Radiotracers in Fluorine Chemistry. Fluorine-18 Exchange between Group I Fluorides and Trifluoroacetyl Fluoride or Sulphur Tetrafluoride. The Effect of Group I Fluorides on Chlorine-36 Exchange between Chlorine and Sulphur Chloride Pentafluoride

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Fluorine-18 exchange has been observed between Group I fluorides (Cs–Li inclusive) and trifluoroacetyl fluoride or sulphur tetrafluoride at 150 and 50 °C. In all cases the order of exchange observed is Cs > Rb > K > Na > Li. Chlorine-36 exchange between chlorine and sulphur chloride pentafluoride at 150 °C is enhanced by the presence of Group I fluorides. The order of enhancement parallels the order of fluorine-18 exchange ability. The results are discussed in relation to the formation of the anions $C_2F_5O^-$ and SF_5^-.

CAESIUM fluoride behaves as a catalyst for the addition of fluorine [1] or chlorine monofluoride [2] across the carbonyl group of a perfluoroacyl fluoride, to form a perfluoroalkyl-fluoroxo compound or -hypochlorite respectively, and in the formation of sulphur chloride pentafluoride from sulphur tetrafluoride and ClF.[3] Chlorine and CsF react with SF_4 or trifluoromethyl sulphur trifluoride to give SF_5Cl or trifluoromethyl sulphur chloride tetrafluoride.[4] These reactions, and others which are initiated or catalysed by fluoride ion,[5] may involve complex fluoro-anions, *e.g.* $(R_f)_2CFO^-$, SF_5^-, as intermediates. The use of metal fluorides other than CsF leads either to decreased yields or to alternative products. For example, a detailed study of the reaction between carbonyl fluoride and F_2 in the presence of various fluorides has shown that although CsF is a good catalyst for the formation of CF_3OF, CF_3OOCF_3 is the main product when silver fluoride catalysts are used.[6]

Radiotracer studies using ^{18}F and ^{36}Cl are being undertaken in an attempt to further the understanding of the role of metal fluorides in this type of reaction. In this paper we report the results of ^{18}F exchange between Group I fluorides (Cs—Li inclusive) and $CF_3C(O)F$ or SF_4, systems for which the logical intermediates $C_2F_5O^-$ or SF_5^-, have been, at least partially, characterised,[4a,7] and the effect of Group I fluorides on the ^{36}Cl exchange between Cl_2 and SF_5Cl.

The use of ^{18}F as a tracer is well established.[8] Exchange in the NaF, UF_6 system occurs *via* Na_2UF_8,[9] and ^{18}F labelled BF_3, SiF_4, PF_5, POF_3, AsF_5, SF_4, SOF_2, and SeF_4 have been prepared by their passage over heated $Li^{18}F$.[10] In one of the few cases where the behaviour of different metal fluorides has been compared, exchange between Group I fluorides and hexafluoropropene has been described.[11]

EXPERIMENTAL

Standard vacuum and dry-box techniques were used throughout. Sulphur chloride pentafluoride (Peninsular ChemResearch) and chlorine (Matheson C.P. Grade) were dried over P_2O_5 for several hours, sulphur tetrafluoride (Peninsular ChemResearch) was purified *via* its adduct with BF_3.[12] Trifluoroacetyl fluoride, hexafluoroacetone, and hexafluoropropene (all from Peninsular ChemResearch) and boron trifluoride (Air Products Ltd.) were used as received. No impurities were evident in their i.r. spectra except for a small quantity of SF_6 in SF_5Cl, and no hydrolysis was detected in subsequent exchange reactions. Group I fluorides (B.D.H. Optran grade) were dried by at least three cycles of pumping at 20° and heating *in vacuo* at 150 °C for 3 h.

Radioactivity Measurement.—^{18}F and ^{36}Cl activities were determined using a NaI well scintillation counter (Ekco Instruments), well dimensions $\frac{25}{16} \times \frac{25}{32}$ in. diameter, samples being contained in Pyrex ampoules of uniform bore and fitted with P.T.F.E., glass stop-cocks (Fischer and Porter). Solids were counted as aqueous solutions (5 ml), and volatile compounds in the gas phase. The pressure variation over the range used was found to have no effect on the counting efficiency. Reproducible counts were obtained in all cases.

Preparation of Labelled Compounds.—^{18}F was prepared by neutron irradiation (1 h; flux = 3×10^{12} n cm^{-2} s^{-1}) of lithium carbonate (2 g, B.D.H. AnalaR) according to $^6Li(n, \alpha)t$; $^{16}O(t, n)^{18}F$ in the Scottish Universities Research Reactor, East Kilbride. Aqueous solutions of $Cs^{18}F$ were prepared according to the scheme [13]

$$Li^{18}F \xrightarrow[\text{distil}]{50\%\ H_2SO_4} H^{18}F \xrightarrow[0\,°C]{\text{CsOH aq}} Cs^{18}F\ \text{aq}$$

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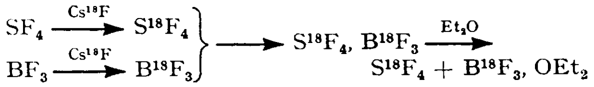
[13] J. E. Whitley, Scottish Research and Reactor Centre Report, No. 26/28.

