RADIOTRACERS IN FLUORINE CHEMISTRY.   PART VIII.

FLUORINE-18 EXCHANGE REACTIONS INVOLVING URANIUM(VI) OR URANIUM(V)

FLUORIDES.   EVIDENCE   FOR SURFACE COMPLEXATION AND COMPARISONS

WITH LIGAND EXCHANGE REACTIONS [1]

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SUMMARY

Fluorine-18 exchange between UF_6, β-UF_5, or the UF_6^- anion and [^{18}F]-labelled BF_3 or Me_3SiF is observed readily at ambient temperature and below, both under heterogeneous conditions and in acetonitrile solution.   The behaviour of [^{18}F]-labelled BF_3, PF_5, or SF_4 towards β-UF_5 is significantly different from that towards α-UF_5, and suggests that   small quantities of the Lewis acid fluorides are retained by β-UF_5.   This is confirmed for SF_4 by ^{35}S studies.   The lability of U^V-F bonds with respect to substitution implied by the ^{18}F results, is confirmed by the formation of U^V chlorofluoride mixtures from reactions of β-UF_5, or UF_5 in MeCN with BCl_3 or $B[OCCl(CF_3)_2]_3$. Complete replacement of F- by MeO-ligands in reactions between UF_5 and Me_3SiOMe in MeCN is not observed.   An insoluble solid is formed whose stoichiometry is $UF_3(OMe)_2$.

INTRODUCTION

The radiotracer fluorine-18 is a useful means of probing fluorine exchange between covalent fluorides in situations where ^{19}F n.m.r. spectroscopy is not applicable [2].   In this paper we describe the results of ^{18}F exchange reactions between uranium hexafluoride, α- or β- uranium pentafluoride, or the hexafluorouranate(V) anion and various

Lewis acid fluorides under heterogeneous conditions, and in acetonitrile solution. Comparisons are made between ^{18}F exchange and ligand substitution reactions, and evidence for the formation of surface complexes involving β-UF_5 is presented.

RESULTS AND DISCUSSION

Exchange reactions are discussed in terms of ^{18}F transferred from the initially labelled, to the initially unlabelled reactant, the fraction of activity exchanged (f) being defined by the relationship

Fraction of ^{18}F in the initially unlabelled fluoride after reaction
Fraction of total F(mg atom) in the initially unlabelled fluoride

Complete exchange corresponds to f = 1. When f is > 1, an interaction additional to ^{18}F exchange has occurred, for example retention of SF_3^{18}F by CsF [3]. This situation was encountered in many of the reactions studied in the present work; its observation is a reflection of the sensitivity of the radiotracer technique.

^{18}F Exchange between UF_6 and BF_2^{18}F or Me_3Si^{18}F

Exchange between UF_6 and [^{18}F]-labelled boron trifluoride is readily observed at room temperature, and the reaction is a good method for the preparation of UF_5^{18}F. Representative results are given in Table 1. Values of f are ⩾ 0.88, and in one reaction f > 1 was observed. However, there was no evidence for any interaction apart from ^{18}F exchange. Although these reactions were carried out nominally under heterogeneous conditions, the homogeneous, gas-phase reaction will be an important pathway. ^{18}F exchange also occurs readily between UF_6 and trimethylsilyl [^{18}F]-fluoride, and is observable at ca. 210 K (Table 1). Mixtures of these compounds are dark violet or brown, however there was no evidence for a chemical reaction at this temperature. A reaction does occur to a small extent at ambient temperature.

The behaviour of UF_6 towards Me_3Si^{18}F may be compared with our earlier study of hexafluoride, Et_3Si^{18}F reactions [2] to obtain a qualitative order of hexafluoride bond lability towards R_3Si^{18}F. The order is UF_6 ∿ MoF_6 > WF_6 > TeF_6. The behaviour of BF_3 towards

$Et_3Si^{18}F$ is intermediate between that of MoF_6 and WF_6. In view of the rapid exchange between UF_6 and $BF_2^{18}F$ or $Me_3Si^{18}F$, a detailed mechanistic study was not attempted, but it can be argued that the lability of a $U^{VI}-F$ bond is the result both of the effective Lewis acid centre, U^{VI}, and of the donor properties of F bound to U^{VI}.

TABLE I

^{18}F Exchange reactions between UF_6 and $BF_2^{18}F$ or $Me_3Si^{18}F$

UF_6	$BF_2^{18}F$ or $Me_3Si^{18}F$		Time	Temperature	Fraction exchanged
mmol		mmol	min	K	f
0.91	$BF_2^{18}F$	1.33	45	292	0.94
1.74	$BF_2^{18}F$	0.28	45	293	0.88
0.74	$BF_2^{18}F$	2.48	50	292	1.11
0.63	$Me_3Si^{18}F$	4.99	60	207	0.74
0.79	$Me_3Si^{18}F$	5.00	60	208	0.90
0.87	$Me_3Si^{18}F$	10.39	65	207	0.93

Comparison between ^{18}F exchange and ligand substitution reactions involving UF_6

