879. *A Polarographic Investigation into the Redox Behaviour of Quinones: The Roles of Electron Affinity and Solvent.*

By M. E. Peover.

One-electron reduction potentials, E_1, of thirty quinones in aprotic conditions have been determined. A comparison with published molecular-orbital calculations shows that electron addition takes place to the lowest unoccupied molecular orbital. The E_1 values are linearly related to the electron affinity of the quinones. Intramolecular hydrogen bonding leads to an enhanced electron affinity in some α-hydroxy-quinones and apparently also in an unconjugated hydroxy-quinone. Although some E_1 values for hydroxylic solvents parallel those for aprotic solvents, there are marked deviations for halogeno- and cyano-quinones. It is tentatively suggested that changes in hydrogen bonding with the hydroxylic solvent account for this.

In connection with studies of polyquinone[1] and charge-transfer systems,[2] it was desirable to find a readily measured parameter which would describe the electron affinity of the quinone and closely reflect changes in the relevant energy level brought about by substitution in the quinone nucleus. Whereas conventional redox potentials (at zero pH) for the reaction, Quinone + 2e + $2H^+ \rightleftharpoons$ Quinol, have proved of considerable practical value in indicating the oxidising or reducing power of a system, and have been successfully correlated with the gain in resonance energy in passing from an unsubstituted quinone to its quinol, there are notable anomalies, in particular for halogens, when substituents are introduced.[3] Also the use of these conventional redox potentials as a measure of the electron affinity of the molecule has not been very successful. Since Hoijtink and his co-workers[4] showed that one-electron redox potentials measured in virtually aprotic conditions for a series of aromatic hydrocarbons are linearly related to the energies of the lowest unoccupied molecular orbitals, we have determined the potentials, E_1, corresponding to the reaction, Quinone + e $\rightleftharpoons$ Quinone$^-$, for a series of *ortho*- and *para*-quinones and substituted quinones, mainly in acetonitrile, and investigated their correlation with the calculated energies of the lowest unoccupied molecular orbitals. We then hoped to interpret the redox behaviour of quinones in terms of their electronic energy and environmental factors. To this end, a set of E_1 values has been determined in hydroxylic solvents and compared with the results in acetonitrile.

---

[1] Peover and Lindsey, *Chem. and Ind.*, 1961, 1273.

[2] Peover, *Nature*, 1961, **191**, 702.

[3] Evans and de Heer, *Quart. Rev.*, 1954, **4**, 94.

[4] Hoijtink, Van Schooten, de Boer, and Aalbersberg, *Rec. Trav. chim.*, 1954, **73**, 355; Hoijtink, *ibid.*, 1955, **74**, 1525.

Earlier work [5] has indicated that polarography provides a convenient means of measuring the one-electron potentials in non-proton-active solvents. Polarography, being a dynamic process, yields potentials which are virtually equilibrium values only if the electron transfer is rapid and associated chemical reactions are slow.[6] This can be conveniently investigated by AC polarography. A small alternating voltage is superimposed on the usual direct voltage applied to the cell. In the region of a redox reaction the AC admittance results in a peak-shaped polarogram whose summit potential lies at the corresponding DC half-wave potential. The magnitude of the faradaic current i_f depends on the rate constant of the electron-transfer process: [7]

$$i_\mathrm{f} = \frac{Vn^2\boldsymbol{F}^2CA\omega^{1/2}D^{1/2}}{2\sqrt{2\boldsymbol{R}T}} \,.\, \sin\phi, \tag{1}$$

$$\text{where } \sin\phi = \frac{1}{\sqrt{\left[1 + \frac{1}{k}\sqrt{\frac{\omega D}{2}}\right]^2 + 1}} \tag{2}$$

in which V is the amplitude of the applied AC voltage, n is the number of electrons per molecule involved, $\boldsymbol{R}$, $\boldsymbol{F}$, and T have their usual significance, C is the bulk concentration of the electroactive species, A is the area of the electrode surface, ω is the AC frequency, D is the diffusion constant of the reduced and the oxidised form (assumed equal), k is the rate constant of electron transfer at the standard potential and ϕ is the phase angle between the current and the applied voltage. Where a range of frequencies is available, k can be determined from eqns. (1) and (2). However, when only one frequency is available, eqns. (1) and (2) can be used in the following manner.

