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Literature Survey of the Aqueous Chemistry of Technetium Related to Photolysis

H. A. Friedman

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LITERATURE SURVEY OF THE AQUEOUS CHEMISTRY OF TECHNETIUM RELATED TO PHOTOLYSIS

H. A. Friedman

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LITERATURE SURVEY OF THE AQUEOUS CHEMISTRY OF TECHNETIUM RELATED TO PHOTOLYSIS

H. A. Friedman

ABSTRACT

A literature survey was made to accumulate information about the chemistry of technetium as it relates to photolysis. The electrochemical potentials and the reactions of the various technetium compounds and complexes are discussed, along with the various absorption spectra of the different species.

The $TcCl_6^{2-}$ ion has been shown to be photochemically active in HCl solutions. Hexachlorotechnetate(IV) is oxidized when exposed to sunlight in concentrated HCl. A ligand change occurs when it is exposed to either 254- or 340-nm radiation in more dilute HCl. No other photolysis reactions were found in the literature.

It is possible that, under appropriate conditions, other valence states of technetium would be photochemically active, resulting in either redox or ligand exchange reactions. Proposals for investigating the photochemical reduction of the pertechnetate in HNO_3 and other media are discussed.

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1. INTRODUCTION

Numerous periodicals,[1-114] as well as a number of review articles[3,11,12,18,74,97,111-113] and several books,[16,57,114] have been written about the chemistry of technetium. The purpose of this report is to present a survey of the chemistry of technetium as it relates to the study of the photolysis of technetium, including (1) its properties and the procedures for preparing and purifying the various starting compounds that are to be photolyzed; (2) conditions that alter valence states, including electrochemical; (3) the stability (ease of oxidation or reduction of one valence state to another) and complex formation of the various technetium species in solution; and (4) use of chemical and spectrophotometric means to identify the various oxidation states and species.

The study of the photochemical reactions of technetium is of interest both as a basic scientific investigation and as a possible means of altering the valency of the technetium ion to offer a better method for separating technetium from other components. One species of technetium, $TcCl_6^{2-}$, has already been shown to be photochemically active in HCl solutions.[29,106,107] Other oxidation states or species in different media may also be light-sensitive.

Photolysis could be used as a means for altering the valence state of a technetium species. One potential application of photolysis might be in the separation of technetium from uranium. Pertechnetate ions are coextracted by uranyl ions from aqueous nitric acid into TBP.[115] If TcO_4^- were reduced by photolysis, the distribution coefficient of the reduced species would probably be significantly different from that of TcO_4^- and thus might facilitate the separation of uranium from technetium. Moreover, the reduced specimen would interact differently, and probably less strongly, than pertechnetate.[115]

2. DISCUSSION

2.1 Technetium Chemistry

Technetium is found as the metal, as oxides, halides, oxyhalides, complexes, and hydroxides, and probably in other forms as well. All oxidation states from -1 through +7 may be expected.[3] The +7 is the most important of these, although +4, +5, and +6 are of considerable interest.[3] It is quite possible for a single solution to contain various valence states.[2] Disproportionation, complex formation, and hydrolysis must also be considered.[2]

2.1.1 Technetium(VII)

Technetium(VII) exists as the heptaoxide, Tc_2O_7, the pertechnetate, TcO_4^-, and as pertechnyl chloride, TcO_3Cl. The pertechnetate is the most common form.

Oxide and acid. Technetium heptaoxide is a pale-yellow crystalline, very hygroscopic solid[16] that dissolves in water to form

pertechnic acid, $HTcO_4$. Pink, then red, and finally very dark red needles crystallize out when a concentrated solution of $HTcO_4$ is evaporated to dryness. The weight of the crystals is consistent[10] with the formula $Tc_2O_7 \cdot H_2O$ or anhydrous $HTcO_4$.

Both the acid ($HTcO_4$) and the heptaoxide have rather high vapor pressures even at low temperature.[17] Technetium(VII) may be distilled from concentrated H_2SO_4, possibly as Tc_2O_7.[18] In the distillation of sulfuric acid—water mixtures, a substantial amount of the technetium, possibly as $HTcO_4$, is found in the low-boiling aqueous fraction.[3] Once the water has been removed, the distillation appears to follow a first-order rate law, with the rate constant being dependent on the apparatus and reflux ratio.[3] A Kjeldahl head should be used to avoid contamination by spray, and the flask should be heated electrically by means of a heating mantle with quartz fabric insulation for optimum reproducibility.[3]

Salts. Potassium pertechnetate, $KTcO_4$, is a white crystalline solid which is very stable thermally.[16] It undergoes a reversible color change on heating,[19] becoming bright yellow at 500°C, although some color is evident at 200°C. Heating to 500°C is sufficient to ensure a water-free sample[20] that melts at 540°C and sublimes at about 1000°C.[19]

Ammonium pertechnetate, NH_4TcO_4, is a stable, nonhygroscopic,[10] white crystalline solid[6] at ambient temperature but decomposes with heat. The white crystals of ammonium pertechnetate appear[21] as an aqueous pertechnic acid solution is neutralized with ammonia and evaporated to dryness. Some researchers report[22] that ammonium pertechnetate decomposes fairly rapidly even at 90 to 100°C. However, other investigators[18] claim that it shows no sign of decomposition after being heated for several hours at 100°C. It can be purified by sublimation in vacuum[5] but decomposes to TcO_2 on heating in vacuum[11] to 550°C. The ammonium pertechnetate is also decomposed to Tc_2O_7 when an 18 N H_2SO_4 solution is taken almost to dryness.[23]

Oxychloride. Technetium trioxide chloride (pertechnyl chloride, TcO_3Cl) is reported to form[19,40] when a cold solution of potassium pertechnetate in 18 M H_2SO_4 is treated with small amounts of 12 M HCl. The

fact that the compound can be extracted into chloroform, carbon tetrachloride, or hexane clearly indicates that it is the monochloride species.[19] It is a colorless liquid which decomposes on gentle heating to a red solid, thought to be TcO_3, although the bulk of the liquid can be distilled unchanged.[16]

Oxidation-reduction reactions. Technetium(VII) is reduced to lower oxidation states by various commonly used reductants. The pertechnetate ion is rapidly reduced by active metals in sufficiently acid solution to yield technetium dioxide.[24] This product is reduced by ammonium thiocyanate in acid solution to give complexes[16] of Tc(IV) and Tc(V). In 3 to 5 M H_2SO_4 or in HCl medium, thiocyanate reduces Tc(VII) to a red Tc(V) thiocyanate complex and, to some extent, a yellow Tc(IV) thiocyanate complex.[25]

Hydrazine, hydroxylamine, ascorbic acid, or stannous chloride produces a state in a dilute sulfuric acid medium that readily yields the hydrated dioxide.[26] The shift of the half-wave potential in polarograms from $E_{1/2}$ = -0.75 V to more positive values in pertechnetate solutions of p(OH) = 1 containing hydrazine confirmed the reduction of Tc(VII) to a lower state by hydrazine.[27] The variations of the half-wave potentials and color changes of the solution during the reduction of TcO_4^- with changes in hydrazine concentrations are given in Table 1. In the absence of HCl, TcO_4^- is reduced by ascorbic acid only to Tc(V); in the presence of 20% HCl, however, it is reduced[28] to Tc(IV).

The reduction of Tc(VII) by $SnCl_2$ in acid media proceeds only by prolonged boiling, and a mixture of reduced species consisting mainly of Tc(V) is generally obtained.[28] Reduction in 1 to 2 M HCl by stannous chloride gave a Tc(IV) species[29] with a uv-absorbance band at 322 nm. In 0.5 to 0.75 M HCl, a second oxygenated species with an absorption band at 350 nm was also obtained.[29]

In alkaline media, reduction of ^{99}Tc(VII) proceeds with hydrazine, hydroxylamine, ascorbic acid, or stannous chloride only with prolonged boiling.[26] On the other hand, reduction of ^{99m}Tc(VII) with hydrazine at pH 11 was very rapid.[27,30] Below or above this pH value, the reduction

Table 1. Variations of half-wave potentials during the reduction of $^{99}TcO_4^-$ by hydrazine $[TcO_4^-] = 0.58 \times 10^{-3}$ M in 0.1 N NaOH[a]

	Concentration of hydrazine (M)							
	0	0.25×10^{-4}	2.5×10^{-4}	5.0×10^{-4}	7.5×10^{-4}	1.0×10^{-3}	1.25×10^{-3}	1.5×10^{-3}
Half-wave potential of the first step reduction, V	−0.75	−0.74	−0.65	−0.56	−0.54	−0.48	−0.45	Disappears
Half-wave potential of the second step reduction, V	−1.00	−1.00	−0.95	−0.88	−0.85	−0.78	−0.78	Disappears
Change of color	Colorless	Slightly pink	Pink	Slightly brown	Brown	Dark brown	Dark brown	Dark brown precipitate

[a]Ref. 27.

was much slower or did not take place. This is based on the fact that hydrazine is completely dissociated[27,30] at pH 11 but only partially dissociated at other pH levels. Reduction of TcO_4^- to a cationic form of Tc(IV) by using hydrazine at pH 8 or 9 or hydriodic acid has been reported.[31]

A concentrated solution of $HTcO_4$ is a sufficiently strong oxidant to be sensitive to the presence of contaminants such as dust and organic vapors. Black particles of TcO_2 appear in 1 M solutions of $HTcO_4$ when they are exposed to the dust and atmosphere.

Technetium(IV) is readily oxidized to Tc(VII) by nitric acid, hydrogen peroxide, or atmospheric oxygen.[26]

2.1.2 Technetium(VI) and (V)

Pentavalent and hexavalent technetium are somewhat more difficult to prepare than the Tc(IV) or Tc(VII) states and, therefore, have not been too well characterized. They are of interest in this study because they may appear as intermediate ions or complexes, either via direct photolysis or during sample preparation.

