[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Observations on Some Chemical and Physical Properties of Technetium and its Compounds

BY CHARLES L. RULFS AND W. WAYNE MEINKE

The composition of Tc_2S_7 has been confirmed by analysis. Activity measurements on solutions prepared from this compound are in good agreement with recently reported precision values. The absorption spectrum of the pertechnetate ion has been examined.

Introduction

Early work on the activity of the long-lived Tc^{99} isotope resulted in estimates of its half-life varying between 2 and 9×10^5 years. The work of Fried, *et al.*,[1] establishes a half-life of 2.12×10^5 years. The lower activity implied by a half-life value of 5.5×10^5 years represents an earlier estimate by Parker, Reed and Ruch[2] which was based on a weight of the higher sulfide of assumed composition, Tc_2S_7 (by analogy with Re_2S_7). It is important to know the cause of the discrepancy, *i.e.*, whether it is due to an impure sulfide or to a composition other than that postulated.

The limited material available in the present work did not permit measurements of the order of accuracy employed by Fried, *et al.*,[1] but sufficed to answer the question just posed. Examination of the sulfide has established its composition and provides an adequate explanation of the previous discrepancy.

As a result of the purifications necessary for the available technetium material, some observations of possible value may be made regarding certain of the recommendations in the earlier literature.

The spectrophotometric absorption curve for a pure pertechnetate solution was determined. These data are recorded since they differ markedly from previous data.[2] Later workers,[1] however, have noted absorption maxima in accord with our findings.

Experimental

The starting material consisted of approximately 6 ml. of an aqueous solution reputed to contain only ammonia, hydrogen peroxide and 1 mg. of Tc^{99} as ammonium pertechnetate.[3] Careful evaporation of this solution left a large white residue (very faint trace of pink) which, after drying at 100°, weighed slightly over 40 mg. Prolonged drying at this temperature gave a slight additional loss in weight, but the pink color changed to brown. The dissolution of Tc_2S_7 in ammonia and hydrogen peroxide always results in the formation of large amounts of ammonium sulfate. After numerous attempts, it was concluded that ammonium pertechnetate (prepared the wet way) was unsuitable as a primary standard for three reasons: *viz.*, its solubility is comparable in magnitude to that of the accompanying ammonium sulfate, ammonium sulfate is insufficiently volatile at 100°, and the decomposition of ammonium pertechnetate is fairly rapid even at 90 to 100°.

The heptasulfide, an important compound in the usual purification scheme for technetium, has been found suitable as a primary standard (*i.e.*, a weighable starting point) for technetium work provided that any excess sulfur is removed.

Recent workers have reported the useful fact that pertechnetate is not precipitated by H_2S from 9 N hydrochloric acid, permitting its isolation from Re_2S_7 which is insoluble in this medium. While acidities from 2 to 8 N have been variously recommended as suited for the precipitation of Tc_2S_7, the range from 2 to 4 N appears to be best suited for quantitative work in the case of hydrochloric acid. Precipitation usually begins promptly, but complete precipitation requires long saturation, digestion and resaturation, etc.

The residue from our original material was reoxidized with ammoniacal peroxide, evaporated to near dryness, dissolved in 8 ml. of 4 N hydrochloric acid, and thoroughly saturated with H_2S. The washed, black sulfide was dissolved in ammonia and hydrogen peroxide solution, evaporated to a small volume, and diluted to 5 ml. with 9 N hydrochloric acid. Saturation of this solution with H_2S gave a black sulfide which was estimated (by volume) to contain nearly one-fourth of the total heavy-metal. Dissolution of this material and its examination both spectrophotometrically and radiochemically indicated that it consisted primarily of rhenium; it was retreated twice more and the technetium centrifugate recombined with the main body of the technetium solution.

The technetium centrifugates were retreated several times by precipitation of Tc_2S_7 from 4 N hydrochloric acid followed by dissolution of the sulfide in ammoniacal peroxide. The purified solution would give no further evidence of sulfide precipitation from the 9 N medium. With the centrifuge these purification steps may be conducted quite efficiently. Care must be exercised that no evaporation steps are conducted on acidic pertechnetate solutions lest serious losses occur because of the volatility of Tc_2O_7 or $HTcO_4$. In the final steps, a minimal quantity of ammonia and peroxide should be employed in dissolving the sulfide, and the excess peroxide should be removed or destroyed by evaporation of the alkaline solution prior to acidification.

