# **431.** *The Mechanism of the Electrolytic Reduction of a Heterocyclic Chalcone Analogue,* 1-p-*Methoxyphenyl*-3-2′-*quinolylprop*-2-*en*-1-*one: a Polarographic and Controlled-potential Macroelectrolysis Study.*

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The compound named in the title gives three main polarographic diffusion-controlled reduction waves at the dropping-mercury electrode in 50% aqueous ethanol over apparent pH range 1·36—13·9 at 25°. By comparison with polarographic and macroelectrolysis results for quinoline-2-aldehyde, it is shown that the first wave has a one-election potential-controlling process, but includes two competitive secondary processes. One leads to dimeric carbonyl-containing products without further electron uptake, the other involves a further univalent reduction to a monomeric ketonic dihydro-derivative, which has also been studied polarographically. The proportion of the latter process under polarographic conditions is ~100% up to pH 9, falling to zero at pH 13·9. Under macroelectrolysis conditions, the proportion is ~50% up to at least pH 7, falling to zero at pH 13·9. The second wave, which has an adsorption pre-wave and is partly adsorption-controlled, and the third wave are due to successive univalent reductions at the carbonyl group. Even for the first wave, primary attack occurs at the carbonyl group, but subsequent rearrangement leads to reduction of the ethylenic bond. Two further waves at more negative potentials occur at certain pH values, but have not been interpreted.

In this paper we compare the behaviour at the dropping-mercury electrode of 1-*p*-methoxyphenyl-3-2′-quinolylprop-2-en-1-one (Ia), which is a heterocyclic analogue of chalcone (Ib), with that of chalcone, furfurylideneacetophenone (Ic), and some of their derivatives. For all the last-named compounds, three reduction waves are in general obtained,[1–7] although at low pH the third wave sometimes becomes obscured by the hydrogen discharge wave, and occasionally the second wave, the half-wave potential ($E_{\frac{1}{2}}$) of which is much less pH-dependent than those of the other waves, merges with the first wave as pH rises.

$R{\cdot}CH{=}CH{\cdot}CO{\cdot}R'$ (a) $R = $ 2-quinolyl, $R' = p\text{-MeO}{\cdot}C_6H_4$. (b) $R = R' = Ph$. (c) $R = $ 2-Furyl, $R' = Ph$.

(I)

For chalcone, Pasternak [1] reports that the ethylene group is always reduced before the carbonyl group, but Korshunov and Vodzinskii [2] consider that the carbonyl and not the ethylene group is attacked. The effect of substitution by hydroxyl, alkoxyl, and acetoxyl groups in either ring of chalcone was studied by Geissman and Friess [3] who found that, when conjugated with the carbonyl group, hydroxyl and methoxyl groups decrease, and acetoxyl groups increase, the ease of reduction. The kinetics [6] and equilibria [4,6] of reactions 2-hydroxychalcones $\rightleftharpoons$ flavanones have been followed polarographically; the equilibria are independent of pH in the range 5—9, shifting to the left at high pH; the velocities of both reactions rise with pH. The rate of formation of a chalcone from the corresponding acetophenone and benzaldehyde has also been determined polarographically.[6]

Few heterocyclic analogues of chalcone have been studied in detail polarographically.

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[1] (*a*) Pasternak, *Helv. Chim. Acta*, 1948, **31**, 753; (*b*) Pasternak and von Halban, *ibid.*, 1946, **29**. 190.

[2] Korshunov and Vodzinskii, *Zhur. fiz. Khim.*, 1953, **27**, 1152.

[3] Geissman and Friess, *J. Amer. Chem. Soc.*, 1949, **71**, 3893.

[4] Schraufstätter, *Experientia*, 1948, **4**, 192.

[5] Cassidy and Whitcher, *J. Phys. Chem.*, 1959, **63**, 1824.

[6] Corvaisier and Tirouflet, *Compt. rend.*, 1960, **251**, 1641.

[7] Tirouflet and Boichard, *Compt. rend.*, 1960, **251**, 1861.

Cassidy and Whitcher[5] found that the furyl analogue (Ic) and several of its derivatives give three waves at somewhat less negative $E_{\frac{1}{2}}$ than corresponding chalcones; electron-releasing substituents decrease, and electron-withdrawing groups increase, the ease of reduction. For ferrocene analogues, $C_5H_5 \cdots Fe \cdots C_5H_4{\cdot}CO{\cdot}CH{=}CHR$ and $C_5H_5 \cdots Fe \cdots C_5H_4{\cdot}CH{=}CH{\cdot}COR$ (R = aryl or heteroaryl), Tirouflet and Boichard[7] obtained an anodic wave due to oxidation of the ferrocene skeleton and a single cathodic wave due to reduction of the CO·CH:CH group; for R = phenyl, thienyl, furyl, or pyrryl, this wave resembled the first wave of chalcones in corresponding to one electron in acid and 2 in alkali; for R = pyridyl, it was a 2-electron wave at all pH's examined.

In an attempt to elucidate the mechanism of the polarographic reduction of compound (Ia), controlled-potential coulometric electroreductions have now also been carried out.

