CHAPTER III

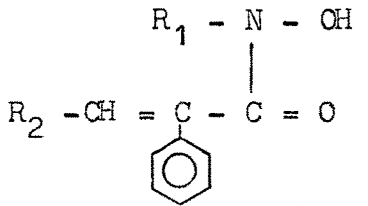
THERMODYNAMIC IONIZATION CONSTANTS OF HYDROXAMIC ACIDS

RESUME

The thermodynamic ionization constants of hydroxamic acids have been determined in different mole fractions of dioxan (0.174-0.33) at 25 and 35±0.1°C. The pK_a varies linearly with the mole fraction of dioxan and the linear relationship have been obtained using the method of least square. The relevant correlation coefficients have also been calculated. The thermodynamic parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$ are calculated. The effect of substituent on ionization of hydroxamic acids is discussed.

INTRODUCTION

The knowledge of ionization constant is essential to know the order of basicity of the ligand and extraction equilibria of the metal ions. Further for the calculation of the metal ligand stability constants, the ionization constant plays an important role. With this view, in the present investigation the thermodynamic ionization constants of substituted α-phenyl cinnamohydroxamic acids (I)



(I)

(R_1= Phenyl, p-Cl-phenyl, p-tolyl or m-tolyl and R_2= aryl or substituted aryl etc.)

have been determined in dioxan-water media at 25° and 35°C.

Since most of the hydroxamic acids are sparingly soluble in water, the mixed aqueous media has been used to obtain the desired constants.

The pK_a were determined by the pH titration method using glass and saturated calomel electrode. The details of the method and calculations etc. are essentially the same as described by Agrawal (1).

Since these acids are insoluble in water but highly soluble in dioxan, the dioxan-water media have been choosen for the determination of ionization constants. Moreover, the dioxan is completely miscible with water and has a neutral character. The boiling range of both the solvents are approximately same. Many of the physical properties of dioxan-water mixtures, needed for studying the proton-ligand and metal ligand ionic equilibria, are accurately known and are easily available (1,2).

Thermodynamic ionization (proton-ligand stability) constants

The thermodynamic dissociation constants $K_{a(aq)}$ of hydroxamic acid, HA,

$$HA \rightleftharpoons H^+ + A^-$$

in an aqueous medium is given by equations (I) and (II).

$$K_{a(aq)} = \frac{[H^+]\ [A^-]}{[HA]} \quad \frac{y_{H^+} \cdot y_{A^-}}{y_{HA}} \qquad (I)$$

$$pK_{a(aq)} = -\log [H^+] + \log \frac{[HA]}{[A^-]} - 2 \log y_{\pm} \qquad (II)$$

where $y_{\pm}$ is the mean activity coefficient of a univalent ions ($y_{H^+} + y_{A^-} = y_{\pm}$) at a given temperature and medium, it is assumed that the activity coefficient of the unionized acid y_{HA} is unity (3,4).

If the medium is altered by addition of dioxan, then according to Van Uitert and latter Agrawal et al. (5-10) the stoichiometric hydrogen ion concentration $[H^+]$ can be obtained from pH meter readings (B) by the following equation (III)

$$- \log [H^+] = B + \log U^\circ_H + \log y_\pm \qquad \text{(III)}$$

The values of log U°H were determined experimentally by Agrawal and given in the Appendix I, Table 1.

Then from equation (II) and (III) we get

$$pK_a = B + \log U^\circ_H + \log \frac{[HA]}{[A^-]} + \log {}^1/y_\pm \qquad \text{(IV)}$$

The pK_a values, thus determined, are termed as thermodynamic values, for that include correction due to activity coefficients. The equation (IV) can be written as

$$pK_a = B + \triangle \qquad \text{(V)}$$

Where $\triangle = \log U^c_H + \log \frac{[HA]}{[A^-]} + \log {}^1/y_\pm$

The values of $\triangle$ calculated by Agrawal (1) are summarised in Appendix I, Tables 2-3.

If the hydrolysis of the salt is taken into consideration, the equation II can be written as

$$pK_{a\,(aq)} = -\log [H^+] + \log \frac{[HA] + [OH^-]}{[A^-] - [OH^-]} + 2 \log {}^1/_{y_\pm} \qquad (VI)$$

and for mixed aqueous media.

$$pK_a = B + \log U_H^{\circ} + \log \frac{[HA] + [OH^-]}{[A^-] - [OH^-]} + \log {}^1/_{y_\pm} \qquad (VII)$$

Relevant values of pK_w as given by Agrawal (1) summarised in Appendix I, Table 4, are used to evaluate the hydroxyl ion concentration.

