

ride), bis-iodomethyl mercury and benzyl chloromethyl mercury. The primary product of the interaction of diazomethane and *p*-tolylmercuric chloride undergoes disproportionation, yielding mercury di-*p*-tolyl and bis-chloromethyl mercury; that from phenylmercuric chloride behaves analogously.

2. There are described the reactions with alcoholic hydrogen chloride and those with mercuric chloride of bridged mercury compounds prepared in this work. With the former reagent benzyl chloromethyl mercury yields toluene and chloromethylmercuric chloride and no benzylmercuric chloride.

3. Aliphatic diazo compounds react also with some other types of mercury compounds and with certain salts and organic derivatives of metals other than mercury. Mercuric chloride and *diphenyldiazomethane* interact forming, apparently, diphenylchloromethylmercuric chloride. The latter displays interesting decomposition reactions.

4. Certain theoretical implications of the results of the investigation are discussed.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

AN OPTICAL METHOD FOR THE STUDY OF REVERSIBLE ORGANIC OXIDATION-REDUCTION SYSTEMS.

I. PARA-BENZOQUINONES¹

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Introduction

Extensive studies have been made on the reduction potentials of reversible organic oxidation-reduction systems.² In one of these investigations, Conant and Fieser^{2b,k} determined the oxidation-reduction potentials of a number of systems composed of a quinone and its hydroquinone referred to the solid, dissolved and gaseous states.

¹ (a) The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Donovan E. Kvalnes in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931. This paper was prepared by the junior author after the death of Dr. W. H. Hunter.—L. I. Smith. (b) Presented at the spring meeting of the American Chemical Society, New Orleans, 1932.

² (a) Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921); (b) Clark, *J. Wash. Acad. Sci.*, **10**, 225 (1920); (c) Clark, *Science*, **54**, 557 (1921); (d) Biilmann, *Ann. chim.*, **15**, 109 (1921); (e) Conant, Kohn, Fieser and Kurtz, *THIS JOURNAL*, **44**, 1382 (1922); (f) La Mer and Baker, *ibid.*, **44**, 1954 (1922); (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922); (h) Conant and Fieser, *ibid.*, **45**, 2194 (1923); (i) Biilmann, *Trans. Faraday Soc.*, 676 (1923); (j) Conant and Fieser, *THIS JOURNAL*, **46**, 1858 (1924); (k) Conant, *ibid.*, **49**, 293 (1927); (l) Fieser, *ibid.*, **51**, 3101 (1929).

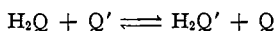
They found that in general the order of the potentials is alcoholic solution > aqueous solution > solid state > gaseous state; that the introduction of methyl groups progressively and regularly decreases the potentials; that in all but the gaseous state the introduction of chlorine into the quinone first raises and then lowers the potential.

In a few cases the potentials of the corresponding chloro and bromo quinones have been determined.^{2f,g,i} These results, together with the data of Conant and Fieser^{2j} on derivatives of naphtho and anthraquinones and the data of Clark³ on oxidation-reduction indicators show that the effect of the introduction of chlorine and bromine is identical within the limits of the significance of the data.

Since the potential of a quinone-hydroquinone combination depends upon the state of the system, *i. e.*, whether solid, dissolved or gaseous, the question arises as to which is the preferred state in which to study the result of substitution of the parent compound. Conant^{2k} believes that the gaseous state is the one to be selected, with a dilute solution as second choice, in order to eliminate secondary effects such as solubilities or the affinity of the quinone and hydroquinone molecules for each other.

Since there is no general agreement among the potentials of a series of quinones, determined in different states, and since potential measurements have been used as evidence in problems of chemical constitution, it seemed advisable to attack this question of oxidizing strength by some method other than an electrochemical one. This has been accomplished in the following manner.

If one mole of a hydroquinone (H_2Q) is in solution with one mole of some quinone (Q'), an equilibrium will eventually result, as shown by the equation



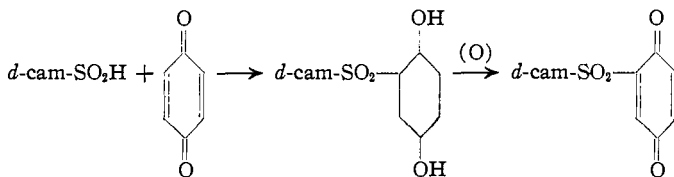
The same equilibrium may be reached by starting with one mole each of Q and H_2Q' . If the H_2Q - Q pair were an optically active hydroquinone and quinone, it would be possible to measure the concentration of each substance involved in the equilibrium. This would afford a means of grading the oxidizing strength of a series of hydroquinone-quinone pairs, represented by $H_2Q'-Q'$, against a given optically active pair, $H_2Q^*-Q^*$, used as a standard. If the $H_2Q'-Q'$ pair were a stronger oxidizing agent than the standard pair, and if a mole each of H_2Q^* and Q' were used at the start, then at equilibrium there would be proportionately more Q^* present than H_2Q^* . The reverse would be true if the $Q'-H_2Q'$ pair were a weaker oxidizing agent than the standard pair.

