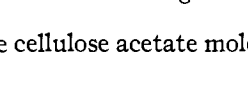
after the cellulose acetate had been in contact with the solvent for three days and, therefore, indicate an equilibrium state of affairs with no description of the rate at which this equilibrium was reached. In every case where all the fractions ultimately dissolved, the rate of solution was invariably in the order D:C:B:A. Thus, with methyl acetate, the D fraction dissolved in eight minutes, C in twenty minutes, B in one hour and A in three hours.

All the fractions show a greater tendency to swell and dissolve in the lower member of an homologous series. If the most prominent atomic grouping in the cellulose acetate molecule is taken, as  , it may be said in a broad sense that cellulose acetate tends to swell and dissolve in those liquids that resemble it most closely in chemical structure. This is in general agreement with the views of Sheppard[8] and Whitby.[9]

Summary

1. A sample of a commercial acetone-soluble cellulose acetate has been fractionally precipitated. The fractions have the same chemical composition but different physical properties; this has been attributed to a difference in the state of aggregation of the glucose anhydride units in the micelles.

2. The solubility of cellulose acetate in organic liquids has been shown to be a function of its state of aggregation as well as its acetyl content.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE REDUCTION POTENTIALS OF VARIOUS PHENANTHRENEQUINONES

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RECEIVED MAY 31, 1929 PUBLISHED OCTOBER 5, 1929

The problem of correlating the structures of the quinones with their reduction potentials divides itself naturally into two distinct parts: a comparison of the potentials of the parent quinones which are derived from the various aromatic hydrocarbons and heterocycles, and a study of the manner in which substituent groups influence the oxidizing power of a given substance. The results of the present electrochemical study of a number of quinones of the phenanthrene series thus fall into two groups and each of these may be considered in the light of one or the other of the two aspects of the general problem.

[8] S. E. Sheppard, *Nature*, **73**, March 17 (1921).

[9] G. S. Whitby, "Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York City, Vol. IV, **1926**, p. 203.

1. Isophenanthrenequinones.—While all of the homonuclear quinones of benzene, naphthalene and anthracene have been investigated by the electrochemical method, and while rational interpretations have been found for the values of the reduction potentials of these substances, only one of the four possible homonuclear phenanthrenequinones, the 9,10-derivative, has been studied and no adequate account of the potential of this compound has been given. With the object of completing the data for this series, and with the hope that an explanation of the potential of 9,10-phenanthrenequinone might be suggested by a knowledge of the values for the isomeric quinones, 1,2-, 1,4- and 3,4-phenanthrenequinone and a few of their substitution products have been prepared[1] and the normal reduction potentials have been determined by standard methods.

The results are summarized in Table I. The normal potential, E_0, was determined by the electrometric titration of a solution of either the oxidant or the reductant, as indicated by the nature of the titrating reagent. This potential is equal to the e.m.f. of the cell Pt | Solvent, Oxidant, Reductant || Solvent, H_2 | Pt, at the point of half-reduction or half-oxidation. Under ΔE_1 and ΔE_2 are given the average differences between E_0 and the potential at 20% and at 80% reduction or oxidation. The theoretical value is 17.8 mv. The two unsubstituted ortho-quinones, Nos. 1 and 3, are destroyed by an acidic solution too rapidly to permit the preparation and titration of a solution of the oxidant, but the reductant could be titrated so rapidly that the decomposition of the quinone involved an error which was estimated to be less than 3 mv.

