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Radiotracers in fluorine chemistry.
Part 16 [1]. A fluorine-18 study of the formation and lability of heptafluorotungstate(VI) and heptafluoromolybdate(VI) anions in acetonitrile and under heterogeneous conditions

M. Fouzi Ghorab and John M. Winfield*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ (UK)

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Abstract

An [^{18}F]-fluorine exchange study between various $[WF_7]^-$ salts and $WF_5{}^{18}F$ in MeCN at room temperature indicated that, as expected, exchange is rapid and complete. Rapid exchange also occurs between $[WF_7]^-$ and $MoF_5{}^{18}F$ and between $[MoF_7]^-$ and $WF_5{}^{18}F$ under similar conditions; the two heptacoordinate anions co-exist with their hexafluorides in MeCN solution. More surprisingly, there is observable [^{18}F] exchange between $[WF_7]^-$ salts and $WF_5{}^{18}F$ under heterogeneous conditions at room temperature. The behaviour observed and the behaviour of $MF_5{}^{18}F$, M = Mo or W, towards CsF under heterogeneous conditions, are interpreted in terms of exchange reactions occurring on the surface between $[MF_7]^-$ and adsorbed $MF_5{}^{18}F$.

Introduction

The formation of complex fluoro anions, in which the central atom has a coordination number greater than six, is a characteristic property of many high oxidation state binary fluorides. There has been renewed interest in this topic following the report of a good synthesis for anhydrous tetramethylammonium fluoride [2] and several seven- and eight-coordinated anions containing tellurium(VI) or iodine(VII) have been characterized structurally and spectroscopically [3]. It has been shown also that the structures of the salts containing the pseudo seven-coordinate anion $[IF_6]^-$ depend on the nature of the cation, the anion being dimeric in its $[Me_4N]^+$ salt and tetrameric with the smaller $[NO]^+$ cation [4].

The formation of high coordination number fluoro anions by the widely used, d-block Lewis acids MoF_6 and WF_6 is also well documented. The crystal structures of hepta- and octa-fluoromolybdates(VI) and their tungsten(VI) analogues have apparently not been reported but the vibrational spectra of several Group I salts, originally prepared from the Group I fluorides and the hexafluorides in IF_5 [5], have been used to infer structures for $[MF_7]^-$ and $[MF_8]^{2-}$, M = Mo or W. For example, D_{5h} symmetry has been suggested for

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*Author to whom all correspondence should be addressed.

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$[MF_7]^-$ in its Cs^+, Rb^+ [6] and $[NO]^+$ [7] salts, D_{5h} symmetry for $[WF_7]^-$ in its $[NF_4]^+$ salt [8] and D_{4d} symmetry for the anion in A_2MoF_8, A = Rb or K [6] and A_2WF_8, A = Cs, Rb, K [6] and $[NO]^+$ [7]*.

^{19}F NMR spectroscopic studies of the $[WF_7]^-$ anion in solution, while being consistent with the presence of the discrete anion, suggest that it may be in equilibrium with F^- and WF_6 [8–10]; certainly, exchange between $[WF_7]^-$ and WF_6 is rapid on the NMR timescale [9]. It appears, therefore, that W–F bonds in the anion are labile and following our recent [^{18}F]-fluorine radiotracer studies of bond lability in $[BF_4]^-$ and various hexafluorometallate(V) anions, both in MeCN [11] and under heterogeneous conditions [12], it was logical to examine the [^{18}F]-exchange behaviour of this anion. We find that the behaviour of $[WF_7]^-$ and $[MoF_7]^-$ (the latter has been examined in solution, apparently for the first time) differs from those anions previously examined, since [^{18}F] exchange is observable both in solution and under heterogeneous conditions.

Experimental

Except where noted below, instrumentation and the methods used to purify reagents and to prepare [^{18}F]-labelled compounds have been described previously [11, 12]. Thallium(I), solvated copper(II) and $[NO]^+$ heptafluorotungstates(VI) were prepared using literature methods [7, 9]. Caesium $[WF_7]^-$ and $[MoF_7]^-$ salts were prepared from CsF and the appropriate hexafluoride in MeCN at room temperature [11]. The combining ratio CsF MF_6 was 1:1 in both cases, the results of mass balance and [^{18}F] measurements (Table 1) being in excellent agreement.