The pentavalent and hexavalent states are not noted for their stability in aqueous solutions. It is generally accepted as characteristic for these species to undergo disproportionation as follows:[28]

$$3TcO_4^{2-} + H_2O \rightleftharpoons 2TcO_4^- + TcO_3^{2-} + 2OH^- , \qquad (1)$$

$$3TcO_3^- + H_2O \rightleftharpoons TcO_4^- + 2TcO_3^{2-} + 2H^+ . \qquad (2)$$

The TcO_4^{2-} ions were generated by potential-controlled cathodic reduction of $((CH_3)_4N)TcO_4$ in $((CH_3)_4N)ClO_4^-$-acetonitrile solution, with the formation of olive $((CH_3)_4N)_2TcO_4$ crystals at a platinum sheet electrode and by the reduction of $KTcO_4$ in $(CH_3)_2SO_4$ solution with formation of violet-blue K_2TcO_4 at a mercury cathode.[39]

The TcO_4^{2-} species has been prepared by the reduction of TcO_4^- with hydrazine [3.1 x 10^{-2} M] at 90°C.[2] Continued heating resulted in the formation of Tc(IV).[2]

Technetium(VI) was also obtained by the reduction of cold, alkaline pertechnetate solutions with hydrazine.[26] Since these experiments were carried out with ^{99m}Tc, which has a half-life of 6 h, the compound had to be characterized by radiochemical techniques. It is not extracted by ketones or pyridine, or precipitated by ferric hyroxide, but is carried quantitatively by molydenum 8-hydroxyquinolate as well as by silver and lead molybdate. In the presence of dioximes, it can be extracted into inert solvents such as chloroform. At an OH^- concentration of 0.02 to 0.05 N, the compound slowly disproportionates to Tc(VII) and Tc(IV) in the ratio of ~2:1. The above facts are consistent with its identification as TcO_4^{2-}.

The reduction of TcO_4^- with hydrazine [1.82 mM TcO_4^-, 0.015 M N_2H_4, and 0.7 M OH^-] was followed spectrophotometrically as a reddish-brown compound (absorbing at 500 nm) reported to be TcO_4^{2-} was formed.[40] The TcO_4^{2-} then disproportionated to TcO_4^- and TcO_2, according to reaction (2). Other investigators[41] claim that the reddish-brown compound[40] is more likely to be a (V) rather than a (VI) state since there are a number of absorption bands near 490-520 nm which may well characterize Tc(V) or (V)-oxo structures. Technetium(V)-oxo structures[42] show a strong ligand band at 400 nm and a weaker (ε* = ~3000) band near 520 nm.

Evidence was obtained[25] for the formation of Tc(VI), Tc(V), and Tc(IV) in the potentiometric titration of TcO_4^- by Ti(III) in 12 M H_2SO_4. In this medium, Tc(VI) disproportionates to Tc(V) and Tc(VII) within 3 to 4 min, whereas Tc(V) disproportionates to Tc(VII) and Tc(IV) within 1 h. In 2 M H_2SO_4 or 2 M HCl saturated with $(NH_4)_2SO_4$ and NH_4Cl, respectively, a red color (absorption maximum about 500 nm) was observed at the stoichiometric end point of Tc(V). No such color was observed in 10 to 12 M acid.[25]

---

*Unit for molar extinction coefficient (ε) is L $mole^{-1}$ cm^{-1}.

An intermediate oxidation state of technetium has been observed[3] in the reduction of TcO_4^- to $TcCl_6^{2-}$ by 6 to 8 M HCl. At 100°C, the reaction is complete in about 12 h. The intermediate oxidation state, which forms during the first 2 h, extracts into hexone with a partition coefficient of >30 (compared with approximately 11 for TcO_4^-), absorbs light strongly at 235 nm (molar extinction coefficient*, ~3 x 10^4), and forms a red complex with thiocyanate.[3] It was later shown that this complex (ε = 52,000 at 513 nm) was due to Tc(V).[25] The intermediate oxidation state could possibly be the hydrolyzed oxo-complex $TcO(OH)Cl_4^{2-}$ [absorption band at 238 nm].

Some of the earlier observations[25,53] were confirmed by another observer,[29] who reported chlorocomplexes of Tc(V) in solution. Potassium pertechnetate was reduced directly to Tc(V) without the formation of detectable intermediate components in 12 M HCl, 12 M H_3PO_4, or 8 M HCl. It was suggested that the tetrachlorooxotechnetate(V) ion, as $TcOCl_4^-$, was formed[29] even though no derivatives were isolated. The absorption spectrum of the complex, showing peaks at 292.5 and 230 nm (ε = 4700 and 10,400, respectively),[24] are very close to the absorbance peaks [294 and 228 nm] of the oxo-complex, $TcOCl_5^{2-}$, reported below. Further reduction to hexachlorotechnetate(IV) occurred only slowly. The technetium(V) complex, while stable in 3 M HCl, disproportionated to pertechnetate and the hydrolysis product of hexachlorotechnetate in 1 M acid.[29]

The oxo-complex, K_2TcOCl_5, was prepared[52] by treating $KTcO_4$ with high-purity 11.5 M HCl. The precipitated green crystals of potassium oxochlorotechnetate were separated from the solution, washed with alcohol and ether, and dried under vacuum at room temperature. The resulting product was hydrolyzed in 3 M HCl at room temperature and by heating on a water bath, accelerating the reaction to produce $K_2TcO(OH)Cl_4$. Well-formed crystals of the hydrolyzed salt with a Tc:Cl ratio of 1:4 were obtained by dissolving the K_2TcOCl_5 in minimum amounts

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*Unit for molar extinction coefficient (ε) is L $mole^{-1}$ cm^{-1}.

of 3 M HCl, heating on a water bath, and concentrating the solution under vacuum until crystals separated.[52]

The stability of the Tc(V) species is temperature dependent.[54] According to Shukla, the pertechnetate ion is immediately and completely reduced to a pure solution of Tc(V) by concentrated HCl at 0°C.[54] Radiochromatograms revealed the presence of species other than Tc(V) at 8 and 23°C. Even after 96 days, the 0°C solution held at this temperature contained only 22% Tc(VII) and 1.1% Tc(IV). The same amount of Tc(VII) and Tc(IV) was found after 8 h at 8°C as after 2 h at 23°C. Less decomposition of Tc(V) occurred in 10 months at 0°C than in 17 days at room temperature.[54]

A solution of Tc(V) in concentrated HCl held at room temperature for 15 months[54] still contained 11% Tc(V). A solution aged for 18 months[55] contained 5.5% Tc(V) and 94.5% Tc(IV). After 1 year,[55] a solution of technetium held at 0°C in concentrated HCl contained 88.4% Tc(V), 9.9% Tc(VII), and 1.7% Tc(IV). In the initial stages the amount of Tc(VII) increased, but the Tc(VII) gradually disappeared as more Tc(IV) was produced.[55]

2.1.3 Technetium(IV)

Technetium(IV) is a stable form, the particular species being dependent on the medium and its pH. Technetium(IV) exists as TcO_2 at pH 3 and precipitates[45] in chloride medium above pH 2. At a concentration of 0.01 M, TcO_2 exists in the colloidal state[92] above pH 5. It is possible that other species such as TcO^{2+}, $TcO(OH)^{+}$, and Tc^{4+} occur[45] in highly acid media [pH <1.5]. A pink species of Tc(IV) has been observed during the electrolytic reduction of pertechnetate solution in the presence of phosphate ion,[54] but nothing is known about its properties.

Technetium dioxide. Technetium dioxide can be prepared free of other cations for use in solutions to be photolyzed. The anhydrous TcO_2 has been prepared[4,21] by the thermal decomposition of NH_4TcO_4 and by dehydrating[21] the dihydrate in a vacuum at 300°C. The dihydrate has been produced by reducing pertechnetate solution with zinc and HCl,[21] followed by the addition of a large excess of ammonium

hydroxide.[16] Technetium dioxide has also probably been prepared by the electrolytic reduction of alkaline pertechnetate solutions.[34] The black deposit, formed by electrolysis, was assumed to be the dioxide and not the metal because it was solubilized in an ammonia—hydrogen peroxide mixture which does not dissolve technetium metal. It is possible that the product was either a lower oxide of technetium or very finely divided reactive metal.[16]

Anhydrous TcO_2 is a very stable compound which can be sublimed at about 1000°C in vacuum.[21] It can be reduced to the metal by hydrogen at 500°C or oxidized to the heptaoxide by heating in oxygen. It reacts with chlorine to give a mixture of technetium oxide and technetium chloride, and with bromine to give an oxide-bromide mixture.[16] In aqueous suspension the hydrated dioxide is converted to pertechnetate by H_2O_2 plus alkali, by neutral Ce(IV), or by bromine water.[35]