The mean limiting DC diffusion current over the drop-time t is given by the Ilkovič equation:

$$i_\mathrm{d} = \frac{1{\cdot}31n\boldsymbol{F}CAD^{1/2}}{\pi^{1/2}t^{1/2}} \tag{3}$$

Hence

$$\frac{i_\mathrm{f}}{i_\mathrm{d}} = \frac{V\boldsymbol{F}\,\omega^{1/2}\pi^{1/2}t^{1/2}n\sin\phi}{3{\cdot}71\sqrt{2\boldsymbol{R}T}} \tag{4}$$

For a given frequency, voltage, and temperature we have:

$$\frac{i_\mathrm{f}t^{-1/2}}{i_\mathrm{d}} = \text{Constant}.\ n \sin\phi. \tag{5}$$

For very large values of k, ϕ is $\pi/4$ (cf. refs. 6, 7). Half-wave potentials are virtually equilibrium potentials [6] when $k > 2 \times 10^{-2}$ cm. sec.$^{-1}$; with a frequency of 35 cycles/sec. and $D^{1/2} = 3 \times 10^{-3}$ cm. sec.$^{\frac{1}{2}}$ one obtains $\sin\phi = 0{\cdot}35$. Here the magnitude of expression (5) will be taken as a qualitative indication of the value of k and hence of the reversibility of the electrode process. Use of eqn. (5) has the advantage over the direct use of eqn. (1) that it contains D only in ϕ; comparison of molecules having fairly different values of D is thereby facilitated.

Notes indicating the relevance of some of the results to the electron affinities of quinones [8] and charge-transfer studies [2] have appeared.

---

[5] (*a*) Wawzonek, Berkey, Blaha, and Runner, *J. Electrochem. Soc.*, 1956, **103**, 456; (*b*) Given, Peover, and Schoen, *J.*, 1958, 2674; (*c*) Given and Peover, in " Advances in Polarography " ed. Longmuir, Pergamon Press, Oxford, 1960, p. 948.

[6] Delahay, " New Instrumental Methods in Electrochemistry," Interscience Publ., Inc., New York, 1954, p. 85.

[7] (*a*) Ershler, *Discuss. Faraday Soc.*, 1947, **1**, 269; (*b*) Randles, *ibid.*, 1947, **1**, 11; (*c*) Aten, Büthker, and Hoijtink, *Trans. Faraday Soc.*, 1959, **55**, 324.

[8] Peover, *Nature*, 1962, **193**, 475.

EXPERIMENTAL

Materials.—Dimethylformamide was fractionally distilled. Eastman Kodak " Spectrograde " acetonitrile was used as received. Tetraethylammonium iodide was prepared as described in ref. 5*b*; the perchlorate was obtained by addition of magnesium perchlorate followed by repeated recrystallisation from hot water. *p*-Benzoquinone was sublimed; *o*-benzoquinone,[9] 1,8-diphenoquinone,[10] chloro-1,4-benzoquinone,[11] and trichloro-1,4-benzoquinone [12] were prepared as in the refs. cited. The *o*-benzoquinone was prepared in dilute ethereal solution and used directly. Phenyl-1,4-benzoquinone and trimethyl-1,4-benzoquinone were kindly supplied by Dr. A. S. Lindsey. Tetrafluoro-1,4-benzoquinone was supplied by Dr. Pedler of Birmingham University. Tetrabromo- and 2,3-dichloro-5,6-dicyano-quinol were prepared from the quinones by hydrogenation with tetralin.[13] Other materials were of laboratory grade and were recrystallised. The water content of the solvents was 0·01—0·05%.

Apparatus.—A Cambridge pen-recording polarograph with " Univector " AC unit was used. The measured frequency and amplitude of the AC voltage was 35·0 cycles/sec. and 26·5 mv. The Univector unit is primarily designed for analytical work and incorporates a phase-sensitive bridge to eliminate capacitative currents due to the electrode double layer. For the present purpose the properties of the AC unit were investigated with the equivalent electrode circuit shown in Fig. 1 (the cell resistance was about 300 Ω and so was omitted from the equivalent circuit). The electrode reaction elements R_f and C_f are in parallel with the electrode double-layer capacity C_l. It was found that the measured current was unaffected by C_l provided $C_l \leqslant C_f$ for a variety of R_f and C_f such that the phase angle through the reaction element was 18—70°. However, even in the absence of C_l, the measured current through R_f and C_f depended on the phase angle in an unusual manner approaching the calculated value for small ϕ and increasing less than that required as ϕ increases. In the range of currents usually required, the variation closely follows the law

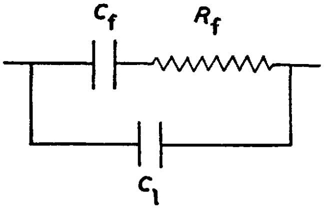


FIG. 1. Equivalent electrode circuit.

$$i_m = i \cos \phi, \qquad (6)$$

where i_m is the measured alternating current.* Thus equation (5) becomes

$$A \equiv i_m t^{-1/2}/i_d = \text{Constant} \,.\, n \sin \phi \cos \phi. \qquad (7)$$

A three-compartment cell was used, consisting of the working compartment with mercury-pool anode, separated by a sinter (porosity 4) from a renewable liquid bridge in turn separated by a sinter (porosity 1) from an agar (N-KNO_3) bridge and saturated calomel electrode (S.C.E.). Provision was made for passing oxygen-free " White-spot " nitrogen through the test solution. The resistance of the cell (dropping-mercury electrode to S.C.E.) was 1—2000 ohms. Measurements were made at 25° ± 0·05°. The measured potentials are reproducible to a least ±0·005 v. The dropping-mercury electrode had a drop time in acetonitrile of 4·2 sec. A rotating platinum electrode used for some experiments was constructed from a piece of platinum wire fused into the axis of a thick-walled glass capillary and ground flat; it was rotated at 500 r.p.m.

