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Kinetic and Mechanistic Study of the Reaction of CCl_4 with Prefluorided Chromia to Form CCl_3F and CCl_2F_2

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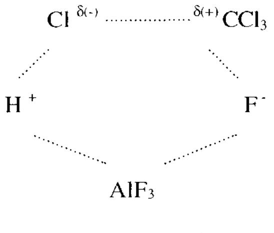
The reaction of CCl_4 with prefluorided chromia (prefluorided to multilayer depth) has been studied using the transient techniques of temperature programmed reaction (TPR), temperature programmed desorption (TPD) and gas adsorption chromatography (GAC). The reaction has been shown to proceed by a Langmuir–Hinshelwood mechanism in which the chemisorbed CCl_4 molecule exchanges its chlorine atoms with the fluoride ions on the surface of fluorided chromia. Mono and di-exchange, forming CCl_3F and CCl_2F_2, has been shown to occur simultaneously with an activation energies of $\sim$63 kJ mol^{-1} for both. The facile reaction of the chemisorbed CCl_4 with the surface F^- ion to form CCl_3F is rationalised in a four centre exchange mechanism in which the CCl_4 is bonded to the fluorided chromia surface through a chlorine atom of the CCl_4 molecule bonding to a surface Cr^{3+} ion. The C atom of CCl_4 molecule bonds to a surface F^- species. Di-exchange which occurs simultaneously with mono exchange, the two reactions having the same activation energy, is accounted for by the CCl_4 being bonded through two Cl atoms to two surface Cr^{3+} ions, with the carbon being loosely associated with two surface F^- ions. This configuration which has been shown to be geometrically possible on the (001) surface of CrF_3 allows for simultaneous double exchange of the halogens.

INTRODUCTION

The need to replace the environmentally damaging chlorofluorocarbons (CFCs) has resulted in interest in the new replacement ozone friendly hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). These are manufactured by catalytic hydrofluorination. The industrial preparation of CFCs, HCFC, and HFCs is carried out mainly by gas–solid heterogeneous catalysis, using a metal oxide catalyst, e.g., Cr_2O_3, Fe_2O_3, Al_2O_3, Sb_2O_3, and gas phase HF. At present, however, little definite is known about the mechanism or the energetics of this process. Since the mechanism of the formation of industrially relevant hydrofluoroalkanes (e.g., $C_2H_2F_4$) is complex, the reaction of simple HCFCs (e.g., CCl_4 and CHF_2Cl) with HF over various metal oxides or fluorides (e.g., Cr_2O_3, CrF_3, $CrCl_3$) has been studied as a means of elucidating the generic mechanism of the hydrofluorination process (1–4).

Kemnitz *et al.* (1) reported on the reaction between gas phase CCl_4 and HF over CrF_3. They have attempted to distinguish between a Langmuir–Hinshelwood mechanism and a Rideal–Eley mechanism for this reaction. Unambiguous discriminative evidence has not been found and they have suggested that a modified Langmuir–Hinshelwood mechanism occurs, deriving from the reactants, HF and halomethane, exhibiting quite different chemical behaviour. They have not observed competitive adsorption in their experiments and suggested that the reactants enter at different places on the catalyst surface.

Gambaretto *et al.* (2) have investigated the gas–solid hydrofluorination of CCl_4 by HF using an anhydrous aluminium fluoride catalyst with the aim of determining the mechanism of the reaction. They discussed two possible schemes, through which the fluorination process might be thought to take place: (i) through the formation of intermediate complexes between the catalyst and the organic substrate, or (ii) an intermediate complex formed between the catalyst and HF. When the reaction is carried out in the liquid phase, the former mechanism is believed to operate; when the process takes place in the gas phase, the authors then believe that a rather ill-defined intermediate of the type shown in below (Scheme 1) occurs, initially by reaction of the AlF_3 catalyst with the HF. Rowley and co-workers using radiolabelled hydrogenfluoride ($H^{18}F$) to monitor the reaction have suggested that the fluorination reaction occurs through the chloroalkane being fluorinated by oligomeric hydrogen fluoride $(HF)_nHF$, both of which



SCHEME 1. The intermediate complex formed between HF/AlF_3 and CCl_4 suggested by Gambaretto *et al.* (2) for the gas phase reaction of CCl_4 with HF over AlF_3.

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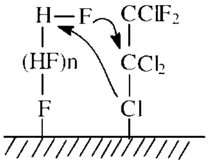
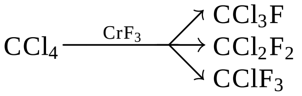


SCHEME 2. The mechanism for surface catalysed fluorination reaction proposed by Rowley and co-workers (3).

are adsorbed on the fluorided metal oxide surface. The intermediate proposed (Scheme 2) is shown above.

Coulson and co-workers (4), in a mechanistic study of dismutation of chlorodifluoromethane catalysed by chromium oxide have suggested that catalysts for the dismutation of CFCs and for the formation of HCFCs are usually the same ones found to be active in isomerization and halogenation of these compounds. They also suggested that the active sites for all of these processes are the same or very similar. They have proposed that a coordinatively unsaturated Cr^{3+} centre is a necessary component of the active site of the dismutation reaction of CHF_2Cl over chromium oxide. The reactive centres they believe must contain Cr–X (X = F or Cl) bonds, which results in an enhancement of their Lewis acidity. While rejecting a Rideal–Eley mechanism involving the reaction of gas phase CHF_2Cl with adsorbed CHF_2Cl, their data do not allow them to conclude that the mechanism involves a monomolecular halogen exchange reaction of the HCFC with the metal halide site. Okazaki (5), on the other hand, has studied the dismutation of CCl_3F over $FeCl_3$ on charcoal and has concluded that the kinetics obeyed a Rideal–Eley mechanism, where the rate-determining step involved the reaction of complexed CFC with free CCl_3F.

The purpose of this paper is to investigate the kinetics and mechanism of the hydrofluorination of chloroalkanes using CCl_4 as a model reactant. In order to simplify the evaluation of the kinetics of the process the reaction of CCl_4 will be carried out on a prefluorided Cr_2O_3 in the absence of gas phase HF using the transient techniques of temperature programmed desorption and reaction. Even though it is the simplest example of a fluorination reaction, the mechanism of the reaction [1] has not been precisely described.



$$CCl_4 \xrightarrow{CrF_3} \begin{cases} CCl_3F \\ CCl_2F_2 \\ CClF_3 \end{cases} \qquad [1]$$

EXPERIMENTAL

Preparation of the Catalyst

Chromium (III) oxide was prepared by dehydration of chromium hydroxide that was obtained by a slow and continuous addition ($10\ cm^3\ min^{-1}$) of ammonia solution (5 *M*) to chromium nitrate (0.5 *M*) (6). The resulting solution (hydroxide form) was constantly stirred and heated at 353 K for at least 1 h. The hydroxide gel thus obtained was filtered and washed thoroughly with hot distilled water three times, then the filtered gel was air-dried at 363 K for 16 h (7). The final step of thermal treatment was followed by heating the olive green catalyst from room temperature to 623 K ($3\ K\ min^{-1}$) under a flow of He ($30\ cm^3\ min^{-1}$, 1 bar) and was left at 623 K for 8 h. The chromium (III) oxide formed was cooled to room temperature under He.

