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RADIOTRACERS IN FLUORINE CHEMISTRY. PART XIV. THE LABILITY OF THE FLUOROANIONS BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, NbF_6^- AND TaF_6^- IN ACETONITRILE SOLUTION. A FLUORINE-18 RADIOTRACER STUDY [1,2]

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SUMMARY

Fluorine-18 exchange between BF_4^- or PF_6^- and the [^{18}F]-labelled hexafluorides MoF_6, WF_6 or UF_6 and between NbF_6^- or TaF_6 and $WF_5{}^{18}F$ in acetonitrile is rapid at room temperature. Rapid ^{18}F exchange is observed also between AsF_6^- and $UF_5{}^{18}F$ under identical conditions but is not observed between AsF_6^- and $MoF_5{}^{18}F$ or $WF_5{}^{18}F$. No ^{18}F exchange is observed between SbF_6^- and any of the three hexafluorides. On this basis SbF_6^- is the anion of choice in situations where a kinetically inert anion is required.

INTRODUCTION

Fluoroanions such as BF_4^-, PF_6^- and AsF_6^- are often used when an inert counter-anion is required in solution studies. They are kinetically inert with respect to hydrolysis in aqueous acid, although hydrolysis is catalysed by hard acids, for example, Be^{II} or Al^{III} [3]. The observation suggests that coordination to a positive centre via a fluorine ligand is possible and indeed several instances of F^- ion abstraction in solution from BF_4^- [4] or PF_6^- anion [5] have been reported under a variety of conditions.

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The behaviour of many fluoroanions, for example BF_4^- and EF_6 E = P, As, Sb, Nb and Ta, towards high oxidation state binary fluorides, BF_3 or MF_5, M = P, As, Sb, Nb and Ta, in solution is well documented from n.m.r. studies. In most cases attention has been focussed on complex formation involving E-F-E or E-F-M bridges [6]. Fluorine exchange which is fast on the n.m.r. time scale has been reported in some cases but the lability of bonds in these anions has never been compared systematically using a common reference acid under identical conditions. We have undertaken this comparison using fluorine-18 (β^+ decay, $t_{1/2}$ = 110 min) as a radiotracer and the hexafluorides MoF_6, WF_6 and UF_6 as reference Lewis acids. The hexafluorides are very useful probe molecules for this type of investigation since their Lewis acidities are significantly weaker than those of SbF_5 or AsF_5 which have been used most often in previous ^{19}F n.m.r. investigations.

EXPERIMENTAL

Preparation of Reagents

Standard vacuum and glove-box techniques were used throughout. Binary fluorides, commercial products or prepared by F_2 fluorination of the appropriate element, were purified by distillation or sublimation immediately before use. Acetonitrile (Rathburn HPLC Grade S) was purified as described previously [7]. The pentafluorides, AsF_5, SbF_5, NbF_5 and TaF_5, were manipulated as their 1:1 adducts with MeCN, the latter being characterized by their vibrational spectra [8]. Lithium, fluoroanion salts were prepared on the 5 mmol scale from reactions between lithium fluoride (B.D.H. Optran Grade) and the appropriate binary fluoride or its MeCN adduct in MeCN at room temperature. Syntheses were carried out in Pyrex double limb vessels fitted with P.T.F.E., Pyrex stop-cocks (J. Young). All salts were colourless and were very soluble in MeCN so could be separated from unchanged LiF by decanting the solution. Samples were recrystallised from MeCN before use. Their i.r. spectra contained bands due to the appropriate anion, BF_4^-, AsF_6^-, SbF_6^- or TaF_6^- [9,10]. There was no evidence for coordinated MeCN. Satisfactory Raman spectra were obtained only for $LiSbF_6$; decomposition occurred in the other cases. The salt $[Cu(NCMe)_5][NbF_6]_2$ was prepared as described previously for the TaF_6^- analogue [10] and was characterized by its spectra.

Caesium heptafluorotungstate(VI) was prepared from caesium fluoride (5.0 mmol; B.D.H. Optran Grade), WF_6 (4.0 mmol) and MeCN (5 cm^3). This mixture, contained in a flamed out, double limb, Pyrex vessel, was shaken for several hours at room temperature. The solution was decanted and a colourless solid isolated after removal of volatile material. The i.r. and Raman spectra of the solid contained strong bands at 620 and 714 cm^{-1} respectively, assigned to the ν_3 and ν_1 modes of the D_{5h}, WF_7^- anion [11]. No bands due to coordinated MeCN were observed.

