Radiotracers in Fluorine Chemistry. Part IV.[1] Fluorine-18 Exchange between labelled Alkylfluorosilanes and Fluorides, or Fluoride Methoxides, of Tungsten(VI), Molybdenum(VI), Tellurium(VI), and Iodine(V) †

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Exchange of ^{18}F between labelled alkylfluorosilanes and fluoride methoxides gives the sequences of rates $WF_6 < WF_5(OMe) \geqslant WF_4(OMe)_2 > WF_3(OMe)_3 > WF_2(OMe)_4$, $MoF_6 \gg MoF_{6-n}(OMe)_n$ (n = 4 or 5), and $IF_4(OMe) > IF_5$. Exchange with tellurium compounds is too slow to measure. An associative mechanism is proposed for the ^{18}F-exchange reactions, and the exchange reactions are compared with similar substitution reactions.

WE have shown previously [1] that the extent of fluorine-18 exchange between ^{18}F-labelled fluorotrimethylsilane and substituted tungsten(VI) fluorides, $WF_{6-n}X_n$ (X = OMe, OPh, OC_6F_5, or NEt_2), depends both on the identity and on the number of substituents present. This paper describes the results of a more detailed ^{18}F-exchange study, in which the effect of the methoxide ligand on the lability of various element–fluorine (M–F) bonds (M = W^{VI}, Mo^{VI}, Te^{VI}, or I^{V}) has been determined.

EXPERIMENTAL

Vacuum and inert-atmosphere (Lintott inert-atmosphere box, $\leqslant$10 p.p.m. of water) techniques were used throughout. Tungsten and molybdenum hexafluorides and iodine pentafluoride (from Alfa Inorganics or Fluorochem Ltd.) were purified by trap-to-trap distillation and stored over NaF. Fluoride methoxides of W^{VI}, Mo^{VI}, and I^{V} were prepared by literature methods.[2] Tellurium hexafluoride and tellurium(VI) pentafluoride methoxide were gifts from Dr. G. W. Fraser, Strathclyde University. Alkylfluorosilanes were either commercial samples (PCR Inc.) or were prepared by the fluorination of other alkylsilyl compounds.[2] Hexafluorobenzene (Fluorochem Ltd.) was dried and stored over sodium.

Compounds were labelled with ^{18}F usually by exchange at room temperature in a stainless-steel vessel with solid $Cs^{18}F$ (*ca.* 0.1 mCi).[3] Labelled $WF_4(OMe)_2$ was prepared from $SiMe_2(OMe)_2$ and $W^{18}F_6$. In each case the radiochemical purity was checked by decay-curve determination ($t_{\frac{1}{2}}$ 110 min) over at least three half-lives. Fluorine-18 activity was measured by a NaI-well scintillation counter (Ekco Instruments) as described previously.[3]

The reactants were selected to ensure rapid separation by distillation *in vacuo* after exchange. Reactions were carried out on a small scale (typically 0.6 mmol) in calibrated Pyrex counting tubes (*ca.* 2 cm^3) fitted with polytetrafluoroethylene stopcocks (Fischer and Porter), because of ready hydrolysis of the compounds. In order to minimise concentration errors, reaction mixtures were made up by weight rather than by volume. Allowance was made for components present in the vapour phase by using measured values of the partial pressures.

The reaction procedure was as follows. A stock solution of the unlabelled involatile component in C_6F_6, which did not undergo ^{18}F exchange under the conditions used, was prepared *in vacuo*, and aliquot portions were transferred to counting tubes in the inert-atmosphere box using a calibrated Pasteur pipette. After degassing and weighing, a weighed quantity of the labelled volatile component, whose ^{18}F activity had been previously determined, was added to each tube. As far as possible, solution volumes and mole ratios of reactants were kept constant for a given run. The reaction mixtures were rapidly warmed to the desired temperature and thermostatted. After a suitable time a mixture was frozen, the components separated, and counted either in C_6F_6, or after hydrolysis, in aqueous acetone. When both components were volatile, each sample in a run was prepared individually.

