The Electrolytic Reduction of Simple Nitrate Esters[1]

BY FREDERICK KAUFMAN, HELEN J. COOK AND STANLEY M. DAVIS

The polarography and large scale reduction of ethyl and cyclohexyl nitrate were studied. Between pH 3 and 13, a pH-independent reduction wave was obtained and the reduction found to be diffusion controlled. A two-electron reduction mechanism with alcohol and nitrite ion as products was established and found to be consistent with all observations. The polarography of these nitrate esters in the presence of Ce^{+++}, La^{+++}, UO_2^{++} was also studied and the behavior of nitrite ion at the dropping mercury electrode in the presence of uranyl ion was reinvestigated.

Introduction

In the course of various investigations into the physical and chemical properties of propellants it became apparent that the electrochemistry of even the simple nitrate esters had never been studied. An investigation of the polarography of nitrate esters was therefore begun with the aim of examining its possible usefulness in analysis as well as establishing the mechanism of reduction at the dropping mercury electrode. Added interest in such a study came from the somewhat anomalous behavior of inorganic nitrate and nitrite ion. While in early work on the polarography of NO_2^- and NO_3^- in the presence of Ce^{+++}, La^{+++}, Li^+ and UO_2^{++2-4} the observed waves had been ascribed to a catalytic reduction of nitrate or nitrite, Meites[5] has recently shown that for Li^+ and Ce^{+++} this wave is actually due to the catalytic reduction of water or hydronium ion. The same interpretation will undoubtedly apply to La^{+++}, but the effect of UO_2^{++}, which produces a catalytic wave at a much more positive potential will probably require a different explanation. The polarographic behavior of ethyl and cyclohexyl nitrate was therefore examined both in the absence and presence of Ce^{+++}, La^{+++} and UO_2^{++}. Experiments on large scale cathodic reduction were also run to test polarographic results and suggested reduction mechanisms.

Cyclohexyl nitrate was chosen for much of this investigation since it is less volatile than the lower members of the series, contains a ring structure and secondary ester linkage, and thereby represents a closer analogy to the sugar nitrates and cellulose nitrate which are of general interest to this Laboratory.

Experimental

All polarograms were obtained on a Leeds and Northrup Electrochemograph, Model 42200-Al, using three different capillaries. Because of the time lag of the instrument, all half-wave potentials were determined manually. The temperature was controlled to ±0.2°.

All inorganic chemicals were reagent grade. Clark and Lubs buffer solutions were prepared from recrystallized boric acid, potassium dihydrogen phosphate and potassium acid phthalate.

Oxygen removal turned out to be an unpleasant problem. After trying several methods we adopted the following procedure: the solution containing everything except the ni-trate ester was thoroughly deaerated with purified nitrogen, a concentrated solution of the ester was added, a magnetic stirrer turned on for a few seconds, and the polarogram recorded.

Preparations.—Ethyl nitrate was fractionally distilled twice and the middle fraction used.

Cyclohexyl nitrate was prepared by simultaneous slow addition of cyclohexanol and 100% nitric acid to acetic anhydride at room temperature followed by washing, drying and repeated fractional distillation at reduced pressure; b.p. 171° at 760 mm., 92–93° at 37 mm., d^{25}_{25} 1.099, $n^{24}D$ 1.4542.

Anal. Calcd. for $C_6H_{11}O_3N$: C, 49.64; H, 7.64. Found: C, 49.92; H, 7.21.

Large scale reductions were carried out using an all-electronic constant potential reduction and oxidation apparatus to be described elsewhere.[6] In several reduction experiments on ethyl and cyclohexyl nitrate in aqueous and alcoholic solutions, the total quantity of electrical charge was measured by mercury coulometer and also by graphical integration of the current *vs.* time plot using a calibrated ammeter.

The ethyl alcohol produced was analyzed by fractional distillation, density measurements, and preparation of derivatives. Cyclohexanol was determined with far less accuracy by ether extraction and weighing.

Nitrite ion concentration was determined by a modification of the Griess test on a Beckman spectrophotometer, model DU. In this method, 5 ml. of the unknown nitrite solution (diluted to 1 to 5 × 10^{-5} M) was treated with 0.5 ml. of a 1% solution of sulfanilic acid in glacial acetic acid, and with 0.5 ml. of a solution containing 0.1 g. of α-naphthylamine in 75 ml. of glacial acetic acid and 175 ml. of water. The resulting solution was allowed to stand at room temperature for 10 minutes and its optical density at 4700 Å. was measured. Known solutions of alkali nitrites served as standards. Nitrate esters did not interfere.

