62. **Morizo Ishidate, Takashi Isshiki, and Keizo Tada**: Nonaqueous Polarography of Quinones. IV. Polarography of *p*-Benzoquinone and 1,4-Naphthoquinone in Glacial Acetic Acid, and Resonance Effect upon Half-wave Potentials of *p*-Quinones.

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Relative to the series of work,[1,2] these experiments were carried out on the simple quinones like benzoquinone (I) and 1,4-naphthoquinone (II) for the following reasons: Interesting behavior in nonaqueous polarography in glacial acetic acid, although their polarographic literatures were voluminous; their weak carcinogenic activities, in spite of quinoid structures, particularly (I); necessity of comparing, under identical conditions, the polarographic behavior of these quinones with more complicated ones reported previously.[1,2]

The experiments were commenced, at first, in the same way as described previously,[1] but difficulties were encountered immediately, such as an unexpected appearance of an extremely large maximum[3] in each polarogram (shown in Fig. 1) and too great a positive shift of their reduction-waves as anticipated from the works of Conant and Fieser,[4] and Adkins.[5]

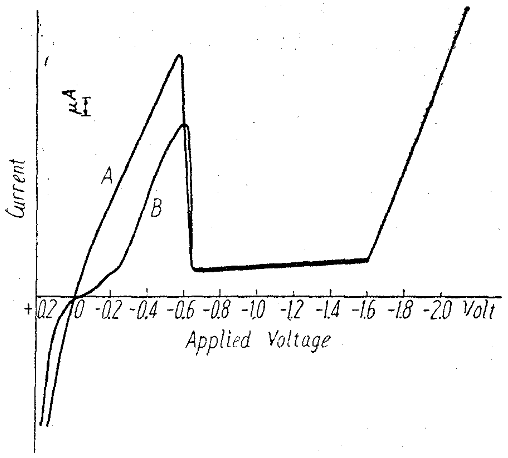

Fig. 1. Maximum Waves of (I) and (II), No addition of Maximum-Suppressor at 25±0.2°C

A : Polarogram of (I) } against Int. Anode
B : 〃 (II) }

(uncorrected for IR drop.)

Concentration : $4.60_2 \times 10^{-4}$ mol./L

Maximum Galvanometer-Sensibility : $3.64_9 \times 10^{-9}$ A/mm. m.

$m^{2/3}t^{1/6}$: 1.1_{76}

The first obstacle was rather easily solved by the addition of such maximum-suppressor as gelatine or methylcellulose into each cell solution at the final concentration of more than 0.02%, without any practical influence[6] upon their diffusion currents. With (II), the half-wave potential was satisfcatorily measured by using saturated mercurous sulfate electrode (S. M. E.) as reference electrode instead of S. C. E. and the diffusion current was also obtained from the polarograms even from the applied-voltage of +0.2 volt against the internal anode.[7] With (I), no precise results, not only for half-wave potential but also for the diffusion currents, were obtained by the usual drawing

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[1] Takashi Isshiki, Keizo Tada: This Bulletin, **2**, 266 (1954).

[2] K. Tada: *Ibid.*, **2**, 270; **2**, 272.

[3] M. Maruyama reported (II) produced a slight "maximum" in ethanol-benzene: Japan Analyst, **1**, 85 (1952).

[4] J. B. Conant, L. F. Fieser: J. Am. Chem. Soc., **44**, 2480 (1922).; **46**, 1859 (1924).

[5] R. H. Baker, H. Adkins: *Ibid.*, **62**, 3305 (1940).

[6] Y. Shimada, *et al.*, reported influences of gelatine-addition upon wave-heights and wave-form of (II) in aqueous buffered solution. cf. Japan Analyst, **1**, 17 (1952).

[7] Ordinary cell having an internal mercury pool was used.

methods[8] although these were useful in the case of (II), from both polarograms taken against S. M. E. and internal anode. A novel method was therefore employed which is described in detail later.

In relation to the above, the following should be added. IR drop caused by the inner resistance (i.e., 20,000～50,000 Ω) through the circuit was so large that a correction for it was necessary at each run. The inner resistance was measured by the method reported previously[1] immediately after each experiment. The potential of S. M. E. vs. S. C. E. was reported to be 0.41 volt, but it was found that this value deviated in the range of more than ±10 mV. This was accurately measured against S. C. E. immediately before each run by the method which is described later (in Experimental Section).

