J. Electroanal. Chem., 92 (1978) 85—99

POLAROGRAPHIC REDUCTION OF PERTECHNETATE

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(Received 9th September 1977; in revised form 5th January 1978)

ABSTRACT

Oxidation states were identified for the products of electrolytic reduction of pertechnetate at the mercury cathode in a variety of media, and for the products of reoxidation upon reversing the cell current. Tast polarography, pulse polarography and triangular-wave voltammetry were employed. The first cathodic wave in acidic phosphate was identified as Tc(VII) → Tc(III) by means of the ratio between it and the Tc(III) → Tc(IV) reoxidation wave obtained on anodic-sweep pulse polarography. This wave was then used as a standard to determine values of n in other media of the same ionic strength. The first wave in acidic media occurred at pH-dependent potential and was found generally to correspond to the formation of Tc(III). The Tc(III) could in some media be reoxidized at the electrode to Tc(IV) or Tc(V). For the second wave in acidic media, which occurred at —0.9 V, diffusion current measurements indicated that $n \leq 7$ with a catalytic component preventing determination of the exact value. In alkaline or unbuffered media the first wave occurred at —0.8 V and a second wave was sometimes seen at —1.0 V. The wave heights in alkaline media, while generally proportional to concentration of pertechnetate and varying with drop time in the manner expected for a diffusion current, often corresponded to non-integral values of n. In certain basic media the reduction of pertechnetate led to the formation of an insoluble oxidizable surface film. Under all conditions investigated the reduction of pertechnetate proved to be irreversible.

INTRODUCTION

The chemistry of technetium remains poorly understood despite the immense practical importance of technetium-containing pharmaceuticals in diagnostic medical scintigraphy. These pharmaceuticals are usually chelates of unknown structure in which the oxidation state of the technetium is likewise unknown. No stable isotope of technetium exists, and the hazard and inconvenience of working with radioactive materials has no doubt discouraged study. There was a brief flurry of interest by electrochemists when the element became available in the late 1950's but only sporadic reports have appeared since 1964. In the meantime diagnostic scanning agents containing technetium, developed by trial and error, have assumed a major role in modern medical practice. The

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chemistry of these agents is the redox and complex chemistry of a transition metal, a field in which electrochemistry has much to contribute. A link between the electrochemistry and the pharmaceutical radiochemistry of technetium was forged by our demonstration that controlled-potential electrolysis could be used for the synthesis of medically important technetium chelates, even at the tracer concentrations (10^{-9} M) used in practice [1]. This permits correlation between radiochemical and electrochemical studies.

A simple but important question is that of the oxidation state of technetium in chelates of medical interest. More subtle but also important is the question

TABLE 1

Previous polarographic measurements of number of electrons transferred, n, and half-wave potential $E_{1/2}$ (vs. SCE)
i = ill defined wave, m = maxium

Medium	First wave		Second wave	
	n	$E_{1/2}/\mathrm{V}$	n	$E_{1/2}/\mathrm{V}$
Magee et al., 1959 [3]				
6 M H_2SO_4		i		
4 M HCl		−0.15		−0.35
2 M NaOH	3	−0.85		−1.0 m
2 M KCl	3	−0.65		−1.3 m
Miller et al., 1960 [4]				
10 M H_2SO_4		i		
2 M H_2SO_4		i		
4 M $HClO_4$		i		
P_2O_7—PO_4 pH 7	3	−0.68		−1.35
Borate pH 10	2	−0.79		
0.1 M NaOH	2	−0.8		−1.0 i
0.1 M NH_4Cl		−0.8		−1.2 m
0.1 M KCl	3	−0.8		−1.2 m
Colton et al., 1960 [5]				
4 M $HClO_4$		i		
4 M HCl	1	−0.52	3	−0.68
0.1 M KOH	2	−0.85	3	−1.15
0.1 M KCN	3	−0.81		
2 M KCl			8	−1.1
Salaria et al., 1963 [6,7]				
0.01 M HCl, 0.49 M KCl	4	−0.14		−0.91
0.1 M KOH, 0.15 M K_2SO_4	3	−0.81	4	−1.02
0.1 M KOH, 0.4 M KCl	3	−0.78	4	−1.02
Astheimer and Schwochau, 1964 [8]				
0.1—1 M NaOH	2	−0.8	3	−1.1
0.1—1 M LiCl	2	−0.8		
Munze, 1964 [9]				
0.1 M NaOH, 0.5 M $NaClO_4$	2		3	
0.1 M NaOH, 1.0 M "Na-citrate"	2		3	
0.1 M KOH, 0.5 M KSCN	2		3	
0.1 M KOH, 0.5 M KCN	3		4	

TABLE 2

Measurement of number of electrons transferred, *n*, by controlled-potential coulometry