Characterisation of the Catalyst

The chromium (III) oxide prepared by the above procedure was crushed and sieved into particle size of 300 to 350 μm. The total surface area of the catalyst was determined to be $200\ m^2\ g^{-1}$ by appling the BET method, using N_2 adsorption at 77 K. X-ray diffraction (XRD) of the powder showed that the material contained only amorphous chromium oxide.

Pretreatment of Catalyst for Reaction

The chromium (III) oxide ($\approx$0.2 g) prepared as above was loaded into a U-shaped (30-cm long, 0.6-cm ID) Monel microreactor tube; it was heated under helium ($25\ cm^3\ min^{-1}$, 1 bar) to 623 K and was left at this temperature for 30 min to remove any adsorbed water. The catalyst was then fluorinated *in situ* by 10% HF in He ($25\ cm^3\ min^{-1}$, 1 bar) for approximately 1 h at 623 K. The total amount of HF passed was always $200\ cm^3$, or 8.2×10^{-3} mol or 2.5×10^{22} fluorine per gram of catalyst. The surface area of the fluoride chromia was measured *in situ* to be $103\ m^2\ g^{-1}$ so that, assuming unit reaction probability of the HF with the oxide, this corresponds to a coverage of the oxide with fluoride ions of 1.9×10^{17} ions cm^{-2} which, if the assumption is correct, means that the surface and several layers of the bulk of the Cr_2O_3 have been fluorinated. The fluorided Cr_2O_3 was cooled from 623 K to ambient under a He flow ($25\ cm^3\ min^{-1}$, 1 bar, $\sim$30 min) to desorb all HF. The catalyst was then sealed and transported to the mass spectrometer.

APPARATUS

A line diagram of apparatus is shown in Fig. 1. This system consisted of a gas-handling panel and a micro-reactor which was connected to an on-line computer interrogated mass spectrometer. It is used for temperature-programmed reaction (TPR), temperature-programmed desorption (TPD), and *in-situ* surface area measurements.

The gas-handling system allows any mixture of up to four separate gases to be passed over the catalyst at a pressure of 101 kPa. However, the pressure inside the chamber was not allowed to exceed 1×10^{-4} Torr to protect the mass spectrometer filament and, therefore, only a small fraction of the gas stream was admitted. The by-pass system on the

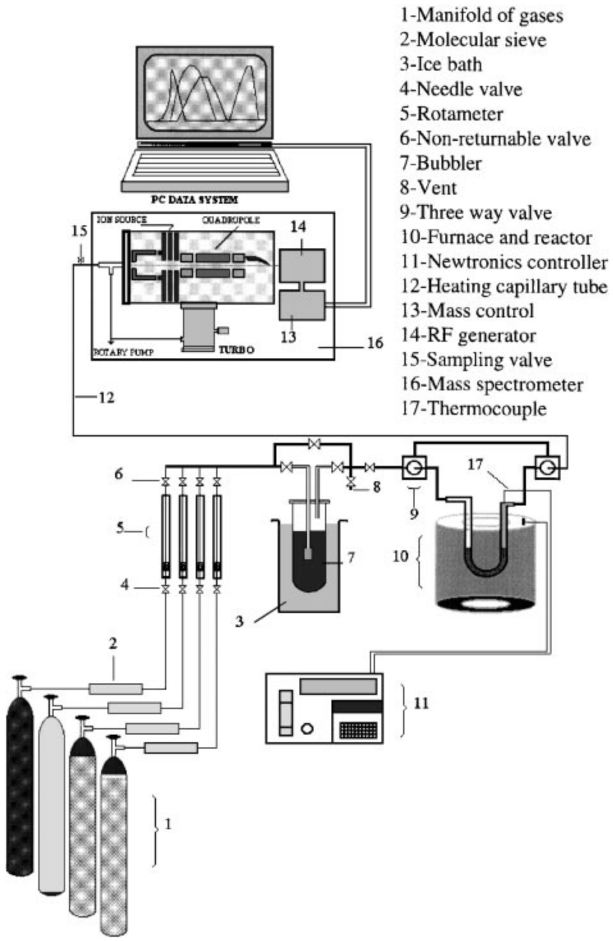


FIG. 1. Line diagram of multipurpose micro-reactor.

micro-reactor allowed HF gas to be used for catalyst pretreatment. It also allowed the transfer of the HF activated Cr_2O_3 to the quadrupole mass spectrometer (Hiden Analytical, Warrington, England) without exposure to air by removing the gaseous HF by flushing the system in He for 30 min before sealing it. The reactor itself was constructed of Monel for its resistance to corrosion by HF at high temperatures. The reactor was positioned in an electrically heated furnace. A thermocouple was embedded in the catalyst to allow accurate temperature reading to be obtained. The temperature of the reactor was controlled from 77 to 1073 K by a Newtronics temperature programming controller.

A CCl_4 mixture (4% CCl_4, 1 bar) was produced by bubbling He (25 ml min^{-1}, 1 bar) through liquid CCl_4 held at 273 K.

Experimental Techniques

Temperature-programmed techniques are a series of catalyst characterisation methods which involve thermal transient analysis. During temperature-programmed experiments, the sample was exposed to different gaseous environments and the sample temperature was increased linearly with time. The response of the system to the thermal transient was monitored by measuring the consumed gas concentration or product gas concentration. Temperature-programmed reaction (TPR) was used to measure the rates and energetics of individual reactions when several proceed in parallel. Temperature-programmed desorption was used to determine surface coverages and desorption activation energies.

The total surface area, adsorption isotherm, desorption kinetics, surface reaction mechanisms, are examples of *in-situ* measurements which can be made on the micro-reactor system.

RESULTS

Isothermal Adsorption of CCl_4 over HF Pretreated Cr_2O_3

The adsorption isotherm of CCl_4 on prefluorided Cr_2O_3 at 293 K and its isothermal heat of adsorption were obtained by gas adsorption chromatography (GAC) (8).

A line shape of the detector response (mass spectrometer detector) during a gas adsorption chromatographic experiment is shown in Fig. 2. A flow of helium (25 cm^3 min^{-1}, 1 bar) is passed over the catalyst at 293 K; after 2 min it is switched (at the point t_0) to a He/CCl_4 flow (4% CCl_4 in He, 1 bar). The time from t_0 to t_1 is the time to sweep out the dead volume of the system and at point t, the CCl_4 is seen to break through on the mass spectrometer. The integral $(t - t_1) \times$ height is the frontal uptake, shown by the hatched area in Fig. 2 is the amount of CCl_4 adsorbed at 293 K on the catalyst. At the point of t_3 the He/CCl_4 flow is switched back to the helium flow. The time difference $t_4 - t_3$ is the time to sweep out the dead volume of the system.

Each point along the falling trailing edge of the eluted curve is proportional to the differential of the adsorption isotherm, i.e. to the differential of the number of moles adsorbed with respect to the gas phase concentration (9). One can therefore do a stripwise integration, i.e. horizontal integration, of the eluted line shape, the area of the strip being proportional to the number of moles CCl_4 adsorbed while the height of each strip is proportional to the gas phase concentration of CCl_4 to produce the isotherm shown in Fig. 3.

