

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE POTENTIALS AND THE DECOMPOSITION REACTIONS OF ORTHO QUINONES IN ACID SOLUTION

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With the development of a method of measuring accurately the potentials of unstable oxidation-reduction systems,<sup>1a</sup> it seemed desirable to apply this new method to a re-examination of some of the systems for which the reported values are in the nature of approximations. It is particularly difficult to characterize the systems from the ortho quinones by simple electrometric titration, because of the great instability of the oxidants. We have thus made use of the method of discontinuous titration in a further study of the ortho quinones derived from benzene, naphthalene and phenanthrene, and we have attempted wherever possible to establish the course of the reactions leading to the destruction of the oxidant.

### $\beta$ -Naphthoquinone

The instability of dilute solutions of this substance in alcoholic hydrochloric acid was noted by Conant and Fieser,<sup>2</sup> who reported the results of titrations of the oxidant and some preliminary observations concerning one of the decomposition products. In extending these results we first established the normal oxidation-reduction potential of the system by the discontinuous titration of pure  $\beta$ -naphthohydroquinone, with the results given in Table I. Solutions of the material were treated with varying quantities of an oxidizing agent and the initial potential in each experiment

TABLE I

DISCONTINUOUS TITRATION OF  $\beta$ -NAPHTHOHYDROQUINONE (25°)

0.0003 mol. eq. in 220 cc. of 70% alcohol, 1 *M* in HCl and 0.2 *M* in LiCl, required 34.2 cc. of  $K_2Mo(CN)_8$  solution.

Molybdi- cyanide soln., cc.	Initial potential, v.	Fraction of Mo soln. un- reacted ( <i>m</i> )	$\frac{[Oxid]}{[Red]}$	Normal potential $E_0$ , v.	Velocity constant, $\Delta E/t$
8	0.5623	0.008	0.302	0.5776	0.0003
10	.5653	.009	.408	.5768	.0003
12	.5673	.010	.532	.5754	.0003
14	.5705	.011	.680	.5755	.0004
16	.5732	.012	.859	.5751	.0003
18	.5764	.013	1.083	.5754	.0003
				Average .5760	

was established by extrapolation of the time-potential curve. The oxidizing agent employed was potassium molybdicyanide. With this reagent the potentials of the organic and inorganic systems are so close together

<sup>1</sup> This communication is in partial fulfilment of the requirements for the degree of Master of Arts at Radcliffe College.

<sup>1a</sup> Fieser, *THIS JOURNAL*, **52**, 4915 (1930).

<sup>2</sup> Conant and Fieser, *ibid.*, **46**, 1858 (1924).

that the oxidation of the hydroquinone does not go to completion and in calculating the correct ratio of oxidant to reductant (Column 4) the amount of unreacted reagent present (Column 3) must be taken into consideration, as explained in the first paper cited. On account of this overlapping in potentials, no end-point can be obtained in acid solution. The  $\beta$ -naphtho-hydroquinone solution was thus compared with the molybdicyanide by titration in a neutral alcoholic buffer solution, for here the potential of the inorganic system is considerably higher than that of the other system.  $\beta$ -Naphthoquinone was found to be perfectly stable in this solution and we were thus able to use the continuous method of titration.

The velocity constants given in the last column of the table were calculated for a monomolecular reaction; they are numerically equal to the decrease in potential per minute. It may be noted that the decomposition of the oxidant was much slower than in the earlier work in which impure  $\beta$ -naphthoquinone was employed.

In order to study the products of the decomposition of  $\beta$ -naphthoquinone, we dissolved a quantity of the pure quinone in the alcoholic buffer solution and allowed the decomposition reaction to proceed to completion (about three hours). This solution was found to contain the oxidant of a stable system and the reductant of another, unstable system. The oxidant could be titrated with titanous chloride, but the titration of the reductant presented a more difficult problem. Some indication of the normal potential of the unstable system was furnished by rapid titrations of the reductant with tetrabromo-*o*-benzoquinone. The value found (0.576 v.) was very close to that of the  $\beta$ -naphthoquinone system (0.5760 v.), and the velocity of decomposition was identical with that noted. It was not possible, however, to carry out a discontinuous titration with molybdicyanide in just the manner described above, for on attempting to determine the end-point in neutral solution it was found that this oxidizing agent attacks the oxidant of the other stable system present. The same disturbing reaction prevented the use of ceric sulfate, which has a high enough potential to give an end-point in acid solution. Tetrabromo-*o*-benzoquinone is free from this objection, and has a sufficiently high potential, but the compound is not stable enough in solution to permit its use in the time-consuming discontinuous titration.

