various substituents. The polarity is discussed in terms of the electronic structure of benzene.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE]

ELECTROMETRIC STUDIES ON THE 2-HYDROXYNAPHTHALENE SULFONIC ACIDS. PREPARATION OF PURE 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID

BY KARL H. ENGEL AND A. WITT HUTCHISON

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The purpose of the investigation was to study the neutralization curves, as obtained by electrometric titrations, of the 2-hydroxynaphthalenesulfonic acids in order to characterize them as acids and to determine especially the effect on the second dissociation constant of the position of the sulfonic acid group.

Preparation of Pure 2-Hydroxynaphthalene-6-sulfonic Acid.—In the study of this acid an especially pure material was desired. Though the preparation of metallic salts of the acid in a pure state may be accomplished by repeated recrystallization from their solutions, this cannot be done with the free acid because of its extreme solubility in water, alcohol, acetone, ether, etc.

It was found that the free acid may be precipitated from its aqueous solution by the addition of hydrogen chloride. This permitted a complete separation of the acid from excess sulfuric acid remaining in the sulfonation mass and from any isomeric compounds that may have been formed.

Schaeffer[1] first prepared the free acid from the lead salt by means of hydrogen sulfide. He obtained a crystalline compound which, when dried over concentrated sulfuric acid, melted at 125°. Later Ebert and Merz[2] used the same method of isolation and found a melting point of 122° but accepted Schaeffer's higher value as the correct one. Analyses of the compounds were not given in either case.

Preparation of the Free Acid from Hydrogen Chloride Solutions.—A mixture of 100 g. of 2-hydroxynaphthalene (Merck's resublimed) and 100 g. of sulfuric acid (100%) was stirred for seventy-five minutes at a temperature of 85°. The sulfonation mass, which had begun to solidify, was poured into a mixture of 500 g. of ice and water.

An aliquot portion of the solution was made alkaline with sodium carbonate and titrated with a standard solution of 1-diazo-2-methylbenzene hydrochloride. It was found that the solution contained 70% of the theoretically possible amount of the 2-hydroxynaphthalene-6-sulfonic acid.

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[1] Schaeffer, *Ann.*, **152**, 296 (1869).

[2] Ebert and Merz, *Ber.*, 9, 609 (1876).

Traces of insoluble substances were removed by filtration from the solution of the sulfonation mass. The filtered solution was saturated with dry hydrogen chloride and a crystalline precipitate of the 2-hydroxynaphthalene-6-sulfonic acid appeared. Previous tests had shown that neither the isomeric 2-hydroxynaphthalene-8-sulfonic acid, nor the two 2-hydroxynaphthalenedisulfonic acids, 3,6- and 6,8-, which might have been formed during the sulfonation, could be precipitated in this way. The crystals were removed from the mother liquor by filtration and washed with hydrochloric acid (30%). They were redissolved in water and reprecipitated with hydrogen chloride until, after four such recrystallizations, a test with barium chloride showed the absence of sulfuric acid.

Analytical.—The purified crystals were allowed to stand for four weeks in a desiccator over potassium hydroxide sticks (Baker's Analyzed). A sample tested at this time with silver nitrate solution showed the absence of chloride ions.

Anal. Calcd. for $C_{10}H_6OH \cdot SO_3H \cdot 2H_2O$: S, 12.32. Found: S, 12.23.

Melting point determinations were made by means of capillary tubes in a bath of sulfuric acid. The dihydrate melted sharply and without apparent decomposition at 118° corr. The dihydrate was stable at the water vapor tension of air at room temperatures. When placed in a desiccator over concentrated sulfuric acid or phosphorus pentoxide at 20°, a loss in weight corresponding to one mole of water occurred.

Anal. Loss calcd. for one mole of H_2O: 6.915%. Found over P_2O_5, 6.96%; over H_2SO_4, 6.92%. Samples regained their original weights when exposed to the air. The monohydrate melted sharply without decomposition at 129° corr.

A sample of the dihydrate when dried over phosphorus pentoxide in an atmosphere of dry nitrogen at 65° showed a loss corresponding to two moles of water.

Anal. Loss calcd. for two moles of H_2O: 13.83%. Found: 13.79%.

Samples regained their original weights when exposed to the air. The anhydrous acid melted sharply without decomposition at 167° corr.

It should be noted that the melting point of 125° given by Schaeffer agrees best with the value the authors have found for the monohydrate. Undoubtedly this was the compound he had prepared since he had dried the acid over concentrated sulfuric acid.

Materials and Apparatus.—The potassium salt of the 2-hydroxynaphthalene-6-sulfonic acid was prepared as suggested by Schaeffer.[1] The potassium salt of the 2-hydroxynaphthalene-1-sulfonic acid was prepared according to the method of Nietzki.[3] The 2-hydroxynaphthalene-6-sulfonic acid was prepared as described above.

