroge as adsorbate. Samples which had not been exposed to HF had surface areas in the range 60±2 - 65±2 $m^2 g^{-1}$ (Table 4.1). After passage of HF at 623 K and reaction of the chlorofluoroethane at 623 K, surface areas of chromia catalysts were in

Table 4.1 Surface Areas of Chromia Samples.

Sample	Description	Surface Area (m^2g^{-1})
1	Unused, no pre-treatment	65±2
2	Unused, no pre-treatment	60±2
3	8.5h. HF/$C_2Cl_2F_4$ flow	34±2
4	HF(22cm^3 liquid), 175 mmol $C_2Cl_2F_4$	30.9±1.5
5	600h.HF/Chlorofluoroethane flow	20±1
6	1500 HF/Chlorofluoroethane flow	13±1
7	1500 HF/Chlorofluoroethane flow	13±1

the range 30.9±1.5 - 34±2 m^2g^{-1}. Used catalyst, which had been used for several hundred hours in an industrial plant in a mixed HF/chlorofluoroethane flow, had the lowest surface areas, these being in the range 13±1 - 20±1 m^2g^{-1}. The reduction in surface area with increasing HF treatment suggests that the chemical nature of the surface changed under conditions of HF flow and reaction. Laboratory pre-fluorinated catalysts with surface areas in the range 31 - 34 m^2g^{-1} contained up to 10% w/w fluorine, while used, extensively fluorinated catalysts with surface areas of ca. 13 m^2g^{-1} contained 30% w/w fluorine[70]. The slow replacement of Cr^{III}-O bonds by Cr^{III}-F bonds has been suggested to account for these observations.[26]

4.4 Interaction of [^{18}F]-Fluorine Labelled Hydrogen Fluoride with Unused Chromia.

The uptake of HF ~~or~~ pre-dried and pre-fluorinated chromia was determined by flowing [^{18}F]-fluorine labelled HF over chromia at 623 K. The subsequent removal of adsorbed [^{18}F]-fluorine activity by N_2 or N_2/HCl gas flow was determined to establish the extent to which HCl displaced adsorbed [^{18}F]-fluorine.

Flowing $H^{18}F$ over chromia at 623 K resulted in the uptake of [^{18}F]-fluorine activity in the range 1.04±0.02 - 1.4±0.1 mmol $H^{18}F$ (g catalyst)$^{-1}$(Table 4.2). There appeared to be no relationship between the quantity of HF admitted in the pre-treatment and the uptake of [^{18}F]-fluorine following pre-treatment.

Table 4.2 Uptake of $H^{18}F$ by Chromia at 623 K.

Experiment	HF used in pretreatment at 623 K (cm^3 liquid)	$H^{18}F$ treatment		$[^{18}F]$-Fluorine count rate of chromia count s^{-1}(g catalyst)$^{-1}$	Equivalent $H^{18}F$ uptake (mmol[g catalyst]$^{-1}$)
		(cm^3 liquid)	flow time(min)		
1	3.0	3.0	60	312±2	1.3±0.1
2	9.0	4.0	60	152±10	1.4±0.1
3	10.0	4.0	60	406±5	1.34±0.04
4	7.0	4.0	60	432±9	1.38±0.04
5	7.0	3.0	60	260±4	1.04±0.02
6	8.0	4.0	60	92±2	1.12±0.04

4.5.1. Removal of adsorbed [^{18}F]-fluorine by dinitrogen and dinitrogen/hydrogen chloride gas flow.

Chromia pretreated with H^{18}F was purged in a flow of N_2 or N_2/HCl gas. Flowing dinitrogen at 623 K at a rate of 15 - 20 cm^{3}min^{-1} for 40 min reduced the [^{18}F]-fluorine count rate to 52-61% of that observed immediately following H^{18}F gas flow. After a further 40 min in the dinitrogen gas flow a further portion of [^{18}F]-fluorine was removed (Table 4.4). [^{18}F]-Fluorine determined after 80 min dinitrogen flow was in the range 34-58% of that determined after 40 min dinitrogen flow. A previous [^{18}F]-fluorine study[25] of the behaviour of H^{18}F on chromia reported that *ca*. 15% of the adsorbed [^{18}F]-fluorine, resulting from the passage of H^{18}F over the catalyst at 623 K, was removed by 10 min dinitrogen flow. From the results obtained in the present study it appears that relatively more [^{18}F]-fluorine was removed in the early stages of the dinitrogen purge, 15% after 10 min, 39-48% after 40 min and 66-82% after 80 min. This observation suggests that it becomes increasingly more difficult to remove [^{18}F]-fluorine as the concentration of the adsorbed fluorine-containing species falls.

Flowing HCl vapour in a stream of dinitrogen (0.08 mmol HCl, flow rate 15-20 cm^{3}min^{-1}) over [^{18}F]-fluorine labelled chromia for 40 min reduced the [^{18}F]-fluorine to 52-68% of that determined immediately following H^{18}F treatment (Table 4.3). Since dinitrogen flow in the absence of HCl vapour removed 52-61% of the adsorbed [^{18}F]-fluorine, it can be concluded that HCl vapour had no greater affect than dinitrogen

Table 4.3 $[^{18}F]$-Fluorine activity removed by N_2 or N_2/HCl gas flow during 40 min at 623 K.

Experiment †	Initial $[^{18}F]$Count Rate (count s^{-1})	Gas Flow (40 min)	Final $[^{18}F]$Count Rate (count s^{-1})	$[^{18}F]$-Fluorine activity retained (%)
1	312±2	N_2	161±1	52
2	152±10	N_2	93±4	61
3	406±5	N_2/HCl	277±10	68
4	432±9	N_2/HCl	223±4	52
5	260±4	N_2/HCl	169±11	65
7	67±1	N_2/HCl	35±1	52

† Corresponds to numbers in Table 4.2.

Table 4.4 $[^{18}F]$-Fluorine activity removed by N_2 gas flow during 80 min at 623 K.

Experiment	$[^{18}F]$Count Rate after 40 min N_2 flow (count s^{-1})	$[^{18}F]$count rate after 80 min N_2 flow (count s^{-1})	$[^{18}F]$-fluorine activity retained (%)
8	155±2	91±3	58
9	273±8	93±2	34

NOTE: $[^{18}F]$count rates were not determined immediately after passage of $[^{18}F]$-HF.

on the removal of catalyst [^{18}F]-fluorine. Chlorine uptakes on pre-fluorinated chromia following N_2/HCl flow, under identical conditions of flow rate and temperature to the experiments in Table 4.3, were determined to be <u>ca</u>. 0.2 mmol Cl(g catalyst)$^{-1}$ (Table 5.8). Compared with [^{18}F]-fluorine uptake from passage of $H^{18}F$, the uptake of chlorine from HCl was small. Any displacement of catalyst [^{18}F]-fluorine by HCl flow would therefore have been expected to be small, and may have had no detectable effect in these experiments.

4.5.2. <u>Hydrolysis of Fluorine Adsorbed on Chromia.</u>

When samples of fluorinated chromia were stored in glass sample bottles etching of the glass occurred. This phenomen~~um~~ was caused by the reaction of HF with silica to form silicon tetrafluoride. The catalyst is hygroscopic and replacement of HF by H_2O can be proposed to account for this observation. The removal of weakly bound water from the surface of chromia during HF flow could involve the volatile species HF---H_2O.[71] The reverse of this process can be proposed to account for desorption of HF when the catalyst is allowed to come into contact with water vapour.

CHAPTER FIVE

THE BEHAVIOUR OF HYDROGEN CHLORIDE ON CHROMIA

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THE BEHAVIOUR OF HYDROGEN CHLORIDE ON CHROMIA.

5.1 Introduction.

The uptake of hydrogen chloride on chromia was determined using neutron activation analysis. [^{36}Cl]-Chlorine labelled hydrogen chloride was used to investigate the behaviour of adsorbed chloride. The fate of the adsorbed [^{36}Cl]-chlorine during subsequent reactions involving chlorofluoroethanes or hydrogen fluoride was established by determining [^{36}Cl]-chlorine count rates in the eluant fractions and on the catalyst.

The experiments were carried out using reactor A (Section 2.2.2). Catalyst samples were treated at 623 K using dry dinitrogen flow before use. This treatment was expected to remove a proportion of the water present in the catalyst. Samples of the pelleted chromia catalyst were removed for analysis from various positions along the catalyst bed. Since the catalyst is hygroscopic, pellets were not returned to the reactor for use in further experiments.

5.2. Treatment of [^{36}Cl]-Chlorine Count Rate Data.

Chlorine uptakes on chromia, from passage of $H^{36}Cl$, can be calculated from the quotient of the [^{36}Cl]-chlorine count rate on chromia and the specific [^{36}Cl]-chlorine count rate of $H^{36}Cl$, determined as $Ag^{36}Cl$, (Section 2.8.3).

$$\text{Uptake of } [^{36}\text{Cl}]\text{-chlorine HCl} = \frac{\text{Chromia}[^{36}\text{Cl}]\text{-chlorine count rate}}{\text{Specific}[^{36}\text{Cl}]\text{-chlorine count rate of H}}$$

<u>where</u> Uptake is in mol HCl(g catalyst)$^{-1}$

Chromia [^{36}Cl]-chlorine count rate is in count s^{-1}

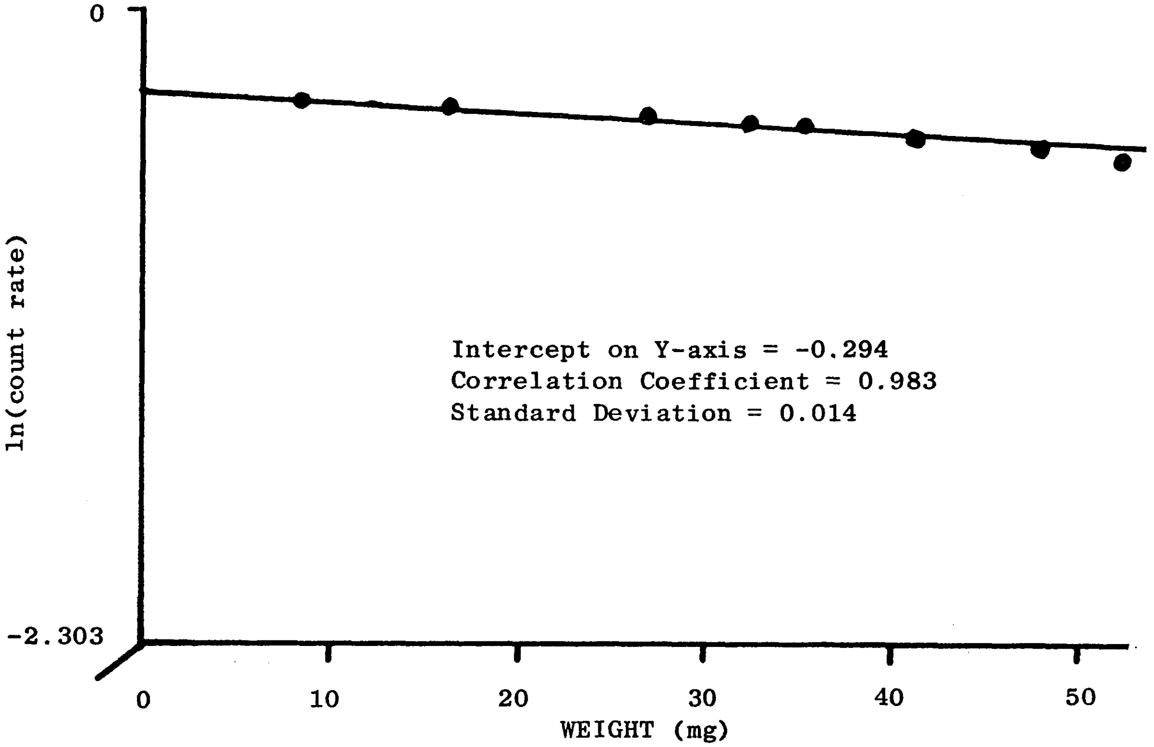
Specific [^{36}Cl]-chlorine count rate of HCl is in count s^{-1}(mol HCl)$^{-1}$ and is determine as Ag^{36}Cl.

<u>Equation (5.1)</u>

However, two problems arose in using equation (5.1). First , two different solids were counted, chromia and silver chloride. Second , [^{36}Cl]-chlorine in the two solids was subject to different self-absorption effects. Although [^{36}Cl]-chlorine count rates determined for Ag^{36}Cl and [^{36}Cl]-chlorine labelled chromia were corrected for self-absorption, the corrections were not to zero self-absorption. Instead, [^{36}Cl]-chlorine count rates were corrected to the lowest sample weight for which reliable readings could be obtained, which was 20mg in each case. For sample weights of less than 20mg, for both Ag^{36}Cl and [^{36}Cl]-chlorine labelled chromia, a certain proportion of [^{36}Cl]-chlorine β-emissions continued to be absorbed by the surrounding matter.

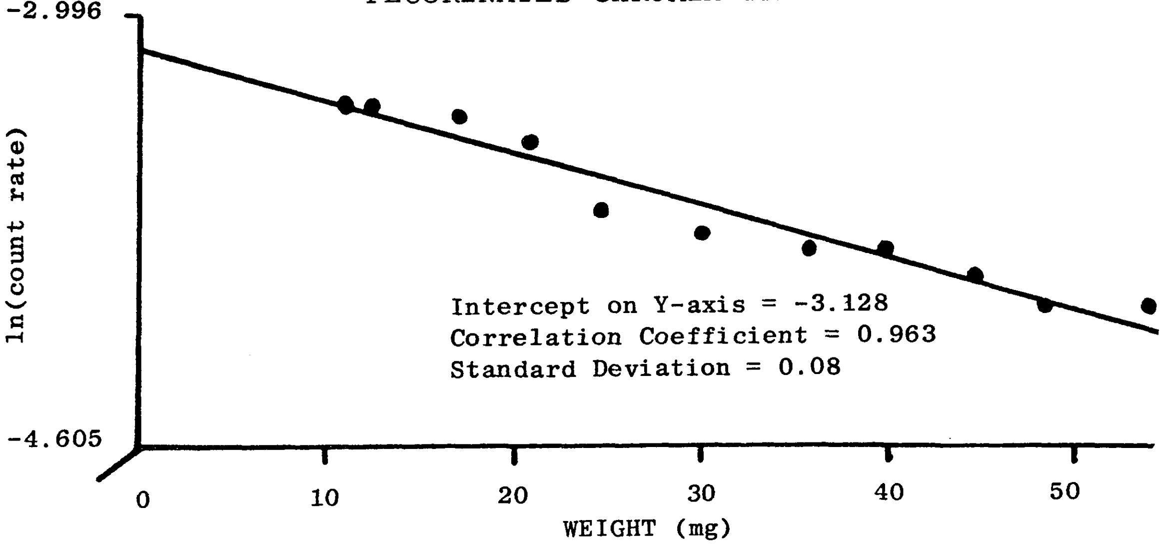
Figures 5.1 and 5.2 demonstrate the effect of self-absorption on Ag^{36}Cl and [^{36}Cl]-chlorine labelled chromia samples respectively. These plots show a linear relationship between ℓn(count rate) and sample weight, and are

FIGURE 5.1 [^{36}Cl] -CHLORINE SELF-ABSORPTION IN Ag^{36}Cl.



Intercept on Y-axis = -0.294
Correlation Coefficient = 0.983
Standard Deviation = 0.014

FIGURE 5.2 [^{36}Cl] -CHLORINE SELF-ABSORPTION FOR PRE-FLUORINATED CHROMIA TREATED USING H^{36}Cl.



Intercept on Y-axis = -3.128
Correlation Coefficient = 0.963
Standard Deviation = 0.08

derived from the self-absorption curves in Figures 2.11 and 2.12. Extrapolation of the lines in Figures 5.1 and 5.2 to the y-axis enables the extent of self absorption below a sample weight of 20mg to be estimated. This estimate assumes that the linear relationship between ℓn(count rate) and sample weight does not change for very small weights. The [^{36}Cl]-chlorine count rates for Ag^{36}Cl and [^{36}Cl]-chlorine labelled chromia for 50mg and 20mg samples, together with the extrapolated value for [^{36}Cl]-chlorine count rate, are shown in Table 5.1.

Table 5.1 [^{36}Cl]-Chlorine Count Rates for Ag^{36}Cl and [^{36}Cl]-Chlorine Labelled Chromia.

Sample	Weight (mg)	[^{36}Cl]-Chlorine Count Rate (count s^{-1})
Ag^{36}Cl	50	0.62
	20	0.70
	extrapolated to y-axis	0.75
^{36}Cl -chlorine labelled chromia	50	0.017
	20	0.031
	extrapolated to y-axis	0.044

Using the data in Table 5.1, self-absorption of [^{36}Cl]-chlorine for a 20mg sample could be compared with self-absorption for a 50mg sample. [^{36}Cl]-chlorine self-absorption for a 20mg sample of Ag^{36}Cl was 38% of that for a 50mg sample. In the case of [^{36}Cl]-chlorine labelled chromia, self-absorption for a 20mg sample was 48% of that for a 50mg sample. The difference between [^{36}Cl]-chlorine self-absorption for 20mg samples of Ag^{36}Cl and [^{36}Cl]-chlorine labelled chromia was therefore small enough to be ignored. [^{36}Cl]-Chlorine count rates, from H^{36}Cl flow experiments on chromia, corrected to sample weights of 20mg could therefore be used to obtain reliable estimates of [^{36}Cl]-chlorine uptakes on chromia using equation (5.1).

5.3 Total Chlorine Contents of Chromia Catalysts Used in Hydrogen Chloride Adsorption Studies, Determined by Neutron Activation Analysis.

The total chlorine contents of pre-fluorinated catalysts treated with HCl or used in reactions involving $C_2Cl_2F_4$ were determined using neutron activation analysis (Section 2.10). Since this method determined the intensity of a γ-emission peak associated with the β^- decay of [^{38}Cl]-chlorine, self-absorption was not expected to occur and both surface and, if present, bulk chlorine species would have been detected. In contrast, self-absorption of β^- particles from [^{36}Cl]-chlorine adsorbed on chromia limited the utility of [^{36}Cl]-chlorine count rate data to determination of species at or near the surface of chromia.

Used catalyst, with several hundred hours use in a chlorofluoroethane/HF environment, contained 13±1 - 15±1 μmol Cl(g catalyst)$^{-1}$ as received (Table 5.2). Admission of HCl (HCl/N_2 gas flow = 15-20 cm^{3}min^{-1}, 0.08 mol HCl admitted) to used chromia at 693 K resulted in the uptake of chlorine by the catalyst. Following HCl flow, the total chlorine content of used catalyst was in the range 64±4 - 88±7 μmol (g catalyst)$^{-1}$, (Table 5.2). Uptake of chlorine on fresh, pre-fluorinated chromia following HCl flow at 623 K (N_2/HCl flow rate = 15 - 20 $cm^3 min^{-1}$) was in the range 171±6 - 200±14 μmol(g catalyst)$^{-1}$, substantially above the range determined for used catalyst. The uptake of chlorine from HCl treatment of pre-fluorinated chromia was much smaller than the uptake of fluorine from HF. Admission of ca. 0.08 mol HCl to fresh, pre-fluorinated chromia at 623 K resulted in uptake of 171±6 - 200±14 μmol Cl(g catalyst)$^{-1}$ compared with an uptake of 1.04±0.02 - 1.4±0.1 mmol F (g catalyst)$^{-1}$ from admission of ca. 0.14 mol HF.

Reaction of $C_2Cl_2F_4$ at 693 K on used chromia, previously treated at 623 K with HF followed by HCl, formed C_2ClF_5, ca. 17 mol %, $C_2Cl_2F_4$, ca. 78 mol % and $C_2Cl_3F_3$, ca. 5 mol %. Chlorine contents determined following reaction of $C_2Cl_2F_4$ were 66±3 and 92±6 μmol (g catalyst)$^{-1}$ (Table 5.3).

Admission of $C_2Cl_2F_4$ to fresh, pre-fluorinated chromia resulted in reaction to form $C_2Cl_3F_3$ and C_2ClF_5 as the principal products. Chlorine contents determined for fresh, pre-fluorinated chromia following HCl/N_2 flow at 623 K and reaction of ca. 20 mmol $C_2Cl_2F_4$ at 693 K were 312 and 343 μmol(g catalyst)$^{-1}$ (Table 5.3). The products from reaction of $C_2Cl_2F_4$ comprised C_2ClF_5, ca. 55 mol %, $C_2Cl_2F_4$, ca. 32 mol % and $C_2Cl_3F_3$, ca. 13 mol %.

Reaction of $C_2Cl_2F_4$ at 693 K (ca. 79 mmol) on a pre-fluorinated catalyst resulted in chlorine contents, determined two days after removal of the catalyst, in the range 635 - 746 μmol (g catalyst)$^{-1}$ (Table 5.3). However, after allowing the catalyst to stand in air for three weeks chlorine contents

Table 5.2 Chlorine contents of chromia catalyst determined by Neutron Activation Analysis.

Chromia treated with 0.08 mol HCl.

Conditions.	Pellet (1)	Chlorine content (μmol Cl[g catalyst]$^{-1}$)
Unused, pre-fluorinated	1	200±14
chromia.	10	177±3
HCl flow	19	199±6
Catalyst temperature 623K	28	171±6
Used, extensively	-	13±1
fluorinated chromia	-	15±1
As received		
Used, extensively	13	64±4
fluorinated chromia.	18	88±7
HCl flow		
Catalyst temperature 693K		

Note 1 = Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

Table 5.3 Chlorine contents of chromia catalyst determined by Neutron Activation Analysis.