In order to make an evaluation of the normal potential which would be more reliable than that furnished by rapid titration, the following expedient was adopted. Portions of the solution of the decomposition products were treated with varying amounts of molybdicyanide solution and the initial potentials, velocity constants and the fraction of unreacted molybdicyanide ( $m$ ) were obtained in the usual manner (Table II). The approximate value for the normal potential of 0.576 v. was then used to calculate from these results values for the ratio [Oxid]/[Red], and from these figures

TABLE II

TITRATION OF THE REDUCTANT FORMED IN THE DECOMPOSITION OF  $\beta$ -NAPHTHOQUINONE<sup>a</sup>

Molybdi- cyanide soln., cc.	Initial potential, v.	<i>m</i>	$\frac{[\text{Oxid}]}{[\text{Red}]}$	End- point, cc.	Normal potential, $E_0$ , v.	Velocity constant, $\Delta E/t$
4	0.5612	0.007	0.311	16.7	0.5762	0.0003
6	.5694	.011	.589	15.9	.5769	.0003
8	.5745	.013	.876	16.9	.5759	.0003
10	.5806	.016	1.41	16.8	.5761	.0004
12	.5863	.019	2.19	17.1	.5751	.0004
				Average 16.7	Av. .5760	

<sup>a</sup> Solvent: See Table I.

values were obtained for the theoretical end-point of oxidation. The average end-point was then used to calculate values for the normal potential (next to last column). The constancy of the results, and the agreement with the approximate value, justifies this interpretation.

The normal potential found is the same as that for  $\beta$ -naphthoquinone (0.5760 v.), but it is also not far from the potential reported<sup>2</sup> for a known product of the acid decomposition of this quinone, namely, dinaphthyl-diquinhydrone. A special study of this compound (see below) showed that the potential is indeed close to that found here, but that the compound is perfectly stable under the conditions of the experiment and that it is thus excluded as a possible product. On the other hand, a comparison of the values given in Tables I and II for both the normal potentials and the velocity constants leaves little doubt but that the reductant produced in the decomposition of  $\beta$ -naphthoquinone is  $\beta$ -naphthohydroquinone.

There remained the identification of the oxidant which is produced, and the determination of the relative amounts of the two decomposition products. The plan of attack was to reduce the oxidant and then to titrate in succession the reductant of each system with the same oxidizing agent. The reagent chosen was tetrabromo-*o*-benzoquinone. In each of the experiments listed in Table III a 20-cc. portion of the solution of the decomposition products was first titrated to an end-point with titanous chloride. This gave the value for the normal potential of the stable

TABLE III

TITRATION OF THE TWO DECOMPOSITION PRODUCTS OF  $\beta$ -NAPHTHOQUINONE<sup>a</sup>

Stable system		Unstable system			Molecular ratio of the two de- composition products: Col. 6/Col. 3	
Titration of oxidant with $\text{TiCl}_3$ , $E_0$ , v.	Titration of re- ductant with $\text{C}_6\text{Br}_4\text{O}_2$ , $E_0$ , v.	End-point, cc.	$\text{C}_6\text{Br}_4\text{O}_2$ soln. added, cc.	Initial potential, v.		
0.3560	0.3568	24.5	4	0.5547	25.0	1.02
.3570	.3568	25.4	8	.5660	25.5	1.00
.3558	.3572	23.4	10	.5722	23.5	1.00
.3572	.3572	29.6	10	.5674	29.8	1.01
.3562	.3569	24.2	12	.5755	24.6	1.02
.3568	.3568	23.1	16	.5859	23.3	1.01
.3562	.3572	23.7	20	.5952	24.5	1.03
Av. .3565	Av. .3569					Av. 1.01

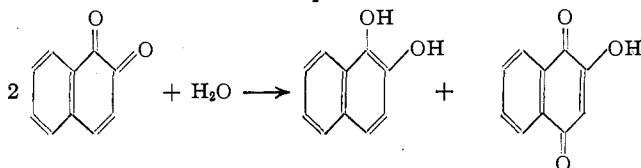
<sup>a</sup> Solvent: See Table I.