Source	Medium	pH	E/V vs. SCE	n
Thomason, 1958 [10	Phosphate	7	−0.84	4
Miller et al., 1960 [4]	Phosphate-pyrophosphate	7	−0.68	4
Terry and Zittel, 1963 [11]	Tripolyphosphate	4.7	−0.70	4
Salaria et al., 1963 [6,7]	H_2SO_4	~0	−0.05	4
	HCl	~1	−0.30	4
	Phosphate-pyrophosphate	7.4	−0.71	3
			−0.85	4
	Carbonate	~10	−0.75	3
	KOH	~13	−0.85	3
			−1.12	4

of reaction mechanism in the electrolytic syntheses. For answers it is appropriate to turn to conventional polarographic methods. The existing literature, summarized in Tables 1 and 2, is sparse and inconsistent. No previous studies have employed current-reversal methods to identify additional oxidation states. No data are available for media of interest to the pharmaceutical chemist: for commonly used non-toxic injectable buffers or with medically important chelating agents. Reduction of pertechnetate is reported to form an insoluble surface film at the hanging mercury drop [2] but there has been no discussion of how this might affect polarographic measurements. For these reasons we considered it appropriate to re-examine the polarographic reduction of pertechnetate.

To be more specific let us identify some points of controversy in the polarographic literature (summarized in Table 1). For the first reduction wave of pertechnetate in NaOH or KOH there are two reports that $n = 3$ and four that $n = 2$. For the first wave in neutral chloride there are two reports that $n = 3$ and one that $n = 2$. Erratic results below pH 1 have been attributed by Salaria et al. to the direct chemical reduction of pertechnetate by mercury, but only they have reported a 4-electron wave in acid media [6]. Even though some pertechnetate may react with the mercury pool, it is strange that no one else has identified a 4-electron wave for unreacted pertechnetate. Turning now from the first wave to the second, in KOH or NaOH we have reports both that $n = 3$ and $n = 4$. There is a solitary report of an 8-electron second wave in neutral chloride. No author has been able to decide between $n = 7$ and $n = 8$ for the second wave in acid. Thus there is no consensus on the oxidation states formed in the polarographic reduction of pertechnetate.

Coulometry affords another means to determine n values. Results from the literature, summarized in Table 2, indicate that $n = 4$ in acid and, depending on potential, $n = 3$ or $n = 4$ in base. However, Munze has questioned the validity of using these data to determine polarographic n values (9). He explained a 1-electron discrepancy between his polarographic and coulometric data by postulating a slow second 1-electron step in the coulometric reduction, too slow to be detectable on the polarographic time scale. Salaria et al. reported that coulometric n values for pertechnetate are quite sensitive to the choice of electrode potential

[6]. This fact, which we can confirm from our own experience, makes it difficult to interpret the coulometric data with confidence or to compare them directly with the results of polarography. For these reasons we have undertaken to determine *n* by purely polarographic means.

Previous polarographic determinations of *n* for the reduction of pertechnetate have all been based on the Ilkovic or Koutecky equation, using a diffusion coefficient obtained conductometrically. An alternative approach, discussed at some length by Meites [12], entails finding two reactions with different *n* values so that their ratio admits but one plausible interpretation. We have found and used two such pairs of reactions. One pair is the 4-electron reduction of pertechnetate in acidic phosphate and the one-electron reoxidation of the product by anodic-sweep normal pulse polarography (starting from the plateau of the cathodic wave). The other pair is the 4-electron reduction in citrate and the 2-electron reoxidation of the product in two poorly separated 1-electron steps. Our method differs from that discussed by Meites only in requiring the appropriate diffusion-theory correction [13,14] in order to compare the cathodic (tast) with anodic (normal pulse) current. After we determined *n* in this way for phosphate and citrate, and found the results to agree with each other, the phosphate medium was then used as a standard and *n* determined by proportion in other media of the same ionic strength. In this way most potential sources of error in the polarographic measurement of *n* could be eliminated.

METHODS

Apparatus

Polarographic and voltammetric measurements were carried out by means of a Princeton Applied Research Corp. Model 174A polarograph (Princeton, N.J.) with a Model 175 Universal Programmer. Polarograms and voltammograms were recorded on either a Hewlett-Packard Model 7043A XY recorder (Palo Alto, Calif.) or a Tektronix Model 5113 dual beam storage oscilloscope (Beaverton, Ore.). A Metrohm Model E410 hanging mercury drop electrode (distributed by Brinkmann Instruments, Westbury, N.Y.) was used for voltammetry. Polarography and voltammetry were performed in a conventional polarographic H-cell with KCl-agar salt bridge.

