Synthesis of a new volatile technetium(VII) oxofluoride, $TcOF_5$

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Krypton difluoride reacts with TcO_2F_3 in HF at room temperature to yield the last member of the Tc^{VII} oxofluoride series, $TcOF_5$, which is characterized in solution by ^{19}F and ^{99}Tc NMR spectroscopy and in HF solution and in the solid state by Raman spectroscopy

Technetium-99, a low energy β-emitter (293 keV β^-; $t_{\frac{1}{2}}$ = 2.13 × 10^5 y), makes up approximately 6% of the uranium fission products produced by commercial nuclear reactors. Fluorination of the unspent nuclear fuel, in the form of UO_2, for re-enrichment of ^{235}U yields volatile TcO_3F, TcF_6 and possibly other technetium oxofluorides which must be separated from UF_6 process feeds prior to enrichment by gaseous diffusion. Technetium-99 enters the gaseous diffusion stream and remains as a low-level contaminant in ^{235}U enriched UF_6 which may be released into the environment when nuclear fuel elements are refabricated. Consequently, an understanding of the fluoride and oxofluoride chemistry of high-valent technetium is of fundamental importance to the reprocessing of nuclear fuels.[1]

Unlike their rhenium analogues, ReO_3F, ReO_2F_3 and $ReOF_5$, which have been known for some time,[2,3] the members of the technetium(VII) oxofluoride series have proven more difficult to synthesize. Pertechnyl fluoride, TcO_3F, a volatile yellow liquid was prepared by passing fluorine gas over TcO_2 at 150 °C[4] and by the solvolysis of pertechnetate salts in anhydrous HF and has been spectroscopically characterized.[5] Over 30 years elapsed before the next highest oxofluoride, TcO_2F_3, was prepared in our laboratory by the solvolysis of Tc_2O_7 in anhydrous HF to give TcO_3F followed by fluorination with XeF_6, which also served to scavenge water formed in the solvolysis step, to give near quantitative yields of TcO_2F_3.[6] The bright yellow solid was characterized by Raman spectroscopy and single-crystal X-ray diffraction and shown to be an open chain fluorine-bridged structure consisting of TcO_2F_4 units in which the oxygens are *cis* to each other and the bridge fluorines are *trans* to the oxygen atoms. Reaction of TcO_2F_3 with XeF_6 in HF led to the formation of $XeF_5^+TcO_2F_4^-$ and did not result in further fluorination to give $TcOF_5$.

In addition to $ReOF_5$,[3] the only other +7 oxidation state, six-coordinate species reported thus far are IOF_5[7] and $OsOF_5$.[8] In view of the recent successful synthesis of *cis*-OsO_2F_4 from OsO_4 and KrF_2,[9] a similar approach was used to prepare $TcOF_5$. Technetium(VII) oxide pentafluoride was prepared according to eqn. (1) by the reaction of TcO_2F_3 with a twofold excess of KrF_2

$$TcO_2F_3 + KrF_2 \xrightarrow{HF} TcOF_5 + \tfrac{1}{2}O_2 + Kr \qquad (1)$$

in anhydrous HF at room temperature in an FEP (perfluoroethylene–perfluoropropylene copolymer) reactor.† Because TcO_2F_3 has a negligible solubility in HF, reaction mixtures were periodically sonicated to give bright orange solutions of $TcOF_5$ over a period of 24 h. The solvent and remaining gaseous products were pumped off at −78 °C leaving behind a volatile orange solid, which was sublimed into a side-arm of the FEP reactor. The unreacted KrF_2, which sublimed along with $TcOF_5$, was allowed to decompose at room temperature and its presence was monitored by observing the intense $\nu_1(\Sigma_g^+)$ stretching mode of KrF_2 at 462 cm^{-1} in the Raman spectrum.[10] Pure $TcOF_5$ melts reversibly and without decomposition at 57–58 °C and is deep red–orange in the liquid state. The solid is stable for at least two weeks at room temperature when kept under anhydrous conditions.

