# A Kinetic and Mechanistic Study of the Cl/F Exchange Reaction of CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, and CClF<sub>3</sub> with Prefluorided Chromia

## A. Farrokhnia, B. Sakakini, and K. C. Waugh\*

Department of Chemistry, Faraday Building, UMIST, PO Box 88, Manchester M60 1QD, U.K. Received: February 26, 2002; In Final Form: June 17, 2002

Chromium oxide has been fluorided to several monolayers depth by interaction with HF at 625 K. The interaction of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> with these surface chromium fluoride layers has been studied by temperatureprogrammed reaction. In the case of the reaction of CCl<sub>3</sub>F, mono- and bi-exchange occurs with the surface monolayer fluoride, forming CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> simultaneously at a peak maximum temperature of 520 K. Exchange with the subsurface fluoride layers occurs at a peak maximum temperature of 680 K, as the fluoride ions from the bulk migrate to the surface and chloride ions on the surface migrate inward. In both temperature regions, mono-exchange predominates by a factor of about  $10^2$ . Line-shape analysis of the temperature dependence of the rates of production of CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> gave activation energies of 53 and 54 kJ mol<sup>-1</sup> for exchange with the surface fluoride, so the difference in rates must be the need for special dimer-type surface sites for the bi-exchange. The activation energy for exchange of F ions evolving from the bulk calculated by line-shape analysis is 83 kJ mol<sup>-1</sup> for mono-exchange and 100 kJ mol<sup>-1</sup> for bi-exchange. These higher values than those obtained by reaction with the surface fluoride ion derive from the added activation energy for migration of the fluoride ion from the bulk to the surface.

#### Introduction

The Montreal protocol in 1989 banned production and use of chlorofluorocarbons (CFCs) because of their ability to destroy the ozone layer. This is thought to be accomplished by the following chain reaction (reactions 1-3), which leads to the net destruction of O<sub>3</sub> and O<sup>•</sup> atoms.

$$\mathrm{RC-Cl} \xrightarrow{h\nu} \mathrm{RC}^{\bullet} + \mathrm{Cl}^{\bullet} \tag{1}$$

$$Cl^{\bullet} + O_3 \rightarrow ClO + O_2 \tag{2}$$

$$ClO + O^{\bullet} \rightarrow Cl + O_2 \tag{3}$$

The CFCs have been replaced by hydrofluorocarbons (HFAs), which are not sufficiently stable to rise through the atmosphere to the ozone layer. One of the HFA replacements is 1,1,1,2-tetrafluoroethane (**134a**), which is produced by reaction of 1,1,2-trichloroethene with HF over a prefluorided chromia catalyst. The reaction is considered to proceed according to the following mechanism.

$$\operatorname{CCl}_2 = \operatorname{CHCl} + \operatorname{HF} \xrightarrow{\operatorname{CrF}_3} \operatorname{CFCl}_2 \operatorname{CH}_2 \operatorname{Cl} (\mathbf{131a}) \qquad (4)$$

$$CFCl_2CH_2Cl + CrF_3 \rightarrow CF_2ClCH_2Cl (132a) + CrF_2Cl (5)$$

$$CrF_2Cl + HF \rightarrow CrF_3 + HCl$$
 (6)

$$CF_2CICH_2CI + CrF_3 \rightarrow CF_3CH_2CI (133a) + CrF_2CI (7)$$

$$CF_3CH_2Cl + CrF_3 \rightarrow CF_3CH_2F$$
 (134a) +  $CrF_2Cl$  (8)

This mechanism (reactions 4-8) is based on our previously published work on the fluorination of CCl<sub>4</sub> in which we showed that the fluorination reaction proceeds by the exchange of the chlorine atom of the CCl<sub>4</sub> with the F atom/ion of the fluorided chromium (usually surface CrF<sub>3</sub>).<sup>1,2</sup> The role of the HF was considered to be to refluoride the surface of the CrF<sub>3</sub>, which had been partially chlorided (reaction 6).

In the study reported in this paper, we have determined the kinetics and mechanism of the fluorination of  $CCl_3F$  and  $CCl_2F_2$  over a prefluorided  $Cr_2O_3$  ( $CrF_3$ ) as models for reactions 5 and 7, respectively, of the above mechanism. We use these model systems to avoid complications of reactions involving chlorine/ fluorine exchange on the second C atom.

### **Experimental Section**

**Apparatus.** The microreactor and gas-handling system have been previously reported.<sup>1</sup> The microreactor is a U-shaped (30 cm long, 0.6 cm i.d.) monel microreactor tube, which was connected via a heated capillary to an on-line, computerinterrogated, mass spectrometer (Hiden Analytical, Warrington, England). It is used for temperature-programmed reaction (TPR), temperature-programmed desorption (TPD) in which 16 masses can be followed with temperature/time and in-situ surface area measurements.

