[CONTRIBUTION FROM ANALYTICAL CHEMISTRY BRANCH, U. S. NAVAL ORDNANCE TEST STATION]

Polarographic Reduction of Polynitrate Esters

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The polarographic behavior of ethylene glycol dinitrate, glycerol trinitrate and pentaerythritol tetranitrate was studied in an ethanol–water system with tetramethylammonium chloride as the supporting electrolyte. Diffusion currents of the esters are well-defined in neutral, alkaline and weakly acidic solutions. The reduction process at the dropping mercury electrode was found to be diffusion controlled and from *p*H 4.0 to 11.0 appeared to be independent of *p*H. The diffusion current constants for the esters increased proportionally with the number of ONO_2 groups in the molecule. Diffusion coefficients for these compounds and *n*-butyl nitrate were experimentally determined in the same media. Values for the number of electrons (n) involved in the polarographic reduction of one molecule of these nitrate esters were calculated from the experimentally determined diffusion coefficient data. More precise values of n were determined by this method than by the use of the Stokes–Einstein equation. The studies revealed a value for n of two for each ONO_2 group in the molecule.

Introduction

The simple nitrate esters have been studied at the dropping mercury electrode.[1,2] Reduction mechanisms have been suggested and a two-electron reduction with alcohol and nitrite ion as products has been established for ethyl and cyclohexyl nitrate.[1] In these studies the value for the number of electrons involved in the reduction of one molecule of the ester was determined by large scale electrolysis experiments or by the Ilkovic equation ($n = i_d/607D^{1/2}Cm^{2/3}t^{1/6}$). When using the Ilkovic equation one must know the diffusion coefficient (D) for the ion in question. However, in organic polarography the value for (D) is very often unknown and ions of comparable size must be found and their diffusion coefficients substituted for the ion in question. The available experimental data on diffusion coefficients are insufficient and are many times of doubtful accuracy or not in media suited for polarographic investigations. The application of experimentally determined diffusion coefficient data in the Ilkovic equation revealed very reliable data for reduction mechanism studies.

Ethylene glycol dinitrate (EGDN), glycerol trinitrate (NG) and pentaerythritol tetranitrate (PETN), representing two, three and four ONO_2 groups in the molecule, were chosen for this investigation. *n*-Butyl nitrate ($BuNO_3$) was also studied in the same media.

Experimental

Apparatus.—Polarograms were obtained in a constant-temperature bath at 30° (±0.2°) and recorded with a Sargent Model XXI polarograph. Two capillaries were used as dropping mercury electrodes. Capillary 1 had a drop rate of 6.5 sec. per drop at zero applied potential with a value of 1.351 mg.$^{2/3}$sec.$^{-1/2}$ for $m^{2/3}t^{1/6}$ at a 91.5 cm. head of mercury. Capillary 2 had a drop rate of 9.0 sec. per drop at zero applied potential with a value of 1.048 mg.$^{2/3}$ sec.$^{-1/2}$ for $m^{2/3}t^{1/6}$ at a 91.5 cm. head of mercury. All half-wave potentials, unless stated otherwise, were referred to the saturated calomel electrode ($E_{1/2}$ *vs.* S.C.E.) and were determined with a Fisher Elecdropode.[3] All alcoholic solutions except the 90% ethanol solution, used in these studies had a cell resistance of less than 1000 ohms and the iR drop correction was therefore negligible in computing $E_{1/2}$ values.[4] Viscosities of the solutions were determined by means of an Ostwald viscosimeter and densities were obtained by means of a pycnometer. Small Pyrex beakers (30 ml.) were used as polarographic cells. Dissolved oxygen was removed from all solutions with pure nitrogen just prior to the polarographic examination. The nitrogen was passed through a portion of the solution being examined polarographically and finally through the solution in the polarographic cell. "Apparent" *p*H values for the alcohol solutions were determined with a model "G" Beckman *p*H meter.