The shape of the curve is characteristic of a Langmuir adsorption isotherm for which the dynamic equilibrium is

$$CCl_4 + CrF_3\ (\text{surface}) \Leftrightarrow CCl_4\text{–}CrF_3\ (\text{surface}). \qquad [1]$$

The fractional coverage (θ) of the Cr_3F by adsorbed CCl_4 is given by

$$\theta = \frac{Kp}{1 + Kp} \quad \text{or} \quad \theta = \frac{K[CCl_4]}{1 + K[CCl_4]}, \qquad [2]$$

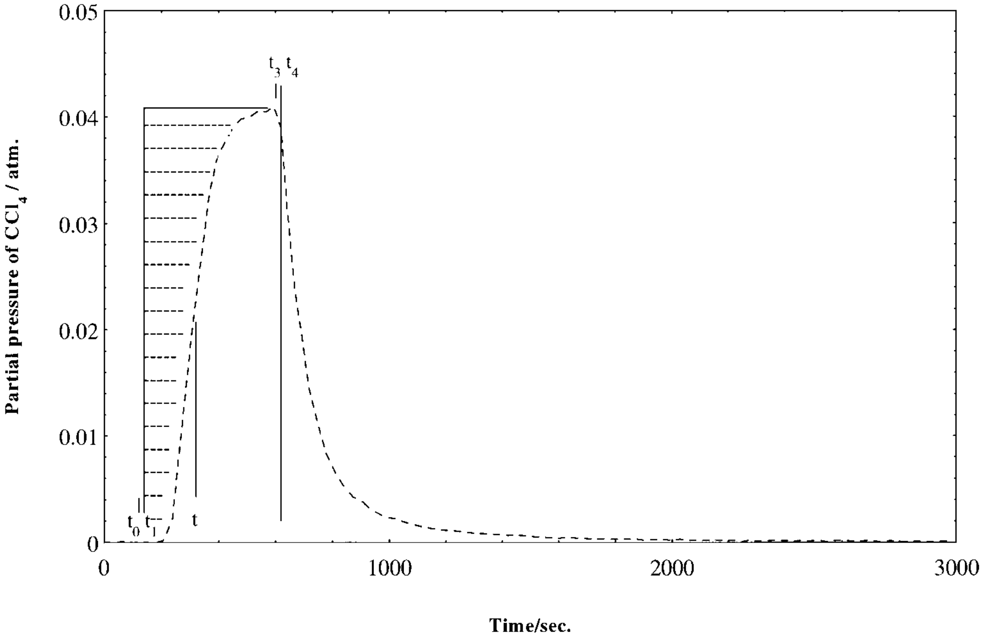


FIG. 2. The gas adsorption chromatography frontal uptake and desorption trailing edge for the interaction of CCl_4 at 293 K with an HF pretreated Cr_2O_3.

where $K = k_a/k_d$, p is the partial pressure/atm and $[CCl_4]$ is concentration of CCl_4/mol.

If $\theta = V/V_m$, where V_m is volume corresponding to monolayer coverage, Eq. [2] can be rewritten as

$$[CCl_4]/V = [CCl_4]/V_m + 1/(KV_m). \qquad [3]$$

The plot of $[CCl_4]/V$ against $[CCl_4]$ taken from Fig. 3 gives a straight line of slope $1/V_m$ and intercept $1/KV_m$ (10). It is shown in Fig. 4. The least-square best line has an intercept at $[CCl_4] = 0$, 5.2277×10^{-8} and a slope of 0.45307. The slope (0.45307) is $1/V_m$ and so V_m is 2.207 cm^3. This corresponds to a coverage of 4.2264×10^{14} molecule cm^{-2} or an area of

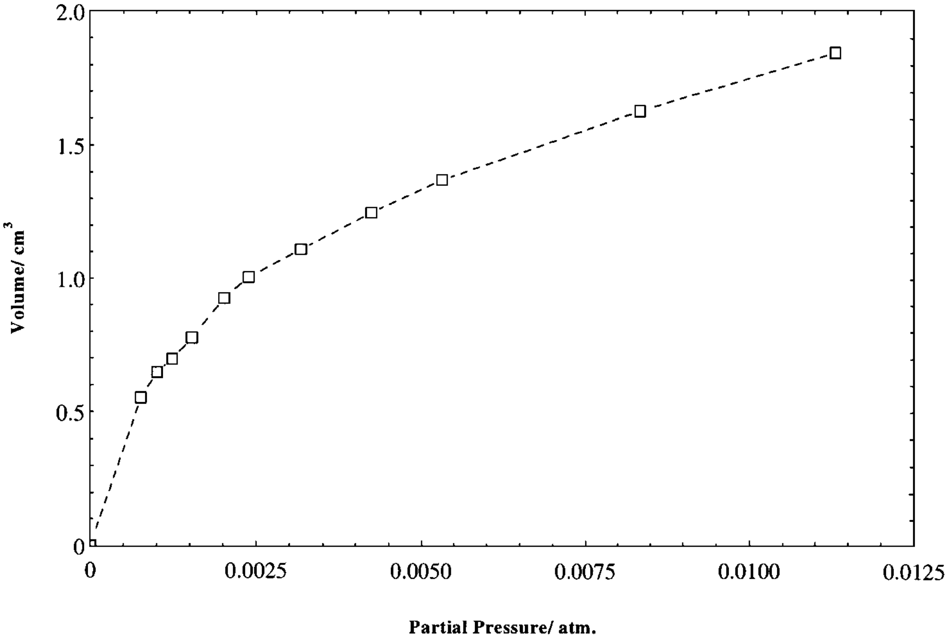


FIG. 3. The adsorption isotherm of CCl_4 over HF pretreated Cr_2O_3 at 293 K by stripwise integration of the trailing edge of the gas adsorption chromatographic line shape of Fig. 4.

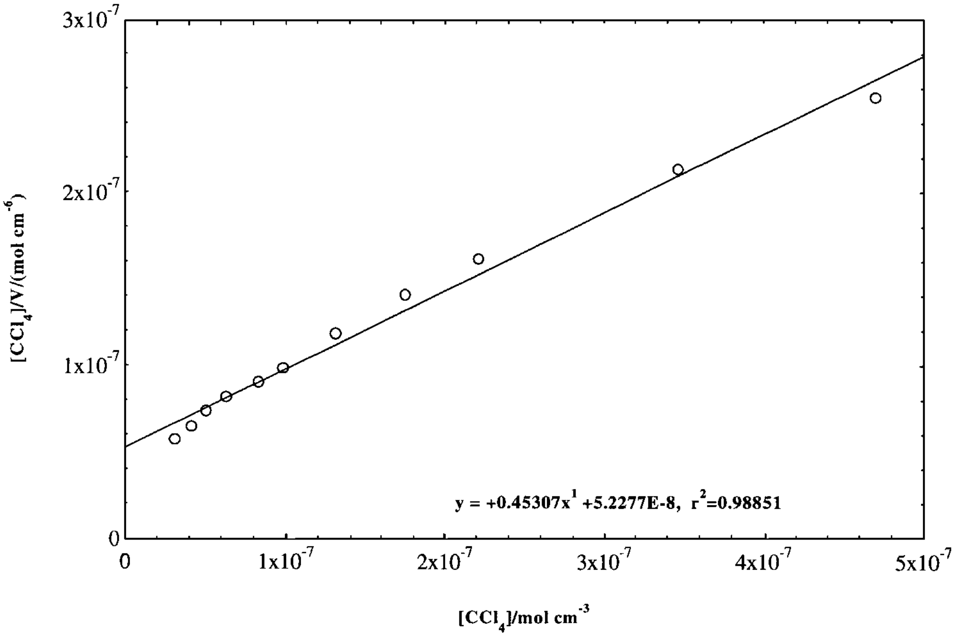


FIG. 4. The plot of $[CCl_4]/V$ against $[CCl_4]$ for the adsorption of CCl_4 over HF pretreated Cr_2O_3 at 293 K.