**Catalyst.** The catalyst that was used in this study is gel chromium oxide. The preparation of this catalyst has been previously described. The calcined chromium(III) oxide was crushed and sieved into particles size of 300 to 350  $\mu$ m. The total surface area of the catalyst was determined to be 200 m<sup>2</sup> g<sup>-1</sup> by applying the BET method, using N<sub>2</sub>, adsorption at 77 K. X-ray diffraction (XRD) of the powder showed that the material contained only amorphous chromium oxide.

**Catalyst Pretreatment.** The chromium(III) oxide catalyst ( $\sim 0.2$  g) was loaded into the microreactor tube, and before any

<sup>\*</sup> To whom correspondence should be addressed. Tel: 44 (0) 161 200 4503. Fax: 44 (0) 161 200 4430. E-mail: ken.waugh@umist.ac.uk.



Figure 1. Temperature-programmed reaction of CCl<sub>3</sub>F over HF-pretreated Cr<sub>2</sub>O<sub>3</sub>.

measurement and reaction, it was heated under helium (25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa) 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<sup>3</sup> min<sup>-1</sup>, 101 kPa) for approximately 90 min at 623 K. The total amount of HF passed was always 200 cm<sup>3</sup> or  $8.2 \times 10^{-3}$  mol or  $2.5 \times 10^{22}$  fluorine atoms per gram of catalyst. The surface area of the fluorided chromia was measured in situ to be 103 m<sup>2</sup> g<sup>-1</sup>, so assuming unit reaction probability of the HF with the oxide, this corresponds to a coverage of the oxide with fluoride ions of  $1.9 \times 10^{17}$  ions cm<sup>-2</sup>, which, if the assumption is correct, means that the surface and several layers of the bulk of the Cr<sub>2</sub>O<sub>3</sub> have been fluorinated. The catalyst was then sealed, removed from the fluorinating unit, and connected to the mass spectrometer.

## **Results and Discussion**

The Temperature-Programmed Reaction of CCl<sub>3</sub>F over Fluorided Cr<sub>2</sub>O<sub>3</sub>. The temperature-programmed reaction of CCl<sub>3</sub>F on fluorided Cr<sub>2</sub>O<sub>3</sub> is shown in Figure 1. A CCl<sub>3</sub>F mixture (~4% CCl<sub>3</sub>F, 101 kPa) was produced by bubbling He (25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa) through liquid CCl<sub>3</sub>F held in a slush bath of liquid nitrogen/chlorobenzene at 228 K. Initially, the CCl<sub>3</sub>F/ He mixture was flowed over the catalyst for 12 min at 296 K to ensure adsorption equilibrium, after which the temperature was increased linearly from 296 to 773 K at a rate of 5 K min<sup>-1</sup>, following masses m/z = 117 (CCl<sub>4</sub>), m/z = 101 (CCl<sub>3</sub>F), m/z =85 (CCl<sub>2</sub>F<sub>2</sub>), and m/z = 69 (CClF<sub>3</sub>) on the mass spectrometer. The temperature-programmed reaction profile so produced is shown in Figure 1.

Several points can be made by inspection of the Figure 1. The initial increase in CCl<sub>3</sub>F concentration between 300 and 350 K derives from the desorption of physisorbed CCl<sub>3</sub>F from the surface of the catalyst. The remaining profile can be divided into two regions: (i) the low-temperature region, where the ion-exchange reaction between CCl<sub>3</sub>F (m/z = 101) and the catalyst, CrF<sub>3</sub>, begins at around 400 K, and (ii) the high-temperature region, where the bulk to surface fluorine/chlorine ion-exchange reaction begins at about 600 K.

Figure 2a shows the temperature dependence of the rate of production of  $CCl_2F_2$  with the curve fitting used to determine



**Figure 2.** The temperature dependence of the rate production and curve fit (a) for  $CCl_2F_2$ , m/z = 85 and (b) for  $CCl_3$ , m/z = 69. The solid line is the experimental data; the dashed line is the curve fitting to the data.

the kinetics of the surface exchange reaction and to determine the kinetics of the exchange reaction of  $CCl_3F$  with a F ion on the surface, which had migrated there from the bulk. The temperature dependence of the rate of production of  $CClF_3$  (with the curve fitting) is shown in Figure 2b. It is clear from these figures that mono-exchange (producing  $CCl_2F_2$ ) and bi-exchange (producing  $CClF_3$ ) occur simultaneously. Simultaneous monoand bi-exchange had been observed previously with  $CCl_4$  as the reactant.<sup>1</sup>