Reagents

Ammonium pertechnetate was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tenn. as aqueous solution. Its stated concentration, which had been determined radiometrically, agreed within 2% with the value measured in our laboratory by ultraviolet spectrophotometry. Linde prepurified grade nitrogen was saturated with water vapor and used for deaeration without further purification. Other chemicals were commercial products of reagent grade. The following abbreviations are used: EDTA, ethylenediaminetetraacetic acid; DTPA, diethylenetriaminepentaacetic acid; TRIS, tris(hydroxymethyl)methylamine.

Procedures

Polarography. Initial experiments demonstrated that the first cathodic wave and first anodic-sweep pulse wave in phosphate buffer had the ratio predicted for $n = 4$ and $n = 1$, respectively. The ratio of anodic to cathodic currents predicted by diffusion theory [13,14] for the instrument parameters employed was 0.722; the measured value was 0.725 ± 0.010 (95% confidence limits from Student's t distribution, 6 measurements). Measurements in test solutions of copper and lead salts agreed similarly with theory. As discussed in the introduction, this led to positive identification of the cathodic wave as a 4-electron reduction. Phosphate was then used as a reference for further measurements (0.1 M H_3PO_4, 0.1 M NaH_2PO_4). Aliquots of pertechnetate stock solution were delivered to the medium under study and to the reference medium, diffusion currents were measured in both, and the diffusion current for the medium under study was expressed relative to that for the reference medium. The ratio was multiplied by 4 (the value of n for the reference medium) so that the tabulated relative diffusion currents are in units of n (Tables 4 and 5). Measurements were repeated twice each, alternating the reference with the unknown, and were found to be quite reproducible (±0.1 unit in Table 4) even without using a water bath as long as the media had ample time to reach room temperature (22—25° C) before use. Elimination of the water bath was desirable from the standpoint of radiation safety because it simplified the manipulations and the cleanup of spills. Diffusion currents were measured near the shoulder of the wave and corrected for the background current at the same potential in buffer alone.

The data reported here refer to 0.15 mM pertechnetate concentrations, though in preliminary experiments the concentration was varied from 0.15 to 0.9 mM with no evident deviations from linearity. As a rule the ionic strength of the medium was 0.1 M. Diffusion control was verified by variation of diffusion current with concentration, variation of diffusion current with drop time, or comparison of measured with predicted ratio of tast to pulse wave height. An interval of 2 s was used from drop formation to pulse onset and the current was sampled for the last 17 ms of a 57 ms pulse. Reversibility was determined by pulse polarographic criteria [13]. No maximum suppressor was used; when maxima occurred the measurements were made outside the region of the maximum. Potentials refer to the saturated calomel electrode.

Voltammetry. Triangular-wave voltammetry was performed at scan rates from 0.2 V s^{-1} to 20 V s^{-1} in preliminary experiments, without detecting any qualitative differences between high and low scan rates. Therefore, for convenience in recording, the slower rate of 0.2 V s^{-1} was adopted as the routine to obtain the data reported here. When repetitive cycling ("cyclic triangular-wave voltammetry") was used, there was no hysteresis during the first few cycles other than that attributable to concentration changes. However, after many cycles, the mercury drop generally became passivated and could not be restored by anodization. A fresh drop and a single cycle were therefore used for each measurement reported here. The diffusibility of an electroactive reaction product was determined by pausing for 60 s during the anodic phase of the cycle. A non-diffusible peak due to a surface film would persist after the pause, while a diffusible peak would disappear.

TABLE 3

Half-wave potential $E_{1/2}$ and number of electrons transferred n for pertechnetate reduction and for reoxidation of products by anodic-sweep pulse polarography
Potentials are vs. SCE; (i) = ill formed wave

pH	Medium	Wave I $E_{1/2}$ (n)/V	Wave II $E_{1/2}$ (n)/V	Anodic sweep from I		Anodic sweep from II	
				$E_{1/2}$ (n)/V	$E_{1/2}$ (n)/V	$E_{1/2}$ (n)/V	$E_{1/2}$ (n)/V
1.0	$HClO_4$	−0.06(4)	−0.88(7?)	—	—	—	—
1.7	Sulfate	−0.13(4)	−0.94(7?)	+0.06(1)	—	—	—
2.0	Phosphate	−0.15(4)	−0.89(7?)	+0.01(1)	—	—	—
3;0	Citrate	−0.26(4)	−0.98(7?)	−0.08(2)	—	—	—
3.7	DTPA	−0.34(4)	−0.99(i)	−0.2(i)	—	−0.2(i)	—
4.0	Ascorbate	−0.45(4)	−0.97(7?)	−0.32(1)	—	—	—
4.8	Acetate	−0.41(4)	−0.95(7?)	−0.4(1)	+0.04(4?)	+0.01(1)	—
6.5	EDTA	−0.60(4)	−1.1(5?)	−0.44(1)	−0.25(2?)	−0.42(1)	−0.25(2)
8.0	Pyrophosphate	−0.69(3)	−0.98(4)	−0.08(3)	—	−0.50(1)	−0.02(4)
8.8	Borate	−0.77 [a]	−1.28(i) −1.73(i) [b]	−0.18(2)	+0.01 [a]	−0.8(1?)	−0.17 [a] +0.01 [a]
9.5	TRIS [c]	−0.67 [a]	−1.05(5?)	−0.7 [a]	−0.29 [a]	−0.7 [a]	−0.28 [a]
9.8	Ammonium	−0.70 [a]	−1.0(i)	−0.19 [a]	—	−0.75 [a]	−0.22 [a]
9.8	Carbonate	−0.75(3)	−1.10(i)	−0.26 [a]	−0.15 [a]	−0.59 [a]	−0.29 [a]
13.0	KOH	−0.80(2)	−1.08(3)	−0.42(2)	—	−0.40(3)	—
	KCl	−0.78(3)	—	−0.17(3)	—	—	—
	KSCN	−0.85(3)	—	−0.20(i)	—	—	—
	KCN	−0.79 [a]	—	—	—	—	—

