When 23 g. of *dl-s*-butyl alcohol in 100 cc. of ordinary benzene was treated with boron fluoride, the mixture turned lavender. After 16 g. of catalyst had been absorbed, a vigorous reaction occurred and two layers separated. After standing overnight, the mixture was washed, dried and fractionaly distilled; yield, 24 g. (55.9%), b. p. 61–62° (18 mm.), $n^{20}\text{D}$ 1.4880. The discrepancy in refractive index seems to arise from impurity in the benzene (thiophene), since using thiophene-free benzene or washing the impure product with cold concentrated sulfuric acid gave material with the correct physical properties. Fractional distillation was ineffective in removing the impurity from the product, and it is interesting to note that the impurity does not alter the molecular refractivity of the *s*-butylbenzene.

***l-s*-Butylbenzene.**—When 23.0 g. of *d-s*-butyl alcohol ($[\alpha]^{20}\text{D}$ +11.36) was condensed with thiophene-free benzene as above, using boron fluoride as the catalyst, 20.3 g. (48%) of *l-s*-butylbenzene was obtained, b. p. 61° (18 mm.), $n^{20}\text{D}$ 1.4891, $[\alpha]^{20}\text{D}$ $-0.16°$ (observed rotation $-0.27°$). The properties of this material were unaffected by washing with cold concentrated sulfuric acid, by refractionation or by standing for over a month.

A preliminary experiment using ordinary benzene and *d-s*-butyl alcohol ($[\alpha]^{20}\text{D}$ +11.05) gave optically active material, but, as with the other products using ordinary benzene, it had a low index of refraction ($n^{20}\text{D}$ 1.4848, d^{20}_4 0.8558, $M^{20}\text{D}$ (calcd.) 44.79, $M^{20}\text{D}$ (found) 44.86, $[\alpha]^{20}\text{D}$ -0.16). Washing with cold concentrated sulfuric acid raised the index of refraction without affecting the optical activity ($n^{20}\text{D}$ 1.4880, d^{20}_4 0.8612, $M^{20}\text{D}$ (calcd.) 44.79, $M^{20}\text{D}$ (found) 44.82, $[\alpha]^{20}\text{D}$ $-0.15°$).

Summary

The alkylation of benzene with *d-s*-butyl alcohol using boron fluoride as a catalyst yielded *s*-butylbenzene which was levo-rotatory. With aluminum chloride as a catalyst the product was racemic.

URBANA, ILLINOIS RECEIVED AUGUST 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY, WORCESTER POLYTECHNIC INSTITUTE]

Indicator Properties of 8-Hydroxyquinoline-5-sulfonic Acid and its Derivatives

BY HARRY B. FELDMAN AND ARNET L. POWELL[1]

Van Urk[2] has investigated the indicator properties of 7-iodo-8-hydroxyquinoline-5-sulfonic acid, a compound used in medicine. It acts as a monochromatic amphoteric indicator with a maximum color intensity at *p*H 4. The decrease in color intensity with increase or decrease in *p*H suggests the application of indicators of this type in the field of *p*H measurements.

In the present work the indicator properties of 8-hydroxyquinoline-5-sulfonic acid, the parent acid of the above compound, as well as some of its derivatives were determined.

Experimental

Materials.—8-Hydroxyquinoline-5-sulfonic acid was prepared by sulfonation of 8-hydroxyquinoline in the cold using the method of Claus and Posselt.[3] The final product, after recrystallization from dilute hydrochloric acid, was washed free of chlorides and dried at 98°. Its decomposition point was found to be 300°.

7-Iodo-8-hydroxyquinoline-5-sulfonic acid was obtained from the Eastman Kodak Co., who stated that its purity, based on the iodine content, was 98–99.5%.

7-Bromo-8-hydroxyquinoline-5-sulfonic acid and 7-chloro-8-hydroxyquinoline-5-sulfonic acid were prepared by bromination and chlorination, respectively, of 8-hydroxyquinoline-5-sulfonic acid.[4] *Anal.* Calcd. for $C_9H_6O_4NSBr$: Br, 26.28. Found: Br, 25.07. Calcd. for $C_9H_6O_4NSCl$: Cl, 13.66. Found: Cl, 12.63.

