conclusions from the $E_{1/2}$ of the peroxide wave in this medium, and possibly from the log plot also. The peroxide branch of the diagram in Fig. 2 was obtained from the first half of the wave, which can be observed fairly well in ammonia and in phosphate solution (*p*H 8) before the mercury dissolution wave completely obscures it. In general the wave appeared to be symmetrical in shape, with an apparent *n* value (on the basis of a reversible wave) of about 1.5. There is unfortunately only a narrow range of *p*H in which the peroxide wave can be observed in a truly irreversible state.

Discussion.—It may be worthwhile to discuss a simple model for the oxygen mechanism and compare the consequences with the experimentally observed facts. Thus the specific effects of *p*H and buffer components on the oxygen wave in acid and neutral medium may be dismissed as absorption effects, and the electron transfer be taken as the rate-determining step. The essential *p*H-independence of the reduction $E_{1/2}$ would require the following mechanism

$$O_2 + ne^- \longrightarrow O_2^{-n} \text{ (rate-determining)}$$
$$2H^+ + O_2^{-n} + (2 - n)e^- \rightleftarrows H_2O_2$$

where $n = 1$ or 2. By the same token the $E_{1/2}$ of the peroxide wave would be *p*H dependent, as is observed experimentally, since the rate-determining electron transfer would be preceded by an equilibrium involving the hydrogen ion. On the basis of absolute rate theory, for a unit change in *p*H the $E_{1/2}$ would be expected to shift $0.059/\beta$ v. for $n = 2$, and $0.059/1/2(1 + \beta)$ for $n = 1$, where β is the transfer coefficient for the oxidation reaction. From the data available it would appear that the actual shift lies somewhere between 0.059×1 and 0.059×2, a condition that could be satisfied by either value of *n*.

According to the same theory,[20] the apparent *n* value n_b of the oxidation reaction, as determined from the log plot, should be 2β and $1 + \beta$ for $n = 1$ and $n = 2$, respectively. If it is assumed that $\alpha = 1 - \beta$, it follows that the relation $n_b = 2 - n_a$ should hold regardless of the value of *n*. As stated above, $n_b = ca.$ 1.5, hence the apparent *n* value n_a of the oxygen reduction wave should be *ca.* 0.5. It has been shown that a reliable value for n_a cannot be measured, because of the deformation of the oxygen wave in different media. However, if the average of the two slopes in Fig. 7 is used, one obtains $n_a = 0.47$. In view of the uncertain value of both n_a and n_b, one must be cautious in attaching significance to this agreement.

The behavior mentioned in paragraph 3 is not consistent with the simple model discussed above. As the *p*H reaches values at which the reverse reaction (peroxide oxidation) becomes important, one would expect the reduction wave to move to more negative potentials along its entire length, and not have one part of the wave move backward while the other moves forward. The observed behavior suggests a radical change in the mechanism of reduction as the reaction approaches reversibility. It is conceivable, though unlikely, that the presence of HO_2^- in the solution in significant quantities might be connected with such a change in mechanism.

Acknowledgment.—The author is indebted to Prof. J. J. Lingane for helpful advice in the course of these experiments.

(20) D. M. H. Kern, THIS JOURNAL, **76**, 4234 (1954).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

Polarography of Nitrate Ion

BY JUSTIN W. COLLAT AND JAMES J. LINGANE

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The reduction of nitrate ion in the presence of certain catalysts has been studied by the method of controlled potential coulometric electrolysis at a large mercury cathode. Electricity consumption and chemical analyses show that in the presence of uranyl ion nitrate is reduced chiefly to hydroxylamine, while in the presence of lanthanum or cerous ions the predominant reduction products are hydroxylamine and ammonia. Reasons are given why these products should also obtain at the dropping mercury electrode. Polarographic reduction of nitrate ion in acid medium without any specific catalyst present has been discovered. Under these conditions nitrite is a major, although probably not the only, product.

Introduction

That nitrate and nitrite produce polarographic waves in certain supporting electrolytes is well known,[1] but there is no agreement among previous investigators on the nature of the reduction products.