23 Å^2 per CCl_4 molecule. This value corresponds roughly to the close-packed hard sphere area of a physisorbed CCl_4.

The normally assumed value of the desorption preexponential (A_d) is 10^{13} s^{-1} and, since the adsorption of CCl_4 is probably nonactivated, the adsorption A-factor will equal the standard collision number. If the units of the A-factor are in cm^3 mol^{-1} s^{-1} the standard collision number has a value of 10^{13} cm^3 mol^{-1} s^{-1}. Therefore $A_a \approx A_d$ and

$$K = \exp(\Delta H/RT) \qquad [4]$$

so that $\Delta H = RT \ln K = 8.314 \times 293 \times 15.975 = 39$ kJ mol^{-1}.

This value for the enthalpy of adsorption of CCl_4 over the catalyst is slightly higher than that of the physisorption but the s-shape of the uptake suggests that upon adsorption diffusional pore filling has occurred and, therefore, the value of the enthalpy derived using a sharp cutoff at t_0 should be regarded with caution.

The amount of CCl_4 adsorbed in equilibrium with 4% CCl_4 in the gas phase can be determined by measurement of the frontal uptake (Fig. 2). Its value is 1.045×10^{-4} mol (on 0.127 g) corresponding to a coverage of 4.8×10^{14} molecule cm^{-2}, a value which is in good agreement with that obtained above by the linearisation of the Langmuir isotherm.

When the flow is switched from the CCl_4/He stream to He, CCl_4 is desorbed from the catalyst, the amount being 8.69×10^{-5} mol on the 0.127 g of fluorided catalyst used (Fig. 2). This leaves 1.76×10^{-5} mol CCl_4 "irreversibly" adsorbed at room temperature. The coverage of this chemisorbed material is 8.2×10^{13} molecule cm^{-2}. This constitutes an initial estimate of the numbers of active centres.

Temperature Programmed Desorption of CCl_4 over HF Pretreated Cr_2O_3

The chemisorbed CCl_4 obtained from the GAC experiment described above was desorbed from the fluorided Cr_2O_3 by temperature programming (5 K min^{-1}) in a He stream (25 cm^3 min^{-1}), having first flushed the system in that He stream for 1 h at 293 K to remove any remaining weakly held CCl_4. The temperature programmed desorption spectrum is shown in Fig. 5.

Inspection of Fig. 5 allows several points to be made regarding the mechanism of reaction. First, the reactant molecule (CCl_4) is chemisorbed. The desorption activation energy can be obtained by solution of the Redhead equation (Eq. [5]) at the peak maximum temperature (11),

$$\frac{E_d}{RT_m^2} - \frac{A}{\beta} e^{E_d/RT_m} = 0, \qquad [5]$$

where E_d is the desorption activation energy, β is the heating rate, and T_m is the peak maximum temperature. Equation [5] can be solved for a heating rate of 5 K/min and an assumed value of the preexponential term of 10^{13} s^{-1}. The activation energy at the peak maximum temperature (343 K) so obtained is 95.3 kJ mol^{-1}. This is a strong chemisorptive bond and so the reaction occurs by a Langmuir–Hinshelwood mechanism, there being no gas phase nor weakly held species in the system. The desorption half life

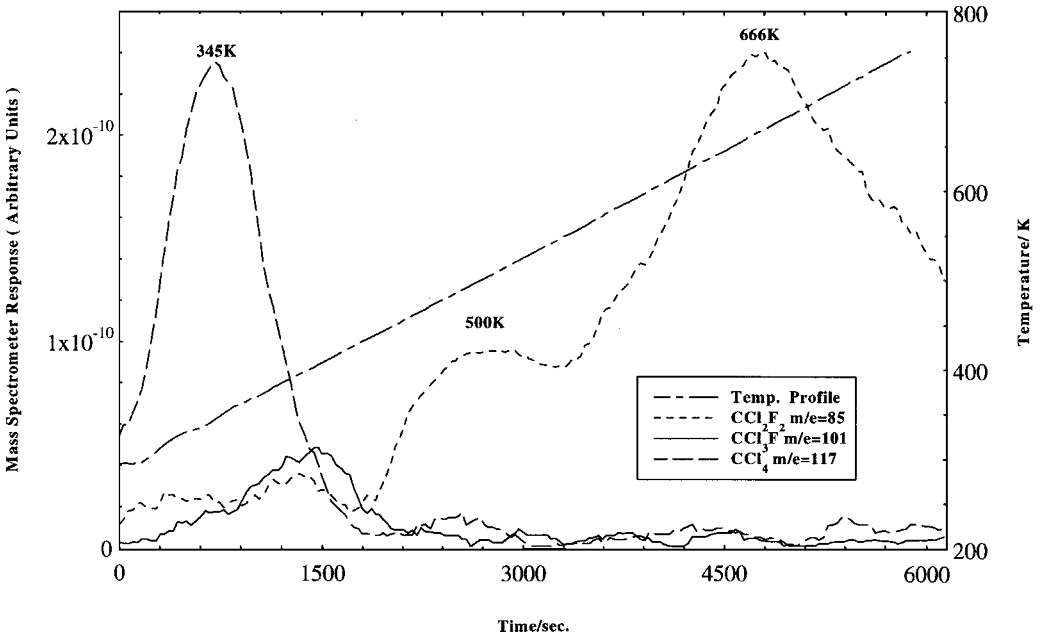


FIG. 5. The temperature programmed desorption spectrum of CCl_4 adsorbed on HF pretreated Cr_2O_3.

of the chemisorbed CCl_4 is given by

$$t_{1/2} = \frac{\ln 2}{A} e^{E_d/RT_m}, \qquad [6]$$

where E_d, T_m, and A have the same meaning in Eq. [5]. Its value is 2 h, which is considerably larger than the elution time so that the chemisorbed amount is a good estimate of the number of active centres.

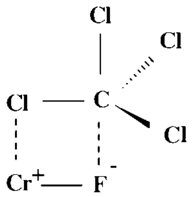
As stated above, the total amount of chemisorbed CCl_4 is 8.2×10^{13} molecule cm^{-2} $\approx$8% of monolayer. The sum of the CCl_4 ($m/z = 117$, the CCl_3^+ ion), CCl_3F ($m/z = 101$, the CCl_2F^+ ion), and CCl_2F_2 ($m/z = 85$, the $CClF_2^+$ ion) desorbed is 8.9×10^{13} molecule cm^{-2}, indicating a near exact carbon balance. These ions are the major peaks in the mass spectra of CCl_4, CCl_3F, and CCl_2F_2. The CCl_3^+ peak of CCl_3F makes a negligible contribution to the 117 peak used for CCl_4, while the CCl_2F^+ peak of CCl_2F_2 also makes a negligible contribution to the peak used for CCl_3F. Since the reaction is occurring between chemisorbed CCl_4 and surface CrF species, this correspondence between the small amount of CCl_4 chemisorbed at the outset (~8% of a monolayer) and the sum of the amounts of CCl_4 desorbed and reacted suggests that the active centre is of a highly specific geometric nature which may be similar to that proposed by Coulson and co-workers (4).

