

SPECTROPHOTOMETRIC STUDIES OF LOWER OXIDATION STATES OF TECHNETIUM

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(Received 26 April 1963. Accepted 14 June 1963)

Summary—The spectrophotometric behaviour of lower oxidation states of technetium, obtained by reducing pertechnetate under different conditions by various methods, has been examined. Contrary to some of the previously advanced conclusions regarding the ascorbic acid reduction of pertechnetate, it was found that the technetium is reduced to a quadrivalent state. The latter product does not appear to involve a tightly-bound ascorbate species; neither does it significantly react or complex with α -picolinic acid to give a new species.

THE lower oxidation states of technetium resulting from chemical or electrochemical reduction of technetium^{VII}, present as pertechnetate in solution, have not been clearly defined for a variety of reactions.¹ Surveys of the polarographic reduction patterns of technetium^{VII} solutions,^{2,3} supplemented by more detailed studies,⁴⁻⁶ begin to decrease the uncertainties involved in characterising the lower oxidation levels.

Spectrophotometric data should provide further information regarding the technetium species involved, but the data so far reported are limited and somewhat contradictory. The absorption spectrum of pertechnetate ion is well known^{7,8} and a technetium^V-thiocyanate system has been carefully characterised.⁹ Spectra have also been given for technetium^{IV} and technetium^{III},^{10,11} and undefined lower states,¹⁰ sometimes over very narrow ranges of wavelength and for unspecified concentrations.

The present paper presents additional data relating to the spectrophotometry of technetium ter- and quadrivalent states. Based on evidence now available, a re-interpretation is suggested for the technetium^V,^{VI}- α -picolinate spectrophotometric method.¹⁰

EXPERIMENTAL

Apparatus

A Beckman Model 2400 DU instrument was used with 1.000-cm quartz cells for the spectrophotometric measurements. Polarographic measurements were made with a Fisher Electrode and an H-cell thermostatically controlled at $25.0 \pm 0.1^\circ$; one leg of the cell contained a saturated calomel electrode (S.C.E.). pH was measured with a Leeds and Northrup No. 7664 pH meter.

Reagents

Technetium solutions: A solution of ammonium pertechnetate in water (pH 4) containing 46.75 mg of ⁹⁹Tc/ml and 3×10^{-6} mc of ^{95m}Tc/g of ⁹⁹Tc was obtained from the Oak Ridge National Laboratory; coulometric studies substantiate the stated concentration.^{4,5} Pertechnetate stock solution I was prepared by diluting 10 ml of this solution to 250 ml; 10 ml of solution I were further diluted to 100 ml to give stock solution II (technetium concentration: 1.89 mM).

Ascorbic acid, α -picolinic acid and sulphosalicylic acid solutions: 10% w/v aqueous solutions were prepared from reagent-grade chemicals (ascorbic acid was U.S.P.).

Tin^{II} chloride solution: 20 g of SnCl₂·2H₂O were dissolved in 6M hydrochloric acid with warming, then diluted to 100 ml with the same acid.

Nitrogen: Oil-pumped and used without further purification for purging all solutions of oxygen.

Buffer solutions: A pH 1 buffer solution was prepared by diluting to 200 ml a mixture of 97 ml of 0.2M hydrochloric acid and 2.983 g of potassium chloride. A pH 2 buffer solution was prepared by diluting to 500 ml a mixture of 26.5 ml of 0.2M hydrochloric acid and 125 ml of 0.2M potassium chloride. The measured pH values of these buffer solutions were 1.0 and 2.0, respectively.

All other chemicals used were C.P. grade.

Polarographic procedure

Twenty-five ml of pertechnetate solution II and 25 ml of ascorbic acid solution were diluted to volume in a 250-ml volumetric flask with pH 2 buffer. About 15-ml portions of this solution (technetium^{VII} concentration 0.189 mM) were transferred to the H-cell at different intervals of time after preparation of the solution, deoxygenated with nitrogen for 10 to 15 min, then polarographed over the potential range of 0.0 to -1.5 V vs. S.C.E. $E_{\frac{1}{2}}$ and i_d were determined graphically, utilising the maximum deflections.