The preparation of activated caesium [^{18}F]-fluoride has been described elsewhere [12]. [^{18}F]-Fluorine labelled MoF_6 and WF_6 (5-10 mmol) were prepared by exchange with solid $Cs^{18}F$ at 348 K for 0.5 h in a stainless steel vessel (Hoke, 70 cm^3). They were transferred by distillation to a Pyrex vessel containing activated NaF before use. [^{18}F]-Labelled MoF_6 (5-10 mmol) was also prepared by exchange with [^{18}F]-BF_3 (30 mmol) [12] at room temperature for 0.5 h. The mixture was contained in a Monel metal vessel (Hoke, 90 cm^3) and $BF_2{}^{18}F$ was removed after the exchange by distillation at 195 K. [^{18}F]-Labelled UF_6 was prepared in a similar manner. [^{18}F]-Labelled $NO^+PF_6^-$ and

$NO^+AsF_6^-$ salts were prepared in situ from reactions between [^{18}F]-labelled PF_5 or AsF_5 [12] and nitrosyl fluoride [13] in MeCN. [^{18}F]-Labelled Li^+ salts were prepared from the labelled pentafluoride and LiF as described above.

In all cases radiochemical purity was checked by determination of the ^{18}F γ-ray spectrum and half-life. Specific ^{18}F count rates were $>10^4$ count min^{-1} $mmol^{-1}$.

[^{18}F]-Fluorine Exchange Reactions

The fraction of [^{18}F]-fluorine exchanged between a [^{18}F]-labelled hexafluoride and a fluoroanion in MeCN at room temperature was determined using a single limb Pyrex counting vessel which fitted into a well scintillation counter (Ekco and Nuclear Enterprises; well dimensions 1.56 x 0.78 ins. diameter). The counting vessel was fitted with a loop to minimise loss of involatile material during separations and a P.T.F.E., Pyrex stop cock. A quantity of the fluoroanion salt was loaded into the flamed out vessel in the glove box, and its mass determined. Solvent, MeCN (1 cm^3) was added by distillation and the mass of the solution determined. A known mass of [^{18}F]-labelled hexafluoride was then added by distillation, the mixture was warmed quickly to room temperature, 293 ± 2 K, and the reaction was allowed to proceed. Preliminary experiments with $WF_5{}^{18}F$ and PF_6^- salts indicated that apparent equilibrium was attained within 20 mins and this time was used in all cases. The mixture was counted during the reaction and the ^{18}F specific count rate (count min^{-1} $mmol^{-1}$) of the labelled hexafluoride used was also determined by counting a measured mass of $MF_5{}^{18}F$ in MeCN under identical conditions.

The components of the reaction mixture were separated rapidly by distillation and the ^{18}F count rates and the masses of the solid fluoroanion salt and hexafluoride solution in MeCN determined. All counts were corrected for background and ^{18}F decay. Radiochemical balances were >95%. Experiments in which the involatile component was initially labelled were carried out in an analogous fashion.

Difficulty was encountered in achieving rapid quantitative separations in some experiments due to the high solubilities of the Li^+ salts. This had little effect on the precision of the ^{18}F exchange determinations since the fraction of ^{18}F activity exchanged (f) was determined solely from the volatile fluoride specific count rates using the relationship

$$f = S_0 - S_t/S_0 - S_\infty$$

where S_0 and S_t were the ^{18}F specific count rates (count min^{-1} mmol^{-1}) determined for the volatile fluoride before and after the exchange and S_∞ was the specific count rate calculated on the basis of complete exchange.

Fluoride Ion Transfer Reactions

Reactions between $CsWF_7$ and BF_3, PF_5, $AsF_5.NCMe$ and $SbF_5.NCMe$ in MeCN at room temperature were carried out in Pyrex double limb flasks equipped with Pyrex capillaries, enabling samples of the solutions to be withdrawn for Raman spectroscopy (Spex Ramalog with Ar^+ or Kr^+ laser sources). Solids remaining after removal of volatile material were examined by i.r. spectroscopy (PE 983, Nujol mulls between AgCl plates).

RESULTS AND DISCUSSION

There is no evidence that chemical reactions occur between the anions BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, NbF_6^- or TaF_6^- and the hexafluorides, MoF_6, WF_6 or UF_6 in acetonitrile at room temperature but rapid ^{18}F exchange occurs in many cases. Exchange is essentially complete between $MF_5{}^{18}F$, M = Mo, W and U, and the BF_4^- anion, Table 1, or the PF_6^- anion, Table 2, after 20 min, indicating an upper limit for the exchange half-life of ca.5 min. Exchange is complete also between $PF_5{}^{18}F^-$ and MoF_6 under similar conditions, Table 2, and was also demonstrated qualitatively between $PF_5{}^{18}F^-$ and WF_6. The behaviour observed is consistent with the complete ^{18}F exchange previously demonstrated between $LiBF_4$ and $BF_2{}^{18}F$ in MeCN [12].

