In view of the rapid exchange of sulfurous acid with water, but not of peroxide and water, it is very likely that in forming the ester, the S–O rather than O–O bond is severed. The formation of the doubly labelled sulfate can take place by an intramolecular rearrangement of the persulfurous acid, or by the interaction of two molecules. Of these the second seems less likely since the extent of transfer is independent of an extreme variation in the ratio of H_2O_2/SO_2aq. The tracer result makes it unlikely that a major part of the reaction proceeds by a free radical mechanism, but does not exclude a minor contribution by this path. A slight participation by a free radical path is suggested by the observation that H_2O_2 induces the reaction of O_2 and $SO_3^=$,[11] but not at all efficiently.

The work of Winter and Briscoe[2] showed that in the reaction of hydrogen peroxide and sulfite in water, an atom of oxygen is released to the solvent for each molecule of H_2O_2 consumed. The present work shows that in acidic solutions this atom is derived from the sulfite rather than from the peroxide. In more alkaline solution the formation of the ester may be slow, and it seems possible that only one atom of oxygen is transferred from the peroxide to the sulfite on reaction.

The data on the catalyzed reaction of H_2O_2 and $S_2O_3^=$ are too incomplete to justify a definite conclusion. The experimentally measured value of $n = 1$ is in harmony with the view that a permolybdic acid (molybdate and hydrogen peroxide react very rapidly to form permolybdic acid) which is almost certainly an intermediate, will act by transferring oxygen atoms. This type of mechanism can be expected when any strongly polarizing group such as HMO_3 or HSO_3, is attached to $O–O^=$ thereby weakening the O–O linkage. The experiment is of some interest in showing the exchange of sulfur intermediates in the oxidation to sulfate is less rapid than the oxidation.

The excess of the value of n over 2 observed for the reaction of oxygen and sulfite may be due to isotope fractionation. A deviation in the observed direction can be expected if O_2^{16} reacts more rapidly than oxygen containing O^{18}. A more thorough study will be necessary to discover whether the deviation is entirely due to this cause, or whether a real exchange effect exists.

The efficient transfer observed in the reaction of sulfite with MnO_2 suggests that sulfite makes bonds with the oxygen atoms rather than with the metal ions at the surface of the solid. Permanganate ion, or the unknown oxidation state which attacks the sulfite apparently operates largely by electron transfer.

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[11] H. L. J. Bäckstrom, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 15 (1927).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Anodic and Cathodic Voltammetry of Thallium at the Rotated Platinum Wire Electrode

BY I. M. KOLTHOFF AND JOSEPH JORDAN[1]

The anodic oxidation of thallous to thallic thallium at the rotated platinum wire electrode was studied at various pH, using an automatic recording instrument. Proportionality between diffusion current and concentration was found in sodium hydroxide solutions. This amperometric method is suitable for the determination of thallium in a concentration range between 10^{-5} and 10^{-3} *M*. Good results can be obtained with a manual polarograph provided that diffusion currents are measured after the same time of electrolysis. Limiting anodic potentials in various supporting electrolytes have been determined. In alkali hydroxide the oxygen overvoltage was found to be negligible. Anodic dissolution patterns of thin layers of metallic thallium and cathodic dissolution patterns of thallic oxide are presented. The standard potential of the reaction

$$2Tl^+ + 6OH^- \rightleftarrows Tl_2O_3\,(s) + 3H_2O + 4e$$

was found to be -0.23 ± 0.02 volt *vs.* S.C.E. ($+0.02$ *vs.* N.H.E.) at 25°.

Thallous–thallic potentials have been studied by various authors[2–5] in acid solutions. Jonas[6] investigated the characteristics of a thallium storage battery in alkaline medium. Recently Delahay and Stiehl[7] described the anodic oxidation of thallous thallium at a rotated platinum micro-anode using a manual technique. They obtained well defined waves in alkaline solutions; however, large deviations (from 5 to 20%) from proportionality between diffusion current and concentration were observed.

Experiments with an automatic recording polarograph, and also with a manual apparatus, reported in this paper, show that anodic diffusion currents of thallous thallium are proportional to concentration to better than 2%. Evidence is given that the anodic reaction involves two electrons. Anodic dissolution patterns of micro-quantities of metallic thallium and cathodic dissolution patterns of thallic oxide are presented and discussed.

Experimental

Materials Used.—Thallous sulfate, C. P., was obtained from Fairmount Company.

