# 647. *The Polarography of Quinoline Derivatives. Part VII.* The Reduction Waves of Quinoline*-3-, -5-, -6-, *and* -7-*carboxylic Acids.*

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The polarography of quinoline-3-, -5-, -6-, and -7-carboxylic acid in buffered solutions of constant ionic strength, covering the approximate pH range 2—12, and in 0·1M-sodium hydroxide, has been examined. In general, the behaviour of these acids resembles that of the other three isomers. Except for quinoline-6-carboxylic acid, the order of increasing (negative) half-wave potentials in strongly alkaline solution of the seven isomers approximates closely to the order of increasing electron densities at the carbon atoms at which the substituent is attached.

The polarographic behaviour of quinoline-2- and -8-carboxylic acid in buffered solutions has been studied by Stock,[1,2] and Casimir and Lyons [3] have examined the 4-isomer. The behaviour of quinoline-2-carboxylic acid in solutions of low buffer capacity at an electrode of short drop-time has also been described.[4] Preliminary observations concerning the 6- and the 7-isomer have been reported.[5] The present work completes the examination of all seven of the quinolinemonocarboxylic acids. As in previous studies, deoxygenated well-buffered solutions covering a pH range of about 2—12 were used. In the present case, however, the solutions were of higher but constant ionic strength. The behaviour in 0·1M-sodium hydroxide ("pH 13") was also examined.

## EXPERIMENTAL

*Apparatus.*—Current–voltage curves at 25° ± 0·1° were obtained with a Leeds and Northrup Type E Electrochemograph, operated without damping. Data for wave analysis and determination of half-wave potentials were obtained by manual operation. The polarographic cell, reference electrode, coulometric apparatus, and general technique were as used previously.[6] On open circuit in 0·1M-potassium chloride at 25°, the characteristics of the dropping-mercury electrodes were (*A*) $m = 1{\cdot}752$ mg. sec.$^{-1}$, $t = 3{\cdot}88$ sec, and (*B*) $m = 1{\cdot}622$ mg. sec.$^{-1}$, $t = 3{\cdot}97$ sec. Electrode (*A*) was used with quinoline-6-carboxylic acid solutions, those of the other three isomers being examined with electrode (*B*).

All potentials are with reference to the saturated calomel electrode at 25° and are corrected for *iR* drop.

*Reagents.*—Quinoline-3-carboxylic acid, m. p. 273° (lit., 275°,[7] 270—272° [8]), was prepared from 3-bromoquinoline.[8] Quinoline-5-carboxylic acid, m. p. 338—339° (lit.,[9] 342°), was synthesized by the method of Bradford, Elliott, and Rowe.[9] Quinoline-6-carboxylic acid, m. p.

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* Part V, *J.*,1949, 2470; *Metallurgia*, 1949, **40**, 179, 229, is regarded as being Part VI of this work.

[1] Stock, *J.*, 1944, 427.
[2] Stock, *J.*, 1949,763.
[3] Casimir and Lyons, *J.*, 1950, 783.
[4] Wenger, Monnier, and Epars, *Helv. Chim. Acta*, 1952, **35**, 561.
[5] Pinchin and Stock, *Chem. and Ind.*, 1953, 1204; 1954, 347.
[6] Stock, *J.*, 1957, 4532.
[7] Mills and Watson, *J.*, 1910, **97**, 71.
[8] Gilman and Spatz, *J. Amer. Chem. Soc.*, 1940, **62**, 446.
[9] Bradford, Elliott, and Rowe, *J.*, 1947, 437.

291° (lit.,[10] 291°) (Found: C, 69·3; H, 4·1; N, 8·3. Calc. for $C_{10}H_7O_2N$: C, 69·3; H, 4·1; N, 8·1%), and quinoline-7-carboxylic acid, m. p. 251—252° (lit.,[9] 251°) (Found: C, 69·1; H, 4·1%), were obtained by the dichromate oxidation of the corresponding methylquinolines.[11, 12] A second sample of quinoline-6-carboxylic acid (Distillation Products Corpn.), washed with water and dried *in vacuo*, gave polarographic waves indistinguishable from those of the first sample and was used in the greater part of the work with this acid.