By this method of determining the concentrations, the equilibrium can in no way be affected. However, for accurate measurements it would be necessary to employ an optically active quinone and hydroquinone with a

³ Clark, *Chem. Reviews*, **2**, 127 (1925).

relatively large difference in specific rotations, since the actual rotation would be a summation of the rotations due to each in the equilibrium mixture. A search of the literature failed to show any optically active compounds fulfilling these requirements and, therefore, the first part of this work dealt with the preparation of a series of such compounds.⁴

Optically Active Quinones and Hydroquinones.—The optically active hydroquinones were prepared by treating a quinone with *d*-camphorsulfonic acid, to give the *d*-camphorsulfone of the hydroquinone, according to the method of O. Hinsberg.⁵ A few of the corresponding optically active quinones were made by oxidation of the respective hydroquinones.



The specific rotations of the hydroquinones are given in Table I.

TABLE I
ROTATIONS OF OPTICALLY ACTIVE HYDROQUINONES

<i>d</i> -Camphorsulfone of	$[\alpha]_{546}^{25}$ in benzene
Hydroquinone	+46.5°
2,6-Dibromohydroquinone	37.9
2,6-Dichlorohydroquinone	35.4
2,5-Dibromohydroquinone	19.6
2,5-Dichlorohydroquinone	29.9
2,5-Dimethylhydroquinone	24.2

With regard to this table, it will be noted that the unsubstituted hydroquinone has the highest rotation, while the introduction of methyl groups or halogen atoms causes a lowering of the rotation. The position of substitution is of importance since the 2,6-dihalogen derivatives have higher rotations than have the corresponding 2,5-dihalogen compounds. This is much more marked in the case of the bromo than in the chloro compound.

The rotations of the quinones are given in Table II.

TABLE II
ROTATIONS OF OPTICALLY ACTIVE QUINONES

<i>d</i> -Camphor sulfone of	$[\alpha]_{546}^{25}$ in benzene
Benzoquinone	+305.5
α -Naphthoquinone	237
<i>p</i> -Xyloquinone	223

⁴ While this research was in progress, a paper by Hill and Adams [THIS JOURNAL 53, 3453 (1931)] appeared, in which an optically active quinone was prepared and resolved, although the corresponding hydroquinone was not resolved.

⁵ Hinsberg, *Ber.*, 27, 3259 (1894); *ibid.*, 28, 1315 (1895); *ibid.*, 29, 2025 (1896).

The unsubstituted quinone has the highest rotation. Two methyl groups, in the 2,5-positions, have a greater lowering effect than a condensed ring. The rotations of the quinones are much greater than those of the corresponding hydroquinones. This would be expected due to the change of the benzenoid to the quinoid structure, since unsaturation has a marked effect on rotations.

Choice of a Standard.—The hydroquinone–quinone pair chosen as a standard was the *d*-camphorsulfone of 2,5-dimethylhydroquinone and the corresponding quinone. These two compounds are fairly easy to obtain in a pure condition and have a large difference in specific rotations. Benzene was selected as a solvent because it is a non-polar liquid and, therefore, larger specific rotations are secured.⁶

Soon after the addition of a quinone to the H_2Q^* , there are present in the solution two hydroquinones and two quinones



Furthermore, there is the possibility of the formation of the following four quinhydrones: (H_2Q^*-Q') , $(H_2Q^*-Q^*)$, $(H_2Q'-Q')$, $(H_2Q'-Q^*)$. If one of these is formed more readily than the others, the point of equilibrium will not be the same as it would if there were no quinhydrones present. However, it is impossible to determine the exact amounts or the specific rotations of the quinhydrones.

It is not possible to measure the effect of an optically inactive quinone on the rotation of the optically active hydroquinone, and *vice versa*, because of immediate oxidation and reduction to form new compounds according to the equation above. However, by adding definite amounts of the H_2Q^* to the Q^* and determining the resulting rotation, it is possible to ascertain whether or not there is any effect on the individual rotations of the two compounds due to association or quinhydrone formation. If the resultant rotation is the sum of the individual rotations, observed under the same conditions, then no association has occurred.