Evaluation of the Detailed Energetics of the Process by Line-Shape Analysis of Figure 1. *The Heat of Adsorption of CCl*<sub>3</sub>*F*. The temperature dependence of the CCl<sub>3</sub>*F* line shape in the temperature range 300-350 K in Figure 1 contains data for the measurement of the heat of adsorption of CCl<sub>3</sub>*F*. Figure 3 shows an expanded version of the profile of the temperature



Figure 3. A profile of temperature dependence of CCl<sub>3</sub>F desorption from fluorided Cr<sub>2</sub>O<sub>3</sub>.

dependence of the rate of desorption of  $CCl_3F$ . If the rate of desorption is given by

$$\frac{-\mathrm{d}[\mathrm{CCl}_{3}\mathrm{F}]}{\mathrm{d}t} = A_{\mathrm{ex}} \,\mathrm{e}^{-E/(RT)} \,[\mathrm{CCl}_{3}\mathrm{F}] \tag{9}$$

where [CCl<sub>3</sub>F] is the amount of CCl<sub>3</sub>F that is desorbed in units of mol cm<sup>-3</sup>,  $A_{ex}$  and E are the A-factor and desorption activation energy, which in this physisorption process is equal to  $\Delta H_a$ , the heat of adsorption. The rate of desorption is proportional to the height, h, of the mass spectrometer response, and the amount of [CCl<sub>3</sub>F] adsorbed is proportional to the area, A, of the CCl<sub>3</sub>F peak. Equation 9 can be rewritten as

$$k_1 h = A_{\rm ex} e^{-E/(RT)} k_2 A$$
 (10)

or

$$\ln\left(\frac{h}{A}\right) = \ln A_{\rm ex} + \ln\frac{k_2}{k_1} - \frac{E}{RT} \tag{11}$$

where  $k_1$  and  $k_2$  are calibration constants.

A plot of  $\ln(h/A)$  versus 1/T gives the desorption activation energy. The integration of the area was taken to 339 K, because this was the temperature at which a minimum in the rate of desorption of CCl<sub>3</sub>F was observed. The desorption activation energy of CCl<sub>3</sub>F is obtained by plotting  $\ln(h/A)$  versus 1/T in the temperature range 293–303 K for the line shape shown in Figure 3, which gives a straight line is shown in Figure 4. A value of 34 kJ mol<sup>-1</sup> is obtained for desorption activation energy, which is characteristic of physical adsorption.<sup>3</sup>

The Activation Energies for the Formation of  $CCl_2F_2$  and  $CClF_3$ . The activation energies for the interaction of chemisorbed  $CCl_3F$  with surface and bulk  $F^-$  ions of the prefluorided  $Cr_2O_3$  forming  $CCl_2F_2$  and  $CClF_3$  can be obtained by line-shape analysis of the temperature dependence of the  $CCl_2F_2$  peaks at 520 and 684 K and of the  $CCl_3F$  peaks at 520 and 680 K. The line-shape analysis technique for calculation of the activation energies of the above reactions is as follows. The halogen

exchange reaction occurs between chemisorbed  $CCl_3F$  and surface  $F^-$ . (The loss of gas-phase  $CCl_3F$  upon the production of  $CCl_2F_2$  shows the chemisorbed material to be replenished from the gas phase.) Assuming the reaction to be first-order in  $CCl_3F$ , the reaction is described by eq 12 and the rate of production of  $CCl_2F_2$  is given by eq 13.

$$\operatorname{CCl}_{3}F + F_{(s)}^{-} \rightarrow \operatorname{CCl}_{2}F_{2} + \operatorname{Cl}_{(s)}^{-}$$
(12)

$$\frac{d[CCl_2F_2]}{dt} = A e^{-E/(RT)} [CCl_3F][F_{(s)}]$$
(13)

where [CCl<sub>3</sub>F], [CCl<sub>2</sub>F<sub>2</sub>], and [F<sup>-</sup><sub>(s)</sub>] are the concentrations of each species in units of mol cm<sup>-3</sup> and  $A_{ex}$  and *E* are the A-factor and activation energy, respectively, for the exchange reaction. Figure 5 shows the rate of production of CCl<sub>2</sub>F<sub>2</sub>. The concentrations of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> are given by the height of the mass spectrometer response. Each of these species is multiplied by its respective calibration constant, that is, [CCl<sub>3</sub>F] in mol cm<sup>-3</sup> =  $k_1h_1$  and [CCl<sub>2</sub>F<sub>2</sub>] in mol cm<sup>-3</sup> =  $k_2h_2$  and the surface F<sup>-</sup> ion concentration is given by the area, *A*, under the CCl<sub>2</sub>F<sub>2</sub> peak so that eq 13 can be rewritten as

