

The IONIZATION CONSTANT  
of  
PARA CYANOBENZOIC ACID

Thesis

by

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# THE IONIZATION CONSTANT OF PARA-CYANO-BENZOIC ACID.

## PURPOSE

The purpose of this research was to determine the ionization constant  $K_A$  of p-cyanobenzoic acid <sup>and</sup> its position in the para substituted benzoic acid series.

## THEORY

Since the ionization constant of the para substituted benzoic acids is a measure of the electron attraction of the substituting radical, it was necessary to determine the  $K_A$  of p-cyanobenzoic acid in order to place the cyanide radical in this scheme.

According to the Mass Law the expression

$$\begin{aligned} \text{HX} &= \text{H}^+ + \text{X}^- \\ c(1-\gamma) & \quad c\gamma \quad c\gamma \\ \frac{(c\gamma)^2}{c(1-\gamma)} &= K_A \end{aligned} \quad \text{must hold, where } \gamma \text{ is the}$$

amount ionized and  $c$  is concentration in mols per liter.

It is known that  $\frac{\Lambda_c}{\Lambda_\infty} = \gamma$  = amount ionized, where  $\Lambda_c$  is the equivalent conductance of the acid at a known concentration and  $\Lambda_\infty$  the equivalent conductance at infinite dilution. The problem then resolved into preparing the pure acid and measuring the conductance of known concentration of the acid.

## PREVIOUS WORK.

No reference could be found in the literature to the  $K_A$  of p-cyanobenzoic acid, probably because Sandmeyer<sup>1</sup> reported that it was unstable and changed into terephthalamide upon crystallization from hot water. However, Kattwinkel and Wolffenstein<sup>2</sup> showed that p-cyano benzoic acid is stable, and can be prepared by the Sandmeyer reaction from p-aminobenzoic acid. It has a M.P. of 219° C. and crystallizes in white plates. These investigators report no yields.

## EXPERIMENTAL METHODS and RESULTS.

The experimental work carried out was the preparation of p-nitrobenzoic acid, the p-aminobenzoic acid, and p-cyanobenzoic acid, which was purified and used for conductivity measurements.

## Preparation of P-nitrobenzoic Acid.

The procedure given in Organic Syntheses<sup>3</sup> was used.

Three batches were run.

200 gm.	72% yield.
180 "	65% "
206 " (by John Akers)	74% "

- (1) Sandmeyer B. 18, 1497 (1885).
- (2) Kattwinkel and Wolffenstein B. 34, 2423 (1901)
- (3) Organic Syntheses Wiley. Vol. II p. 53.

### Preparation of P-aminobenzoic Acid.

Wilbrand and Beilstein<sup>4</sup>, and Vanino<sup>5</sup> reduced the nitro compound with Tin and Hydrochloric acid, but give no yields. The method finally adopted here was to mix 150 grams p-nitrobenzoic acid and 320 grams tin in a 5 li. ballon flask. Then 350 c.c. of conc. HCl were added in small portions. It is advisable to add hot dilute HCl at first so that the reaction can be started under control. If too much conc. HCl is added at first, the reaction becomes too violent. When the reaction was completed the solution was evaporated to dryness, the mass treated with conc.  $\text{NH}_4\text{OH}$ , and the stannous oxide filtered off. The ammonia solution was boiled to remove the excess ammonia, acidified with acetic acid, and allowed to crystallize. The crystals were filtered off and, after they were recrystallized from hot water, came out as brown needles.

Yield (75 gm.)      60 %      M.P. 182-183° C. (unc.)

(4) Wilbrand and Beilstein      A. 128, 261 (1863).

(5) Vanino, p. 573, "Preparative Chemie" (Enke)

Vol. 2 (1923) p. 573. (In this method the chloride of p-aminobenzoic acid crystallizes out.)

Fischer<sup>6</sup> reduced the p-nitrobenzoic acid with  $H_2S$  in an ammoniacal solution. This was tried in the following manner. Ten gm $\phi$ . p-nitrobenzoic acid was dissolved in 125 cc. dilute  $NH_4OH$  and  $H_2S$  was passed in until the solution was saturated. It was then heated and more gas introduced until a red brown color developed. The flow of  $H_2S$  was discontinued and the solution evaporated until the color changed to yellow. The sulfur formed was filtered off; the solution acidified with acetic acid; evaporated to 50 cc. , and set aside to cool. Yellow crystals formed. These were all soluble in  $NaOH$  but not completely soluble in  $HCl$ , thus showing that some unchanged p-nitrobenzoic acid was present. The product, recrystallized from hot water, formed long yellow needles.

Yield (4.3 gms.) 53 %. M.P. 181.5-182.5° C (unc).

This procedure is less difficult than the one in which tin and  $HCl$  are used.

#### Preparation of P-cyanobenzoic Acid.

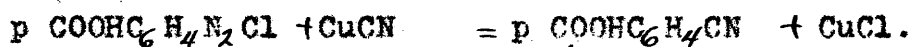
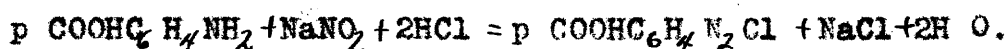
Kattwinkel and Wolffenstein<sup>2</sup> found that p-cyanobenzoic acid existed, had a M.P. of 219° C and crystallized from hot water in white plates. Hantsch<sup>7</sup> showed that syn and anti forms of the  $N=N-CN$  radical exist; of which the

(6) Fischer A. 127, 142 (1863).

(7) Hantsch B. 28, 666 (1895).

anti is stable and will not enter into the Sandmeyer reaction. Earl D. Stewart<sup>8</sup> found that the stable form could be prevented by having the cuprous cyanide solution in the Sandmeyer reaction alkaline with  $\text{Na}_2\text{CO}_3$ .