Spectrophotometric procedures

(1) In a 10-ml volumetric flask, 0.5 ml of pertechnetate solution II was well mixed with 5 ml of pH 2 buffer and 1 ml of ascorbic acid solution, heated at *ca.* 70° under an infrared lamp for 20 min, cooled and diluted to volume with pH 2 buffer; the spectrum of the resulting solution was measured at different intervals of time against a blank containing 1 ml of ascorbic acid solution diluted to 10 ml with pH 2 buffer. This procedure was also used with 0.5 ml of α -picolinic acid solution present in addition to the ascorbic acid.

(2) In a 10-ml volumetric flask, 0.5 ml of pertechnetate solution II was thoroughly mixed with 4 ml of pH 1 buffer solution and 0.2 ml of tin^{II} chloride solution, then diluted to volume with pH 1 buffer. The absorption spectrum was measured against a blank containing 0.2 ml of tin^{II} chloride solution diluted to 10 ml with pH 1 buffer. A similar procedure was employed with the addition of 1 ml of sulphosalicylic acid solution in addition to the tin^{II} chloride.

RESULTS AND DISCUSSION

Al-Kayssi, Magee and Wilson¹⁰ reduced technetium^{VII} in hydrochloric acid solution with either tin^{II} chloride or ascorbic acid to give a postulated quadri- or quinquevalent state complex with α -picolinic acid; the resulting pink solution showed a molar absorptivity (ϵ) of about 4,400 at 480 m μ .

On treating pertechnetate with ascorbic acid by the same method¹⁰ but in the absence of α -picolinic acid, reduction occurs very slowly (*cf.* Table I) with the molar

TABLE I.—SPECTRA AND POLAROGRAPHY AT 25° OF TECHNETIUM^{VII} SOLUTION REDUCED BY ASCORBIC ACID

Elapsed time, hr	Molar absorptivity, ϵ^a		Wave I ^b i_d , μA
	418 m μ	490 m μ	
0	0	0	(6.25)
2	21	42	—
24	516	824	5.12
48	1160	1860	4.19
72	1600	2690	4.25
96	1850	3210	3.64
120	1990	3460	2.94
144	2075	3650	2.29
168	2120	3820	1.42
192	2180	3880	0.82
216	2190	3950	0.44
	(2380)	(4300)	(0.00)

^a Solution was 0.095 mM in technetium; a complete spectrophotometric run took about 30 min.

^b $E_{\frac{1}{2}}$ was between -0.150 and -0.158 V vs. S.C.E.; the value of 6.25 μA is the current obtained for a similar technetium solution in the absence of ascorbic acid.

absorptivities finally approaching 4,300 at 485 $m\mu$ (maximum) and 2,380 at 418 $m\mu$ (minimum). The prior or subsequent addition of α -picolinic acid in this procedure results in no change in the position or intensity of these absorption characteristics (curve A of Fig. 1).

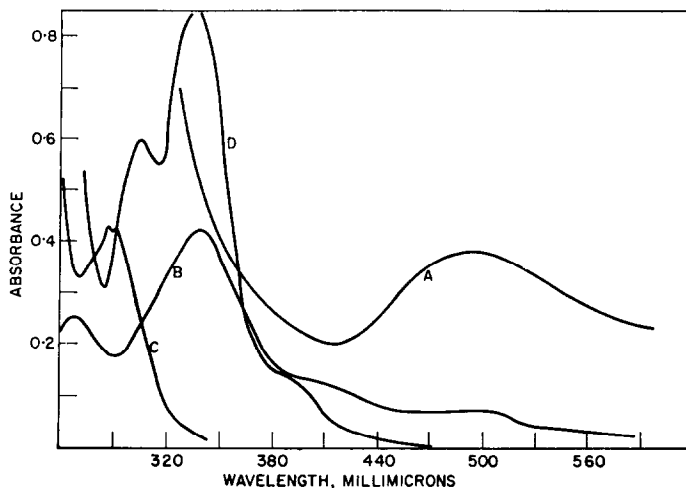


FIG. 1.—Absorption spectra:

- (A) 0.095 mM technetium^{IV} solution resulting from ascorbic acid reduction;
- (B) partially re-oxidised technetium^{III} via coulometry (56% technetium^{VII} and 44% technetium^{III}) equivalent to 0.090 mM ;
- (C) 0.095 mM pertechnetate ion;
- (D) 0.189 mM $(TeCl_6)^{2-}$ ion.

The rate of decrease in the first polarographic reduction wave of pertechnetate^{4,5} in the presence of ascorbic acid is in agreement with the increase in molar absorptivity. The half-wave potential of this wave, which represents the reduction of technetium^{VII} to technetium^{III}, is not significantly shifted by the presence of the ascorbic acid; the slope is also unchanged. While this wave does shift in the expected manner⁴ as a function of pH, it is irreversible (slope criterion) and its failure to shift here is not incontrovertible evidence of the non-existence of ascorbate complexes of the reduced technetium state or states.

The partial extraction by chloroform of the "quadri- or quinquevalent α -picolinate complex" of technetium has been noted.¹⁰ In the present study, the red solutions obtained by the reduction of pertechnetate with ascorbic acid were made 0.05–6 M in sulphuric acid and extracted with equal volumes of chloroform. Radiometric assay of the two layers indicated an extraction of 2.5–5.5%, corresponding to a low distribution coefficient of 0.03–0.06. Better extraction of technetium^{IV}, for example, is obtained with ether from 0.0–6 M hydrochloric acid solution. However, these results correspond to distribution coefficients of less than 0.1, and are not indicative of the existence of significant amounts of organic solvent soluble technetium-ascorbate species.

In order to ascertain whether the ascorbate-reduced solution contained any technetium^{III}, a yellow-green technetium^{III} solution, prepared by the macroscale reduction at a mercury cathode of an acidic pertechnetate solution,⁵ was rapidly examined spectrophotometrically after dilution. (The spectrum obtained had nothing

in common with that observed for technetium^{III} in pH 7 phosphate solution between 400 and 750 $m\mu$.⁶) The appreciable amount of technetium^{VII}, which developed as a result of rapid air oxidation, was determined polarographically and the spectrophotometric curve was corrected by subtracting the absorbance from technetium^{VII} to give curve B of Fig. 1; inaccuracies in this correction, from the presence of technetium^{IV} or technetium^V, may account for the apparent features at 270 and 290 $m\mu$; however, the peak at 340 $m\mu$ is essentially free of any effects from technetium^{VII}.

Based on the absence in the ascorbate-reduced solution (curve A of Fig. 1) of the 340- $m\mu$ peak observed in the technetium solution, it can be safely asserted that the ascorbate-reduced solution does not contain appreciable amounts of technetium^{III}; this is confirmed by the presence in the ascorbate-reduced solution of an absorption maximum at 485 $m\mu$ which is absent in the technetium^{III} solution.

The nature of the technetium^{IV} species obtained by ascorbate reduction, as indicated by its spectrum (curve A of Fig. 1), is different from the technetium^{IV} species obtained by reduction in hydrochloric acid (curve D of Fig. 1). The latter spectrum is that of pertechnetate, which was allowed to stand for about 1 month in 9M hydrochloric acid, then examined against a blank of 9M hydrochloric acid; the molar absorptivity of 9,100 at 338 $m\mu$ is in general agreement with the value of 11000, reported for spectrophotometry in 1M hydrochloric acid after reduction in 9M hydrochloric acid.¹¹

Consequently, it may be concluded that ascorbic acid, in the absence of thiocyanate, reduces pertechnetate very slowly to a technetium^{IV} species, which shows a maximum at 485 $m\mu$ with a molar absorptivity of 4,300 to 4,400 as previously reported.¹⁰ The red colour of the technetium^{IV} species and the absence of a precipitate of technetium dioxide suggests the formation of an ascorbate complex, but the polarographic behaviour of the partially reduced solution is contrary to such a postulation, *i.e.*, formation of a technetium^{IV}-ascorbate complex should involve a shift in $E_{\frac{1}{2}}$, which does not occur.