Reproducible counts were obtained in each case, but the best data [10^4—10^6 counts (100 s)$^{-1}$] were obtained with a 1 : 1 mol ratio of reactants. Mass balances were $\geqslant$98% and radiochemical balances were $\geqslant$95%. The latter were very sensitive to hydrolysis, and as such were used as a criterion of purity. For each solution the fraction of ^{18}F activity exchanged (f) was determined, where f is defined as in equation (1); A_1 and A_2 (counts s^{-1}) are the activities,

$$\frac{A_1}{A_1 + A_2} \cdot \left(\frac{xm_1}{xm_1 + ym_2}\right)^{-1} \qquad (1)$$

corrected for decay, after exchange between m_1 and m_2 mmol of the components 1 and 2 containing x and y exchangeable F atoms. Because of the short half-life of ^{18}F, complete exchange was not demonstrated in all cases, and x and y were assumed to equal the numbers of F atoms in the molecules.

The extent of exchange varied from being complete within the time of mixing to being unobservable after 2 h (count rate <25 counts s^{-1}). For the intermediate cases plots of $\log[1/(1-f)]$ against time were obtained according to the McKay equation.[4] Rates of exchange were obtained from linear plots by least-squares fitting. Relative errors in f were <5%; the uncertainty in the rates is considered to be $< \pm 15\%$. Rate data from different systems may be compared as the stoicheiometries and solution volumes were similar in each case.

Fluorine-18 exchange between $SiMe_3{}^{18}F$ and $WF_5(OMe)$ or $WF_4(OMe)_2$ was rapid enough for concentration-variation studies to be carried out. Counting and solubility considerations limited the $WF_5(OMe)$ concentration range to 0.2—2.0 mol (kg C_6F_6)$^{-1}$, and the requirement that the volume of $SiMe_3F$ should be small with respect to that of

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† No reprints available

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C_6F_6 limited the $SiMe_3F$ concentration to < 1 mol (kg $C_6F_6)^{-1}$. Temperature-variation studies in the $SiMe_3{}^{18}F$–$WF_5(OMe)$ system were limited (283—303 K) by the m.p. of C_6F_6 and by the thermal instability of $WF_5(OMe)$.

RESULTS

The results of the ^{18}F-exchange reactions are given in Tables 1—3.* Exchange between $WF_5(OMe)$ and $B^{18}F_3$ in C_6F_6 at 293 K was essentially complete within 1 h (Table 3), and exchange was readily observed between $WF_5(OMe)$ and $SiMe_3{}^{18}F$, $SiMe_2{}^{18}F$, or $W^{18}F_6$ under similar conditions (Table 1). Although $WF_5(OMe)$ is monomeric in C_6F_6,[2a] and thus contains structurally non-equivalent fluoride ligands, the linear McKay plots obtained (see also ref. 1) indicate that, within experimental error, all F ligands exchange at similar rates. The alternative explanation, that four F ligands (*cis* to OMe) exchange but that the fifth does not, is considered unlikely.

TABLE 1

Fluorine-18 exchange reactions involving tungsten(VI) fluoride methoxides [a]

Reactants and concentrations [mol (kg $C_6F_6)^{-1}$]				No. of points on McKay plot	10^3 Rate of exchange [b] mol (kg $C_6F_6)^{-1}$ min^{-1}
$WF_5(OMe)$	1.002	$SiMe_3{}^*F$	1.093 (av)	6	1.94
$WF_5(OMe)$	0.986	$SiMe_3{}^*F$	1.117 (av)	6	2.66
$WF_5(OMe)$ [c]	0.979	$SiMe_3{}^*F$	1.020 (av)	3	1.54
$WF_5(OMe)$ [d]	0.979	$SiMe_3{}^*F$	0.980 (av)	3	3.98
$WF_4(OMe)_2$ [e]	1.037	$SiMe_3{}^*F$	0.927 (av)	5	1.36
$W^*F_4(OMe)_2$ [e]	1.020	$SiMe_3F$	1.054 (av)	5	1.69
$WF_4(OMe)_2$	0.997	$SiMe_3{}^*F$	1.025 (av)	6	4.95
$WF_3(OMe)_3$	0.996	$SiMe_3{}^*F$	1.114 (av)	6	0.70
$WF_2(OMe)_4$	1.055	$SiMe_3{}^*F$	1.206		*f*
$WF_5(OMe)$	1.042	$SiMe_2{}^*F_2$	0.890 (av)	6	2.74
$WF_5(OMe)$	1.003	$SiMe_2{}^*F_2$	0.972 (av)	6	3.37
$WF_4(OMe)_2$ [e]	1.011	$SiMe_2{}^*F_2$	1.148 (av)	6	2.65
$WF_5(OMe)$	0.968	W^*F_6	0.892 (av)	5	10.1
$WF_5(OMe)$	0.966	W^*F_6	1.032 (av)	6	9.50