A close similarity between reactions of tungsten (VI) fluoride, methoxides with $Me_3Si^{18}F$ or Me_3SiOMe has been noted previously [2], and a similar situation obtains for UF_6. For example, the lability of UF_6 towards $Me_3Si^{18}F$ is paralleled by facile, low-temperature substitution reactions between UF_6 and Me_3SiOMe to give $UF_{6-n}(OMe)_n$, n = 1 - 6. The fluorine ligands in the products undergo rapid, intermolecular exchange [4]. Reactions between UF_6 and BCl_3 [5] or $B(OTeF_5)_3$ [6] which lead to UCl_6 and $U(OTeF_5)_6$ respectively, may be

ompared with the behaviour of UF_6 towards $BF_2{}^{18}F$. Substitution reactions involving WF_6 are very much slower, and complete replacement of F- by other ligands is often not achieved [e.g.2]. The difference in lability between a $U^{VI}-F$ and a $W^{VI}-F$ bond is one of the factors responsible for the difference in chemical reactivity between the two hexafluorides.

^{18}F Exchange between $UF_6{}^-$ and $BF_2{}^{18}F$ or $UF_5{}^{18}F$

^{18}F exchange reactions between the hexafluorouranate(V) anion, with Cu^{II} or Tl^{III} counter-cations, and $BF_2{}^{18}F$ at room temperature result in values of f > 1, both in MeCN solution and under heterogeneous conditions (Table 2). The most obvious explanation is that both ^{18}F exchange, and retention of small quantities of $BF_2{}^{18}F$ by the salts, occur. Mass balance data are consistent with retention, and the near i.r. spectrum of $UF_6{}^-$ in MeCN, to which BF_3 has been added, shows that both $UF_6{}^-$ and $UF_5(NCMe)_x$ [7] are present. Evidently transfer of F^- ion from $UF_6{}^-$ to $BF_3 \cdot NCMe$ occurs to some extent. Although it is possible that the ^{18}F activity is retained as $BF_2{}^{18}F \cdot NCMe$ rather than $BF_3{}^{18}F^-$, this is less likely in view of the high degree of dissociation found for $BF_3 \cdot NCMe$ in the gas phase at ambient temperature [8].

^{18}F exchange between solid $UF_6{}^-$ salts and gaseous $UF_5{}^{18}F$ at room temperature is substantial, $f \geqslant 0.72$ (Table 2), but there is no evidence for retention. Rapid exchange between these species in MeCN has been reported previously [9].

Clearly the $UF_6{}^-$ ion is a good donor in both thermodynamic and kinetic senses. In this respect it is similar to the hexafluorotungstate(V) anion [10].

^{18}F Exchange between α- or β- UF_5 and Lewis acid fluorides under heterogeneous conditions

The two structural modifications of uranium pentafluoride behave very differently towards $BF_2{}^{18}F$ at room temperature. For β- UF_5 under the conditions used, f > 1, whereas between α- UF_5 and $BF_2{}^{18}F$ far less interaction is observed (Table 3). Mass balance data from β- UF_5 reactions indicate the possible retention of BF_3 by β- UF_5, although attempts to verify this spectroscopically were unsuccessful.

TABLE 2

^{18}F Exchange reactions between UF_6^- and $BF_2^{18}F$ or $UF_5^{18}F$

	Reactants			Time	Temperature	Fraction exchanged
	mmol			min	K	f
UF_6^-, Cu^{II}Salt in MeCN	0.59	$BF_2^{18}F$	0.61	75	293	1.38
UF_6^-, Tl^{III}Salt in MeCN	0.73	$BF_2^{18}F$	0.46	60	294	1.18
$Cu(UF_6)_2 5MeCN$	0.35	$BF_2^{18}F$	0.61	60	293	1.34
$Tl(UF_6)_2 5MeCN$	0.12	$BF_2^{18}F$	0.46	65	294	1.48
$Cu(UF_6)_2 5MeCN$	0.29	$UF_5^{18}F$	0.91	40	292	0.72
$Cu(UF_6)_2 5MeCN$	0.24	$UF_5^{18}F$	0.55	40	293	0.81

Although UF_5 forms complexes with the strong Lewis acid antimony pentafluoride [11], and evidence for complexation with arsenic penta-fluoride in anhydrous HF below room temperature has been reported [12], the possibility of complexation between β- UF_5 and the weaker Lewis acid, BF_3 was surprising. Accordingly interactions between β- or α- UF_5 and [^{18}F]-labelled BF_3, phosphorus pentafluoride, or sulphur tetrafluoride were examined in more detail by following the transfer of ^{18}F activity from gas-to-solid with time. Typical plots of ^{18}F count rate versus time for gas-plus-solid, gas only, and the derived plot of solid count rate versus time are shown in Figure 1 for the $BF_2^{18}F$, β-UF_5 system. Derived solid count rate versus time plots for the systems β- UF_5, $PF_4^{18}F$ or $SF_3^{18}F$ are shown in Figure 2.

