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THERMODYNAMIC PARAMETERS OF SOME *N*-ARYLHYDROXAMIC ACIDS AND APPLICATION OF THE HAMMETT EQUATION

PARAS C. MARU AND PADMAKAR V. KHADIKAR
School of Studies in Chemistry, Vikram University, Ujjain – 456 010 (India)
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ABSTRACT

The thermodynamic parameters ΔG°, ΔH° and ΔS° for six *N*-arylhydroxamic acids are reported in three different dioxane–water mixtures. Thermodynamic ionisation constants required for this have also been determined employing a pH titration technique at 25 and 35 °C. An attempt has also been made to correlate the thermodynamic ionisation constants with Hammett's equation.

INTRODUCTION

N-Arylhydroxamic acids are characterised by a remarkable versatility as reagents in organic and inorganic analysis[1–5]. Recently, Maru and Khadikar[6] have synthesised *N*-*p*-chlorophenyl-*p*-methoxybenzohydroxamic acid and have observed it to be a versatile reagent for the spectrophotometric determination of vanadium. The selectivity and sensitivity of the relevant analytical reactions of these hydroxamic acids requires a knowledge of their corresponding thermodynamic ionisation constants. In connection with our previous work[7] the present communication deals with the determination of the thermodynamic ionisation constants of six *N*-arylhydroxamic acids by a pH titration method in aqueous dioxane media with the hope of developing a reagent with superior analytical potentialities. The thermodynamic parameters, i.e. ΔG°, ΔH° and ΔS°, have also been calculated. Since these acids are sparingly soluble in water, recourse to the use of a mixed solvent had to be taken. These determinations have been restricted to 50, 60 and 70% dioxane–water mixtures only because of the inadequate solubility of hydroxamic acids in mixed aqueous solvents of low dioxane concentration.

EXPERIMENTAL

All the chemicals used were of AR and GR grades of B.D.H. and E-Merck, respectively.

TABLE 1

THERMODYNAMIC p*K* OF *N*-ARYLHYDROXAMIC ACIDS AT 25 °C AND 35 °C IN DIOXANE/WATER

N-p-chloro-phenyl-hydroxamic acid	*Dioxane (% v/v)*		
	50	*60*	*70*
(1) -*p*- methoxybenzo-	10.86 (10.76)*	11.35 (11.25)	12.03 (11.89)
(2) -*p*- methylbenzo-	10.70 (10.55)	11.14 (11.04)	11.85 (11.78)
(3) -benzo-	10.64 (10.35)	11.06 (10.96)	11.76 (11.70)
(4) -furo-	10.57 (10.28)	10.98 (10.81)	11.49 (11.28)
(5) -*p*- fluorobenzo-	10.56 (10.25)	10.96 (10.74)	11.45 (11.27)
(6) -*p*- nitrobenzo-	10.07 (9.90)	10.75 (10.65)	11.28 (11.12)

* Values in parenthesis are at 35 °C.

Hydroxamic acids

N-Arylhydroxamic acids (Table 1) were prepared employing the method described by Agrawal and Tandon[8] who recrystallised them before use from mixtures of benzene and petroleum ether and dried them in vacuum over P_2O_5. However, we observed that better crystallisation can be achieved from dry acetone and this was done in the present case. The final purity was established by m. p., elemental analysis, UV and IR spectra.

Solvents

B.D.H. "Analar" *p*-dioxane was purified by the method described by Weissberger and Proskauer[9].

Glass-distilled water was redistilled over alkaline potassium permanganate and the middle fraction was used. Absence of carbonate was tested for by the method of Kolthoff and Sandell[10].

Carbonate-free sodium hydroxide solution was prepared by the Vogel electrolytic method[11], standardised against potassium hydrogen phthalate, and diluted to 0.1 M with dioxane/water in the same ratio as employed in preparing the titre solutions.

Apparatus

A Beckman pH-meter type GS equipped with a glass and calomel electrode was used for pH measurements and was calibrated before use with Beckman standard buffer solutions. The titration procedure for the determination of pK_a was basically the same as that described by Albert and Sergeant[12].