Reference Potential.—DC potentials were measured directly against the standard calomel

---

* This is in agreement with the Jessop principle used in the bridge.

[9] Willstätter and Müller, *Ber.*, 1908, **41**. 2580.

[10] Willstätter and Kalb, *Ber.*, 1905, **38**, 1232.

[11] Levy and Schultz, *Annalen*, 1881, **210**, 138.

[12] Oliveria, *Gazzetta*, 1948, **78**, 108.

[13] Braude, Brook, and Linstead, *J.*, 1954, 3569.

electrode and corrected for *iR* drop, but for AC measurements polarograms were run against the mercury-pool anode to minimise the cell resistance. In 0·1N-iodide the mercury anode provides a sufficiently stable reference electrode,[14] but in perchlorate solution the anode potential drifts considerably. AC summit potentials were then determined from separate polarograms by using the standard calomel electrode as anode. The bridge solution was the supporting electrolyte. The aqueous–non-aqueous liquid junction potentials differ by about 80 mv for the two organic solvents. The potentials in dimethylformamide are corrected by this amount so that all results include the acetonitrile–water liquid-junction potential.

Solutions were freed from oxygen by passing nitrogen through them for 10—15 min.; nitrogen was passed over the solution during a polarogram. In general, the concentration of reducible material was varied from ~0·2 to 0·6 mM in 0·1N-supporting electrolyte.

Preparative Electrolyses.—Semiquinone ions were prepared by micro-electrolysis of 5 ml. of 1—4mM-quinone in 0·1N-tetraethylammonium perchlorate in the chosen solvent at a stirred mercury cathode (area 3·5 cm.^{2}) maintained at the desired potential. The anode was of mercury in contact with a saturated lithium chloride solution separated from the main cell by a sinter (porosity 4). A dropping-mercury electrode *in situ* was used to follow the reduction.

RESULTS

The numerical results are collected in Tables 1 and 2, where $E_{\frac{1}{2}}$ and I are respectively the DC half-wave potential and the DC diffusion current constant ($i_d/Cm^{2/3}t^{1/6}$, where i_d is the limiting current in μA, C the concentration in mmoles per l., m the mass of mercury flowing in mg. sec.$^{-1}$, and t the drop-time in seconds), and A is the AC : DC diffusion current ratio defined by eqn. (7). As the AC summit potentials agree with the DC half-wave potentials within 0·01 v they are not included in the Tables.

TABLE 1.

Polarography of quinones in acetonitrile at 25° (supporting electrolyte 0·1N-NEt_4ClO_4).

	$E_{1/2}$ (v), *vs.* S.C.E.		I [a]		A [b]	
Quinone	E_1	E_2	1	2	1	2
1,4-Benzoquinone	−0·51 [cd]	−1·14	1·91	1·31	1·66	1·65
2,3-dichloro-5,6-dicyano-	+0·51	−0·30	1·56	1·56	1·68	1·67
tetrabromo-	0·00	−0·72	1·13	1·13	1·54	1·48
tetrachloro-	+0·01 [ef]	−0·71 [f]	1·72	1·71	1·68	1·57
trichloro-	−0·08	−0·78	1·56	1·56	1·45	1·45
2,5-dichloro-	−0·18	−0·81	1·91	1·60	1·58	1·60
2,6-dichloro-	−0·18	−0·81	1·72	1·70	1·57	1·61
chloro-	−0·34	−0·92	1·74	1·51	1·41	1·40
tetrafluoro-	−0·04	−0·82	1·63	1·51	1·22	1·38
tetramethyl-	−0·84	−1·45	1·62	1·34	1·56	1·50
trimethyl-	−0·75	−1·35	1·71	1·42	1·41	1·57
2,5-dimethyl-	−0·67	−1·27	1·80	1·61	1·70	1·52
methyl-	−0·58	−1·10	2·02	1·53	1·53	1·50
2,5-di-t-butyl-	−0·73	−1·24	1·72	1·41	1·50	1·45
phenyl-	−0·50	−1·03	1·66	1·51	1·49	1·45
1,2-Benzoquinone	−0·31	−0·90	— [g]	— [g]	—	—
1,4-Naphthaquinone	−0·71	−1·25	1·71	1·45	1·27	1·50
2-methyl-	−0·77	−1·28	1·67	1·21	1·38	1·51
2-amino-	−0·92	−1·40	1·42	1·38	1·22	1·25
5-hydroxy-	−0·52	−0·99	2·16	1·98	1·36	1·50
1,2-Naphthaquinone	−0·56	−1·02	1·63	1·27	1·61	1·55
1,4-Anthraquinone	−0·75	−1·25	1·55	1·34	1·58	1·42
9,10-Anthraquinone	−0·94	−1·45	1·52	1·50	1·70	1·50
2-sulphonate (Na)	−0·91	−1·40	1·21	1·00	1·67	1·39
9,10-Phenanthraquinone	−0·66	−1·22	1·53	1·41	1·50	1·17
1,8-Diphenoquinone	−0·24	−0·41	1·52	1·40	1·68	1·53

