667. *Electrochemical Measurements in Pyridine. Part II.**
The Redox Potentials of Some Quinones.

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The redox potentials of a series of quinone–quinol systems have been measured in anhydrous pyridine, and in some cases the entropies of reduction have also been determined. The use of this solvent allows measurements to be made on compounds where this had been impracticable because of their low solubility in water or alcohol, including higher polycyclic quinones for which predicted values are available for comparison. Sufficient agreement has been found between calculated and measured values to show that the empirical relations used to predict redox potentials are of considerable practical value, but appreciable discrepancies exist, and the possible reasons for these have been discussed. In the case of anthraquinone, the reduction to anthraquinol anion in anhydrous pyridine has also been investigated, and a very large semiquinone formation constant found.

A KNOWLEDGE of the free energies of reduction of the carbonyl groups of quinones is of practical importance in connection with vat dyes, and of theoretical interest because such free energies can, with certain limitations, be correlated with structure in a large number of cases (Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, 1945; Diatkina and Syrkin, *Acta Physicochim. U.R.S.S.*, 1946, **21**, 921; Carter, *Trans. Faraday Soc.*, 1949, **45**, 597; Evans, *ibid.*, 1946, **42**, 113), and also in many cases with the rates of reduction of quinones or with the rates of oxidation of quinols (Barron, *J. Biol. Chem.*, 1932, **97**, 287; Dimroth, *Z. angew. Chem.*, 1933, **46**, 571; Hammett and Pfluger, *J. Amer. Chem. Soc.*, 1933, **55**, 1079). The measurement of redox potentials affords an extremely convenient method for determining free energies of reduction, but in the usual solvent, water, its application is limited by solubility difficulties. Its range can be somewhat extended by the use of alcohol as solvent (Kvalnes, *ibid.*, 1934, **56**, 670; Fieser and Fieser, *ibid.*, p. 1565) or by using mixtures of water and organic solvents (Geake and Lemon, *Trans. Faraday Soc.*, 1938, **34**, 1409), but the redox potentials of most vat dyes remain inaccessible, as do those of the unsubstituted polycyclic quinones which are of particular interest in testing proposed relationships between structure and redox potential. Sulphuric acid is a good solvent for these compounds, but attempted measurements in that medium have had only limited success (Geake, *ibid.*, 1941, **37**, 68).

In the present work the technique developed in Part I * for potentiometric measurements in anhydrous pyridine has been used to determine the redox potentials in that solvent of a number of quinones and other compounds, in some cases at two different temperatures, the process studied being the reduction to the leuco-compounds by addition of hydrogen atoms. The reduction of quinones to their leuco-anions by addition of electrons is of greater interest from the technical point of view, and the redox potential of the system anthraquinone–anthraquinol anion was measured in pyridine, but the experimental difficulties proved so great that no other compounds were investigated under the same conditions. Potentiometric measurements proved generally more difficult in pyridine than in water, and could not be made with the same accuracy, but the potentials

* Part I, preceding paper.

observed in pyridine were sufficiently stable and reproducible in most cases to yield useful information. As in water, the main limitation was still set by solubility considerations; some of the compounds (especially pyranthrone) were only very slightly soluble even in pyridine, and their solutions consequently gave less well poised potentials. This tendency was more marked at higher temperatures, presumably because of insulation difficulties, and in the worst cases the potentials were then too unsteady to measure. In addition, measurements above room temperature could not be made on p-benzoquinone or 1 : 4-dibenzamidoanthraquinone, in the first case because of reaction with pyridine hydrochloride (presumably to give a halogenated quinol), and in the second because of decomposition of the reduced compound.

Systems Q–QH$_2$.—The significance of the potential–composition curves obtained was tested by applying the usual equation

$$E = E_0 + (RT/F) \ln [\text{H}^+] + (RT/2F) \ln [\text{ox.}]/[\text{red.}] \quad . \quad . \quad . \quad . \quad (1)$$

where [H$^+$] = concentration of pyridine hydrochloride, *i.e.*, complete ionization of the latter is assumed and the pyridinium ion is taken as equivalent to the H$_3$O$^+$ ion in water; [ox.] = concentration of total oxidised form; [red.] = concentration of total reduced form; and [H$^+$] $\gg$ [ox.] + [red.]. The assumptions implicit in equation (1) appeared to be reasonably justified at constant ionic strength, since the calculated E_0 values were constant in each case to ± 3 mv or better over the range 20—80% oxidised, the reproducibility in successive experiments being of the same order, except for pyranthrone. If, however, the ionic strength was varied, by varying the pyridine hydrochloride concentration or by adding a neutral salt, E_0 varied appreciably, as shown in Table 1.