TABLE I

REDUCTION POTENTIALS AT 25°

Solvents: A, 0.1 *N* HCl; B, 50% Alcohol, 0.1 *N* in HCl and 0.2 *N* in LiCl

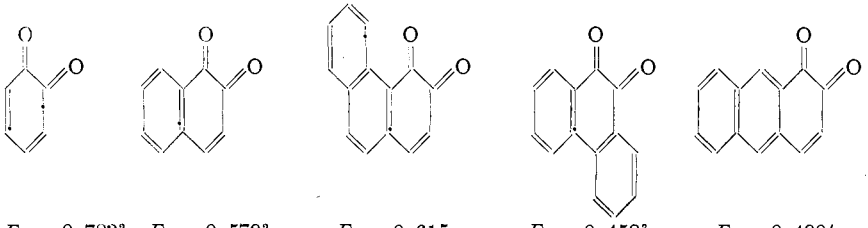
No.	Compound	Solvent	Titrated with	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0(av.), v.
1	1,2-Phenanthrenequinone[1b]	B	$C_6Br_4O_2$[a]	0.650	0.652	0.651	18.5	18.5	0.651
2	1,2-Phenanthrenequinone-4-sulfonic acid[1b]	A	$TiCl_3$	.651	.651	.651	18.9	19.0	.651
		B	$TiCl_3$	.685	.685		17.1	17.4	.685
3	3,4-Phenanthrenequinone[1a]	B	$C_6Br_4O_2$	.615	.614		19.7	21.2	.615
4	3,4-Phenanthrenequinone-1-sulfonic acid[1a]	A	$TiCl_3$	.664	.664	.663	16.9	18.6	.664
		B	$TiCl_3$	.677	.677		17.2	17.8	.677
5	1-Methyl-5,6-(1,2-naphtho)-3,4-coumaranquinone[1a]	B	$TiCl_3$	.461	.460		18.3	17.9	.461
6	1,4-Phenanthrenequinone[1d]	B	$C_6Br_4O_2$	.522	.524	.524	20.0	19.3	.523
7	2 - Hydroxy - 1,4 - phenanthrenequinone[1b]	B	$TiCl_3$	.410	.411	.409	17.9	17.9	.410
8	2 - Methoxy - 1,4 - phenanthrenequinone[1b]	B	$TiCl_3$	.418	.418	.418	18.0	18.3	.418
9	3 - Hydroxy - 1,4 - phenanthrenequinone[1a]	B	$TiCl_3$	.395	.396	.396	17.7	17.4	.396
10	3 - Methoxy - 1,4 - phenanthrenequinone[1a]	B	$TiCl_3$	.408	.409	.410	18.4	18.1	.409

[a] Tetrabromo-*o*-benzoquinone.

[1] (a) Fieser, THIS JOURNAL, **51**, 940 (1929); (b) **51**, 1896 (1929); (c) **51**, 1935 (1929); (d) **51**, 2460 (1929); (e) **51**, 2471 (1929).

Examination of the table will show that the relationships between the ortho- and para-isophenanthrenequinones and between the substituted and unsubstituted members of the series are much the same as those found with the corresponding naphtho- and anthraquinones, though there are some deviations for which it is not easy to account. Thus the two ortho quinones, Nos. 1 and 3, differ considerably in potential, though their sulfonated derivatives, Nos. 2 and 4, are quite similar. From the fact that 3,4-phenanthrenequinone differs in potential from its sulfonate and from 1,4-phenanthrenequinone by normal increments, while the corresponding differences for 1,2-phenanthrenequinone are smaller than would be anticipated, it may be argued that it is 1,2-phenanthrenequinone which exhibits a somewhat abnormal character.

With this minor irregularity, the isophenanthrenequinones form a distinct group, and it is important to establish the exact relationship between this and other series of quinones. A comparison of the normal reduction potentials of the ortho quinones I-V will show that there is little similarity



$E_0 = 0.783$[2] $E_0 = 0.579$[2] $E_0 = 0.615$ $E_0 = 0.458$[3] $E_0 = 0.490$[4]

I II III IV V

between the two phenanthrene derivatives III and IV or between the isophenanthrenequinone, III, and the isoanthraquinone, V. The difference between 3,4- and 9,10-phenanthrenequinone is not surprising in view of the fact that the former has a terminal quinonoid nucleus while in the latter the quinone grouping is flanked by benzene rings. That 1,2-anthraquinone has a peculiarly low potential has been attributed[4] to a unique structure of anthracene, and the present results furnish no indication that this interpretation should be altered.