[a] Mixed oxidation states. [b] Third wave. [c] Tris(hydroxymethyl)methylamine.

RESULTS

The results of polarographic measurements are summarized in Tables 3 and 4. Table 3 shows the waves present, their half-wave potentials and the assigned values for the number *n* of electrons transferred. Tables 4 and 5 show the diffusion current data on which the *n* values of Table 3 are based. The diffusion currents are all measured relative to the diffusion current for pertechnetate in 0.1 *M* H_3PO_4, 0.1 *M* NaH_2PO_4, for which $n = 4$. In these units they provide a direct estimate of the number of electrons transferred. (The total current for each wave is given, not the difference between one wave and the next.) For anodic-sweep pulse waves the diffusion current is also given relative to the 4-electron reduction wave for pertechnetate in phosphoric acid buffer, but in order that these numbers will also represent an estimate of the number of electrons transferred, the ratio was divided by 2.89, the theoretical ratio for a reverse pulse to forward tast diffusion wave for the instrument parameters employed [13,14]. Where maxima interfered with $E_{1/2}$ measurement by tast polarography, the $E_{1/2}$ for the normal pulse polarogram is given; otherwise, the data of Table 4 refer to tast polarograms.

Acidic media

In acidic media the initial wave corresponded to a 4-electron diffusion-controlled wave. The half-wave potential varied linearly with pH and could be

TABLE 4

Polarographic diffusion currents relative to that in phosphate ($n = 4$), times 4
Tast polarography was used for the cathodic waves and anodic-sweep pulse polarography for the anodic waves
i = ill defined; m = maximum; c = catalytic

pH	Medium [b]	I	II	Anodic sweep from I		Anodic sweep from II	
1	$HClO_4$	4.0	m	—	—	—	—
1.7	Sulfate	4.1	7.5	1.0	—	—	—
2.0	Phosphate	(4.0) [a]	m	1.0	—	—	—
3.0	Citrate	3.9	m	2.0	—	0.6	—
3.1	DTPA	4.0	i	i	—	i	
4.1	Ascorbate	4.0	i	1.1	—	—	—
4.8	Acetate	4.0	m	0.9	4i	0.8	—
6.5	EDTA	4.2	c	0.9	1.6	0.9	1.8
8.0	Pyrophosphate	2.9	3.9	2.9	—	1.0	4.1
8.8	Borate	2.5	i	2.0	2.4	0.7	3.3, 3.6
9.5	TRIS	3.4	5.0	0.6	1.2	0.5	1.3
9.8	Ammonium	3.6	i	3.3	—	0.5	2.4
9.8	Carbonate	2.8	i	1.4	2.6	0.8	3.6
13.0	KOH	2.2	3.0	1.9	—	2.9	—
	KCl	3.0	—	2.8	—	—	—
	KSCN	3.2	—	i	—	—	—
	KCN	2.6	—	—	—	—	—

[a] By definition. [b] Ionic strength 0.1.

