reduction to ammonia. If an oxidation does occur, a logical intermediate would be hyponitrite, the generally accepted intermediate in the reduction of nitrates to ammonia and nitrogen. The experimental data presented here suggesting that nitrous oxide is a competitive inhibitor of the nitrogen fixation reaction in *Azotobacter* can be interpreted as some support for this view.[11]

It is assumed that nitrous oxide affects some reaction prior to formation of ammonia, because inhibition cannot be demonstrated in the presence of this compound (Table II). These initial steps in the fixation process have escaped detection, and the enzyme or enzymes involved are not known. Nitrous oxide apparently competes for an enzyme active in this reaction. If nitrous oxide or a related compound were an intermediate in the nitrogen fixation reaction, one would anticipate not only competitive inhibition but also ready utilization. Since nitrous oxide is not assimilated by *Azotobacter* the most likely present explanation is that nitrous oxide has properties similar enough to some intermediate to enable it to compete for the enzyme—*i.e.*, analogous to the action of an antimetabolite. If nitrous oxide has the same effect on the symbiotic nitrogen fixing system as on that of *Azotobacter*, Kriegel's discovery confirmed by Taylor, *et al.*,[12] that nitrous oxide is one of the most abundant constituents of soil air could have important practical implications for agriculture.

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[11] In a note published in *Chemistry and Industry*, no. 4, 87 (1952), T. G. G. Wilson and E. R. Roberts report independent confirmation of this important conclusion.

[12] R. C. Taylor, R. A. Brown, W. S. Young and C. E. Headington, *Anal. Chem.*, **20**, 396 (1948).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF LOUISVILLE]

Polarography of Some Substituted 8-Quinolinols

BY QUINTUS FERNANDO[1] AND J. P. PHILLIPS

The polarographic behavior of 2-, 3- and 4-methyl substituted 8-quinolinols in the *p*H range 2–12 was compared with that of 8-quinolinol. The 3-methyl derivative resembled 8-quinolinol much more closely than the other compounds. The addition of aluminum ion had no effect on the waves of 2-methyl- and 2,3-dimethyl-8-quinolinol in alkaline solution, indicating no chelate formation.

As part of a study of the properties of substituted 8-quinolinols[2a,b,3] the polarography of the 2-, 3- and 4-methyl and 2,3-dimethyl derivatives was studied. In spite of the close structural relationship of these compounds differences in reduction at the mercury cathode were anticipated from the greater activities of 2- and 4-substituents compared to 3-substituents in quinolines, and also from the anomalous behavior of 2-substituted 8-quinolinols in forming no chelates with aluminum ion.[2a,4,5]

Experimental

A Sargent Model XXI Polarograph and an H-type cell kept at 25 ± 0.01° were employed for all determinations. Measurements were made against a saturated calomel electrode. The characteristics of the dropping mercury electrode, determined in 0.1 *N* potassium chloride on open circuit, were: $m = 2.30$ mg./sec., $t = 4.00$ sec.

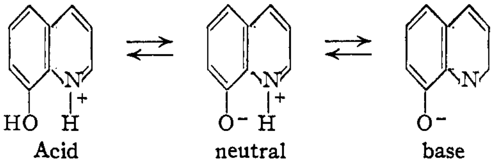
Polarograms were run on each compound at nine or more *p*H values between 2 and 12 and at concentrations ranging from 0.0001 to 0.001 *M*. Britton and Robinson buffers (consisting of acetic, phosphoric and boric acids with sodium hydroxide) were used after polarographic examination for reducible impurities. Oxygen was removed from the solutions with nitrogen. An instrument sensitivity of 0.100 was usually suitable.

The preparation and purification of the compounds have been previously described.[2a]

Results and Discussion

The polarographic reduction of substituted 8-quinolinols shows great variations with *p*H. It is convenient to consider the polarograms in acidic, neutral and basic solutions separately since there are three different molecular species involved

I



In acid solutions the reduction of 8-quinolinol and presumably of its methyl derivatives, is known to give the 1,2,3,4-tetrahydro derivative.[6,7] Polarographically it is not possible to establish the reduction process because of a catalytic wave due to the quinolinium ion.[8] The magnitude of the catalytic wave, as well as its potential, decreases with increasing *p*H (Figs. 1–3), because an increase in *p*H shifts the equilibrium of equation I to give decreasing amounts of quinolinium ion in solution. In all the compounds a small preliminary wave at the foot of the catalytic wave was noticeable but the interference of the following catalytic wave made analysis impossible. The preliminary wave was most pronounced in 2,3-dimethyl-8-quinolinol.