The standard sodium hydroxide solution used in the titrations was prepared free from carbonates by diluting the required amount of a saturated sodium hydroxide solution with recently boiled distilled water. Fused benzoic acid was used as a standard.

The materials used in the calomel cells were reagents prepared by Leeds and Northrup Company especially for electromotive force measurements.

Experimental.—Fifteen-cc. portions of 0.1 molar solutions of the acids were titrated with 0.1 molar sodium hydroxide solution. The progress of the titrations was followed by measuring potential differences between a hydrogen electrode and a saturated calomel half-cell by means of a Leeds and Northrup Type K potentiometer. A suspended coil galvanometer with a sensitivity of 126 megohms was used as a null point instrument.

Data and Calculations.—The data obtained are listed in the tables. *P*H values were calculated from the equation.

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[3] Nietzki, *Ber.*, **15**, 305 (1882).

$$\frac{E(\text{obs.}) - E(\text{calcd.})}{0.00019837\ T} = \log \frac{1}{(\text{H})} = P_{\text{H}}$$

Values for pK and, from these, values for the usual dissociation constants were obtained from the equation

$$pK = P_{\text{H}} + \log \frac{\text{moles acid—moles base}}{\text{moles salt}}$$

as suggested by Clark.[4]

TABLE I

TITRATION OF 15 CC. OF 0.1 M SOLUTION OF THE POTASSIUM SALT OF 2-HYDROXYNAPHTHALENE-1-SULFONIC ACID WITH 0.1 N SODIUM HYDROXIDE

Temperature, 22 ± 0.5°; E, calcd. at 22°, 0.2480 volt

NaOH, cc.	Volt	P_{H}	$\log \frac{\text{moles acid—moles base}}{\text{moles salt}}$	pK	$K \times 10^{11}$
0.0	0.6455	6.80			
.1	.7691	8.90			
.3	.7987	9.42			
.6	.8122	9.64			
1.0	.8269	9.89			
2.0	.8456	10.22			
3.05	.8572	10.41			
4.06	.8657	10.58			
5.08	.8741	10.70	0.29	10.99	1.02
6.09	.8802	10.80	.17	10.97	1.08
7.11	.8866	10.91	.05	10.96	1.11
8.12	.8919	11.01	9.93-10	10.94	1.15
9.14	.8976	11.11	9.81-10	10.92	1.21
10.15	.9032	11.19	9.68-10	10.87	1.35
11.16	0.9071	11.26			
12.18	.9123	11.35			
13.20	.9167	11.43			
14.21	.9209	11.50			
15.22	.9242	11.57			
16.23	.9277	11.61			
17.25	.9307	11.66			
18.25	.9341	11.68			
22.32	.9444	11.91			

These values have been plotted in the curve of Fig. 1.

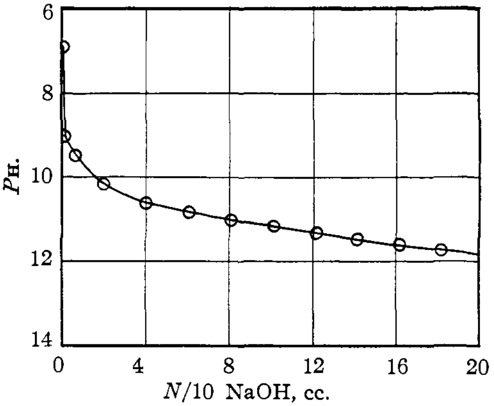

Fig. 1.—Titration of 15 cc. of $N/10$ potassium salt of 2-hydroxynaphthalene-1-sulfonic acid.

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[4] Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 1923.

TABLE II

TITRATION OF 15 CC. OF 0.1 M SOLUTION OF THE POTASSIUM SALT OF 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID WITH 0.1 N SODIUM HYDROXIDE

Temperature, 18° ± 0.5°; E, calcd. at 18°, 0.2506 volt

NaOH, cc.	Volt	P_H	$\text{Log}\ \frac{\text{moles acid—moles base}}{\text{moles salt}}$	pK	$K \times 10^9$	NaOH, cc.	Volt	P_H
0.0	0.4945	3.98				13.65	0.8204	9.87
.1	.6147	4.23				14.21	.8287	10.01
.2	.6597	6.31				14.71	.8416	10.24
1.0	.7030	7.83				14.82	.8440	10.28
2.0	.7222	8.17				15.01	.8504	10.39
3.05	.7329	8.35				15.22	.8589	10.53
4.06	.7430	8.53				15.42	.8604	10.66
5.08	.7502	8.65	0.29	8.95	1.14	15.62	.8753	10.82
6.09	.7578	8.79	.17	8.95	1.12	15.83	.8841	10.97
7.11	.7650	8.91	.05	8.96	1.11	16.04	.8893	11.07
7.62	.7687	8.98	9.99–10	8.96	1.11	16.24	.8967	11.20
8.12	.7730	9.05	9.93–10	8.98	1.05	16.64	.9063	11.40
9.14	.7798	9.17	9.81–10	8.98	1.05	17.05	.9130	11.49
10.15	.7865	9.28	9.68–10	8.96	1.10	18.25	.9266	11.70
11.16	.7941	9.41				19.27	.9329	11.83
12.18	.8020	9.55				20.30	.9385	11.92
13.20	.8130	9.74				22.33	.9459	12.06

These values have been plotted in the curve of Fig. 2.