When the value thus obtained is represented by E_M, half-wave potentials vs. S. M. E. corrected for IR drop by $E^M_{1/2}$, and the real value vs. S. C. E. by $E_{1/2}$, the following equation is introduced.

$$E_{1/2} = E^M_{1/2} + E_M$$

All conversions from $E^M_{1/2}$ into $E_{1/2}$ were done according to the above equation.

Results

p-Benzoquinone (I)

Fig. 2 shows a special drawing method for the determination of its half-wave potential applied at first on the recorded polarogram taken against S. M. E., where each polarogram obtained from both empty solution (leere Lösung) and test-solution was placed in such a way that the prolonged parts of each anodic wave of mercury overlapped, and a tangent drawn in parallel with the diffusion current plateau of test solution along the residual curve of empty solution. The value of 0.33_0 volt vs. S. C. E. thus obtained was, however, not expected to be quite correct because of the probability of partial overlapping of the reduction-wave with the anodic wave of mercury.

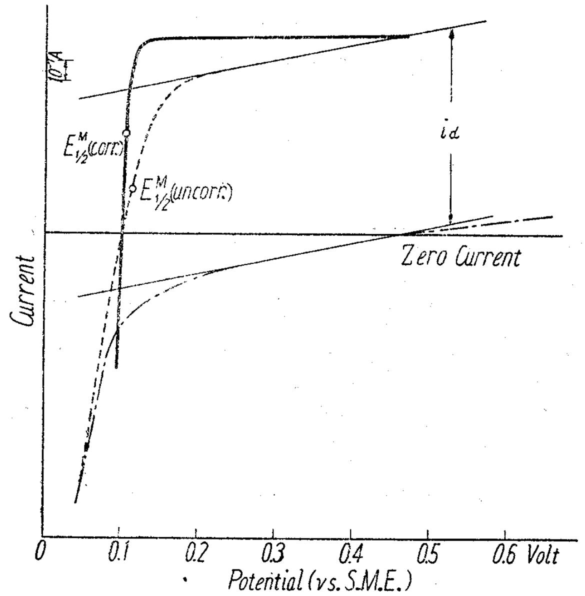

Fig. 2. Current-Potential Curves of (I) at 25±0.2°C

Broken line : Recorded wave taken against S.M.E (+0.431_1 volt. vs. S. C. E.) (Cell resistance $4.5 \times 10^4 \Omega$)

Solid line : Corrected wave for both IR drop and residual current

Chain line : Residual current of empty solution taken against S. M. E.

Concentration : $1.78_2 \times 10^{-4}$ mol/L

Gelatine : 0.03%

Maximum Galvanometer-Sensibility : $5.9_3 \times 10^{-10}$ A/mm. m.

$m^{2/3}t^{1/6}$: 1.8_{76}

The $\log i/i_d - i$ was then plotted against various potentials (vs. S. C. E.) over the corrected wave, giving the diagram shown in Fig. 3. This indicated the distinct existence of two extremely different types of slopes, in which one gave the value of 2.2_2 for the number of electrons participating in the reduction of (I), while the other was entirely

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8) cf. Takashi Isshiki, *et al.* : This Bulletin, **2**, 257 (1954).

different. This fact provides us with evidence that the reduction wave in Fig. 2. was composed of two elements, a typical reversible reduction wave involving two electron-exchange per molecule (line A) and an anodic wave of mercury (line B).

The value of -0.33_8 volt vs. S. C. E. obtained by the intersection of line A and potential-axis is somewhat more positive (i.e., 8 mV.) than the above value (0.33_0 volt). It is, however, considered to be more accurate because line A is not contaminated with any other.

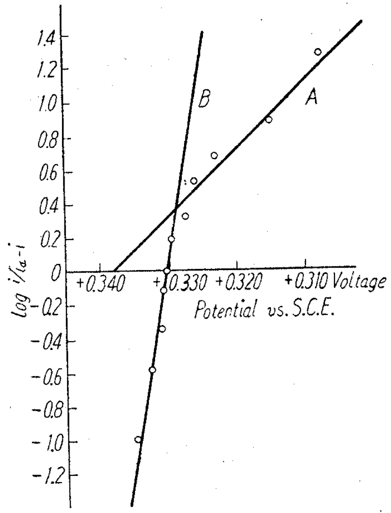

Fig. 3. $\log i/i_a-i$-Potential Diagram for (I) (calculated from solid curve in Fig. 2)

Under various concentrations, the diffusion currents were measured both against the internal anode and S. M. E., and determined actually by the first drawing method. These values are given in Table I.