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[1] On leave from the Hebrew University, Jerusalem, Israel.

[2] G. Grube and A. Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] J. R. Partington and H. I. Stonehill, *Trans. Faraday Soc.*, **31**, 1365 (1935).

[4] M. S. Sherrill and A. G. Haas, Jr., THIS JOURNAL, **58**, 953 (1936).

[5] A. A. Noyes and C. S. Garner, *ibid.*, **58**, 1268 (1936).

[6] L. Jonas, *Z. Elektrochem.*, **9**, 523 (1903).

[7] P. Delahay and G. L. Stiehl, THIS JOURNAL, **73**, 1655 (1951).

Apparatus and Technique.—A platinum wire microelectrode, synchronously rotated at 600 r.p.m.,[8] a saturated calomel reference electrode and salt bridge described by Hume and Harris[9] were used. The platinum wire was 0.1 cm. thick and 1 cm. long, with an exposed area of 0.31 sq. cm. A 150-ml. Pyrex beaker served as electrolysis cell which was closed with a rubber stopper with appropriate holes for inserting the platinum electrode, salt bridge and in-and-outlets for nitrogen. Fifty ml. of solution was used in each experiment, unless otherwise stated. The resistance of the circuit in 0.1 M sodium hydroxide was approximately 600 ohms. Oxygen was removed with Linde nitrogen purified through a vanadous sulfate gas train.[10] Nitrogen was passed through the cell for 15 minutes before the start of an experiment and continuously during the actual recording of the polarograms.

A Sargent Model XXI visible recording polarograph was used to record current-voltage curves. The rate of voltage change, $\Delta E/\Delta t$, was 2.47 mv./sec., unless otherwise stated. When desired, a manual setup[8] was used.

pH values were measured with a Beckman model G pH meter, except in sodium hydroxide solutions, where the pH was calculated from Latimer's[11] activity tables.

All experiments were carried out at 25 ± 0.02°.

Potentials refer to the saturated calomel electrode (S.C.E.); in accordance with polarographic conventions cathodic currents are denoted as positive and anodic current as negative. Decomposition potentials of supporting electrolytes were estimated from their current-voltage curve, in air saturated solutions.

Results and Discussion

Pretreatment of the Platinum Electrode.—In agreement with Rogers, *et al.*,[12] it was found that the reproducibility of an experiment greatly depends upon the kind of pretreatment of the electrode. As a rule, the electrode was stored in 10 M nitric acid and washed with distilled water shortly before each experiment. Prolonged storage of the electrode in water gives rise to abnormally large and irreproducible residual currents. Furthermore, it was found necessary to immerse the electrode for at least 15 minutes in the test solution, before actually recording the current-voltage curves. These were found perfectly reproducible when the electrode was kept in the test solution for 15 to 60 minutes; upon longer times irregularities were observed.

Limiting Anodic and Cathodic Potentials.—In aqueous solutions the limiting anodic potentials are usually considered to be determined by oxidation of hydroxyl ions to oxygen. In sodium hydroxide solutions the decomposition potentials actually correspond to this oxidation. It is seen from the data in Table I that the overvoltage of oxygen in alkali hydroxide at the rotated wire electrode is very small. The overvoltage is known to increase with current density and the absence of overvoltage in our experiments may be accounted for by the small current density at the potentials where oxygen evolution starts (of the order of 10^{-6} a./sq. cm.^{2}).

In the buffer solutions listed in Table I the decomposition potentials are more negative than those corresponding to the decomposition potential of oxygen, indicating anodic oxidation of the buffer and of ammonia.[13] The rotated platinum electrode seems to be ideally suitable for further studies of these anodic oxidations.

TABLE I

ANODIC DECOMPOSITION POTENTIALS (S.C.E.) OF AIR-SATURATED SUPPORTING ELECTROLYTES

Supporting electrolyte	pH (glass electrode)	Observed decomposition potentials	Thermodynamic oxygen evolution potentials[a]
0.1 M Acetic acid	2.7	1.12	1.31
Acetate buffer[b]	4.0	0.90	1.23
Acetate buffer[b]	5.0	.90	1.17
Acetate buffer[b]	6.0	.90	1.11
Phosphate buffer[c]	7.0	.94	1.05
Phosphate buffer[c]	8.0	.88	0.99
0.1 M NH_3 + 1 M NH_4Cl	8.3	.68	.97
0.1 M NH_3 + 0.1 M NH_4Cl	9.3	.60	.91
1 M NH_3 + 0.1 M NH_4Cl	10.4	.50	.85
1 M ammonia	11.4	.44	.79
0.01 M NaOH	12.0[d]	.75	.76
0.1 M NaOH	12.9[d]	.72	.70
1 M NaOH	13.8[d]	.60	.65

[a] Calculated from Latimer's data. [b] Total concentration in acetic acid and sodium acetate was 0.1 M. [c] Total phosphate concentration in buffer was M/30. [d] pH calculated using Latimer's activity coefficients.

