[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

REDUCTION POTENTIALS OF QUINONES. II. THE POTENTIALS OF CERTAIN DERIVATIVES OF BENZOQUINONE, NAPHTHOQUINONE AND ANTHRAQUINONE

BY JAMES B. CONANT AND LOUIS F. FIESER

RECEIVED MARCH 22, 1924 PUBLISHED AUGUST 5, 1924

In the first paper of this series[1] we reported our measurements of the reduction potentials of certain derivatives of *p*-benzoquinone in aqueous solution, in alcoholic solution and referred to the solid state. It was found that the results obtained with a series of quinones under these three different conditions were so nearly parallel that significant comparisons may be made by considering the reduction potentials[2] in either aqueous or alcoholic solution. We have now determined the reduction potentials in alcoholic solution of some 35 additional derivatives of benzoquinone, naphthoquinone and anthraquinone as a further step towards the discovery of the principles underlying the relationship between the structure, of quinones and the free energy of their reduction.

The general method of determining the reduction potential by titration requires little comment as it has been considered in detail elsewhere both as applied in aqueous[3] and alcoholic solutions.[1b] The apparatus employed in this investigation was identical with that previously described. The solvents employed were mixtures of alcohol and water containing sufficient

[1] (a) THIS JOURNAL, **45**, 2194 (1923); see also (b) Conant and Fieser, *ibid.*, **44**, 2480 (1922).

[2] Professor G. S. Forbes has kindly called our attention to a question of terminology which, perhaps, was not made sufficiently clear in our previous papers. We have defined the normal reduction potential of a quinone as the electromotive force of a cell composed of an inert electrode immersed in a solution of equimolecular amounts of quinone and hydroquinone and a hydrogen electrode immersed *in the same solvent.* Such a combination is free from liquid-junction potentials and its electromotive force is a direct measure of the free energy of the reduction (by hydrogen) of the quinone *in the solvent in question.* The numerical value of such a reduction potential in non-aqueous solvents is obviously somewhat different from the single electrode oxidation-reduction potential referred to the normal hydrogen electrode in aqueous solution. Such single electrode potentials may be evaluated from our results when sufficient data are available in regard to the potential difference between the hydrogen electrode in the solvent in question and the normal hydrogen electrode. Since the solvents we have so far employed contained at least 5% of water, the actual difference is probably not great [compare Lapworth, *J. Chem. Soc.*, **99**, 242 (1911)]. Although it is common electrochemical practice to refer all single electrode potentials to the normal hydrogen electrode, we have preferred to define our reduction potentials of quinones in terms of a hydrogen electrode in the same solvent, as only this reduction potential is a direct measure of the free energy of the chemical process with which we are concerned.

[3] (a) Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920); (b) *Pub. Health Repts.*, **38**, 933, 1669 (1923). (c) Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922). (d) LaMer and Baker, *ibid.*, **44**, 1954 (1922).

hydrogen chloride to be 0.5 N or 1.0 N; in a few cases the quinones were sufficiently soluble to be measured in aqueous solution. Where the solubility permitted, 50% alcohol was used in preference to 95% as better conductivity was obtained in the former solvent; the solutions of the quinones were 0.001–0.005 M. All measurements were made at 25°; a correction of the hydrogen electrode to standard conditions was not necessary as this correction is less than the other experimental errors. The symbol

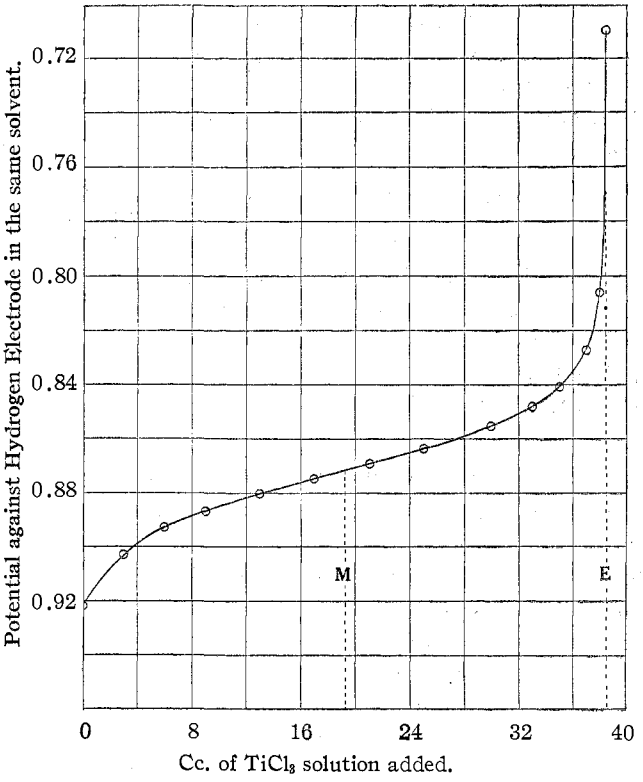


Fig. 1.—Titration curve of tetrabromo-*o*-benzoquinone in 50% alcoholic 0.5 N HCl. End-point (E) by inspection is 38.5 cc., hence mid-point of reduction (M) is 19.25 cc. and π_0 is 0.872 v.

π_0 is used throughout this paper for the normal reduction potential in the solvent in question, being th e.m.f. of the cell:

$$H_2, Pt, \quad \begin{matrix} \text{Solvent} \\ [HCl] = x \end{matrix} \Big| \begin{matrix} \text{Solvent,} \\ [HCl] = x \end{matrix} \quad \begin{matrix} Pt \\ [Q] = [QH_2] \end{matrix}$$

This normal potential was evaluated from the titration curve by interpolating the potential at the mid-point of reduction rather than by calculating π_0 from each individual point on the curve with the aid of the theoretical equation. This convenient method was adopted because it has already been

found to yield values in good agreement with those obtained by the more detailed process and because it is free from any error which might arise if the theoretical equation fails to hold in unmodified form, due, for example, to a high degree of quinhydrone association.[4] A typical titration curve and the method of interpreting it are shown in Fig. 1. This curve is of particular interest because the potentials are among the highest yet observed. It will be seen that the potential of the solution of the pure quinone (0.922 v.) corresponds to a considerable amount (2.1%) of the hydroquinone and not to an infinitely small concentration as would be expected. However, an inspection of the curve shows that the position of the mid-point is but slightly affected by a 2% error in regard to the origin or the end-point of the titration curve and the combined probable errors would not affect the value of π_0 by more than 1 millivolt. The curve closely approximates the equation, π (obs.) $= \pi_0 + 0.0295 \log \frac{[\text{quinone}]}{[\text{hydroquinone}]}$. Thus the difference between the potential at the mid-point and at 20% and 80% reduction, respectively, is 17 and 19 mv., while the calculated value is 18 mv. For the sake of brevity we have omitted this detailed information for the other compounds studied and reported in the following tables only the interpolated values for π_0. Suffice it to say that, with the exceptions noted below, the titration curves correspond to the equation within a few millivolts.

I. Ortho- and Para-Quinones

o-**Benzoquinone.**—This compound was prepared by oxidizing pyrocatechol in absolute ether with specially prepared silver oxide according to the directions of Willstätter and Pfannenstiel.[5] In order to obtain a pure sample without recrystallization, only the first crop of crystals separating from the ethereal solution was employed. The quinone has no definite melting point. From the descriptions of this compound it would seem that the chance of obtaining a stable aqueous or alcoholic solution for potential measurements was very slight. Willstätter states that the quinone is soluble in water but suffers rapid change. On standing a few days the solid substance decomposes to give a black-brown product. Jackson and Koch,[6] failing to obtain even a solution of the quinone in alcohol on treating the lead salt of pyrocatechol with iodine, believed that the quinone was attacked by the alcohol as soon as it was formed. Their attempts to isolate the solid substance always led to a brown substance soluble in chloroform and a black substance insoluble in chloroform. They assigned to the black product the formula, $O_2(OH)H_2C_6—C_6H_3(OH)_2$. It appears, moreover, that acids, which must be employed in potential

[4] Compare Ref. 3 c.

