

Received June 24, 1984; accepted October 17, 1984

RADIOTRACERS IN FLUORINE CHEMISTRY. PART IX
FLUORINATION OF CHLOROFLUOROETHANES BY CHROMIA CATALYSTS
TREATED WITH HYDROGEN FLUORIDE OR HYDROGEN [¹⁸F]-FLUORIDE

JERZY KIJOWSKI, GEOFFREY WEBB and JOHN M. WINFIELD.

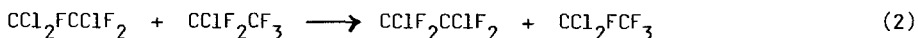
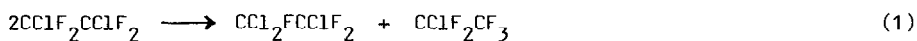
Chemistry Department, The University of Glasgow, Glasgow G12 8QQ
Scotland (U.K.)

SUMMARY

Passage of dichlorotetrafluoroethane isomers or 1,1,2-trichloro-1,2,2-trifluoroethane at temperatures ≥ 623 K over chromia catalysts, previously treated with hydrogen fluoride at 623 K, leads to the formation of fluorinated and chlorinated products. Incorporation of fluorine-18 radioactivity in the products is observed when hydrogen [¹⁸F]-fluoride is used in the catalyst pretreatment, indicating the involvement of a surface fluorine-containing species. The reactions observed are described in terms of series of F-for-Cl and Cl-for-F halogen exchange reactions occurring at the catalyst surface.

INTRODUCTION

Although the fluorination of chlorofluoroethanes by hydrogen fluoride in the presence of aluminium trifluoride, chromia, or alumina-based catalysts has received widespread study [1-5], the main emphases have been on product identification and on designing conditions for the efficient preparation of chloropentafluoroethane. On the basis of observed product distributions the reactions which occur under heterogeneous conditions have been discussed [2,4] in terms of reorganisation (disproportionation) and isomerisation processes, for example, equations 1 and 2:



An ionic mechanism has been postulated for the Cl-F exchange process [2], and for nickel-doped AlF_3 and chromia, a redox function for the catalyst has been suggested on the basis of an e.p.r. study [6]. However, little is known about the interactions which occur at a catalyst surface. We have obtained direct evidence for the involvement of a surface fluorine-containing species in the fluorination of dichlorotetrafluoroethane isomers and 1,1,2-trichloro-1,2,2-trifluoroethane over fluorinated chromia catalysts by means of a fluorine-18 ($t_{1/2} = 110$ min) study. Our results cast doubt on the importance of concerted reorganisation and isomerisation reactions and an alternative reaction scheme is proposed. A preliminary account of this work has been given [7].

EXPERIMENTAL

The pelleted, chromia catalysts used in this work were commercial samples. Experiments were performed both with fresh catalyst, surface area $66.5 \text{ m}^2 \text{ g}^{-1}$, and with samples that had been used for catalytic fluorination, surface areas $9.8 - 11.0 \text{ m}^2 \text{ g}^{-1}$. Chlorine and fluorine contents of the latter were in the range $0.20 - 0.64$ and $24.1 - 28.0$ w/w % respectively. The surface area of the fresh catalyst fell to $22.0 \text{ m}^2 \text{ g}^{-1}$ after use in 1,1,2-trichloro-1,2,2-trifluoroethane experiments and its chlorine and fluorine contents were 0.78 and 8.4 w/w % respectively.

Hydrogen fluoride (Matheson or I.C.I. P.L.C., nominally 99.8%), dichlorotetrafluoroethane (Fluorochem) and trichlorotrifluoroethane (I.C.I. P.L.C.) were used as received. Their ^{19}F n.m.r. spectra indicated that the mole ratio $\text{CClF}_2\text{CClF}_2 : \text{CCl}_2\text{FCF}_3$ was $12.8 : 1.0$, and that $\text{CCl}_2\text{FCClF}_2$ contained a trace of the isomer CCl_3CF_3 .

Fluorine-18 was prepared by the sequence ${}^6\text{Li}(n, \alpha){}^3\text{H}$, ${}^{16}\text{O}({}^3\text{H}, n){}^{18}\text{F}$ using the Scottish Universities' Research Reactor, East Kilbride. Work-up of the irradiated product gave $\text{Cs}^{18}\text{F}(\text{aq})$ [8] which was evaporated to dryness and dried further in vacuo above 373 K. Hydrogen [^{18}F]-fluoride was prepared by an exchange reaction between $\text{HF}(\text{ca. } 3-5 \text{ cm}^3 \text{ liquid})$ and $\text{Cs}^{18}\text{F}(\text{ca. } 1 \text{ g}; 20 \mu\text{Ci})$ at $293 - 523$ K in a Monel metal pressure vessel (95 cm^3) attached to a Monel metal vacuum system. ^{18}F count rates were determined using a NaI well scintillation counter (Ekco and Nuclear Enterprises), well dimensions 1.56×0.78 ins diameter. Aliquots of H^{18}F complexed by predried CsF were contained in F.E.P. counting tubes fitted with Monel valves (Whitey). Specific count rates of H^{18}F determined by this means were $> 100 \text{ count s}^{-1} \text{ mmol}^{-1}$. Radiochemical purity was established by half-life determination and all count rates were corrected for background and decay.

