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Technetium Electrochemistry. 5.[1] Spectroelectrochemical Studies on the Hexachlorotechnetate(IV) and Hexabromotechnetate(IV) Complexes in Aqueous Media[2]

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Thin-layer spectroelectrochemical techniques have been employed to show that the TcX_6^{2-} (X = Cl, Br) complexes undergo a reversible one-electron reduction in concentrated HX/NaX aqueous media (typically, 2.0 M HX and 3.0 M NaX). A single 4-min Tc(IV) → Tc(III) → Tc(IV) cycle in the thin-layer cell generates a completely equilibrated $TcX_6^{2-}/TcX_5(H_2O)^-$ Tc(IV) system, even though these substitution-inert Tc(IV) complexes normally require several days to reach equilibrium at room temperature. Spectropotentiostatic experiments conducted as a function of [H⁺] and [X⁻] show that the bromo system is 160 mV easier to reduce than is the chloro system and that both hydrogen and halide ions are lost from the Tc center upon reduction from Tc(IV) to Tc(III). The numbers of H⁺ ions lost from the chloro and bromo systems are 1.2 ± 0.1 and 1.6 ± 0.3, respectively; the number of chloride ligands lost is 2.7 ± 0.1, while the number of bromide ligands lost is 5.9 ± 0.5. A general reaction scheme consistent with these results is presented, and implications are drawn about the relatively high lability and low halide affinity of the Tc(III) center in aqueous media.

Introduction

The inorganic chemistry of technetium complexes has received a considerable amount of attention over the past few years, largely because of the widespread use of technetium-99m in diagnostic nuclear medicine.[3–5] Despite this attention, there are still many aspects of the fundamental chemistry of technetium coordination complexes that are not well understood. We have been utilizing electrochemical and spectroelectrochemical techniques in order to elucidate some of these aspects,[1,6–9] and in this paper we focus our attention on the classical hexahalotechnetate(IV) complexes TcX_6^{2-} (X = Cl, Br).

The title complexes have been known ever since chemical amounts of technetium became available in the early 1950s,[3,10] and they are widely used as starting materials in the syntheses of other technetium complexes.[3,8,11] These TcX_6^{2-} anions have been characterized by a variety of structural,[12–15] spectral,[16] photochemical,[17,18] electrochemical,[7,19,20] and kinetic[21–23] studies.

However, despite this extensive literature, the aqueous solution chemistry of the TcX_6^{2-} anions is still not completely understood. For instance, the factors governing the lability of the Tc–X bond remain unclear; quantitative kinetic studies on the rate of hydrolysis[21,22] and on the rate of halide exchange[23] of TcX_6^{2-} complexes establish that in strongly acidic media the Tc–X bond is substitution inert, but yet these complexes yield insoluble $TcO_2 \cdot nH_2O$ within seconds of being placed in neutral or weakly acidic media.[3] The present study was undertaken in order to characterize the redox chemistry of the TcX_6^{2-} anions in strongly acidic aqueous media and to determine whether or not redox phenomena might play a role in the complicated aqueous chemistry of these complexes.

Experimental Section

Caution! Technetium-99 emits a low-energy (0.292-MeV) β-particle with a half-life of 2.15×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination and inadvertent ingestion or inhalation of this isotope.

Reagents. All common laboratory chemicals were reagent grade and were used as received unless otherwise noted. $NH_4^{99}TcO_4$ of >99% radiochemical purity was obtained from Oak Ridge National Laboratory Oak Ridge, TN. Ammonium salts of the hexahalotechnetate(IV) complexes were prepared as described by Dalziel et al.,[24] then recrystallized from hot hydrohalic acid, and finally washed with cold 3 M hydrohalic acid.

Apparatus and Instrumentation. The optically transparent thin-layer electrodes were constructed with a 100 wire/in. gold minigrid as previously described[25] and enclosed in a Plexiglas box fitted with quartz windows as well as inlet and outlet ports for maintaining a constant stream of argon gas. The cell volumes and optical path lengths were calibrated by using standard solutions of ferricyanide and *o*-tolidine.[25] Potentials were measured versus a saturated sodium chloride calomel electrode (SSCE), and a platinum wire served as the auxiliary electrode. Electrochemical measurements were made with either (i) a Princeton Applied Research Model 173 potentiostat/galvanostat, Model 179 digital coulometer, and Model 175 universal programmer or (ii) a Bioanalytical