It will be observed that the potential of 3,4-phenanthrenequinone is of the same order of magnitude as that of β-naphthoquinone, and this suggests that the isophenanthrenequinones should be considered in comparison with the corresponding naphthoquinones. Such a comparison, given in Table II, indicates that the isophenanthrenequinones are higher in potential than the naphthoquinones by a fairly regular increment. The chief structural difference between the two series, or between the quinones II

[2] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

[3] Fieser and Ames, *ibid.*, **49**, 2604 (1927).

[4] Fieser, *ibid.*, **50**, 465 (1928).

TABLE II

DIFFERENCE IN POTENTIAL BETWEEN ISOPHENANTHRENEQUINONES (X) AND NAPHTHOQUINONES (−Y) IN MILLIVOLTS

Substituent.....	None	$-SO_3H$	$-OH$	$-OCH_3$	$-CH_2CH(CH_3)O-$
1,2-Phenanthrenequinones	+72	+21, 49[a]	.....	.....	..
3,4-Phenanthrenequinones	+36	+34, 41[a]	.....	.....	+55
1,4-Phenanthrenequinones	+30	.....	+40, 54[b]	+56, 65[b]	..

Average difference, 48 mv.

[a] The two figures give the differences observed in solvents A and B, respectively.

[b] The first figure refers to the 2-derivative, the second to the 3-substituted isomer.

and III, is that in the tricyclic compounds a naphthylene, rather than a phenylene, group is attached to the quinonoid nucleus. The presence of the phenylene group is responsible for a decrease in the reduction potential of *o*-benzoquinone amounting to 204 mv. (compare I and II), an effect which has been attributed to the stabilization of the benzoquinone by the incorporation of one of the otherwise reactive quinonoid ethylene linkages in an aromatic ring.[2] In the same way 3,4-phenanthrenequinone may be regarded as *o*-benzoquinone with a fused-on naphthylene group, and this group may be said to produce a decrease in the potential of 168 mv. (compare I and III). That the effect is less than for the phenylene group is entirely consistent with the fact that naphthalene is a more reactive hydrocarbon, that it is less "aromatic," than benzene.

That a reasonable interpretation of the potentials of the isophenanthrenequinones is thus found in comparing these compounds with the naphtho- and benzoquinones, is of assistance in seeking an explanation of the potential of 9,10-phenanthrenequinone. The value is abnormally high, that is, it is 83 mv. higher than one would be led to expect from the relationship between quinones I and II. This means either that 9,10-phenanthrenequinone possesses an added reactivity or that its hydroquinone is abnormally inert. Since 1,2-, 1,4- and 3,4-dihydroxyphenanthrene appear to be quite normal, it is highly probable that this is also true of the 9,10-derivative and hence that an account of the observed deviation is to be sought in the structure of 9,10-phenanthrenequinone.

Two explanations of the peculiarly great oxidizing power of 9,10-phenanthrenequinone suggest themselves. The molecule appears to be in a condition of some strain and it is possible that this strain is the result of a configuration in which the two benzene rings are coplanar but not co-axial, the nuclei being spread apart by the carbonyl groups on one side of the diphenyl linkage. It is also possible, and perhaps somewhat more probable, that the two benzene rings are co-axial but not coplanar, that is, that, owing to the normal spatial requirements of the carbonyl groups, the diphenyl skeleton suffers a distortion or twisting which produces a strain within the molecule. It may be possible to distinguish between these two

hypotheses, for according to the latter suggestion a monosubstituted phenanthrenequinone should have an asymmetrical configuration.

2. Substituted 9,10-Phenanthrenequinones.—Table III summarizes the results of a study of a number of compounds of the type indicated.

TABLE III

REDUCTION POTENTIALS AT 25°

Solvents: A, 0.1 *N* HCl; B, 50% Alcohol, 0.1 *N* in HCl and 0.2 *N* in LiCl; C, 37% Alcohol, 0.047 *M* in KH_2PO_4 and 0.047 *M* in Na_2HPO_4; D, 95% Alcohol, 0.2 *N* in HCl and 0.2 *N* in LiCl.