Miller *et al.*⁶ coulometrically reduced technetium^{VII} in pH 7 phosphate buffer to a pink quadrivalent state, which absorbed at 515 $m\mu$ with an ϵ of 380. Apparently, the technetium^{IV} forms a stable red-coloured complex as indicated by the shift of the absorption maximum from 485 to 515 $m\mu$ and the decrease in molar absorptivity from 4,300 to 380. Similar pink or pale-violet solutions were obtained by the present authors after coulometric reduction of technetium to a quadrivalent state in non-complexing acidic media.^{4,5}

Reduction of 0.189 mM pertechnetate in 0.1M hydrochloric acid by tin^{II} chloride, which is complete in about 30 min, gives an orange-coloured solution (maximum at 445 $m\mu$, $\epsilon = 670$). Polarography of this solution does not show any portion of the wave from the reduction of technetium^{VII} to technetium^{III} ($E_{\frac{1}{2}} = +0.02$ V *vs.* S.C.E.). The polarographic wave, which does appear at $E_{\frac{1}{2}}$ of -0.41 V *vs.* S.C.E., is that from the reduction of tin^{II}; however, the current is 224 μ A, compared to 206 μ A observed for tin^{II} alone. The increase may be caused by reduction of tin^{IV} formed and to further reduction of technetium to the metal (the reduction of technetium^{III} to technetium⁰ normally occurs at $E_{\frac{1}{2}}$ of *ca.* -0.9 V at the acidity involved).

Reduction of pertechnetate in 0.1M hydrochloric acid by tin^{II} chloride in the presence of sulphosalicylic acid gives in 30 min a solution having an absorption maximum at 430 $m\mu$ of $\epsilon = 1120$. The changes in absorption would indicate formation

of a sulphosalicylate complex by the reduced technetium. Earlier workers¹⁰ have reported for a similar operation a maximum at 460-470 m μ , without mentioning the molar absorptivity; this maximum was ascribed by them to a technetium^V complex.

Acknowledgments—One of the authors (G. B. S. S.) wishes to thank the National Academy of Sciences (U.S.A.) for an appointment supported by the International Cooperation Administration under the Visiting Research Scientist Program.

Zusammenfassung—Das spektralphotometrische Verhalten durch Reduktion von Perotechnetat unter verschiedenen Bedingungen und nach verschiedenen Methoden erhaltener niedriger Oxydationsstufen von Tc wurde untersucht. Im Gegensatz zu einigen früher gezogenen Folgerungen über die Reduktion von Perotechnetat mit Ascorbinsäure wurde gefunden, daß Tc zur vierwertigen Stufe reduziert wird. Das Produkt enthält offenbar kein Ascorbat fest gebunden; auch reagiert es nicht nennenswert mit α -Picolinsäure zu einer neuen Verbindung.

Résumé—On examine le comportement spectrophotométrique de l'état inférieur d'oxydation du technetium, obtenu par réduction du perotechnetate dans différentes conditions et par diverses méthodes. Contrairement à de nombreuses conclusions antérieures, la réduction du perotechnetate par l'acide ascorbique, il a pu être montré que le technétium est réduit à l'état d'oxydation (IV). Ce dernier ne semble pas être fortement lié aux molécules d'acide ascorbique et ne réagit pas, d'une manière caractéristique, ni ne fournit de complexe avec l'acide α -picolinique.

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