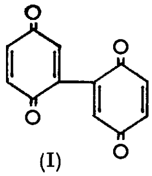
881. *Polymeric Quinones. Part II.*[1] *The Electrochemical and Physicochemical Behaviour of Some Methylene-linked Polybenzoquinones.*

By A. S. Lindsey, M. E. Peover, and N. G. Savill.

The reduction of dimeric and trimeric methylene-linked benzoquinones has been found polarographically to take place in acetonitrile by one-electron additions, giving multiradical structures, and in acid buffers by separated two-electron steps. The electron spin resonance spectrum of the semiquinone of the dimer (II) indicates that configurational interaction with the methylene protons, and charge-transfer between the rings, if they occur, are small. The electrochemical behaviour of two polymeric benzoquinone systems has been interpreted in terms of near-neighbour interactions between reduced and non-reduced units of the polymer chain. Physicochemical examination shows that reversible and irreversible changes occur within the polymer structure during several quinone–quinol conversion cycles.

Recent studies of polymeric quinones by Cassidy[2] and Manecke[3] and their colleagues indicated that the polymeric environment, as well as the nature of the vicinal groups and linkages, affect appreciably the electrochemical and physicochemical behaviour of quinone groups incorporated in a polymer matrix. Our investigations have therefore been directed particularly towards studying the nature of the electrochemical and chemical changes occurring at the molecular level in the polymer chain and associated with the quinone–quinol conversion.

The chemical and physical structures of two closely similar polymeric quinones, which were used in this study, were confirmed by examination of their infrared absorption spectra and by measurement of their redox capacities and water-regain properties. These measurements also indicated the extent to which irreversible structural changes occurred during repeated treatment with inorganic oxidising and reducing agents.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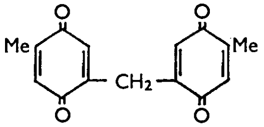
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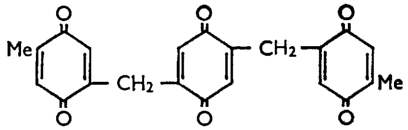
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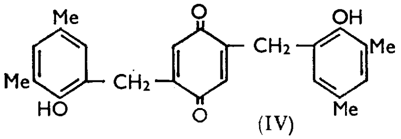
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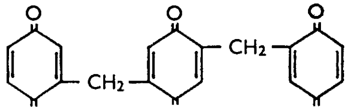
(V)

The electrochemical properties of the polyquinone segments whose synthesis was reported in the preceding paper have been determined polarographically for both buffered (aqueous ethanol) and aprotic (acetonitrile, dimethylformamide, and dimethyl sulphoxide) solutions, and electron spin resonance measurements have been attempted on the semiquinone ions derived from the quinones (II—IV). (A note describing some of these results has appeared.[4]) These results are then used to interpret the electrochemical behaviour and mid-point potentials of the polymeric quinones.

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[1] Part I, preceding paper.

[2] Robinson, Fernandez-Rofojo, and Cassidy, *J. Polymer Sci.*, 1959, **39**, 47; and earlier papers cited therein.

[3] Manecke, *Z. Elektrochem.*, 1953, **57**, 189; 1954, **58**, 363, 369; Manecke and Bahr, *ibid.*, 1958, **62**, 311.

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

EXPERIMENTAL AND RESULTS

Materials.—The di- and tri-quinones were synthesised as reported.[1] Dibenzoquinone was prepared by a known method.[5] Dimethyl sulphoxide was distilled through a short column under reduced pressure. Materials for buffers were of " AnalaR " grade. Other compounds and solvents were either prepared as previously described [6] or were of laboratory grade. The buffers consisted of 75% ethanol solutions of 0·05N-sodium acetate and acetic acid (apparent pH 6·40) and 0·05N-perchloric acid (apparent pH 1·70).

Polyquinones used in this study were: polymer (VII), the oxidised form of an acid-catalysed 1 : 1 : 3 polycondensate of quinol, phenol, and formaldehyde; polymer (VIIIP), the oxidised product of the polyquinol obtained from poly-(2,5-dimethoxy-1,4-phenylenemethylene) by demethylation with pyridinium chloride; and polymer (VIIIH), the same as (VIIIP) but prepared by using hydriodic acid for demethylation. Some data on these are in Table 1.

TABLE 1.

Polyquinones: analytical data, etc.

	(VII)			(VIIIP)			(VIIIH)		
	C (%)	H (%)	Ash (%)	C (%)	H (%)	Ash (%)	C (%)	H (%)	Ash (%)
As prepared	70·0	4·6	0·1	69·5	4·9	0	68·9	4·8	0
Calc.	74·7	5·4	nil	68·8	5·0	0	68·8	5·0	0
After cyclic treatment:									
reductant Ti^{3+}	69·7	4·9	2·8	64·6	4·6	0·6	62·5	4·7	0·6
reductant $S_2O_4^{2-}$	72·0	5·2	0·5	60·7	4·4	1·5	62·8	4·5	0·3
Change (%) in wt. after cyclic treatment:									
reductant Ti^{3+}		—			+15·7			+8·7	
reductant $S_2O_4^{2-}$		+2			—16·0			—38·4	

Infrared Absorption.—Infrared absorption spectra of the dry ground polymers dispersed in potassium chloride discs were measured on a Grubb–Parsons GS3 double-beam grating instrument. The spectral absorption bands were rather broad and the band maxima are recorded:

Polymer (VII): (i) fully oxidised, *ca.* 3370, 1653, 1609, 1510, 1473, 1427, 1317, 1210, 1108, 998, and 820 cm.$^{-1}$.

(ii) fully reduced, *ca.* 3330, 1635sh, 1604, 1595sh, 1497, 1465sh, 1422, 1316, 1184, 1095, 994, 812, and 751 cm.$^{-1}$ (sh = shoulder).

(iii) after cyclic treatment (reductant Ti^{3+}), *ca.* 3386, 1691sh, 1646, 1609, 1500, 1463sh, 1425, 1325sh, 1200, 1097, 994, 819, and 756 cm.$^{-1}$.