Chromia used in reaction of $C_2Cl_2F_4$

Conditions.	Pellet (1)	Chlorine content (μmol Cl[g catalyst]$^{-1}$)
Unused, pre-fluorinated chromia.	13	343±10
HCl flow followed by 20 mmol $C_2Cl_2F_4$	18	312±9
Used, extensively fluorinated chromia	13	66±3
HCl flow followed by 17 mmol $C_2Cl_2F_4$	18	92±6
Unused, pre-fluorinated chromia. No HCl treatment 79 mmol $C_2Cl_2F_4$		
(a) Analysis two days after removal from reactor	7	746±83
	13	746±83
	19	635±111
(b) Analysis after leaving to stand in air for 3 weeks.	1	417±19
	18	442±22
	25	312±19
	30	343±19

Note. (1) = Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

in the range 312 - 442 μmol (g catalyst)$^{-1}$ were determined (Table 5.3). The difference between the chlorine contents determined in the two analyses can be accounted for if desorption of a surface chlorine containing species occurs. Desorption of hydrogen fluoride from fluorinated chromias was observed when the catalyst was allowed to stand in air (Section 4.5) and hydrolysis is the most likely explanation for the loss of HF. It is reasonable to suggest that desorption of the chlorine-containing species from the catalyst is also due to hydrolysis.

Desorption of the catalyst chlorine-containing species has important implications for the determination of [^{36}Cl]-chlorine count rates. Counting times for [^{36}Cl]-chlorine determinations ranged between 1 and 5h for each pellet. The effect on the count rates of [^{36}Cl]-chlorine desorbing from the catalyst was minimised by determining [^{36}Cl]-chlorine count rates for all the pellets as quickly as possible, usually within 36 h of removal from the reactor. [^{36}Cl]-Chlorine count rates for pellets were always determined in numerical sequence, with pellet one counted first. However, desorption of [^{36}Cl]-chlorine may have been a significant source of error in experiments involving [^{36}Cl]-chlorine count rate determinations.

5.4 Uptake of [^{36}Cl]-Chlorine on Chromia Following Admission of $H^{36}Cl$.

Admission of $H^{36}Cl$ (0.08 mol at a $N_2/H^{36}Cl$ flow rate of 15 - 20 cm^{3}min^{-1}) to fresh pre-fluorinated chromia at 623 K resulted in uptake of [^{36}Cl]-chlorine from the gas phase on to the catalyst. The [^{36}Cl]-chlorine count rate data for these experiments are tabulated in Tables 5.4 - 5.7. Using the [^{36}Cl]-chlorine count rate data, corrected for self-absorption on chromia, the average [^{36}Cl]-chlorine count rate for each experiment was plotted against the [^{36}Cl]-chlorine count rate of Ag^{36}Cl (derived from the H^{36}Cl substrate) (Figure 5.3). The plot is not linear, indicating that the uptakes of [^{36}Cl]-chlorine in the flow experiments were not identical. The experimental variables which may have led to the variations in [^{36}Cl]-chlorine uptake among the experiments include the quantity of fluorine adsorbed during pre-treatment of the catalyst with HF, the surface area of the catalysts and the flow rate of N_2/HCl vapour over the catalysts.

Values for [^{36}Cl]-chlorine uptakes were obtained by substituting the [^{36}Cl]-chlorine count rates determined on chromia and Ag^{36}Cl into equation (5.1). By comparing the [^{36}Cl]-chlorine uptakes on chromia pellets removed from similar positions along the catalyst bed in each of the four experiments, the range of [^{36}Cl]-chlorine uptake along the catalyst bed was calculated. From the experimental data in Tables 5.4 - 5.7, [^{36}Cl]-chlorine uptakes were calculated for four pellets, each pellet representing the uptake in one region of the catalyst bed (Table 5.8). Within 95% confidence limits (±2 standard deviations), [^{36}Cl]-chlorine uptakes on unused chromia were in the range equivalent to 119-323 μmol HCl (g catalyst)$^{-1}$. This compared with the

Table 5.4 [^{36}Cl]-Chlorine activity on unused chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, HF (5cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol. at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pre-treatment = (1.10 ± 0.02)x10^5 count s^{-1} (mol Cl)$^{-1}$

	Pellet Number (1)				
	1	7	12	18	25
Weight Counted (mg)	49.5	56.7	49.0	52.8	52.9
Counts accumulated	10010	13204	12026	11038	10603
Count s^{-1} (2)	0.741 ±0.007	0.891 ±0.008	0.793 ±0.007	0.710 ±0.007	0.675 ±0.007
Count s^{-1}, corrected for self absorption on chromia	1.264 ±0.013	1.678 ±0.015	1.337 ±0.013	1.271 ±0.013	1.208 ±0.013

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.5 [^{36}Cl]-Chlorine activity on unused chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, HF (6 cm^3 liquid at 623 K)
H^{36}Cl (0.1 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pre-treatment = (6.04±0.06)x10^4 count s^{-1} (mol Cl)$^{-1}$

	Pellet number (1)							
	1	7	8	14	15	20	25	26
Weight Counted (mg)	51.1	50.9	48.1	49.6	53.1	49.9	49.5	54.1
Counts accumulated	10448	10942	17986	17486	19179	17100	16280	10500
Count s^{-1} (2)	0.584 ±0.005	0.504 ±0.005	0.492 ±0.004	0.467 ±0.004	0.551 ±0.004	0.448 ±0.003	0.407 ±0.003	0.449 ±0.004
Count s^{-1}, corrected for self absorption on chromia	1.022 ±0.009	0.880 ±0.009	0.820 ±0.006	0.797 ±0.006	0.986 ±0.007	0.764 ±0.006	0.694 ±0.006	0.814 ±0.008

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.6 $[^{36}Cl]$-Chlorine activity on unused chromia following passage of $H^{36}Cl$ at 623 K.

Catalyst pre-treatment, HF (7 cm^3 liquid at 623 K)
$H^{36}Cl$ (0.08 mol. at 623 K)

$[^{36}Cl]$-chlorine count rate of $H^{36}Cl$ admitted in pre-treatment = $(1.42\pm0.01)\times10^5$ count s^{-1} (mol Cl)$^{-1}$.

	Pellet Number (1)					
	1	2	3	4	5	6
Weight Counted (mg)	51.1	54.5	50.6	53.6	53.7	54.5
Counts Accumulated	12250	13179	10078	10668	11046	11131
Count s^{-1} (2)	0.736 ±0.007	0.891 ±0.008	0.794 ±0.007	0.829 ±0.008	0.903 ±0.008	0.920 ±0.009
Count s^{-1}, corrected for self absorption on chromia	1.280 ±0.012	1.619 ±0.015	1.349 ±0.012	1.495 ±0.014	1.633 ±0.016	1.663 ±0.016

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 6 = bottom.

(2) Corrected for background.

Table 5.7 [^{36}Cl]-Chlorine activity on unused chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, HF (7cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol. at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (1.46±0.07)x10^5 count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)			
	1	2	3	4
Weight Counted (mg)	50.7	51.7	53.5	50.2
Counts Accumulated	12150	13339	14199	14010
Count s^{-1} (2)	0.619 ±0.005	0.718 ±0.006	0.789 ±0.007	0.774 ±0.007
Count s^{-1}, corrected for self absorption on chromia.	1.068 ±0.009	1.254 ±0.011	1.431 ±0.012	1.320 ±0.011

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 4 = bottom

(2) Corrected for background.

FIGURE 5.3 UPTAKE OF [^{36}Cl] -CHLORINE , FROM PASSAGE OF H^{36}Cl , ON CHROMIA.

([^{36}Cl] -Chlorine count rate on chromia) versus ([^{36}Cl] -Chlorine count rate of Ag^{36}Cl).

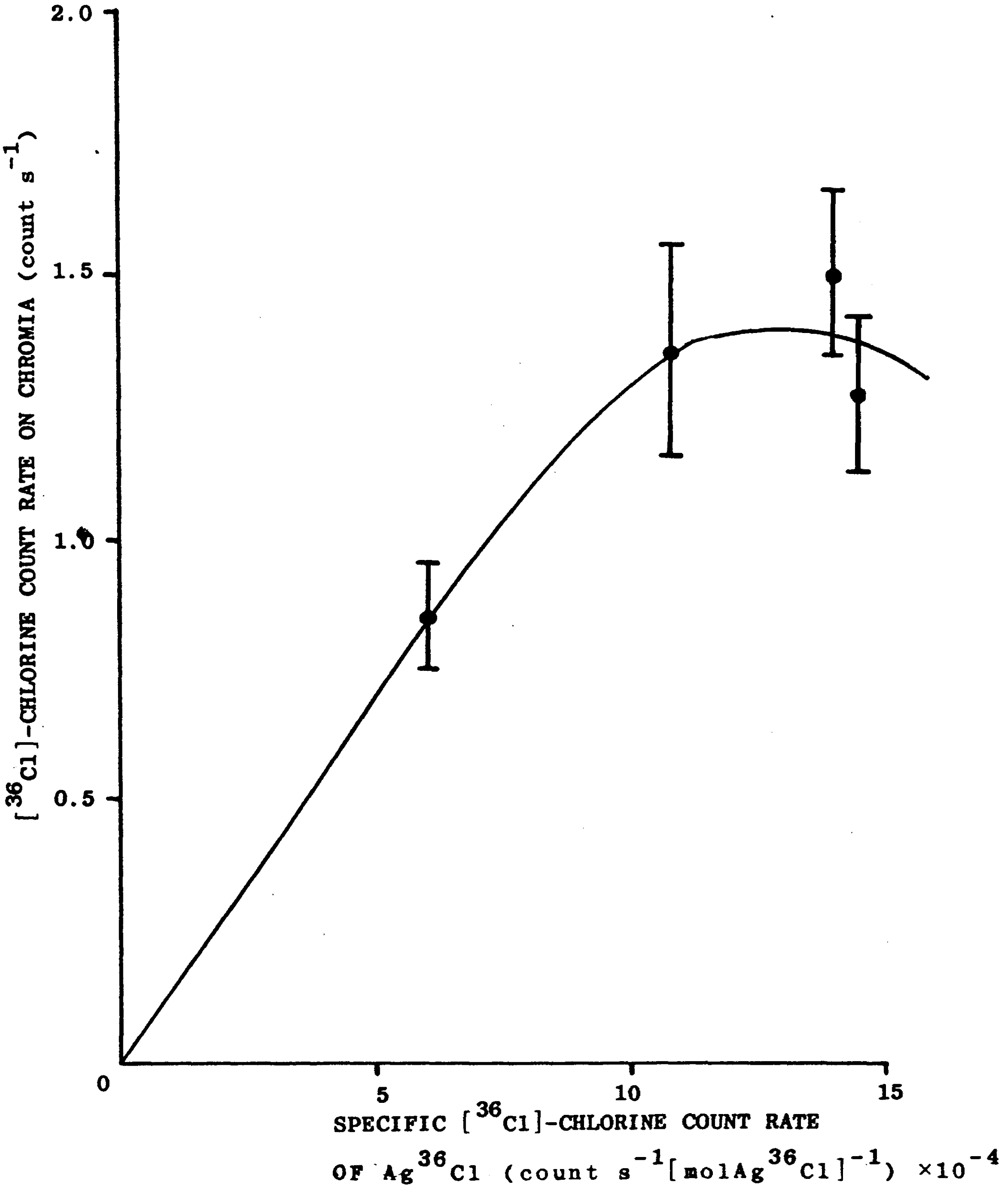


Table 5.8 [^{36}Cl]-Chlorine uptake on unused chromia.

H^{36}Cl admitted to fresh, prefluorinated chromia at 623 K.

Position in Reactor.	Table	Pellet	Equivalent H^{36}Cl uptake (μmol[g catalyst]$^{-1}$)	Average Equivalent H^{36}Cl uptake
1st Quarter	5.4	1	232±5	221±82
	5.5	1	332±7	
	5.6	1	176±2	
	5.7	1	145±7	
2nd Quarter	5.4	7	269±6	228±59
	5.5	7	287±5	
	5.6	3	189±2	
	5.7	2	166±8	
3rd Quarter	5.4	18	218±5	227±56
	5.5	15	368±5	
	5.6	4	198±2	
	5.7	3	183±9	
4th Quarter	5.4	25	208±5	209±21
	5.5	25	232±5	
	5.6	6	216±3	
	5.7	4	181±9	

[Note: Errors are based on counting errors only]

Uptake is in a range equivalent to 119-323 μmol H^{36}Cl(g catalyst)$^{-1}$, within 95% confidence limits.

range 171±6 - 200±14 μmol Cl(g catalyst)$^{-1}$ determined using N.A.A. (Section 5.3).

On used, extensively fluorinated chromia, uptakes of [^{36}Cl]-chlorine were smaller than those determined on fresh catalyst. Uptake of [^{36}Cl]-chlorine at 623 K was in the range equivalent to 59±4 - 104±5 μmol HCl(g catalyst)$^{-1}$ (Table 5.11). At 688 K uptake of [^{36}Cl]-chlorine was greater than at 623 K, in the range equivalent to 77±2 - 125±2 μmol H^{36}Cl (g catalyst)$^{-1}$. However, the distribution in chlorine uptakes determined on fresh catalysts (Table 5.8) suggests that the apparent difference between uptakes determined at 623 K and 683 K may have been due to experimental variables other than temperature, for example the amount of HF adsorbed in the pre-treatment of the catalysts.

Uptakes of [^{36}Cl]-chlorine by unused chromia not previously treated with HF were derived from the [^{36}Cl]-chlorine count rate data in Tables 5.12 and 5.13. Equation (5.1) was used to calculate the [^{36}Cl]-chlorine uptakes, and the self-absorption characteristics of unfluorinated chromia were assumed to be identical to those of fluorinated chromia. [^{36}Cl]-Chlorine uptakes derived from the two experiments were in the ranges equivalent to 897±30 - 997±33 μmol H^{36}Cl (g catalyst)$^{-1}$ and 414±10 - 486±14 μmol H^{36}Cl (g catalyst)$^{-1}$, using 6 and 30 pellet charges respectively (Table 5.14). Although there was great variation in [^{36}Cl]-chlorine uptake between the two experiments, uptake of [^{36}Cl]-chlorine was greater than on pre-fluorinated chromia in both cases .

Table 5.9 [^{36}Cl]-Chlorine activity on used chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, HF (8 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (9.7±0.4)x10^4 count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	51.7	50.2	55.3	50.3	48.2	50.5	47.9	48.6	52.3	50.1
Counts Accumulated	10278	14886	15682	11160	15365	10395	11401	15223	10597	14273
Count s^{-1} (2)	0.213	0.234	0.260	0.296	0.250	0.297	0.295	0.246	0.240	0.253
	±0.002	±0.002	±0.002	±0.003	±0.002	±0.003	±0.003	±0.002	±0.002	±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.379	0.399	0.480	0.505	0.417	0.507	0.486	0.415	0.427	0.432
	±0.004	±0.003	±0.004	±0.005	±0.003	±0.005	±0.004	±0.003	±0.004	±0.004

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.10 [^{36}Cl]-Chlorine activity on used chromia following passage of H^{36}Cl at 688 K.

Catalyst pre-treatment, HF (7cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 688 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (1.31±0.02)x10^5 count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	50.3	52.9	51.7	48.6	51.6	50.4	49.1	53.3	49.9	50.
Counts Accumulated	21637	11318	10162	20509	10158	9237	10604	17073	8427	959
Count s^{-1} (2)	0.459 ±0.003	0.460 ±0.004	0.457 ±0.004	0.422 ±0.003	0.484 ±0.005	0.394 ±0.004	0.421 ±0.004	0.307 ±0.002	0.298 ±0.003	0.30 ±0.00
Count s^{-1}, corrected for self absorption on chromia.	0.783 ±0.005	0.823 ±0.008	0.798 ±0.008	0.707 ±0.005	0.851 ±0.008	0.672 ±0.007	0.710 ±0.007	0.556 ±0.004	0.508 ±0.006	0.51 ±0.00

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.11 $[^{36}Cl]$-Chlorine uptake on used chromia at 623 K and 688 K.

Pellet	Equivalent $H^{36}Cl$ uptake (μmol[g catalyst]$^{-1}$)	
	at 623 K (Data from table 5.9)	at 688 K (Data from table 5.10)
1	59 ± 4	119 ± 2
6	80 ± 3	118 ± 2
7	91 ± 4	117 ± 2
12	92 ± 3	111 ± 2
13	88 ± 3	125 ± 2
18	104 ± 5	102 ± 2
19	104 ± 5	110 ± 2
24	86 ± 3	80 ± 2
25	84 ± 4	77 ± 2
30	82 ± 3	77 ± 2

[NOTE: Errors are based on counting errors only]

Range of $[^{36}Cl]$-chlorine uptake over all pellets, within 95% confidence limits, = 61 - 129 μmol (g catalyst)$^{-1}$

Table 5.12 [^{36}Cl]-Chlorine activity on unused and unfluorinated chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, H^{36}Cl (0.08 mol at 623 K).

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (5.39±0.17)x10^{4} count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)					
	1	2	3	4	5	6
Weight Counted (mg)	49.1	52.6	50.2	49.2	53.2	50.3
Counts Accumulated	11040	11094	11317	11378	11835	12084
Count s^{-1} (2)	1.418 ±0.013	1.429 ±0.014	1.473 ±0.014	1.486 ±0.014	1.577 ±0.015	1.627 ±0.015
Count s^{-1}, corrected for self absorption on chromia.	2.405 ±0.023	2.542 ±0.024	2.513 ±0.024	2.519 ±0.024	2.823 ±0.027	2.775 ±0.026

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 6 = bottom

(2) Corrected for background.

Table 5.13 [^{36}Cl]-Chlorine activity on unused and unfluorinated chromia following passage of H^{36}Cl at 623 K.

Catalyst pre-treatment, H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (8.0±0.2)x10^{4} count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	51.2	53.9	54.5	49.4	49.4	52.3	50.8	51.9	53.7	50.5
Counts Accumulated	12645	10588	10833	11616	11467	10915	11218	9819	10858	10512
Count s^{-1} (2)	0.526 ±0.005	0.509 ±0.005	0.526 ±0.005	0.656 ±0.006	0.631 ±0.006	0.539 ±0.005	0.590 ±0.006	0.489 ±0.005	0.530 ±0.005	0.472 ±0.005
Count s^{-1}, corrected for self absorption on chromia.	0.920 ±0.008	0.922 ±0.009	0.965 ±0.009	1.119 ±0.011	1.077 ±0.010	0.965 ±0.009	1.030 ±0.010	0.860 ±0.009	0.960 ±0.009	0.815 ±0.008

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.14 $[^{36}Cl]$-Chlorine uptake on unused, unfluorinated chromia at 623 K.

Date from table 5.12		Data from table 5.13	
Pellet	Equivalent $H^{36}Cl$ uptake (μmol[g catalyst]$^{-1}$)	Pellet	Equivalent $H^{36}Cl$ uptake (μmol[g catalyst]$^{-1}$)
1	909 ± 31	1	438 ± 12
2	897 ± 30	6	422 ± 11
3	928 ± 31	7	429 ± 11
4	948 ± 31	12	496 ± 14
5	997 ± 33	13	486 ± 14
6	935 ± 31	18	444 ± 13
		19	466 ± 12
		24	417 ± 12
		25	433 ± 11
		30	414 ± 10

NOTE: Errors are based only on counting errors.

5.5 Removal of Adsorbed [^{36}Cl]-Chlorine Originating from [^{36}Cl]-Chlorine Labelled Hydrogen Chloride.

5.5.1 Removal of adsorbed [^{36}Cl]-chlorine by N_2 gas flow

Before removing the catalyst to determine [^{36}Cl]-chlorine count rates, the reactor was flushed with dry N_2 gas at 623 K. This treatment prevented possible contamination of the laboratory environment with any [^{36}Cl]-chlorine originating from weakly bound species on the chromia samples. Weakly adsorbed [^{36}Cl]-chlorine could not, therefore, be determined using this technique, unlike the situation with [^{18}F]-fluorine which was counted *in situ* and consequently presented no laboratory contamination hazard.

5.5.2 Removal of adsorbed [^{36}Cl]-chlorine by $H^{18}F$ gas flow.

The uptake of [^{18}F]-fluorine following admission of $H^{18}F$ to chromia previously treated with HF followed by $H^{36}Cl$ was equivalent to 1.3±0.3 mmol (g catalyst)$^{-1}$, within the range previously determined (Section 4.4). [^{36}Cl]-Chlorine count rates (Tables 5.15 and 5.16), determined following the decay of [^{18}F]-fluorine activity to background, were equivalent to $H^{36}Cl$ uptake in the range 23±1 - 45±1 μmol (g catalyst)$^{-1}$ (Table 5.17). On the basis of the results described in Section 5.4, the initial uptake of [^{36}Cl]-chlorine on pre-fluorinated chromia, following $H^{36}Cl$ flow, was assumed to have been in the range 119 - 323 μmol(g catalyst)$^{-1}$. [^{36}Cl]-Chlorine adsorbed on chromia was therefore removed by HF flow and HF was adsorbed on to the catalyst.

Table 5.15 [^{36}Cl]-Chlorine activity remaining on unused chromia, treated with H^{36}Cl, following passage of HF at 623 K.