Twenty-five cc. of benzene containing 0.0855 g. of H_2Q^* and 0.0850 g. of Q^* gave 98.8% of the calculated rotation, and gave 100% of the calculated value when diluted to 50 cc. Accordingly, subsequent measurements were carried out with solutions sufficiently dilute to obviate association.

General Procedure

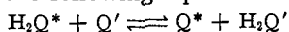
A weighed amount of a given quinone was added to a weighed sample of H_2Q^* . Enough benzene was added to dissolve the two compounds and the solution was allowed to stand for several hours. It was then diluted to a definite volume and the rotation was determined. Rotations were again observed after various periods of time. The rotation of the solution rose slowly to a definite value, remained constant at this point for several hours

⁶ Rule and McLean, *J. Chem. Soc.*, 674 (1931).

to a day and then dropped, often quite abruptly. The equilibria were established after lengths of time varying from a few hours to two days. Several determinations were carried out at different concentrations, and the equilibrium constants thus calculated served to check the separate runs.

Because the equilibrium points are not rapidly reached, it was necessary to determine whether or not the rotations of the optically active compounds change with time. The optically active hydroquinone showed no change in rotation even after several days. However, the rotation of the optically active quinone dropped slowly during the same period of time. Although this introduces an error into the determinations, it is a small one. Moreover, since the observed equilibrium points, using various quinones, are reached in approximately the same length of time, this error does not affect the comparative results.

Calculation of Conversions.—If a quinone Q' be added to H_2Q^* , in equimolecular amounts, the following equilibrium will be reached



If the concentrations of H_2Q^* and Q' , at the start, be represented by 1, and the concentrations of Q^* and H_2Q' at equilibrium be represented by β , then the concentrations of H_2Q^* and Q' at equilibrium will each be $(1-\beta)$. The equilibrium constant for the reaction is given by the equation $K = \beta^2/(1-\beta)^2$. To calculate β it is necessary to know the actual rotation of H_2Q^* at the start (A), the actual rotation of Q^* , if all the H_2Q^* were changed to Q^* , (B), and the observed rotation (C). These values must be calculated for definite concentrations in a given solvent. At equilibrium, the contribution of H_2Q^* to the observed rotation will be $A(1-\beta)$ and the contribution of Q^* will be $B\beta$. The observed value for the rotation of the solution (C) will be the sum of the above two values. $C = A(1-\beta) + B\beta$; from which $\beta = (C - A)/(B - A)$. β will be a measure of the oxidizing strength of the system H_2Q' and Q' referred to the standard system, H_2Q^* and Q^* , in the solvent used. The conversion β_0 of any quinone Q' , will be defined as the percentage change at equilibrium of H_2Q^* into Q^* when equimolecular amounts of H_2Q^* and Q' are used. Thus, if the system chlorohydroquinone-chloroquinone is a stronger oxidizing agent than the system hydroquinone-benzoquinone, referred to the standard system, chloroquinone will have a higher conversion, (β_0), than benzoquinone. The calculation of the benzoquinone equivalent may be illustrated as follows. The conversion value for 2,6-dichloroquinone is 51.2; that is, one mole of 2,6-dichloroquinone added to one mole of H_2Q^* would cause 51.2% of the latter to be oxidized to Q^* . It is possible to calculate how many moles of benzoquinone it is necessary to add to one mole of H_2Q^* to cause 51.2% of the latter to be oxidized to Q^* , knowing the equilibrium constant for benzoquinone to be 0.114.

$$\frac{(\beta_0)^2}{(1 - \beta_0)(X_0 - \beta_0)} = 0.114$$

X_0 will be the number of moles of benzoquinone which would be required to cause a conversion equal to β_0 , obtained by using only one mole of the quinone in question. X_0 may be called the *benzoquinone equivalent*. Thus 5.2 moles of benzoquinone are necessary to give the same β as is given by one mole of 2,6-dichloroquinone.

Results

Table III gives a list of quinones, with their equilibrium constants, conversions, (β_0), and benzoquinone equivalents, (X_0), in relation to the standard system. For the purposes of comparison, the potentials in the solid, dissolved and gaseous states for the same quinones are given. The latter were determined by Conant and Fieser^{2h,k} unless otherwise noted.