or

$$fk_2h_2 = A_{\rm ex} \,{\rm e}^{-E/(RT)} \,k_1h_1A$$
 (14)

$$\ln\left(\frac{h_2}{h_1A}\right) = \ln(A_{\text{ex}}) - \frac{E_{\text{ex}}}{RT} + \ln\left(\frac{k_1}{fk_2}\right)$$
(15)

where *f* is the flow rate in  $\text{cm}^3 \text{ s}^{-1}$ .

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<sub>2</sub>F<sub>2</sub> is obtained by plotting  $\ln(h_2/(h_1A))$  versus 1/T in the temperature range 400–490 K for the deconvoluted [CCl<sub>2</sub>F<sub>2</sub>] line shape shown in Figure 5. The Arrhenius plot for the determination of the surface exchange activation energy is shown in Figure 6 from which a value of 53 kJ mol<sup>-1</sup> is obtained for the reaction of an adsorbed CCl<sub>3</sub>F molecule with a surface



Figure 4. Arrhenius plot of  $\ln(h/A)$  versus 1/T for determination of desorption activation energy.



Figure 5. Temperature dependence of the rate of production of CCl<sub>2</sub>F<sub>2</sub>.

 $F^-$  ion. Justification of the assumption that the 520 K CCl<sub>2</sub>F<sub>2</sub> peak results from the exchange of CCl<sub>3</sub>F with a surface  $F^-$  and the assumption that the 684 K peak results from exchange with a bulk  $F^-$  ion is found by calculation of the amounts of  $F^-$  exchanged in each peak; see below and Table 1.

An identical analysis of the temperature dependence of the rate of production of  $CCl_2F_2$  in the temperature range 640–666 K gave an activation energy of 83 kJ mol<sup>-1</sup> for the surface exchange reaction between chemisorbed  $CCl_3F$  and a F<sup>-</sup> ion that had evolved at the surface by diffusion from the bulk of the fluorided chromia. The Arrhenius plot for this reaction is shown in Figure 7. The same analysis was used for the temperature dependence of the rate of formation of  $CCl_3$  from which a value of 54 kJ mol<sup>-1</sup> for exchange with F<sup>-</sup> ions emanating at the surface from the bulk. The nearly identical values for the activation energy for the mono- and bi-exchange

TABLE 1: The Amounts of CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> Formed in the Low-Temperature Region (at 520 K) and the High-Temperature Region (at 680 K) by Temperature-Programmed Reaction of CCl<sub>3</sub>F over Fluorided Chromia Catalyst

	surface F reaction peak (520 K)	exchange reaction with a F ion that had migrated from the bulk to the surface			
CCl <sub>2</sub> F <sub>2</sub>					
amount	$2.03 \times 10^{20}$ molecule or	$5.2 \times 10^{20}$ molecule or			
	$1.6 \times 10^{21}$ molecule g <sup>-1</sup>	$4.1 \times 10^{21}$ molecule g <sup>-1</sup>			
selectivity	98.7%	99.8%			
	CClF <sub>3</sub>				
amount	$3.3 \times 10^{18}$ molecule or	$4.9 \times 10^{19}$ molecule or			
	$2.6 \times 10^{19}$ molecule g <sup>-1</sup>	$3.9 \times 10^{20}$ molecule g <sup>-1</sup>			
selectivity	1.3%	0.2%			

suggests that a similar type of intermediate is involved in both reactions; see later.



Figure 6. Arrhenius plot of  $\ln[h_2/(h_1A)]$  versus 1/T for the determination of the activation energy of CCl<sub>3</sub>F with surface F<sup>-</sup> to form CCl<sub>2</sub>F<sub>2</sub>.



**Figure 7.** Arrhenius plot of  $\ln[h_2/(h_1A)]$  versus 1/T for the determination of the activation energy for the exchange reaction (to form  $CCl_2F_2$ ) between  $CCl_3F$  and  $F^-$  ions evolving at the surface from the bulk of the fluorided chromium oxide.