system listed in Column 1 of the table. A somewhat more reliable evaluation of the same potential was obtained when the reductant was then titrated with tetrabromo-*o*-benzoquinone, Column 2. At the conclusion of this titration a certain quantity of the oxidizing agent was quickly added and the potential was followed and extrapolated to zero time, giving the initial potential of the unstable system (Column 5). From this potential and the normal potential of the system the amount of oxidizing agent required for complete oxidation was calculated (Column 6). It is obvious that the amount of reagent consumed in the titration of the reductant of the stable system (Column 3) gives a measure of the quantity of the oxidant of that system which was originally present. It will be observed that the end-point of the titration is not the same in each experiment. This is because solutions of tetrabromo-*o*-benzoquinone in the alcoholic buffer are not altogether stable. A fresh solution was made up for each experiment, and in warming the solvent to effect dissolution, a certain variable quantity of the reagent was always destroyed. While separate experiments are thus not comparable, the titer of the quinone solution does not change appreciably in the short amount of time required to carry out the two separate titrations in each solution and the two end-points are strictly comparable. A comparison of the figures in Columns 3 and 6 thus gives a measure of the relative amounts of the two decomposition products formed, and this is indicated in the last column of the table. It is clear that the substances are produced in equimolecular proportion.

The potential of the more stable of the two systems (av., 0.3567 v.) suggests that the oxidant in question is 2-hydroxy-1,4-naphthoquinone. The value of 0.356 v. has been reported<sup>2</sup> for this compound, and we have found the average value of 0.3570 v. from a further series of determinations.<sup>3</sup> Any doubt as to the identity of the substance was dispelled by the isolation of hydroxynaphthoquinone from the solution.

### The Mechanism of the Decomposition

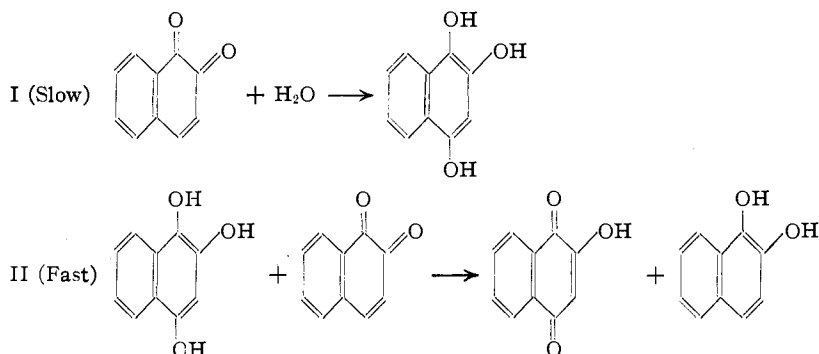
The above results show that  $\beta$ -naphthoquinone in dilute alcoholic solution decomposes into equimolecular amounts of  $\beta$ -naphthohydroquinone and 2-hydroxy-1,4-naphthoquinone. While the final result thus represents a disproportionation, there is further evidence which shows that the reaction does not follow the simple course:



<sup>3</sup> The quinone was hydrogenated and titrated with potassium molybdicyanide. Individual results agreed within 0.1 mv.

Such a reaction, in an aqueous-alcoholic medium, would be bimolecular. The reaction velocity measurements summarized in Tables I and II show, on the other hand, that the reaction is strictly monomolecular. The values obtained for the monomolecular constant agreed well in each individual experiment, as well as when the concentration of  $\beta$ -naphthoquinone was varied. A mechanism which postulates the intermediate formation of dinaphthylidiquinhydrone is likewise excluded, for this would be a bimolecular reaction.

The only mechanism which fits all of the facts is that  $\beta$ -naphthoquinone first adds a molecule of water as in I, and that the trihydroxynaphthalene



thus formed is oxidized at once by unchanged  $\beta$ -naphthoquinone, as in II. Oxidation-reduction reactions of the type of II are extremely rapid, and the speed of the first reaction thus controls the velocity of decomposition. Hydration of the ketonic substance is thus responsible for the final disproportionation in the present case. It may be noted that our results do not preclude the possibility that it is alcohol rather than water which adds to the quinone. If this reaction took place, it would lead to the formation of 4-ethoxy-1,2-naphthoquinone, a substance which would be hydrolyzed and isomerized to give 2-hydroxy-1,4-naphthoquinone under the conditions of the experiment.<sup>4</sup>

