version to 3-furyl isocyanate, which was not isolated, particularly because of its pronouncedly offensive properties.

3-Benzoylaminofuran.—The benzene solution of 3-furyl isocyanate was added dropwise to an ether solution of phenylmagnesium bromide, observing customary precautions for interaction of isocyanates with Grignard reagents. Hydrolysis with a 10% solution of ammonium chloride gave 3-benzoylaminofuran, which after crystallization from benzene melted at 142°.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.58; H, 4.81. Found: C, 70.40; H, 5.26.

2-Methyl-3-furoyl Hydrazide.—This hydrazide was prepared from ethyl 2-methyl-3-furoate in a 91% yield; and after crystallization from aqueous methanol it melted at 148°.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.43; H, 5.71. Found: C, 51.11; H, 6.11.

The hydrazide was transformed as usual to the azide and this, in turn, to the isocyanate. The 2-methyl-3-furyl isocyanate was converted by the addition of water to the corresponding urea, *sym*-di-(2-methyl-3-furyl) urea, which melted at 226° after crystallization from alcohol.

2-Methyl-3-benzoylaminofuran.[2]—The same sequence of reactions was used here as with the 3-benzoylaminofuran, and the 2-methyl-3-benzoylaminofuran melted at 135° after crystallization from water.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.14; H, 5.47. Found: C, 71.02; H, 5.93.

Hydrolysis of 2-Methyl-3-benzoylaminofuran.—The benzoylamino compound is rather resistant to hydrolysis both by aqueous or alcoholic potassium hydroxide. However, hydrolysis is promptly effected by sulfuric acid. In an orienting experiment with 1 g. of compound, the acid hydrolysate was made slightly alkaline with potassium hydroxide and the resulting mixture was steam distilled at once and in an inert atmosphere. The clear distillate had an odor remindful of naphthylamine and gave a carbylamine test. An aliquot of the steam distillate was diazotized, and the resulting solution was treated with β-naphthol to give a yellow-greenish precipitate. The diazotized solution with dimethylaniline gave a bright red solid which gradually darkened on long standing in the light.

The residue from steam distillation was acidified and then extracted to give a quantitative yield of benzoic acid.

2-Methyl-3-acetaminofuran, 2-$CH_3C_4H_2ONHCOCH_3$-3.—This acetaminofuran was prepared in a manner essentially identical with that in the synthesis of 2-methyl-3-benzoylaminofuran. The amide melts at 148°, and alkaline hydrolysis gives the corresponding amine, the hydrochloride of which has been diazotized.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.43; H, 6.61. Found: C, 60.48; H, 6.61.

Acknowledgments.—The author is grateful to Miles McCorkle for assistance; to the Miner Laboratories and Quaker Oats Co. for chemicals; and to the Rockefeller Fluid Research Fund for fellowship support.

Summary

Incidental to the use of β-furandiazonium salts for purposes of orientation, 3-benzoylaminofuran, 2-methyl-3-benzoylaminofuran and 2-methyl-3-acetaminofuran have been prepared from the furyl isocyanates and the appropriate Grignard reagents.

AMES, IOWA RECEIVED SEPTEMBER 11, 1933

---

[2] This compound was described recently by Blomquist and Stevenson [THIS JOURNAL, 56, 146 (1934)].

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

An Optical Method for the Study of Reversible Organic Oxidation–Reduction Systems. II. Halogenated Benzoquinones

BY D. E. KVALNES[1]

It has been shown[2] that the relative potentials of various oxidation–reduction systems can be measured without recourse to the potentiometric method by the use of an optically active quinone–hydroquinone pair (Q^* and H_2Q^*) as a reference system, and by observing the rotation of equilibrium mixtures such as that resulting from the interaction in a suitable solvent of a quinone, Q', with the optically active hydroquinone

$$H_2Q^* + Q' \rightleftharpoons Q^* + H_2Q' \qquad \text{(I)}$$

The particular value of the new method is in the fact that it permits a study of the organic systems in non-polar solvents, where potentiometric measurement is impossible. It should, of course, be equally applicable to solutions in polar solvents, and a series of measurements in aqueous or in alcoholic solution would indeed be of great value in affording a means of testing the reliability and the accuracy of the new method by comparison with the results obtained by the electrical method. Unfortunately experiments in this direction so far have met with no success; the hydroxylic solvents

---

[1] National Research Fellow in Chemistry.

