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THERMODYNAMIC PROTON—LIGAND STABILITY CONSTANTS IN DIOXANE—WATER MEDIA. pK_a, ΔG^0, ΔH^0 AND ΔS^0 VALUES FOR *N-p*-CHLOROPHENYL SUBSTITUTED HYDROXAMIC ACIDS

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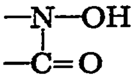
ABSTRACT

The thermodynamic ionisation constants of *N-p*-chlorophenyl substituted hydroxamic acids have been determined in different mole fractions of dioxane (0.174—0.330) at 25 and 35 ± 0 1°C. The thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, are calculated. The effect of solvent, the change in free energy from mixed aqueous to aqueous media, δ, the Hammett correlation function and the effect of substituents on the ionisation constants of hydroxamic acids are discussed.

INTRODUCTION

Analytical application of hydroxamic acids requires the knowledge of their ionisation constants [1—3]. Ionisation constants are essential for understanding the physico-chemical properties of the reagents which are of considerable importance in their application as analytical reagents. It is observed that the substituents affect the ionisation constants (pK_a) of the acids [4—8].

The hydroxamic acids, functional group (I), have a dissociatable hydrogen



$$\begin{array}{l} -\mathrm{N}-\mathrm{OH} \\ \;\;\; | \\ -\mathrm{C}=\mathrm{O} \end{array}$$

(I)

and their pK_a varies between 8 and 14. With this objective a series of *N-p*-chlorophenyl substituted hydroxamic acids were synthesised [9] and their ionisation constants are reported for possible analytical applications.

The pK_a values of hydroxamic acids are determined by the pH-titration method using glass and saturated calomel electrodes. The necessary corrections for "medium effect" and "activity coefficients" to obtain the thermodynamic pK_a values are made [10—13].

EXPERIMENTAL

All chemicals used were of AnalaR and G.R. grades of B.D.H. or E. Merck unless otherwise stated. Dioxane was purified by the method of Weissberger

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et al. [14]. Carbonate-free potassium hydroxide was prepared by the electrolytic method of Vogel [15]. The acids were prepared as described elsewhere [9]. They were recrystallised before use and the purity was checked by elemental analysis, UV and IR spectra. A systronics digital pH meter, Model 335, was used for pH measurements and standardised by standard buffers [16].

The details of the experimental procedure and calculations of pK_a are essentially the same as reported elsewhere [1]. Briefly, 0.5 mmole of hydroxamic acid in 47.5 ml of solvent mixture were titrated with 0.1 M KOH in 0.5 ml increments using a thermostatted (25 or 35°C) three-necked titration vessel, equipped with an inlet for nitrogen, glass and calomel electrodes and a limb for the burette tip. The solution was stirred with nitrogen, presaturated with solvent medium. The highest drift-free pH meter reading was noted. If the hydroxamic acids were insoluble, the titrations were performed using lower concentrations of the acids.

From the thermodynamic pK_a values at two different temperatures, the change in free energy, ΔG^0, enthalpy, ΔH^0 and entropy, ΔS^0, associated with the ionisation equilibrium, i.e. $HA \rightleftharpoons H^+ + A^-$ (HA = hydroxamic acid), can be readily evaluated on the basis of the following equations

$$\Delta G^0 = 2.303RT\text{p}K_a \qquad (1)$$

For simplicity, eqn. (1) can be written as

$$\text{At } 25^\circ\text{C: } \Delta G^0_{(298.2^\circ\text{C})} = 1.365\ \text{p}K_a\ (\text{in kcal}) \qquad (1a)$$

$$\text{at } 35^\circ\text{C: } \Delta G^0_{(308.2^\circ\text{C})} = 1.411\ \text{p}K_a\ (\text{in kcal}) \qquad (1b)$$