[5] Willstätter and Pfannenstiel, *Ber.*, **37**, 4744 (1904).

[6] Jackson and Koch, *Am. Chem. J.*, **26**, 10 (1901).

measurements, catalyze the formation of the black condensation product. It was by treating β-naphthoquinone with dil. sulfuric acid that Stenhouse and Groves[7] were able to effect its condensation, and Schmidlin[8] found that *o*-benzoquinone behaved in the same way excepting that the reaction was practically instantaneous.

Discouraging as these statements appear, it was nevertheless possible to obtain good titration curves for *o*-benzoquinone. The first attempts were unsuccessful. The sample was placed in a small glass cup which was suspended above the solvent in the titration vessel. When all preparations for carrying out a titration had been made, a few cubic centimeters of reducing agent was run in, the cup was immersed in the well-stirred solvent, and the potential read at once. The potential was fairly constant but another small increment of reducing agent was more than enough to react with all of the free quinone that remained. Nearly all of the quinone had been converted into the black condensation product the instant it touched the acid. Believing that the condensation would take place less readily the more dilute the initial solution, the sample was then slowly sprinkled into the solvent which was rapidly stirred. Only a small amount of the black substance was formed and the main part of the sample dissolved to give a clear, yellow solution. Since it is not necessary to remove the oxygen from the cell when the hydroquinone is perfectly stable in air, the hydrogen electrode, siphon and buret could be placed in readiness, the solvent brought to the desired temperature, and the titration could be commenced within a few seconds after the quinone solution had been prepared. It was also found that electrode equilibrium was attained with the greatest rapidity, so that the titration could be completed in the space of a few minutes, and only an exceedingly rapid decomposition could vitiate the results.

The stability of a solution is readily determined by observing the constancy of the potentials with time. Using 0.1 *N* acid a fall in the potential (indicating destruction of the quinone) of only 0.1 mv. in ten minutes was observed. In normal acid the potential fell as much as 1.0 mv. in two to three minutes, and the recorded values may be 2–3 mv. too low. Decomposition was also accelerated by the presence of alcohol so that, while the weaker acid gave solutions sufficiently stable to permit good titrations, in using normal alcoholic-aqueous acid the potentials fell so rapidly that no satisfactory results could be obtained.

1,2-Naphthoquinone.—A light yellow sample of this quinone was prepared by oxidizing carefully purified 1,2-aminonaphthol hydrochloride with sodium dichromate in dil. sulfuric acid at 0°. It has no definite melting point, and cannot be purified by recrystallization; titrations of its

[7] Stenhouse and Groves, *Ann.*, **194**, 205 (1878).

[8] Schmidlin, *Ber.*, **43**, 1299 (1910).

oxidizing equivalent showed that it was at least 99% pure. Values for the reduction potential of this compound in 0.2 *N* alcoholic-aqueous acid have already been reported ($\pi_0 = 0.579$). On attempting to extend these results to include measurements in solutions of higher acid concentration, it was discovered that in 0.5 *N* alcoholic hydrochloric acid solution β-naphthoquinone undergoes decomposition at a velocity readily measured potentiometrically. After allowing the solution to stand until all of the β-naphthoquinone had been destroyed, a normal titration curve was obtained, indicating a reduction potential for the unknown decomposition product of 0.358 in 0.5 *N* 50% alcoholic acid, and of 0.360 in 0.5 *N* 95% alcoholic acid. In the first of these solutions the reduction potential is very close to that of hydroxy naphthoquinone ($\pi_0 = 0.356$) but in 95% alcohol, in which solvent the potential of the latter compound is 0.352, the difference is so great that the compounds cannot be identical. That the unknown material is not dinaphthyldiquinhydrone[7,9] (formed by allowing β-naphthoquinone to stand in contact with dilute acids) was evident from the titration of a sample of the dinaphthyldiquinhydrone which was found to have a value of π_0 of 0.579 in 0.5 *N* 50% alcoholic acid. It is hoped that a further investigation of this problem may be made at some later time.

9,10-Phenanthrenequinone.—The titration of a pure sample (m. p., 203°) of this compound presented no difficulties.

1-Methyl-7-*iso*propyl-9,10-phenanthrenequinone (Retenequinone).—Retene (m. p., 95.5°) was oxidized with chromic acid according to the method of Bamberger and Hooker.[10] An excess of solvent was used to avoid troublesome by-products and the yield was only 27%. The quinone was purified by repeated precipitation from a chloroformic solution with alcohol, when it melted constantly at 197°.

1,4-Naphthoquinone.—This substance was prepared by oxidizing 1,4-aminonaphthol hydrochloride; it was best purified by sublimation under diminished pressure in a current of steam, a light yellow crystalline material melting at 125.5° being obtained. When purified by recrystallization from gasoline the substance was brown but melted at 125.5°. Both samples had the same reduction potential in alcoholic solution. It will be observed (Table I) that the reduction potential is 10 mv. higher in 95% than in 50% alcoholic solution. This is not surprising, since the potential in any solvent is dependent upon the solubility relationships of the quinone and hydroquinone, but it is somewhat unusual. LaMer and Baker[3d] measured the potential in aqueous solution and found it to be 0.4698.

[9] *Ber.*, **17**, 3019 (1884).

[10] Bamberger and Hooker, *Ann.*, **229**, 117 (1885). For proof of structure see *Ann.*, **229**, 102 (1885); *Monatsh.*, **25**, 452 (1904); **29**, 763 (1908); THIS JOURNAL, **32**, 374 (1910).

9,10-Anthraquinone.—A recrystallized sample of commercial material (m. p., 273°) was used. Titrations are somewhat tedious because of the length of time required before equilibrium is established after the addition of each increment of reducing agent. The potentials were, however, perfectly constant once equilibrium was reached. Electrode equilibrium was especially slow towards the completion of the reduction and the end-point was not sharp; this is due largely to the low reduction potential of the quinone, since the difference in potential between the quinone and reducing agent influences to some extent the speed of reduction and also determines the extent of the drop in potential at the end-point.

1,2-Anthraquinone.—This compound was prepared according to the method of Dienel[11] by oxidizing 2-amino-1-anthrol which in turn was prepared from 1-anthrol through the nitroso compound and reduction. The material was purified by repeated solution in alcohol and precipitation with water as recommended by Lagodzinski.[12] This treatment removed effectively a small amount of a black, insoluble product and the pure material was light orange; it melted with decomposition at about 185°. Equilibrium in the titrations was reached with considerable rapidity and the potentials were always constant.

TABLE I

NORMAL REDUCTION POTENTIALS AT 25° IN VOLTS

	Aqueous solution		50% alc. sol.		95% alc. sol.	
	0.1 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl
o-Benzoquinone	0.787	0.776	0.783	...	...	...
	.786	.777	.784	...	...	...
Phenanthrenequinone	...	...	...	...	0.470	0.472
	...	...	...	...	.471	.470
1 - Methyl - 7 - *iso*propyl - phenanthrenequinone	...	...	...	...	.409	.411
	...	...	...	...	.406	.411
1,4-Naphthoquinone	...	...	.483	.483	.492	.492
	...	...	.484	.483	.495	.492
9,10-Anthraquinone	...	...	...	...	.157	.154
	...	...	...	...	.154	.153
1,2-Anthraquinone	...	...	...	...	.490	.486
	...	...	...	...	.491	.487

Discussion

In comparing the reduction potentials of these quinones, since there is no good reason for selecting any one particular solvent as the basis for such a comparison, all of the values reported above will be given consideration. This may be done by simply averaging all values for a compound in aqueous and in alcoholic solution and employing both averages. An exception

[11] Dienel, *Ber.*, **39**, 926 (1906).

