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On the existence of $[TeF_6]^{2-}$ and $[SeF_6]^{2-}$

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Abstract

The reduction processes of the volatile hexafluorides TeF_6 and SeF_6 have been studied in CH_2Cl_2 using electrochemical methods with a vacuum-tight electrochemical cell. At −78 °C the half-wave potential for the $[TeF_6]^{0/2-}$ step occurs at −0.88 V vs. SCE, while the less reversible $[SeF_6]^{0/2-}$ reduction is observed at the more positive potential, $E_{1/2} = -0.1$ V. The complex ion $[TeF_7]^-$ is irreversibly reduced in MeCN at −0.7 V. These results are interpreted using an orbital framework. The results of Extended Hückel calculations on model systems are discussed. In each case, reduction results in the population of a metal–ligand antibonding orbital which is dominated by the metal valence s orbital.

Introduction

There have been long-standing discussions about the existence of an octahedral anion $[TeF_6]^{2-}$ [1] and $[SeF_6]^{2-}$ [2]. Although $[TeX_6]^{2-}$ and $[SeX_6]^{2-}$ (X = Cl, Br) anions have a regular octahedral configuration [3, 4], the most stable complexes of tellurium(IV) fluoride and selenium(IV) fluoride are the distorted pseudo-octahedral $[TeF_5]^-$ [5] and $[SeF_5]^-$ [6] anions. The distortion is attributed to the occupation of one co-ordination site by the valence s^2 lone pair of electrons.

Interest in the anion $[TeF_6]^{2-}$ has been renewed by the synthesis of '$[NH_4]_2[TeF_6]$' [7], and its inconclusive structural analysis by Raman [8] and X-ray spectroscopy [9]. Two salts containing the unstable $[SeF_6]^{2-}$ anion were reported in the 1950s [10]; however, their existence has been questioned [6].

A recent theoretical study at the SCF level suggests that both $[TeF_6]^{2-}$ and $[SeF_6]^{2-}$ are more stable in a non-octahedral C_{3v} geometry, although inclusion of electron correlation at the MP2 level reverses this conclusion for the selenium species. For both elements, the +4 state was found to be less stable than the +6 state in both O_h and C_{3v} geometries [11].

The first evidence for a tellurium species which retains its ligands in oxidation states +4 and +6 was obtained in an electrochemical study of the $OTeF_5^-$ ligand for which a two-electron reduction step $[OTeF_5]^{-/3-}$ was observed in CH_2Cl_2 at −1.9 V vs. SCE [12]. In the present work we have studied the electrochemical properties of TeF_6, $[TeF_7]^-$ and SeF_6, all in the formal +6 oxidation state, in non-aqueous solutions in order to obtain an indication of the relative stability of the possible anions $[TeF_6]^{2-}$ and $[SeF_6]^{2-}$.

Results and discussion

The redox properties of the volatile hexafluorides TeF_6 (b.p. −35.5 °C) and SeF_6 (b.p. −34.5 °C) have been studied in carefully purified CH_2Cl_2 at room temperature and below in a sealed system under vacuum. The complex salt $[Me_4N][TeF_7]$ was similarly studied using MeCN as solvent. Under these conditions, ^{19}F, ^{77}Se and ^{125}Te NMR spectra show that solutions of both hexafluorides and the heptafluorotellurate anion are stable for several days.

The cyclic voltammograms obtained for SeF_6 and TeF_6 at various temperatures are shown in Fig. 1. At room temperature, the cyclic voltammograms of both hexafluorides at scan rates slower than 100 mV s^{-1} showed one irreversible reduction process. Upon cooling to −78 °C, a re-oxidation wave appears for the $[TeF_6]^{0/2-}$ reduction step, while the reduction of SeF_6 remains strictly irreversible. Although faster scan rates produced a re-oxidation wave for both reduction processes, the re-oxidation wave was more pronounced for the tellurium case. Use of faster scan rates in combination with low temperature was limited by the substantial ohmic drop of the solvent system. Under conditions optimized for reversibility (see Table 1), TeF_6 was reduced at $E_{1/2} = -0.88$ V vs. SCE while the reduction step of SeF_6 occurred at $E_{1/2} = -0.1$ V. Complementary results were obtained by alternating current (a.c.) techniques (Table 1).

