456. *Polarographic Behaviour of Technetium.*

By G. B. S. Salaria, Charles L. Rulfs, and Philip J. Elving.

The electrochemical reduction of pertechnetate ion and related species has been examined polarographically and by macroscale electrolysis, including coulometry, over the pH range of −0·6 to 13·30.

Technetium(VII) is reduced in two or three stages. In acidic media the first stage usually involves addition of four electrons, giving technetium(III); a poorly separated (IV) ⟶ (III) step is sometimes discernible. In non-complex-forming media of pH >4, the first stage of reduction proceeds only to technetium(IV); in macroscale electrolyses this product is largely precipitated as TcO_2. Subsequent reduction is quite profound, equivalent at least to the level of metallic technetium, and the complex nature of this stage may justify the postulation of technetium hydrides analogous to rhenium hydrides. In solutions of pH 11—13 the reduction step of technetium(IV) to metal (?) breaks into two stages, an adsorption-controlled (IV) ⟶ (III) step preceding further reduction.

Prior work [1-4] on the polarographic reduction of technetium is relatively incomplete and, in some respects, inconclusive. We have made a more elaborate and systematic study of the polarographic and coulometric behaviour of technetium, primarily to elucidate the reduction pattern of pertechnetate ion and the succeeding oxidation states.

The septivalent state is the most available and stable oxidation level for technetium and comprises the logical starting point for study. The modest activity of the ^{99}Tc isotope (0·29 Mev) provides a convenient means of monitoring such aspects as the loss of $HTcO_4$ by volatilization, slow reduction by mercury, etc.

In a preliminary communication Magee, Scott, and Wilson [1] survey the polarography of pertechnetate ion in neutral salt, two alkaline, and two acidic media; as they worked with 10^{-5}M-solutions and without coulometric or other auxiliary data, their conclusions must be regarded as tentative. Miller, Kelley, and Thomason [2] reported a more detailed polarographic study which was supplemented by coulometry and other types of data. In the present study we have been able to duplicate much, though not all, of the latter work and report our observations based on considerable additional work. For example, both groups of workers cited expressed surprise that "well-formed" waves were not observed in such media as 6—10M-sulphuric or 4M-perchloric acid; this appears to be due to the ready reduction of technetium(VII) by mercury in concentrated solutions of acids.

Results

Since it was evident from a preliminary survey of the polarographic behaviour of technetium(VII) that the wave pattern varied in a complex fashion with pH, a systematic survey was undertaken, in the first stage of which about 70 polarographic runs were made over a pH range of −0·6 to 13·3. Apart from the various buffer solutions examined, the results for which are discussed below, the bulk of the runs involved 0·4—0·5M-potassium chloride or 0·25—0·4M-potassium sulphate solutions with hydrochloric or sulphuric acid, respectively, or potassium hydroxide, as necessary. The results in unbuffered chloride and sulphate media exhibit only very minor differences and will be discussed together.

In very strongly acidic media, especially with hydrochloric acid, the apparent $E_{\frac{1}{2}}$ of the first wave may be simply the point at which anodic dissolution of mercury permits the wave to be observed; for the same reason, the toe of such a wave is not defined. The half-wave

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[1] Magee, Scott, and Wilson, *Talanta*, 1959, **2**, 376.

[2] Miller, Kelley, and Thomason, in Longmuir's "Advances in Polarography," Pergamon Press, London, 1960, Vol. II, pp. 716—726.

[3] Anders, "The Radiochemistry of Technetium," U.S. Atomic Energy Commission, Bulletin NAS-NRC 3021, 1960.

[4] Colton, Dalziel, Griffith, and Wilkinson, *J.*, 1960, 71.

potentials of the first wave (I-A in Fig. 1) were shifted from slightly positive potentials in the most strongly acidic solutions to about $-0{\cdot}4$ v at pH 4. The shift of $E_{\frac{1}{2}}$ from the earliest meaningful potentials at pH ~ 1 to pH 4 conforms, in either medium, to an approximately eighth-power dependence on hydrogen-ion concentration (Fig. 2). The average value of the diffusion-current constant for pertechnetate ion in this pH region indicates a diffusion coefficient, D, at 25° of about $2{\cdot}1 \times 10^{-5}$ cm.^{2}/sec. (calculated from the Ilkovic equation for $n = 4$).