TABLE III
CONVERSIONS OF QUINONE-HYDROQUINONE SYSTEMS

Quinone	K (av.)	β_0	X_0	E_s	Normal reduction potentials E_0				E_g
					0.1 N HCl H ₂ O	1.0 N HCl alc.-H ₂ O	0.5 N HCl alc.-H ₂ O	1.0 N HCl alc.-H ₂ O	
<i>p</i> -Xyloquinone	0.00059	2.4	0.03	0.582	0.590	..	0.600	0.597	0.486
Toluquinone	.00437	6.2	0.10	.623	.645	.641	..	.656	..
Benzoquinone	.114	25.2	1.000	.681	.699	.696	..	.711	.570
Chloroquinone	.669	45.0	3.7	.678	.713	.710	..	.736	.611
Bromoquinone	.853	48.0	4.4	..	7
2,6-Dichloroquinone	1.09	51.2	5.2	.689	.722	.719	..	.748	.636
2,6-Dibromoquinone	1.43	54.5	6.3
Trichloroquinone670731	.726	.649
Tetrachloroquinone	1.27	53.0	5.8	.664695	.703	.657
Tetrabromoquinone	1.69	56.5	7.0
2,5-Dichloroquinone	1.73	56.8	7.1	.689	7	.719	.740	.734	..
2,5-Dibromoquinone	9.04	75.0	20.5	..	7

Since conversions and benzoquinone equivalents do not yield to ready comparison with the potentials determined electrochemically, a series of potentials, (E^*), has been calculated from the equilibrium constants given in Table III. This has been accomplished by use of the equation $E = (RT/nF) \log_e K$ in which T is 300. A system which has the same oxidizing strength as the optically active standard system will have a value of E^* equal to zero. Weaker oxidizing systems will have negative values of E^* and stronger oxidizing systems will have positive values of E^* . It is convenient to change the E^* values to a series in which the benzoquinone-hydroquinone system is represented by zero. This series is given in Table IV under the heading ΔE^* .

⁷ La Mer and Baker^{2f} give the following: chloroquinone, 0.7125; bromoquinone, 0.7151; whereas Billmann²ⁱ gives: chloroquinone, 0.7124 and bromoquinone, 0.7120; 2,5-dichloroquinone, 0.7230 and 2,5-dibromoquinone, 0.7228.

In order to calculate the potentials for a system in benzene from the E_g values determined by Conant it would be necessary to know the vapor pressures of the components of the system and their solubilities in benzene. As yet these data are not available. An interesting series of potentials could be calculated if the E_g value of benzoquinone, 0.570, were arbitrarily chosen as the potential of benzoquinone in benzene. To this could be added the ΔE^* values. Since these potentials might be misleading, an alternative procedure has been used. The E_g value of benzoquinone has been set equal to zero and ΔE_g values calculated accordingly. These results are given in Table IV.

TABLE IV
RELATIVE POTENTIALS OF QUINONE-HYDROQUINONE SYSTEMS IN BENZENE

Quinone	$\log_{10} K$	E^*	ΔE^*	ΔE_g
<i>p</i> -Xyloquinone	-3.22915	-0.09613	-0.0681	-0.084
Toluquinone	-2.35952	- .07024	- .0422
Benzoquinone	-0.94310	- .02808	.0000	.000
Chloroquinone	- .17457	- .00520	+ .0229	+ .041
Bromoquinone	- .06905	- .00206	+ .0260
2,6-Dichloroquinone	+ .03743	+ .00111	+ .0292	+ .066
2,6-Dibromoquinone	+ .15534	+ .00462	+ .0327
Tetrachloroquinone	+ .10380	+ .00309	+ .0312	+ .087
Tetrabromoquinone	+ .22789	+ .00678	+ .0349
2,5-Dichloroquinone	+ .23805	+ .00709	+ .0352
2,5-Dibromoquinone	+ .95617	+ .02847	+ .0566

Discussion

The results indicate that this method gives a quantitative evaluation of the oxidizing strength of a series of hydroquinone-quinone systems, compared to a standard system. Certain generalizations are apparent from the data in Table III. A methyl group lowers and a halogen raises the conversion value of the parent compound. Furthermore, a methyl group is more effective than a halogen atom. In general, the successive introduction of like groups causes the conversion values to change consistently in the same direction, the first group always being more effective than the succeeding ones. The position of the groups is of importance since the 2,5-dihalogenated quinones have much higher conversion values than anticipated, even higher than those of the tetrasubstituted quinones. A similar difference due to position was pointed out in the consideration of the rotations of the optically active halogenated hydroquinones, shown in Table I. In both cases this difference is far more marked in the brominated compounds than in the chlorinated compounds. The introduction of bromine gives systems which are stronger oxidizing agents than are the analogous chlorinated systems. The difference between the two is quite uniform except in the abnormal 2,5-dihalogenated quinones.

Comparison with Electrochemical Data.—The relative order of the

potentials of *p*-xyloquinone, toluquinone, benzoquinone and chloroquinone is the same whether the potentials are determined for the solid, dissolved or gaseous state. Thus benzoquinone has a higher potential than has *p*-xyloquinone, in all three states.^{2h,k,8} The results obtained in this research also show the same relative order for these four quinones.

