116. *The Reduction of Quinaldinic Acid at the Dropping-mercury Cathode.*

By John T. Stock.

Current–voltage curves of quinaldinic acid in well-buffered aqueous solutions of pH 1·5—12 have been constructed, reduction occurring over the entire pH range. The principal reduction product appears to be dihydroquinaldinic acid. Since the wave heights are proportional to the concentration of quinaldinic acid, this acid may be estimated polarographically.

THE systematic development of the technique of amperometric titration by means of the dropping-mercury electrode (see, *e.g.*, Kolthoff and Lingane, " Polarography," New York, 1941, pp. 447—478) indicated the utility of certain of the well-known organic precipitants for metallic ions in this connection. Quinaldinic acid, a reagent for the gravimetric determination of copper, zinc, and cadmium (Hopkin and Williams, Ltd., " Organic Reagents for Metals," 1943, pp. 122—125), has potential uses in this procedure, and the present work concerns its behaviour at the dropping-mercury cathode.

Current–voltage curves of quinaldinic acid (0·001M) in well-buffered aqueous solutions at 25° over the pH range 1·5—12 have been constructed. Müller (*Chem. Rev.*, 1939, **24**, 107) has stressed the importance of

Fig. 1.
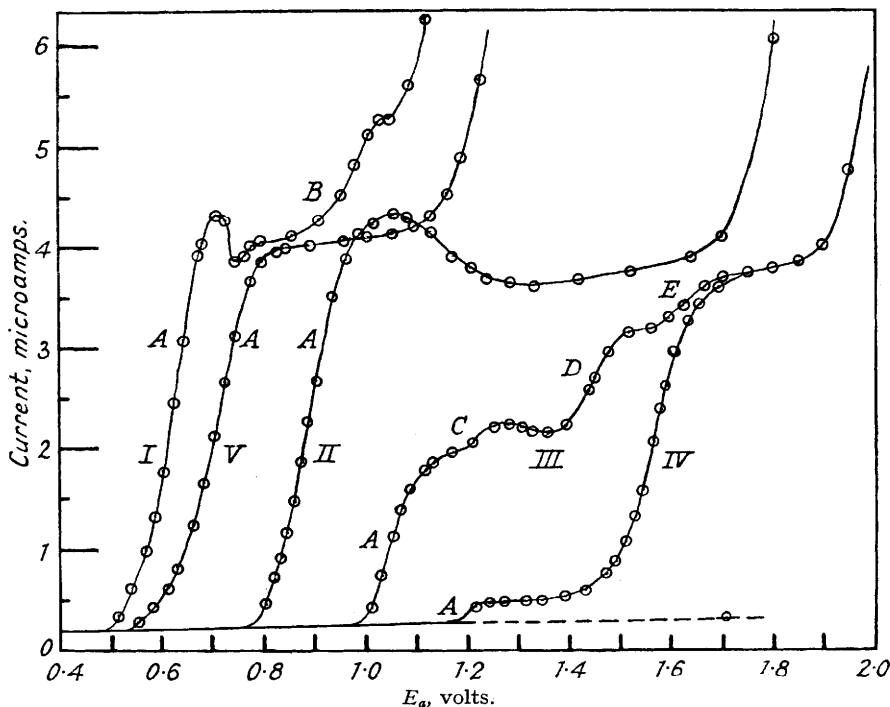
Curve I, pH 1·50; *II*, pH 5·75; *III*, pH 7·91; *IV*, pH 10·69; *V, as I, but* 0·02% *gelatin added.*

adequate buffering in studying the electroreduction of organic compounds. Quinaldinic acid was found to be reducible over the entire pH range examined. In strongly acid solutions the first wave A (Fig. 1, curve I) is surmounted by a " maximum " and followed by a second, smaller wave B which immediately precedes the rapid rise in current due to the decomposition of the supporting electrolyte. Under these conditions quinaldinic acid, in common with other quinoline derivatives, decreases the overvoltage of hydrogen. As the pH of the solution is increased, wave A is displaced to more negative potentials, the maximum broadening considerably. At the same time, wave B decreases in height, vanishing completely at about pH 4 (Fig. 1, curve II). In the region of neutrality the current–voltage curves become very complicated, no less than four waves A, C, D, and E appearing (Fig. 1, curve III). Wave C can be distinguished in the pH range 6·4—8 and decreases in height with increase in pH. Its appearance coincides with a marked decrease in the height of wave A. Wave D appears at pH 5·5 and wave E at about pH 7·4. Both increase in height with increase in pH, the former merging into the latter in the region of pH 9. In solutions more alkaline than pH 9, wave A becomes very small (Fig. 1, curve IV). It is, however, still distinguishable at pH 12·3. In 0·1M-sodium hydroxide solution it was not observed.