Polymer (VIIIP): (i) fully oxidised, *ca.* 3367, 1646, 1608, 1562sh, 1493sh, 1437, 1174, 1038, 876, and 783 cm.$^{-1}$.

(ii) fully reduced: *ca.* 3350, 1606, 1577sh, 1481, 1412, 1150, 1031, 926, 854, and 775 cm.$^{-1}$.

(iii) after cyclic treatment (reductant Ti^{3+}): *ca.* 3340, 1698sh, 1635sh, 1610, 1566sh, 1490, 1436, 1188, 1040, 876, and 783 cm.$^{-1}$.

Polymer (VIIIH): (i) as prepared, *ca.* 3352, 1638, 1610, 1426, 1175, 1030, 870, and 783 cm.$^{-1}$.

(ii) after cyclic treatment (reductant Ti^{3+}): *ca.* 3386, 1691sh, 1641, 1610, 1436, 1174, 1040, 876, and 783 cm.$^{-1}$.

The spectra of polymer samples after cyclic treatment with sodium dithionite as reductant were similar to those reported for Ti^{3+} as reductant.

Xanthone: 1646, 1599, 1472, 1338sh, 1327, 1233, 1207, 1140, 1095, 1022, 928, 876, 839, 804, and 756 cm.$^{-1}$.

Xanthen: 1597, 1572, 1483, 1452, 1297, 1262, 1213, 1198, 1147, 1112, 1088, 1031, 961, 920, 885, 863, 853, 796, 780, 746, and 694 cm.$^{-1}$.

Water-regain Properties of Polymer (VIIIP).—The water-regain properties of duplicate samples of polymer (VIIIP) in the reduced form and in the oxidised form measured by the method of Pepper, Reichenberg, and Hale [7] gave the following results (duplicate measurements in good

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[5] Borsche and Scholten, *Ber.*, 1917, **50**, 604.
[6] Peover, *J.*, 1962, 4540.
[7] Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.

agreement) expressed as g. of water per g. of dry resin, for polymer (VIIIP) in the H- and Na-form, respectively: fully reduced, 1·35, 2·60; fully oxidised, 1·33, 2·86.

It will be noted that (i) alkali treatment swells both the reduced and the oxidised forms of the polymers to the same extent (within experimental error) and by ~100% compared to the H-form (however, since quinones are sensitive to aqueous alkalis it is not possible to assess the significance of this result), and (ii) an " apparent " degree of cross-linking of 6—7% could be obtained on the assumption that the water-regain properties of the dihydroxybenzyl polymer were similar to those of sulphonated polystyrene.

Oxidation-Reduction Capacities of Polyquinones.—Duplicate samples of the moist polymers (granule size 0·5—0·25 mm.) were weighed into sintered-glass tube filters (capacity 15 ml.) so that the equivalent of 100 mg. of dried resin (based on predetermined moisture contents) was introduced into each tube. All resin-solution reactions were carried out under nitrogen with deoxygenated solutions, and the samples were subjected to either one of the following two cyclic treatment procedures:

Procedure T: The resin samples were washed with N-sulphuric acid (25 ml.) and treated with ~0·5N-titanous sulphate in N-sulphuric acid (50 ml.) for several days, and the cycle was then commenced at treatment (ii). T-Cycle: (i) 0·1N-Titanous sulphate in N-sulphuric acid (10 ml.) was added daily after draining of previously added solution which was titrated against 0·1N-ferric ammonium sulphate in N-sulphuric acid. This process was continued until daily variation in capacity fell below 0·1 mequiv. per g. of dry resin. (ii) The resin was washed with N-sulphuric acid until no titanium was detected in the eluate (hydrogen peroxide test). (iii) 0·1N-Ferric ammonium sulphate in N-sulphuric acid was added daily, after draining of previously added solution which was titrated against 0·1N-potassium dichromate until the capacity variation fell below 0·1 mequiv. per g. of dry resin. (iv) The resin was washed with N-sulphuric acid until no Fe^{3+} was detected in the eluate (ammonium thiocyanate test). (v) Operations (i)—(iv) were repeated.

Procedure D: This was similar to procedure T except that the reducing agent was ~0·25M-sodium dithionite in N-sodium hydroxide. In the D-cycle the resin samples were always thoroughly washed with distilled water before addition of acid solutions.

Very good agreement of the capacity values of duplicate samples was obtained by both procedures. Results are in Fig. 1.

Polarographic Technique.—The polarographic cell was as described elsewhere.[6] A Cambridge Instrument pen-recording polarograph was used with an A.C. " Univector " unit. The characteristics of this unit have been described.[6] The polarograms for aqueous buffer solution were run at a speed of 1·25 mv/sec. and with organic solvents at 5 mv/sec. The temperature was maintained at 25° ± 0·1°. " White-spot " oxygen-free nitrogen saturated with the solvent vapour was used to purge the test solutions of oxygen. D.C. polarograms were made against a calomel electrode whilst A.C. polarograms were made against a mercury-pool anode to reduce the cell resistance. The A.C. potentials are therefore only approximate. Measurements in organic solvents were made with a bridge of acetonitrile and so include the acetonitrile-water liquid-junction potential.[6]

For measurements on polymer suspensions, about 50 mg. of material were ground in a ball-mill in about 0·3 ml. of a 10% solution of " Petrosil " wetting agent, and an amount equivalent to 1·5 mg. of material added to 10 ml. of buffer. A 75% ethanol-acetate buffer or a borate buffer in water, each of pH 6·4, was used. Nitrogen was passed quickly through the suspension while the polarogram was taken. The suspension was then filtered and the filtrate repolarographed to establish that the polarograms were not due to material in solution. Both D.C. and A.C. polarograms were recorded, a saturated calomel electrode serving as reference electrode.

A large-scale electrolytic reduction of polymer (VII) was carried out on a suspension of 0·5 g. at a stirred-mercury cathode (area about 50 cm.^{2}) maintained at a potential of $-1·7$ v *vs* S.C.E. Nitrogen was passed continuously through the suspension. The initial current of 40 mA dropped to 15 mA after about 5 hr.