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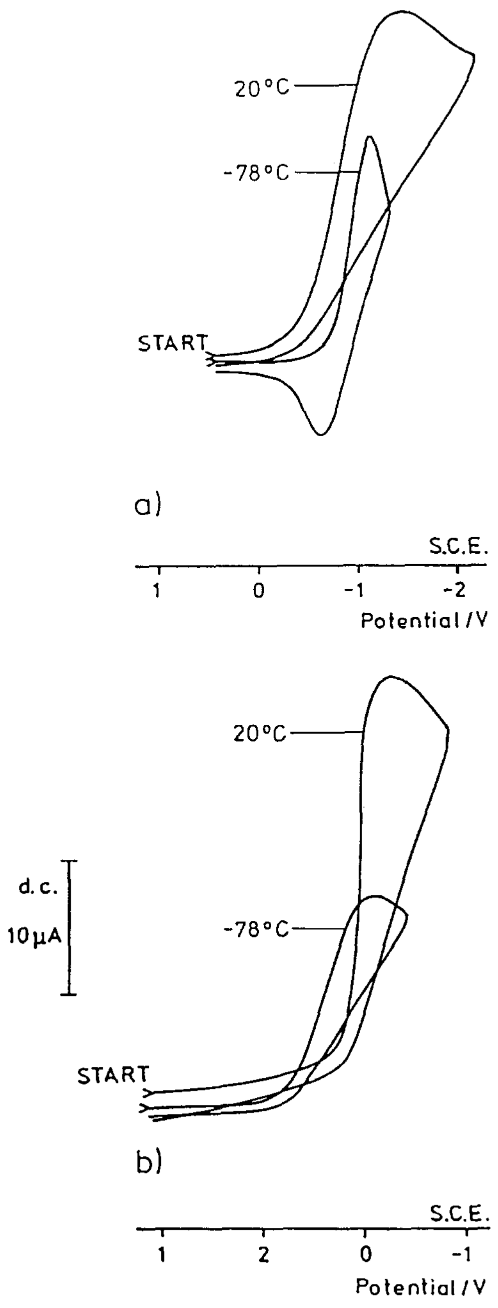

Fig. 1. Cyclic voltammograms of (a) TeF_6 and (b) SeF_6 in CH_2Cl_2 ($\nu = 100$ mV s^{-1}) showing the effect of lowering the temperature on the TeF_6 sample.

TABLE 1. Electrochemical data for TeF_6, SeF_6, $[MeN_4][TeF_7]$ and $[Et_4N][OTeF_5]$

	Cyclic voltammogram (cv)			Alternating current polarogram (a.c.)[a]	
	T (°C)	E_{pa} (V)[b]	E_p (mV)	$E_{1/2}$ (V)	$E_{p/2}$ (mV)[c]
TeF_6[d]	+20	−1.3	irrev.	−0.9	300
	−78	−0.88[f]	250	–	–
SeF_6[d]	+20	−0.3	irrev.	−0.1	400
	−78	−0.2	irrev.	–	–
$[Me_4N][TeF_7]$[e]	+20	−0.9	irrev.	−0.7	300
$[Et_4N][OTeF_5]$[d]	+20	−2.3	irrev.	−1.9	150

[a] $\omega = 350$ Hz, $\nu = 10$ mV s^{-1}.
[b] All potentials measured against $FeCp_2/FeCp_2^+$ as internal standard and referred to SCE, $\nu = 50$–1000 mV s^{-1}.
[c] Half-width of the curves.
[d] Supporting electrolyte (0.5 mol l^{-1}), $[Bu_4N][PF_6]$ in CH_2Cl_2.
[e] $[Et_4N][PF_6]$ (0.1 mol l^{-1}) in MeCN.
[f] $E_{1/2}$ measured, $\nu = 1000$ mV s^{-1}.

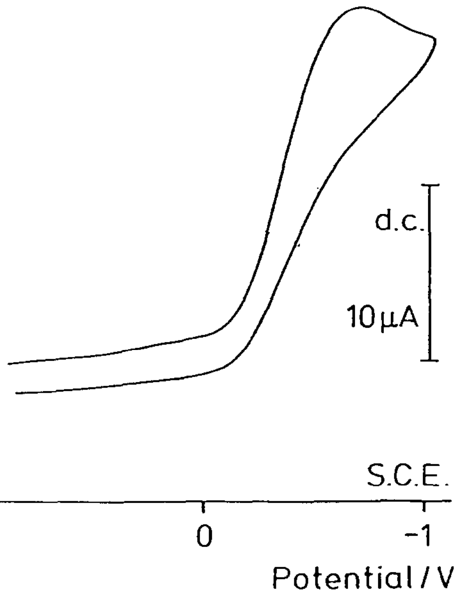

Fig. 2. Cyclic voltammogram of $[Et_4N][TeF_7]$ in MeCN ($\nu = 100$ mV s^{-1}).