From the relative heights of the cadmium ion and nitrate ion waves in the presence of multi-charged cations Tokuoka and Ruzicka[2] concluded that reduction proceeds all the way to ammonia. This conclusion rests on the assumption of equal diffusion coefficients for nitrate and cadmium ions, whereas in fact the diffusion coefficient of nitrate ion is more than twice as large as that of cadmium ion.

Kolthoff, Harris and Matsuyama[3] pointed out that the observed diffusion current constants, coupled with the assumption that the diffusion coefficient of nitrate ion in the test solutions is the same as at infinite dilution, indicates hydroxylamine as the reduction product in lanthanum chloride solution and elemental nitrogen in acidic uranyl solutions. This is, however, only a tentative conclusion. The fact that the true diffusion coefficient of nitrate ion in the actual solutions is uncertain makes impossible a more definite conclusion than that the *n*-value is close to 5 or 6, and probably not as large as 8.

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 2nd ed., 1952, p. 533.

(2) M. Tokuoka, *Collection Czech. Chem. Communs.*, **4**, 444 (1932); M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

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

Sinyakova and Karanovich[4] claimed that reduction of nitrate in cerous chloride solutions of *p*H 2.5 proceeds to elemental nitrogen, that nitride and hydroxylamine are the products in lanthanum and neodymium chloride solutions, and that nitrogen is not the reduction product in acidic uranyl solutions.

Most recently Meites[5] interpreted the nitrate wave in lithium and cerous chloride solutions as not being due to reduction of nitrate at all but the result of catalytic reduction of hydrogen ion. This conclusion is based mainly on coulometric electrolysis with the dropping electrode. The results were quite anomalous and susceptible to more than one interpretation.

Kaufman, Cook and Davis[6] expressed the opinion, unsupported by experimental evidence, that the nitrate and nitrite waves in acidic uranyl solutions may be the result of catalytic reduction of hydrogen ion rather than reduction of nitrate and nitrite ions.

These highly discordant conclusions reflect the uncertainties of the indirect evidence on which they are based. In the present study this problem has been attacked directly by coulometric analysis on the macro scale with a mercury cathode at controlled potential, in conjunction with direct identification and quantitative determination of the reduction products. The aim was to determine the reduction products under conditions that corresponded as closely as possible to those extant in the polarographic procedures, particularly as regards concentration of nitrate, and composition of supporting electrolyte.

In the experiments with lanthanum and cerous chlorides as "catalysts" the solutions were only slightly acid and unbuffered, just as in the polarographic procedures, and, since the reduction of nitrate removes hydrogen ion, the *p*H was observed continuously with a glass electrode and standard hydrochloric acid solution was added as needed to maintain the *p*H within narrow limits. Since the current density during the macro electrolysis was approximately the same as it would be at the dropping electrode, this technique ensured that the *p*H at the electrode surface (which, of course, is considerably higher than in the bulk of the solution) would be as closely as possible the same as with the dropping electrode. Buffers were not used for *p*H control because this would have produced conditions at the electrode surface drastically different from the polarographic conditions.

Although the value of the controlled potential coulometric technique for identifying polarographic reactions has been demonstrated with many different types of reactions,[7] it is not infallible. The possibility must be recognized that the actual final products of a prolonged electrolysis, whether on a macro scale with a mercury pool or on a micro scale with the dropping electrode itself, may differ from those primarily produced under polarographic conditions at the dropping electrode as a result of nonelectrolytic reactions subsequent to the primary electrode reaction (rearrangements, disproportionation, etc.).[7] A difference in the over-all *n*-value in the two cases is also possible if the current under polarographic conditions is controlled by kinetic factors rather than by diffusion. However, as far as we are aware, no case has yet been encountered in which the *n*-value determined by macro coulometric electrolysis has been found to differ from the *n*-value under polarographic conditions. In the present case the lack of any contra evidence lends confidence to the conclusion that the products we observed in the macro electrolyses are also those produced at the dropping electrode.