Polarography in Aqueous-ethanolic Buffer.—Polarographic measurements were made in buffered 3 : 1 v/v ethanol-water at apparent pH values (glass electrode) of 6·4 and 1·7. Complete reversibility was established for compounds (II) and (III) by starting with the quinol and the quinone severally and mixtures of the two, identical results being obtained. The absence of adsorption, kinetic, or catalytic effects was shown by the normal variation of current with mercury pressure at five points along the waves for all the compounds in Table 2. Dimer formation was ruled out for compound (II) by the invariant shape of the curves over a ten-fold change in concentration. The pH variation of potential of all the compounds was normal.

The curves obtained for the simple quinones and compound (IV) did not deviate significantly from the theoretical shape for a two-electron process. However, the curves for the polymeric quinone showed significant deviations in shape (index potentials ~35 mv; cf. 14 mv). Two separate, two-electron steps are discernible in the polarogram of compound (II) (Fig. 2). One two-electron step and a complex four-electron wave is given by compound (III) (Fig. 3), and (V) behaves similarly. The four-electron wave was analysed by a modification of Geake's procedure [8] into two two-electron components. The results are collected in Table 2.

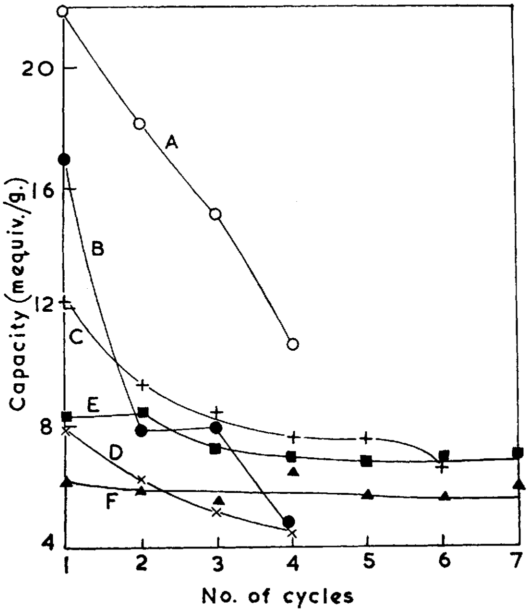

FIG. 1. Reduction capacity plotted against number of cycles for reduction by, respectively, $Na_2S_2O_4$ and $Ti_2(SO_4)_3$ of: polymer (VIIP) A, B; polymer (VIIIH), C, D; and polymer (VII), E, F.

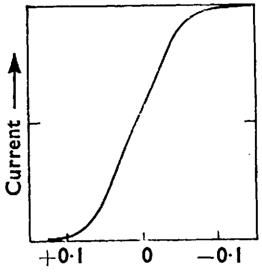

FIG. 2. Polarogram of diquinone(II) in 75% ethanol–acetate buffer of pH 6·4.

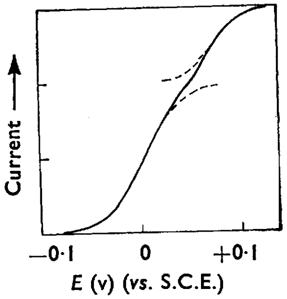

FIG. 3. Polarogram of triquinol(III) in 75% ethanol–acetate buffer of pH 6·4.

In alkaline aqueous ethanol the quinols from compounds (II) and (III) are ionised. The polarograms, which involve only electron-transfer, show a central plateau at half-reduction, as found by Appleton and Geake [9] for certain di- and tri-anthraquinones in alkaline aqueous pyridine. Because of the instability of the solutions and the need to control the species formed for electron spin resonance measurements, further investigations under these conditions were abandoned in favour of aprotic solvents.

[8] Geake, *Trans. Faraday Soc.*, 1938, **34**, 1395.

[9] Appleton and Geake, *Trans. Faraday Soc.*, 1941, **37**, 60.

TABLE 2.

Quinone	Concn. (mM)	E_0 [a] (v) *			I_d [b]
1,4-Benzoquinone	0·2—1·0	0·700			2·31
Methyl-1,4-benzoquinone	0·2—1·0	0·643			2·30
2,5-Dimethyl-1,4-benzoquinone	0·2—1·0	0·589			2·26
Diquinone (II)	0·1—1·0	0·598	0·665		3·36
Triquinone (III)	0·06—0·10	0·624 [c]	0·652 [c]	0·703	3·90
Compound (IV)	0·20	0·652			1·40
Triquinone (V)	0·19	0·635	0·690 [c]	0·728 [c]	4·11

* Against normal hydrogen electrode.

[a] Calc. to apparent pH 0. [b] Total value, $I_d = i_d/(cm^{2/3}t^{1/6})$, where i_d = diffusion current in μA, m = mass of mercury in mg. flowing per second, t = drop time in sec., c=concentration in mM. [c] Calc. from curve (see text).

Polarography in Aprotic Solvents.—The characteristics of the reduction processes of quinones in aprotic solvents [6, 10, 11] show a marked similarity to the reduction in highly alkaline media.

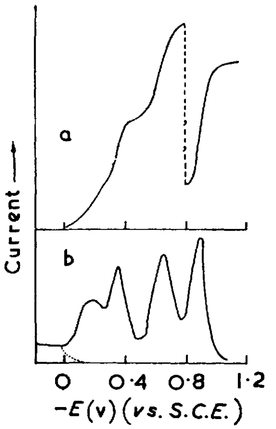

FIG. 4.

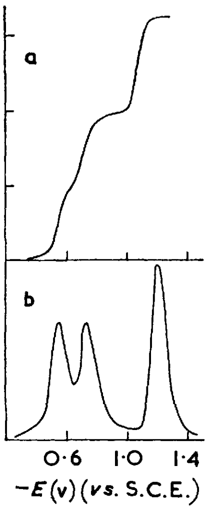

FIG. 5.