TABLE 1.   (Quinone concentration 0·001M throughout.)

Temp.	[HCl], M	[LiCl], M	E_0 (anthraquinone),mv	Temp.	[HCl],M	[LiCl], M	E_0 (anthraquinone), mv
18°	0·013	—	−298	18°	0·049	0·124	−346
,,	0·049	—	−308	95	0·090	—	−406
,,	0·115	—	−329	,,	0·194	—	−420
,,	0·216	—	−332	,,	0·232	—	−421
,,	0·61	—	−349				

It seems likely that the variations represent changes in activity coefficients, but no attempt was made to correct for these. Instead, measurements were made throughout at an ionic strength of approximately 0·2. The results are shown in Table 2.

TABLE 2.

Compound	E_0 ($T_1°$), mv		E_0 ($T_2°$), mv		ΔS, cal. °c^{-1} mole^{-1}
p-Benzoquinone	199	(25°)	—		—
1 : 4-Naphthaquinone	− 23	(18°)	—		—
9 : 10-Anthraquinone	−332	(18°)	−420	(95°)	51
9 : 10-Phenanthraquinone	− 21	(25°)	− 60	(95°)	25
Perylene-3 : 10-quinone	0	(25°)	− 51	(95°)	41
Anthanthrone	−238	(25°)	—		—
3 : 4-8 : 9-Dibenzopyrenequinone ...	−242	(25°)	−287	(75°)	41·5
Pyranthrone	*ca.* −330	(25°)	—		—
Dibenzanthrone	−222	(18°)	—		—
1 : 4-Dibenzamidoanthraquinone...	−410	(18°)	—		—
16 : 17-Dimethoxydibenzanthrone	−277	(18°)	−305	(70°)	25
Indanthrone	−223	(25°)	—		—
Indigo	−220	(25°)	—		—

Branch and Calvin (*op. cit.*) and Carter (*loc. cit.*) have given empirical relationships between the relative redox potentials of a series of unsubstituted quinones and the numbers of Kekulé forms of the quinones and the corresponding quinols, and have tested these relations for compounds with up to 5 rings by comparison with values determined in alcoholic solution. The present work allows a test to be made for compounds with up to 9 rings.

Table 3 gives the experimental values at room temperature and those calculated from Carter's equation, their zero being adjusted to make $\Sigma[E_0 \text{ (exp.)} - E_0 \text{ (calc.)}]^2$ a minimum.

The agreement between the experimental and the calculated redox potentials is certainly sufficient to give information of practical value with a quinone of unknown potential, but the larger deviations are clearly outside the range of experimental error. It is therefore of interest to examine possible reasons for the discrepancies.

Both Carter's and Branch and Calvin's methods for calculating redox potentials depend on the assumptions that reduction takes place exclusively to the quinol; that the relative free energies of reduction of a series of quinones depend almost exclusively on the differences in resonance energy between quinones and quinols; that the resonance energies can be represented by an equation which takes account of Kekulé forms only; and finally, that steric " ortho "-effects can be allowed for by a small number of empirical corrections.

TABLE 3.

	E_0 (exp.), mv	E_0 (calc.), mv	Diff., mv		E_0 (exp.), mv	E_0 (calc.), mv	Diff., mv
p-Benzoquinone	199	205	− 6	Anthanthrone	−238	−291	+53
1 : 4-Naphthaquinone	− 23	− 30	+ 7	3 : 4-8 : 9-Dibenzo-			
9 : 10-Anthraquinone...	−332	−342	+10	pyrenequinone	−242	−274	+32
9 : 10-Phenanthra-				Pyranthrone .... *ca.*	−330	−316	−14
quinone	− 21	+ 2	−23	Dibenzanthrone	−222	−258	+36
3 : 10-Perylenequinone	0	+ 87	−87				