[12] Lagodzinski, *Ann.*, **342**, 80 (1905).

should be made in the case of α-naphthoquinone, however, since its reduction potential varies with the alcohol percentage. Since such variation does not occur with *p*-benzoquinone, and inasmuch as anthraquinone could only be studied in 95% alcohol, only the value of α-naphthoquinone in 95% alcohol will be considered in comparing the *p*-quinones. Table II is prepared according to these principles. The potentials are given in millivolts; the differences given in the last columns are between the successive members of each series.

TABLE II

	Av. red. potential		Difference		
	Water Mv.	Alcohol Mv.	Water Mv.	Alcohol Mv.	Av. Mv.
(A) *para*-Quinones					
p-Benzoquinone	699	711	229	218	224
1,4-Naphthoquinone	470[a]	493			
9,10-Anthraquinone	...	155	...	338	338
(B) *ortho*-Quinones					
o-Benzoquinone	782	784	235	205	220
1,2-Naphthoquinone	547	579			
Phenanthrenequinone	...	471	...	108	108
1,2-Anthraquinone	...	489	...	...	...

[a] From the results of LaMer and Baker, Ref. 3d.

These results confirm and extend the qualitative observations of Willstätter and Parnas,[13] and others,[14] regarding the "stabilization" of the quinonoid structure which always occurs when one or more of its ethylene linkages is shared between the quinonoid and a benzenoid nucleus. It is apparent from the table that one phenylene group "stabilizes" this linkage in *p*- and *o*-benzoquinone to about the same extent. It should be observed that the potential is lowered in both cases by a certain number of millivolts (average, 222) and not by a constant percentage of the initial potential.

A second phenylene group, on the other hand, produces an entirely different effect on the two naphthoquinones, for when attached to the *para* isomer the potential is lowered 338 millivolts while a similar group attached to 1,2-naphthoquinone lowers the potential only 108 millivolts. It is significant that in neither case is the effect at all close to the above value of 222 millivolts. The comparison of 9,10-anthraquinone and 1,2-anthraquinone and phenanthrenequinone is, of course, not strictly analogous to these simpler cases, but it is interesting to note that the 9,10-anthraquinone has a potential 316 millivolts below that of phenanthrenequinone. An adequate interpretation of all these facts must take into account, undoubtedly, both the structural formulas of the quinones

[13] Willstätter and Parnas, *Ber.*, **40**, 1406 (1907).

[14] Beschke and Diehm, *Ann.*, **384**, 173 (1911). Kalb, *Ber.*, **47**, 1724 (1914). Scholl, *Ann.*, **433**, 163 (1923).

and the hydroquinones and thus the constitution of anthracene and phenanthrene themselves. Without going into this interesting aspect of the problem at this time, we can safely draw the following conclusions: *o*-quinones have a considerably higher potential than the isomeric *p*-quinones, the difference being nearly the same in the benzene and naphthalene series; the attachment of a phenylene group to a quinonoid nucleus (either *ortho* or *para*) lowers the reduction potential, this lowering being about 220 millivolts for one phenylene group but much greater for a second attached to a *para* quinone and much less for a second attached to an *ortho* quinone. The difference in the effect of phenylene groups as compared to alkyl groups, observed qualitatively by Willstätter and Parnas will be discussed in another paper in which measurements on alkyl quinones and tetrahydronaphthoquinone will be presented; it may be noted here, however, that the potentials of xyloquinone and thymoquinone[1a] are only 110 millivolts less than that of benzoquinone as compared with a difference of 220 millivolts between benzoquinone and naphthoquinone. The introduction of 4 methyl groups into *p*-benzoquinone lowers the potential 245 millivolts;[1a] two phenylene groups lower it 556 in 9,10-anthraquinone. The phenylene group, therefore, seems to be much more effective than simple alkyl groups.

II. Hydroxy- and Alkoxy-Quinones

Hydroxy-*p*-Benzoquinone.—Oxidation of the hydroquinone with silver oxide[15] gave hydroxybenzoquinone in 60% yields; the compound crystallized from benzene in fine, yellow needles. It has no definite melting point but passes into a black substance when heated. Possibly because of a rearrangement into an *o*-quinone derivative this compound is not altogether stable even in the solid state and changes within a week into a black solid which resembles the decomposition product of *o*-benzoquinone. Some of this material is formed when the compound is dissolved in water, though it is apparently too insoluble to enter into an oxidation-reduction equilibrium. Because of this instability it was considered inadvisable to prepare the solution more than one to two minutes before a titration was commenced, and because of the suspected instability of the hydroquinone towards oxygen the removal of this gas was considered necessary. Consequently the sample was suspended in a cup above the surface of the solvent, the cell was swept free of air with nitrogen, the cup plunged into the solvent and a titration commenced at once.

2,5-Dihydroxy-*p*-benzoquinone.—Saponification of 2,5-dimethoxy quinone[16] with concd. sodium hydroxide solution yielded 2,5-dihydroxybenzoquinone. It was purified by solution in warm alkali and precipitation with acid; it was obtained as yellow crystals decomposing at about 210°. (Previous investigators give about 215–220°.)

[15] Willstätter and Müller, *Ber.*, **44**, 2180 (1911).

[16] Knoevenagel and Bückel, *Ber.*, **34**, 3993 (1901).

2-Hydroxy-1, 4-naphthoquinone (Naphthalenic Acid).—1, 2, 4-Trihydroxy-naphthalene-triacetate (prepared from α-naphthoquinone and acetic anhydride) was saponified with alcoholic potassium hydroxide; the resulting hydroquinone was dissolved in methyl alcohol and potassium hydroxide and oxidized by a current of air. On acidification, the hydroxynaphthoquinone was obtained as red needles melting at 182°; another sample precipitated from a hot solution of the barium salt was yellow and melted at 186°. O. Miller has pointed out[17] that the melting point of this substance has been reported from 179° to 191° and there is no regularity in the melting point or color of pure preparations of this quinone.

8-Hydroxy-1,4-naphthoquinone (Juglone).—1,5-Dihydroxy-naphthalene was oxidized with sodium dichromate and the quinone extracted by the method of Bernthsen and Semper.[18] The quinone was purified by evaporation of its solution in chloroform after precipitation of impurities with petroleum ether. A brown-red powder was obtained which decomposed at about 145°. The titration curves were considerably steeper in the initial stages of reduction than the theoretical curve.

1-Hydroxy-anthraquinone.—This compound[19] was prepared by diazotizing 1-amino-anthraquinone in glacial acetic acid and heating the diazonium compound with water; after purification by solution in hot alkali and precipitation with acid it melted at 192°.

1-Hydroxy-4-chloro-anthraquinone.—Following the directions of Ullmann and Conzetti[20] hydroxy-anthraquinone was treated with sulfuryl chloride and the product crystallized from glacial acetic acid. It formed bright orange needles, melting at 188°.

2,5-Dihydroxy-3,6-dichloro-*p*-benzoquinone (Chloranilic Acid).—Pure chloranil was treated with sodium hydroxide according to the method of Graebe[21] and purified through the sodium salt. It melted in a sealed tube at 282–284°. In titrating this compound (and bromanilic acid) rather wide divergences from the theoretical slope of the curve were observed in some of the solutions investigated.

2,5-Dihydroxy-3,6-dibromo-*p*-benzoquinone (Bromanilic Acid).—This compound was prepared from bromanil by the same procedure as that used for the preparation of chloranilic acid. It decomposed at 270°.