TABLE 5

Comparison between *n* values measured by tast and by pulse polarography
m = maximum; i = ill formed

Medium	pH	First wave		Second wave	
		Tast *n*	Pulse *n*	Tast *n*	Pulse *n*
Sulfate	1.7	4.1	4.2	7.5	7.8
Phosphate	2.0	4.0	4.0	m	7.6
Citrate	3.0	3.9	4.2	m	8.0
Ascorbate	4.1	4.0	4.3	i	6.8
Borate	8.8	2.5	2.6	i	4.7
TRIS	9.5	3.4	3.4	5.0	5.1
Ammonium	9.8	3.6	3.7	i	4.6
KOH	13	2.2	2.0	3.0	i

described approximately by the relationship $E_{1/2} = -0.10$ (pH) over the pH range from 0 to 7. (Additional data defining this relationship are presented in our earlier report [1].) Diffusion control was verified by varying the drop time from 1 to 5 s, by varying the concentration from 0.1 to 0.9 m*M*, and by comparing the pulse with the tast diffusion current. Anodic-sweep pulse polarography from the plateau of the first wave sometimes demonstrated reoxidation of the Tc(III) to Tc(IV) or Tc(V). A second wave was consistently observed in acidic media at a half-wave potential of approximately —0.9 V. The measured diffusion currents corresponded to values for *n* between 7 and 8. In at least one example, but near neutrality (EDTA at pH 6.5), this wave had a clearly catalytic component.

Alkaline media

In alkaline media the first wave occurred consistently in the neighborhood of —0.8 V. The measured value for the number of electrons transferred ranged from 2 to 4 and was often non-integral, although this wave was at least approximately diffusion-controlled. Waves obtained by anodic-sweep pulse polarography from the plateau of the first wave also gave non-integral values for *n*. A second wave was usually seen in alkaline media at approximately —1.0 V (—1.27 in borate) when pulse polarography was used. In tast polarography this wave sometimes disappeared at higher concentrations of pertechnetate (1.0 m*M*). Anodic-sweep pulse polarography from the plateau of the second wave generally yielded two anodic waves, one at the same potential as a wave seen on anodic sweep from the first wave and another at a potential near that of the first cathodic wave. The height of the second cathodic wave generally corresponded to a 4—5 electron transfer when measured by pulse polarography, but in a few media (e.g. ammonia buffer) varied non-linearly with concentration. To confirm the non-integral values for *n* obtained by tast polarography the diffusion current was also compared with that of the reference standard using pulse polarography. The results show close agreement between the two methods (Table 5). The pulse method tended to give very slightly higher *n* values. This may be related to the occurrence of a maximum in the phosphate reference standard; *n* values by pulse polarography would be about 5% lower were citrate buffer used as the reference standard.

Unbuffered media

The half-wave potential of the first wave in unbuffered solutions, like that in alkaline media, was around −0.8 V. This probably reflects alkalinization of the solution adjacent to the electrode as hydrogen ions are consumed in the reduction of pertechnetate. The wave is diffusion-controlled, at least approximately. A small prewave was seen in KSCN and KCl at low pertechnetate concentrations, which has not been reported previously. The prewave could be mimicked by adding traces of acid, and was proportional to the acid added, so that it too is probably related to the consumption of protons by the electrode process. Unlike buffered alkaline media, no wave was observed near −1.0 V. At more negative potentials a large catalytic wave was sometimes found.

Voltammetry

Triangular-wave voltammetry at the hanging mercury drop served to confirm qualitatively the polarographic findings and to identify non-diffusible surface films. Table 6 shows the results. A cathodic peak was consistently seen at the potential of the first polarographic wave. A second cathodic peak was sometimes seen at the potential of the second polarographic wave, but often this was lost in the cathodic background. Anodic peaks were identified at potentials corresponding to waves on the anodic-sweep pulse polarogram. Non-diffusible films which failed to disappear with time were obtained in alkaline media (hydroxide, carbonate, ammonia). Apart from these no surface films were identified which

TABLE 6

Half-peak potentials by cyclic voltammetry (vs. SCE)
(d) = diffusible (nd) = not diffusible

pH	Medium	Cathodic $E_{p/2}$/V	Anodic $E_{p/2}$/V
1.0	$HClO_4$	−0.05	None
1.7	Sulfate	−0.10	None
2.0	Phosphate	−0.09	0.0(d)
3.0	Citrate	−0.25	−0.15(d)
4.8	Acetate	−0.42	−0.38
6.5	EDTA	−0.61	−0.42, −0.22, −0.12
8.0	Pyrophosphate	−0.69, −0.98	−0.52(d), −0.07(d), −0.02(d)
9.5	TRIS [a]	−0.80	−0.22, −0.12
9.8	Ammonium	−0.71, −0.96	−0.16(nd)
9.8	Carbonate	−0.76	−0.55(d), −0.25(d), −0.14(nd)
13.2	KOH	−0.82, −1.08	−0.44(d), −0.37(d), −0.30(nd)
	KCl	−0.78	−0.19(d)
	KSCN	−0.78	−0.18(d)

[a] Tris(hydroxymethyl)methylamine.

either formed peaks or caused unexpected hysteresis in the voltammogram. (Although no change in electrode properties was seen on a few repetitions, continued repetitions of the triangular wave did lead to eventual passivation.) We were unable to learn anything from voltammetry about the second wave in acid, perhaps reduction to metallic Tc, because no corresponding cathodic peak was obtained and no anodic peak was produced by sweep reversal from the cathodic background.