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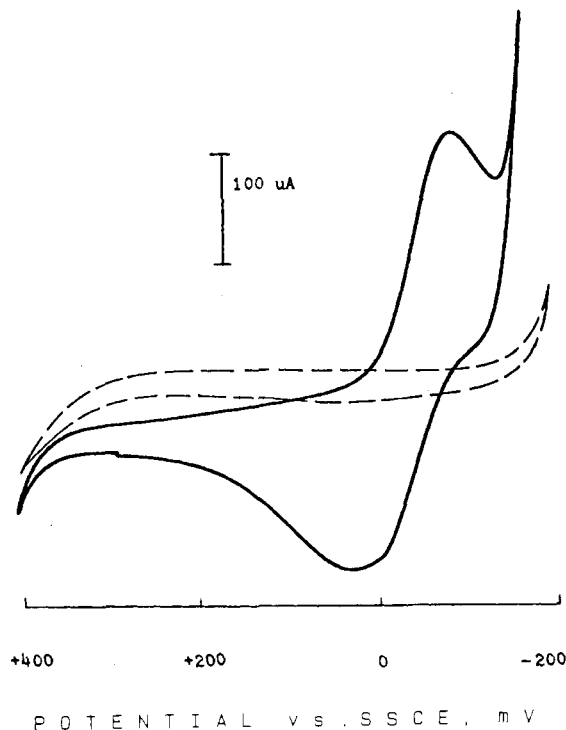
Figure 1. Thin-layer cyclic voltammograms of 3 mM $[NH_4]_2TcCl_6$ in 2.0 M HCl, 2.0 M NaCl (solid line) and of 2.0 M HCl, 2.0 M NaCl alone (dashed line). Scan rate = 5 mV/s.

Systems CV-1A or DCV-4 voltammetry instrument. Spectrophotometric measurements were made with a Harrick RSS-B Rapid-Scanning spectrometer; on-line experiment control, data acquisition, and data reduction were accomplished by an 8080 microprocessor system.[26] Bulk solution cyclic voltammograms were obtained by using a gold-button electrode, were displayed on a Tektronix 5103 oscilloscope, and were recorded with a Tektronix C-5 oscilloscope camera.

Procedures. Experiments were generally conducted as previously described[1,25,27] by using 1–3 mM solutions of technetium complex in aqueous HX/NaX media (X = Cl, Br). For most experiments, solutions were deaerated with an argon stream for 30 min prior to conducting electrochemistry, and then a blanket of argon gas was maintained over the solution during the experiment. Subsequent studies showed that the observed electrochemistry is not affected by dissolved oxygen, and thus a few experiments were also conducted in an aerobic environment. All experiments were conducted at room temperature.

Results and Discussion

The Tc(IV) complexes $TcX_6{}^{2-}$ (X = Cl, Br) rapidly hydrolyze in neutral or weakly acidic aqueous media to yield insoluble $TcO_2 \cdot H_2O$. For this reason most electrochemical investigations of these complexes have employed nonaqueous solvents, even though only irreversible processes are observed in these media.[7,20] However, hydrolysis does not occur in concentrated HX/X⁻ aqueous media, and in the course of this investigation we encountered HX/X⁻ concentration conditions under which the $TcX_6{}^{2-}$ complexes apparently undergo reversible electrochemical reduction. Similar concentration conditions were employed in a previous, brief study of the electrochemical reduction of $TcX_6{}^{2-}$ anions in aqueous media.[19]