TABLE 1

Reactions between CsF and [^{18}F]-labelled hexafluorides at room temperature in the presence of MeCN (1 cm^3)

Reactants (mmol)		Uptake of MF_6 (mmol) as determined from	
CsF	$MF_5{}^{18}F$	Mass balance	[^{18}F] count rate of solid[a]
0.58 ± 0.01	0.72 ± 0.01(Mo)	0.56 ± 0.02	0.53 ± 0.04
0.74 ± 0.01	1.36 ± 0.01(W)	0.75 ± 0.02	0.75 ± 0.04

[a] Calculated on the basis of complete consumption of CsF and complete [^{18}F] exchange between the product and unchanged $MF_5{}^{18}F$.

***Note added in proof**

X-Ray crystal structures of some $[WF_7]^-$, $[MoF_7]^-$ and $[WF_8]^{2-}$ salts reported very recently (A.-R. Mahjoub, S. Giese and K. Seppelt, *ACS 11th Winter Fluorine Conf.*, St. Petersburg, FL, Jan. 1993, Abs. 34) indicate that the anions have capped octahedral and square antiprismatic structures, respectively.

[^{18}F]-exchange reactions in MeCN

Exchange reactions were carried out in a Pyrex counting vessel whose body fitted into the well scintillation counter. The cell was fitted with a semicircular loop to prevent loss of solid during rapid separation of the reaction components by vacuum distillation and terminated in a Pyrex/PTFE stopcock (J. Young) and standard cone fitting. Solutions were made up by weight, solid $[MF_7]^-$ salts being added in a glove-box (H_2O content < 10 ppm) and MeCN (1 cm^3) being added by vacuum distillation. A weighed aliquot of [^{18}F]-labelled hexafluoride, whose specific count rate had been determined, was added to the mixture by distillation, and the mixture was warmed quickly to room temperature or to the reaction temperature to be used. During the reaction, the [^{18}F] count rate of the mixture was determined. After a suitable time, the components (solid and hexafluoride plus MeCN) were separated, counted in cells of identical geometry and their masses determined. Count rates were corrected for [^{18}F] decay and background. Radiochemical balances were always $>90\%$ and usually $>95\%$. Radiochemical counting errors were $<1\%$. The fraction of activity (f) exchanged between $MF_5{}^{18}F$ and the heptafluorometallate(VI) salt was determined from the relationship $f = (S_0 - S_t)/(S_0 - S_\infty)$, where S_0, S_t and S_∞ are respectively the specific [^{18}F] count rates [count min^{-1} (mmol MF_6)$^{-1}$] of $MF_5{}^{18}F$ before reaction, after reaction, and after reaction calculated on the basis of complete exchange.

[^{18}F]-exchange reactions under heterogeneous conditions

These reactions were carried out in a Pyrex double-limb counting vessel. Each limb was of identical geometry and fitted the well scintillation counter. The counting vessel was fitted with three Pyrex/PTFE stop-cocks, one on each limb and the third dividing the vessel into two compartments. The cell was calibrated before use. A weighed quantity of solid was added to one limb in the glove box and a weighed quantity of [^{18}F]-labelled hexafluoride, of measured specific count rate, added to the other limb by vacuum distillation. The quantity of $MF_5{}^{18}F$ was such that it was all in the vapour phase at room temperature. The stop-cock dividing the two limbs was opened and the hexafluoride vapour allowed to equilibrate between the two compartments. Each limb was counted alternately over 0.75–1.0 h and plots of decay-corrected [^{18}F] count rates due to solid plus vapour and due to vapour only, both versus time, constructed. Subtraction of the latter from the former gave the relationship between the [^{18}F] count rate of the solid versus time. After reaction, $MF_5{}^{18}F$ was removed by vacuum distillation, added to MeCN (1 cm^3) and both components were counted and weighed.