2-Hydroxy-3-chloro-1,4-naphthoquinone.—2, 3-Dichloronaphthoquinone was moistened with a little alcohol and warmed with a very concentrated solution of potassium hydroxide.[22] Hydrochloric acid converted the red crystalline paste into a bright yellow precipitate of the

[17] Miller, *J. Russ. Phys.-Chem. Soc.*, **43**, 440 (1911).
[18] Bernthsen and Semper, *Ber.*, **20**, 938 (1887).
[19] Roemer, *Ber.*, **15**, 1793 (1882).
[20] Ullmann and Conzetti, *Ber.*, **53**, 829 (1920).
[21] Graebe, *Ann.*, **263**, 24 (1891).
[22] *Ann.*, **149**, 13 (1869).

hydroxychloroquinone. After repeated precipitations from hot alkaline solutions, it was obtained in the form of yellow needles melting at 213°; yield, 76%.

2,5-Dimethoxy-benzoquinone.—This substance was prepared by treating quinone with alcohol and zinc chloride.[16] The crude product was crystallized from large volumes of either glacial acetic acid or alcohol and finally sublimed, giving light yellow crystals which decomposed at about 250°.

2,5-Diethoxy-benzoquinone.—This was prepared in a similar manner to the methoxy compound but the yields are much poorer. It was repeatedly crystallized from alcohol after boiling with animal charcoal; it melted at 182.5°.

2,6-Dimethoxy-benzoquinone.—We are indebted to Professor Hunter and Mr. A. Levine of the University of Minnesota for a pure sample of this material which melted at 249°.

TABLE III

NORMAL POTENTIALS AT 25° IN VOLTS

	Aqueous solution		50% alc. soln.		95% alc. soln.	
	0.1 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl
Hydroxy-benzoquinone	0.596	0.594	0.601	0.598	...	...
	.595	.592	.600	.597	...	...
2,5-Dihydroxy-benzoquinone	.442	.441	.433	.435	...	...
	.443	.439	.435	.433	...	...
2-Hydroxy-1,4-naphthoquinone	...	...	.357	.356	0.351	...
	...	...	.356	.356	.353	...
8-Hydroxy-1,4-naphthoquinone	...	...	.452	.449	...	...
	...	...	.452	.450	...	...
1-Hydroxy-anthraquinone	...	...	...	...	.131	0.133
	...	...	...	...	.133	.130
1-Hydroxy-4-chloro-anthraquinone	...	...	...	...	.142	.145
	...	...	...	...	.142	.137
	...	...	...	...	.141	.141
2,5 - Dihydroxy - 3,6 - dichloro - benzoquinone (chloranilic acid)	.420	.449	.443	.453	.422	.422
	.419	.450	.442	.450	...	...
2,5 - Dihydroxy - 3,6 - dibromo - benzoquinone (bromanilic acid)	...	...	.427	.437	.402	.420
	...	...	.426	.437	.403	.416
2-Hydroxy-3-chloro-1,4-naphthoquinone	...	...	.352	.352	.348	...
	...	...	.351	.352	.348	...
2,5-Dimethoxy-benzoquinone	...	...	...	...	.477	.460
	...	...	...	...	.475	.458
2,5-Diethoxy-benzoquinone	.465	.460	.474	...	.480	.475
	.464	.458	.474	...	.477	.482
2,6-Dimethoxy-benzoquinone	...	...	.527	...	.530	.529
	...	...	.528	...	.528	.532
2,3-Diphenoxy-1,4-naphthoquinone	...	...	...	...	.457	.454
	...	...	...	...	.453	.455

2,3-Diphenoxy-1,4-naphthoquinone.—Dichloro-naphthoquinone was condensed with anhydrous potassium phenolate and the resulting diphenoxynaphthoquinone repeatedly crystallized from xylene;[23] it formed red needles melting at 199° (204° corr.).

Discussion

It is evident from an examination of the data presented in Table III, that the reduction potentials of chloranilic acid and bromanilic acid are very markedly affected by the concentration of the acid employed, whereas the potentials of the other quinones are essentially the same in 0.5 and 1 *N* alcoholic-hydrochloric acid.

The behavior of chloranilic and bromanilic acids is undoubtedly connected with the fact that these compounds are acids of strength comparable to that of the mineral acids.[24] They will in consequence be more or less dissociated in almost all of the solutions investigated, whereas the dissociation of the same phenolic groups in the hydroquinones will be less pronounced in these same solutions. Then unless, as is very unlikely, the dissociation constants of these phenolic groups of the quinone and hydroquinone are identical, the process of reduction involves a change in the degree of dissociation of these acidic groups and, conversely, the "apparent normal potential" which was measured above will not be constant but will be a function of these dissociation constants and of the hydrogen-ion concentration of the solution used. Without a knowledge of these hydrogen-ion concentrations the above results are of only qualitative significance.

The existence of oxidation-reduction systems of just this nature has been anticipated by Clark and Cohen[25] in an analysis of the theoretical relations between reduction potentials and Sörensen values. One of their equations and curves might be applied with a minor modification, to the system under discussion. From their analysis it is clear that the "apparent normal potential" should increase with increasing hydrogen-ion concentration and, if one regards only the pairs of determinations in each aqueous or alcoholic solution, it is seen that this is the case except with chloranilic acid in 95% alcohol. Here a value constant with changing hydrogen-ion concentration is obtained.

In the present attempt to correlate reduction potential and structure it was hoped to avoid this interesting problem rather than to solve it. It is obvious, for example, that the recorded measurements for chloranilic

[23] Ullmann and Ettisch, *Ber.*, **54**, 261 (1921).

[24] Coffetti, *Gazz. chim. ital.*, [2] **30**, 241 (1900), found by sugar inversion measurements that the dissociation constants of hydrochloric, bromanilic and chloranilic acids were in the proportion of 1:0.322:0.319.

[25] Clark and Cohen, "Studies on Oxidation-reduction." II, *U. S. Pub. Health Repts.*, **38**, 666 (1923).

acid are not comparable with other reduction potentials where the complication of changing ionization of another group is absent. It is only when both oxidant and reductant differ by only two hydrogen atoms that significant reduction potentials may be directly measured. Fortunately, a simple means is at hand of determining whether or not this is true, for the constancy of the potential with changing acid concentration indicates that the desired condition is realized. Thus all the reduction potentials of the hydroxyquinones, except the two above, are believed to be significant measures of the free energy of the addition of two hydrogen atoms to the quinone molecule, because the potentials are essentially independent of the acid concentration.

For purposes of comparison the measurements in all of the solutions used will be given equal weight by averaging the values, as usual. While all the compounds have not been studied in the same solutions, all pairs of compounds have been dealt with under comparable conditions and the effect of a substituent in benzoquinone ought to be capable of classification with its effect in anthraquinone even though the individual determinations were carried out in different solvents. Such a comparison is given in Table IV.

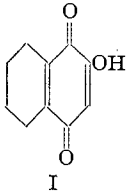
TABLE IV

THE EFFECT OF THE HYDROXYL GROUP

Hydroxy-substituted compound	Potential lowering in mv. due to introduction of hydroxyl group: Alc. soln.	Aq. soln.	Position of substituent group
Hydroxy-benzoquinone	112	105	Quinonoid nucleus
2,5-Dihydroxy-benzoquinone[a]	129	139	
2-Hydroxy-1,4-naphthoquinone	134	...	
8-Hydroxy-1,4-naphthoquinone	32	...	Aromatic nucleus (α pos.)
1-Hydroxy-anthraquinone	23	...	
1-Hydroxy-4-chloro-anthraquinone	33	...	

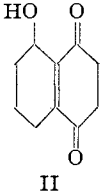
[a] The effect of each substituent is here considered to be one-half of the effect of the two groups.