Reactions between HF and $C_2Cl_2F_4$ or CCl_2FCClF_2 were carried out in a Monel metal (o.d. = 0.25 ins)- 'Pyrex' flow system, Monel needle valves (Whitey or Nupro) and P.T.F.E./glass stop-cocks (Rotaflo) being used as appropriate. The reaction vessel was a vertical Monel tube, o.d. = 0.5 ins, containing a heated zone, 7 ins, within which the catalyst was supported on a copper gauze. The temperature of the heated zone was determined by a centrally mounted thermocouple and gas flow was from top to bottom. The flow system had separate chlorofluorocarbon and HF feed and exit lines and a by-pass line for the reactor. Both reactor and product exit lines were pumped for several hours to minimise the build-up of less volatile, highly chlorinated products.

Catalyst samples were given several pre-treatments with HF vapour at 623 K before use in a series of experiments. Before each experiment the apparatus was flushed with dry nitrogen while the catalyst was heated to 623 K. HF vapour, dispensed from a measured volume of liquid HF in a Monel vessel at 333 K, was passed over the heated catalyst, its flow rate being controlled by a differential-pressure flow-meter. HF not retained by the catalyst was passed through a Kel-F trap, in which aqueous HF was collected, the remaining effluent was absorbed in NaF - soda lime towers. The reactor was flushed with dry N_2 for 10-30 min while the catalyst was brought to the desired temperature for reaction. A chlorofluorocarbon vapour stream, generated by passing helium at a constant flow rate through a weighed quantity of $C_2Cl_2F_4$ held at 258 K or CCl_2FCClF_2 held at 298 K, was allowed to react with the fluorinated catalyst. Reaction products, after removal of trace HF by a small NaF scrubber, were monitored by regular, 5-15 min, sampling of the gas stream using a PE.F11 chromatograph (3 m, 0.125 ins ad. column packed with D.P.N. on Porasil C, thermal conductivity detector). Members of the series $C_2Cl_{6-n}F_n$, $n = 2-6$, were quantitatively determined but it was not possible to differentiate between isomeric forms. Identification of isomers was accomplished by ^{19}F n.m.r. spectroscopy of larger product samples. Constant chlorofluorocarbon flow rates were not always achieved, particularly for reactions involving CCl_2FCClF_2 \leq 623 K, and heating the exit line and NaF trap to 373 K made no improvement. The problem was circumvented to some extent by determining flow rates at the exit as GC samples were taken. Mean values with their standard deviations are quoted.

Fluorine-18 tracer studies were carried out in a similar manner with the addition of an F.E.P. counting tube at 90° to the reactor at its upper end. The reactor assembly could be removed from the flow system without

loss of integrity, in order that the ^{18}F count rates of the top three pellets could be determined after flows of H^{18}F and the chlorofluorocarbon. Separate experiments established that the sampling point temperature was 10 - 30 K higher than at the mid-point of the reactor and that the variation of ^{18}F count rate over the catalyst bed (ca. 20 pellets) corresponded to H^{18}F uptakes of 0.9 - 1.0 mmol (g catalyst) $^{-1}$.

[^{18}F]-labelled chlorofluorocarbon products were collected in a low temperature fractionation train, and counted, and weighed either *in situ*, or for highly volatile products, after transfer *in vacuo* to small volume counting cells. The composition of each fraction was determined by ^{19}F n.m.r. spectroscopy. Mass balances were > 90% unless $\text{CCl}_3\text{CClF}_2$ was a large component. Radiochemical balances were > 90% except in some experiments at > 623 K where large ^{18}F losses, presumed to be loss of labile H^{18}F from the catalyst, were encountered.

