Radiotracers in Fluorine Chemistry. Part II.[1] Fluorine-18 Exchange between Carbonyl Fluoride and Group I Fluorides. Effect of Dipolar, Aprotic Solvents †

By **C. Joy W. Fraser, David W. A. Sharp, Geoffrey Webb,** and **John M. Winfield,*** Chemistry Department, University of Glasgow, Glasgow G12 8QQ

Fluorine-18 exchange between carbonyl fluoride and Group I fluorides (Cs—Li inclusive) varies in the order Cs > Rb ≫ K > Na, Li at 423 K, and in the order Cs > Rb ≫ K, Na, Li at 323 K. Exchange is enhanced in the presence of acetonitrile or diglyme, the effect of the latter being particularly marked for LiF and NaF, but not in the presence of benzene or diethyl ether. The results are discussed in terms of the solvents' properties.

We have shown previously that fluorine-18 exchange between gaseous trifluoroacetyl fluoride or sulphur tetrafluoride and solid Group I metal fluorides varies in the order Cs > Rb > K > Na > Li.[1] The logical intermediates for these exchange reactions, $C_2F_5O^-$ or SF_5^-, belong to the class of complex fluoro-anions which are postulated as intermediate in reactions, which are catalysed or initiated by fluoride ion.[2] For example, fluorinated ethers may be prepared by reactions in which it is postulated that perfluoroalkoxide ions generated *in situ* react with olefins,[3] or perfluoroepoxides.[4] Related reactions involving perfluoroacyl fluorides can lead to perfluoroesters.[5] Fully or partially fluorinated alkoxides of Group I metals are well known.[6] They are often prepared using dipolar, aprotic solvents, for example, acetonitrile (MeCN) or diethylene glycol dimethyl ether (diglyme). Compounds such as $Cs^+OCF(CF_3)_2^-$ and $Cs^+OC_2F_5^-$ are appreciably soluble in these solvents unlike CsF. These solvents are also often used as media for reactions involving fluoride ion catalysis.[2-4]

For these reasons we wished to determine the effect of dipolar aprotic solvents on ^{18}F exchange between ionic and covalent fluorides, in particular to determine whether the identity of the cation would be dominant as is the case in gas–solid exchanges.[1] Carbonyl fluoride was chosen as the substrate for the following reasons. ^{18}F Exchange between F_2CO and Group I fluorides is readily observed. Trifluoromethoxides of Li and Na apparently cannot be isolated and those of K, Rb, and Cs decompose in MeCN at 298 K in the absence of a pressure of F_2CO.[6a] Reaction conditions could therefore be chosen such that the formation of solid $M^+OCF_3^-$ compounds, which would complicate the exchange results, would be unlikely.

The present work shows that ^{18}F exchange is enhanced in the presence of MeCN or diglyme, but not in the presence of benzene or diethyl ether. The effect of diglyme is particularly marked for NaF and LiF.

EXPERIMENTAL

Standard vacuum techniques were used throughout. Group I fluorides (B.D.H. Optran grade) were dried by at least three cycles of pumping at 293 K and heating *in vacuo*

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† No reprints available.

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at 423 K for 3 h. Carbonyl fluoride was prepared from carbonyl chloride (British Oxygen Co.) and NaF in MeCN,[6,7] and pentafluoropropionyl fluoride was prepared similarly from $C_2F_5C(O)Cl$ (Peninsular Chem Research). Both compounds were purified by low temperature trap-to-trap distillation and were stored in metal vessels over NaF. Their purity was monitored by their i.r. spectra and by molecular weight determination. MeCN, diglyme, C_6H_6, Et_2O, and dimethyl sulphoxide (DMSO) were purified and dried by standard methods,[8] and stored *in vacuo* over activated molecular sieves.

Radioactivity measurements and the preparation of ^{18}F labelled compounds were carried out as described previously.[1,9]

Exchange Reactions.—Gas–solid exchanges were performed in Monel metal vessels (95 ml) as described previously.[1] The radiochemical balance was $\geqslant 95\%$ in all cases. Exchanges in the presence of dipolar solvents were performed similarly, all manipulations being carried out *in vacuo* or in a Lintott inert atmosphere box where the concentrations of O_2 and H_2O were $\leqslant 10$ p.p.m. The metal vessels were thermostatted at 298 ± 0.5 K. There was no evidence for hydrolysis or alkoxide formation (i.r. spectra and mass balance) but the radiochemical balance was less satisfactory ($\geqslant 90\%$ for the results in MeCN or diglyme; $\geqslant 95\%$ for the results in benzene or diethyl ether).