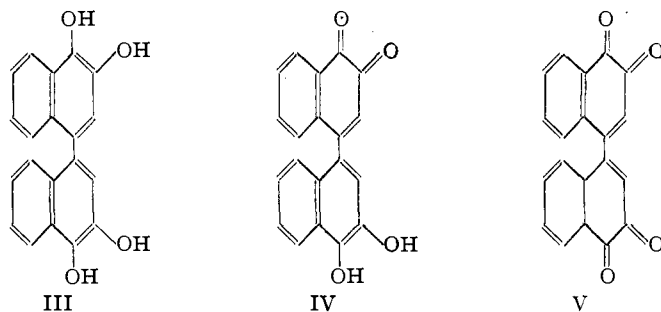
It is a well-known fact that  $\beta$ -naphthoquinone can be converted almost quantitatively into dinaphthylidiquinhydrone by the action of mineral acids, and yet no trace of this material was detected in the present experiments. The difference is easily accounted for. When a small amount of  $\beta$ -naphthoquinone is dissolved in a large amount of alcoholic acid, as in our experiments, the monomolecular reaction consumes the material. The reaction is slow and it is not accelerated by increasing the concentration of the reactant. Thus when a large amount of the quinone is stirred into a relatively small quantity of acid, the speed of the monomolecular reaction remains unchanged, while the condensation of two molecules of the quinone

<sup>4</sup> Fieser, THIS JOURNAL, 48, 2922 (1926).

to give dinaphthylidiquinhydrone, being a bimolecular reaction, is greatly accelerated.

### Dinaphthylidiquinhydrone (IV) and Dinaphthylidiquinone (V)

Since the compounds named are ortho quinones, they are appropriately included in this study. When dinaphthylidiquinhydrone, III, was titrated in alcoholic acid solution with ceric sulfate, a curve was obtained having



two distinct inflections, as shown in Fig. 1. The reactants present appeared to be perfectly stable and no drift in the potentials was observed

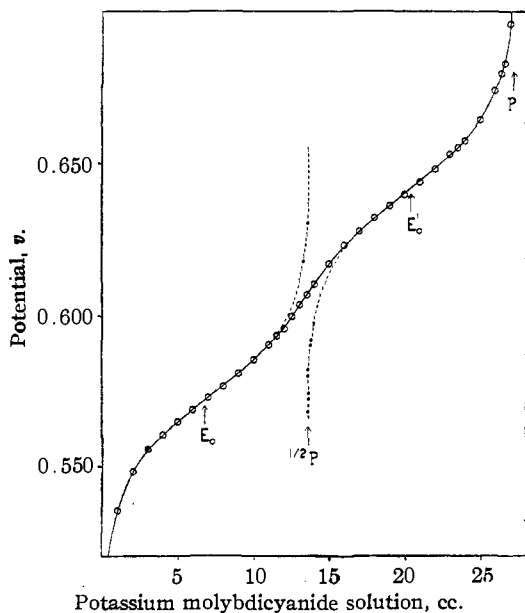


Fig. 1.—The titration of dinaphthylidiquinhydrone.

except at the very end of the titration. This drift is attributable to an oxidation of the solvent alcohol by ceric sulfate when an excess of the latter is present. The lower half of the curve refers to the potentials of the system formed by the reductant, III, and the monoquinone, IV, for a similar curve was obtained by the titration of the latter substance with titanous chloride. The upper half of the double curve obviously refers to the equilibrium between the monoquinone and the diquinone, V. The complete curve has a distinct end-point, and the "end-point" of each single curve can be taken as half of this value; but it is not permissible to take as the normal potentials of the two systems the mid-points of the two curves, for the normal potentials lie so close together that at almost

any potential level all three of the organic substances are present in finite concentration. Such approximate values for the normal potentials were, however, employed in calculating more reliable figures in the following manner. From each of the potentials of the lower system, and the approximate normal potential of the upper system, we calculated the amount of diquinone present, and thus the true ratio of the monoquinone to its reductant. This permitted a calculation of the normal potential of the lower system from each observation. The process was then reversed, and the normal potential of the upper system was calculated. A summary of a few calculations from the results which are reported graphically in Fig. 1 is given in Table IV. In Fig. 1 the dotted lines represent the theoretical

TABLE IV  
TITRATION OF DINAPHTHYLDIHYDROQUINONE (25°)

Solvent: 70% alcohol, 1 *M* in HCl, 0.2 *M* in LiCl. End-point of complete oxidation = 27.2 cc. of ceric sulfate solution.

Monoquinone system				Diquinone system			
Ceric sulfate soln., cc.	Potential, v.	Fraction, <i>m</i>	Normal potential, v.	Ceric sulfate soln., cc.	Potential, v.	Fraction, <i>m</i>	Normal potential, v.
2	0.5483	0.001	0.5709	16	0.6231	0.018	0.6431
4	.5610	.002	.5723	18	.6321	.009	.6416
6	.5693	.003	.5724	20	.6397	.006	.6413
8	.5771	.005	.5727	22	.6480	.003	.6420
10	.5857	.012	.5731	24	.6573	.002	.6423
		Av.	.5723			Av.	.6420

potentials of the two systems if each were free to function independently; it is obvious that the experimental curve is the resultant of these two.

