74. *Polarographic Reduction of Aromatic Hydrocarbons and Carbonyl Compounds in Dimethylformamide in the Presence of Proton-donors.*

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Phenol is sufficiently acidic to act as an effective proton-donor in polarographic reduction in dimethylformamide, but does not give a hydrogen discharge wave in this medium. A wide variety of changes in behaviour is observed in the polarography of the substances studied as increasing amounts of phenol or benzoic acid are added: new waves appear in some cases either because the mechanism is changed or because more extensive reduction is made possible by protonation of the ions first formed. The effectiveness of the weak acids at low concentrations in some cases (molar ratios, acid : substrate, = 2—4) suggests that the undissociated acid rather than the proton takes part in the protonation; and the shape of the waves is consistent with this.

It has been shown[1] that some aromatic hydrocarbons are more extensively reduced polarographically in 75% than in 96% dioxan–water, which was accounted for[1] by supposing that neutralization of the charges on the dinegative ions by proton-addition from the water made further addition of electrons possible. It has also been shown that in the presence of hydrogen iodide and benzoic acid, respectively, the two waves given by anthracene[1] and anthraquinone[2] coalesce to one wave; water in high concentration has the same effect on anthraquinone.[2] The object of the work reported here was to ascertain in more detail the behaviour of a selection of hydrocarbons and carbonyl compounds on polarography in the presence of proton-donors, particularly phenol, as a background to current work[3,4] on the reduction of solvent extracts of coals. The compounds studied were mostly those whose behaviour in dimethylformamide in the absence of proton-donor has been reported previously.[5,6]

Benzoic acid and hydrogen iodide are of limited usefulness as proton-donors in polarographic studies because they give hydrogen discharge waves which may interfere with the waves of the substance being studied. We find, however, that phenol is a strong enough acid in dimethylformamide to act as an effective proton-donor but is too weak to give a hydrogen discharge wave at any potential less negative than the decomposition potential of the supporting electrolyte. Water, on the other hand, is too weak an acid to be of much value for the purpose. In the work to be described, phenol and benzoic acid have been used as proton-donors; the latter could be used with a few compounds only and then usually at molar ratios, acid : substrate, not more than two.

Experimental and Results

The polarograph and methods were as described previously.[5] The materials were " pure " grades, obtained commerically, except that 9,10-dihydroxynaphthacene-11,12-quinone was kindly supplied by Drs. L. Blom of the Central Laboratory of the Dutch State Mines; phenol, 2-naphthol, and benzoic acid were " AnalaR " samples. The dimethylformamide contained less than 0·02% of water. 0·1N-Tetraethylammonium iodide was used as supporting electrolyte, and potentials were referred to a mercury pool anode in this medium.

Particular attention was paid to the manner in which the behaviour of each substance changed with increasing concentration of proton-donor; the variation is more informative than the behaviour at one concentration. The concentration of the substance to be reduced was

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

[2] Wawzonek, Berkey, Blaha, and Runner, *J. Electrochem. Soc.*, 1956, **103**, 456.

[3] Given and Schoen, *J.*, 1958, 2680.

[4] Given, Lupton, and Peover, Proc. Inst. Fuel Conf., " Science in the Use of Coal," Sheffield, 1958, p. A–38.

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

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

1 mM, unless otherwise stated, and polarograms were run at 3—5 concentrations of proton-donor; in a few cases the measurements were repeated at a low concentration of substrate (about 0·25 mM). The polarographic behaviour of diphenyl, phenanthrene, perylene, 9,10-diethoxyanthracene, phenanthraquinone, and 9,10-dihydroxynaphthacene-11,12-quinone in the absence of proton-donor in dimethylformamide has not been reported previously.

Five types of behaviour were observed, of which types B, C(*b*), and E have not been reported previously. They are listed in Table 1 together with the substrate–acid pairs that showed each type. A brief description of what is believed to be the mechanism responsible for the various types of behaviour is also included (justification for these mechanisms will be given below). A selection of the numerical results is in Table 2. A diffusion current constant, *I*, of 1·8—2·0 corresponds to a one-electron addition.[5,6]

TABLE 1. *Change in polarographic behaviour as concentration of proton-donor is increased.*