Catalyst pre-treatment, HF (12 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (7.4±0.1)x10^4 count s^{-1}(mol Cl)$^{-1}$

Further HF admitted = 4 cm^3 liquid at 623 K.

	Pellet Number (1)			
	1	2	3	4
Weight Counted (mg)	48.1	56.9	54.8	52.1
Counts Accumulated	10457	13133	12607	12622
Count s^{-1} (2)	0.083 ±0.001	0.092 ±0.001	0.066 ±0.001	0.067 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.140 ±0.001	0.174 ±0.002	0.122 ±0.001	0.119 ±0.001

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 4 = bottom

(2) Corrected for background.

Table 5.16 [^{36}Cl]-Chlorine activity remaining on unused chromia, treated with H^{36}Cl, after passage of HF at 623 K.

Catalyst pre-treatment, HF (12 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (7.1 0.2)x10^4 count s^{-1}(mol Cl)$^{-1}$

Further HF admitted = 4 cm^3 liquid at 623 K.

	Pellet Number (1)			
	1	2	3	4
Weight Counted (mg)	46.6	48.7	49.3	49.4
Counts Accumulated	10443	10314	10980	10753
Count s^{-1} (2)	0.057 ±0.001	0.048 ±0.001	0.092 ±0.001	0.077 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.092 ±0.001	0.080 ±0.001	0.157 ±0.002	0.132 ±0.002

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 4 = bottom

(2) Corrected for background.

Table 5.17 $[^{36}Cl]$-Chlorine remaining on chromia following HF flow at 623 K.

Data from table 5.15		Data from table 5.16	
Pellet	Equivalent $H^{36}Cl$ uptake (μmol[g catalyst]$^{-1}$)	Pellet	Equivalent $H^{36}Cl$ uptake (μmol[g catalyst]$^{-1}$)
1	39 ± 1	1	28 ± 1
2	41 ± 1	2	23 ± 1
3	30 ± 1	3	45 ± 1
4	31 ± 1	4	38 ± 1

NOTE: Errors are based on counting errors only.

Range of $[^{36}Cl]$-chlorine uptake over all pellets, within 95% confidence limits = 20-48 μmol(g catalyst)$^{-1}$

5.5.3 Removal of adsorbed [^{36}Cl]-chlorine activity during reaction of chlorofluoroethane on pre-fluorinated chromia treated with H^{36}Cl.

During the reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ at temperatures >623 K on pre-fluorinated chromia treated with H^{36}Cl, the distributions of fluorinated and chlorinated derivatives of reactant chlorofluoroethane did not differ from those observed on pre-fluorinated chromia not treated with H^{36}Cl (Section 3.1). The eluant product fractions contained [^{36}Cl]-chlorine activity which must have originated from the chromia catalyst. Determinations of [^{36}Cl]-chlorine activity in the product fractions are described in detail in Chapter 6.

Following the reaction of chlorofluoroethane, the catalyst was flushed with dry N_2 gas at 623 K and removed from the reactor. [^{36}Cl]-Chlorine count rates from these samples (Tables 5.18 - 5.22) cannot be considered as [^{36}Cl]-chlorine uptakes, since reaction of chlorofluoroethane involves retention of radiochemically inactive chlorine originating in the reacting molecules (Section 5.3). [^{36}Cl]-Chlorine count rates determined following reaction of $C_2Cl_2F_4$ can only be converted to [^{36}Cl]-chlorine uptakes, using equation (5.1), if the specific [^{36}Cl]-chlorine count rate of H^{36}Cl, admitted to the catalyst in pre-treatment, is known. Incorporation of inactive chlorine from reacting molecules will reduce the specific [^{36}Cl]-chlorine count rate of H^{36}Cl compared to that of H^{36}Cl admitted in pre-treatment.

Table 5.18 [^{36}Cl]-Chlorine activity remaining on unused chromia treated with H^{36}Cl, following passage of $C_2Cl_2F_4$ at 623 K.

Catalyst pre-treatment, HF (6 cm^3 liquid at 623 K)
H^{36}Cl (0.1 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = $(8.1\pm0.1)10^4$ count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 31 mmol

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	50.5	51.6	51.8	47.6	50.7	49.5	53.0	47.5	47.5	53.2
Counts Accumulated	11616	10385	11460	9434	10412	10265	10446	11652	11273	13216
Count s^{-1} (2)	0.122 ±0.001	0.081 ±0.001	0.083 ±0.001	0.079 ±0.001	0.082 ±0.001	0.077 ±0.001	0.083 ±0.001	0.123 ±0.001	0.110 ±0.001	0.175 ±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.211 ±0.002	0.142 ±0.002	0.146 ±0.002	0.130 ±0.002	0.142 ±0.002	0.142 ±0.002	0.148 ±0.002	0.203 ±0.002	0.181 ±0.002	0.313 ±0.003

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.19 **[^{36}Cl]-Chlorine remaining on unused chromia, treated with H^{36}Cl, following passage of $C_2Cl_2F_4$ at 623 K.**

Catalyst pre-treatment, HF (6 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = $(1.12\pm0.01)\times10^5$ count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 17.7 mmol

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	51.0	52.3	48.4	47.6	51.5	52.3	47.5	49.1	49.5	53.8
Counts Accumulated	12167	11864	11682	10891	10973	10943	10920	11064	10851	11845
Count s^{-1} (2)	0.140 ±0.001	0.130 ±0.001	0.124 ±0.001	0.098 ±0.001	0.101 ±0.001	0.100 ±0.001	0.099 ±0.001	0.104 ±0.001	0.096 ±0.001	0.130 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.245 ±0.002	0.230 ±0.002	0.208 ±0.002	0.161 ±0.002	0.176 ±0.002	0.178 ±0.002	0.163 ±0.002	0.175 ±0.002	0.164 ±0.002	0.236 ±0.002

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.20 [^{36}Cl]-Chlorine activity remaining on unused chromia, treated with H^{36}Cl, following passage of $C_2Cl_2F_4$ at 623 K.

Catalyst pre-treatment, HF (7 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl] -chlorine count rate of H^{36}Cl admitted in pretreatment = (1.72±0.06)x10^5 count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 13.4 mmol

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	51.7	52.4	50.6	48.7	54.7	49.7	52.5	49.2	49.5	53.2
Counts Accumulated	21420	17501	8598	7868	18104	15216	15834	10481	15696	16236
Count s^{-1} (2)	0.424 ±0.003	0.293 ±0.002	0.309 ±0.003	0.286 ±0.003	0.313 ±0.002	0.226 ±0.002	0.238 ±0.002	0.238 ±0.002	0.233 ±0.002	0.251 ±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.741 ±0.005	0.521 ±0.004	0.533 ±0.006	0.479 ±0.005	0.574 ±0.004	0.385 ±0.003	0.423 ±0.003	0.404 ±0.004	0.395 ±0.003	0.455 ±0.004

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.21 [^{36}Cl]-Chlorine activity remaining on unused chromia, treated with H^{36}Cl, after passage of $C_2Cl_2F_4$ at 683 - 693 K.

Catalyst pre-treatment, HF (7 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (1.20± 0.02)x10^5 count s^{-1} (mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 93.2 mmol.

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	53.4	51.3	50.7	48.8	49.6	53.7	52.8	45.7	48.3	51.8
Counts Accumulated	12350	11982	11968	12024	12005	12784	11135	13393	13128	14836
Count s^{-1} (2)	0.122 ±0.001	0.109 ±0.001	0.109 ±0.001	0.111 ±0.001	0.110 ±0.001	0.136 ±0.001	0.135 ±0.001	0.156 ±0.001	0.148 ±0.001	0.205 ±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.221 ±0.002	0.190 ±0.002	0.189 ±0.002	0.187 ±0.002	0.189 ±0.002	0.247 ±0.002	0.246 ±0.002	0.251 ±0.002	0.249 ±0.002	0.360 ±0.003

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.22 [^{36}Cl]-Chlorine activity remaining on unused chromia, treated with H^{36}Cl, following passage of $C_2Cl_3F_3$ at 623 K.

Catalyst pre-treatment, HF (10 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (6.8±0.3)x10^4 count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_3F_3$ reacted = 25.9 mmol.

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	50.6	48.6	48.3	54.6	47.5	52.5	49.9	54.1	51.9	51.5
Counts Accumulated	15271	12748	15341	11367	15731	12056	15969	16210	16023	15994
Count s^{-1} (2)	0.050 ±0.001	0.058 ±0.001	0.053 ±0.001	0.081 ±0.001	0.073 ±0.001	0.086 ±0.001	0.085 ±0.001	0.097 ±0.001	0.087 ±0.001	0.086 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.085 ±0.001	0.098 ±0.001	0.089 ±0.001	0.149 ±0.001	0.120 ±0.001	0.152 ±0.001	0.145 ±0.001	0.178 ±0.001	0.144 ±0.001	0.142 ±0.001

(1) **Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom**

(2) **Corrected for background.**

Table 5.23 $[^{36}Cl]$-Chlorine, remaining from pre-treatment of fresh, pre-fluorinated chromia with $H^{36}Cl$ at 623 K, following reaction of chlorofluoroethane.

Pellet	Data from Table:					Average $[^{36}Cl]$-chlorine remaining μmol (g catalyst^{-1})
	5.18	5.19	5.20	5.21	5.22	
	$[^{36}Cl]$-Chlorine remaining from pretreatment (μmol[g catalyst]$^{-1}$)					
1	51±1	43±1	84±3	34±2	25±2	47± 23
6	34±1	39±1	59±2	31±2	31±1	39± 12
7	35±1	38±1	62±2	31±2	28±1	39± 14
12	34±1	30±1	59±2	32±2	41±2	39± 12
13	34±1	30±1	66±2	31±2	38±2	40± 15
18	34±1	30±1	48±2	38±2	41±2	38 ± 7
19	35±1	30±1	48±2	38±2	44±2	39 ± 7
24	53±1	32±1	49±2	45±2	50±2	46 ± 8
25	47±1	30±1	49±2	42±2	42±2	42 ± 7
30	73±1	39±1	51±2	58±2	42±2	53 ±14

NOTE: Errors based on counting errors only.

Range for $[^{36}Cl]$-Chlorine remaining, within 95% confidence limits, over all pellets = 18-66 μmol Cl(g catalyst)$^{-1}$

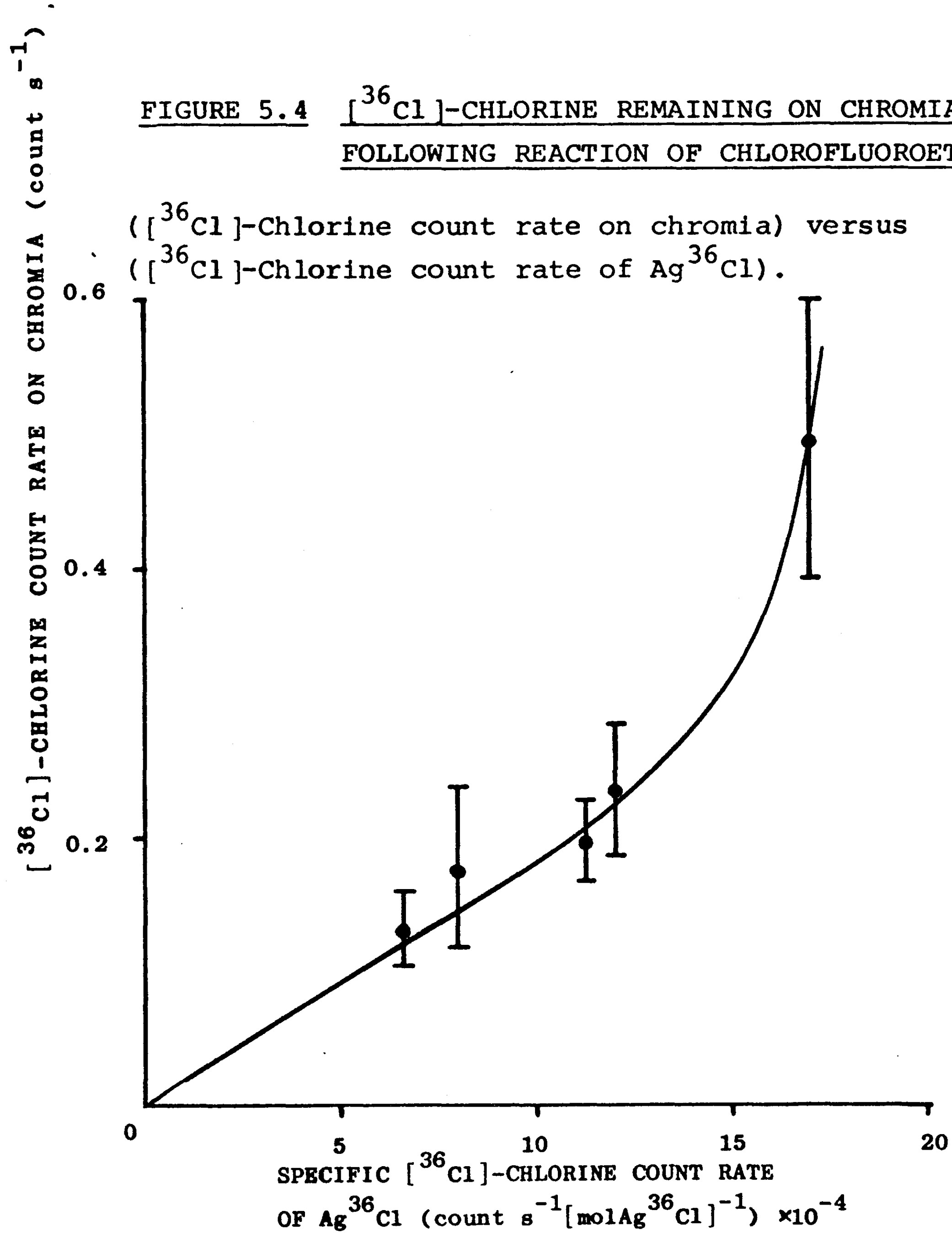
Instead, the [^{36}Cl]-chlorine count rates determined following reaction of chlorofluoroethane were used to derive the quantity of [^{36}Cl]-chlorine remaining from the pre-treatment, using the specific [^{36}Cl]-chlorine count rate of the $H^{36}Cl$ admitted prior to reaction of chlorofluoroethane. The data represent the extent to which [^{36}Cl]-chlorine, originally present on the catalyst, was removed, but they give no indication of the total chlorine content of the catalyst.

A plot of (average [^{36}Cl]-chlorine count rate), corrected for self-absorption of [^{36}Cl]-chlorine on chromia, against (specific [^{36}Cl]-chlorine count rate of $Ag^{36}Cl$), derived from the $H^{36}Cl$ substrate admitted in each experiment, for the five experiments involving fresh catalyst and chlorofluoroethane is shown in Figure 5.4. The plot is not linear, indicating that the quantity of [^{36}Cl]-chlorine retained from pre-treatment was not the same in each case. [^{36}Cl]-Chlorine uptakes, derived from the [^{36}Cl]-chlorine count rate data (Tables 5.18 - 5.22), are tabulated in Table 5.23. Within 95% confidence limits, [^{36}Cl]-chlorine remaining from pre-treatment was in the range equivalent to 18 - 66 μmol $H^{36}Cl$ (g catalyst)$^{-1}$. This compares with an expected initial [^{36}Cl]-chlorine uptake, based on the results in Section 5.4, in the range 119 - 323 μmol(g catalyst)$^{-1}$.

Used catalyst, pre-treated with HF followed by $H^{36}Cl$ was expected to adsorb [^{36}Cl]-chlorine in the range 61 - 129 μmol(g catalyst)$^{-1}$ (Table 5.11). Following reaction of $C_2Cl_2F_4$ at 683 K, [^{36}Cl]-chlorine remaining from pre-treatment,

FIGURE 5.4 [^{36}Cl]-CHLORINE REMAINING ON CHROMIA FOLLOWING REACTION OF CHLOROFLUOROETHANE.

([^{36}Cl]-Chlorine count rate on chromia) versus
([^{36}Cl]-Chlorine count rate of Ag^{36}Cl).



derived from the [^{36}Cl]-chlorine count rates (Table 5.24), was in the range 5±2 - 19±2 μmol(g catalyst)$^{-1}$ (Table 5.25). This range is lower than that determined following reaction of chlorofluoroethane on fresh catalyst and is consistent with the lower uptakes of H^{36}Cl determined on used catalyst.

5.5.4 Removal of [^{36}Cl]-chlorine during reaction of $C_2Cl_2F_4$ on chromia pre-treated with H^{36}Cl at 623 K.

Reaction of $C_2Cl_2F_4$ at 693 K on fresh chromia treated with H^{36}Cl formed ca. 39 mol % C_2ClF_5, 55 mol % $C_2Cl_2F_4$ and 6 mol % $C_2Cl_3F_3$. [^{36}Cl]-Chlorine activity was detected in the eluant fractions. The observation that reaction can occur in the absence of catalyst pre-treatment involving HF is discussed in Chapter 7. The quantity of [^{36}Cl]-chlorine remaining on the catalyst following reaction of $C_2Cl_2F_4$, derived from the [^{36}Cl]-chlorine count rates (Table 5.26), was in the range 32±1 - 166±7 μmol(g catalyst)$^{-1}$ (Table 5.27). [^{36}Cl]-Chlorine remaining from pre-treatment of unfluorinated chromia was greater than on fluorinated chromia. This is consistent with the greater uptake of [^{36}Cl]-chlorine on unfluorinated chromia (Table 5.14).

5.5.5 Removal of adsorbed [^{36}Cl]-chlorine by digesting chromia, treated with H^{36}Cl, in concentrated sodium hydroxide solution.

Chromia pellets containing [^{36}Cl]-chlorine in the range equivalent to 208 - 269 μmol H^{36}Cl(g catalyst)$^{-1}$

Table 5.24 [^{36}Cl]-Chlorine remaining on used chromia, treated with H^{36}Cl, following passage of $C_2Cl_2F_4$ at 683 K.

Catalyst pre-treatment, HF (5 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = $(6.4 \pm 0.1) \times 10^4$ count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 17.3 mmol

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	53.8	50.2	50.7	50.1	50.9	66.7	52.9	54.8	48.7	-
Counts Accumulated	12380	12470	12480	12110	11258	18670	12527	8108	12852	-
Count s^{-1} (2)	0.019	0.022	0.022	0.010	0.025	0.030	0.024	0.027	0.034	-
	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	-
Count s^{-1}, corrected for self absorption on chromia.	0.034	0.038	0.038	0.017	0.043	0.065	0.043	0.050	0.059	-
	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	<±0.001	-

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.25 [^{36}Cl]-Chlorine, remaining from pre-treatment of used chromia with H^{36}Cl at 623 K, following reaction of $C_2Cl_2F_4$ at 683 K.

Pellet	[^{36}Cl]-Chlorine remaining * from pre-treatment (μmol g catalyst $^{-1}$)
1	9±2
6	12±2
7	12±2
12	5±2
13	14±2
18	15±2
19	13±2
24	15±2
25	19±2

NOTE: Errors based on counting errors only.

* derived from [^{36}Cl]-chlorine count rates in Table 5.24

Table 5.26 [^{36}Cl]-Chlorine activity remaining on unused chromia, pre-treated with H^{36}Cl only, following passage of $C_2Cl_2F_4$ at 693 K.

Catalyst pre-treatment, H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = $(4.50 \pm 0.17) \times 10^4$ count s^{-1}(mol Cl)$^{-1}$

$C_2Cl_2F_4$ reacted = 62.1 mmol

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	53.4	49.5	40.8	47.8	54.4	51.1	52.3	49.9	49.6	52.0
Counts Accumulated	8209	8421	8141	8711	8843	9451	9704	9848	9781	9529
Count s^{-1} (2)	0.047 ±0.001	0.068 ±0.001	0.040 ±0.001	0.097 ±0.001	0.109 ±0.001	0.171 ±0.001	0.196 ±0.002	0.210 ±0.002	0.204 ±0.002	0.179 ±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.084 ±0.001	0.115 ±0.001	0.059 ±0.001	0.159 ±0.002	0.202 ±0.002	0.298 ±0.003	0.347 ±0.004	0.359 ±0.004	0.347 ±0.004	0.316 ±0.004

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(2) Corrected for background.

Table 5.27 [^{36}Cl]-Chlorine, remaining from pre-treatment of fresh, unfluorinated chromia with H^{36}Cl at 623 K, following reaction of $C_2Cl_2F_4$ at 693 K.

Pellet	[^{36}Cl]-Chlorine remaining * from pre-treatment (μmol [g catalyst]$^{-1}$)
1	35±1
6	52±2
7	32±1
12	74±3
13	82±3
18	130±5
19	166±7
24	160±6
25	156±6
30	135±5

NOTE: Errors based on counting errors only.

*derived from [^{36}Cl]-chlorine count rates in Table 5.26.

were left to digest in concentrated aqueous NaOH solution for 48 h. Upon filtering and drying the green/black residue, [^{36}Cl]-chlorine in the range equivalent to 8±1 - 51±2 μmol $H^{36}Cl$(g catalyst)$^{-1}$ was determined (Table 5.29).