Fig. 4 shows a linear relationship between C and $i_a/m^{2/3}t^{1/6}$. I_D of 3.1_{86} was also obtained as the mean value of those given in Table I, which indicates that the experimental error was within ±1.5%.

TABLE I.

C $10^{-4}M$	$i_a/m^{2/3}t^{1/6}$ 10^{-7}A	I_D $i_a/c\cdot m^{2/3}t^{1/9}$	Electrode Used
1.0_{71}	3.5_{00}	3.1_{41}	Int. Anode
1.5_{50}	4.9_{99}	3.2_{26}	Int. Anode
1.5_{50}	4.8_{70}	3.1_{42}	S. M. E.
1.7_{82}	5.6_{56}	3.2_{40}	Int. Anode
1.8_{82}	5.5_{59}	3.1_{91}	S. M. E.
2.4_{42}	7.7_{63}	3.1_{64}	S. M. E.
2.6_{94}	8.6_{20}	3.1_{98}	Int. Anode

mean value 3.1_{86}

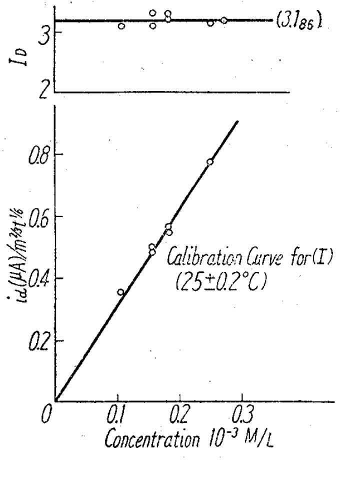

Fig. 4. Calibration Curve for (I) (25±0.2°C)

1,4-Naphthoquinone (II)

The corrected polarogram taken against S. M. E. is shown in Fig. 5, where a one-step, well-defined reduction wave appeared with its half-wave potential at $+0.10_5$ volt vs. S. C. E.

The diffusion currents were measured under various concentrations against both the internal anode and S. M. E. These are given in Table II (half-wave potential and diffusion currents were drawn by the usual method[8]).

A linear relationship between C and $i_a/m^{2/3}t^{1/6}$ is shown in Fig. 6, and I_D of 3.1_{46}

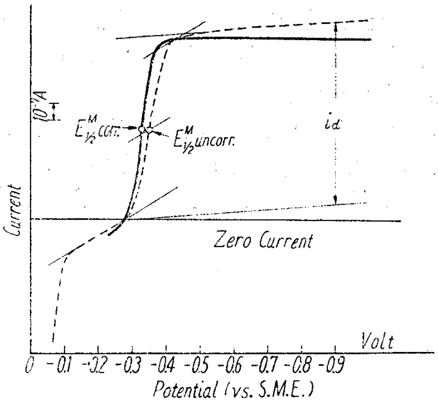

Fig. 5. Current-Potential Curves of (II) at 25±0.2°C

Broken line : Recorded wave taken agsinst S.M.E. (+0.431$_8$ volt vs. S. C. E.)
Solid line : Corrected wave for both IR drop and residual current (Inner resistance $3.5\times10^4\Omega$)
Concentration : $2.87_4\times10^{-4}$ mole/L
Methylcellulose : 0.02$_7$%
Maximum Galvanometer-Sensibility : $1.16_0\times10^{-9}$A/mm. m.
$m^{2/3}t^{1/6}$: 1.1$_{85}$

TABLE II.