Classes of behaviour	Explanation	Systems in class *	Remarks †
A. 1st wave grows in height at expense of 2nd till latter disappears	R^- protonated to RH· which is reduced at same potential	Naphthalene–P	Complete with $m = 4$
		Anthracene–P	Incomplete with $m = 14$
		Biphenyl–P	Complete with $m = 8$
		Benzophenone–P	Complete with $m = 2$
		Anthraquinone–B	Nearly complete at $m = 5$
B. New wave appears between the two original waves, and grows in height at expense of 2nd	Connected with dimerisation of R′ (?)	Benzaldehyde–P	
		Xanthone–P	
		Purpurogallin–P	Effect more marked with B than P
		Purpurogallin–B	
C. Waves grow in height with little change of potentials; new wave(s) may appear	(*a*) R^- protonated, RH· reduced at same potential; protonation makes further reduction possible	Pyrene–P	
		Perylene–P	New 3rd wave
		Phenanthrene–P	New 2nd wave
		2-Naphthol–P	,, ,,
	(*b*) Protonation makes further reduction possible: mechanism not clear	9,10-Diethoxyanthracene–P	
		9,10-Diacetoxyanthracene–P	
		Anthraquinone–P ‡	New 4th wave
		Phenanthraquinone–P ‡	New 3rd wave
		9,10-Dihydroxynaphthacene-11,12-quinone–P ‡	,, ,,
		1,4-Dihydroxyanthraquinone–P ‡	,, ,,
D. 1st wave unchanged, 2nd shifts to less negative potentials	R^{2-} but not R^- protonated; 2nd wave dependent on concentration of acid	Anthraquinone–P	With $m = 14$ waves nearly coalesced
		1,4-Dihydroxyanthraquinone–P	Effect small at $m = 5$
		Phenanthraquinone–P	Nearly complete at $m = 10$
E. New wave appears, *less* negative than original waves, grows at expense of them	Prior protonation of R to RH^+ (?)	Benzophenone–B	Complete with $m = 2$
		Benzaldehyde–B	Completion needs $m > 2$
		Xanthone–B	,, ,, some class A behaviour when $m = 0·5$

* P = phenol; B = benzoic acid. † *m* = molar ratio, proton-donor : substrate.

‡ These entries concern further reduction of the molecule after quinone groups have been reduced.

The references in Table 1, classes A and D, to anthraquinone and phenanthraquinone concern the behaviour of the waves representing reduction of the quinone groups. Anthraquinone shows also a small third wave whose height in the absence of proton-donor is less than proportional to concentration.[6] In the presence of phenol this wave grows in height and splits into two waves, each eventually of height equivalent to the addition of two electrons. 1,4-Dihydroxyanthraquinone, phenanthraquinone, and 9,10-dihydroxynaphthacene-11,12-quinone do not show a corresponding wave in the absence of phenol, but one appears as phenol is added.

TABLE 2*a*. *Polarographic results: effect of proton-donors (behaviour classes A, B, and C)* (1 mM-solutions of substrate in 0·1N-tetraethylammonium iodide).

Class of behaviour	Substance	Acid	Molar ratio acid : subst.	$-E_{\frac{1}{2}}$ (v) *vs* Hg pool	I *	ΣI
A	Benzophenone	None	0	1·22, 1·51	2·0, 1·55	3·55
		Phenol	1·0	1·17, 1·54	2·8, 0·65	3·45
		Phenol	2·0	1·16 —	3·50	3·50
	Anthraquinone	None	0	0·32, 0·99	1·80, 1·70	3·50
		Benzoic	0·55	0·31, 0·98	2·75, 1·10	3·85
	Naphthalene	None	0	1·98	2·8	2·8
		Phenol	4·0	1·95	4·9	4·9
	Diphenyl	None	0	2·07	3·7	3·7
		Phenol	8·0	2·04	6·25	6·25
B	Purpurogallin	None	0	0·88, 1·50	1·45, 1·60	3·05
		Phenol	1·90	0·89, 1·27, 1·45	1·45, 0·30, 1·50	3·25
		Benzoic	1·90	0·895, 1·26, 1·43	1·85, 1·35, 0·60	3·8
	Benzaldehyde	None	0	1·30, 1·86	2·05, 1·55	3·60
		Phenol	3·83	1·22, 1·48, 1·78	2·30, 1·70, 0·50	4·5
C(*a*)	Perylene	None	0	1·13, 1·67	1·55, 1·45	3·0
		Phenol	2·0	1·13, 1·54	1·60, 2·00	3·6
		Phenol	8·0	1·14, 1·52, 1·71	1·50, 2·45, 1·45	5·4
	Pyrene	None	0	1·56, 2·03	2·0, 1·05	3·05
		Phenol	7·5	1·56, 2·03	2·45, 3·10	5·55
		Phenol	14·4	1·56, 2·03	2·75, 4·30	7·05
	Phenanthrene	None	0	1·95,	2·4	2·4
		Phenol	8·0	1·91, 2·10	4·3, 3·6	7·9
	2-Naphthol	None	0	1·97,	1·02	1·02
		Phenol	10	2·0, ca. 2·15	10·85 total	10·85
(*b*)	9,10-Diethoxyanthracene	None	0	1·42, 1·98	1·60, 7·2	8·8
		Phenol	18·1	1·43, 1·98	2·80, 9·90	12·7
	9,10-Diacetoxyanthracene	None	0	1·20, 1·65, 2·01, 2·13	1·4, 2·05, 1·35, 2·1	6·9
		Phenol	15·6	1·23, 1·67, 1·83	1·45, 3·65, 3·8	8·9
	Phenanthraquinone	None	0	0·12, 0·69	1·70, 1·45	0 †
		Phenol	21·2	0·12, 2·21	3·1, 13·0	13·0 †
	9,10-Dihydroxynaphthacene-11,12-quinone	None	0	0·23, 0·74	1·55, 1·45	0 †
		Phenol	13·0	0·22, 0·74, 1·91	1·45, 1·35, 8·35	8·35 †
			22·9	0·23, 0·74, ~1·97	1·45, 1·45, 14·8	14·8 †

