

iodo- and tetraiodoquinone prevented measurement in this solvent.

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### Summary

The determination of the oxidation potentials of the known haloquinones has been completed.

Iodoquinone was synthesized for this purpose. The relative potentials in benzene of these quinones were calculated by arbitrarily assigning a value to the benzoquinone-hydroquinone system. The influence of the halogen and the positions occupied by the halogens upon the potential has been discussed. The relative potentials in benzene have been compared with the electrochemically determined potentials in aqueous solvents to illustrate the effect of the solvent upon the potential.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## An Optical Method for the Study of Reversible Organic Oxidation-Reduction Systems. III. Preparation and Use of a New Optically Active Standard

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In the preceding papers of this series<sup>2</sup> an optically active hydroquinone-quinone pair was used to determine the relative potentials in benzene of certain benzoquinones. This standard pair is adequate for the measurement of quinones whose potentials are in the range of about 700 to 800 mv., *i. e.*, benzoquinone and the halogenated quinones. It was of importance to develop another optically active pair of lower oxidation-reduction level and such a one has been found in the *d*-camphor-10-sulfonyl- $\alpha$ -naphthohydroquinone and the corresponding quinone. The molecular rotations of the two are +137 and +1320°, respectively. This large difference in rotation, together with the fact that benzoquinone, and quinones whose potentials are as much as 100 mv. lower than that of benzoquinone, can be studied with this standard, makes it admirably suited for the present study.

Table I gives the equilibrium constants ( $K_2$ ) of the reactions resulting from the mixing of a quinone ( $Q'$ ) with the optically active  $\alpha$ -naphthohydroquinone,  $(H_2Q^*)_2$ . By arbitrarily assigning the value of 0.711 v., as the potential of benzoquinone in benzene solution, as was done in the previous paper,<sup>2b</sup> the potential of the new optically active standard is calculated to be 0.637 v. The potentials in the fourth column of the table were calculated from this figure and the various equilibrium constants.

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(2) (a) Hunter and Kvalnes, *THIS JOURNAL*, **54**, 2869 (1932); (b) Kvalnes, *ibid.*, **55**, 667 (1934).

TABLE I  
NORMAL POTENTIALS IN VARIOUS SOLVENTS (25°)

System named as oxidant, -quinone $Q'$	Ox. of $(H_2Q^*)_2$ by $Q'$ , $\beta_2$ (%)	Eq. const., of mixture $(H_2Q^*)_2 + Q'$ , $K_2$	Rel. pot. in benzene: benzoquinone, 0.711 v., $E_0$ , v.	Normal pot. by e. m. f. meas., $E_0$ , v.
Benzo-	96.3	664	0.711	0.711 <sup>a</sup>
Tolu-	72.7	7.1	.653	.658 <sup>a</sup>
Ethyl-	70.4	5.7	.650	.658 <sup>a</sup>
Hydroxy-	25.3	0.115	.600	.598 <sup>a</sup>
Methoxy-	63.4	3.00	.642	.594 <sup>a</sup>
<i>m</i> -Xylo-	31.4	0.208	.607	...
<i>p</i> -Xylo-	28.5	.164	.604	.597 <sup>a</sup>
Thymo-	23.7	.096	.597	.589 <sup>a</sup>
2,6-Dimethoxy-	35.5	.310	.612	.530 <sup>a</sup>
3,5 - Dibromo - 2,6 - dimethoxy-	74.4	8.4	.655	.641 <sup>a</sup>
Dibromo- <i>p</i> -xylo-	64.5	3.3	.643	.609 <sup>a</sup>
2,5-Diphenoxy-	55.7	1.58	.633	...
$\beta$ -Naphtho-	60.4	2.32	.638	.576 <sup>a</sup>
6-Bromo- $\beta$ -naphtho-	61.1	2.47	.639	...
<i>p</i> - Tolylsulfonyl - $\alpha$ - naphtho-	59.8	2.21	.638	.605 <sup>a</sup>
<i>p</i> - Bromophenyl - sulfonyl- $\alpha$ -naphtho-	65.4	3.57	.644	.609 <sup>a</sup>
<i>d</i> -Camphor-10-sulfonyl- $\alpha$ -naphtho-	50.0	1	.627	.598 <sup>a</sup>

$(H_2Q^*)_2 = d$ -camphor-10-sulfonyl- $\alpha$ -naphthohydroquinone.

The introduction of a methyl group into benzoquinone results in a marked decrease in the rela-

(3) 95% Alcohol, 1.0 *M* in HCl: Conant and Fieser, *ibid.*, **45**, 2194 (1923).

(4) 95% Alcohol, 1.0 *M* in HCl: Conant and Fieser, *ibid.*, **46**, 1858 (1924).

(5) 70% Alcohol, 1.0 *M* in HCl and 0.2 *M* in LiCl: Fieser, *ibid.*, **52**, 5223 (1930).

(6) 70% Alcohol, 1.0 *M* in HCl and 0.2 *M* in LiCl: Fieser and Peters, *ibid.*, **53**, 793 (1931).