TABLE 2

FREE ENERGY, ENTHALPY AND ENTROPY CHANGES FOR IONISATION OF *N*-ARYL HYDROXAMIC ACIDS

N-p-chlorophenyl-hydroxamic acid		*Dioxane (% v/v)*		
		50	*60*	*70*
-*p*- methoxybenzo-	ΔG°	14.82	15.49	16.42
(ΔH° 4.77)		(15.18)*	(15.87)	(16.78)
	$-\Delta S^\circ$	33.73	35.97	39.08
		(33.58)	(35.81)	(38.72)
-*p*- methylbenzo-	ΔG°	14.61	15.21	16.18
(ΔH° 4.49)		(14.59)	(15.58)	(16.62)
	$-\Delta S^\circ$	33.94	35.95	39.20
		(33.53)	(35.75)	(39.12)
-benzo-	ΔG°	14.54	15.10	16.10
(ΔH 4.91)		(14.60)	(15.46)	(16.51)
	$-\Delta S^\circ$	27.59	29.47	32.67
		(26.74)	(29.51)	(32.88)
-furo-	ΔG°	14.43	14.99	15.68
(ΔH° 7.43)		(14.50)	(15.25)	(15.92)
	$-\Delta S^\circ$	16.88	18.76	21.09
		(16.47)	(18.88)	(21.02)
-*p*- fluorobenzo-	ΔG°	14.41	14.96	15.63
(ΔH° 9.99)		(14.46)	(15.15)	(15.90)
	$-\Delta S^\circ$	14.95	16.59	19.02
		(14.85)	(16.75)	(19.17)
-*p*- nitrobenzo-	ΔG°	13.75	16.67	15.40
(ΔH° 6.03)		(13.97)	(15.03)	(15.69)
	$-\Delta S^\circ$	25.88	28.99	31.42
		(25.80)	(29.00)	(31.14)

* Values in parenthesis are at 35 °C.

The experimental set-up, procedure and method of calculation was the same as described earlier[7].

RESULTS AND DISCUSSION

The *N*-arylhydroxamic acids studied in the present investigation are weak acids, sparingly soluble in water as well as in mixed aqueous solvents of low dioxane concentration. The thermodynamic ionisation constants in three different dioxane/water mixtures along with the various thermodynamic parameters are recorded in Tables 1 and 2.

Table 1 shows that pK_a values follow the order $OCH_3 > CH_3 > H > F \approx$ Furo $> NO_2$.

Temperature effect

The ionisation constant of a weak acid is a function of temperature. It has a maximum value, K_a (max) or pK_a (min) near room temperature. Table 1 reveals that the pK_a values of all the hydroxamic acids investigated in the present study, decrease with increase of temperature.

Medium effect

The change of pK_a with mole fraction of dioxane is of considerable magnitude and is linear. This is due to the fact that the solvent of low dielectric constant increases the electrostatic force between the ions and facilitates the formation of molecular species which increase the pK_a value. The values of pK_a given in Table I are in accordance with this statement.

Thermodynamic parameters

The value of ΔG°, ΔH° and ΔS° have been calculated in the usual way. ΔH° has been calculated by the temperature coefficient method. This method is subjected to large error because the enthalpy change is small and pK_a values are not determined at a series of temperatures which would have allowed the use of a more precise method[13]. The values of ΔH° are approximate because the heats of ionisation vary with temperature. We observed that an error of 0.01 in pK_a causes an error of 0.42 k cal/mole in ΔH°. The magnitude of the error depends upon the addition or cancellation of errors in the individual pK_a values determined at two different temperatures. In all cases, ΔH° values are found to be positive and the ionisation process up to 25 °C is endothermic. Table 2 shows that the change in ΔH° with change in solvent composition is relatively small and is within experimental error.

The precision of the pK_a values is found to be between 0.02 and 0.03 causing an error in ΔG° of between 0.03 and 0.04 kcal/mole.

Substitution effect

In the benzoic acid series, regardless of electronic type, nearly all the substituents are acid strengthening in the *ortho*-position[14], but may be either acid weakening or strengthening when they are in the *meta* or *para* positions, depending on the character. In the present case (Table I) the acid strengthening effect is observed in all cases. The effect of *para* substituents on the pK_a of hydroxamic acids, except the furo derivative, is similar to that for benzoic acid, viz. $OCH_3 > CH_3 > H > F > NO_2$.

Applicability of the Hammett equation

The pK_a of hydroxamic acids when plotted against the corresponding pK_a of the benzoic acids, gives a straight line. Also, there is a linear relationship between the pK_a values of *N*-arylhydroxamic acids and the pK_a values of corresponding *para*-substituted benzoic acids. The plot of the pK_a values of *N*-arylhydroxamic acids against Hammett's σ function gives a straight line indicating that the Hammett equation is applicable in the present case also.

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