C $10^{-4}M$	$i_d/m^{2/3}t^{1/6}$ 10^{-7}A	I_D $i_d/c\cdot m^{2/3}t^{1/6}$	Electrode Used
0.9_{58}	3.1_{13}	3.2_{50}	Int. Anode
1.5_{92}	4.8_{10}	3.0_{80}	Int. Anode
2.4_{19}	7.5_{79}	3.1_{34}	Int. Anode
2.8_{74}	9.0_{32}	3.1_{57}	S. M. E.
3.1_{96}	9.9_{39}	3.1_{10}	Int. Anode

mean value 3.1_{46}

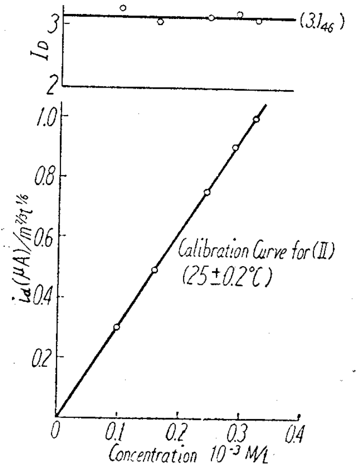

Fig. 6. Calibration Curve for (II) (25±0.2°C)

was obtained as the mean value of those given in Table II.

The log i/i_d-i was plotted as in the case of (I) giving a linear relationship as shown in Fig. 7, whose slope, 1.8$_0$, indicates that the reduction was reversible involving two electron-exchange per molecule.

Half-wave potentials ($E_{1/2}$) and diffusion current constants (I_D) of (I) and (II), and those of *p*-quinones reported previously$^{1,2)}$ are summarized in Table III with their normal redox potentials measured by Conant and Fieser.$^{4,9)}$

TABLE III.

	$E_{1/2}$(V)*	ε(V)**	$\varepsilon-E_{1/2}$(V)	I_D
p-Benzoquinone (B. Q.)	$+0.33_8$	0.71_1	0.37_3	3.1_{86}
1,4-Naphthoquinone (N. Q.)	$+0.10_5$	0.49_2	0.38_7	3.1_{46}
Anthraquinone (A. Q.)	-0.24_0	0.15_5	0.39_5	3.1_{86}
1,2-Benzanthraquinone (B. A. Q.)	-0.16_8	0.22_8	0.39_6	2.5_{07}
1,2,5,6-Dibenzanthraquinone (D. B. A. Q.)	-0.13_7	0.26_7	0.40_4	2.4_{26}

* vs. S. C. E. corrected for IR drop.
** vs. Hydrogen electrode measured potentiometrically by Conant and Fieser in 95% EtOH.

The relationship between their structures and $E_{1/2}$ (or ε) will be discussed in the next section according to the resonance theory, although some theoretical interpretations have been made in this regard by Fieser,$^{9)}$ Badger,$^{10)}$ Calvin and Branch,$^{11)}$ and Carter.$^{12)}$

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9) L. F. Fieser, E. M. Dietz : J. Am. Chem. Soc., **53**, 1128 (1931).
10) G. M. Badger : "The Structures & Reactions of the Aromatic Compounds," 87 (1954).
11) Calvin, Branch : "The Theory of Organic Chemistry," 303.
12) Carter : Trans. Faraday Soc., **45**, 597 (1947).

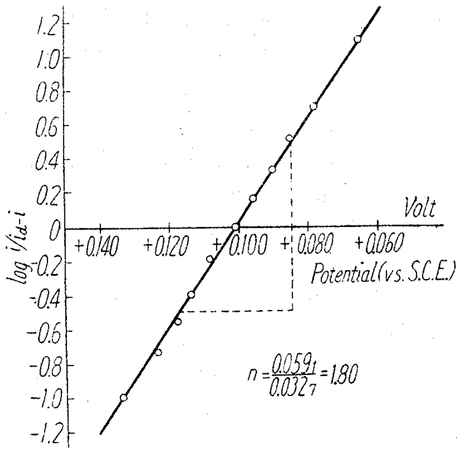


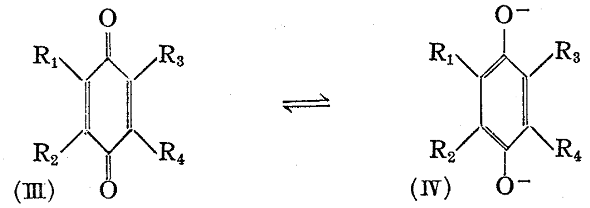
Fig. 7. log i/i_d-i-Potential Diagram for (Ⅱ) (calculated from solid curve in Fig. 5)