[2] Hunter and Kvalnes, THIS JOURNAL, 54, 2869 (1932).

investigated either lacked sufficient solvent power or else they attacked the quinone structure before a condition of equilibrium had been attained.

In benzene solution, however, the optical method does yield results which are reproducible and which appear to be quite reliable. The procedure has been improved somewhat in the course of the present study and the earlier results have now been extended to include a comparison of all of the known halogenated benzoquinones and of one new one (iodoquinone).

It is obvious that only the relative potentials of a series of quinones in benzene solution are thus obtainable; but for the sake of comparison with the known absolute values in polar solvents it is convenient to adopt some arbitrary standard for reference. Thus in summarizing in Table I the results of this as well as of the previous investigation, we have arbitrarily assigned to the benzoquinone–hydroquinone system in benzene solution the normal potential of 0.711 v., the accepted value in alcoholic solution. The equilibrium constant (K_1) of equation 1 is related to the normal potentials (E_0) of the two systems as follows: $\log_e K_1 = nF/RT\ (E_0' - E_0^*)$. From the experimentally determined value of K_1 for benzoquinone, using *d*-camphor-10-sulfonyl-*p*-xyloquinone and its reductant as the reference system, it is found that the potential of this system on the arbitrary reference scale is 739 v. The potentials given in the fourth column of the table were calculated from this figure and from the various equilibrium constants.

TABLE I

NORMAL POTENTIALS IN VARIOUS SOLVENTS (25°)

System named as oxidant, -quinone, Q'	Ox. of H_2Q^* by Q', β_0 (%)	Eq. const. of mixture $H_2Q^* + Q'$, K_1	Rel. pot. in benzene: benzoquinone 0.711 v. E_0', v.	Normal pot. by e. m. f. meas. Alcoholic soln.,[3] E_0, v.	Aqueous soln., E_0, v.
Benzo-	25.2	0.114	0.711	0.711	0.699
Chloro-	45.0	.669	.734	.736	.712[4,6]
2,6-Dichloro-	51.2	1.09	.740	.748	.722[5,6,7]
2,5-Dichloro-	56.8	1.73	.746	.734	.722[5,6]
2,3-Dichloro-	64.0	3.15	.750	.711	.708[5,6]
Trichloro-	67.6	4.33	.755	.726	...
Tetrachloro-	53.0	1.27	.742	.703	...
Bromo-	48.0	0.85	.737	.735	.715[4,6]
2,6-Dibromo-	54.5	1.43	.744	...	.722[6]
2,5-Dibromo-	75.0	9.04	.768	...	.723[5,6]
Tribromo-	71.7	6.38	.763	...	.709[5]
Tetrabromo-	56.5	1.69	.746	...	...
Iodo-	48.5	0.89	.737	...	.706[6]
2,6-Diiodo-	57.1	1.78	.746	...	...

H_2Q^* = *d*-camphor-10-sulfonyl-*p*-xylohydroquinone.

It is of interest to compare the relative potentials in benzene with those in alcohol and water, the solvents used in most of the potentiometric studies and the last two columns in the table give what are regarded as the most accurate and the most representative potential values for the compounds in question. The introduction of any one of the three halogens results, in aqueous solution, in only a slight increase in the potential (13 mv., 16 mv., and 7 mv., for Cl, Br and I); but in alcoholic solution the increase amounts to 25 mv., and 26 mv., and in benzene solution it is practically the same (23 mv., 26 mv., and 26 mv.). The two organic solvents are thus more nearly comparable than the two hydroxylic solvents. On comparing the results in alcoholic and in benzene solution for the polychloro compounds, it is found that in the latter solvent the potentials are relatively higher than in alcohol but that in each case with the progressive accumulation of substituents there is eventually a falling off in potential and the tetrachloro compound is in each case lower in potential than the trichloro compound. The relationship indeed approaches more nearly that for the gaseous state[8] in benzene than in either of the other two solvents.

Any conclusions regarding the influence of the positions of the substituents seem hardly justified. Among the isomeric dichloroquinones there are distinct differences in potential, but there is no agreement in the order of the potentials in the three solvents. The differences noted are thus probably too small to be of great significance.