Experimental

An automatic potentiostat[7,8] was used for the controlled potential electrolysis, and the quantity of electricity passed was measured with a hydrogen–oxygen coulometer.[9]

The requirement of working with nitrate concentrations as small as those under ordinary polarographic conditions (1 millimolar or less in most experiments) necessitated electrolysis of a relatively large volume of solution to obtain sufficient quantities of reduction products for analyses. The electrolysis cell consisted of a 1-liter flask, with a mercury pool cathode in the bottom, connected to the separate anode compartment by a wide side arm closed by a sintered glass disk.[10] The mercury–electrolyte interface was stirred vigorously with a glass propellor stirrer, and air was removed from the solution with nitrogen.

In the experiments with lanthanum and cerous chloride solutions, the electrolyte was first deaerated and electrolyzed with the cathode controlled at the desired potential against a saturated calomel reference electrode until the background current decayed to about 5 milliamp. The nitrate was then added (as standard potassium nitrate solution), and electrolysis was continued until the current decreased from an initial value of *ca.* 100 milliamp. to the original background value (3–3.5 hr.). The *p*H was observed continuously during the electrolysis with a glass electrode, and standard hydrochloric acid was added as needed from a buret to maintain the *p*H between about 5 and 7.

In the uranium-catalyzed reductions the supporting electrolyte plus nitrate was first deaerated and the electrolysis was started by adding a measured volume of standard uranyl chloride solution. Electrolysis was continued until the current decreased to a constant minimal value (2–2.5 hr.). At the end of the electrolysis the uranium was found to be present entirely in the +4 state, and appropriate correction was applied for the quantity of electricity corresponding to the reduction of the uranyl ion. Since the quantity of hydrochloric acid originally present was a large excess over that consumed in the nitrate reduction, no additional acid was put in during the electrolysis.

The following methods, all of which were tested with synthetic solutions, and which are described in complete detail in the thesis of the junior author,[11] were employed to analyze the solutions resulting from the electrolyses.

Nitrate.—In all cases nitrate was determined by the polarographic method of Kolthoff, *et al.*[3]

Nitrite.—Nitrite was detected by the Griess test and, when present, was determined by the polarographic method of Keilen and Otvos,[12] or by the spectrophotometric method of Rider and Mellon.[13]

Hydroxylamine.—Hydroxylamine was determined by reduction to ammonia with chromous ion in alkaline tartrate

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(4) S. I. Sinyakova and G. G. Karanovich, *Trudy Komisii Anal. Khim., Otdel Khim. Nauk. Akad. Nauk S.S.S.R.*, **2** [5], 65 (1949).

(5) L. Meites, THIS JOURNAL, **73**, 4115 (1951).

(6) F. Kaufman, H. J. Cook and S. M. Davis, *ibid.*, **74**, 4997 (1952).

(7) J. J. Lingane, Electroanalytical Chemistry, Interscience Publishers, Inc., New York, N. Y., 1953, p. 368.

(8) J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).

(9) J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

(10) See, *e.g.*, ref. 7, p. 371.

(11) J. W. Collat, Ph.D. Thesis, Harvard University, 1953.

(12) B. Keilin and J. W. Otvos, THIS JOURNAL, **68**, 2665 (1946), modified as follows: a polarogram of nitrate plus nitrite was recorded; then in another sample the nitrite was destroyed with sodium azide (*cf.* Haslam and Cross, *J. Soc. Chem. Ind.*, **64**, 259 (1945). A polarogram of this solution was then made and the nitrate and nitrite content of the sample calculated from both polarograms.

(13) B. F. Rider and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 96 (1946).

TABLE I

CONTROLLED POTENTIAL ELECTROLYSES

Volume of solution 750 ml., solutions electrolyzed 3–3.5 hr., *p*H maintained between 5 and 7.