## EXPERIMENTAL

*Materials*.—Compound (Ia), prepared as directed by Ariyan and Suschitzky,[8] was purified by column chromatography on alumina (Spence's type H) with benzene as solvent and eluant; the small initial zone of colourless ultraviolet-fluorescent material did not depress the m. p. (133°) of the main yellow fraction, but it was discarded. A $10^{-2}$M-stock solution in " AnalaR " (99—100%) ethanol was diluted with aqueous buffers to give solutions for polarography which contained 50% v/v of ethanol, and at least 100 : 1 molar ratios of buffer constituent to compound (Ia), and were adjusted where possible to final ionic strength 0·1 with " AnalaR " potassium chloride. All solutions containing compound (Ia) were kept in the dark during preparation, storage, or experimental investigations, since, in ethanol or benzene, the material is photolysed in daylight to a purple product (which is being further investigated). Buffer constituents were of " AnalaR " grade excepting ethanolamine (EA), triethanolamine (TEA), sodium formate (all reagent grade), and boric acid (B.P.). Buffer pH values in water and apparent values (pH′) for the same buffer mixture in 50% aqueous ethanol were determined at 25° with the Pye " Dynacap " pH-meter; in both solvents an aqueous saturated calomel electrode and either a Pye lithium-glass or a Cambridge wide-range glass electrode were used, without significant difference in the results. The system was standardised against aqueous buffers at pH 4·01, 6·99, and 9·15 supplied with the " Dynacap " meter, and also against 0·1M-aqueous potassium trihydrogen tetraoxalate (pH 1·50). The values found were:

| Buffer | 0·1N-HCl | $CH_2Cl{\cdot}CO_2^-$ | $H{\cdot}CO_2^-$ | $AcO^-$ | TEA |
|---|---|---|---|---|---|
| pH ($H_2O$) ......... | 1·12 | 2·38 | 3·04 | 4·13 | 7·28 |
| pH′ (50% EtOH) | 1·33 | 3·13 | 3·65 | 5·02 | 7·01 |

| Buffer | TEA | EA | Borate | Borate | 0·1N-NaOH | N-NaOH |
|---|---|---|---|---|---|---|
| pH ($H_2O$) ......... | 8·27 | 9·52 | 8·79 | 10·23 | 12·86 | — |
| pH′ (50% EtOH) | 7·98 | 9·22 | 10·14 | 11·59 | *ca.* 13·05 | *ca.* 13·9 |

The pH′ of 0·1N-NaOH was 12·70 initially, drifting to 13·42 after about 20 min. For N-NaOH, no pH′ could be read.

Calomel and mercury for calomel and mercury-pool electrodes were of " AnalaR " grade, but for the dropping-mercury electrode the mercury was further treated with acetone, followed by dilute nitric acid, dried, and triply vacuum-distilled. Commercial agar (B.D.H.) was used for the salt-bridge in controlled-potential electrolysis. Quinoline-2-aldehyde (from Messrs. L. Light and Co.) was steam-distilled and recrystallised from water shortly before use, and shielded from light. Cylinder nitrogen was deoxygenated and presaturated by passage through sintered-disc wash-bottles containing successively Fieser's solution (alkaline dithionite-reduced sodium anthraquinone-2-sulphonate), aqueous sodium hydroxide, and 50% v/v aqueous ethanol.

*Apparatus*.—Polarograms were obtained by means of a Sargent model XXI pen-recording polarograph incorporating a fast pen-recorder (full-current scale-deflection requiring 1 sec.) and used without damping, so that maximum, and not an average, current during a mercury drop-life was recorded. The polarographic cell assembly maintained usually at 25° ± 0·1°

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[8] Ariyan and Suschitzky, *J.*, 1961, 2242.

in a water thermostat-bath, was similar to that of Cooper and Stonehill,[9] incorporating two dip-type saturated calomel reference electrodes of slightly modified type (Fig. 1), placed on either side of the dropping-mercury electrode, one being used to carry the polarographic current, the other to measure the true potential within 1 mv of the electrode, free from errors due to ohmic potential drop,[10] at selected points along the polarogram, with the aid of a Cambridge Instrument Co. vernier potentiometer. Two Sargent Pyrex dropping-mercury electrode capillaries were used, which were connected to the mercury reservoir by polyvinyl chloride tubing and had the following characteristics, measured with no applied potential in borate buffer, of ionic strength 0·1, in 50% aqueous ethanol (apparent pH′ 11·59) at 25°: $m$ (mercury flow rate) = 3·70 and 3·92 mg. sec.$^{-1}$; $t$ (drop-time) = 2·18 and 2·10 sec., respectively.

Controlled-potential electrolytic reductions were carried out at room temperature in an apparatus similar to that of Pasternak.[1] The cathode was a magnetically stirred mercury pool, the anode was a piece of silver foil, and the catholyte was separated from the saturated potassium chloride anolyte by a sintered-glass disc backed on the anode side by a plug (1 cm. in length) of 2% agar solution saturated with potassium chloride. Both anolyte and catholyte were continuously stirred by a stream of nitrogen bubbles, which served for the pre-electrolytic deoxygenation of the solution. Current was supplied from a Radford Labpack D.C. supply unit, supplemented when necessary by NiFe-alkaline accumulators. By means of a series resistor, the applied potential was frequently adjusted manually to maintain constancy of the potential difference (measured with a Cambridge vernier potentiometer) between the cathode and an auxiliary saturated calomel reference electrode, the agar–potassium chloride salt-bridge of which terminated about 1 mm. above the mercury cathode surface. Current was measured frequently with an Avo milliameter, and the number of coulombs passed was determined by graphical integration of current against time.

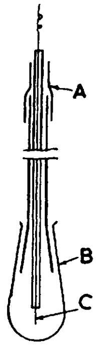

FIG. 1. Dip-type calomel electrode.