Thin-Layer Cyclic Voltammetry. Figure 1 shows a typical thin-layer cyclic voltammogram obtained for $TcCl_6{}^{2-}$ in a 2.0 M HCl, 2.0 M NaCl medium. A negative potential scan initiated at the open-circuit potential (+0.400 V vs SSCE) yields a distinct reduction wave (E_{pc} = -0.06 V), and then a reverse scan reveals a coupled oxidation wave (E_{pa} = +0.05 V). Repetitive cycling between the two redox forms yields no apparent change in the cyclic voltammogram. Similar results are obtained for the $TcBr_6{}^{2-}$ analogue (E_{pc} = +0.03 V, E_{pa} = +0.07 V).
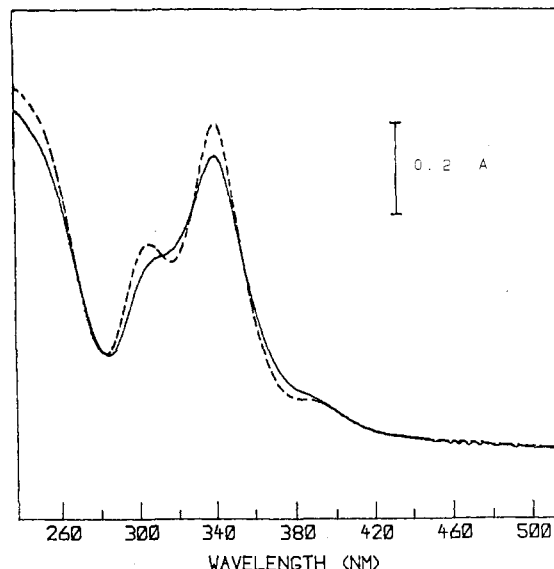
Figure 2. Results of performing a single thin-layer cyclic voltammetry scan from Tc(IV) to Tc(II) and back to Tc(IV). The dashed line shows the spectrum of $[NH_4]_2TcCl_6$ in 2.0 M HCl, 2.0 M NaCl before the scan, while the solid line shows the spectrum after the scan. Each trace represents the average of 1024 individually recorded spectra; the background absorbance has been subtracted.

Bulk Solution Cyclic Voltammetry. The thin-layer cyclic voltammetric experiment requires about 4 min to complete and is thus suitable for investigating systems that achieve redox equilibrium slowly. In order to qualitatively probe the kinetics of the redox process depicted in Figure 1, bulk solution cyclic voltammetry experiments were also conducted by employing scan rates from 100 mV/s to 100 V/s. At the slower scan rates the redox process of Figure 1 is observed, but as the scan rates increase, the difference in potential between the oxidation and reduction waves increases and the peak magnitudes decrease. At scan rates greater than 10 V/s, no oxidation or reduction process is observed. These observations imply either that the electrode processes involved in the redox cycle are slow or that the redox process is coupled to a chemical reaction that occurs relatively slowly. The latter implication is consistent with data obtained from thin-layer spectroelectrochemistry (vide infra), and in this context it is worth noting that at a scan rate of 10 V/s, approximately 80 ms is required to cycle from one oxidation state to the other.

Thin-Layer Coulometry. The n value associated with each of the two redox couples observed in the cyclic voltammetry experiments was determined by thin-layer coulometry.[25] For the chloro complex n = 1.00 ± 0.06 (average and standard deviation of 14 independent measurements), while for the bromo complex n = 1.00 ± 0.09 (average and standard deviation of 15 independent measurements). Thus, for both complexes the electrode process involves consumption of one electron per Tc(IV) center, corresponding to a formal reduction of Tc(IV) to Tc(III).

Thin-Layer Spectrochemistry. Even though the thin-layer cyclic voltammetry (CV) experiments do not detect any electrochemical variation through several repetitive cycles, careful monitoring of the visible–UV spectrum of the solution during CV establishes that a definite spectrophotometric change occurs after the first electrochemical cycle, but *only* after this first cycle. This result is illustrated in Figure 2, wherein the dashed line represents the spectrum of $TcCl_6{}^{2-}$ *before* the first CV scan and the solid line represents the spectrum *after* this first scan. Repetitive cycles engender no additional changes in the visible–UV spectrum. The initial spectrum (dashed line) is that of pure $TcCl_6{}^{2-}$, while the second spectrum (solid line) corresponds very well to that of the equilibrium mixture of $TcCl_6{}^{2-}$ and $TcCl_5(H_2O)^-$ obtained upon allowing $TcCl_6{}^{2-}$ to stand for several days in the CV medium (2.0 M HCl, 2.0 M NaCl). The spectrum of this equilibrium mixture also agrees very well with that obtained by Kawashima et al. upon allowing $TcCl_6{}^{2-}$ to reach equilibrium in 4.0 M HCl at 80 °C.[21]