Using Stewart's idea the following procedure was devised.



To <sup>1/2 of</sup> the CuCN solution <sup>prepared</sup> according to the directions given in Organic Syntheses<sup>9</sup> was added 60 gms.  $\text{Na}_2\text{CO}_3$  (anhydrous). The diazotized solution was prepared by treating a mixture of 40 gm. p-aminobenzoic acid in 61 cc. conc. HCl (C.P.), 100 cc. water cooled with 300 gm. ice; with 20 gm. sodium nitrite in 50 cc. water until a starch iodide <sup>test</sup> was positive. Then the diazotized solution was added to the CuCN solution at an average temperature of 50-60° C with an active evolution of gas. When the gassing stopped, the solution was acidified with HCl, (slowly), the precipitated CuCN and p-cyano benzoic acid were filtered off and washed. The solid was treated with about 75 cc. of conc.  $\text{NH}_4\text{OH}$  and filtered. The filtrate was acidified with HCl, precipitating the p-cyanobenzoic acid as a

(8) Earl D. Stewart Senior Thesis California Institute of Technology. 1925.

(9) Organic Syntheses Vol. III p. 53.

Vol. IV p. 69.

brown mass. Yield crude 45 %. M.P. 106-110° C. (unc.)

The product was purified by treating its hot water solution 5 times with prepared charcoal. This treatment gave a pure product of white plates.

Yield (13 gms.) 30 % M.P. 218.5-219° C (cor.)

Its solubility was found to be about .12 grams in 100 cc. of water at 20° C, and about 4 gms. at 100° C.

#### DETERMINATION of IONIZATION CONSTANT.

The relations used in determining the conductivity of the solution are:

$$\frac{\bar{L}}{L} = k = \text{cell constant}$$

$\bar{L}$  = specific conductance

$$L = \text{actual conductance} = \frac{1}{R}$$

$$\Lambda_c = \frac{1000 \bar{L}}{c} = \frac{1000 k}{c R}$$

$\Lambda_c$  = equivalent conductance

R = actual resistance

c = concentration in mols per liter

Thus R is the only value to be measured. This can be determined by <sup>measuring</sup> the resistance of a known solution by the Kohlrausch method, using, however, an A C galvanometer for detecting balance instead of a telephone receiver.

## EXPERIMENTAL DATA

Conductivity Cell # 5. k .186 Temp. 25° C.

Number	Concentration	Resistance		
1	.007446 N	352.9	Ohms	70.8
2	.006936	367.5		73.0
3	.006909	369.6		72.8
4	.004141	494.0		90.9
5	.002059	755.3		119.6
6	.0008235	1347.0		167.6

Since the amount of ionization

$$y = \frac{\Lambda_c}{\Lambda_\infty}$$

the value of  $K_A$  can be calculated from the formula

$$\frac{(cy)^2}{c(1-y)} = K_A$$

$$\Lambda_\infty = \Lambda H^+ + \Lambda X^-$$

An examination of the known equivalent conductances of the para substituted benzoate ions shows that the greater *number* are approximately 32 or 33. Further Ostwald<sup>10</sup> gives for the m-cyanobenzoic acid  $\Lambda_\infty = 354$ . This is using however, a  $\Lambda_\infty H^+ = 320$  (18° C ?) giving a value of 34 to the m-cyanobenzoate ion. It would seem logical to adopt 33 as the equivalent conductance of p-cyanobenzoate ion. The calculation of  $K_A$  is therefore based on the value  $(347 + 33) = 380$  for  $\Lambda_\infty$  of p-cyanobenzoic acid.  $\Lambda H^+ = 347$ . (25° C)

(10) Ostwald Zeit. Phy. Chem. 3, 241 (1889).

(11) Ostwald Zeit. Phy. Chem. 3, 172 (1889).



## Calculated Results.

$$\Lambda_{\infty} = 380.$$

Temp. 25 °C.

Number	Concentration	$\Lambda$	$\gamma$	$K_A \times 10^{-5}$
1	.007446 N	70.8	.186	31.6
2	.006936	73.0	.192	31.7
3	.006909	72.8	.192	31.5
4	.004141	90.9	.239	31.1
5	.002059	119.6	.315	29.8
6	.0008235	167.6	.441	28.6

$$\text{Average } K_A \times 10^{-5} = 31.2.$$

Even when a value of 30 is used for the p-cyanobenzoate ion, or 377 for  $\Lambda_{\infty}$ , the value of  $K_A \times 10^{-5}$  is 31.5 or 1 % higher.

Terephthalamide, produced by the action of  $H_2O_2$  on p-cyanobenzoic acid<sup>12</sup>, proved to be too insoluble to allow conductivity measurements to be made. Yet its  $K_A$  can be determined by the hydrolysis of its sodium salt. Lack of time prevented making this determination.

## Conclusion.

This work was carried out under the direction of Professor Howard J. Lucas. I am also indebted to Dr. Albert Raymond and Mr. Howard Winegarden for the use their conductivity apparatus; and to Dr. Stuart J. Bates for suggestions concerning the physical chemistry involved.

SUMMARY.

Para cyanobenzoic acid was prepared by the Sandmeyer reaction, as modified by Earl D. Stewart<sup>s</sup>, and its ionization constant determined by conductivity methods. The constant was found to be  $31.2 \times 10^{-5}$ . (The meta acid has a value of  $19.9 \times 10^{-5}$ .)<sup>10</sup>

The solubility of p-cyanobenzoic acid is about .12 gm. in 100 cc. water at 20°C.

The  $K_A$  value of  $31.2 \times 10^{-5}$  places the CN radical below the  $NO_2$  radical in the p-substituted benzoic acids.