The expression for standard enthalpy change, ΔH^0, is obtained by integration of the Van't Hoff equation at two temperatures, T_1 and T_2

$$\log K_2/K_1 = \frac{\Delta H^0(T_2 - T_1)}{4.576T_1T_2} \qquad (2)$$

From the pK_a at two temperatures, the standard enthalpy change, ΔH^0, is estimated using eqn. (2). From measurements at 25 and 35°C, eqn. (2) can be simplified as

$$\Delta H^0 = 42.07\Delta\ \text{p}K_a\ (\text{kcal}) \qquad (2a)$$

where

$$\Delta\ \text{p}K_a = \text{p}K_{a(25^\circ\text{C})} - \text{p}K_{a(35^\circ\text{C})}$$

Standard enthalpy change, ΔS^0, is computed from the Gibbs—Helmholtz equation

$$\Delta S^0 = \frac{\Delta G^0 - \Delta H^0}{T} \qquad (3)$$

At 25 and 35°C, eqn. (3) can be reduced to the following forms

$$\text{at } 25^\circ\text{C: } -\Delta S^0\ (\text{kcal}) = 3.354 \times 10^{-3}(\Delta G^0 - \Delta H^0) \qquad (3a)$$

$$\text{at } 35^\circ\text{C: } -\Delta S^0\ (\text{kcal}) = 3.244 \times 10^{-3}(\Delta G^0 - \Delta H^0) \qquad (3b)$$

RESULTS AND DISCUSSION

The thermodynamic ionisation constants at 25 and 35°C are given in Table 1. The pK_a values are accurate to ±0.03. The empirical data for the mole fraction of dioxane and ΔG^0, ΔH^0 and ΔS^0 values are given in Tables 2 and 3, respectively. The pK_a values increase with increase in dioxane content (mole fraction of dioxane) because of the decrease in the dielectric constant of bulk solvent. As the dielectric constant decreases, the ion interaction involving the proton and anionic oxygen on the ligand decreases to a greater extent than the ion dipole interaction between the proton and the solvent molecule. A plot of pK_a vs. mole fraction of dioxane (Fig. 1) shows a linear relationship of the form p$K_a = mn_2 + C$.

It has also been pointed out by Gurney [17] and Agrawal et al. [1,18] that the standard free energy change accompanying the proton transfer, $\Delta G^0_{\mathrm{diss.}}$, may be split up into two distinct parts, electrostatic and non-electrostatic.

$$\Delta G^0_{\mathrm{diss.}} = \Delta G^0_{\mathrm{el}} + \Delta G^0_{\mathrm{non.}} \tag{4}$$

The electrostatic contribution to free energy change is estimated by the

TABLE 1

pK_a of *N*-*p*-chlorophenyl substituted hydroxamic acids at 25 and 35°C[a]

Compd. No.	*N*-*p*-Chlorophenylbenzo-hydroxamic acids	pK_a		
		Mole fraction of dioxane (n_2)		
		0 174	0.24	0.33
I	Benzo-	10.91	11.77	12.87
		(10.68)	(11.53)	(12.64)
II	*p*-Methoxy-	11.25	12.10	13.15
		(10.93)	(11.80)	(12.84)
III	*p*-Ethoxy	11.95	12.70	13.75
		(11.70)	(12.50)	(13.55)
IV	*p*-Fluoro-	10 80	11.61	12.76
		(10.60)	(11.45)	(12 60)
V	*p*-Chloro-	10 82	11.72	12.80
		(10.50)	(11.34)	(12 45)
VI	*p*-Bromo-	10.65	11.45	12.59
		(10.47)	(11.30)	(12.41)
VII	*p*-iodo-	10.60	11.35	12 45
		(10.40)	(11.21)	(12.30)
VIII	2-Naphtho-	11 00	11.70	12.69
		(10.70)	(11.37)	(12.30)
IX	Cinnamo-		11.82	12.73
			(11.26)	(12.27)
X	Monochloroaceto-	10.27	11 05	11.95
		(10.05)	(10.75)	(11.65)

The values given in parentheses are at 35°C.