No.	-Phenanthrenequinone	Solvent	Titrated with	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0 (av.), v.
11	Phenanthrenequinone	A	.....	...	...	...	..	..	0.442[3]
		B	.....	...	...	...	..	..	.458[3]
		C	$K_3Fe(CN)_6$	0.460	0.459	0.461	19.3	18.9	.460
		D	.....	...	...	...	..	..	.471[2]
12	1-Hydroxy-[1d]	B	Quinone	.408	.408		21.2	25.7	.408
13	2-Hydroxy-[5]	B	$TiCl_3$	.457	.457		18.3	18.3	.457
		D	$TiCl_3$	.459	.459		18.5	18.6	.459
14	3-Hydroxy-[6]	B	Quinone	.405	.405	.404	18.3	19.3	.405
15	4-Hydroxy-[7]	B	$TiCl_3$	.459	.458	.458	51	35	.458
16	1,2-Dihydroxy-[1c]	B	Quinone	.379	.381	.379	18.9	19.5	.380
17	1,4-Dihydroxy-[8]	B	Quinone	.379	.380	.379	20.3	22.5	.379
18	3,4-Dihydroxy-[1a]	B	Quinone	.385	.386	.384	18.3	18.6	.385
19	2,6-Dihydroxy-[1e]	B	Quinone	.401	.401	.402	20.2	20.4	.401
20	2,7-Dihydroxy-[1e]	D	$TiCl_3$	.448			18.2	17.8	.448
21	3,6-Dihydroxy-[1e]	D	$TiCl_3$	.344	.345	.344	19.6	18.9	.344
22	1,2,4-Trihydroxy-[1c]	B	Quinone	.340	.340	.340	18.8	20.4	.340
23	1,3,4-Trihydroxy-[1c]	B	Quinone	.281	.281	.281	19.7	22.1	.281
24	3-Acetoxy-[6]	B	Quinone	.467	.467	.467	21.9	19.7	.467
25	3,4-Diacetoxy-[1a]	B	Quinone	.488	.489	.488	20.8	19.2	.488
26	3-Methoxy-[6]	B	$TiCl_3$	.421	.419	.418	18.9	18.8	.419
27	3,6-Dimethoxy-[1e]	D	$TiCl_3$	.387	.387	.388	17.7	18.5	.387
28	2-Amino-[5,9]	C	$K_3Fe(CN)_6$	.444	.443	.443	18.7	18.7	.443
		B	$TiCl_3$	.493	.490	.490	19.9	20.1	.491
29	3-Amino-[10]	C	$K_3Fe(CN)_6$	.362	.361	.362	18.5	18.8	.362
30	4-Amino-[9]	C	$K_3Fe(CN)_6$	.432	.432		18.3	18.1	.432
31	1-Methyl-[11]	B	$TiCl_3$	.394	.394		20.5	25.5	.394
32	1-Methyl-7-*iso*propyl-	D	.....	...	...	...	..	..	.408[2]
33	3-Bromo-[12]	D	$TiCl_3$	.500	.499	.499	18.0	18.5	.499
34	2-Nitro-[7,13]	D	$TiCl_3$	.540	.540	.540	18.7	18.7	.540
35	3-Nitro-[10,14]	D	$TiCl_3$	.562	.562	.562	18.2	18.3	.562
36	4-Nitro-[7,13]	D	$TiCl_3$	.528	.528		17.2	18.0	.528
		B	$TiCl_3$	.513	.513		18.4	21.1	.513
37	2,5-Dinitro-[15,16]	D	$TiCl_3$	.569	.570		18.2	18.1	.569
38	2,7-Dinitro-[15]	D	$TiCl_3$	.590	.590		16.6	17.9	.590
39	( )-1-Sulfonic acid[1a]	A	$TiCl_3$	.464	.465	.465	19.8	20.9	.465
40	( )-2-Sulfonic acid[17]	A	$TiCl_3$	.466	.466	.466	20.3	20.1	.466
		B	$TiCl_3$	.490	.490		18.4	17.9	.490
41	( )-3-Sulfonic acid[18]	A	$TiCl_3$	.472	.472	.472	20.2	20.0	.472
42	3-Cyano-[18]	D	$TiCl_3$	.546	.547	.548	19.0	19.6	.547
43	( )-3-Carboxylic acid[18]	D	$TiCl_3$	.520	.519	.520	16.5	20.3	.520
44	Methyl ( )-3-carboxylate[19]	D	$TiCl_3$	.529	.529	.530	18.6	17.9	.529
45	3-Benzoyl-[20]	D	$TiCl_3$	.530	.531	.530	17.6	18.0	.530
46	5,6 - Dihydroxy - 1,4-naphthoquinone[21]	B	Quinone	.427	.427	.426	19.5	19.9	.427

[5] Schmidt and Spoun, *Ber.*, **55**, 1194 (1922).