The reduction potential of wave A as determined by the " 45° tangent " method (Heyrovsky, *Coll. Czech. Chem. Comm.*, 1935, **7**, 198) is displaced to more negative potentials with increase in pH. Up to pH 5, this displacement is linear, the reduction potential being given by $E = -(0·42 + 0·06 \text{ pH})$ volt. All potentials are referred to the saturated calomel electrode at 25°.

To permit analysis of the results, attempts were made to suppress the maximum surmounting wave A. Methyl-red and methylene-blue fail completely, even when added in concentrations large enough to increase the residual current considerably. Thymol is also ineffective. The maximum is completely suppressed by the addition of 0·02% of gelatin, but at the same time wave A is displaced to a more negative potential range, while wave B is completely eliminated (Fig. 1, curve V). The lateral displacement of wave A is similar to the effect observed by Kolthoff and Barnum (*J. Amer. Chem. Soc.*, 1941, **63**, 521) in their work on cystine. Applic-
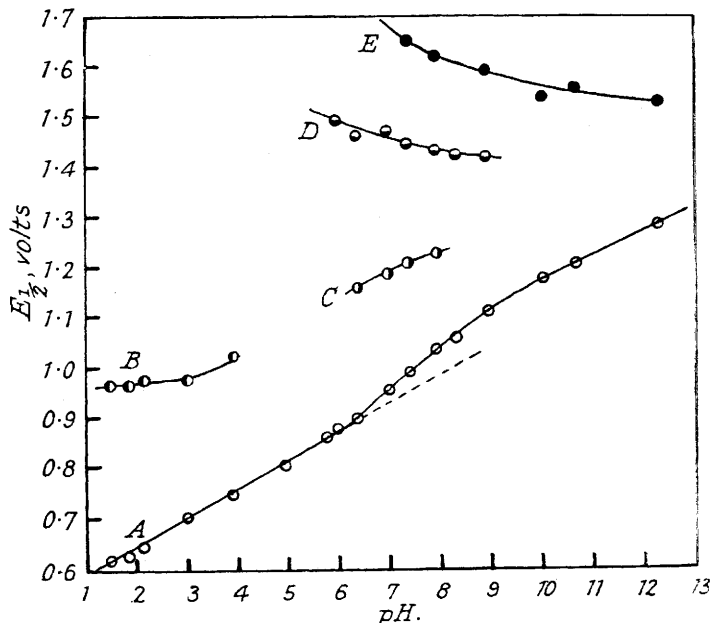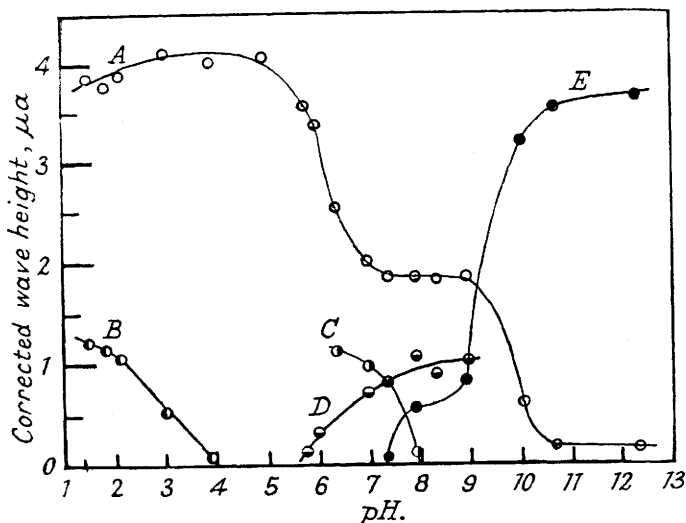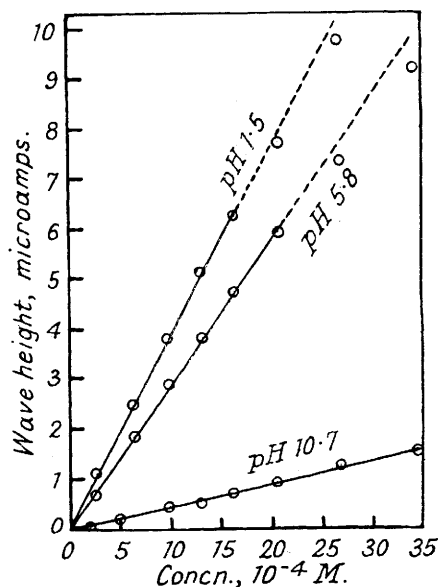