Materials.—Tetramethylammonium chloride (Eastman Kodak, practical grade) was used as the supporting electrolyte for polarographic and diffusion coefficient studies. Several solutions were used in this work. Solution A was 75% ethanol and 0.1 M in tetramethylammonium chloride. Solution B was 90% ethanol and 0.1 M in tetramethylammonium chloride. Both solutions contained 10 ml. of a 0.1% alcoholic solution of methyl red per 500 ml. of solution. Solution C was 75% ethanol and 0.5 M tetramethylammonium chloride. Redistilled mercury was used as the anode in all beakers for polarographic studies. Potassium chloride, C.P. grade, was used in standardizing the cells for diffusion coefficient measurements. Glycerol trinitrate was obtained from Kieselguhr dynamite by a high-vacuum distillation in a Hickman still. The material analyzed 99.2% by the titanous chloride method.[5] A semi-micro Dumas nitrogen analysis showed the material contained 18.33% nitrogen. This value agrees with the titanous chloride analysis. Ethylene glycol dinitrate was prepared by the method of Rinkenbach.[6] The material had a sp. gr. of 1.485 at 25°.

Pentaerythritol tetranitrate was prepared by nitration of a good grade of pentaerythritol. The material analyzed 99.8% by the titanous chloride method.

n-Butyl nitrate was obtained from City Chemical Company, New York. The material was not further purified and had a value for n^{25}D of 1.4050. Buffer solutions used in polarographic studies were Britton and Robinson buffers.[7] Five milliliters of the buffer was added to 25 ml. of ethanol–water system. The buffer concentration was about 0.1 M in all solutions.

Diffusion Coefficient Measurements.—The diffusion coefficients were determined by a procedure adapted from that employed by Stokes.[8] In this method, porous diaphragm cells were used, which embodied a magnetic stirring mechanism. The cells were calibrated by the usual method of allowing 0.1 M potassium chloride to diffuse into water at 25° until 25% had passed through the diaphragm. The diffusion constant of potassium chloride for these conditions is known to be 1.867×10^{-5} cm.^{2}/sec. (Stokes above).

Results and Discussions

Polarographic Studies.—The nitrate esters were studied polarographically in 0.1 and 0.5 M $(CH_3)_4NCl$ solutions that were 75 and 90% ethanol, respectively. Since the hydrogen ions have a standard free energy that is different in alcoholic media than in aqueous media, the *p*H of these solutions is only an "apparent *p*H." The "apparent *p*H" of these solutions was 5.1 with a *p*H meter.

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[1] F. Kaufman, H. J. Cook and S. M. Davis, THIS JOURNAL, **74**, 4997 (1952).

[2] N. Radin and T. DeVries, *Anal. Chem.*, **24**, 971 (1952).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 192.

[4] Reference 3, p. 193.

[5] W. W. Becker, *Ind. Eng. Chem., Anal. Ed.*, **5**, 152 (1933).

[6] William Rinkenbach, *Ind. Eng. Chem.*, **18**, 1195 (1926).

[7] H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1456 (1931).

[8] R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

Glycerol trinitrate gives one well-defined wave in neutral media (*p*H 5.1). In alkaline media, however, the one wave appears to break up into two small waves whose combined wave height is only about 25% that of the one wave in neutral media (Table I). Apparently an alkaline hydrolysis of the polynitrate ester occurs. Results with *n*-butyl nitrate did not produce a double wave. This suggests that the secondary ONO_2 group in glycerol trinitrate may be more readily attacked by hydroxyl ion; while a primary ONO_2 group, such as present in *n*-butyl nitrate, may be quite resistant to hydroxyl ion at room temperature. Glycerol trinitrate in acidic media gives one poorly defined wave. The end of the wave is made indefinite through encroachment of a wave apparently due to hydrogen ion. As the apparent *p*H of the solution approaches five, the definity of the glycerol trinitrate wave improves. Excellent waves are obtained around *p*H 5.0. The same effect was observed with butyl nitrate.

TABLE I

MILLIMOLAR SOLUTION OF GLYCEROL TRINITRATE (75% Ethanol, 0.1 *M* $(CH_3)_4NCl$)

*p*H "Apparent"		$E_{1/2}$, volts	i_d, μa.	Remarks
1.5[a]		−1.02	20.90	Wave poorly-defined
5.1		−0.83	9.48	Wave well-defined
12.8[b]	(1)	−0.60	1.38	Wave fairly well-defined
	(2)	−1.16	0.66	Wave fairly well-defined

[a] Contains 2 drops of concentrated HCl per 20 ml. [b] Contains 5 drops of a 10% solution of $(CH_3)_4NOH$ per 20 ml.