(7) 50% Alcohol, 0.1 *M* in HCl and 0.2 *M* in LiCl: Kvalnes (experimental part).

tive potential of the quinone. This change (59 mv.) is more than twice as great as that caused by a halogen atom and is in the opposite direction. The effect of the second methyl group is not quite as great as the first and its position is of no importance since the two xyloquinones have about the same potential. On the other hand, the decrease in the potential due to the first methoxyl group is more than twice that due to the second methoxyl group (69 and 30 mv., respectively). Judging on the basis of the disubstituted compounds, a phenoxy group is less efficient than a methyl or methoxyl group in decreasing the potential of the quinone structure. With an increase in the size of the substituted alkyl group little change in the potential results; this is observed by comparing the potentials of tolu- and ethylquinone and *p*-xylo- and thymoquinone. An hydroxyl group produces a profound lowering of the potential (111 mv). The introduction of two bromine atoms in 2,6-dimethoxyquinone and *p*-xyloquinones causes a rise in the potential of about 40 mv. This is not as great as the difference between benzoquinone and 2,5-dibromoquinone (57 mv.)<sup>2a</sup>; however, tetrasubstituted quinones have lower potentials than would be predicted from an algebraic addition of the individual effect of each group upon the potential of benzoquinone. The attachment of a sulfone group to a quinone results in a tremendous increase in the potential. Thus the *d*-camphor-10-sulfonyl group raises the relative potential of *p*-xyloquinone by 135 mv.

The slight solubility in water of these quinones makes it impossible to obtain potentiometric measurements in this solvent. The last column in the table gives the potentials as determined in this investigation and by previous workers, but since various alcoholic solutions were used the results are not strictly comparable. In general the relative potentials in benzene are higher than the potentiometrically determined potentials in alcoholic solutions. This is particularly true of the methoxy compounds and the highly substituted quinones. However, the solvent appears to have little effect in the case of the alkyl quinones and hydroxyquinone.  $\beta$ -Naphthoquinone is unstable in aqueous acid solution, but its potential has been carefully determined by Fieser and Peters.<sup>8</sup> A benzene solution of this quinone appears to be perfectly stable. The relative potentials of  $\beta$ -naph-

thoquinone and of 6-bromo- $\beta$ -naphthoquinone are about 60 mv. higher than the potential of  $\beta$ -naphthoquinone in alcoholic solution.

The two standard pairs which have been used adequately serve for the study of systems which lie in the important interval between 590 and 790 mv. It is apparent that other standard pairs should be developed to extend this range and investigations in this direction are now in progress.

TABLE II  
EQUILIBRIUM CONSTANTS OF MIXTURES  $(H_2Q^*)_2 + Q'$

Quinone (Q')	Q' (moles)		$\beta$	$K_2$	$K_2$ (av.)	$\beta_2$
	$(H_2Q^*)_2$	(moles)				
Benzo-	1	96.2	641			
	1	96.8	915			
	0.75	74.5	435	664	96.3	
Tolu-	1	72.3	6.8			
	1	72.5	6.9			
	0.75	61.8	7.6	7.1	72.7	
Ethyl-	1	70.7	5.8			
	1	70.4	5.7			
	0.75	59.6	5.7	5.7	70.4	
Hydroxy-	1	25.0				
	1	25.3				
	1	25.3				
	1	25.5		0.115	25.3	
Methoxy-	1	63.7				
	1	62.3				
	1	63.9				
	1	63.7		3.00	63.4	
<i>p</i> -Xylo-	1	27.1				
	1	29.7				
	1	28.8		0.164	28.5	
<i>m</i> -Xylo-	1	31.2	0.205			
	1	31.3	.207			
	1	31.6	.213	.208	31.4	
Thymo-	1	23.7				
	1	23.7				
	1	23.6		.096	23.7	
2,6-Dimethoxy-	1	35.1				
	1	37.8				
	1	33.4				
	1	37.5				
	1	33.8		.310	35.5	
3,5 - Dibromo - 2,6 - di- methoxy-	1	74.0	8.1			
	1	74.7	8.7	8.4	74.4	
Dibromo- <i>p</i> -xylo-	1	64.5	3.3			
	1	64.8	3.4			
	0.75	54.1	3.1	3.3	64.5	
2,5-Diphenoxy-	1	65.1				
	1	66.5				
	1	65.1		3.60	65.5	
2,5 - Dibromo - 3,6 - diethoxy-	1	55.6				
	1	55.7		1.58	55.7	
$\beta$ -Naphtho-	1	60.0				
	1	60.4				
	1	61.0		2.32	60.4	
6-Bromo- $\beta$ -naphtho-	1	61.3				
	1	61.4				
	1	60.7				
	1	61.1		2.47	61.1	
<i>p</i> - Tolylsulfonyl - $\alpha$ - naphtho-	1	59.5				
	1	60.1				
	1	59.8		2.21	59.8	
<i>p</i> - Bromophenylsul- fonyl- $\alpha$ -naphtho-	1	64.0				
	1	65.5				
	1	66.6		3.6	65.4	

(8) Fieser and Peters, THIS JOURNAL, 53, 793 (1931).