A, Polyvinyl chloride tubing (connector). B, Ground glass joint (C 7). C, Platinum wire, sealed in glass.

Absorption spectra were measured with an Optica UV recording spectrophotometer and a Perkin–Elmer Infracord model 137 recording infrared spectrophotometer.

*Procedure.*—Solutions (*ca.* 1mM) of compound (Ia) or of quinoline-2-aldehyde were polarographed in the dark at 25° over the potential range 0—1·8 v against the saturated calomel electrode. A nitrogen stream flowed through the polarographic cell above the solution during polarography. The various buffer supporting electrolytes in 50% v/v aqueous ethanol were separately polarographed to confirm the absence of polarographically active impurities. Half-wave potentials were corrected for ohmic potential drop by means of an auxiliary calomel reference electrode. Polarograms were usually recorded for mercury column heights, $h$, of 28, 35, 45, and 60 cm., and the slopes of graphs of log $i$ ($i$ = limiting current) against log $h$ for each wave were used to distinguish between diffusion, adsorption, and kinetic waves, for which the theoretical slopes are 0·5, 1·0, and <0·5, respectively.

Controlled-potential electrolytic reductions of compound (Ia) were carried out at potentials corresponding to the upper plateaux of each of the three polarographic waves A, D, and F of Table 1, with 0·5—0·8mM-solutions in 75% v/v aqueous-ethanolic triethanolamine–hydrochloric acid buffers (ionic strength 0·25M) at initial pH′ 7·01, 7·93, or 13·05. For quinoline-2-aldehyde, a 5 × 10$^{-2}$M-solution in 50% v/v aqueous-ethanolic triethanolamine–hydrochloric acid buffer (ionic strength 0·5M) of initial pH′ 7·2 was electrolysed at a potential corresponding to

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[9] Cooper and Stonehill, *J.*, 1958, 3341.

[10] Arthur, Lewis, Lloyd, and Vanderkam, *Analyt. Chem.*, 1961, **33**, 488.

the plateau of the first polarographic wave. The pH′ of these solutions increased slightly during electrolysis, since the concentration ratios of electroactive to buffer constituents were much higher than those used in polarography. The buffer supporting electrolytes were pre-electrolysed, and the cathode mercury was replaced by fresh mercury, before addition of electroactive material. Electrolysis was continued until the current had fallen to a low constant level approximating to that obtained with the buffer supporting electrolyte without electroactive material. The resulting suspensions of sparingly soluble products were heated, diluted 10-fold with hot water, and cooled to cause complete precipitation, and the solid was filtered off, washed with water, and dried in a vacuum over $P_2O_5$, to give in general a ~90% yield calculated on the weight of starting material. The products from compound (Ia) were chromatographed in benzene on alumina, with elution by benzene containing increasing amounts of ethyl acetate; the main fraction was recrystallised from light petroleum with or without benzene, or from acetone. The product from quinoline-2-aldehyde was recrystallised from dioxan. For some of the fractions, infrared and ultraviolet absorption spectra and the cryoscopic molecular weight in benzene or camphor were determined. Since with compound (Ia) polarographic tests indicated the presence of unchanged starting material after the current stopped falling, control electrolyses with larger quantities were carried out, in which current was continued until a larger number of faradays per molecule had been passed than in the smaller-scale experiments.

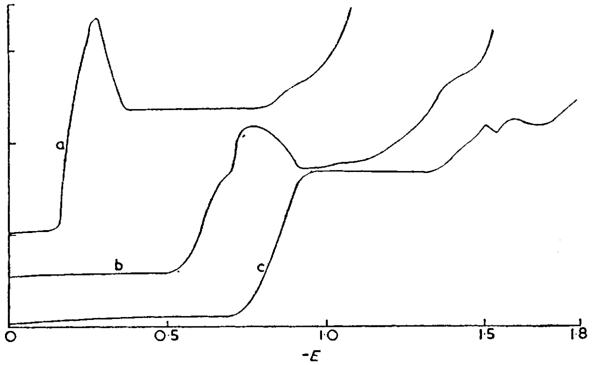

FIG. 2. Typical polarograms of compound (Ia) (*i* in arbitrary units; $-E$ in mv *vs* S.C.E.). pH′: (a) 1·36, (b) 7·01, (c) 10·14.

## RESULTS

*Polarographic Results*.—Table 1 gives the detailed polarographic results for compound (Ia). Typical polarograms are shown in Fig. 2. The successive waves in order of increasingly negative $E_{\frac{1}{2}}$ are designated A—F. In general, $E_{\frac{1}{2}}$ values are given for mercury column height $h = 60$ cm., but in some indicated cases, where a lower $h$ caused a single wave to split into two, $E_{\frac{1}{2}}$ is given for $h = 45$ cm. The values for d log $i$/d log $h$ indicate that wave A is a diffusion wave, B is in general an adsorption wave, C is controlled by adsorption and diffusion, and D by diffusion; for E and F, there are insufficient results for a decision.

The effect of variation of temperature and of $h$ upon $E_{\frac{1}{2}}$ and $i$ for one typical solution is illustrated by Table 2. Wave A has $E_{\frac{1}{2}}$ virtually independent of $h$ and shifting to more negative values with rise of temperature; the temperature coefficient of $i$ for this wave is ~2·5% per °c at $h = 28$ cm., rising to 2·9% at $h = 60$ cm., confirming the view that the wave is diffusion-controlled. For wave B, however, although $E_{\frac{1}{2}}$ is also only slightly dependent on $h$, it is shifted to more positive values at higher temperatures, while $i$ has the negative temperature coefficient expected of an adsorption wave. The fragmentary results for wave C suggest adsorption control.