6-Methyl-8-hydroxyquinoline-5-sulfonic acid was prepared starting with 6-methylquinoline. The latter was sulfonated using the method of Lubavin[5] to form 6-methylquinoline-8-sulfonic acid which was converted to 6-methyl-8-hydroxyquinoline by fusion with sodium hydroxide according to Fischer and Willmack.[6] Isolation of the product from the fusion mass by crystallization from alcohol was found unsatisfactory but was accomplished by depositing the product by sublimation on the bottom of a beaker filled with cold water. Sulfonation of this product by the method of Claus and Posselt[3] yielded 6-methyl-8-hydroxyquinoline-5-sulfonic acid which had a melting point of 210°, identical with that given in the literature.[7]

Buffer solutions in the range of *p*H less than 2 were prepared by dilution of 0.1 *N* hydrochloric acid. McIlvaine's standard buffer solutions prepared from citric acid and disodium phosphate were used for the *p*H range 2.2 to 8.0 and solutions of *p*H 9.2, 10.0, and 11.0 were prepared from Kolthoff and Vlesschhouwer's alkaline soda–borax buffers. The *p*H of each buffer solution below *p*H 9 was checked electrometrically with the quinhydrone electrode.

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(1) The material presented in this paper constitutes a portion of the thesis presented by Arnet L. Powell to the Faculty of Worcester Polytechnic Institute in partial fulfillment of the requirements for the degree of Master of Science.

(2) H. W. van Urk, *Z. anal. Chem.*, **77**, 12 (1929).

(3) Claus and Posselt, *J. prakt. Chem.*, [2] **41**, 33 (1889).

(4) German Patent 73,145; *Friedlaender, Fortschritte der Theerfarbenfabrikation*, **3**, 966.

(5) Lubavin, *Ber.*, **2**, 400 (1869).

(6) Fischer and Willmack, *ibid.*, **17**, 441 (1884).

(7) German Patent 84,063; *Friedlaender, Fortschritte der Theerfarbenfabrikation*, **4**, 1146.

Method.—In determining the dissociation curves and acid and basic dissociation constants the following procedure was used: forty ml. each of a series of buffer solutions ranging in *p*H from 1.3 to 11.0 were placed in 50-ml. Nessler tubes. To each was added 2 ml. of the proper indicator solution made by dissolving 1 part of indicator in 100 parts of water containing sufficient sodium hydroxide to dissolve the solid. After thorough mixing the tubes were viewed longitudinally above a white background and an attempt was made to determine the solution of maximum color intensity. In all cases the solution appeared to possess a maximum color intensity over a range of *p*H of about one. The *p*H of the middle of this range was selected as the arbitrary maximum.

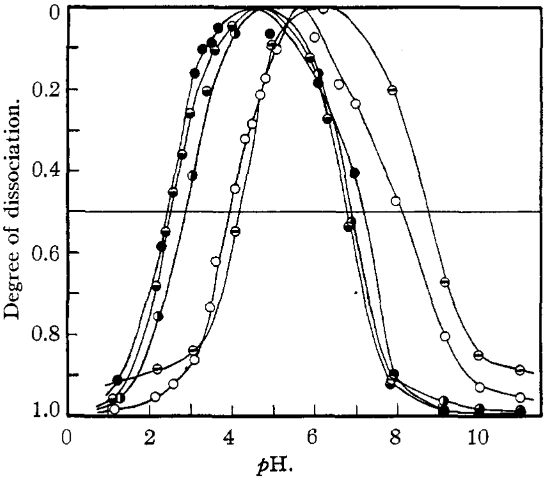

Fig. 1.—Dissociation curves of indicators: ○, 8-hydroxyquinoline-5-sulfonic acid; ●, 7-iodo-8-hydroxyquinoline-5-sulfonic acid; ◒, 7-bromo-8-hydroxyquinoline-5-sulfonic acid; ◑, 7-chloro-8-hydroxyquinoline-5-sulfonic acid; ⊖, 6-methyl-8-hydroxyquinoline-5-sulfonic acid.

Ten ml. of this buffer solution was now placed in one of the tubes of a Duboscq colorimeter and the relative color intensity of 10 ml. of each of the other mixtures was determined by comparison with the arbitrary maximum. From these results a preliminary curve of degree of dissociation *versus* *p*H was plotted for each indicator and the true color maximum obtained by extending the curves corresponding to acid and basic dissociation until they intersected. In this way the *p*H at minimum dissociation was secured. The experiment was now repeated using as the solution of maximum color intensity one prepared by mixing 40 ml. of a buffer solution corresponding to this point and 2 ml. of indicator solution. The degrees of dissociation corresponding to the relative color intensities were now plotted *versus* *p*H (Fig. 1). On the assumption that the color of the solution is due to undissociated molecules of the indicator, the point of maximum color intensity corresponds to approximately zero per cent. dissociation.