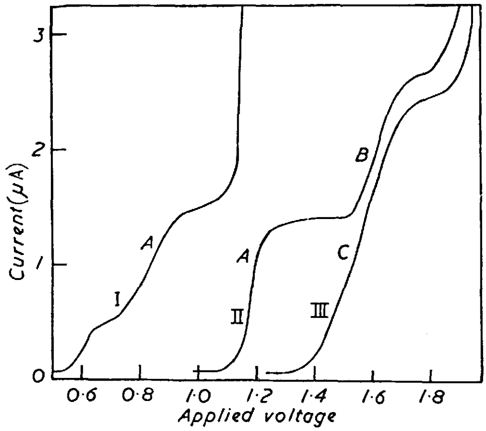
Buffer solutions of ionic strength 0·5 [6] were checked polarographically for absence of reducible impurities.

*Preparation of Solutions.*—The low solubilities of the above four quinolinemonocarboxylic acids and of their sodium salts precluded the use of stock solutions. For each run, the appropriate acid was therefore weighed directly into the buffer solution contained in the polarographic cell and dissolved by passage of nitrogen through the solution. Except in current-concentration experiments, a concentration of 5·0 × $10^{-4}$M of quinolinecarboxylic acid was used throughout.

## RESULTS

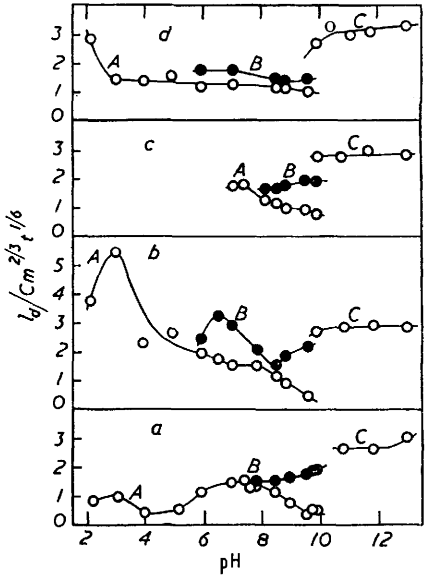
*Quinoline-3-carboxylic Acid.*—Within the approximate pH limits 2—7, quinoline-3-carboxylic acid yields one major wave *A* (Fig. 1), which is accompanied by a pre-wave. A second wave *B* is visible in the pH interval 7—10. Whereas the half-wave potential ($E_{\frac{1}{2}}$) of wave *B* is −1·61 v and independent of pH, that of wave *A* varies with pH according to $-E_{\frac{1}{2}} = 0{\cdot}77 + 0{\cdot}067\text{pH}$ in the pH range 2—5, or according to $-E_{\frac{1}{2}} = 0{\cdot}50 + 0{\cdot}100\text{pH}$ in solutions of pH greater than 5. Waves *A* and *B* therefore coalesce at about pH 11 to form a single wave *C*. At pH 9, waves *A* and *B* are both well-defined and their individual or combined wave-heights increase linearly with the concentration of quinoline-3-carboxylic acid when this concentration does not exceed about 1·5 × $10^{-3}$M. The diffusion-current constants of the waves are markedly pH-dependent (Fig. 2*a*).

FIG. 1. *Polarograms of* 5 × $10^{-4}$M-*quinoline*-3-*carboxylic acid.*



*Curve* I, pH 3·05; II, pH 7·82; III, pH 10·82.

FIG. 2. *Diffusion-current constant*—pH *relations.*



(*a*) *Quinoline*-3-, (*b*) -5-, (*c*) -6-, *and* (*d*) -7-*carboxylic acid.*

*Quinoline*-5-*carboxylic Acid.*—The polarographic behaviour of quinoline-5-carboxylic acid qualitatively resembles that of the 2-isomer.[1] A large ill-defined wave *A*, accompanied by a

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[10] Alamela and Dey, *Proc. Natl. Inst. Soc. India*, 1941, **7**, 215.

[11] Seibert, Norton, Benson, and Bergstrom, *J. Amer. Chem. Soc.*, 1946, **68**, 2721.

[12] Glenn and Bailey, *J. Amer. Chem. Soc.*, 1941, **63**, 641.

small pre-wave, is obtained in the pH range 2—5. Above pH 5, the definition of this wave improves and a second wave *B* appears. The diffusion-current constants of both waves are highly pH-dependent (Fig. 2*b*), that of wave *A* becoming negligible at pH 11. Above pH 6 the equation of wave *A* is $-E_{\frac{1}{2}}$ = 0·59 + 0·095pH, but the equation $-E_{\frac{1}{2}}$ = 0·73 + 0·125pH for wave *B* holds up to pH 8 only. In more alkaline solutions, the half-wave potential of wave *B* is nearly independent of pH. At pH 6, the individual or combined heights of the two waves increase linearly with the concentration of quinoline-5-carboxylic acid when this concentration does not exceed $3 \times 10^{-3}$M.