[a] At 293 ± 0.1 K except where otherwise indicated. Under similar conditions ^{18}F exchange between $SiEt_3F$ and $W^{18}F_6$ is negligible. Rate of exchange ~10^{-4} mol (kg $C_6F_6)^{-1}$ min^{-1}. [b] Estimated uncertainty ± 15%. [c] At 283 ± 0.1 K. [d] At 303 ± 0.1 K. [e] Freshly prepared sample. [f] No measurable exchange after 4 h.

TABLE 2

Fluorine-18 exchange between alkylfluorosilanes and molybdenum(VI) or iodine(V) fluorides [a]

Reactants and concentrations [mol (kg $C_6F_6)^{-1}$]				No. of points on McKay plot	10^3 Rate of exchange [b] mol (kg $C_6F_6)^{-1}$ min^{-1}
Mo^*F_6	0.766	$SiEt_3F$	1.048		*c*
$MoF_2(OMe)_4$	0.957	$SiMe_3{}^*F$	0.959		*d*
$MoF(OMe)_5$	0.964	$SiMe_3{}^*F$	0.969		*d*
IF_5	1.072	$SiMe_2{}^*F_2$	0.901 (av)	4	0.32
$IF_4(OMe)$	0.973	$SiMe_2{}^*F_2$	1.113 (av)	6	5.09

[a] At 293 ± 0.1 K. Under similar conditions no measurable exchange was observed between $SiEt_3{}^{18}F$ and TeF_6 or $TeF_5(OMe)$. [b] Estimated uncertainty ±15%. [c] Complete exchange observed within 1 h; the solution was dark brown and the colour persisted to some extent in the MoF_6 fraction on separation. However the mass and radiochemical balances were satisfactory. [d] No measurable exchange after 4 h.

TABLE 3

Fluorine-18 exchange reactions involving B^*F_3 in C_6F_6 [a]

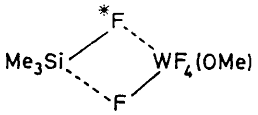
Reactants and concentrations (mmol)				*t*/min	Fraction exchanged, *f*
$WF_5(OMe)$	0.834	B^*F_3	0.748	60	0.954 ± 0.014
$WF_5(OMe)$	0.843	B^*F_3	0.739	180	0.951 ± 0.020
IF_5	0.819	B^*F_3	0.574	45	0.598 ± 0.003
IF_5	0.590	B^*F_3	0.549	180	0.876 ± 0.005
$SiEt_3F$	0.620	B^*F_3	0.544	75	0.144 ± 0.002
$SiEt_3F$	0.622	B^*F_3	0.596	180	0.342 ± 0.004

[a] At 293 ± 0.1 K; B^*F_3 added to solutions which were *ca.* 1 mol (kg $C_6F_6)^{-1}$ in reactant.