### 3,4-Phenanthrenequinone

The normal potential of the unstable system formed by morphol and its oxidation product was determined in exactly the same manner as in the case of  $\beta$ -naphthohydroquinone. The explanation given of Table I thus applies equally well to the results listed in Table V. The normal potential

TABLE V  
DISCONTINUOUS TITRATION OF MORPHOL (25°)

0.0003 Mol. eq. in 220 cc. of 70% alcohol, 0.5 *M* in HCl and 0.2 *M* in LiCl, required 25.2 cc. of  $K_2Mo(CN)_6$  solution

Molybdi-cyanide soln., cc.	Initial potential, v.	Fraction of Mo soln. unreacted ( <i>m</i> )	$\frac{[Oxid]}{[Red]}$	Normal potential, v.	Velocity const., $\Delta E/t$
2	0.5906	0.035	0.083	0.6227	0.0003
4	.6007	.051	.177	.6228	.0003
6	.6055	.060	.289	.6214	.0003
8	.6093	.069	.419	.6205	.0003
10	.6140	.082	.573	.6211	.0003
12	.6175	.094	.759	.6208	.0003
14	.6212	.105	.989	.6213	.0003
				Av.	.6215

of this system is so close to that of the molybdicyanide system (0.6760 v.) that at the mid-point of the titration as much as 10% of the molybdicyanide fails to react and remains in the equilibrium mixture. The correction which must be applied to give the true ratio of organic oxidant to reductant is thus large and there is more uncertainty about the value found for the normal potential than in the previous cases studied. In order to obtain the most reliable results possible, we thus confined our experiments to measurements at the lower potentials.

The decomposition products of 3,4-phenanthrenequinone were studied by the method described in connection with Table III, above, and the results are included in Table VI. In the present case it was found that when the oxidant of the stable system was titrated with titanous chloride,

TABLE VI

TITRATION OF THE TWO DECOMPOSITION PRODUCTS OF 3,4-PHENANTHRENEQUINONE<sup>a</sup>

Stable system Titration of reductant with $C_6Br_4O_2$		Unstable system			End- point calcd., cc.	Mol. ratio of decomp. products Col. 6/Col. 2	Unstable system	
$E_0$ , v.	End- point, cc.	$C_6Br_4O_2$ soln. added, cc.	Initial potential, v.	Velocity constant			[Oxid] [Red]	$E_0$ , v.
0.3976	24.7	6	0.6049	0.0003	27.8	1.12	0.280	0.6212
.3972	24.8	10	.6137	.0003	28.0	1.13	.571	.6209
.3972	26.3	12	.6162	.0003	30.1	1.14	.698	.6208
.3974	24.3	14	.6220	.0003	27.4	1.13	1.08	.6211
.3978	25.2	16	.6246	.0003	28.4	1.13	1.33	.6209
Av. .3974						Av. 1.11		Av. .6210
After an interval of 30 hours								
0.3980	24.6	10	0.6121	0.0003	30.9	1.26		

<sup>a</sup> Solvent, see Table V.

the electrode equilibrium was not good and the values thus found for the normal potential are less reliable than those obtained in the back titration and they are not reported. A further variation from the other procedure was that we employed a single series of measurements for the calculation of the normal potentials, as well as of the relative concentrations, of the two decomposition products. This was possible because all the indications were that the reductant which is produced in the decomposition is morphol. We thus used the normal potential found for the system from this compound in calculating from each initial potential for the unstable system the amount of oxidizing agent which would be required for complete oxidation. These figures are given in Column 6, and a comparison with the end-points in the titrations of the stable reductant (Col. 2) gives the relative proportion of the two decomposition products (Col. 7). Having established the ratio between the concentrations of these products, the titer of the stable reductant could be regarded as a standardization of the tetrabromo-*o*-benzoquinone solution in each experiment. The ratio of the



components of the unstable system was then calculated from the expression:  $[\text{Oxid}]/[\text{Red}] = (\text{oxid. agent added})/[(\text{titer of stable Red}) \times 1.11 - (\text{Oxid agent added})]$ . The normal potential was then calculated from these values (see last column).

