547. *Polarography of Some Aromatic Carbonyl Compounds in Dimethylformamide.*

By P. H. Given, M. E. Peover, and J. Schoen.

Half-wave potentials for the polarographic reduction of anthraquinone and some of its hydroxy-derivatives, 12 : 12′-dimethoxydibenzanthrone, benzaldehyde, acetophenone, benzophenone, xanthone, benzanthrone, and purpurogallin in dimethylformamide are uniformly more negative than those in aqueous solutions, and in most cases two waves are observed. The behaviour when tetraethylammonium iodide is used as supporting electrolyte is consistent with a mechanism involving two one-electron steps. Quinones are reduced to the quinol ions.

As we wanted to study the polarography of oxygen-containing groups in solvent extracts of coals, which are not soluble in the aqueous or partially aqueous media previously used for carbonyl compounds, but are soluble in dimethylformamide, we investigated several aromatic carbonyl compounds, chosen to include a number in which the carbonyl group is strongly conjugated to the aromatic system, in this solvent. Since dimethylformamide does not ionize to yield protons, one would expect a different mechanism from that accepted for aqueous solutions, and different half-wave potentials.

Dimethylformamide was used for the polarography of aromatic hydrocarbons by Wawzonek *et al.*[1] In the present work lithium chloride and tetraethylammonium iodide were used as supporting electrolytes. Some characteristics of these solutions as polarographic media are described; for further details see ref. 2.

Experimental

Materials.—Lithium chloride and dimethylformamide from George and Becker were used as received. The water content of the solvent was 0·02—0·1% (Karl Fischer). Tetraethylammonium iodide was prepared by heating an equimolecular mixture of triethylamine and

---

[1] Wawzonek, Blaha, Berkey, and Runner, *J. Electrochem. Soc.*, 1955, **102**, 235.

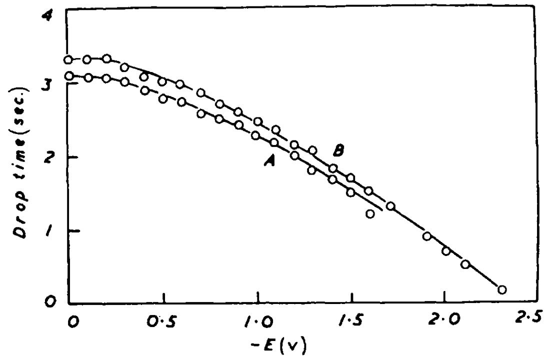
[2] Given and Peover, *J.*, in the press.

ethyl iodide in nitrobenzene * for 2 hr. at 80°; the salt was precipitated on cooling, and was washed on the filter with much carbon tetrachloride, and repeatedly crystallised from alcohol.

Apparatus.—A Tinsley polarograph, model 14/3, was used with a simple type of cell in which the mercury pool served as anode. The cell had two side-tubes with sintered-glass plates across their mouths for the introduction of oxygen-free nitrogen.

Procedure.—1·0N-Lithium chloride and 0·1N-tetraethylammonium iodide solutions were used. The concentration of reducible substance in these supporting solutions was about 0·1—1·0 mM. Nitrogen (" oxygen-free " from a cylinder) was bubbled for 20 min. through the solutions to remove oxygen. Usually the mercury pool was added *after* this, and nitrogen was then passed for a few more minutes. This procedure was recommended by Arthur and Lyons;[4] its neglect caused the appearance of a spurious wave near 0 v.

Results.—(1)*Polarography in dimethylformamide solutions.* Half-wave potentials are referred to the potential of the mercury pool; this eliminates the risk of contamination introduced by an aqueous calomel electrode and avoids liquid-junction potentials. The potential of the pool against a saturated aqueous calomel electrode was —0·47 v when covered by N-lithium chloride in dimethylformamide and —0·50 v under 0·1N-tetraethylammonium iodide. These values are close to the potential of the pool covered by solutions of tetra-*n*-butylammonium iodide in certain other organic solvents (collected values are discussed by Hoijtink *et al.*[5]). The potential of the pool, when measured in an H-cell against the saturated calomel electrode, remained constant during a polarogram when the pool was the anode and the half-wave potentials of most of the substances studied were independent of concentration. The pool therefore provides a stable and reproducible reference potential. Galvanometer zero was —0·01 v against the pool anode in 0·1N-tetraethylammonium iodide.



