

and tris-(2,3-dihydroxypropyl)-hexadecylammonium chlorides have been compared.

2. The substitution of hydroxyethyl groups for methyl groups in trimethyldodecylammonium chloride does not greatly modify the colloidal prop-

erties; however, the substitution of 2,3-dihydroxypropyl groups results in a decided modification. A similar substitution in trimethylhexadecylammonium chloride is without a significant effect.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## The Dissociation Constants of Some Mono-substituted Benzeneseleninic Acids<sup>1</sup>

BY JAMES D. McCULLOUGH AND EDWIN S. GOULD

### Introduction

The benzeneseleninic acids are white crystalline solids analogous to benzenesulfonic acids in the sulfur series. They are weak acids of strengths comparable to that of acetic acid. A series of thirteen of these compounds has been prepared, six members of which have not been previously described in the literature. Acidic dissociation constants were determined by titration of approximately 0.005*F* solutions of the acids with standard (0.1*N*) carbonate-free sodium hydroxide using a model H Beckman *pH* meter. The dissociation constants thus obtained have been correlated with the Hammett  $\rho$ - $\sigma$  treatment<sup>2</sup> and a  $\rho$  value for the ionic dissociation observed. The effects of small temperature changes on the dissociation constants have been noted for a number of the acids and have been found to be similarly small.

### Experimental

I. Syntheses.—The seleninic acids were prepared from the corresponding diselenides through oxidation with concentrated hydrogen peroxide.



A. Preparation of Diselenides.—The diselenides were prepared by the two methods described by Campbell and McCullough.<sup>3</sup> The numbers in Table I refer to the numbering of the methods used by those authors.

B. Oxidation of Diselenides.—Two methods were employed depending on whether the diselenide was liquid or solid.

1. Solid Diselenides.—Ten grams of the diselenide was added to 10 ml. of 1,4-dioxane and the mixture warmed to about 60° to dissolve as much solid as possible. It was then cooled to below 5° and *C. P.* concentrated hydrogen peroxide (20–28%) was added dropwise, stirring the mixture and cooling externally to keep the temperature under 10°. After addition of a threefold excess of peroxide, fifteen grams of ice was added and the resulting solid (which was almost white) was filtered off and washed with 10 ml. of ice water.

2. Liquid Diselenides.—Ten grams of the diselenide was dissolved in 15 ml. of diethyl ether. Concentrated hydrogen peroxide was added dropwise; but after each five or six drops, the solution was swirled vigorously over a warm water-bath at 45° to ensure as complete a reaction as

possible. If the temperature of the mixture rose above 38°, it was cooled to below 34°, ether being added from time to time to replace that lost by evaporation. After addition of a threefold excess of peroxide, the ether was stripped off at room temperature with a water pump, leaving a mixture of white seleninic acid and orange oil impurities.

If the amount of orange oil was excessive, 30 cc. of 6*N* ammonia was added to the residue, dissolving the acid. The solution was washed twice with 20-ml. portions of ether, removing a large part of the orange residue. The aqueous layer was acidified with dilute sulfuric acid, and an excess of potassium iodide was added along with an additional 15 ml. of ether to reduce the acid back to the original diselenide. The mixture was shaken thoroughly, and just enough sodium thiosulfate solution was added to reduce the  $I_3^-$  formed. The ether layer, containing the diselenide, was separated, washed twice with dilute sodium hydroxide, twice with distilled water, and reoxidized with hydrogen peroxide as before.

C. Purification Method.—One of two methods was used, depending upon the solubility in water of the seleninic acid involved.

1. Slightly Soluble Acids.—A ten per cent. excess of 15*N* ammonia was added to the solid acid, and the solution was stirred until no white solid remained. The solution was filtered, decolorized twice with Norite, and the acid reprecipitated by slow addition of *C. P.* 6*N* hydrochloric acid. The solid was washed with ice water, dissolved in a minimum volume of methanol, and the methanolic solution added dropwise to boiling water until cloudiness formed. At that point, 25% more boiling water was added, the solution filtered hot, decolorized if necessary, then cooled rapidly with scratching to 0°. After thirty minutes, the crystallized acid was filtered off and recrystallized as before, this time cooling very slowly. The crystals, usually needles, were filtered off, dried in a vacuum desiccator over calcium chloride for two days, and a preliminary melting point taken. If the melting point was above 120°, the acid was dried in an oven for an hour at 90°. If the melting point was below 120°, the solid was kept in the vacuum desiccator for three additional days. Difficulty was encountered in removing the last traces of water from the solid; for if it were dried too persistently, the product turned pink, indicating decomposition. For this reason, the equivalent weights of some of the acids were as much as 1% low while some were 3 or 4% high. This difficulty should not, however, affect the accuracy of the dissociation constants.