Fig. 2.

Fig. 3.

Fig. 4.

ation of the wave heights measured in the presence of gelatin to the corresponding curves obtained in its absence permits a fair estimate of the half-wave potentials ($E\frac{1}{2}$). Up to pH 6 the relation $E\frac{1}{2} = -(0·52 + 0·06 \text{ pH})$ volt holds for wave A. No maximum suppressor is necessary with solutions of pH >7. Fig. 2 shows the $E\frac{1}{2}$– pH relationships of the various waves, constructed directly from current–voltage curves obtained in the absence of gelatin (except in the case of wave A up to pH 7, when the method described was used).

The magnitude of the waves also depends markedly on pH, as is shown by Fig. 3. The wave heights are corrected both for the residual current of the supporting solution and for the varying drop-time of the capillary

due to the occurrence of the waves at different potentials (Lingane and Kolthoff, *J. Amer. Chem. Soc.*, 1939, **61**, 831). The heights of wave A up to pH 7 are those recorded after the addition of gelatin; other measurements were made in the absence of this agent.

Though the effect of pH on wave A is remarkable, the wave height is directly proportional to the concentration of quinaldinic acid in buffers of widely differing pH. As shown in Fig. 4, this relationship holds for concentrations up to 2×10^{-3}M. (Wave heights here are corrected for residual current only.) Accordingly, the measurement of the height of wave A provides a means of estimating quinaldinic acid polarographically. The total wave height in alkaline solution, *viz.*, the sum of the heights of waves A and E, is also proportional to the concentration. At concentrations $>2 \times 10^{-3}$M, in the presence of gelatin, the rising portion of wave A is seen to be composite, the lower half being steeper than the upper half. $E\frac{1}{2}$ becomes slightly less negative with increasing concentration of quinaldinic acid, probably due to the displacing effect of the constant concentration of gelatin being partly counteracted.

To permit application of Ilkovič's equation (*Coll. Czech. Chem. Comm.*, 1934, **6**, 498), the diffusion coefficient (D) of the quinaldinate ion was calculated from the relation $D = \mathbf{R}T\Lambda_0/zF^2$, where Λ_0 is the equivalent conductance of the ion at infinite dilution and z its valency (Lingane and Kolthoff, *loc. cit.*, p. 825). Use of the data due to Ostwald (*Z. physikal. Chem.*, 1889, **3**, 369; International Critical Tables, **6**, 293) in the above equation gives $D = 0.80 \times 10^{-5}$ cm.² sec.⁻¹ at 25°.

Ilkovič's equation is usually expressed as $I_d = 605nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}$, where I_d is the diffusion current (wave height) in microamps., n the number of electrons involved per mol., C the concentration (in millimols./l.), m the rate of flow of mercury from the capillary (in mg./sec.), and t the drop time (in secs.). By applying this equation to wave A at pH 5 (at which value no other waves are detectable, see Fig. 3), n was found to be 2·05. Since quinaldinic acid is incompletely ionised under these conditions, this result is an approximation, but is sufficient to show that wave A at its fullest development corresponds with a reduction involving 2 electrons per mol. In 0·1M-sodium hydroxide solution, E is the only wave detectable. Application of Ilkovič's equation here yields the value $n = 1.96$. Hence wave E also corresponds with a 2-electron reduction.