EGDN and PETN give one well-defined wave, respectively, in 0.1 *M* $(CH_3)_4NCl$ ethanol solutions (Table II). The diffusion current (i_d) increases with an increasing number of ONO_2 groups in the molecule and the half-wave potentials become more positive with an increasing number of ONO_2 groups in the molecule (Table II). The larger number of ONO_2 groups in the molecule affect the slope of the wave considerably. For example, a millimolar solution of *n*-butyl nitrate requires about 0.3 volt increment in voltage for polarographic reduction, while glycerol trinitrate requires about 0.6 volt range.

TABLE II

MILLIMOLAR SOLUTIONS OF NITRATE ESTERS IN ETHANOL ("APPARENT" *p*H 5.1)

Nitrate ester	Concn., m*M*/l.	$E_{1/2}$, volts	i_d, μa.	Remarks
$C_4H_9ONO_2$	1.09[a]	−1.02	3.72	Wave well-defined
$C_2H_4(ONO_2)_2$	2.16[a]	−0.92	12.60	Wave well-defined
$C_3H_5(ONO_2)_3$	1.00[a]	− .83	9.48	Wave well-defined
$C_5H_8(ONO_2)_4$	1.00[b]	− .80	11.94	Wave well-defined

[a] 75% Ethanol, 0.1 *M* $(CH_3)_4NCl$. [b] 90% Ethanol, 0.1 *M* $(CH_3)_4NCl$.

In order to test the electrode process for diffusion control, the height of the mercury column (*h*) was changed and the effect of i_d with this change was studied (Table III). From the data it appears that the diffusion current (i_d) is dependent upon the height of the mercury column (i_d varies as $h^{-1/2}$) and thus the reduction is diffusion-controlled. Since $E_{1/2}$ appears to depend upon concentration (Table IV), although the change is slight in the range studied, and since plots of log $i/(i_d - i)$ do not give a linear relationship, the process at the cathode appears to be irreversible.

TABLE III

EFFECT OF MERCURY COLUMN HEIGHT ON i_d OF GLYCEROL TRINITRATE

75% Ethanol, 0.1 *M* $(CH_3)_4NCl$ with 0.01% methyl red; Capillary 1, $m^{2/3}t^{1/6}$ = 1.35 mg.$^{2/3}$ sec.$^{-1/2}$

Mercury column(*h*), cm.	i_d, μa.	$i_d h^{-1/2}$
100.3	10.62	1.06
91.5	10.47	1.09
75.6	9.96	1.15
52.1	7.50	1.04

Since hydrogen ions participate in the electrode reaction with most organic reductions,[9] the *p*H of the solution must be kept constant if $E_{1/2}$ values are to be duplicated. Table IV shows the effect of a buffered and unbuffered solution upon the $E_{1/2}$ value of glycerol trinitrate. The $E_{1/2}$ values are 130–140 millivolts more positive in the unbuffered solutions. From *p*H 4.0 to 11.0 the reduction seems to be independent of *p*H (Table V). Since diffusion currents were poorly defined in acidic media through encroachment of a hydrogen ion wave with that of the ester, no accurate comparison of i_d values could be ascertained. However, from *p*H 6.0 to 11.0 only slight lowering of the diffusion current constant was observed. This may be due to some alkaline hydrolysis of glycerol trinitrate in the alkaline solutions. With simple nitrate esters, Kaufman, *et al.*, found no appreciable change in i_d with *p*H beyond a *p*H of 6.0. No change in i_d was observed for *n*-butyl nitrate in unbuffered solutions at *p*H values of 5 and 13, respectively (Table VI).

TABLE IV

GLYCEROL TRINITRATE IN BUFFERED AND UNBUFFERED SOLUTIONS

75% Ethanol, 0.5 *M* $(CH_3)_4NCl$ with 0.01% methyl red; Capillary 2, $m^{2/3}t^{1/6}$ = 1.048 mg.$^{2/3}$ sec.$^{-1/2}$

Buffered (0.1 *M*, *p*H 9)			Unbuffered		
Concn. m*M*/l.	i_d μa.	$E_{1/2}$, volts	Concn., m*M*/l.	i_d, μa.	$E_{1/2}$, volts
0.50	4.86	−0.83	0.53	5.46	−0.70
1.00	9.60	− .84	1.00	9.60	− .70
2.00	19.50	− .85	2.00	18.75	− .71
3.00	29.70	− .85	3.06	27.22	− .72
..	...	....	5.21	46.65	− .75

TABLE V

EFFECT OF *p*H ON i_d AND $E_{1/2}$ OF GLYCEROL TRINITRATE

75% Ethanol, 0.5 *M* $(CH_3)_4NCl$ with 0.01% methyl red, 0.1 *M* buffer; Capillary 2, $m^{2/3}t^{1/6}$ = 1.048 mg.$^{2/3}$ sec.$^{-1/2}$

