

Electron Spin Resonance Spectroscopy Studies of ^{99}Tc in Aqueous Solutions.
Part II.

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SUMMARY

The addition of NaNO_2 to aqueous NH_4TcO_4 yielded paramagnetic Tc complexes when reduced in HCl solutions. Similar or identical complexes are produced by reduction of NH_4TcO_4 with hydroxyl amine in acidic, neutral, and basic solutions.

Key Words: Technetium, ESR Spectrum, Radiopharmaceuticals, Arsenite Reduction, Ferrous Sulfate Reduction

INTRODUCTION

In a previous paper (1) we reported esr spectra for ^{99}Tc having 10 hf lines in acidic solution. We had obtained these solutions by reducing NH_4TcO_4 in HCl with ascorbic acid, potassium iodide, or stannous chloride. All the work was done with a 7-year-old supply of NH_4TcO_4 solution, which was exhausted by the time the experimental work was completed. New supplies of NH_4TcO_4 failed to give these esr spectra by the same reactions mentioned above. A long search for the cause followed until a study of the

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†"Paramagnetic" is used in this paper to mean detectable by Tc 10-line esr spectrum.

Roussin complexes (2) suggested the formation of a nitroso complex similar to compounds reported by Eakins et al. (3) and later by Armstrong and Taube (4). These authors reported some Tc complexes of low valence containing the NH_2OH and nitrosyl (+NO) ligands in different compounds. By adding NaNO_2 to the new NH_4TcO_4 and then reducing with ascorbic acid, KI, or SnCl_2 , respectively, in HCl we attempted to obtain similar Tc complexes of low valence. The complexes exhibited the characteristic 10-line Tc esr spectrum in each case (1).

All we could learn about the 7-year-old NH_4TcO_4 , which was different from the newer supplies, was that the older material had been prepared in 0.5 M NH_4OH , whereas the other samples were all prepared in water. Later we found that Rigg et al. (5) had produced nitrite by irradiating aqueous ammonia solutions with 200 keV x-rays. This finding suggested that the beta radiation of the ^{99}Tc could have produced nitrite in our old NH_4TcO_4 solution. We have initiated a long term experiment to verify this hypothesis.

In the interim since our previous paper (1), we found that in addition to the reductants and reactions already mentioned, Tc esr spectra can also be reproduced by reducing nitrite-containing NH_4TcO_4 with (a) arsenite and (b) ferrous iron in HCl, respectively, or by reducing nitrite-free NH_4TcO_4 with NH_2OH in (a) acid, (b) water, and (c) base. In acid solution the hydroxylamine reduction of NH_4TcO_4 yields two paramagnetic Tc species, which have been separated from each other but not yet isolated.

In this paper we will deal with this reaction in some detail and report a survey of reactions and media that yield Tc esr spectra. We will also report on some methods used in analyzing these solutions and thereby indicate our progress toward isolating and characterizing these Tc complexes.

EXPERIMENTAL

Reagents. From an approximately 0.3 M aqueous solution of NH_4TcO_4 was prepared a 0.03 M NH_4TcO_4 working dilution. A sample of "Aliquat 336" (methyl tricaprylammonium chloride; MTC) was supplied by General Mills, Chemical Division, Kankakee, IL.

Equipment. All esr spectra were obtained with a Varian E-9 electron spin resonance spectrometer. All radiochromatograms were scanned with a Varian

Berthold Radiochromatogram Scanner, Model #LB2723. A rudimentary paper electrophoresis apparatus with a Gelman power supply was constructed in this laboratory.

Sample Preparation. See Table I. For components of the nitrite reaction (N category) 100 μl of 0.03 M $(\text{TcO}_4)^-$ was placed in a 1 dram vial, using an Eppendorf pipet; an excess of solid NaNO_2 and then the reductant in 6 M HCl were added to a total volume of about 1 ml. For components of the hydroxylamine reaction (H category) 100 μl of 0.03 M $(\text{TcO}_4)^-$ was placed in a 1 dram vial, using an Eppendorf pipet, and 6 M HCl , H_2O , or 1 M NaOH was added to a volume of about 1 ml; then an excess of solid $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added. In both categories, the samples were scanned for esr spectra immediately after they were mixed in order to observe any change of amplitude with time.