DISCUSSION

First wave in acidic media

Of the conflicting reports cited in the introduction our findings agree most closely with those of Salaria et al. [6,7]. They found, and we confirm, that the first polarographic wave below pH 4 is an irreversible 4-electron reduction. They sometimes observed a 3-electron wave poorly separated from the 4-electron one. This we did not see, but we did find evidence for Tc(IV) species on anodic-sweep pulse polarograms, which often showed reoxidation of Tc(III) to Tc(IV) (Table 3). Salaria et al. believed that the mechanism changed above pH 4, but we think this was the consequence of their using strong acid rather than buffer to adjust the pH so that above pH 4 the medium was in effect unbuffered. We found the transition to occur in buffered media not at pH 4 but at pH 7 [1]. We found the same dependence of half-wave potential on pH reported by Salaria et al.: approximately 0.10 V pH^{-1}. This is consistent with a mechanism in which the rate-determining step is the discharge of $HTcO_4$, preceded by a fast protonation reaction with equilibrium far to the left. For this mechanism one can calculate that $n_a\alpha = 0.6$ from the measured pH-dependence of half-wave potential. Another estimate of $n_a\alpha$ can be calculated from the experiments of Table 3. The values of $n_a\alpha$ were calculated from the slope of the tast polarogram at its inflection point using the readily derived equation:

$$i_d \left.\frac{dE}{di}\right|_{i=i_d/2} = \frac{0.103}{n_a\alpha}\ \text{V}$$

These values clustered around 0.5 in acid media (1.0 in base) in agreement with the estimate based on the proposed mechanism.

All pertechnetate reduction waves studied were irreversible by the criteria of anodic-sweep pulse polarography [13]. In a few cases anodic waves occurred at potentials close to a cathodic wave, suggesting reversibility, but the diffusion current data showed in each case that fewer electrons were involved in the anodic than in the cathodic reaction.

The polarographic findings were further supported by triangular-wave voltammetry at the hanging mercury drop (Table 6). A cathodic peak was found with half-peak potential matching the half-wave potential for the first wave. An anodic peak was sometimes found (for example, in acetate buffer) corresponding in potential to the cathodic peak, but this did not indicate reversibility, corresponding instead to the situation described in the previous paragraph. The anodic peaks were all due to diffusible Tc(III) species and not to insoluble surface films.

Although phosphate proved a satisfactory reference medium for this study, we would recommend citrate for further work. In 0.1 *M* sodium citrate, 0.1 *M* citric acid there are no maxima for either classical or normal-pulse waves, unlike phosphate. The plateau is nearly parallel to the background and corresponds, as shown here, to $n = 4$. While one can use phosphate and simply avoid the maximum, as we did, citrate would be more convenient.

Second wave in acidic media

Salaria et al. described a second wave in acid occurring at a pH-independent half-wave potential of −0.93 V [6,7]. Its variation with drop time indicated diffusion control, but it was not linear with concentration. A visible film was formed on the surface of the electrode, thought to be most probably metallic technetium. The value of *n* could not be definitely ascertained. Others have suggested that this might be an 8-electron wave as reported for rhenium [5,15]. Coulometry does not help since no endpoint is reached, evidently because of catalytic water reduction [6]. Anodic-sweep pulse polarography failed to disclose any waves attributable to the primary reaction product. (Tables 3 and 4. No electroactive species could be demonstrated on sweeping anodically from the plateau of the second wave when it was diffusion-controlled and without maxima; otherwise traces of electroactive species could be obtained having the same half-wave potentials as those identified for higher oxidation states.)No peak was observed on triangular-wave voltammetry which corresponded to the second polarographic wave, the cathodic background supervening instead.

Nevertheless the data of Table 5 do permit a decision between $n = 7$ and $n = 8$. Coulometric and voltammetric evidence clearly indicate some catalytic reduction of water coincident with the second wave. Since this must cause the measured *n* value to be too high, our observed values between 7 and 8 indicate that $n \leqslant 7$, compatible with a 7-electron but not an 8-electron reduction. The possibility that $n < 7$ cannot be excluded, but no value significantly under 7 has been observed below pH 5.

First wave in alkaline medium

Salaria et al. described the first wave in base as an irreversible diffusion-controlled 3-electron process occurring at the pH-independent half-wave potential −0.78 [6,7]. Astheimer and Schwochau subsequently contended that it was a 2-electron process and that it was fairly reversible by a.c. polarographic criteria [8]. Munze described it also as a 2-electron process (3-electron in cyanide) which was reversible and had pH-dependent half-wave potential [9]. Salaria et al. presented coulometric data to support their assignment of *n*, but the coulometric data are difficult to interpret because the results are quite sensitive to the potential used. It has also been suggested that the coulometric data may disagree with the polarographic because of slow chemical reactions which remain undetected on the polarographic time scale but become important in the time required for classical coulometry [9]. Thin-layer coulometry has yet to be performed with pertechnetate.