Hexachlorotechnetate(IV). Potassium hexachlorotechnetate(IV), K_2TcCl_6, has been prepared by the reduction of potassium pertechnetate.[3,26,29,56,57] Concentrated[56,57] or strong[3,26] HCl alone serves as an effective agent for this reduction, although the reaction is slow at room temperature[58] and proceeds through several intermediate oxidation steps.[3,26] The reaction is 100 times more rapid at the boiling point.[58] This has been shown to be a complicated reduction. The first stable complex[29] is one of Tc(V), perhaps $TcOCl_4^-$ [or $TcOCl_5^{2-}$], which slowly reduces to $TcCl_6^{2-}$. In 12 N HCl, $^{99m}TcO_4^-$ is reduced immediately to Tc(V),[56] which disproportionates to Tc(IV) [$TcCl_6^{2-}$] and Tc(VII) [TcO_4^-]. Although the reduction is slower[56] in 8 N HCl than in 12 N HCl, the products are the same. With $^{99m}TcO_4^-$, Tc(V) is not formed;[56] however, TcO_4^-, $TcCl_6^{2-}$, and TcO_2 are the end products. A later chromatographic investigation[59] confirmed the formation of Tc(V) when $^{99m}TcO_4^-$ was reduced with concentrated HCl, but in lesser amounts than with $^{99}TcO_4^-$. When ammonium chloride in slight excess of the stoichiometric quantity is added to a concentrated solution of ammonium pertechnetate followed by concentrated HCl and the solution is boiled

down to a small volume, golden-yellow ammonium hexachlorotechnetate(IV) crystallizes.[60]

When 6 N HCl is distilled into a pertechnetate—80% H_2SO_4 solution at 180 to 200°C, most of the technetium is reduced to the nonvolatile +4 state.[61]

Some KI is normally added to facilitate the reduction[4,21,62] of the pertechnetate in HCl. Red crystals of an intermediate oxide halide, thought to be pentachlorohydroxytechnetate(IV), $K_2TcCl_5(OH)$,[16] usually separate out in this method. When these crystals are digested with large quantities of HCl, they dissolve to give a reddish solution which slowly becomes light yellow and deposits golden-yellow octahedral crystals of hexachlorotechnetate(IV) on cooling.[16]

The hexachlorotechnetate(IV) ion is not stable and hydrolyzes in dilute HCl, neutral, and basic solutions. (Hydrolysis occurs[56] in 0.3 N and 1 N HCl and in 9:1 $CH_3OH:H_2O$.) It undergoes hydrolysis even in 3 M HCl, judging from changes in its absorption spectrum.[11] In 1 M HCl, it decomposes to an unidentified oxygenated species with the ultimate formation of pertechnetate ion.[29] In aqueous solution, it hydrolyzes slowly[11] to TcO_2; in basic solution, it hydrolyzes promptly[26,34] to the dioxide. The solubilities of the hexachlorotechnetates (see Table 2) appear to be independent of the acid concentration.[63]

The $TcCl_6^{2-}$ ion is oxidized[3,26] to Tc(VII) by HNO_3, H_2O_2, Cl_2, Ce(IV), or MnO_4^-, but appears to be more resistant to air oxidation than the oxygenated species of Tc(IV).

2.1.4 Technetium(III) and lower valence states of technetium

The (III) and lower valence states of technetium are easily oxidized and, therefore, very difficult to maintain in solution. However, they are discussed here since they could be formed during photolysis.

Three hybrid oxides of technetium have been reported. Technetium forms two hydrous oxides, Tc_3O_4 and Tc_4O_7, as surface films. These compounds were identified in both anodic polymerization of the metal and cathodic reduction of $Tc(OH)_4$ deposited electrolytically on the

Table 2. Solubility of M_2TcCl_6 compounds at 25°C[a]

Compound	Solubility (M)		
	10 M HCl	5.0 M HCl	3.0 M HCl
$(NH_4)_2TcCl_6$	4.01×10^{-3}	4.1×10^{-3}	4.12×10^{-3}
K_2TcCl_6	1.17×10^{-3}	1.175×10^{-3}	1.16×10^{-3}
Rb_2TcCl_6	3.68×10^{-4}	3.69×10^{-4}	3.66×10^{-4}
Cs_2TcCl_6	2.91×10^{-4}	2.9×10^{-4}	2.87×10^{-4}

[a]Ref. 63.

metal.[36] The third hydrous oxide, Tc_2O_3, has been prepared by electrolytic reduction[37,38] of TcO_4.

Both hexachlorotechnetate(IV)[44] and pertechnetate[43] were quantitatively reduced to a trivalent compound by carefully controlling the cathode potential. A green solution containing Tc(III) was prepared[43] by controlled cathode potential electrolysis of TcO_4^- in a phosphate buffer at a pH of 7. These Tc(III) solutions have strong reducing properties and are easily air oxidized[45] to Tc(IV).

Reduction of technetium in the quadrivalent state with hydroxylamine ion produces the chloride complex cation containing hydroxylamine and ammonia in ligands.[60] A solid separating from the solution after the reaction of ammonium hexachlorotechnetate with hydroxylamine hydrochloride contained a pink cation complex of bivalent technetium with an empirical formula $[Tc(NH_2OH)_2(NH_3)_3]\cdot Cl_2$, which could not be distinguished from $[Tc(NH_2OH)_2(NH_3)_3H_2O]\cdot Cl_2$ because of the accuracy of the results. At least two other compounds, one of which was mobile (as a cation) in paper electrophoresis and one of which was an uncharged species,[60] were also observed.

The reaction of TcO_4^- with a mixture of concentrated HCl in concentrated H_2SO_4 resulted in an instantaneous formation of a dark blue solution.[1] The formation of compounds with technetium in an oxidation state no higher than (III) was confirmed by the change of the blue color to light green over a period of hours under the influence of atmospheric oxygen. The spectrum of the light green solution was identical to that of hexachlorotechnetate(IV).

An oxidation state lower than (IV) is obtained[26] via the reduction of TcO_4^- by zinc in concentrated HCl.

Reaction of ammonium hexachlorotechnetate with zinc and HCl gave a mixture from which salts of the acid $H_3Tc_2Cl_8$ were isolated.[60,65] The ammonium salt was $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$ (technetium valence = 2.5). The salts were isolated by crystallization from fairly concentrated HCl, a medium in which they are soluble and oxidize only slowly. Later x-ray evidence confirmed the formula for the $Tc_2Cl_8^-$ group.[64] Oxidation and

hydrolysis of the $Tc_2Cl_8^{3-}$ species occur rapidly to form hexachlorotechnetate[60] in dilute HCl and to form TcO_2 in water.

If the reduction of hexachlorotechnetate(IV) with zinc in concentrated HCl is carried out at 75°C instead of 100°C, the formation of a black unidentified precipitate which occurs at 100°C can be almost entirely eliminated.[66] The reduced technetium compounds thereby obtained from ammonium and magnesium hexachlorotechnetate(IV) were black and chocolate brown powder, respectively.[66] The black powder containing ammonium ions, $(NH_4)_3[Tc_2Cl_8]2H_2O$, dissolved in nondeoxygenated, concentrated HCl with a blue color, with no evidence of red from intermediates or contamination with yellow hexachlorotechnetate(IV) salts. The brown powder containing magnesium ions dissolved with a brown color,[66] as previously reported.[60] Prolonged oxygenation leads to the re-formation of hexachlorotechnetate(IV).[66]

Crystals[67] calculated from analyses to be $(NH_4)_8(Tc_2Cl_8)_3 \cdot 2H_2O$ and $K_8(Tc_2Cl_8)_3 \cdot 4H_2O$ were salted out from the mother liquor of ammonium pertechnetate in 11.5 M HCl that had been heated at 170°C in an autoclave at an initial H_2 pressure of 30 atm.

A valency of +1 has been reported for technetium in a cyanide complex.[50] Potassium pertechnetate was reduced with potassium amalgam in the presence of excess KCN to green $Tc(CN_6)^{5-}$. Potassium hexachlorotechnetate, K_2TcCl_6, made from $KTcO_4$, KI, and HCl, forms $K_3[Tc(OH)_3(CN)_4]$ on treatment with KOH and KCN. Aqueous solutions of $K_3[Tc(OH)_3(CN)_4]$ also form $K_5[Tc(CN)_6]$ by reduction with potassium amalgam in 60 to 80% yield,[50] based on NH_4TcO_4.

2.1.5 Technetium metal

Technetium metal is available and, therefore, can be considered as a source or a starting material for conversion to a higher oxidation state. The metal oxidizes in HNO_3, aqua regia, and hot concentrated H_2SO_4 (ref. 3) but is insoluble[6,8] in HCl and neutral or alkaline H_2O_2. Technetium has been reported to dissolve[57] in acid — 5% H_2O_2. It tarnishes slowly in moist air.[3]

Oxidation of the metal is a very complex procedure. When it is exposed to dry oxygen in a high-vacuum line, Tc_2O_7 is the major product;[5] contrary to some reports in the literature,[10-13] however, lower oxides of technetium are always produced in small quantities,[5] and purification by simple resublimation[14] is not possible. The formation of small quantities of a second volatile compound [possibly TcO_3 or $HTcO_4$] has been observed by some investigators.[14]

2.2 Electrolysis

2.2.1 Characterization and potentials

Information about the electrochemical reactions and the potentials of a substance are useful in predicting its photochemical behavior in solutions and in furnishing a method to adjust, by either oxidation or reduction, its valence state before photolysis. The precipitate that forms in solutions during electrolysis will probably also form if reduction is effected by photolysis. All things being equal, the larger the potential difference between a "stable" form and another oxidation state, the less likelihood of a change in the oxidation state of the "stable" form and, therefore, the less likelihood of a redox reaction by photolysis.

Both the electrode potentials and the number of electrons involved in the reaction (i.e., the "n" value) may be obtained from the polarograms. If a multistep reduction is shown in the polarogram, $n > 1$, and the same conditions indicated for the polarogram are used, the intermediate valence states will be unstable regardless of how they were produced.

Coulometric reduction of a pertechnetate solution generally results in either a three-electron or a four-electron change, depending on: (1) pH, (2) nature of the supporting electrolyte, and (3) applied potential.[37,38,40] The four-electron reduction yields either a green

solution[38,40,70,71] or a brown to black precipitate. The green solution is believed to be a Tc(III) complex species, while the dark precipitate could be the sesquioxide Tc_2O_3, or the dioxide (TcO_2) resulting from a subsequent disproportionation or from air or solvent oxidation of the Tc(III).