In neutral solutions from *p*H 4 to 9.5 the analysis of the polarographic waves is complicated by the unknown position of the equilibria of equation I. The waves in this portion of the *p*H range showed greater variations from compound to compound than anywhere else. With all compounds pronounced maxima were obtained at a potential of

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[1] International Fellow from Colombo, Ceylon, sponsored by Joseph E. Seagram and Sons, Inc., Louisville, Kentucky.

[2] (a) J. P. Phillips and L. L. Merritt, THIS JOURNAL, **71**, 3984 (1949); (b) J. P. Phillips and F. J. O'Hara, *ibid.*, **73**, 583 (1951).

[3] J. P. Phillips and H. P. Price, *ibid.*, **73**, 4414 (1951).

[4] L. L. Merritt and J. K. Walker, *Anal. Chem.*, **16**, 387 (1944).

[5] H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

[6] O. Fischer, *Ber.*, **14**, 1368 (1881).

[7] C. J. Cavallito and T. H. Haskell, THIS JOURNAL, **66**, 1166 (1944).

[8] S. Wawzonek, *Anal. Chem.*, **21**, 61 (1949).

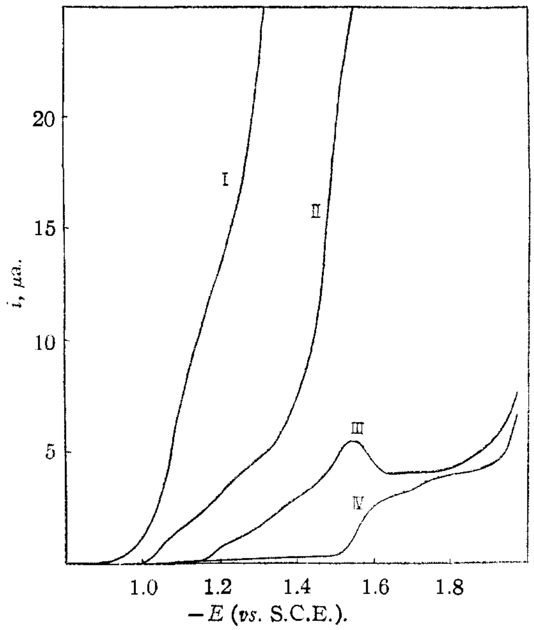

Fig. 1.—Polarograms of 2-methyl-8-quinolinol: I, pH 2.5, 9.1×10^{-4} *M*; II, pH 6.4, 6.7×10^{-4} *M*; III, pH 8.2, 5.0×10^{-4} *M*; IV, pH 11.1, 5.3×10^{-4} *M*.

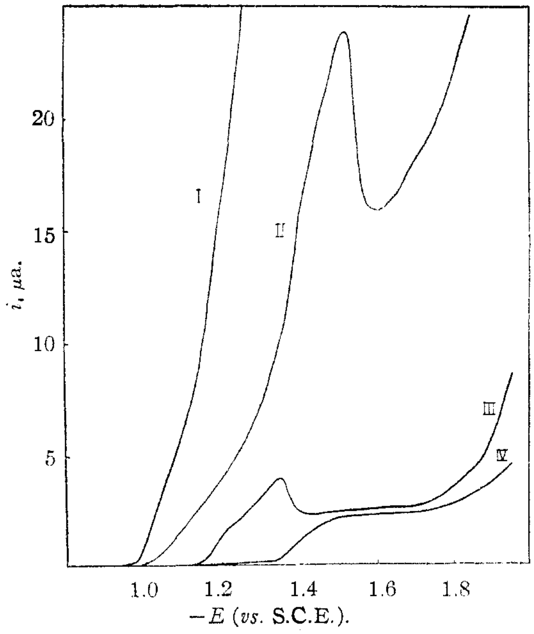

Fig. 2.—Polarograms of 3-methyl-8-quinolinol: I, pH 2.0, 5.0×10^{-4} *M*; II, pH 5.4, 5.0×10^{-4} *M*; III, pH 7.4, 5.0×10^{-4} *M*; IV, pH 9.4, 5.0×10^{-4} *M*.

