

## THERMODYNAMIC PROTON-LIGAND STABILITY CONSTANTS OF SOME HYDROXAMIC ACIDS

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The present communication deals with the determination of thermodynamic proton-ligand stability constants,  ${}^T K_a$ , of ten hydroxamic acids by the pH titration method in the aqueous medium at  $25 \pm 0.1^\circ \text{C}$ . Since most of these compounds are sparingly soluble in water, recourse to the use of mixed solvents had to be made in various instances. Values of  ${}^T K_a$  thus obtained from different dioxan-water mixtures were then extrapolated to 100% aqueous medium, after the validity of such an extrapolation was found to hold good.

### Experimental

Hydroxamic acids (Table 1) were prepared by the method of Priyadarshini and Tandon.<sup>1</sup> Carbonate-free potassium hydroxide was prepared by the electrolytic method,<sup>2a</sup> standardized against potassium hydrogen phthalate,<sup>2b</sup> and diluted to 0.1M. B.D.H. dioxan was purified as recommended by Weissberger and Proskauer.<sup>3</sup>

### Determination of Proton-Ligand Stability Constants

The titration procedure for the determination of  ${}^T K_a$  was essentially the same as that described by Albert and Serjeant.<sup>4</sup> Measurements of pH were made with a Radiometer pHM-4c pH-meter, saturated calomel reference electrode and a glass electrode. Hydroxamic acid (0.5 mmol) was introduced into a titration cell and was dissolved in water or dioxan-water mixture of desired composition; the initial volume was 47.5 ml in all the titrations. Pre-saturated nitrogen (with solvent of appropriate composition) was continually bubbled through the solution. After about 10 min, the titration was started by adding 0.5-ml increments of 0.1M KOH each time and noting the highest pH-meter reading which remained steady. Titrations, carried out in duplicate, were reproducible within  $\pm 0.01$  pH unit.

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<sup>1</sup> Priyadarshini, U., and Tandon, S. G., *J. chem. Engng Data*, 1967, **12**, 143.

<sup>2</sup> Vogel, A. I., "A Text-book of Quantitative Inorganic Analysis." 3rd Edn, (a) p. 240; (b) p. 243. (Longmans: London 1961.)

<sup>3</sup> Weissberger, A., and Prosskauer, E. S., "Organic Solvents." Vol. 7, p. 372. (Interscience: New York 1955.)

<sup>4</sup> Albert, A., and Serjeant, E. P., "Ionization Constants of Acids and Bases." p. 28. (Methuen: London 1962.)

### Calculations

For an organic acid, say HA, in an aqueous medium, it can be shown that

$$\text{Tp}K_a = \text{pH} + \log([\text{HA}]/[\text{A}^-]) + \log(1/\gamma_{\pm})$$

and in a mixed aqueous solvent

$$\text{Tp}K'_a = B + \log U^{\circ}_{\text{H}} + \log([\text{HA}]/[\text{A}^-]) + \log(1/\gamma_{\pm})$$

where  $\text{Tp}K_a$  and  $\text{Tp}K'_a$  stand for the negative logarithm of the thermodynamic proton-ligand stability constant in the aqueous and mixed aqueous solvent medium respectively, and  $B$  represents the pH-meter reading obtained in the latter. Applying a correction for hydrolysis of the salt which may be appreciable in the end of the titration (i.e. at  $\text{pH} > 10$ ), the final expression for  $\text{Tp}K_a$  is given by the relation

$$\text{Tp}K_a = \text{pH} + \log\{([\text{HA}] + [\text{OH}^-])/([\text{A}^-] - [\text{OH}^-])\} + \log(1/\gamma_{\pm})$$

Values of the correction factor,  $\log U^{\circ}_{\text{H}}$ , and the mean activity coefficients of uni-valent ions,  $\gamma_{\pm}$ , are given elsewhere.<sup>5</sup>

TABLE 1

THERMODYNAMIC PROTON-LIGAND STABILITY CONSTANTS AT 25°C OF HYDROXAMIC ACIDS  $\text{R-N(OH)-CO-R'}$

For compounds (1), (2), and (4) the mole fraction  $n_2$  of dioxan employed was 0.0–0.174, for the rest 0.05–0.174.

Com- pound	R	R'	TpK <sub>a</sub> in Aqueous Medium			TpK <sub>a</sub> = $a + bn_2$
			Expt.	Extrap.	Lit. <sup>a</sup>	
(1)	H	Ph	8.91	8.95	8.92 <sup>b</sup>	$8.95 + 9.98n_2$
(2)	Ph	Pr	8.84	8.87		$8.87 + 15.06n_2$
(3)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Pr	ins.	9.02		$9.02 + 14.91n_2$
(4)	Ph	Ph	8.38	8.46	8.38, <sup>b</sup> 8.31 <sup>c</sup>	$8.46 + 14.95n_2$
(5)	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	ins.	8.58		$8.58 + 14.47n_2$
(6)	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	ins.	8.67		$8.67 + 14.04n_2$
(7)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	ins.	8.72		$8.72 + 13.82n_2$
(8)	Ph	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	ins.	8.41		$8.41 + 14.37n_2$
(9)	Ph	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	ins.	8.53		$8.53 + 14.61n_2$
(10)	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	ins.	8.64		$8.64 + 14.52n_2$

<sup>a</sup> Reported stoichiometric constants ( $^{\circ}\text{p}K_a$ ) have been converted into thermodynamic constants ( $\text{Tp}K_a$ ) after appropriate correction on the basis of equation  $\text{Tp}K_a(\text{aq.}) = ^{\circ}\text{p}K_a(\text{aq.}) + 0.5\sqrt{I_m}$  where  $I_m$  is the ionic strength calculated.

<sup>b</sup> Jaimini, J. P. C., and Sogani, N. C., *J. Indian chem. Soc.*, 1970, **47**, 247.

<sup>c</sup> Dyrssen, D., *Acta chem. scand.*, 1956, **10**, 353.

### Results

$\text{Tp}K_a$  values of ten hydroxamic acids are given in Table 1. The values, which are accurate to  $\pm 0.03$  unit, are thermodynamic constants since in the calculation activities of individual species have been taken into account. Titrations could be done in the aqueous medium with compounds (1), (2), and (4) only. Values of  $\text{Tp}K'_a$

<sup>5</sup> Shukla, J. P., Ph.D. Thesis, Jabalpur University, 1968.

determined in 10, 20, 30, 40, 45, and 50% (v/v) aqueous dioxan were subjected to least-squares analysis which showed that for all the compounds the best fit is obtained with an equation of first order. The linear equations for these lines thus computed are also given in Table 1.

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