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THE IONIZATION CONSTANT OF PARA-CYANOBENZOIC ACID

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It has been pointed out by one of us[1] that from the ionization constants of the para-substituted benzoic acids it is possible to obtain an approximate value of the relative electron attractions of radicals. It has been assumed that in such acids the substituent groups are so far removed in space from the carboxyl group that their effect upon the latter is largely the result of electron displacements through the benzene ring and not of electrostatic influences operating across space. It is therefore desirable to know the ionization constants of all of the para-substituted benzoic acids. In this paper are described the methods by which *p*-cyanobenzoic acid was prepared and its ionization constant determined.

In the process of replacing amino by cyano it is necessary to avoid, first, the formation of *anti*-diazocyanide,[2] second, the decomposition of the sodium cuprous cyanide when the acid, which is present in the diazotized solution, is added and, third, the hydrolysis of the cyano group in the final product. As the replacement reaction is not especially rapid it was found necessary to maintain a temperature of 50–60°. Since *syn*-diazotates may at this temperature change to the stable *anti*-forms, it was thought best to keep the diazo solution acid until it could react with the cuprous cyanide. The addition of sodium carbonate to the cuprous cyanide solutions,[3] following a procedure which had been developed previously in this Laboratory in connection with other work,[4] seemed to overcome these difficulties fairly well, since the yield of crude *p*-cyanobenzoic acid, m. p. 206–210° (uncorr.), was 45%, and of the pure acid, m. p. 218.5–219° (corr.), after five crystallizations from hot water was 30%.[5]

From measurements on the conductance of aqueous solutions of the pure *p*-cyanobenzoic acid the ionization constant has been found to be

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[1] Lucas, THIS JOURNAL, **48**, 1837 (1926).

[2] Hantzsch and Schulze, *Ber.*, **28**, 666 (1895), showed that the *anti*-diazocyanides are stable and do not readily decompose to yield nitriles.

[3] "Organic Syntheses," John Wiley and Sons, **1925**, Vol. IV, p. 69. In the preparation of the tolunitriles sodium carbonate is added to the cold solution of the diazotized amine. The modification here described is more convenient.

[4] E. D. Stewart, "Senior Thesis," California Institute of Technology, **1925**.

[5] Sandmeyer, *Ber.*, **18**, 1497 (1885), reported that the acid is unstable and changes into terephthalamide upon crystallization from hot water. However, Kattwinkel and Wolffenstein, *ibid.*, **34**, 2423 (1901), showed that the cyano acid can be prepared by the Sandmeyer method and can be recrystallized from hot water to give a product melting at 219°.

3.1×10^{-4}, the calculation being made according to the usual expressions

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

where $\gamma = \Lambda_c/\Lambda_0$, Λ_0 = the conductance at zero concentration and Λ_c = the conductance at the concentration c.

A comparison of the ionization constant of this acid with those of other para-substituted benzoic acids indicates that CN has a lower electron attraction than NO_2 and a greater one than SO_2NH_2, since the constant of *p*-$C_6H_4NO_2COOH$ is 4.0×10^{-4} and that of *p*-$C_6H_4SO_2NH_2COOH$ is 2.6×10^{-4}.

The solubility of *p*-cyanobenzoic acid is approximately 0.12 g. in 100 g. of water at 20° and 4 g. at 100°.

Terephthalamide, produced by the action of hydrogen peroxide on *p*-cyanobenzoic acid,[6] has such a low solubility that no measurements of its conductivity were undertaken.