Exchange between $WF_5{}^{18}F$ and the NbF_6^- or TaF_6^- anions is also complete under these conditions, Table 3. The behaviour of MoF_6 and UF_6 towards these anions was not investigated but previous ^{18}F studies [14,15] strongly suggest that WF_6 is the least labile of the three hexafluorides. It is likely therefore that BF_4^-, PF_6^-, NbF_6^- and TaF_6^- should be bracketed in respect of their lability.

The AsF_6^- anion appears to be less labile with respect to ^{18}F exchange. Complete exchange occurs between AsF_6^- and $UF_5{}^{18}F$ within 20 min in MeCN at room temperature but there is no observable exchange with $MoF_5{}^{18}F$ or $WF_5{}^{18}F$ under identical conditions, Table 4, and transfer of ^{18}F from $AsF_5{}^{18}F^-$ to MoF_6 is negligible.

TABLE 1

^{18}F Exchange reactions between $LiBF_4$ and ^{18}F labelled hexafluorides in acetonitrile at room temperature for 20 min

Reagents (mmol)			^{18}F Specific count rate (count min^{-1} mmol^{-1})		Fraction ^{18}F exchanged
			Before reaction	After reaction	
$LiBF_4$ 1.02±0.03	+	$MoF_5{}^{18}F$ 0.82±0.02	26170±451	15004±277	0.94±0.07
$LiBF_4$ 1.16±0.03	+	$WF_5{}^{18}F$ 1.08±0.01	29701±487	18328±307	0.92±0.10
$LiBF_4$ 0.86±0.03	+	$WF_5{}^{18}F$ 0.50±0.01	27692±974	12611±433	1.02±0.06
$LiBF_4$ 0.90±0.03	+	$UF_5{}^{18}F$ 0.55±0.01	99478±1832	46272±935	1.02±0.05
$LiBF_4$ 1.21±0.03	+	$UF_5{}^{18}F$ 0.40±0.01	84275±2215	26397±728	1.03±0.05

The SbF_6^- anion is the least labile of those examined since there is no observable ^{18}F exchange with any of the hexafluorides, Table 5. The inertness of an Sb^V-F bond with respect to exchange is reflected also in the lack of observable exchange between $SbF_5.NCMe$ and $WF_5{}^{18}F$ in MeCN at room temperature. In contrast, exchange between $WF_5{}^{18}F$ and $AsF_5.NCMe$ under identical conditions is >80%, Table 6.

TABLE 2

^{18}F Exchange reactions between $LiPF_6$ or $NOPF_6$ and hexafluorides in acetonitrile at room temperature for 20 min

Reagents (mmol)			^{18}F Specific count rate ($count\ min^{-1}\ mmol^{-1}$)		Fraction ^{18}F exchanged
			Before reaction	After reaction	
$LiPF_6$ 0.62±0.02	+	$MoF_5{}^{18}F$ 0.65±0.02	20204±760	9425±365	1.04±0.10
$NOPF_5{}^{18}F$ 0.80±0.02	+	MoF_6 0.98±0.02	39557±1404	15984±1515	0.97±0.08
$LiPF_6$ 0.41±0.02	+	$WF_5{}^{18}F$ 0.25±0.01	50714±1863	19883±1400	0.99±0.10 [a]
$LiPF_6$ 0.41±0.02	+	$WF_5{}^{18}F$ 0.59±0.01	60504±2295	35617±1176	0.99±0.10
$LiPF_6$ 0.42±0.02	+	$UF_5{}^{18}F$ 0.39±0.01	127141±4849	71574±2744	0.92±0.10
$LiPF_6$ 0.42±0.02	+	$UF_5{}^{18}F$ 1.22±0.01	52230±578	37639±497	1.09±0.10

[a] ^{18}F exchange between $LiPF_5{}^{18}F$ and WF_6 in MeCN was also demonstrated qualitatively.