Table 1 lists the amount of CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> by both the surface exchange reaction and by exchange of F<sup>-</sup> ion that had migrated to the surface from the bulk. The total surface fluoride, which removed from the catalyst in the first two peaks, was  $1.7 \times 10^{21}$  atoms g<sup>-1</sup> (0.127 g catalyst, total surface area 103 m<sup>2</sup> g<sup>-1</sup>), while the amount in the higher temperature peaks was  $4.9 \times 10^{21}$  fluorine ions g<sup>-1</sup>. The total amount of fluorine removed from the catalyst in the higher temperature region constitutes  $4.74 \times 10^{15}$  ions cm<sup>-2</sup>. This is greater than five monolayers of fluorine confirming that the higher temperature peaks derive from F<sup>-</sup> in bulk CrF<sub>3</sub> migrating to the surface.

The product percentage ratio of  $CCl_2F_2/CClF_3$  in the first two peaks was 98.7:1.3 and in the second two peaks was 99.8:0.2, which clearly shows that the reaction is highly selective for mono-exchange producing  $CCl_2F_2$ . The low selectivity to  $CClF_3$  is probably a function of the low surface coverage of appropriately spaced  $\rm Cr^{3+}$  sites for bidentate adsorption of the CCl\_3F.

A final point of note is that the total amount of fluorine in the 520 K CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> peaks, which is considered to be the surface exchange reaction, is  $2.08 \times 10^{20}$  atoms, corresponding to a surface coverage of  $1.59 \times 10^{15}$  ions cm<sup>-2</sup> or a fluorine ion area of 6.3 Å<sup>2</sup> or a fluorine ion radius of 1.4 Å. This latter value accords well with the quoted value of the fluorine ion radius of 1.33 Å.<sup>4</sup> This results gives added credence to the suggestion that the 520 K peaks derive from exchange of the surface F<sup>-</sup> species.

The activation energy for mono chloro/fluoro exchange of  $CCl_4$  is 65 kJ mol<sup>-1</sup>.<sup>1</sup> This is slightly higher than the value of 53 kJ mol<sup>-1</sup> found here for  $CCl_3F$ . Our previous paper<sup>1</sup> postulated that the ion exchange reaction proceeds by a

TABLE 2: C–Cl and C–F Bond Dissociation Energies (kJ  $mol^{-1}$ ) in Chlorofluoromethane<sup>4</sup>

Х	$X-CF_3$	$X-CClF_2$	$X-CCl_2F$	$X-CCl_3$
F	546	514.6	460	426
Cl	360.7	318	305	306

Langmuir—Hinshelwood mechanism through a four-center intermediate. The structure of four-center intermediate that we consider is likely to be involved is shown in intermediate 1.



Intermediate 1 - The four centre intermediate for production of  $CCl_2F_2$  from the reaction of  $CCl_2F$  over fluorided  $Cr_2O_3$ .

The exchange reactions of both CCl<sub>4</sub> and CCl<sub>3</sub>F require the breaking of a C–Cl and a Cr–F bond and, at the same time, the formation of a C–F and a Cr–Cl bond. As a result, during the exchange process, the formation of the reaction intermediate depends on the strengths of the bonds being formed or broken. The bond strengths of C–F and C–Cl bonds in different chlorofluoromethanes are reported in Table 2.<sup>4</sup>

Because the bond strengths of Cr–F and Cr–Cl are similar (~356 kJ mol<sup>-1</sup>), the driving force for the reaction is the formation of the stronger C–F bond. The fluorination of CCl<sub>4</sub> to form CCl<sub>3</sub>F requires 306 kJ mol<sup>-1</sup> of energy to dissociate the Cl–CCl<sub>3</sub> bond, which is more than compensated for by the formation of the F–CCl<sub>3</sub> bond (D(C–F) = 426 kJ mol<sup>-1</sup>), eq 16. On the other hand, in the fluorination of CCl<sub>3</sub>F to form CCl<sub>2</sub>F<sub>2</sub>, dissociation of the Cl–CCl<sub>2</sub>F bond requires 305 kJ mol<sup>-1</sup>, while the formation of the F–CCl<sub>2</sub>F bond releases 460 kJ mol<sup>-1</sup>, eq 17.

$$\operatorname{Cl} \xrightarrow{306} \operatorname{CCl}_3 \xrightarrow{\operatorname{CrF}_3} \operatorname{F} \xrightarrow{426} \operatorname{CCl}_3 \qquad E_a = 65 \text{ kJ mol}^{-1} (16)$$

$$\operatorname{Cl} \xrightarrow{305} \operatorname{CCl}_2 F \xrightarrow{\operatorname{Cr}_3} F \xrightarrow{460} \operatorname{CCl}_2 F \qquad E_a = 53 \text{ kJ mol}^{-1} (17)$$

Therefore because of the formation of the stronger C–F bond in the fluorination of  $CCl_3F$ , the exchange activation energy of  $CCl_3F$  is smaller than that of  $CCl_4$ .