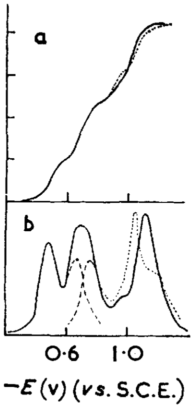

FIG. 6.

FIG. 4. (a) D.C. and (b) A.C. polarograms of diquinone (I) in acetonitrile–0·1N-NEt_4ClO_4 (A.C. potential scale approximate; sensitivity of D.C. = 7/3 × that of A.C.).

FIG. 5. (a) D.C. and (b) A.C. polarograms of diquinone (II) (conditions as for Fig. 4, but sensitivity factor = 2).

FIG. 6. (a) D.C. and (b) A.C. polarograms of triquinone (III) (conditions as for Fig. 4, but sensitivity factor = 5/3). The full lines give results in the presence of "Rhodopas."

In the present work acetonitrile was chosen as solvent for most of the polarographic work, with a few measurements in dimethylformamide and dimethyl sulphoxide to facilitate comparisons and to obtain data for electron spin resonance experiments. Figs. 4—6 show the D.C. and A.C. polarograms of the quinones (I—III) in acetonitrile. The diquinone (I) exhibits a pre-wave of less than one-electron height in both the A.C. and D.C. polarograms in both acetonitrile and dimethylformamide. From the nature of the dependence of the current of this wave on the mercury pressure it can be concluded that this is probably due to adsorption. For both the diquinones (I and II) the first two one-electron additions are clearly resolved and for the triquinone (III) the first three one-electron steps can be separated. There then follows a central plateau and the final electron additions take place at similar potentials for a given

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

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

compound. Adsorption also plays a part in the reduction of the triquinone (III), as shown in Fig. 6; here it is the final wave which is affected and normal behaviour can be induced by addition of a surface adsorbent (" Rhodopas ").

Logarithmic analysis of the first two waves of compounds (I) and (II) and the first wave of (III) in acetonitrile indicated diffusion-controlled one-electron reduction. The diffusion-current constants I_d (Table 3) are as expected for one-electron processes; *e.g.*, anthraquinone gives a value of 1·52 in acetonitrile.[6] The diffusion currents after the central plateau are less than expected for a two- or a three-electron change; this is usual for a charged organic species [6, 11] and is probably due to repulsion from the electrode surface; the low value for the composite wave of compound (III) is also probably due to this factor. The dependence of current on mercury pressure indicates diffusion control. The A.C. polarograms show (Figs. 4—6) well-developed peaks. Where single-electron steps are involved, the half-peak width is 100—110 mv; the theoretical for one-electron transfer is 90—95 mv.[12, 13] The large A.C. peaks corresponding to the addition of the final electrons are lower than expected for a reversible process and it is highly probable that proton is being added to the quinol ions; in these conditions this leads to a lowering of the A.C. admittance.[14] Similar observations with the other solvents indicate that a similar mechanism operates. The magnitude of the A.C. peak current depends on the rate constant of electron-transfer.[14, 15] The following expression can be used as an indication as to whether the rate constant is sufficiently large for diffusion control: [6] $i_f t^{-1/2}/i_d$ = Constant × $n \sin \phi$, where i_f is the peak faradaic current, i_d the D.C. limiting current, t the drop time, n the number of electrons involved, and ϕ is the phase shift which is related to the rate constant k by: [14]

TABLE 3.

Quinone	Concn. (mM) in MeCN	$-E_{\frac{1}{2}}$ (V) [a]			I_d [b]	A [c]
		MeCN	DMF [d]	Me_2SO		
(I)	0·6—0·9	0·35 [e]	0·38 [e]	—	1·50 [f]	1·70 [f]
		0·65	0·74	—	1·48	1·25
		0·88	1·29	—	1·70	1·17
(II)	0·2—1·0	0·55	0·57	0·50	1·63	1·59
		0·72	0·77	0·66	1·63	1·70
		1·08	1·48	1·23	2·16	1·60
(III)	0·1—0·25	0·49	0·51	—	1·45	1·45
		0·67	0·71	—	2·23	1·6
		0·73				1·6
		1·05	1·20	—	2·87	0·98
(IV)	0·7 [g]	—	0·32	—	1·43 [g]	1·76 [g]
		—	0·68	—	1·43 [g]	1·50 [g]

[a] Against standard calomel electrode; values include liquid-junction potential (see text). [b] In acetonitrile except (IV); $I_d = i_d/cm^{2/3}t^{1/6}$ (see footnotes to Table 2). [c] In acetonitrile; $A = (i_m/i_d t^{1/2})\, n \sin \phi \cos \phi$ for this apparatus; i_m = measured AC current in μA; i_d = D.C. current in μA; t in sec.; ψ is phase angle, n = no. of electrons added. [d] DMF = Dimethylformamide. [e] Excluding pre-wave. [f] Pre-wave included. [g] In dimethylformamide.

$$\sin \phi = 1/\{\sqrt{[1 + \sqrt{(\omega D/2)}/k]^2 + 1}\},$$

where D is the mean diffusion coefficient of the electroactive species and ω the frequency of the A.C. voltage. For the Univector unit the above equation in the range of current densities used becomes: [6] $A = i_m t^{-1/2}/i_d$ = Constant × $n \sin \phi \cos \phi$, where i_m is the measured A.C. current. For diffusion control $k > 2 \times 10^{-2}$ cm. sec.$^{-1}$, which leads to the condition $1{\cdot}70n \geqslant A > 1{\cdot}06n$ when $D = 10^{-5}$ cm.^{2} sec., for the apparatus used.[6]

From Table 3 it can be seen that this condition is fulfilled at least up to half-reduction for these quinones.

Apparent Oxidation–Reduction Potentials of Polyquinones by Potentiometric Titration.—Samples of the moist polymers (granule size 0·25—0·15 mm.) were accurately weighed into 12

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[12] Aten, Thesis, Free University, Amsterdam, 1959.