RESULTS

Reactions of dichlorotetrafluoroethanes with HF- and H^{18}F - treated catalysts

Flowing HF over pelleted chromia catalyst at 623 K results in the uptake of HF by the catalyst. The magnitude of the HF uptake, determined by using H^{18}F of measured specific count rate, depends on the catalyst sample's history, for example those of previously fluorinated samples are less than those obtained using fresh catalyst, however uptake is always in the range 0.3 - 1.2 mmol HF (g catalyst) $^{-1}$, Table 1. Dichlorotetrafluoroethane, mole ratio $\text{CClF}_2\text{CClF}_2$ (114) : CCl_2FCF_3 (114a) = 12.8 : 1.0, react with HF-treated fresh catalyst under flow conditions at 698 K to give CClF_2CF_3 (115) and $\text{C}_2\text{Cl}_2\text{F}_4$ isomers as major products. The compounds $\text{CCl}_2\text{FCClF}_2$ (113) and $\text{CCl}_3\text{CClF}_2$ (112a) are minor products and a trace of C_2F_6 (116) is also observed.

A typical product distribution with time, determined by gas chromatography, is shown in Figure 1(a). Assuming that the feed rate (F molecule min^{-1}) of $\text{C}_2\text{Cl}_2\text{F}_4$ is constant and is the quotient of the number of feed molecules and the time, the number of molecules contacting the catalyst at any given time is Fvx^{-1} , where $v \text{ cm}^3$ is the catalyst volume and $x \text{ cm}^3 \text{ min}^{-1}$ is the flow rate. It then follows that the number of substrate molecules reacting (Z) is given by equation (3)

$$Z = Fvx^{-1} - (\text{number in effluent}) \quad (3)$$

TABLE 1

^{18}F treatment of catalysts and catalyst count rates

| Experiment* | ^{18}F used cm^3 liq. | ^{18}F treatment at 623 K flow time min | Initial Count rate [†] count s^{-1} | ^{18}F taken up by catalyst mmol g^{-1} | Count rate after reaction [†] count s^{-1} | ^{18}F retained by catalyst % |
|-------------|--|--|---|---|--|--|
| 1 | 3.5 | 25 | 942 ± 3 | 0.94 | 777 ± 3 | 82.4 |
| 2 | 3.5 | 30 | 2169 ± 5 | 1.02 | 2067 ± 5 | 95.3 |
| 3 | 3.5 | 20 | 729 ± 3 | 0.97 | 425 ± 2 | 58.3 |
| 4 | 3.5 | 30 | 2712 ± 5 | 1.19 | 2825 ± 5 | |
| 5 | 4.0 | 25 | 409 ± 2 | 0.30 | 232 ± 2 | 56.7 |
| 6 | 3.5 | 25 | 836 ± 3 | 0.25 | 407 ± 2 | 48.6 |
| 7 | 3.5 | 30 | 793 ± 3 | 1.06 | 505 ± 2 | 63.6 |
| 8 | 3.5 | 25 | 349 ± 2 | 0.83 | 241 ± 2 | 69.0 |
| 9 | 3.5 | 25 | 1077 ± 3 | 0.45 | 399 ± 2 | 37.0 |
| 10 | 4.0 | 30 | 859 ± 3 | 0.33 | 629 ± 3 | 73.2 |
| 11 | 4.0 | 30 | 564 ± 2 | 0.31 | 322 ± 2 | 50.6 |

* Nos. 1 - 4 and 7 - 8 fresh catalyst; nos. 5 - 6 and 9 - 11 used catalyst.

† Determined by counting a catalyst sample in situ. Nos. 1 - 6 reactions with $\text{C}_2\text{Cl}_2\text{F}_4$; nos. 7 - 11 reactions with $\text{CCl}_2\text{FCClF}_2$.

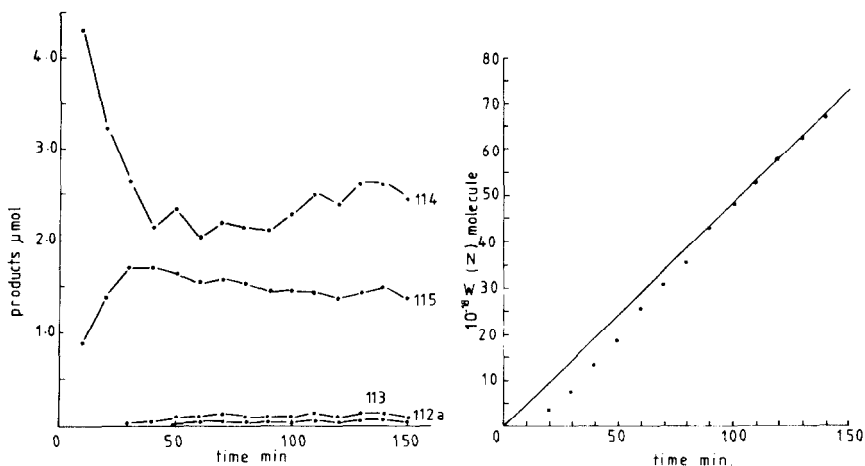


Fig. 1(a) Product distribution with time in the reaction $C_2Cl_2F_4$ + HF-treated catalyst at 698 K. (b) $\Sigma(Z)$ molecule vs. time (min) for the same reaction.

