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 and 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

$$\begin{array}{ccccc} HX & = & H^+ & + & X^- . \\ c(1-\gamma) & & c\gamma & & c\gamma \end{array}$$

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

must hold, where γ 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 Λ_c is the equivalent conductance of the acid at a known concentration and Λ_∞ 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[1] reported that it was unstable and changed into terephthalamide upon crystallization from hot water. However, Kattwinkel and Wolffenstein[2] 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[3] 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[4], and Vanino[5] 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. NH_4OH, 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.)

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

(5) Vanino, p.573, "Praparative Chemie" (Enke) Vol. 2 (1923) p. 573. (In this method the chloride of p-aminobenzoic acid crystallizes out.)

Fischer[6] reduced the p-nitrobenzoic acid with H_2S in an ammoniacal solution. This was tried in the following manner. Ten gms. 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[2] found that p-cyanobenzoic acid existed, had a M.P. of 219° C and crystallized from hot water in white plates. Hantsch[7] 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[8] found that the stable form could be prevented by having the cuprous cyanide solution in the Sandmeyer reaction alkaline with Na_2CO_3.

Using Stewart's idea the following procedure was devised.

$$p\ COOHC_6H_4NH_2 + NaNO_2 + 2HCl = p\ COOHC_6H_4N_2Cl + NaCl + 2H\ O.$$

$$p\ COOHC_6H_4N_2Cl + CuCN = p\ COOHC_6H_4CN + CuCl.$$

To 1/4 of the CuCN solution prepared according to the directions given in Organic Syntheses[9] was added 60 gms. Na_2CO_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 test 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 precipatated CuCN and p-cyano benzoic acid were filtered off and washed. The solid was treated with about 75 cc. of conc. NH_4OH and filtered. The filtrate was acidified with HCl, precipatating 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.

DERTERMINATION of IONIZATION CONSTANT.

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

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

$\bar{L}$ = specific conductance

L = acutal conductance $= \frac{1}{R}$

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

Λ_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 measuring 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

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

the value of K_A can be calculated from the formula

$$\frac{(c\gamma)^2}{c(1-\gamma)} = K_A.$$

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

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[10] 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 Λ_∞ 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	Λ	γ	$K_A \times 10^{-5}$.
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

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

Even when a value of 30 is used for the p-cyanobenzoate ion, or 377 for Λ_∞, 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[12], 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.

(12) Kattwinkel and Wolffenstein B. 37, 3221 (1904)

SUMMARY.

Para cyanobenzoic acid was prepared by the Sandmeyer reaction , as modified by Earl D. Stewart,[8] and its ionization constant determined by conductivity methods. The constant was found to be 31.2×10^{-5}. (The meta acid has a value of 19.9×10^{-5}.)[10]

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

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