PARA-SUBSTITUTED BENZOHYDROXAMIC ACIDS: THERMODYNAMIC IONIZATION CONSTANTS AND APPLICABILITY OF HAMMETT EQUATION

By Y. K. AGRAWAL*† and J. P. SHUKLA*‡

[Manuscript received 16 October 1972]

Abstract

Thermodynamic ionization constants were determined in aqueous media at 25°. An attempt was made to correlate these constants with Hammett's equation.

Introduction

The hydroxamic acids are important in the field of analytical chemistry. In view of this it was desirable to obtain a knowledge of their ionization constants. Only a few concentration constants have been reported.¹⁻³ Therefore, in the present investigation the thermodynamic ionization constants of *p*-substituted benzohydroxamic acids have been determined in aqueous medium at 25°. These constants were correlated with Hammett's σ function.

Experimental

Hydroxamic Acids

The *p*-substituted hydroxamic acids were prepared by adapting the modified method described previously.⁴

Determination of Ionization Constants

The weighed quantity of hydroxamic acid (0.05 mol) was placed in a four-neck titration cell and dissolved by adding 47.5 ml of water. The solution was stirred for several minutes under an

* Department of Chemistry, Government Polytechnic, Jabalpur, M.P., India.

[†] Present address: Department of Chemistry, Indian Institute of Technology, Powai, Bombay-76, India. Author to whom correspondence should be addressed.

[‡] Present address: Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-85, India.

¹ Wise, W. W., and Brandt, W. W., J. Am. chem. Soc., 1955, 77, 1058.

- ² Green, A. L., Sainburg, G. L., Saville, B., Stansfield, M. J., J. chem. Soc., 1958, 1983.
- ³ Hackley, B. E., Jr, Plapinger, R., Stolberg, M., Jauregg, T. W., J. Am. chem. Soc., 1955, 77, 3651.

⁴ Shukla, J. P., Agrawal, Y. K., and Kuchya, K. P., J. Indian chem. Soc., in press.

Aust. J. Chem., 1973, 26, 913-5

atmosphere of nitrogen and titrated with 0.1M carbonate-free potassium hydroxide in 10 increments. After each addition the pH was recorded after 1 min.

Results and Discussion

The thermodynamic ionization constants, pK_a , are given in Table 1. In Figure 1 the pK_a of benzohydroxamic acids are plotted against pK_a of the benzoic acids to give a straight line. Equation (1) is obtained by the method of least squares:

$$pK_a = 1.02 K_0 + 4.62 \tag{1}$$

TABLE 1

THERMODYNAMICIONIZATION CONSTANTS OF *p*-SUBSTITUTED BENZOHYDROXAMIC ACIDS $XC_6H_4CONHOH$ The experimental pK_a values are the average of nine results. pK_a difference is $(pK_a exptl) - (pK_a least squares)$

X	pK _a exptl	σ ^a	pK_a least squares	pK _a Hammett	pK _a difference	pK_a benzoic acids
н	8.91		8.91		0.00	4.21
CH₃	9.05	-0.170	9.05	9.08	0.00	4.34
OCH ₃	9.15	-0.268	9.18	9.18	-0.03	4.47
F	8.81	+0.062	8.84	8.85	-0.03	4.14
Cl	8.70	+0.227	8.69	8.69	+0.01	3.99
Br	insol.	+0.232	8.70	8.68	· <u>-</u> .	4.00
I	insol.	+0.276	8.63	8.63	_	
NO ₂	8.12	+0.778	8.13	8.13	0.00	3.44
NH ₂	9.42	-0.660		· · · · · · · · · · · · · · · · · · ·	<u> </u>	
CN	8.26	+0.660	8.24	8.25	+0.02	3.55

^a From Jaffe, H. H., Chem. Rev., 1953, 53, 191.



Fig. 1.— pK_a of *p*-substituted benzohydroxamic acids against pK_a of *p*-substituted benzoic acids.

The pK_a values in Table 1 established experimentally and calculated by the Hammett equation⁵ $[\log(K/K_0) = \rho\sigma]$ and least squares are in good agreement, having a maximum $\pm 0.03pK_a$ unit deviation. Similarly, the plot of pK_a values of

⁵ Hammett, L. P., Chem. Rev., 1935, 17, 125.

914

p-substituted benzohydroxamic acids against Hammett's σ function gives a straight line with the slope $\rho = 1.00$ in agreement with the experimental values (Table 1).

Acknowledgment

The authors are indebted to Professors A. B. Biswas and S. C. Bhattacharyya of I.I.T., Bombay, for providing facilities.