[13] Aten and Hoijtink, in " Advances in Polarography," ed. Longmuir, Pergamon Press, Oxford, 1960, p. 777; Baver, *Austral. J. Chem.*, 1962, **15**, 13.

[14] Aten, Büthker, and Hoijtink, *Trans. Faraday Soc.*, 1959, **55**, 325.

[15] Breyer and Hacobian, *Austral. J. Chem.*, 1954, **7**, 225.

glass tubes each of 20 ml. capacity and fitted with a B19 ground-glass cone and stopper at the top and a sintered disc and tap at the bottom, so that the equivalent of 100 mg. of dry resin (based on a predetermined moisture content) was introduced into each tube. The resins were then fully reduced by means of 0·25N-sodium dithionite in N-sodium hydroxide which was renewed three times; the solids were then washed with deoxygenated distilled water until neutral and finally with deoxygenated N-sulphuric acid.

No oxidant was added to the first tube, but accurately measured quantities of 0·1N-ferric ammonium sulphate in increasing amounts were added to the second and later tubes so that the eleventh and twelfth tubes contained ~10% and 20% excess over the calculated amount required to oxidise the sample completely. Each tube was then completely filled with N-sulphuric acid under oxygen-free nitrogen, stoppered, and shaken for 72 hr.

A platinum electrode and agar–potassium chloride bridge were inserted into each tube in turn, under nitrogen, and the electrode potential was measured at room temperature (23—25°) against a saturated calomel electrode by means of a Pye Universal pH meter and millivoltmeter. A steady reading was usually reached within a few minutes of insertion of the electrode. After the electrode potential of each tube had been recorded, the stoppered tubes were again shaken for 24 hr. and the electrode potentials redetermined. Absence of significant alteration of the corresponding electrode potentials was considered evidence of equilibrium. The amount of Fe^{2+} present in each tube was calculated from the measured electrode potential, by applying the Nernst equation with the assumption that the ratio of the activity coefficient of Fe^{3+}/Fe^{2+} ions was close to unity, and from the known amount of ferric ammonium sulphate added. The amount of Fe^{2+} present was taken to be equivalent to the amount of resin oxidised. From the known capacity and weight of resin the potentials were plotted against the degree of oxidation of the resin. The midpoint potential of the resin thus derived, and corrected to pH 0, gave the "apparent" oxidation–reduction potential. In this way polymer (VII) had $E_0 = 628 \pm 10$ mv, and in a similar way but with 0·1N-solution of ferric perchlorate in 0·1N-perchloric acid as oxidant a value $E_0 = 730 \pm 20$ mv was obtained for polymer (VIIIP).

Electron Spin Resonance Measurements.—These were made at room temperature with a superheterodyne spectrometer operating at 9000 Mc/sec. with phase-sensitive detection and derivative recorder presentation.

Conventional methods of preparation of the semiquinones proved to be completely unsatisfactory owing to the instability of the quinones in alkali, so aprotic conditions were tried. Excellent spectra of the semiquinones of *p*-benzoquinone and its 2,5-dimethyl derivative as their tetraethylammonium salts in dimethyl sulphoxide solution were obtained by this method.

The solutions for electron spin resonance were prepared by a modification of the procedure used by Austen *et al.*[16] and were 2—4mM in quinone in 0·1N-tetraethylammonium perchlorate in the chosen solvent; 5-ml. portions were electrolysed in a micro-cell[6] at a stirred mercury cathode (area 3·5 cm.^{2}) under nitrogen. The potential of the cathode was maintained at the potential corresponding to the top of the polarographic wave at which the desired number of electrons are added. Electrolysis was continued (3—4 min.) until the current had fallen to about 5% of its initial value (~15 mA). Samples of the solution were withdrawn by syringe, sealed *in vacuo* in tubes to fit the spectrometer cavity, and kept in liquid nitrogen until measurement.

The diquinone (II), when electrolysed in dimethyl sulphoxide at a potential such that a mononegative ion would be formed, gave a dark green solution exhibiting an electron spin resonance spectrum that changed rather rapidly with time, new lines appearing and the spectrum becoming asymmetric presumably owing to decomposition. Fig. 7 shows the derivative spectrum recorded as early as possible after preparation. Some asymmetry is already present but it appears that the spectrum consists of six main lines; the intensities in two preparations were in the ratio 0·7 : 4·1 : 10 : 10·1 : 6·3 : ~1·5; 1 : 5·8 : 10 : 11·7 : 6·3 : 2 which is fairly close to that expected for equal coupling with five protons (1 : 5 : 10 : 10 : 5 : 1); further resolution could not be obtained. The splitting was 1·4 gauss, which contrasts with the value 2·1 gauss obtained here for 2,5-dimethylbenzoquinone. Similar results were obtained in a 5 : 7 mixture of dimethylformamide and benzene although greater decomposition had occurred, but only a very poor concentration of radicals could be obtained in acetonitrile. An attempt to produce the dinegative ion from quinone (II) gave a green solution with a strong electron spin resonance

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

signal but a highly complex spectrum suggesting much decomposition. The instability of the semiquinone ion did not allow meaningful spectra of compound (II) or (IV) to be taken.

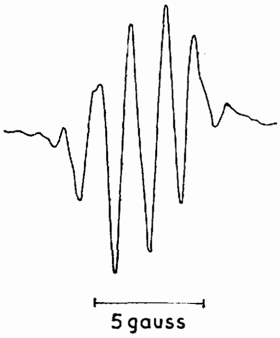
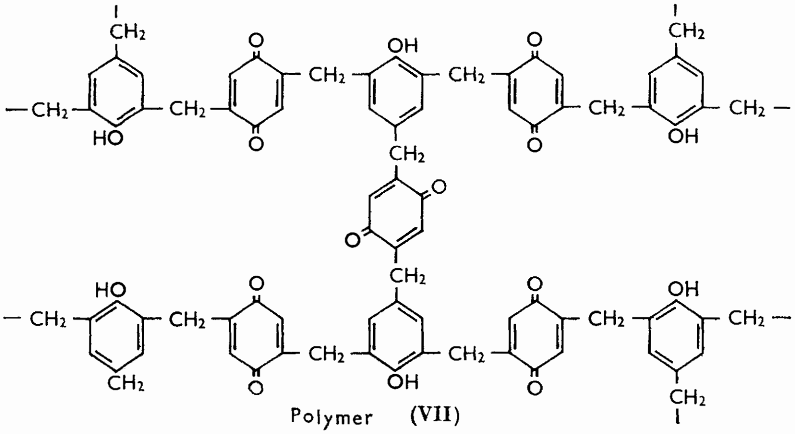
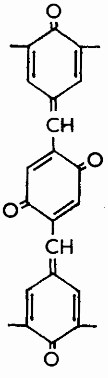


FIG. 7. Derivative electron spin resonance spectrum of the free-radical produced by electrolysis of diquinone (II) in dimethyl sulphoxide.