The reduction process of the hepta-coordinated tellurium(VI) in the complex salt $[Me_4N][TeF_7]$ was studied in MeCN. Only one irreversible reduction process was observed at −0.7 V at all temperatures employed between +20 °C and −40 °C. Figure 2 shows the cyclic voltammogram obtained for $[Me_4N][TeF_7]$ in MeCN at −40 °C.

The reduction processes for TeF_6 and SeF_6 in CH_2Cl_2 at −78 °C are shown in eqns. (1) and (2). Owing to the non-reversible character of the reductions observed in this study, the number of electrons transferred could not be determined. However, from the wealth of evidence regarding the stable oxidation states of tellurium and selenium, we would expect a two-electron reduction to M(IV) rather than a one-electron reduction to the elusive M(V) (M = Se, Te).

$$TeF_6 + 2e^- \rightleftharpoons [TeF_6]^{2-} \qquad (1)$$

$$SeF_6 + 2e^- \longrightarrow \text{'}[SeF_6]^{2-}\text{'} \longrightarrow \text{decomposition} \qquad (2)$$

Table 1 lists the electrochemical data obtained together with the reduction potential for the

$[OTeF_5]^{-/3-}$ step [12]. Oxidation processes for TeF_6, SeF_6 or $[TeF_7]^-$ were not observed in the potential range up to +3.0 V vs. SCE.

The electrochemical findings suggest that $[TeF_6]^{2-}$, $[SeF_6]^{2-}$ and $[TeF_7]^{3-}$ are unstable in solution at room temperature. Although the reversibility of the reduction process $[TeF_6]^{0/2-}$ improved with lower temperature and faster scan rates, it can, at best, only be considered as quasi-reversible.

Using an orbital model, the resistance of these Se^{VI} and Te^{VI} compounds to reduction may be understood in terms of the high energy of their respective acceptor orbitals. Figure 3 shows the energy and topology of the frontier orbitals of TeF_6, $OTeF_5^-$ and TeF_7^-. The results for SeF_6 were essentially the same as for TeF_6. In each case, the LUMO is dominated by the metal valence s orbital (67% Se 4s in SeF_6; 67% Te 5s in TeF_6; 68% Te 5s in TeF_7^- and 63% Te 5s in $OTeF_5^-$). Furthermore, in each case the LUMO is antibonding with respect to the ligands and corresponds directly to the stereochemically inactive lone pair of the VSEPR model. These conclusions regarding the nature of the LUMO in MF_6 compounds are in agreement with those which have been reached for SF_6 after numerous studies [13–16]. The orbital energies of the HOMO and LUMO of the three compounds, as well as those of SeF_6, are very similar. The HOMO for SeF_6, TeF_6 and TeF_7^- is a fluorine lone-pair type orbital. For $OTeF_5^-$, the 6e HOMO is oxygen lone-pair based, a conclusion which agrees completely with the results of Hartree–Fock calculations described previously [17]. However, at the Extended Hückel level of approximation, it is not possible to explain the observed differences among the reduction potentials for these three compounds in terms of the absolute energy of the acceptor orbitals. One reason for this may be that the energy of the LUMO is extremely sensitive to the M−F bond lengths; small variations in this term can cause greater changes in the LUMO energy than the variation obtained amongst the four species studied here.