* $I = i/cm^{\frac{2}{3}}t^{\frac{1}{6}}$.

† Reduction of carbonyl excluded.

TABLE 2*b*. *Polarographic results: effect of proton-donors (behaviour classes D and E).*

Class of behaviour	Substance	Acid	Molar ratio acid : subst.	$-E_{\frac{1}{2}}$ (v) vs Hg pool	I	ΣI
D	Anthraquinone	None	0	0·32, 0·99	1·80, 1·70	3·5
		Phenol	1·8	0·32, 0·63	2·15, 1·80	3·95
		Phenol	7·35	0·32, 0·54	2·15, 1·85	4·0
	Phenanthraquinone	None	0	0·12, 0·69	1·70, 1·45	3·15
		Phenol	1·22	0·13, 0·41	2·15, 0·85	3·0
E	Benzophenone	None	0	1·22, 1·51	2·0, 1·55	3·55
		Benzoic	0·25	1·04, 1·23, 1·53	0·2, 2·00, 1·45	3·65
		Benzoic	0·74	1·05, 1·23, 1·54	1·20, 1·40, 0·85	3·45
		Benzoic	1·49	1·06, 1·22, 1·51	2·75, 0·41, 0·38	3·54
		Benzoic	2·0	1·07	3·40	3·40
	Benzaldehyde	None	0	1·30, 1·86	2·05, 1·55	3·60
		Benzoic	1·2	1·13, 1·28, 1·78	1·50, 0·71, 1·80	4·01
		Benzoic	2·6	1·13	3·70	3·70
	Xanthone	None	0	1·22, 1·68, 2·22	2·15, 1·30, 1·45	3·45 †
		Benzoic	1·51	1·20, 1·70, 2·21	2·65, 0·72, 1·20	3·37 †
		Benzoic	3·52	1·08,* 1·62, 2·20	3·35,* 0·33, 1·80	3·68 †

* New wave, wave at −1·20 v having disappeared.

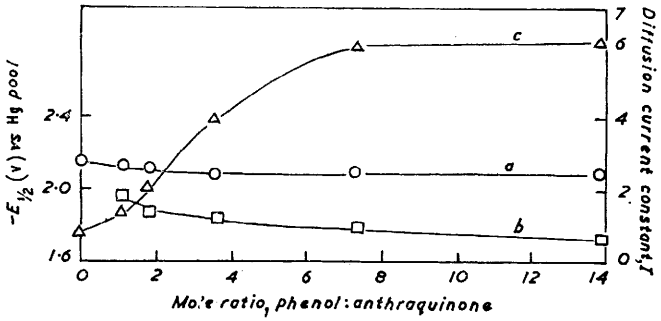
† Reduction of carbonyl only.

The behaviour of anthraquinone is shown in some detail in Fig. 1, and that of the other substances is summarized in Table 2*a*, class C. Owing to the difficulty of resolving the two anthraquinone waves at the lower concentrations of phenol, only the total height of the waves (uncorrected for change in drop time with applied potential) is given in Fig. 1; at $m = 7{\cdot}6$ the corrected values of I were 4·5 and 4·55, and at $m = 13{\cdot}9$ were 4·3 and 4·6.

It has been reported[6] that 9,10-diacetoxyanthracene adds nearly four electrons, instead of the two expected of an anthracene derivative containing non-reducible substituents; it is now found that the 9,10-diethoxy-derivative behaves similarly. In the presence of phenol the total wave heights increase from 4 to 5 and 5 to 6½ electrons respectively.

