549. *Polarography of Conjugated Systems in Dimethylformamide.*

By P. H. Given.

The polarographic reduction of naphthalene, anthracene, phenanthrene, pyrene, and coronene at the dropping-mercury electrode in dimethylformamide suggests that the mechanism is that previously established [1] for the reduction of aromatic systems in dioxan–water mixtures. Pyridine and quinoline give waves indicating reduction by a similar mechanism. The reduction of the aromatic systems in 2-naphthol, 2-methoxynaphthalene, anthraquinone, and 9 : 10-diacetoxyanthracene provides examples of the behaviour of oxygen-containing derivatives; all three substances showed waves suggesting that the aromatic systems were being reduced.

The reduction of polycyclic aromatic hydrocarbons at the dropping-mercury electrode has been studied in dioxan–water,[1-3] acetonitrile,[4] and 2-methoxyethanol,[5] and its mechanism discussed.[1,4] The results are of theoretical interest, since half-wave potentials have been taken as measures of the energy states of the hydrocarbon molecules.[6] The experimental data have now been extended to some polycyclic aromatic hydrocarbons in dimethylformamide, and also to some oxygenated derivatives and two nitrogen heterocycles. Although the polarographic reduction of aromatic bases in an aprotic solvent and of the aromatic systems in oxygenated derivatives has not been reported previously, dimethylformamide was used for the polarography of some hydrocarbons related to stilbene.[4]

Experimental

The supporting electrolyte, 0·1M-tetraethylammonium iodide in dimethylformamide, apparatus, and procedure were as previously described.[7] Naphthalene, anthracene, 2-naphthol, anthraquinone, pyridine, and quinoline were " pure " commercial samples, used as received. Phenanthrene was treated (by Coggan) with sodium and distilled. Pyrene and coronene were purified samples kindly supplied by Dr. N. Sheppard. 9 : 10-Diacetoxyanthracene, prepared by reductive acetylation of anthraquinone with zinc dust, sodium acetate, and acetic anhydride,[7a] crystallized from acetic acid and had m. p. 265° (lit., 261°); polarography showed the absence of anthraquinone.

The reported potentials are all referred to the mercury pool anode, which is stable and reproducible under our conditions.[7] The diffusion current constants $A = i_d/(cm^{\frac{2}{3}}t^{\frac{1}{6}})$ (see ref. 8) were corrected for the change of drop-time with applied potential as described by Hoijtink *et al.*[1]

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

[2] Laitinen and Wawzonek, *J. Amer. Chem. Soc.*, 1942, **64**, 1765, 2365.

[3] Hoijtink and van Schooten, *Rec. Trav. chim.*, 1952, **71**, 1089.

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

[5] Bergman, *Trans. Faraday Soc.*, (*a*) 1954, **50**, 829; (*b*) 1956, **52**, 690.

[6] Hoijtink, de Boer, and van Schooten, *Rec. Trav. chim.*, 1955, **74**, 1525.

[7] Given, Peover, and Schoen, *J.*, 1958, 2674.

[7a] Calderbank, Johnson, and Todd, *J.*, 1954, 1285.

Results.—The experimental results are collected in the Table.

Substance	Concn. range (mmole/l.)	$-E_{\frac{1}{2}}$ (v)	*A*		*n* *	$-E_{\frac{1}{2}}$ in Bu_4NI in 90% dioxan–water (v) †
			Partial	Total		
Naphthalene	0·2 —1·3	1·99	1·85	1·85	1	2·04
Anthracene	0·25—1·5	1·41, 1·88	2·2, 1·9	4·1	2	1·42, 1·88
Phenanthrene	0·5 —1·9	1·93	2·1	2·1	1	1·94
Pyrene	0·5 —2·0	1·56, 2·03	2·0, 1·3	3·3	2	1·54, 2·01
Coronene	0·2 —0·8	1·53, 2·03	1·9, 4·6	6·5	4	1·49, 1·88
2-Naphthol	0·5 —1·5	1·99	1·25	1·25	?	—
2-Methoxynaphthalene	0·4 —1·3	2·03	2·05	2·05	1	—
Anthraquinone	0·2 —1·1	2·15	— ‡	—	—	—
9 : 10-Diacetoxyanthracene	0·3 —1·3	1·19, 1·65 2·02, 2·12	1·5, 2·95, $i_3 + i_4 = 3{\cdot}45$	7·90	4	—
Pyridine	0·7 —1·3	2·01	4·55	4·55	2	—
Quinoline	0·25—0·9	1·53	3·75	3·75	2	—

* For overall change, calculated by means of Ilkovič equation; see below. † Results due to Hoijtink *et al.*,[1] for comparison. ‡ The waves due to reduction of the quinone groups are not included; a reliable wave-height cannot be given for reasons stated in the text.