*p*H "Apparent"	$E_{1/2}$, volts	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	Remarks
4.0	−0.83	..	End of wave poorly-defined
5.0	− .83	..	End of wave poorly-defined
6.3	− .83	9.33	Wave well-defined
7.9	− .82	9.22	Wave well-defined
9.2	− .82	9.16	Wave well-defined
11.1	− .82	8.76	Wave well-defined

The effect of the number of ONO_2 groups in the molecule on $E_{1/2}$ and the diffusion current constant

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(9) Reference 3, p. 624.

TABLE VI

1.09 MILLIMOLAR SOLUTION OF *n*-BUTYL NITRATE IN UNBUFFERED SOLUTION

75% Ethanol, 0.1 *M* $(CH_3)_4NCl$

*p*H "Apparent"	$E_{1/2}$, volts	i_d, μa.	Remarks
1.5[a]	−1.07	9.00	Wave poorly-defined
5.1	−1.02	3.72	Wave well-defined
12.8[b]	−0.83	3.72	Wave well-defined

[a] Contains 2 drops concd. HCl per 20 ml. [b] Contains 5 drops of 10% solution of $(CH_3)_3NOH$ per 20 ml.

(*I*) of the nitrate esters was studied in 75 and 90% ethanol solutions, respectively, that were 0.1 *M* in $(CH_3)_4NCl$ (Table VII). Values for $E_{1/2}$ appear to decrease about 100 millivolts for each ONO_2 group in the molecule, while values of *I* increased somewhat proportionally with each additional ONO_2 group present. Since the process measured, in determining values of *I*, is diffusion controlled, the result is in very good agreement with the number of electrons taking part in the cathodic reduction of one molecule of the ester as determined experimentally (Table IX).

TABLE VII

EFFECT OF NUMBER OF ONO_2 GROUPS IN THE MOLECULE ON $E_{1/2}$ AND DIFFUSION CURRENT CONSTANTS OF SOME POLYNITRATE ESTERS

Nitrate ester	Concn., m*M*/l.	$E_{1/2}$, volts	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
$C_4H_9ONO_2$	1.09[a]	−1.02	3.26
$C_2H_4(ONO_2)_2$	2.16[a]	−0.92	5.56
$C_3H_5(ONO_2)_3$	1.00[a]	− .83	9.05
$C_5H_8(ONO_2)_4$	1.00[b]	− .70	11.39

[a] 75% Ethanol, 0.1 *M* $(CH_3)_4NCl$. [b] 90% Ethanol, 0.1 *M* $(CH_3)_4NCl$.

The influence of solvent on $E_{1/2}$ and i_d values was studied with a millimolar solution of NG in acetone or ethanol. The supporting electrolyte was 0.1 *M* $(CH_3)_4NCl$. Only in 60, 75 and 95% ethanol solutions and the 90% acetone solutions was the wave for NG well-defined (Table VIII). Two poorly defined waves were obtained for NG in the lower ethanol concentrations. The $E_{1/2}$ value for NG was about 250 millivolts more negative in acetone than in ethanol. Both $E_{1/2}$ and i_d values are dependent upon solvent.

TABLE VIII

EFFECT OF SOLVENT ON $E_{1/2}$ AND DIFFUSION CURRENT CONSTANT OF A MILLIMOLAR SOLUTION OF GLYCEROL TRINITRATE (1.055 *M*, 0.1 *M* $(CH_3)_4NCl$)

Solvent, %	$E_{1/2}$ (*vs.* Hg pool), volts	*id*, μa,	Remarks
90[a]	−1.00	7.80	One wave, well-defined
15[b]	−0.54[c]	11.13[c]	Two waves, poorly-defined
25[b]	− .61[c]	10.26[c]	Two waves, poorly-defined
50[b]	− .75[c]	9.00[c]	Two waves, poorly-defined
60[b]	− .79	9.39	One wave, well-defined
75[b]	− .84	9.54	One wave, well-defined
95[b]	− .77	12.48	One wave, well-defined

[a] Acetone. [b] Ethanol. [c] Values determined on total wave.