Numbers of effluent molecules are calculated from G.C. traces, making allowance for the difference in catalyst and sampling loop volumes.

Summations of G.C. data for two experiments, Table 2, indicate mass balances are > 95%, that the yields of $CClF_2CF_3$ are 36 - 34%, and that the ratio $CClF_2CF_3 : C_2Cl_2F_4$ in the product is 0.58. Plots of $\Sigma(Z)$ vs. time, Figure 1(b), are linear in the later stages of the reaction but deviate initially. The observed behaviour indicates that the reaction is zero order with respect to gaseous $C_2Cl_2F_4$ at least in its later stages.

The behaviour of $C_2Cl_2F_4$ when flowed over $H^{18}F$ -treated catalyst is similar to that described above except that its degree of conversion to fluorinated and chlorinated products was lower due to the necessarily shorter reaction times. Radiochemical data for the reactions are given in Tables 1 and 3 and the identified products in Table 4. In each case retention of ^{18}F activity by the catalyst after $C_2Cl_2F_4$ flow is significant, for example after reactions at 698 - 703 K, the proportion of ^{18}F activity remaining is in the range 59-48%. Obviously not all of the fluoride species on the catalyst is catalytically active.

TABLE 2
Reactions of $C_2Cl_2F_4$ or CCl_2FCClF_2 with HF-treated catalysts*

| Reactant | Wt. of Catalyst | Temperature K | Flow time min | Av. flow rate $cm^3 \text{ min}^{-1}$ | G.C. data | |
|----------------|---------------------|------------------|------------------|--|--|--|
| | | | | | $\Sigma(\text{Reactant contacting catalyst})$ μmol | $\Sigma(\text{Products})$ μmol |
| $C_2Cl_2F_4$ | 6.2619 [†] | 698 | 120 | 32.6 ± 6.2 | 247.8 | 2.1 4.4 153.4 89.5 2.7 |
| $C_2Cl_2F_4$ | 6.2619 [†] | 698 | 150 | 30.0 ± 0.6 | 291.0 | 2.6 5.8 170.6 99.3 trace |
| CCl_2FCClF_2 | 4.4330 [‡] | 703 | 180 | 21.0 ± 0.8 | 291.0 | 33.8 206.3 34.7 9.3 - |

* Catalysts treated by flowing HF for 30 - 55 min at 623 K. 112a, CCl_3CClF_2 ; 113, CCl_2FCClF_2 ; 114, $CClF_2CClF_2$; 114a, CCl_2FCF_3 ; 115, $CClF_2CF_3$; 116, C_2F_6 .

[†] Fresh catalyst. [‡] Used catalyst.

TABLE 3
Reactions of $C_2Cl_2F_4$ with [^{18}F]-labelled catalysts

| Experiment* | CClF ₂ CClF ₂ + CCl ₂ FCF ₃ | | Flow time min | Temperature K | Count rate of product collected at | | Incorporation of ¹⁸ F in total product %† |
|-------------|---|------|------------------|------------------|---------------------------------------|--------------------------------|---|
| | mmol | mmol | | | 173 K count s ⁻¹ | 113 K count s ⁻¹ | |
| 1 | 7.27 | 0.57 | 30 | 623 | 692 ± 3 | - | 8.7 |
| 2 | 7.54 | 0.59 | 30 | 623 | 2052 ± 5 | - | 11.3 |
| 3 | 8.69 | 0.68 | 30 | 698 | 1280 ± 4 | 45 ± 1 | 21.6 |
| 4 | 8.50 | 0.66 | 30 | 698 | 3938 ± 7 | 332 ± 2 | 18.7 |
| 5 | 5.75 | 0.45 | 30 | 698 | 387 ± 2 | 97 ± 1 | 22.4 |
| 6 | 9.00 | 0.70 | 35 | 703 | 181 ± 1 | 12 ± 1 | 2.8 |

* Numbers correspond to those in Table 1.