TABLE 2

Empirical correlation of pK_a with mole fraction of dioxane (n_2)

Compd. No.	p$K_a = mn_2 + C$				
	Least squares method			Graphically	
	m	C	r[a]	m	C
I	12.54	8.74	1.00	12.50	8.76
	(12.55)	(8.50)	(1.00)	(12.50)	(8.50)
II	12.15	9.15	1.00	12.10	9.15
	(12.21)	(8.83)	(0.99)	(12.00)	(8.85)
III	11.56	9.93	1.00	11.50	9.91
	(11.92)	(9.63)	(1.00)	(11.80)	(9.65)
IV	12.58	8.60	1.00	12.80	8.60
	(12.82)	(8.37)	(1.00)	(12.70)	(8.37)
V	12.65	8.64	0.99	12.50	8.65
	(12.49)	(8.32)	(1.00)	(12.50)	(8.33)
VI	12.45	8.48	0.99	12.50	8.49
	(12.43)	(8.31)	(1.00)	(12.50)	(8.30)
VII	11.88	8.52	1.00	11.80	8.50
	(12.19)	(8.28)	(1.00)	(12.10)	(8.27)
VIII	10.84	9.11	0.99	10.70	9.10
	(10.26)	(8.91)	(0.99)	(10.20)	(8.90)
IX	10.71	8.44	0.99	10.60	8.40
	(10.25)	(8.28)	(1.00)	(10.50)	(8.23)

The values given in parantheses are at 35°C.

[a] r = Correlation coefficient.

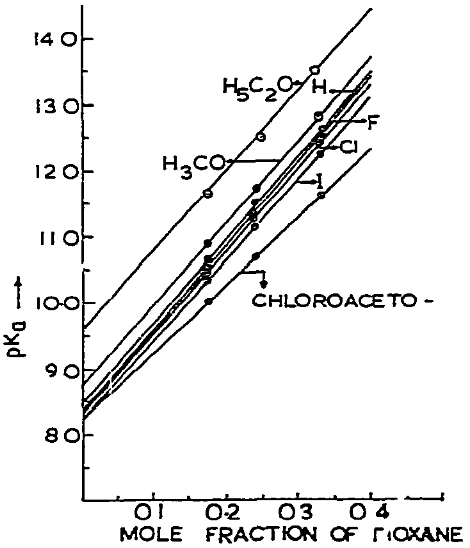


Fig. 1 Plot of pK_a of substituted hydroxamic acids vs. mole fraction of dioxane at 35°C.

TABLE 3

ΔG^0, ΔH^0, ΔS^0 and δ values for hydroxamic acids

Compd. No.	Mole fraction of dioxane (n_2)														
	0 [a]			0.174				0.24				0.33			
	ΔH^0	ΔG^0	$-\Delta S^0$	ΔH^0	ΔG^0	$-\Delta S^0$	δ	ΔH^0	ΔG^0	$-\Delta S^0$	δ	ΔH^0	ΔG^0	$-\Delta S^0$	δ
I	10.1	11.93	6.2	9.7	14.89	17.5	2.96	10.1	16.07	20.1	4.14	9.7	17.57	26.5	5.64
		(11.99)	(6.2)		(15.07)	(17.5)	(3.08)		(16.27)	(20.1)	(4.28)		(17.84)	(26.5)	(5.85)
II	13 5	12.49	−3.3	13.5	15.36	6.4	2.87	12.6	16.52	13.1	4.03	12.2	17.95	19.3	5.46
		(12.46)	(−3.3)		(15.42)	(6.4)	(2.96)		(16.65)	(13.1)	(4.19)		(18.12)	(19.2)	(5.66)
III	12 6	13.55	3.1	10.5	16.31	19.4	2.76	8.4	17.34	30.0	3.79	8.4	18.77	34.8	5.22
		(13.59)	(3.2)		(16.51)	(19.4)	(2.92)		(17.64)	(30.0)	(4.05)		(19.12)	(34.8)	(5 53)
IV	9.7	11.74	6.9	8.4	14.74	21.2	3.00	6.7	15 85	30.6	4.11	6.7	17.42	35.9	5.68
		(11.81)	(6.9)		(14.96)	(21.3)	(3.15)		(16.16)	(30.6)	(4.35)		(17.78)	(35.9)	(5.97)
V	13.0	11.79	−4.2	13.5	14.77	4.4	2.98	16.0	16.00	0.1	4.21	14.7	17.47	9.2	5.68
		(11.75)	(−4.2)		(14.82)	(4.4)	(3.07)		(16.00)	(0.1)	(4.25)		(17.57)	(9.3)	(5.82)
VI	7.2	11.58	14.9	7.2	14.52	24.7	2.94	7.2	15.66	28.5	4.08	7.6	17.18	32.2	5.60
		(11.73)	(14.9)		(14.77)	(24.7)	(3.04)		(15.94)	(28.5)	(4.21)		(17.51)	(32.3)	(5.78)
VII	10.1	11.63	5.2	8.4	14.47	20.3	2.84	5.9	15.49	32.2	3.86	6.3	16.99	35.8	5.36
		(11.68)	(5.2)		(14.67)	(20.3)	(2.99)		(15.82)	(32.2)	(4.14)		(17.36)	(35.9)	(5.32)
VIII	8.4	12.44	13.5	12.6	15.02	8.1	2.58	13.9	15.97	7.0	3.53	16.4	17.32	3.1	4.88
		(12.57)	(13.5)		(15.10)	(8.1)	(2.53)		(16 04)	(7.0)	(3.47)		(17.36)	(3.1)	(4.79)
X	6.7	11.52	16.1	9 3	14.02	16.0	2.50	12.6	15.08	8.3	3.56	12.6	16.31	12.4	4.79
		(11.68)	(16.1)		(14.18)	(16.0)	(2.50)		(15.17)	(8.3)	(3.49)		(16.44)	(12.4)	(4.76)