### Experimental

The polariscopic measurements were made in the same manner as that described elsewhere.<sup>2a</sup> Table II gives the equilibrium constants for the reactions of the quinones and the optically active  $\alpha$ -naphthohydroquinone.

The e. m. f. measurements were made by titrating a solution of the hydroquinone with tetrabromo-*o*-benzoquinone at 25°. The reaction cell was connected to a hydrogen electrode by a bridge containing the buffer solution. In the case of the highly substituted compounds the establishment of equilibrium was slow and consequently the end-points were not well defined.

#### Preparation of Materials

The directions as given in the literature were followed in the preparation of most of the quinones.

**2,5-Dibromo-3,6-diethoxyquinone.**—Dibromo-diphenoxyquinone was treated with sodium ethoxide in a manner analogous to that described by Jackson<sup>9</sup> for the dichloro compound. The resulting hemiacetal was decomposed to yield the quinone by gentle warming with acetic anhydride, m. p. 140–141°. A mixed melting point with the compound obtained by treating bromanil with absolute alcohol and sodium carbonate<sup>10</sup> proved the structure of the latter to be the para isomer.

***d*-Camphor-10-sulfonyl- $\alpha$ -naphthohydroquinone.**—An alcoholic solution of  $\alpha$ -naphthohydroquinone was added slowly, with stirring, to an excess of an acidified solution of zinc *d*-camphor sulfinate. The dark red solution was stirred for two hours and was diluted with water. This caused the precipitation of a solid, or an oil which slowly solidified. This product was separated, moistened with alcohol and warmed with an HCl-SnCl<sub>2</sub> solution until decolorization was effected. The mixture was cooled and diluted with water. The white precipitate was filtered off, dried, dissolved in dry ether, filtered, and precipitated by the addition of petroleum ether. The yield was nearly quantitative, m. p. 159–160°. It is very soluble in ether and alcohol, fairly soluble in benzene and chloroform and only slightly soluble in petroleum ether:  $[\alpha]_{5461}^{25} + 44.7^\circ$ ,  $c = 0.3916$  in benzene,  $\alpha = 0.35^\circ$ ,  $l = 2$ .

*Anal.* Calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>5</sub>S: C, 64.17; H, 5.88. Found: C, 63.96; H, 5.74.

***d*-Camphor-10-sulfonyl- $\alpha$ -naphthoquinone.**—A sample of this quinone much better than that previously described<sup>2a</sup>

(9) Jackson and Grindley, *Proc. Am. Acad. Arts Sci.*, **30**, 432 (1895).

(10) Bentley, *Am. Chem. J.*, **20**, 479 (1898).

was obtained by slowly adding a concentrated solution of ferric chloride to a solution of the pure hydroquinone in alcohol. The substance separated in the form of yellow plates and was crystallized by the concentration of a solution in dry ether. It formed small bright yellow plates melting at 131°. The compound is quite soluble in most organic solvents, slightly soluble in ether:  $[\alpha]_{5461}^{25} + 355^\circ$ ,  $c = 0.2524$  in benzene,  $\alpha = +1.79^\circ$ ,  $l = 2$ .

*Anal.* Calcd. for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>S: C, 64.5; H, 5.4. Found: C, 64.2; H, 5.2.

***p*-Tolylsulfonyl- $\alpha$ -naphthohydroquinone.**—To an acidified solution of sodium *p*-tolylsulfinate in aqueous methyl alcohol was added a methyl alcohol solution of  $\alpha$ -naphthoquinone. The yellow color of the quinone very rapidly disappeared with the subsequent formation of a white precipitate. Crystallization from aqueous alcohol gave minute crystals of m. p. 181°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>4</sub>S: C, 64.97; H, 4.46. Found: C, 64.42; H, 4.40.

***p*-Tolylsulfonyl- $\alpha$ -naphthoquinone**, prepared by the method given above, formed light yellow crystals from benzene-ligroin, m. p. 172–173°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>S: C, 65.39; H, 3.85. Found: C, 65.43; H, 3.99.

***p*-Bromophenylsulfonyl- $\alpha$ -naphthohydroquinone.**—*p*-Bromobenzene sulfonyl chloride was reduced with sodium sulfite and the product added to  $\alpha$ -naphthoquinone in the usual manner. Crystallization from aqueous acetic acid gave tan colored needles, which melted at 221–222° with decomposition. This compound is much less soluble than the *p*-tolyl sulfone.

*Anal.* Calcd. for C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>SBr: C, 50.66; H, 2.90. Found: C, 50.77; H, 3.32.

***p*-Bromophenylsulfonyl- $\alpha$ -naphthoquinone** formed small bright yellow crystals from alcohol, m. p. 175–176°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>9</sub>O<sub>4</sub>SBr: C, 50.93; H, 2.39. Found: C, 50.71; H, 2.62.

### Summary

A new optically active hydroquinone-quinone pair has been prepared and has been used to determine the relative potentials in benzene of certain quinones. The effect of substitution upon the potential of these quinones has been discussed and the results have been compared with the potentiometric measurements upon the same compounds in alcoholic solution.

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