[a] $I = i_d/Cm^{2/3}\ 3t^{1/6}$, in μA mmole^{-1} l. mg.$^{-2/3}$ sec.$^{-1/6}$. [b] See eqn. 7. [c] In satd. $NaNO_3$ value is −0·50 v. [d] At a rotating Pt electrode value is −0·52 v. [e] In satd. $NaNO_3$ value is 0·00 v. At a rotating Pt electrode values are −0·01 and −0·80 v. [g] Concn. unknown.

---

[14] Given and Peover, *J.*, 1959, 1602.

TABLE 2.

Polarography of quinones in dimethylformamide at 25° (supporting electrolyte $0{\cdot}1\text{N-NEt}_4\text{ClO}_4$ or $0{\cdot}1\text{N-NEt}_4\text{I}$).

	$E_{1/2}$ (v) *vs*. S.C.E.		I [a]		A [b]		
Quinone	E_1	E_2	1	2	1	2	NEt_4 salt
1,4-Benzoquinone	−0·54	−1·23	1·91	1·32	1·61	1·23	ClO_4
	—[c]	−0·81	—[c]	1·21	—	—	I
tetrachloro-	−0·02	−0·90	1·71	1·60	1·50	1·35	ClO_4
2,5-dimethyl-	−0·68	−1·34	1·85	1·35	1·53	1·20	ClO_4
	—[c]	−1·41	—[c]	1·30	—[c]	1·60	I
9,10-Anthraquinone ...	−0·98	−1·74	1·41	1·38	1·56	1·14	ClO_4
	−0·98	−1·69	1·50	1·30	1·67	1·21	I
1-hydroxy-	−0·77	−1·39	1·96	1·68	1·48	1·56	ClO_4
1,8-dihydroxy-	−0·64	−1·42	1·71	1·32	1·57	1·15	ClO_4
2-ethyl-	−1·12	−1·69	1·51	1·25	1·67	1·33	I
-2-sulphonate (Na)...	−0·98	−1·64	1·24	1·00	1·31	1·49	I
1,4-Naphthaquinone ...	−0·72	−1·63	1·60	1·43	1·33	0·49	ClO_4
2-hydroxy-	−0·64 [d]	−1·20	1·25	0·63	0·25	1·27	ClO_4
5-hydroxy-	−0·51	−1·17	2·12	0·90	0·96	0·30	ClO_4
(Anthracene	−2·05	−2·57	2·00	1·56	1·59	0·33	ClO_4)

[a, b] See Table 1. [c] Maximum. [d] In the presence of " Gepolit " (see text).

Previously reported results for *p*-benzoquinone [5a, 15] were markedly affected by the halide ion of the supporting electrolyte.* The behaviour in perchlorate solution is normal.

In contrast to all the other compounds, which gave first waves of close to theoretical shape for a one-electron process, 2-hydroxy-1,4-naphthaquinone showed a drawn-out first wave of one-electron height in both solvents, and the AC polarograms showed sharp peaks characteristic of adsorption effects.[17] The addition of a surface-active polymer (" Gepolit," a polystyrene–polyvinyl chloride copolymer) produced a shift of about 0·2 v. The AC admittance was still abnormally low but showed no adsorption peaks. Protonation of the mononegative ion [7c, 18] or tautomerism to the *ortho*-quinone may play a part.[19]

The value of A (see eqn. 7) for very fast electron-transfer is given by putting $\phi = \pi/4$. The DC wave ceases to be diffusion-controlled under our conditions when $\sin \phi = 0{\cdot}35$; the criterion for reversibility becomes $1{\cdot}70n \geqslant A > 1{\cdot}06n$. (If A were to exceed the upper limit it would suggest abnormal capacitative current due to absorption effects.) This criterion is well satisfied by all the compounds listed in Tables 1 and 2 for $n = 1$, except for 2-hydroxy-1,4-naphthaquinone. Anthracene has been included in Table 2 since the value of k for the first-electron addition is known from Aten and Hoijtink's work [20] to be of the order 1 cm. sec.$^{-1}$; the A value is close to the upper limit as expected. The E_1 values for the dichlorodicyanoquinone and anthraquinone were identical with those of the semiquinone ions produced by addition of sodium iodide and by electrolysis, respectively.

The second half-wave potentials are some 0·7 and 0·6 v more negative than the first wave in dimethylformamide and acetonitrile, respectively. The values given by Wawzonek *et al.*[5a] for *p*-benzoquinone, tetramethylbenzoquinone, and anthraquinone in acetonitrile give a corresponding difference of some 0·8 v; the discrepancy may be due to the tetrabutylammonium salt used by those workers.

