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Ionization Constants of Some Hindered Aromatic Acids[1,2]

BY MELVIN S. NEWMAN AND HERBERT BODEN

The ionization constants of a number of aromatic acids in 50% dioxane–water at 40° are recorded and their values discussed.

In the solid state many polynuclear aromatic hydrocarbons and derivatives thereof are forced into non-planar structures because of intramolecular overcrowding.[3] We have long been interested in the synthesis of this type of compound and in the optical resolution of the hydrocarbons or derivatives thereof.[4] With the synthetic problems essentially solved, our interest has turned to the chemistry of derivatives of such overcrowded hydrocarbons. In this paper we report on the ionization constants of the six carboxybenzo[c]phenanthrenes,[5] together with those of a few other acids of interest (see Table I), in 50% dioxane–water at 40°. This solvent and temperature were chosen because of the solubilities of the acids involved.

TABLE I
IONIZATION CONSTANTS OF ACIDS

Acid	pK_a	Neutralization Equivalent Calcd.	Found
Benzoic	6.21	122.1	122.1
o-t-Butylbenzoic[a]	5.93	178.2	179.1
1-Naphthoic	6.05	172.2	171.3
2-Naphthoic	6.17	172.2	172.0
4-Phenanthroic	5.43	222.2	222.1
9-Phenanthroic	5.98	222.2	221.7
1-Benzo[c]phenanthroic	6.65	272.3	273.7
2-Benzo[c]phenanthroic	6.34	272.3	272.5
3-Benzo[c]phenanthroic	6.20	272.3	272.6
4-Benzo[c]phenanthroic	6.20	272.3	271.3
5-Benzo[c]phenanthroic	5.97	272.3	272.6
6-Benzo[c]phenanthroic	5.87	272.3	271.5

[a] We thank Prof. H. Shechter for a sample of this acid.

In o-substituted benzoic acids and highly branched aliphatic acids two opposing steric effects on acid strength have been observed: o-substituted benzoic acids are stronger than the para analogs, regardless of the polar nature of the substituent[6]; and highly branched aliphatic acids are appreciably weaker than acetic acid.[7] In explaining these facts,

two factors have been considered: decrease of solvation due to steric factors, and steric inhibition of resonance.

In both aromatic and aliphatic acids, solvation would be expected to stabilize the carboxylate anion relative to the free acid. Hence solvation of the ion should be an acid-strengthening factor. If steric factors decrease the amount of solvation of the anion the acid should be correspondingly weaker. The magnitude of this decrease has been demonstrated in the case of several hindered aliphatic acids.[7]

The resonance factor comes into play only with aromatic (or unsaturated) acids. Here resonance involving transfer of electrons from the ring into the carboxyl function should be more important in the free acid (neutral) than in the carboxylate anion (negatively charged) and hence should be an acid-weakening factor. If such resonance is decreased by steric factors, as in the case in o-substituted benzoic acids,[8] an acid-strengthening effect is to be expected. Since o-substituted benzoic acids are stronger than the corresponding p-isomers[8] it is apparent that steric inhibition of resonance is more important than decrease of solvation in this series. Furthermore the ratio of the strength of o-t-butylbenzoic acid to the p-isomer is greater than the corresponding ratio of the toluic acids. This indicates that as the steric factor increases in mono-o-substituted aromatic acids, the steric inhibition of resonance acid-strengthening effect becomes more pronounced than the inhibition-of-solvation acid-weakening effect.[9]

In assessing the influence of o-substituents on the strength of aromatic acids, the relative effect of a t-butyl group as compared to that of two continuously fused angular aromatic rings is of interest.[10] Comparison (see Table I) shows that 4-phenanthroic acid is appreciably stronger than o-t-butylbenzoic acid. This indicates that two continuously angularly fused rings are slightly more

(1) The material herein presented was taken from the Ph.D. thesis of H. Boden, O.S.U., 1960.

(2) We gratefully acknowledge support of this work by Grant G-9482 of the National Science Foundation.

(3) See A. O. McIntosh, J. M. Robertson and V. Vand, J. Chem. Soc., 1661 (1954), and E. Harnik, F. H. Herbstein, G. M. J. Schmidt and F. L. Hirshfeld, ibid., 3288 (1954), and references therein. F. Bell and D. H. Waring, ibid., 2689 (1949), originated the term "intramolecular overcrowding."

(4) See M. S. Newman and R. M. Wise, THIS JOURNAL, 78, 450 (1956), for leading references; also M. S. Newman and D. Lednicer, ibid., 78, 4765 (1956).

(5) For the syntheses, see M. S. Newman and H. Boden, J Org. Chem., 26, in press (1961).

(6) See for, example, G. S. Hammond in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 430.

(7) G. S. Hammond and D. H. Hogle, THIS JOURNAL, 77, 338 (1955).

(8) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University, Ithaca, N. Y., 1953, p. 744.

(9) For example, the following pKa values may be cited: o-toluic (3.91), p-toluic (4.34); o-t-butylbenzoic (3.46), p-t butylbenzoic (4.40). See E. A. Braude and F. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 588.