Electrocapillarity curves for A, N-lithium chloride; B, 0·1N-tetraethylammonium iodide in dimethylformamide. —E is the potential of the dropping-mercury electrode against the mercury pool.

We attempted to use a calomel electrode made up in dimethylformamide saturated with lithium chloride (about 2N). The potential of the pool against a freshly-prepared electrode of this kind was reproducibly —0·45 v, but the electrode appeared to be unstable and it is not clear what the potential-determining reaction is.[2] Half-wave potentials of anthraquinone measured in an H-cell with a dimethylformamide–calomel electrode as anode are included in Table 2. The first and second waves were 0·465 and 0·48 v respectively more negative than the values referred to the mercury pool.

Electrocapillarity curves with lithium chloride and tetraethylammonium iodide as the base electrolytes are shown in the Figure. The curves are similar to that reported by Bergman[6] for tetrabutylammonium iodide–2-methoxyethanol solutions and are not quite the usual inverted parabolas. The maxima occur near 0 v (referred to the pool anode). The drop time in tetraethylammonium iodide becomes extremely short at potentials more negative than

---

* The use of nitrobenzene as a solvent in the preparative use of the Menschutkin reaction is, we believe, new. It is well known (see for example Laidler[3]) that the reaction velocity in certain solvents, of which nitrobenzene is one, is 100—1000 times higher than it is in the more common aliphatic solvents. We have used the same procedure with success in the preparation of the higher tetra-alkylammonium iodides, though there the solubilities of the salts are less convenient.

[3] Laidler, " Chemical Kinetics," McGraw-Hill, New York, 1950, p. 116.

[4] Arthur and Lyons, *Analyt. Chem.*, 1952, **24**, 1422.

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

[6] Bergman, *Trans. Faraday Soc.*, 1954, **50**, 829.

−1·9 v, so diffusion currents of all substances giving half-wave potentials more negative than −1 v were corrected for the change of drop-time with applied potential.

The cell resistance, measured with a Mullard conductivity bridge operating at 3000 c./sec., was about 550 ohms with 0·1N-tetraethylammonium iodide. The *iR* drop was therefore 0·5—5 mv and was ignored.

(2) *Reduction of carbonyl compounds.* Except for the dibenzanthrone derivative, all the substances gave well-defined waves. The results are collected in Tables 1 and 2. The term *A* (the diffusion-current constant) is the value of $i_d/(cm^{2/3}t^{1/6})$ where i_d is the diffusion current (μA), *c* the concentration (mmole l.$^{-1}$), *m* the mass (mg.) of mercury flowing per sec., and *t* the drop-time (sec.). Results were obtained for all substances over a range of concentrations; figures for only one representative concentration are given unless the behaviour was concentration-dependent.

Logarithmic analysis of the first waves in some polarograms in lithium chloride and all those in tetraethylammonium iodide gave good straight lines of slope *ca.* 0·059; if the reactions were known to be reversible this would indicate that they were one-electron changes. Irregularities in the waves in lithium chloride are discussed later. The second waves gave fairly good straight lines of slope usually *ca.* 0·07—0·08, but with acetophenone it was 0·12, with benzaldehyde 0·11, and with purpurogallin (0·5—1·0 mM) 0·14. The waves for these substances are possibly composite. In tetraethylammonium iodide the half-wave potential of none of the carbonyl compounds, except benzanthrone, anthraquinone, and purpurogallin, varied with concentration, but the relative heights of the waves changed somewhat. Purpurogallin, a benzotropolone, gave three waves in very dilute solution, but at higher concentrations the third could not be resolved. Xanthone also gave three waves, but the third was much larger than the other two. The diffusion currents of anthraquinone gave a straight-line plot against the square-root of the corrected wave-height.

TABLE 1. *Aromatic carbonyl compounds in tetramethylammonium iodide–dimethylformamide*

Substance	Concn. (mmole/l.)	$-E_{\frac{1}{2}}$ (v)	*A*
Anthraquinone	0·385	0·33, 0·90	1·75, 1·65
	1·10	0·33, 0·96	1·70, 1·45
1 : 4-Dihydroxyanthraquinone	1·00	0·07, 0·58	2·15, 1·75
1-Hydroxyanthraquinone	0·74	0·16, 0·73	1·75, 1·15
Benzaldehyde	0·43	1·30, 1·83	2·50, 3·10
Acetophenone	0·27	1·49, 1·89	1·70, 3·90
Benzophenone	0·36	1·22, 1·47	1·47, 1·49
Xanthone	0·40	1·15, 1·55, 2·10	1·85, 1·80, 3·0
Benzanthrone	0·36	0·72, 1·30	1·37, 1·64
	1·50	0·74, 1·38	1·26, 1·22
Purpurogallin	0·10	0·89, 1·41, 1·72	1·50, 1·71, 1·36
	1·00	0·87, 1·50	1·56, 1·72