Some measurements were made in 0·1N-sodium hydroxide in 75% ethanol. The quinols are stable under these conditions in the absence of air, but the quinones are extremely unstable. The semiquinone ions have appreciable life-times. Polarograms were therefore confined to

---

* Given and Peover [16] recently reported work on some stilbenequinones in dimethylformamide–iodide solution; the results were probably markedly affected by the use of iodide as supporting electrolyte.

[15] Given and Peover, *J.*, 1960, 394.

[16] Given and Peover, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3195.

[17] Breyer and Hacobian, *Austral. J. Sci. Res.*, 1952, **5**, *A*, 500.

[18] Aten and Hoijtink, *Z. phys. Chem.* (*Frankfurt*), 1959, **21**, 192; Given and Peover, *J.*, 1960, 385.

[19] Fieser, *J. Amer. Chem. Soc.*, 1928, **50**, 465.

[20] Aten and Hoijtink, in "Advances in Polarography," ed. Longmuir, Pergamon Press, Oxford, 1960, p. 777; Aten, Thesis, Free University, Amsterdam, 1959.

oxidation of the ionised quinol form, except for anthraquinone derivatives. A few determinations could be carried out at the dropping-mercury electrode. Mostly, only the more negative wave could be resolved and the overall mid-point potential was determined. The potentials corresponding to the addition of the first electron to the quinone (E_1 in Table 4) were obtained from the measured mid-point potential by adding 0·07 v, the average value for the separation under these conditions. The results are collected in Table 3; diffusion-current constants are not given because of uncertainties in concentration. Some measurements were made at a rotating platinum electrode and gave fair agreement with those at the dropping-mercury electrode.

TABLE 3.

Polarography of quinols in 75% ethanol at 25° (supporting electrolyte 0·1N-NaOH; potentials in v *vs.* S.C.E., ±0·01 v).

Quinol	$E_{\rm m}$	E_1	E_2
9,10-Anthraquinol-2-sulphonate	−0·75	−0·67	−0·82
1,4-Naphthaquinol	−0·52	−0·44	−0·59
Quinol	−0·31	—*	−0·38
tetrabromo-	−0·16	—*	−0·23
chloro-	−0·23	—*	−0·31
2,6-dichloro-	−0·17	—*	−0·24
trichloro-	−0·13	—*	−0·20
tetrachloro-	−0·11	—*	−0·18
2,3-dichloro-5,6-dicyano-	0·25 †	—	—

* Oxidation of mercury interferes. † At rotating platinum electrode.

DISCUSSION

Theoretical Significance of the Potentials in Non-hydroxylic Solvents.—All the quinones studied give two well-defined DC waves of similar height. It has previously been shown by controlled-potential electrolysis,[5b] coulometry,[5b,15] and electron-spin resonance[21] in dimethylformamide, and by electrolysis in acetonitrile,[5a] that anthraquinone is reduced by two one-electron steps to the mononegative ion (semi-quinone ion) and quinol di-ion at potentials corresponding to the first and second half-wave potential, respectively. Also, electrolysis of 2,5-dimethyl-1,4-benzoquinone at −0·80 v was found in this laboratory to yield a solution giving a strong E.S.R. signal and exhibiting the hyperfine structure characteristic of the semi-quinone ion.[22] From the polarographic similarities it can thus reasonably be assumed that all these quinones are reduced by the same mechanism. The results indicate that the polarographic half-wave potentials can be identified with the equilibrium potentials and it is permissible to attempt a correlation with other molecular properties. The free-energy changes corresponding to the measured potentials will be composed of two factors, one dependent on environmental factors such as solvation-energy changes and the other a property of the electronic structure of the molecule. It is assumed that the first of these is constant in the series of quinones to be compared. It appears that this type of assumption often has considerable justification, for example, from the successful use of similar potentials for a wide range of aromatic hydrocarbons.[4] Molecular-orbital calculations of the energy levels of a series of quinones have been published by Kuboyama[23] and Mme. Pullman.[24] Kuboyama used a method based on a self-consistent field treatment of *o*- and *p*-benzoquinone,[25] but the details of Pullman's method are not yet available. In any such calculations values have to be assigned to the parameters termed the coulomb and resonance integrals referred to the oxygen atoms

---

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

[22] Venkataraman and Fraenkel, *J. Chem. Phys.*, 1955, **23**, 588.

[23] Kuboyama, *Bull. Chem. Soc. Japan*, 1958, **31**, 752; 1959, **22**, 1226; 1960, **33**, 917.

[24] Pullman, *Compte rend.*, 1961, **253**, 1210.

[25] Nagakura and Kuboyama, *J. Amer. Chem. Soc.*, 1954, **76**, 1003.