The normal potential of 0.3974 v. found for the more stable of the two systems is sufficiently close to the value of 0.396 v. reported for 3-hydroxy-1,4-phenanthrenequinone<sup>5</sup> to show that one of the decomposition products of the ortho quinone under consideration is the corresponding hydroxy-*p*-quinone. The potential of the unstable system agrees well with that found for the system morphol/3,4-phenanthrenequinone. The identity of the two decomposition products thus seems clear. There is one point of difference, however, from the results obtained with  $\beta$ -naphthoquinone. The amount of the hydroquinone is in excess of the amount of the hydroxyquinone. The experiment reported in the last line serves to account for this difference. It shows that when the solution was allowed to stand for over a day, the relative proportion of the hydroxyquinone was even less than in the experiments carried out in succession on a solution prepared twelve hours in advance. It is known that 3-hydroxy-1,4-phenanthrenequinone undergoes cleavage very readily in alkaline solution,<sup>6</sup> and that it differs in this respect from hydroxynaphthoquinone. It now appears that acid cleavage is also possible. A certain quantity of the material was destroyed by cleavage during the time allowed for the completion of the decomposition reaction; a further amount had been destroyed during the thirty-hour period.

This interpretation of the experiments leads to the conclusion that the mechanism of the decomposition of this ortho quinone is exactly like that of  $\beta$ -naphthoquinone.

It is worth noting that the value found for the normal potential of the 3,4-phenanthrenequinone system by a method which involves a rather large correction factor (Table V) is well confirmed by the results of Table VI, in which no such correction was required. The value of 0.621 v. thus may be accepted as a reliable constant to replace the approximate figure of 0.615 v. reported by one of us.<sup>5</sup>

### 1,2-Phenanthrenequinone

Since there is apparently a considerable error in at least one of the earlier, admittedly approximate, determinations, it seemed advisable to reinvestigate other ortho quinone systems by the discontinuous titration method. The results for one of these are given in Table VII. The potential here is so high that potassium molybdicyanide cannot be used as a titrating agent, and tetrabromo-*o*-benzoquinone is not stable enough to use

<sup>5</sup> Fieser, *THIS JOURNAL*, 51, 3101 (1929).

<sup>6</sup> Fieser, *ibid.*, 51, 940 (1929).

TABLE VII

DISCONTINUOUS TITRATION OF 1,2-DIHYDROXY-PHENANTHRENE (25°)  
 0.0003 Mol. eq. in 220 cc. of 70% alcohol, 0.5 *M* in HCl and 0.2 *M* in LiCl, required  
 23.6 cc. of ceric sulfate solution.

Ceric sulfate soln., cc.	Initial potential, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Velocity constant	Normal potential, v.
4	0.6380	0.204	0.0003	0.6584
6	.6446	.291	.0004	.6604
8	.6514	.513	.0004	.6600
10	.6563	.735	.0005	.6602
12	.6605	1.03	.0005	.6599
14	.6651	1.46	.0006	.6603
18	.6762	3.22	.0006	.6612
				Av. .6601

in the discontinuous titration method. We consequently used ceric sulfate even though the reaction of this substance with alcohol near the end-point of the titration introduces a slight uncertainty regarding the end-point. The new value, however, is certainly more reliable than that previously reported.<sup>5</sup>

### Ortho Benzoquinone

Since ortho benzoquinone and catechol are soluble in water, this solvent was used in carrying out titrations of catechol so that ceric sulfate could be used as the oxidizing agent without any disturbing reaction of this reagent with the solvent. The results given in Table VII do not differ materially from those which have been obtained with other systems. There is a slight trend in the uncorrected values for the normal potential and it is in such a direction as to indicate an association between the oxidant and the reductant. A correction factor, *c*, was consequently applied in the manner explained before.<sup>1</sup> The velocity constants correspond well with the requirements for a monomolecular decomposition reaction. We did not investigate the reaction further, because we were unable to find a satisfactory method of establishing the normal potential of the probable decomposition product.

Conant and Fieser<sup>2</sup> carried out rapid titrations of ortho benzoquinone with titanous chloride and obtained the values of 0.786 v. and 0.776 v. for 0.1 *N* and 1 *N* hydrochloric acid solutions, respectively. The present results show that these early figures are much too low. There does appear to be some slight increase in the potential with decreasing acidity of the solution. The potential of the system in neutral buffer is probably somewhat greater than 0.794 v. In a neutral alcoholic solution a potential about ten millivolts higher would be anticipated. Thus the value of 0.810 v. which was estimated by one of us<sup>7</sup> by a purely indirect method does not appear to be very far in error.

<sup>7</sup> Fieser, *THIS JOURNAL*, 52, 5204 (1930).