The present results make possible for the first time a comparison of the three types of haloquinones. Chloro- and bromo- and iodoquinone do not differ appreciably in potential in benzene or in alcoholic solution, and the slight differences in aqueous solution can hardly be of great significance. Among the dihaloquinones of similar structure there is again no significant difference between the three types. In the chlorine and bromine series the effect of tri- and tetra-substitution is again very nearly the same. The only serious divergence from the rule that the three halogens are, within the limits of significance of such results, practically identical in their effect[9] is

---

(3) 95% Alcohol, 1.0 *N* HCl; Conant and Fieser, THIS JOURNAL, **45**, 2194 (1923).

(4) La Mer and Baker, *ibid.*, **44**, 1954 (1922).

(5) Biilmann, *Trans. Faraday Soc.*, 676 (1923).

(6) Kvalnes, using 0.5 *N* H_2SO_4 (experimental part).

(7) Values reported for 0.1 *N* HCl, 0.2 *N* HCl and 1 *N* HCl are as follows: 0.723,[5] 0.721[4] and 0.719.[6]

(8) Conant, THIS JOURNAL, **49**, 293 (1927).

(9) Compare Conant and Fieser, *ibid.*, **46**, 1858 (1924), for the effect of bromine and chlorine.

in the case of iodanil, which appears considerably lower in potential than bromanil and chloranil; but it may be said that the measurement of this compound was subject to considerable inaccuracy and that the value must be regarded as uncertain.

Experimental

Determination of Conversions.—The standard procedure used was the following. Weighed amounts of *d*-camphor-10-sulfonyl-*p*-xylohydroquinone and a quinone were dissolved in 50 cc. of benzene. These solutions varied from 0.0003 to 0.0004 *M* with respect to the optically active hydroquinone. Within the range of concentrations used the rotations of the optically active compounds are directly proportional to the concentration. The solutions were allowed to stand in a dark, constant temperature room (25 ± 1°) and after twelve to fifteen hours their rotations were observed at intervals until the equilibrium point had been reached and maintained for some time. No abrupt drops in the rotations were observed in this work as were occasionally noticed in the preliminary investigation. In the great majority of cases the rotation would rise slowly after the equilibrium condition had been maintained for a period of time. In general the equilibrium point was reached in about twenty-four to thirty-six hours, the rotation then remaining constant for a number of hours to several days. The rate of the reaction is dependent to some extent upon the structure of the quinone, the tendency being for the highly substituted quinones to react more slowly than the simpler quinones.

An increase of β_0 of 1.0, which is the average limit of accuracy attained in this work, results in an increase in the relative potential of 1.0 mv. Consequently the potentials reported are accurate to ±1.0 mv., unless otherwise stated.

TABLE II

EQUILIBRIUM CONSTANTS OF THE MIXTURES $H_2Q^* + Q'$

Quinone (Q')	$\frac{Q' \text{ (moles)}}{H_2Q^* \text{ (moles)}}$	β	K_1	K_1 (av.)
2,3-Dichloro-	0.75	54.7	3.25	
	1.00	64.0	3.16	
	1.00	63.6	3.05	3.15
Trichloro-	0.75	57.8	4.60	
	.80	60.0	4.50	
	1.00	67.2	4.20	4.33
Tribromo-	0.50	44.7	6.82	
	.75	60.2	6.15	
	.75	60.2	6.15	6.38
Iodo-	1.00	48.2		
	1.00	48.8		
	1.00	48.5		0.89
2,6-Diiodo-	0.50	37.9	1.91	
	.50	37.3	1.75	
	.70	46.7	1.76	
	.70	47.0	1.81	
	1.00	57.7	1.86	1.78
Tetraiodo-	0.294	13.4	0.130	
	.50	12.7	.050	
	.50	15.6	.084	
	.60	19.8	.122	
	.60	24.2	.215	0.12

The results for tetraiodoquinone are not very accurate because low solubility required the use of solutions more dilute than ordinary and the dark color of the solutions rendered accurate reading of the rotations more difficult.

Preparation of Materials

2,6-Diiodoquinone.—Triiodophenol was oxidized with cold fuming nitric acid. The yield was poor. Upon repeating Metzeler's directions[10] for the preparation of a diiodoquinone the only compound isolated was 2,6-diiodoquinone, m. p. 177–179°. There was no lowering of the melting point when mixed with a sample prepared by the first method.