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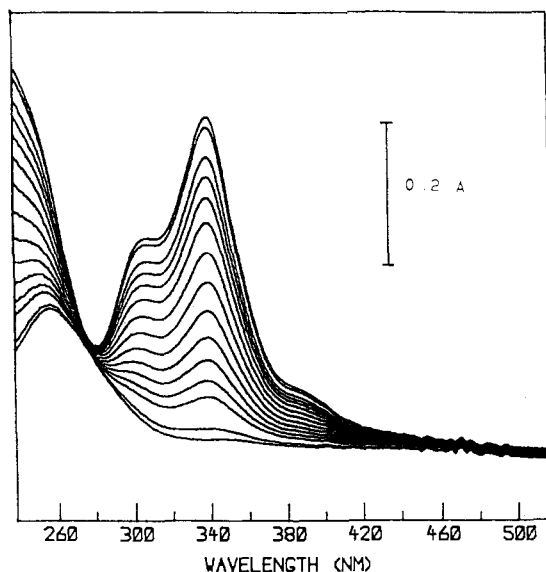
Figure 3. Spectra recorded during thin-layer spectropotentiostatic experiments on 1.3 mM [NH$_4$]$_2$TcCl$_6$ in 2.0 M HCl, 3.0 M NaCl. Applied potentials range from +400 mV (fully oxidized, top) to –230 mV (fully reduced, bottom) vs SSCE. Each trace represents the average of 1024 individually recorded spectra; the background absorbance has been subtracted.
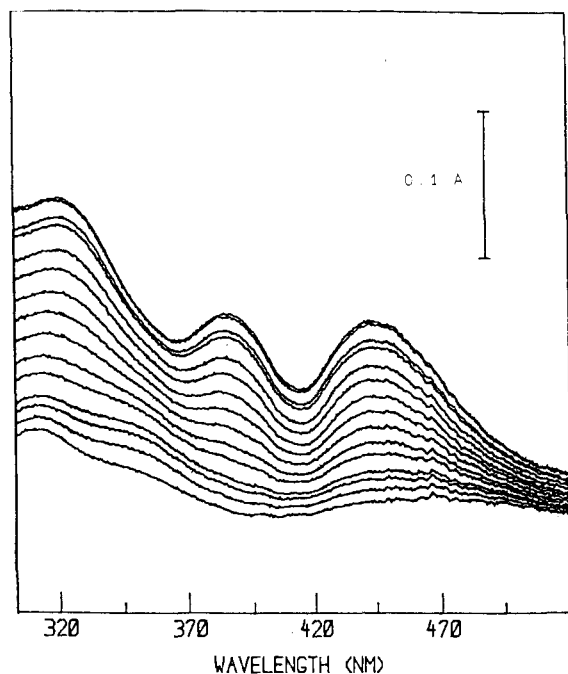
Figure 4. Spectra recorded during thin-layer spectropotentiostatic experiments on 1.1 mM [NH$_4$]$_2$TcBr$_6$ in 2.0 M HBr, 3.0 M NaBr. Applied potentials range from +200 mV (fully oxidized, top) to –200 mV (fully reduced, bottom) vs SSCE. Each trace represents the average of 1024 individually recorded spectra; the background absorbance has been subtracted.

Thus, even though TcCl$_6{}^{2-}$ is a substitution-inert complex (the half-life for Tc–Cl bond aquation is estimated to be several days at room temperture[21]), a single 4-min thin-layer CV cycle suffices to equilibrate TcCl$_6{}^{2-}$ with TcCl$_5$(H$_2$O)$^-$. Since all thin-layer studies reported in this paper were conducted on solutions that had undergone at least one CV cycle, they are therefore studies of equilibrium mixtures of TcX$_6{}^{2-}$ and TcX$_5$(H$_2$O)$^-$. The equilibrium constants governing these mixtures at high temperatures and a total halide concentration of 4.0 M have been reported by Kawashima et al.[21] From these reported data it can be estimated that under the conditions of most of our experiments (25 °C, total halide concentration 5.0 M), the [TcX$_6{}^{2-}$]/[TcX$_5$(H$_2$O)$^-$] ratio
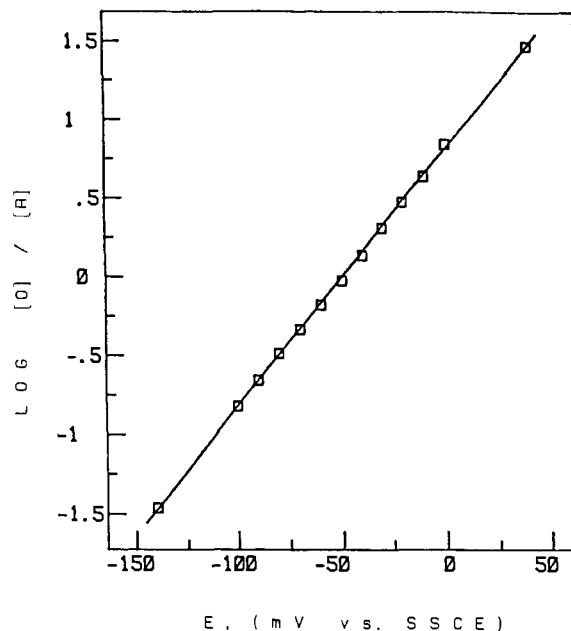
Figure 5. Nernst plot of the spectropotentiostatic data shown in Figure 3.