Benzoic acid by itself gave a wave at $-1{\cdot}27$ v, with $I\ (= i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}) = 1{\cdot}5$, and a second much smaller wave at $-1{\cdot}7$ v ($I = 0{\cdot}15$). When excess of the acid was added to a reducible substance of half-wave potential less negative than $-1{\cdot}27$ v, the acid wave at this potential was usually observed; in some cases, however, this wave was not seen, and it was the wave at $-1{\cdot}7$ v that appeared and grew in height with increasing concentration of acid. In accord with Delahay[7] we tentatively identify the two acid waves with two modes of hydrogen discharge:

FIG. 1. *Effect of phenol on reduction of ring system in anthraquinone* (1mM in 0·1N-NEt$_4$I).



(*a*) *and* (*b*), *Half-wave potentials.* (*c*) *Total height of the two waves* (*for accuracy see text*).

$$H^+ + \varepsilon \longrightarrow H$$

and $$HA + \varepsilon \longrightarrow H + A^-$$

DISCUSSION

The normal mechanism of reduction of aromatic hydrocarbons and carbonyl compounds in the absence of proton-donors is:[1,2,5,6,8]

$$R + \varepsilon \rightleftharpoons R^- \quad \text{. . . . . (1)}$$

$$R^- + \varepsilon \rightleftharpoons R^{2-} \quad \text{. . . . . (2)}$$

$$R^{2-} + 2H^+ \longrightarrow RH_2 \quad \text{. . . . . (3)}$$

Hoijtink *et al.*[1] have shown by molecular-orbital calculations that the electron affinity of a radical RH•, obtained by protonating the ion R$^-$, is always greater than that of the parent molecule, R, when R is an alternant aromatic hydrocarbon. Consequently, if the rate of proton addition to R$^-$ is greater than its rate of diffusion from the electrode surface, RH• is formed and reduced at the potential of the first wave and no second wave is observed. As already noted, Hoijtink *et al.*[1] describe the polarography of anthracene in the presence of hydrogen iodide as an example of this type of behaviour (class A in Table 1). The calculation referred to concerned hydrocarbons only; the presence of oxygen substituents will presumably not alter greatly the energy levels of R and RH•.

In dimethylformamide, naphthalene, phenanthrene, and biphenyl each give only one wave of height about equivalent to the addition of one electron; the second wave must lie beyond the decomposition potential of the supporting electrolyte. In the presence of phenol the wave given by all three hydrocarbons grows to nearly twice the previous height, and with phenanthrene a second wave becomes visible, also of height equivalent to the addition of two electrons (phenanthrene also shows two two-electron waves in the proton-active solvent, 2-methoxyethanol).[9]

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[7] Delahay, *J. Amer. Chem. Soc.*, 1951, **73**, 4944.

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

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

The mononegative ions formed by anthracene and benzophenone have been shown not to dimerise during electrolysis at a potential corresponding to the top of the first wave [10] (contrast benzaldehyde, below). Phenanthrene on the other hand dimerises to some extent.[11]

Behaviour of type B may be connected with the fact that, at a potential corresponding to the top of the first wave, the mononegative ion dimerises more rapidly than it can diffuse away or be protonated: electrolysis of benzaldehyde in the absence of phenol at this potential afforded a good yield of hydrobenzoin; moreover, addition of phenol has little effect on the height of the first wave. On the other hand, the height and half-wave potential of the new second wave of benzaldehyde are strongly dependent on the concentration of phenol, and electrolysis in the presence of phenol at this more negative potential (—1·6 v) yields benzyl alcohol (80%). Thus, when enough phenol is present and the potential is negative enough the mononegative ion, R^-, may be protonated and the product RH• immediately reduced further at the same potential.* The second waves given by some carbonyl compounds in the absence of added proton-donor appear composite; [5] this may be due to some contribution to the polarogram by class B behaviour resulting from protonation by the solvent alone (or water in it).

The change in behaviour of pyrene and perylene (type C) when phenol is added is similar to that observed when the same hydrocarbons are polarographed in dioxan–water of increasing water concentration,[1] and the same explanation (loss of reducible material by diffusion when the rate of proton addition is low) no doubt holds. Phenanthrene and 2-naphthol behave similarly. The total height of the waves of all four substances is increased to four electrons by phenol in the molar ratio 7—13 : 1.