However, for the polyhalogenated quinones there is no agreement among the potentials for the three states. The potentials of the tri- and tetrachloroquinones, in the solid state and in solution, are lower than that of benzoquinone. In the gaseous state the potentials of the polychloro compounds are higher than that of benzoquinone. Our results are well in accord with those obtained by Conant for the gaseous state, as can be seen by Table III.

The introduction of two methyl groups into benzoquinone causes a decided drop in both E_g and β_0 . The successive introduction of a chlorine atom causes an increase in E_g and β_0 , the first chlorine being more effective than the second, and it in turn more effective than the next. Two methyl groups decrease E_g and β_0 to a greater extent than two chloro groups increase them. It would be unwarranted to predict close agreement between the ΔE^* and ΔE_g values, given in Table IV, though values of the same order of magnitude would be expected. Conant did not determine the E_g value of 2,5-dichloroquinone or of any bromoquinones.

Electrochemical studies of analogous chloro and bromo compounds give potentials differing by less than the experimental error. Our method, however, shows that these compounds differ decidedly in oxidizing strength.

The electrochemical results for alcoholic solutions cannot be checked by this method because the optically active quinones do not give reproducible rotations in alcohol. In some cases the rotations are so abnormal as to indicate possible reaction between the quinone and the alcohol. The present method is further limited because a quinone-hydroquinone pair that is weaker in oxidizing strength than is the 2,5-dimethylhydroquinone-quinone pair cannot be measured accurately, due to the low rotations resulting. To overcome this difficulty a new standard pair for a different range must be obtained.

The junior author is continuing the investigation of this field.

Experimental

Experimental Determination of Conversions.—An extensive study of the system hydroquinone-benzoquinone, in the presence of the standard pair, was first carried out. A number of runs at several different concentrations were made to obtain the equilibrium constant. All determi-

⁸ Information obtained from absorption spectra of molecular compounds involving these four quinones also indicates the same relative order (unpublished work by W. H. Hunter and E. H. Northey).

nations were made at 27°. A weighed quantity of benzoquinone was added to a weighed sample of H_2Q^* , together with enough benzene to dissolve the two compounds. In a few minutes a green precipitate formed. After letting the solution stand for about two hours, enough benzene was added to dissolve the precipitate, and the whole was diluted to a definite volume. Benzoquinone was the only quinone used that resulted in a precipitation of a quinhydrone. Because of this quinhydrone formation it was possible to arrive at the equilibrium point much sooner than in any other case.

TABLE V
EQUILIBRIUM CONSTANTS OF SYSTEM STANDARD PAIR—BENZOQUINONE-HYDROQUINONE

H_2Q^* (g.)	$\frac{\text{Moles Benzo Q}}{\text{Moles } H_2Q^*}$	β	K	K (av.)
0.1825	1	25.0	0.111	
.1823	1	24.8	.109	
.1311	1	25.2	.114	0.111
.1980	2	35.1	.115	
.1815	2	36.2	.125	
.1859	2	34.2	.107	
.1281	2	35.0	.114	
.1275	2	35.8	.122	
.1826	2	35.4	.118	.117
.1765	3	41.4	.113	
.1862	3	41.9	.117	
.1016	3	40.5	.106	.115
.1040	4	46.1	.112	.112

$\beta_0 = 25.2$ for benzoquinone.

Average of K 's .114

The equilibrium was now approached from the other side. Hydroquinone was added to an equimolecular amount of Q^* . The hydroquinone was dissolved in warm benzene and cooled before it was added to Q^* , since hydroquinone dissolves very slowly in benzene. No quinhydrone formed in this experiment. The rotation slowly dropped during the first twenty-four hours and then remained constant for about twenty hours before it began to drop again. From the rotation at equilibrium it was determined that 74.9% of the optically active quinone had been converted into the H_2Q^* . This value agrees very well with the conversion value (β_0) of 25.2%.

Below are given the results of a typical determination, using an equimolecular mixture of 2,6-dichloroquinone and H_2Q^* .

$$\begin{aligned}
 &0.1228 \text{ g. of } H_2Q^* \quad 0.0618 \text{ g. of 2,6-dichloroquinone} \\
 &\frac{0.1228}{0.1240} \times 0.24 = 0.238^\circ = A = \text{rotation due to } H_2Q^* \text{ in 25 cc. benzene, 2-dec. tube} \\
 &\frac{0.1228}{0.1042} \times \frac{350}{352} \times 1.82 = 2.180^\circ = B = \text{rotation if all of } H_2Q^* \text{ were changed to } Q^*, \\
 &\quad \text{in 25 cc. benzene, 2-dec. tube.}
 \end{aligned}$$

The two compounds were dissolved in 25 cc. of benzene and allowed to stand for thirteen hours before being diluted to 50 cc.