The solution activities were typically 0·2 mCi. Neutralisation with 40% HF followed by evaporation and drying (1 h; i.r. lamp) gave solid $Cs^{18}F$ which was further dried *in vacuo*.

Volatile fluorides were labelled by exchange with $Cs^{18}F$ in either a Monel metal (95 ml) or a stainless steel (75 ml) pressure vessel (Hoke Ltd.) fitted with a Hoke needle valve. Typical conditions and activities are given in Table 1. It was convenient to label and purify SF_4 at the same time by the scheme:



$$\left.\begin{array}{l} SF_4 \xrightarrow{Cs^{18}F} S^{18}F_4 \\ BF_3 \xrightarrow{Cs^{18}F} B^{18}F_3 \end{array}\right\} \longrightarrow S^{18}F_4,\ B^{18}F_3 \xrightarrow{Et_2O} S^{18}F_4 + B^{18}F_3,\ OEt_2$$

The radiochemical purity of all ^{18}F labelled compounds was checked by decay curve determination over at least three half-lives. Calculated $t_{\frac{1}{2}}$ values agreed with the previously reported [14] value of 110 min.

$^{36}Cl_2$ was prepared from $K_2S_2O_8$ and $H^{36}Cl$ (Radiochemical Centre, Amersham) and diluted with inactive Cl_2 to give a specific activity of *ca.* 100 counts s^{-1} $mmol^{-1}$.

Exchange Reactions.—(*a*) *With* ^{18}F. A known weight of the labelled volatile fluoride whose specific activity had been determined, was allowed to exchange with a known weight of dried, inactive metal fluoride in a Monel metal or stainless steel pressure vessel under appropriate conditions. The volatile fraction was removed, reweighed, and the activities of both fractions were determined and corrected for ^{18}F decay. In all cases the radiochemical balance was $\geqslant 95\%$ and there was no evidence for hydrolysis or other chemical reactions.

(*b*) *With* ^{36}Cl. These were performed in the same manner as the ^{18}F exchange experiments. Known weights of $^{36}Cl_2$ and inactive SF_5Cl were allowed to exchange in the presence of a dried metal fluoride. Some experiments at lower temperatures were performed in glass bulbs (100 ml). The volatile fraction was separated by fractional distillation, SF_5Cl being held at −78 °C and Cl_2 at −120 °C. Traces of Cl_2 present in SF_5Cl were removed by shaking with mercury.

RESULTS AND DISCUSSION

The results of the exchange reactions (Tables 2—5) are expressed in terms of the fraction (f) of ^{18}F or ^{36}Cl exchanged; f is defined [11,15] by the expression

$$f = \frac{A_1}{A_1 + A_2} \Big/ \frac{n_1 m_1}{n_1 m_1 + n_2 m_2}$$

where A = activity (counts s^{-1}) after exchange, m (mmol) = quantity of a species with n exchangeable F or Cl atoms, and subscripts 1 and 2 refer to the initially inactive and active species respectively. Comparison between the $CF_3C(O)F$, $Cs^{18}F$ and the $(CF_3)_2CO$, $Cs^{18}F$ systems (Table 1) indicates that only one F atom in $CF_3C(O)F$ is readily exchanged under the conditions used. In all other cases n is assumed to equal the number of F or Cl atoms in the molecule. Errors in f due to weighings are negligible and those quoted arise from count rate determinations. Other sources of uncertainty arise from loss of radioactivity ($\leqslant 5\%$) and from variations in the composition of reaction mixtures. The variations in f with composition for the $CF_3C(O)^{18}F$, CsF and $S^{18}F_4$, CsF systems are relatively small, and it is considered that qualitative comparisons between different fluorides are valid.

TABLE 1

^{18}F Exchange between covalent fluorides and $Cs^{18}F$

Compound [a]	Conditions	Specific activity/ counts s^{-1} $mmol^{-1}$
SF_4	1 h, 150°	10,000
$CF_3C(O)F$	1 h, 150°	7000
$(CF_3)_2CO$	2 h, 150°	75
$CF_3{\cdot}CF{:}CF_2$	2 h, 150°	2000

[a] 20 mmol in each case, $Cs^{18}F$ = *ca.* 0·2 mCi.