Results and discussion

Lability of $[MF_7]^-$, M = W or Mo, anions in MeCN

[^{18}F] exchange between $WF_5{}^{18}F$ and the $[WF_7]^-$ anion in MeCN solution is rapid and complete at room temperature (Table 2) as expected from previous NMR studies [8–10]. [^{18}F] exchange at 252 K is substantial; the different values obtained for the fraction of [^{18}F] activity exchanged (f) from

Tl^I and Cu^{II} salts (Table 2) is probably a reflection of the lower solubility of the latter resulting in incomplete dissolution at 252 K. In no case was there any evidence for a chemical reaction. Exchange was observed also between $NO[WF_6{}^{18}F]$, prepared *in situ* from FNO and $WF_5{}^{18}F$ [7], and WF_6 in MeCN at room temperature after 20 min. The behaviour observed can therefore be described by eqn. (1).

$$[WF_7]^- + WF_5{}^{18}F \rightleftharpoons [WF_6{}^{18}F]^- + WF_6 \qquad (1)$$

$[^{18}F]$ exchange between $[WF_7]^-$ and $MoF_5{}^{18}F$ and between $[MoF_7]^-$ and $WF_5{}^{18}F$ is substantial in MeCN at room temperature, i.e. $f > 0.9$ (Table 2). Although there was no evidence for a chemical reaction in the $NO[WF_7] + MoF_6$ case, the solid product isolated after the $Cs[WF_7] + MoF_6$ exchange reaction contained bands in its Raman spectrum attributable to both $[WF_7]^-$ and $[MoF_7]^-$; $\nu_{max.}$ 713 (vs), 442 (m) and 683 (m) cm^{-1} assigned to $\nu_1(A_1)$ and $\nu_8(E_1)$ of $[WF_7]^-$ and to $\nu_1(A_1)$ of $[MoF_7]^-$, respectively [6]. In the reaction between $Cs[MoF_7]$ and $WF_5{}^{18}F$, mass balance and Raman data both indicated substantial displacement of MoF_6 by WF_6 in the solid, $\nu_{max.}$ being 714 (vs), 442 (m) and 683 (w) cm^{-1}. It is concluded that the two anions exist in equilibrium with the hexafluorides in MeCN at room temperature [eqn. (2)]:

$$[MoF_7]^- + WF_6 \rightleftharpoons [WF_7]^- + MoF_6 \qquad (2)$$

but that when Cs^+ is the countercation, isolation of a solid product favours $Cs[WF_7]$.

The behaviour of $[MoF_7]^-$ and $[WF_7]^-$ in MeCN resembles that of $[BF_4]^-$, and most hexafluorometallate(V) anions that have been examined [11]. Only $[SbF_6]^-$ and to a lesser extent $[AsF_6]^-$ can be regarded as kinetically inert. It is not possible to distinguish between dissociative and associative pathways since the exchange reactions are too rapid.

A dissociative mechanism has been proposed to account for exchange in $[WF_7]^-$ [10] and this is consistent with the small quantity of insoluble

TABLE 2

$[^{18}F]$ exchange between heptafluorometallates(VI) and hexafluorides in MeCN[a]

Reactants	Temperature (K)	Time (min)	Fraction of $[^{18}F]$ exchanged[b]
$Tl[WF_7] + WF_5{}^{18}F$	293	7–60	$\geqslant 0.95 \pm 0.03$ (4 expts.)
$Tl[WF_7] + WF_5{}^{18}F$	252	20	0.92 ± 0.07
$[Cu(NCMe)_5][WF_7]_2 + WF_5{}^{18}F$	293	20	1.01 ± 0.03
$[Cu(NCMe)_5][WF_7]_2 + WF_5{}^{18}F$	252	10–20	0.63 ± 0.03 (2 expts.)
$[NO][WF_7] + MoF_5{}^{18}F$	293	20	1.10 ± 0.10 (2 expts.)
$Cs[WF_7] + MoF_5{}^{18}F$	293	20	0.93 ± 0.08[c]
$Cs[MoF_7] + WF_5{}^{18}F$	293	20	$\geqslant 0.89 \pm 0.04$[d] (2 expts.)