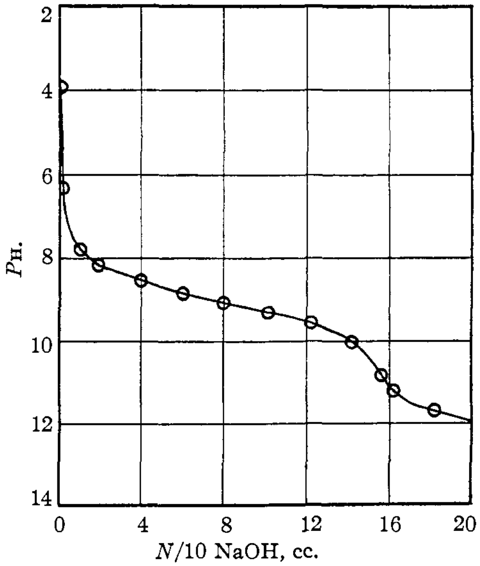

Fig. 2.—Titration of 15 cc. of $M/10$ potassium salt of 2-hydroxynaphthalene-6-sulfonic acid.

TABLE III

TITRATION OF 15 Cc. OF 0.01 *M* SOLUTION OF 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID WITH 0.1 *N* SODIUM HYDROXIDE SOLUTION

Temperature, 17 ± 0.5°; *E* calcd. at 17°, 0.2513 volt

NaOH, cc.	Volt	P_H	$\text{Log}\ \frac{\text{moles acid}-\text{moles base}}{\text{moles salt}}$	pK	$K \times 10^2$
0.0	0.3139	1.09			
.5	.3141	1.09			
1.0	.3144	1.10			
1.5	.3153	1.12			
2.0	.3172	1.15			
3.05	.3193	1.19			
4.06	.3226	1.24			
5.08	.3258	1.30	0.29	1.59	2.59
6.09	.3331	1.42	.17	1.59	2.59
7.11	.3361	1.47	.05	1.52	3.03
7.62	.3377	1.50	9.99–10	1.48	3.25
8.12	.3406	1.55	9.93–10	1.48	3.25
9.14	.3440	1.61	9.81–10	1.42	3.81
10.15	.3480	1.68	9.68–10	1.36	4.37
11.16	.3543	1.79			
11.60	.3591	1.92			
12.18	.3637	1.95			
13.20	.3769	2.18			
13.65	.3861	2.35			
14.21	.4030	2.64			
14.51	.4217	2.96			
14.72	.4544	3.55			
14.91	.6182	6.41			
15.22	.6759	7.38			
15.62	.6964	7.27			
16.24	.7152	8.06			
17.25	.7317	8.39			
18.26	.7425	8.54			
19.28	.7506	8.68			$K \times 10^9$
20.30	.7573	8.80	0.26	9.06	0.87
21.31	.7644	8.92	.13	9.06	.87
22.33	.7713	9.04	.02	9.06	.87
23.34	.7775	9.15	9.90–10	9.05	.89
24.36	.7846	9.27	9.78–10	9.05	.89
25.37	.7906	9.37	9.65–10	9.02	.95
26.38	.7985	9.51	9.50–10	9.01	.97
27.40	.8074	9.67	9.32–10	8.99	1.00
28.41	.8201	9.88			
29.44	.8351	10.15			
29.64	.8414	10.26			
29.84	.8472	10.36			
30.04	.8544	10.49			
30.25	.8622	10.62			
30.45	.8717	10.78			
30.65	.8793	10.92			

Table III (*Concluded*)

NaOH cc.	Volt	P_H
30.85	0.8892	11.09
31.15	.8973	11.23
31.45	.9056	11.36
31.75	.9111	11.47
32.04	.9155	11.53
33.49	.9311	11.81
34.49	.9370	11.92
35.50	.9414	12.01
36.50	.9451	12.05

These values have been plotted in the curve of Fig. 3.