^{18}F *Exchange.*—The degree of ^{18}F exchange between $CF_3C(O)^{18}F$ and Group I fluorides (Table 2) at 150 °C varies in the order Cs ≫ Rb > K > Na > Li, and a similar order, Cs ≫ Rb > K > Na ~ Li, is found at 50 °C. The fraction exchanged after 1 h with CsF is similar at both temperatures, but is considerably less with the other fluorides at 50 °C. Exchange between $S^{18}F_4$ and Group I fluorides (Table 3) at 150 °C varies

TABLE 2

^{18}F Exchange after 1 h between labelled $CF_3C(O)F$ and Group I fluorides

$CF_3C(O)F$ (mmol)	Group I fluorides (mmol)	Temperature (°C)	Fraction exchanged [a] f
3·05	2·23 (Cs)	150	0·160 ± 0·004
3·23	2·51 (Cs)		0·175 ± 0·004
3·38	5·40 (Cs)		0·206 ± 0·004
4·55	3·66 (Rb)		0·087 ± 0·003
4·16	2·63 (K)		0·048 ± 0·001
4·37	4·35 (Na)		0·026 ± 0·004
3·10	2·81 (Li)		0·0046 ± 0·0004
2·03	2·31 (Cs)	50	0·152 ± 0·006
5·88	6·05 (Rb)		0·036 ± 0·001
1·44	2·73 (K)		0·012 ± 0·002
1·04	1·39 (Na)		0·003 ± 0·001
2·94	1·67 (Li)		0·003 ± 0·001

[a] Defined in the text assuming only one F in $CF_3C(O)F$ is exchangeable.

TABLE 3

^{18}F Exchange after 1 h between labelled SF_4 and Group I fluorides

SF_4 (mmol)	Group I fluoride (mmol)	Temperature (°C)	Fraction exchanged [a] f
3·26	2·35 (Cs)	150	0·173 ± 0·004
2·32	1·82 (Cs)		0·237 ± 0·004
2·40	2·60 (Cs)		0·175 ± 0·004
1·88	4·39 (Cs)		0·144 ± 0·004
2·96	3·23 (Rb)		0·018 ± 0·001
3·56	2·52 (K)		0·0155 ± 0·0008
5·53	4·93 (Na)		0·0055 ± 0·0003
5·09	4·58 (Li)		0·0052 ± 0·0003
3·24	2·39 (Cs)	50	0·018 ± 0·002
3·80	3·49 (Rb)		0·007 ± 0·001
3·85	3·64 (K)		0·004 ± 0·001
2·27	2·44 (Na)		0·006 ± 0·002

[a] Defined in text assuming all F atoms are exchangeable.

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[14] The Radiochemical Manual, 2nd Edn., 1966, The Radiochemical Centre, Amersham.

[15] R. M. Adams, R. B. Bernstein, and J. J. Katz, *J. Chem. Phys.*, 1954, **22**, 13.

in the order Cs ≫ Rb ∼ K > Na ∼ Li. At 50 °C less exchange is observed in all cases, the order being Cs ≫ Rb ∼ K ∼ Na.

It has been shown previously that the stability of Group I element pentafluoroethoxides with respect to decomposition to MF + $CF_3(O)F$, increases with increasing size of M^+. $CsOC_2F_5$ decomposes rapidly at 80 °C and $RbOC_2F_5$ at 50 °C. The adduct formed between KF and $CF_3C(O)F$ decomposes at 20 °C, and no evidence has been found for adduct formation between NaF and $CF_3C(O)F$.[7] SF_4 is absorbed by CsF in a sealed reaction vessel above 110 °C to give $CsSF_5$, which dissociates to a significant extent at 150 °C.[4a] Apart from a brief mention of a $Me_4N^+F^-$, SF_4 adduct,[16] other SF_4 adducts with F^- ion appear to be unknown, but it is reasonable to suppose that their stabilities would depend on the size of the cation involved.

The results of the ^{18}F studies parallel previous synthetic work on $C_2F_5O^-$ and SF_5^- anions. It is considered that the anions are plausible models for the transition states in the exchange reactions, although their lifetimes will be very short under the conditions used. The situation is similar to that in the LiF, SiF_4 system where ^{18}F exchange occurs at lower temperatures than that required to form Li_2SiF_6.[10a] This work is also consistent with the postulate that CsF catalysed reactions of $CF_3C(O)F$ and of SF_4 involve complex fluoroanion intermediates.