*Quinoline*-6-*carboxylic Acid.*—In contrast to all other isomers, quinoline-6-carboxylic acid yields no measurable wave in acid solutions.[5] The lowering of the hydrogen overpotential normally caused by quinoline derivatives is, however, apparent. In neutral or alkaline solutions a well-defined wave *A* of equation $-E_{\frac{1}{2}}$ = 0·35 + 0·105pH is observed. A second wave *B*, of pH-independent half-wave potential −1·60 v, appears at about pH 8. Between the pH limits 8—10, the sum of the heights of these two waves is constant and approximately equal to that of the single wave *C* which is formed by their coalescence in strongly alkaline solutions (Fig. 2*c*).

*Quinoline*-7-*Carboxylic Acid.*—The polarographic behaviour of quinoline-7-carboxylic acid qualitatively resembles that of the 8-isomer.[2] Within the approximate pH limits 2—5, quinoline-7-carboxylic acid yields one major wave which is accompanied by a pre-wave and a small maximum. The half-wave potential, −0·96 v at pH 2·1, first rises as the pH is increased to −1·19 v at pH 4·9, falls to −0·99 v at pH 6, and then rises again as the pH is further increased. At pH 6 a second wave, of half-wave potential −1·23 v, becomes visible. This half-wave potential rises to −1·51 v at pH 7·5 and is then almost unaffected by further pH increase or by the merging in of the first wave at about pH 10. Until the two waves merge, the heights of both decrease as the pH is increased (Fig. 2*d*).

## DISCUSSION

Since the polarography of quinoline derivatives has already been reviewed,[13] probable reaction mechanisms are here only outlined.

The diffusion-current constants of the single wave obtained in strongly alkaline solutions are about the same, not only for the present four quinolinemonocarboxylic acids, but also for the other isomers.[1,2,3] Coulometric electrolysis and, in the case of the 2-isomer, conductivity data,[1] indicate that, in such solutions, the reduction involves the uptake of two electrons per molecule.

Apart from the large wave (probably due to catalytic discharge of hydrogen ion) given by quinoline-5-carboxylic acid in solutions of pH about 3, there is no indication that the reduction of any of the quinolinemonocarboxylic acids proceeds beyond the dihydro-stage. The magnitude of the diffusion-current constants of waves *A* and *B* for the 3, 6-, and 7-isomers indicates that these waves are each associated with the uptake of one electron per molecule. Since their heights are approximately proportional to the square root of the pressure of mercury at the dropping-mercury electrode, these waves are diffusion-controlled.[14] Hydrogen ions are presumably involved directly in the electrode reaction associated with wave *A*, but not in that associated with wave *B*.

Exaltation of wave *B* of the 5-isomer in the pH range 6—8 may be due to the inclusion in the measured height of almost coincident small waves associated with secondary processes (cf. the complex wave system of quinoline-2-carboxylic acid in this pH range [1,4]).

Logarithmic analysis [15] of the waves listed in Table 1 yields linear curves. In

TABLE 1. *Wave analysis of quinolinemonocarboxylic acids.*

| Isomer | 3 | | | | 5 | | | | 6 | | 7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH ......... | 6·93 | 8·83 | 8·83 | 10·75 | 6·43 | 8·50 | 9·90 | 9·90 | 8·14 | 11·74 | 6·93 | 8·83 | 8·83 |
| Wave ...... | *A* | *A* | *B* | *C* | *A* | *B* | *A* | *B* | *A* | *C* | *A* | *A* | *B* |
| α ............ | 0·70 | 1·20 | 0·66 | 0·37 | 0·89 | 0·79 | 0·42 | 0·64 | 0·51 | 0·54 | 0·66 | 1·39 | 0·53 |

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[13] Stock, Proc. 1st Internat. Polarographic Congr., Prague, 1951, 371.

[14] Kolthoff and Lingane, "Polarography," Interscience Publ. Inc., New York, 1952, 2nd edn., Vol. I, p. 274.

[15] Kolthoff and Lingane, ref. 14, p. 215.

practically all cases, the reciprocal slopes of these curves are considerably greater than those required for reversible electron uptake and hence lead to fractional α-values in the Kolthoff–Lingane equation.[16] The waves therefore appear to be associated with irreversible processes.