5.6 Hydrolysis of [^{36}Cl]-Chlorine Adsorbed on Chromia.

Unused, pre-fluorinated chromia pellets, treated with $H^{36}Cl$ at 623 K, were left to hydrolyse in air following determination of [^{36}Cl]-count rates. The samples, corresponding to the experiment described in Table 5.6, were recounted after standing in air for three weeks. [^{36}Cl]-Chlorine count rates determined after exposure to air (Table 5.31) were smaller in all cases, but [^{36}Cl]-chlorine count rates for pellets 1 and 3 were less changed than those for pellets 2,4 and 6. The reason for the different behaviour of pellets 1 and 3 compared with the remainder of the sample is not known. The loss of [^{36}Cl]-chlorine from the catalyst is most likely accounted for by hydrolysis accompanied by loss of $H^{36}Cl$. Desorption of HF from chromia left to stand in air was also observed (Section 4.5). In the case of HF, however, etching of the glass sample bottle, characteristic of the interaction between HF and silica, was not observed until several months had elapsed.

Table 5.28 [^{36}Cl]-Chlorine activity on unused chromia, treated with H^{36}Cl, after digestion in concentrated sodium hydroxide solution (1)

Catalyst pre-treatment, HF (5 cm^3 liquid at 623 K)
H^{36}Cl (0.08 mol at 623 K)

[^{36}Cl]-chlorine count rate of H^{36}Cl admitted in pretreatment = (1.10 0.02)x 10^{5}count s^{-1} (mol Cl)$^{-1}$.

	Pellet Number (2)			
	2 - 6	8 - 11	13 - 17	19 - 25
Weight Counted (mg)	51.2	48.7	50.3	52.5
Counts Accumulated	11625	11070	9262	17314
Count s^{-1} (3)	0.166 ±0.002	0.138 ±0.001	0.047 ±0.001	0.017 <±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.304 ±0.003	0.245 ±0.002	0.095 ±0.001	0.045 <±0.001

(1) Pellets from same experiment as Table 5.4

(2) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom

(3) Corrected for background.

Table 5.29 [^{36}Cl]-Chlorine, remaining from pre-treatment of unused, pre-fluorinated chromia with H^{36}Cl at 623 K, after leaving to digest in concentrated sodium hydroxide solution for 48h.

Pellet	[^{36}Cl]-Chlorine remaining * (μmol[g catalyst]$^{-1}$)
1	51±2
2	42±2
3	16±1
4	8±1

NOTE: Errors based on counting errors only.

*derived from [^{36}Cl]-count rates Table 5.28.

Table 5.30 [^{36}Cl]-Chlorine activity remaining on unused chromia, pre-treated with H^{36}Cl at 623 K, after leaving to stand in air for 3 weeks.

Catalyst and pre-treatment - as Table 5.6

	Pellet Number (1)				
	1	2	3	4	6
Weight Counted (mg)	53.7	51.1	52.7	49.1	51.8
Counts Accumulated	13014	12547	13381	12132	11837
Count s^{-1} (2)	0.668 ±0.006	0.575 ±0.005	0.742 ±0.007	0.492 ±0.005	0.433 ±0.004
Count s^{-1}, corrected for self absorption on chromia.	1.211 ±0.011	1.004 ±0.010	1.319 ±0.012	0.839 ±0.008	0.765 ±0.007

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 6 = bottom

(2) Corrected for background.

Table 5.31 **[^{36}Cl]-Chlorine count rates for chromia determined before and after leaving to stand in air.**

Unused, pre-fluorinated chromia treated with $H^{36}Cl$ and left to stand in air for three weeks.

Pellet	[^{36}Cl]-Chlorine count rate (count s^{-1},[g chromia]$^{-1}$)	
	On Removal (1)	After 3 weeks in air (2)
1	25.05±0.25	22.55±0.23
2	29.71±0.30	19.64±0.19
3	26.66±0.27	25.02±0.25
4	27.89±0.28	17.08±0.17
5	30.41±0.30	n/d
6	30.51±0.31	14.76±0.15

NOTES: (1) From table 5.6

(2) From table 5.30

n/d = not determined.

Errors based on counting errors only.

CHAPTER SIX

THE REACTIONS OF CHLOROFLUOROETHANES WITH THE SURFACE CHLORIDE SPECIES

CHAPTER SIX.

The Reactions of Chlorofluoroethanes with the Surface Chloride Species.

6.1 Introduction

Reaction of $C_2Cl_2F_4$ or $C_2Cl_3F_3$ on pre-fluorinated chromia resulted in an increase in the catalyst chlorine content (Section 5.3). Pre-fluorinated chromia samples, treated using $H^{36}Cl$ and then subjected to reaction with $C_2Cl_3F_3$ or $C_2Cl_2F_4$, were found to have lower [^{36}Cl]-chlorine count rates than samples subjected only to $H^{36}Cl$ treatment. [^{36}Cl]-Chlorine activity was detected in the reactor eluant.

The interaction between chlorine originating from CCl_2FCF_3 and pre-fluorinated chromia was studied using [^{36}Cl]-CCl_2FCF_3, prepared by the method described in Section 2.6.3. The fate of adsorbed [^{36}Cl]-chlorine, originating either from reaction of [^{36}Cl]-CCl_2FCF_3 or $H^{36}Cl$ flow, was investigated by reacting $C_2Cl_3F_3$ or $C_2Cl_2F_4$ on chromia containing [^{36}Cl]-chlorine. ^{19}F N.m.r. and liquid scintillation counting were used to determine the distribution of [^{36}Cl]-chlorine in the reaction products.

6.2 Uptake of [^{36}Cl]-Chlorine on Chromia Following Reaction of [^{36}Cl]-CCl_2FCF_3

The products from reaction of [^{36}Cl]-CCl_2FCF_3 at 688 K on fresh, pre-fluorinated chromia were C_2ClF_5, ca. 55 mol %, $C_2Cl_2F_4$, ca. 30 mol % and $C_2Cl_3F_3$, ca. 15 mol %. CCl_3CClF_2 was present in the reactor eluant in trace quantities and the isomer CCl_2FCCl_2F (< 1 mol %) was detected during one experiment. This was the only occasion that CCl_2FCCl_2F was detected in the present work. For all experiments the gas flow rate (N_2 + F.C.114a) was in the range 23 - 30 cm^3min^{-1}. [^{36}Cl]-Chlorine activity was detected in the reactor eluant and on the catalyst at the end of the reaction.

Values for [^{36}Cl]-chlorine uptake on chromia were obtained from the [^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined as $Ag^{36}Cl$, and the [^{36}Cl]-chlorine count rates of the catalysts (Tables 6.1 - 6.3) by substitution into equation (5.1). The [^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3 was derived from the [^{36}Cl]-chlorine count rates of [^{36}Cl]-Cl_2, used in the synthesis of [^{36}Cl]-CCl_2FCF_3, and $H^{36}Cl$, produced in the synthesis, using equation (2.5).

[^{36}Cl]-Chlorine uptake from the reaction of [^{36}Cl]-CCl_2FCF_3 at 688 K on fresh, pre-fluorinated chromia was in the range 44 - 380 μmol(g catalyst)$^{-1}$ over the whole catalyst bed (Table 6.4). [^{36}Cl]-Chlorine uptakes at the beginning of the catalyst bed were higher than those at the end. In the three experiments (Tables 6.1 - 6.3) uptake of [^{36}Cl]-chlorine was in the range 192 - 358 μmol(g catalyst)$^{-1}$ for pellets 1 - 13 and 19 - 275 μmol(g catalyst)$^{-1}$ for pellets 18 - 30 (Table 6.4). A plot of [^{36}Cl]-chlorine uptake versus (position of pellet in bed) is shown in Figure 6.1.

[^{36}Cl]-Chlorine uptake on fresh, pre-fluorinated chromia following reaction of a [^{36}Cl]-$CCl_2FCF_3/CClF_2CClF_2$

Table 6.1 [^{36}Cl]-Chlorine activity on unused chromia following reaction of [^{36}Cl]-CCl_2FCF_3 at 688 K.

Catalyst pre-treatment, HF (12 cm^3 liquid at 623 K)

[^{36}Cl]-CCl_2FCF_3 reacted = 7.7 mmol

[^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(3.73 \pm 0.08) \times 10^4$ count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	53.1	50.1	48.0	50.4	50.0	50.4	50.3	50.8	50.9	50.6
Counts Accumulated.	9689	10390	9664	9256	10407	7476	8476	8278	8462	8181
Count s^{-1} (2)	0.302 ±0.003	0.372 ±0.004	0.298 ±0.003	0.348 ±0.003	0.374 ±0.004	0.164 ±0.002	0.181 ±0.002	0.161 ±0.002	0.180 ±0.002	0.152 ±0.002
Count s^{-1}, corrected for self absorption on chromia.	0.548 ±0.006	0.643 ±0.006	0.496 ±0.005	0.601 ±0.006	0.646 ±0.006	0.283 ±0.003	0.312 ±0.003	0.278 ±0.003	0.310 ±0.003	0.262 ±0.003

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.2 [^{36}Cl]-Chlorine activity on unused chromia following reaction of [^{36}Cl]-CCl_2FCF_3 at 688 K.

Catalyst pre-treatment, HF (13 cm^3 liquid at 623 K)

[^{36}Cl]-CCl_2FCF_3 reacted = 14.1 mmol

[^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined on $Ag^{36}Cl$ = (3.73±0.08)x10^4 count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	54.2	52.3	48.0	49.9	51.3	54.7	54.9	51.8	53.9	50.6
Counts Accumulated.	10846	11537	11703	11349	10474	9763	10739	9182	9047	9095
Count s^{-1} (2)	0.249 ±0.002	0.318 ±0.003	0.335 ±0.003	0.299 ±0.003	0.212 ±0.002	0.138 ±0.001	0.238 ±0.002	0.083 ±0.001	0.069 ±0.001	0.074 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.451 ±0.004	0.566 ±0.005	0.558 ±0.005	0.511 ±0.005	0.372 ±0.004	0.258 ±0.003	0.437 ±0.004	0.146 ±0.002	0.125 ±0.001	0.126 ±0.001

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.3 $[^{36}Cl]$-Chlorine activity on unused chromia following reaction of $[^{36}Cl]$-CCl_2FCF_3 at 688 K.

Catalyst pre-treatment, HF (12 cm^3 liquid at 623 K)

$[^{36}Cl]$-CCl_2FCF_3 reacted = 17.3 mmol

$[^{36}Cl]$-chlorine count rate of $[^{36}Cl]$-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(3.73 \pm 0.08) \times 10^4$ count s^{-1} (mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	54.4	51.5	51.3	49.5	48.5	50.7	49.4	50.3	51.9	54.1
Counts Accumulated.	11143	11482	11059	11083	11405	11585	11051	9971	9585	9431
Count s^{-1} (2)	0.279 ±0.003	0.313 ±0.003	0.270 ±0.003	0.273 ±0.003	0.305 ±0.003	0.323 ±0.003	0.270 ±0.003	0.162 ±0.002	0.123 ±0.001	0.108 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.481 ±0.005	0.549 ±0.005	0.475 ±0.005	0.465 ±0.004	0.511 ±0.005	0.560 ±0.005	0.460 ±0.004	0.276 ±0.003	0.216 ±0.002	0.186 ±0.002

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.4 Uptake of $[^{36}Cl]$-chlorine on unused chromia following reaction of $[^{36}Cl]$-CCl_2FCF_3 at 688 K.

Pellet	$[^{36}Cl]$-Chlorine uptake (μmol $[g\ catalyst]^{-1}$)			
	Data from Table 6.1	Data from Table 6.2	Data from Table 6.3	Average
1	277±7	223±6	237±6	246±28
6	344±9	290±7	286±7	307±32
7	277±7	312±8	248±6	279±32
12	325±8	247±7	252±6	275±44
13	345±9	195±5	282±7	274±75
18	151±4	124±3	296±8	190±93
19	167±4	214±5	250±6	210±42
24	147±4	76±2	147±4	123±41
25	163±4	62±2	112±3	112±51
30	139±4	67±2	92±2	99±37

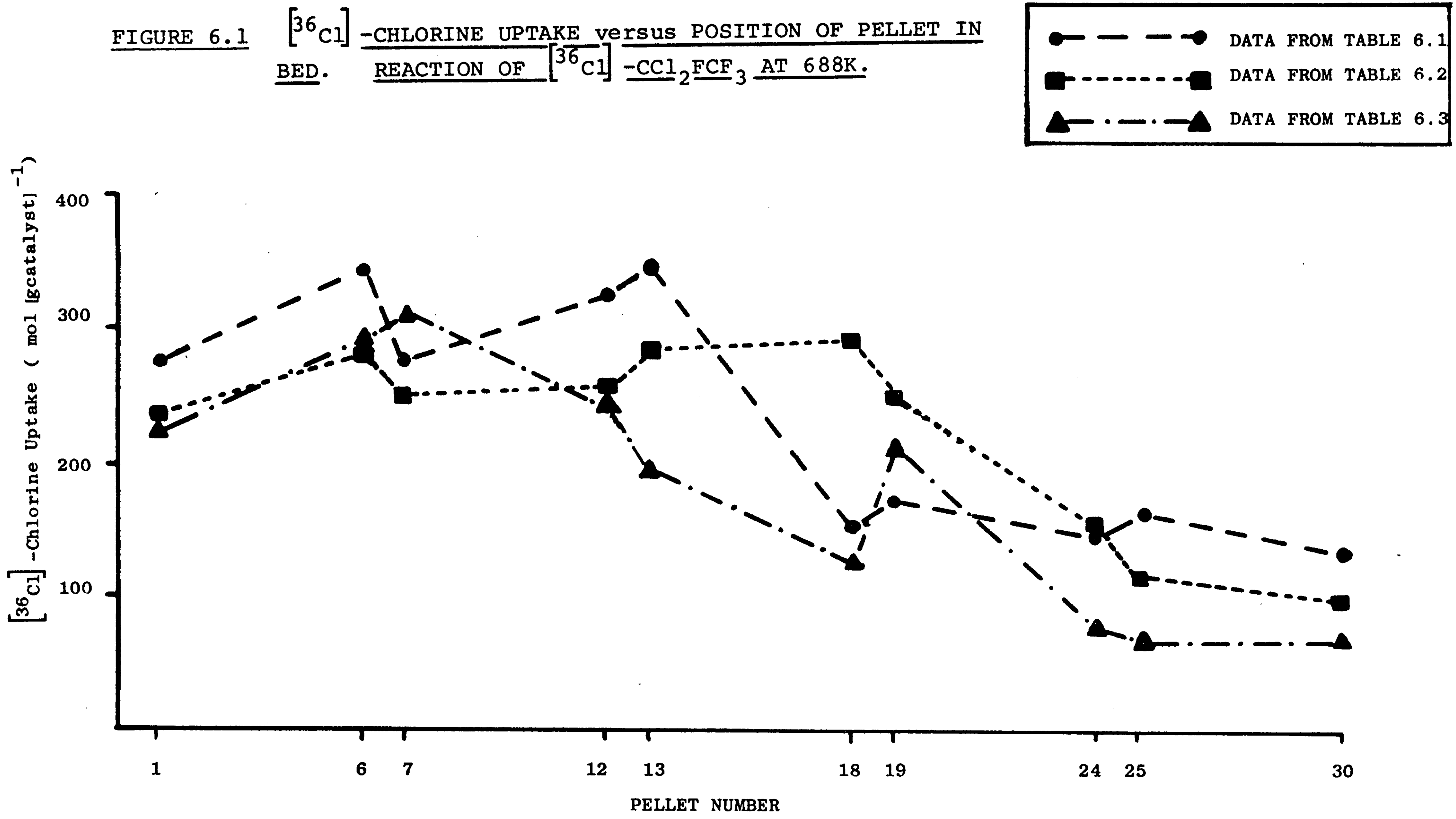
Range of $[^{36}Cl]$-chlorine uptake, within 95% confidence limits:

over all pellets = 44 - 380 μmol Cl$(g\ catalyst)^{-1}$

over pellets 1-13 = 192 - 358 μmol Cl$(g\ catalyst)^{-1}$

over pellets 8-30 = 19 - 275 μmol Cl$(g\ catalyst)^{-1}$

FIGURE 6.1 $[^{36}Cl]$-CHLORINE UPTAKE versus POSITION OF PELLET IN BED. REACTION OF $[^{36}Cl]$-CCl_2FCF_3 AT 688K.



mixture (55.1 mmol, mole ratio [^{36}Cl]-CCl_2FCF_3:$CClF_2CClF_2$ = 1.2:1) at 676 - 693 K was in the range 178 - 630 μmol (g catalyst)$^{-1}$ (Table 6.6). The reaction products comprised C_2ClF_5, ca. 38 mol %, $C_2Cl_2F_4$, ca. 55 mol %. and $C_2Cl_3F_3$, ca. 7 mol % (Table 6.19). [^{36}Cl]-Chlorine was more evenly distributed along the catalyst bed than was the case following reaction of [^{36}Cl]-CCl_2FCF_3 alone (Tables 6.4 and 6.6). The range for [^{36}Cl]-chlorine uptake following reaction of the [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ mixture on the catalyst is slightly higher than the range determined following reaction of [^{36}Cl]-CCl_2FCF_3. This observation is surprising since, although a greater [^{36}Cl]-chlorine uptake might have been expected from reaction of the [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ mixture, due to the greater quantity of [^{36}Cl]-CCl_2FCF_3 reacted (29.9 mmol compared with 7.7 - 17.9 mmol), chlorination of $CClF_2CClF_2$ would have been expected to remove catalyst [^{36}Cl]-chlorine, resulting in a lower [^{36}Cl]-chlorine uptake compared with experiments involving reaction of [^{36}Cl]-CCl_2FCF_3 alone. The strong inference is that the principal route to formation of C_2ClF_5 is from the asymmetric isomer. Gas chromatographic analysis of the reaction products (Table 6.19) indicated that the average mole ratio of the asymmetric:symmetric isomers of $C_2Cl_2F_4$ in the reactor eluant was (1.2±0.2):1. This compared with a reactant asymmetric:symmetric isomer ratio of 1.2:1. Since the isomer $CClF_2CClF_2$ was not involved in chlorination reactions to any significant extent the unchanged asymmetric: symmetric isomer ratio in the reaction products must be

Table 6.5 $[^{36}Cl]$-Chlorine activity on unused chromia ; Reaction of $[^{36}Cl]$-CCl_2FCF_3 and $CClF_2CClF_2$ (mole ratio $[^{36}Cl]$-F.C. 114a:F.C.114 = 1.2:1) at 676 - 693 K.

Catalyst pre-treatment, HF(11 cm^3 liquid at 623 K)

$[^{36}Cl]$-CCl_2FCF_3 reacted = 29.9 mmol
$CClF_2CClF_2$ reacted = 25.2mmol
admitted to catalyst as an isomeric mixture.

$[^{36}Cl]$-chlorine count rate of $[^{36}Cl]$-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(2.28 \pm 0.08) \times 10^4$ count s^{-1} (mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	50.7	45.7	50.7	51.6	50.9	51.0	49.8	48.8	55.1	55.3
Counts Accumulated.	9248	9782	11648	13031	12979	9908	9940	8061	8097	8126
Count s^{-1} (2)	0.162 ±0.002	0.162 ±0.002	0.150 ±0.001	0.323 ±0.003	0.317 ±0.003	0.343 ±0.004	0.348 ±0.004	0.304 ±0.003	0.311 ±0.003	0.317 ±0.004
Count s^{-1}, corrected for self absorption on chromia.	0.276 ±0.003	0.261 ±0.003	0.256 ±0.002	0.568 ±0.005	0.540 ±0.005	0.585 ±0.006	0.594 ±0.006	0.501 ±0.006	0.571 ±0.006	0.582 ±0.006

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.6 Uptake of [^{36}Cl]-Chlorine on unused chromia following reaction of [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ isomer mixture

mole ratio [^{36}Cl]-F.C.114a:F.C.114 = 1.2:1

Pellet	[^{36}Cl]-Chlorine uptake * µmol Cl(g catalyst)$^{-1}$
1	235 ± 9
6	247 ± 9
7	220 ± 8
12	480 ± 17
13	462 ± 16
18	503 ± 18
19	524 ± 19
24	450 ± 17
25	455 ± 17
30	461 ± 17

*Derived from [^{36}Cl]-chlorine count rate data in Table 6.5

Range of [^{36}Cl]-chlorine uptake, within 95% confidence limits:

Over all pellets = 178 - 630 µmol Cl(g catalyst)$^{-1}$

Over pellets 12-30 = 425 - 528 µmol Cl(g catalyst)$^{-1}$

accounted for by conversion of $CClF_2CClF_2$ to CCl_2FCF_3.

On used, extensively fluorinated chromia, [^{36}Cl]-CCl_2FCF_3 underwent reaction at 695 K to yield C_2ClF_5, ca. 15 mol %, $C_2Cl_2F_4$, ca. 71 mol %, $C_2Cl_3F_3$ ca. 13 mol %, and $C_2Cl_4F_2$, ca. 1 mol %. Conversion of the [^{36}Cl]-chlorine count rate data (Table 6.7) to [^{36}Cl]-chlorine uptakes gave [^{36}Cl]-chlorine uptake in the range 36 - 76 μmol (g catalyst)$^{-1}$ (Table 6.8). [^{36}Cl]-Chlorine uptake on used chromia was smaller than the uptake on fresh chromia, regardless of whether the [^{36}Cl]-chlorine originated from [^{36}Cl]-CCl_2FCF_3 or $H^{36}Cl$. Reaction of [^{36}Cl]-CCl_2FCF_3 with fresh chromia produced approximately four times more C_2ClF_5 than with used chromia and the uptake of [^{36}Cl]-chlorine on the fresh chromia was a factor of approximately four greater than on the used chromia. The relationship between [^{36}Cl]-chlorine uptake and the extent of C_2ClF_5 production provides further evidence for a series of halogen exchange reactions which can account for the reactions of chlorofluoroethanes on chromia.