The reproducibility of diffusion currents corresponding to wave I-A in acidic media is not always satisfactory, owing in part to the experimental difficulties mentioned above and in some cases, to the rather ambiguous definition of the first wave. There is some tendency for a stepwise separation of the (VII) ⟶ (IV) from the (IV) ⟶ (III) stage, which tends to be more prominent at higher acidities and in sulphuric acid (compared with hydrochloric acid) solutions. As shown by the first five coulometric runs of Table 1, an n value of 3 can be obtained by careful electrolysis just at the half-wave potential. This is readily done in sulphuric acid; continued electrolysis on the resulting suspension of black technetium dioxide TcO_2 at a more negative potential does not result in further reduction. However, initial electrolysis of pertechnetate at a more negative potential gives an n value of 4; the resulting brown-black suspension is apparently the sesquioxide Tc_2O_3. It is also possible to obtain an n value of 3 in hydrochloric acid, resulting in a suspension of black dioxide, but one need only have the initial potential just on the plateau of the wave to obtain an n value of 4 and a green solution, which still exhibits polarographic wave II.

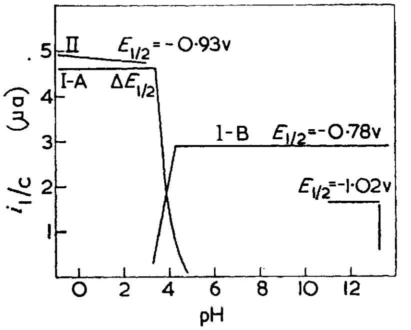

FIG. 1. Variation with pH of the limiting current of polarographic waves of pertechnetate in sulphate or chloride media. (Half-wave potentials are indicated; Δ indicates a variation with pH.)

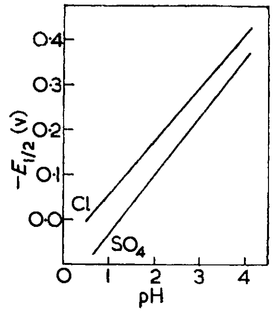

FIG. 2. Variation of the half-wave potential of pertechnetate wave I-A with pH.

TABLE 1.

Coulometric determination of the number of electrons involved in the reduction of pertechnetate ion.*

Solution	pH	Applied E (v)	n
M-H_2SO_4	$-0{\cdot}30$	$0{\cdot}12$	3·05
M-H_2SO_4	$-0{\cdot}30$	$-0{\cdot}05$	4·08
0·5M-(KCl + HCl)	0·80	$-0{\cdot}03$	3·05
0·5M-(KCl + HCl)	1·30	$-0{\cdot}30$	3·81
0·5M-(KCl + HCl)	2·00	$-0{\cdot}16$	3·08
KCl, $Na_2HPO_4,7H_2O$, $H_3C_6H_5O_7,H_2O$ (ionic strength 0·427M)	6·80	$-0{\cdot}66$	3·03
0·1M-$K_4P_2O_7$ 0·1M-K_2HPO_4, 0·1M-KH_2PO_4	7·40	$-0{\cdot}71$	3·02
		$-0{\cdot}85$†	1·00
0·5M-KCl, 0·2M-Na_2CO_3, 0·1M-$NaHCO_3$	9·80	$-0{\cdot}75$	3·03
0·5M-(KCl + KOH)	13·10	$-0{\cdot}85$	2·95
0·5M-(KCl + KOH)	13·10	$-1{\cdot}12$	4·07
0·25M-(K_2SO_4 + KOH)	13·00	$-0{\cdot}85$	2·92
0·25M-(K_2SO_4 + KOH)	13·00	$-1{\cdot}15$	4·02

* 18·7 mg. of Tc were present in each experiment. † The applied potential was stepped up to $-0{\cdot}85$ v *after* the run at $-0{\cdot}71$ v.

Whether wave I-A has the appearance of a single or of a composite wave, its slope indicates an irreversible process. The current-dependence on mercury head and temperature indicates the process as diffusion-controlled (Table 2).

TABLE 2.

Temperature and drop-time (mercury-head) dependence of limiting currents.*

Medium	pH	Wave	$(di/dt)/i$ (%)	$i = kh^m$ (m)	Current control
Chloride	1·75	I–A	1·7	0·61	Diffusion
		II		0·60	Diffusion
Chloride	2·00	I–A		0·60	Diffusion
		II		0·58	Diffusion
Sulphate	2·90	I–A		0·52	Diffusion
		II		0·43	Diffusion
Sulphate	3·95	I–A	2·0	0·60	Diffusion
		I–B	7(?)	*ca.* 0·0	Kinetic
Sulphate	13·0	I–B		0·53	Diffusion
		II–B	$<1·0$	1·2	Adsorption
Chloride	13·1	I–B		0·57	Diffusion
		II–B	$<1·0$	1·1	Adsorption

* The mercury head (h) was corrected for back-pressure.