Table I. Results of Spectropotentiostatic Experiments on TcX$_6{}^{2-}$ Complexes

TcCl$_6{}^{2-}$			TcBr$_6{}^{2-}$		
[Cl$^-$], M	[H$^+$], M	$E,^a$ mV	[Br$^-$], M	[H$^+$], M	$E,^a$ mV
2.0	2.0	+17 ± 1	3.0	2.0	+41 ± 3
2.5	2.0	–5 ± 2	3.5	2.0	+28 ± 4
3.0	2.0	–17 ± 1	4.0	2.0	+7 ± 2
3.5	2.0	–28 ± 2	5.0	2.0	–23 ± 4
4.0	2.0	–35 ± 2	5.1	1.2	–19 ± 4
4.5	2.0	–47 ± 2	5.1	2.1	–33 ± 3
5.0	2.0	–51 ± 1	5.1	3.0	–56 ± 2
5.1	1.2	–34 ± 2	5.1	4.0	–62 ± 3
5.1	2.1	–51 ± 3			
5.1	3.0	–63 ± 1			
5.1	4.0	–72 ± 2			

^{a} Versus SSCE. Average and standard deviation of three or four independent measurements.

is about 5 for the chloro complex and about 7 for the bromo complex; more extensively aquated species are not present in significant amounts under these concentration conditions.[21]

The results of typical spectropotentiostatic experiments on the TcCl$_6{}^{2-}$ and TcBr$_6{}^{2-}$ systems are shown in Figures 3 and 4, respectively. In each case the initially recorded spectrum is consistent with the solution containing an equilibrium mixture of TcX$_6{}^{2-}$ and TcX$_5$(H$_2$O)$^-$, with the latter species being present at less than 20% of the amount of the former.[21] As reduction from Tc(IV) to Tc(III) occurs, the characteristic charge-transfer bands of the TcX$_6{}^{2-}$ anions disappear. For the chloro system (Figure 3), the Tc(III) product exhibits a broad absorbance centered at about 260 nm, while in the bromo system (Figure 4) the Tc(III) product does not exhibit a distinctive absorption maximum. Figure 5 presents a Nernst plot[25] resulting from the spectropotentiostatic data of Figure 3; linear least-squares analysis of this plot yields a midpoint potential, E_{mp}, of –0.049 V vs SSCE and n = 0.97 (the midpoint potential is defined as that potential at which the concentration of oxidized species equals the concentration of reduced species). An equivalent analysis of the data shown in Figure 4 yields E_{mp} = 0.023 V vs SSCE and n = 0.98. The independently measured n values support the results of the thin-layer coulometry experiments and confirm that the electrochemical process being monitored involves net reduction of Tc(IV) to Tc(III).

The results of similar spectropotentiostatic experiments, conducted over a range of concentrations of HX and NaX, are summarized in Table I for both the chloro and bromo systems.
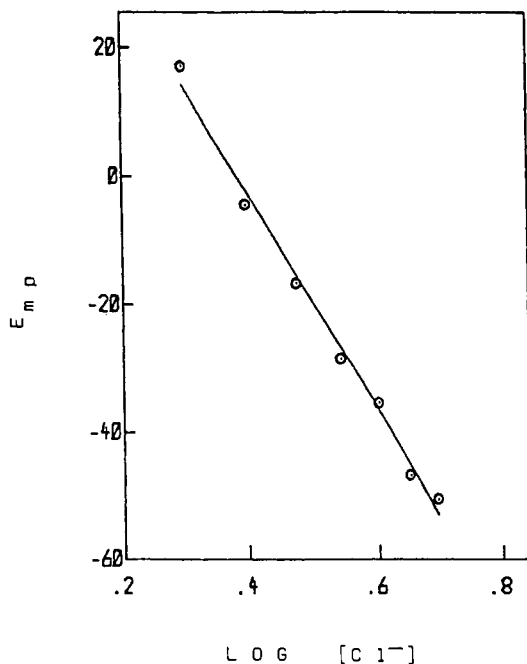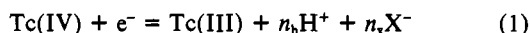
Figure 6. Plot of E_{mp} vs log [Cl⁻] for [NH$_4$]$_2$TcCl$_6$; data acquired at [H⁺] = 2.0 M.