Thermodynamics functions for ionic equilibria

The standard free energy $\Delta G°$ of the ionization reaction, $HA \rightleftharpoons H^+ + A^-$, can be determined from the equation (VIII).

$$\Delta G° = 2.303\ RT\ pK_a \qquad (VIII)$$

which can be written in a simplified form :

$$\Delta G°\ (298.2°) = 5.711\ pK_a\ (KJ) \qquad (IX)$$

$$\Delta G°\ (308.2°) = 5.904\ pK_a\ (KJ) \qquad (X)$$

The expression for the standard enthalphy of reaction, $\Delta H°$ (KJ), is obtained by integrating the Vant Hoff equation for two temperature T_1 and T_2 :

$$\log \frac{K_2}{K_1} = \frac{\Delta H°\ (T_2 - T_1)}{19.146\ T_1 T_2} \qquad (XI)$$

Equation (XI) is approximate, since $\Delta H°$ varies with temperature. For measurements at 25° and 35°C equation (XI) can be simplified as

$$\Delta H° \text{ (KJ)} = 176.02 \, \Delta \, pK_a \qquad \text{(XII)}$$

Standard entropy changes, $\Delta S°$, is computed from Gibbs-Halmholtz equation (XIII).

$$- \Delta S° = \frac{\Delta G° - \Delta H°}{T} \qquad \text{(XIII)}$$

At 25 and 35°C equation (XIII) can be reduced to the following forms :

At 25°C $-\Delta S° \text{ (KJ)} = 14.033 \times 10^{-3} (\Delta G° - \Delta H°)$ (XIV a)

At 35°C $-\Delta S° \text{ (KJ)} = 13.573 \times 10^{-3} (\Delta G° - \Delta H°)$ (XIV b)

EXPERIMENTAL

The details of the chemicals and reagents used are described in CHAPTER II.

Hydroxamic acids

These are described in CHAPTER II and recrystalized, before use, from the mixture of benzene and petroleum ether.

Distilled water

Pure distilled water redistilled over alkaline potassium permanganate and freed from carbon dioxide was used. It was tested for the absence of carbonate by Kolthoff's method (11).

Dioxan

p-Dioxan was purified by the method of Weissberger (12). It was refluxed over the pellets of KOH for about 8-10 hrs, distilled and middle fraction of the distillate refluxed over metallic sodium for 5-6 hrs. and fractionally distilled. The middle fraction was used. Its purity was established by freezing points which varied from 11.65° to 11.80°C (uncorrected) against the reported range 11.65° to 12.00°C (13, 14).

Volume percent dioxan

All solutions were made up by volume and the designation. X percent dioxan (v/v) refers to the mixture obtained by mixing X ml of dioxan with (100-X) ml of water. Due allowance for the contraction in volume on mixing of two solvents, was made whenever necessary (7,8). Mole fraction of dioxan was calculated using appropriate values of densities (4).

APPARATUS

A digital Systronics pH meter Model 324 equipped with a combined glass and calomel electrode was used for the pH metric measurements. The pH meter was calibrated in dioxan-water mixtures as described elsewhere (9,10).

DETERMINATION OF IONIZATION CONSTANTS

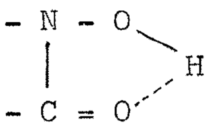
The titration procedure for determining ionization constants, was essentially the same given by Agrawal (1,2). In a titration vessel (thermostated at 25 and 35±0.1°C). 0.01 M hydroxamic acid in 47.5 ml of the solvent of desired composition was titrated, with 0.5 ml increments of 0.1 M tetrabutylammonium hydroxide, after being dearated by passage of nitrogen (presaturated with solvent) for 15 min. The highest steady B value (pH meter reading) being noted after each increment.

RESULTS AND DISCUSSION

Experimental observations on the determination of pK_a for a few sets of titrations are reported in Tables 1-3. So far thermodynamic pK_a of none of these acids have been reported. The data on the thermodynamic ionization constants of substituted α-phenyl cinnamohydroxamic acids in various dioxan-water media at 25°and 35°C are given in Tables 4-5. The average pK_a generally falls within a spread of ± 0.02 but not beyond ± 0.03 in any case.

In Figs. 1-9, the pK_as are plotted against the mole fraction of dioxan, n_2, in the solvent mixtures and empirical relations derived therefrom are given in Table 6. The values of thermodynamic functions $\Delta G°$, $\Delta H°$ and $\Delta S°$ are summarised in Table 7.

The hydroxamic acids are very weak acids but stronger than phenols, and their acidity have been attributed essentially to the -OH group. The decrease in the acid character may be due to intramolecular hydrogen bonding (II) which has been proved by ir spectroscopic studies (15-17).