In both sulphate and chloride media of pH $< \sim 3·5$ a second pH-independent wave, II in Fig. 1, occurs at $E_{\frac{1}{2}}$ $-0·93$ v. Wave II is of about the same magnitude as wave I-A, but evidently corresponds to the 3 *e* reduction of technetium(III) to the metal; an alternative hypothesis might involve the formation of technetium hydrides. Attempted coulometry at potentials appropriate to wave II resulted in electrolysis continuing beyond the stage where $n = 7$, while the pH of the unbuffered solution rises continuously. While such behaviour might result from postulated cyclic processes involving technetium hydride(s), a simpler possibility exists. Wave II is closely followed by what appears to be a catalytic hydrogen-discharge wave.* Such a wave may well exist because of the removal of the high hydrogen overvoltage of mercury by deposition of a thin film of metallic technetium; in coulometry, an ordinary faradaic current consumption due to reduction of hydrogen ion may be involved. In polarography, the appearance of the dropping-mercury electrode when it is at a potential more negative than $E_{\frac{1}{2}}$ of wave II is similar to that of mercury droplets shaken with acidic pertechnetate solutions; the film or deposit of metallic (?) technetium may be chemically extracted and shows β-activity in both cases.

Owing to the proximity of wave II to the following catalytic wave, it was not possible to obtain reliable temperature coefficients. The dependence of the current on the height of mercury is normal for diffusion control. The slope indicates irreversibility.

Within the narrow pH range of $\sim 3·5$—4·0, a very fundamental change occurs in the nature of the polarographic reduction pattern of pertechnetate ion. At higher pH, wave I-A disappears, becoming what we shall term wave I-B, which involves 3, rather than 4, electrons; $E_{\frac{1}{2}}$ of wave I-B is invariant with pH at $-0·78$ v. Simultaneously, wave II " disappears " or, in any case, is no longer distinguishable from the immediately following catalytic hydrogen discharge. Within the narrow pH range 3·0—4·2, portions of all of waves I-A, I-B, and II may be present. In this region the temperature coefficients and mercury-head dependence of the current are erratic and difficult to reproduce, but they indicate a kinetic factor in the current control.

Over a limited pH range, $\sim 11·2$—13·1, in the alkaline region a wave (II-B of Fig. 1) moves forward of the limiting current discharge and may be moderately well defined. This wave ($E_{\frac{1}{2}} = -1·02$ v) corresponds to a one-electron reduction of technetium(IV) to technetium(III). Coulometric runs 10 and 12 of Table 1 may be compared with runs 9 and 11, respectively. In macroscale electrolysis at pH 13, the product is a precipitate of technetium dioxide or sesquioxide for runs 9 and 11 or 10—12, respectively. The temperature coefficient of current for wave II-B is difficult to reproduce but appears to be less than 1%; the variation with mercury head corresponds to a first-power dependence (Table 2); these features indicate adsorption control.

* It should be noted in relation to our usage of the term " catalytic hydrogen discharge " that these large current discharges always occur earlier (*i.e.*, at less negative potentials) in the presence of technetium than is the case for the supporting electrolyte discharge alone (Tc absent).

Various acetate, phosphate, pyrophosphate, carbonate, and ammonia buffer systems covering the pH range 4·0—9·8 were also examined as background electrolytes for the polarographic reduction of pertechnetate ion. In such media between pH 4·0 and ~7, only a single wave is observed whose $E_{\frac{1}{2}}$ shifts from −0·38 to −0·65 v. Between pH 7 and 8, a small and ill-defined second wave appears. Throughout this region (pH 4—8), the composite (?) primary wave(s) appear to involve the reduction of technetium(VII) to technetium(III), with some tendency for a separation of the (IV) ⟶ (III) reduction. There is only a small change in the diffusion current of the primary wave up to pH 9·8, where the steadily shifting $E_{\frac{1}{2}}$ has become −0·75v. Starting at pH 8·2 and persisting through pH 9·8, there is a substantial second wave at $E_{\frac{1}{2}} = -1{\cdot}0$v. Coulometric runs 6, 7, and 8 (Table 1) show that either a three- or a four-electron process might be argued for the " primary " wave depending on whether electrolysis is conducted just at a potential corresponding to $E_{\frac{1}{2}}$ or at the plateau of the wave. As reported previously,[2] when complex-forming anions are present to prevent precipitation of technetium dioxide, a three-electron run may be continued at a more negative potential for the transmission of an additional electron (runs 7a and 7b of Table 1).