Discussion.—The reduction of quinoline at the dropping-mercury cathode has been studied by Pech (*Coll. Czech. Chem. Comm.*, 1934, **6**, 126), by Tachi and Kabai (*J. Electrochem. Assoc. Japan*, 1935, **3**, 250; *Chem. Abstracts*, 1936, **30**, 2500) and by Adkins and Cox (*J. Amer. Chem. Soc.*, 1938, **60**, 1151). In neutral and alkaline solution Pech reported two waves of equal height which he attributed to the formation of dihydro- and tetrahydro-quinoline severally. According to the Japanese workers the reduction product is dihydroquinoline. Apart from quinine (Pech; Tachi and Kabai, *locc. cit.*), no derivatives of quinoline have been examined polarographically.

Interpretation of the results is rendered difficult by the known tendency to polymerisation of dihydroquinoline and its derivatives. According to Meerwein (Houben's " Die Methoden der organischen Chemie," Leipzig, 1925, **2**, 620), only the N-substituted derivatives are known in the monomeric form. Ahrens (*Z. Elektrochem.*, 1896, **2**, 580) studied the electrolytic reduction of quinoline and quinaldine in sulphuric acid solution using a lead cathode and obtained monomeric, dimeric, and trimeric dihydro-compounds. Levchenko (*J. Gen. Chem., U.S.S.R.*, 1941, **11**, 686) further studied the reduction of quinoline in alkaline solution, using a mercury cathode. He reported a 30% yield of trimeric 1 : 4-dihydroquinoline with smaller amounts of the monomeric and the dimeric form. In sulphuric acid solution the trimer only was obtained. Accordingly, the reaction products discussed below may, in fact, exist in polymerised forms.

The step-like form of the pH—wave height curve of wave A (Fig. 3) is peculiar. In accordance with the composite appearance of this wave in acid solution, logarithmic analysis (Kolthoff and Lingane, *op. cit.*, p. 144) under these conditions gives a curve which is linear over the portion corresponding to the lower half-wave, but which deviates markedly beyond this. The occurrence of two reactions at potentials very close to one another is a possible explanation. Since on increasing the pH, wave C appears as the height of wave A shows a marked decrease, it seems that the composite wave splits up into its components due to the increased separation of the two reduction potentials. The constant height of wave A over the pH range 7·5—9 yields a value $n = 0.95$ when inserted into Ilkovič's equation, corresponding to a one-electron reaction which is probably reversible, since logarithmic analysis yields linear curves of reciprocal slope 0·064 (cf. Laitinen and Wawzonek, *J. Amer. Chem. Soc.*, 1942, **64**, 1765). Since $E\frac{1}{2}$ varies with pH, hydrogen ions are involved in the electrode reaction. Waves A and C being considered together, these are taken to represent two successive one-electron additions, of which the first is complete up to pH 9 and shows evidence of reversibility. It is suggested that the product of this reaction is a free radical such as (I) or (II). (Ionic dissociation is disregarded here.)

(I.)   (II.)   (III.)
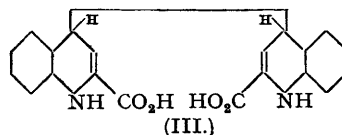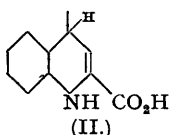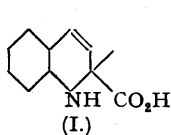
The second reaction, which begins to decrease at about pH 5 and ceases at pH 8 (disappearance of wave C), is attributed to the reduction of (I) or (II) to dihydroquinaldinic acid. By analogy with the work of Levchenko (*loc. cit.*), Meisenheimer and Stotz (*Ber.*, 1925, **58**, 2330), and Knowles and Watt (*J. Amer. Chem. Soc.*, 1943, **65**, 410), the 1 : 4-isomer is the expected product. This reaction may be partly inhibited by the union of two free

radicals to yield a dimer of type (III). Coincident with the first decrease in the height of wave A, the badly-defined wave D appears, increasing in height as wave C becomes smaller. This indicates a third reaction, alternative to the second one, which is favoured by increase in pH. The effect of pH on wave D with respect to $E\frac{1}{2}$ is quite different from that on waves A and C (Fig. 2). With the last two waves, $E\frac{1}{2}$ is displaced to more negative potentials with increase in pH; with wave D, the small displacement observed is in the opposite direction. This indicates that hydrogen ions take part in the potential-determining reactions indicated by waves A and C, but that electron-capture is the primary process associated with wave D, followed by abstraction of a proton from the solvent as a non-potential-determining reaction.