It is at once evident that the influence of the hydroxyl group on the potential falls into two classes depending on whether it is substituted for a hydrogen atom of the quinonoid nucleus (I) or for hydrogen attached to an adjacent benzenoid ring (II and III). In the first case the average



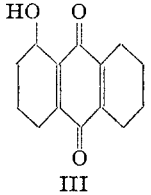
I

2-Hydroxy-naphtho-quinone



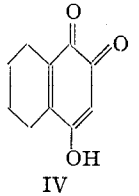
II

Juglone



III

1-Hydroxy-anthraquinone



IV

decrease in the potential is 124 mv., while in the second case the decrease is only 27 mv., or about one-fifth as great. Dimroth and Hilcken[26] have come to similar conclusions from a qualitative examination of the oxidizing power of certain hydroxyquinones and have also shown that the effect of the hydroxyl group is greater, the nearer it is to the quinonoid system.

Like the methyl radical, the hydroxyl group lowers the potential of benzoquinone, but its effect is about twice as great. Since the two sets of figures in Table II, although they do not show very exact agreement, exhibit no pronounced trend from series to series, the effect of the hydroxyl group is approximately independent of the oxidizing power of the quinone into which it is introduced.

Another point which deserves mention at the present time is the question of the structure of hydroxy-naphthoquinone. In accordance with the general practice[27] it has been assumed that this compound is a *p*-quinone (I) though there is no definite chemical evidence to show that its structure is not that of an *o*-quinone (IV). In fact O. Miller[17] believed that hydroxy-naphthoquinone consists of an equilibrium mixture containing the *para* and the *ortho* forms in the ratio of 1: 8. But the evidence on which this conclusion was based is not convincing. The quinone was neutralized with ammonia, the silver salt precipitated with silver nitrate and treated with ethyl iodide in the usual manner. The product contained two isomeric ethers in the ratio of 1: 8 and the structure of each was proved by conversion into the corresponding anilide. While this is an interesting fact in connection with the general problem of the isomerism of hydroxyquinones in salt formation, it is obviously without bearing on the question of the structure of hydroxy-naphthoquinone as it exists in the solid state or in acid solution. O. Miller found that the melting point of pure samples of this compound may differ by as much as 11° and that its color and crystal form may differ according to the conditions under which it is prepared. But a red and a yellow sample, whose melting points differed by 4°, gave identical titration curves which were in every way normal, and measurements made on a freshly-prepared and a year-old sample were identical. Since the potentials of α- and β-naphthoquinone differ by about 80 millivolts, the existence in the solutions investigated of two stable isomers could hardly escape notice and the conclusion is justified that either only one isomer is present, or that both isomers are in a mobile tautomeric equilibrium.[28]

Of course, this does not indicate which isomer is exclusively stable or which tautomer predominates in acid solution. But from Table IV

[26] Dimroth and Hilcken, *Ber.*, **54**, 3050 (1921).

[27] Dimroth, *Ber.*, **42**, 1616 (1909); *Ann.*, **411**, 341 (1916). Scholl and Zinke, *Ber.*, **51**, 1421 (1918).

[28] Cohen, Gibbs and Clark, *U. S. Pub. Health Repts.*, **39**, 390 (1924).

it is clear that the effect of introducing the hydroxyl group is about the same in the case of the first three compounds which are *assumed* to be *p*-quinones. If they are all assumed to be *o*-quinones, equally consistent results are obtained but if, however, it is supposed that hydroxy-naphthoquinone is an *o*-quinone while hydroxy-benzoquinone is a *p*-quinone, the effect of the hydroxyl group is found to be quite different in the two cases, namely 225 millivolts[29] and 109 millivolts.[30]

Thus the hydroxy derivatives of benzoquinones and naphthoquinones must have similar structures or if we are dealing with a tautomeric mixture the proportions of the tautomers must be nearly the same. If hydroxy-naphthoquinone is considered to be an *o*-quinone it is not only necessary to formulate hydroxy- and 2,5-dihydroxy-benzoquinone in a similar fashion but the same structure must also be assigned to chlorohydroxy-naphthoquinone and to chloranilic and bromanilic acids. But in all of these cases the *p*-quinonoid formulation has been assumed without question. Thus there was no doubt in the minds of Willstätter and Müller[15] as to the structure of hydroxy-benzoquinone for in color, stability and tendency to quinhydrone formation it was quite similar to *p*-benzoquinone and to methoxy-*p*-benzoquinone and quite different from *o*-benzoquinone and its methoxy derivative. Therefore, although the present work constitutes no proof of the case, it is highly probable that all of these hydroxyquinones including hydroxy-naphthoquinone exist in acid solution at least very largely as *p*-quinones.

In connection with the measurements of the alkoxy quinones it was observed that the slopes of the titration curves are rather irregular and abnormal in the case of the 2,5-dimethoxy compound. For 2,5-diethoxyquinone and 2,6-dimethoxyquinone the normal potential changes slightly with an increase in the concentration of alcohol, a small rise being observed in each case.

Regarding the interpretation of these data it is at once evident that within the limits in which these measurements, by their very nature, can be considered as significant, the methoxy and ethoxy groups may be considered as identical. This is perhaps particularly important inasmuch as the two compounds concerned exhibit widely different physical properties; the diethoxy compound is decidedly more soluble and lower-melting than the dimethoxy homolog. This conclusion is in accord with the fact pointed out in the previous paper that the effects of the methyl and *iso*-propyl groups are practically indistinguishable. On the other hand, the phenoxy group appears to be very different in character from the alkoxyl groups. Though no comparison of the compound studied above with

[29] This value was found by subtracting the potential of hydroxy-naphthoquinone in alcoholic solution from that of β-naphthoquinone in the same solvent.

[30] *Average value* from Table IV.

similar alkoxy and hydroxy derivatives can at present be made, the fact that the two *ortho* phenoxy groups lower the potential of the parent compound only 38 mv. seems to show that this group is distinctly different in character from the alkoxy radicals.

In Table V average values are collected and compared with the values found for 2,5-dihydroxyquinone. Why the potential of the dihydroxy compound falls on passing from aqueous to alcoholic solution while the reverse is the case with its ethers is not known, but even when allowance is made for this somewhat irregular behavior there can be no doubt that the alkoxy group is less effective in its power to bring about a decrease in reduction potential, than the hydroxyl group. It is also evident that of two isomeric dialkoxy quinones the one in which the substituent groups are in the *meta* position has a higher reduction potential than the *para* isomer.

TABLE V

REDUCTION POTENTIALS OF ALKOXY-BENZOQUINONES

Substituents	2,6-$(OCH_3)_2$	2,5-$(OC_2H_5)_2$	2,5-$(OH)_2$
50% alc.	0.529	0.474	0.434
Aq. soln.	.514[a]	.462	.441

[a] From the results of LaMer and Baker, Ref. 3 d.

When it is recalled that the same relationship exists between the *m*- and *p*-dichloroquinones (previous paper) one is led to suspect that the potential of the *meta* compound is always higher than that of the *para* isomer regardless of the substituents. Whether or not this will be found to be generally true, it suggests the existence of other similarities between otherwise dissimilar groups. And, indeed, just as the potential of *p*-dichloroquinone is lower than would be predicted if the effect of the chlorine atom were additive, so the potential of *p*-dihydroxy-quinone is much lower than that expected from a consideration of the monohydroxy derivative. This is in contrast to the methyl derivatives, in which the effect of *para* disubstitution is just twice that of mono substitution (previous paper).

III. The Effect of Chlorine and Bromine

Bromo-benzoquinone.—Bromo-hydro-quinone was oxidized in ether solution with silver oxide, a 76% yield of the bromoquinone being obtained. The product was unstable, as Sarauw[31] has observed, but when crystallized from petroleum ether it separates in the form of large, reddish-yellow crystals, melting at 56.5°, which can be kept for several weeks.