ΔG^0 and ΔH^0 in kcal mole^{-1}, ΔS^0 in cal mole^{-1} K^{-1}.
The values given in parantheses are at 35°C.
[a] Extrapolated values at 0% dioxane.

Born equation [19].

$$\Delta G^0_{\text{el.}} = W = \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{5}$$

where r_+ and r_- are radii of the solvated ions and D is the dielectric constant of the solvent [20,21]. Hence,

$$\Delta G^0_{\text{diss.}} = \Delta G^0_{\text{non.}} + \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{6}$$

Further, on substitution of $\Delta G^0_{\text{diss.}}$ from eqn. (1), eqn. (6) becomes

$$\mathrm{p}K_a = \frac{\Delta G^0_{\text{non.}}}{2.303RT} + \frac{Ne^2}{4.606RTD}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{7}$$

It is conventional to plot pK_a vs. $1/D$ assuming $\Delta G^0_{\text{non.}}$ to be independent of solvent. When the pK_a of *N*-*p*-chlorophenyl substituted hydroxamic acids are plotted vs. $1/D$ it is observed that the plots possess a distinct curvature. The same observations were recorded by earlier workers [1,3,22]. It seems evident that non-electrostatic factors exert a considerable influence on the dissociation of hydroxamic acids.

Further, the plot of change in free energy from mixed aqueous media, δ, vs. % dioxane is shown in Fig. 2. In this plot we have expressed these results as

$$\delta = \Delta G^0_s - \Delta G^0_w \tag{8}$$

In eqn. (8), ΔG^0_w and ΔG^0_s refer to the standard free energy change from pure water as solvent and in aqueous or organic mixtures as solvent, respectively. A distinct curvature is observed between aqueous to 70% aqueous dioxane mixture at both temperatures (25 and 35° C).

The errors induced in the determination of pK_a are reflected in all the values of all thermodynamic functions. Therefore, an estimate of error is necessary to show how reliable these results are. The pK_a values have been deter-

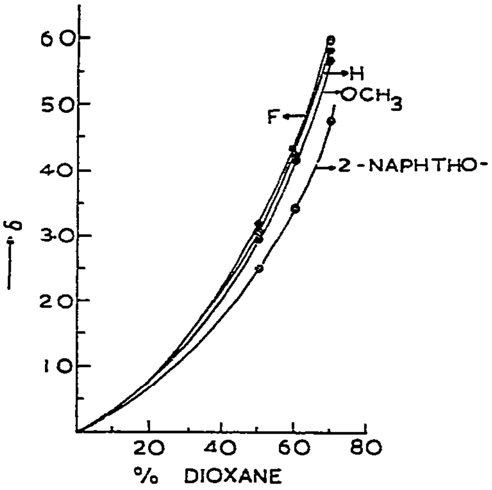


Fig. 2. Plot of free energy change, δ, of the substituted hydroxamic acids vs. % dioxane.