^{18}F *Activities in Group I Fluorides in Solution.*—Samples of $M^{18}F$ (M = Cs—Li inclusive) containing M^+OH^- as a carrier were shaken with MeCN, DMSO, or diglyme (25 ml) for 1 h at room temperature. The solutions were filtered and the ^{18}F activities of 1 ml aliquots determined using a NaI well counter (Quartz Silice) and 100 channel analyser. The specific activities of all solutions were similar and were in the range 10^{-7}—10^{-8} Ci l^{-1}. It was not possible to establish whether equilibrium was obtained due to the short half-life of ^{18}F (112 min[10]). For this reason also it was not possible to make quantitative comparisons, but qualitatively for each solvent the activities of $Cs^{18}F$–CsOH solutions were less than those of $Li^{18}F$–LiOH. Solutions of $Li^{18}F$–LiOH in diglyme had greater activities than those in MeCN. In all cases the solution activities were very much less than those of the undissolved $M^{18}F$–MOH parts.

RESULTS AND DISCUSSION

^{18}F *Exchange in the Absence of Solvents.*—The results of exchange between labelled F_2CO and Group I fluorides at 423 and 323 K (Table 1) are expressed in terms of the fraction of ^{18}F activity exchanged (f). This is defined throughout unless stated to the contrary by the expression

$$f = \frac{A_1}{A_1 + A_2} \Big/ \frac{m_1}{m_1 + 2m_2}$$

where A_1 and A_2 (counts s^{-1}) are the activities of m_1 and m_2 (mmol) of Group I fluoride and F_2CO respectively. The quoted errors on f arise from count rate determinations. By analogy with the behaviour of $CF_3C(O)F$,[1] both F atoms in F_2CO are expected to be exchangeable and this is demonstrated in the F_2CO–CsF system.

A range of f values is observed in this system at 423 K which is not simply related to changes in stoicheiometry. The variations probably arise from changes in the surface properties of the CsF from sample to sample, and are readily apparent due to the large values of f. Nevertheless, the results (Table 1) clearly show that the exchange varies in the order Cs > Rb $\gg$ K > Na, Li at 423 K, and in the order Cs > Rb $\gg$ K, Na, Li at 323 K.

TABLE 1

^{18}F Exchange after 1 h between labelled F_2CO and Group I fluorides

F_2CO (mmol)	Group I fluorides (mmol)	Fraction exchanged f
(*a*) at 423 K		
1·93	1·84 (Cs)	1.07 ± 0.01
1·19	1·70 (Cs)	0.959 ± 0.006
2·13	2·21 (Cs)	0.550 ± 0.008
4·04	3·85 (Rb)	0.404 ± 0.007
1·86	1·63 (K)	0.131 ± 0.003
3·84	3·80 (Na)	0.048 ± 0.002
5·08	4·44 (Li)	0.033 ± 0.001
(*b*) at 323 K		
2·31	2·30 (Cs)	0.533 ± 0.004
2·97	2·90 (Rb)	0.351 ± 0.003
2·46	2·38 (K)	0.077 ± 0.002
2·78	2·80 (Na)	0.034 ± 0.002
3·62	3·71 (Li)	0.012 ± 0.0002
(*c*) at 298 K		
2·05	1·92 (Cs)	0.013 ± 0.001
2·18	1·35 (Cs)	0.010 ± 0.001

The exchanges are greater than in the corresponding $CF_3C(O)F$ systems,[1] the differences being particularly marked for CsF and RbF. In contrast ^{18}F exchange between $C_2F_5C(O)F$ and Group I fluorides is very small. For $C_2F_5C(O)F$ (1·55 mmol) and CsF (1·61 mmol) at 423 K $f = 0.101 \pm 0.001$ (assuming one exchangeable F atom[1]), and values for the other fluorides are <0.01. Exchange decreases between CsF and RC(O)F in the order R = F > CF_3 > C_2F_5 which is the order of decreasing electronegativity and increasing size of R. We suggest that both effects are important.

The pattern of exchange results reinforces a previous observation[1] that there is a strong correlation between the ability of a Group I fluoride to undergo exchange with RC(O)F molecules and the stability with respect to decomposition of the corresponding solid perfluoroalkoxide.[6a] It is also significant that $CF_3C(O)F$ and F_2CO can be separated by gas chromatography using a CsF, CaF_2 column, F_2CO having the longer retention time.[11] Chemisorption of the volatile substrate by the metal fluoride during the exchange process is strongly implied.

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^{18}F *Exchange in the Presence of Dipolar, Aprotic Solvents.*—The data in Tables 2—4 show that exchange between F_2CO and Group I fluorides is greatly enhanced in the presence of MeCN or diglyme but not in the presence of C_6H_6 or Et_2O. Considerable variations in the fractions exchanged are found for the MeCN and diglyme systems (the *f* values in Tables 2 and 3 are the maximum and minimum observed). Greater variation within a given F_2CO, MF system is expected with the introduction of a third component but it could result from the contamination of MF by quantities of alkoxide which would not be detected by i.r. spectroscopy or by the mass balance

TABLE 2

^{18}F Exchange after 1 h at 298 K between labelled F_2CO and Group I fluorides in the presence of acetonitrile (5 ml)