The reduction of Tc(VII) ion takes place on the platinum electrode via absorbed hydrogen atoms.[81] The overall scheme for the reduction of Tc(VII) to Tc(IV) should be:

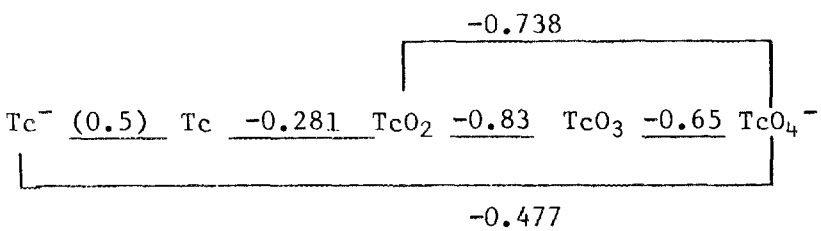
$$3H^+ + 3e^- \rightarrow 3H_{ads} \ ,$$

$$TcO_4^- + 3H_{ads} + H^+ \rightarrow TcO_2 + 2H_2O \ .$$

No appreciable reduction is detected when H_2 gas is bubbled into a solution of Tc(VII) ion at any pH value; however, Tc(VII) is reduced to TcO_2 or to TcO_2 plus Tc_2O_3 in the presence of platinum black.

The reduction to TcO_2 and Tc_2O_3 on platinum occurs via the intermediate hydrogen atoms; however, these compounds are formed as charge transfer products on mercury.[81]

Several oxidation-reduction diagrams for acid solutions have been proposed.[11,33,73] The earliest one[33] has been shown to be inaccurate because oxygen was present in the solution when the TcO_2^--TcO_4^- potential was measured.[73] A typical diagram[11] is:



The standard electrode potentials have been calculated from the established free energies of formation, and the results have been reported.[74]

The polarographic behavior of the pertechnetates in acid, neutral, basic, and complexing media containing a wide range of supporting electrolytes has been summarized by other authors.[72,74] Reduction of pertechnetate is possible in various media, although most of the results

have been obtained in chloride,[35,37,38,45] sulfate,[37,38,40,75] and perchlorate.[45,76-78] However, interpretations of polarographic waves are contradictory with regard to the nature of the oxidation states involved during the reduction of TcO_4^- in acidic and alkaline media.

2.2.2 Acid media

Most polarographic and coulometric data from studies made in acid media have been interpreted as four-electron reduction at the first step.[37,38,45,72,77,79-83] Some exceptions have been noted.[28,35,74-76,84]

Several investigators have proposed two-step polarographic reduction[37,38,45,72] of TcO_4^- in acidic media involving a four-electron change[37,38,45,72] [Tc(VII)/Tc(III)] for the first wave and a three-electron change for the second wave[37,38,45] [Tc(III)/Tc(0)]. Grassi has reported a third reduction wave that is related to the catalytic reduction of hydrogen.[45] Exchange of four electrons for the first wave was confirmed by controlled-potential coulometry measurements [E = -0.5 V] that gave $n = 3.98 \pm 0.14$ in both chloride and sulfate media[45] at a pH of 2. During the course of the coulometry, however, part of the Tc(III) was transformed by an unknown reaction to various electrochemically inactive species which could not be identified.[45]

The polarographic properties of pertechnetate in perchlorate media are the same as those observed in sulfate and chloride. Although Tc(III) is formed at pH 1 to 3.5 during the first reduction step, the reduced technetium is reoxidized[45] by the ClO_4^-. The potential for the first cathodic wave [Tc(VII)/Tc(III)] in acid solution is pH dependent but occurs at -0.8 V in alkaline or buffered media.[72] Diffusion current measurement for the second wave in acid media,[72] which occurred at -0.9 V, indicated that $n \leq 7$; the catalytic component prevented determination of the exact value. The formation of technetium metal during the second step, demonstrated by radiopolarographic measurements,[83] confirmed the value of 7. The reduction of pertechnetate proved to be irreversible under all conditions investigated.[72]

The previous scheme was contested by other investigators,[75,76] who suggested that the first step involved the reduction of Tc(VII) to Tc(IV) and subsequent formation of TcO_2. It was established[76] that the polarographic wave observed at $E_{1/2} = -0.8$ V corresponds to a three-electron reduction with the formation of TcO_2. Addition of $HClO_4$ to this system produced a new wave at $E_{1/2} = -0.6$ V, which increased in height and moved to less negative potentials as the acidity was increased.[76]

Although the polarographic reduction of pertechnetate ion in unbuffered acidic solutions of pH < 4 gives an initial wave due to a four-electron process,[37]

$$TcO_4^- + 8H^+ + 4e^- \rightarrow Tc^{3+} + 4H_2O \ ,$$

some tendency exists for a stepwise separation of the (VII)/(IV) from the (IV)/(III) stage which tends to be more prominent at higher acidities, especially with H_2SO_4 as compared with HCl solutions.[37,38] An "n" value of 3 can be obtained just at the half-wave potential[37] in the appropriate media [e.g., H_2SO_4 (ref. 38)], resulting in a black suspension of TcO_2. Continued electrolysis at a more negative potential does not effect further reduction.[37,38] However, initial electrolysis of Tc(VII) at a more negative potential does give an n value of 4, with an accompanying black suspension[37,38] that is apparently Tc_2O_3. It is also possible to obtain n = 3 in HCl, resulting in a brown TcO_2 suspension; however, one only need to have the initial potential just on the plateau of the wave to obtain n = 4 and a green solution which still exhibits polarographic wave II.[37,38] An n value of 4 $\pm$ 2% can be obtained if coulometry in HCl is made at -0.30 V vs S.C.E. [on the plateau of the wave] and the pH is maintained constant within 0.01 unit by adding acid.[38]

The separation between (VII)/(IV) and (IV)/(III) becomes more prominent near pH 1.75; a value of 3 for n can be obtained by electrolyzing on the plateau of the first wave, while n = 4 can be obtained by initially electrolyzing at a more negative potential.[38] The reaction pathway is hindered, at a pH > 4, probably due to the absorption of some intermediate (e.g., TcO_3 or TcO_2) on the mercury surface.[38]

While carefully regulated coulometric runs can give either a three-electron or a four-electron reduction, the product of macroscopic electrolysis[37] is, respectively, the insoluble dioxide (TcO_2) or the sesquioxide (Tc_2O_3). In either case, the suspension shows no further electrochemical activity.[37]

The reduction of Tc(VII) at mercury electrodes in acidic chloride media, yielding Tc(III) as the product of the first totally irreversible step,[79] was first order with respect to TcO_4^- and second order with respect to hydrogen ion in the rate-determining step.[79] Technetium(III), which is the product of the electrode reaction, probably exists in the hydrolyzed form [$TcO(OH)$, $Tc(OH)_3$, Tc_2O_3] or as a chloride complex but cannot be identified[79] on the basis of the spectrophotometric measurements due to a lack of data for the absorption spectrum of Tc^{3+}. The reduction of pertechnetate in acid media is given by the overall reaction[79]

$$TcO_4^- + 5H^+ + 4e \rightarrow TcO(OH) + 2H_2O \ .$$

This reaction is irreversible and involves a single slow rate-determining step which can be written as

$$TcO_4^- + 2H^+ + e^- \rightarrow TcO_3 + H_2O \ .$$

In some media, the Tc(III) could be reoxidized to Tc(IV) or Tc(V) at the electrode.[72] Neither oxidation nor reduction current was observed after coulometric oxidation of Tc(III) [E = -0.05 V] at pH 2. This shows that the oxidation product of Tc(III) was unstable, possibly due to the formation of a chemically inactive complex.[45]

Reduction of pertechnetate in strong acids does not produce any well-defined waves.[16,35,76,89] In 2 M H_2SO_4,[89] 10 M H_2SO_4,[89] and 4 M $HClO_4$,[16,35,76,89] the current increased gradually to the voltage of the reduction of the supporting electrolyte[16,35] or hydrogen discharge[89] and started in the potential region corresponding to the anode dissolution of mercury, suggesting that the chemical reduction of TcO_4^- by mercury was possible.[76] Similarly, an ill-defined wave that spread over a wide potential range was observed at low pH values in the presence of HCl,[98] $HClO_4$,[35,84] and H_2SO_4.[35,84]

In tests made by using applied potentials of -0.25 to -0.45 V vs S.C.E., a mercury pool cathode, and a 1 M H_2SO_4 solution which was protected from O_2 by a N_2 flush and blanket, the average coulometric n value for the [(VII)/(III)] reduction was found to be 3.65 from Ce(IV) titrations of the product-solution aliquants.[40] The chemical reduction of Tc(VII) by the mercury appears to account for most of the coulometric vs titrimetric discrepancy.[40]

Conflicting results are reported in 4 M HCl. Two ill-defined irreversible waves were observed[35] with half-wave potentials vs S.C.E. of -0.52 and -0.68 V, corresponding to a one-electron and a two-electron reduction, respectively. Others[84] obtained waves at $E_{1/2}$ = -0.15 and -0.35 V, with a third wave commencing at -0.7 V.

In very strong acidic media, especially HCl, the apparent $E_{1/2}$ of the first wave may simply be the point at which the anodic dissolution of mercury permits the wave to be observed.[57] For some reason, the top of such a wave is not defined. The potential of the first wave was shifted[37] from slightly positive potentials in the more strongly acidic solution to about -0.4 V at pH 4.

