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Tc(VII) OXYFLUORIDES; PREPARATION AND STUDY BY ^{99}Tc NMR, RAMAN SPECTROSCOPY AND X-RAY CRYSTALLOGRAPHY

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Although TcO_3F can be prepared by solvolysis of TcO_4^- in anhydrous HF and ReO_2F_3 and $ReOF_5$ have been known for some time, the preparations of the higher oxyfluorides of Tc(VII) have not been reported.

The noble-gas fluorides KrF_2 and XeF_6 are potent oxidative fluorinating agents and provide a ready means to the syntheses of the higher oxyfluorides of Tc(VII). Thus, XeF_6 and KrF_2 oxidative fluorinations of TcO_3F in HF media lead to the stepwise elimination of O_2 gas and fluorination of Tc(VII), resulting in the syntheses of TcO_2F_3 and $Tc_2O_5F_4$. The latter is the subject of a x-ray single crystal structure and vibrational study.

Technetium-99 NMR spectroscopy has been used to monitor the above reactions and to characterize the diamagnetic Tc(VII) products in solution. Technetium-99 possesses a quadrupole moment, Q ($I = 9/2$). Quadrupole relaxation is expected to broaden ^{99}Tc NMR signals, but due to the favorable magnitude of Q and large I, the extent of line broadening is not severe. In the case of TcO_2F_3, the line width is narrow enough in the non-cubic environment of ^{99}Tc to permit the observation of the first ^{99}Tc-^{19}F spin-spin coupling.

The fluoride ion donor properties of TcO_3F are also reported, leading to the isolation of $TcO_3F{\cdot}AsF_5$ from HF solution. ^{99}Tc and ^{17}O NMR studes confirm the presence of TcO_3^+ in solution. Solid state Raman spectroscopy indicates that the TcO_3^+ cation is fluorine bridged to the AsF_6^- anion.