In all cases the decrease in ^{18}F count rate observed in the gas phase is too great to be accounted for solely by ^{18}F exchange. This, and the rapid increase in the β- UF_5 count rate with time, can be accounted for if ^{18}F exchange occurs via a strongly adsorbed, surface species which is retained to some extent by β- UF_5. Equilibrium

TABLE 3

^{18}F Exchange reactions between $BF_2{}^{18}F$ and β- or α- UF_5

UF_5		$BF_2{}^{18}F$	Time	Temperature	Fraction exchanged
	mmol	mmol	min	K	f
β- UF_5	0.23	0.22	50	293	1.29
β- UF_5	0.29	0.61	55	293	1.24
β- UF_5	1.11	0.93	60	293	1.15
β- UF_5	0.14	0.22	100	293	1.25
α- UF_5	0.48	0.70	55	293	0.24
α- UF_5	0.26	0.70	55	293	0.30
α- UF_5	0.21	2.73	60	293	0.22

distribution of ^{18}F was not observed in these experiments unless a very small sample of β- UF_5 was used, however the f values obtained (Table 4) indicate that the degree of interaction increases in the order $SF_3{}^{18}F < BF_2{}^{18}F < PF_4{}^{18}F$, the order of increasing Lewis acidity. Similar behaviour was found between β- UF_5 and $[^{18}F]$-labelled gaseous UF_6, WF_6, or Me_3SiF, however interpretation of these systems is complicated by condensation at the β- UF_5 surface during the reaction.

Confirmation of a surface species formed by SF_4 at β- UF_5 is provided by using ^{35}S as a tracer. Admission of $^{35}SF_4$ to β- UF_5 results in the immediate detection of a surface β$^-$ count rate which remains constant over 2h. It is unaffected by removal of gaseous $^{35}SF_4$, admission of additional $^{35}SF_4$, or by admission of inactive SF_4.

In marked contrast to the behaviour of β- UF_5, ^{18}F count rates produced in a α- UF_5 by reaction with $BF_2{}^{18}F$, $PF_4{}^{18}F$, or $SF_3{}^{18}F$ are small, and only small increases with time are observed. Under conditions comparable to those used in Figures 1 and 2 and Table 4, f values are < 0.1. A small surface ^{35}S count rate is detectable when $^{35}SF_4$ is admitted to α- UF_5 but it decreases to zero when the gas is removed, and no retention is observed.

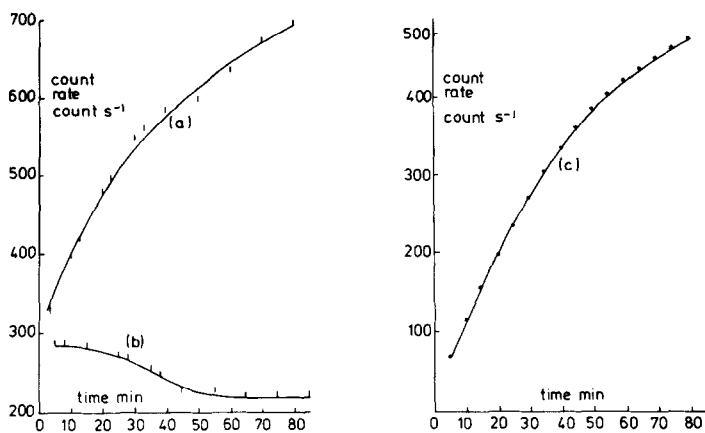Fig. 1. ^{18}F count rate vs. time for β- UF_5 (0.93 mmol) + $BF_2{}^{18}F$ (2.81 mmol); (a) gas + solid, (b) gas, (c) solid, derived from (a) - (b).

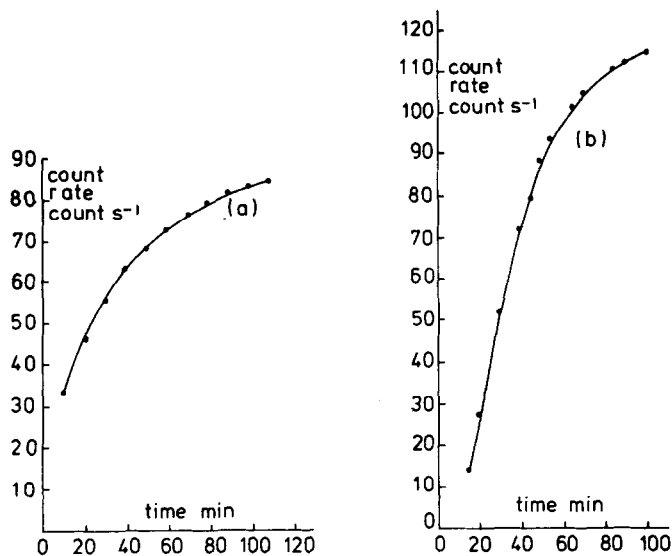Fig. 2. Derived ^{18}F count rate vs. time from solid; (a) β- UF_5 (0.42 mmol) + $PF_4{}^{18}F$ (2.75 mmol), (b) β- UF_5 (0.66 mmol) + $SF_3{}^{18}F$ (2.75 mmol).