Some reduction of Tc(VII) does occur with mercury.[38] Only the second wave was observed in a 2.4 M HCl solution previously shaken with mercury, which indicates that Tc(VII) was reduced almost quantitatively to Tc(IV) or Tc(III).[38] There was also some reduction to still lower states since a 20 to 47% decrease in the height of the second wave was found. Both Tc(VII) waves appear in 0.1 M HCl or 2 M H_2SO_4 solutions previously shaken with mercury, but the first wave was reduced by 87 and 59%, respectively.[38]

2.2.3 Reversible reactions in complexing media

The formation of a green Tc(III) phosphate complex by the coulometric reduction of Tc(III) in phosphate-buffered solutions of pH 5 to 7 has been noted in several articles.[37,40,43,70,71] This coulometric process in a (III)-complexing medium, such as phosphate at pH 4.7, is reproducible[71] within n = 4 $\pm$ 0.04. It appears that a four-electron

reduction also takes place in solutions of higher pH when an appropriate complexing agent is present.[71]

When $KTcO_4$ dissolved in a potassium phosphate-buffered solution of pH 7 is electrolyzed at -0.80 V vs a Ag-AgCl reference electrode, the solution first becomes pink (after a few minutes) but then turns green at the completion of the process.[43] A long electrolysis time and the absence of air are necessary to obtain the green product[40] since the Tc(III) will be oxidized to the pink Tc(IV) phosphate complex as it contacts air.[40,43] The electrolytic reduction of the pink phosphate complex to the green complex involves a one-electron change.[43]

A green-colored Tc(III) is also formed[40] when a dilute H_2SO_4 solution of ferrous ammonium sulfate containing H_3PO_4 is contacted with Tc(VII). In the absence of H_3PO_4, the solution darkens and TcO_2 finally precipitates. The green-colored product transforms to a yellow-orange Tc(IV) species on standing in air; however, the conversion is delayed[40] by the increase of H_3PO_4.

When Tc(VII) is coulometrically reduced at a controlled potential of -0.70 V vs S.C.E. in an acetate-buffered sodium tripolyphosphate ($Na_5P_3O_{10}$) medium of pH 4.7, Tc(III) is quantitatively formed.[71] (A more negative potential than that at $E_{1/2}$ must be applied for complete reduction.) The $E_{1/2}$ (V vs S.C.E.) for the reduction at other pH levels are:

pH	$E_{1/2}$ (V)
4.0	-0.44
5.5	-0.66
6.4	-0.67
7.2	-0.68
9.0	-0.79
9.0-9.5	-0.81

The first step corresponds to a four-electron reduction.[71] The second step, which is associated with the reduction of Tc(III), is not completed because Tc(II) reacts with the medium.[71]

As the medium becomes more basic, the reduction of Tc(VII) to Tc(III) occurs at a more negative applied potential and the break between Tc(VII) → Tc(III) and Tc(III) → Tc(II) reduction becomes less pronounced.[71]

The color changes in the reduction of Tc(VII) to Tc(III) in the various media indicate that the reduction may be sequential.[71] Colorless Tc(VII) in an acetate-buffered sodium tripolyphosphate medium at pH 4.7 is reduced to Tc(IV), which is pink; and Tc(IV) is reduced to Tc(III), which is initially orange but finally becomes yellow. In phosphate-buffered sodium tripolyphosphate medium (pH = 7.0), the colors are slightly different: colorless Tc(VII), pink Tc(IV), gray Tc(IV) and Tc(III), and finally green Tc(III), corresponding to the results obtained previously by Thomason.[43]

The Tc(IV) → Tc(III) couple is reversible since Tc(III) can be oxidized to Tc(IV) at -1.0 V vs S.C.E.

The time required to reduce Tc(VII) in unbuffered medium is considerably longer than that required in buffered medium.[71] As the pH decreases, the potential required for the Tc(VII) → Tc(III) reduction becomes less negative.[71]

As in the case of the technetium phosphate complexes, the cathodic process for $TcCl_6^{2-}$ is practically reversible[93] and the first step involves a single-electron change: $TcCl_6^{2-} + H_2O + e \rightarrow TcCl_5OH^{3-} + Cl^- + H^+$. The $TcCl_5OH^{3-}$ is oxidized, anodically or by air, in 1 N HCl solution again to $TcCl_6^{2-}$.[93,94] In the region of the second step at -0.45 V vs S.C.E., the mercury electrode begins to drop irregularly. The gold electrode becomes coated with a brown deposit.[93]

It may be necessary to reduce the pertechnetate in a complexing medium to prevent the formation of technetium oxide. Table 3 lists the applied potentials necessary to reduce the pertechnetate, along with some results of the solution changes and the media in which precipitation does and does not occur.

Table 3. Coulometric determination of the Faradaic n value for Tc(VII) involved in the reduction of pertechnetate

pH[a]	Solution	Potential (applied V vs S.C.E.)	Value of n	Solution change	Reference
-0.3	1 M H_2SO_4	+0.12	3.05	Brown ppt.	37,38
-0.3	1 M H_2SO_4	-0.05	4.09	Black ppt.	37,38
0.8	0.5 M (HCl + KCl)	-0.03	3.05	Brown ppt.	37,38
1.1(1.3)	0.5 M (HCl + KCl)	-0.30	3.81	Green soln.	37,38
2.0(7)	0.5 M (HCl + KCl)	-0.16	3.08	Brown ppt.	37,38
1.0[b]	HCl + KCl	-0.3	3.92	Green soln.	38
1.1[b]	HCl + KCl	-0.3	3.94	Green soln.	38
1.75[b]	HCl + KCl	-0.3	3.05	Brown ppt.	38
1.75[b]	HCl + KCl	-0.5	3.74	Green soln.	38
4.7	Tripolyphosphate	-0.70	4		71
6.80	KCl, $Na_2HPO_4.7H_2O$, $H_3C_6H_5O_7.H_2O$ (ionic strength, 0.427 M)	-0.66	3.03		37
7	Phosphate	-0.84	4		43
7	Phosphate-pyrophosphate	-0.68	4		70
7.40	0.1 M $K_4P_2O_7$ + 0.1 M K_2HPO_4	-0.71	3.02		37
7.40	0.1 M $K_4P_2O_7$ + 0.1 M K_2HPO_4	-0.85[c]	1.00		37
9.80	0.5 M KCl, 0.2 M Na_2CO_3, 0.1 M $NaHCO_3$	-0.75	3.03		37
13.10	0.5 M (KCl + KOH)	-0.85	2.95		37
13.10	0.5 M (KCl + KOH)	-1.12	4.07		37
13.00	0.25 M (K_2SO_4 + KOH)	-0.85	2.92		37
13.00	0.25 M (K_2SO_4 + KOH)	-1.15	4.02		37

[a]Numbers in parentheses indicate the pH at the end of electrolysis.
[b]Acid was added during these runs to keep the pH constant.
[c]The applied voltage was stepped up to -0.85 V after the run made at -0.7 V.

2.2.4 Neutral and basic media

Reduction in neutral and basic media involves two or three electrons in the first step.[27,28,35,37,38,70,75,76,78,79,84,90,91,95,96] A three-electron step [Tc(VII)/Tc(IV)] followed by a one-electron step [Tc(IV)/Tc(III)] has been proposed from results of coulometric measurements[37,38] and from various polarographic studies in buffered and unbuffered media.[72,96] In both buffered and unbuffered media,[72] the first wave appears at -0.8 V and the second at -1.0 V [-1.27 V in borate solution].

Other authors[35,70,75,76,78,84,90,91] have suggested an alternative scheme with Tc(V) as the intermediate and Tc(IV) as the final oxidation step. In 0.1 M KOH,[35] the first wave occurs at -0.85 V and the second at -1.15 V. There is no marked variation of the n value with concentration. Both waves are irreversible.[35]

Other investigators[28] found only a single-step reduction, corresponding to a two- or three-electron transfer, depending on the medium. In aqueous solutions of 0.1 M KOH, 0.1 M NaOH, 0.1 M KCl, and 0.1 M $NaClO_4$, the single-step reduction corresponds to a two-electron transfer at -0.8 V.[28] In 0.1 M potassium cyanide, $KTcO_4$ gave a single well-defined irreversible wave with a half-wave potential of 0.81 V, corresponding to a three-electron reduction to Tc(IV).[28] In a solution containing 0.1 M HCN and 1 M sodium citrate, only a single three-electron transfer was observed at a half-wave potential[28] of -0.88 V.

In basic solutions, the electrolytic reduction of the pertechnetate in uncomplexing media usually results in a precipitate. A black-brown precipitate, possibly TcO_2, formed[40] when the pertechnetate in a 0.25 M NaOH solution was electrolyzed at -1.15 V vs S.C.E. with an n value of 3.46.

When the pertechnetate in 2 M NaOH was electrolyzed at -1.1 V vs S.C.E., more than 95% of the technetium was precipitated, probably as the oxide since the product was later dissolved in a mixture of ammonium hydroxide and hydrogen peroxide.[34]

2.3 Absorption Spectra

Absorption spectra are useful for identifying ions or complexes in solution, for measuring the concentrations of the various species, and for determining when a reaction has occurred.

Representative absorption spectra for some of the various valence states of technetium, including Tc(VII) through the lower valence states, are given in Figs. 1-3 (see also Table 4). Insufficient absorption data have been found to determine the concentrations of the various species in any one solution if photolysis occurs.