Results and Discussion

The Polarography of Cyclohexyl Nitrate.—For reasons of solubility most of the work on cyclohexyl nitrate was carried out in 11.25% ethanol by weight (1 ml. of 95.5% ethanol and 6 ml. of water). In this medium a well-developed single wave was obtained at all pH values between 3 and 13 in buffered solutions containing 0.1 to 0.5 M KCl, LiCl or $N(CH_3)_4Cl$. In buffered solutions of higher ethanol concentrations with LiCl, or $(CH_3)_4NCl$, as supporting electrolyte as well as in all similar solutions of ethyl nitrate (there ranging from completely aqueous to 95.5% ethanol) a single wave was observed with $E_{1/2}$ values from about -0.6 to -1.3 v. depending on exact composition and described in greater detail below.

In order to test diffusion control and reversibility, two criteria were applied: The dependence of the diffusion current, i_d, on the height, h, of the mercury column was determined, and from the data in Table I the reduction appears to be diffusion-controlled.

Reversibility was tested by plotting $\log i/(i_d - i)$

(1) Presented in part at the Detroit Meeting of the American Chemical Society, April, 1950.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 314–317.

(3) I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

(4) B. Keilin and J. W. Otvos, *ibid.*, **68**, 2665 (1946).

(5) L. Meites, *ibid.*, **73**, 4115 (1951).

(6) To be submitted shortly for publication to *Anal. Chem.*

TABLE I

2.48 mM CYCLOHEXYL NITRATE IN 11.25 WT. % ETHANOL, 0.5 M LiCl, 0.01% GELATIN

h_{eff}, cm.	i_d, μa.	$i_d h^{-1/2}$
53	14.9	2.05
48	14.0	2.03
43	13.4	2.04
38	12.5	2.03
33	11.5	2.00

$h_{eff} = h_{measured} - 2$ cm.

vs. E along several waves. Such plots were not entirely linear and even in the nearly linear portion, calculated values of n, the number of electrons taken up, turned out to be only 0.5 to 0.6. Moreover, $E_{1/2}$ was found to depend on concentration as shown in Table II.

TABLE II

CYCLOHEXYL NITRATE IN 11.25 WT. % ETHANOL, 0.5 M LiCl, 0.01% GELATIN

C, mM	$E_{1/2}$ vs. S.C.E.[a]
2.48	−0.65
1.24	− .60
0.62	− .57
0.31	− .56

[a] With a measured cell resistance of 400 Ω, the iR correction to $E_{1/2}$ is negligible.

The reduction therefore is irreversible, especially in view of the clear result that $n = 2$ from other experimental evidence described below.

Even though the reproducibility of i_d values was never as high as that of entirely non-volatile compounds, the proportionality of i_d and C was found to hold quite well (Table III).

TABLE III

CYCLOHEXYL NITRATE IN 11.25 WT. % ETHANOL, 0.5 M KCl, 0.1 M BUFFER pH 9, 0.01% GELATIN

C, mM	i_d, μa.	$\dfrac{i_d}{C}$, $\dfrac{μa.}{mM}$
2.80	15.0	5.36
2.16	11.63	5.38
1.08	5.85	5.42
0.72	3.84	5.33
.54	3.03	5.61

Polarograms were run at many different pH values between 1 and 13 and the results are presented in Table IV.

TABLE IV

2.27 mM CYCLOHEXYL NITRATE IN 11.25 WT. % ETHANOL, 0.5 M LiCl, 0.1 M BUFFER, 0.01% GELATIN, $m^{2/3}t^{1/6} = 1.84$ MG.$^{2/3}$ SEC.$^{1/2}$

pH	$E_{1/2}$ vs. S.C.E.	i_d, μa.	pH	$E_{1/2}$ vs. S.C.E.	i_d, μa.
1	[a]	36	6	−0.63	12.7
2	[a]	35	9	− .63	13.0
3	−0.61	14.2	10	− .65	13.0
4	− .64	12.7	13	− .61	12.4
5	− .64	12.7			

[a] Long drawn-out double wave.