[6] Werner, *Ann.*, **322**, 135 (1902).

[7] Schmidt and Schairer, *Ber.*, **44**, 740 (1911).

[8] Brass and Stadler, *ibid.*, **57**, 133 (1924). The sample was kindly supplied by Professor Brass, to whom the author wishes to express his thanks.

[9] Brass and Ferber, *ibid.*, **55**, 541 (1922).

[10] Brass and Nickel, *Ann.*, **441**, 217 (1925).

[11] Pschorr, *Ber.*, **39**, 3106 (1906).

[12] Schmidt and Lumpp, *ibid.*, **43**, 423 (1910).

[13] Schmidt and Austin, *ibid.*, **36**, 3730 (1903).

[14] Schmidt and Söll, *ibid.*, **41**, 3679 (1908).

[15] Schmidt and Kämpf, *ibid.*, **36**, 3738 (1903).

[16] Schmidt and Kämpf, *ibid.*, **36**, 3745 (1903). Regarding the structure, see, Christie and Kenner, *J. Chem. Soc.*, 470 (1926); Christie, Holderness and Kenner, *ibid.*, 671 (1926).

[17] Sandqvist, *Ann.*, **379**, 79 (1911).

[18] Werner, *ibid.*, **321**, 248 (1902).

[19] Phenanthrene-3-carboxylic acid (ref. 18) was converted by the action of methyl iodide on the silver salt into the methyl ester: colorless plates, m. p. 97°. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.00; H, 5.10. This was oxidized at 70° in the usual manner and the quinone was crystallized from glacial acetic acid, giving orange-yellow needles, m. p. 212°. Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 71.86; H, 3.94.

[20] A solution of phenylmagnesium bromide was slowly added to a stirred and well-cooled solution of 3-phenanthroyl chloride (distilled and crystallized from ligroin, m. p. 118°) in benzene. The benzoyl-3-phenanthrene which resulted was not obtained in a pure condition, for the reaction product was an oil which failed to solidify. Oxidation of this oil with chromic acid in glacial acetic acid solution yielded an orange oil from which 3-benzoylphenanthrenequinone was obtained easily by crystallization from glacial acetic acid. The quinone forms golden-yellow plates melting at 205–206°. The substance is not easily burned. Analyses in a copper oxide tube, even with the use of the Dennstedt contact star, gave low values for carbon. The difficulty was overcome completely by the use of a combustion tube packed with small lumps of fused lead chromate, and by heating the tube to a full red glow. Calcd. for $C_{21}H_{14}O_3$: C, 80.75; H, 3.87. Found: C, 80.59; H, 4.04. This procedure, which was suggested by an observation of Bamberger and Hooker, *Ann.*, **229**, 118 (1885), has been of great service in the analysis of certain other substances which could not be burned completely either by the platinum star method or with the use of cuprous chloride according to Haas, *J. Chem. Soc.*, **89**, 570 (1906).

[21] Dimroth and Roos, *Ann.*, **456**, 177 (1927). The author wishes to thank Professor Dimroth for kindly furnishing him with a sample of this substance.

The quinones which have been described by other investigators were prepared according to the methods indicated in the references and purified until they corresponded in properties to the best samples known. The electrometric titration curve often reveals the presence of an impurity, and in one case, that of 4-hydroxyphenanthrenequinone, the sample appeared to be somewhat contaminated and the results may be somewhat in error for this reason.

