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THE REDOX PROPERTIES OF UF_6, MoF_6 AND WF_6 IN MeCN

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Previous work in this laboratory and elsewhere has established the relative order of oxidizing ability $UF_6 > MoF_6 > WF_6$, both in the gas phase, and in MeCN solution. We have now compared the hexafluorides' redox properties in MeCN with other redox couples using cyclic voltammetry, and by carrying out the appropriate redox reactions under carefully controlled conditions. The order of oxidizing ability established is $UF_6,UF_6^- > MoF_6,MoF_6^- > Tl^{3+},Tl^+ > NO^+,NO > Cu^{2+},Cu^+ \geqslant WF_6,WF_6^- > Ag^+,Ag^0 > I_2,I^- > MoF_6^-,Mo^{IV} > Cu^+,Cu^0 > Tl^+,Tl^0 > WF_7^-,W^V > WF_6^-,W^{IV}$. MoF_6 oxidizes Cu^0 to Cu^{2+}, and the latter is reduced by Cu^0 to Cu^+. In both cases the counter-anion is MoF_6^-; there is no evidence for MoF_6^{2-} or MoF_7^-. The analogous WF_6 system is described by the redox and F^- ion transfer equilibria, $Cu^{2+} + WF_6^- \rightleftharpoons Cu^+ + WF_6$ and $WF_6^- + WF_6 \rightleftharpoons WF_7^- + WF_5$, WF_7^- being redox inactive. Tl^0 is oxidised to Tl^{3+} by MoF_6 or UF_6, providing $[MF_6] \geqslant$ ca. 2 mol dm^{-3}. At lower $[MF_6]$, mixtures of Tl^+ and Tl^{3+} with MF_6^- counter-anions are formed, presumably because the process $Tl^+ \rightarrow Tl^{3+}$ is relatively slow. As expected from previous studies of MoF_6 and WF_6 in the gas phase or in SO_2 solution, WF_6^- is oxidized by NO^+, and both hexafluorides oxidize I^-. The products from the WF_6,I^- reaction in MeCN are I_2, WF_7^-, and WF_6, but with MoF_6 oxidation of I_2 occurs and $[I(NCMe)_2][Mo^VF_6]$ is isolated from solution.