Listed pH values are nominal and strictly correct only in aqueous solution, the effect of the ethanol having been neglected. The effect of gelatin, the
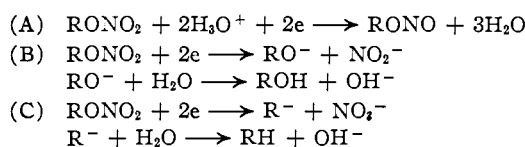
maxima suppressor, on $E^{1/2}$ and i_d was checked on unbuffered and buffered solutions of the ester in 11.25 wt. % ethanol, 0.5 M KCl. There was no change in i_d and only a slight change in $E^{1/2}$, with the half-wave potential about 0.03 v. more positive in the presence of gelatin. (Throughout this investigation, mercury drop times at −1.2 v. were between 3.5 and 4 sec.)

From pH 3 to 13 the reduction seems entirely independent of pH. In acid solution (pH 1 and 2), a large smeared-out double wave is obtained. This double wave looks like a superposition of the smaller ester wave as obtained at higher pH plus the wave given by free nitrous acid, a comparison which is described later in greater detail for ethyl nitrate (Fig. 1). The Ilkovic equation

$$n = \frac{i_d}{607 C D^{1/2} m^{2/3} t^{1/6}}$$

as well as large scale electrolysis experiments can be utilized to determine n, the number of electrons taken up. Setting $C = 2.27$ mM per liter $m^{2/3}t^{1/6} = 1.84$ mg.$^{2/3}$ sec.$^{-1/2}$, $i_d = 13.0$ μa. one still needs a value for D, the diffusion coefficient. From conductance data on ions of comparable size such as benzoate, o-chlorobenzoate, acid phthalate and o-nitrobenzoate, a range for D from 8 to 9 × 10^{-6} cm.^{2} sec.$^{-1}$ seems reasonable. i_d is then corrected for the ethanol content of the solvent by assuming that cyclohexyl nitrate behaves similarly to ethyl nitrate whose i_d is given in a later section as a function of % ethanol (Table VIII). This correction can be regarded as a viscosity effect, but it is apparent from the calculation that its exact magnitude is not critical. The range of values for n obtained in this manner is 1.99 to 2.08, so undoubtedly $n = 2$.

Several possible two electron reductions may now be considered.

(A) $RONO_2 + 2H_3O^+ + 2e \longrightarrow RONO + 3H_2O$

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

(C) $RONO_2 + 2e \longrightarrow R^- + NO_3^-$
 $R^- + H_2O \longrightarrow RH + OH^-$

Schemes A and C are not borne out by large scale reductions. Neither nitrite ester nor hydrocarbon was ever found to be a product of the reduction, whereas alcohol and nitrite ion were actually found in good yield. Moreover, cyclohexyl nitrite was found to be reducible at approximately the same potential as cyclohexyl nitrate, giving diffusion currents of comparable magnitude.

The polarographic behavior of cyclohexyl and ethyl nitrate at pH 1 and 2 is further evidence for scheme B. As stated earlier, the nitrate ester wave in acid solution can be described as the sum of the ester wave and the diffuse wave given by acidified nitrite ion solutions. Such a correlation is shown in Fig. 1. Curve 1 is the total wave of ethyl nitrate at pH 2. Curve 2 is constructed by subtracting the pH-independent ester wave of an equal concentration of ester from curve 1. This should represent the contribution due to nitrous acid at pH 2 which was obtained independently in curve 3. The match of 2 and 3 is reasonably good. It should be noted, also, that the concentration of

nitrous acid in curve 3 is considerably lower than that produced in the reduction of the ester. This is not surprising, since the HONO in the acid ester wave is supplied to the dropping mercury electrode by the diffusion of ester whose diffusion coefficient is certainly lower than that of HONO.

Large Scale Reduction Experiments.—Controlled potential reductions at a mercury cathode of ethyl and cyclohexyl nitrate confirmed the polarographic results (Tables V and VI).

TABLE V

REDUCTION OF CYCLOHEXYL NITRATE IN 67.4 WT. %
ETHANOL, 0.5 M $(CH_3)_4NCl$, E = -1.1 to -1.3 v. vs. S.C.E.

Quantity, mole	Faradays per mole	Yield ROH, %	Yield NO_2^-, %
0.070	2.02	72	72
.054	2.26	..	56
.039	2.38	52	105

TABLE VI

REDUCTION OF ETHYL NITRATE IN 1 M Na_2SO_4, E = -1.8 v. vs. S.C.E.