TABLE 4

^{18}F Exchange reactions at room temperature between β- UF_5 and $BF_2^{18}F$, $PF_4^{18}F$, or $SF_3^{18}F$

β- UF_5	XF_n	Time	Fraction exchanged
mmol	mmol	min	f
0.93	2.81 ($BF_2^{18}F$)	95	0.91
0.93	2.95 ($BF_2^{18}F$)	95	0.66
0.24	1.80 ($BF_2^{18}F$)	82	1.58
0.45	3.08 ($PF_4^{18}F$)	120	2.34
0.42	2.75 ($PF_4^{18}F$)	120	2.04
0.52	1.62 ($SF_3^{18}F$)	120	0.72
0.66	2.75 ($SF_3^{18}F$)	100	0.67

The different behaviour of α- and β- UF_5 towards these Lewis acid fluorides can be compared with their structures. α- UF_5 contains octahedrally coordinated U^V with trans-F-bridges [13], whereas β- UF_5 is $[UF_{6/2}F_2]_\infty$, in which the coordination polyhedron about U^V is intermediate between a square antiprism and a dodecahedron [14]. Retention of $^{35}SF_4$ by a CsF fluoride surface has been demonstrated previously [15], and the retention of $^{35}SF_4$ by β- UF_5, and by implication that of $BF_2^{18}F$ and $PF_4^{18}F$, suggests that β- UF_5 has more basic surface sites for the adsorption of Lewis acid fluorides than does α- UF_5. This may be a consequence of the greater extent of F-bridging in the β- isomer.

^{18}F Exchange and ligand substitution reactions involving UF_5

The behaviour of $BF_2{}^{18}F$ towards UF_5 in MeCN at room temperature is very similar to that observed for $\beta-$ UF_5 in the absence of a solvent in that f values > 1 are observed (Table 5). $Me_3Si^{18}F$ behaves similarly, and even below room temperature, significant inter-action is observed (Table 5). In view of these results, substitution of F- ligands in UF_5 using BX_3 or Me_3SiX reagents should be facile.

TABLE 5

^{18}F Exchange reactions between UF_5 in MeCN and $BF_2{}^{18}F$ or $Me_3Si^{18}F$

UF_5*	$BF_2{}^{18}F$ or $Me_3Si^{18}F$		Time	Temperature	Fraction exchanged
mmol	mmol		min	K	f
0.29	$BF_2{}^{18}F$	0.39	55	293	1.52
0.33	$BF_2{}^{18}F$	0.37	45	293	1.50
0.51	$BF_2{}^{18}F$	2.74	70	293	1.13
0.59	$Me_3Si^{18}F$	4.48	50	294	1.16
0.55	$Me_3Si^{18}F$	4.30	55	294	1.19
0.49	$Me_3Si^{18}F$	3.93	60	296	0.97
0.80	$Me_3Si^{18}F$	6.50	60	273	0.50
0.42	$Me_3Si^{18}F$	5.02	75	273	0.58
0.50	$Me_3Si^{18}F$	2.96	65	208	0.40[+]

* In MeCN (3cm^3). [+] Heterogeneous conditions, no solvent, $\beta-$ UF_5.

It has been shown elsewhere that $\alpha-$ or $\beta-$ UF_5 react with a large excess of boron trichloride at ambient temperature, in the absence of a solvent, to give $\beta-$ uranium pentachloride [16]. We find that when the mole ratio $\beta-$ $UF_5:BCl_3$ is 1:2, substitution is not complete. The products are a mixture of haloboranes, $BF_{3-n}Cl_n$, n = 0 – 3, and a brown solid whose near i.r. spectrum in MeCN (Figure 3a) indicates the presence of U^V chlorofluorides. The spectrum is distinct from that of UCl_5 in MeCN, but resembles that of 'UF_2Cl_3' the product obtained from the reaction of UF_5 in MeCN with trimethylchlorosilane,

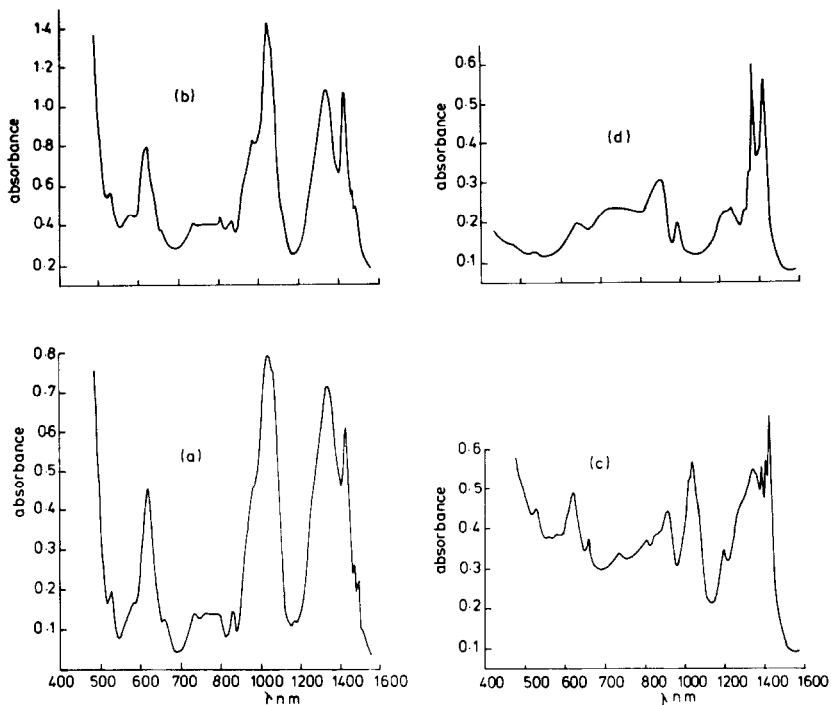Fig. 3.   Near i.r. - visible spectra in MeCN of (a) the solid product
from β- UF_5 + $2BCl_3$ [U^V] ~ 0.2 mol dm^{-3}, (b) the solid product from
UF_5 + $B[OCCl(CF_3)_2]_3$ in MeCN, [U^V] ~ 0.3 mol dm^{-3}, (c) the reaction
mixture 2.9 UF_5 + $B[OCCl(CF_3)_2]_3$ in MeCN, [U^V] ~ 0.1 mol dm^{-3},
(d) UF_5 ~ 0.14 mol dm^{-3}.