DISCUSSION

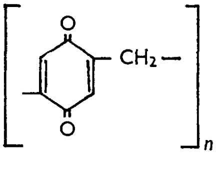
Before examining the electrochemical behaviour of the polyquinones it is first necessary to consider their chemical structures. Polymer (VII) is considered to possess structure (VII) on the basis of the analytical, infrared, and capacity data, and the known mode of formation of phenolic polymers from given precursors. However, the possibility of small regions in the matrix where mainly phenol or quinone groups are linked together cannot be excluded. Fully reduced polymer (VII) exhibited infrared absorption at ~1640, 1604, and 1595 cm.$^{-1}$, and after oxidation of the polymer at 1653 and 1609 cm.$^{-1}$ (quinonoid absorption). The presence of a 1640 cm.$^{-1}$ band in the reduced polymer suggests the presence of xanthone (1646 cm.$^{-1}$) or hydrogen-bonded carbonyl groups [*e.g.*, the quinone segment (IV) has bands at 1638 and 1597 cm.$^{-1}$).[4] The presence of groupings such as (VIIa) also cannot be discounted. Although monomeric phenol does not show an absorption band near 1640 cm.$^{-1}$, monomeric quinol (1628 cm.$^{-1}$) and 2,6-dimethylphenol (1652 cm.$^{-1}$) show weak absorption in this region.


Polymer (VII)


(VIIa)

After polymer (VII) had passed through several oxidation–reduction cycles a medium-strength absorption band appeared in the spectrum at ~1690 cm.$^{-1}$, and slight broadening of the 3 μ band (*ca.* 3370 cm.$^{-1}$) occurred. This indicates the formation of carboxyl groups. However, since initial and final carbon and hydrogen contents of the treated polymer showed little change, and since the weight variation after treatment with sodium dithionite was slight and the fall off in capacity small, it is probable that carboxyl is formed only to a small extent.

The initial structures of polymers (VIIIP) and (VIIIH) must differ from each other since the initial oxidation–reduction capacity of the latter is approximately half that of the former. Polymer (VIIIP), however, has an initial capacity close to the theoretical value. In view of this, of its mode of preparation, and of the analytical data, it must almost certainly possess the general structure shown. However, some degree of cross-linking must be present, as indicated by the solubility charactersitics of the poly-(2,5-dimethoxy-1,4-phenylenemethylene) precursor [1] and the water-regain properties of the oxidised and the reduced form of the resin. The general structure of polymer (VIIIH) is uncertain. Although demethylation of the precursor by hydriodic acid may lead to xanthone-type structures within the polymer framework, causing a reduction in the initial capacity value, the infrared absorption spectrum does not offer conclusive evidence on this point.



Polymer (VIII P)

Fully reduced polymer (VIIIP) showed no infrared carbonyl absorption and both (VIIIP) and (VIIIH) revealed strong quinonoid absorption when oxidised. When these two polymers passed through several oxidation–reduction cycles a medium-to-strong infrared band appeared at 1690—1700 cm.$^{-1}$ and the $3\ \mu$ band broadened [markedly in the case of (VIIIP), slightly in that of (VIIIH)], indicating carboxyl formation.

The results (Fig. 1) of repeated treatment of the polyquinones with inorganic oxidising and reducing agents showed that with titanous sulphate as reductant polymers (VII) and (VIIIP) possessed initial capacities near their theoretical values (8·3 and 16·5 mequiv./g., respectively), whereas that of polymer (VIIIH) was approximately half the expected value. With sodium dithionite as reductant the initial capacities were somewhat higher. The capacity values of all three polymer samples fell with cycling. The value for polymer (VII), however, became approximately constant after the third cycle. By reweighing the polymer samples after several cycles of treatment it was found that polymers (VIIIP) and (VIIIH), which had been treated with dithionite solution, had decreased in weight, whilst polymer (VIII) was almost unchanged in weight. Polymer (VIIIP) and (VIIIH) when treated with titanous sulphate, increased in weight to a small extent and contained a small amount of inorganic material, irreversibly bound within the polymer. The loss in weight in the first instance (with sodium dithionite) indicates some degradative removal of polymer. The capacity values shown in Fig. 1 have been corrected for the weight variations.

The marked stability of polymer (VII) towards the inorganic oxidising and reducing agents used and the near-constancy of its redox capacity after a few cycles is in contrast to the much lower stability of polymers (VIIIP and H) and is probably associated both with the higher degree of cross-linking present in polymer (VII) and with the greater separation of the quinone groups in the polymer matrix.

We turn now to a consideration of the polarographic measurements made on the polyquinone segments in various solvents. In a discussion of the effect of structure on the electrochemical behaviour of these polyquinones, three intramolecular effects have to be considered: inductive effects on the σ-bond and thence π-bond networks; conjugative effects on the π-system including hyperconjugation; and other effects dependent on the geometry of the molecule. Evidence has been presented elsewhere [6,17] to show that in monomeric quinones substituent effects can be represented by the potentials obtained in aprotic conditions, which, to a good approximation, are directly related to the energy of the lowest unoccupied molecular orbital of the molecule. The results obtained for acetonitrile solutions will, therefore, be considered first, and an attempt made to understand the conventional redox potentials in the light of the resulting conclusions. The effect of solvent on the free-energy change will be assumed to be the same for all the quinones compared.