In dilute solutions, the TcO_4^- ion absorbs chiefly in the ultraviolet region and not in the visible. Two partially resolved envelopes of bands, with peaks evident at 244 and 248 nm on one band and a peak at 288 nm on the other band (see Fig. 1 and Table 4), have been reported by several investigators.[10,11,18,19,22-24,32,40,57,97-101]

The spectrum of the pertechnetate ion is influenced by the type and concentration of acid in the solution but is independent of moderate temperature changes. The molar extinction coefficients for the bands in the ultraviolet are not affected significantly by moderate temperature changes; they remain[40] within 2% from 10 to 60°C. The molar extinction coefficient increases with the type of acid in the following order: $HClO_4 < HNO_3 < H_2SO_4 < HCl$.[100] The effect of acid or base (up to 1 N) is negligible.[40] The band at 288 nm is present in neutral solutions and in $HClO_4$ and H_2SO_4 solutions <7 M but gradually disappears with increasing acidity.[40] A new band of lower wavelength than 244 nm, which grows in and increases in absorbance with acidity, strongly influences the peaks at 244 and 248 nm.[40]

Two bands, one in the 230- to 240-nm region and the other at 293 nm, have been reported for TcO_4^- in HCl at high acid concentrations; a single band has been observed for low acid concentrations.[100] The location of the first band is acid dependent, while that of the second band is not. For example, the 230- to 240-nm band is nonexistent in 1 M HCl, occurs at 230 nm in 10 M HCl, and shifts to 240 nm[100] in 11 M HCl. The molar absorbance increases with increasing acidity above 7 to 7.5 M acid.[40]

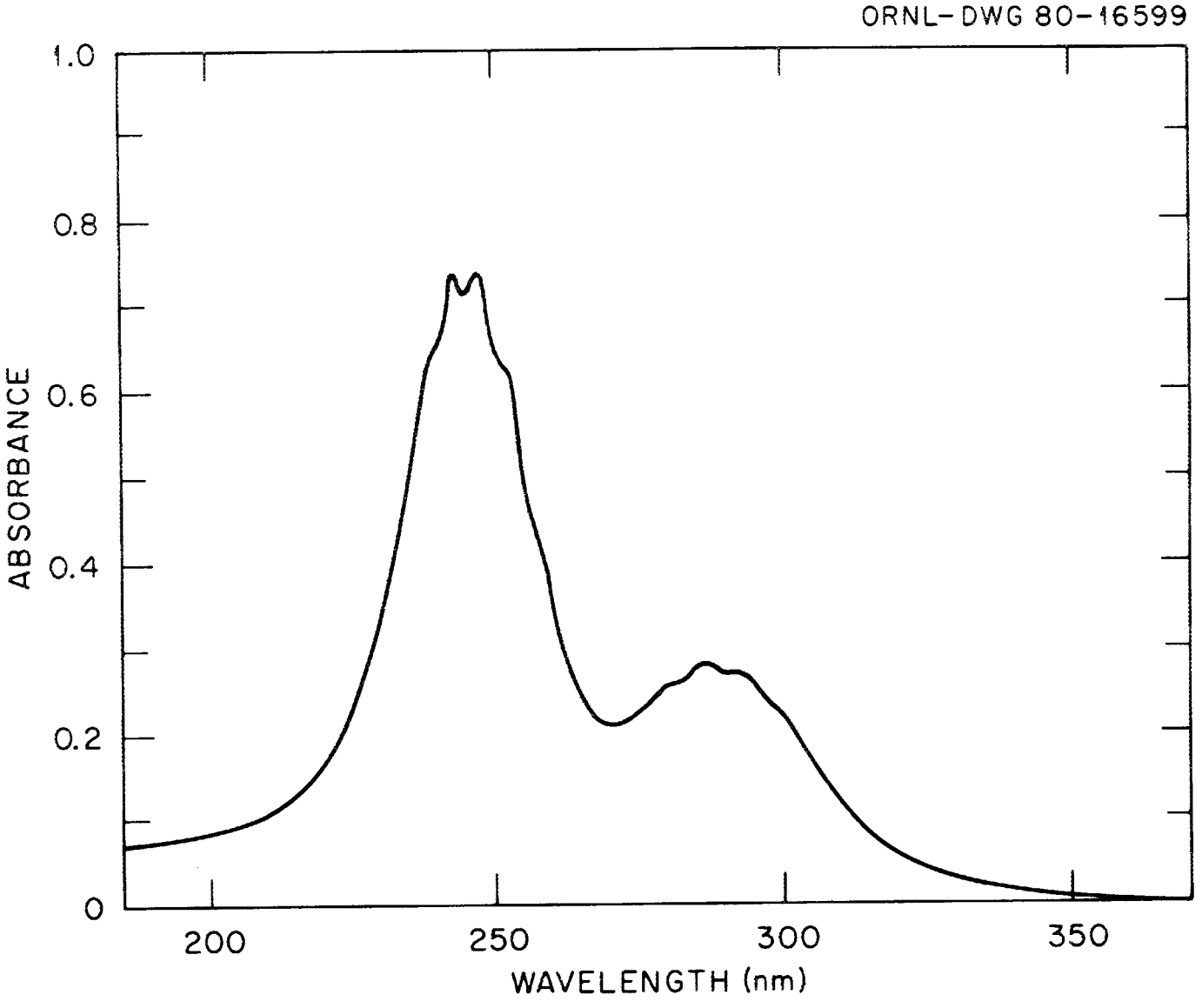


Fig. 1. Ultraviolet absorption spectrum (185 to 350 nm) of 1.22×10^{-4} M $KTcO_4$ (1-cm cell). [Adapted from ref. 11]

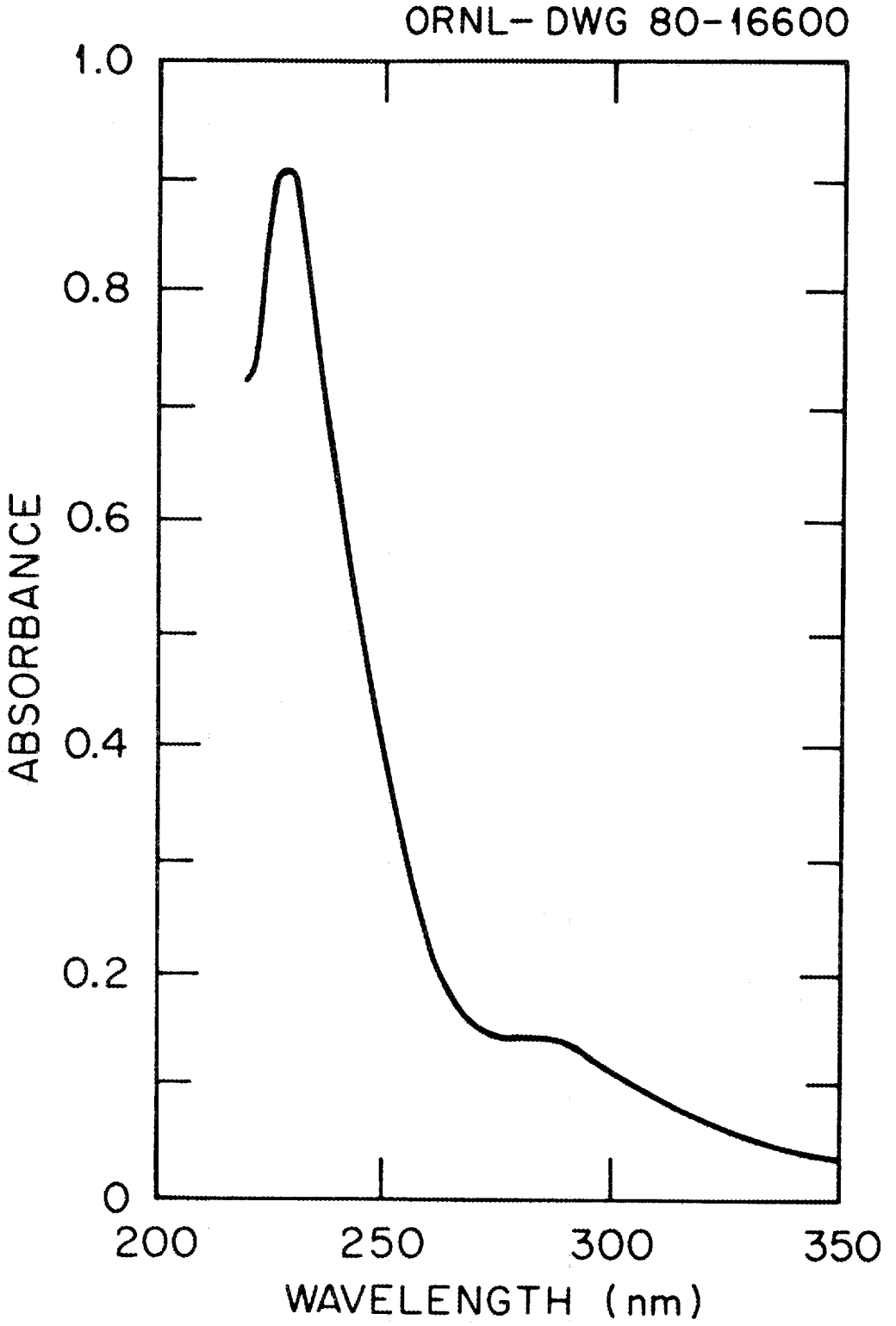


Fig. 2. Ultraviolet absorption spectrum (200 to 350 nm) of 1.8×10^{-6} M TcO_4^{2-} (1-cm cell). [Adapted from ref. 2]