[a] Reaction conditions: $[MF_7]^-$, 0.1–0.3 mmol; MF_6, 1–2 mmol; MeCN, 1 cm^3.
[b] Defined in the text.
[c] The reaction $[WF_7]^- + MoF_6 \rightarrow [MoF_7]^- + WF_6$ occurred to some extent.
[d] The reaction $[MoF_7]^- + WF_6 \rightarrow [WF_7]^- + MoF_6$ occurred.

material (presumably TlF) observed when Tl[WF_7] was redissolved in MeCN; the insoluble material dissolved on adding WF_6 to the solution. Reactions between $[MF_7]^-$ and MF_6, M = Mo, W [eqn. (2)] are, however, analogous to those between $[WF_6(X)]^-$, $X^- = N_3^-$ or $(CN)^-$, and WF_6 [13] for which associative (WF_6 displacement [14]) mechanisms have been proposed on the basis of variable-temperature NMR studies. Associative mechanisms are also more consistent with the [^{18}F]-exchange behaviour observed under heterogeneous conditions.

Lability of the $[WF_7]^-$ anion under heterogeneous conditions

The behaviour of $WF_5{}^{18}F$ vapour towards solid Tl^I Cu^{II} and $[NO]^+$ heptafluorotungstates at room temperature was examined with the results shown in Fig. 1. In each case, a growth in [^{18}F] activity from the solid was observed on exposure to $WF_5{}^{18}F$ vapour, although the shape of the [^{18}F] growth curve depended to some extent on the salt under examination. Mass balance data (Table 3) indicate that some WF_6 was retained by the Tl^I salt, in one case, and the Cu^{II} salts after removal of material volatile at room temperatures. Determinations of [^{18}F] specific count rates (Table 4) indicate that, rather surprisingly, exchange occurred in all cases. The [^{18}F] growth curves for Tl^I and Cu^{II} salts [Fig. 1(a) and (b)] are the result, therefore, of

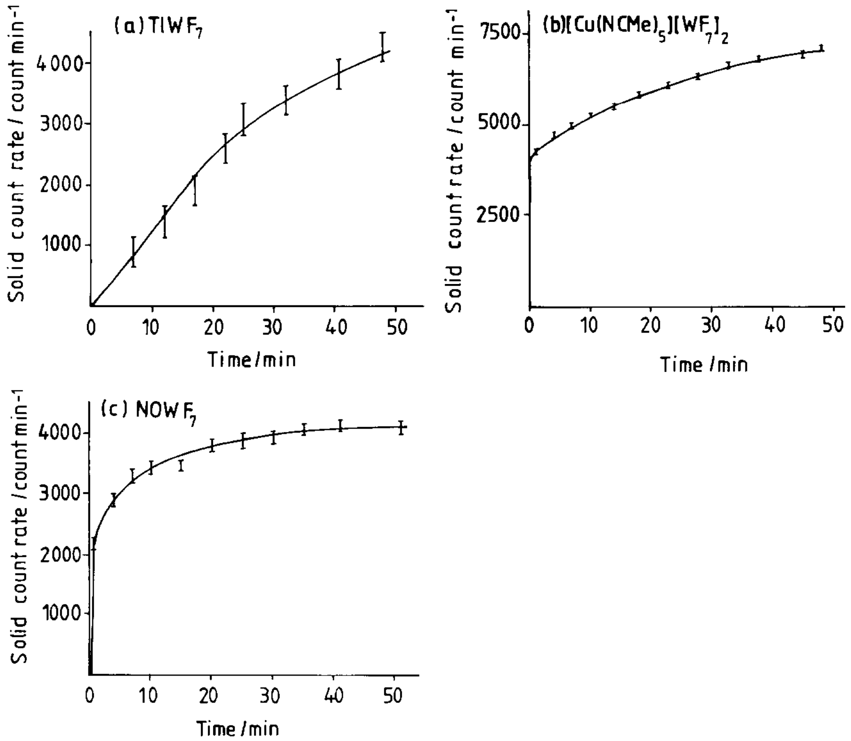

Fig. 1. [^{18}F] growth curves for solid (a) $TlWF_7$, (b) $[Cu(NCMe)_5][WF_7]_2$ and (c) $NOWF_7$ on exposure to $WF_5{}^{18}F$ vapour at room temperature.

TABLE 3

Uptake of WF_6 by heptafluorotungstates(VI) at room temperature under heterogeneous conditions

$A[WF_7]_x$	Quantity (mmol)[a]	WF_6 (mmol)[a]	Uptake of WF_6 [mmol (mmol$[WF_7]^-$ salt)$^{-1}$]
$Tl[WF_7]$	0.82	2.43	0.13±0.05
$Tl[WF_7]$	0.57	0.85	0.02±0.05
$[Cu(NCMe)_5][WF_7]_2$	0.69	1.56	0.26±0.05
$[Cu(NCMe)_5][WF_7]_2$	0.16	0.92	0.41±0.05
$[NO][WF_7]$	0.20	1.16	0

[a] ±0.01 mmol.