Discussion

From Table Ⅲ, the ease with which *p*-quinones are reduced at the dropping mercury electrode is shown by the sequence :

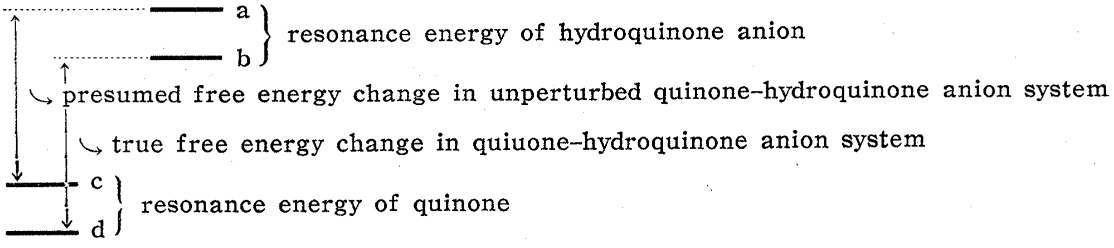
$$\text{B. Q.} > \text{N. Q.} > \text{D. B. A. Q.} > \text{B. A. Q.} > \text{A. Q.} \qquad (1)$$

In discussing these results, it is necessary to presume that the reduction is one simple mechanism, although, in reality, it is very complicated. If it is assumed to be reversible and further, if quinones and hydroquinone-anions are represented by only one structure such as (Ⅲ) and (Ⅳ), respectively, the free energy change from quinone to hydroquinone-anion, consequently half-wave potential which is closely related to the free energy change, should be identical in all five quinones in question, because the same numbers of bonds are formed or destroyed during reduction without regard to the nature of R_1, R_2, R_3, and R_4 groups (i.e., two C=O bonds and one C—C bond are destroyed and two C—O$^{(-)}$ bonds and one C=C bond are formed). But this is not actually the case.


(Ⅲ) (Ⅳ)

This discrepancy may be ascribed to the assumption that quinone and hydroquinone be represented by only one structure such as (Ⅲ) and (Ⅳ), respectively. According to the resonance theory, any compound composed of conjugated systems can never be expressed perfectly by a single unperturbed structure. It is well known that, if for any given compound more than one structure can be written differing only in the distribution of

Fig. 8. Schematic Representation of Energy Level and Free Energy Change



line a : Presumed energy level of unperturbed structure of hydroquinone anion
line b : True energy level of hydroquinone anion
line c : Presumed energy level of unperturbed structure of quinone
line d : True energy level of quinone

bonds, such compound is better expressed as a hybrid of those structures. Thus it seems that the reduction of quinones becomes easier as the hydroquinone anions acquire a larger contribution of many principal limiting structures,[*] as there is an attendant continuous fall in the energy level of hydroquinone anion. On the other hand, the reduction of quinone becomes more difficult as the number of structures contributing to the resonance of quinone increases, because the resonance energy of quinone cancels the lowering in the energy level of hydroquinone anion which is caused by resonance. These relationships are illustrated in Fig. 8.

Thus, it is to be expected that the reduction of quinone at the dropping mercury electrode will be easier as the ratio of number of resonance structures for hydroquinone anion to those for quinone increases. The values which may be reached concerning the number of principal limiting structures discussed, are illustrated in Table IV.

TABLE IV.

Number of Principal Limiting Structures Contributing to the Resonance and Ratios of Hydroquinone Anion to Quinone in the Number of Limiting Structures

	Benzo-	Naphtho-	Anthra-	Benzanthra-	Dibenzanthra-
hydroquinone	2	3	4	7	12
quinone	1	2	4	6	9
ratio $\left(\frac{\text{hydroquinone}}{\text{quinone}}\right)$	2	1.5	1	1.17	1.33

It is obvious from Table IV that, for the five quinones in question, the ratios decrease in the following order :

$$\text{B. Q.} > \text{N. Q.} > \text{D. B. A. Q.} > \text{B. A. Q.} > \text{A. Q.} \qquad (2)$$

This is in accordance with sequence (1), and indicates that the resonance structures contributing to both quinone and hydroquinone anion have an unquestionable relationship to the oxidation-reduction equilibrium between them. Consequently, it is understandable that half-wave potentials of quinones do not shift uniformly with the number of condensed angular benzene rings.