The extensive reduction undergone by the anthracene derivatives was quite unexpected. Reasons have been given [2,5,6] for supposing that the stable product of reduction is the 9,10-dihydroxyanthracene di-ion, as the tetraethylammonium salt. This di-ion would no doubt be reluctant to accept further negative charges but, as excess of phenol is added, increasing proportions of the neutral quinol molecule could exist in equilibrium:

$$C_{14}H_8O_2^{2-} + 2PhOH \rightleftharpoons C_{14}H_8(OH)_2 + 2PhO^-$$

and the neutral molecules can evidently be reduced. The wave at —1·7 to —1·9 v involves addition of protons as well as electrons, since its half-wave potential changes markedly with phenol concentration; it presumably represents reduction to the 9,10-dihydro-derivative. One would expect addition of two electrons and protons in the 9,10-positions, giving what is in effect a benzene derivative, incapable of further reduction in the nucleus before decomposition of the supporting electrolyte. In further experiments [12] it has been found by electrolysis in dimethylformamide at a controlled potential of —2 to —2·15 v that anthraquinone (in the presence of phenol) and 9,10-diacetoxyanthracene yield 9,10-dihydroanthracene, and xanthone with phenol gives xanthen: that is, the extra addition of electrons leads to scission of carbon–oxygen bonds rather than hydrogenation of the nuclei. Presumably 9,10-diethoxyanthracene reacts similarly. On the other hand, since phenanthrene can undergo a four-electron change, to the 1,2,3,4-tetrahydro-derivative, the 7—8-electron reduction of phenanthraquinone in the presence of phenol could represent either hydrogenation to 1,2,3,4,9,10-hexahydro-9,10-dihydroxyphenanthrene or carbon–oxygen scission (no definite products could be isolated from the products of electrolysis). There is a similar uncertainty about the reaction of the dihydroxynaphthacenequinone.

The effect of phenol on the polarography of the carbonyl groups in anthraquinone (class D) resembles that of water on the same substance,[2,5] though it is effective at much lower concentrations. Since it is only the second wave that is affected, it is the dinegative

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* The authors are indebted to Professor Hoijtink for this suggestion.

[10] Austen, Given, Ingram, and Peover, *Nature*, 1958, **182**, 1784.

[11] Wawzonek and Wearring, *J. Amer. Chem. Soc.*, 1959, **81**, 2067.

[12] Given and Peover, *Nature*, 1959, **184**, 1064.

ion that is protonated[2] (compare the effect of benzoic acid on anthraquinone, above). The behaviour of the carbonyl groups in phenanthraquinone is predominantly of the same type, but with some type A features superimposed.

It is possible that the new, less negative, wave that appears when benzoic acid is added to benzophenone (class E behaviour) is due to prior protonation of the ketone. This might involve the formation merely of a hydrogen-bonded complex:

$$\mathrm{R} + \mathrm{HX} \rightleftharpoons \mathrm{R{,}HX} \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$\mathrm{R{,}HX} + \varepsilon \rightleftharpoons \mathrm{RHX}^- \longrightarrow \mathrm{RH}\cdot + \mathrm{X}^- \quad \ldots\ldots\ldots \quad (5)$$

or complete proton transfer

$$\mathrm{R} + \mathrm{HX} \rightleftharpoons \mathrm{RH}^+ (+\,\mathrm{X}^-) \xrightarrow{+\,\epsilon} \mathrm{RH}\cdot \quad \ldots\ldots\ldots \quad (6)$$

In either case the addition of a second electron occurs at the same potential:

$$\mathrm{RH}\cdot + \varepsilon \longrightarrow \mathrm{RH}^- \xrightarrow{\mathrm{HX}} \mathrm{RH}_2 + \mathrm{X}^- \quad \ldots\ldots\ldots \quad (7)$$

Benzophenone is known to be protonated in this way in concentrated sulphuric acid, but not to a measurable extent in dilute benzoic acid solutions in dimethylformamide. [The frequency of the hydroxyl vibration of phenol in dimethylformamide (4mM) shows hydrogen bonding with the solvent, but no change of frequency occurs when benzophenone is added; and the longest-wavelength electronic band of neither benzophenone nor benzaldehyde changes when benzoic acid is added, again in dilute solution in dimethylformamide.] However, the presence of a small concentration of the protonated form on the electrode could lead to the production of the wave provided the rate of protonation of R according to equation (4) or (6) is greater than its rate of diffusion to the electrode.

Hoijtink and Aten have found that A.C. polarograms of benzophenone in the presence of benzoic acid show a small peak at the potential of the new first wave and another, slightly larger, at the potential of the original first wave.* The appearance of the peaks and their frequency dependence indicate that the new first electron-addition is reversible but fairly slow; the electron-transfer at the original first wave is faster, so that a mechanism of type A takes over when the potential is negative enough. The behaviour is more consistent with reactions (4) and (5) than (6); in the former a presumably irreversible dissociation intervenes between the two electron additions so that the second addition does not disturb the reversibility of the first.