Discussion of Results.—The value of 1.1×10^{-11} determined for the dissociation constant of the hydroxy group of the 2-hydroxynaphthalene-1-sulfonic acid shows it to be an exceedingly weak acid. This is evident from the curve (Fig. 1) in which no break appears at the end-point of the titration. It is perhaps of interest to note that the value assigned to the constant for phenol is 1.3×10^{-10}.[5]

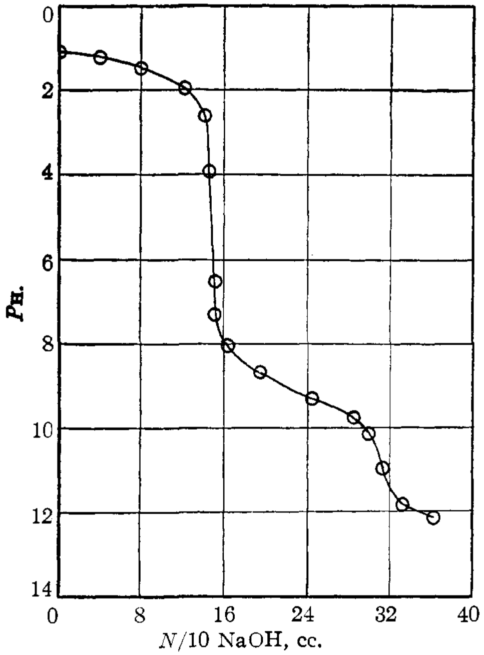

Fig. 3.—Titration of 15 cc. of $M/10$ 2-hydroxynaphthalene-6-sulfonic acid.

In the case of the constant for the hydroxy group of the 2-hydroxy-naphthalene-6-sulfonic acid the value 1×10^{-9} obtained both from the titration of the free acid and from that of its potassium salt is larger. Inspection of the curves (Fig. 2 and Fig. 3) shows that a definite break does occur at the end of the titration. It may be classed with the weak acids such as hydrogen sulfide, $K = 5.7 \times 10^{-8}$, or hydrocyanic acid, $K = 7.2 \times 10^{-10}$.[6] The break occurring in the curve of this acid makes possible its quantitative estimation in the presence of the 2-hydroxynaphthalene-1-sulfonic acid or of neutral salts.

The value of 3.3×10^{-2} found for the first dissociation constant of the 2-hydroxynaphthalene-6-sulfonic acid places it with the fairly strong

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[5] Clark, Ref. 4, Appendix.

[6] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, **1926**, Tables.

acids, the value for the second hydrogen of sulfuric acid being 3×10^{-2}; for the first constant of oxalic acid, 3.8×10^{-2}.[6] The very sharp break occurring at the end-point of the curve of the free acid (Fig. 3) lends itself well to the quantitative estimation of the acid.

Summary

1. 2-Hydroxynaphthalene-6-sulfonic acid has been purified by recrystallization of the acid from aqueous solutions by means of the addition of hydrogen chloride. The identity of a monohydrate and a dihydrate has been established. Melting points for these three compounds have been determined.

2. The 2-hydroxynaphthalene sulfonic acids have been studied electrometrically and values determined for their acid dissociation constants. The nature of the curve obtained for the 2-hydroxynaphthalene-6-sulfonic acid shows that the quantitative estimation of the acid or of its salts might be possible in the presence of the isomeric 2-hydroxynaphthalene-1-sulfonic acid, or of neutral salts.

STATE COLLEGE, PENNSYLVANIA

[COMMUNICATION FROM THE DEPARTMENT OF CHEMISTRY, SMITH COLLEGE]

RESEARCHES ON CYCLIC ACETALS. I. FORMATION OF CYCLIC ACETALS OF 4,5-DIHYDROXY-2,6-OCTADIENE[1]

BY C. PAULINE BURT AND FRANCES HOWLAND

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The tendencies toward formation of cyclic acetals have been investigated by Hibbert and co-workers.[2] In the majority of these investigations both the aldehyde and the glycol used were of the saturated type. More recently[3] work has been published on the tendencies of unsaturated glycols. The present investigation deals with a saturated glycol to form acetals with both the saturated and unsaturated type of aldehyde.

Experiments were carried out on the condensation of 4,5-dihydroxy-2,6-octadiene (dipropenyl glycol), $CH_3CH{=}CHCHOHCHOHCH{=}CHCH_3$, with acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde, acetone, benzaldehyde, crotonaldehyde, cinnamaldehyde and chloral, using sulfuric acid as a catalyst. The yields of cyclic acetals obtained were taken as a basis of comparison for the tendencies of the aldehydes toward cyclic acetal formation.

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[1] This paper is constructed from a dissertation submitted in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

[2] Hibbert and co-workers, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921); THIS JOURNAL, **45**, 734, 2433, 3108, 3117, 3124 (1923); **46**, 1283 (1924); **50**, 1411, 2235, 2242 (1928).

[3] Hibbert, Houghton and Taylor, *ibid.*, **51**, 611 (1929).