2-Chloro-1,4-naphthoquinone.—Naphthoquinone was converted into the dichloride which on treatment with sodium acetate lost hydrogen chloride and formed the monochloro-naphthoquinone.[32] The substance

[31] Sarauw, *Ann.*, **209**, 105 (1881).

[32] Zincke and Schmidt, *Ber.*, **27**, 2757 (1894).

was obtained as light yellow needles after recrystallizing it from alcohol, and melted at 111°.

2-Bromo-1,4-naphthoquinone.—This was prepared from naphthoquinone dibromide by Zincke's method. It crystallized from alcohol in yellow plates melting at 130.5°.

2,3-Dichloro-1,4-naphthoquinone.—The convenient method of preparing this compound from α-naphthol recently developed by Ullmann and Ettisch[33] gave an 83% yield of crude quinone. The material was purified by crystallization from glacial acetic acid after passing a little chlorine into the hot solution or after adding some chromic acid. A final crystallization from alcohol gave a product melting at 188.5° (192.5° corr.).

Tetrachloro-*o*-benzoquinone.—This was prepared from tetrachloropyrocatechol by oxidation with nitric acid according to the directions of Jackson and Carleton;[34] it melted at 130°.

Tetrabromo-*o*-benzoquinone.—This compound was prepared from tetrabromo-pyrocatechol according to the directions of Jackson and Shaffer;[35] after recrystallization from glacial acetic acid it melted at 150°.

1-Chloro-anthraquinone.—A sample of commercial material was recrystallized from benzene, melted at 157.5° (161° corr.), and was identical with a sample prepared by passing chlorine into a dil. hydrochloric acid solution of anthraquinone-α-sulfonic acid at the boiling point.[36]

2-Chloro-anthraquinone.—This compound was obtained in 64% yield by adding sodium chlorate to a boiling solution of anthraquinone-β-sulfonic acid; after crystallization from benzene it melted at 206–207°.

2,7-Dichloro-anthraquinone.—A commercial material was recrystallized from benzene; it melted at 212°.

2-Methyl-anthraquinone.—This compound was prepared from *p*-toluyl-*o*-benzoic acid by condensation with fuming sulfuric acid. After crystallization from alcohol it was obtained in the form of long, silken needles, almost colorless and melting at 173.5° (176° corr.).

2-Chloromethyl-anthraquinone.—Although it has been claimed in the patent literature that this compound may be obtained by treating β-methylanthraquinone with chlorine at the melting point[37] or with sulfuryl chloride at 160°,[37] and although this is one of a series of derivatives whose conversion into anthraflavone has been patented,[38] no description of the compound appears to have been given.

[33] Ullmann and Ettisch, *Ber.*, **54**, 261 (1921).

[34] Jackson and Carleton, *Am. Chem. J.*, **39**, 496 (1908).

[35] Jackson and Shaffer, *ibid.*, **34**, 461 (1905); see also *ibid.*, **39**, 83 (1908).

[36] Ger. pat., 205,195.

[37] Ger. pat., 216,715.

[38] Ger. pat., 199,756.

Since ω-bromomethyl-anthraquinones are conveniently prepared by brominating methyl-anthraquinone in nitrobenzene solution,[39] the same solvent might be expected to be suitable for chlorination. However, the treatment of β-methyl-anthraquinone in nitrobenzene solution at 160° with chlorine has been patented[40] as a method of preparing anthraquinone-β-carboxylic acid. Since this oxidation can be brought about by means of the oxides of nitrogen alone in an indifferent solvent,[41] it is presumably oxides of nitrogen, formed from nitrobenzene and chlorine, which bring about the oxidation in this reaction.

In order to test these statements, β-methyl-anthraquinone (7 g.) was dissolved in 20 cc. of boiling nitrobenzene in a brominating flask and treated with a slow stream of chlorine for seven hours in the sunlight. The reaction mixture, from which a few crystals separated on cooling, was treated with two volumes of alcohol and the precipitate (about 2 g.) filtered off. This precipitate was dissolved in hot, dilute ammonia solution, precipitated with acid, filtered off and dried. It was chlorine-free and was found by a mixed-melting-point determination to be anthraquinone-β-carboxylic acid. The filtrate was concentrated by distilling the solvent in a vacuum and the residue was dissolved in and recrystallized from alcohol. It melted at 163–164° and was found to be β-monochloro-methyl-anthraquinone. Thus this reaction is capable of giving two products.

On chlorinating β-methyl-anthraquinone in an indifferent solvent (chlorobenzene), no oxidation occurred but the reaction could not always be stopped at just the stage desired and a mixture of the starting material, the mono- and the di-chloro compounds usually resulted. Since the monochloro compound is much more soluble in alcohol than the dichloro derivative, separation of these two is not difficult. Consequently, β-methyl-anthraquinone was dissolved in the least amount of boiling chlorobenzene in a brominating flask and treated with chlorine until a test portion, dissolved in alcohol and allowed to crystallize, gave a product melting above 160°. The main product was then washed out with a little alcohol, filtered off, and fractionally crystallized from alcohol, and the lower-melting fraction crystallized from alcohol-benzene and from benzene until the melting point remained constant at 164.5°.

Anal. Calc. for $C_{15}H_9O_2Cl$: Cl, 13.82. Found: Cl, 13.57.

β-Chloromethyl-anthraquinone forms pale yellow, almost colorless, shining plates, soluble in alcohol, very soluble in benzene, and melting at 164.5°. Contrary to the statement[42] that all ω-halogenated methyl-anthraquinones are decomposed by sulfuric acid while nuclear halogenated

[39] Ullmann and Klingenberg, *Ber.*, **46**, 717 (1913).

[40] Ger. pat., 259,365.

[41] Ger. pat., 250,742.

[42] Ger. pat., 269,249.

derivatives are stable, it may be recovered unchanged after being heated in concd. sulfuric acid for one hour on the steam-bath. The solution may be heated to 165° before hydrogen chloride is given off and at a temperature much above this, deep-seated decomposition begins.

The position of the halogen atom in this compound was shown by the fact that, on further chlorination, it passed into the known ω-dichloromethyl-anthraquinone which was fully identified.

TABLE VI

NORMAL REDUCTION POTENTIALS AT 25° IN VOLTS

	Aqueous solution		50% alc. sol.		95% alc. sol.	
	0.1 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl
Chloro-benzoquinone[a]	0.713	0.710	0.736	0.736	...	...
Bromo-benzoquinone	.714	.710	.734	.735	...	...
	.714	.710	.734	.734	...	...
2-Chloro-1,4-naphthoquinone	...	...	...	...	0.508	0.512
	...	...	...	...	.509	.510
2-Bromo-1,4-naphthoquinone	...	...	...	...	.506	.511
	...	...	...	...	.507	.512
Tetrachloro-*o*-benzoquinone	.827	.829	.876	.870	...	...
	.827	.827	.876	.870	...	...
Tetrabromo-*o*-benzoquinone	.822	.817	.872	.870	...	...
	.823	.817	.873	.868	...	...
2,3-Dichloro-1,4-naphthoquinone	...	...	...	...	.499	.494
	...	...	...	...	.498	.501
1-Chloro-anthraquinone	...	...	...	...	.175	.173
	...	...	...	...	.173	.178
	...	...	...	...	.174	.174
	...	...	...	...	.174	.172
2-Chloro-anthraquinone	...	...	...	...	.200	.203
	...	...	...	...	.202	.200
2,7-Dichloro-anthraquinone	...	...	...	...	.226	.222
	...	...	...	...	.224	.231
2-Methyl-anthraquinone	...	...	...	...	.150	.150
	...	...	...	...	.152	.150
2-Chloromethyl-anthraquinone	...	...	...	...	.175	.177
	...	...	...	...	.183	.182

[a] From previously published results, Ref. 1.