(α_O and β_O, respectively), which it is assumed are valid for the series of molecules. It is usual to express α_O and β_O in the form $\alpha_O = \alpha + \delta\beta$, $\beta_O = \gamma\beta$, where α and β are the corresponding parameters for carbon. Recent work on the odd-electron distribution in semiquinone ions suggests that one set of values for δ and γ can be used to give an adequate description of the molecule at least for a series of *para*-quinones,[26] but there are considerable differences of opinion as to what are the best values for δ and γ. Kuboyama [23] took $\delta = 1{\cdot}3$, $\gamma = 1{\cdot}0$, for both *ortho*- and *para*-quinones; Vincow *et al.*[26] use $\delta = 1{\cdot}20$, $\gamma = 1{\cdot}56$, and Brandon and Lucken [26] use $\delta = 0{\cdot}39$, $\gamma = 1{\cdot}06$, for *para*-quinones. Nevertheless, as is shown in Fig. 2, the correlation between the one-electron half-wave potentials measured in acetonitrile, E_1 (MeCN), and Kuboyama's calculated lowest unoccupied orbital energies is good for both *ortho*- and *para*-quinones, except for diphenoquinone. It has been indicated that the assumptions made in the calculations for diphenoquinone are probably in error.[8] The equation of the line is $E_1 = [2{\cdot}07(E - \alpha)/\beta] - 1{\cdot}03$. The similar plot for Pullman's results in Fig. 2 (the substituted quinones being excluded) gives an equation

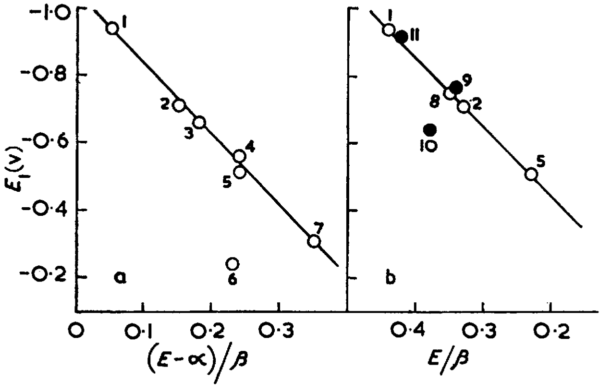


FIG. 2. Dependence of E_1 (in acetonitrile) on energy E of lowest unoccupied molecular orbital, calculated by (a) Kuboyama, (b) Pullman.

(1) 9,10-Anthraquinone. (2) 1,4-Naphthaquinone. (3) 9,10-Phenanthraquinone. (4) 1,2-Naphthaquinone. (5) *p*-Benzoquinone. (6) 1,8-Diphenoquinone. (7) *o*-Benzoquinone. (8) 1,4-Anthraquinone. (9) 2-Methyl-, (10) 2-hydroxy- (in $NMe_2{\cdot}CHO$), and (11) 2-amino-1,4-naphthaquinone.

$E_1 = (2{\cdot}00E/\beta) - 0{\cdot}05$. The slopes of the two lines are in good agreement and appear to give the reasonable value for β of about 2 v. The few measurements made in dimethylformamide indicate that similar results are obtained with this solvent. It seems reasonable to conclude that electron addition takes place to the lowest unoccupied molecular orbital and that the one-electron half-wave potential gives a parameter related linearly to the electron affinity of the molecule. The correlation with the conventional redox potentials, on the other hand, is poor.[8]

In considering the effect of substituents in the quinone nucleus on the electron affinity of the molecule by the use of molecular-orbital calculations, further difficulties are introduced as suitable parameters have to be assigned to the substituents. Pullman's results for 2-substituted 1,4-naphthaquinones are plotted with the measured E_1 (MeCN) values in Fig. 2b. There is good agreement for the amino- and fair agreement for the methyl derivative. The anomalous position of the hydroxy-derivative could be due in part to the uncertain polarographic behaviour of this compound, but, for several other hydroxy-quinones investigated, values of E_1 in acetonitrile or dimethylformamide are also considerably more positive than for the parent compound. It is well known that introduction of a hydroxyl substituent shifts the conventional redox potential to a more negative

---

[26] Vincow and Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333; Brandon and Lucken, *J.*, 1961, 4273.

value, as indicated by Pullman's calculation. The large, reverse effect found in non-hydroxylic solvents is discussed below.

The half-wave potentials for substituted benzoquinones in Table 1 indicate that electron-releasing groups (methyl, t-butyl) increase the energy of the lowest unoccupied orbital, the potentials becoming more negative with increasing number of substitutents. On the other hand, electronegative substituents (halogen, cyanide) decrease this energy, leading to more positive potentials, and the potentials are affected regularly by the number of substituents; here inductive far outweigh any conjugative effects. The effect of halogen is greater than that of methyl; cyanide has the greatest effect. A phenyl group has virtually no disturbing effect on the potential. These half-wave potentials describe the electron affinity of the molecule (including α-hydroxy-quinones) very satisfactorily in connection with a series of charge-transfer spectra of the quinones with a given donor. The energy of the longest-wavelength charge-transfer absorption band is given to a good approximation by $\nu_{\text{max.}} = I_D - E_A + \text{Constant}$, where I_D is the ionisation potential of the donor (here constant), and E_A is the electron affinity of the acceptor. A straight-line relation is found between $\nu_{\text{max.}}$ and the half-wave potential of the quinone, with a slope close to unity. The details of this work will be published separately.[27] It can thus be concluded that for substituted quinones also, the E_1 (MeCN) potentials can be taken as a parameter linearly related to the electron affinity of the molecule.