Tungsten(VI) pentafluoride methoxide decomposed slowly at room temperature according to equation (2), and while there was no evidence for decomposition in the samples used the lower rate obtained for a given reaction is probably

$$WF_5(OMe) \longrightarrow WF_4O + MeF \qquad (2)$$

more reliable. The apparent activation energy for the exchange between $SiMe_3{}^{18}F$ and $WF_5(OMe)$ is *ca.* 33 kJ mol^{-1}, and the entropy of activation is negative. The limited data from the accessible concentration range indicates a rate $\propto [SiMe_3{}^{18}F][WF_5(OMe)]^2$, consistent with an associative mechanism but not with a simple four-centred transition state, (I).



(I)

The compounds $WF_{6-n}(OMe)_n$ (n = 2—4) are monomeric in C_6F_6, and, when n = 2 or 4, exist as *cis* isomers.[2a] It was not possible to separate the *cis* and *trans* isomers of $WF_3(OMe)_3$, and a mixture was therefore examined. Ex-

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* Solution stoicheiometries and *f* values used in calculating the rates are contained in Supplementary Publication No. SUP 21772 (4 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full size copies).

cept for *cis*-$WF_2(OMe)_4$, where exchange was too slow to be measured, linear McKay plots were obtained with $SiMe_3{}^{18}F$ or $SiMe_2{}^{18}F_2$. As with $WF_5(OMe)$, it is considered that the non-equivalent F ligands within a compound exchange at comparable rates.

Rates of exchange involving *cis*-$WF_4(OMe)_2$ were markedly dependent on the history of the sample. Smaller exchange rates were obtained with freshly prepared samples (Table 1). The McKay plots had positive values of $\log[1/(1-f)]$ at zero time, but these are too small to be due to a very fast exchange process involving two of the F ligands in $WF_4(OMe)_2$. The reaction order with respect to $WF_4(OMe)_2$ also depended on the history of the sample in contrast to the behaviour found for $WF_5(OMe)$. The compound $WF_4(OMe)_2$ is known to isomerise slowly at room temperature [equation (3)],[2a] and the observed exchange behaviour

$$cis\text{-}WF_4(OMe)_2 \longrightarrow WF_4O{\cdot}OMe_2 \qquad (3)$$

may be explained by postulating an additional fast exchange between $SiMe_3{}^{18}F$ and $WF_4O{\cdot}OMe_2$. Although the latter compound could not be detected by n.m.r. spectroscopy, its presence to a small extent may distort the results obtained, particularly for aged samples. Rates determined from freshly prepared samples are considered to be more relevant to the pure compound.

The variation in exchange rates (Table 1) between $SiMe_3{}^{18}F$ and the compounds $WF_{6-n}(OMe)_n$ was small, but a decrease in rate with increasing n was apparent, *i.e.* $WF_5(OMe) \geqslant WF_4(OMe)_2 > WF_3(OMe)_3 > WF_2(OMe)_4$. The compound $SiMe_2{}^{18}F_2$ undergoes exchange with $WF_4(OMe)_2$ more readily than does $SiMe_3{}^{18}F$, and at a rate comparable to that observed between $SiMe_2{}^{18}F_2$ and $WF_5(OMe)$.

Complete exchange occurred between $B^{18}F_3$ and $WF_4(OMe)_2$ or $WF_2(OMe)_4$ within the time of mixing; however the n.m.r. spectra of the solutions indicate that F-for-OMe exchange also occurred [equations (4) and (5)].

$$WF_4(OMe)_2 + BF_3 \longrightarrow WF_5(OMe) + BF_2(OMe) \qquad (4)$$

$$WF_2(OMe)_4 + BF_3 \longrightarrow WF_5(OMe) + B(OMe)_3 \qquad (5)$$

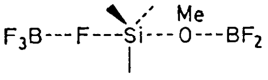
Similar reactions have been observed previously between $WF_2(OMe)_4$ and $WF_5(OMe)$[2a] and between WF_6 and $B(OMe)_3$.[5]