The values of K_a and K_b, the acid and basic dissociation constants for each indicator, were determined from the dissociation curves in the conventional manner. The values of K_a and K_b for the indicators investigated are given below in Table I.

TABLE I

ACID AND BASIC DISSOCIATION CONSTANTS OF 8-HYDROXYQUINOLINE-5-SULFONIC ACID AND ITS DERIVATIVES

Indicator	$K_a \times 10^{-8}$	$K_b \times 10^{-12}$
......	0.8	80
7-Iodo-	7.1	2.8
7-Bromo-	20	3.2
7-Chloro-	16	8.0
6-Methyl-	0.2	160

Discussion of Results

All the compounds investigated formed yellow colored solutions at the point of maximum color intensity and functioned as amphoteric indicators, the intensity of the yellow coloration decreasing as the *p*H of the solution varied from that corresponding to the isoelectric point. The halogenated derivatives differed from the others in that the color intensities corresponding to the same degree of dissociation were much greater for the former. Moreover, no difference in maximum color intensities for these three compounds could be detected, the three halogens being equally powerful auxochromes.

The indicator properties of the iodo compound were found to agree closely with those reported by van Urk,[2] the only difference being that the *p*H of maximum color intensity was found by the authors to be 4.5 as compared with 4.0.

The introduction of the methyl group in the "6" position in the 8-hydroxyquinoline-5-sulfonic acid molecule produced no appreciable intensification of color, the methyl group exhibiting no appreciable auxochromic power.

From Fig. 1 as well as Table I it can be seen that there is little difference in the behavior of the three halogenated compounds. The chlorine derivative is the easiest to prepare and for this reason is the most practical for general use.

The fact that these indicators change color over a *p*H range of as much as 6 units suggests their application in investigating *p*H changes of solutions, the initial and final *p*H values of which lie on opposite sides of the maximum. It should be noted, however, that each indicator exhibits the same color intensity for two different *p*H values.

Summary

1. The dissociation curves and acid and basic dissociation constants of 8-hydroxyquinoline-5-sulfonic acid and its 7-iodo, 7-bromo, 7-chloro- and 6-methyl derivatives were determined.

2. Of the compounds investigated, 7-chloro-8-hydroxyquinoline-5-sulfonic acid was found to be the most practical for use as an indicator.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonds Involving the C-H Link. XI.[1] Effect of Structure on Bonding of Donor and Acceptor Molecules

BY C. S. MARVEL, M. J. COPLEY AND EMANUEL GINSBERG

Heat of mixing data have been used by several investigators to study the formation of compounds of halogenated hydrocarbons, such as chloroform, bromoform, pentachloroethane and trichloroethylene with solvents such as ethers, esters and amines.[2] The more recent experimenters in this field have concluded that this is a satisfactory