Absorption Spectrum of Pertechnetate Ion

A solution of the purified pertechnetate in 0.1 N hydrochloric acid was examined spectrophotometrically with the Beckman model DU instrument. Unfortunately, the technetium concentration of the solutions was not accurately known at this stage, hence only approximate values may be stated for the extinction coefficients. These data were obtained at 25° using 1-cm. path silica cells.

The character of the curve (Fig. 1) is similar to that shown earlier by Parker, Reed and Ruch,[2] but the location of its points is radically displaced along the wave length axis toward the ultraviolet region. Well-defined absorption maxima are exhibited at 247 mμ and at 290 mμ while a possible third maximum centers near 226 mμ (not easily definable with the concentration employed). The order of magnitude of the molar extinction coefficients for 1-cm. path and at 25° for the points at 290, 247 and 226 mμ are estimated to be: 15,000, 40,000, and greater than 100,000, respectively.

The point at 247 mμ would seem to coincide with the 2440 Å. point for Tc(VII) in perchloric acid recently mentioned by Fried, *et al.*[1] A 2490 Å. point mentioned by these same authors is not

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[1] S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, *Phys. Rev.*, **81**, 741 (1951).

[2] G. W. Parker, J. Reed and J. W. Ruch, Atomic Energy Commission Report, AECD-2043.

[3] Source: Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tennessee.

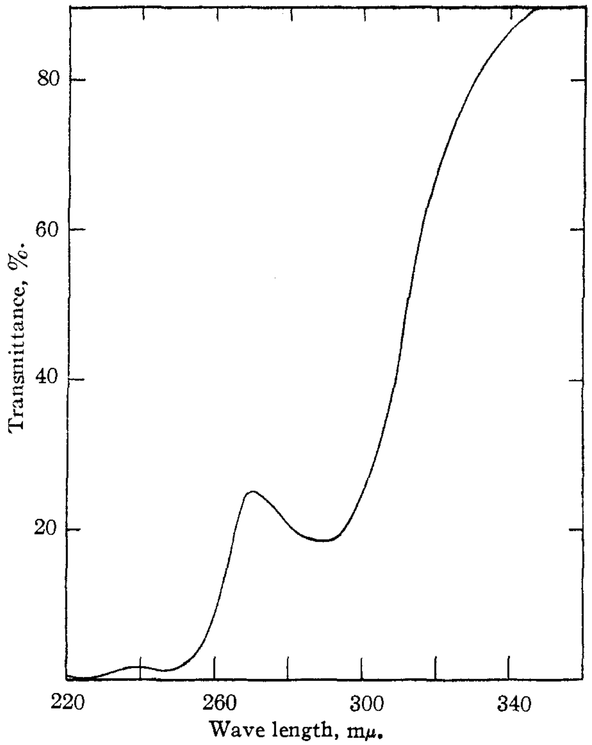

Fig. 1.—Percentage transmittancy of 0.5 millimolar pertechnetate ion in 0.1 *N* hydrochloric acid, 1-cm. path, 25°. The transmittancy approaches 100% at 450 mμ and there is no absorption out to 1000 mμ.

evident within the limits of resolution of our instrument.[4]

Composition of Tc_2S_7.—Purified Tc(VII) solutions were dispensed into small porcelain crucibles and the sulfide was brought down from a 4 *N* hydrochloric acid medium. The supernatant liquid was filtered off through fine porcelain frit filtersticks; and crucible, stick and precipitate were dried at 110° and weighed. The sulfide was then extracted with several successive 1-ml. portions of carbon bisulfide, redried and reweighed. Constant weight was achieved after two to three such treatments, but in the early extractions as much as 21% (run a) to 12% (run b) of the total weight of precipitate was lost.

The purified sulfides were dissolved in the minimum quantities of ammoniacal peroxide and evaporated to near dryness. The residues were taken up in 0.1 *N* hydrochloric acid and diluted to exact volumes. Aliquots of these solutions were used for counting measurements (run a, only) and gravimetric sulfate determinations (replicates on runs a and b, both).