Exp.	Electrolyte	Cathode potential, volts *vs.* S.C.E.	Nitrate at start, mmoles	Electricity passed, meq.	Acid consumed, mmoles	Ammonia found, mmoles	Hydroxylamine found, mmoles	Nitrate left in soln. mmoles	Reducing power, meq.	Accounted for in nitrate reduction (%)		
										Elec.	H^+	Nitrogen
1	0.1 *M* $LaCl_3$	−1.40	0.80	4.92	6.23	0.31	0.35	0.06	2.50	93	89	90
2	.1 *M* $LaCl_3$	−1.40	.79	4.88	5.98	0.26	.41	.05	2.31	93	92	91
3	.1 *M* $CeCl_3$	−1.70	.77	5.13	5.96	..	.31	.13	1.85	88[a]	92[a]	
4	.1 *M* $CeCl_3$	−1.70	.77	5.55	6.54	0.35	.08	.11	0.49	60	62	70

[a] Calculated assuming balance of nitrate is reduced to ammonia.

medium.[14] The ammonia formed was determined by conventional distillation and titration where possible. When the amount of hydroxylamine was less than 0.02 millimole, the ammonia was finally determined by nesslerization. The hydroxylamine content thus determined was corrected for nitrate and/or nitrite and/or ammonium present.

Reducing Power of the Solution.—This was determined by bromate titration,[15] which oxidizes hydroxylamine and nitrite to nitrate, and hydrazine to nitrogen, but does not oxidize ammonia. This determination could be made on the product solution from uranyl-catalyzed reduction only after the solution had been aerated until all the uranium was present in the +6 state. Aeration was found to leave hydroxylamine unchanged. Since nitrite and hydrazine were not products in the uranyl-catalyzed electrolysis, it proved to be a good method for oxidizing +4 uranium in the mixture.

Hydrazine.—The amount of hydrazine present could be calculated from the reducing power determination and the known amount of hydroxylamine in the sample, but it was never found.

Ammonia.—Ammonia was determined in the sample in which the reducing power had been determined. The sample was made alkaline, and the ammonia was distilled from it and determined by titration, or, if necessary, by nesslerization.

Hydrogen Ion.—The hydrogen ion consumed in the nitrate reduction with lanthanum or cerous ion as catalyst was calculated from the amount of hydrochloric acid added during the electrolysis. In the uranyl-catalyzed reductions, where the supporting electrolyte was *ca.* 0.01 *M* in hydrochloric acid, the exact hydrogen ion concentration before and after electrolysis was measured by titration. An aliquot of the solution containing +6 uranium (starting solution or aerated product solution) was titrated with standard sodium hydroxide in the presence of dipotassium hydrogen phosphate. Potassium uranyl phosphate precipitates quantitatively releasing one mole of dihydrogen phosphate ion per mole of uranyl ion. The solution was titrated to the *p*H of a pure monohydrogen phosphate solution, and correction was applied for the hydrogen ion liberated by the precipitation of the uranium.

Reagents.—Lanthanum chloride solutions were prepared by dissolving a lanthanum oxide–carbonate mixture in the requisite amount of hydrochloric acid. The oxide–carbonate mixture had been prepared by Behrens[16] and had been shown to be free of other rare earths. The solutions resulting from this treatment had a *p*H between 6 and 7.

Cerous chloride solutions were prepared by repeatedly evaporating hydrochloric acid solutions of diammonium ceric hexanitrate (G. F. Smith Chemical Co.). Excess hydrochloric acid was removed from the resulting solutions either by electrolytic reduction at a mercury cathode whose potential was kept at −1.7 to −1.8 volt *vs.* S.C.E., or by precipitation of cerous hydroxide with ammonia and solution of the cerous hydroxide in less than an equivalent amount of hydrochloric acid, with centrifugal separation of the excess solid. The latter method gave a solution contaminated with ammonium ion. Thus, in experiment 3 of Table I, determinations which involved ammonia or its production could not be made precisely on the product solution because of the large background quantity of ammonium ion. The solution used for experiment 4 was neutralized by electrolysis and was free of ammonium ion.

Results and Discussion

Reduction in Presence of Lanthanum and Cerous Ions.—Results of the controlled potential reductions in presence of lanthanum and cerous chlorides are summarized in Table I. Considering the difficulties involved in determining the very small concentrations of reaction products, the percentages of electricity, hydrogen ion, and nitrogen accounted for by the quantities of ammonia and hydroxylamine found are quite satisfactory. The data leave no doubt that hydroxylamine and ammonia are the chief products of the reduction in both electrolytes. The small fraction of the nitrogen unaccounted for may have been lost as elemental nitrogen or nitrous oxide. The very good agreement between the total reducing power and the independently determined hydroxylamine shows that neither nitrite nor hydrazine is produced in significant amounts.