Table 3 illustrates, for a single representative pH′, the proportionality between $i$ and $c$ (concentration) for wave A (but not B), and the variation of $E_{\frac{1}{2}}$ with $c$ for these waves.

For quinoline-2-aldehyde, the polarogram at $c = 1$mM, pH′ 11·59, and 25°, consisted of two waves with a broad maximum on the upper plateau of the first. Addition of a trace

TABLE 1.

Half-wave potentials (*vs.* S.C.E.), limiting current constants, and variation of limiting currents with mercury column height, for compound (Ia).

| pH′ | Concn. (mM) | Wave | A | B | C | D | E | F |
|---|---|---|---|---|---|---|---|---|
| 1·36 | 0·8 | $-E_{\frac{1}{2}}$ (mv) | ~177 ¶ | — | 830 | — | — | ~1205 |
| | | $I = i/cm^{2/3}\,t^{1/6}$ | 2·38 | — | 0·32 | — | — | — |
| | | $S = \mathrm{d}\log i/\mathrm{d}\log h$ | 0·47 | — | 0·97 | — | — | — |
| 3·13 | 0·8 | $-E_{\frac{1}{2}}$ | 304 ¶ | 842 | ~966 | 1052 | — | ~1286 |
| | | $I$ | 2·44 | 0·38 | 0·42 | 0·76 | — | — |
| | | $S$ | 0·48 | 0·9 | — | — | — | — |
| 3·65 | 0·8 | $-E_{\frac{1}{2}}$ | 372 ¶ | 840 | ~984 | 1111 †† | — | 1356 †† |
| | | $I$ | 2·53 | 0·27 | 0·4 | — | — | — |
| | | $S$ | 0·53 | 1·04 | * | 0·49 | — | — |
| 5·02 | 0·8 | $-E_{\frac{1}{2}}$ | 484 ¶ | 897 | 1073 | 1141 | — | 1186 |
| | | $I$ | 2·44 | 0·22 | 0·57 | 1·49 | — | 0·63 |
| | | $S$ | 0·51 | 1·03 | ~0·5 | — | — | * |
| 7·01 | 1·0 | $-E_{\frac{1}{2}}$ | 620 § ** | 1020 | 1196 | 1338 | — | 1528 |
| | | $I$ | 2·36 | 0·11 | 0·66 | 1·45 | — | 1·23 |
| | | $S$ | 0·63 | ~0 | 0·73 | 0·55 | — | — |
| 7·98 | 1·0 | $-E_{\frac{1}{2}}$ | 688 ‡ ** | 1089 | 1256 | 1378 | — | ~1558 |
| | | $I$ | 2·37 | 0·11 | 0·74 | 0·83 | — | 1·45 |
| | | $S$ | 0·6 | 0·32 | 0·49 | † | — | — |
| 9·22 | 1·0 | $-E_{\frac{1}{2}}$ | 757 | 1173 | 1336 | 1463 ‡ | 1562 | 1658 ‡ |
| | | $I$ | 2·24 | 0·10 | 0·98 | 0·95 | 0·370 | 0·18 |
| | | $S$ | 0·58 | * | * | * | * | — |
| 10·14 | 1·0 | $-E_{\frac{1}{2}}$ | 838 | — | 1401 ‡ | 1533 § | 1716 | 1743 |
| | | $I$ | 2·19 | — | 0·63 | 0·12 | 0·580 | 0·27 |
| | | $S$ | 0·57 | — | ~0 | ~0·1 | — | ~0 |
| 11·59 | 1·0 | $-E_{\frac{1}{2}}$ | 880 | — | 1493 †† | ~1580 †† | — | 1736 †† |
| | | $I$ | 1·84 | — | 1·08 | 0·101 | — | — |
| | | $S$ | 0·50 | — | 0·79 | 0 | — | ~0·48 |
| 13·05 | 0·8 | $-E_{\frac{1}{2}}$ | 943 ‡ | — | ~1514 | ~1574 | ~1685 | ~1790 |
| | | $I$ | 1·42 | — | 0·26 | 0·475 | 1·22 | 1·24 |
| | | $S$ | 0·46 | — | * | — | — | — |
| ~13·9 | 0·8 | $-E_{\frac{1}{2}}$ | 987 ‡ | — | 1495 ‡ | ~1651 †† | ~1683 †† | ~1772 |
| | | $I$ | 1·16 | — | 0·56 | — | — | 2·75 |
| | | $S$ | 0·51 | — | 1·4 | — | — | — |

* Indefinite. † Negative. ‡ Small maximum. § Maximum. ¶ Large maximum. ** Maximum diminishes as *h* falls. †† For *h* = 45 cm.

TABLE 2.