Quantity, mole	Faradays per mole	Yield ROH, %	Yield NO_2^-, %
0.060	2.15	..	75
.060	1.94	..	64
.121	2.35	97	..

The average value of n was 2.18 ± 0.14, an accurate determination of ethanol gave a 97% yield, while the very much poorer analysis for cyclohexanol gave 50 to 70%. Nitrite ion analysis was complicated by the fact that nitrite ion was itself slowly reduced at a potential of -1.8 v. This would lead to high values for n and low yields of nitrite. Moreover, a few reduction experiments on two dinitrates, cis- and trans-1,2-cyclohexanediol dinitrate, gave n = 4 with high accuracy, and produced the corresponding diols in good yields

The Influence of Chemical Structure and Solvent on the Polarography of Nitrates.—The effect of changing the alkyl group R in $RONO_2$ on $E_{1/2}$ and i_d was studied only in a few instances (Table VII).

TABLE VII

$RONO_2$ IN 11.25 WT. % ETHANOL, 0.5 M LiCl, 0.01% GELATIN

R	$\dfrac{i_d}{Cm^{2/3}t^{1/6}}$	$E_{1/2}$ vs. S.C.E.
Ethyl	3.39	-0.82
Cyclohexyl	3.06	$-$ .63
n-Hexyl	2.53	$-$ .54

The diffusion current decreases with increasing size as expected. The considerable decrease from cyclohexyl to n-hexyl may be somewhat too large, i.e., the i_d of n-hexyl nitrate too low. This could have been caused by the low solubility of that ester in the solvent so that on addition to water of a concentrated alcoholic solution, not all of the ester was immediately mixed. Moreover, the ester would have a higher vapor pressure, being closer to saturation than the other two, which would lead to greater volatilization losses. The trend in the $E_{1/2}$ values is not clear, though it should be remembered that here, too, differences in solvation, rather than in the nature of R, may have a controlling
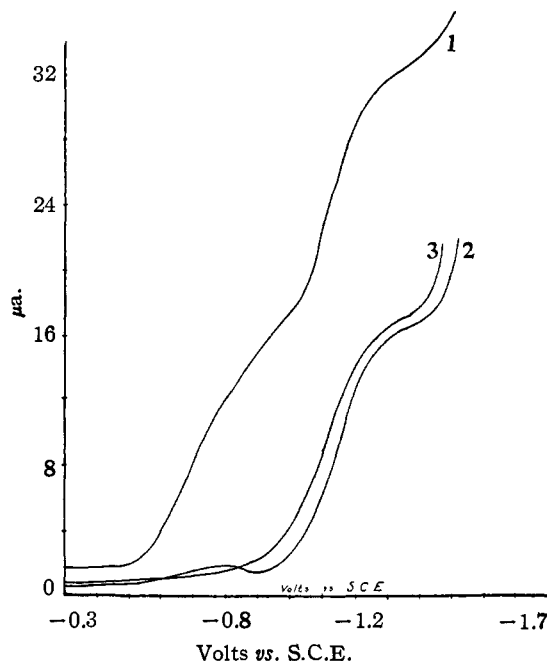

Fig. 1.—Comparison of polarograms of ethyl nitrate and sodium nitrite in acid solution: 1, 1.35 mM $C_2H_5ONO_2$ in 11.25 wt. % ethanol, 0.5 M LiCl, 0.01 M HCl, 0.01% gelatin; 2, (1) minus polarogram of 1.35 mM $C_2H_5ONO_2$, 11.25 wt. % ethanol, 0.5 M LiCl, 0.1 M buffer pH 10, 0.01% gelatin; 3, 1.09 mM $NaNO_2$ in same electrolyte as (1).

effect. Thus, the order of increasing solubility is also that of decreasing ease of reduction. Such an explanation would, of course, only be valid if the differences in solvation of the intermediates or products of the electrode reaction would be small compared to those of the reactants.

The influence of the solvent on i_d and $E_{1/2}$ was studied for ethyl nitrate over a wide range of ethanol-water mixtures (Table VIII).

TABLE VIII

ETHYL NITRATE IN ETHANOL–WATER, 0.3 M LiCl

Ethanol by weight, %	$\dfrac{i_d}{Cm^{2/3}t^{1/6}}$, obsd.	$E_{1/2}$ vs. S.C.E.[a]	$\dfrac{i_d}{Cm^{2/3}t^{1/6}}$, calcd.
0	3.96	-0.61	3.96
13.2	3.27	-0.85	3.08
37.3	3.00	-1.04	2.46
64.5	2.97	-1.17	2.55
95.5	4.02	-1.31	3.36

[a] The cell resistance was from 300 to 600 Ω, the iR drop correction therefore negligible.