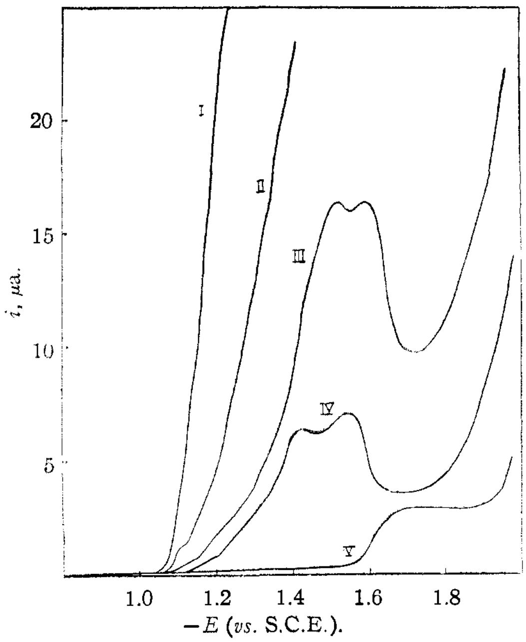

Fig. 3.—Polarograms of 4-methyl-8-quinolinol: I, pH 2.4, 4.6×10^{-4} *M*; II, pH 4.0, 4.6×10^{-4} *M*; III, pH 5.9, 6.0×10^{-4} *M*; IV, pH 6.7, 6.0×10^{-4} *M*; V, pH 11.3, 6.0×10^{-4} *M*.

about −1.4 volts. The maxima decreased with increasing pH and eventually disappeared altogether; they could be suppressed with gelatin but suppression altered the potential of the wave. 3-Methyl-8-quinolinol resembled 8-quinolinol[9] very closely in this region; the other compounds were notably different. It does not seem advisable to attempt a more exact interpretation of the results, since there are evidently quite a number of competing reduction processes possible in this pH range.

In alkaline solutions of pH 10–12 well defined waves with diffusion currents proportional to concentration were obtained. The variations of half wave potentials with increasing pH follow equations (Table I) which indicate[10] that the reduction process involves combination with hydrogen as well as a gain of electrons. Application of the Ilkovic equation using the same diffusion coefficient as that estimated for 8-quinolinol[9] shows that the reduction involves one electron (1.0 ± 0.2) for all compounds. The magnitude of the diffusion currents (Table II) is slightly larger for the two compounds containing a 3-methyl group; the half wave potentials do not differ enough to draw any conclusions about the relative ease of reduction of these compounds. The behavior of 8-hydroxyquinaldine is peculiar in that the empirical equa-

TABLE I

HALF-WAVE POTENTIAL–pH RELATIONS FOR SUBSTITUTED 8-QUINOLINOLS IN ALKALINE SOLUTION

Substituent	$-E_{1/2}$ (*vs.* S.C.E.)
None[a]	0.90 + 0.057 pH
2-CH_3	.59 + .084 pH
3-CH_3	.91 + .056 pH
4-CH_3	.86 + .064 pH
2,3-$(CH_3)_2$	.82 + .069 pH

[a] Although independently determined this equation is almost identical to that of Stock.[9]

TABLE II

$E_{1/2}$–i_d RELATION AT pH 11.6 ± 0.1 IN 0.001 *M* SOLUTION

Substituent	$E_{1/2}$, volts	i_d, μa.
2-CH_3	−1.57	2.92
3-CH_3	−1.56	4.00
4-CH_3	−1.62	2.85
2,3-$(CH_3)_2$	−1.61	3.70

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(9) J. T. Stock, *J. Chem. Soc.*, 586 (1949).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 185.

tion (Table I) for its half wave potential–pH relationship is unlike the others and also in that a second small wave is found (Fig. 1) after the main wave. It is possible that this additional wave corresponds to reduction of the dimer formed as the result of the first one electron reduction. An unidentified dimer from the reduction of quinaldine on mercury has been reported,[11] and apparently a similar dimer was not found in the reduction of quinoline. This might account for the different behavior of 8-hydroxyquinaldine compared to the other substituted 8-quinolinols.

Since aluminum has been found not to form insoluble chelates with 2-substituted 8-quinolinols,[4,5] the effect of adding aluminum ion on the polarographic wave in alkaline solution was investigated as a very sensitive check on this fact. Precipitation of an aluminum chelate as well as a decrease in wave height was obtained with 3- and 4-methyl-8-quinolinols at a pH of 12. No significant decrease in wave height and no precipitation was observed with the 2-methyl and 2,3-dimethyl derivatives.

Acknowledgments.—This work was supported in part by a grant from the Research Corporation. The authors are also grateful to Joseph E. Seagram & Sons, Inc., Louisville, Kentucky, in whose laboratories most of this work was done, and also to Edward J. Kimmel of the Seagram research department for technical assistance with the polarograph.