Second, all of the adsorbed CCl_4 and CCl_3F is desorbed by ~400 K. This occurs before formation of CCl_2F_2 and so the CCl_2F_2 must be formed between 293 and 400 K. The activation energy to its formation must, therefore, be low. Additionally, since the CCl_2F_2 appears in the gas phase at 500 and 666 K, its appearance must be limited by its rate of desorption. The peaks at 500 and 666 K must therefore derive from the CCl_2F_2 being held with desorption energies of 138 and 184 kJ mol^{-1}.

It is impossible to state here whether the reaction is sequential, i.e.

$$\begin{array}{ccccc} CCl_{4(a)} & \rightarrow & CCl_3F_{(a)} & \rightarrow & CCl_2F_{2(a)} \\ & & CCl_3F_{(g)} & & CCl_2F_{2(g)} \end{array} \qquad [7]$$

or whether the CCl_4 forms CCl_3F and CCl_2F_2 simultaneously on different sites. Since there is no gas phase or chemisorbed HF, the Cl/F exchange reaction must occur between the chemisorbed CCl_4 and surface fluoride ion of the fluorided chromia. The lowest energy pathway for such an exchange is through a four-centre intermediate in which the energy required to break the C–Cl and Cr–F bonds is compensated for by the formation of the C–F and Cr–Cl bonds. Such a four-centre intermediate, labelled Intermediate 1, is shown below. This could account for the highly specific nature of the active centre. It is a more detailed description of that proposed by Coulson and co-workers (4).



INTERMEDIATE 1. The four-centre intermediate for chloro fluoro exchange reaction.

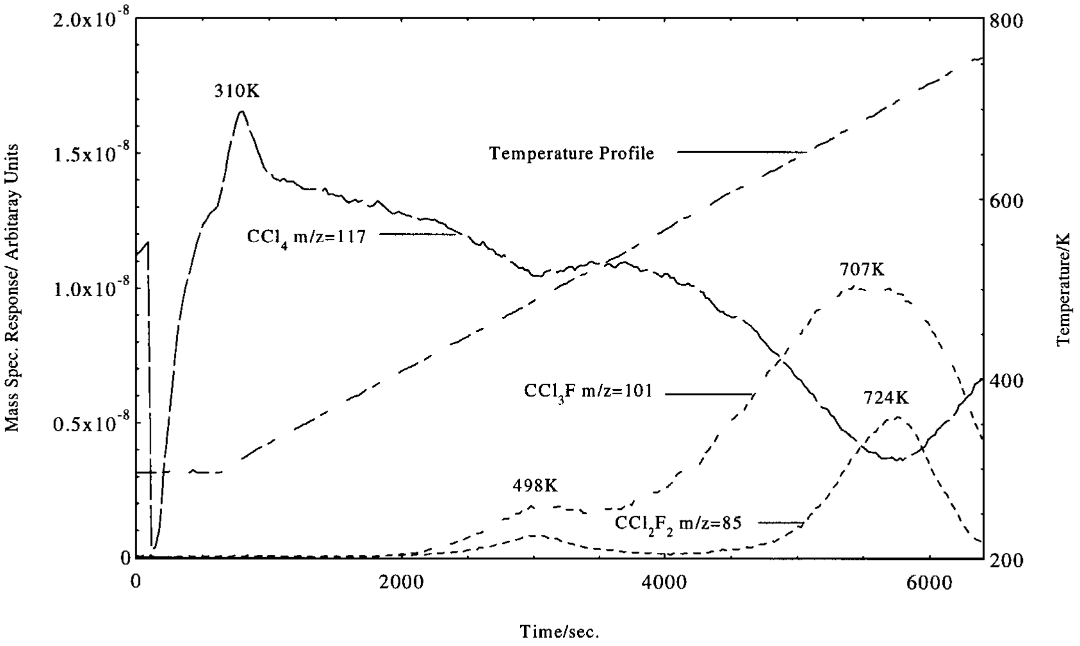


FIG. 6. Temperature programmed reaction of CCl_4 over HF pretreated Cr_2O_3.

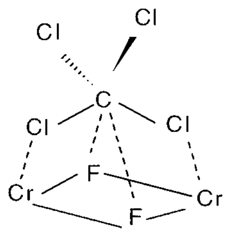
Temperature-Programmed Reaction of CCl_4 over HF Pretreated Cr_2O_3

Figure 6 is the temperature programmed reaction mass spectrum obtained by flowing CCl_4 in He (4% CCl_4, 25 cm^3 min^{-1}, 1 bar) continuously over the HF pretreated Cr_2O_3, increasing the temperature linearly at 5 K min^{-1}. The CCl_4 was flowed through the by-pass for 2 min to establish the flow after which the CCl_4/He flow was switched over the catalyst. The carbon tetrachloride (m/z = 117) was first flowed over the catalyst for 10 min at 293 K to ensure adsorption equilibrium, after which the temperature of the sample was increased linearly from 293 to 773 K at a rate of 5 K/min.

Several points can be made by inspection of Fig. 6. The initial decrease in CCl_4 concentration derives from the uptake of CCl_4 onto the prefluorided Cr_2O_3. Its amount is 1.48×10^{-4} mol (on 0.127 g catalyst) or a coverage of 6.81×10^{14} molecule cm^{-2}. Of this amount 1.07×10^{-4} mole of CCl_4 desorbs before 400 K (the temperature of the onset of reaction) in a peak whose maximum occurs at 310 K. At 400 K, therefore, the temperature of the onset of reaction, 4.08×10^{-5} mol of CCl_4 (1.88×10^{14} molecule cm^{-2}) is chemisorbed on the prefluorided chromia. Nevertheless the rate of reaction above 400 K is such that not only is the preadsorbed CCl_4 consumed in the reaction, its surface population has to be replenished from the gas phase. This can be quite clearly seen in Fig. 6, where the decrease in the gas phase CCl_4 concentration mirrors the increase in the concentration of the products.

The products of the reaction are CCl_3F (m/z = 101) and CCl_2F_2 (m/z = 85). No $CClF_3$ (m/z = 69, the CF_3^+ ion) was detected. Surprisingly, the line shapes of the temperature dependence of the production of CCl_3F and CCl_2F_2 are identical. The CCl_3F and CCl_2F_2 molecules are, therefore, formed with the same kinetics. This is confirmed by line shape analysis of the temperature dependence of both products—see later. The formation of CCl_2F_2 cannot be sequential from CCl_4 through CCl_3F. The CCl_3F and CCl_2F_2 are formed simultaneously from CCl_4. It is clear from the preceding section that the CCl_3F is formed from the CCl_4 through the four-centre intermediate shown by Intermediate 1. For the CCl_2F_2 species to be formed with identical kinetics, the intermediate must be virtually identical to the four–centre intermediate (Intermediate 1), but it must allow both exchange reactions to occur simultaneously.

The intermediate (Intermediate 2) proposed is shown below. It has two chlorine atoms of the CCl_4 bonded to two chromium ions, allowing simultaneous exchange of two



INTERMEDIATE 2. The four-centre intermediate for di-substitution.