Our findings support the contention of Salaria et al. that the first wave in base is irreversible, diffusion-controlled, and pH-independent. Irreversibility was clearly demonstrated by cyclic voltammetry and anodic-sweep pulse polarography. Diffusion control was demonstrated by examining the variation of wave height with drop time and concentration, and by comparing the wave height for tast and pulse polarography. The measured diffusion currents in base ranged from 2 to 4 and were often non-integral despite the apparently diffusion-limited character of the wave. An average value of 1.0 was observed for $n_a\alpha$.

Since reduction began at a potential virtually independent of the composition of the medium, the initial discharge of pertechnetate ion is probably the rate-determining step. Subsequent fast competing reactions apparently lead to a mixture of oxidation states, catalytic reduction of water, or both. The catalytic reduction of water is suggested by the failure to date to isolate oxides of technetium lower than TcO_2 despite apparent 4-electron coulometric reductions of alkaline pertechnetate. Since the resulting wave is diffusion-limited, the species which reacts with water must not be regenerated by subsequent reactions, unlike the usual catalytic wave. Another possible explanation of non-integral *n* values would be the formation of species with metal-metal bonds (such as the known $Tc_2Cl_8^{3-}$), but the data of Table 4 do not suggest consistent formation of such species.

One might be tempted to attribute the non-integral diffusion current ratios of Table 4 to a change in the chemical form of pertechnetate on passing from acidic to basic media, resulting in a changed diffusion coefficient. However, no single correction factor for the diffusion coefficient will bring all the ratios measured in alkaline media to integral values. Furthermore pertechnetate is believed (from spectral data, for example) to be the conjugate of a strong acid and to exist as the same mononegative species in both acidic and basic media.

The existence of competing concurrent reactions when pertechnetate is reduced in alkaline media has been recognized in the tracer radiochemistry of technetium [16]. When technetium chelates are prepared by the reduction of pertechnetate by stannous ion in the presence of chelon, high chelon concentrations and strongly acidic environments are employed to inhibit competing hydrolytic reactions. Such reactions, catalytic water reduction by short-lived intermediates, or both can account for the non-integral *n* values in what otherwise appear to be diffusion-controlled waves. Catalytic water reduction seems the less likely alternative, since the anodic-sweep data indicate quantitative formation of electroactive species (Table 4) and hydrogen does not react at the dropping mercury electrode.

The species recognized as stable in non-complexing alkaline media are TcO_4^- and insoluble TcO_2. These are the likely fate, after disproportionation or reduction of water, of the intermediates formed at the cathode. However, the anodic-sweep pulse waves for these intermediates (Table 4) show their persistence as diffusible electroactive species for the duration (2 s) of the mercury drop. To the extent disproportionation occurs, a second-order reaction, the process is likely to follow a different course at tracer concentrations (of practical importance as noted above).

Second wave in alkaline media

In base Salaria et al described a 4-electron second wave at a pH-independent half-wave potential of −1.0, sometimes adsorption-controlled [6,7]. Astheimer and Schwochau subsequently described a 3-electron second wave, diffusion-controlled and fairly reversible [8]. Munze reported a 3-electron wave, becoming 4-electron in the presence of cyanide [9]. Our own data indicate *n* values from 3 to 5, sometimes integral, with diffusion-controlled behavior in at least some media (such as KOH or TRIS). This wave tends to disappear at higher pertechnetate concentrations (1.0 m*M*) using classical polarography, but can be demonstrated even at the higher concentrations by pulse methods. (Indeed, in our earlier survey of the polarographic properties of pertechnetate, using only classical methods at high concentrations, we missed this wave entirely [1]) The half-wave potential ranged between −0.98 and −1.10 V except in borate buffer, where it was −1.28 V for an asymmetrical wave. The fairly uniform occurrence of a second wave around −1.0 V in both acid or base may be a clue to the reduction mechanism, but its interpretation escapes us. The anodic-sweep data (Table 4) indicate that some reduction products are not reoxidizable, unlike the first wave, and could represent some catalytic reduction of water.

Unbuffered media

As we have pointed out previously, the polarographic behavior of pertechnetate in unbuffered media resembles that in alkaline media [1]. This might be expected, since any plausible half-cell reaction for the reduction of pertechnetate involves the consumption of protons and consequent alkalinization of the diffusion layer. However, in contrast to the findings in alkaline buffers, we have not observed any wave in unbuffered media between the first wave at −0.7 V and the subsequent large catalytic waves or cathodic background at −1.1 V. In dilute solutions, or in more concentrated solutions if traces of acid are added, a small prewave can be observed. This is proportional to the added acid, and evidently arises from the consumption of protons at the electrode surface. Three-electron waves were found in KCl and KSCN.