TABLE 2. *Behaviour of some quinones in lithium chloride–dimethylformamide.*

Substance	Concn. (mmole/l.)	$-E_{\frac{1}{2}}$ (v)	*A*
Anthraquinone	0·80	0·305, 0·57	1·3, 0·86
	0·91	0·77,* 1·05 *	
1 : 4-Dihydroxyanthraquinone	0·20	0·42, 0·83	1·75 (total height)
	0·60	0·42, 0·55, 0·90	
1-Hydroxyanthraquinone	0·385	0·10, 0·54	0·93, 1·20
1 : 2 : 5 : 8-Tetrahydroxyanthraquinone	0·20	0·37, 0·70	0·73, 0·89
12 : 12′-Dimethoxydibenzanthrone	0·28	0·56	1·10

* Potential vs. S.C.E. in dimethylformamide.

The polarography of anthraquinone was further studied by controlled-potential electrolysis. Anthraquinone (1·5 g.) in 0·1N-tetraethylammonium iodide in dimethylformamide (500 ml.) was electrolysed at −1·1 v (measured against a small mercury pool in the cathode compartment), a stirred mercury pool being used as cathode (area when quiescent 60 cm.^{2}) and a roll of silver gauze as anode. The two compartments were separated by a fine-porosity sintered-glass disc. The quantity of electricity consumed corresponded to the addition of about 2·4 electrons per molecule. During electrolysis the solution was intensely red, characteristic of alkali-metal salts of 9 : 10-dihydroxyanthracene. This persisted when the current was switched off, provided the solution was not exposed to air. After electrolysis addition of excess of acetic anhydride immediately discharged the colour. From the solution a 75% yield of 9 : 10-diacetoxyanthracene was isolated, whose melting point and polarographic behaviour [7] were identical with those of a sample prepared by reductive acetylation.

When anthraquinone was polarographed in tetraethylammonium iodide solution containing acetic anhydride (*ca.* 20 mM), only one wave was observed, of half-wave potential equal to that of the first wave previously observed and of height equal to the sum of the heights of the two previous waves. Benzophenone and xanthone behaved similarly, but here the half-wave potentials of the single waves were slightly less negative (about 0·1 v) than the values for the first waves observed in the absence of the anhydride.

Anthraquinone and its 1- and 1 : 4-hydroxy-derivatives were studied in both lithium chloride and tetraethylammonium iodide solutions. The behaviour of the first two was similar in both. The first waves given by each substance were more negative in tetraethylammonium iodide–dimethylformamide by an amount approximately equal to the difference in the potential of the pool in the two base solutions (0·04 v); the second waves were considerably more negative; the wave-heights were greater in the iodide solution and the two waves given by each substance were more nearly equal in height. There were some puzzling features in the behaviour of anthraquinone and 1 : 4-dihydroxyanthraquinone in the lithium chloride solution which suggest that this salt is a less satisfactory supporting electrolyte than tetraethylammonium iodide. The half-wave potentials of anthraquinone varied with concentration and the total diffusion current constant was low for a two-electron wave (the latter was also true of all the substances in lithium chloride). The behaviour of 1 : 4-dihydroxyanthraquinone in lithium chloride was complex, since at some concentrations three waves were distinctly resolved. At the lowest concentrations (0·04 and 0·1 mM) the first two waves were seen as a single, fairly regular wave of slope about 0·06. At higher concentrations (0·2—0·4 mM) the wave was composite, but could not be resolved. At the highest concentrations used (0·6—0·8 mM) all three waves were resolved, but not well enough for reliable logarithmic analysis of the first two waves to be made. The slope of the third wave was 0·035, which would correspond to $n = 1{\cdot}7$ if the reaction were reversible. The relative heights of the waves varied with both concentration and temperature. With increasing concentration the second wave grew at the expense of the other two, so that at 0·8 mM its height was more than double that of either of the others. From 8° to 50° and at 0·3 mM, the height of the third wave decreased with increasing temperature; the temperature coefficient for the total diffusion current was about +1·5% per degree, which is a normal value (see ref. 8, p. 93), and the half-wave potential of the third wave decreased steadily from −0·86 v at 8° to −0·82 v at 50°. The potential of the third wave also shifted somewhat towards more negative values with concentration. On the other hand, 1 : 4-dihydroxyanthraquinone showed only two waves in tetraethylammonium iodide, the first rising immediately from 0 v and the galvanometer zero. The other hydroxyanthraquinone did not show these complexities within the range of conditions used.