As is clear from Figure 2a,b, the production of  $CCl_2F_2$  and  $CCl_3$  from  $CCl_3F$  occurs simultaneously. Because the temperature dependences of the rates of production of  $CCl_2F_2$  and  $CClF_3$  are identical, it is highly unlikely that the production of  $CCl_3F_2$ . Were it to have been sequential, a small delay in the rate of production of  $CClF_3$  would have been expected. The intermediate that would allow bi-exchange, is a "bi-four-center" intermediate (intermediate 2).



Intermediate 2-The intermediate for di-substitution to form CCIF<sub>3</sub> from reaction of CCl<sub>3</sub>F over fluorided chromium oxide.

The adsorption of  $CCl_3F$  on the 001 surface of  $CrF_3$  for the bi-exchange reaction is shown in Figure 8. The  $Cl^-$  and  $F^-$  ions



**Figure 8.** A cut-away model of the (001) face of  $CrF_3$  with a  $CCl_3F$  molecule adsorbed on it for bi-exchange reaction together with the product  $CClF_3$  and the catalyst after the reaction.

and the smaller chromium ions are shown to scale. The  $CCl_3F$  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  $CCl_3F$  molecule and substitution of them by the F of the surface.

Another point of note in relation to Figure 1 is the production of  $CCl_4$  from  $CCl_3F$ . This reaction would occur through a fourcenter intermediate (intermediate 3) resulting from the reaction of chemisorbed  $CCl_3F$  with partially chlorided catalyst ( $CrF_2$ -Cl) shown in Figure 8.



Intermediate 3-The four centre intermediate for mono-substitution to form CCl<sub>4</sub> from reaction of CCl<sub>3</sub>F over prefluorided  $Cr_2O_3$ .

Temperature-Programmed Reaction of  $CCl_2F_2$  over HF Prefluorided  $Cr_2O_3$ . The temperature-programmed reaction of  $CCl_2F_2$  over prefluorided chromium(III) oxide is shown in Figure 9. The catalyst is pretreated with HF, using 10% HF in He (25 cm<sup>2</sup> min<sup>-1</sup>, 101 kPa) for approximately 1 h at 623 K.

The reactant gas, 5%  $CCl_2F_2$  in He (25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa), is prepared by choosing the appropriate flow rates of both  $CCl_2F_2$  and helium using flow meters. The temperatureprogrammed reaction profile (Figure 9) is obtained by passing  $CCl_2F_2$  (5% in He) continuously over the catalyst while raising the temperature from ambient to 773 K at 5 K min<sup>-1</sup>.

Only CClF<sub>3</sub> is observed. No CF<sub>4</sub> is detected. Therefore, whereas mono- and bi-exchange were observed with CCl<sub>4</sub> and CCl<sub>3</sub>F as the reactants, bi-exchange is not observed with CCl<sub>2</sub>F<sub>2</sub> as the reactant. Because the availability of the appropriately spaced two Cr<sup>3+</sup> ions on the surface CrF<sub>3</sub> in the catalyst is the same and because the distance between the Cl atoms on CCl<sub>2</sub>F<sub>2</sub> will be the same as that between two Cl atoms on CCl<sub>4</sub> and CCl<sub>3</sub>F, the lack of observation of bi-exchange cannot be structural. It must therefore be energetic.

It could be a function of the reaction dynamics. If the first Cl/F exchange occurs fractionally before the second, then in the case of the reaction of  $CCl_2F_2$ , the first product will be  $CCl_3F$ , the C–Cl bond strength of which is 361 kJ mol<sup>-1</sup>. This high C–Cl bond strength probably prevents the near-simulta-



Time/ s

Figure 9. Temperature-programmed reaction of CCl<sub>2</sub>F<sub>2</sub> over HF-pretreated Cr<sub>2</sub>O<sub>3</sub>.





Figure 10. Temperature dependence of the rate production of CClF<sub>3</sub>.

neous bi-exchange from occurring. It also suggests that, whereas in the cases of the bi-exchange of CCl<sub>4</sub> and CCl<sub>3</sub>F we had argued that bi-exchange was a concerted and simultaneous process, it is probable that the first exchange occurs fractionally earlier (say  $10^{-10}$  s) than the second. (It should be noted that no exchange reaction is observed with CClF<sub>3</sub> as reactant (see later). This observation supports the C–Cl bond-strength argument.)

Another point to note in relation to Figure 9 is the production of  $CCl_3F$  from  $CCl_2F_2$ . It is being suggested here that the chlorination reaction of  $CCl_2F_2$  to  $CCl_3F$  occurs with the same mechanism as that involved in the fluorination reaction. Here, however, it can be seen from Figure 9 that production of  $CClF_3$ only occurs after some significant production of  $CClF_3$  is observed, which produces a considerably chlorided surface.