mined with a precision of ±0.02 to ±0.03 and the error in ΔG^0 is estimated to be between ±0.03 and ±0.04 kcal. It is apparent from eqn. (2a) that an error of 0.01 in pK_a causes an error of 0.42 kcal in ΔH^0 while the magnitude of error in ΔpK_a depends on the cancellation or addition of errors of an individual set of pK_a values determined at two temperatures. In view of the inherent weakness of the method, no definite trends in the magnitude of the values of ΔH^0 with the change of media could be observed. The positive value of ΔH^0 is found in all solvent media and has a real significance for all hydroxamic acids: it implies that the ionisation process at 25°C is endothermic and will be exothermic only above T_{max}. Further, it is certain that the magnitude of change in ΔH^0 with change of media is relatively small and within the range of experimental error. It is observed that there is a general tendency for ΔS^0 to increase with increase in dioxane content of the solvent medium.

Hammett [23] and Jaffe [24] correlated the effect of substitution on the reactivity of benzene derivatives. Agrawal et al. [8,25] have made an attempt to correlate the pK_a of substituted benzohydroxamic acid with benzoic acid and obtained good agreement between the two sets of values. In the present investigation, a correlation is established between the pK_a values of the *N*-*p*-chlorophenylbenzohydroxamic acids and Hammett's equation

$$\log \frac{K}{K_0} = \rho\sigma \tag{10}$$

where ρ is the reaction constant, σ is the substituent constant, K and K_0 are the pK_a values of substituted and unsubstituted hydroxamic acids, respectively.

The pK_a values given in Tables 4 and 5 indicate that the experimental values (extrapolated) and those calculated by Hammett's equation and least squares method are in good agreement.

TABLE 4

Hammett pK_a values of substituted *N*-*p*-Chlorophenylbenzohydroxamic acids in aqueous media at 35°C

Substituent X	pK_a [a]	pK_a [b]	σ	pK_a [c]	pK_a [d] (Hammett)	pK_a Benzoic acid
H	8.50	8.50		8.52		4.21
OCH_3	8.85	8.83	−0.268	8.79	8.77	4.47
OC_2H_5	9.65	9.63				
F	8.37	8.37	+0.062	8.45	8.37	4.14
Cl	8.33	8.33	+0.227	8.30	8.27	3.99
Br	8.30	8.31	+0.232	8.31	8.27	4.00
I	8.27	8.28	+0.276	8.24	8.22	3.93

[a] pK_a in aqueous media, extrapolated values.
[b] pK_a in aqueous media by least squares.
[c] pK_a obtained by $pK_a = 1.02\,x + 4.23$.
[d] pK_a obtained from the Hammett σ function.

TABLE 5

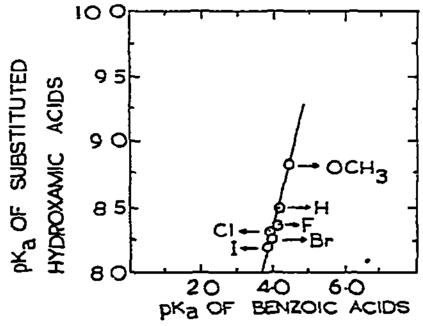
Hammett pK_a values of *N*-*p*-chlorophenylbenzohydroxamic acids ın different dioxane—water medıa at 35°C

Substituent	Mole fraction of dioxane (n_2)							
	0 *		0.174		0.24		0.33	
	Least squares	pK_a = 1.02 x + 4 23	Least squares	pK_a = 0 98 x + 6.55	Least squares	pK_a = 1.1 x + 6.91	Least squares	pK_a = 0.95 x + 8.62
H	8.50	8.52	10.68	10 68	11.51	11.54	12.64	12.62
OCH$_3$	8 83	8.79	10.95	10.93	11.76	11.83	12.86	12.87
F	8 37	8.45	10.60	10.61	11.45	11.46	12.60	12 55
Cl	8.33	8.30	10.50	10.46	11.33	11.30	12.45	12.41
Br	8.31	8.31	10 47	10.47	11.29	11.31	12.41	12.42
I	8.28	8.24	10 40	10.40	11 21	11.23	12.30	12.35

* Extrapolated values at 0% dioxane.