It is interesting to know how far behaviour remains diffusion-controlled when proton-donors are present.† When sufficient acid is present to ensure that further addition does not alter wave heights, the rate of diffusion to the electrode is evidently faster than the rate of reaction, *i.e.*, under these conditions one would expect the process to be diffusion-controlled. In fact, we have found the current to be directly proportional to the square root of the corrected height of the mercury reservoir when enough phenol is added to benzophenone and naphthalene to cause complete coalescence of the waves. This proportionality was also found with the systems named when the acid present was enough to cause only partial coalescence. With other systems, where the amount of proton-donor required to produce complete coalescence or the appearance of further waves is relatively large, it might be possible to detect the expected partial dependence of current on reaction rate, but we have not explored this possibility.

It is striking that the weak acids used as proton donors in this study were effective at such low concentrations, particularly with benzophenone. Neither acid is much ionized in dimethylformamide.‡ Hence it is probable that the rate of protonation of the ions in

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* We are indebted to Professor Hoijtink and Dr. Aten for undertaking the A.C. polarograms on our behalf, and for permitting us to quote the results. We are also indebted to Professor Hoijtink for much of the above discussion of benzophenone–benzoic acid polarography.

† We are indebted to Dr. P. Zuman for pointing out to us the importance of this point.

‡ The equivalent conductivities of phenol and benzoic acid in dimethylformamide are very low: aaout 0·2 and 0·5 mho at 0·01N-concentration.

polarographic reduction depends on the rate of diffusion of undissociated acid rather than solvated proton. The efficiency of the acids at low concentration in protonating the benzophenone and naphthalene ions led us to consider whether it might be the undissociated acid that reacts with the free-radical ions rather than the proton,

that is: $$\mathrm{R^- + HX \longrightarrow RH\cdot + X^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8a)$$

rather than: $$\mathrm{R^- + H^+ \longrightarrow RH\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8b)$$

(It has already been suggested that the water in dioxan–water mixtures protonates hydrocarbon ions in this manner, that is, that the undissociated water molecule is effective.[13]) These alternative modes of protonation, (8a) and (8b), would give waves having different equations, since in the latter case the dissociation constant of the acid would appear, but not in the former.

Hoijtink and his colleagues [14] have shown by A.C. polarography that the waves given by several of the compounds used in this study are reversible. With hydrocarbons, if conditions are such that protonation of the dinegative ion, R^{2-}, is fast, the second peak in the polarogram disappears, showing that protonation steps are irreversible; however, protonation of $R\text{–}O^-$ ions may well be reversible (for quinol ions it obviously is; with ketones protonation of R^- might be reversible if the electron adds to the positive end of the carbonyl dipole and the proton to the oxygen atom, thus: $>\mathrm{C^+\text{–}O^-} \xrightleftharpoons{+\epsilon} >\dot{\mathrm{C}}\mathrm{\text{–}O^-} \xrightleftharpoons{+\mathrm{H}^+} >\dot{\mathrm{C}}\text{–OH}$). It is justifiable therefore to apply the Nernst equation to the electrochemical changes. In what follows we deduce the equation of the wave found in class A behaviour when the amount of proton-donor is enough to make the original second wave disappear completely, according to the mechanism below. [The description of reaction (10) as " fast " is merely a recognition of the fact that RH• is formed fast enough to ensure that the wave is diffusion-controlled; see above.]

$$\mathrm{R + \varepsilon \rightleftharpoons R^-} \quad . \; . \; . \; . \quad \text{(9) (reversible)}$$

$$\mathrm{R^- + HX \longrightarrow RH\cdot + X^-} \quad . \; . \quad \text{(10) (fast, may be irreversible)}$$

$$\mathrm{RH\cdot + \varepsilon \rightleftharpoons RH^-} \quad . \; . \; . \; . \quad \text{(11) (reversible)}$$

$$\mathrm{RH^- + HX \longrightarrow RH_2 + X^-} \quad . \; . \quad \text{(12) (may be irreversible)}$$

Equating the rate of diffusion of R to the drop to the rate of removal of R^- by protonation, we have:

$$k_{\mathrm{R}}(C_{\mathrm{R}} - C^\circ_{\mathrm{R}}) = kC^\circ_{\mathrm{R}^-}C^\circ_{\mathrm{HX}} \quad . \; . \; . \; . \; . \; . \; . \quad (13)$$

where C_{R} and C_{HX} are the concentrations of R and HX in the bulk phase, C°_{R}, C°_{HX}, etc., are the corresponding concentrations on the electrode surface, k_{R} and k_{HX} are constants proportional to the square roots of the respective diffusion coefficients, and k is a velocity constant. The current, i, is equal to the rate of conversion of R into R^- plus the rate of reduction of RH•, so that:

$$i = k_{\mathrm{R}}(C_{\mathrm{R}} - C^\circ_{\mathrm{R}}) + kC^\circ_{\mathrm{R}^-}C^\circ_{\mathrm{HX}} \quad . \; . \; . \; . \; . \quad (14)$$