An explanation must be given of the considerations which determined the choice of solvent and the method of measurement employed. The most convenient means of determining the reduction potential of a quinone in an acidic solution consists in the electrometric titration of the oxidant with titanous chloride, but this reagent often forms complex compounds

with substances having ortho hydroxyl groups or with *o*-hydroxyquinones. For this reason it seemed expedient in many cases to prepare a solution of the reductant by catalytic hydrogenation and to titrate with an organic oxidizing agent such as benzoquinone. It was found that nitrophenanthrenequinones can be reduced to the hydroquinones by titanous chloride in acid solution without reduction of the nitro group; a sharp inflection of the titration curve occurred at a point corresponding to just two equivalents of reducing agent. There were indications that the nitrohydroquinones slowly undergo a disproportionation after the end-point has been reached, but this does not affect the results of the titration.

The solvent most generally employed was a 50% alcoholic hydrochloric acid solution containing lithium chloride to increase the sensitivity of the readings; in some cases a higher concentration of alcohol was required to bring the quinone into solution. It has appeared to the author advisable to compare the potentials of the various quinones under conditions which permit of no dissociation of moderately acidic or basic groups of either the oxidant or the reductant. For this reason, in studying the aminophenanthrenequinones, a solvent ("C") was selected which is probably about neutral and in which the amino group doubtless is undissociated. In one case (No. 28) results in an acidic solution are also included, though they are of little value for the purpose of relating potential and structure.

In the case of the acetoxy-, the di- and triacetoxyphenanthrenequinones, a number of which were studied, it was found that a group in the 1-position interfered with the attainment of electrode equilibrium and the results were not satisfactory. Hydroxyl and sulfonate groups in this position exhibited no such influence, but with 1-methylphenanthrenequinone a constant potential was reached only very slowly.

Considerable information is available from previous work concerning the effect of substituents in a quinonoid nucleus on the potential of a quinone, but little is known regarding substitutions at points more distant from the quinone grouping except that the effect is considerably less. The phenanthrenequinones afford a particularly favorable series in which to study such substitutions because the number of possible isomers is great and because the potential of the parent quinone is subject to considerable change as the result of substitution. Thus the potential range of the quinones here studied is from 0.281 to 0.590 v.

The most striking and novel feature of the results given in Table III is the pronounced influence of the position of a substituent on the potential. A hydroxyl group in the 1-position causes a decided drop in the potential of phenanthrenequinone, the effect is negligible in the 2-substituted isomer, a considerable lowering is produced by substitution in the 3-position and 4-hydroxyphenanthrenequinone has the same potential as the parent compound. This seems rather surprising until it is considered that the 1- and

3-positions are ortho and para, respectively, to one of the quinonoid carbonyl groups, while the 2- and 4- are meta positions. It is not odd that the effect of the hydroxyl group in the ortho and para positions, or in the two meta positions, is about the same. This regularity is not confined to the hydroxyl group or, indeed, to groups which cause a lowering in the potential. Table IV shows that a para amino group lowers the potential considerably more than does a meta-(2) group or a meta-(4) group. A para nitro group produces a greater increase in the potential than does a nitro group in either of the meta positions.

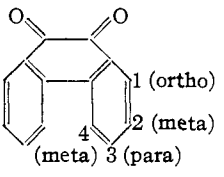


TABLE IV

THE INFLUENCE OF THE POSITION OF THE SUBSTITUENT

Effect in millivolts on the potential of substituting a group in the positions

	Ortho-Para		Meta	
Substituent	1	3	2	4
OH	−50	−53	− 1	0
NH_2	..	−98	−17	−28
NO_2	..	+91	+69	+57
SO_3H	+21	+30	+24	..

In the case of the sulfonic acid group the influence on the potential is so slight that the effect of the position of the substituent may well be masked. There is sufficient evidence to warrant the generalization that the effect on the potential of a substituent in the ortho (1) and para (3) positions is about the same, and that it is greater than the effect of a group in either meta position (2 or 4). This conclusion harmonizes well with the known facts concerning the directive influence of substituents in the benzene ring.