Liquid-Liquid Extraction. To the aqueous sample preparations in the original 1 dram reduction vials was added an equal volume of 5-10% MTC in toluene. The tightly capped vials were shaken for about 1 min. The toluene layers were transferred with disposable pipets to other vials containing an equal volume of 2.5 M HClO_4 . The capped vials were then extracted by shaking for about 1 min.

Paper Electrophoresis. This technique was performed in an electrolyte, 0.5 M HClO_4 , on a 22 x 1 cm strip of Whatman No. 1 chromatography paper at an applied voltage of 150 V for 1 hr.

Paper Partition Chromatography. A 14 x 4 cm strip of Whatman No. 1 paper was dipped in 3 M HCl , blotted between two sheets of white absorbent paper, and pressed to remove excess moisture. The spotted paper was then developed for 2 hr in a 2% toluene solution of MTC that had been equilibrated with 3 M HCl .

RESULTS AND DISCUSSION

As the first three reductants in the nitrite reaction of Table 1 were discussed in our previous paper (1), we present only the last two, ferrous sulfate and sodium arsenite, as new reductants capable of yielding paramagnetic Tc complexes. However, we will discuss only arsenite in any

detail. In the hydroxylamine reaction, all reactions are new, but only the 6 M HCl solution was studied in any detail.

Colors of Paramagnetic Solutions. The colors of solutions of the products in the nitrite reaction are generally greenish yellow. The nitrite-free blanks were clear yellow and probably contain the Tc(IV) complex anion $(\text{TcCl}_6)^{4-}$, which is pale yellow. A visible-UV spectral study of these various complexes has been undertaken and will be reported later (6). The Tc(IV) state has been verified in the case of the KI reduction blank by a non-titrimetric method employing amperometry (7).

Comparison of ESR Spectra of the Two Categories. We found that the spectra of some solutions of the hydroxylamine category were identical to those of N-1 and N-2 (Table 1). We believe that this indicates that the same Tc complex is formed by two different pathways. Although we found similarities in spectra of complexes of the two categories in HCl, we found distinct differences in a basic medium such as NaOH. The hyperfine interactions are much larger than those in HCl, indicating a considerably different ligand field for the Tc ion. These spectral features and other related topics will be reported in a future publication (8).

Analysis of Hydroxylamine Reduced NH_4TcO_4 in 6M HCl

By Liquid-Liquid Extraction. An atypical esr spectrum was obtained (Table 1) in the hydroxylamine reduction of NH_4TcO_4 in 6 M HCl (Fig. 1A). This indicated that possibly more than one paramagnetic Tc complex was present.

Employing Salaria's method (9), one paramagnetic Tc complex was extracted into toluene with 10% MTC, leaving another paramagnetic complex of unknown polarity behind in the aqueous HCl (Fig. 1B). The separated MTC-toluene phase was reextracted with an equal volume of 2.5 M HClO_4 . This ion-exchange operation, suggested by Salaria (9), was necessary so that the Tc complex would be in an acidic aqueous medium, similar to the original HCl solution.

*Caution: In this HClO_4 medium the Tc complex, if anionic, could exist as the acid and it should be treated as volatile.