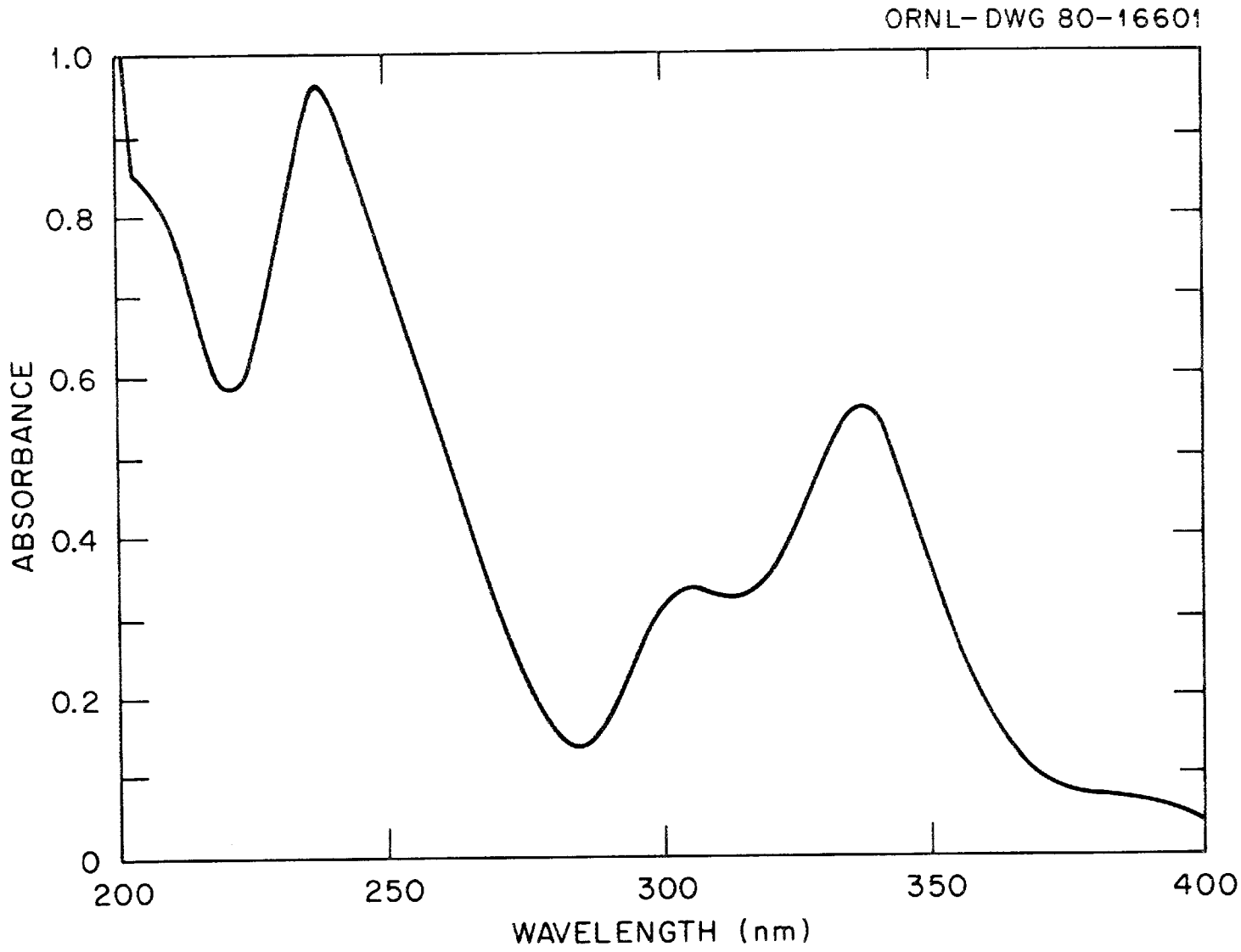


Fig. 3. Absorption spectrum (200 to 400 nm) of 5.09×10^{-5} M K_2TcCl_6 in 1 M HCl (1-cm cell). [Adapted from ref. 11]

Table 4. Absorbance bands for technetium species

Species	Wavelength (nm)	Extinction coefficient	Remarks	Reference
Technetium(VII)				
TcO_4	244.3 ± 0.3 248.1 ± 0.3 287.5 ± 0.3	6148 ± 67 6165 ± 61 2316 ± 33	At pH 0.35 to 12.2, effect of acid or base up to 1 N negligible Extinction coefficient between 10 and 60°C within ±2%	40
TcO_4^-	230, 293 at 10 M HCl		Spectral change and molar absorption not affected up to 7.0-7.5 M. At higher acidities, spectra change and molar absorption increases. Absorbance of TcO_4^- increases in following order: $HClO_4$ < HNO_3 < H_2SO_4 < HCl.	100
TcO_4^-	240, 293 at 11 M HCl			
TcO_4^-	No 230 or 240, 293 at 1 M HCl			
Technetium(VI)				
TcO_4^{2-}	231		Alkaline medium	2
Tc(VI)	500	200 (est.)	Reddish-brown color [may be Tc(V)][a]	40
Technetium(V)				
Tc(V)	513 235	52,200 30,000	In HCl solution	97
Tc(V)	292.5 230.0	4700 10,400	Made by dissolving $KTcO_4$ in 12 M HCl	29
K_2TcOCl_5	600 480 294 228		Made by treating $KTcO_4$ with 11.5 M HCl	52

Table 4 (continued)

Species	Wavelength (nm)			Extinction coefficient	Remarks	Reference
$K_2TcO(OH)Cl_4$	625 357 238				Hydrolyzed K_2TcOCl_5 in 3 M HCl and heated	52
Tc:Cl ratio of 1:45	325 238				Hydrolyzed species that occurred with $TcOCl_5^{2-}$ in 3 to 3.7 M HCl	52
Tc(V)	326			7800	Unknown Tc(V) species formed by oxidation of $TcCl_6^{2-}$ by sunlight	29
Technetium(IV)						
$TcCl_6^{2-}$		1163(s)[c]			Measured in strong HCl solutions	
	1121[b]	1124(w)				104
	1095	1096				57
	1046	1049				107
	(1031)	1029				
	709					
	704	705				
		616				
	(385)	388		1380[b]		
	338	338	340[d]	10,600		
	240		241	18,000		
$Tc(OH)_2(SO_4)_2^{2-}$ (believed to be)		500			Made by electrolysis of TcO_4^-; disappears in acidity of less than pH 4	105
Tc(IV) phosphate complex		540 385		540 1700	Yellow-orange anionic phosphate complex resulting from the reduction of TcO_4^- with ferrous ion	40
Tc(IV) phosphate complex	Broad absorption from 500-540 nm				Pink phosphate solution; made by electrolytic reduction of TcO_4^-	43

Table 4 (continued)

Species	Wavelength (nm)	Extinction coefficient	Remarks	Reference
Technetium(III)				
Tc(III)	595	250	Green, uncharged phosphate resulting	40
	500	140	from reduction with ferrous ion	
Tc(III)	760-350		Phosphate-buffered solution from electrolysis; broad absorption band; no fine structure; green in color	43
Technetium (hybrid)				
$[Tc_2Cl_8]^{3-}$	1695	630		110
	735(w)	35		
	637	172	Unsymmetrical band decomposed to show second weak band at 735 nm	
	500	10	Could be obscured under lower edge of uv absorption	
	318	3900		
	269	5600	Shoulder	
	230	14,000	Maximum	
$[Tc_2Cl_8]_3^{8-}$	1670	540		67
	1595	565		
	1520	510		
	650	190		
	506	20		
	320	2550		
	~260	>>2550		

[a]Ref. 41.
[b]Data in this column taken from ref. 104.
[c]Data in this column taken from ref. 57.
[d]Data in this column taken from ref. 107.

The major band for TcO_4^{2-}, according to Rulfs et al.,[40] is at 500 nm. However, Majumdar et al.[41] claim that this product is Tc(V) instead of Tc(VI). As TcO_4^- is reduced to Tc(VI) or Tc(V) by hydrazine, the absorbance from 650 to 386 nm increases as the amount of reduced product increases.[40] Below 385 nm, the absorbance decreases as Tc(VII) is reduced.[40]

The major band in the ultraviolet for TcO_4^{2-}, also made by the reduction of TcO_4^- with hydrazine,[2] is found at 231 nm (see Table 4 and Fig. 2).

The peaks for the major bands of $TcCl_6^{2-}$ in the uv region are at 240 and 338 nm (see Fig. 3 and Table 4).

The electrolytic reduction of TcO_4^- yields different complex species (Table 4), depending on the media. The reduction of TcO_4^- in sulfate solutions results in an ion believed to be $Tc(OH)_2(SO_4)_2^{2-}$, which disappears[105] in media with acidities greater than pH 4. Its absorption bands are at 500 and 320 nm.[105] The electrolytic reduction of TcO_4^- in a phosphate solution produces a pink Tc^{4+} solution which shows broad absorbance from 500 to 540 nm.[43] Further reduction in the phosphate-buffered solution forms a green Tc^{3+} solution that shows absorbance between 760 and 350 nm and has no fine structure.[43]

A yellow-orange anionic phosphate—Tc^{4+} complex that has bands at 650 and 385 nm results from the reduction of TcO_4^- with ferrous ion in phosphate solution.[40] Further reduction in this solution forms a green Tc^{3+} complex with bands at 595 and 500 nm (Table 4).[40]

As shown in Table 4, lower-valent technetium species[67] are $[Tc_2Cl_8]^{3-}$ and $[Tc_2Cl_8]_3^{8-}$.

Most of the spectral data reported in the literature, with the exception of the pertechnetate, were for technetium chlorides; however, several references were concerned with phosphate complexes and a sulfate. No data were found for nitrates or perchlorates, possibly because of a lack of interest of technetium in these media or because technetium species (except for the pertechnetate) are unstable in these media. Regardless of which solutions of technetium are photolyzed, more spectral data need to be obtained.

2.4 Photolysis

The $TcCl_6^{2-}$ ion has been shown to be photochemically active in HCl following exposure to uv irradiation[106,107] or to sunlight.[29] No other photosensitive reactions have been reported.