The next point of interest is to compare the effects produced by the different kinds of substituent groups. In view of the above generalization, the most favorable series for such a study is that of the 1- or 3-substituted phenanthrenequinones, and one is justified in comparing a 1-derivative with a 3-derivative. This has been done in constructing Table V, though the results for both positions are included wherever available. The figures represent the differences in the potentials of the substituted and unsubstituted quinones in the same solvent. In a few instances two such comparisons are possible for a single substituent.

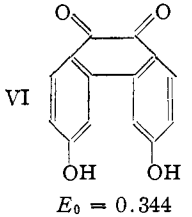
TABLE V

THE EFFECT ON THE POTENTIAL OF PHENANTHRENEQUINONE OF VARIOUS SUBSTITUTENT GROUPS IN THE ORTHO-PARA (1 OR 3) POSITIONS

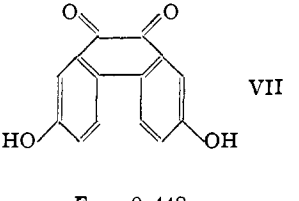
Substituent	Effect on potential, mv.	Substituent	Effect on potential, mv.	Substituent	Effect on potential, mv.
NO_2	+91	COOH	+49	OCH_3	−39
CN	+76	Br	+28	OH	−50, 53
COC_6H_5	+59	SO_3H	+23, 30	CH_3	−64
$COOCH_3$	+58	$OCOCH_3$	+ 9	NH_2	−98

From the results given in the table it will be seen that all of the unsaturated substituent groups cause an increase in the potential of phenanthrenequinone. The nitro group is the most effective, the sulfonic acid group is the least so and the cyano, ketone and carboxylate groups occupy intermediate positions. Methoxyl, hydroxyl, methyl and amino groups all lower the potential of the parent quinone. The effect of an hydroxyl group is eliminated, and to a slight extent reversed, by acetylation. In general, an ortho-para directing group lowers the potential and a meta directing group causes an increase, though the bromine atom constitutes an exception to this rule, for the substitution of hydrogen by bromine results in an appreciable increase in the potential. Aside from this exception, and aside from the fact that the effect of a methyl group appears to be surprisingly pronounced, the order here indicated for the various substituents is much the same as that found by other methods of comparison. The exact theoretical significance of the present results is not yet completely clear, for there are certain complicating aspects of the whole question of the effect of substituent groups on the potential. Thus, for example, it is not easy to decide whether the substituent alters the nature of the oxidant, of the reductant or of both components of the reversible system. Experiments designed to settle this and other points are now in progress and a more thorough consideration of the above comparison of groups will be reserved until this work is completed.

The potentials of the polysubstituted phenanthrenequinones would present a perplexing problem if one had no knowledge of the difference between the ortho-para and the meta types of substitution. Thus 3,6-dihydroxyphenanthrenequinone, VI, and the 2,7-isomer, VII, differ in potential by 104 mv., but this difference is understandable when it is observed



$E_0 = 0.344$



$E_0 = 0.448$

that in one case each hydroxyl group is para to a quinonoid carbonyl group while in the other compound both hydroxyls are in meta positions. Furthermore, the difference in potential between 3,6-dihydroxyphenanthrenequinone and 3(or 6)-hydroxyphenanthrenequinone is nearly the same as that between the mono-substituted derivative and phenanthrenequinone. In other words, the effect of the second substituent is approximately equal to that of the first. In order to determine whether this is generally true, a comparison is given in Table VI of the observed total effect of two or

more substituents with the effect calculated on the assumption that the influence of each group is the same as in a mono-substitution product.