Discussion

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

$$\mathrm{TcO_4^- + 8H^+ + 4e^- \longrightarrow Tc^{3+} + 4H_2O} \tag{1}$$

There is always some tendency for separation of the (IV) ⟶ (III) stage into a separate step (composite wave). The wave is polarographically irreversible, but diffusion-limited. The shift of half-wave potential with pH, which conforms to a consumption of 8·1 (in HCl) or 8·9 (in H_2SO_4) hydrogen ions per technetium atom, follows the equations:

$$E_{\frac{1}{2}} = 0{\cdot}12 - 0{\cdot}11_3\ \mathrm{pH}\ (0{\cdot}25\mathrm{M\text{-}K_2SO_4 + H_2SO_4}); \tag{2}$$

$$E_{\frac{1}{2}} = 0{\cdot}50 - 0{\cdot}12_4\ \mathrm{pH}\ (0{\cdot}5\mathrm{M\text{-}KCl + HCl}). \tag{3}$$

While carefully regulated coulometric runs can give either the three- or the four-electron reduction, the products of such macroscale electrolyses are, respectively, the insoluble dioxide TcO_2 or sesquioxide Tc_2O_3. In either case, the suspension shows no further electrochemical activity before the decomposition potential of the supporting electrolyte. In macroscale electrolysis, less than eight hydrogen ions per technetium atom would be involved, owing to hydrolysis of technetium-(IV) or -(III) to the oxide.

The second wave in media of pH <4 occurs at a $E_{\frac{1}{2}}$ of −0·93 v and does not shift with pH; it appears to be irreversible, but diffusion-limited. The originating process is presumed to involve the further reduction of technetium(III) to metal, which appears as an insoluble film on the surface of the dropping-mercury electrode. A closely following catalytic hydrogen discharge may be ascribed to the lowering of the hydrogen overpotential resulting from the technetium electrodeposit.

The lower concentration of hydrogen ion in unbuffered solutions of pH >4 will no longer support reaction (1); the first wave in such media involves only a three-electron reduction to the (IV) state ($E_{\frac{1}{2}} = -0{\cdot}78$v and is pH-independent); the wave is irreversible, but diffusion-limited above pH 4·5 (HCl) and pH 5·0 (H_2SO_4). In either micro- or macro-scale electrolysis, the end product may now be insoluble technetium dioxide. No subsequent polarographic waves are definable, except that at pH ~ 12 ± 1 an adsorption-controlled further reduction to sesquioxide occurs ($E_{\frac{1}{2}} = -1{\cdot}02$ v) just before the hydrogen discharge. In the immediate vicinity of pH 4, the four-electron and the three-electron wave may coexist; in this environment, the latter wave appears by the usual criteria to have some kinetic character.

Experimental

Reagents.—A solution of ammonium pertechnetate in water (pH 4) containing 46·75 mg. of ^{99}Tc per ml. and $0{\cdot}3 \times 10^{-5}$ mc of 95m Tc per g. of ^{99}Tc was obtained from the Oak Ridge

National Laboratory. The integral *n* values (generally, within ±1%) obtained in coulometric studies by using aliquot parts of this solution substantiate the stated concentration.

Technetium stock solution I was prepared by diluting 10 ml. of the ammonium pertechnetate solution in a 250-ml. volumetric flask; 10 ml. of solution I were further diluted to 100 ml. to give stock solution II.

Nitrogen (oil-pumped) was used, without further purification, for purging solutions.

Apparatus.—The Fisher Elecdropode, and Leeds and Northrup Electro-Chemograph model E, were used for polarographic measurement. pH was measured with the Leeds and Northrup pH meter. Negative values of pH were not measured and represent only a formalized device for incorporating the results of a few runs made in N- and 2N-acid.

A thin-window Geiger counter (Nuclear Chicago model 151A) and a flow-transfer-type scintillation well-counter (Atomic Instrument Company, model 162) were used to measure the β-activity of technetium samples.

The dropping-mercury electrode essentially consisted of a capillary connected to a mercury reservoir with "Tygon" tubing. It was calibrated by noting the time of flow and the mass of 40 drops of mercury collected in each supporting electrolyte at the half-wave potentials of waves I and II. The drop time of the electrode was measured at $E_{\frac{1}{2}}$ of the solution being scanned in the case of the Fisher Elecdropode and at the top of the wave for the Electro-Chemograph.