Edsberg [9] has studied the polarography of anthraquinone in dimethylformamide with lithium chloride as supporting electrolyte, and reports waves at more negative potentials than ours (−0·83 v and −1·17 v against aqueous S.C.E.) with $i_d/c = 2{\cdot}0$. However, various acid anhydrides and lithium hydroxide were also present in his solution.

The waves given by 1 : 2 : 5 : 8-tetrahydroxyanthraquinone and 12 : 12′-dimethoxydibenzanthrone (the latter was selected as an example of a complex highly condensed quinone) in lithium chloride solution were superimposed on a steady rise in current and so were somewhat drawn-out (see Fig. 1 in the following paper) and not susceptible to satisfactory logarithmic analysis. The slope of the first wave given by the anthraquinone derivative was about 0·06, but the log $i/(i_d - i)$ plot (where i is the current at any point on the wave) for the single wave given by the dye was linear only over its centre portion, and the slope of this portion was abnormally high (*ca.* 0·1): the wave is perhaps composite.

---

[7] Given, *J.*, 1958, 2684.

[8] Kolthoff and Lingane, " Polarography," Interscience, New York, 2nd Edn., 1952.

[9] Edsberg, *Analyt. Chem.*, 1953, **25**, 798.

DISCUSSION

The diffusion constant of anthracene in dimethylformamide has been measured by Coggan and Given[10] by the porous-diaphragm method. The results, taken with polarographic data for the hydrocarbon in the same solvent,[7] indicate that a diffusion current constant of about 4 corresponds to a two-electron addition to a molecule of this size in this solvent. On this basis it can be seen from Table 1 that for all the substances studied the total wave heights (of first two waves only where more than two were observed) are reasonable for two-electron additions (due allowance being made for differences in molecular size and shape). This view is confirmed for anthraquinone by the recovery of a high yield of 9 : 10-diacetoxyanthracene from controlled-potential electrolysis followed by acetylation. The two waves were of roughly equal height (except those of acetophenone), the relative heights did not vary much with concentration, and the i_d/c ratios were constant over a range of concentrations; hence neither wave is due to adsorption on the mercury surface,* and it may be accepted that reduction of the various carbonyl compounds takes place by two one-electron steps. The observed variation of the anthraquinone limiting currents with the height of the mercury reservoir indicates that both waves are diffusion-controlled.

Hoijtink *et al.*[5] have made an illuminating analysis of possible mechanisms of reduction at the dropping-mercury electrode, which, though originally in reference to hydrocarbons, is quite general. They point out that at a voltage above the start of the first wave the ion R^- formed by reversible addition of one electron must suffer one of two fates: either (*a*) diffuse into the bulk of liquid, where $R^- + H^+ \longrightarrow RH$, or (*b*) react with a proton to form a radical RH• which then adds an electron to become RH^-, followed by $RH^- + H^+ \longrightarrow RH_2$. If the basicity of R^- and the availability of protons is such that (*b*) is faster than (*a*), then the RH• radical formed on the electrode surface immediately adds a second electron, with no further change in potential, because, with hydrocarbons at least, the reduction potential of a radical is always less negative than that of the molecule from which it is derived. Consequently only one wave is observed, of height equivalent to a two-electron addition but of slope corresponding approximately to $n = 1$.† On the other hand, if proton addition is slow compared with diffusion away from the electrode surface, two waves are observed, each of slope corresponding to $n = 1$. The second wave corresponds to the addition of a further electron to R^-. Even in dioxan–water mixtures containing 25% of water, proton addition is slow and most hydrocarbons show behaviour of type (*a*).[5, 7] Hoijtink *et al.*[5] found that if a proton donor, such as hydrogen iodide, is added in sufficient amount (*e.g.*, 4 mmoles of HI per l.) the height of the second wave becomes very small or vanishes while that of the first increases without great change in half-wave potential, *i.e.*, behaviour changes to type (*b*). Wawzonek *et al.*[1] found the same effect when water (3 moles/l.) or benzoic acid (4 mmoles/l.) is added to anhydrous dimethylformamide or acetonitrile.