In each system, increasing either the concentration of acid (while decreasing NaX to keep X⁻ constant) or the concentration of halide ion makes it more difficult to reduce Tc(IV) to Tc(III). These results can be interpreted within the following half-reaction and Nernst analysis:

$$Tc(IV) + e^- = Tc(III) + n_hH^+ + n_xX^- \qquad (1)$$

$$E = E° - 0.059(n_h)(\log [H^+]) - 0.059(n_x)(\log [X^-]) + 0.059(\log ([Tc(IV)]/[Tc(III)])) \qquad (2)$$

where $E°$ represents the formal reduction potential of the couple. When $E = E_{mp}$, then [Tc(IV)]/[Tc(III)] is unity and eq 2 becomes

$$E_{mp} = E° - 0.059(n_h)(\log [H^+]) - 0.059(n_x)(\log[X^{-1}]) \qquad (3)$$

Plots of E_{mp} vs log [H⁺] (at constant [X⁻]), and of E_{mp} vs log [X⁻] (at constant [H⁺]), are linear, as illustrated by Figure 6, wherein E_{mp} for the chloro system at [H⁺] = 2.0 M is plotted vs log [Cl⁻]. Considering the very high ionic strengths involved in these studies and the fact that the ionic strength could not be held constant while [X⁻] was varied at constant [H⁺] (the Tc(III) species reacts rapidly with supporting-electrolyte anions such as nitrate, chlorate, or perchlorate), the linearity of these plots is probably somewhat fortuitous. However, these plots do justify a more extensive analysis of the data according to eq 3.

Nonlinear least-squares analysis[28] within eq 3 of all E_{mp}, [H⁺], and [X⁻] data obtained for each TcX$_6$²⁻ complex yields the following optimized n_h, n_x, and $E°$ values: for TcCl$_6$²⁻, n_h = 1.2 ± 0.1, n_x = 2.7 ± 0.1, and $E°$ = 0.082 ± 0.004 V vs SSCE; for TcBr$_6$²⁻, n_h = 1.6 ± 0.3, n_x = 5.9 ± 0.5, and $E°$ = 0.240 ± 0.017 V vs SSCE. The optimized $E°$ values indicate that, as expected,[7,20] the bromo system is easier to reduce than is the chloro system. The 160-mV difference in $E°$ values is consistent with the results of a previous study of the dihalobis(L-L)technetium(III) complexes, *trans*-[Tc(L-L)$_2$X$_2$]⁺ (L-L = chelating di(tertiary phosphine or arsine)); in this system the dibromo complexes are consistently about 100 mV easier to reduce to Tc(II) than are the corresponding dichloro complexes.[8] Clearly, bromo ligands stabilize the lower technetium oxidation states better than do chloro ligands, and the effect is larger for complexes that contain a greater number of halo ligands.