The validity of the first assumption is seldom questioned, yet the possibility always exists of reduction to the keto-form (I) tautomeric with the quinol (II). In the case of anthraquinone the keto-form (oxanthrone) is well known, though the normal equilibrium between (I) and (II) lies at 97% of (II) in alcohol (Meyer, *Annalen*, 1911, **379**, 37). Data on keto–enol equilibria for other quinols are scanty, but the considerations used to predict


the relative free energies of the change quinone→quinol for a series of compounds should be equally applicable to predicting the relative free energies of the change (I)→(II). Hence, structures which favour the quinone relatively to the quinol should also favour the oxanthrone form, and, solvent effects apart, the greatest equilibrium proportion of keto-form would be expected in the reduction products of those quinones with the lowest predicted redox potentials; but, in fact, $[E_0$ (exp.) − E_0 (calc.)] does not seem to vary systematically with E_0 (calc.), and it appears either that no appreciable amount of keto-form is produced from any of the quinols, or that the same proportion is formed in all cases. The former is the more likely explanation, since in alcohol only 3% of keto-form occurs at equilibrium with anthraquinol, even though anthraquinone has one of the lowest predicted redox potentials.

The second assumption has been discussed by Evans and de Heer (*Quart. Reviews*, 1950, **4**, 94), who point out that the differences in the heats and entropies of solvation of quinones and quinols are the most likely factors to vary, apart from the differences in resonance energies, and that the entropy of reduction, for example, varies with the solvent. Table 2 shows that for four unsubstituted quinones in pyridine the entropy of reduction varies considerably, but it is surprising that in spite of the large entropy contribution to the total free-energy change, these variations in ΔS are not reflected in E_0(exp.) − E_0(calc.). The conclusion seems to be that the heat change of reduction is also varying appreciably, in such a way as to obscure the effect of the variations in ΔS. Direct measurement of heats of solvation would throw light on this point.

The third assumption has been tested by Carter (*loc. cit.*), who has shown that his empirical equation agrees surprisingly well with the results of molecular-orbital calculations, even up to undecacyclic compounds. The fourth assumption may well be partly incorrect, and individual corrections may be needed if a wide range even of unsubstituted compounds is to be covered, but as Evans and de Heer have pointed out, the nature of these " ortho "-

effects is not always clear, and quantitative treatment of them is usually impossible.   In any case the observed variation of ΔS, and the probable accompanying variation of ΔH, are amply large enough to account for the observed discrepancies without involving further variables.

System Q–Q⁻.—The potential–composition curve obtained for the system anthraquinone–anthraquinol anion in pyridine at 18° is shown in the figure.   Analysis by Michaelis and Schubert's method (*Chem. Reviews*, 1938, **22**, 437) showed that the potentials measured were in fact thermodynamically significant, and that the reaction $AQ^- \rightleftharpoons AQ + 2e$ proceeds in two distinct one-electron steps, the free energies of which are so different that the first is completed before the second occurs to any appreciable extent. Consequently, an equimolecular mixture of AQ and AQ⁻ in pyridine consists almost entirely of the semiquinone SQ⁻ formed by the reaction $AQ + AQ^- \rightleftharpoons 2SQ^-$, for which the equilibrium constant $K = [SQ^-]^2/[AQ][AQ^-]$ is in this case *ca.* 5×10^4.   No
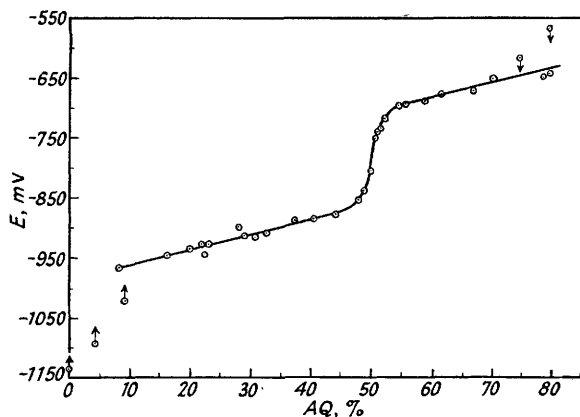
Redox curve of AQ–AQ⁻ *in pyridine at* 18° c.

dimerization of the semiquinone could be detected.   From the results its appears that E_1 and E_2, the standard potentials of the steps

$$AQ + e \longrightarrow SQ^- \ (E_1) \qquad SQ^- + e \longrightarrow AQ^- \ (E_2)$$

are respectively -635 and -922 mv.

