Journal of Fluorine Chemistry, 9 (1977) 333–336

Received: September 13, 1976

SHORT COMMUNICATION

Proton-Ligand Stability Constants of Halo-N-Arylhydroxamic Acids

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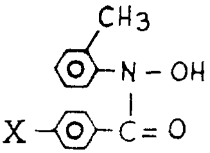
In a previous communication [1] we described the preparation and ionisation constants of hydroxamic acid. We now report further work on the halogen substituted N-arylhydroxamic acids (I), their proton ligand stability constants and correlation with Hammett σ function.



(X = F, Cl or Br)

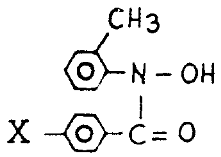
The thermodynamic pK_a for N-arylhalodroxamic acids are given in Table 1. The values on the thermodynamic parameters are shown in Table 2. The plot of change in free energy from mixed aqueous to aqueous media δ versus dioxane precent is shown in Fig. 1. In these plots we have expressed these results as δ where

$$\delta = \Delta G^{o}_{s} - \Delta G^{o}_{w} \qquad (1)$$

In eqn. (1) ΔG^{o}_{w} and ΔG^{o}_{s} refer to the standard free energy changes in pure water as solvent and in aqueous or organic mixture as solvent, respectively. It is interesting to note in dioxane-water mixtures, the effect of increased organic content on δ is in the same order as F > Cl > Br.

TABLE 1

Thermodynamic proton ligand stability constants of halo N-arylhydroxamic acid



Dioxane		X = F		X = Cl		X = Br	
n_2 (mole fraction)	% (v/v)	25°	35°	25°	35°	25°	35°
0.023	10	8.80	8.60	8.70	8.48	8.68	8.46
0.050	20	9.20	9.00	9.11	8.90	9.09	8.88
0.083	30	9.71	9.50	9.61	9.38	9.60	9.37
0.123	40	10.33	10.15	10.22	9.99	10.20	9.98
0.147	45	10.73	10.52	10.58	10.35	10.56	10.35
0.174	50	11.08	10.87	11.01	10.75	10.98	10.75
0.240	60	12.16	11.95	12.03	11.75	12.00	11.73
0.330	70	13.50	13.30	13.41	13.15	13.38	13.18
25°:	$pK_a =$	$15.41\ n_2 + 8.44$		$15.37\ n_2 + 8.34$		$15.20\ n_2 + 8.33$	
35°:	$pK_a =$	$15.37\ n_2 + 8.24$		$15.17\ n_2 + 8.13$		$15.49\ n_2 + 8.07$	

It is observed that a linear relationship exists between the pK_a and the mole fraction of dioxane of the form

$$pK_a = mn_2 + C \qquad (2)$$

The values of slope, m, and the constant were obtained by the method of least squares and given in Table 1. While a plot of pK_a against reciprocal of the dielectric constant of dioxane is not linear at 25° and 35°C and evidently non-electrostatic factors exert a considerable influence on the dissociation [2, 3] as shown by the Born equation, eqn.(4)

$$pK_a = \frac{\Delta G^0{}_{non}}{2.303\ RT} + \frac{Ne^2}{2\ D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

where r_+ and r_- are the radii of the ions and D is the dielectric constant of the dioxane. The pK_a values in Table 1 established experimentally and calculated by the Hammett equation, $-\log K/K_0 = \rho\,\sigma$, and the least squares are in good agreement.

TABLE 2

Thermodynamic parameters of halo N-arylhydroxamic acid

X		Dioxane							
		10	20	30	40	45	50	60	70
	ΔG^{o}	12.01 12.13	12.56 12.70	13.25 13.40	14.10 14.32	14.65 14.85	15.12 15.34	16.60 16.86	18.43 18.77
F	ΔH^{o}	8.4	8.4	8.8	7.6	8.8	8.8	8.8	8.4
	$-\Delta S^{o}$	12.01 12.10	13.95 13.95	14.93 14.92	21.80 21.80	19.62 19.59	21.20 21.22	26.16 26.15	33.64 33.64
	ΔG^{o}	11.88 11.97	12.44 12.56	13.12 13.24	13.95 14.10	14.44 14.60	15.03 15.17	16.42 16.58	18.30 18.55
Cl	ΔH^{o}	9.3	8.8	9.7	9.7	9.7	10.9	11.8	10.9
	$-\Delta S^{o}$	8.65 8.66	12.21 12.20	11.44 11.48	14.25 14.27	15.90 15.90	13.85 13.85	15.50 15.51	24.82 25.82
	ΔG^{o}	11.85 11.89	12.41 12.47	13.09 13.19	13.92 14.07	14.41 14.60	14.97 15.18	16.37 16.62	18.22 18.60
Br	ΔH^{o}	10.5	10.5	10.1	9.7	8.8	8.8	8.4	7.1
	$-\Delta S^{o}$	4.53 4.51	6.41 6.39	10.03 10.02	14.16 19.10	18.82 18.81	20.69 20.70	26.66 26.67	37.30 37.31

The values at the upper line are at 25°C and at the lower line are at 35°C. ΔG^{o} and ΔH^{o} are in kcal mole^{-1}, $-\Delta S^{o}$ is in cal mol^{-1} deg^{-1}

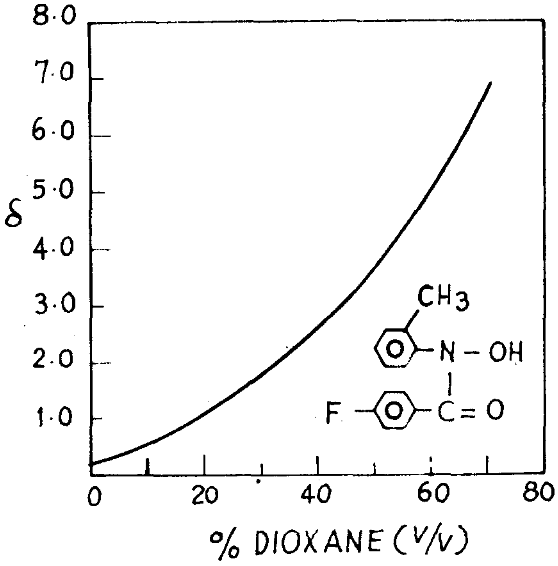


Figure 1.

The titration procedure was essentially the same as recommended elsewhere [5, 6]. Generally 0.05 mmole of hydroxamic acid in 47.5 ml of solvent were placed in a three necked titration vessel (thermostated at 25° or 35°) carrying a glass electrode, calomel electrode and microburette. Nitrogen gas presaturated with solvent was passed through the solution which was titrated with 0.1 M tetrabutyl ammonium hydroxide in 0.5 ml aliquots and noting the highest appropriate drift free reading on the pH meter.

We would like to thank Prof. A.S. Kapur, Head, Department of Chemistry, Government Science College, Satna for providing the necessary facilities.

1 Y.K. Agrawal, V.P. Khare and A.S. Kapur, J. Fluorine Chem., 5 (1976) 447.
2 M. Kilpatric, Chem. Revs., 30 (1942) 159.
3 R.G. Bates, in B. Pesce (ed.), Electrolytes, Pergamon, Oxford, 1962.
4 M. Born, Z. Phys., 1, (1920) 45.
5 Y.K. Agrawal and S.G. Tandon, Talanta, 17 (1972) 700.
6 A. Albert and E.P. Serjeant, Ionisation Constants of Acids and Bases, Methuen, London, 1962.