NOTES

Thermodynamic Functions of the Ionisation of Aminobenzoic Acids

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Studies of the ionisation of substituted benzoic acids have received the attention of numerous workers in recent years.[1-5] Besides the value of the knowledge of pK and related functions in chelate chemistry,[6] these data have been found to be extremely significant in elucidating a number of structural features, such as hydrogen bonding and the dipolar ion.[7] It is for the latter purposes that not only the change in the free energy of ionisation but also such other thermodynamic quantities as the changes in entropy or in heat content, have been found to be of importance. It was, therefore, considered worthwhile to undertake a systematic study of the thermodynamic functions of the ionisation of a few substituted benzoic acids; the results of the investigation of *o*-, *m*- and *p*-aminobenzoic acids will be reported in the present communication.

Experimental

Oxalic acid and *m*-aminobenzoic acid were analar samples of B. D. H. *o*-Aminobenzoic acid was crystallised from alcohol while *p*-aminobenzoic acid was recrystallised from water.[8] Sodium hydroxide was a Mercks guaranteed reagent.

Procedure.—pH metric titrations were carried out with a Beckman pH meter model H2. The temperature was maintained with an accuracy of ±0.1°C. Nitrogen was bubbled in the solution before and during the titrations.

Results and Discussion

pK values were calculated by plotting the values of pH against (HA)/(A$^-$), where the terms in parantheses refer to the activity of undissociated acid and the anions. The concentration of anions present at any stage of titration was calculated by the method of Britton,[9] while the activity coefficients were calculated in the usual manner, using the values of the Debye and Hückel constant given by Bales and his coworkers;[10] the activity coefficient of undissociated acid was taken as unity.

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[1] S. P. Datta and A. K. Grzybowski, *Trans. Faraday Soc.*, **54**, 1179 (1958).

[2] K. Laidler, ibid., **55**, 1725 (1959).

[3] E. King, *J. Am. Chem. Soc.*, **88**, 3577 (1960).

[4] N. A. Ramaiah and R. K. Chaturvedi, *Proc. Ind., Acad. Sci.*, **51**, 177 (1960).

[5] R. K. Chaturvedi and S. S. Katiyar, This Bulletin, **35**, 1416 (1962).

[6] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., p. 386.

[7] H. C. Brown, D. H. McDaniel and O. Haflinger, "Determination of Organic Structures by Physical Methods," Ed. by E. A. Braude and F. C. Nachod, Acad. Press, New York (1937), pp. 59, 2365.

[8] "Dictionary of Organic Compounds," Vol. I, Eyre and Spottiswoode, London (1946), p. 60.

[9] H. T. S. Britton, "Hydrogen Ions," Chapman and Hall, London (1955), p. 170.

[10] G. G. Manov, R. G. Bates, W. H. Hamer and S. E. Acree, *J. Am. Chem. Soc.*, **65**, 1765 (1943).

Figure 1 gives a typical set of titration curves of *o*-aminobenzoic acid at different temperatures. It may be seen that these curves show a marked inflexion, as is the case with most of the benzoic acids. Similar titration curves were obtained for other acids also. The values of p*K* at different temperatures were obtained by the graphical procedure given in Fig. 2. These data are given in Table I.

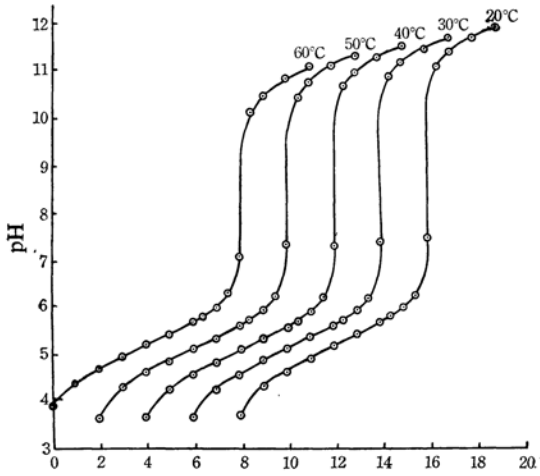

Fig. 1. pH metric titration of *o*-aminobenzoic acid.