Various relationships have been described in attempts to correlate the reduction potentials of aromatic hydrocarbons with some fundamental property related to molecular structure.[17,18] In strongly alkaline solution, where the quinolinemonocarboxylic acids will exist as anions, the two-electron mechanism of reduction is consistent with Hoijtink's scheme [19] of reaction for conditions where the rate of protonation is high. The reduction may consist of the reversible addition of an electron, followed by the rapid addition of a proton. This makes possible the immediate addition of the second electron at the same reduction potential, followed by the abstraction of another proton from the solvent (in this case water). In the following schemes R represents the quinolinemonocarboxylic acid anion:

$$\mathrm{R} + \mathrm{e} \rightleftharpoons \mathrm{R}^- \quad . . . . . . . \quad (1) \qquad \mathrm{RH}\cdot + \mathrm{e} \longrightarrow \mathrm{RH}^- \quad . . . . . \quad (3)$$

$$\mathrm{R}^- + \mathrm{H}^+ \longrightarrow \mathrm{RH}\cdot \quad . . . . . . \quad (2) \qquad \mathrm{RH}^- + \mathrm{H}^+ \longrightarrow \mathrm{RH}_2 \quad (4)$$

Reactions (2) and (4) are probably irreversible, and thus the overall process for these compounds may appear to be irreversible, as deduced above. The view that the potential-determining step involves only one electron is not universally accepted [17] but this does not affect the present argument.

Reaction (1) may be regarded as a nucleophilic attack by an electron on the quinoline ring system. The electron need not be localised at this stage.[20] Reduction in a given medium will be facilitated (for attack by a nucleophilic reagent) by a substituent which withdraws electrons from the ring, and made more difficult by a substituent which increases the charge on the quinoline nucleus. According to Gore,[21] a reactivity number of a position (such as the localisation energy) can be taken, as a first approximation, as a measure of the extent to which conjugation will take place when a substituent is in that position, at least in alternant hydrocarbons. The electron density of the carbon atom to which the substituent is attached may serve as a suitable reactivity number, and will determine the magnitude of the effect on the electron density at the point of attack. Thus the electron density at the carbon atoms in the quinoline ring will indicate approximately the relative ease of reduction of the isomeric quinolinemonocarboxylic acids, which in 0·1M-sodium hydroxide will exist as anions in which the carboxyl group will tend to push electrons into the ring.

TABLE 2. *Half-wave potentials of quinolinemonocarboxylic acids in* 0·1M-*sodium hydroxide.*

| Isomer ........... | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| $-E_{\frac{1}{2}}$ .............. | 1·53 [1] | 1·71 | 1·51 [3] | 1·70 | 1·64 | 1·59 | 1·74 [2] |

TABLE 3. *Electron densities for quinoline.*

| Position of atoms | N | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Coulson [22] ..................... | 1·63 | 0·79 | 0·98 | 0·77 | 0·96 | 0·99 | 0·95 | 1·00 |
| Brown and Harcourt * [23] ... | 1·22 | 0·89 | 1·01 | 0·93 | 0·99 | 1·00 | 0·98 | 1·01 |

* Abbreviated to three significant figures, for $h = 0·5$, $h' = 0$, $k = 1·0$ (from ref. 23).

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[16] Kolthoff and Lingane, ref. 14, p. 267.

[17] Gardner, *Nature*, 1959, **183**, 320.

[18] Gergeley and Iredale, *J.*, 1953, 3226; Coulson, Crowell, and Tendich, *J. Amer. Chem. Soc.*, **1957**, **79**, 1354; Given, *Nature*, 1958, **181**, 1001; *J.*, 1958, 2684.

[19] Hoijtink, van Schooten, de Boer, and Aalbersberg, *Rec. Trav. chim.*, 1954, **73**, 355.

[20] Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

[21] Gore, *J.*, 1954, 3166.

[22] Coulson, " Valence," Oxford, 1952, p. 243.

[23] Brown and Harcourt, *J.*, 1959, 3451.

The half-wave potentials in 0·1M-sodium hydroxide, wherein the effect of changes in pH and in ionic strength upon the polarographic characteristics is small, are listed in Table 2. Difficulty of polarographic reduction of the acid anions thus increases in the order 4 $\approx$ 2,7,6,5,3 $\approx$ 8. Except for the 6-isomer this approximates closely to the order of increasing electron density at the carbon atoms at which the substituent is attached. According to Coulson [22] this order is 4,2,7,5,3,6,8 and according to Brown and Harcourt [23] it is 2,4,7 $\approx$ 5,6,3 $\approx$ 8 (Table 3).

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