TABLE VI
DETERMINATION OF THE CONVERSION OF 2,6-DICHLOROQUINONE

<i>l</i> , dm.	Benzene, cc.	Zero	Obs.	$\alpha = c$	β	<i>A</i>	<i>B</i>	<i>B - A</i>	<i>C - A</i>	Time, hrs.
3	50	5.13	5.85	0.72	37.2	0.178	1.635	1.457	0.542	14
3	75	5.13	5.70	.57	46.5	.119	1.090	0.971	.451	20
3	75	5.13	5.72	.59	48.5	.119	1.090	.971	.471	24
3	75	5.13	5.74	.61	50.6	.119	1.090	.971	.491	36
3	100	5.13	5.59	.46	51.0	.089	0.817	.728	.371	39
3	100	5.13	5.59	.46	51.0	.089	.817	.728	.371	48
3	100	5.13	5.52	.39	41.3	.089	.817	.728	.301	60

$$\beta = \frac{C - A}{B - A}$$

$\beta_0 = 51.0$ for this determination.

TABLE VII
EQUILIBRIUM CONSTANTS OF STANDARD PAIR—QUINONE—HYDROQUINONE PAIRS

Quinone	H ₂ Q*, moles	Q, moles	β	<i>K</i>	<i>K</i> (av.)
Monochloroquinone	1	1	45.0	0.669	
	1	1	45.0	0.669	0.669
2,5-Dichloroquinone	1	0.75	48.4	1.71	
	1	0.75	48.0	1.64	
	1	1.00	56.5	1.69	
	1	1.00	57.4	1.82	
	1	1.00	57.0	1.76	1.73
2,6-Dichloroquinone	1	0.75	44.0	1.11	
	1	1.00	51.0	1.08	1.09
Tetrachloroquinone	1	0.50	35.1	1.27	
	1	1.00	53.0	1.27	1.27
Monobromoquinone	1	0.75	40.9	0.830	
	1	0.75	40.7	0.815	
	1	0.80	43.0	0.877	
	1	1.00	48.4	0.880	
	1	1.00	47.2	0.799	
	1	1.50	58.7	0.914	0.853
2,5-Dibromoquinone	1	0.50	45.7	8.95	
	1	0.80	65.8	8.92	
	1	0.80	66.0	9.15	
	1	1.00	75.0	9.00	
	1	1.00	75.2	9.20	9.04
2,6-Dibromoquinone	1	0.50	35.9	1.43	
	1	0.75	46.5	1.42	
	1	0.75	46.3	1.39	
	1	1.00	53.0	1.49	1.43
Tetrabromoquinone	1	0.50	36.9	1.65	
	1	0.50	37.4	1.77	
	1	1.00	56.8	1.73	
	1	1.00	55.9	1.61	1.69

TABLE VII (Concluded)

Quinone	H ₂ Q,* moles	Q, moles	β	K	K (av.)
Toluquinone	1	1.00	6.3	0.00452	
	1	2.00	8.6	.00423	
	1	3.00	10.6	.00434	0.00437
<i>p</i> -Xyloquinone ⁹	1	1.00	2.3	.00056	
	1	3.00	4.2	.00062	0.00059

Preparation of Materials

The common derivatives of benzoquinone were prepared by the ordinary methods. Zinc *d*-camphorsulfinate was made according to the method of Smiles and Hilditch.¹⁰

***d*-Camphorsulfones of Hydroquinones.**—The quinone, dissolved in alcohol, was added slowly to an excess of zinc *d*-camphorsulfinate, dissolved in dilute acid. The reaction was very rapid in the case of benzoquinone and the halogenated quinones and the yellow color of the quinone disappeared very rapidly. On standing for a few hours or by concentration *in vacuo* precipitation took place or an oil settled out. In the latter case several days was sometimes necessary to effect crystallization. The sulfones are quite soluble in all the common organic solvents. Recrystallization is accomplished from dilute alcohol. The *d*-camphorsulfone of 2,5-dimethylhydroquinone when dissolved in alcohol is easily precipitated, by the addition of water, to give a cotton-like mass. The hydroquinones are soluble in alkali and are reprecipitated by the addition of acids, but are not obtained in a pure state. The hydroquinones give no color with ferric chloride but reduce an ammoniacal silver nitrate solution. By dissolving a small amount of any one of these hydroquinones, together with a little benzoquinone, in ether a small amount of a purple quinhydrone remains on evaporation of the solvent. The hydroquinones are white and odorless. The yields are practically quantitative.