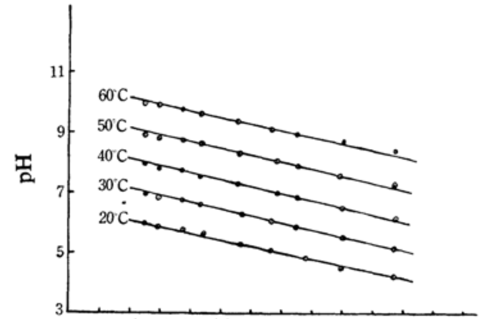

Fig. 2

TABLE I. THERMODYNAMIC DISSOCIATION CONSTANTS OF AMINOBENZOIC ACIDS

Temp. °K	*o*-Aminobenzoic acid pK_a	*m*-Aminobenzoic acid pK_a	*p*-Aminobenzoic acid pK_a
293	5.125	4.90	4.95
303	5.025	4.75	4.90
313	5.030	4.675	4.95
323	5.100	4.600	5.10
333	5.200	4.70	5.25

The variation in p*K* with the temperature has been studied theoretically by Harned and Robinson.[11] When the data in Table I are examined on the basis of the equation of Harned and Robinson, the following equations were derived:

o-Aminobenzoic acid

$$TpK = 13.589\times10^3 - 83.07T + 1.427\times10^{-1}T^2$$

m-Aminobenzoic acid

$$TpK = 12.929\times10^3 - 76.12T + 1.261\times10^{-1}T^2$$

p-Aminobenzoic acid

$$TpK = 13.73\times10^3 - 85.9T + 1.5\times10^{-1}T^2$$

The validity of these equations was established by the close agreement between observed and calculated values of p*K*. From the parameters of these equations, the values of the thermodynamic functions of ionisation were calculated in the usual way.[11] These are given in Table II.

TABLE IIA. THERMODYNAMIC FUNCTIONS OF IONISATION OF *o*-AMINOBENZOIC ACID

Temp. °K	ΔF kcal./mol.	ΔH kcal./mol.	ΔS cal./degree, mol.	ΔC_p cal./mol., degree
293	6.916	6.091	−2.636	−386.3
303	6.963	2.242	−15.63	−396.4
313	7.191	−1.793	−28.74	−409.6
323	7.558	−6.243	−41.85	−422.6
333	7.971	−10.23	−54.87	−435.6

TABLE IIB. THERMODYNAMIC FUNCTIONS OF IONISATION OF *m*-AMINOBENZOIC ACID

Temp. °K	ΔF kcal./mol.	ΔH kcal./mol.	ΔS cal./degree, mol.	ΔC_p cal./mol., degree
293	6.643	9.665	10.17	−335.7
303	6.597	6.229	−1.283	−350.1
313	6.689	2.655	−12.92	−360.8
323	6.825	−1.013	−24.39	−373.3
333	7.191	−4.817	−39.02	−385.0

TABLE IIC. THERMODYNAMIC FUNCTIONS OF IONISATION OF *p*-AMINOBENZOIC ACID

Temp. °K	ΔF kcal./mol.	ΔH kcal./mol.	ΔS cal./degree, mol.	ΔC_p cal./mol., degree
293	6.643	3.938	−9.166	−402.9
303	6.825	−0.142	−22.82	−416.6
313	7.101	−3.93	−36.67	−430.4
323	7.558	−8.758	−50.42	−444.1
333	8.061	−13.25	−64.16	−458.0

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[11] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

As was expected on the basis of the resonance effect and in accordance with deductions from physico-chemical measurements(12) the data obtained in the present work also suggest that there is a greater tendency for meta acid than for ortho and para acids to exist in the form of the dipolar ion.

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12) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corporation, New York (1943), p. 147.