Discussion

LaMer and Baker[3d] found the reduction potentials of chloroquinone and bromoquinone in 0.2 *N* hydrochloric acid to be 0.7125 and 0.7151, respectively. The difference of 2.6 mv. between these figures and the direction of the difference, representing the bromo substituent as being the more "negative" in contradiction to the usual relations between the halogens, was regarded by these authors as significant. Considering the known variations of potentials with solvent conditions there is little justification for supposing that any conclusion is established by measure-

ments made on one compound in but one solution, especially when the observed difference between the potentials of the compounds compared is so very slight. In order to test further the relative effect of chlorine and bromine on the reduction potentials of quinones, the above measurements have been made on a variety of chloro- and bromoquinones in addition to the measurements with chloroquinone already reported.

Concerning the two compounds investigated by LaMer and Baker, their statement that bromoquinone has the higher potential in dil. hydrochloric acid is confirmed. On the other hand, the two are identical in more concentrated aqueous acid while, in alcoholic solution, the potential of chloroquinone is the higher of the two. Taking the monosubstituted compounds as a whole it may be said that the difference between the chloro and bromo derivatives is in some cases slightly greater than the experimental error and it may be either positive or negative in sign for the same pair of compounds. At the present stage of our knowledge of reduction potentials such slight and irregular variations are meaningless, and we may conclude that *within the limits of the significance of such data chloro and bromo monosubstitution derivatives are identical in potential.*

These data are interesting in another respect. It has been pointed out in comparing quinone and chloroquinone that the effect of the chlorine atom on the potential appears to be 13 millivolts if the comparison is made in aqueous solution and 25 millivolts if alcohol is taken as a reference solvent. It is reassuring to find that this same, rather erratic, fluctuation occurs for the bromine atom. It is somewhat unusual that a reduction potential should increase with an increase in the acid concentration as is observed for chloro-naphthoquinone. However, bromonaphthoquinone exhibits the same behavior.

The most exacting test of the point in question is to be found in comparing the *o*-benzoquinones in Table VI. Here the benzo-quinonoid nucleus is completely surrounded by halogen atoms and in the last compound the proportion of bromine is 75%. Moreover the change in potential in passing from aqueous to alcoholic solution is the most extensive yet observed. In view of these facts it is perhaps extraordinary that the potentials of the chloro and bromo compounds show such small differences as they do. These differences amount to 3.5, 1, 4.5 and 10 millivolts in the four solvents investigated, the chloro compound always being of higher potential. It is difficult to decide whether these differences are significant or not.

On comparing the effect of a substituted chlorine atom on the potential of benzoquinone and of α-naphthoquinone it is found that, if all pairs of measurements made under comparable conditions be considered, the average increase in potential is 19 millivolts for benzoquinone and 17 millivolts for α-naphthoquinone. Like the hydroxyl group, the chlorine

atom produces the same effect when attached to the quinonoid nucleus of each of these compounds. This analogy is further brought out by comparing the *o*-dichloroquinones of the benzene and naphthalene series. In the first case[43] the average increase in potential due to the two chlorine atoms is 11 mv. while with 2,3-dichloro-naphthoquinone it amounts to 5 mv. The introduction of the second chlorine atom into benzoquinone involves a decrease in potential of 9 mv. while with naphthoquinone a decrease is again observed, the potential falling 12 mv.

In considering the anthraquinones it should be borne in mind that the experimental difficulties in making these determinations, in particular the low potentials and slight solubilities encountered, tend to decrease the accuracy of the results. The extent to which this is true, however, depends so greatly on the nature of the compound in question that no general statement of the probable error can be made. As an inspection of the tables will show this differs considerably from compound to compound. Since problems are conceivable which might be solved by the use of a variety of different substituents, it may be well to state that in the anthraquinone series the most successful results were obtained with the sulfonic acids, the 2-methyl derivative, anthraquinone-2-carboxylic acid and its esters, and 1-chloro-anthraquinone. With the other chloro derivatives the end-point was less sharp, electrode equilibrium was reached slowly, and slight solubility often necessitated the use of very dilute solutions (0.001 *M*) with the attendant increase in the tendency towards slow attainment of electrode equilibrium.

This is an unfortunate situation, for the chloro-anthraquinones present a complex problem which is no more than indicated by the present data. This is evident from Table VII.

TABLE VII

INCREASE IN POTENTIAL DUE TO CHLORINE ATOM IN ANTHRAQUINONE

1-Chloro	2-Chloro	2.7-Dichloro (each)	2-Chloromethyl
Mv. 19	46	36	29

The first of the relations which appear abnormal is the fact that substitution of this atom in any position of the aromatic nucleus produces a greater

[43] On repeating the titration of 2,3-dichloro-benzoquinone subsequent to the publication of the values for π_0 of 0.739 and 0.711 for 0.5 *N* and 1.0 *N* 95% alcoholic hydrochloric acid, it was discovered that titrations made at different times and with different electrodes gave rather divergent results, though all attempts to discover the cause of this behavior were fruitless. As a result of 17 determinations the above values were revised to 0.730 and 0.719, respectively. The reported reduction potentials for this compound in aqueous solution were, however, perfectly reproducible as were all of the other published results with the possible exception of those for 2,5-dichloroquinone, for which compound we now consider the average value of 0.737 for 0.5 *N* and 1.0 *N* 95% alcoholic acid as more nearly correct than the reported values of 0.740 and 0.734, respectively. These changes do not affect our earlier conclusions.

effect than substitution in the quinonoid nucleus of benzoquinone or naphthoquinone. Secondly, of the two isomers the one in which the substituent is further from the carbonyl group has the higher reduction potential. Moreover even when the chlorine atom is substituted in the side chain which is in the beta position its effect is greater than that of the α-chloro atom.

Further investigations of halogen derivatives of anthraquinone and naphthoquinone are necessary before any very satisfactory solution of this problem can be formulated. We hope to present further data along this line at some later time and in particular to be able to obtain significant measurements with chloro-naphthoquinones having chlorine atoms in the non-quinonoid nucleus, and derivatives of benzoquinone having halogen atoms in the side chain.

IV. The Effect of the Sulfonic Acid and Carboxyl Groups

The following measurements with certain sulfonic acids of anthraquinone and naphthoquinone are supplementary to the work reported in earlier papers.

Sodium Anthraquinone-2-sulfonate.—This material was kindly furnished by Dr. E. K. Bolton of E. I. Du Pont de Nemours and Company. It was further identified by conversion into 2-chloro-anthraquinone, the sulfochloride and sulfonamide.

Potassium 1,2-Naphthoquinone-4-sulfonate.—This compound was prepared from 1-amino-2-naphthol-4-sulfonic acid according to the directions of Böniger.[44] The salt crystallized from water in bright orange crystals.

Potassium-1,2-naphthoquinone-4,6-disulfonate.—1-Amino-2-naphthol-4-sulfonic acid was converted into the nitroso compound which was reduced and sulfonated by adding hydrochloric acid to its solution in sodium bisulfite. The resulting 1-amino-2,4,6-naphthol-disulfonic acid was oxidized with nitric acid to the quinone which was isolated as the potassium salt and crystallized from hot water.[44]

Anthraquinone-2-carboxylic Acid.—Oxidation of β-methyl-anthraquinone with chromic acid in glacial acetic acid gave a 25% yield of the acid, 57% of unchanged material being recovered. After re-precipitation from very dilute aqueous ammonia, the acid melted at 282° (291° corr.).