The gross structure of $TcOF_5$ was established by ^{19}F NMR spectroscopy. At −110 °C in SO_2ClF solvent, the ^{99}Tc–^{19}F scalar couplings are quadrupole collapsed as a result of the long rotational correlation time of the $TcOF_5$ molecule at this temperature.[11] The spectrum [Fig. 1(*a*)] consists of a doublet at δ 364.1 and a quintet at δ 62.0 having integrated intensities of 4.00 : 1.00, and are assigned to the equatorial (F_e) and the axial (F_a) fluorines, respectively, confirming the pseudo-octahedral geometry **I** expected for the $TcOF_5$ molecule. The two-bond fluorine–fluorine scalar coupling, $^2J(^{19}F_a–^{19}F_e)$ 75 Hz, is very similar in magnitude to that observed for $ReOF_5$ (69 Hz).[12] At 35 °C in HF solvent [Fig. 1(*b*)], the ^{19}F resonances of $TcOF_5$ occurred at δ 371.7 ($\Delta\nu_{\frac{1}{2}}$ 4930 Hz) and δ 45.0 ($\Delta\nu_{\frac{1}{2}}$ 1840 Hz), respectively, but were broadened by the partially quadrupole collapsed spin–spin coupling to the ^{99}Tc nucleus (I = $^9/_2$) that results from shorter rotational correlation times.‡ The saddle shape of the low-frequency resonance indicates that $^1J(^{19}F_a–^{99}Tc)$ is larger than $^1J(^{19}F_e–^{99}Tc)$, and is consistent with a Tc–F_a bond that is more covalent than the Tc–F_e bonds. The *trans* influence of the oxo ligand does not appear to be dominant in this case. This observation is consistent with the results of normal coordinate treatments for $ReOF_5$ and $OsOF_5$ which

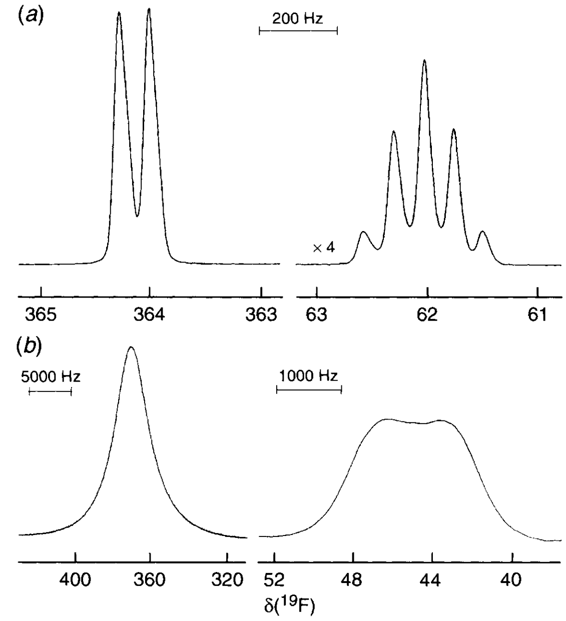

Fig. 1 The ^{19}F NMR spectrum (282.409 MHz in ppm relative to $CFCl_3$ at 25 °C) of $TcOF_5$ (*a*) in SO_2ClF at −110 °C and (*b*) in HF at 35 °C

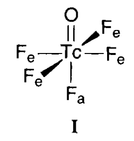

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Table 1 Vibrational frequencies and assignments for $TcOF_5$ compared to those of $ReOF_5$