Sulfate determinations with barium chloride were made on each solution. The precipitates were monitored and found to contain small amounts of technetium. The technetium present was estimated very roughly from its activity and corrections applied to the precipitates on the assumption that it was present as $Ba(TcO_4)_2$. The magnitude of these corrections, expressed as equivalent milligrams of barium sulfate per the one-fifth aliquots used in each sulfate run, was never greater than 0.04 mg.

The results of two runs which were made on Tc_2S_7 (which had been extracted to constant weight) are shown in Table I. The agreement for the Tc found by difference with that calculated from theory (on the assumed formula Tc_2S_7), while slightly low in both cases (*i.e.*, sulfur is high), is within 3%. This agreement is all that could be hoped for considering the quantities of material available. All weighings were made on an Ainsworth type TCX semi-micro balance reproducible to plus or minus 0.005 mg.

TABLE I

Run	Tc_2S_7, mg.	$BaSO_4$ on $^1/_5$ aliquots, mg. (cor.)	Total *S*, mg.	Tc, mg. Found	Tc, mg. Theory
a	0.540	0.425	0.292	0.246	0.253
		.430	.295		
b	0.715	.550	.378	0.328	.335
		.575	.395		

The formulation Tc_2S_7 appears to be justified. A reasonably pure compound can be prepared by aqueous precipitation followed by drying and extraction with carbon bisulfide. The initial precipitate contains up to 20% sulfur, which accounts in part for the lower values of earlier activity measurements based on this compound. The remaining discrepancy is, perhaps, attributable to metallic impurities such as rhenium or to limitations of the counting techniques then employed.

Activity of Tc from Tc_2S_7.—As an independent check on the purity of the Tc_2S_7, aliquots of solutions of the purified sulfides were subjected to radioactivity measurements, using standard Geiger counting techniques. It was first established by aluminum absorption measurements that the Tc^{99} was free from contaminating radioisotopes, then its specific activity was measured.

150 λ aliquots containing 2.70 micrograms of Tc were discharged onto brass sample discs. Two drops of concentrated NH_4OH were added to the slightly acid aliquot to prevent volatilization of the Tc, and two drops of detergent solution were added to help spread the active solution uniformly over the entire plate. The liquid was then evaporated slowly to dryness under a heat lamp.

The sample was counted with an end-window alcohol-quenched argon-filled Geiger–Müller tube with a window of 2.6 mg./cm.^{2} thickness, used in conjunction with a scale of 64 counting circuit. Comparison with a Co^{60} standard indicated that the Tc samples contained 3.32×10^4 dis./min. μg. This value is within about 12% of the value of 3.78×10^4 dis./min. μg., determined by Fried, *et al.*, by precision coincidence counting methods, and is within the accuracy expected for the amount of material and equipment used in our experiments.

In these specific activity measurements the 0.31 Mev. Co^{60} β-radiation was used to calibrate the counter since its spectrum is very similar to that of the Tc^{99} β-radiation (0.312 Mev). Since about 4.6 mg./cm.^{2} of absorber (window and air) was traversed by the β particles before they were counted, correction was made for the Tc/Co counting-rate ratio due to this absorption. This correction was based on data presented by Fried, *et al.*[1] A Tracerlab Co^{60} standard was used for this calibration. This standard, purportedly correct to ±10%, consists of a thin layer of Co^{60} plated on a thick brass disc and covered with thin aluminum foil.

In standardization measurements with the Co^{60} β-particles it is very important to ensure identical backscattering of the β-particles in both sample and standard. Hence the Tc samples were evaporated on sample holders identical in composition and size with those of the Tracerlab standards. Self-absorption of the weak β-particles presents a further complication, especially since the Tc samples may contain salt and foreign material up to 40 times the weight of the Tc in the Tc_2S_7 before dissolution. In precise work, counting rate corrections should be made for this self-absorption.

ANN ARBOR, MICHIGAN

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(4) It is possible that the point 2490 Å. represents an error of transposition and was intended to be 2940 Å., which is in reasonable coincidence with our point at 290 mμ. This work[1] is to be published shortly.