TABLE 4

$[^{18}F]$ exchange between $WF_5{}^{18}F$ and heptafluorotungstates(VI) at room temperature under heterogeneous conditions

$A[WF_7]_x$[a]	$[^{18}F]$ specific count rate of $WF_5{}^{18}F$ (count min^{-1} mmol^{-1})		Fraction of $[^{18}F]$ activity exchanged[b]
	Initial	Final	
$Tl[WF_7]$	33578±168	31363±181	0.24±0.03
$Tl[WF_7]$	169894±5530	155100±1955	0.20±0.03
$[Cu(NCMe)_5][WF_7]_2$	29138±315	26164±246	0.20±0.03
$[Cu(NCMe)_5][WF_7]_2$	84150±230	81133±102	0.12±0.03
$[NO][WF_7]$	19960±238	19196±309	0.23±0.03

[a] Stoichiometry of the reactions as in Table 3.
[b] Defined as described in the text.

both $[^{18}F]$ exchange and uptake of WF_6. IR spectra of the solid Tl^I and Cu^{II} salts, recorded after exposure to $WF_5{}^{18}F$, contained additional bands, $\nu_{max.}$ 710 (m), 515 (w, sh) and 425 (m) cm^{-1} (Tl^I salt) and 710 (mw), 480 (mw) and 410 (mw) cm^{-1} (Cu^{II} salt). These were not obviously due to any known fluoro-tungstate(VI) anion and, by analogy with the spectra of fluorine-bridged adducts [15], they are tentatively assigned to a fluorine-bridged species derived from WF_6.

The behaviour of the $[NO][WF_7]$ sample differed slightly in that while $[^{18}F]$ exchange occurred on exposure to $WF_5{}^{18}F$ (Table 4), there was no detectable uptake of WF_6 (Table 3). $[^{18}F]$ exchange between solid $[NO][WF_6{}^{18}F]$ and WF_6 vapour was also detected after 1 h and, in this experiment, the uptake of WF_6 (mmol mmol^{-1}) determined from mass balance data was 0.04±0.02 mmol. In the reaction between solid $[NO][WF_7]$ (0.59±0.01 mmol) and $MoF_5{}^{18}F$ (0.83±0.02 mmol) vapour, the fraction of $[^{18}F]$ activity exchanged after 1 h (*f*) was 0.40±0.02 and there was a marginal uptake of MoF_6. The $[^{18}F]$ growth curve resembled that of $[NO][WF_7]$ versus $WF_5{}^{18}F$ [Fig. 1(c)].

In view of the results described above, the behaviour of solid $CsMoF_7$ towards $WF_5{}^{18}F$ vapour was examined. Two experiments were carried out and in both cases the *f* values after 1 h exposure were similar, 0.13 and

0.15 (both ±0.03). Uptake of WF_6 was observed, 0.31±0.03 mmol (mmol $CsMoF_7)^{-1}$, in only one case. The [^{18}F] growth curve resembled that of $TlWF_7$ versus $WF_5{}^{18}F$ [Fig. 1(a)]. In this, as with the other heterogeneous systems examined, a degree of irreproducibility from sample to sample is apparent.

The most noteworthy feature in these reactions is that partial exchange is observed in all cases. This behaviour is in contrast to the behaviour of $[AsF_6]^-$, $[BF_4]^-$ and $[SF_5]^-$ (all Cs^+ salts) which do not undergo observable [^{18}F] exchange with AsF_5, BF_3 or SF_4, respectively, at room temperature under heterogeneous conditions [12]. Fluoro ligands in hepta-coordinate $[MF_7]^-$ anions are evidently more labile than those in anions of lower coordination numbers.