Methyl Anthraquinone-2-carboxylate.—This compound was prepared by esterifying the acid in the usual manner. It was re-crystallized from alcohol and formed faintly yellow needles melting at 165°.

Anal. Calc. for $C_{16}H_{10}O_4$: C, 72.2; H, 3.8. Found: C, 71.8; H, 4.0.

Ethyl Anthraquinone-2-carboxylate.—This compound was prepared by esterifying the corresponding acid.[45] It melted at 145° after crystallization.

[44] Böniger, *Ber.*, **27**, 3050 (1894).

[45] *Ber.*, **17**, 888 (1884).

TABLE VIII

NORMAL REDUCTION POTENTIALS AT 25° IN VOLTS

	Aqueous soln.		50% alc. soln.		95% alc. soln.	
	0.1 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl	0.5 *N* HCl	1.0 *N* HCl
Anthraquinone-1-sulfonic acid[a]	0.195	...	...	...	...	...
Anthraquinone-1,5-disulfonic acid[a]	.239	...	...	...	...	...
Anthraquinone-1,8-disulfonic acid[a]	.206	...	...	...	...	...
Anthraquinone-2-sulfonic acid[a]	.187	...	0.197	0.197	...	...
	...	...	.198	.195	...	...
Anthraquinone-2,6-disulfonic acid[a]	.228	...	...	...	...	...
Anthraquinone-2,7-disulfonic acid[a]	.229	...	...	...	...	...
1,4-Naphthoquinone-2-sulfonic acid[b]	.534	.532	.558	...	0.552	...
1,2-Naphthoquinone-4-sulfonic acid	.629	.628	.635	.636	...	...
	.627	.628	.636	.637	...	...
1,2-Naphthoquinone-4,6-disulfonic acid	.661	.663	.652	.660	...	...
	.659	.661	.652	.658	...	...
Anthraquinone-2-carboxylic acid	...	...	...	...	.208	.213
	...	...	...	...	.213	.213
Methyl anthraquinone-2-carboxylate	...	...	...	...	.222	.221
	...	...	...	...	.225	.220
Ethyl anthraquinone-2-carboxylate	...	...	...	...	.222	.221
	...	...	...	...	.221	.225

[a] The measurements in aqueous solution have been reported in an earlier paper, Ref. 3c.

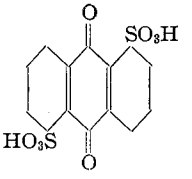
[b] From previously published results, Ref. 1 b.

Discussion

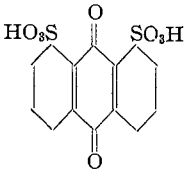
The present data, together with average values for compounds studied in previous papers, are summarized in Table VIII. It will be observed that the results for the carbethoxy and carbomethoxy compounds are identical, the potential being 67 mv. higher than for anthraquinone. The effect of the carboxyl group is a little less, causing an increase of only 57 mv. These facts are in accord with the experiments with alkoxy and hydroxy quinones where it was found that the methoxy and ethoxy group were equivalent but that the hydroxyl group lowered the potential more than the alkoxy group. If the effects of the COOH or COOR group are an algebraic sum of the effects of the $C{=}O$ and OH or OR groups, respectively, we should expect the substitution of OR by OH to lower the potential just as is found.

Since the potential of anthraquinone (0.155) is known only in 95% alcohol, it is not strictly comparable with that of the β-sulfonic acid derivative. Such a comparison indicates, however, that this group increases the reduction potential by 42 mv., a value in good agreement with that obtained for the introduction of a second group in the beta position, which is 42 mv. and 41 mv., respectively, for the 2,6 and 2,7 isomers. On the other hand, the effect of substituting a second group in the alpha

position (V) is slightly greater (44 mv.), while the potential of anthraquinone-α-sulfonic acid itself is 8 mv. higher than that of the beta isomer. This difference is probably attributable to the difference in proximity of the substituent to the carbonyl group.



V



VI

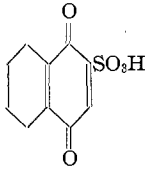
While these relationships appear to be quite regular, an abnormal behavior is encountered in the 1,8-disulfonate (VI). Here the substitution of a second sulfonic acid group has increased the potential by only 11 mv. or, judging from the other results, the effect of each of the two groups is only 27 mv. as compared with the normal value of 44 mv. Perhaps this irregularity is connected with the fact that of the disulfonates the 1,8 isomer is the only one in which the substituent groups are somewhat near to each other in the molecule.

The effect of the sulfonic acid group when attached to the quinonoid nucleus of α- and β-naphthoquinones may be summarized as follows.

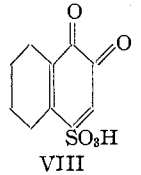
INCREASE IN POTENTIAL DUE TO SULFONIC ACID GROUP

	In aq. soln. Mv.	In alc. soln. Mv.
α-Naphthoquinone	63	70
β-Naphthoquinone	81	57

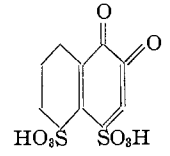
Though the substituent in Compounds VII and VIII is somewhat differently situated with regard to the carbonyl groups, it is attached directly to a quinonoid nucleus in each case and the effect appears to be about the same. The average value of 68 mv. is higher than the normal value of 44 mv. for the substitution of the sulfonic acid group in the α-position



VII



VIII



IX

in anthraquinone. This is in accord with the difference in the effect of the hydroxyl group when substituted in the quinonoid and in the aromatic nucleus except that in the present case the difference is much less pronounced.

Regarding the disulfonated naphthoquinone (IX), if its potential be compared with that of the monosubstituted compound (VIII) it is found

that the second group in the 6-position has caused an additional increase in potential of only 15 to 33 mv. By analogy with the anthraquinones an increase of about 42 mv. might be expected, but this lower value is found.

We wish to acknowledge our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for two grants which have greatly aided this work, and to Dr. E. K. Bolton of E. I. du Pont de Nemours and Company for generously supplying us with a number of compounds used in this investigation.

Summary

1. The reduction potentials of a variety of derivatives of benzoquinone, naphthoquinone and anthraquinone have been measured in alcoholic solution. The reduction potential as determined is a direct measure of the free energy of reduction of the quinone by hydrogen in the particular solvent employed. A few of the quinones were sufficiently soluble in water to permit measurements to be made also in aqueous solution.

2. A study of the unsubstituted quinones showed that the reduction potential of *o*-quinones is considerably higher than that of the corresponding *p*-quinones; in the case of unsubstituted benzoquinones and naphthoquinones the difference appears to be nearly constant. The attachment of a phenylene group to a quinonoid nucleus (either *ortho* or *para*) lowers the reduction potential, this lowering being about 220 mv. for one phenylene group, but much greater for a second attached to a *p*-quinone and much less for a second attached to an *o*-quinone. The phenylene group is more effective than two alkyl groups.

3. The introduction of a hydroxyl group into the molecule lowers the reduction potential, the effect being greatest when the group is directly attached to the quinonoid nucleus; the methoxy and ethoxy group are nearly identical in their influence which is a little less than that of the hydroxyl group. The results obtained with certain so-called hydroxy-*p*-quinones give additional support to the *p*-quinonoid structure for these substances.

4. The effects of chlorine and bromine are identical within the limits of the significance of the data. Substitution of hydrogen by one chlorine atom increases the potential both in the benzoquinone, naphthoquinone and anthraquinone series; no satisfactory correlation can be made as yet between the position of the substituent atom and the magnitude of its effect.

5. Experiments with derivatives of anthraquinone and naphthoquinone show that the carboxyl group, the carbalkoxyl group and the sulfonic acid group when introduced into the molecule all raise the potential greatly.

CAMBRIDGE 38, MASSACHUSETTS