The behaviour of $MoF_2(OMe)_4$ and $MoF(OMe)_5$ towards $SiMe_3{}^{18}F$ is similar to that of $WF_2(OMe)_4$; however in contrast to WF_6, exchange between MoF_6 and $SiEt_3{}^{18}F$ in C_6F_6 was rapid at 293 K (Table 2). It is possible that MoF_6 and $SiEt_3F$ react to a very small extent, although there was no evidence for this. The compounds MoF_6 and $SiMe_3F$ formed an intense yellow liquid whose components could not be completely separated by fractional vacuum distillation, and a solution of MoF_6 in C_6F_6 is dark red. The colours are ascribed to contact charge-transfer interactions,[6] and it is likely that the dark brown colour of the $SiEt_3F$–MoF_6–C_6F_6 solution has a similar origin. It is noteworthy that MoF_6 undergoes exchange with $SiEt_3{}^{18}F$ more readily than does BF_3 (Table 3), even though the latter compound is usually considered to be the stronger Lewis acid.

Substitution of a fluoride by a methoxide ligand in iodine pentafluoride labilises the remaining F ligands towards exchange with $SiMe_2{}^{18}F_2$ (Table 2). Linear McKay plots were obtained for both compounds, although the rates of exchange are greater than for their tungsten(VI) counterparts. The ^{19}F n.m.r. spectrum of IF_5 in C_6F_6 indicates that the molecule has C_{4v} symmetry, although there may be weak interactions between neighbouring molecules.[7] The structural evidence for $IF_4(OMe)$ is not definitive, but its n.m.r. spectra are consistent with a square-pyramidal structure in which the OMe ligand occupies the axial position.[2c] In contrast, the six-co-ordinate compounds TeF_6 and $TeF_5(OMe)$ [8] do not undergo measurable exchange with $SiEt_3{}^{18}F$ under similar conditions.

DISCUSSION

Substitution reactions at a four-co-ordinate silicon centre characteristically occur *via* associative mechanisms involving five-co-ordinate transition states.[9] Retention or inversion of the sterochemistry about Si may occur, depending on the nature of the entering and leaving groups.[10] For example, in the reactions of fluoro(methyl)-(α-naphthyl)phenylsilane with LiR (R = alkyl or aryl group) the stereochemistries of the products depend on the nature of R.[11] Of particular relevance to the present work are the reactions of optically active SiRR′R″(OMe) compounds with BF_3 or $OEt_2{\cdot}BF_3$ in pentane or OEt_2, which occur with predominant inversion of stereochemistry at Si. This is not explicable on the basis of a simple four-centre transition state. The proposed reaction scheme is second order in BF_3 and involves the transition state (II).[12]



(II)

Far less mechanistic information is available on substitution reactions of high-oxidation-state transition-metal fluoride derivatives, but ligand-exchange reactions of the type $MF_5L + L^* \rightleftharpoons MF_5L^* + L$ occur by an associative process.[13] A possible scheme for the ^{18}F-exchange reaction between $WF_5(OMe)$ and $SiMe_3F$ is in equations (6) and (7) which requires a transition state

$$WF_5(OMe) + SiMe_3{}^{18}F \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (MeO)F_4WFSiMe_3{}^{18}F,\ k_2 > k_1 \qquad (6)$$

$$(MeO)F_4WFSiMe_3{}^{18}F + WF_5(OMe) \longrightarrow \text{exchange} \qquad (7)$$

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containing seven-co-ordinate tungsten. The geometry of the transition state is expected to be non-rigid in solution, accounting for the absence of *cis* or *trans* effects due to the OMe ligand. Formally, $WF_5(OMe)$ is required to behave both as a donor and as an acceptor. The latter property is characteristic of high-oxidation-state fluorides,[14] and the behaviour of $WF_5(OMe)$ towards $B^{18}F_3$ and $W^{18}F_6$ is consistent with its function as a donor. Fluorine-18 exchange occurs more readily with these compounds than with the weaker Lewis acids $SiMe_2{}^{18}F_2$ and $SiMe_3{}^{18}F$. It is considered that the donor site in $WF_5(OMe)$ is an F rather than the OMe ligand which would have a larger steric requirement. The function of the OMe ligand is to reduce the effective nuclear charge at tungsten, either *via* π (ref. 15) or *via* σ orbitals, with consequent increase in electron density at the F ligands. N.m.r. studies on the compounds $WF_{6-n}(OMe)_n$ show that the OMe ligand effect is transmitted most strongly to the *trans* F ligands,[16] thus the *trans* F ligand in $WF_5(OMe)$ may be the preferred donor site.