2. Soluble Acids.—If the acid was quite soluble in cool water, treatment with ammonia was omitted, the crude product dissolved directly in a minimum quantity of hot (but not boiling) water (80°), the solution filtered hot, decolorized with norite until a pale yellow, and the acid reprecipitated by cooling. A second recrystallization was then made. The drying procedure was that described above.

D. Special Method.—*m*-Nitrobenzeneseleninic acid was prepared by nitration of benzeneseleninic acid nitrate as described by Friend.<sup>4</sup> The procedure was modified by

(1) Based on research carried out under Task Order I of Contract N6onr-275, between the Office of Naval Research and the University of California, Los Angeles. Presented at the Chicago meetings of the American Chemical Society, April, 1948.

(2) Louis P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1941.

(3) Tod W. Campbell and James D. McCullough, *THIS JOURNAL*, **67**, 1965 (1945).

(4) Friend, "Text-book of Inorganic Chemistry," Vol. XI, Charles Griffin and Company, Ltd., London, 1937, p. 48.

TABLE I  
IONIZATION CONSTANTS FOR SUBSTITUTED BENZENESSELENINIC ACIDS

Substituent	Preparation			M. p., °C.	$pK_{25}$	$n$	Mean dev.	$\sigma$	Equivalent weight			Se, %		
	D	O	P						Theor.	Acid	Ox. $\times 3^a$	Theor.	Anal. <sup>b</sup>	
1	None	2	1	2	121	4.79	4	0.03	0.00	189.2	188.2	189.8	41.7	41.7
2	<i>p</i> -CH <sub>3</sub>	2	1	1	170	4.88	3	.05	-.170	203.2	206.3			
3	<i>m</i> -CH <sub>3</sub>	1	2	2	121 dec.	4.80	3	.03	-.069	203.2	208.2			
4	* <i>p</i> -F	1	2	2	132-140 dec.	4.50	2	.005	.062	207.2	205.3	206	38.1	38.8
5	* <i>m</i> -F	1	2	2	115-124 dec.	4.34	2	.003	.337	207.2	212.2	209	38.1	38.5
6	<i>p</i> -Cl	2	1	1	170-185	4.48	3	.006	.227	223.7	229.3			
7	<i>m</i> -Cl	1	1	1	145-147 dec.	4.47	3	.06	.373	223.7	224.3	223		
8	<i>p</i> -Br	2	1	1	177-181	4.50	3	.03	.232	268.1	269.7	268		
9	* <i>m</i> -Br	1	1	1	157-159	4.43	3	.01	.391	268.1	269.5	270		
10	* <i>p</i> -CH <sub>3</sub> O	1	2	2	101	5.05	2	.01	-.268	219.2	219.4			
11	* <i>m</i> -CH <sub>3</sub> O	1	2	2	118	4.65	2	.01	.115	219.2	220.0	220	36.1	35.6
12	<i>m</i> -NO <sub>2</sub>			2	152	4.07	2	.02	.710	234.2	236.3	235		
13	* <i>o</i> -C <sub>6</sub> H <sub>5</sub>	2	2	2	89	4.67	1	...	None	263.2	263.0	264	30.0	29.7

\* Denotes new compound. D, denotes method of preparation of diselenide. O, denotes oxidation method. P, denotes purification method.  $n$ , denotes the number of determinations.  $\sigma$ , denotes Hammett's substituent constant.

reducing the heating time to thirty minutes and by diluting the starting material with an equal weight of concentrated nitric acid. The product is white, not yellow, as reported by Friend. (It is possible that the di-nitro compound is described.)