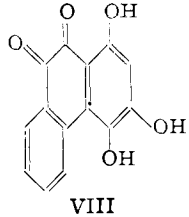
TABLE VI

THE EFFECT OF POLY-SUBSTITUTION

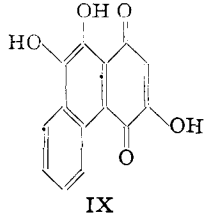
Substituents	Positions of substituents	Effect of substituents on the potential, mv. Found	Calcd.	Diff.
1,2-$(OH)_2$	*o*, *m*	− 78	− 51	−17
1,4-$(OH)_2$	*o*, *m*	− 79	− 50	−19
3,4-$(OH)_2$	*p*, *m*	− 73	− 53	−20
2,6-$(OH)_2$	*m*, *p*	− 57	− 53	− 4
2,7-$(OH)_2$	*m*, *m*	− 23	− 2	−21
3,6-$(OH)_2$	*p*, *p*	−127	−106	−21
3,6-$(OCH_3)_2$	*p*, *p*	− 84	− 74	−10
2,5-$(NO_2)_2$	*m*, *m*	+ 98	+126	−27
2,7-$(NO_2)_2$	*m*, *m*	+119	+138	−19
1,2,4-$(OH)_3$	*o*, *m*, *m*	−118	− 51	−68
1,3,4-$(OH)_3$	*o*, *p*, *m*	−177	−103	−74

It will be observed that with the disubstituted phenanthrenequinones the calculated value is in every case slightly more positive than the value found. The difference is remarkably constant, the average being 18 mv., and this is true regardless of whether the substituents raise or lower the potential and of whether they are situated in the same or in different rings. It appears that the effect of a second substituent is greater by about 18 mv. than that of the first; if the potential is increased (or decreased) by a single substitution, it is increased (or decreased) to a slightly greater extent by a second such substitution, regardless of the positions. From the results with the two tri-substituted quinones it may be concluded that the potential lowering produced by three hydroxyls is greater than that expected from the known effect of each separate group by about 72 mv. The influence of a substituent thus becomes progressively greater as substitution proceeds.

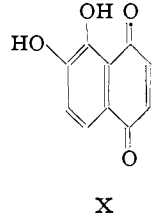
One further question of interest in connection with the present results is that of the possible tautomerism of certain of the hydroxyphenanthrenequinones. It is conceivable, for example, that 1,3,4-trihydroxyphenanthrenequinone, VIII, as the result of a tautomeric change, exists largely in



VIII



IX



X

the form of the para quinone, IX. There is some chemical evidence in support of Structure VIII,[1c] and it is of interest to inquire if this conclusion

is in accord with such electrochemical evidence as is available. The reduction potential of the quinone is 0.281 v., a value which appears to be consistent with Structure VIII, though it does not necessarily confirm this structure. One can arrive at a prediction concerning the potential of a quinone having the structure of IX by considering that it is derived from 5,6-dihydroxy-1,4-naphthoquinone, X, by the attachment of a phenylene and an hydroxyl group. Thus: potential of IX = 0.427 v. (5,6-dihydroxy-1,4-naphthoquinone) + [0.396 v. (3-hydroxy-1,4-phenanthrenequinone) − 0.356 v. (3-hydroxy-1,4-naphthoquinone)] − [0.523 v. (1,4-phenanthrenequinone) − 0.396 v. (3-hydroxy-1,4-phenanthrenequinone)] = 0.340 v. This calculation gives a result which is much higher than the potential found for the compound. According to the theory that an hydroxyquinone should exist in that tautomeric form having the lowest possible reduction potential,[22] this means that the quinone in question does not have the structure of IX, a conclusion which is consistent with the other evidence. Similar reasoning supports the 9,10-phenanthrenequinone structure for all of the hydroxy quinones studied.

Summary

The normal reduction potentials at 25° of 43 phenanthrenequinones have been determined and an analysis of the data has led to the following conclusions: (1) an isophenanthrenequinone, such as 1,4-phenanthrenequinone, has a somewhat higher potential than the corresponding naphthoquinone; the difference results from the substituting of a naphthylene group for the less reactive phenylene group. (2) The abnormally high potential of 9,10-phenanthrenequinone is due to a strain resulting from some peculiar spatial arrangement of the molecule. (3) Among the substituted 9,10-phenanthrenequinones, a group has the same effect on the potential when it is ortho or para to a quinonoid carbonyl group and the effect is much greater than when the substituent occupies either of the meta positions. A second substituent has a somewhat greater influence than the first. The potential is increased by the substitution of nitro, cyano, ketone, carboxyl, bromo and sulfonate groups; it is decreased by amino, alkyl, hydroxyl and methoxyl groups.

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[22] Fieser, THIS JOURNAL, 50, 439 (1928).