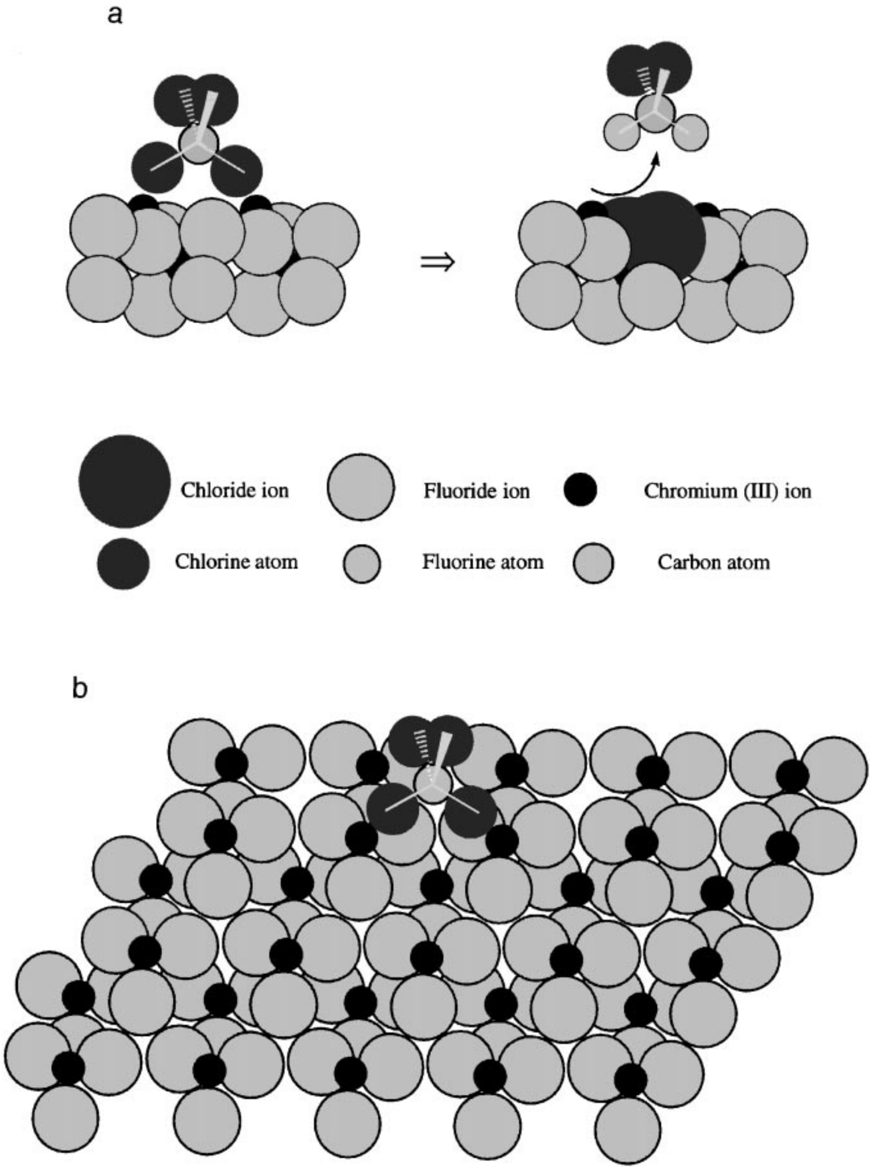


FIG. 7. (a) A cut-away model of the (001) face of CrF_3 with a CCl_4 molecule adsorbed on it for di-exchange reaction, together with the product CCl_2F_2 and the catalyst after the reaction. (b) A plan model of the (001) Face of CrF_3 with the adsorbed CCl_4 molecule on it.

chlorine/fluorine atoms. Since the reaction is the same as the mono exchange the energetics will be identical.

Figure 7a shows a cut-away model of the (001) face of CrF_3 with a CCl_4 molecule adsorbed on it. Figure 7b shows a plan model the same surface and the adsorbed CCl_4 molecule; the F^- ions and the smaller Cr^{3+} ions are shown to scale. This model is being used here simply to illustrate that the atomic arrangement in CrF_3 does allow for this type of adsorption. It should not be taken to imply that the fluorination of Cr_2O_3 would be considered to produce crystalline CrF_3, only that adsorption sites of this type do exist on the CrF_3 surface.

It can be seen from Figs. 7a and 7b that the CCl_4 molecule can adsorb with two of the Cl atoms interacting with two exposed Cr^{3+} ions. This will allow simultaneous abstraction of the Cl atoms from the adsorbed CCl_4 molecule and substitution of them by the F of the surface. The energetics of this process should be the same as that of monosubstitution. The difference in the rates of substitution (monosubstitution is at least twice as fast as di-substitution) probably derives from the relative numbers of the appropriate active centres.

It could be considered that Intermediate 2 is the only intermediate and that mono and di-exchange derive simply from the propensity of this intermediate to undergo exchange once preferentially to twice. However, the fact that mono and di-exchange reactions have the same activation energy means that, for the mono exchange to occur twice as

TABLE 1

The Amounts of CCl_3F and CCl_2F_2 Formed in the Two Peaks at 498 K and 707–742 K by Temperature-Programmed Reaction of CCl_4 with Prefluorided Cr_2O_3

	In first peak (498 K)	In second peak (707–742 K)
CCl_3F	7.2×10^{19} molecule or 5.7×10^{20} molecule g^{-1}	3.6×10^{20} molecule or 2.8×10^{20} molecule g^{-1}
CCl_2F_2	8.4×10^{18} molecule or 6.6×10^{19} molecule g^{-1}	3.7×10^{19} molecule or 2.9×10^{20} molecule g^{-1}

fast as the di-exchange, the value of the preexponential term for mono exchange must be twice that of di-exchange. This would be highly unlikely, given that mono and di-exchanges have the same activation energy and derive from the same intermediate. A predisposition of the same intermediate for mono, rather than di-exchange, given that both processes have the same activation energy, therefore appears to be highly unlikely. The co-existence of two nearly identical intermediates (Intermediate 1 and Intermediate 2) appears to be the more reasonable conclusion, the difference in the rate being accounted for in the difference in surface population of the respective intermediates—Intermediate 2 is obviously less likely than Intermediate 1.

A final point of note in relation with Fig. 6 is that the products are formed in three distinct peaks, at 498, 710, and 742 K. Table 1 lists the amounts of CCl_3F and CCl_2F_2 formed in each peak. The total amount of fluorine removed from the catalyst in the first two peaks is 7.02×10^{20} atoms g^{-1} (0.127 g surface area, 103 m^2 g^{-1}), i.e. the sum of the CCl_3F (5.7×10^{20} molecule g^{-1}) and the CCl_2F_2 (6.6×10^{19} molecule g^{-1}, 1.32×10^{20} fluorine ions g^{-1}) formed while that in the second two peaks (707 and 742 K peaks) is 3.38×10^{20} fluorine ions g^{-1} ($CCl_3F = 2.8 \times 10^{21}$ molecule g^{-1}, $CCl_2F_2 = 2.9 \times 10^{20}$ molecule g^{-1} or 5.8×10^{20} fluorine ions g^{-1}). The total amount of fluorine removed from the catalyst in the second two peaks constitutes 4.5×10^{15} ions cm^{-2} which is greater than four monolayers of fluorine and so these higher temperature peaks must come from bulk CrF_3. The lower temperature peak at 498 K comprising (7.02×10^{20} ions g^{-1} or 6.8×10^{14} ions cm^{-2}) fluorine probably originates from reaction of the adsorbed CCl_4 with surface fluoride ions. Indeed, the fluorine ion radius which can be calculated from the coverage of 6.8×10^{14} ions cm^{-2} is 2.1 Å, a value which is in reasonable accord with the quoted value of the fluorine ion radius of 1.33 Å (12), bearing in mind that some of the surface is occupied by Cr^{3+} ions. Whereas the kinetics and mechanism of the surface exchange reaction in both peaks are the same, the higher temperature of the second two peaks is accounted for in the slow bulk to surface fluorine/chlorine ion exchange.