Polarographic measurements were made in an H-cell thermostatically controlled at 25° ± 0·1°. The macro-electrolysis cell contained a stirred massive mercury cathode, which was connected by means of a potassium chloride–agar salt bridge to a large saturated calomel electrode which served as the working anode. A Fisher Powerhouse supplied the working potential; the Fisher Elecdropode was used as a potentiometer to monitor the electrode potential.

All potentials are with reference to the saturated calomel electrode at 25° unless otherwise stated.

Polarographic Procedure.—The polarographic test solution was usually prepared by diluting 5 ml. of stock solution II to 50 ml. in a volumetric flask with the desired supporting electrolyte to give a 0·1889-mM-technetium solution. The pH of this solution was measured, and about 15 ml. were transferred to the H-cell, deoxygenated with nitrogen for 10—15 min. and then polarographed over the desired potential range. Triton X-100 (concentration 0·0013%) was added in a few cases to suppress maxima. $E_{\frac{1}{2}}$ and i_d were determined graphically, by utilizing the average of the recorder trace. In the case of the Elecdropode, the maximum deflection was plotted to determine $E_{\frac{1}{2}}$ and i_d.

Coulometric Procedure.—For coulometry and macroscale electrolysis at controlled potential, the buffer solution (50 ml.) was added to the coulometer cell, with a large mercury pool cathode, and deoxygenated for about 10 min. The solution was pre-electrolyzed at a potential several tenths of a volt more negative than that at which the electrolysis was to be run, until the current fell to its minimum value, generally 1—2 ma.

A known volume of technetium stock solution I was deoxygenated and introduced into the coulometer cell; the coulometer was connected (the hydrogen–oxygen coulometer was pre-saturated with the gases), and the electrolysis at the desired potential started. Nitrogen was continuously passed through the solution being electrolyzed. The volume of hydrogen–oxygen evolved was plotted against time in order to establish the optimum stopping point. From the curve thus obtained, the volume of the gas evolved during the electrolytic reduction was determined and corrected for residual current volume; *n* was calculated after appropriate temperature, pressure, and vapour-pressure corrections had been made.

Sources of Error.—Two sources of error noted during the present study have features of general interest.

Pertechnetate solution [0·189 mM-TcO_4^-, 0·5M-(KCl + HCl) to pH 1·00] (15 ml.) was placed in the polarograph cell at 25° and purged with nitrogen for 10 min. Nitrogen and pertechnetic acid escaping from the cell were led into a tube containing ammonia solution, whose β-activity was measured with a scintillation well counter. The activity acquired by the ammonia solution was 0·84% of the technetium in the test solution, as calculated against a standard sample similarly counted. This loss would, of course, be larger at higher temperatures, with longer bubbling, or from solutions with higher concentrations of acid; it may be minimized by presaturating the nitrogen in an appropriately thermostat-controlled prebubbler containing an identical solution. For personnel safety, effluent gases from acidic media should be trapped in alkali.

The direct chemical reduction of technetium(VII) by hydrochloric acid more dilute than 2M appears to be *very* slow at room temperature. However, even with more dilute acid or with sulphuric acid, some direct chemical reduction occurs in the presence of mercury. Under extreme conditions, *i.e.*, higher concentration of acid, considerable reduction occurs, giving intermediate oxidation states. In all cases a minute fraction (perhaps 0·001% during the time required to run a polarogram) of the technetium appears as a grey film (metal ?) on the surface of the mercury. Because of such reduction it is difficult to obtain reliable, reproducible data for the first reduction wave of technetium(VII) in solutions more acid than pH 1. This reaction between technetium and mercury is being investigated more fully.

As a consequence of direct chemical reduction, a small anomalous wave usually appears in solutions of pH $-0{\cdot}6$ to $+1$ at about $-0{\cdot}25$ to $-0{\cdot}45$ v, even when polarograms are rapidly run on freshly prepared solutions. On the basis of thiocyanate tests and other indirect evidence, this is tentatively ascribed to reduction of technetium(V), produced in the chemical reduction. The fact that the electrochemical reduction of technetium(V), *per se*, occurs at a different potential from that of technetium-(VII) to -(III) is not surprising in view of the irreversibility of both processes. In careful work, the magnitude of this wave was only about one-tenth of that of the primary reduction wave. To avoid obscuring an already complicated picture, the existence of this wave has been ignored in the discussion.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICHIGAN, U.S.A.

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