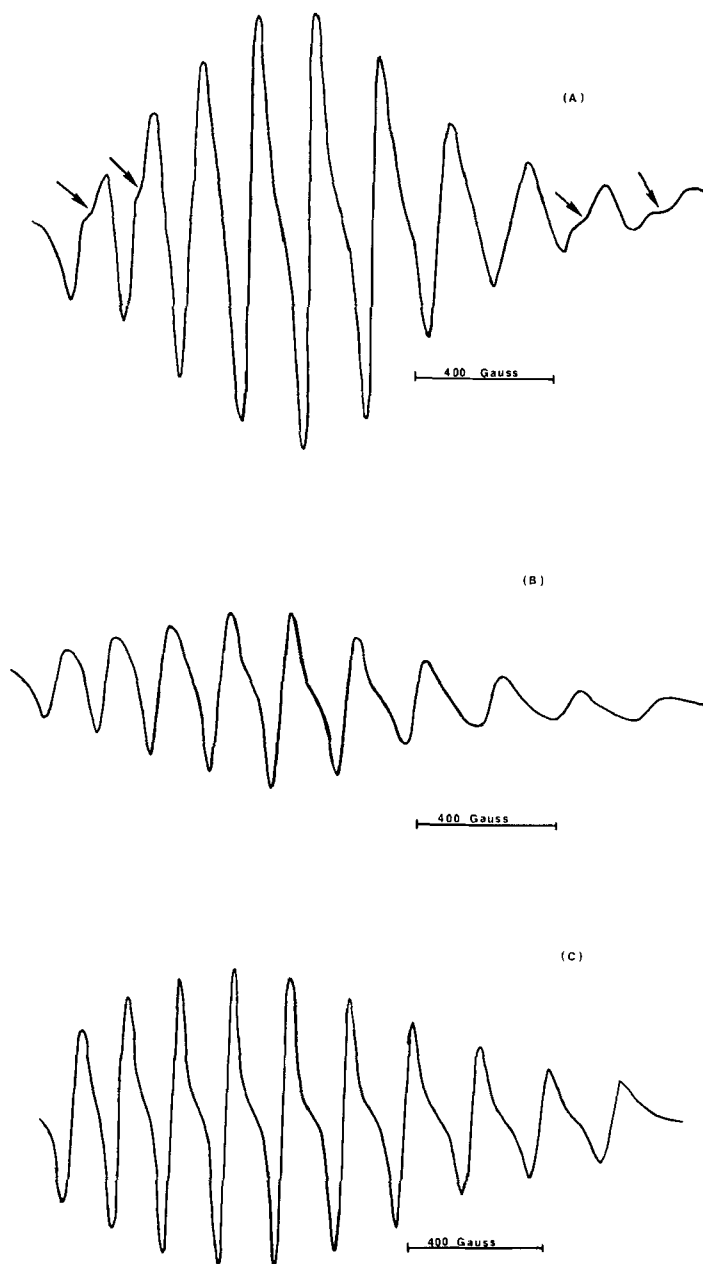


Fig. 1. ESR spectrum of (A) solution resulting from reaction of ammonium pertechnetate and hydroxylamine in 6 M HCl at room temperature (arrows show anomalies); (B) aqueous phase (6 M HCl) after extraction with 5% MTC in toluene; (C) 2.5 M HClO_4 solution containing Tc complex extracted from toluene phase, B.

The esr spectrum of the HClO_4 solution is shown in Fig. 1C. It can be seen from these two single spectra that the components of the original spectrum (Fig. 2) were resolved. Two questions were raised at this point: Were these two complexes final products or was one just an intermediate, convertible to the other? By heating some of the solution that gave the original esr spectrum (Fig. 1A), it was found that one species diminished while the second grew, yielding an almost pure spectrum of the latter.

By Paper Partition Chromatography in 6 M HCl (H-1 and N-5). Based on the above extraction system for $\text{Tc(VII)} + \text{NH}_2\text{OH}$ in 6 M HCl, a two-phase paper partition chromatographic method was developed which revealed more Tc complexes than were found by extraction. At least 4 Tc bands were indicated, three of which were well separated from each other (Fig. 2).

When the solution containing the arsenite reduction products ($\text{Tc(VII)} + \text{NO}_2^- + \text{As(III)}$ in 6 M HCl) was examined by paper partition chromatography, its chromatogram had only two Tc bands (A, Fig. 3). The chromatogram of the nitrite-free blank showed only one Tc band near the solvent front (B, Fig. 3).

By Electrophoresis. Since both liquid-liquid extraction and paper partition chromatography provided evidence for anionic paramagnetic Tc complexes, we again attempted to confirm the report by Eakins et al. that they found a cationic Tc band (3). Paper electrophoresis of solution H-3 revealed a pink cationic band and a purple anionic band which darkened to brown upon standing (Fig. 4). The system is essentially the same as that of Eakins et al. except that we start with $(\text{TcO}_4)^-$ and they start with $(\text{TcCl}_6)^{3-}$.

This finding of the cationic pink Tc band led us to consider the pink complex of Armstrong and Taube for esr study (4). This work is under way and will be reported elsewhere (8).