1:3 mole ratio.   This may not be a single compound [17].   Similar
behaviour is observed for UF_5 and BCl_3, 1:1 mole ratio, in MeCN.
Redistribution reactions of F and Cl at boron are facile, both in the
gas phase [18] and in MeCN solution [19], also UF_5 and UCl_5 undergo
halogen redistribution in MeCN [17].   However, these reactions alone
are not sufficient to account for the behaviour observed, and it is
necessary to postulate that at least some of the halogen exchange
reactions between U^V and boron chlorofluorides are reversible.   This
is not the case for Me_3Si^- versus U^V exchange [17].

Reactions between UF_5 and tris[1-chloro-1-(trifluoromethyl)-2,2,2,-trifluoroethyl] borate in MeCN are facile at room temperature, but do not yield the expected $UF_{5-n}[OCCl(CF_3)_2]_n$ derivatives. The products obtained are BF_3, hexafluoroacetone, and U^V chlorofluorides. To some extent the identities of the latter depend on the stoichiometry used. The near i.r. spectrum of the product from a 1:1 reaction is virtually identical to that obtained from UF_5 + $2BCl_3$ (Figure 3a and b), and an identical spectrum is obtained from a 3:2, $UF_5 : B[OCCl(CF_3)_2]_3$ reaction mixture in MeCN. The spectrum of $3UF_5$ + $B[OCCl(CF_3)_2]_3$ in MeCN is intermediate between those of UF_5 and the 1:1 product (Figure 3 b,c, and d), and resembles the spectrum of 'UF_4Cl', obtained from UF_5 and Me_3SiCl, 1:1 mole ratio, in MeCN [17].

Apparently the U^V-$OCCl(CF_3)_2$ moiety is unstable with respect to the elimination of $(CF_3)_2CO$ and the formation of a U^V-Cl bond. The alternative explanation, that $B[OCCl(CF_3)_2]_3$ decomposes to give BCl_3 and $(CF_3)_2CO$ in the presence of $UF_5(NCMe)_x$, seems less plausible.

Trimethyl(methoxo)silane reacts with UF_5 in MeCN at ambient temperature to give Me_3SiF, in essentially quantitative yield for UF_5: Me_3SiOMe mole ratios up to 1:2. The major uranium-containing compound under all conditions, mole ratios up to 1:50, is an insoluble, yellow-green solid, which analyses as $UF_3(OMe)_2$. The solid's electronic spectrum shows the presence of U^V, but is distinct from those of $UF_5(NCMe)$ and β- UF_5. A prominent i.r. band at $1030cm^{-1}$ suggests that bridging, rather than terminal MeO- ligands are present [20], and a strong absorption at 465, 505(sh) cm^{-1} is presumed to be due to U^V-F stretching modes. Solid $UF_3(OMe)_2$ undergoes substantial ^{18}F exchange with $Me_3Si^{18}F$ at room temperature (Table 6), but little or no reaction occurs between $UF_3(OMe)_2$ and Me_3SiOMe in the presence of MeCN. A small quantity of a brown solid, soluble in MeCN and in benzene, is obtained after one week. Its electronic spectrum suggests that it is $U(OMe)_5$ or a related species [21], but insufficient material was obtained for characterisation. An identical material is obtained as a trace product in reactions between UF_5 and Me_3SiOMe in MeCN, when the solution is dilute.

TABLE 6

^{18}F Exchange reactions between $UF_3(OMe)_2$ and $Me_3Si^{18}F$

$UF_3(OMe)_2$	$Me_3Si^{18}F$	Time	Temperature	Fraction exchanged
mmol	mmol	min	K	f
0.21	4.13	50	293	0.82
0.43	2.75	50	293	0.84
0.43	3.30	45	294	0.82
0.36	3.30	50	294	0.64

Although the evidence is not definitive, the solid $UF_3(OMe)_2$ appears to be a single compound rather than a fortuitous mixture. Its difference in behaviour towards $Me_3Si^{18}F$ and Me_3SiOMe could be a thermodynamic consequence of the presumably, polymeric solid.