Effects of varying temperature and mercury column height, for 0·8mM-solutions of compound (Ia) at pH′ 13·05.

| | Wave A | | | | | | Wave B | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *h* | $-E_{\frac{1}{2}}$ (mv) | | | $i$ (μA) | | | $-E_{\frac{1}{2}}$ (mv) | | | $i$ (μA) | | |
| (cm.) | 25° | 35° | 45° | 25° | 35° | 45° | 25° | 35° | 45° | 25° | 35° | 45° |
| 28 | 940 | 940 | 954 | 2·22 | 2·70 | 3·10 | 1563 | 1530 | 1533 | 1·34 | 0·68 | 0·98 |
| 35 | 939 | 943 | 952 | 2·34 | 3·00 | 3·54 | 1568 | 1541 | 1532 | 1·66 | 1·08 | 1·02 |
| 45 | 940 | 949 | 952 | 2·72 | 3·42 | 4·00 | 1568 | 1552 | 1530 | 1·88 | 1·54 | 1·38 |
| 60 | 943 | 938 | 952 | 3·04 | 3·96 | 4·78 | 1558 | 1534 | 1522 | 1·60 | 1·60 | 1·26 |

| | Wave C | | | | | |
|---|---|---|---|---|---|---|
| *h* | $-E_{\frac{1}{2}}$ (mv) | | | $i$ (μA) | | |
| (cm.) | 25° | 35° | 45° | 25° | 35° | 45° |
| 28 | — | — | 1653 | — | — | 1·62 |
| 35 | — | — | 1642 | — | — | 1·62 |
| 45 | — | — | 1647 | — | — | 1·88 |
| 60 | 1685 | — | 1620 | 2·68 | — | 1·30 |

TABLE 3.

Effect of varying concentration on half-wave potentials and limiting currents of compound (Ia) at pH′ 7·98.

| | Wave A | | | Wave B | | |
|---|---|---|---|---|---|---|
| $c$ (mM) | $-E_{\frac{1}{2}}$ (mv) | $i$ (μA) | $I = i/cm^{2/3}\,t^{1/6}$ | $-E_{\frac{1}{2}}$ (mv) | $i$ (μA) | $I$ |
| 0·1 | 690 | 0·66 | 2·31 | 1067 | 0·04 | 0·14 |
| 0·4 | 688 | 2·72 | 2·38 | 1099 | 0·39 | 0·27 |
| 1·0 | 690 | 6·75 | 2·37 | 1094 | 0·35 | 0·12 |

(*ca.* 5 × $10^{-5}$M) of compound (Ia) suppressed this maximum, and the resulting wave had $E_{\frac{1}{2}}$ = −888 mv, $I = i/cm^{2/3}t^{1/6}$ = 1·84, d log *i*/d log *h* = 0·6 (diffusion wave); logarithmic analysis [11] yielded a good straight line of slope 68 mv. The second wave had $E_{\frac{1}{2}}$ = approx. −1540 mv, *I* = 0·90.

*Controlled-potential Electrolyses.*—Details are given in Table 4. For compound (Ia), small-scale electrolyses (Nos. 1, 3, and 5) at potentials corresponding to the plateaux of polarographic waves A, D, and F gave values of *n* (electron uptake per molecule) of 1, 1·8, and 2·3. However, polarographic examination of the electrolysed solution no. 1 showed that wave A of compound (Ia) was still present to an extent indicating the presence of about one-third of the original compound. A larger-scale repetition (no. 2) of this electrolysis, in which passage of current was continued until *n* = 1·5, gave a solution whose polarogram no longer exhibited wave A, but gave waves similar to B, C, and D for compound (Ia). Experiment no. 4, a large-scale repetition of no. 3, with current maintained until *n* = 3·5, gave results like those from no. 3. No. 6, a large-scale repetition of no. 5 in which the high value *n* = 8 is due to considerable hydrogen evolution, produced gums. The red colour observed at the two most negative potential regions is probably due to free-radical electrolysis products which rapidly dimerise or otherwise react. Experiment no. 7, a large-scale electrolysis at the plateau of wave A in more strongly alkaline solution, gave dimeric, red, uncrystallisable products.

TABLE 4.

Controlled-potential electrolyses.

| Expt. no. | Cpd. (Ia) (g.) | Initial pH′ | Potential (mv *vs.* S.C.E.) | *n* (faradays/mole) | Product: yield and m. p. of main fraction | Remarks |
|---|---|---|---|---|---|---|
| 1 | 0·06 | 7·01 | −600 to −700 | 1 | 0·035 g., 103° | *a* |
| 2 | 2 | 7·5 | −700 | 1·5 | 1·8 g., 103° | *b* |
| 3 | 0·175 | 7·93 | −1450 | 1·8 | 0·162 g., 98—99·5° | *c, d, e* |
| 4 | 2 | 7·5 | −1450 | 3·5 | 1·81 g., 102—104° | *e, f* |
| 5 | 0·20 | 7·93 | −1640 to −1700 | 2·3 | 0·153 g., 99—100° | *g, h* |
| 6 | 2 | 9·5 | −1800 | 8 | 1·1 g., gum | *g* |
| 7 | 2 | 13·05 | −1170 | 1·3 | 1·86 g., amorphous | *i* |
| 8 | 0·631 g. of quinoline-2-aldehyde | 7·2 | −1000 to −1020 | 1·02 | 0·554 g., 205—208° (decomp.) | *j* |