TABLE 3

^{18}F Exchange reactions between $[Cu(NCMe)_5][NbF_6]_2$ or $LiTaF_6$ and $WF_5{}^{18}F$ in acetonitrile at room temperature for 20 min

Salt (mmol)	$WF_5{}^{18}F$ (mmol)	^{18}F Specific count rate of $WF_5{}^{18}F$ (count min^{-1} $mmol^{-1}$) Before reaction	After reaction	Fraction ^{18}F exchanged
$[Cu(NCMe)_5][NbF_6]_2$ 0.13±0.01	1.14±0.01	34621±395	28618±169	0.93±0.10
$LiTaF_6$ 0.65±0.01	1.98±0.01	13930±99	10557±120	0.98±0.02

These results relate to the behaviour of the fluoroanions in situations where thermodynamic control is absent and the differences observed must be kinetic in origin. In the reactions where ^{18}F exchange occurred the rates were too fast to be determined precisely and therefore mechanistic discussion is speculative. The simplest possibility is that ^{18}F exchange could occur via a dissociative process (equation 1)

$$EF_{n+1}{}^{-} \rightleftharpoons EF_n.NCMe \quad + \quad F^{-} \quad (n = 3 \text{ or } 5) \qquad (1)$$

followed by rapid exchange involving $MF_5{}^{18}F$, M = Mo, W and U, and $EF_n.NCMe$ or F^-. This pathway seems unlikely, at least for the $AsF_6{}^-$ anion, in view of the different exchange behaviour observed for $AsF_5{}^-$ and $AsF_5.NCMe$, Tables 4 and 6.

TABLE 4

^{18}F Exchange reactions between $LiAsF_6$ and ^{18}F labelled hexafluorides in acetonitrile at room temperature for 20 min

Reagents (mmol)			^{18}F Specific count rate (count min^{-1} $mmol^{-1}$)		Fraction ^{18}F exchanged
			Before reaction	After reaction	
$LiAsF_6$ 0.55±0.02	+	$MoF_5{}^{18}F$ 0.75±0.02	20173±669	20866±692	0
$LiAsF_6$ 0.62±0.02	+	$MoF_5{}^{18}F$ 1.33±0.02	20317±387	20404±388	0 [a]
$LiAsF_6$ 0.39±0.02	+	$WF_5{}^{18}F$ 0.47±0.01	266967±4433	277816±6293	0
$LiAsF_6$ 0.51±0.02	+	$WF_5{}^{18}F$ 0.75±0.01	31414±787	31585±745	0
$LiAsF_6$ 0.48±0.02	+	$UF_5{}^{18}F$ 0.70±0.01	61250±1334	33931±753	1.09±0.08
$LiAsF_6$ 0.41±0.02	+	$UF_5{}^{18}F$ 0.41±0.01	70146±2406	34271±1188	1.00±0.08

[a] In a reaction between $NOAsF_5{}^{18}F$ (0.95±0.02 mmol) and MoF_6 (1.19±0.02 mmol) under similar conditions < 3% of the initial ^{18}F activity was transferred to MoF_6 after 20 min.

TABLE 5

^{18}F Exchange reactions between $LiSbF_6$ and ^{18}F labelled hexafluorides in acetonitrile at room temperature for 20 min

Reagents (mmol)			^{18}F Specific count rate (count min^{-1} $mmol^{-1}$)		Fraction ^{18}F exchanged
			Before Reaction	After reaction	
$LiSbF_6$ 0.51±0.02	+	$MoF_5{}^{18}F$ 0.68±0.02	27786±636	28589±636	0
$LiSbF_6$ 0.56±0.02	+	$MoF_5{}^{18}F$ 0.85±0.02	26959±491	27706±504	0
$LiSbF_6$ 0.51±0.02	+	$WF_5{}^{18}F$ 1.68±0.01	13930±79	13399±99	0
$LiSbF_6$ 0.60±0.02	+	$WF_5{}^{18}F$ 2.16±0.01	8588±72	9244±96	0
$LiSbF_6$ 0.51±0.02	+	$UF_5{}^{18}F$ 0.85±0.01	35620±666	36263±700	0
$LiSbF_6$ 0.51±0.02	+	$UF_5{}^{18}F$ 0.93±0.01	30765±526	31002±674	0

Equation 1 has been postulated to account for the rapid ^{19}F exchange within $AgBF_4$ in MeCN above room temperature [16] but addition of BF_3 accelerates the rate of exchange. This observation, and others made on related reactions by ^{19}F n.m.r. spectroscopy have been taken as indicating associative mechanisms [6,16].