This effect is illustrated in Fig. 4, which plots the HOMO and LUMO energies of TeF_6 as a function of d(Te−F). Recent high-level SCF calculations predict a bond lengthening of almost 0.30 Å for both the selenium and tellurium hexafluorides upon reduction to the dianion. (Equilibrium bond lengths for SeF_6 have been calculated to be 1.66 Å, while for SeF_6^{2-} constrained to O_h symmetry this value became 1.94 Å. For tellurium, the values were 1.81 and 2.10 Å, respectively [11].) The intercepts at these SCF bond lengths are indicated in Fig. 4. At the very least, reduction to TeF_6^{2-} should be accompanied by an enormous amount of reorganizational energy as the bonds lengthen. It is therefore not surprising that this reduction is not fully reversible. We have also performed calculations which show that the removal of a single fluoride ligand causes a rehybridization of the $3a_{1g}$ orbital of TeF_6^{2-} into the $6a_1$ lone-pair type orbital of TeF_5^- and that this process causes a comparable degree of stabilization of the orbital

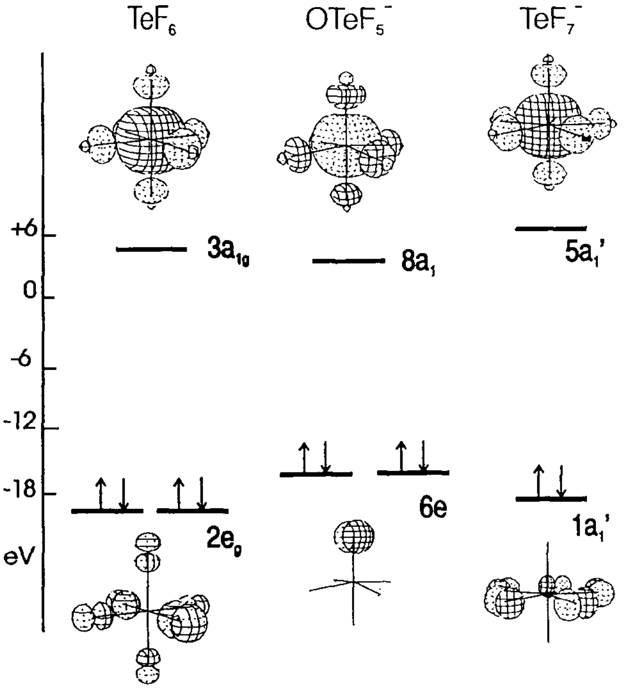

Fig. 3. Frontier orbital energies and orbital topologies for TeF_6, $OTeF_5^-$ and TeF_7^- from Extended Hückel calculations. For degenerate orbitals, only one example of the topology is shown.

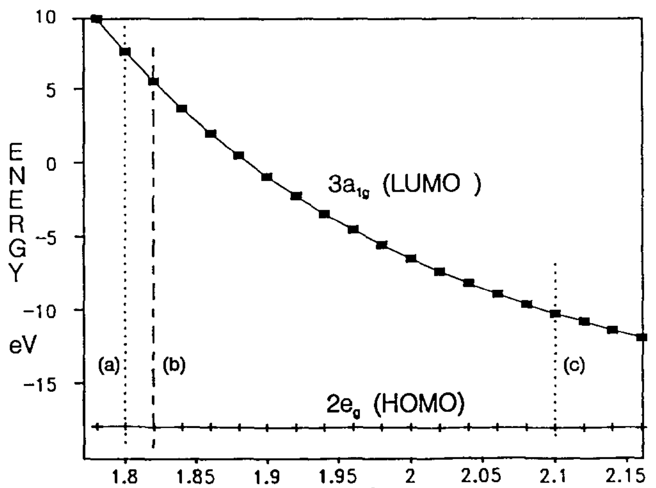

Fig. 4. Walsh diagram showing the effect of simultaneously changing the Te−F bond lengths of TeF_6 on the frontier orbital energies. The $3a_{1g}$ LUMO orbital is the acceptor orbital and becomes the HOMO of TeF_6^{2-}. Dashed intercepts indicate (a) the SCF equilibrium geometry of TeF_6, (b) the experimental geometry of TeF_6 used in the Extended Hückel calculations and (c) the SCF equilibrium geometry of TeF_6^{2-} (taken from ref. 11).

as does increasing all the bond lengths simultaneously to 2.10 Å. Hence decomposition of $TeF_6{}^{2-}$ according to eqn. (3) is entirely plausible:

$$TeF_6{}^{2-} \longrightarrow TeF_5{}^{-} + \text{‘}F^{-}\text{’} \qquad (3)$$

The improved reversibility of the reduction process at low temperature is explainable by both models.