The cathodic limiting potentials in the supporting electrolyte used correspond to those of hydrogen evolution.

Anodic and Cathodic Current-Voltage Curves in the Thallium-Thallous-Thallic System.—Current-voltage curves of thallium were run "forward" (*i.e.*, from positive to negative potentials) and "backward." Figure 1 shows polarograms of 10^{-4} M thallous ion in 0.1 M sodium hydroxide over the potential range between hydrogen and oxygen evolution. The "forward" polarogram (Curve I) first records a potential region where a well defined anodic diffusion current, i_a, is obtained; in this region the electrode becomes covered with a yellow deposit which Jonas[6] has identified as Tl_2O_3. Consequently the anodic reaction is

$$2Tl^+ + 6OH^- \longrightarrow Tl_2O_3(s) + 3H_2O + 4e^- \quad (1)$$

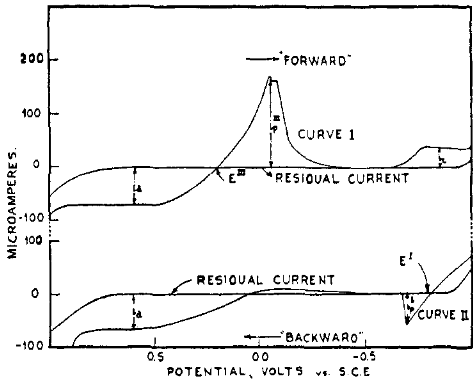

Fig. 1.—Current-voltage curves of 10^{-4} M Tl^+ in 0.1 M NaOH: curve I, forward; curve II, backward. Curves are shifted arbitrarily along vertical axis.

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(8) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

(9) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

(10) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(11) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 323-325.

(12) L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, *Anal. Chem.*, **21**, 777 (1949).

(13) See, *e.g.*, S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., Inc., New York, N. Y., 1936.

With increasing negative potential the anodic current decreases, the current–voltage curve intersecting the "residual current line" at a potential E^{III}. A cathodic current is then obtained, which reaches a maximum (i_p^{III}) and subsequently drops abruptly to the residual current value. This "current bulge" pattern corresponds to the cathodic dissolution of the thallic deposit off the electrode. At more negative potentials the familiar reduction wave of thallous ion to thallium is observed with a cathodic diffusion current i_c.

The "backward" polarogram (curve II in Fig. 1) starts out with a reduction current where both thallium and hydrogen are formed at the electrode. With increasing positive potentials the current becomes equal to zero at a potential E^I, and then the typical dissolution pattern of the metallic thallium deposit is observed. At potentials slightly more positive than 0.0 volt the thallous–thallic wave starts with a well-defined diffusion current at a potential of about +0.6 volt. The anodic diffusion currents, i_a, in the "forward" and "backward" experiments were 67 and 68 μa., respectively, while the cathodic one was 34 μa.; hence

$$i_a = 2i_c \tag{2}$$

This relation shows conclusively that the anodic oxidation involves two electrons [*cf.* equation (1)]. A marked overvoltage of oxygen is apparent in both forward and backward polarograms when the electrode is coated with thallic oxide.

The dissolution patterns are of analytical importance. They may serve for the detection of extremely thin films while the current–time area can be made use of in the coulometric determination of microquantities of coated material on the electrode.

The Anodic Waves.—Examples of anodic current–voltage curves at varying *p*H in different supporting electrolytes are shown in Fig. 2. At a *p*H greater than 8 a deposit of thallic oxide is observed on the electrode. In acid solution the thallic thallium is soluble. A poorly defined diffusion current is observed in 0.1 *M* acetic acid, while in the *p*H region between 3 and 9 the anodic currents of the supporting electrolytes interfere with the thallic wave. In a phosphate buffer of *p*H 8, however, an ill-defined wave is obtained and a deposit is formed on the electrode (at *p*H 7 a wave was not obtained and no oxide coat was observed). The dissolution pattern of this deposit yielded two cathodic areas instead of one (see Fig. 1), about 0.45 volt apart. The complex phenomena in the phosphate buffer of *p*H 8 may be due to the formation of a mixed film of thallic oxide and thallic phosphate.