F_2CO (mmol)	Group I fluorides (mmol)	Fraction exchanged *f*
3·42	2·26 (Cs)	0·582 ± 0·008
2·26	2·39 (Cs)	0·524 ± 0·008
2·05	2·08 (Rb)	0·672 ± 0·008
3·04	2·63 (Rb)	0·416 ± 0·006
1·78	1·01 (K)	0·415 ± 0·006
2·00	1·82 (K)	0·167 ± 0·002
3·45	3·87 (Na)	0·010 ± 0·001
1·63	1·88 (Na)	0·016 ± 0·001
3·95	2·51 (Li)	0·060 ± 0·001
2·43	2·31 (Li)	0·033 ± 0·001

TABLE 3

^{18}F Exchange after 1 h at 298 K between labelled F_2CO and Group I fluorides in the presence of diglyme (5 ml)

F_2CO (mmol)	Group I fluorides (mmol)	Fraction exchanged *f*
2·64	2·63 (Cs)	0·407 ± 0·003
3·23	1·46 (Cs)	0·289 ± 0·002
2·37	2·27 (Rb)	0·475 ± 0·003
3·49	4·04 (Rb)	0·181 ± 0·001
1·45	1·38 (K)	0·856 ± 0·01
2·20	1·91 (K)	0·390 ± 0·003
2·28	2·12 (Na)	0·489 ± 0·003
3·32	4·08 (Na)	0·140 ± 0·002
3·20	3·25 (Li)	0·405 ± 0·003
3·85	3·86 (Li)	0·189 ± 0·002

TABLE 4

^{18}F Exchange after 1 h at 298 K between labelled F_2CO and CsF in the presence of diethyl ether or benzene (5 ml)

F_2CO (mmol)	CsF (mmol)	Fraction exchanged *f*
1·62	2·55 (ether)	0·063 ± 0·008
2·07	1·22 (ether)	0·033 ± 0·004
1·46	1·66 (benzene)	0·033 ± 0·002
1·86	2·20 (benzene)	0·010 ± 0·001

^{18}F Exchange in the presence of MeCN at 298 K varies in the order Cs, Rb > K ≫ Li, Na, the *f* values being comparable to, or larger than, those observed at 423 K in the absence of solvent. In the presence of diglyme there is no clear relationship between *f* and the identity of the Group I cation, but significant exchange is observed in each case. For CsF exchange is greater in the presence of MeCN than in the presence of diglyme, and the same is probably true for RbF. For the other three fluorides the reverse is the case, the differences being particularly marked for NaF and LiF.

Group I fluorides are normally regarded as being insoluble or of very low solubility in dipolar aprotic solvents. The only solubility data in the literature pertinent to the present work appears to be for NaF and KF in MeCN. The values at 298 K are 0·071 and 0·041 mmol/100 g solvent respectively.[11] An attempt was made in this work to determine the relative orders of solubility in MeCN, diglyme, and DMSO by measuring the ^{18}F activities of saturated solutions of $M^{18}F$ which was free from $M^{19}F$. The results may be ambiguous due to the short half-life of ^{18}F and to the presence of MOH as carrier but qualitative conclusions may be drawn. In each solvent LiF appears to be more soluble than CsF, analogous to the situation for other Group I halides in MeCN [12] or DMSO.[13] LiF appears to be more soluble in diglyme than in MeCN. There is little variation between the solutions however, and in all cases solubilities are very low.

The most obvious effect of a solvent is to allow exchange to occur under homogeneous conditions between solvated $(MF)_n$ ion aggregates and solvated F_2CO molecules *via* a transition state of the type $M^+(solv)OCF_3^-(solv)$. It is considered that heterogeneous exchange occurs also and is enhanced either by the solvent continuously exposing a fresh MF surface, or by co-ordination of solvent molecules at the M^+ surface sites decreasing interactions between M^+ and F^-, or by a combination of both effects. Both the dielectric constant of the solvent and its solvating properties are important therefore.

Of the four solvents examined, only MeCN has a high bulk dielectric constant [14] (at 298 K, MeCN **36**, C_6H_6 2·3, Et_2O 4·3). The dielectric constant of diglyme apparently has not been reported, but its dielectric permeability at 298 K is 7·23 compared to Et_2O which is 4·18.[15] Cation solvation by dipolar aprotic solvents is more important than anion solvation.[16] MeCN is a poor solvating agent to Group I cations,[17] and a similar situation will obtain for benzene and diethyl ether. Group I cations are strongly solvated by polyethers, particularly macrocyclic ethers,[18] and diglyme

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complexes for example $[K(diglyme)_3][Mo(CO)_5I]$ and $[M(diglyme)_n][Mo(CO)_5I]$ (M = Group I element) are well known.[19] Although F_2CO cannot be quantitatively recovered from DMSO, suggesting that a complex is formed in solution, there is no evidence for similar behaviour between F_2CO and MeCN, Et_2O, C_6H_6, or diglyme.

For ^{18}F exchange to be enhanced it is necessary that the solvent should have a high dielectric constant, for example MeCN, and/or should be a good donor towards the Group I cation, for example diglyme. The latter property is particularly important when smaller cations are involved. Solvents without either property, for example diethyl ether or benzene, have little or no effect on the exchange.

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