TABLE VIII

DISCONTINUOUS TITRATIONS OF CATECHOL WITH CERIC SULFATE (25°)

A. Solvent: 0.5 N H <sub>2</sub> SO <sub>4</sub> ; end-point, 25.0 cc.						
Ceric sulfate soln., cc.	Initial potential, v.	[Oxid] [Red]	Correction factor, <i>c</i>	Velocity const.	Normal potential, E <sub>0</sub> uncorr.	E <sub>0</sub> corr.
3	0.7676	0.136	1.03	0.0006	0.7932	0.7941
4	.7719	.191	1.04	.0006	.7932	.7937
5	.7760	.250	1.02	.0006	.7938	.7942
6	.7790	.316	1.02	.0006	.7938	.7942
7	.7822	.388	0.98	.0007	.7943	.7947
8	.7847	.471	.97	.0006	.7943	.7946
9	.7867	.564	1.10	.0007	.7941	.7943
12	.7944	.923	..	.0008	.7943	.7943
15	.8001	1.50	1.15	.0008	.7949	.7947
			Av. 1.03			Av. .7943
B. Solvent: 1 N H <sub>2</sub> SO <sub>4</sub> ; end-point, 20.4 cc.						
4	0.7682	0.244	1.15	0.0005	0.7863	0.7894
6	.7770	.417	1.17	.0005	.7882	.7890
8	.7826	.645	1.14	.0006	.7882	.7891
10	.7888	.962	..	.0007	.7891	.7891
12	.7950	1.43	1.30	.0008	.7904	.7896
14	.7996	2.19	1.06	.0008	.7896	.7889
16	.8089	3.64	1.20	.0010	.7933	.7895
			Av. 1.17			Av. .7891

### Experimental Part

**Materials.**—From a review of the literature it seems clear that neither  $\beta$ -naphthoquinone nor its reduction product has been prepared in completely pure form. After many trial experiments we concluded that the most promising source of such samples was 1,2-diacetoxynaphthalene. In preparing this compound by the reductive acetylation of ordinary samples of  $\beta$ -naphthoquinone<sup>8</sup> a certain amount of dinaphthyldiquinhydrone was always formed and this itself underwent acetylation. The amount of the by-product may be reduced to a minimum by adding the quinone in small portions to a mixture of sodium acetate, acetic anhydride and zinc dust and by adding fresh portions of zinc dust as required to insure the rapid decolorization of the quinone. The crude product obtained was always oily. It was treated with ether, which left a residue of the solid tetra-acetate of dinaphthyldihydroquinone. The ethereal solution was washed well with sodium carbonate and dried over calcium chloride. Evaporation of the ether left a greenish-black oil which is not easily purified by crystallization. The material distills well, however, at diminished pressure, and after two distillations a colorless product was obtained. The 1,2-diacetoxynaphthalene formed small, colorless crystals from alcohol; yield 50%; m. p. 109.5° (Korn, 102–104°).

For the hydrolysis of the diacetate in the absence of oxygen, and for many similar operations, we have found the following simple apparatus to be of great service. The reaction vessel was a three-necked flask, carrying through one opening a tube for the admission of purified nitrogen. Through the central opening a tube was inserted which ordinarily served as the outlet for nitrogen but which could be pushed to the bottom of the flask when it was desired to transfer a solution to another piece of apparatus under

<sup>8</sup> Compare Korn, *Ber.*, 17, 3025 (1884).

pressure of nitrogen gas. The third tubulature carried a separatory funnel for the admission of solution. In order to sweep this solution free of oxygen, a tube extending to the bottom of the funnel was connected to the nitrogen outlet by a length of rubber tubing. The glass tube passed through a large tube which was inserted in the stopper of the funnel, and through which, by means of a side-T, the nitrogen escaped. The advantage of the arrangement is that different reagents may be freed of oxygen rapidly and introduced in succession to the reaction flask.

For the preparation of *pure  $\beta$ -naphthohydroquinone* 10 g. of 1,2-diacetoxynaphthalene was dissolved in 75 cc. of alcohol, the solution was swept with nitrogen and treated with a solution of 8 g. of sodium hydroxide in 50 cc. of water. When the hydrolysis was complete the faintly yellow solution was acidified with 130 cc. of 1 *M* hydrochloric acid, and diluted with about 400 cc. of oxygen-free water. The material crystallized on cooling in the form of large colorless plates melting at 105.5° (4 g.). The melting point of 60° reported for samples of this compound prepared by reduction of the quinone<sup>9</sup> indicates that this is not a satisfactory method of preparation. By adding an excess of ferric chloride to the mother liquor from the above crystallization, the remaining material was converted into an excellent sample of crystalline  $\beta$ -naphthoquinone (2.6 g.).