## II. Physical Measurements

A half-millimole sample of acid was weighed into a 250-ml. beaker and dissolved in 100 ml. of distilled water previously boiled twenty minutes to remove carbon dioxide. The titration was made with standard, approximately 0.1 *N* carbonate-free sodium hydroxide delivered from a 10-ml. buret. The solution was stirred and protected from carbon dioxide during the titration. Readings were taken with a Beckman Model H pH meter at the start and after each milliliter of base added. In the region of the endpoint the pH value was read at each drop. The temperature of the solution was noted during each titration. The equivalence point was assumed to be at a pH value of 8.0 and the pH at half-neutralization was obtained either by interpolation or graphically. Complete titration curves were prepared for a number of the acids and with the remainder, readings were taken only in the vicinities of the half-neutralization and the equivalence points. In order to get an approximate evaluation of the temperature coefficients of the dissociation constants, the pH at half-neutralization was determined at both 25 and 35° for five of the acids.

## Results and Discussion

A typical titration curve, that for the *p*-methoxy acid, is shown in Fig. 1. A summary of results is shown in Table I. The melting points are in some cases rather sharp while in others a decomposition takes place which appears to involve a loss of water to give the anhydride. Further heating then causes the anhydride to melt. This behavior is noted for some acids in the table. The rather large discrepancies between the observed and theoretical equivalent weights is probably due to the difficulty of drying the acids without decomposition as previously noted. The tendency toward high experimental values is prob-

(5) McCullough, Campbell and Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

ably due to incomplete drying. This should not affect the accuracy of the  $pK$  values determined.

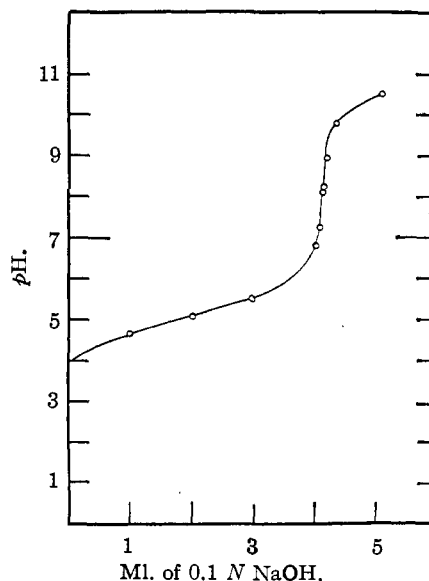


Fig. 1.—Titration curve for *p*-methoxybenzeneselenenic acid.

In calculating the  $pK$  values from the pH at half-neutralization, correction was made for the activity coefficient of the acid anion. This was done as follows

$$K = \frac{a_{H^+} a_{X^-}}{a_{HX}} = \frac{a_{H^+} C_{X^-} \gamma_{\pm}}{C_{HX} \gamma_{HX}} \quad (1)$$

Since the activity coefficient of the un-ionized acid is practically unity, we have

$$-\log K = -\log a_{H^+} - \log \frac{C_{X^-}}{C_{HX}} - \log \gamma_{\pm} \quad (2)$$