These data disprove Meites' claim[5] that nitrate is not reduced in cerous chloride solution and that the current results from catalytic reduction of hydrogen ion. Unrecognized factors in Meites' experiments must have been responsible for the anomalous results he obtained.

The production of hydroxylamine and ammonia in approximately equal proportions corresponds to an average *n*-value close to 7. Although Kolthoff, Harris and Matsuyama[3] concluded that *n* was 6 under polarographic conditions with lanthanum chloride supporting electrolyte, the uncertainty in the diffusion coefficient of nitrate ion, on which this conclusion depends, is sufficient to cause an *n*-value of 7 to be just as consistent with their diffusion current constant data as a value of 6. Thus the diffusion current constant data support our conclusion that the average *n*-value is the same in the reduction of nitrate ion at the dropping electrode and at the macro mercury cathode. Conceivably, of course, the primary products produced at the dropping electrode might be different, provided that they were formed in proportions corresponding to an average *n*-value of 7, and provided also that they were capable of subsequent non-electrolytic reaction to produce hydroxylamine and ammonia. We know of no possible intermediates which could satisfy both these conditions.

At both the dropping electrode and the macro mercury cathode hydroxylamine and ammonia doubtless result from a series of rapid consecutive reactions, probably both electrolytic and non-electrolytic. Some of these reactions must consume hydrogen ion, and the relative proportions and rates of these must be *p*H sensitive. Such *p*H dependence very likely underlies the well established

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[14] J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **21**, 622 (1949).

[15] A. Kurtenacker and J. Wagner, *Z. anorg. allgem. Chem.*, **121**, 261 (1922).

[16] E. E. Behrens, Ph.D. Thesis, Harvard University (1931).

TABLE II

CONTROLLED POTENTIAL ELECTROLYSES OF NITRATE IN PRESENCE OF URANYL ION

700 ml. solution, 0.1 *M* KCl, 0.01 *M* HCl, 0.0002 *M* UO_2^{++}; cathode potential −1.1 volt *vs.* S.C.E., time of electrolysis 2–2.5 hr.

Exp.	Nitrate at start, mmoles	Elec. passed, meq.	H^+ consumed, mmoles	Nitrate found at end, mmoles	NH_2OH found, mmoles	Reducing power, millieq.	N acct., %	Ratio of elec. balance to H^+ balance
1	0.187	2.13	2.06	0.008	0.149	0.845	84	0.96
2	.187	2.07	1.96	.003	.183	.870	99	1.02
3	.187	2.50	2.47	.004	.158	.900	87	0.93
4	1.87	14.9	16.4[a]	.11	1.44	.848	83	0.95
5	0.187	2.54	1.98	.003	0.130	.860	71	1.38
6	.187	2.33	2.38	...	.137	.821	73	0.87
7	.175	1.80	1.98	...	.127[b]	.716	71	0.70
							Av.	1.0 ± 0.1

[a] 0.031 *M* HCl initially in this expt. [b] 0.005 millimole NH_3 found in this expt.

fact that the diffusion current constant of nitrate ion, and thus the proportions of hydroxylamine and ammonia formed, varies significantly with nitrate concentration and concentration of lanthanum or cerous chlorides.[1] In nearly neutral and unbuffered solution the hydrogen ion required for the nitrate reduction must be supplied by water with the consequent liberation of hydroxide ion. The greater the concentration of nitrate ion the greater will be the *p*H increase at the electrode surface. Lanthanum or cerous ion, by combining with hydroxide ion, limits the *p*H increase at the electrode surface, and the extant *p*H evidently will be smaller the greater the lanthanum or cerous ion concentration in the body of the solution.