CONCLUSION

Several new reactions yielding paramagnetic complexes of Tc have been reported. One example of each of the two major reaction categories has been studied by liquid-liquid extraction and paper partition chromatography, which proved successful for isolating the paramagnetic complexes. Both techniques have given positive evidence for anionic complexes in both the nitrite and the

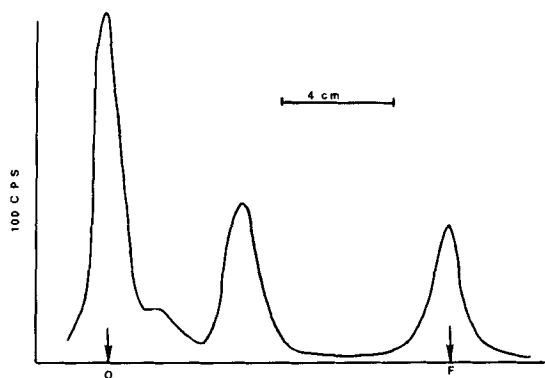


Fig. 2. Radiochromatogram of solution resulting from reaction of ammonium pertechnetate and hydroxylamine in 6 M HCl.

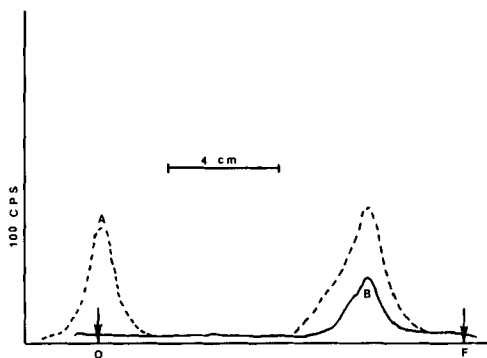


Fig. 3. Radiochromatogram of (A) solution resulting from reaction of ammonium pertechnetate and sodium arsenite in 6 M HCl; (B) blank: pertechnetate and 6 M HCl.

Table 1. Two major categories of reactions yielding Tc esr spectra in solution.

General Nitrite Reaction: $(\text{NH}_4\text{TcO}_4 + \text{NaNO}_2) + \text{Reductant in HCl}$

Colors obtained in solution

Reductant	(paramagnetic)	Color
N-1. Ascorbic acid		Greenish yellow
N-2. Potassium iodide		Greenish yellow (I_2 removed by extraction)
N-3. Stannous chloride		Greenish yellow
N-4. Ferrous sulfate		Greenish yellow (Fe(III) , Fe(NO)_x^{+n} interfere)

General Hydroxylamine Reaction: $(\text{NH}_4\text{TcO}_4 + \text{NH}_2\text{OH.HCl in Medium})$

Colors obtained in solution

Medium	(paramagnetic)	Color
H-1. 6 M HCl, pH << 7		green-yellow
H-2. H_2O , pH < 7		deep red-purple
H-3. H_2O , NH_3 (pH = 7)		purple-violet
H-4. NaOH, pH >> 7		pale pink

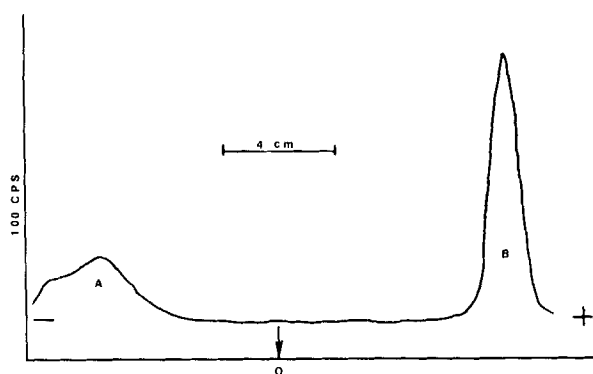


Fig. 4. Electropherogram of solution resulting from reaction of pertechnetate and hydroxylamine hydrochloride, first in water, then by addition of ammonia to pH 7. The cationic band (A) was pink; the anionic band was purple, but changed to brown.

hydroxylamine reactions in HCl, while electrophoresis of solution H-3 showed cationic and anionic Tc bands.

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