CONCLUSIONS

Although the interpretation of ^{18}F exchange reactions involving UF_6, UF_5, or UF_6^- is complicated by additional reactions which occur, notably complexation between Lewis acid fluorides and $\beta-UF_5$, the results of this study indicate that both $U^{VI}-F$ bonds in UF_6, and U^V-F bonds in a variety of environments, are labile with respect to substitution by ^{18}F. Their lability is an important factor in accounting for the chemical reactivity of these fluorides, and in some cases there is a close analogy between ^{18}F exchange and ligand substitution behaviour.

The relationship between the lability and the electronic properties of a bond is speculative, but in a recent X-ray P.E. spectroscopic investigation of uranium halides, it has been proposed that the ionicity of uranium-halogen bonds increases with increasing oxidation state of U,

and with the halogen's electronegativity [22].   A degree of ionic character in U-F bonds is implied by the crystal structures of SbF_5 adducts with UF_5 [11b], UOF_4, and UO_2F_2 [23], and would account for the behaviour observed in this ^{18}F study.

EXPERIMENTAL

All operations were carried in vacuo or in an Ar-atmosphere glove box (H_2O < 5 p.p.m.).   Synthesis and spectroscopic procedures have been described previously [24].   The fluorides UF_6, WF_6, PF_5, and BF_3 were commercial products which were purified by low temperature trap-to-trap distillation over activated NaF. SF_4 was prepared from S_8 and IF_5 and purified via its BF_3 adduct [25].   The reagents Me_3SiF, Me_3SiOMe, and BCl_3 (all commercial products) were purified by low temperature distillation, and were stored over activated 4A molecular sieves. $B[OCCl(CF_3)]_3$ was prepared from BCl_3 and $(CF_3)_2CO$ [26];   its mp. agreed with that previously reported. Cu^{II} and Tl^{III} hexafluorouranates(V) were prepared as reported previously [9], and α- and β- UF_5 according to literature methods [13,7].   MeCN (Rathburn HPLC grade) was purified and dried by a modification of a standard procedure [27].

Radioactivity measurement

^{18}F activity was determined using a NaI well scintillation counter (Ekco and Nuclear Enterprises), well dimensions 1.56 x 0.78 ins. diameter, samples being contained in calibrated Pyrex ampoules (ca. 7 or 62 cm^3) fitted with P.T.F.E., glass stop-cocks.   Calibrated double limb counting tubes (ca. 62 cm^3) were used to study exchange with time in gas-solid reactions, each limb being intercalibrated before use.   Reproducible counts were obtained in all cases, and linear count-rate versus pressure relationships were obtained for all volatile compounds studied.

Experiments involving ^{35}S were performed in an evacuable Pyrex reaction vessel incorporating two, intercalibrated Geiger-Müller detectors to allow surface ^{35}S activity to be determined directly [28].

Preparation of labelled compounds

^{18}F was prepared by the sequence ^{6}Li$(n,\alpha)^{3}$H; ^{16}O$(^{3}$H,n$)^{18}$F using
the Scottish Universities' Research Reactor, East Kilbride. Work up
of the irradiated product gave Cs^{18}F(aq.) [29] which was evaporated
to dryness and dried in vacuo above 373 K. Volatile fluorides were
labelled by exchange (1h) with Cs^{18}F (ca.1g; 20 µCi) in a Monel metal
bomb (95 cm^{3}) under the following conditions: BF$_{2}$^{18}F, 2.5 - 3.0 x 10^{3}
Torr, 358 K; PF$_{4}$^{18}F, 2.5 - 3.0 x 10^{3} Torr, 378 K; Me$_{3}$Si^{18}F, 10-20
mmol, 298 K; WF$_{5}$^{18}F, 2-5 mmol, 313 K; UF$_{5}$^{18}F and SF$_{3}$^{18}F were prepared
by exchange with BF$_{2}$^{18}F at 298 and 95 K respectively, exchange in the
latter case occurring via [^{18}F]-SF$_{3}$$^{+}BF_{4}$$^{-}$ which was decomposed using
Et$_{2}$0. ^{35}SF$_{4}$ was prepared as previously described [25]. Radio-
chemical purity of [^{18}F]-labelled compounds was established by γ-ray
spectrum and half-life determinations.

Exchange reactions

^{18}F exchange reactions were carried out in counting vessels,
mixtures being made up by weight, or, in the case of [^{18}F]-labelled
BF$_{3}$, PF$_{5}$, or SF$_{4}$, using a calibrated manifold and Bourdon gauge
(Heise, ± 1 Torr). The initially active reagent was counted prior to
its addition, and both components were counted after their separation
by vacuum distillation. Radiochemical balances were > 95% and mass
balances > 98%, however in reactions involving β- UF$_{5}$ or UF$_{6}$$^{-}$ salts,
the solids consistently showed small mass increases (> 35 mg) after
reaction. The stoichiometries and specific activities used were
chosen to minimise counting errors.