Thus the behaviour of carbonyl compounds in tetraethylammonium iodide solutions reported here (the existence of two waves, the wave heights and slopes, the constancy of behaviour with change of concentrations, and the formation of highly coloured ions during electrolysis) is consistent with the view that reduction takes place by two one-electron steps, the rate of addition of protons (or other ions) to the product of the first step being slow. Of course, in pure dry dimethylformamide only behaviour of type (*a*) would be possible. Since the results indicate that the rate of proton addition is low enough not to influence behaviour, the presence of a little water appears not to be significant. This

---

* The authors are indebted to a Referee for drawing attention to this possibility.

† The distinction between the significance of the values of *n* derived from the wave height and the slope is not always made clear in the literature; the first refers to the overall chemical change, the second refers to the mechanism of the potential-determining step.

[10] Coggan and Given, unpublished work.

conclusion is confirmed by the fact that the half-wave potentials were mostly not concentration-dependent, as one would expect them to be if uptake of protons from water were an important step; moreover, addition of 1% of water (550 mM) to 0·566 mM-anthraquinone in dimethylformamide containing less than 0·02% of water caused no significant change in the first half-wave potential of either diffusion current constant; the half-wave potential of the second wave became about 0·03 v less negative. The effect of adding acetic anhydride to a solution of a carbonyl compound before polarographic reduction parallels the effect of proton donors on the reduction of hydrocarbons, that is, the rate of removal of the mononegative ion by reaction becomes greater than its rate of diffusion from the electrode surface; in this case the reaction is not proton-addition but $RO' + Ac_2O \longrightarrow ROAc + OAc'$.

The product of addition of two electrons to a quinone is the quinol di-ion. The strong red colour of the anthraquinone solution during controlled potential electrolysis and its immediate discharge on the addition of acetic anhydride indicate that the di-ion remains stable, as the tetraethylammonium salt. The stationary-state analysis of Hoijtink *et al.*[5] shows two interesting consequences of the fact that, in the reduction of hydrocarbons in dioxan–water, protons are supplied to the *di*-negative ions from the water in the solvent, which is unbuffered: the second half-wave potential should be concentration-dependent, and logarithmic analysis of the wave should give a line of slope 0·084, not 0·059, at 25°. These predictions are found correct in the behaviour of hydrocarbons, but in the reduction of carbonyl compounds in dimethylformamide, where the di-negative ions are removed from the electrochemical equilibrium by a different process, the slope of the wave is indeed about 0·084, but its half-wave potential does not appear to be concentration-dependent for most of the substances within the concentration range studied. It is not easy to explain these facts.

In the reduction of ketones the di-negative ion has the structure $R_2C^-{-}O^-$, which may remain as a stable entity.[11] However if this captured a proton by reaction with the solvent (or the water contained in it), then the alkoxide ion, $R_2CH{-}O^-$, would undoubtedly be stable. Wawzonek *et al.*[1] showed that in the reduction of hydrocarbons in dimethylformamide and acetonitrile the di-negative ions do indeed abstract protons from the solvent, the negative solvent ion then decomposing or polymerizing.

The third wave given by xanthone appears to correspond to the addition of two further electrons, this time to the aromatic system. Purpurogallin also gave a third wave in very dilute solution, but this was small and perhaps was an adsorption post-wave; colchicine and colchiceine, which are structurally related to it, give small adsorption waves in aqueous buffer solution.[12]

No explanation can yet be given for the various peculiarities of behaviour in lithium chloride solutions. Some of the behaviour of 1 : 4-dihydroxyanthraquinone is consistent with the view that the third wave is due to adsorption of the quinone. However it should be borne in mind that this compound contains a hydroxyl group in the *peri*-position and proton transfer from this to the mononegative ion would be simple (this is also true of purpurogallin). The setting up of a tautomeric equilibrium of this kind would clearly interfere with the reduction process. The lithium ion can also form chelate complexes, whereas the tetraethylammonium ion cannot.

The authors are indebted to Mr. S. Marinkowič for some of the experimental work in this and the following paper. This paper and the two following are published by permission of this Association.

British Coal Utilisation Research Association,
Leatherhead, Surrey.

[*Received, April* 12*th*, 1957.]

---

[11] Rausch, McEwen, and Kleinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 3622.

[12] Brdicka, *Časopis Českého Lékárnictva*, 1945, **58**, 37.