Frequency/cm^{-1}				
$ReOF_5$ (g)[a]	$TcOF_5$ (s)[b]	$TcOF_5$ (HF soln.)[b,c]	Assignment C_{4v}	Approx. mode description
990s	933(28)	937(4), p	$\nu_1(A_1)$	$\nu_{sym}(MO)$
740vs	702(100)	702(100), p	$\nu_2(A_1)$	$\nu_{sym}(MF_a + MF_{4e})$
713s[d]	—[e]	—[e]	$\nu_8(E)$	$\nu_{as}(MF_{4e})$
652m	616(8)	624(8), dp	$\nu_5(B_1)$	$\nu_{as}(MF_{2e} - MF_{2e})$
640m	601(5)	598(2, sh), dp	$\nu_3(A_1)$	$\nu_{sym}(MF_a - MF_{4e})$
367s	351(10)	346(10), dp	$\nu_{10}(E)$	$\delta_{as}(OMF_e)$, scissors
334s	328(10)	329(10), dp	$\nu_7(B_2)$	$\delta_{as}(MF_{4e})$, scissors
309vw	278(5)	289(2), dp	$\nu_4(A_1)$	$\delta_{sym}(MF_{4e})$, umbrella
260s[e]	—[e]	—[e]	$\nu_9(E)$	$\delta_{as}(OMF_a + F_eMF_e)$
234vw	206(2)	199(2), dp	$\nu_6(B_1)$	$\delta_{as}(MF_{4e})$, out-of-plane pucker
125vw	131(1)	135(1 br), dp	$\nu_{11}(E)$	$\delta_{as}(OMF_a - F_eMF_e)$

[a] From 14; relative intensities are denoted by strong (s), very strong (vs), medium (m), very weak (vw). [b] Raman spectra were recorded at 25 °C in the FEP reaction tubes using 647.1 nm excitation from a krypton ion laser; relative intensities are given in parentheses. [c] The abbreviations denote a shoulder (sh), polarized (p), depolarized (dp) and broad (br) Raman bands. [d] IR frequency; band too weak to be observed in the Raman spectrum. [e] Too weak to be observed in the Raman spectrum.

showed that the M–F_a force constants are significantly larger than the M–F_e force constants.[13] The ^{99}Tc NMR spectrum (67.520 MHz) of $TcOF_5$ recorded at 35 °C in HF and at 30 °C in SO_2ClF showed broad resonances at δ 394.5 ($\Delta\nu_{\frac{1}{2}}$ = 440 Hz) and δ 433.8 ($\Delta\nu_{\frac{1}{2}}$ = 6680 Hz), respectively (relative to 0.1 M aqueous $NH_4^+TcO_4^-$ at 25 °C). No $^1J(^{99}Tc–^{19}F)$ couplings could be resolved in either the ^{19}F or ^{99}Tc NMR spectra because of quadrupolar broadening resulting from the fast relaxation rate of the ^{99}Tc nucleus.

Fifteen vibrational modes are expected for $TcOF_5$, all of which are Raman active and the A_1 and E modes are IR active: $\Gamma_{vib} = 4A_1 + 2B_1 + B_2 + 4E$. Nine of the expected eleven Raman bands have been observed and are assigned by analogy with the vibrational frequencies of $ReOF_5$ (Table 1). The vibrational frequencies of $TcOF_5$ are generally lower than their $ReOF_5$ counterparts. The trend is opposite to that expected based on the reduced mass effect alone even though the metal undergoes displacement in all normal coordinates except $\nu_5(B_1)$ and $\nu_7(B_2)$. The trend is consistent with Tc–F and Tc–O bond strengths that are lower than those of the rhenium analogue. Similar frequency decreases with decreasing mass have been noted for TcF_6/ReF_6, TcF_6^-/ReF_6^-, MoF_6/WF_6 and MoF_6^-/WF_6^-.[15]

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Footnotes

† All work involving ^{99}Tc was performed according to the regulations and recommendations of the Canadian Atomic Energy Control Board as outlined in AECB Radioisotope Safety Poster INFO-0142-1/Rev. 2, *Rules for Working with Radioisotopes in a Basic Laboratory*.

‡ Similar results were reported in an earlier paper in which the reaction between TcO_3F and KrF_2 in HF was investigated.[16] However, no products were isolated and the new ^{99}Tc resonance was mistakenly attributed to TcO_2F_3, mainly because of the failure to observe the equatorial fluorine resonance at high frequency in the ^{19}F NMR spectrum.

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