† Based on initial count rates of the catalyst (Table 1)

TABLE 4

Product from reactions of $C_2Cl_2F_4$ with [^{18}F]-labelled catalysts

| Experiment* | Collected at 173 K mmol | | | | Collected at 113 K mmol | | |
|-------------|-------------------------|------|------|------|-------------------------|---------|------|
| | 113 | | 114 | | 114a | | 115 |
| | 113a | 113 | 114a | 114 | 114a | 114a | 115 |
| 1 | - | - | 6.99 | 0.42 | 0.15 | - | - |
| 2 | - | - | 7.14 | 0.40 | 0.06 | - | - |
| 3 | 0.34 | 0.06 | 6.82 | 0.62 | 0.62 | 0.0200g | - |
| 4 | 0.21 | 0.02 | 7.37 | 0.52 | 0.39 | 0.08 | 0.01 |
| 5 | 0.27 | - | 4.79 | 0.35 | - | 0.51 | 0.04 |
| 6 | - | - | 8.24 | 0.60 | - | 0.47 | 0.04 |

* Numbers correspond to Tables 1 and 3. Product analyses by ^{19}F n.m.r. spectroscopy. For count rates see Table 3. 113, CCl_2FCClF_2 ; 113a, CCl_3CF_3 ; 114, $CClF_2CClF_2$; 114a, CCl_2CF_2 ; 115, $CClF_2CF_3$.

Although incorporation of ^{18}F activity in the products is observed in all cases, the degree of incorporation observed depends on the reaction temperature and on the history of the catalyst sample. Reactions carried out at 698 K with previously unused catalyst (reactions 3 and 4 in Table 3) result in approximately 20% ^{18}F incorporation, the products (Table 4) being $\text{CClF}_2\text{CClF}_2$, CCl_2FCF_3 , CClF_2CF_3 , some $\text{CCl}_2\text{FCClF}_2$, and a trace of CCl_3CF_3 . At 623 K incorporation of ^{18}F in the products, $\text{CClF}_2\text{CClF}_2$, CCl_2FCF_3 , and CClF_2CF_3 , is only 9 - 11% (reactions 1 and 2, Tables 3 and 4). The behaviour of extensively fluorinated catalysts (e.g. reactions 5 and 6 in Tables 3 and 4) is less reproducible. The yield of CClF_2CF_3 in reaction 5 is very small although ^{18}F incorporation in the products is significant, but in reaction 6 ^{18}F incorporation is barely detectable and no CClF_2CF_3 was observed. Although it was not possible to determine specific ^{18}F count rates of the individual products, their relative order may be estimated from those reactions in which two product fractions were counted and analysed by n.m.r. spectroscopy. For example the data obtained from reaction 4 indicate the order of specific count rates $\text{CClF}_2\text{CF}_3 > \text{CClF}_2\text{CClF}_2$, the derived values, assuming that $\text{C}_2\text{Cl}_3\text{F}_3$ isomers are inactive and that specific count rates of $\text{C}_2\text{Cl}_2\text{F}_4$ isomers are equal, are 436 and 1277 count $\text{s}^{-1} \text{mmol}^{-1}$ respectively. Although the derived count rates depend upon the assumptions made, the relative order does not. The data are not consistent with all components having equal specific count rates.

Reactions of 1,1,2-trichloro - 1,2,2-trifluoroethanes with HF- and H^{18}F - treated catalysts

The reaction between $\text{CCl}_2\text{FCClF}_2$ and HF-treated, extensively fluorinated catalyst at 703 K results in a mixture of $\text{CCl}_3\text{CClF}_2$ (112a), $\text{CCl}_2\text{FCClF}_2$ (113), $\text{C}_2\text{Cl}_2\text{F}_4$ isomers (114 + 114a) and CClF_2CF_3 (115), Table 2. The latter is a minor component and was not observed as a product in reactions involving HF-treated, fresh catalyst at 623 K, Table 5. The G.C. mass balance for the 703 K reaction was satisfactory but those at 623 K were not, however overall ratios of products were determined, Table 5. Formation of more highly chlorinated products is a feature of these reactions, and the distribution of products sampled at various times during a reaction, Figure 2, indicates that $\text{CCl}_3\text{CClF}_2$ is 'held-up' significantly in the reactor and exit line. This may mean that a 'build-up' of chlorine-containing species occurs on the catalyst during the early stages of its use.

TABLE 5

Reactions of $\text{CCl}_2\text{FCClF}_2$ with HF-treated catalyst at 623 K*

| Wt. of Catalyst g | Flow time min | Av. flow rate $\text{cm}^3 \text{min}^{-1}$ | Overall product ratio determined from G.C. sampling | | |
|----------------------|------------------|--|--|-------|-------|
| | | | 112a | : 113 | : 114 |
| 4.4191 | 135 | 31.8 ± 0.8 | 2.4 | 2.6 | 1.0 |
| 4.4165 | 180 | 24.2 ± 1.5 | 2.2 | 2.7 | 1.0 |
| 4.4165 | 165 | 26.7 ± 1.7 | 2.5 | 3.1 | 1.0 |

* Fresh catalyst treated by flowing HF for 20-30 min at 623 K. 112a, $\text{CCl}_3\text{CClF}_2$; 113, $\text{CCl}_2\text{FCClF}_2$; 114, $\text{CClF}_2\text{CClF}_2$.