Exchange behaviour was compared in terms of the fraction of ^{18}F
activity exchanged (f) determined by

$$f = \frac{A_1}{A_1 + A_2} \left(\frac{xm_1}{xm_1 + ym_2} \right)^{-1} = \frac{(A_o - A_2)(xm_1 + ym_2)}{A_o\, xm_1}$$

A_1 and A_2 count s^{-1} are the count rates, corrected for decay, after exchange between m_1 and m_2 mmol of reactants (1 being inactive initially) containing respectively x and y F atoms. A_o count s^{-1} is the corrected count rate of reactant 2 before exchange. The second relationship was used in gas-solid reactions, where counting efficiencies of the two reactants were significantly different.

The distribution of ^{18}F activity with time in UF_5, XF_n systems was studied by loading a known mass of UF_5 into one limb of a double limb counting vessel, and condensing a measured quantity of $[^{18}F]-XF_n$, whose count rate had been determined, into the other limb. The gas was warmed rapidly to room temperature, and count rates were determined from alternate limbs at regular intervals. After a specified time, the components were counted separately, and f values calculated. Count rates for the solid component at various times during the reaction were obtained by subtraction of the gas count rate from that of gas-plus-solid, using the plots of count rate versus time.

The interaction of $^{35}SF_4$ with α- or β- UF_5 was studied using the procedure previously developed for $^{35}SF_4$ or ^{36}ClF with CsF [10]. In some experiments treatment of α- UF_5 with $^{35}SF_4$ or $SF_3^{18}F$ resulted in a green colouration of the solid's surface, suggesting the possibility of α → β isomerisation. However the radiochemical behaviour of the two isomers was always different, and there was no evidence of a chemical reaction. α- UF_5 appeared to be more susceptible to trace hydrolysis than was the β- isomer.

Substitution reactions of UF_5

(a) With BCl_3

A mixture of β- UF_5 (1.74 mmol) and BCl_3 (3.48 mmol), allowed to react at room temperature for 0.5 h, gave a dark brown solid and volatile material. The latter was identified by i.r. spectroscopy as a mixture of $BCl_{3-n}F_n$, n = 0-3 [18]. Addition of MeCN to the solid produced initially a yellow, and finally a green solution, whose electronic spectrum (Figure 3a) indicated that U^V chlorofluorides [17] were present. A mixture of β- UF_5 (1.84 mmol) and BCl_3 (1.81 mmol) in MeCN (6 cm^3), allowed to react at room temperature for 18 h, gave a

green solid after removal of $BCl_{3-n}F_n$. The i.r. spectrum of the
solid indicated the presence of co-ordinated MeCN, in particular
the presence of BCl_3.NCMe [30]. The electronic spectrum of the
solid redissolved in MeCN, was very similar to Figure 3a, being
identical in the 600-700 and 900-1100 nm region, and differing only
in relative intensities of the bands in the 1200-1500 nm region.

(b) With $B[OCCl(CF_3)_2]_3$

A mixture of β- UF_5 (1.56 mmol) and $B[OCCl(CF_3)_2]_3$ (1.54 mmol)
in MeCN (6 cm^3), allowed to react at room temperature for 18 h, gave
a yellow-green solution. Removal of volatile material, shown to be
a mixture of $(CF_3)_2CO$, BF_3, and MeCN by i.r. spectroscopy, left a
green solid. The electronic spectrum of the latter, redissolved in
MeCN, (Figure 3b) was almost identical to that obtained from β- UF_5 +
$2BCl_3$. The solid's i.r. spectrum contained bands due to co-ordinated
MeCN, and a strong band at 505 cm^{-1}. The electronic spectrum of
β- UF_5 (0.38 mmol) and $B[OCCl(CF_3)_2]_3$ (0.28 mmol) in MeCN (4 cm^3) was
identical to Figure 3b, and that obtained from β- UF_5 (0.41 mmol) and
$B[OCCl(CF_3)_2]_3$ (0.14 mmol) in MeCN (4 cm^3) (Figure 3c) was intermediate
between those of Figure 3b and UF_5 in MeCN (Figure 3d). In neither
case did the spectrum change with time. The reaction between β- UF_5
(0.62 mmol) and $B[OCCl(CF_3)_2]_3$ (1.86 mmol) in MeCN (6 cm^3) was similar
to those described above, but the solid product appeared to contain
unreacted borate.

(c) With Me_3SiOMe

A mixture of β- UF_5 (0.33 mmol), Me_3SiOMe (0.33 mmol) and MeCN
(2.08 g), allowed to react at room temperature for 1h, gave a yellow-
green solid and a brown solution. The volatile material was a mix-
ture of MeCN and Me_3SiF (0.35 mmol), identified by i.r. spectroscopy.
A similar reaction between β- UF_5 (0.47 mmol) and Me_3SiOMe (0.94 mmol)
in MeCN (3.71 g) gave Me_3SiF (0.89 mmol). Analysis of the yellow-
green, insoluble solid isolated from β- UF_5 (3.3 mmol) and Me_3SiOMe
(21.3 mmol) corresponded to uranium(V) trifluoride dimethoxide.
Found C, 6.6; H, 1.6; F, 15.8; U, 66.7. $C_2H_6F_3O_2U$ requires
C, 6.7; H, 1.7; F, 16.0; U, 66.7%. The electronic spectrum of

$UF_3(OMe)_2$ (Nujol mull) was: λ_{max} 1565(m), 1430(w,br), 1045(m), 885(sh) nm. The spectrum of $\beta-UF_5$, obtained under similar conditions was: λ_{max} 1400(s), 1370(s), 1200(m, br), 935(s), 900(sh) nm, and that of solid UF_5(NCMe) was: λ_{max} 1430(s), 1405(sh), 1330(vw), 1170(sh), 1122(w, br), 700(w, br) nm. The spectra of solid products obtained using different mole ratios of reactants were identical.