Kuboyama [23] has shown that a large energy gap separates the first and the second unfilled orbital in quinones. The second one-electron half-wave potentials (E_2) presumably represent addition of the electron to the same orbital as the first, the difference in potential ($E_2 - E_1$) reflecting the repulsion forces from the negative charge in the molecule, offset by solvation-energy changes. Indeed a correlation is found for these potentials E_2 with the energy of the lowest unoccupied molecular orbital but not with that of the next unoccupied level.[8]

TABLE 4.

Potentials of some quinones (in v *vs.* S.C.E.).

Quinone	pK_1 [a]	pK_2 [a]	E_0(pH 0) [b] (H_2O)	E_m(pH > pK_2) (H_2O), calc.	E_1(pH > pK_2) (75% EtOH)	E_1 (MeCN)	E_m(H_2O) $-E_1$(MeCN)	E_1(EtOH) $-E_1$(MeCN)
9,10-Anthraquinone -2-sulphonate	—	—	−0·059	−0·62 [c]	−0·67	−0·91	0·29	0·24
1,4-Naphthaquinone	9·4	10·9	0·224	−0·37	−0·44	−0·71	0·34	0·27
1,4-Benzoquinone ...	9·9	11·1	0·433	−0·17	−0·24	−0·51	0·34	0·27
methyl-	10·1	11·6	0·399	−0·24	—	−0·58	0·34	—
tetramethyl-	11·25	12·7	0·220	−0·49	—	−0·84	0·35	—
chloro-	—	—	0·466	—	−0·16	−0·34	—	0·18
2,6-dichloro-	7·3	10·0	0·475	−0·04	−0·10	−0·18	0·14	0·08
trichloro- ...	—	—	0·486 [d]	—	−0·06	−0·08	—	0·02
tetrachloro-	—	—	0·452 [d]	−0·04 [e]	−0·04	0·01	0·05	−0·05
tetrabromo-	—	—	—	—	−0·09	0·00	—	−0·09
2,3-dichloro-5,6-dicyano	—	—	1·0 [d]	—	0·32 [f]	0·51	—	−0·19

[a] From Baxendale and Hardy, *Trans. Faraday Soc.*, 1953, **49**, 1140. [b] From Clark, " Oxidation Reduction Potentials of Organic Systems, " Baillière, Tindall, and Cox, London, 1960. [c] Direct determination, from Gill and Stonehill, *J.*, 1952, 1845. [d] In ethanol. [e] For tetrachloroquinol in 0·1N-NaOH, at r.p.e. [f] At r.p.e.

Behaviour in Hydroxylic Solvents.—In view of the anomalies encountered in the conventional redox potentials of halogenoquinones,[3] a solvent effect is to be expected, and we shall now consider to what extent the correlations discussed above hold in hydroxylic media.

---

[27] Peover, *Trans. Faraday Soc.*, 1962, **58**, 1656.

The determination of E_1 values for solutions in hydroxylic solvent can be achieved, in principle, under highly alkaline conditions, although in practice the quinones are often very unstable. Some values derived from measurements in 75% ethanol are collected in Table 4 together with calculated mid-point potentials, E_m, in water. The E_m values, which differ from the corresponding E_1 values by about 0·02 v,[28] were obtained from the conventional redox potentials (E_0, at zero pH) and the quinol dissociation constants by assuming normal pH variation.

Except for the halogeno-quinones, the last two columns of Table 4 indicate that the E_1 or E_m values in alcohol or water parallel the E_1 values in acetonitrile, and so bear a similar relation to the electron affinities. However, the conventional redox potentials, E_0, reflect the one-electron potentials, and so also the electron affinities, only so far as the pK values of the quinols are similar.

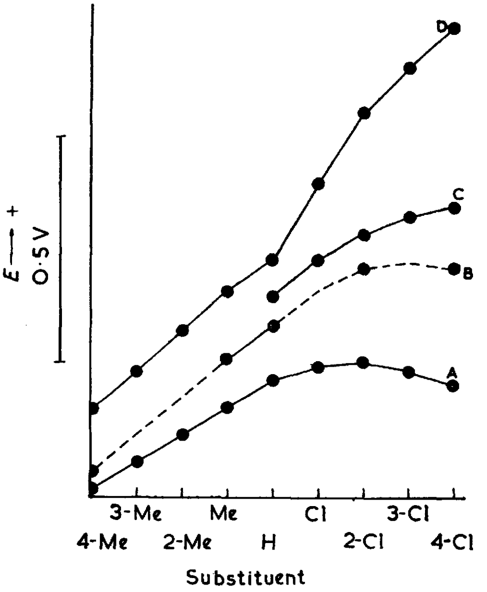


FIG. 3. Variation in redox potential with solvent and substitution in *p*-benzoquinone.