^{18}F data and product yields for reactions of $\text{CCl}_2\text{FCClF}_2$ with H^{18}F -treated, fresh or previously fluorinated catalysts are given in Tables 6 and 7 respectively, and the appropriate H^{18}F uptakes are contained in Table 1. Reactions at 623 K using fresh catalyst (nos. 7 and 8) lead to $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCClF}_2$, $\text{CClF}_2\text{CClF}_2$, and minor quantities of CCl_2FCF_3 . Incorporation of ^{18}F in the products is 24 - 28%. One of the fluorinated catalysts used (reaction 8) shows similar behaviour, although product yields are lower and a small quantity of CCl_3CF_3 is produced. Specific ^{18}F count rates determined for the products from this reaction, assuming $\text{CCl}_3\text{CClF}_2$ to be inactive, are 161 and 2139 $\text{count s}^{-1} \text{mmol}^{-1}$ for $\text{C}_2\text{Cl}_3\text{F}_3$ and $\text{C}_2\text{Cl}_2\text{F}_4$ isomers respectively. The other fluorinated catalyst used was less effective, and no reaction was observed below 703 K. Even at this temperature the extent of reaction is small (reactions 10 and 11).

TABLE 6
 Reactions of $\text{CCl}_2\text{FCClF}_2$ with [^{18}F]-labelled catalysts

| Experiment* | $\text{CCl}_2\text{FCClF}_2$ mmol | Flow time min | Temperature K | Count rates of products collected at | | Incorporation of ^{18}F in products % [†] |
|-------------|--------------------------------------|------------------|------------------|---|--------------------------------|--|
| | | | | 233 K count s ⁻¹ | 173 K count s ⁻¹ | |
| 7 | 9.32 | 40 | 623 | 1095 ± 3 | 196 ± 2 | 23.8 |
| 8 | 7.16 | 30 | 623 | 570 ± 2 | 93 ± 1 | 27.8 |
| 9 | 8.20 | 25 | 623 | 1392 ± 4 | 481 ± 2 | 32.9 |
| 10 | 14.1 | 35 | 703 | 1119 ± 3 | 45 ± 1 | 16.5 |
| 11 | 14.7 | 35 | 703 | 895 ± 3 | 62 ± 1 | 20.7 |

* Numbers correspond to those in Table 1. † Based on initial count rates of the catalyst (Table 1).

TABLE 7

Products from reactions of $\text{CCl}_2\text{FCClF}_2$ with [^{18}F]-labelled catalysts

| Experiment* | Collected at 233 K mmol | | | | Collected at 173 K mmol | | | | | |
|-------------|-------------------------|-------|------|------|-------------------------|------|------|-------|-------|-------|
| | 112a | 113 | 113a | 114 | 114a | 112a | 113 | 113a | 114 | 114a |
| 7 | 0.22 | 6.37 | - | 0.61 | 0.04 | - | 0.82 | - | 0.36 | 0.03 |
| 8 | 0.27 | 4.85 | - | 0.67 | 0.05 | 0.04 | 0.65 | - | 0.58 | 0.07 |
| 9 | 0.06 | 6.20 | 0.04 | 0.13 | 0.05 | - | 0.85 | 0.01 | 0.16 | trace |
| 10 | - | 10.99 | 0.19 | 0.12 | 0.07 | - | 0.68 | trace | trace | trace |
| 11 | 0.08 | 11.48 | 0.03 | 0.13 | 0.09 | 0.01 | 1.09 | 0.01 | trace | trace |

* Numbers correspond to Tables 1 and 6. Product analyses by ^{19}F n.m.r. spectroscopy. For count rates see Table 6. 112a, $\text{CCl}_3\text{CClF}_2$; 113, $\text{CCl}_2\text{FCClF}_2$; 113a, CCl_3CF_3 ; 114, $\text{CClF}_2\text{CClF}_2$; 114a CCl_2FCF_3 .