LOUISVILLE 8, KENTUCKY RECEIVED DECEMBER 18, 1951

[11] V. V. Levchenko, *Zhur. Obshchei Khim.*, **18**, 1245 (1948).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

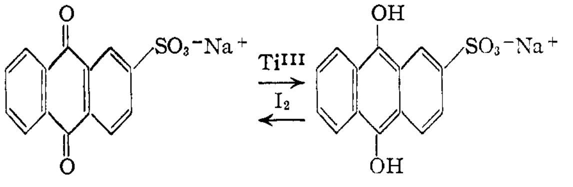
Oxidation–Reduction. III. The Kinetics of the Reduction of Sodium Anthraquinone β-Sulfonate by Titanous Ion and the Oxidation by Iodine

BY CARL E. JOHNSON, JR.,[1] AND S. WINSTEIN

RECEIVED AUGUST 2, 1951

The kinetics of the reduction of sodium anthraquinone β-sulfonate by titanous ion have been investigated spectroscopically. In general, the rate-law for the production of the hydroquinone was found to be of the form: $d(R)/dt = (Ti^{III})[k_1(T)^{1/2}(R)^{1/2} + k_2(T)(R) + k_3(T)^{3/2}(R)^{1/2}]$ where T and R represent the quinone and hydroquinone, respectively. A mechanism has been proposed involving three reaction paths: (1) the reduction of S, the semiquinone, by Ti^{III}; (2) the reduction of S·S, a semiquinone dimer, by Ti^{III}; and (3) the reduction of T·S, a molecular complex composed of one molecule of the quinone and one molecule of the semiquinone, by Ti^{III}, or such alternatives as the reaction between S and a complex ion containing one Ti^{III} ion and one T molecule. The rate of reduction of the quinone molecule itself by titanous ion is insignificant with respect to these three rate-determining reactions. The oxidation of sodium anthrahydroquinone β-sulfonate by iodine proved to be too rapid for accurate kinetic analysis. Under all of our experimental conditions it appears to be much faster than the reduction of the quinone by titanous ion.

The oxidation of hydroquinones by molecular oxygen has been extensively investigated, principally by Weissberger and co-workers[2] and by LuValle and Weissberger[3] who correlated their kinetic data on the basis of semiquinone theory. On the other hand, with the exception of the work of Dimroth[4] on the relation between over-all free energy change and the rate of reduction of a series of quinones, little attention appears to have been paid to the kinetics and mechanism of the reduction of quinones. For this reason, and because of the connection with the already reported[5] catalysis of the titanous chloride–iodine reaction by sodium anthraquinone β-sulfonate (I), we have studied separately the kinetics of reduction of sodium anthraquinone β-sulfonate (I) by titanous ion and the oxidation of the hydroquinone II by iodine. The first portion of this paper presents an analysis of the kinetics of the reduction which was followed spectroscopically. The last portion presents results obtained for the oxidation which proved to be too rapid to lend itself to kinetic analysis by similar methods.



I II

The Reduction by Titanous Ion.—Since the anthrahydroquinone II exhibits a sharp maximum in its light absorption at 382 mμ, while the anthraquinone I absorbs very much less and the titanous chloride and other reagents are transparent in this region, the course of the reduction could be followed spectrophotometrically at 382 mμ. Figure 1 shows optical density plotted *vs.* wave length for various combinations of sodium anthrahydroquinone β-sulfonate II and titanous chloride in acid solution. It is seen that titanous ion, even at concentrations higher than those employed in the rate determinations, and titanic ion have no specific effect on the absorption of the hydroquinone II, for an identical absorption is obtained for the hydroquinone II whether produced by reduction of I with excess titanous ion or with zinc dust. Absorption due to sodium anthraquinone β-sulfonate (I) at the beginning of typical reductions amounted to *ca.* 3–

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[1] Department of Chemistry, University of Illinois, Urbana, Illinois.

[2] (a) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937); (b) T. H. James, J. M. Snell and A. Weissberger, *ibid.*, **60**, 2084 (1938); (c) A. Weissberger and G. Kornfeld, *ibid.*, **61**, 361 (1939); (d) A. Weissberger, J. E. LuValle and D. S. Thomas, Jr., *ibid.*, **65**, 1934 (1943); (e) A. Weissberger and J. E. LuValle, *ibid.*, **69**, 1576 (1947).

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[4] O. Dimroth, *Z. angew. Chem.*, **46** 571 (1933).

[5] (a) C. E. Johnson, Jr. and S. Winstein, THIS JOURNAL, **73**, 2601 (1951); (b) *ibid.*, **74**, 755 (1952).