6.3 [^{36}Cl]-Chlorine Remaining on Chromia, from Reaction of [^{36}Cl]-CCl_2FCF_3, Following Reaction of Chlorofluoroethane.

Reaction of [^{36}Cl]-CCl_2FCF_3 at 688 K on fresh, pre-fluorinated chromia resulted in the uptake of [^{36}Cl]-chlorine by the catalyst in the range 44 - 380 μmol (g catalyst)$^{-1}$ (Section 6.2). The quantity of [^{36}Cl]-chlorine remaining from the initial reaction of [^{36}Cl]-CCl_2FCF_3, following reaction of chlorofluoroethane, was determined using the [^{36}Cl]-

Table 6.7 [^{36}Cl]-Chlorine activity on used chromia following reaction of [^{36}Cl]-CCl_2FCF_3 at 695 K.

Catalyst pre-treatment HF(12 cm^3 liquid at 623 K)

[^{36}Cl]-CCl_2FCF_3 reacted = 16.0 mmol

[^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined on Ag^{36}Cl = $(2.87\pm0.09)\times10^4$ count s (molCl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	48.0	48.8	50.3	50.4	49.4	49.5	56.9	48.1	53.5	51.6
Counts Accumulated.	12004	10776	9368	12405	12330	12279	12483	9136	12029	11892
Count s^{-1} (2)	0.036 <±0.001	0.047 <±0.001	0.050 ±0.001	0.056 ±0.001	0.052 ±0.001	0.050 ±0.001	0.060 ±0.001	0.045 <±0.001	0.037 <±0.001	0.030 <±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.064 ±0.001	0.080 ±0.001	0.085 ±0.001	0.097 ±0.001	0.089 ±0.001	0.086 ±0.001	0.113 ±0.001	0.080 ±0.001	0.067 ±0.001	0.053 ±0.001

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet = bottom.

(2) Corrected for background.

Table 6.8 Uptake of [^{36}Cl]-Chlorine on used chromia following reaction of [^{36}Cl]-CCl_2FCF_3 at 695 K.

Pellet	[^{36}Cl]-Chlorine uptake * μmol(g catalyst)$^{-1}$
1	46 ± 2
6	57 ± 2
7	59 ± 2
12	67 ± 2
13	63 ± 2
18	60 ± 2
19	69 ± 2
24	54 ± 2
25	44 ± 2
30	36 ± 1

* Derived from [^{36}Cl]-chlorine count rate data in Table 6.7

Range of [^{36}Cl]-chlorine uptake over all pellets, within 95% confidence limits = 36 - 76 μmol Cl(g catalyst)$^{-1}$

chlorine count rate on chromia and the [^{36}Cl]-chlorine count rate of Ag^{36}Cl derived from [^{36}Cl]-CCl_2FCF_3 (Tables 6.9 - 6.11). The method of calculation is described in Section 5.2. [^{36}Cl]-Chlorine remaining on chromia following the reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ at 623 - 693 K was in the range 11 - 83 μmol (g catalyst)$^{-1}$ (Table 6.12). This range compares with the range 18 - 66 μmol (g catalyst)$^{-1}$ determined for [^{36}Cl]-chlorine remaining from H^{36}Cl pretreatment of chromia followed by reaction of $C_2Cl_2F_4$ (Section 5.5.3).

6.4 Determination of [^{36}Cl]-Chlorine Activity in the Reactor Eluant by Liquid Scintillation Counting

6.4.1. [^{36}Cl]-Chlorine activity in the products from reaction of [^{36}Cl]-CCl_2FCF_3

[^{36}Cl]-Chlorine activities in [^{36}Cl]-CCl_2FCF_3 and in the products from reaction on chromia were determined by liquid scintillation counting (Section 2.11). [^{36}Cl]-Chlorine count rates for reactant [^{36}Cl]-CCl_2FCF_3 were determined by condensing a known weight of [^{36}Cl]-CCl_2FCF_3 into a vessel containing the scintillator solution (Figure 2.15). Three determinations of [^{36}Cl]-chlorine count rates, on three samples of [^{36}Cl]-CCl_2FCF_3 from the same preparation, were undertaken to establish the precision of [^{36}Cl]-chlorine count rate determination by this method (Table 6.13).

Table 6.9 $[^{36}Cl]$-Chlorine activity on unused chromia; Reaction of $[^{36}Cl]$-CCl_2FCF_3 followed by reaction of $C_2Cl_2F_4$ both at 693 K.

Catalyst pre-treatment, HF (14 cm^3 liquid at 623 K)

$[^{36}Cl]$-CCl_2FCF_3 reacted = 15.9 mmol

$C_2Cl_2F_4$ reacted = 37.9 mmol

$[^{36}Cl]$-chlorine count rate of $[^{36}Cl]$-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(3.73\pm0.08)\times10^4$ count $s^{-1}mol^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	49.3	49.6	52.2	48.0	52.6	48.7	49.5	48.2	50.5	47.8
Counts Accumulated.	9347	9069	8987	8912	8850	8735	8501	8776	8814	8676
Count s^{-1} (2)	0.099 ±0.001	0.071 ±0.001	0.063 ±0.001	0.056 ±0.001	0.049 <±0.001	0.038 <±0.001	0.055 ±0.001	0.042 <±0.001	0.046 <±0.001	0.032 <±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.169 ±0.002	0.122 ±0.001	0.112 ±0.001	0.093 ±0.001	0.088 ±0.001	0.064 ±0.001	0.093 ±0.001	0.070 ±0.001	0.078 ±0.001	0.053 ±0.001

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.10 [^{36}Cl]-Chlorine activity on unused chromia ; Reaction of [^{36}Cl]-CCl_2FCF_3 at 683 K followed by reaction of $C_2Cl_2F_4$ at 673 - 693 K.

Catalyst pre-treatment, HF (11 cm^3 liquid at 623 K)

[^{36}Cl]-CCl_2FCF_3 reacted = 9.9 mmol

$C_2Cl_2F_4$ reacted = 43.3 mmol

[^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(3.0\pm0.2)\times10^4$ count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	49.3	47.8	52.1	52.8	54.4	47.1	50.3	49.9	49.2	51.1
Counts Accumulated.	12425	12510	12407	12258	12267	12150	12096	12559	11944	12660
Count s^{-1} (2)	0.054 ±0.001	0.060 ±0.001	0.053 ±0.001	0.045 <±0.001	0.043 <±0.001	0.036 <±0.001	0.032 <±0.001	0.063 ±0.001	0.022 <±0.001	0.070 ±0.001
Count s^{-1}, corrected for self absorption on chromia.	0.092 ±0.001	0.099 ±0.001	0.094 ±0.001	0.080 ±0.001	0.079 ±0.001	0.059 ±0.001	0.056 ±0.001	0.107 ±0.001	0.038 <±0.001	0.122 ±0.001

(1) **Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.**

(2) **Corrected for background.**

Table 6.11 [^{36}Cl]-Chlorine activity on unused chromia ; Reaction of [^{36}Cl]-CCl_2FCF_3 at 693 K followed by reaction of $C_2Cl_3F_3$ at 623 K.

Catalyst pre-treatment, HF (12 cm^3 liquid at 623 K)

[^{36}Cl]-CCl_2FCF_3 reacted = 16.6 mmol

$C_2Cl_3F_3$ reacted = 30.0 mmol

[^{36}Cl]-chlorine count rate of [^{36}Cl]-CCl_2FCF_3, determined on $Ag^{36}Cl$ = $(2.87\pm0.09)\times10^4$ count s^{-1}(mol Cl)$^{-1}$

	Pellet Number (1)									
	1	6	7	12	13	18	19	24	25	30
Weight Counted (mg)	48.7	49.8	50.9	48.2	48.6	48.5	49.2	51.9	50.0	-
Counts Accumulated.	8981	9108	7033	9062	8977	8371	8782	8888	8771	-
Count s^{-1} (2)	0.035 <±0.001	0.048 <±0.001	0.016 <±0.001	0.043 <±0.001	0.035 <±0.001	0.028 <±0.001	0.015 <±0.001	0.026 <±0.001	0.014 <±0.001	-
Count s^{-1}, corrected for self absorption on chromia.	0.059 ±0.001	0.082 ±0.001	0.028 <±0.001	0.073 ±0.001	0.058 ±0.001	0.046 ±0.001	0.026 <±0.001	0.046 ±0.001	0.024 <±0.001	-

(1) Gas flow in reactor from top to bottom; pellet 1 = top, pellet 30 = bottom.

(2) Corrected for background.

Table 6.12 $[^{36}Cl]$-Chlorine from pre-reaction of $[^{36}Cl]$-CCl_2FCF_3 at 683 - 693 K, remaining on unused chromia, following reaction of $C_2Cl_2F_4$ or $C_2Cl_2F_3$.

Pellet	$[^{36}Cl]$-Chlorine remaining from pre-treatment (μmol [g catalyst]$^{-1}$)			
	Data from Table 6.9 $C_2Cl_2F_4$ at 693 K	Data from Table 6.10 $C_2Cl_2F_4$ at 673-693K	Data from Table 6.11 $C_2Cl_3F_3$ at 623K	Average
1	92±2	62±4	42±1	65±25
6	66±2	69±5	57±2	64±6
7	58±2	59±4	19±1	45±23
12	52±2	48±3	53±1	51±3
13	45±2	49±3	44±1	46±3
18	35±1	41±3	33±1	36±4
19	50±1	37±2	19±1	35±16
24	39±1	71±5	31±1	47±21
25	41±1	26±2	19±1	29±11
30	30±1	79±5	-	-

Range for $[^{36}Cl]$-chlorine remaining on catalyst, within 95% confidence limits = 11 - 83 μmol Cl(g catalyst)$^{-1}$

Table 6.13 [^{36}Cl]-Chlorine activity in three samples of [^{36}Cl]-CCl_2FCF_3 from the same preparation.

Weight Counted (mg)	Counts accumulated	[^{36}Cl]-Chlorine activity[1] (Bq mg^{-1})
268.6	406878	31
207.9	69652	24
152.0	201424	32

NOTE: 1. Corrected to 100% counting efficiency.

Errors on the count rate data in Table 6.13 are << 1 % but the distribution of [^{36}Cl]-chlorine activities derived from the data is large, being 29±4 Bq mg^{-1}. The errors arose from difficulty in transferring all the scintillator/ chlorofluoroethane solution to the crimped vial and an unknown amount of chlorofluoroethane was lost due to incomplete transfer. For large sample weights these errors are reduced but for the small sample weights in the present work the errors were significant. The percentage error in the determination of [^{36}Cl]-chlorine activity in [^{36}Cl]-CCl_2FCF_3 was used to estimate the errors for all the results obtained using liquid scintillation counting.

[^{36}Cl]-CCl_2FCF_3 reacted at 688 K on fresh, pre-fluorinated chromia to give C_2ClF_5, ca. 55 mol %. $C_2Cl_2F_4$, ca. 30 mol % and $C_2Cl_3F_3$, ca. 15 mol %. The reaction products were collected over sodium hydroxide granules to remove any $H^{36}Cl$ formed during the reaction. Samples greater than 50 mol % in one of the fractions C_2ClF_5, $C_2Cl_2F_4$ or $C_2Cl_3F_3$ were obtained by distillation. In all cases (Runs 1 - 4, Table 6.14) [^{36}Cl]-chlorine activities in the products from reaction of [^{36}Cl]-CCl_2FCF_3 were lower than in the reactant. In general, the fractions containing relatively more of the chlorinated products, $C_2Cl_3F_3$ and $C_2Cl_4F_2$, had higher [^{36}Cl]-chlorine activities than those containing more of the fluorinated product, C_2ClF_5 (Runs 3 and 4, Table 6.14). No conclusion can be drawn as to whether C_2ClF_5 contained [^{36}Cl]-chlorine. Although ^{19}F n.m.r data were not determined for Run 1, fraction 1, comparison with the other data in Table 6.14 suggests that relatively more of the chlorinated products were present in fraction 1 compared with fraction 2.

Plots of the concentrations of C_2ClF_5 and $C_2Cl_2F_4$ against ([^{36}Cl]-chlorine activity in fraction), figures 6.2 and 6.3, from the data in Table 6.14, show that there is not a simple relationship between the concentration of $C_2Cl_2F_4$ or C_2ClF_5 and the [^{36}Cl]-chlorine activity of the reaction products. [^{36}Cl]-Chlorine activities in Run 4 were corrected for the different [^{36}Cl]-chlorine activity of [^{36}Cl]-CCl_2FCF_3 in Run 4 compared with Runs 1 - 3. The data in figures 6.2 and 6.3 show that the [^{36}Cl]-chlorine activity in the fractions increased with increasing concentration of $C_2Cl_2F_4$ and decreased with increasing concentration of C_2ClF_5. This observation is consistent both with the halogen exchange and with the dismutation models. It was not possible to determine the [^{36}Cl]-chlorine activities of the products C_2ClF_5, $C_2Cl_2F_4$ and $C_2Cl_3F_3$ from the experimental data.

Table 6.14 [^{36}Cl]-Chlorine activity in the products from reaction of [^{36}Cl]-CCl_2FCF_3 at 688K on fresh, pre-fluorinated chromia.

Run	Fraction	Product Distribution By ^{19}F n.m.r. (mol %)								Scintillation Count			Reference Table.
		112	112a	113	113a	114	114a	115	116	Weight Counted (mg)	Counts Accumulated	[^{36}Cl]-Chlorine Activity (Bq mg^{-1})	
1	Reactant	-	-	-	-	2.8	97.2	-	-	268.6	406878	29±4	6.9
	1	not determined								73.0	82232	22±3	
	2	-	-	1.9	12.9	2.4	13.6	69.2	-	47.6	11553	4.6±0.6	
2	Reactant	-	-	-	-	2.8	97.2	-	-	207.9	69652	29±4	6.11
	1	-	0.2	1.6	10.9	7.0	49.8	30.5	-	255	35790	2.7±0.4	
	2	-	-	-	0.7	7.0	13.8	78.4	-	172	31516	3.5±0.5	
3	Reactant	-	-	-	-	2.8	97.2	-	-	152.0	201424	29±4	6.7
	1	0.2	1.2	2.4	11.4	5.6	67.0	12.2	-	515.2	512873	24±3	
	2	0.8	3.4	1.4	2.6	9.4	32.1	50.3	-	29.6	8788	5.7±0.8	
4	Reactant	-	-	-	-	2.8	97.2	-	-	179.1	406370	55±8	—
	1	-	-	2.0	4.5	1.4	63.4	28.5	-	378.1	530353	46±6	
	2	-	-	-	4.7	5.5	70.9	18.9	-	410.1	679110	42±6	
	3	-	-	1.1	7.5	4.1	34.4	52.7	-	75.3	39506	11±2	

FIGURE 6.2 $[^{36}Cl]$-CHLORINE ACTIVITY IN C_2ClF_5 FORMED IN THE REACTION OF $[^{36}Cl]$-CCl_2FCF_3

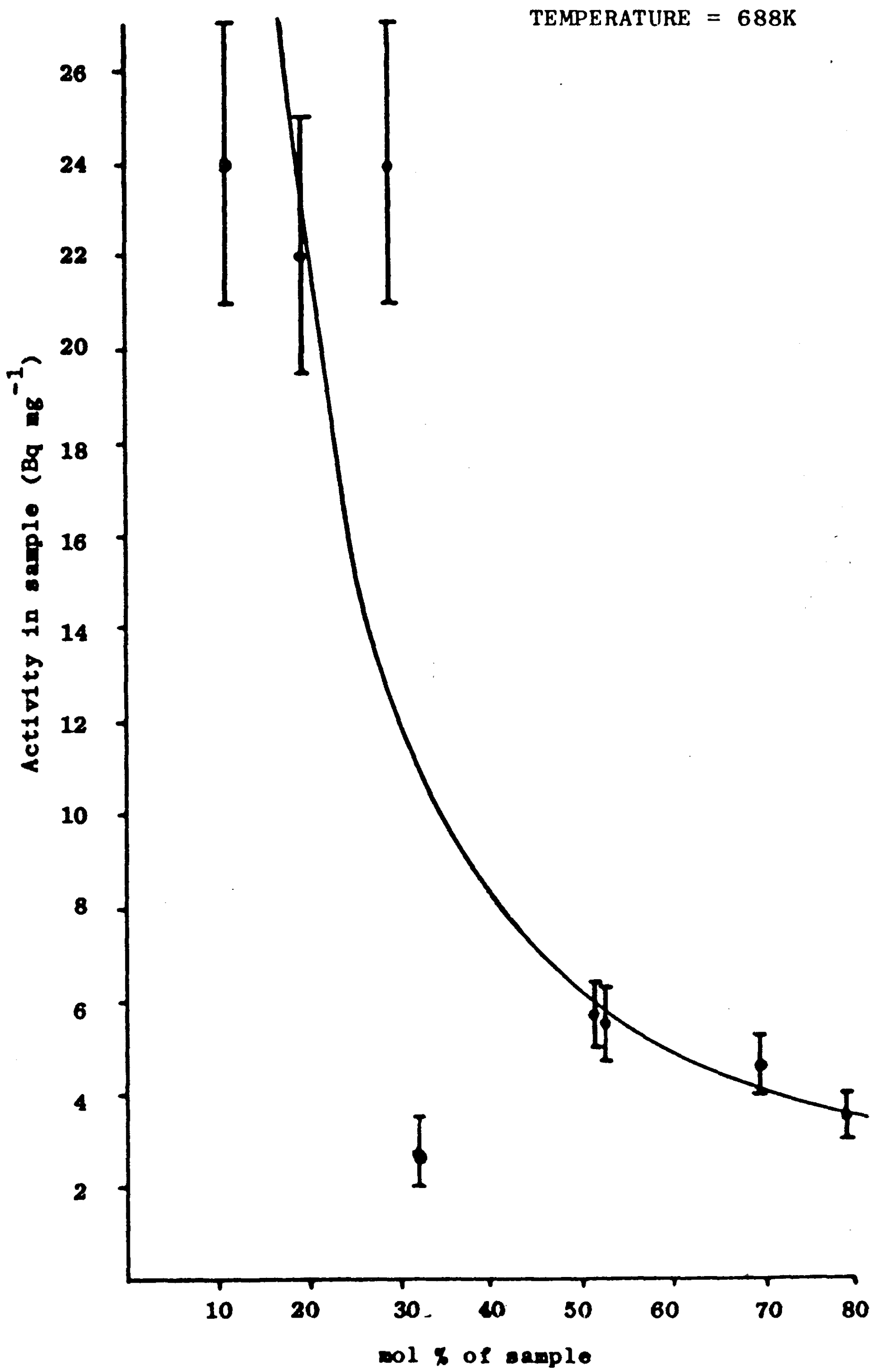
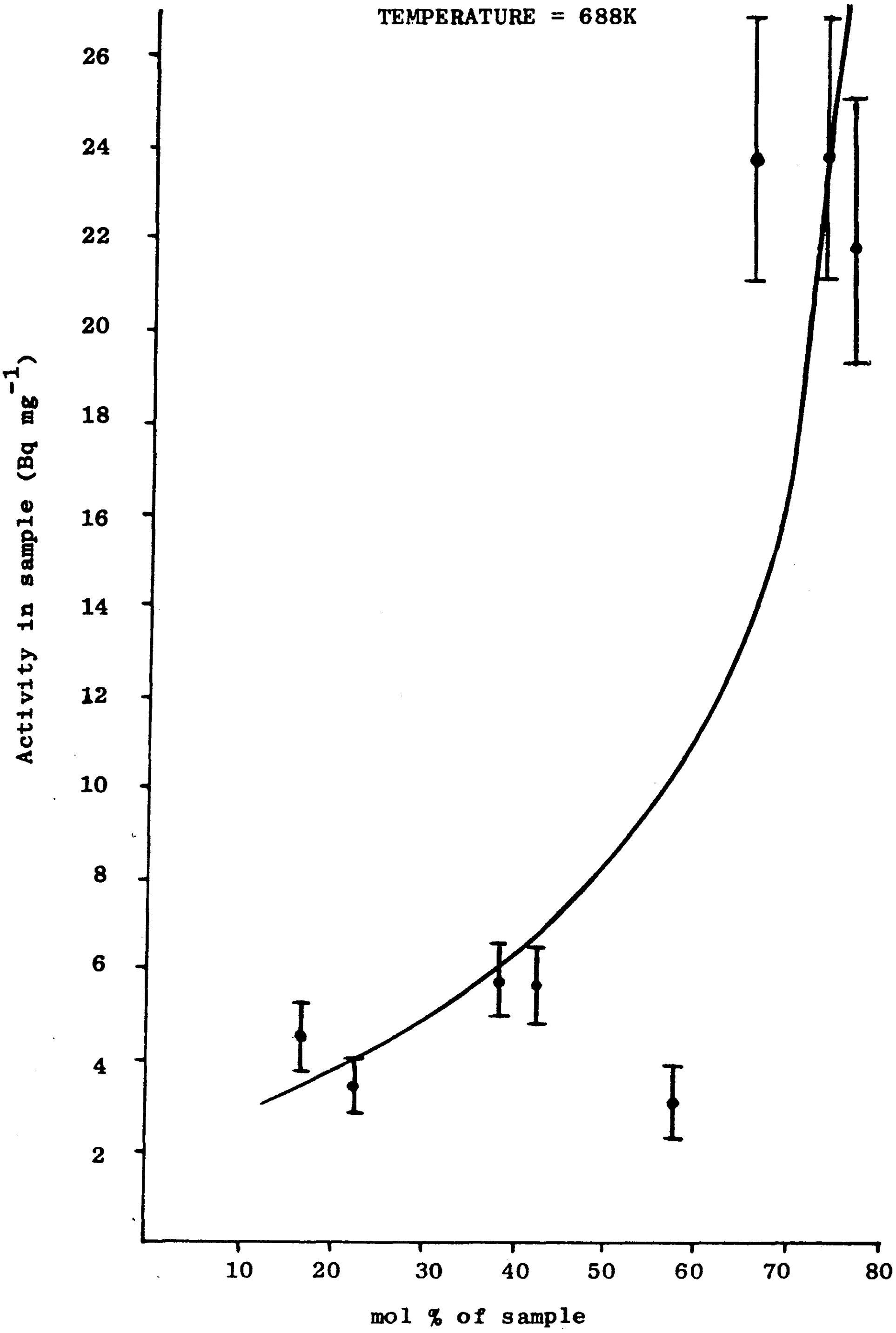


FIGURE 6.3 [^{36}Cl] -CHLORINE ACTIVITY IN $C_2Cl_2F_4$ FORMED IN THE REACTION OF [^{36}Cl]-CCl_2FCF_3



6.4.2. [^{36}Cl]-Chlorine activity in the products from the reaction of CCl_2FCClF_2 or $CClF_2CClF_2$ on pre-fluorinated chromia previously used in the reaction of [^{36}Cl]-CCl_2FCF_3.