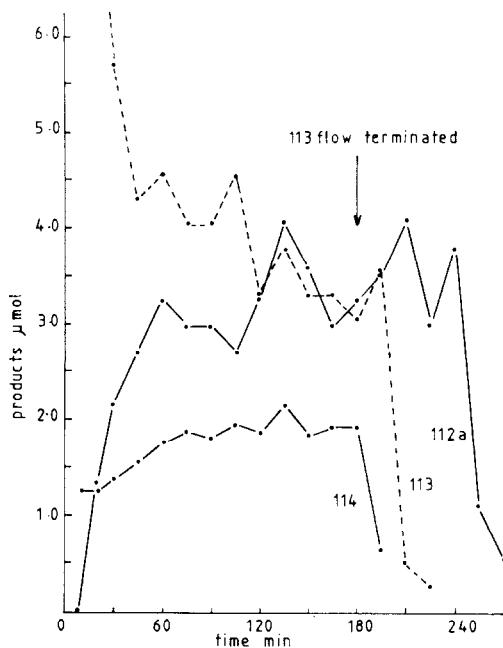
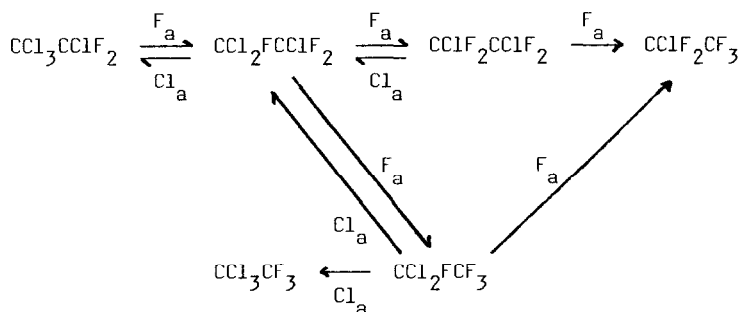


Fig. 2. Product distribution with time in the reaction $\text{CCl}_2\text{FCClF}_2 + \text{HF}$ -treated catalyst at 623 K.

DISCUSSION

The present work differs from the synthetic investigations carried out previously [1,2,4] in that HF or H^{18}F and the chlorofluorocarbon were flowed separately over the chromia catalyst rather than as a mixture. This procedure results in relatively low conversions to fluorinated products, but it enables the involvement of a surface fluorine-containing species to be unambiguously demonstrated. Although adsorption of HF has been inferred from the reaction kinetics of carbon tetrachloride fluorination in the presence of aluminium trifluoride [9], the use of [^{18}F]-labelled HF allows the adsorption to be directly monitored, and demonstrates that it is not completely reversible. In all the reactions studied there is significant ($\geq 37\%$ Table 1) retention of ^{18}F by the catalyst. Evidently other reactions, for example fluorination of chromia, occur during catalyst use.

The behaviour of 1,1,2-trichloro-1,2,2-trifluoroethane and the dichlorotetrafluoroethanes can be rationalised on the basis of a series of related halogen-exchange reactions. These are summarised in the Scheme, in which F_a and Cl_a represent fluorine- and chlorine- containing species present on the chromia surface.



Scheme

The ^{18}F tracer experiments provide direct evidence for the fluorination steps $CClF_2CClF_2 \longrightarrow CClF_2CF_3$ and $CCl_2FCClF_2 \longrightarrow CClF_2CClF_2$; both are important reactions under the conditions used. The reaction $CCl_2FCClF_2 \longrightarrow CCl_2FCF_3$ is of minor importance but does occur. From the limited data obtained for the process $CCl_2FCF_3 \longrightarrow CClF_2CF_3$, it appears that the asymmetric isomer is fluorinated more readily than is $CClF_2CClF_2$.

The product distributions observed from both substrates, CCl_2FCClF_2 and $C_2Cl_2F_4$ isomers, are consistent with the ease of fluorination of a C-Cl bond increasing in the order $-CClF_2 < -CCl_2F$. This is in keeping with the results obtained using other fluorinating agents, for example Sb^{III} , Sb^V , chloride, fluoride mixtures [10]. Exact descriptions for the transition states of the fluorinations cannot be given, but it is likely that prior adsorption of the chlorofluoroethane is required. Adsorption of $CClF_2CClF_2$ and chlorofluoromethanes on lanthanide trifluorides and other trihalides has been suggested from an i.r. study [11]. Although direct evidence for adsorption in the present case has not yet been obtained, circumstantial evidence comes from the reaction of $C_2Cl_2F_4$ which approximates to zero-order in gaseous $C_2Cl_2F_4$, Figure 1(b).

The observation of $\text{CCl}_2\text{FCClF}_2$ and $\text{CCl}_3\text{CClF}_2$ as products from reactions involving $\text{C}_2\text{Cl}_2\text{F}_4$ isomers and $\text{CCl}_2\text{FCClF}_2$ indicates that the chlorination reactions $\text{CClF}_2\text{CClF}_2 \longrightarrow \text{CCl}_2\text{FCClF}_2$, $\text{CCl}_2\text{FCClF}_2 \longrightarrow \text{CCl}_3\text{CClF}_2$, and possibly $\text{CCl}_2\text{FCF}_3 \longrightarrow \text{CCl}_2\text{FCClF}_2$ occur. The observation of CCl_3CF_3 as a trace product in some reactions, Table 7, suggests that $\text{CCl}_2\text{FCF}_3 \longrightarrow \text{CCl}_3\text{CF}_3$ is possible. Chlorination is particularly important in experiments involving $\text{CCl}_2\text{FCClF}_2$ at 625 K. The fate of chlorine-containing species formed from the fluorination reactions was not investigated, but it is reasonable to assume that they are present, at least in part, as surface species on chromia and can take part in further reaction.