In conclusion, it seems that in contrast to the known heavier homologues $[TeX_6]^{2-}$ with X = Cl and Br, the $5s^2$ electron pair in $[TeF_6]^{2-}$ cannot be accommodated easily in a stable octahedral or a non-octahedral C_{3v} configuration. The same line of reasoning applies to the selenium compounds. Not surprisingly, electrochemical reduction of the anions $[TeF_7]^-$ and $[OTeF_5]^-$ also did not give stable products. Attempts to prepare salts of the form $M_2[TeF_6]$ or $M_2[SeF_6]$ synthetically should take into account that these salts can be stable in solution only in a reducing medium and at low temperature.

Electrochemical studies on $[MX_6]^{2-}$ (M = Se, Te; X = Cl, Br and I) are in progress. Preliminary results suggest a very rich electrochemistry with complex oxidation and reduction steps.

Experimental

^{19}F, ^{77}Se and ^{125}Te NMR spectra were obtained using a JEOL FX 90 Q instrument at various temperatures with CH_2Cl_2 and MeCN as solvents, the spectra being referenced to external $CFCl_3$, SeO_2/H_2O and H_6TeO_6/H_2O, respectively. Volatile materials were manipulated in standard glass or metal vacuum lines. All non-volatile substances were handled in an argon filled dry-box (Braun GmbH, Oberschleißheim, Germany).

TeF_6 and SeF_6 were synthesized by direct fluorination of the corresponding metals [18] and $[Me_4N][TeF_7]$ [19] was prepared by the reaction of TeF_6 with $[Me_4N]F$ [20] in anhydrous acetonitrile [21]. Dichloromethane (Merck, analytical grade) was dried by distilling from P_2O_5 under argon and stored over activated 3 Å molecular sieves. Ferrocene served as internal standard and was sublimed prior to use. The electrolyte, $[Et_4N][PF_6]$, was prepared by neutralization of Et_4NOH with HPF_6 (pH meter), recrystallized from boiling ethanol and dried *in vacuo* for 24 h at 80 °C. $[Bu_4{}^nN][PF_6]$ (Aldrich) was recrystallized first from methanol, then from ethyl acetate/diethyl ether and dried *in vacuo* at room temperature. The electrolyte was then dissolved in a small amount of CH_2Cl_2 and filtered through a high-grade ashless filter paper to remove any oily droplets until the solution appeared crystal clear. The CH_2Cl_2 was removed under vacuum and the electrolyte dried for 24 h at 40 °C.

Phase-sensitive alternating current (a.c.) measurements ($\omega = 350$ Hz, 10 mV s^{-1}) and cyclic voltammograms (cv) with scan rates $\nu = 50$–500 mV s^{-1} were measured on a PAR model 173 potentiostat, model 175 universal programmer, model 5208 lock-in-amplifier and a Linseis LY 18100 X-Y-Y recorder. Cyclic voltammograms with faster scan rates $\nu = 1$–100 V s^{-1} were traced using a storage oscilloscope.

Electrochemical experiments were performed on a platinum three-electrode system in a vacuum-tight all-glass cell with integrated cooling finger as described previously [22]. The platinum electrode connection to the glass wall was made vacuum-stable by the use of a molybdenum wire. The addition of electrolyte, ferrocene and $[Me_4N][TeF_7]$ to the cell was achieved using break–seal techniques. TeF_6, SeF_6 and solvents were transferred into the cell with the help of a vacuum line. The internal resistance/impedance of the solutions (iR-comp.) was compensated manually and measurements started with the determination of a satisfactory electrochemical window.

Molecular orbital calculations were performed by the Extended Hückel method using the CACAO package running on a 66 MHz Intel 486 computer [23]. The Se parameters are those of ref. 24 and the Te are from ref. 25. Idealized octahedral geometries were used for MF_6 with the Se−F and Te−F distances at 1.70 Å and 1.82 Å, respectively [26]. A Walsh diagram was constructed by varying all the Te−F bond lengths simultaneously over the range 1.78–2.20 Å. The geometry used for $OTeF_5{}^-$ was C_{4v} with $d(Te{-}O) = 1.79$ Å, $d(Te{-}F_{ax}) = 1.85$ Å, $d(Te{-}F_{eq}) = 1.85$ Å; the F_{eq} atoms were 5.2° below the plane [17]; for $TeF_7{}^-$, an idealized D_{5h} geometry was employed with $d(Te{-}F_{ax}) = 1.79$ Å and $d(Te{-}F_{eq}) = 1.86$ Å [27].

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