The only predictable effect on i_d is that due to a change in D. If the Einstein–Stokes equation holds, this means that D = Const. η^{-1} where η is the viscosity of the solvent, and that therefore i_d = Const $\eta^{-1/2}$. i_d is calculated in this way in column 4 of Table VIII. The constant was obtained from i_d in water and interpolated viscosities used from the "Handbook of Chemistry and Physics" (1949 Edition). While the general trend is correctly represented, the numerical agreement is poor. The large change in $E_{1/2}$ with increasing ethanol content of the solvent is somewhat surprising, especially when it is considered that for Cd^{++}, $E_{1/2}$ is unchanged from 0 to about 50%

ethanol when measured under similar conditions. A possible explanation might be that an intermediate such as $RONO_2^-$ is first formed and that this ion would be more stable in a medium of high dielectric constant.

The Polarography of Nitrates in the Presence of Ce^{+++}, La^{+++} and UO_2^{++}.—Polarograms of ethyl and cyclohexyl nitrate in the presence of Ce^{+++}, La^{+++} and UO_2^{++} appeared as the superposition of the ester wave and of that attributed to nitrite ion (similar to nitrate). In Ce^{+++} and La^{+++} solutions, the normal (pH-independent) ester wave preceded the sharp nitrite wave as would be expected, since the pH of the solutions was above 3. In the case of uranyl ion, on the other hand, the supporting electrolyte contains 0.01 M HCl and the drawn-out wave characteristic of the reduction of ester in acid solution precedes the sharp nitrite wave at -0.98 v. (Figs. 2, 3, 4).
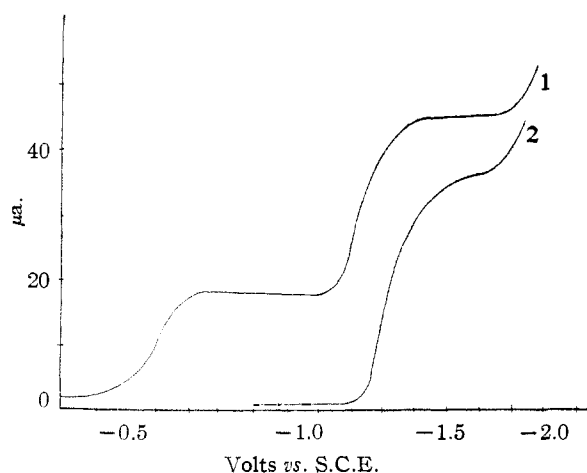
Fig. 4.—Uranyl chloride supporting electrolyte: 1, 1.05 mM $C_2H_5ONO_2$, 0.1 M KCl, 0.01 M HCl, 2 × 10^{-4} M UO_2Cl_2; 2, 0.695 mM $NaNO_2$ in same supporting electrolyte.

in the presence of 2.10^{-4} M UO_2Cl_2 and 0.01 M HCl. To these solutions, enough sulfamic acid or sodium azide was added to give concentrations of 0.01 M and the solutions were polarographed again. The nitrite wave had disappeared entirely and only the small blank due to UO_2^{++} remained. This was to be expected since the reactions

$$HN_3 + HONO \longrightarrow N_2 + N_2O + H_2O \quad (1)$$
$$NH_2SO_3^- + HONO \longrightarrow N_2 + HSO_4^- + H_2O \quad (2)$$
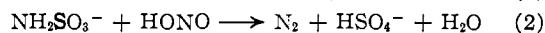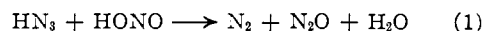
are known to go rapidly to completion in acid solution. Then, a similar sequence of polarograms was run substituting ethyl nitrate for nitrite ion. The results here were quite different. Addition of either azide or sulfamate left the second wave (due to NO_2^-) entirely unchanged, showing that the nitrite ion formed as an intermediate gives rise to a catalytic wave before the rapid reactions (1) or (2) can decrease its concentration.