Hydroquinone *d*-Camphorsulfone. Melting point 159–160°, $[\alpha]_{5461}^{27} +46.55$, $c = 0.3366$ in benzene, $\alpha = 0.47^\circ$, $l = 3$.

Anal. Calcd. for C₁₆H₂₀O₃S: C, 59.26; H, 6.17. Found: C, 59.25; H, 6.7.

Diacetate of Hydroquinone *d*-Camphorsulfone.—This was obtained by treating the hydroquinone with acetic anhydride. It was recrystallized from aqueous alcohol. It is soluble in organic solvents and insoluble in water or alkali; m. p. 119–122°. The rotation of the diacetate is slightly lower than that of the hydroquinone, $[\alpha]_{5461}^{27} +17.5$, $c = 0.5448$ in abs. alc., $\alpha = 0.18^\circ$, $l = 2$.

Anal. Calcd. for C₂₀H₂₄O₅S: C, 58.8; H, 5.9. Found: C, 58.7; H, 5.9.

2,5-Dichlorohydroquinone *d*-Camphorsulfone.—M. p. 169–173°, $[\alpha]_{5461}^{27} +29.99$, $c = 0.3398$ in benzene, $\alpha = 0.305^\circ$, $l = 3$.

Anal. Calcd. for C₁₆H₁₂O₃Cl₂S: C, 48.86; H, 4.6. Found: C, 49.0; H, 4.6.

2,6-Dichlorohydroquinone *d*-Camphorsulfone.—M. p. 104–106°, $[\alpha]_{5461}^{27} +35.4^\circ$, $c = 0.3716$ in benzene, $\alpha = 0.395^\circ$, $l = 3$.

Anal. Calcd. for C₁₆H₁₂O₃Cl₂S: C, 48.86; H, 4.6. Found: C, 48.91; H, 4.6.

2,5-Dibromohydroquinone *d*-Camphorsulfone.—M. p. 172–173°, $[\alpha]_{5461}^{27} +19.6^\circ$, $c = 0.5260$ in benzene, $\alpha = 0.31^\circ$, $l = 3$.

Anal. Calcd. for C₁₆H₁₂O₃Br₂S: C, 39.83; H, 3.74. Found: C, 39.55; H, 4.0.

⁹ The results for *p*-xyloquinone are not as reliable as for the other quinones since the observed rotations were close to that due to the unchanged optically active hydroquinone added.

¹⁰ Smiles and Hilditch, *J. Chem. Soc.*, 91, 519 (1907).

2,6-Dibromohydroquinone *d*-Camphorsulfone.—M. p. 108–112°, $[\alpha]_{5461}^{27} +37.9^\circ$, $c = 0.3568$ in benzene, $\alpha = 0.395^\circ$, $l = 3$.

Anal. Calcd. for $C_{16}H_{18}O_6Br_2S$: C, 39.83; H, 3.74. Found: C, 40.7; H, 4.4.

2,5-Dimethylhydroquinone *d*-Camphorsulfone.—M. p. 176–177°, $[\alpha]_{5461}^{27} +24.22$, $c = 0.4960$ in benzene, $\alpha = 0.24^\circ$, $l = 2$.

Anal. Calcd. for $C_{18}H_{24}O_6S$: C, 61.36; H, 6.82. Found: C, 61.12; H, 6.84.

Diacetate of 2,5-Dimethylhydroquinone *d*-Camphorsulfone.—M. p. 103–106°, $[\alpha]_{5461}^{27} +21.7^\circ$, $c = 0.4758$ in benzene, $\alpha = 0.31^\circ$, $l = 3$.

Anal. Calcd. for $C_{22}H_{28}O_8S$: C, 60.55; H, 6.42. Found: C, 60.50; H, 6.47.

The *d*-Camphorsulfones of Quinones.—The *d*-camphorsulfones of benzoquinone and *p*-xyloquinone were prepared by oxidation of the corresponding hydroquinones. The latter were dissolved in ether and an excess of either lead dioxide or silver oxide was added. The mixture was stirred from three to ten minutes and was then filtered. The residue was well washed with dry ether. The combined ether filtrates were concentrated, using a water pump. The yellow quinones crystallized from the concentrated solutions. The quinones were filtered off and washed with a little cold ether. The yields ranged from 30 to 80%.

The optically active quinones are yellow, crystalline compounds, quite soluble in alcohol, benzene, chloroform, acetic acid and acetone. They are less soluble in ether and are insoluble in water. They are not volatile with steam and do not have an odor. The values for their specific rotations are considerably higher than those of the corresponding hydroquinones. In the case of the *d*-camphorsulfone of benzoquinone the rotation in alcohol is very little higher than that of the hydroquinone, but in benzene solution there is a considerable difference in their rotations.