TABLE I

HEAT OF MIXING DATA FOR MIXTURES OF DONOR AND ACCEPTOR LIQUIDS

Acceptor	Donor	Mole fraction of acceptor	Heat of mixing per mole of solution at 3°, cal.
$CHCl_3$	n-$C_4H_9NH_2$	0.500	700^a
$CHCl_3$	$C_6H_{11}NH_2$	.500	800^a
$CHCl_3$	$C_6H_{11}N(CH_3)_2$	.565	1166
$CHCl_3$	$C_6H_5N(CH_3)_2$	.600	280^b
$CHCl_3$	$CH_3CON(CH_3)_2$	.500	920^c
$CHCl_3$	$C_6H_5CON(C_2H_5)_2$	.453	1090
$CHCl_3$	n-C_4H_9CN	.477	390
$CHCl_3$	C_6H_5CN	.505	297
$CHCl_3$	$CN(CH_2)_3CN$	.507	233
$CHCl_3$	$CN(CH_2)_3CN$	.666	253
$CHCl_3$	$CN(CH_2)_3CN$	.680	261
$CHCl_3$	$C_6H_5NO_2$	.444	118
$CHCl_3$	$C_2H_5ONO_2$	.448	113
$CHCl_3$	CH_3NO_2	.500	None
$CHCl_3$	$C_6H_5OCH_3$	.509	175
$CHCl_3$	$C_6H_{11}OCH_3$	.471	665
$CHCl_3$	$(C_2H_5)_2O$	.5	700^d
$CHCl_3$	CH_3COCH_3	.458	495
$CHCl_3$	$CH_3CO_2C_2H_5$	.513	544
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.540	249
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.614	285
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.663	270
$CHCl_3$	$(C_2H_5O)_2SO_2$	.577	257
$CHBr_3$	C_5H_5N	.486	498^e
$CHBr_3$	$CH_3CON(CH_3)_2$	.468	918^e
$CHBr_3$	$CH_3CON(CH_3)_2$	.515	901^e
$CHBr_3$	$(C_2H_5)_2O$	.483	515^e
$CHBr_3$	CH_3COCH_3	.592	342^e
CH_2Cl_2	$CH_3CON(CH_3)_2$	.520	527
CH_2Cl_2	$(C_2H_5)_2O$	.382	245
CH_2Br_2	$CH_3CON(CH_3)_2$	.483	400
CH_2Br_2	$(C_2H_5)_2O$	.461	200
CH_2I_2	$CH_3CON(CH_3)_2$	.506	100^f
CH_2I_2	$(C_2H_5)_2O$	.50	None^f
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	.376	426
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	.600	500
$C_6H_5CHCl_2$	$(C_2H_5)_2O$	.484	232
$C_6H_5CHCl_2$	CH_3COCH_3	.451	200
$(C_6H_5)_2CHCl$	$CH_3CON(CH_3)_2$	.495	208^g
$(C_6H_5)_2CHCl$	$(C_2H_5)_2O$	.500	Very sl.^{g}
$HCCl_2CCl_2H$	C_5H_5N	.482	589
$HCCl_2CCl_2H$	C_5H_5N	.545	605
$HCCl_2CCl_2H$	C_6H_5CN	.505	362
$HCCl_2CCl_2H$	$C_6H_5NO_2$	.5	140^h
$HCCl_2CCl_2H$	C_6H_6	.5	125^h
$HCCl_2CCl_2H$	CH_3COCH_3	.481	610
$HCCl_2CCl_2H$	CH_3COCH_3	.587	610
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	.496	608
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	.520	572
$CCl_2{=}CHCl$	$CH_3CON(CH_3)_2$	.720	212
$CCl_2{=}CHCl$	$C_6H_5NO_2$	.5	None^h
$CCl_2{=}CHCl$	C_6H_6	.5	None^h
$CCl_2{=}CHCl$	$(C_2H_5)_2O$	.541	278
$CCl_2{=}CCl_2$	$CH_3CON(CH_3)_2$	.5	None
$CCl_2{=}CCl_2$	$(C_2H_5)_2O$	.5	None
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	.298	249
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	.494	305
$C_6H_5CF_3$	$CH_3CON(CH_3)_2$	.535	120
CH_3NO_2	$CH_3CON(CH_3)_2$	.535	118
$HC(OC_2H_5)_3$	$CH_3CON(CH_3)_2$	.483	Sl. cooling
$HC(OC_2H_5)_3$	n-C_6H_{14}	.469	Cooling
$CH_2(OC_2H_5)_2$	$CH_3CON(CH_3)_2$	.482	Sl. cooling
$CH_2(OC_2H_5)_2$	n-C_6H_{14}	.504	Cooling

[a] R. W. Spence, private communication. [b] Ref. 2b. [c] C. E. Holley, private communication. [d] Ref. 2d. [e] Measured at 10° instead of 3°. [f] Measured at 7° instead of 3°. [g] Measured at 14° instead of 3°. [h] Measured at 5° instead of 3°.

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(1) For the tenth communication in this series see Marvel, Dietz and Copley, THIS JOURNAL, **62**, 2273 (1940).

(2) (a) Guthrie, *Phil. Mag.*, (5) **18**, 495 (1884); (b) Weissenberger and others, *Monatsh.*, **45**, 425 (1924); **46**, 47, 57, 281, 295, 301 (1925); (c) Trew, *Trans. Faraday Soc.*, **28**, 509 (1932); Trew and Watkins, *ibid.*, **29**, 1310 (1933); (d) McLeod and Wilson, *ibid.*, **31**, 576 (1935); (e) Zellhoefer and Copley, THIS JOURNAL, **60**, 1343 (1938); (f) Copley and Holley, *ibid.*, **61**, 1599 (1939).