The plot of E_{de} against log $i/(i_d - i)$ (see preceding paper) for the first wave given by each substance was a good straight line; in cases where two or more waves were observed, the slope of this line was approximately 0·06 (values in the range 0·055—0·066 were obtained). Where a substance gave only one wave, the slope was higher (0·07—0·09). For the second waves, where they were observed, the slope was always greater than 0·059 (usually about 0·08). Bergman [5] has estimated the diffusion coefficients of a number of hydrocarbons by means of the Stokes–Einstein equation, suitably corrected, and concludes that for a molecule of the size of anthracene a diffusion current constant of about 3·0 corresponds to a two-electron reduction, and for molecules the size of pentacene the value is nearer 2·0. Approximate diffusion coefficients for anthracene, pyrene, and coronene in dimethylformamide were obtained by Coggan and Given; [8] their use in the Ilkovič equation gives the values of *n* shown in the Table and suggests that the values of the diffusion current constant corresponding to Bergman's figures of 3 and 2 are higher for dimethylformamide (about 4 and 3), which is consistent with its lower viscosity than that of Cellosolve. The other values of *n* in the Table were obtained by use of the above approximate figures for the diffusion current constant per two electrons added. The half-wave potentials of none of the substances studied changed with concentration in the range stated.

The wave given by anthraquinone at $-2{\cdot}15$ v was not clearly resolved from that of the decomposition of the supporting electrolyte and was anomalous in certain respects. The diffusion current " constant " decreased from 2·65 at 0·236 mM (*i.e.*, $n \approx 1{\cdot}3$) to 1·65 at 1·09 mM. If 0·1—0·4% of water (about 50—200 mM) was added the diffusion current constant increased markedly and became more nearly independent of the concentration of anthraquinone (about 4·0 at water : anthraquinone mole ratio of 200, and about 5·2 when the ratio was 400). At any given concentration of anthraquinone (with no added water) the diffusion current gave an approximately straight-line plot against the height of the mercury reservoir (corrected for back pressure).

The addition of water (0·2—1·0%) to millimolar solutions of anthracene or pyrene made the half-wave potentials of the second waves less negative by 0·03—0·04 v and in the case of pyrene increased the height of the first wave by about 10%.

Discussion

The half-wave potentials of the five hydrocarbons studied in dimethylformamide are strikingly similar to the corresponding values measured in 96% dioxan–water, if all potentials are referred to the mercury pool. The agreement is still noteworthy, though less striking, if all potentials are referred to the aqueous calomel electrode. The same five compounds have also been studied in 2-ethoxyethanol,[5] and anthracene in acetonitrile as

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[8] Coggan and Given, unpublished work.

well;[4] the potentials are on the whole similar to those in the Table. The anode potentials in the four media mentioned differ much less among themselves than any one of them differs from the calomel potential. Theoretically one might expect not only the anode potentials but also the solvation energies of the ions to differ in different solvents; moreover in any comparison of potentials in different solvents a liquid junction potential is necessarily implied. The similarities observed are therefore unexpected; they are too numerous to be dismissed as coincidence, and must be significant.

The other characteristics of polarographic reduction of hydrocarbons in dimethylformamide (number of waves, heights and slopes of waves) also resemble those observed in other solvents, particularly 96% dioxan–water. For anthracene, pyrene, coronene, and 9 : 10-diacetoxyanthracene these characteristics are those expected, on the analysis of mechanism by Hoijtink *et al.*,[1] for reductions by one-electron potential-determining steps in which proton addition to the intermediate mononegative ions is slow (cf. the reduction of quinones [7]); in the case of coronene, the dihydro-derivative evidently has a higher electron affinity than coronene itself, since two further electrons are added with no decrease in potential (pyrene behaves similarly in 75% dioxan–water [1]). All the other substances in the Table show one wave only. According to the mechanism of Hoijtink *et al.*[1] one wave is found when the rate of addition of protons to the mononegative ion is fast compared with the diffusion of the ion from the electrode surface; in these circumstances the monohydro-radical at once adds a second electron without change in potential, since all such hydrocarbon radicals necessarily have higher electron affinities than their parent hydrocarbons.[1] Logarithmic analysis of the single wave should give a line of slope about 0·08—which in this context indicates a one-electron potential-determining step—but the wave-height should correspond to the addition of two electrons. The slopes of the single waves observed in dimethylformamide solutions are in agreement with these conclusions, but their heights are in many cases surprisingly low.