The ^{18}F-exchange behaviour of the other fluoride methoxides towards alkylfluorosilanes may be rationalised on a similar basis. In the series $WF_{6-n}(OMe)_n$, donor properties will increase with increase in n, but acceptor properties will decrease for both steric and electronic reasons. Both properties are necessary as neither WF_6, which is a good F acceptor in solution,[14b] nor $WF_2(OMe)_4$, $MoF_2(OMe)_4$, nor $MoF(OMe)_5$, readily undergo ^{18}F exchange.

The greater lability of IF_5 and $IF_4(OMe)$ compared with the tellurium(VI) compounds arises partly from the square-pyramidal structures of these molecules which facilitate the formation of donor–acceptor interactions. The shielding effect of the 'lone pair' in IF_5 on the iodine(V) nuclear charge is less than that of the fluoride ligands and relatively short $F\cdots I{-}F$ polar contacts exist both in solid IF_5 and in $XeF_2\cdot IF_5$.[17] Similarly there is good evidence that liquid IF_5 is associated to some extent,[18,7] and the compound forms weak complexes with organic donor molecules.[19]

There is a close correspondence between the behaviour of a fluoride methoxide $MF_{x-n}(OMe)_n$ towards $SiMe_3{}^{18}F$ or $SiMe_2{}^{18}F_2$ and its behaviour towards further substitution with $SiMe_3(OMe)$ or $SiMe_2(OMe)_2$. The following observations are relevant. The compound $WF_5(OMe)$ reacts rapidly with $SiMe_3(OMe)$ or $SiMe_2(OMe)_2$ to give *cis*-$WF_4(OMe)_2$, but the next two substitution steps are considerably slower. Substitution beyond $n = 4$ in the series $WF_{6-n}(OMe)_n$ does not occur at room temperature using $SiMe_3(OMe)$, and is very slow using $SiMe_2(OMe)_2$.[2a] Similar reactions designed to produce $MoF_{6-n}(OMe)_n$ ($n = 1$—3) are very vigorous, and the products are thermally unstable. Further substitution, giving products with $n = 4$ or 5, occurs very slowly and is achieved only with $SiMe_2(OMe)_2$.[2b] Complete replacement of F ligands in IF_5 by OMe occurs with $SiMe_2(OMe)_2$, although the final step is slow. The reactions are complicated by the lability of $IF_3(OMe)_2$ which dismutates to $IF_4(OMe)$ and $IF_2(OMe)_3$. Both IF_5 and $IF_4(OMe)$ react with $SiMe_3F$, giving $SiMe_2F_2$ as one product.[2c] In contrast, TeF_6 does not react with $SiMe_3(OMe)$, and the compounds $TeF_{6-n}(OMe)_n$ ($n = 1$ or 2) are prepared either from TeF_6 and MeOH,[8] or from $Te(OMe)_6$ and HF.[20]

Although the mechanisms of OMe-for-F substitution and of ^{18}F exchange may differ in detail, in both cases donor and acceptor properties of each reactant are important. The ^{18}F-exchange results have a predictive value therefore in future synthetic work.

The absence of specific *cis*- or *trans*-labilising effects due to the OMe ligands in the $WF_{6-n}(OMe)_n$ series suggests that the preference for a *cis* configuration when $n = 2$ or 4 has a thermodynamic rather than a kinetic origin. The preference may result from a significant $(p-d)\pi$ bonding contribution in the W^{VI}–O bonds. This suggestion has been advanced to explain the thermochemical differences between tungsten(VI) chloride fluorides and fluoride methoxides,[21] and it is noteworthy that some $TeF_4(OR)_2$ and $TeF_2(OR)_4$ compounds, in which $(p-d)\pi$ bonding should be less important, exist as *cis–trans* mixtures.[8,20]

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