The Activation Energies for the Formation of  $CCl_3F$  and  $CClF_3$ . The activation energies for the interaction of chemisorbed  $CCl_2F_2$  with surface and bulk  $F^-$  ions of the fluorided  $Cr_2O_3$  to form  $CClF_3$  can be obtained by line-shape analysis of the temperature dependence of the two product peaks at 570 and 600 K. The line-shape analysis technique for calculation of the activation energies of the above reactions is exactly the same one that was used for the  $CCl_3F$  and  $CCl_4$  reaction. The crude deconvolution of the  $CClF_3$  reaction profile used to calculate the exchange activation energies is shown in Figure 10. Again the reaction is assumed to be first-order in  $CCl_2F_2$  (eq 18), and the rate of production of  $CClF_3$  is given by eq 19.

$$\operatorname{CCl}_2 F_2 + F_{(s)}^{-} \rightarrow \operatorname{CCl} F_3 + \operatorname{Cl}_{(s)}^{-} \tag{18}$$

$$\frac{d[CClF_3]}{dt} = A_{ex} e^{-E/(RT)} [CCl_2F_2][F_{(s)}]$$
(19)

where [CCl<sub>2</sub>F<sub>2</sub>], [CClF<sub>3</sub>], and [ $F^-_{(s)}$ ] are the concentration of each species in units of mol cm<sup>-3</sup> and  $A_{ex}$  and E are the A-factor and activation energy, respectively, for the exchange reaction. The concentrations of CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub> are given by the height of the mass spectrometer response.



Figure 11. Arrhenius plot of  $\ln[h_2/(h_1A)]$  versus 1/T for the determination of the activation energy of  $CCl_2F_2$  with surface  $F^-$  to form  $CClF_3$ .



Figure 12. Temperature-programmed reaction of CCIF<sub>3</sub> over prefluorided Cr<sub>2</sub>O<sub>3</sub>.

As explained in the previous equation, 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 CCIF<sub>3</sub> is obtained by plotting  $\ln(h_2/(h_1A))$  versus 1/T in the temperature range 550–575 K for the deconvoluted [CCIF<sub>3</sub>] line shape shown in Figure 10. The Arrhenius plot for the determination of the surface exchange activation energy is shown in Figure 11 from which a value of 84 kJ mol<sup>-1</sup> is obtained for the surface F/Cl exchange and 110 kJ mol<sup>-1</sup> for the exchange with F<sup>-</sup> ions emanating at the surface from the bulk.

As Figure 10 clearly shows the mono-exchange reaction occurs at around 650 K. This is higher than mono-exchange reaction of  $CCl_4$  and  $CCl_3F$  so the activation energy is expected to be higher, as we have found.

$$\operatorname{Cl} \xrightarrow{318} \operatorname{CClF}_2 \xrightarrow{\operatorname{CrF}_3} \operatorname{F} \xrightarrow{515} \operatorname{CClF}_2 \qquad E_a = 84 \text{ kJ mol}^{-1} \quad (20)$$

The C-Cl bond in CCl<sub>2</sub>F<sub>2</sub> is 318 kJ mol<sup>-1</sup>, which is higher than that in CCl<sub>3</sub>F and CCl<sub>4</sub> (~305 kJ mol<sup>-1</sup>), and although this is conpensenated for by a higher C-F bond strength (D(C-F) in CCl<sub>2</sub>F<sub>2</sub> = 515 kJ mol<sup>-1</sup>), the net effect is a higher activation energy for the exchange reaction.

Temperature-Programmed Reaction of CClF<sub>3</sub> over CrF<sub>3</sub> and CrCl<sub>3</sub>. The final part of this study is to investigate the possibility of substitution of the chlorine atom of CClF<sub>3</sub> with a  $F^-$  atom. For this purpose, first the reaction of CClF<sub>3</sub> was investigated over fluoride chromia. Figure 12 is the temperature-programmed reaction mass spectrum obtained by flowing CClF<sub>3</sub> in He (5% CClF<sub>3</sub>, 25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa) continuously over the catalyst (CrF<sub>3</sub>), while raising the temperature from ambient to 773 K at a heating rate of 5 K min<sup>-1</sup>.