Coincident with the second decrease in the height of wave A beyond pH 9, wave E rapidly increases in height up to pH 10·5, whereupon the rate of increase becomes small. As in the case of wave A at its greatest height, wave E corresponds with a two-electron reduction. Since the effect of pH on $E\frac{1}{2}$ is similar to that observed in the case of wave D, the general nature of the reaction is also one of electron-capture. Logarithmic analysis of wave E at pH 10·7 yields a linear curve, the reciprocal slope of which is 0·089. The theoretical value for a reversible two-electron reaction is 0·030, and for a reversible one-electron reaction, 0·059. Hence it is concluded that reduction in alkaline solution affords no evidence of reversibility.

Only the major waves A and E being considered, the system of two waves of equal maximum height, one preponderating in acid, the other in alkaline solutions, resembles that observed in the polarography of substances capable of existence in two forms, *e.g.*, tautomers (cf. Müller and Baumberger, *J. Amer. Chem. Soc.*, 1939, **61**, 590; Langer, *Ind. Eng. Chem. Anal.*, 1942, **14**, 283). It is hoped when conditions permit to examine the reduction on a larger scale by the controlled potential method developed by Lingane, Swain, and Fields (*J. Amer. Chem. Soc.*, 1943, **65**, 1348), for isolation of the products should throw more light on the reaction mechanism. Until then, the author adopts Tachi and Kabai's suggestion (*loc. cit.*) that the " dissociated " (quinolinium) molecules are more readily reduced than those existing in the " undissociated " (quinolinium hydroxide) form.

The small wave B occurring in strongly acid solutions is taken to indicate some formation of tetrahydro-quinaldinic acid (Wieland, Hettche, and Hoshino, *Ber.*, 1928, **61**, 2377). Since wave A does not attain its maximum height until pH 3, when wave B has become very small, the formation of the tetrahydro-derivative occurs directly without proceeding through the dihydro-stage.

<center>EXPERIMENTAL.</center>

Quinaldinic Acid.—The B.D.H. anhydrous product was recrystallised from benzene and dried at 105°; m.p. 157° (corr.). A 0·025M-stock solution in 50% aldehyde-free alcohol was prepared and diluted 25 times or as required with the appropriate buffer. The introduction of these small concentrations of alcohol was found to be without measurable effect upon the pH. Aqueous solutions made by neutralising the acid with sodium hydroxide grew moulds.

Buffer Solutions.—These were prepared from " AnalaR " reagents and examined polarographically for reducible impurities. Solutions of pH 5·8 and below were sulphuric acid–acetate mixtures 0·2M in sodium acetate, and Clark and Lubs's phosphate and borate buffers were used over the remainder of the range.

Apparatus.—Manual apparatus similar to that described by Kolthoff and Lingane (*op. cit.*, p. 215) was used. A saturated calomel half cell with an electrode area of 16 cm.² served as external anode, being connected to the test solution by means of a salt bridge. Dissolved oxygen was removed from the solution by a stream of purified nitrogen which was first passed through a bubbler containing a little of the solution under examination. Bubbler, electrolysis cell, and calomel half cell were all maintained at 25·0°±0·2° in a large thermostat. The characteristics of the dropping electrode were : $m = 0·917$ mg. sec.$^{-1}$, $t = 3·39$ secs., $m^{2/3}t^{1/6} = 1·157$ (determined in 0·1M-potassium chloride solution at 25°). Applied voltage was measured by means of a " Granta Minor " potentiometer, and was corrected for the IR drop due to the resistance of the cell. The current was measured by a calibrated Tinsley galvanometer with enclosed lamp and scale. The pH of the solutions was determined at 25° by the hydrogen electrode, values below 8 being checked by the quinhydrone electrode.

The author thanks the Chemical Society for a grant.

UNIVERSITY COLLEGE, SOUTHAMPTON.