Reactions between caesium fluoride and [^{18}F]-labelled hexafluorides under heterogeneous conditions

One of the early applications of [^{18}F] in inorganic chemistry involved a study of the solid–gas NaF, UF_6 reaction and the identification of the complex formed as 2NaF,UF_6 rather than 3NaF,UF_6 [16]. This was confirmed in subsequent work [17] and it was further shown that, using NaF previously activated by sorption and desorption of UF_6, it was possible to prepare both NaF,MF_6 and 2NaF,MF_6, M = Mo, W or U, complexes depending on the conditions used [18]. Caesium fluoride can be activated for this type of Lewis acid–base reaction by thermal decomposition of $Cs[OCF(CF_3)_2]$ [12], and it was of interest, therefore, to follow the formation of $Cs[MF_7]$, M = Mo or W, under heterogeneous conditions at room temperature by using [^{18}F].

Three batches of CsF were used. Batch 1 was converted completely to $Cs[OCF(CF_3)_2]$ by reaction with $(CF_3)_2CO$ in the presence of MeCN [19] followed by thermal decomposition *in vacuo* [12]. Batch 2 was treated similarly, except that insufficient $(CF_3)_2CO$ to achieve complete conversion to $Cs[OCF(CF_3)_2]$ was used; it would be expected that the degree of activation in batch 2 would be less than that in batch 1. Batch 3 was merely treated with MeCN, followed by its removal *in vacuo*; no activation would be expected from this treatment [12].

Eight reactions were carried out with $WF_5{}^{18}F$ and five with $MoF_5{}^{18}F$, all at room temperature under conditions similar to those used for the heterogeneous exchange reactions. Although there was some spread in the uptake and [^{18}F]-exchange data, the general pattern of the results was clear.

Uptake of [^{18}F]-labelled hexafluorides was observed in all cases and in all experiments but one (involving $MoF_5{}^{18}F$). There was a substantial decrease in the specific [^{18}F] count rate of the hexafluoride after reaction, indicating that substantial exchange had occurred. The provenance of the CsF determined the extent of the reaction, particularly for those involving $WF_5{}^{18}F$. [^{18}F] growth curves for $WF_5{}^{18}F$ versus CsF (batch 1 top curve, batch 3 bottom curve) are shown in Fig. 2. The uptakes in these experiments were respectively 0.69±0.03 and 0.13±0.03 mmol (mmol $CsF)^{-1}$. In two other experiments using batch 1 CsF, the uptake of $WF_5{}^{18}F$ was 1.00±0.03 mmol (mmol

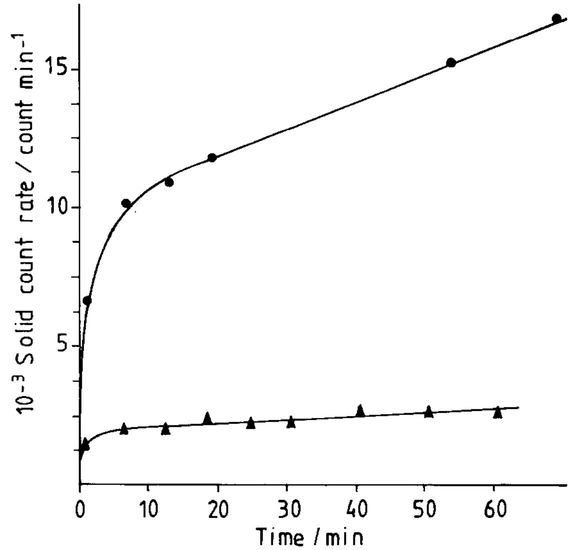

Fig. 2. Uptake of [^{18}F] activity by CsF on exposure to $WF_5{}^{18}F$ at room temperature; ●, CsF = 1.59 ± 0.02, $WF_5{}^{18}F$ = 3.28 ± 0.01 mmol; initial [^{18}F] specific count rate of $WF_5{}^{18}F$ = 9008 ± 60 count min^{-1} mmol^{-1}; ▲, CsF = 1.62 ± 0.02, $WF_5{}^{18}F$ = 4.6 ± 0.01 mmol; initial ^{18}F specific count rate of $WF_5{}^{18}F$ = 11395 ± 86 count min^{-1} mmol^{-1}.