The total amount of fluorine removed from the catalyst at the end of the reaction (4.08×10^{21} molecule g^{-1}) is roughly six times less than the total amount of HF passed over the catalyst. This is in accord with the visual observation of a breakthrough (by bubbling the reactor exit gas through water containing Methyl red indicator) after 10 min of the 30-min fluorination period of the Cr_2O_3 at 623 K. It is probable that after the monolayer fluorination was complete that the migration of the subsurface oxide anions to the surface with the concomitant diffusion of surface fluoride ion to the bulk was the rate-determining process. Therefore, after the monolayer coverage of the oxide by fluorine was complete, the reaction probability of the HF with the catalyst surface will decrease markedly.

Evaluation of the Detailed Energetics of the Process by Line Shape Analysis of Fig. 6

(i) *The heat of adsorption of CCl_4.* The temperature dependence of the CCl_4 line shape contains data for the measurement of the heat of adsorption of CCl_4 and for the evaluation of the activation energies for the transformation of CCl_4 to CCl_3F and CCl_2F_2. Concentrating initially on the temperature dependence of the CCl_4 mass spectrometer response, the temperature dependence of the rising edge of the CCl_4 peak at 310 K is proportional to the heat of adsorption through Eq. [8] (13),

$$\frac{dy}{dT} = y\frac{\Delta H_a}{RT^2}, \qquad [8]$$

where y is mole fraction of CCl_4, R is the gas constant, T is the temperature/K, ΔH_a, is the heat adsorption/J mol^{-1}.

From Fig. 6, dy/dT has a value of 8.28×10^{-4} mol K^{-1} at 305 K when $y = 0.048$, from which ΔH_a has a value of 12.5 kJ mol^{-1}. This low heat of adsorption is consistent with the majority of the CCl_4 being physisorbed. The value obtained here however is lower than the value of 39 kJ mol^{-1} using gas adsorption chromatography, emphasising the inaccuracy produced by ignoring the diffusional aspects encountered in the GAC experiment.

(ii) *The activation energies for the formation of CCl_3F and CCl_2F_2.* The activation energies for the interaction of chemisorbed CCl_4 with surface and bulk F^- ions of the fluorided Cr_2O_3 to form CCl_3F and CCl_2F_2 can be obtained by line shape analysis of the temperature dependences of the two peaks at 498 and 707 K for CCl_3F and at 498 and 742 K for CCl_2F_2.

The technique involved is the same for the determination of the activation energies for the interaction of CCl_4 with the surface and bulk F^- ion forming CCl_3F and CCl_2F_2. For brevity it will be exemplified for the interaction of CCl_4 with surface F^- to form CCl_3F.

It is clear that, although the reaction occurs between chemisorbed CCl_4 and surface F^-, the loss of gas phase CCl_4 upon the production of CCl_3F shows the chemisorbed material to be replenished from gas phase. Assuming the reaction to be first order in CCl_4, the rate of production of

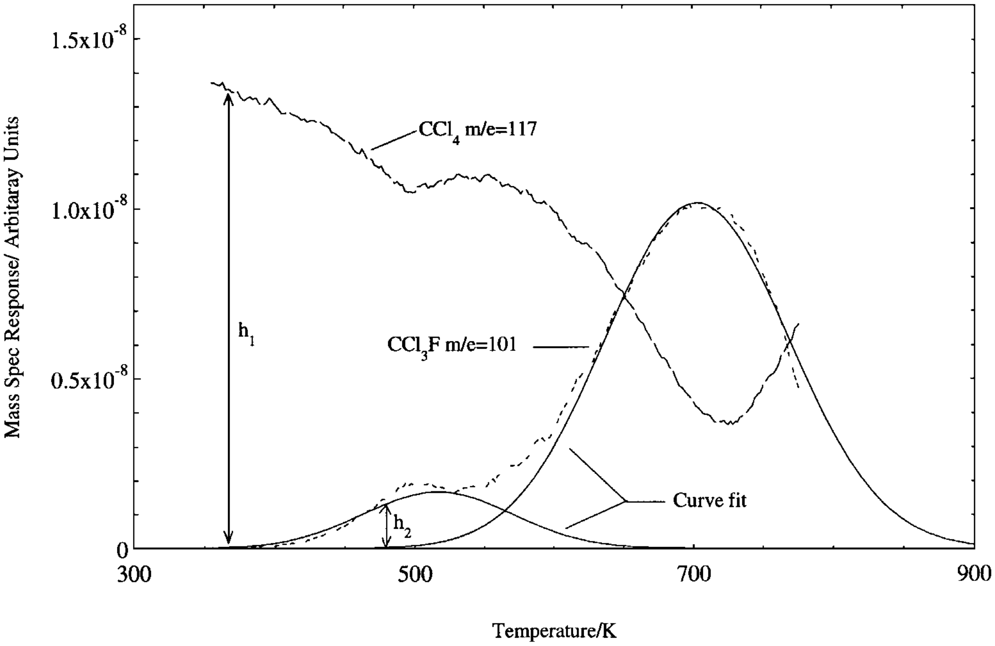


FIG. 8. Temperature dependence of the rate of production of CCl_3F.

CCl_3F is given by

$$\frac{d[CCl_3F]}{dt} = A_{ex}e^{-E/RT}[CCl_4][F^-_{(s)}], \qquad [9]$$

where $[CCl_4]$, $[CCl_3F]$, and $[F^-_{(s)}]$ are the concentration of each species in units of mol cm^{-3}, and A_{ex} and E_{ex} are the A-factor and activation energy for the exchange reaction.

The concentrations of CCl_4 and CCl_3F are given by the height of the mass spectrometer response for each of these species multiplied by its respective calibration constants, i.e. $[CCl_4]$/mol $cm^{-3} = k_1h_1$ and $[CCl_3F]$/mol $cm^{-3} = k_2h_2$ and the surface F^- ion concentration is given by the area, A of the CCl_3F peak so that Eq. [9] can be rewritten as

$$Fk_2h_2 = A_{ex}e^{-E_{ex}/RT}k_1h_1 \cdot A \qquad [10]$$

or

$$\ln\left(\frac{h_2}{h_1A}\right) = \ln(A_{ex}) - \frac{E_{ex}}{RT} + \ln\left(\frac{k_1}{Fk_2}\right), \qquad [11]$$

where F is the flow rate/cm^3 s^{-1}.

A plot of $\ln(h_2/h_1A)$ versus 1/T gives the exchange activation energy. The surface exchange activation energy for the formation of CCl_2F_2 is obtained by plotting $\ln(h_2/h_1A)$ versus 1/T in the temperature range 420 to 490 K for the deconvoluted $[CCl_3F]$ line shape shown in Fig. 8. The Arrhenius plot for the determination of the surface exchange activation energy is shown in Fig. 9 from which a value of 65 kJ mol^{-1} is obtained.

An identical analysis of the temperature dependence of the rate of CCl_3F in the temperature range 550 to 690 K gave an activation energy of 90 kJ mol^{-1} for the surface exchange reaction between chemisorbed CCl_4 and a F^- ion which had evolved at the surface by diffusion from the bulk of the fluorided chromia. The Arrhenius plot for this reaction is shown in Fig. 10.