Surface films

Insoluble films sometimes form upon mercury or solid electrodes during the reduction of pertechnetate [1,2]. The film formed at the hanging mercury drop in KOH has been used for analysis by stripping voltammetry [2]. The influence of film formation on the polarography of pertechnetate has not previously been investigated. We therefore used cyclic voltammetry at the hanging mercury drop to better define the conditions under which non-diffusible films are formed. Table 6 shows that non-diffusible oxidizable films (lower oxides?) are produced in some, but not all, alkaline media at potentials on the negative side of the first polarographic wave. While films are formed in voltammetric experiments, they are not formed under polarographic conditions, at least when low concentrations of pertechnetate (0.15 m*M*) are employed. The anodic-sweep pulse polarographic data of Table 4 show diffusion currents of the magnitude predicted for a diffusion process, and maximum currents would be expected for an insoluble electroactive product. At higher concentrations than those used here, film effects may become important even in polarography. A film effect could account for the disappearance of the tast second wave and persistence of the pulse second wave at high concentrations of pertechnetate in basic media.

CONCLUSIONS

In buffered acidic media, pertechnetate is reduced in multiple steps. The first is a diffusion-controlled 4-electron reduction at half-wave potential which varies with pH as:

$E_{1/2} = -0.10\ \text{pH} \qquad (\text{V vs. SCE}) \quad 0 < \text{pH} < 7$

The presence of complexing agents has little effect on the half-wave potential. The rate-determining step is probably:

$HTcO_4 + e^- \rightarrow HTcO_4^-$

Pertechnetic acid is a minority species being a strong acid. The product, $HTcO_4^-$, is subsequently reduced in a sequence of fast reactions to Tc(III), which can often be reoxidized to Tc(IV) or Tc(V) by triangular-wave voltammetry or by anodic-sweep pulse polarography. A second wave appears at −0.9 V with $n \leqslant 7$, perhaps corresponding to the reduction of pertechnetate to metallic technetium. This wave usually has a catalytic component so that only an upper limit can be given for n. Further waves, observed at more cathodic potentials, are so large as to be clearly catalytic.

Multiple waves are also found in buffered alkaline media. The first occurs consistently at −0.8 V regardless of the presence of complexing agents and probably corresponds to the rate-determining step:

$TcO_4^- + e \rightarrow TcO_4^{2-}$

(This reaction is known to occur at platinum cathodes in anhydrous acetonitrile, but the technetate ion produced is unstable in the presence of water [17].) The exact fate of the technetate formed in aqueous polarography is obscure. Though this wave is diffusion-controlled, non-integral values between 2 and 4 are observed for the total number of electrons transferred. The non-integral value appears to reflect formation of mixed oxidation states by competing fast reactions or, less likely, the concurrent reduction of water. If reduction of water occurs, the mechanism is not such as to result in a typical catalytic current, but rather one that mimics a diffusion current. A second wave is often seen at −1.0 V, especially when low pertechnetate concentrations or pulse techniques are used, which corresponds to n values between 4 and 5. The second wave thus appears at similar potentials in both acid and alkaline media.

Results in unbuffered media resemble those in buffered alkaline media except for absence of the wave at −1.0 V. The alkaline environment produced at the electrode surface during pertechnetate reduction accounts for this similarity; almost any plausible half-cell reaction involves consumption of protons. The consumption of hydrogen ion can be directly verified since the addition of traces of acid to unbuffered media results in the appearance of a prewave having height proportional to the acid concentration. A similar prewave can also be observed at low pertechnetate concentrations in the absence of added acid.

Contrary to some previous reports, no reversible waves were found for pertechnetate reduction in any media. The formation of insoluble surface films could be demonstrated in some alkaline media by triangular-wave voltammetry at the hanging mercury drop, but not under polarographic conditions at low concentrations of pertechnetate (0.15 m*M*).

In future work we suggest that the first wave in citrate buffer be used as a standard 4-electron pertechnetate reduction wave for purposes of reference. This medium (0.1 *M* citric acid, 0.1 *M* sodium citrate) yields a well-defined wave free of maxima and nearly parallel to the background whether pulse or classical polarography is used.

ACKNOWLEDGMENTS

We are grateful for advice given by Professors Fred Anson, Dennis Evans, and Janet Osteryoung. Ms. Linda Askew, Ms. Jane Haley, and Mrs. Doris Miller helped prepare the manuscript. This work was supported by the Veterans Administration Hospital, Birmingham, Alabama, and by the Department of Radiology, University of Alabama, Birmingham.

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