Finally for the rate of diffusion and consumption of HX we have

$$k_{\mathrm{HX}}(C_{\mathrm{HX}} - C^\circ_{\mathrm{HX}}) = 2kC^\circ_{\mathrm{R}^-}C^\circ_{\mathrm{HX}} \quad . \; . \; . \; . \; . \quad (15)$$

Solving these equations for C°_{R} and $C^\circ_{\mathrm{R}^-}$, we obtain:

$$C^\circ_{\mathrm{R}} = (2k_{\mathrm{R}}C_{\mathrm{R}} - i)/2k_{\mathrm{R}}$$

and $$C^\circ_{\mathrm{R}^-} = ik_{\mathrm{HX}}/2k(k_{\mathrm{HX}}C_{\mathrm{HX}} - i)$$

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[13] Kolthoff and Lingane, " Polarography," Interscience, New York, 2nd edn., pp. 634—639.

[14] Aten, Büthker, and Hoijtink, *Trans. Faraday Soc.*, 1959, **55**, 324; Hoijtink, personal communication.

Now the potential of the dropping electrode is given by:

$$E_{\mathrm{de}} = E_0 + \frac{RT}{F}\ln\frac{C^\circ_{\mathrm{R}}}{C^\circ_{\mathrm{R^-}}}$$

$$= E_0 + \frac{RT}{F}\ln\frac{k}{k_{\mathrm{R}}k_{\mathrm{HX}}} + \frac{RT}{F}\ln\frac{i_{\mathrm{d}} - i}{i} + \frac{RT}{F}\ln\left(k_{\mathrm{HX}}C_{\mathrm{HX}} - i\right)$$

(note that $i_{\mathrm{d}} = 2k_{\mathrm{R}}C_{\mathrm{R}}$). If we assume that the ratio of the square roots of the diffusion coefficients of proton-donor and reductant is unity (so that $k_{\mathrm{HX}} = k_{\mathrm{R}}$) and write the ratio $C_{\mathrm{HX}}/C_{\mathrm{R}} = m$, we finally obtain for the equation of the wave:

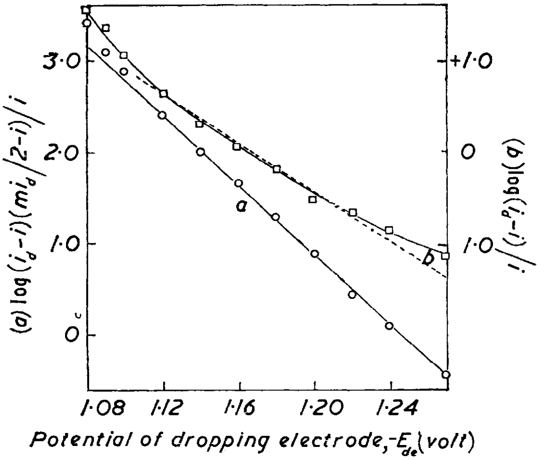
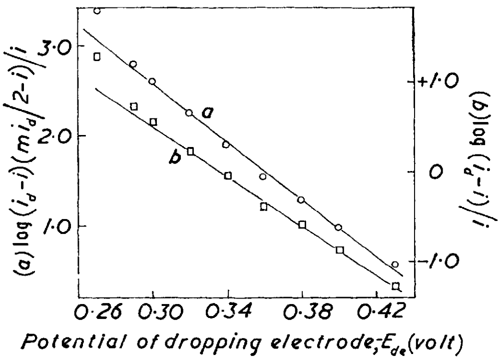


FIG. 2. *Logarithmic analysis of wave of benzophenone with phenol in molar ratio m* = 2·0.

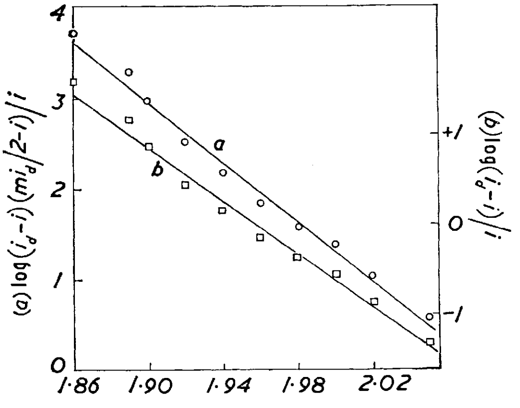
Slopes: (*a*) 53·5 mv, (*b*) 75 mv.

FIG. 3. *Logarithmic analysis of wave of anthraquinone with benzoic acid in molar ratio m* = 4·5.