(A) E_0 in alcohol, pH 0. (B) E_m in water, pH > pK_2 (calc.). (C) E_1 in 75% ethanol, pH > pK_2. (D) E_1 in acetonitrile. (Curves displaced arbitrarily along voltage axis.)

A very large exception to the parallelism between E_0 and the half-wave potential in acetonitrile is provided by the halogeno-quinones as illustrated in Fig. 3. Their conventional redox potentials have always appeared somwhat anomalous[3] in that they show an unbroken increase with number of substituents only when converted to the gaseous state;[29] even then, four chlorine substituents enhance the potential by only 0·087 v in contrast to 0·5 v in acetonitrile. Fig. 3 and the last two columns of Table 4 show that the mid-point or one-electron potentials at high pH are anomalous. The expected increase in electron affinity, as exemplified by the results in acetonitrile, is offset in hydroxylic solvents. The fact that the dichlorodicyano-quinone gives a value of [E_1 (EtOH) − E_1 (MeCN)] more negative than that for the tetrachloro-quinone shows that the effect is not specific to halogen substitutents. If only general solvation-energy differences are concerned in the behaviour in the hydroxylic and aprotic solvents, the solvation energy associated with these quinones must be either greater in acetonitrile or less in water or alcohol than for other quinones. Since the half-wave potentials in acetonitrile adequately describe processes involving one-electron transfer[2,27] it appears that it is the behaviour in alcohol and water that is exceptional. However, it may be not only general solvation

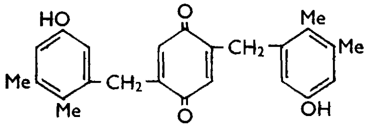
---

[28] Gill and Stonehill, *J.*, 1952, 1845.

[29] Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 293.

changes which affect the potentials. The outstanding difference in the properties of the two solvents is the capacity of water (and hydroxylic solvents generally) for hydrogen bonding. Indeed, in hydroxylic solvents, carbonyl compounds are known to be more or less hydrogen-bonded with the solvent, as shown by the blue shift in the $n \longrightarrow \pi^*$ electronic transitions of these compounds which occurs in passing from weakly to strongly hydrogen-bonding solvents (although the band for benzoquinone shows strong deformation and increased extinction, indicating complicating factors).[30]

Some evidence on the effect of hydrogen-bonding on redox potentials is forthcoming from the behaviour of α-hydroxy-naphthaquinones and -anthraquinones, which have a greatly enhanced reduction potential in dimethylformamide or acetonitrile. The effect in the aprotic solvents is undoubtedly due to intramolecular hydrogen bonding between the hydroxyl-hydrogen and the quinone and semiquinone oxygen. (It is assumed that at the concentrations used, 10^{-4}—10^{-3}M, intermolecular interaction is negligible.) In a conjugated system a general change in electronic structure by transmission through the


(I)

system[31] is caused by such intramolecular bonding. However, in the molecule (I) transmission of electronic changes through the molecule is largely blocked by methylene bridges; yet this molecule shows an enhancement of its reduction potential (in dimethylformamide, $E_1 = -0{\cdot}32$ v), even over that of unsubstituted quinone, but is normal in its conventional redox potential.[1, 32] Thus the hydrogen bonding, which approximates to the intermolecular case, results in a considerable increase in apparent electron affinity of the molecule.

A similar situation may exist in hydroxylic solvents (the E_1 potentials are about 0·3 v more positive than in acetonitrile, in the absence of halogen substitutents). The presence of extra lone pairs in halogeno-quinones and the lower basisity of their semiquinone ions could distinguish them from other quinones in regard to hydrogen-bonding effects.

Spectroscopic studies are in progress to obtain further information on the extent and effect of hydrogen-bonding to quinones and their ions.

The author is indebted to Dr. A. Horsfield for the electron spin resonance measurement and to Mr. J. D. Davies for technical assistance.

National Chemical Laboratory, D.S.I.R.,
Teddington, Middlesex.
[*Received, January* 31*st*, 1962.]

---

[30] Kasha, in "Luminescence of Biological Systems," ed. Johnson, Amer. Assoc. Adv. Sci., 1955, Chapter 2; Chandra and Basu, *Trans. Faraday Soc.*, 1960, **56**, 632.

[31] Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247; Shigorin, Schcheglova, Dokunikhin, and Puchkov, *Proc. Acad. Sci.* (*U.S.S.R.*), 1960, **132**, 565.

[32] Hunt and Lindsey, *Chem. and Ind.*, 1961, 1272; Lindsey, Peover, and Saville, *J.*, 1962, 4558.