The reaction of [^{36}Cl]-CCl_2FCF_3 at 683 K on fresh, pre-fluorinated chromia resulted in the uptake of [^{36}Cl]-chlorine by the catalyst in the range 44 - 380 μmol Cl (g catalyst)$^{-1}$ (Section 6.2). The reaction of $C_2Cl_2F_4$ or $C_2Cl_3F_3$ on a catalyst treated in this manner resulted in the incorporation of catalyst [^{36}Cl]-chlorine activity in the reaction products (Section 6.3). The error on [^{36}Cl]-chlorine activity determinations was assumed to be ±14%, as determined for [^{36}Cl]-CCl_2FCF_3 (Section 6.4.1).

Reaction of $C_2Cl_2F_4$ (mole ratio $CClF_2CClF_2$:CCl_2FCF_3 = 17:1) at 673 - 693 K on fresh, pre-fluorinated chromia formed C_2ClF_5, ca. 18 mol %, $C_2Cl_2F_4$, ca. 73 mol %, $C_2Cl_3F_3$, ca. 8 mol %, and $C_2Cl_4F_2$, ca. 1 mol % (Runs 1 - 3, Table 6.15). [^{36}Cl]-Chlorine detected in the products must have originated from the catalyst and chlorine-for-fluorine exchange must account, at least in part, for [^{36}Cl]-chlorine labelled products. In general, the fractions containing relatively more of the chlorinated products, $C_2Cl_3F_3$ and $C_2Cl_4F_2$, had higher [^{36}Cl]-chlorine activities than those containing more of the fluorinated product, C_2ClF_5. The [^{36}Cl]-chlorine activities determined for fractions 1 and 3 in Run 3 were similar, although fraction 1 contained 53 mol % chlorinated products compared with 0 mol % in fraction 3. The higher [^{36}Cl]-chlorine activity determined for fraction 3 may be accounted for by the

Table 6.15 [^{36}Cl]-Chlorine activity in the products from reaction of $CClF_2CClF_2$ at 673-693K on chromia previously used in the reaction of [^{36}Cl]-CCl_2FCF_3

Run	Reactant	Fraction	Product Distribution By ^{19}F n.m.r. (mol %)								Scintillation Count			Reference Table.
			112	112a	113	113a	114	114a	115	116	Weight Counted (mg)	Counts Accumulated	^{36}Cl -Chlorine Activity (Bq mg^{-1})	
1	$C_2Cl_2F_4$	1	-	0.5	3.7	4.6	60.4	14.7	16.1	-	79.2	11284	2.7±0.4	6.9
		2	-	0.8	1.3	11.7	25.7	16.7	43.8	-	888.1	9333	0.20±0.03	
2	$C_2Cl_2F_4$	1	-	7.9	14.6	34.1	28.0	13.4	2.1	-	206.9	24833	2.8±0.4	6.10
		2	-	3.6	9.5	19.0	39.3	16.7	11.9	-	1035.5	22225	1.2±0.2	
		3	-	-	1.0	3.2	29.5	11.8	54.6	-	826.7	21150	0.9±0.1	
3	$C_2Cl_2F_4$	1	-	6.7	30.5	15.9	43.3	3.7	-	-	179.9	15844	1.8±0.2	-
		2	-	-	6.1	3.6	83.7	6.6	-	-	305.3	9655	0.6±0.1	
		3	-	-	-	-	59.0	6.8	34.1	-	209.4	19635	1.9±0.3	
4	$C_2Cl_3F_3$	1	-	1.4	23.9	22.3	34.3	17.8	0.3	-	474.7	49321	2.7±0.4	6.11
		2	-	-	-	1.1	36.1	35.3	27.5	-	71.5	15356	4.1±0.6	

presence of $H^{36}Cl$ not removed by treatment of the products with NaOH, since hydrogen chloride condenses at the lower temperature (< 193 K) at which C_2ClF_5 was collected.

Reaction of $C_2Cl_3F_3$ at 623 K on fresh, pre-fluorinated chromia, previously used in the reaction of $[^{36}Cl]$-CCl_2FCF_3, produced $C_2Cl_2F_4$, <u>ca</u>. 26 mol %, $C_2Cl_3F_3$, <u>ca</u>. 54 mol %, and $C_2Cl_4F_2$, <u>ca</u>. 19mol%, C_2ClF_5, <u>ca</u>. 1 mol % was also detected. Fraction 1 (Run 4, Table 6.15) contained very little $C_2Cl_4F_2$, indicating an inefficient transfer of sample from the eluant collection vessels. The $[^{36}Cl]$-chlorine activity of this fraction was substantial, indicating that $C_2Cl_3F_3$ contained $[^{36}Cl]$-chlorine activity.

Incorporation of $[^{36}Cl]$-chlorine in $C_2Cl_3F_3$ can be accounted for either by Cl-for-Cl exchange between reactant $C_2Cl_3F_3$ and chromia, chlorination of $C_2Cl_3F_3$ followed by fluorination, or fluorination of $C_2Cl_3F_3$ followed by chlorination (Scheme 6.1).

$$C_2Cl_3F_3 \xrightarrow{[^{36}Cl]\text{-chlorine/chromia}} [^{36}Cl]\text{-}C_2Cl_4F_2 + [^{36}Cl]\text{-}C_2Cl_3F_3 + C_2Cl_2F_4$$

$$C_2Cl_2F_4 \xrightarrow{[^{36}Cl]\text{-chlorine/chromia}} [^{36}Cl]\text{-}C_2Cl_3F_3$$

Scheme 6.1 <u>Possible routes to $[^{36}Cl]$-$C_2Cl_3F_3$ from reacting $C_2Cl_3F_3$</u>

6.4.3 [^{36}Cl]-Chlorine activity in the products from reaction of $CClF_2CClF_2$ on pre-fluorinated chromia treated with $H^{36}Cl$.

Pre-fluorinated chromia, previously treated using $H^{36}Cl$ at 623 K, was used to catalyse the reaction of $CClF_2CClF_2$ at 623 - 683 K. Admission of $H^{36}Cl$ at 623 K to pre-fluorinated chromia resulted in the uptake of [^{36}Cl]-chlorine by the catalyst in the range 119 - 323 μmol (g catalyst)$^{-1}$ (Section 5.4). At a reaction temperature of 623 K and a flow rate of 14 cm^3 min^{-1} the reactor eluant comprised C_2ClF_5, *ca.* 29 mol %, $C_2Cl_2F_4$. *ca.* 64 mol %, and $C_2Cl_3F_3$, *ca.* 7 mol %. At the same flow rate and a temperature of 683 K the reaction products were C_2ClF_5, *ca.* 46 mol %. $C_2Cl_2F_4$, *ca.* 44 mol %, and $C_2Cl_3F_3$, *ca.* 9 mol %. C_2F_6 and $C_2Cl_4F_2$ were detected in trace quantities. A light pink colour was occasionally detected in the product collection traps. The species was volatile and the colour was maintained when the traps were allowed to warm to room temperature. Over a period of time, during which the samples were exposed to light, the pink colour was discharged. Several Cr^{VI} species are red or pink in colour and the observed properties of the species corresponded closely to chromium dioxide dichloride,[72] CrO_2Cl_2.

Reaction of $CClF_2CClF_2$ (17.8 mmol) at 623 K (Run 1, Table 6.16) gave an eluant containing [^{36}Cl]-chlorine activity. The [^{36}Cl]-chlorine activity of fraction 1 was found to be 2.8 Bq mg^{-1} while that for fraction 2 was 0.4 Bq mg^{-1}. The composition of fraction 2 was not determined.

Table 6.16 [^{36}Cl]-Chlorine activity in the products from reaction of $CClF_2CClF_2$ at 623-683K on pre-fluorinated chromia treated with H^{36}Cl.

Run	Fraction	Product Distribution By ^{19}F n.m.r. (mol %)								Scintillation Count			Reference Table.
		112	112a	113	113a	114	114a	115	116	Weight Counted (mg)	Counts Accumulated	[^{36}Cl]-Chlorine Activity (Bq mg^{-1})	
1	1	-	1.6	6.2	14.1	53.3	15.7	9.0	-	189.4	26398	2.8±0.4	5.19
	2	not determined								189.7	203	0.41±0.06	
2	1	-	0.4	1.0	4.5	58.2	18.7	17.3	-	361.4	242033	1.3±0.2	5.24
	2	-	-	-	-	49.4	14.3	35.1	-	78.5	2600	0.13±0.02	
3a.	1	-	0.7	2.6	2.6	88.3	5.5	0.3	-	226.5	26013	2.3±0.3	5.21
	2	not determined								*ca* 100	271	0.16±0.02	
3b	1	-	0.9	6.6	26.8	31.8	19.4	14.4	-	547.0	44787	0.04±0.01	
	2	-	-	5.1	3.8	29.5	17.9	43.6	-	19.7	820	0.03±0.01	
3c	1	-	0.1	0.5	0.6	85.3	5.7	7.9	-	609.7	19013	0.04±0.01	

However, on the basis of the data in Tables 6.14 and 6.15 fraction 2, which was collected at 193 K, was assumed to contain a higher concentration of C_2ClF_5 compared with fraction 1, which was collected at 233 K. Run 2 (Table 6.16) gave similar results to Run 1. [^{36}Cl]-Chlorine activity corresponding to 1.3 Bq mg^{-1} was detected in fraction 1, which contained $C_2Cl_3F_3$ and $C_2Cl_4F_2$. Fraction 2, which contained only $C_2Cl_2F_4$ and C_2ClF_5 contained 0.1 Bq mg^{-1} [^{36}Cl]-chlorine.

Run 3a (Table 6.16) gave similar results to Runs 1 and 2. Reaction of $CClF_2CClF_2$ (18.2 mmol) at 683 K resulted in 2.3 Bq mg^{-1} [^{36}Cl]-chlorine activity in fraction 1. Fraction 2, which was expected to contain relatively more fluorinated product, contained less [^{36}Cl]-chlorine activity, namely 0.1 Bq mg^{-1}. Further reaction of $CClF_2CClF_2$ on the same catalyst gave only traces of [^{36}Cl]-chlorine in the products (Run 3b, 23.5 mmol $CClF_2CClF_2$; Run 3c, 51.6 mmol $CClF_2CClF_2$). After removal of the catalyst, following Run 3c, [^{36}Cl]-chlorine corresponding to a retention of 31 - 58 μmol Cl(g catalyst)$^{-1}$ was determined (Table 5.21). [^{36}Cl]-Chlorine retentions determined for the catalysts used in Runs 1 and 2 were in the ranges 30 - 43 μmol Cl(g catalyst)$^{-1}$ and 9 - 15 μmol (g catalyst)$^{-1}$ respectively (Tables 5.19 and 5.24). Substantial quantities of [^{36}Cl]-chlorine activity could therefore be removed from chromia treated with H^{36}Cl during reaction of <u>ca</u>. 20 mmol $CClF_2CClF_2$. Further reaction of $CClF_2CClF_2$ did not remove an additional quantity of catalyst [^{36}Cl]-chlorine. Catalyst [^{36}Cl]-chlorine determined following reaction of ca. 20 mmol $CClF_2CClF_2$ was therefore more strongly bound than catalyst [^{36}Cl]-chlorine which can be removed during the reaction and incorporated in the reaction products.

6.4.4 [^{36}Cl]-Chlorine activity in the products from reaction of $CClF_2CClF_2$ on chromia pre-treated only with $H^{36}Cl$.

Treatment of unfluorinated chromia with $H^{36}Cl$ resulted in the uptake of [^{36}Cl]-chlorine by the catalyst in the range 414 - 997 μmol(g catalyst)$^{-1}$ (Table 5.14). Admission of $CClF_2CClF_2$ (34 mmol) at 693 K resulted in reaction to form C_2ClF_5, ca. 39 mol %, $C_2Cl_2F_4$, ca. 55 mol %, and $C_2Cl_3F_3$, ca. 6 mol %. Table 6.17 shows the [^{36}Cl]-chlorine activity detected in the products. The catalyst [^{36}Cl]-chlorine count rates indicated that [^{36}Cl]-chlorine had been removed from the catalyst (Table 5.27). The mass balance for the reaction, calculated from the gas chromatographic data, was 76 % and compared with mass balances > 92 % for the reactions on pre-fluorinated chromias (Section 3.2).

[^{36}Cl]-Chlorine activity corresponding to 2.7 Bq mg^{-1} was detected in fraction 1, which comprised 50.5 mol % chlorinated products (Table 6.17). Fraction 3, which comprised 42.7 mol % C_2ClF_5, contained [^{36}Cl]-chlorine corresponding to 1.3 Bq mg^{-1}, significantly greater than fraction 2, which contained 0.2 Bq mg^{-1} [^{36}Cl]-chlorine and comprised 19.7 mol % C_2ClF_5. Fractions 2 and 3 contained similar quantities of chlorinated product, 6.9 and 4.0 mol %

Table 6.17 **[^{36}Cl]-Chlorine activity in the products from reaction of $CClF_2CClF_2$ at 693 K on chromia pre-treated only with $H^{36}Cl$.**

Fraction	Product Distribution By ^{19}F n.m.r. (mol %)								Scintillation Count			Reference Table.
	112	112a	113	113a	114	114a	115	116	Weight Counted (mg)	Counts Accumulated	[^{36}Cl]-Chlorine Activity (Bq mg^{-1})	
1	-	2.0	6.9	41.6	39.6	9.9	-	-	402	39672	2.7±0.4	5.26
2	-	-	1.0	5.9	55.7	17.7	19.7	-	481	4587	0.20±0.03	
3	-	-	-	4.0	50.0	3.2	42.7	-	292	18239	1.3±0.2	

respectively. This apparent anomaly may indicate the presence of $H^{36}Cl$ in fraction 3. It was not possible to determine the $[^{36}Cl]$-chlorine activities of the products C_2ClF_5, $C_2Cl_2F_4$ and $C_2Cl_3F_3$ from the experimental data.

The observation that reaction occurred on chromia treated only with $H^{36}Cl$ was surprising, since the fluorination reactions required a quantity of fluorine seven times greater than that provided by chlorination reactions (C_2ClF_5, ca. 39 mol % ; $C_2Cl_3F_3$, ca. 6 mol %). The experiment was repeated under similar conditions, but with untreated chromia in the reactor, to verify that the reaction of $C_2Cl_2F_4$ was not promoted by fluoride ion adsorbed either on the walls of the reactor, or on the sodium fluoride pellets used to remove hydrogen fluoride from the reactor eluant. No reaction was observed and the isomeric composition of $C_2Cl_2F_4$ was unchanged following passage through the reactor.

The 76 % mass balance for the reaction indicated that 7.2 mmol of chlorofluoroethane was unaccounted for (34 mmol $C_2Cl_2F_4$ admitted to the catalyst, 26.8 mmol chlorofluoroethane determined in the reactor eluant). Chlorofluoroethane in the reactor eluant included 33 mol %, or 8.8 mmol, corresponding to C_2ClF_5 for which the chlorination reactions could not have provided a source of fluorine. Fluorine from the chlorofluoroethane not determined in the reactor eluant must account for the large quantity of C_2ClF_5 formed. The results are consistent with dissociative adsorption of chlorofluoroethane providing a source of catalyst fluoride ion for the fluorination reactions. However, the D.R.I.F.T.S.

study of the interaction between $C_2Cl_3F_3$ and chromia (Section 3.9) provided no evidence for strongly adsorbed organic species on chromia which had been used for reaction of chlorofluoroethanes.

6.4.5 [^{36}Cl]-Chlorine activity in the products from reaction of [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ on pre-fluorinated chromia.

The reaction of a [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ mixture at 676 - 693 K on fresh, pre-fluorinated chromia (Section 6.1) resulted in uptake of [^{36}Cl]-chlorine by the catalyst and incorporation of [^{36}Cl]-chlorine in the reaction products (Table 6.18). It was not possible to compare [^{36}Cl]-chlorine activities in the symmetric and asymmetric isomers of $C_2Cl_2F_4$ to establish whether [^{36}Cl]-chlorine activity had been incorporated in the symmetric isomer.

Table 6.18 [^{36}Cl]-Chlorine activity in the products from reaction of a [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ mixture at 676-693K on fresh, pre-fluorinated chromia.

Run	Fraction	Product Distribution By ^{19}F n.m.r (mol %)								Scintillation Count			Reference Table
		112	112a	113	113a	114	114a	115	116	Weight Counted	Counts Accumulated	^{36}Cl -Chlorine Activity (Bq mg^{-1})	
1	Reactant	-	-	-	-	41.2	58.8	-	-	422.2	15420	9.0±1.2	6.5
	1	-	77.3	22.7	-	-	-	-	-	25.1	733	5.8±0.8	
	2	-	<1	3.6	15.4	39.3	37.8	2.9	-	187.1	8295	7.3±1.0	
	3	-	-	-	3.0	16.1	29.5	51.4	-	49.3	1198	4.1±0.6	
2	Reactant	-	-	-	-	49.9	50.1	-	-	89.2	5818	12.4±1.6	6.5
	1	-	80.0	20.0	-	-	-	-	-	54.9	2017	7.1±1.0	
	2	not determined								166.1	6754	8.0±1.1	
	3	-	-	-	-	11.5	8.1	80.4	-	133.5	1815	2.6±0.4	

Table 6.19 [^{36}Cl]-CCl$_2$FCF$_3$/CClF$_2$CClF$_2$ Reacting on Fresh, Pre-fluorinated Chromia at 676 - 693 K.

Run 1 mole ratio [^{36}Cl]-F.C.114a:F.C.114 = 58.8:41.2 by ^{19}F n.m.r spectroscopy.

Time (min)	Temp. (K)	Flow Rate [N_2+$C_2Cl_2F_4$] ($cm^3 min^{-1}$)	Product Distribution by G.C. (mol % of eluant)				Mole Ratio 114:114a in eluant
			115	114	114a	113	
20	691	28.0	41.0	25.1	29.5	4.3	0.85
55	689	33.3	39.7	23.4	28.1	8.8	0.83
90	689	26.0	40.9	22.6	27.7	8.6	0.82
120	690	31.9	38.2	20.3	32.8	8.3	0.62
157	693	28.5	37.8	22.5	29.5	9.6	0.76

Run 2 mole ratio [^{36}Cl]-F.C.114a:F.C.114 = 50.1:49.9 by ^{19}F n.m.r spectroscopy

Time (min)	Temp (K)	Flow Rate [N_2+$C_2Cl_2F_4$] ($cm\ min^{-1}$)	Product Distribution by G.C. (mol % of eluant)				Mole Ratio 114:114a in eluant
			115	114	114a	113	
30	681	33.3	34.3	28.4	31.3	5.9	0.91
60	684	34.4	37.8	26.8	28.2	7.2	0.95
95	683	35.2	39.6	28.2	24.8	7.4	1.14
127	684	26.0	41.7	24.4	26.3	7.7	0.93
170	683	31.2	27.9	28.5	37.4	6.1	0.76
195	682	25.0	27.8	29.3	36.1	6.8	0.81
233	682	30.0	31.0	27.1	34.0	7.9	0.80

CHAPTER SEVEN

DISCUSSION

CHAPTER SEVEN

DISCUSSION.

7.1 The Interconversion of Chlorofluoroethanes Using a Chromia Catalyst.

The present work shows the importance of chlorination reactions in the vapour phase process for the manufacture of chlorofluoroethanes. The results of experiments involving $H^{36}Cl$ flow or the reaction of $[^{36}Cl]$-CCl_2FCF_3 show that chlorine containing species, presumably in the form of an adsorbed chloride species, are formed on chromia. Uptake of $[^{36}Cl]$-chlorine from passage of $H^{36}Cl$ at 623 K over fresh, pre-fluorinated chromia was in the range 119 - 323 μmol (g catalyst)$^{-1}$ (Table 5.8). The reaction of $[^{36}Cl]$-CCl_2FCF_3 at 688 K on pre-fluorinated chromia resulted in a similar uptake of $[^{36}Cl]$-chlorine by the catalyst, being in the range 44 - 380 μmol (g catalyst)$^{-1}$ over all the pellets and 192 - 358 μmol (g catalyst)$^{-1}$ over pellets 1 - 13.