TABLE 6

^{18}F Exchange reactions between pentafluoride, acetonitrile (1:1) complexes and $WF_5{}^{18}F$ in acetonitrile at room temperature for 20 min

Pentafluoride complex (mmol)	$WF_5{}^{18}F$ (mmol)	^{18}F Specific count rate of $WF_5{}^{18}F$ (count min^{-1} mmol^{-1})		Fraction ^{18}F exchanged
		Before reaction	After reaction	
SbF_5.NCMe 0.88±0.01	2.11±0.01	13181±151	13350±136	0
SbF_5.NCMe 1.06±0.01	1.52±0.01	13181±151	13191±130	0
AsF_5.NCMe 1.10±0.02	1.21±0.01	34621±395	21504±226	0.89±0.04
AsF_5.NCMe 0.73±0.02	0.24±0.01	34621±395	14487±678	0.81±0.06
NbF_5.NCMe 0.35±0.01	1.49±0.01	12347±147	10288±108	1.01±0.04
NbF_5.NCMe 0.23±0.01	1.61±0.01	12347±147	11135±106	0.92±0.05

TABLE 7

Species identified by vibrational spectroscopy from reaction between $CsWF_7$ and Lewis acid fluorides in MeCN

$CsWF_7$ (mmol)	Lewis acid fluoride (mmol)	Prominent Raman bands MeCN solution ($\Delta\tilde{\nu}/cm^{-1}$)	Prominent i.r. bands solid mixture ($\tilde{\nu}/cm^{-1}$)
0.875	0.52 (BF_3)	775 (ν_1 WF_6)	1100-1035,br,($\nu_3 BF_4^-$)
		712 (ν_1 WF_7^-)	773 (ν_1 BF_4^-)
			630 (ν_3 WF_7^-)
			$\left.\begin{matrix}530\\520\end{matrix}\right\}$($\nu_4$ BF_4^-)
0.75	0.86 (PF_5)	775 (ν_1 WF_6)	830 (ν_3 PF_6^-)
		746 (ν_1 PF_6^-)	560 (ν_4 PF_6^-)
		708 (ν_1 WF_7^-)	
1.10	0.75 (AsF_5)	777 (ν_1 WF_6)	
		714 (ν_1 WF_7^-)	715 (ν_1 WF_7^-) [a]
		684 (ν_1 AsF_6^-)	689 (ν_1 AsF_6^-) [a]
0.59	0.95 (SbF_5) [b]	777 (ν_1 WF_6)	655 (ν_3 SbF_6^-)
		660 (ν_1 SbF_6^-)	

[a] Raman spectrum.

[b] Added as SbF_5.NCMe.

We prefer the hypothesis that the ^{18}F behaviour observed is a result of processes described by equation 2.

$$EF_{n+1}^{-} + MF_6 \rightleftharpoons [EF_n\text{-}F\text{-}MF_6]^{-} \rightleftharpoons EF_n.NCMe + MF_7^{-} \qquad (2)$$

$$(n = 3 \text{ or } 5)$$

Transfer of fluorine occurs via the transition state or short-lived intermediate, $[EF_n\text{-}F\text{-}MF_6]^-$. Equation 2 is thermodynamically favoured from right to left as F^- ion transfer from WF_7^- to EF_n.NCMe, EF_n = BF_3, PF_5, AsF_5 and SbF_5, occurs on mixing the reagents at room temperature, Table 7. Rapid ^{19}F exchange between WF_7^- and WF_6 in MeCN also occurs at room temperature [17].

Lattice energy calculations involving anions derived from BF_3 [18], PF_5 and AsF_5 [19] and ion cyclotron resonance spectroscopic studies of reactions involving WF_6 [20] and UF_6 [21] lead to the order of Lewis acidity

$AsF_5 > PF_5 > BF_3 > WF_6 > UF_6$

and thermochemical comparisons between SbF_5 and AsF_5 are consistent with the former being the stronger Lewis acid [22]. Fluoride ion transfer from WF_7^- to SbF_5.NCMe, AsF_5.NCMe, PF_5.NCMe and BF_3.NCMe is to be expected, since MeCN is a very weak ligand and easily displaced. The very sensitive ^{18}F tracer method is required to observe fluorine transfer in the reverse, energetically unfavourable direction. It is interesting that ^{18}F exchange involving WF_6 is observed only with the stronger conjugate base anions, BF_4^- and PF_6^- but this correlation is probably fortuitous, since there is no a priori connection between kinetic and thermodynamic aspects of fluorine transfer. Exchange between AsF_6^- and $UF_5{}^{18}F$ would not have been predicted on this basis.

What has been established is that in a situation where a kinetically inert anion is required, SbF_6^-, or AsF_6^- as an alternative, should be used rather than the BF_4^- or PF_6^- anions. It has been suggested very recently from evidence that is very different to that used here, that SbF_6^- is superior to BF_4^- or PF_6^- as a counter anion for reactive, Lewis acid organometallic cations [23].

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