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[17] Peover, *Nature*, 1962, **193**, 475; *Trans. Faraday Soc.*, 1962, **58**, 1656.

TABLE 4.

Quinone	$E_{\frac{1}{2}}$ (v) [a]			E_0 (v) [b]			Quinone	$-E_{\frac{1}{2}}$ (v) [a]	E_0 (v)
(I)	0·35	0·65		—			1,4-Benzoquinone	0·51 [d]	0·70
(II)	0·55	0·72		0·67	0·60	0·62	Methyl-1,4-benzoquinone	0·58 [d]	0·64
(III)	0·49	0·65	0·73	0·70	0·65	0·62	2,6-Dimethyl-1,4-benzoquinone	0·67 [d]	0·59
(IV)	0·32 [c]			0·65			Phenyl-1,4-benzoquinone	0·50 [d]	0·69
(V)	—			0·73	0·69	0·64			

[a] Against a standard calomel electrode; one-electron values in acetonitrile (values after half-reduction omitted). [b] Against a normal hydrogen electrode; two-electron values in 75% ethanol. [c] In dimethylformamide. [d] From ref. 6.

The results for acetonitrile show that the half-wave potentials up to half-reduction represent one-electron additions only and are indistinguishable from the equilibrium values. The polarographic results have been collected in Table 4.

In contrast to phenyl-1,4-benzoquinone, which has virtually the same $E_{\frac{1}{2}}$ as *p*-benzoquinone, the diquinone (I) exhibits a considerably enhanced potential, by 0·16 v. A strong electronegative inductive effect of the quinone " substituent " is clearly operating, and conjugation may also play some part though coplanarity of the rings is not possible. If the two quinone rings are separated by a methylene bridge, as in (II), the enhancement of potential (compared, here, with methyl-1,4-benzoquinone) is reduced to 0·03 v; the inductive effect is weakened by transmission through the standard carbon atom and the methylene grouping may itself act in opposition through its electropositive character.

Some evidence on the extent to which the odd electron is delocalised comes from measurements of electron spin resonance. The electron spin resonance spectrum of the semiquinone ion from (II) (it being assumed that no further chemical change has occurred) consists of six lines corresponding to roughly equal interaction with five protons. These lines are assigned to interaction with the 3-methyl and 2-ring protons which in general have similar coupling constants. It appears that configurational interaction produced only a low spin density at the methylene protons; this may be ascribed to steric effects which prevent sufficiently rapid rotation of the semiquinone ring. More complete resolution of the spectra was not possible, so this could not be investigated further.

If transfer of charge from one ring to the other takes place as observed with certain aromatic hydrocarbon anions [18, 19] the frequency must be small compared with the rate of interaction with the protons on one ring, and steric factors are probably involved here also. The electron spin resonance spectrum of the semiquinone ion from (I) has recently been measured [20] and no additional splitting due to charge transfer between the rings was found; also the ring protons were markedly non-equivalent in this case. The small value of the splitting constant for compound (II) compared with those for the 2,5-dimethyl-quinone implies a smaller unpaired electron density on those carbon atoms bearing the ring- and methyl-protons, and consequently a larger density on the other atoms of the conjugated system. Because of the large electronegativity of the second quinone nucleus it is probable that a particularly high electron density resides in the vicinity of the methylene bridge. This may have a bearing on the instability of the semiquinone ion. Thus it seems unlikely that charge-transfer between the rings contributes to the electrochemical behaviour, and the methylene protons may not contribute their usual hyperconjugative effect.

The enhancement of the first $E_{\frac{1}{2}}$ of the triquinone (III), representing electron addition to the central nucleus, by 0·02 v over that for *p*-benzoquinone, reflects the factors discussed in relation to the diquinone (II).

The conventional redox potentials, E_0, in acidic aqueous ethanol, can be understood in terms of the above factors, although modifications are introduced since the relation of E_0 to $E_{\frac{1}{2}}$ in acetonitrile is complex.[6]

The quinone (IV) is exceptional in that it has its first $E_{\frac{1}{2}}$ 0·20 v more positive than that

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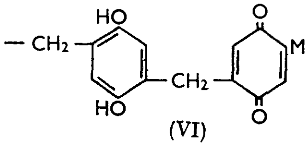
[18] Voevodskii, Solodavnikov, and Chibrikin, *Proc. Acad. Sci.* (*U.S.S.R.*), 1959, **129**, 1083.

[19] McConnell, *J. Chem. Phys.*, 1961, **35**, 508.

[20] Deitz, Hollahan, Dravnieks, and Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

of unsubstituted *p*-benzoquinone. A large inductive effect acting through the methylene bridges can be rejected (cf. the effect of phenyl directly substituted in *p*-benzoquinone), and hydrogen bonding with hydroxyl groups on the phenolic rings is probably responsible for the observations. The infrared carbonyl frequency of compound (IV) in potassium bromide is at 1638 cm.$^{-1}$, to be compared with 1650 cm.$^{-1}$ for (II), in agreement with this. However, in contrast to the very positive value of $E_{\frac{1}{2}}$ the quinone (IV) has E_0 close to that of methyl-1,4-benzoquinone. Now in a hydroxylic solvent hydrogen-bonding of the solvent would probably largely eliminate the intramolecular bonding.[21] Compound (IV) would then not differ greatly from quinones not bearing hydroxyl groups. The E_0 of this quinone will then approximately be represented by a dibenzylquinone. The observed value is in qualitative agreement with this.