Diffusion Coefficient Measurements.—The porous diaphragm cell method with magnetic stirring was selected for this work as a simple, accurate method. The use of magnetic stirring simultaneously limits the diffusion path to the interior of the diaphragm and stirs the compartment of the cell. Identical conditions of diffusion path length and homogeneity of the bulk solutions are assured even if the solutions differ from the calibrating solution in solvent and viscosity, as was the case in these measurements. The concentration of the solutions in the compartments at the conclusion of a diffusion run were determined polarographically and the diffusion coefficient, *D*, was calculated using the equation

$$D = \frac{1}{K_t} \log \frac{C_1 + \frac{v_2}{v_1} C_2}{C_1 - C_2}$$

where *K* is the cell constant determined by KCl calibration, *t* is the diffusion time, v_1 and v_2 are the compartment volumes and C_1 and C_2 are the final concentrations in the two compartments.

For comparison, diffusion coefficients were calculated by means of the Stokes–Einstein equation

$$D_{SE} = \frac{2.96 \times 10^{-7}}{\eta (V_m)^{1/3}} \text{ cm.}^2 \text{ sec.}^{-1} \text{ at } 25°$$

where

η = soln. viscosity in dyne sec. cm.$^{-2}$
V_m = molar volume (mol. wt.)/(density)

The data reported in Table IX compare values of *D* calculated by the Stokes–Einstein equation and the experimental values determined by the magnetic stirring method reported herein. Assuming values of (*n*) and substituting these in the Ilkovic equation the diffusion coefficients calculated are considerably lower than the values obtained experimentally. The value $(D_{SE}/D_m)^{1/2}$ in the table is a measure of the error involved if the Stokes–Einstein equation is used to determine the number of electrons in the reduction of one molecule of the nitrate ester. The data (Table IX) show the ratio approaches 1 as the molecular size increases. This trend in the diffusion coefficient data, as calculated by the Stokes–Einstein equation, has been reported by Radin and DeVries[2] for the nitroalkanes. They indicated that in methanol, for molecules as large as nitrobutane or larger, the Stokes–Einstein equation could be used to calculate diffusion coefficients for polarographic use. Since nitrobutane has a molecular weight of only 103 and the nitrate esters investigated in this work have molecular weights up to 316, it would seem that experimental values for *D* are considerably more reliable for determining the number of electrons involved in the reduction of a

TABLE IX

DIFFUSION COEFFICIENTS AND *n*-VALUES FOR SOME NITRATE ESTERS[a,b]

Nitrate ester	D_{SE} × 10^5	D_m × 10^5	$(D_{SE}/D_m)^{1/2}$	n_m	n_{SE}
$C_4H_9ONO_2$	0.304	0.762	0.671	1.94	1.3
$C_2H_4(ONO_2)_2$	.314	.619	.712	3.90	2.8
$C_3H_5(ONO_2)_3$	.282	.500	.751	6.12	4.5
$C_5H_8(ONO_2)_4$	.346	.433	.834	7.97	6.7

[a] n_{SE} and D_{SE}, calculated from Stokes–Einstein and Ilkovic equations. [b] n_m and D_m, calculated from measured *D* values and Ilkovic equation.

molecule at the dropping mercury electrode. The values of n_{SE} (Table IX) are certainly unreliable. However, the values of n_m as calculated from the average of three experimental values of D are definitely 2, 4, 6 and 8 for butyl nitrate, ethylene glycol dinitrate, glycerol trinitrate and pentaerythritol tetranitrate, respectively.

From the polarographic data and the number of electrons involved in the reduction of one molecule (as calculated from Ilkovic equation with experimentally determined values of D) of a polynitrate ester, it appears that each ONO_2 group in the molecule reduces in a 2-electron step. This has been shown to give an alcohol and nitrite ion as the products

$$RONO_2 + 2e^- \longrightarrow RO^- + NO_2^-$$
$$RO^- + H_2O^- \longrightarrow ROH + OH^-$$

Thus, for glycerol trinitrate the following over-all reduction probably takes place at the dropping mercury electrode in neutral or slightly acidic solutions.

$$C_3H_5(ONO_2)_3 + 6e^- + 3H_2O \longrightarrow C_3H_5(OH)_3 + 3NO_2^- + 3OH^-$$

It may be postulated that in alkaline solution the secondary ONO_2 group is readily attacked by the large concentration of hydroxyl ion and thus a more complicated process is involved. Polynitrate esters are certainly less resistant to attack by hydroxyl ion at room temperature than a simple nitrate ester such as *n*-butyl nitrate. Work now in progress on the alkaline decomposition of glycerol trinitrate may lead to an understanding of the reactions at the dropping mercury electrode in alkaline solution.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