***p*-Cyanobenzoic Acid.**—An alkaline solution of sodium cuprous cyanide is first prepared by adding the cuprous chloride obtained from 160 g. of copper sulfate[7] to a solution of 80 g. of sodium cyanide in 125 ml. of water,[3] followed by the addition of 60 g. of anhydrous sodium carbonate. To the resulting liquid, maintained at a temperature of 50–60°, is added during the course of ten to fifteen minutes the diazotized solution obtained from 40 g. of *p*-aminobenzoic acid, 70 g. of concd. hydrochloric acid (C. P.), 100 g. of water, 300 g. of ice and 20 g. of sodium nitrite (in 50 g. of water). The mixture is maintained at 50–60° for about half an hour, by which time the evolution of nitrogen has practically ceased. It is then cooled and concd. hydrochloric acid is added until no more precipitate comes down. The solid, consisting of *p*-cyanobenzoic acid and cuprous cyanide, is filtered off, washed and treated with about 75 ml. of concd. ammonium hydroxide, which forms the soluble ammonium salt of the organic acid. The solution is filtered from insoluble copper salts and the *p*-cyanobenzoic acid is precipitated as a brown mass on the addition of hydrochloric acid to the filtrate. The product has a melting point of 206–210°; yield, 45%.

Five crystallizations from hot water to which animal charcoal has been added give white plates melting at 218.5–219° (corr.); yield, 30%.

The equivalent weight of the acid was determined by titration of 40.00 ml. of a solution made by dissolving 0.5006 g. in 500 ml. of water at 20° against 0.01660 *N* barium hydroxide. The mean of five titrations gave 16.457 ml. of the base, from which the calculated equivalent weight is 146.6. The theoretical value is 147.1.

The Conductance Measurements.—These were determined by the method of Kohlrausch, employing, however, an a. c. galvanometer for detecting balance instead of a telephone receiver. The cell was immersed in a thermostat at 25°. The results obtained are shown in the accompanying table.

Calculation of the Ionization Constant.—In using the equivalent conductance at zero concentration we have adopted the value of 377 reciprocal ohms, which is the one previously found for *m*-cyanobenzoic

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[6] Kattwinkel and Wolffenstein, *Ber.*, **37**, 3221 (1904).

[7] "Organic Syntheses," John Wiley and Sons, **1923**, Vol. III, p. 33.

TABLE I

CONDUCTANCE MEASUREMENTS ON *p*-CYANOBENZOIC ACID AT 25° ±0.02 (CELL CONSTANT = 0.186)

Expt.	Concn., moles/liter	Resistance in ohms	Λ_c	Λ_c/Λ_0	$K_A \times 10^{-5}$
1	0.007446	352.9	70.79	0.1878	32.2
2	.006936	367.5	72.97	.1936	32.2
3	.006906	369.6	72.48	.1932	32.0
4	.004141	494.0	90.92	.2412	31.7
5	.002059	755.3	119.6	.3172	30.4
6	.0008235	1347.0	167.7	.4448	29.4
				Mean	30.9

acid.[8] The assumption that isomeric *m*- and *p*-cyanobenzoic acids have the same equivalent conductance at zero concentration is warranted from a comparison of other isomeric *m*- and *p*-substituted benzoic acids.[8] If we take the equivalent conductance of hydrogen ion at 25° to be 350 reciprocal ohms,[9] the equivalent conductance of *p*-cyanobenzoic ion is then 27, a value which checks well with that of caproate ion, 27.4.[10]

Summary

By a modification of the Sandmeyer method *p*-cyanobenzoic acid may be obtained in satisfactory yields from *p*-aminobenzoic acid.

The ionization constant of *p*-cyanobenzoic acid as determined by conductivity measurement has a mean value of 3.1×10^{-4} at 25°.

On the assumption that the ionization constants of *p*-substituted benzoic acids are directly related to the electron attraction of radicals, the electron attraction of CN is greater than that of SO_2NH_2 and less than that of NO_2.

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[8] Ostwald, *Z. physik. Chem.*, **3**, 241 (1889), reports a value of 354 expressed in Siemens or mercury units. Compare Scudder, "Conductivity and Ionization Constants of Organic Acids," John Wiley and Sons, New York, **1914**, p. 489.

[9] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922), obtain the value 349.93 at 25°.

[10] Creighton and Fink, "Electrochemistry," John Wiley and Sons, Inc., New York, **1924**, p. 137.