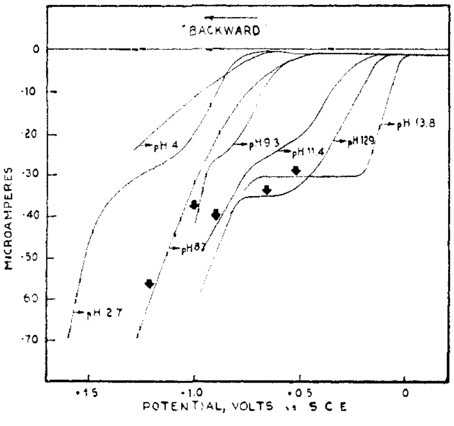

Fig. 2.—Thallous–thallic polarograms: $Tl^+ = 5 \times 10^{-5}$ *M;* supporting electrolytes: *p*H 2.7—acetic acid; *p*H 4—acetate buffer; *p*H 8.3, 9.3—ammonium buffers; *p*H 11.4—ammonia; *p*H 12.9, 13.8—sodium hydroxide; ↓ indicates deposit on electrode.

In 0.1 *M* acetic acid the oxidation corresponds to the reaction

$$Tl^+ \longrightarrow Tl^{+++} + 2e \tag{3}$$

The standard potential of this reaction is 1.00 volt *vs.* S.C.E.[14] The half-wave potential observed in 0.1 *M* acetic acid (0.96 volt, Fig. 2), corrected for the *IR* drop, is 0.97 volt. Thus the oxidation of thallous to soluble thallic thallium at the rotated electrode appears to be reversible in 0.1 *M* acetic acid. In a medium in which the thallic thallium is soluble and does not form a complex the oxidation potential should be independent of *p*H. This could not be verified by measurements of the half-wave potential at higher *p*H, because of interference by the anodic currents of the supporting electrolytes.

Well-defined diffusion currents are observed in a medium which is 0.1 to 1 *M* in sodium hydroxide. The ratio of the diffusion currents in 0.1 and 1 *M* sodium hydroxide was 0.82 while the ratio of the viscosities in these two solutions[15] is 1.023/1.236 = 0.83. From Fig. 3 it is seen that in 0.1 and 1 *M* sodium hydroxide the diffusion current is proportional to the thallous thallium concentration. In 0.1 *M* hydroxide i_d/c was found to be (683 ± 15) μa./millimoles/liter and in 1 *M* hydroxide (560 ± 5) μa./millimoles/liter. The standard deviation is about 2.5 and 1%, respectively. The rotated platinum electrode is ideally suitable for the anodic determination of thallous thallium, 1 *M* sodium hydroxide being recommended as the supporting electrolyte.

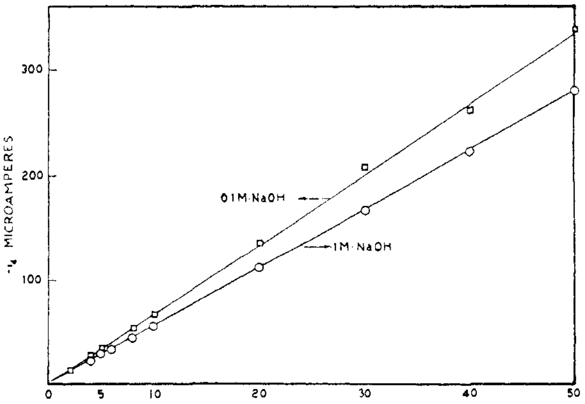

Fig. 3.—Plot of anodic diffusion current *versus* thallium concentration.

Assuming the system to be reversible and in equilibrium during electrolysis and neglecting the solu-

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[14] Reference 11, page 153.