The behaviour of the catalyst-chloride species is independent of the original source of the chloride. Reaction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ at a temperature > 623 K removed 75 - 85% of the $[^{36}Cl]$-chlorine activity from the catalyst. There is no relationship between the quantity of chlorofluoroethane reacted and the quantity of $[^{36}Cl]$-chlorine remaining on the catalyst. The results in Table 5.23 show that the reaction of 93.2 mmol $C_2Cl_2F_4$ did not remove a greater quantity of $[^{36}Cl]$-chlorine than did the reaction of 13.4 - 31.0 mmol $C_2Cl_2F_4$. The reaction of

$C_2Cl_3F_3$ formed relatively more chlorinated products than did the reaction of $C_2Cl_2F_4$. However, [^{36}Cl]-chlorine remaining on the catalyst after the reaction of $C_2Cl_3F_3$ was within the range determined after the reaction of $C_2Cl_2F_4$.

[^{36}Cl]-Chlorine remaining on the catalyst after digestion of the pellets in sodium hydroxide solution was in the range 8 - 51 μmol (g catalyst)$^{-1}$ (Table 5.29). This compares with 18 - 66 μmol Cl(g catalyst)$^{-1}$ determined following reaction of chlorofluoroethane on pre-fluorinated chromia previously treated using $H^{36}Cl$, and 11 - 83 μmol Cl (g catalyst)$^{-1}$ determined following reaction of chlorofluoroethane on pre-fluorinated chromia previously used to react [^{36}Cl]-CCl_2FCF_3 (Tables 5.23 and 6.12 respectively). Flowing HF over pre-fluorinated chromia which had been treated using $H^{36}Cl$ also removed [^{36}Cl]-chlorine from the catalyst. Following HF flow, [^{36}Cl]-chlorine in the range 23 - 45 μmol (g catalyst)$^{-1}$ remained from the initial treatment of the catalyst using $H^{36}Cl$ (Table 5.17).

An inactive chlorine-containing species, inert to reaction with HF or chlorofluoroethane, and retained by the catalyst under basic conditions, which removed _ca_. 75% of the [^{36}Cl]-chlorine taken up by the catalyst, is therefore present on chromia treated with $H^{36}Cl$ or after reaction of [^{36}Cl]-CCl_2FCF_3. This inactive chlorine-containing species comprises 15 - 25% of the chlorine taken up by the catalyst during HCl flow or the reaction of $C_2Cl_2F_4$.

Models to account for the chemistry of chlorofluoroethanes on chromia or aluminium trifluoride, involving either pre-treatment of the catalyst using HF, or reaction of a HF/chlorofluoroethane gas flow, are based on catalyst-halogen exchange, dismutation and isomerisation reactions (Section 1.4.1).

Tatlow and co-workers[17] proposed a catalyst-chloride species to account for the formation of chlorinated products in the reactions of $C_2Cl_3F_3$ using an aluminium trifluoride catalyst. The reactions of chlorofluoroethanes on the catalyst were formulated as a series of chlorination, fluorination and isomerisation reactions. Although there was no experimental evidence to support many of the individual reactions proposed, the model developed by Tatlow being intended only to describe the overall chemical process[73], the concept of a catalytic site for the chlorination reactions was an important development.

Since Tatlow et al [17] first suggested a role for a catalyst-chloride site, the authors of most studies published have relied upon product distribution data to establish the chemistry of the vapour phase system, and models developed to account for the chemistry are derived from these data. The unequivocal establishment of two chlorine-containing species in the present work, together with the fluorine-containing species identified by Kijowski and co-workers[25], is extremely important. The involvement of a fluorine-containing and a chlorine-containing species in the fluorination and chlorination reactions proves the importance of halogen exchange reactions in the catalytic process.

The results of the catalyst-[^{36}Cl]-chlorine/chlorofluoroethane radiotracer studies are consistent with a halogen exchange model involving reaction between chlorofluoroethane and the catalytically active chlorine-containing species. Scheme 7.1 illustrates the possible steps leading to the formation of C_2ClF_5 from CCl_3CClF_2. In this scheme reactions with the labile fluorine and chlorine-containing species are represented by F_a and Cl_a respectively; isomerisation reactions are indicated by 'I'.

The results of a previous [^{18}F]-fluorine radiotracer study[25] provided direct evidence for the fluorination reactions (equation (7.1)):-

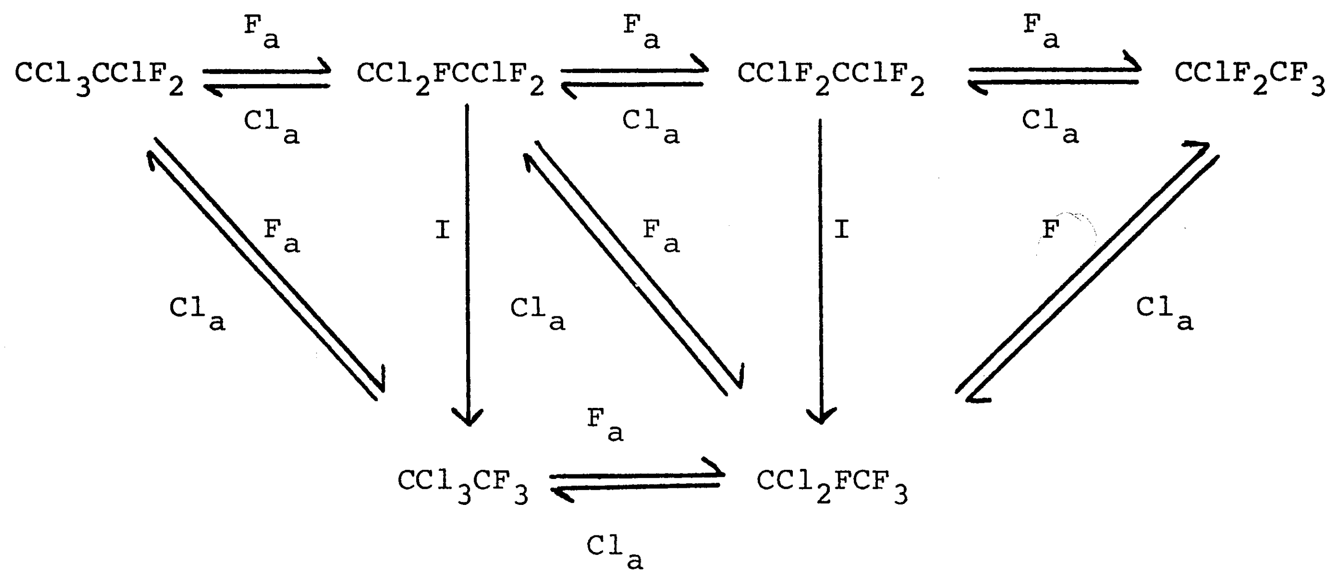
$$\begin{aligned} CCl_2FCClF_2 &\longrightarrow CClF_2CClF_2 \\ CCl_2FCClF_2 &\longrightarrow CCl_2FCF_3 \\ CClF_2CClF_2 &\longrightarrow CClF_2CF_3 \end{aligned}$$

<u>Equation (7.1)</u>

Direct evidence for the reactions in equation (7.2) is provided by the [^{36}Cl]-chlorine analyses of the reactor eluant in the $CClF_2CClF_2$/catalyst-[^{36}Cl]-chlorine and [^{36}Cl]-CCl_2FCF_3/catalyst experiments.

$$\begin{aligned} CClF_2CClF_2 &\longrightarrow CCl_2FCClF_2 \\ CCl_2FCF_3 &\longrightarrow CCl_2FCClF_2 \end{aligned}$$

<u>Equation (7.2)</u>



Scheme 7.1 <u>Interconversion of chlorofluoroethanes by fluorination, chlorination and isomerisation</u>.

The asymmetric isomer CCl_2FCF_3 is more readily fluorinated than the symmetric isomer $CClF_2CClF_2$.

There is no evidence to support the existence of dismutation reactions in the vapour phase process. Any dismutation reaction can be formulated as a series of two halogen exchange reactions as shown, for example, in equation (7.3).

<u>Dismutation</u> $2CClF_2CClF_2 \longrightarrow CCl_2FCClF_2 + CClF_2CF_3$

<u>Halogen Exchange</u> $CClF_2CClF_2 + F^-_{(cat)} \longrightarrow CClF_2CF_3 + Cl^-_{(cat)}$

$CClF_2CClF_2 + Cl^-_{(cat)} \longrightarrow CCl_2FCClF_2 + F^-_{(cat)}$

<u>Equation (7.3)</u>

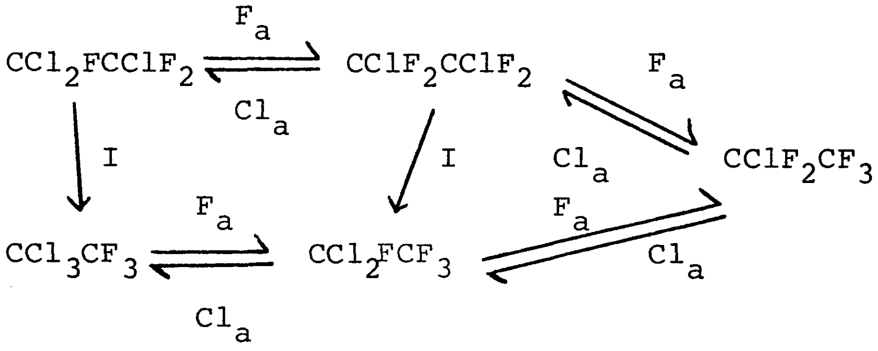
The formation of a catalytically active fluorine-containing species can be inferred from the observation that reaction to form fluorinated products occurred on chromia which had been pre-treated with $H^{36}Cl$ but not HF. Catalyst-[^{36}Cl]-chlorine/chlorofluoroethane exchange is involved in this reaction since [^{36}Cl]-chlorine was removed from chromia and detected in the reaction products. The Cl-F exchange model proposed by Kolditz and co-workers[24] can be ruled out because it involves halogen exchange to form a fluorinated product and desorption of all the exchanged chlorine as HCl. Kolditz ignores the possibility of halogen exchange between a reacting molecule and a catalyst chlorine-containing species and all the chlorinated products determined by Kolditz are accounted for on the basis of the bimolecular dismutation reactions.

The isomerisation reactions (Equation (7.4)) have been proposed by several authors[17,22,23,24]

$$CClF_2CClF_2 \longrightarrow CCl_2FCF_3$$
$$CCl_2FCClF_2 \longrightarrow CCl_3CF_3$$

Equation (7.4)

to account for the formation of asymmetric isomers from symmetric isomer reactants. Scheme 7.1a shows the possible fluorination chlorination and isomerisation reactions of $C_2Cl_2F_4$.



Scheme 7.1a. Fluorination, chlorination and isomerisation reactions from the isomers of $C_2Cl_2F_4$

Reaction of $CClF_2CClF_2$ on pre-fluorinated chromia was always accompanied by the formation of substantial quantities of CCl_2FCF_3 and CCl_3CF_3 (Section 3.1). The concentrations of the two isomers, $CClF_2CClF_2$ and CCl_2FCF_3, at thermodynamic equilibrium can be calculated from the free energy of the isomerisation reaction[27] (Equation (7.5)).

$$CClF_2CClF_2 \longrightarrow CCl_2FCF_3$$

Equation (7.5)

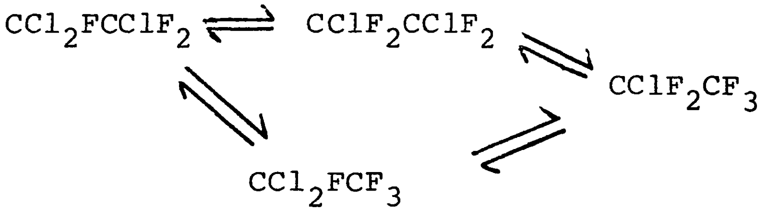
The gas equilibrium constants for the isomerisation reaction in the temperature range 623 - 823 K are shown in Table 7.1.

Table 7.1 Gas Equilibrium Constant for the Isomerisation $CClF_2CClF_2 \rightleftharpoons CCl_2FCF_3$

Temperature (K)	ΔG^o (kJ mol^{-1})	K_p
623	-47.7	$1.0x10^4$
673	-50.2	$8.0x10^3$
723	-52.7	$6.7x10^3$
773	-55.6	$6.1x10^3$
823	-59.4	$6.0x10^3$

On the basis of the thermodynamic data, there is a large excess of CCl_2FCF_3 over $CClF_2CClF_2$ at thermodynamic equilibrium. Increasing temperature shifts the equilibrium towards the left hand side of equation (7.5). However, reaction of $C_2Cl_2F_4$ comprising various isomer mixtures of $CClF_2CClF_2$ and CCl_2FCF_3 (Section 3.5) did not result in the attainment of the predicted equilibrium concentrations of the two isomers. Instead, the product distribution data indicate that the mole ratio of $CClF_2CClF_2$: CCl_2FCF_3 in the eluant tended towards a 1:1 mole ratio for the reaction of all the isomeric mixtures. The results from reaction of a [^{36}Cl]-CCl_2FCF_3/$CClF_2CClF_2$ isomer mixture on pre-fluorinated chromia (Section 6.1) are consistent with the isomer CCl_2FCF_3 reacting preferentially to form C_2ClF_5, whilst the formation of CCl_2FCF_3 from $CClF_2CClF_2$ must account for the unchanged isomer ratio observed in the reaction products. Since the isomer ratio changed from either excess symmetric or excess asymmetric isomer towards a 1:1 symmetric:asymmetric mole ratio, the strong inference is that the kinetic rates of reactions leading to fluorinated and chlorinated products are greater than the rate of the isomerisation reaction. The isomerisation reaction from $CClF_2CClF_2$ to CCl_2FCF_3 can therefore be considered to be kinetically irrelevant.

The route to formation of CCl_2FCF_3 from $CClF_2CClF_2$ (Scheme 7.1b) is more likely to involve the compound



Scheme 7.1b. <u>'Indirect isomerisation' from $CClF_2CClF_2$ to CCl_2FCF_3 involving halogen exchange reactions.</u>

CCl_2FCClF_2 than $CClF_2CF_3$. Fluorination of CCl_2FCClF_2 is achieved readily at a temperature of 623 K or above. The chlorination reaction (Equation (7.6)):

$$CClF_2CF_3 \longrightarrow CCl_2FCF_3 + CClF_2CClF_2$$

Equation (7.6)

has not been studied and the involvement of C_2ClF_5 in the indirect isomerisation of $CClF_2CClF_2$ cannot be ruled out. However, the difficulty of both the fluorination and chlorination reactions generally increases with increasing fluorine content of the chlorofluoroethane. On this basis $CClF_2CF_3$ must be considered unlikely to contribute significantly to the indirect isomerisation of $CClF_2CClF_2$.

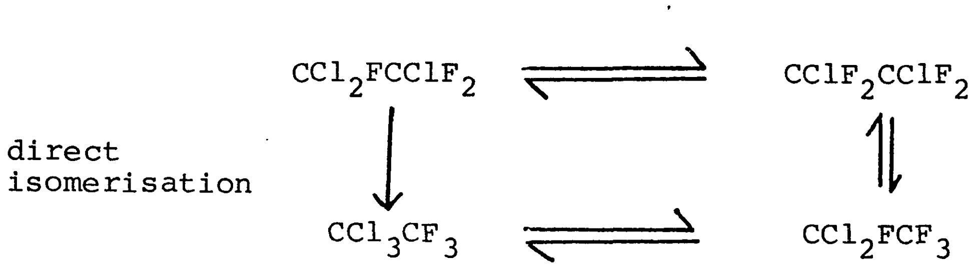
The isomerisation reaction (Equation (7.7)):

$$CCl_2FCClF_2 \longrightarrow CCl_3CF_3$$

Equation (7.7)

is generally accepted[17,23,24] to be an important process in the overall reaction scheme (Scheme 7.1). Reaction of $CClF_2CClF_2$ on pre-fluorinated chromia (to form C_2ClF_5 and $C_2Cl_3F_3$) resulted in symmetric:asymmetric isomer ratios for the eluant $C_2Cl_2F_4$ in the range 10.0:1 - 14.3:1. Symmetric:asymmetric isomer ratios for eluant $C_2Cl_3F_3$ were in the range 2.0:1 - 3.3:1 (Section 3.3, Table 3.2). Symmetric:asymmetric isomer ratios were not determined for the products from the reaction of CCl_2FCF_3. However, the ^{19}F n.m.r. data for the fractions from which the $[^{36}Cl]$-chlorine count rate data were obtained (Table 6.14) indicate that substantial quantities of $CClF_2CClF_2$ were produced and that both CCl_2FCClF_2 and CCl_3CF_3 were formed, the latter being in excess. The observation that $CClF_2CClF_2$ is a significant product from the reaction of CCl_2FCF_3 is consistent with the previous discussion of the isomerisation reaction from $CClF_2CClF_2 \longrightarrow CCl_2FCF_3$.

Formation of CCl_3CF_3 directly from $CClF_2CClF_2$ is not possible and this product must arise either from isomerisation of CCl_2FCClF_2, or from chlorination of CCl_2FCF_3 (Scheme 7.1c).



Scheme 7.1c Possible reactions leading to the formation of CCl_3CF_3

Since CCl_2FCF_3 accumulates during the reaction of $CClF_2CClF_2$, the formation of CCl_3CF_3 can be accounted for by the chlorination reaction $CCl_2FCF_3 \rightarrow CCl_3CF_3$ and it is not necessary to invoke isomerisation to account for the reaction product distributions. The high concentrations of CCl_3CF_3 determined, relative to CCl_2FCClF_2, are consistent with an order of reactivity $CCl_2FCClF_2 > CCl_3CF_3$ towards fluorination. This order of reactivity is supported by the observation that reaction of pure CCl_3CF_3 deactivates the chromia catalyst[23] and is contrary to the general observation that the reactivity of $-CCl_{3-n}F_n$ groups towards fluorination decreases with increasing values of n.[1,28]

7.2 The Role of Hydrogen Chloride in the Vapour Phase Process.

The formation of hydrogen chloride in the reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia (Section 3.4) must involve chlorine from reacting chlorofluoroethanes and hydrogen from HF. The catalyst does retain chlorine from reacting chlorofluoroethanes (Sections 5.3 and 6.2) and the desorption of HCl is consistent with the halogen exchange model.[26] In the absence of HCl desorption, the chlorine-containing species formed in the fluorination reactions build up on the catalyst and the formation of chlorinated products will increase through a concentration effect.

Marangoni and co-workers[22] reported that hydrogen chloride comprised 50-75 mol % of the total eluant hydrogen halide determined for the reaction of a mixed HF/$C_2Cl_2F_4$ gas flow at 718 K on chromia. The HCl is formed in the reaction (Equation (7.8)):-

$$C_2Cl_2F_4 + HF \longrightarrow C_2ClF_5 + HCl$$

<u>Equation (7.8)</u>

In an earlier study of the reaction represented by equation (7.8),[74] Marangoni <u>et.al</u>. observed that increasing the mole ratio of HF:$C_2Cl_2F_4$ decreased the co-production of $C_2Cl_3F_3$. Experiments involving passage of $H^{18}F$ over chromia treated using $H^{36}Cl$ and $H^{36}Cl$ over chromia treated using $H^{18}F$ (Sections 5.5.2 and 4.5.1) established that the interaction between HF and chromia is stronger than that between HCl and chromia. The results of the spectroscopic study using diffuse reflectance i.r. (Section 3.9) indicated that $C_2Cl_3F_3$ is easily removed from chromia and that no chlorofluorocarbons are present on used chromia. The strength of the interaction between chromia and the species HF, HCl and $C_2Cl_3F_3$ is believed to decrease in the order:

$$HF > HCl > C_2Cl_3F_3$$

The decrease in $C_2Cl_3F_3$ production when increased HF flow rates are used can be accounted for on the basis of an increased rate of removal of the chlorine-containing species responsible for the chlorination reactions.

The results from the reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia (Section 3.4) and HF/$C_2Cl_2F_4$ on chromia[22] show that the catalyst-chloride species are readily converted to HCl. Loss of catalyst-chloride occurred when samples treated using HCl or used in the reaction of $C_2Cl_2F_4$ were allowed to hydrolyse (Sections 5.3 and 5.6). In the case of chromia treated with HCl it is not difficult to envisage HCl as the desorbing species. However, desorption of HCl from catalysts used in the reaction of $C_2Cl_2F_4$, and not treated using HCl, indicates that, at least in part, HF admitted to the catalyst in the pre-treatment is adsorbed by the catalyst with retention of both hydrogen and fluorine.