3-Iodo-4-aminophenol.—*m*-Iodophenol (5.5 g.) was dissolved in a small amount of water containing potassium hydroxide (1.4 g.). To this was added a cold solution of diazotized sulfanilic acid, alkalinity being maintained. The mixture was allowed to stand half an hour, sodium hydrosulfite (12 g.) was added and the mixture was warmed. The red dye quickly disappeared and after cooling the precipitate was filtered off and dried. It was dissolved in ether and filtered from a small amount of black material. After evaporation of the ether the product was crystallized from hot water, yielding fine white needles (4.5 g.). The compound darkens at 135° and melts at 140° with charring. It is quite soluble in the ordinary organic solvents.

Anal. Calcd. for C_6H_6ONI: C, 30.64; H, 2.55. Found: C, 30.94; H, 2.69.

Iodoquinone.—One gram of 3-iodo-4-aminophenol was dissolved in 30 cc. of 25% sulfuric acid by gentle warming. The solution was cooled and a concentrated sodium dichromate solution was added to it drop by drop, until a dark brown color was attained. The dark brown precipitate was filtered off and dried (0.95 g.). A good solvent for the crystallization of this compound could not be found and it was purified by careful sublimation. The reddish orange needles melted at 62°. It has a characteristic quinone odor and distils with steam. However, it is quite soluble in water as it is in most organic solvents.

Anal. Calcd. for $C_6H_3O_2I$: C, 30.77; H, 1.28. Found: C, 30.64; H, 1.32.

Iodohydroquinone.—The reduction of the quinone with stannous chloride gave the white crystalline hydroquinone. It was crystallized from chloroform, m. p. 115–116°. It is very soluble in water and the ordinary organic solvents.

Anal. Calcd. for $C_6H_5O_2I$: C, 30.51; H, 2.12. Found: C, 30.92; H, 2.35.

Iodohydroquinone Diacetate.—The reductive acetylation of the quinone gave this compound, which melted at 86–87° after crystallization from aqueous alcohol.

Anal. Calcd. for $C_{10}H_9O_4I$: C, 37.50; H, 2.81. Found: C, 37.48; H, 2.92.

E. m. f. Measurements.—Solutions of the hydroquinones in 0.5 *N* sulfuric acid were titrated with ceric sulfate solution, the temperature being maintained at 25°. The reaction cell was connected to a hydrogen electrode by means of a bridge containing the same solvent as the reaction cell and the hydrogen electrode. Reproducible curves were obtained. The low solubilities of tribromo-2,6-di-

---

[10] Metzeler, *Ber.*, **21**, 2555 (1888).

iodo- and tetraiodoquinone prevented measurement in this solvent.

The author wishes to express his thanks to Mary Fieser and Professor L. F. Fieser for the use of the apparatus for potentiometric measurements and for their aid in making these measurements. He is also deeply indebted to Professor Fieser for his interest and advice during the course of this research.

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.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 28, 1933

[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

BY D. E. KVALNES[1]

In the preceding papers of this series[2] 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–α-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 α-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,[2b] 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.

TABLE I

NORMAL POTENTIALS IN VARIOUS SOLVENTS (25°)

System named as oxidant, -quinone Q'	Ox. of $(H_2Q^*)_2$ by Q', β_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^{3}
Tolu-	72.7	7.1	.653	.656^{3}
Ethyl-	70.4	5.7	.650	.658^{7}
Hydroxy-	25.3	0.115	.600	.598^{4}
Methoxy-	63.4	3.00	.642	.594^{5}
m-Xylo-	31.4	0.208	.607	...
p-Xylo-	28.5	.164	.604	.597^{6}
Thymo-	23.7	.096	.597	.589^{3}
2,6-Dimethoxy-	35.5	.310	.612	.530^{4}
3,5 - Dibromo - 2 6 - dimethoxy-	74.4	8.4	.655	.641^{7}
Dibromo-*p*-xylo-	64.5	3.3	.643	.609^{7}
2,5-Diphenoxy-	55.7	1.58	.633	...
β-Naphtho-	60.4	2.32	.638	.576^{6}
6-Bromo-β-naphtho-	61.1	2.47	.639	...
p - Tolylsulfonyl - α - naphtho-	59.8	2.21	.638	.605^{7}
p - Bromophenyl - sulfonyl-α-naphtho-	65.4	3.57	.644	.609^{7}
d-Camphor-10-sulfonyl-α-naphtho-	50.0	1	.627	.598^{7}

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

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

---

[1] National Research Fellow in Chemistry.

[2] (a) Hunter and Kvalnes, THIS JOURNAL, **54**, 2869 (1932); (b) Kvalnes, *ibid.*, **56**, 667 (1934).

[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).