Uranium-catalyzed Reduction.—Table II summarizes data obtained in the uranium-catalyzed reduction. At the potential employed, the original +6 uranium is reduced to the +3 state.[3] Nitrate ion in acid medium is not reduced at −1.1 v. *vs.* S.C.E. in the absence of uranium. Therefore, it appears that nitrate ion is reduced by the +3 uranium right at the electrode surface, the +3 uranium being oxidized to the +4 or +5 states, which are rapidly re-reduced to produce a catalytic cycle. A similar mechanism probably underlies the molybdenum catalyzed waves of nitrate and nitrite.[17]

From Table II it is seen that reduction of the nitrate to hydroxylamine accounts for three-fourths or more of the total nitrogen. In contrast to the lanthanum- or cerous-catalyzed reduction, only very small quantities of ammonia are produced. No evidence was found for either nitrite or hydrazine as a final reduction product. The small proportion of nitrogen unaccounted for may reflect the production of a small proportion of elemental nitrogen and/or nitrous oxide.

The ratio of electrical balance to hydrogen ion balance in the last column of Table I was obtained by subtracting the quantity of electricity equivalent to the determined quantity of hydroxylamine produced from the total quantity of electricity passed, and dividing by the difference between the total amount of hydrogen ion consumed and that required in the production of the hydroxylamine and in the reduction of the uranyl ion. The closeness of the average value of this ratio to unity strongly suggests that the reduction of nitrate was accompanied by some reduction of hydrogen ion, either by direct electrode reaction or by the +3 uranium. The current efficiency for production of hydroxylamine ranges from 31 to 58%, and in view of the fact that three-fourths or more of the nitrogen is accounted for as hydroxylamine, it is evident that a considerable fraction of the current results from hydrogen ion reduction.

Diffusion current constant data reported by Kolthoff, Harris and Matsuyama[3] for nitrate, and by Kaufman, Cook and Davis[6] for both nitrate and nitrite, support our conclusion that hydroxylamine is also the preponderant product at the dropping electrode. From the measurements of these authors the diffusion current constants of nitrate and nitrite in a supporting electrolyte of the same composition as that in Table II are 13.8 and 9.01 microamp./mmole/l. $mg.^{2/3}$ $sec.^{-1/2}$ at 25°. Since the diffusion coefficients of nitrate and nitrite ions must be closely similar, the ratio of the *n*-values for the two reductions is 13.8/9.01 or 1.53. Making the logical assumption that nitrate and nitrite are reduced to the same final product, the *difference* between the *n*-values must be 2 which, combined with the foregoing ratio, leads to individual *n*-values of 6 and 4, and thus to hydroxylamine as the product. The only other possibility is that nitrate and nitrite are reduced to different products, but this seems to us to be highly improbable and there is no evidence for it.

Uncatalyzed Reduction of Nitrate.—The polarograms in Fig. 1 demonstrate that nitrate ion undergoes reduction in acid medium without any specific catalyst present. The polarograms were recorded with solutions that were 0.1 *M* in potassium chloride, 0.00521 *M* in hydrochloric acid, and with the various millimolar concentrations of nitrate ion indicated for each curve. The polarographic waves themselves result from the reduction of hydrogen ion ($E_{1/2}$ −1.58 v. *vs.* S.C.E.). That reduction of nitrate occurs at potentials about 0.2 v. more negative than the hydrogen ion half-wave potential is shown by the minimum which appears in the diffusion current plateau when nitrate is added, and which deepens with increasing nitrate concentration. This phenomenon is shown more clearly in Fig. 2, in which only the diffusion current sections of the waves are recorded.

The minimum is caused by part of the hydrogen ion which diffuses to the electrode surface being

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(17) M. G. Johnson and R. J. Robinson, *Anal. Chem.*, **24**, 366 (1952); D. T. Chow and R. J. Robinson, *ibid.*, **25**, 1493 (1953).