The completion of the reduction process requires the addition of protons to the negative ions. In our dimethylformamide there are two possible sources of protons, namely, water as impurity (0·02—0·1%; *ca.* 10—50 mM) or the solvent. Water is probably unimportant as a proton donor (except with anthraquinone): deliberate addition of up to 550 mmoles/l. had little effect on the polarography of anthracene or pyrene, although it had some effect on that of anthracene in acetonitrile, but only when 5% (about 3 moles/l.) or more is present. Wawzonek *et al.*[4] showed that although dimethylformamide does not release protons by ionization, hydrocarbon ions can abstract protons from it in a bimolecular reaction: the remaining ion $CO{\cdot}NMe_2^-$ then decomposes. We therefore conclude that the solvent is usually the effective source of protons. The case of anthraquinone is dealt with below. In aqueous solution pyridine and quinoline give [9] catalytic hydrogen waves as well as reduction waves and the polarographic behaviour depends strongly on the supporing electrolyte and pH. As they could not give such waves in an aprotic solvent, their behaviour in dimethylformamide is consistent with the view that the aromatic ring is being reduced.

It is now accepted that the half-wave potential for a hydrocarbon measures the energy needed to place one or more electrons in the lowest unoccupied molecular orbital.[5, 6, 10] Thus electron affinities have been calculated from half-wave potentials [6] by an algebraic method that obviates the necessity of knowing the potentials on the hydrogen scale (see also Matsen [11]) and compared with values calculated from molecular-orbital theory. Bergman [5] has found that when the half-wave potentials of aromatic hydrocarbons are plotted against the frequency (cm.$^{-1}$) of the first *p*-band (in Clar's nomenclature [12]) in the absorption spectrum, the points fall on sets of straight lines of similar slope but differing

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[9] Kolthoff and Lingane, "Polarography," Interscience, New York, 2nd Edn., 1952, pp. 813, 818.
[10] Maccoll, *Nature*, 1949, **163**, 178.
[11] Matsen, *J. Chem. Phys.*, 1956, **24**, 602.
[12] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 2nd Edn., 1952.

intercept according to the type of aromatic system present. The absorption bands in the spectra of pyridine and quinoline have not been identified as *p*, α and β, nor is it clear whether or how this system of classification is applicable to heterocyclic compounds. However, if the frequency of the first band in the spectra of pyridine and quinoline (38,250 and 32,000 cm.$^{-1}$ respectively) is plotted against half-wave potential, the line joining the two points is nearly parallel to Bergman's line for the cata-condensed hydrocarbons (*i.e.*, hydrocarbons with not more than two carbon atoms common to any pair of benzene rings), but of higher intercept on the frequency axis.

No systematic study of the reduction of the aromatic system in substituted derivatives has been made. Provided that the substituent is not itself reducible at the dropping-mercury electrode or capable of giving a catalytic hydrogen wave, the polarographic behaviour should not be much changed by substitution: one might expect a small decrease in half-wave potential to correspond with the small bathochromic shift usually observed in the ultraviolet spectrum (introduction of a methyl group into naphthalene changes the half-wave potential by −0·25 v[13]). The figures in the Table for naphthalene and its derivatives support this view. (Monocyclic phenols do not give hydrogen discharge or reduction waves in dimethylformamide.) If the substituent is reducible, then any further waves observed must represent reduction of the first reduction product. Thus anthraquinone gave a wave at −2·15 v; this presumably represents addition of one or more electrons to the conjugated system in 9 : 10-dihydroxyanthracene or its di-ion. The low values of the diffusion current constant for this wave and their decrease with increasing concentration may be associated with the difficulty of adding further electrons to an ion already doubly-negatively charged. The marked increase in wave height on the addition of water is in accord with this suggestion, since one might expect water partly to hydrolyse the tetraethylammonium salt of 9 : 10-dihydroxyanthracene. The polarography of 9 : 10-dihydroxyanthracene has not been studied, since its ready oxidation makes it difficult to obtain and handle. 9 : 10-Diacetoxyanthracene shows different behaviour from anthraquinone; it apparently undergoes a four-electron reduction. 1-Hydroxy- and 1 : 4-dihydroxy-anthraquinone did not show any wave between the quinone waves and the decomposition potential of the base electrolyte (−2·25 v). A proper understanding of the behaviour of substituted derivatives clearly requires further work.

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[13] Hoijtink and van Schooten, *Rec. Trav. chim.*, 1953, **72**, 691.