The addition of the second electron in acetonitrile to the monoquinones represents complete reduction and is normal. However, with the di- and tri-quinones, the second electron is added at potentials too positive for addition to the same nucleus.[6] Diradical structures are then formed. The second $E_{\frac{1}{2}}$ of quinone (I) thus represents addition to a quinone nucleus substituted by a semiquinone radical-ion. Since this $E_{\frac{1}{2}}$ is 0·14 v more negative than that for *p*-benzoquinone, the substituent acts by induction as a strongly electropositive group. However, some extra contribution to solution changes may be included in the potential as it is an ion and not a neutral molecule that is reduced. It happens that the second $E_{\frac{1}{2}}$ of quinone (II) is 0·14 v more negative than that for methyl-1,4-benzoquinone. Since the electropositive effect of the semiquinone ion will be modified by transmission through the methylene bridge the latter must contribute to the decrease in electron affinity, certainly by induction but to an unknown extent by hyperconjugation.



(VI)

The remaining E_0 values of compounds (II), (III), and (V) show that the reduction of the quinonoid nuclei destroys their ability to act as electronegative substituents. The final nucleus of (V) is reduced at a potential some 90 mv more negative than the first. However the grouping (VI) still has an electronegative character.

The conversion of the diradical or triradical formed from quinones (I—III) in acetonitrile into the fully reduced species takes place by electron addition whose potential separations are very small, resulting in single waves in the polarogram. Since, with such highly charged species, proton addition from the solvent is taking place it cannot be said whether the electron affinity of each semiquinone nucleus in the relevant molecule is very nearly the same or whether the separations are blurred by proton addition.

For the polyquinones (VII) and (VIIIP) the oxidation–reduction potentials were measured both by potentiometry and by polarography. As it was known from earlier work [2, 22] that the normal potentiometric titration was unsatisfactory when applied to aqueous suspensions of the polymers owing to the very slow attainment of a steady electrode potential after addition of titrant, a modified procedure was adopted (see p. 4563). Preliminary experiments showed this method to give reasonably reproducible results. In this way " apparent " oxidation–reduction potentials were obtained for polymers (VII) ($E_0 = 628 \pm 10$ mv) and (VIIIP) ($E_0 = 730 \pm 20$ mv).

Some measurements were also made by D.C. and A.C. polarography on stirred fine suspensions of the polymers in an alcoholic buffer. In similar conditions 2-ethylanthraquinone and chloranil suspensions in aqueous buffer gave D.C. and A.C. waves at potentials close to the values obtained for ethanol solutions. The mechanism by which polarographic currents are produced under these conditions is not known although a number of inorganic and organic suspensions have been found to depolarise the dropping-mercury electrode.[23]

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[21] Caulfield, Rapisarda, and Bauman, *Spectrochim. Acta*, 1961, **34**, 1457.

[22] Luttinger and Cassidy, *J. Polymer Sci.*, 1956, **22**, 271.

[23] Micka, in " Advances in Polarography," ed. Longmuir, Pergamon Press, Oxford, 1960, p. 463.

Adsorption at the mercury surface has been suggested:[24] for the two quinones cited this adsorption must occur at the redox potential. The polymers gave A.C. peaks corresponding to E_m values at zero pH of 630 and 680 mv for polymers (VII) and (VIIIP), respectively. The fraction of the total material in suspension contributing to the polarographic current is small if a comparison is made with the expected current for the same quantity in solution. That actual reduction of the polymer particles occurred was confirmed by controlled-potential electrolysis of a suspension of polymer (VII), which resulted in about 15% reduction as shown by titrations with potassium dichromate. The polarographic and potentiometric titration values of E_m for polymer (VII) are in quite good agreement with the value (650 mv) previously obtained in solution for the corresponding polymer segment (IV). The potentiometric value of E_0 for polymer (VIIIP) (730 mv) is likewise in good, though possibly fortuitous, agreement with the most positive of the values (728 mv) obtained in solution, representing reduction of the central nucleus of the polymer segment (V). The midpoint potential for the titration of the entire segment is 680 mv. The polarographic E_m value for polymer (VIIIP) (680 mv), however, is more in line with the most positive of the values (703 mv) obtained in solution for the polymer segment (III). It may be noted that the free energy change in the conversion of quinone into quinol is made up, not only of factors involving the structural features of the molecule, but also of environmental factors such as solvation-energy changes: in comparing the results for the solid polymer with the results obtained in solution it may not be correct to assume that the solvation-energy changes are the same.

The significance of the midpoint potential in polymer titrations has to be considered. If the quinone groups were so isolated that no interaction occurred the titration curve would be that of the corresponding monomer. It is clear from the electrochemical behaviour of the polymer segments in solution that considerable modification of the properties of the quinone portion occurs, depending on the reduction state of its neighbouring groups. These modifications can be interpreted in terms of the strong electronegative character of the quinone nucleus acting through the methylenes bridges and increasing the electron affinity of a neighbouring quinone nucleus; the quinol nucleus, on the other hand, has had less effect on a neighbouring quinone group. The results on the polymer segments also suggest that interactions other than nearest-neighbour cannot be ignored, at least for a polymer such as (VIIIP). The redox characteristics of the groups in the polymer chain will then depend on the degree of oxidation of the polymer.

As already indicated, the extent to which the methylene-bridge protons can hyperconjugate with the quinone–quinol nuclei appears to depend on steric factors. In the solid polymers rotation of the quinone groups about the methylene bridges will be even more restricted and so a further variable will be introduced to differentiate the individual quinone groups; inhibition of hyperconjugation will make the potentials more positive. As reduction of the polyquinone proceeds, those groups having the most positive redox potential will be first reduced and the curve shows that values of 760 mv must be present; similarly for the almost fully reduced condition values of 680 mv are involved.

The form of the polymer titration curve and its midpoint potential can, therefore, have no direct meaning. The deviation in shape of the titration curve from that of the theoretical has been taken to indicate semiquinone formation;[2,3] this discussion makes it clear that such an interpretation is unnecessary, although it is possible that such intermediates deprived of their normal ability to dimerise of dismutate could be stabilised in the solid form.

The authors are indebted to Dr. A. Horsfield for the electron spin resonance spectra, and to him and Dr. D. H. Whiffen for helpful discussion of these spectra. They also thank Mr. H. M. Paisley for measurement of the infrared spectra and Mr. J. D. Davies for technical help.

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[24] Micka, *Coll. Czech. Chem. Comm.*, 1956, **21**, 647.