(*a*) For main fraction: Found: C, 78·4; H, 6·0; N, 4·4. Calc. for dihydro-deriv., $C_{19}H_{17}NO_2$: C, 78·3; H, 5·8; N, 4·5%. (*b*) For main fraction: Found: *M*, 319 (cryoscopic, in benzene), 258 (Rast); calc. for $C_{19}H_{17}NO_2$: *M*, 291; polarogram of 0·22mM-solution in 50% aq. EtOH, pH′ 7·01, exhibits waves at $E_{\frac{1}{2}}$ −1058, −1182, and −1335 mv, *I* = 1·15, 1·06, and 1·82, respectively. (*c*) Mixed m. p. with main product from no. 1, 101·5°. (*d*) Polarograms of products from no. 1 and no. 3 are identical. (*e*) Transient red coloration for a few mm. above Hg cathode during electrolysis, persisting for a few seconds after current stops. (*f*) Product gives a 2,4-dinitrophenylhydrazone, m. p. 233—236° (decomp.). (*g*) Transient red-yellow colour above cathode, similar to that in (*e*). (*h*) Polarogram of 0·8 mM-solution of crude product at pH′ 9·3 in 50% aq. EtOH exhibits waves at $E_{\frac{1}{2}}$ −1380 (? double wave) and −1590 mv, *I* = 0·46 and 0·38, respectively. (*i*) Main product was a red amorphous solid [Found: *M*, 536 (cryoscopic, in benzene). Calc. for dimerised monohydro-deriv., $C_{38}H_{32}N_2O_4$: *M*, 580]. (*j*) For main product: Found: C, 75·2; H, 5·3; N, 8·6%, *M* (Rast), 288. Calc. for dimerised monohydro-deriv., $C_{10}H_{16}N_2O_2$: C, 75·9; H, 5·1; N, 8·9%; *M*, 316; a 0·07mM-solution in 50% aq. EtOH, pH′ 11·59, gave polarographic waves at $E_{\frac{1}{2}}$ −885 and −1178 mv, both with *I* = ~0·69; product precipitated during electrolytic reduction.

A major fraction (up to *ca.* 50%) of the product of electrolytic reduction of compound (Ia) at pH′ 7—9 at each of the three potential regions employed was a monomeric, presumably dihydro-derivative, m. p. 103°, which was precipitated extensively during electrolysis. Its infrared spectrum includes a strong carbonyl band at 1670 cm.$^{-1}$, and its failure to react with dilute aqueous permanganate [which compound (Ia) does] indicates reduction of the ethylene linkage, so that its structure is (II). The entirely different major product obtained from compound (Ia) by uptake of one electron per molecule at pH′ 13·05, which also has a strong infrared carbonyl band (*ca.* 1680 cm.$^{-1}$), is probably a mixture of various dimeric products such as (IIIa, b, and c).

The electrolytic reduction of quinoline-2-aldehyde gave virtually a single product, dimeric and requiring uptake of one electron per aldehyde molecule in its formation. Its infrared

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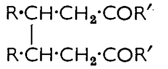
[11] Kolthoff and Lingane, " Polarography," 2nd edn., Interscience Publ., Inc., New York, 1952, Vol. I, p. 193.

spectrum showed no carbonyl band near 1750 cm.$^{-1}$ (contrast the aldehyde), but instead a broad band at 3250 and sharp bands at 1070 and 1316 cm.$^{-1}$, indicating a hydrogen-bonded hydroxyl group. Structure (IV) fits these facts, and is confirmed by the identity of m. p. and of infra-red spectrum with those of an authentic specimen prepared by benzoin condensation of quinoline-2-aldehyde with potassium cyanide (as described by Buechler and Harris;[12] the specimen was kindly presented to us by Dr. H. Suschitzsky, Royal College of Advanced Technology, Salford).

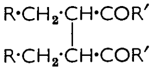
$R\cdot CH_2\cdot CH_2\cdot COR'$

(II)



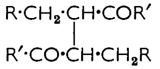
$$\begin{array}{c}R\cdot CH\cdot CH_2\cdot COR'\\ |\\ R\cdot CH\cdot CH_2\cdot COR'\end{array}$$

(IIIa)



$$\begin{array}{c}R\cdot CH_2\cdot CH\cdot COR'\\ |\\ R\cdot CH_2\cdot CH\cdot COR'\end{array}$$

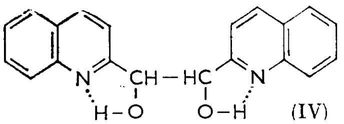
(IIIb)



$$\begin{array}{c}R\cdot CH_2\cdot CH\cdot COR'\\ |\\ R'\cdot CO\cdot CH\cdot CH_2R\end{array}$$

(IIIc)

R = 2-quinolyl; $R' = p\text{-}MeO\cdot C_6H_4$.



(IV)

Ultraviolet absorption spectra of ethanol solutions are in accord with structures (II) and (IV). The strong band at 226 mμ exhibited by quinoline, as well as 4,4′-, 5,5′-, and 8,8′-biquinolyl, is shifted to 246 mμ for quinoline-2-aldehyde, presumably because of conjugation of the quinoline nucleus with the carbonyl group. It reappears for compound (IV) at 222 mμ, because there is now no such conjugation. Similarly, it is shifted to 248 mμ for compound (Ia) but reappears at 228 mμ for (II).