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The optimized n_h values indicate that for each system between one and two hydrogen ions are released upon reduction of Tc(IV) to Tc(III) and that slightly more hydrogen ion is released upon reduction of the bromo system than upon reduction of the chloro system (1.6 ± 0.3 vs 1.2 ± 0.1). In the chloro system approximately three chloride ligands are lost upon reduction, while in the bromo system essentially all six bromide ligands are lost. Given that all of the derived n_h and n_x values are only approximate because of uncontrolled medium effects, the relative magnitudes of these parameters can be rationalized by the set of equilibria
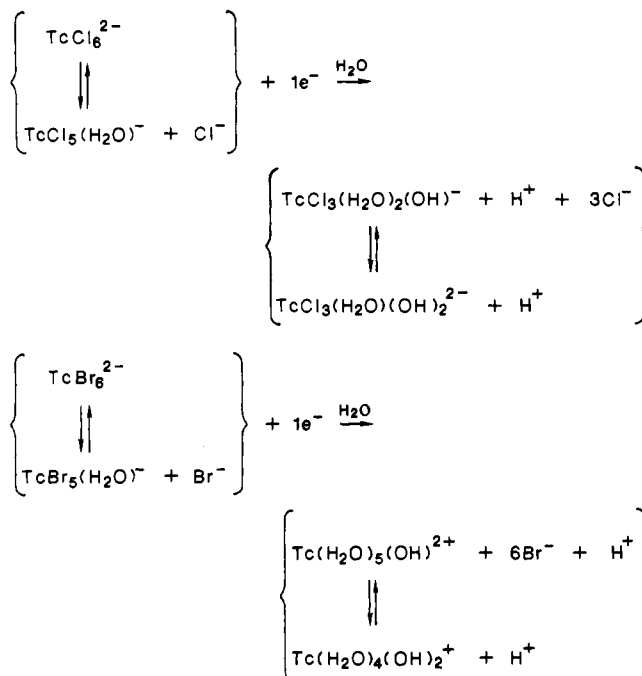
While these proposed equilibria are not unique, they do provide a consistent and chemically reasonable description of the results obtained in this study. Electrochemical reduction of Tc(IV) to Tc(III) reduces the formal charge on the technetium center and consequently promotes loss of the anionic halide ligands. The resulting aquated Tc(III) complex has a reduced negative charge and is sufficiently acidic to completely lose one proton. More halide ligands are lost from the Tc(III) product in the bromo system than in the chloro system, thus generating a more positively charged species, which in turn is more acidic than its chloride counterpart. The more extensive loss of bromide ligands detected in the spectropotentiostatic experiments is also consistent with the spectal changes observed during reduction—the chloro system retains an intense peak after reduction to Tc(III), implying the presence of a chloride ligand in the Tc(III) coordination sphere, while the bromo system does not exhibit any defined peaks in the Tc(III) state (Figures 3 and 4).

Implications for the Aqueous Chemistry of Tc(III). The experiment summarized by Figure 2 clearly shows that in these systems Tc(III) is considerably more labile than Tc(IV). While the Tc(IV) [TcX$_6$²⁻]/[TcX$_5$(H$_2$O)⁻] system normally requires several days to achieve equilibrium at room temperature, a 4-min passage into and out of the Tc(III) state generates a completely equilibrated Tc(IV) state. This can only occur if the Tc(III) state undergoes ligand substitution within a few minutes. But, the bulk cyclic voltammetry experiments imply that substitution on Tc(III) must require longer than about 80 ms. Thus, the half-life for substitution onto Tc(III) in these concentrated HX/X⁻ aqueous media would appear to be in the range of 100 ms to a few minutes.

The strong dependence of E_{mp} on [X⁻] shows that Tc(III) does not have a very high affinity for halide ion, and the resulting n_x values reveal that the affinity of Tc(III) for bromide is less than its affinity for chloride. Even in the presence of 5.0 M bromide, essentially all six bromide ligands of the original Tc(IV) complex are lost upon reduction to Tc(III). This raises the intriguing possibility of preparing [Tc(H$_2$O)$_6$]³⁺ by reduction of a TcX$_6$²⁻

complex in an appropriately noncoordinating, nonoxidizing aqueous medium. Experiments aimed at preparing and characterizing the hexaaquotechnetium(III) ion are currently being undertaken.

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Electron Transfer. 89. Reductions of Carboxylato-Bound Chromium(V) with Mercapto Acids[1]