Slopes: (*a*) 62·5 mv, (*b*) 72 mv.

FIG. 4. *Logarithmic analysis of wave given by naphthalene with phenol in molar ratio m* = 4·0.



Slopes: (*a*) 60·5 mv, (*b*) 68 mv.

$$E_{\mathrm{de}} = \text{Constant} + \frac{RT}{F}\ln\frac{(i_{\mathrm{d}} - i)(mi_{\mathrm{d}}/2 - i)}{i} \quad . \quad . \quad . \quad . \quad (16)$$

whence

$$E_{\frac{1}{2}} = \text{Constant} + \frac{RT}{F}\ln\frac{i_{\mathrm{d}}}{2} + \frac{RT}{F}\ln(m - 1) \quad . \quad . \quad . \quad . \quad (17)$$

The use of the equation is limited to cases where $m > 2$, and a sufficient excess of acid is present to ensure that the waves coalesce completely. However, if m is very large, the logarithmic term in equation (16) reduces to the usual form, ln $(i_d - i)/i$, but the half-wave potential will be concentration-dependent. The logarithmic function of equation (16) has been plotted against E_{de} for benzophenone–phenol mixtures having $m = 1{\cdot}98$ and 3·95, for anthraquinone–benzoic acid mixtures with $m = 3{\cdot}02$, 5·65, and 9·15, and a naphthalene–phenol mixture having $m = 4$. Satisfactory plots of slope $2{\cdot}303\boldsymbol{R}T/F$ were obtained in all cases (the slopes were 52·5, 64, 61, 62·5, 59, 56, and 60·5 mv, respectively); examples are shown in Figs. 2—4, together with plots of the usual function, log $(i_d - i)/i$, for comparison. The half-wave potentials varied with m in the required direction, but by rather less than equation (17) predicts; thus for benzophenone–phenol, if $m = 1{\cdot}98$ and 3·95, $\Delta E_{\frac{1}{2}} = 20$ mv, whereas equation (17) requires 30 mv; and for anthraquinone–benzoic acid, if $m = 3{\cdot}02$ and 9·15, $\Delta E_{\frac{1}{2}} = 30$ mv, equation (17) giving 36 mv. Insufficient data are available for testing the concentration-dependence indicated by the second term of equation (17).

The success of the above analysis in accounting for the observed behaviour in the cases tested confirms the suggestion that the undissociated acid is the effective proton-donor and supports the mechanism used. Moreover, it illustrates the general point that plots of E_{de} against log $(i_d - i)$ having slopes greater than 60 mv do not necessarily indicate the irreversibility of the electrode reaction.

Tables 1 and 2 show that, for any one proton-donor, substances differ widely in the concentration of acid required to complete an effect. Thus, for example, the mononegative ions of benzophenone and naphthalene have higher proton affinities than the ions of anthracene and benzaldehyde; the theoretical reasons for this are not clear. The difference in effect of various proton-donors on the same substrate no doubt arises from differences in the rate constants of protonation reactions such as equation (10); these in turn will depend on the strength of the bond H–X in the acids.

The following general conclusions can be drawn from the work reported: (1) The effect of proton-donors in polarography in dimethylformamide varies widely with the nature of the substance being reduced, and also for any given substance may vary with the nature of the proton-donor. (2) If it is desired to achieve the maximum degree of reduction in the polarography of aromatic systems, it is essential to have a proton-donor present; statements in the literature (cf. ref. 13) that the waves of such systems are independent of pH are misleading. (3) Phenol is a convenient and generally applicable proton-donor for use in dimethylformamide (and no doubt in other non-proton active solvents). (4) Weak acids appear to provide protons by reaction of undissociated acid rather than by ionization. (5) The results with purpurogallin suggest that the presence of phenolic hydroxyl within the molecule reduced does not affect its behaviour by permitting internal protonation.

Note added in proof. We have recently found a possible limitation on the use of phenol as a proton-donor: an adsorption wave appears when 20—40 mmole of phenol is added to 1 mmole of benzophenone. The height of this wave, once it has appeared, is independent of phenol concentration. It is removed by addition of 0·02 gm./l. of a coal extract (the extract seems to be surface-active, since it also suppresses the maximum found on the first wave of benzoquinone in dimethylformamide).

Janz and Danyluk (*J. Amer. Chem. Soc.*, 1959, **81**, 3846) have shown, from conductance studies, that slow solvent–solute interaction precedes the ionization of hydrogen halides in acetonitrile. This suggests, in agreement with the view taken above, that the ionization of weak acids in the similar solvent, dimethylformamide, would be too slow for the solvated proton to have any significant influence on polarography in their presence.

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