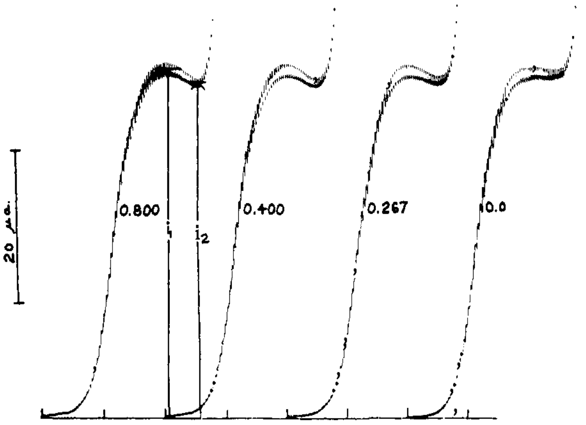

Fig. 1.—Polarograms of nitrate in acid solution. All solutions were 0.1 M in KCl, 0.00521 M in HCl, nitrate concentration in millimole/l. as indicated. All waves begin at −1.2 v. *vs.* S.C.E. One division on voltage scale equals 0.3 v.

consumed in the reduction of nitrate ion, coupled with the fact that the quantity of electricity involved in the nitrate reduction is smaller than that associated with the direct reduction of the number of hydrogen ions consumed in the reduction of each nitrate ion. In accord with this interpretation it was found that, with a constant concentration of hydrogen ion, the minimum finally decreases to a constant value as the nitrate ion concentration is increased.

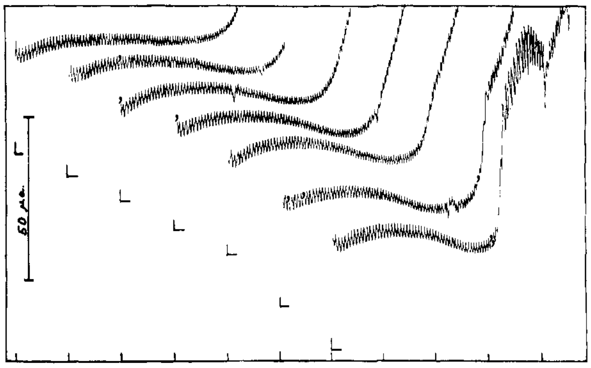

Fig. 2.—Polarograms of nitrate in acid solution. All solutions were 0.1 M in KCl, 0.00477 M in HCl, nitrate concn. (l. to r.), 0.0, 1.00, 2.00, 3.00, 4.00, 5.00, 8.00 millimoles/l. All waves begin at −1.6 v. *vs.* S.C.E. One division on voltage scale equals 0.1 v.

Representing the reduction of nitrate ion by the general equation

$$NO_3^- + ne + qH^+ \longrightarrow \text{Products}$$

it can be shown[11] that the ratio of the constant minimal current observed with excess nitrate to the initial diffusion current of hydrogen ion in the absence of nitrate ion should be very nearly equal to n/q. The observed ratio was 0.84, and thus very close to the $^5/_6$ that would correspond to reduction to nitrogen according to $NO_3^- + 6H^+ + 5e = {}^1/_2N_2 + 3H_2O$. However, the ratio n/q for all possible products is so near the observed value, and varies so little, that there is no justification for concluding that nitrogen is formed. Indeed, evidence from large-scale controlled potential electrolyses indicates that a mixture of nitrite and nitrous acid is a preponderant product.

The large-scale electrolyses were performed at a potential of −1.87 v. *vs.* S.C.E. (corresponding to the minimum in the plateau of the hydrogen wave). To simulate the conditions of excess nitrate ion and approximate neutrality extant at the surface of the dropping electrode, the electrolyses were started with an initially neutral solution of 0.7 to 0.8 millimolar potassium nitrate in 0.1 M potassium chloride to which hydrochloric acid was added in small portions to maintain the current at *ca.* 100 milliamp. for 30 to 50 min. The electrolyses were stopped after about half the original nitrate ion had been reduced, and the final solution was analyzed for nitrite and residual nitrate. The amount of nitrite found in three trials averaged 68% of the amount of nitrate reduced.

For reduction to nitrite ion ($NO_3^- + 2H^+ + 2e = NO_2^- + H_2O$) the ratio n/q is unity, and for reduction to nitrous acid ($NO_3^- + 3H^+ + 2e = HNO_2 + H_2O$) it is $^2/_3$. The observed apparent ratio of 0.84, coupled with the finding of nitrite in the large scale electrolyses, suggests that the pH at the surface of the dropping electrode is such that a mixture of nitrous acid and nitrite ion is produced.

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CAMBRIDGE, MASS.