Though the height of the nitrite wave in the polarograms of ester in the presence of Ce^{+++}, La^{+++} and UO_2^{++} was found to be irreproducible, it was never as high as that produced by an equal concentration of nitrite ion, but about 60% of that value for cyclohexyl and 75% for ethyl nitrate. This is understandable since it is diffusion of ester which furnishes the reducible nitrite. Therefore, the ratio of $I = i_d/Cm^{2/3}t^{1/6}$ for the second ester wave and for NO_2^- should be given by the ratio of $D^{1/2}$ of these species. With $D_{NO_2^-} = 19.2 \times 10^{-6}$, $D_{C_2H_5ONO_2} = 10.7 \times 10^{-6}$ and $D_{C_6H_{11}ONO_2} = 8.7 \times 10^{-6}$ cm.^{2} sec.$^{-1}$, the calculated ratios would be 67 and 75%, respectively, in good agreement with experiment.

After Meites' work[5] on NO_3^- in the presence of Ce^{+++}, it seemed clear that no real meaning could be attributed to any n value derived from diffusion currents of the nitrite wave under similar conditions. It was not surprising, therefore, that coulometric experiments on NO_3^- and NO_2^- in the presence of Ce^{+++} or La^{+++} gave entirely negative results, in agreement with the interpretation of a catalytic evolution of hydrogen. In the presence of uranyl ion, however, a real reduction of NO_3^- or NO_2^- may take place and it was of interest to study the nitrite part of the ester wave under these conditions. If nitrite ion were reduced at the

Fig. 2.—Cerous chloride supporting electrolyte: 1, 2.27 mM $C_6H_{11}ONO_2$ in 11.25 wt. % ethanol, 0.2 M $CeCl_3$, 0.01% gelatin; 2, 2.48 mM $NaNO_2$ in same supporting electrolyte.
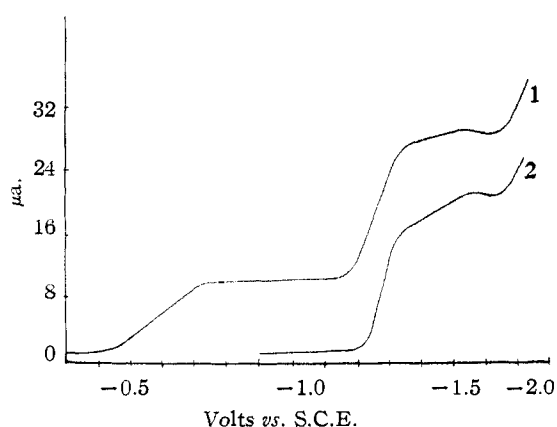
Fig. 3.—Lanthanum chloride supporting electrolyte: 1, 1.53 mM $C_6H_{11}ONO_2$ in 11.25 wt. % ethanol, 0.1 M $LaCl_3$, 0.01% gelatin; 2, 1.00 mM $NaNO_2$ in same supporting electrolyte.

In order to test to some extent whether nitrite ion ever becomes free to diffuse back into the solution, the following experiments were run. Polarograms of dilute nitrite ion solutions were obtained
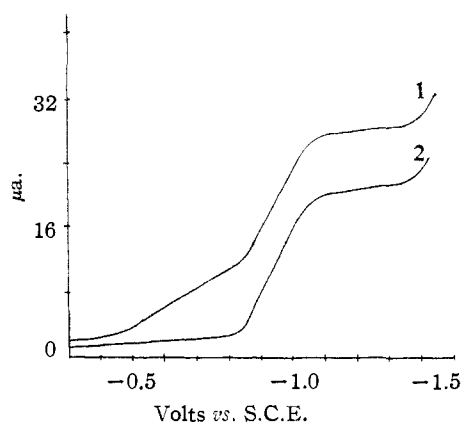
dropping mercury electrode then for a given n its i_d could be predicted from a knowledge of the diffusion coefficient of the ester. Since it was found that the observed waves were always somewhat higher than would be predicted on the basis of Keilin's result of $n = 3$, we decided to re-examine the diffusion currents of nitrite and nitrate ion. Good agreement with Kolthoff, et al.,[3] was obtained on NO_3^-, $I = 13.3$ microamperes/millimole/liter mg.$^{2/3}$ sec.$^{-1/2}$ as against 13.8 found by Kolthoff.