Benzoquinone *d*-Camphorsulfone.—M. p. 135–136°, $[\alpha]_{5461}^{27} +305^\circ$, $c = 0.5696$ in benzene, $\alpha = 3.48^\circ$, $l = 2$.

Anal. Calcd. for $C_{16}H_{14}O_6S$: C, 59.63; H, 5.6. Found: C, 59.73; H, 5.7.

***p*-Xyloquinone *d*-Camphorsulfone.**—M. p. 148–151°, $[\alpha]_{5461}^{27} +223^\circ$, $c = 0.4168$ in benzene, $\alpha = 1.86^\circ$, $l = 2$.

Anal. Calcd. for $C_{18}H_{22}O_6S$: C, 61.7; H, 6.3. Found: C, 61.7; H, 6.7.

α -Naphthoquinone *d*-Camphorsulfone.— α -Naphthoquinone was added to *d*-camphorsulfonic acid. The expected hydroquinone was impure due to partial oxidation to the quinone. This impure product was oxidized in the usual manner to give the optically active quinone, m. p. 144–148°, $[\alpha]_{5461}^{27} +237.3^\circ$, $c = 0.3224$ in benzene, $\alpha = 1.53^\circ$, $l = 2$.

Anal. Calcd. for $C_{20}H_{20}O_6S$: C, 64.5; H, 5.4. Found: C, 64.0; H, 5.6.

Attempted Preparation of Hydroquinone *d*-Bromocamphorsulfone.—It was supposed that the *d*-bromocamphorsulfone of hydroquinone would have a higher rotation than has the unbrominated compound. However, it was found that the zinc-absolute alcohol reduction of *d*-bromocamphorsulfonyl chloride gave zinc *d*-camphorsulfinate instead of the desired zinc *d*-bromocamphorsulfinate.

Summary

1. A number of optically active quinones and hydroquinones have been prepared.
2. The effect of substitution on their rotations has been determined.
3. The oxidizing strength of a number of hydroquinone-quinone pairs has been measured by use of a standard optically active hydroquinone-quinone pair.

4. The effect of substitution on the oxidizing power of a hydroquinone-quinone system has been shown.

5. The results thus obtained have been compared with the electrochemical data in the form of oxidation-reduction potentials.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A QUANTITATIVE STUDY OF SEMICARBAZONE FORMATION

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The interaction between ketones or aldehydes and such substances as phenylhydrazine and hydroxylamine has been the subject of numerous investigations in which the rate of the reaction has been measured. Most of these studies, however, were carried out before the use of the hydrogen electrode had enabled the chemist to define with precision the acidity of his solutions.¹ In recent years it has become apparent that in all these reactions one is dealing with a reversible reaction in which the acidity of the medium plays an important role in determining both the rate of the reaction and the final equilibrium which is reached. The early work of Acree and of Lapworth considered the influence of these factors to the extent that was possible at that time. The recent work of Ölander on the formation of acetoxime is the most complete study of this type of reaction from the modern viewpoint. This work will be referred to again in connection with our own measurements.

We have undertaken to study semicarbazone formation by a variety of carbonyl compounds in aqueous buffer solutions. Our results show the conditions which control the equilibrium in this reaction and the factors which influence the rate of the process. It seems probable that the fundamental principles which we believe we have elucidated can be applied to other similar reactions such as phenylhydrazone and oxime formation; these reactions, therefore, will be briefly discussed in the appropriate place in this paper. We shall first present our own results which are concerned with the equilibrium, then the kinetic study and finally a discussion of the influence of the structure of the carbonyl compound on both the composition of the equilibrium mixture and the rate at which this equilibrium is reached.

¹ The following references are among the most important: (a) Acree and Johnson, *Am. Chem. J.*, **38**, 308 (1907); Acree, *ibid.*, **39**, 300 (1908); (b) Barrett and Lapworth, *J. Chem. Soc.*, **93**, 85 (1908); (c) Ölander, *Z. physik. Chem.*, **129**, 1 (1927); (d) Bodfors, *ibid.*, **109**, 223 (1924); (e) Petrenko-Kritschenko and co-workers, *Ann.*, **341**, 150 (1905); *Ber.*, **34**, 1702 (1901); **39**, 1452 (1906); (f) Stewart, *J. Chem. Soc.*, **87**, 410 (1905); (g) Grassi, *Gazz. chim. ital.*, **38**, II, 32 (1908); *ibid.*, **40**, II, 139 (1910); (h) Michael, *THIS JOURNAL*, **41**, 393 (1919); (i) Ardagh and Williams, *THIS JOURNAL*, **47**, 2976, 2983 (1925).