or

$$pK = pH - \log \frac{C_{X^-}}{C_{HX}} - \log \gamma_{\pm} \quad (3)$$

At the half-neutralization point

$$C_{X^-} = C_{HX} \quad (4)$$

so that

$$pK = (pH)_{1/2} - \log \gamma \pm \quad (5)$$

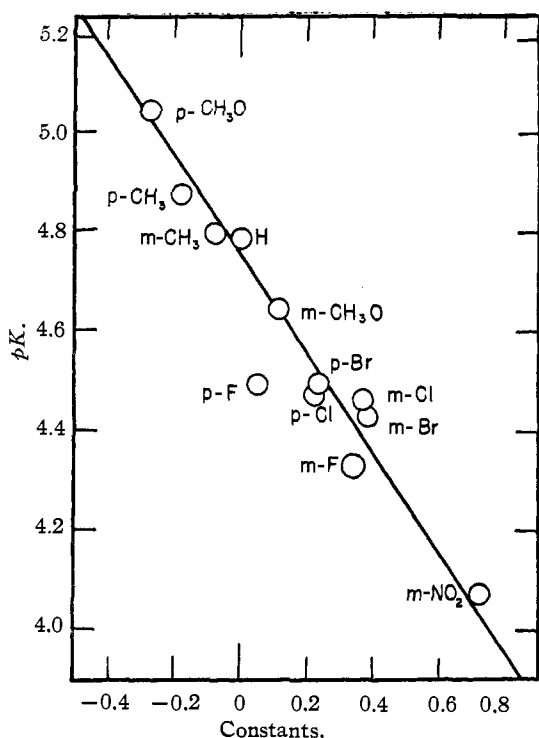


Fig. 2.—Plot of  $pK$  vs. Hammett's substituent constants.

Since

$$-\log \gamma \pm = 0.505Z_1^2\sqrt{\mu} \quad (6)$$

this term has the value 0.025 under our experimental conditions, which leads to

$$pK = (pH)_{1/2} + 0.025 \quad (7)$$

A plot of the  $pK$  values at 25° is made against Hammett's substituent constants ( $\sigma$  values) in Fig. 2 and it is seen that a good approximation to a straight line results. The best straight line through the points has a slope of 1.0 which indicates that the ionization constants of the benzeneseleninic acids have the same susceptibility toward substituents as do the benzoic acids which were the source of the  $\sigma$  values.

The  $pK$  values of the benzeneseleninic acids are rather insensitive to changes of temperature. The five acids investigated were the parent acid,  $p\text{-CH}_3$ ,  $m\text{-CH}_3$ ,  $p\text{-Cl}$  and  $m\text{-Cl}$ . In all cases the  $pK$  increased approximately 0.02 unit per 10° rise in temperature in the range 25–40°.

### Summary

1. Thirteen benzeneseleninic acids have been prepared, six of which are new. Methods of preparation are described.

2. The ionization constants (as  $pK$ ) of these acids have been determined by potentiometric titration using a Beckman  $pH$  meter. The  $pK$  values thus found are a linear function of Hammett's  $\sigma$  values.

3. Approximate temperature coefficients of the  $pK$  values have been noted for five of the acids.

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## The Surface Tension of Aqueous Sulfuric Acid Solutions at 25°

BY R. M. SUGGITT, P. M. AZIZ AND F. E. W. WETMORE

**Introduction.**—In this Laboratory we required values of the surface tension of sulfuric acid solutions at 25° up to the concentration corresponding to maximum conductivity. Morgan and Davis<sup>1</sup> reported values obtained by the drop-weight method; later Harkins and Brown<sup>2</sup> showed that certain corrections must be applied in using this method, but until now the corrected values have not been reported. More recently Sabinina and Terpugov<sup>3</sup> presented data obtained by the method of capillary rise, but gave no experimental details and reported no values for solutions less than 23% by weight acid.

The differential maximum bubble pressure technique described by Sugden<sup>4</sup> was chosen for our measurements, not only because it involves

bubble formation which parallels the experimental arrangement for which we required the data, but also because choice of this technique would afford comparison of data obtained by three different methods.

### Experimental

The solutions were made from C. P. sulfuric acid and twice-distilled water. The individual solutions were standardized by precipitation of barium sulfate and by titration against freshly prepared sodium carbonate.

The apparatus, as shown in Fig. 1, consisted of a pressure generator G and reservoir R (20 liters) connected to the bubble-forming tubes immersed in the liquid, and a sensitive manometer M attached as closely as possible to the tubes. The pressure generator consisted simply of a fine oil stream admitted to a bottle at controlled rate; thus the head required to form bubbles could be maintained at any slow rate of air flow to the tubes. The reservoir minimized pressure fluctuations during the measurements. A connection C to the compressed air line served for setting the initial pressure roughly. The manometer was a water-filled 6 mm. i.d. U-tube enclosed in a thermally lagged box. A glass scale ruled at 0.5 mm.

(1) Morgan and Davis, *THIS JOURNAL*, **38**, 555 (1916).

(2) Harkins and Brown, *ibid.*, **41**, 499 (1919).

(3) Sabinina and Terpugov, *Z. physik. Chem.*, **A173**, 237 (1935).

(4) Sugden, "The Parachor and Valency," George Routledge and Sons, London, 1930, p. 208.