A plot of pK_a values of *N*-*p*-chlorophenylbenzohydroxamic acids vs. the pK_a values of the respective benzoic acids is linear (Fig. 3) with unit slope ($\rho = 1$). A plot of the pK_a values of the hydroxamıc acids (Fig. 4) vs. the Hammett σ functıon, gives a straight lıne of unit slope ($\rho = 1$), in agreement with the experimental values. Further, the dependence of the acidity on substitution on the benzene nucleus was followed by the same reaction constant, ρ, obtained by two different plots (Figs. 3 and 4). The Hammett correlation was also obtained with the pK_a values in different dioxane—water media (50—70%) and the data at 35° C are summarised in Table 5.

In order to understand the relationship between the molecular structure of the hydroxamic acids and their pK_a values it is convenient to examine the parent carboxylic acids. In the present case the hydroxamic acids derived from substituted benzoic acıds ın all mole fractions of dioxane follow the order of pK_a values of benzoic acids. Thus



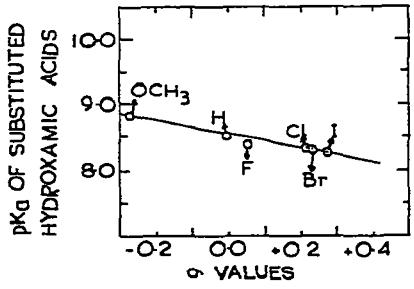


Fig. 3. Plot of pK_a of substituted hydroxamic acids vs. pK_a of benzoic acids at 35°C.

Fig 4. Plot of pK_a of substituted hydroxamic acids vs. σ values at 35°C (Hammett Plot).

pK_a values of benzoic acids: $OC_2H_5 > OCH_3 > H > F > Cl > Br > I$
pK_a values of hydroxamic acids: $OC_2H_5 > OCH_3 > H > F > Cl > Br > I$
Compound No. III > II > I > IV > V > VI > VII

With the introduction of ethoxy or methoxy groups (for compounds II and III) which are the electropositive substituents [6,4], the positive tautomeric effect is much more powerful than the inductive effect and causes a further acid weakening effect thus:

$OC_2H_5 > OCH_3 > H$
Compound No. III > II > I

This order is valid for aqueous and all aqueous—dioxane media.

The large strength of the halogen is explained on the basis that it is believed [6,4] to be a mesomeric effect arising from resonance benzenoid forms and having the negative inductive and tautomeric effect which follows the same order as the pK_a of benzoic acids: F > Cl > Br > I. This same order is followed by substituted *N*-*p*-chlorophenylbenzohydroxamic acids.

F > Cl > Br > I
Compound No. IV > V > VI > VII

The increase in conjugation in the aliphatic chain increases the acidity of the acids as in the case of monochloroaceto and cinnamohydroxamic acids compared to the parent unsaturated acid, as observed here.

pK_a H > monochloroaceto
Compound No. I > X
or
pK_a H > cinnamo
Compound No. I > IX

N-*p*-chlorophenyl-2-napthohydroxamic acid is interesting because it has a lower acidity in 50% dioxane—water medium than *N*-*p*-chlorophenylbenzohydroxamic acid, but beyond 50% a reversible order has been observed as at 50% dioxane—water the pK_a of

H < 2-naphtho
Compound No. I < VIII

and at 60—70% dioxane—water the pK_a of

H > 2-naphtho
Compound No. I > VIII

The reversible order of the pK_a may be due to the non-electrostatic factor, $\Delta G^0_{\text{non.}}$, which may be taking part in the process of ionisation. Hence, it may be said that both $\Delta G^0_{\text{non.}}$ and $\Delta G^0_{\text{el.}}$ are responsible for the ionisation process. It is therefore logical to infer that the relative strength, as measured by the ratio of their ionisation constants, is a function of the medium and several other variables [13].

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