Figure 12 clearly shows that no fluorination, chlorination, or decomposition reaction occurs. This is in agreement with the findings of Kemnitz et al.<sup>5</sup> who have reported that fluorination of CClF<sub>3</sub> by CrF<sub>3</sub> does not occur. As explained earlier for our absence of the observation of the formation of CF<sub>4</sub> from CCl<sub>2</sub>F<sub>2</sub>, the value of the C–Cl bond strength of the CCl<sub>3</sub>F molecule (361 kJ mol<sup>-1</sup>) results in too high an activation energy for the exchange reaction.

Second, another TPR was conducted over  $CrCl_3$  to investigate the possibility of the chlorination reaction on this catalyst. The chromium(III) oxide (0.2 g) was loaded in the microreactor; it was heated under He (25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa) to 623 K and was left at this temperature for 45 min and then was chlorided by 4% CCl<sub>4</sub> in He (25 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa).

Figure 13 shows the temperature-programmed reaction of  $CClF_3$  over  $CrCl_3$  from room temperature to 773 K. There was no indication of any reaction. Therefore, the  $CClF_3$  does not



Figure 13. Temperature-programmed reaction of CClF<sub>3</sub> over CrCl<sub>3</sub>.

react on the  $CrCl_3$  catalyst either. This is probably because this molecule has the highest C-F bond strength, and the exchange of the fluorine atom by a chlorine atom is likely to have a high activation energy.

#### Conclusion

The activation energies of 53 and 54 kJ mol<sup>-1</sup> for the simultaneous mono- and bi-exchange of the chlorine atoms of CCl<sub>3</sub>F with the surface fluoride ions of a prefluorided chromia are lower than that found for CCl<sub>4</sub> (65 kJ mol<sup>-1</sup>). It is probable that this is due to the stronger C–F bond formed in CCl<sub>2</sub>F<sub>2</sub> and CClF<sub>3</sub>, the C–Cl bond strengths in CCl<sub>4</sub> and CCl<sub>3</sub>F being roughly the same.

It is suggested that mono-exchange occurs through a fourcenter intermediate in which the breaking of a C–Cl bond is compensated for by the formation of a C–F bond. Bi-exchange is thought to occur by the adsorption of  $CCl_3F$  by the bonding of two Cl atoms to two appropriately spaced Cr ions on the CrF surface.

Mono-exchange predominates by a factor of  $10^2$  even though the activation energies are nearly the same. It is suggested that this is due to the scarcity of specific sites on the CrF surface for the adsorption of CCl<sub>3</sub>F through two chlorine atoms to two surface Cr ions.

Mono-exchange only is observed in the reaction of  $CCl_2F_2$ , the activation energy for which is 84 kJ mol<sup>-1</sup>. This higher activation energy is due to the higher C–Cl (~318 kJ mol<sup>-1</sup>) bond strength in  $CCl_2F_2$  than in  $CCl_3F$  (D(C-Cl) = 305 kJ mol<sup>-1</sup>). The absence of the occurrence of bi-exchange producing  $CF_4$  is thought to be due to the instantaneous formation of  $CCIF_3$ on the intermediate, which is adsorbed through two chlorine atom where bi-exchange should have been possible. The C–Cl bond strength in  $CCIF_3$  is 361 kJ mol<sup>-1</sup>, this high value prohibiting bi-exchange. This result suggests that, whereas the results of bi-exchange of  $CCl_2F_2$  suggest simultaneous two atom exchange, the detailed dynamics occur by one fluorine/chlorine exchange occurring with  $CCl_2F_2$  being held in a bidentate mode on the Cr–F surface. The second exchange occurs immediately afterward without desorption of the reaction.

No exchange of the C–Cl bond of  $CClF_3$  with the surface CrF was observed. This is probably due to the high bond strength of the C–Cl bond (~361 kJ mol<sup>-1</sup>) in this molecule.

The mechanism presented here accounts for the formation of the fluorohydrocarbon (**134a**) by reaction of 1,1,2-trichloroethene with HF over a prefluorided  $Cr_2O_3$ . Exchange of the chlorine atoms of the adsorbed chlorofluorocarbon occurs with the surface fluoride ions, the resulting surface chloride ion being replaced by exchange with the HF.

### **References and Notes**

(1) Farrokhnia, A.; Sakakini, B.; Waugh, K. C. J. Catal. 1998, 174, 219.

(2) Farrokhnia, A.; Sakakini, B.; Waugh, K. C. Catal. Lett. 2001, 76 (3-4), 241.

(3) Gasser, R. P. H. An Introduction to Chemisorption and Catalysis by Metals; Clarendon Press: Oxford, U.K., 1985.

(4) West, R. C., Ed. *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1987.

(5) Kemnitz, E.; Hansen, G.; Heb, A.; Kohne, A. J. Mol. Catal. 1992, 77, 193.