CsF)$^{-1}$. Growth curves for CsF versus $MoF_5{}^{18}F$ (batch 1 top curve, batch 2 bottom curve) are depicted in Fig. 3. The differentiation is clear but, overall, the dependence of the uptake on the provenance of CsF was less marked, the values over the five experiments being in the range 0.25–0.43 mmol (mmol CsF)$^{-1}$. In both systems, the [^{18}F] exchange was reversible since addition of inactive hexafluoride to [^{18}F]-labelled $CsF(MF_6)_x$ solids led to the detection of $MF_5{}^{18}F$, M = Mo or W, after 45 min exposure. Small uptakes of MF_6 (up to 0.2 mmol) occurred during these reactions.

The Raman and IR spectra of the solids resulting from treatment of activated CsF with MF_6 contained bands attributable to $[MF_7]^-$ anions [6]. However, additional bands, not attributable to $[MF_8]^{2-}$, were also present: $CsF(WF_6)_x$: Raman, 713 (vs), 617 (w), 442 (m) cm^{-1}; IR, 610 (s) cm^{-1}; $CsF(MoF_6)_x$: Raman 629 (s), 596 (w) cm^{-1}. The solid obtained after reaction of unactivated CsF (batch 3) with WF_6 contained no bands attributable to $[WF_7]^-$ in its Raman spectrum, but a strong band at 656 cm^{-1} was possibly due to $[WF_8]^{2-}$ [6].

The reactions of the [^{18}F]-labelled hexafluoride with anhydrous CuF_2 or TlF occurred to a smaller extent than those with activated CsF. Both uptakes and the degrees to which ^{18}F exchange occurred were small.

A possible model for heterogeneous reactions between Lewis acid fluorides and solid ionic fluorides

The results presented here, together with earlier work in which the behaviour of [^{18}F]-labelled AsF_5, BF_3, SF_4 and F_2CO towards CsF was examined

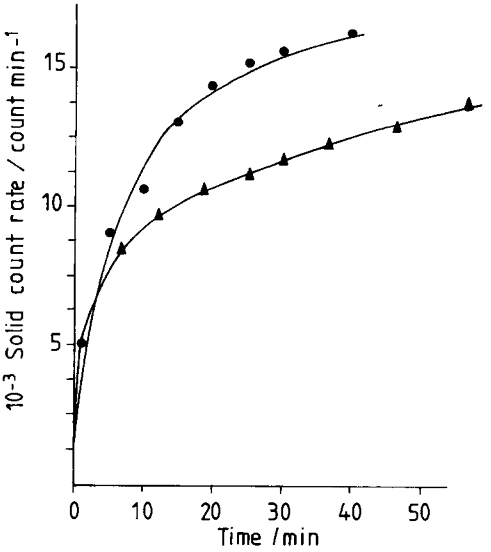

Fig. 3. Uptake of [^{18}F] activity by CsF on exposure to $MoF_5{}^{18}F$ at room temperature; ●, CsF = 1.70 ± 0.02, $MoF_5{}^{18}F$ = 0.64 ± 0.02 mmol; ▲, CsF = 1.48 ± 0.02, $MoF_5{}^{18}F$ = 2.80 ± 0.02 mmol; in both cases, initial [^{18}F] specific count rate of $MoF_5{}^{18}F$ = 23332 ± 580 count min^{-1} $mmol^{-1}$.

[12], enable a tentative model to be proposed for Lewis acid–base reactions occurring under heterogeneous conditions. The model comprises two steps, the reaction between MF_n vapour and solid A^+F^- [eqn. (3)] followed by a reversible reaction involving solid $A[MF_{n+1}]$ and adsorbed MF_n [eqn. (4)].

$$A^+F^-(s) + MF_n(g) \longrightarrow A[MF_{n+1}](s) \qquad (3)$$

$$A[MF_{n+1}](s) + MF_{n-1}{}^*F(ad) \rightleftharpoons A[MF_n{}^*F](s) + MF_n(g) \qquad (4)$$

Although the first step is obvious, verification of the second, particularly its reversibility, requires the use of [^{18}F] as a tracer.

In all cases examined, the first step is rapid at room temperature provided that A^+F^- is activated by some means. It is believed that CsF when activated by $(CF_3)_2CO$ pretreatment exhibits a porous structure to some extent [12]. Also relevant is the observation that NaF has an enhanced capacity for metal hexafluoride sorption after the formation and thermal decomposition of $Na_2[UF_8]$ [18]. It is probable that step 1 occurs via weakly adsorbed MF_n, as the existence of such species has been demonstrated for SF_4 and F_2CO on activated CsF [12].