REFERENCES

1 Presented at the 10th International Symposium on Fluorine Chemistry, 1982; J. Fluorine Chem. 21 (1982) 93, abst. P-13. For Part VII, see ref. 15.

2 R.T. Poole and J.M. Winfield, J. Chem. Soc., Dalton Trans., (1976) 1557.

3 C.J.W. Fraser, D.W.A. Sharp, G. Webb, and J.M. Winfield, J. Chem. Soc., Dalton Trans., (1972) 2226.

4 E.A. Cuellar and T.J. Marks, Inorg. Chem., 20 (1981) 2129.

5 T.A. O'Donnell, D.F. Stewart, and P. Wilson, Inorg.Chem., 5 (1966) 1438.

6 K. Seppelt, Chem. Ber., 109 (1976) 1046; L.K. Templeton, D.H. Templeton, N. Bartlett, and K. Seppelt, Inorg. Chem., 15 (1976) 2720.

7 J.A. Berry, A. Prescott, D.W.A. Sharp, and J.M. Winfield, J. Fluorine Chem., 10 (1977) 247.

8 A.W. Laubengayer and D.S. Sears, J.Am. Chem. Soc., 67 (1945) 164.

9 J.A. Berry, R.T. Poole, A. Prescott, D.W.A. Sharp, and J.M. Winfield, J. Chem. Soc., Dalton Trans., (1976) 272.

10 A Prescott, D.W.A. Sharp, and J.M. Winfield, J. Chem. Soc., Dalton Trans., (1975) 934.

11 (a) R. Bougon and P. Charpin, J. Fluorine Chem., 14 (1979) 235;
   (b) W. Sawodny, K. Rediess and U. Thewalt, Z. Anorg. Allg. Chem., 469 (1980) 81.

12 B. Frlec and D. Gantar, J. Fluorine Chem., 16 (1980) 633.

13 P.G. Eller, A.C. Larson, J.R. Peterson, D.D. Ensor, and J.P. Young Inorg. Chim. Acta, 37 (1979) 129

14 R.R. Ryan, R.A. Penneman, L.B. Asprey, and R.T. Paine, Acta Crystallogr., Sect. B, 32 (1976) 3311; J.C. Taylor and A.B. Waugh, J. Solid State Chem., 35 (1980) 137.

15 G.A. Kolta, G. Webb, and J.M. Winfield, Appl. Catal., 2 (1982) 257.

16 D. Brown, J.A. Berry, and J.H. Holloway, J. Chem. Soc., Dalton Trans., (1982) 1385.

17 J.A. Berry, J.H. Holloway, and D. Brown, Inorg. Nucl.Chem. Lett., 17 (1981) 5.

18 L.P. Lindeman and M.K. Wilson, J. Chem. Phys., 24 (1956) 242; D.F. Wolfe and G.L. Humphrey,J. Mol. Struct., 3 (1969) 293.

19 J.S. Hartman and J.M. Miller, Adv. Inorg. Chem. Radiochem., 21 (1978) 147.

20 D.C. Bradley and A.H. Westlake, Proc. Symp. Co-ord. Chem., Tihans, Hungary, M. Beck (ed.), (1965) 309.

21 D.G. Karraker, Inorg. Chem., 3 (1964) 1618.

22 E. Thibaut, J.-P. Boutique, J.J. Verbist, J.-C. Levet, and H. Noël, J.Am. Chem. Soc, 104 (1982) 5266.

23 R. Bougon, J. Fawcett, J.H. Holloway, and D.R. Russell, J.Chem.Soc. Dalton Trans., (1979) 1881; J. Fawcett, J.H. Holloway, D. Laycock, and D.R. Russell, J. Chem. Soc., Dalton Trans., (1982) 1355.

24 C.J. Barbour, J.H. Cameron, and J.M. Winfield, J. Chem. Soc., Dalton Trans., (1980) 2001.

25 G.A. Kolta, G. Webb, and J.M. Winfield, J. Fluorine Chem., 19 1981/82) 89.

26 E.W. Abel, N. Giles, D.J. Walker, and J.N. Wingfield, J. Chem. Soc. (A), (1971) 1991.

27 M. Walter and L. Ramaley, Anal. Chem., 45 (1973) 165.

28 A.S. Al-Ammar and G. Webb, J. Chem. Soc., Faraday Trans 1, 74 (1978) 195.

29 J.E. Whitley, Scottish Research Reactor Centre Report, No. SRRC 26/68; Nucl. Sci. Abs., 22 (1968) 30592.

30 D.F. Shriver and B. Swanson, Inorg. Chem., 10 (1971) 1354.