[15] International Critical Tables, Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 15.

bility of thallic oxide gives the following expression[16] for the half-wave potential at 25°

$$E^{\mathrm{III}}_{1/2} = E^0 + 0.089 \log \frac{1}{a_{\mathrm{OH}}} - 0.030 \log f_{\mathrm{Tl}^+} - 0.030 \log \frac{C_{\mathrm{Tl}}}{2} \quad (4)$$

where f_{Tl^+} is the activity coefficient of the thallous ion. The difference in half-wave potentials in 0.1 and 1 *M* sodium hydroxide was found to be 0.20 volt which is approximately twice the calculated value. This indicates that the current on the wave is determined not only by the rate of diffusion but also by the rate of electrolysis. This conclusion is substantiated by a plot of log ($i_d - i$) *vs.* the potential of the rotating electrode. Theoretically a straight line with a slope of 0.030 volt should be obtained.[16] Plots of the experimental data yield straight lines, however, with a slope of about 0.160 instead of 0.030 volt. Also, with a ten-fold change in the concentration of thallous ion in a given medium $E_{1/2}$ should change 0.030 volt, while we found a change of 0.045 volt in 1 *M* hydroxide and of 0.0 volt in 0.1 *M* hydroxide.

The Zero Current Potentials.—The potential at the intersection of the dissolution curves with the residual current line (E^{I} and E^{III} in Fig. 1) corresponds to the oxidation potential of the system concerned. This was verified by varying the concentration of thallous ion between 2×10^{-5} and 3×10^{-4} *M* in 0.1 and 1 *M* sodium hydroxide. The zero current potential of the thallium–thallous system agreed within 0.02 volt with the value calculated from the standard potential[14] and activity coefficients given by Latimer.[11]

In Table II are reported the values of the potential of the thallic oxide coated electrode in thallous thallium solutions of varying *p*H. From the data the standard potential of reaction (1) was calculated. This was found to be equal to −0.23 ± 0.02 volt *vs.* S.C.E. (or +0.02 volt *vs.* N.H.E.) over a 500-fold range of thallium concentration and a *p*H range of 3.5. Results obtained with the recording polarograph agreed within 0.01 volt with those obtained manually. The constancy of the calculated standard potential indicates that the system is reversible and in equilibrium with the electrode at the zero current potential.

TABLE II

POTENTIAL OF THALLOUS–THALLIC OXIDE SYSTEM

*p*H	[Tl$^+$]	E_0III (Residual current intersection potential)	Standard potential (*vs.* S.C.E.) for $2\mathrm{Tl}^+ + 6\mathrm{OH}^- \rightleftarrows \mathrm{Tl_2O_3(s)} + 3\mathrm{H_2O} + 4e^-$[a]
9.3	5×10^{-5}	+0.32	−0.23
11.5	5×10^{-5}	+ .10	− .25
12.9	10^{-4}	+ .01	− .23
12.9	1.5×10^{-3}	− .04	− .23
12.9	10^{-2}	− .06	− .20
			Mean = − 0.23 ± 0.02 v.

[a] Calculated on the assumption that E_0^{III} is the thermodynamic equilibrium potential.

Comparison of Manual and Recording Instruments.—Delahay and Stiehl,[7] working with a manual apparatus, did not find satisfactory proportionality between anodic diffusion current and concentration. They attribute this to a variation of the area of the electrode caused by the coat of thallic oxide. We placed our rotating electrode in a 5×10^{-5} *M* thallous solution in 0.1 *M* sodium hydroxide and electrolyzed for 30 minutes at a potential of 0.5 volt the current being of the order of 30 microamperes. Using this coated electrode we found the same diffusion currents as with the uncoated electrode. Thus the thin coat of thallic oxide did not measurably affect the area of the electrode.

The reason why Delahay and Stiehl did not find proportionality between diffusion current and concentration probably is that their solutions became depleted with thallium during the course of an electrolysis experiment. With both recording and manual polarographs we found a decrease of the diffusion current of 0.3% per minute using a volume of 100 ml. and 3% with a volume of 10 ml. This is in good quantitative agreement with the expected depletion, calculated on the basis of Faraday's laws. In two experiments with the recording polarograph, with 30 ml. of 5×10^{-5} *M* thallium in 0.1 *M* sodium hydroxide, in which the rate of voltage change was varied from 2.47 mv. per second to 1.24, we found diffusion currents of 34 and 33 microamperes, respectively. At a given rate of voltage change proportionality between diffusion current and concentration is found. The manual apparatus yields the same relation provided that the various diffusion currents are measured after the same time of electrolysis. The depletion of concentration with time, $\Delta c/\Delta t$, depends on the area of the electrode and the volume of the solution. Using 50 ml. of solution and a wire electrode with approximately 0.3 cm.^{2} area, satisfactory proportionality between diffusion current and concentration is found when the times of electrolysis do not differ more than two minutes.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 3, 1951

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(16) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 155.