Admission of HCl to a HF/$C_2Cl_3F_3$ gas flow decreased the production of $C_2Cl_2F_4$ (Section 3.8, Figures 3.15 - 3.17). The activity of the catalyst towards reaction of $C_2Cl_3F_3$ was greatly reduced, both during $C_2Cl_3F_3$/HF/HCl flow and following termination of the HCl flow. However, the formation of the chlorinated product, $C_2Cl_4F_2$, did not increase during the period of HCl flow. Pre-treatment of the catalyst using either HF followed by HCl, or HCl alone, did not deactivate the catalyst towards the fluorination and chlorination reactions of chlorofluoroethanes (Section 5.4). The composition of the catalyst determined following $C_2Cl_3F_3$/HF/HCl flow, did not differ significantly from the composition determined before use (Table 3.15). However, several weeks elapsed between removal of the catalyst and determination of the chemical composition. The effect of hydrolysis on the chlorine content of the catalyst has been referred to previously (Section 5.3), and a proportion of the chlorine-containing species may have desorbed before the analyses were carried out.

The effect of HCl flow can be accounted for in three ways:

(a) HCl is located on a site responsible for fluorination and prevents the fluorination reaction.

(b) HCl occupies the same site as the chlorofluoroethane molecule and prevents its adsorption.

(c) HCl flow changes the equilibria between the catalyst, HF, chlorofluoroethane and HCl.

There is no evidence to support the uptake of HCl by the catalyst preventing either the reactions of chlorofluoroethanes or the uptake of HF. Uptake of HF and HCl does occur at the same position on the catalyst since one chlorine-containing species is removed by HF flow (Section 5.5.2) and the uptake of HCl by the catalyst is much greater in the absence of HF pre-treatment (Section 5.4). However, there are no significant differences between the product distributions determined for the reaction of $C_2Cl_2F_4$ on pre-fluorinated chromia, when compared with pre-fluorinated chromia which had been treated using HCl. Also, the behaviour of the catalyst-chloride species formed from uptake of HCl is identical to that of the species formed from reaction of CCl_2FCF_3.

The reaction (Equation (7.9)):

$$C_2Cl_3F_3 + HF \longrightarrow C_2Cl_2F_4 + HCl$$

<u>Equation (7.9)</u>

involves desorption of HCl and will be shifted to the left by admission of HCl to the reactor feed. Hydrogen chloride admitted to the reactor in the $HF/C_2Cl_3F_3$ feed comprised <u>ca</u>. 14% of that expected to be formed from fluorinated of $C_2Cl_3F_3$ under the optimum conditions for the fluorination reactions. The HCl formed in the fluorination reaction and then desorbed from the catalyst is indistinguishable from HCl admitted with HF and $C_2Cl_3F_3$, and this suggests that the addition of HCl to the reactants shifts the process in equation (7.9) to the left, rather than altering the overall chemistry of the process. The site at which the chlorine-containing species are formed could be the same site as that at which $C_2Cl_3F_3$ is adsorbed. Retention of chloride at this site, perhaps by a mechanism blocking the formation of HCl, will prevent further adsorption and reaction of $C_2Cl_3F_3$. Circumstantial evidence for this postulate is provided by the observation that the catalyst deactivation was not permanent and that a substantial proportion of the initial activity towards fluorination of $C_2Cl_3F_3$ returned after the catalyst had been left under a dinitrogen atmosphere for 48h. This increase in catalytic activity after 48h. is consistent with a slow desorption of the species responsible for the deactivation.

7.3 The Nature of the Adsorbed Halogen-Containing Species.

The authors of a previous [^{18}F]-fluorine study[26], using [^{18}F]-fluorine labelled hydrogen fluoride to investigate the interaction between HF and chromia, established that three types of fluorine-containing species are formed at 623 K under conditions of HF flow. Only one of the fluorine-containing species is catalytically active towards fluorination of chlorofluoroethanes and this species comprises ca. 70% of the total pool of fluoride on fresh, prefluorinated chromia (Section 1.6.4). Weakly adsorbed and catalytically inactive fluorine-containing species are also present on the catalyst, each comprising ca. 15% of the total pool of fluoride on the catalyst.

Results obtained in the present study show that prolonged purging with dinitrogen at 623 K for 40-80 min removed a larger proportion of the pool of catalyst-fluoride than was removed under the same condition during 10 min (Section 4.4). The removal of catalyst-fluoride was not linear with time. Flowing dinitrogen for 10 min removed ca. 15% of the catalyst-fluoride, 40 min dinitrogen flow removed 32-48% and 80 min dinitrogen flow removed 42-66%. The increased difficulty of fluoride removal with decreasing catalyst-fluoride content is a characteristic of some oligomeric species of HF.[63]

The behaviour of the chlorine-containing species formed from HCl flow or reaction of CCl_2FCF_3 was similar and two catalyst-chloride species were detected in each case. Labile chlorine and fluorine-containing species were also similar in their behaviour. In each case, halide was incorporated in reacting chlorofluoroethanes and the product distribution and count rate data could be accounted for on the basis of halogen exchange reactions alone (Section 7.1). The inactive chlorine-containing species has been proposed to form through the gradual replacement of Cr^{III}-O bonds by Cr^{III}-F bonds.[26] The replacement process is predicted to be slow since Cr(III) compounds are inert to substitution. The inactive chlorine-containing species could be formed by a similar replacement process $Cr^{III}\text{-O} \longrightarrow Cr^{III}\text{-Cl}$.

Used, extensively fluorinated catalysts, which had been used to react chlorofluoroethanes, contained very little chlorine as received, being in the range 13-15 µmol Cl (g catalyst)$^{-1}$. Fresh chromias, pre-fluorinated and used to react $C_2Cl_2F_4$, had chlorine contents > 312 µmol (g catalyst)$^{-1}$ (Section 5.3, determined by N.A.A). Reaction of chlorofluoroethane removed [^{36}Cl]-chlorine from the catalyst, but the total pool of chlorine was not depleted. Chlorine determinations on two pellets, after reaction of $C_2Cl_2F_4$ on chromia previously treated using $H^{36}Cl$, were 312 and 343 µmol (g catalyst)$^{-1}$. There is, therefore, a turnover of chlorine between the catalyst and reacting chlorofluoroethane molecules.

The concentration of the inactive chlorine-containing species might be expected to increase with the age of the catalyst, as Cr^{III}-O bonds are replaced by Cr^{III}-Cl bonds. Determinations of chlorine content for used catalysts show that there is not a large concentration of chlorine on the catalyst, and in fact the concentration of chlorine on used catalysts is smaller than that determined for fresh catalyst used to react chlorofluoroethanes. This result is not unreasonable since the used catalyst was subjected to continuous HF/chlorofluoroethane flow, unlike the fresh catalyst, which was only subjected to pre-fluorination. The small chlorine content of used catalysts can be accounted for in two ways. First, under conditions of HF flow ca. 75% of the chlorine-containing species on the catalyst are removed. Second, the conversion of chromium trichloride to chromium trifluoride using HF is an established process.[75] Under conditions of HF/chlorofluoroethane flow the residence time of the catalytically active chlorine-containing species is shorter than is the case on pre-fluorinated chromia. The formation of the inactive chlorine-containing species from the catalytically active species will therefore be decreased in the HF/chlorofluoroethane system. The concentration of the inactive fluorine-containing species increases over the lifetime of the catalyst.

Direct evidence for the formation of catalyst-fluoride species involving fluorine from reacting chlorofluoroethane molecules is not available, although the existence of such species can be inferred by analogy with catalyst-chloride. A method for synthesising $[^{18}\mathrm{F}]$-fluorine labelled $\mathrm{C_2Cl_4F_2}$ and $\mathrm{C_2Cl_3F_3}$ from $[^{18}\mathrm{F}]$-$\mathrm{UF_6}$ and $\mathrm{C_2Cl_6}$ (Equation (7.10)) has now been developed[76] and in future

$$\mathrm{C_2Cl_6} + [^{18}\mathrm{F}]\text{-}\mathrm{UF_6} \xrightarrow[1\mathrm{h}]{543\ \mathrm{K}} [^{18}\mathrm{F}]\text{-}\mathrm{CCl_2FCCl_2F} + [^{18}\mathrm{F}]\text{-}\mathrm{CCl_3CClF_2} + [^{18}\mathrm{F}]\text{-}\mathrm{CCl_2FCClF_2} + [^{18}\mathrm{F}]\text{-}\mathrm{CCl_3CF_3} + \text{trace } [^{18}\mathrm{F}]\text{-}\mathrm{CClF_2CClF_2}$$

Equation (7.10)

work it should be possible to investigate the interaction between $[^{18}\mathrm{F}]$-fluorine labelled chlorofluoroethanes and chromia.

There is no evidence to support the existence of labile chlorine-containing and fluorine-containing species at two different positions on the chromia catalyst. An adsorbed form of hydrogen chloride provides chlorine for the chlorination reactions and an adsorbed form of hydrogen fluoride provides fluorine for the fluorination reactions. Hydrogen fluoride flow removes all the labile chlorine-containing species and in the absence of HF pre-treatment the quantity of HCl taken up by the catalyst is similar to the HF uptake (Table 5.14). It can be concluded, therefore, that adsorption of HF occurs at the same position on chromia as HCl or chlorine from reacting chlorofluoroethanes.

7.4 The Nature of the Active Halogenating Species.

Fresh chromia, as received, has a surface area of ca. 65 m^2g^{-1}. On the basis of a van der Waals radius for HF of $2.55x10^{-10}m$, the maximum uptake of monomeric HF is predicted to be 0.5 mmol (g catalyst)$^{-1}$, considerably lower than the range 1.0-1.4 mmol (g catalyst)$^{-1}$ determined in the present work (Chapter 4). The difference between the predicted HF uptake and the observed uptake can be accounted for if oligomeric HF species are formed on the fluorinated catalyst. No experimental data have been obtained in the present work to enable the active halogenating species to be identified. However, it is useful to consider which forms these species might adopt.

Hydrogen fluoride is known to exist in oligomeric forms in the gas phase (Section 1.6). Neutral oligomers of the form $(HF)_n$ and charged oligomers of the form $(HF)_nF^-$ have been the subject of widespread study in the literature. Both neutral and charged oligomeric species are strongly hydrogen bonded. A wide range of values for the strengths of the hydrogen bonds within $(HF)_n$ and $(HF)_nF^-$ have been obtained. However Redington[52], in a recent vapour phase analysis of $(HF)_n$ oligomers, determined the energy of the hydrogen bond in $(HF)_2$ to be 23±2 kJ mol^{-1}, which is intermediate in the range of published values. An ion cyclotron resonance determination of fluoride binding energies to Bronsted acids[77] yielded a value of 163±4 kJ mol^{-1} for the hydrogen-bond energy in $(HF)F^-$, also intermediate in the range of published values. The stronger hydrogen-bond in $(HF)F^-$ is a result of the greater electronegativity and small size of fluorine. Clark and co-workers[63], in an ab-initio study, determined values for the dissociation $(HF)_nF^- \longrightarrow (HF)_{n-1}F^- + HF$ (Table 7.2).

Table 7.2 Dissociation Energy for $(HF)_nF^- \rightarrow (HF)_{n-1}F^- + HF$

Species.	H-bond dissociation energy (kJ mol^{-1})	Mean H-bond energy (kJ mol^{-1})
HF_2^-	220	220
$H_2F_3^-$	133	177
$H_3F_4^-$	104	152
$H_4F_5^-$	71	132

In contrast, for $(HF)_n$ intermolecular interactions increase and intramolecular interactions decrease with increasing values of n.

The dimers $(HCl)_2$ and (HF)(HCl) are more weakly hydrogen bonded than $(HF)_2$. Powles and Wojcik[78], in an infra-red spectroscopic study, determined the hydrogen-bond energy in $(HCl)_2$ to be 9.0±0.8 kJ mol^{-1}. An ab-initio study by Kollman[79] obtained a value of 19 kJ mol^{-1} for the hydrogen-bond energy in (HCl)(HF). A review of several experimental studies by Caldwell and Kebarle[80] quoted values for $D(Cl^--HCl)$ of 98.3 kJ mol^{-1} and for $D(Cl^--HF)$ of 91.2 kJ mol^{-1}. Caldwell and Kebarle calculated $D(F^--HCl)$ to be 250 kJ mol^{-1}.

The greater stability in species of the type $(HF)_nF^-$ and the related chlorine containing species compared with

$(HF)_n$ favours the charged species as the sources of catalytically active halide on chromia. The ability of HF to displace the labile chlorine-containing species from the catalyst is consistent with the incorporation of chlorine and fluorine within the same surface species. However, this postulate assumes that the behaviour of the species $(HF)_n$ and $(HF)_nF^-$ on the catalyst is similar to their vapour phase behaviour. The literature contains no information to indicate whether or not this is likely to be the case.

If the species $(HF)_nF^-$ is formed on chromia it must involve dissociative adsorption of HF. Other species adsorb dissociatively on α-chromia, notably dichlorine[81], dioxygen[82] and water.[41] In addition to the dissociative adsorption of water, coordinative chemisorption and physical adsorption are also important. Dioxygen adsorbs in both a molecular and a dissociatively bound state[82], while adsorption of dichlorine is thought to form a monolayer of chlorine atoms which can then react, at temperatures greater than 500 K, to convert Cr^{III}-O bonds to Cr^{III}-Cl bonds.[81]

On α-chromia the adsorptions of dichlorine, dioxygen, water and carbon monoxide are thought to occur at coordinatively unsaturated chromium sites.[81,82,41,83] The structure of α-chromia[84] is that of corundum and cations occupy two-thirds of the octahedral holes in the hexagonal close packed oxygen structure (Figure 7.1). Zecchina and co-workers[85] have proposed that five active sites could be formed on α-chromia by dehydration of the surface. Figure 7.2 represents the dissociative

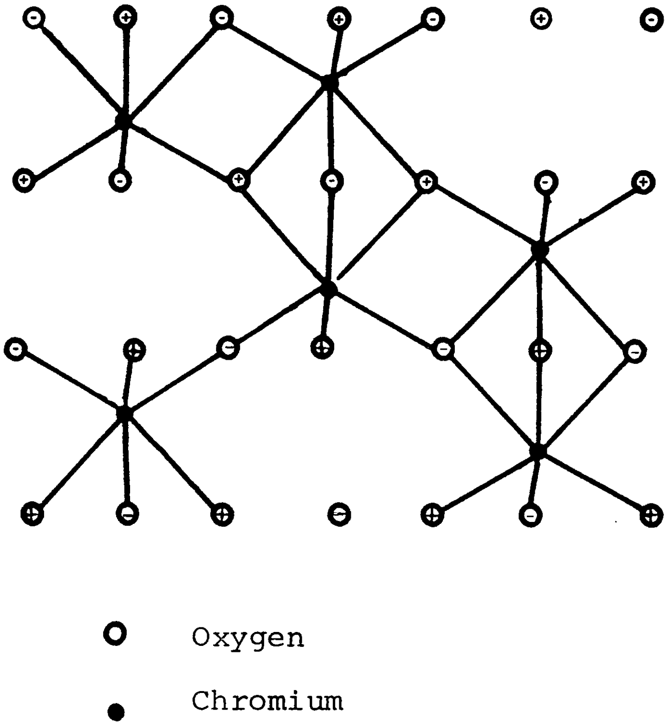


FIGURE 7.1 PROJECTION OF α-Cr_2O_3 ON $(2\bar{1}0)$.
The metal atoms lie in the plane of the page.
(FROM : R.E NEWNHAM and Y.M. De HAAN [84])

adsorption of water at a coordinatively unsaturated chromium ion.

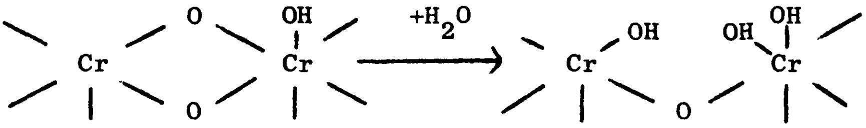


Figure 7.2 Dissociative adsorption of H_2O on α-chromia.

It is clear that a discussion of the generation and properties of coordinative unsaturation on α-chromia will differ in fine detail from the situation on the amorphous chromia used in the present work. However, similar considerations must be involved and it is reasonable to suggest that HF is dissociatively adsorbed on chromia and that surface unsaturation is involved in the adsorption of HF and/or chlorofluoroethane.

The model describing the interactions of HF and HCl with chromia which best fits the experimental observations involves adsorbed species of the general type $(HF)_nF^-$, $(HCl)(HF)_nF^-$ and $(HF)_nCl^-$. These species could be formed by the dissociative adsorption of HF at a Cr-O bond followed by hydrogen bonding of further HF monomers to the Cr-F species. Equilibria of the type shown in Scheme 7.4 can be proposed.

$$(HF)_nF\text{-}Cr \rightleftharpoons (HF)_{n-1}F\text{-}Cr + HF$$

$$(HCl)(HF)_nF\text{-}Cr \rightleftharpoons (HF)_nF\text{-}Cr + HCl$$

$$(HCl)(HF)_nF\text{-}Cr \rightleftharpoons (HCl)(HF)_{n-1}F\text{-}Cr + HF$$

Scheme 7.4 Equilibria for $(HX)_nX^-$ species adsorbed on chromia.

Labile and weakly adsorbed halogen-containing species can be related by the equilibrium shown in equation (7.11). The formation of chromium(III) halide species can be envisaged as a reaction between the labile species and a Cr^{III}-O bond.

$$HX(g) \rightleftharpoons (HX)_nHY_mY\text{-}Cr \longrightarrow Cr^{III}\text{-}Y$$

where X and Y may be either fluorine or chlorine

$(m+n) < 4$

Equation (7.11)

The exact nature of the site with which HF interacts is not clear. An e.p.r. study[44] of unfluorinated chromia concluded that Cr^{III} and oxidation states greater than Cr^{III} are present in amorphous chromia, while temperature-programmed reduction[26] of chromia samples, identical to those used in the present study, showed that Cr^{III}, Cr^{IV} and Cr^{VI} species are present in the catalyst. These latter studies also showed that extensively fluorinated catalyst does not contain Cr^{IV}. Loss of Cr^{IV} may occur very early in the catalyst's life. The species CrF_4 is volatile and this may account for the absence of Cr^{IV} in used, extensively fluorinated catalysts. Chromium tetrafluoride is also unstable with respect to hydrolysis and the disproportionation reaction[86] (Equation (7.12)) can be proposed as an alternative mechanism by which Cr^{IV} is removed from the catalyst.

$$3\ Cr^{4+} \xrightarrow{\text{hydrolysis}} CrO_4^{2-} + 2\ Cr^{3+}$$

Equation (7.12)

Hydrogen fluoride is likely to interact with all the oxidation states of chromium present in the catalyst. Identification of the oxidation states with which HF and HCl interact to form the labile halogenating species is not possible on the basis of the data presented in this thesis. Speculation must involve consideration of Cr^{III} and Cr^{VI} since these are the two oxidation states present in used chromia, which is still active for fluorination and chlorination reactions. Kijowski and co-workers[26] reported little interaction between chromium trifluoride, the final product from replacement of all Cr^{III}-O bonds by Cr^{III}-F bonds. Used, extensively fluorinated catalysts contain up to 30% w/w fluorine and are likely to correspond quite closely to CrF_3. Uptake of [^{36}Cl]-chlorine from $H^{36}Cl$ or [^{36}Cl]-CCl_2FCF_3 was much smaller on used catalysts compared with fresh catalysts (Section 5.4), as was uptake of [^{18}F]-fluorine from $H^{18}F$.[26] The strong inference is that Cr(III) is associated with the formation of the inactive halogen-containing species. By analogy with CrF_3, an interaction between HF and Cr^{III}-F is likely to be small and the active fluorinating species may not be able to form. An interaction between Cr^{VI} and HF is more attractive but further data are required to investigate this possibility.

7.5 General Conclusions

The principal object of the present work was to establish whether the two halogen exchange processes, fluorination and chlorination, are concerted or are related by the active species for chlorination originating from a previous fluorination step.

Two catalyst-chloride species, analogous to the catalytically active and inactive fluoride species determined by Kijowski and co-workers,[26] are formed on chromia during the reaction of chlorofluoroethanes. Within the pool of catalytically active chloride there is a substantial turnover of chlorine; desorption of hydrogen chloride, uptake of chlorine from reacting chlorofluoroethanes and incorporation of chlorine from the catalyst in the reacting molecules are all involved. Taken together with the results of a previous [^{18}F]-fluorine study,[25] the results from the present work have established, for the first time, that a F-for-Cl, Cl-for-F halogen exchange mechanism is involved in the reactions of chlorofluoroethanes on chromia.

There is no evidence for the existence of dismutation reactions in the vapour phase process. Dismutation is unattractive because of the restrictions imposed on the reaction transition states and any dismutation reaction can be formulated as a series of two halogen exchange reactions. Likewise, it is not necessary to propose isomerisation reactions to account for the observed product distributions.

The species hydrogen fluoride, hydrogen chloride and 1,1,2-trichlorotrifluoroethane can be adsorbed on to chromia, the strength of the interaction with chromia decreasing in the order:-

$$HF > HCl > CCl_2FCClF_2$$

Removal of the active chlorine-containing species under conditions of HF flow seems likely to be important in preventing the chlorination reactions.

The results of the $H^{18}F$, $H^{36}Cl$ and $[^{36}Cl]$-CCl_2FCF_3 uptake experiments are consistent with the existence of one catalytically active site for halogenation. Species of the general type $(HX)_nY^-$, where X and Y can be either F or Cl, are attractive by analogy with the established behaviour of other adsorbed species, in particular water[41] on chromia. It is not possible, on the basis of the experimental work undertaken in this project, to identify the site at which the halogenating species are formed. However, since Cr^{III} compounds are known to be inert to substitution an interaction with Cr^{VI} seems more likely.

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