The authors wish to thank Mr. Horioka, Mr. Tsukagoshi and Mr. Kimura for their kind assistance.

Experimental

The experiments were carried out at 25°±0.2°, and glacial AcOH containing 0.25 N $AcONH_4$ was used as a solvent. Except for the following, the apparatus and procedures were all the same

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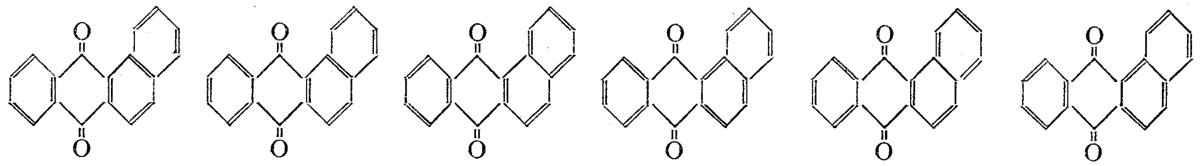
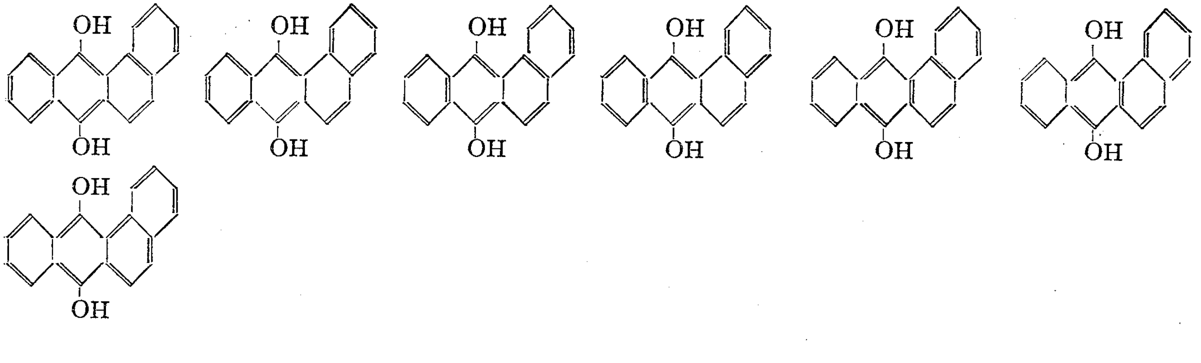
[*] For example, the principal limiting structures contributing to the resonance of 1,2-benzanthraquinone or 1,2-benzanthrahydroquinone are as follows.

1,2-Benzanthraquinone :



1,2-Benzanthrahydroquinone :



as those described previously.[1)]

Reagents—*p*-Benzoquinone and 1,4-naphthoquinone were recrystallized three times from benzene-petr. ether (1 : 3) and again from abs. EtOH, and showed m.p. 116° and 124~125°, respectively.

Apparatus—Instruments : Polarograph improved in our Laboratory and the polarograph P-E-I type (1953) of Yanagimoto Co. were used.

Capillary : A capillary having the constant of either (m 1.92_9 mg./sec. at mercury pressure of 424 mm.) or (m 0.922_7 mg./sec. at mercury pressure of 469 mm.) was used.

Cell Solution—2% Aqueous solution of gelatine, in case of (I), or of methylcellulose, in case of (II), was added into each freshly prepared cell solution at the final concentration of 0.020~0.025%.

Removal of Oxygen—In most cases, hydrogen and in a few cases, nitrogen was used, showing no practical difference.

Measurement of S. M. E. Potential—A standard calomel electrode was at first inserted into the cell-solution filled in the improved H-type of cell,[1)] and the potential of S. M. E. was potentiometrically measured against this S. C. E. as quickly as possible through the X-circuit.

Summary

Relative to complex *p*-quinones, half-wave potentials of both *p*-benzoquinone and *p*-naphthoquinone were measured under the same conditions as described before. From the results of experiments, sequence (1) was obtained in respect to half-waves potentials of five homologous *p*-quinones. The reasons for the irregular shift of these values with increase of condensed benzene rings, is discussed from the standpoint of the resonance theory.

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