Step 2 [eqn. (4)] is proposed to account for the [^{18}F] exchange observed between MF_6 and $[MF_7]^-$, M = Mo or W, salts and during $Cs[MF_7]$ formation, both under heterogeneous conditions. It is not observed where MF_n is AsF_5, BF_3 or SF_4, although [^{18}F] exchange in these systems is observed above room temperature [12]. We believe that room-temperature [^{18}F] exchange and the irreversible uptake of MF_6 are connected, although we have not been able to demonstrate a quantitative relationship. It is suggested tentatively that MF_6 is adsorbed via an F-bridged species $[MF_6{-}F{-}MF_5{}^{18}F]^-$ which is then a plausible intermediate in the $[^{18}F]$-exchange process. Complete exchange between CsF and $MF_5{}^{18}F$ on this basis would not be expected since the pool of 'inactive' fluoride is limited to that fraction directly involved in step 1 [eqn. (3)].

Apparently $[AsF_6]^-$, $[BF_4]^-$ and $[SF_5]^-$ are insufficiently good F-donors to participate in complexation under heterogeneous conditions. $[^{18}F]$ exchange between $Cs[OCF_3]$ and $F^{18}FCO$ is observed at room temperature; this may reflect the relatively weak C—F bonds in the anion, for which there is good evidence for negative fluorine hyperconjugation [20].

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References

1 For part 15, see L. Rowley, J. Thomson, G. Webb, J. M. Winfield and A. McCulloch, *Appl. Catal. A*, *79* (1991) 89.
2 K. O. Christe, W. W. Wilson, R. D. Wilson, R. Bau and J. Feng, *J. Am. Chem. Soc.*, *112* (1990) 7619.
3 K. O. Christe, J. C. P. Saunders, G. J. Schrobilgen and W. W. Wilson, *J. Chem. Soc., Chem. Commun.*, (1991) 837; A.-R. Mahjoub and K. Seppelt, *ibid.*, (1991) 840; A.-R. Mahjoub and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 876.
4 A.-R. Mahjoub and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 323.
5 G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, (1958) 2170, 4390.
6 A. Beuter, W. Kuhlmann and W. Sawodny, *J. Fluorine Chem.*, *6* (1975) 367.
7 W. A. Sunder, A. L. Wayda, D. Distefano, W. E. Falconer and J. E. Griffiths, *J. Fluorine Chem.*, *14* (1979) 299.
8 W. W. Wilson and K. O. Christe, *Inorg. Chem.*, *21* (1982) 2091.
9 A. Prescott, D. W. A. Sharp and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, (1975) 934.
10 R. Bougon, P. Charpin, J. P. Desmoulin and J. G. Malm, *Inorg. Chem.*, *15* (1976) 2532.
11 M. F. Ghorab and J. M. Winfield, *J. Fluorine Chem.*, *49* (1990) 367.
12 K. W. Dixon and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, (1989) 937.
13 B. Glavincevski and S. Brownstein, *J. Inorg. Nucl. Chem.*, *43* (1981) 1827; *Inorg. Chem.*, *20* (1981) 3580.
14 S. Brownstein, A. M. Eastham and G. A. Latremouille, *J. Phys. Chem.*, *67* (1963) 1028.
15 See, for example, J. H. Holloway, G. M. Staunton, K. Rediess, R. Bougon and D. Brown, *J. Chem. Soc., Dalton Trans.*, (1984) 2163.
16 I. Sheft, H. H. Hyman, R. M. Adams and J. J. Katz, *J. Am. Chem. Soc.*, *83* (1961) 291.
17 S. Katz, *Inorg. Chem.*, *3* (1964) 1598; J. G. Malm, H. Selig and S. Siegel, *Inorg. Chem.*, *5* (1966) 130.
18 S. Katz, *Inorg. Chem.*, *5* (1966) 666.
19 M. E. Redwood and C. J. Willis, *Can. J. Chem.*, *45* (1967) 389.
20 W. B. Farnham, B. E. Smart, W. J. Middleton, J. C. Calabrese and D. A. Dixon, *J. Am. Chem. Soc.*, *107* (1985) 4565.