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Received May 28, 1987

The chromium(V) chelate bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) rapidly oxidizes the mercapto acids thiolactic acid (II) and cysteine (III) in solutions buffered with the ligand acid, 2-ethyl-2-hydroxybutyric acid, and its sodium salt. With the thiol acids (RSH) in excess, nearly 2 equiv of reductant is consumed/mol of Cr(V), corresponding to the formation of the disulfide, R_2S_2, and Cr(III). The chromium(III) products consist mainly of a mixture of uncharged bis chelates derived from the ligand anion, each having, in addition, a unidentate coordinating group arising from either the buffering acid or the mercapto reagent. Both reactions are catalyzed by Cr(IV) and pass through thiyl radicals, RS•, for which Cr(IV) and Cr(V) compete. The suggested reaction sequence (eq 2-6), in combination with rate constants for the individual steps resulting from a least-squares refinement of the kinetic data, reproduces the experimental rate profiles. Dependencies of the component-specific rates on [H$^+$] and on the concentration of ligand anion, [Lig$^-$], indicate that oxidations of the two thiol-substituted acids, by both Cr(V) and Cr(IV), require deprotonation and that oxidations of both by Cr(IV) proceed by parallel paths, with a distribution governed by the ratio of [Lig$^-$] to [RSH] in the generating solution. In addition, the 1e oxidation of thiolactic acid by Cr(V) (but not that of cysteine) is subject to kinetic saturation, implying the formation of a Cr(V)–RS$^-$ complex having an association constant near 7×10^2 M^{-1} and a limiting specific rate 3.5×10^2 M^{-1} s^{-1}. Persistence of the chelate rings originally present in the Cr(V) oxidant demonstrates the maintenance of chelation in all steps involving Cr(V) and Cr(IV). Comparisons of calculated electron-transfer rates with those observed for known outer-sphere reactions indicate that at least three of the four steps in the proposed mechanism involve bridged transition states. This is the sixth system in which autocatalysis in the reduction of Cr(V) by anionic donors has been observed. Mechanistic features thought to be common to all such systems are briefly considered.

Of the reported carboxylato complexes of chromium(V),[3] the most robust is the bis chelate of 2-ethyl-2-hydroxybutyric acid (I). Kinetic patterns associated with the reductions of this de-
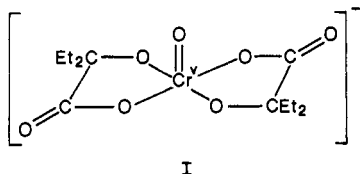
I

rivative to Cr(III) vary greatly in character. Action of 2e reagents, N_2H_4, H_2O_2, and Sn(II),[4] yield straightforward exponential traces, and the same is true for reductions by IrCl$_6^{3-}$ and TiOH^{2+}.[4b,5] Although the latter reactions pass through the atypical oxidation state Cr(IV), this state is, in these instances, reduced very rapidly and its intervention therefore overlooked. With the 1e donors Fe(II) and VO^{2+},[6] however, the formation and decay of a strongly absorbing Cr(IV) intermediate are mirrored in classical biphasic profiles.

Treatment with reductants that undergo both 1e and 2e transactions may lead to more intricate patterns, since four different 1e changes are possible. Depending upon the relative specific rates for the individual steps, slight[7] or severe[8] autocatalysis

Table I. Stoichiometry of the Reactions of Chromium(V) Chelate I with Mercapto Acids[a]

reductant	amt, mmol			$\Delta[red]/$
	Cr^V	red	$\Delta[red]^b$	$\Delta[Cr^V]$
thiolactic acid (II)	0.121	0.517	0.260	2.15
	0.098	0.517	0.225	2.30
	0.166	0.621	0.364	2.19
	0.202	0.621	0.420	2.08
cysteine (III)	0.055	0.393	0.097	1.76
	0.119	0.579	0.210	1.76
	0.221	0.610	0.390	1.77

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt (see Experimental Section). [b] Determined by difference iodometrically (see Experimental Section).

may occur, and slow growth of Cr(IV), followed by its quick decay, may result in a "clocklike" reaction profile.[8]

Among organic reductants, only ascorbic acid, which may donate either one or two electrons,[9] has been shown to generate a Cr(IV) intermediate from a Cr(V) oxidant.[10] In this case, reaction is very rapid and autocatalysis striking. The present extension deals with the oxidations of the mercapto-substituted carboxylic acids thiolactic acid (II) and L-cysteine (III). These

$$CH_3CH(SH)COOH \qquad HSCH_2CH(NH_3^+)COO^-$$
$$II \qquad\qquad\qquad III$$
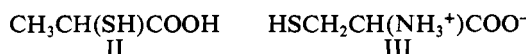
reagents resemble iodide in the polarizability of their donor (–SH) center[11] and in the ease with which they are oxidized.[12,13] They

(1) Joint sponsorship of this work by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
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(12) Formal potentials for thiol–disulfide systems that are devoid of strongly electron-attracting or electron-repelling groups lie between +0.02 and +0.30 V (vs NHE at pH 0).[13a] That for I$^-$–I$_2$ is +0.54 V at 25 °C.[13b]