The activity introduced into hexafluoropropene by reaction with $Cs^{18}F$ is far less than that introduced into $CF_3C(O)F$ or SF_4 under similar conditions (Table 1), and no exchange was detected between $C_3{}^{18}F_6$ and CsF under the conditions used for the other exchange reactions. If the exchange reaction proceeds according to $CF_3CF{:}CF_2 + {}^{18}F^- \rightleftharpoons CF_3{\cdot}\bar{C}F{\cdot}CF_2{}^{18}F$ (ref. 5), the probability of finding $^{18}F^-$ in a 1 : 1 molar mixture of initially labelled C_3F_6 and CsF is only 0·167, even when exchange is complete. The apparent absence of exchange when low specific activities are used may be rationalised if the rates of formation of $^{18}F^-$ ion and of ^{18}F decay are comparable. Previous work,[11] in which ^{18}F exchange between Group I fluorides and C_3F_6 was demonstrated, used much higher ^{18}F activities than those available to us in this work, generally higher temperatures, and a system in which C_3F_6 was continuously circulated over the fluoride while the temperature was varied. The order of exchange observed, Cs > Rb > Li > K > Na, is slightly different than the results obtained here, but is the same as the catalytic effect of metal fluorides on the oxidation of C_3F_6.[11c]

^{36}Cl *Exchange*.—If salts of the type $M^+SF_5^-$ are intermediates in the formation of SF_5Cl from $SF_4 + Cl_2 + MF$, ^{36}Cl exchange between Cl_2 and SF_5Cl might be expected to be enhanced in the presence of MF. This is found to be the case at 150 °C (Table 4), the order of enhancement being Cs > K > Na ∼ Li. Measurements at 50 °C (Table 5) indicate the exchange is enhanced by CsF and that a metal surface has a similar, though smaller, effect. The latter may be due to the formation of a metal fluoride surface layer. At 18 °C no exchange was observed in a glass vessel even in the presence of CsF, although exchange in a metal vessel does occur (Table 4).

TABLE 4

^{36}Cl Exchange after 16 h between labelled Cl_2 and SF_5Cl [a]

Cl_2 (mmol)	SF_2Cl (mmol)	Group I fluoride (mmol)	Temperature (°C)	Fraction exchanged [b] f
2·34	2·13	1·97 (Cs)	150	1·95 ± 0·15
1·94	1·86	1·90 (K)		1·67 ± 0·13
1·33	1·19	1·50 (Na)		1·53 ± 0·12
1·59	1·29	6·21 (Li)		1·48 ± 0·12
2·04	1·50			0·69 ± 0·04
2·04	2·01			0·29 ± 0·03
1·48	1·59			0·38 ± 0·03
1·21	1·12			0·41 ± 0·03
1·23	1·31	1·06 (Cs)	50	1·44 ± 0·12
3·64	5·00			0·38 ± 0·03
4·51	6·16			0·18 ± 0·03
2·20	3·50	1·00 (Cs)	18	0·45 ± 0·06
1·71	1·62	1·10 (Cs)		0·60 ± 0·06
1·17	1·20			0·24 ± 0·06
1·20	1·07			0·24 ± 0·03
3·81	5·30			0·24 ± 0·03

[a] In a metal vessel. [b] Defined in the text assuming all Cl atoms are exchangeable.

TABLE 5

^{36}Cl Exchange at 50 °C after various times between labelled Cl_2 and SF_5Cl in the presence of CsF

Cl_2 (mmol)	SF_5Cl (mmol)	CsF (mmol)	Time (h)	Fraction exchanged [a] f
In a metal vessel [b]				
0·88	1·09	1·06	1	0·21 ± 0·07
1·48	1·38		2	0·34 ± 0·06
1·51	1·54		4	1·03 ± 0·11
1·58	1·38		6	1·45 ± 0·12
1·23	1·31		16	1·44 ± 0·12
In a glass vessel [b]				
0·91	2·27	1·67	1	0·16 ± 0·01
0·93	1·09		2	0·3 ± 0·1
0·66	0·69		4	0·83 ± 0·06
1·50	1·64		6	1·28 ± 0·13
1·95	2·17		16	1·27 ± 0·13

[a] See note *b* Table 4. [b] Using the same sample of CsF in each exchange.

For a homogeneous exchange reaction, a value of $f = 1$ corresponds to complete exchange. The data in Table 5 indicate that measurements made after 16 h correspond to equilibrium. In most cases where a Group I fluoride is present $f > 1$, implying that isotopic fractionation has occurred. Similar effects have been observed in metal surface catalysed reactions of hydrocarbons,[17] but the isotope effect in the present work should be very small. Undoubtedly the mechanism of ^{36}Cl exchange is heterogeneous and complex, and no detailed studies have been attempted.

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CONCLUSIONS

CsF undergoes ^{18}F exchange with SF_4 and with $CF_3C(O)F$ far more readily than do other Group I fluorides, and has the greatest ability to enhance ^{36}Cl exchange between Cl_2 and SF_5Cl. Its behaviour appears to be related to its role in catalytic fluorination and similar reactions, and the use of radiotracers offers a convenient method of comparing ionic fluorides as potential catalysts.

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