## Discussion

At pH′ 7·01, $E_{\frac{1}{2}}$ for the first wave of quinoline-2-aldehyde is almost identical with that of compound (Ia); in fact, this similarity of $E_{\frac{1}{2}}$ extends over pH′ range 1—14.[13] This suggests that a similar potential-determining process operates for both substances. However, for the aldehyde, the coulometry and the dimeric nature of the product of large-scale electrolysis, as well as the $I$ value 1·84, indicate $n = 1$. On the other hand, for compound (Ia) the value of $I$ is *ca.* 2·4 for pH′ 1—9, thereafter falling to 1·2 at pH′ 13·9 (Fig. 3). When the larger size of compound (Ia) than of the aldehyde is taken into account, this suggests that for (Ia) $n$ is 2 up to pH′ 9, thereafter falling until at pH′ 13·9 it is unity. In agreement with this, $I$ values at pH′ ~6 for the assumed 1-electron first-wave reductions of various chalcones and furfurylidenacetophenones are calculated from published results[3,5] to be generally about 1·2 (which should be multiplied by 7/6 to allow for the

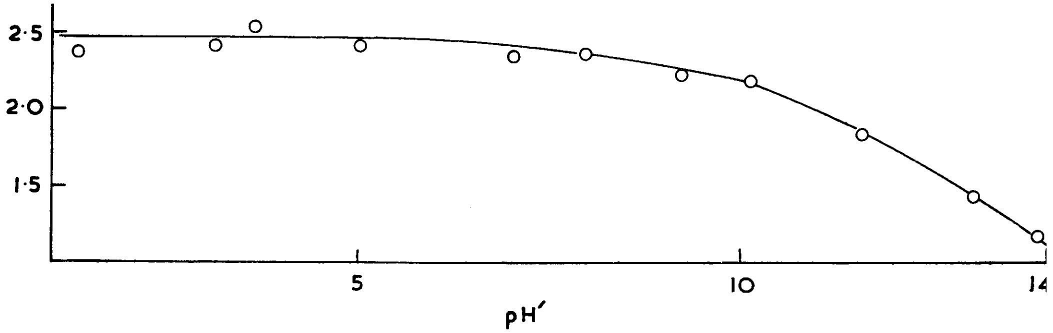


FIG. 3. Limiting-current constant ($I$) for wave A of compound (Ia) as a function of pH′.

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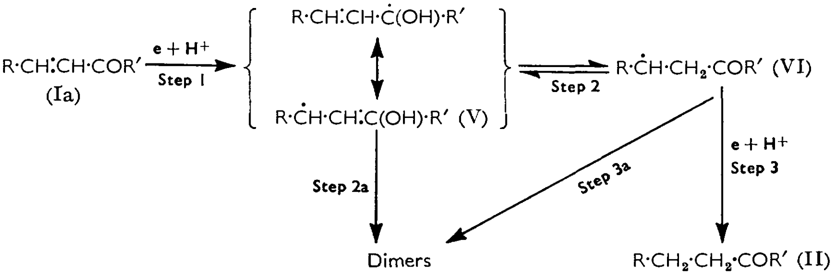
[12] Buechler and Harris, *J. Amer. Chem. Soc.*, 1950, **72**, 5015.

[13] Fornasari, Giacometti, and Rigatti, " Theoretical and Experimental Contributions to Polarography," 1960, Vol. V, 261—267 (Suppl. A to *Ricerca Sci.*, 1960, **30**, Pt. 1).

use of average instead of maximum currents during a single drop-life). Despite this difference of $n$ values, a similar potential-determining step may be postulated for both compound (Ia) and the aldehyde:



(Step 1 is potential-determining.)

For quinoline-2-aldehyde, only steps 1 and 2a occur (since step 2 is impossible), giving $n = 1$ and solely dimeric product. For compound (Ia) it appears that under polarographic conditions only steps 1, 2, and 3 occur at pH′ up to 9, giving $n = 2$; during large-scale electrolysis at pH′ 7·01, however, the concentrations of intermediates (V) and (VI) are much greater, and since the rate of step 2a or 3a is proportional to the square of the appropriate free-radical concentration, while the rate of step 3 is proportional only to the first power of the concentration, step 2a or 3a is accelerated relatively to step 2; the experimental 50% yield of compound (II) corresponds to roughly equal amounts of reaction by routes 2–3 and 2a + 2–3a, resulting in an average $n$ of 1·5 as found. The explanation for the falling-off of $n$ above pH′ 9 is possibly that at this high pH′ the quinoline-nitrogen atom becomes completely unprotonated and is now able to form a hydrogen bond to the hydroxyl group of the enol (V), thus preventing the tautomerisation step 2 and consequently steps 3 and 3a. This view is confirmed by the production of red dimers on large-scale electrolysis at pH′ 13·05. Postulation of step 1 as potential-determining is in agreement with the $E_{\frac{1}{2}}$–pH′ curve (Fig. 4) for wave A, which is linear up to pH′ 10 with a slope of *ca.* 60 mv/pH′ unit, corresponding to a 1 : 1 ratio of protons to electrons. The slope of the curve falls off slightly at higher pH′. This may be due to replacement of step 1 as potential-determining process by a similar process involving no protons as the hydrogen-ion concentration becomes too low, the radical-anion thus produced then abstracting a proton

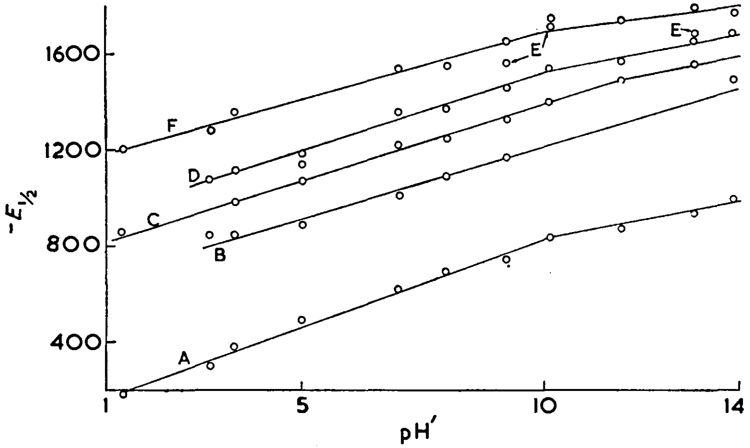


FIG. 4. Variation of half-wave potentials ($-E_{\frac{1}{2}}$, in mv *vs* S.C.E.) with pH

from the solvent to give compound (V); an alternative explanation may be the unreliability of pH′ measurements at very high alkalinities. A further point which may lend support to the view that step 1 is potential-determining is that logarithmic analysis [11] of wave A for compound (Ia) at pH′ 7·01, 7·98, and 13·9 gives reasonably straight lines with slope 59, 69, and 70 mv, respectively.