There are at least three different types of fluoride present on chromia as a result of HF treatment [12] and the ^{18}F labelling of $\text{CCl}_2\text{FCClF}_2$ and $\text{CClF}_2\text{CClF}_2$ observed in the reactions of these compounds could be the result either of direct ^{18}F - for ^{19}F exchange on the H^{18}F -treated chromia, or of sequential chlorination then fluorination reactions. Although the former route cannot be excluded completely, we favour the latter as being more in keeping with the overall experimental observations. When $\text{CCl}_2\text{FCClF}_2$ is flowed over H^{18}F -treated chromia at temperatures below 623 K the degree of ^{18}F incorporation in the products is approximately 10%. The mixture obtained is predominantly $[\text{}^{18}\text{F}]\text{-CCl}_2\text{FCClF}_2$, but traces of $\text{CCl}_3\text{CClF}_2$ and $\text{CClF}_2\text{CClF}_2$ are always present. There is no evidence that ^{18}F exchange occurs prior to the fluorination and chlorination reactions. Similarly flowing $\text{C}_2\text{Cl}_2\text{F}_4$ isomers over H^{18}F -treated chromia at 623 K results in ^{18}F incorporation in the products of approximately 10%, reactions 1 and 2 in Table 3. The products under these conditions, Table 4, are $[\text{}^{18}\text{F}]\text{-C}_2\text{Cl}_2\text{F}_4$ and a small quantity of $[\text{}^{18}\text{F}]\text{-CClF}_2\text{CF}_3$. $\text{CCl}_2\text{FCClF}_2$ is not observed, but under these conditions it would be expected to react readily to give $[\text{}^{18}\text{F}]\text{-CClF}_2\text{CClF}_2$ and $[\text{}^{18}\text{F}]\text{-CCl}_2\text{FCF}_3$, Tables 6 and 7. In those reactions where the specific count rates of $[\text{}^{18}\text{F}]\text{-C}_2\text{Cl}_{6-n}\text{F}_n$ and $[\text{}^{18}\text{F}]\text{-C}_2\text{Cl}_{5-n}\text{F}_{n+1}$, $n = 4$ or 3 , have been compared, those of the fluorinated products are greater than those of the reactants, $\text{C}_2\text{Cl}_2\text{F}_4$ or $\text{C}_2\text{Cl}_3\text{F}_3$. This is to be expected if the labelling route for the latter involves two events at the chromia surface.

Our proposed model involves fluorination and chlorination reactions, related by the active species for the latter originating from the former. However, there is no reason to believe that fluorination and chlorination reactions are concerted as is a requirement for the dismutation reaction postulate [2,4]. Similarly direct isomerization is not a necessary postulate to explain the distribution of products observed.

REFERENCES

- 1 M. Vecchio, G. Gropelli and J.C. Tatlow, *J. Fluorine Chem.*, 4 (1974) 117.
- 2 L. Kolditz, G. Kauschka and W. Schmidt, *Z. Anorg. Allg. Chem.*, 434 (1977) 41.
- 3 L. Kolditz, U. Calov, G. Kauschka and W. Schmidt, *Z. Anorg. Allg. Chem.*, 434 (1977) 55.
- 4 L. Marangoni, C. Gervasutti and L. Conte, *J. Fluorine Chem.*, 19 (1981/82) 21.
- 5 L. Marangoni, G. Rasia, C. Gervasutti and L. Colombo, *Chem. Ind. (Milan)*, 64 (1982) 135.
- 6 L. Kolditz, V. Nitzsche, G. Heller and R. Stösser, *Z. Anorg. Allg. Chem.*, 476 (1981) 23.
- 7 J. Kijowski, G. Webb and J.M. Winfield, *J. Fluorine Chem.*, 24 (1984) 133.
- 8 J.E. Whitley, Scottish Research Reactor Centre, Report No. SRRC 26/68; *Nucl. Sci. Abs.*, 22 (1968) 30592.
- 9 G.P. Gambaretto, F. Avezzu and E. Gola, *J. Appl. Chem. Biotechnol.*, 23 (1973) 175.
- 10 e.g. W.A. Sheppard and C.M. Sharts, 'Organic Fluorine Chemistry,' W.A. Benjamin, Inc., 1969, pp.76-7.
- 11 M.D. Taylor and T.-T. Cheung, *J. Inorg. Nucl. Chem.*, 35 (1973) 3499.
- 12 J. Kijowski, G. Webb and J.M. Winfield, unpublished work.