The Polarography of Thallium(III)[1]

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The polarography of thallium(III) in chloride solutions has been investigated. Two diffusion current plateaus were found in Tl(III) polarograms; the first plateau can be interpreted to correspond to the reduction Tl(III) to Tl(I) and the second to the reduction Tl(III) to Tl(0)(Hg). The magnitude of both diffusion current plateaus is apparently controlled by the rate of diffusion of Tl(III). The diffusion current constants for the two-electron and three-electron reductions Tl(III) to Tl(I) and Tl(III) to Tl(0), were found to be 3.83 ± 0.03 and 5.72 ± 0.08, respectively, in 0.6 M HCl corresponding to a diffusion coefficient, D Tl(III) of 1.00×10^{-5} cm.^{2} sec.$^{-1}$. The diffusion current constant for Tl(I) in 0.6 M HCl was determined from separate experiments with Tl(I) solutions and found to be 2.65 ± 0.03, corresponding to D Tl(I) = 1.91×10^{-5} cm.^{2} sec.$^{-1}$, in reasonably good agreement with previously reported values. Polarograms from solutions containing both Tl(I) and Tl(III) were found to be suitable for analytical determination of Tl(I) and Tl(III). The half-wave potential of the "Tl(I)/(0) wave" for Tl(III) solutions was practically the same as that for Tl(I) in the same supporting electrolyte.

Although the polarography of thallium(I) has been studied extensively,[2-4] apparently only one note, by Hughes and Hush,[5] discusses the polarography of thallium(III). These authors found that for perchloric acid solutions, polarograms of Tl(III) had a "reproducible and well defined" diffusion current plateau which merged with the anodic dissolution current of mercury. This plateau is followed by a wave which on the basis of its half-wave potential was identified with the Tl(I)/(0) wave. The first diffusion current plateau was thus assumed to result from the reduction of Tl(III) to Tl(I), and the second plateau was assumed to result from the reduction of Tl(III) to Tl(0). Since mercury dissolution occurs at a more negative potential than the Tl(III)/(I) reduction potential[6] a polarographic "half-wave" for the Tl(III)/(I) reduction is not observed. No values were given for the diffusion current constants of Tl(III).

The present investigation was primarily concerned with the measurement of diffusion current constants of Tl(III) from the Tl(III)/(I) and the Tl(III)/(0) reduction currents in chloride solution to test the possibility of utilizing polarographic methods for the determination of Tl(I) and Tl(III) in Tl(III)–(I) mixtures. Half wave potentials of the Tl(I)/(0) wave in Tl(III)–(I) mixtures were also measured and compared with previously reported values for Tl(I) solutions.

Experimental

Tl(I) stock solutions (*ca.* 10^{-3} M Tl) were prepared by dissolving recrystallized nitrate-free[7] thallous chloride in 0.1, 0.6 and 1.0 M HCl or 0.1 M KCl containing 5×10^{-3} M HCl. Tl(III) stock solutions were prepared from Tl(I) solutions by oxidation with chlorine gas. Thallium concentrations were determined by iodometric[8,9] titration after removal of the excess chlorine with phenol.

Polarograms were recorded in an air conditioned room at 25 ± 1° with a Sargent Model XXI recording polarograph. A polarographic cell having a capacity of about 20 ml. was used in conjunction with a KCl–agar bridge and a saturated calomel reference electrode. Oxygen (or excess chlorine) was purged from the solutions with nitrogen purified by passing through a train of ammoniacal cuprous chloride or, in some cases, through copper turnings at 500°. When the solutions contained chlorine, the dropping mercury electrode was introduced after the chlorine had been expelled, to

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[3] L. Meites, *ibid.*, **73**, 4257 (1951).

[4] "Bibliography of Polarographic Literature," Leeds and Northrup Co., Philadelphia, Pa., 1950.

[5] G. K. Hughes and N. S. Hush, *Aust. J. Sci.*, **10**, 184 (1948).

[6] The potential of the Tl(I)/(III) couple is −1.25 v. (*vs.* H_2 electrode); W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 2nd Ed., 1952.

[7] By brucine sulfate test—F. Feigl, "Spot Tests," Elsevier Press, New York, N. Y., 3rd Ed., 1946.

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., The Macmillan Co., New York, N. Y., 1947.

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