The suggestion here that the single wave A corresponds to the aggregate of steps 1, 2, 2a, and 3 is not unprecedented. A similar postulation was made by Elving, Rosenthal, Hayes, and Martin [14] to explain the polarographic and controlled-potential electrolysis behaviour of bromomaleic and bromofumaric acid. The reactions postulated above, at least as regards the sequence of steps 1, 2, 3, is broadly similar to those proposed for the polarographic reduction of chalcones [1,3] and of furfurylideneacetophenones,[5] except that in these schemes step 1 alone is assumed to correspond to the first reduction wave and step 3 to the second reduction wave. No evidence based on *n* values and macroelectrolysis products was adduced to support these assignments; for compound (Ia), this evidence excludes such assignments.

The interpretation of waves B—F for compound (Ia) is facilitated by examination of the polarographic data (Table 5) obtained for a specimen of compound (II), produced by macroelectrolysis of compound (Ia) and containing some of the latter unchanged, for which quantitative allowance (on the basis of height of wave A) has been made in evaluating $I$. The waves given by compound (II) are labelled B—F to correspond with those of (Ia), since comparison of $E_{\frac{1}{2}}$ and $S$ values suggests that, at least up to pH′ 11·59, these waves are almost identical for the two compounds. It is concluded that wave B is an adsorption pre-wave associated with wave C, and is due to adsorption of the reduced form of compound (II) produced at wave C. The latter is probably diffusion-controlled, with an $I$ value suggesting (by comparison with wave A of Ia) a one-electron reduction, possibly $R{\cdot}CH_2{\cdot}CH_2{\cdot}COR' + e + H^+ \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}(OH){\cdot}R'$. On this basis, wave D appears to be due to a further one-electron reduction $R{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}(OH){\cdot}R' + e + H^+ \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}R'$. No interpretation can be made of the waves E and F because of the paucity of relevant results; they may correspond to reduction of the quinoline nucleus.

TABLE 5.

Half-wave potentials (*vs.* S.C.E.), limiting-current constants, and variation of limiting currents with mercury column height, for compound (II).

| pH | Concn. (mM) | Wave | B | C | D | E | F |
|---|---|---|---|---|---|---|---|
| 1·36 | 0·76 | $-E_{\frac{1}{2}}$ (mv) | — | 834 | — | — | — |
| | | $I = i/cm^{2/3}t^{1/6}$ | — | 0·43 | — | — | — |
| | | $S = d \log i/d \log h$ | — | ~0·8 | — | — | — |
| 3·65 | 0·76 | $-E_{\frac{1}{2}}$ | 845 | 996 * | — | — | — |
| | | $I$ | 0·33 | ~0·82 | — | — | — |
| | | $S$ | ~0·8 | 0·8 | — | — | — |
| 7·01 | 0·76 | $-E_{\frac{1}{2}}$ | 1022 | 1184 | 1349 | — | — |
| | | $I$ | 0·17 | 1·08 | 0·95 | — | — |
| | | $S$ | ~0·8 | 0·6 | ~0·3 | — | — |
| 9·22 | 0·76 | $-E_{\frac{1}{2}}$ | 1183 | 1320 | 1475 | 1570 | 1666 |
| | | $I$ | 0·30 | 0·95 | 0·99 | 0·27 | 0·64 |
| | | $S$ | ~1·0 | ~0·2 | ~0·2 | ~0 | ~0 |
| 11·59 | 0·44 | $-E_{\frac{1}{2}}$ | — | 1430 | 1574 | — | 1736 |
| | | $I$ | — | 0·83 | 0·15 | — | ~2·02 |
| | | $S$ | — | 0·48 | ~0 | — | 0·52 |
| 13·05 | 0·76 | | No reduction waves | | | | |

* For $h$ = 28 cm.

Detailed comparison of $E_{\frac{1}{2}}$ for waves C of compounds (Ia) and (II) (Tables 1 and 5) shows that up to about pH′ 7 the difference is slight, but as pH′ increases so does the

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[14] Elving, Rosenthal, Hayes, and Martin, *Analyt. Chem.*, 1961, **33**, 330.

difference in $E_{\frac{1}{2}}$. This may be explained in terms of the reduction scheme for compound (Ia), as follows. At lower pH′, wave C for (Ia) is due to reduction of (II) alone, but at higher pH′ to a mixture of compounds (II) and (III), the proportion of the former decreasing to zero at extreme alkalinity; from their structure one would expect similar, but not identical, $E_{\frac{1}{2}}$ values for these compounds. It is noteworthy that at pH′ 13·05 no waves C—F were obtained for compound (II) up to potentials where hydrogen discharge occurred; this was not the case for compound (Ia).

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