The same analysis was used for the temperature dependence of the rate of formation of CCl_2F_2 from which values of 62 kJ mol^{-1} was obtained for the surface exchange and 90 kJ mol^{-1} for exchange with F^- ions emanating at the surface from the bulk.

The nearly identical values for the activation for the mono and di-exchange appear to confirm the postulate of a similar four-centre-type complex for both reactions. Additionally, the smallness of these activation energies (65 and 62 kJ mol^{-1}) accounts for the transformation of chemisorbed CCl_4 to both CCl_3F and CCl_2F_2 at 293 K during the 1 h helium flush prior to desorption of the CCl_4 by temperature programming. The reaction half life for mono exchange is 2×10^{-2} s and for di-exchange is 3×10^{-4} s.

CONCLUSIONS

1. The fluorination of CCl_4 to form both CCl_3F and CCl_2F_2 on a HF prefluorided (to multilayer depth) chromia is a facile reaction having activation energies determined by line shape analysis of the temperature programmed reaction peaks of 65 kJ mol^{-1} for mono exchange and 62 kJ mol^{-1} for di-exchange. The higher rate of the mono-exchange reaction despite the higher activation energy is probably due to the greater number of active centres for this reaction.

2. The facile nature of the exchange reaction in which the Cl atom of the CCl_4 is replaced by an F atom from

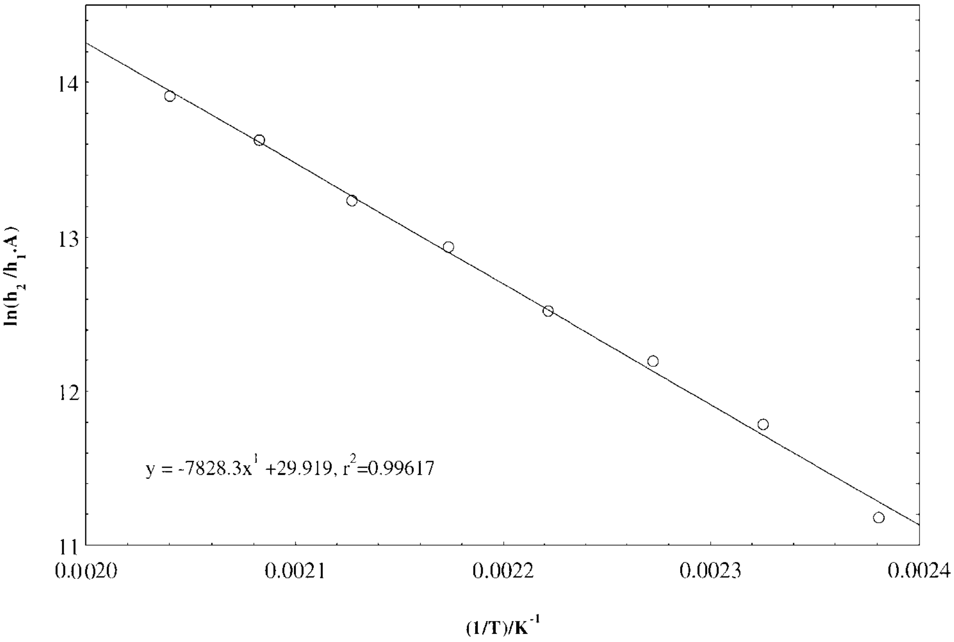


FIG. 9. Arrhenius Plot of $\ln[h_2/(h_1 \cdot A)]$ versus 1/T for the determination of the activation energy of CCl_4 with surface F^- to form CCl_3F.

the fluorided chromia is rationalised for mono exchange in a four-centre intermediate in which the CCl_4 molecule is chemisorbed by a Cl atom bonding to the Cr^{3+} and the C atom bonding to F^- ion on the surface. The mechanism therefore is Langmuir–Hinshelwood. Since the Cr–Cl and Cr–F bond energies are similar, the driving force for the reaction is the formation of the stronger C–F bond (the bond strength of the C–F bond in CCl_3F is 502 kJ mol^{-1} while the C–Cl bond strength in CCl_4 is 305 kJ mol^{-1} (14)). Di-exchange which occurs simultaneously with mono exchange is thought not to be a sequential fluorination of CCl_3F but to occur through an intermediate in which the CCl_4 is chemisorbed by two Cl atoms being bonded to two Cr^{3+} ions on the surface with the C atom, forming a bond

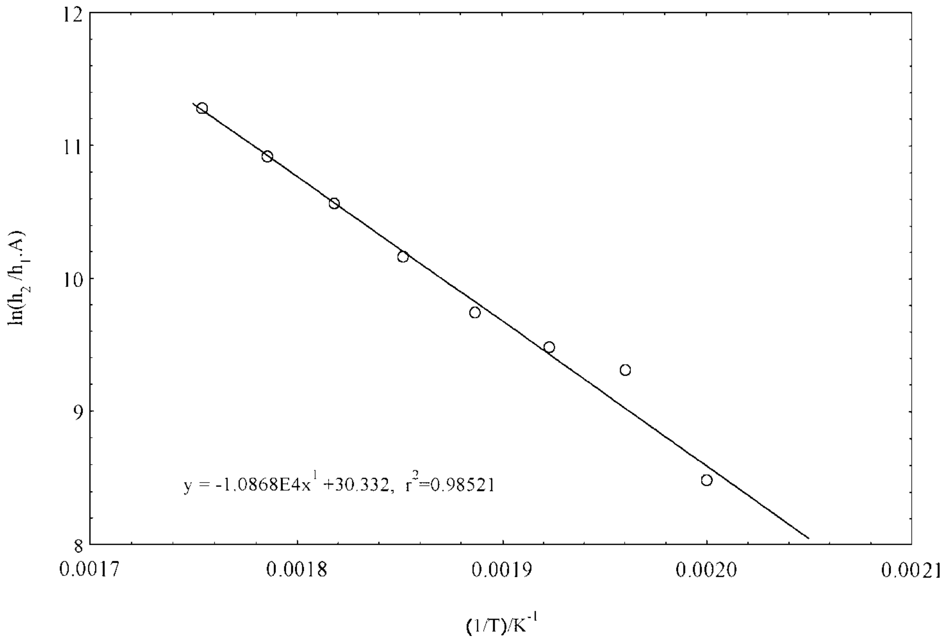


FIG. 10. The arrhenius plot of $\ln(h_2/A\ h_1)$ versus 1/T for the determination of the activation energy of the exchange reaction, forming CCl_3F, between CCl_4 and F^- ions evolving at the surface from the bulk of the fluorided Cr_2O_3.

to two surface F^- ions. This configuration is geometrically possible on the (001) face of CrF_3, and so it allows simultaneous di-exchange.

3. The mono and di-exchange mechanisms proposed here could account for the commercial production of ozone friendly hydrofluorocarbons by the fluorination of chlorohydrocarbons using gas phase HF and fluorided Cr_2O_3. Indeed the mono-exchange mechanism is capable of describing the final fluorination step in the production of the commercially important CF_3CH_2F (134a)—the transformation of CF_3CH_2Cl to CF_3CH_2F. In the overall process, according to the exchange mechanism, the role of the HF is to re-fluoride the catalyst which becomes partially chlorided by the exchange reaction.

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