Geake and Lemon (*loc. cit.*) observed a large increase in K for anthraquinone from water to 50% mixtures of water with pyridine, morpholine, Cellosolve, or ethylenediamine, and it now appears that K continues to increase in going to 100% pyridine.   Since this effect of organic solvents in increasing K does not seem to require the presence in the solvent of any particular atom or group, the most likely explanation of their action is that they affect the dielectric constant of the medium.   The lower the dielectric constant, the greater will be the electrostatic repulsion barrier to the process $2SQ^- \longrightarrow AQ + AQ^-$, while the reverse process will be relatively unaffected.   As the dielectric constant falls, both SQ⁻ and AQ⁻ will tend to form ion-pairs with the cations present, and the two tendencies will very roughly counterbalance each other.   In general, therefore, semiquinone formation should be favoured by a lowering of the dielectric constant of the medium, at the expense of both AQ and AQ⁻, and of any semiquinone dimer.

It is interesting that the semiquinone derived from anthraquinone is only feebly coloured, its solutions in pyridine being pale brown (cf. Geake and Lemon, *loc. cit.*). Presumably it has a strong absorption band outside the visible spectrum.

Finally, by combining the results of the measurements on the AQ–AQH₂ and AQ–AQ⁻ systems, a value can be derived for the dissociation constant $K_A = [AQ^-][H^+]^2/[AQH_2]$, which is found to be 4×10^{-16} g.-mol.²/l.² in pyridine.   A roughly comparable value is that for anthraquinol-β-sulphonate in water, found by Conant *et al.* (*J. Amer. Chem. Soc.*, 1922, **44**, 1882) to be 5×10^{-20}.   The dissociating effect of the more basic solvent is clear.

EXPERIMENTAL

Unless otherwise stated, anhydrous materials of analytical reagent quality were used as such. Pyridine was purified as described in Part I (*loc. cit.*), and pyridine hydrochloride solutions were made by absorbing dry hydrogen chloride in anhydrous pyridine, the concentration being estimated by diluting aliquot portions ten-fold with water and titrating with phenolphthalein as indicator. The majority of the quinones investigated were prepared and purified by the late Dr. P. G. Carter. 3 : 10-Perylenequinone was made from perylene prepared by Dr. Carter, by oxidation with chromic acid followed by recrystallization from nitrobenzene and pyridine. Anhydrous ferric chloride (B.D.H.) and a commercial sample of sodium methoxide were stored *in vacuo* and used as such.

The purification of nitrogen and hydrogen, and the apparatus used, were as described in Part I. The procedure for measurements on the Q–QH_2 systems was to prepare a solution of the reduced form of a given compound in pyridine containing 0.2M-pyridine hydrochloride, and to titrate this solution potentiometrically with an oxidizing agent such as ferric chloride, also dissolved in pyridine. Alternatively, varying amounts of the oxidized form were added to a known amount of the reduced form. Since most of the reduced forms could not be prepared in air, solutions of the oxidized forms were reduced in the potentiometric cell itself, by using hydrogen and the minimum quantity of palladized or platinized asbestos, prepared by alkaline formaldehyde reduction of palladium or platinum chloride absorbed on asbestos-flock. Before the titration was started, residual hydrogen was displaced by nitrogen. It was shown that pyridine was not hydrogenated under the conditions used to reduce the quinones.

For measurements on AQ–AQ^-, solutions of anthraquinone were reduced in pyridine and treated under nitrogen with an excess of sodium methoxide, and the resulting solutions of the sodium salt of anthraquinol were filtered into a burette fitted to the potentiometric cell. Titrations were carried out either by adding a standard anthraquinone solution to a known amount of the standard solution, or *vice versa*. Titration of the anthraquinol anion with a wide variety of inorganic and organic oxidizing agents was attempted, but without success, apparently because of the electrochemical sluggishness of the anthraquinone–anthraquinol anion system, together with its reluctance to enter into chemical equilibrium with other redox systems. Even in the absence of interfering systems, stable potentials were only very slowly established, particularly near the 50% point, where several hours were required for the attainment of equilibrium after each alteration of composition, and below 20% and above 80% of oxidized form. This sluggishness, together with the extreme sensitivity to oxidation of AQ^- and the low working concentration required by its comparatively low solubility, made necessary the most rigorous exclusion of oxygen from the apparatus.

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