*Pure  $\beta$ -naphthoquinone* may be obtained by oxidation of the pure hydroquinone under carefully controlled conditions. Five-tenths g. of  $\beta$ -naphthohydroquinone was dissolved in 10 cc. of alcohol and a mixture of 10 cc. of concentrated hydrochloric acid and 25 cc. of water was added. The solution was cooled to 0° and poured into a cooled solution of 100 cc. of 1 *M* ferric chloride solution also at 0°. The quinone soon began to separate in the form of small orange needles and crystallization was complete in about ten minutes, when the material was collected and washed well with water. In its crystalline character, orange color and freedom from all traces of foreign material, this product differs markedly from the samples obtained by the usual method of preparation. While our attempts to hydrogenate ordinary samples of the compound were no more successful than those of Skita and Rohrmann,<sup>10</sup> the pure quinone was found to be easily reduced by this method.

The preparation of pure morphol<sup>11</sup> and 3,4-phenanthrenequinone<sup>6</sup> have been described. An improved method of preparing *1,2-dihydroxy-phenanthrene*<sup>12</sup> was as follows. The corresponding quinone was reduced in glacial acetic acid solution with zinc dust and the colorless solution was filtered by suction into water. The gray product which separated was distilled in vacuum, thereby removing most of the color. Crystallization from benzene-ligroin gave colorless needles melting at 178°. The sample did not darken on storage.

**Details of the Measurements.**—The solutions of the hydroquinone used in carrying out the titrations reported in Tables I, V and VII were prepared by placing the weighed solid in the three-necked flask referred to above, and adding the oxygen-free buffer solution after removal of all of the oxygen from the flask. The solution was then transferred to a protected reservoir buret of the type described by Cohen,<sup>13</sup> but modified by providing a tip below the lower stopcock through which the solution can enter the buret. This eliminates much delay in drainage. It is convenient to prepare 250 cc. of a solution of such concentration that 20 cc. contains 0.0003 mol. eq. of the reductant. In each experiment this amount was measured into 200 cc. of the buffer solution contained in the electrode vessel and swept free of oxygen.

<sup>9</sup> Liebermann and Jacobson, *Ann.*, 211, 58 (1882).

<sup>10</sup> Skita and Rohrmann, *Ber.*, 63, 1473 (1930).

<sup>11</sup> Fieser, Ref. 6. Further details will be published elsewhere.

<sup>12</sup> Fieser, *THIS JOURNAL*, 51, 1896 (1929).

<sup>13</sup> Cohen, *Ind. Eng. Chem.*, 20, 1238 (1928).

Aqueous solutions of potassium molybdicyanide and solutions of ceric sulfate in either 1 *N* or 0.5 *N* sulfuric acid were employed. The tetrabromo-*o*-benzoquinone was dissolved in the buffer solution with which it was to be used.

Solutions of the decomposition products were prepared by adding the appropriate quinone to the oxygen-free buffer solution. The mixture was shaken well to prevent the formation of any saturated solution during the process of dissolution, and the solution was allowed to stand for five to twelve hours in an atmosphere of nitrogen. During this time the solution of  $\beta$ -naphthoquinone lost its original deep amber color and became pale yellow. The solution of 3,4-phenanthrenequinone remained somewhat red to the end. The solutions were made up to contain approximately 0.0003 *M* of the quinone in 20 cc., the amount used in each experiment.

Hydroxynaphthoquinone was isolated from the solution prepared from  $\beta$ -naphthoquinone by extracting the diluted solution with ether, washing the ether well with water and then extracting with sodium carbonate solution. The soda-soluble material was recovered by extraction of the acidified solution with ether. The product, which melted with decomposition at 194°, was identified by conversion into the ether, m. p. 183.5°, and comparison of an authentic sample, mixed m. p. 183.5°.

For details concerning the potential measurements and the interpretation and calculation of results reference may be made to the first paper cited for no changes in the general procedure were introduced. The values found for the normal potentials of the molybdicyanide system in 70% alcoholic solutions were as follows: 0.5 *M* acid, 0.6760 v.; 1 *M* acid, 0.6867 v.

### Summary

By means of potentiometric analysis it has been found that  $\beta$ -naphthoquinone decomposes in dilute acid solution to give equal parts of  $\beta$ -naphthohydroquinone and hydroxynaphthoquinone. Since the reaction is monomolecular, it is concluded that the first step in the disproportionation is the addition of the elements of water to the quinone. 3,4-Phenanthrenequinone behaves in a similar manner, and it is presumed that the reaction is characteristic of all of the unsubstituted ortho quinones.

The method of discontinuous titration has been used in obtaining values for the normal oxidation-reduction potentials of the ortho quinones derived from benzene, naphthalene and phenanthrene, and the results are considered to supplant the earlier, less reliable, determinations.

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