(10) M. S. Newman and W. H. Powell, J. Org. Chem., 26, in press (1961). In this paper it is pointed out that a benzene ring ortho to a function is roughly equivalent to a methyl group, i.e., an o-tolyl group is roughly equivalent to a 1-naphthyl group. Also two continuously angularly fused rings are roughly equivalent to a t-butyl group, or to a fused ring containing a methyl group in the neighboring peri position.

effective in exerting a steric effect than an *o-t*-butyl group.

More striking, however, is the fact that 1-benzo-[c]phenanthroic acid is appreciably weaker than any of the other isomeric acids studied and is also weaker than benzoic acid. At first glance, one might say that the hindrance to solvation factor has finally overcome the steric inhibition of resonance factor. However, examination of models reveals another feature.[11] In aromatic rings in which the ring system is planar, *ortho* groups cause steric inhibition of resonance of the carboxyl group because they prevent the oxygen atoms from being coplanar with the rings. Thus, in 4-phenanthroic acid and in *o-t*-butylbenzoic acid, the carboxyl group is twisted out of the plane of the rings. However, in 1-benzo[c]phenanthroic acid, *the rings are non-coplanar and the carboxyl group can be essentially coplanar with the ring to which it is attached*. Thus, steric inhibition of resonance between the ring and the carboxyl function does not occur to an appreciable extent and an acid-weakening resonance effect is felt. This, together with the acid-weakening hindrance to solvation effect, accounts for the weakness of 1-benzo[c]-phenanthroic acid.

Explanation of the acid strengths of the other five benzo[c]phenanthroic acids is less clear. As far as steric effects on solvation and resonance the 2- and 3-isomers should be the same. Furthermore, since there are no *o*-substituents in either case one might expect that the acid strength should be essentially the same as that of benzoic and 2-naphthoic acids. This expectation is realized with the 3-isomer, but the 2-isomer is slightly weaker than the 3-isomer. This fact may be accounted for by assuming that there is less acid-weakening resonance effect with the 3-acid than with the 2-acid. This explanation finds support in X-ray crystallographic studies[12] which show that there is more warping of the ring from coplanarity at the 3-position than at the 2-position.[13] If the findings in the solid state carry over to the solutions of the acids involved herein, the differing acid strengths of 2- and 3-benzo[c]phenanthroic acids can be ex-

plained. The two oxygen atoms of the carboxyl function at the 2-position can be coplanar with ring carbons 1 and 3 whereas the two oxygens of the carboxyl function at position 3 cannot be coplanar with carbons 2 and 4 because of the warping of the ring.[13] For this reason one can argue that the acid-weakening resonance factor contributes more in the 2-acid than in the 3-acid and hence the 3-acid is slightly stronger than the 2-acid.

Similar arguments to explain the differences in strengths of the 4-, 5- and 6- acids are less well defined because the resonance factor is affected not only by an adjacent ring fusion in each case but also by different degrees of ring-warping at positions 4, 5 and 6. One would expect that steric effects on solvation at positions 4, 5 and 6 would be about the same. It is noteworthy that the 5-acid is equal in strength to 9-phenanthroic acid whereas the 6-acid is slightly stronger.

Experimental

Ionization Constants.—The ionization constants were determined by potentiometric titration using a Beckman pH meter, model G, a calomel reference electrode, Beckman 1170, and a glass electrode, Beckman 1190–72. The electrodes were inserted directly into the sample solutions and the bath temperature was controlled at 40° by an electronic relay regulated by a mercury-to-mercury thermoregulator, Precision Scientific Co., no. 62510. Standardization was performed before and after each titration with 0.05 M phthalate buffer for pH 4.03, 0.05 M phosphate buffer for pH 6.84, and 0.01 M borax buffer for pH 9.07 as recommended.[14]

An accurately weighed sample of acid was placed in a 180-ml. electrolysis beaker and was dissolved in 50 ml. of pure dioxane pipetted from a reservoir in the constant temperature bath. Then 50 ml. of water was added from a similar reservoir. The solutions were stirred during titrations by a steady stream of nitrogen to maintain a carbon dioxide-free atmosphere. Carbonate-free 0.1003 ± 0.0001 N methanolic sodium hydroxide solution was added from a 25-ml. needle valve buret reading to 0.05 ml. At least two titrations were made on each acid. A plot of pH *versus* volume gave a smooth curve from which the end-point was determined.[15,16] The ionization constants accurate to ± 0.03 pK_a unit, were calculated at the 1/4, 1/2 and 3/4 neutralization points using the Henderson equation,[17] $pK_a = pH - \log([A^-]/[HA])$.

(11) We are indebted to Dr. Carl H. Snyder for this suggestion.

(12) F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954).

(13) See diagrams in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 477.

(14) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, pp. 447–469.

(15) F. Fenwick, *Ind. Eng. Chem., Anal. Ed.*, **4**, 144 (1932).

(16) T. Fukunaga, Ph.D. Thesis, O.S.U., 1959, determined the endpoint of various hindered aliphatic acids using both the Fenwick[15] and Gran methods [G. Gran, *Acta Chem. Scand.*, **4**, 559 (1950)] and obtained results identical within experimental error.

(17) S. Glasstone, "Text-book of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 982.