When $(NH_4)_2TcCl_6$ that had been dissolved in HCl was irradiated with light at 340 or 254 nm, the absorption spectrum changed; on the other hand, the spectrum of a comparable sample kept in the dark remained the same.[106,107] An equilibrium which depended on both the acid concentration and the light intensity was reached on prolonged photolysis at constant temperature.[106] Ligand changes (mainly the loss of Cl^-), but no redox reactions, occurred when the solutions were exposed.[106,107]

Two new species were detected in 3 M HCl solution that had been irradiated for 2 weeks: a neutral species which had been tentatively assigned the formula $TcCl_4$ and may consist of more than one component, and $[TcCl_5(H_2O)]^-$.[106] If the pH of the solution becomes <1, the yellow-colored $TcCl_5(H_2O)]^-$ will decompose into a brownish species as follows: $[TcCl_5(H_2O)]^- \rightarrow [TcCl_5(OH)]^{2-} + H^+$.

The species $[TcCl_5(H_2O)]^-$ is still photochemically active in solutions of greater acidity than 1 M HCl to yield a green-colored species which has tentatively been assigned the formula $TcCl_4(H_2O)_2$. This green complex is easily hydrolyzed to give a brown-colored species which eventually precipitates[106] as TcO_2. Both $[TcCl_5(H_2O)]^-$ and $TcCl_4(H_2O)_2$ were found to be susceptible to oxidation[106] to TcO_4^-.

Quantum efficiencies for $TcCl_6^{2-}$ in chloride-free 1.1 M $HClO_4$ after exposure to 254- and 340-nm radiation were 0.249 and 0.0635, respectively,[106] corresponding to the reaction

$$TcCl_6^{2-} + H_2O \rightleftharpoons [TcCl_5(H_2O)]^- + Cl^- .$$

The quantum yields are inversely proportional to the chloride ion concentration.[106]

An unknown Tc(V) species, presumably a chlorinated type such as $TcCl_6^-$, that has a strong absorption band at 326 nm (ε = 7800) was formed when a 12 M HCl solution of $TcCl_6^{2-}$ was exposed to sunlight.[29]

Another investigator reported no reaction under similar conditions.[108] The oxidation state was established by a spectrophotometric titration with $SnCl_2$. The absorption band for the photolyzed species is similar to the band reported[52] for the suggested hydrolyzed species [Tc:Cl ratio of 1:4.5; absorption maxima at 238 and 325 nm] of oxochlorotechnetate(V), $TcOCl_5^{2-}$, in 3 to 3.7 M HCl. The photolyzed species was slowly reduced back[29] to $TcCl_6^{2-}$ in the 12 M HCl.

In summary, two types of reactions are reported to have occurred when $TcCl_6^{2-}$ was irradiated with sunlight and uv light at 254 and 340 nm. The $TcCl_6^{2-}$ in 12 M HCl was reported to have been oxidized when exposed to sunlight.[29] Only a ligand change occurred when $TcCl_2^{2-}$ in 1, 3, or 6 M HCl was exposed to 254- or 340-nm radiation.[106,107] The discrepancies in the results could be caused by the differences in the acid concentrations or light sources, or by the experimental errors.

2.5 Availability and Safe Handling of Technetium

Ammonium pertechnetate, $NH_4{}^{99}TcO_4$, can be obtained either as the dry salt or in solution from ORNL Isotope Sales at a cost of $55/g plus a $65 handling fee. The metal can be obtained for an additional $50/g. These are the only forms of technetium available.

Subgram quantities of ^{99}Tc can be handled safely in a properly ventilated hood since ^{99}Tc is a weak beta-emitter [beta max. = 0.3 MeV]; however, secondary x-rays (bremsstrahlung) may become important when large amounts of the element are involved.[16] The specific activity for ^{99}Tc is 0.017 Ci/g. Stock solutions of several grams can be contained safely using recommended precautions such as storage of the lead-shielded solutions in a tray, etc. It is essential that a thin-window Geiger-Muller counter survey meter be used to detect ^{99}Tc. As much as 100 mCi of ^{99}Tc has been approved for use in ventilated hoods at this laboratory, and activities from 0 to 100 μCi can be handled on the bench top with approved handling techniques. The handling of dry powders should be avoided, where possible, because of the danger of spreading contamination.

2.6 Proposals for the Investigation of Photochemical Reactions of Technetium

Light-sensitive reactions of technetium, namely the photolysis of $TcCl_6^{2-}$ in HCl, have been demonstrated.[29,106,107] No other photosensitive reactions for technetium were found in the literature. It would be of interest to determine whether other species of technetium in a different medium would also be sensitive to uv irradiation and, if so, to identify the reaction products and to calculate the quantum efficiencies. The photolysis of TcO_4^- in HNO_3, for example, would be of special value if it could provide a means for reducing the pertechnetate, which may in turn facilitate the separation of technetium from uranium by extraction.

The aqueous pertechnetate has an appreciable molar absorbance at 254 and 300 nm [the light output of our lamps], with molar extinction coefficients of approximately 4140 and 1720, respectively.[11] It also has an extinction coefficient of approximately 164 at 345 nm, an area where TcO_4^- can be monitored without interference from moderate NO_3^- concentrations. Thus, the samples could be exposed to uv radiation with the present type of light sources and with equipment[109] similar to that we now have if the sample cell were suitably modified. The progress of the reaction could be followed by observing changes in the spectrum of the solution with the spectrophotometer.

The radioactivity of ^{99}Tc is sufficiently low to permit the samples for our operations to be prepared in a properly ventilated hood and to be handled in reasonable quantities outside the hood. After the prepared sample was loaded into a modified spectrophotometric-photolysis cell,[109] the cell could then be secured in a holder that had been previously aligned in the light path of a Cary 14H spectrophotometer. The operational procedure would be similar to that previously described.[109]

Exposure of the pertechnetate in aqueous solution to uv radiation would proceed in three stages: (1) without the addition of a reducing agent or acid; (2) with a reducing agent such as hydrazine added to the

aqueous solution; and (3) with various concentrations of HNO_3 (or other acid), both with and without the reducing agent. Although HNO_3 will normally oxidize[26] the lower valence states of technetium to TcO_4^-, uv radiation may lead to reduction of the TcO_4^-, especially if hydrazine is present.

A problem may exist in following the reactions, identifying the reaction products, and determining the concentrations of the various species spectrophotometrically in HNO_3 solutions if Tc(VII) is reduced by photolysis. No spectral data could be found for technetium in HNO_3 solutions. A strong likelihood exists that the end products of the reduction would be TcO_2 or Tc_2O_3, which would precipitate or form a colloidal suspension and thus complicate the absorbance values.

Phosphates may be added to prevent precipitation since the phosphate ion complexes the lower oxidation states of technetium. This complexation may actually aid in the photolysis of the pertechnetate.

After the effects of irradiating TcO_4^- have been studied, the pertechnetate would be reduced, either electrochemically or by a reducing agent. Then experiments would be conducted to determine whether the lower oxidation state could be oxidized or whether a ligand change would occur as a result of photolysis.

3. CONCLUSIONS

Mechanisms involving the reactions of technetium are complex, and the resulting products are difficult to identify. Technetium is found as the metal, as well as in the form of chemical compounds and complexes. It is polyvalent, existing in all oxidation states from −1 through +7; +7 appears to be the most important of these, although +4, +5, and +6 are also of interest. Sometimes a single solution can contain several species of various valence states. Disproportionation, complex formation, and hydrolysis must be considered in its reactions.

Coulometric reduction of the pertechnetate generally results in a three-electron or four-electron reduction, depending on pH, nature of the supporting electrolyte, and applied potential. Polarographic and coulometric data in acid media are generally interpreted as a four-electron reduction at the first step with some exceptions. The same types of discrepancies also exist in neutral and alkaline media. Some authors propose a three-electron first step followed by a one-electron step, while others propose a two-electron first step followed by a one-electron step. Regardless of whether the coulometric process results in either a three- or four-electron reduction, the end product will probably be a technetium oxide (which would precipitate) unless a complexing ion, such as phosphate, is present.

Controversy surrounds the results of the photochemical reactions that occur via irradiation of $TcCl_6^{2-}$. The $TcCl_6^{2-}$ ion is known to undergo a reaction when exposed to uv irradiation or sunlight.

Different results have been reported for the photolysis of $TcCl_6^{2-}$. Hexachlorotechnetate(IV), $TcCl_6^{2-}$, is oxidized by sunlight in concentrated HCl. A change in the ligand toward a more hydrolyzed product is formed when this ion is exposed in more dilute acids to uv or visible irradiation.

It is proposed that an effort be made to photolyze TcO_4^-, first in water, then in solutions with hydrazine, and finally in solutions with various concentrations of HNO_3 both in the presence and in the absence of hydrazine. An attempt will be made to photolyze a lower-valent ion or complex of technetium after the pertechnetate photolysis study. The progress of photolysis would be followed spectrophotometrically.

Absorption spectra for TcO_4^- and other technetium compounds, mostly chloride, have been published in the literature; however, no spectra have been reported for nitrates. If photolysis of technetium in HNO_3 solutions does occur, and if the reaction is to be followed by changes in the spectra to determine the changes in concentrations of the various species, then the molar extinction coefficients for the various nitrate species in the acid concentration of the photolyzed solution

will have to be calculated. The reaction products of any photolysis will probably have to be identified and the extinction coefficients of those products determined in the media used for the photolysis.

Although ^{99}Tc is slightly radioactive, subgram amounts can be handled safely, with proper precautions, in a ventilated hood.

The material, ^{99}Tc, can be obtained from Isotope Sales at Oak Ridge National Laboratory.

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