For nitrite ion, on the other hand, results were always higher than those of Keilin and Otvos[4] with

TABLE IX

PASSING N_2 THROUGH 0.448 mM NaNO$_2$ IN 0.1 M KCl, 0.01 M HCl, 0.2 mM UO$_2$Cl$_2$

t, min.	i_d, μa.	$\frac{\Delta i_d}{i_d} \times 100$	ml. N_2 passed through
0	7.62	..	0
15	7.56	0.8	0
25	6.86	9.3	530
40	5.94	13.4	855
60	5.54	6.7	520
75	5.44	1.8	0
155	4.34	20.2	1120

$I = 9.01$ as against 7.45 found by those authors. Their experimental procedure included the deaeration of the acidic nitrite solution with nitrogen. The error introduced by this procedure was estimated by Keilin and Otvos as due to the first-order decomposition of HONO to NO and NO_3^-. This excludes the direct loss of HONO which should be strongly dependent on the flow rate of nitrogen through the solution. The diffusion current of such a solution was therefore measured as a function of time and bubbling rate (Table IX).

The % decrease of i_d (column 3) is seen to be roughly proportional to the amount of N_2 passed through the cell and almost independent of the time interval. This suggests that the higher value of I as obtained by us is correct, but leads to $n = 3.4$. Preliminary coulometric experiments on the reduction of NO_3^- and NO_2^- at a quiescent mercury cathode have so far been unsuccessful and the uranyl-catalyzed nitrate and nitrite wave may also turn out to be a catalytic reduction of water or hydronium ion. Further work will be necessary to clarify this question.

ABERDEEN PROVING GROUND, MD.

Electrochemical Phenomena at a Rotating Mercury Electrode. I. Reduction of Metal Ions

BY T. S. LEE

A new type of polarized electrode is described. The diffusion current of metal ions was found to be strictly proportional to concentration in the range 10^{-4} to 10^{-7} M. In the same concentration range the half-wave potential of a given metal ion was found to be independent of concentration. Equations were derived for (1) the decrease of current with time at constant potential, (2) the dependence of current on potential, and (3) the relation of half-wave potentials to polarographic half-wave potentials. The theoretical equations were tested and were verified within experimental limits of error. The rotating mercury electrode is useful for the analysis of electro-reducible substances at very low concentrations in aqueous solutions.

The value of the *dropping mercury* electrode, as compared with other polarized electrodes, in analysis and in physico-chemical studies is due, in a large measure, to the following facts[1]: (1) electrochemical reactions at the dropping mercury electrode are highly reproducible, and, in the case of metal ions, usually reversible, and (2) the exceptionally high overvoltage of hydrogen on mercury permits the reduction of substances that are, thermodynamically, more difficult to reduce than the solvent, water or alcohol. The *rotating platinum* electrode (or the stationary platinum electrode in a stirred solution), which is also of considerable importance in analysis,[2] has the following advantages: (1) it yields a high diffusion current

for low concentration of reducible or oxidizable substances, and (2) the current does not fluctuate as does the current of the dropping mercury electrode. A *rotating mercury* electrode has not, apparently, been constructed previously, but the idea of combining the advantages of the dropping mercury and rotating platinum electrodes is probably familiar to many of those who are interested in polarography, voltammetry, amperometric titrations, and coulometric determinations. The rotating mercury electrode described below does, in fact, possess all of the advantages mentioned, but certain limitations as well.

Experimental

Electrode.—The details of the construction of the electrode and of the technique of analytical applications are described elsewhere.[3] The brief description given here is chiefly for the purpose of clarifying the discussion of results and theory. Figure 1 shows the electrode: a round plastic cup (one inch in diameter) with an annular groove on the inside edge. One-tenth ml. of mercury was put in the groove before each experiment. The centrifugal force on the mercury was five times that of gravity when the speed of rotation was 1200 r.p.m. Electrical contact with the mercury was made by platinum, gold or silver wire, the outer part of

(1) (a) J. Heyrovsky, "Polarographie," Springer-Verlag, Vienna, 1941, p. 11; (b) J. Heyrovsky, "Polarographisches Praktikum" in "Anleitungen für die chemische Laboratoriumspraxis," Vol. IV, Springer-Verlag, Berlin, 1948, p. 1; (c) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, Chap. IX and XII; (d) M. v. Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter and Co., Berlin, 1950, p. 6; (e) O. H. Müller, "Polarographic Method of Analysis," Chemical Education Publishing Co., Easton, Pa., p. 29.

(2) (a) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941); (b) I. M. Kolthoff and D. L. Leussing, *Z. anorg. Chem.*, **262**, 160 (1950).

(3) T. S. Lee, *Anal. Chem.*, in press.