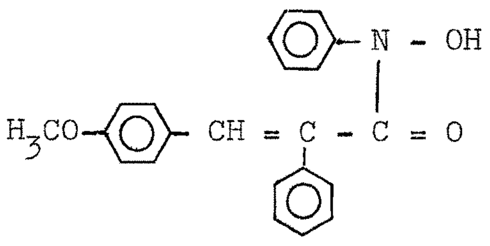


(II)

TABLE 1

Determination of pK_a of N-phenyl-α-phenyl-p-methoxy cinnamohydroxamic acid in 50% (v/v) dioxan-water media

Structural formula	Mol. wt.	Temperature	log U_H^o
	345.40	25±0.1°C	0.20



Concentration : 0.01 M at half neutralization. N-Phenyl-α-phenyl-p-methoxycinnamohydroxamic acid (0.1727 g) was dissolved in 23.75 ml of dioxan and 23.75 ml of water.

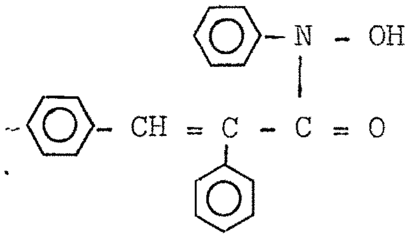
I Titrant 0.1000 M Bu_4NOH ml	II B	III Stoichiometric concentration [HA]	 [A⁻]	IV $\frac{[HA]}{[A^-]}$	V log of column IV	VI $\log \frac{1}{y_\pm}$	VII pK_a
0.00	7.74	0.010	0.000	-	-	-	-
0.50	9.91	0.009	0.001	9/1	0.954	0.038	11.10
1.00	10.22	0.008	0.002	8/2	0.602	0.071	11.09
1.50	10.43	0.007	0.003	7/3	0.368	0.097	11.10
2.00	10.63	0.006	0.004	6/4	0.176	0.107	11.11
2.50	10.78	0.005	0.005	5/5	0.000	0.119	11.10
3.00	10.95	0.004	0.006	4/6	-0.176	0.128	11.10
3.50	11.13	0.003	0.007	3/7	-0.368	0.134	11.10
4.00	11.37	0.002	0.008	2/8	-0.602	0.143	11.11
4.50	11.72	0.001	0.009	1/9	-0.954	0.150	11.12

$$pK_a = B + \log U_H^o + \log \frac{[HA]}{[A^-]} + \log \frac{1}{y_\pm}$$

Results : Average pK_a = 11.10±0.02

TABLE 2

Determination of pK_a of N-phenyl-α-phenylcinnamohydroxamic acid in 60% (v/v) dioxan-water media

Structural formula	Mol. wt.	Temperature	$\log U_H^{\circ}$
	315.37	35±0.1°C	0.42

Concentration : 0.01 M at half neutralisation N-Phenyl-α-phenyl cinnamohydroxamic acid (0.1577 g) was dissolved in 28.5 ml of dioxan and 19.0 ml of water.

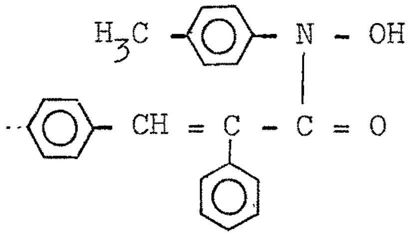
I Titrant 0.1000 M Bu_4NOH ml	II B	III Stoichiometric concentration		IV $\triangle$	V pK_a
		$[HA]$	$[A^-]$		
0.00	7.80	0.010	0.000	-	-
0.50	9.89	0.009	0.001	1.47	11.36
1.00	10.21	0.008	0.002	1.16	11.37
1.50	10.41	0.007	0.003	0.95	11.36
2.00	10.58	0.006	0.004	0.77	11.35
2.50	10.74	0.005	0.005	0.61	11.35
3.00	10.89	0.004	0.006	0.45	11.34
3.50	11.08	0.003	0.007	0.27	11.35
4.00	11.30	0.002	0.008	0.05	11.35
4.50	11.64	0.001	0.009	-0.29	11.35

$$pK_a = B + \triangle, \text{ where } \triangle = \log U_H^{\circ} + \log \frac{[HA]}{[A^-]} + \log \frac{1}{y_{\pm}}$$

Results : Average $pK_a = 11.35 \pm 0.02$

TABLE 3

Determination of pK_a of N-p-tolyl-α-phenylcinnamohydroxamic acid in 70% (v/v) dioxan-water media

Structural formula	Mol. wt.	Temperature	$\log U^{\circ}_{H}$
	329.40	25±0.1°C	0.80

Concentration : 0.01 M at half neutralisation, N-p-tolyl-α-phenylcinnamohydroxamic acid (0.1647 g) was dissolved in 33.25 ml of dioxan and 14.25 ml of water.

I Titrant 0.1000 M Bu_4NOH ml	II B	III Stoichiometric concentration		IV $\triangle$	V pK_a
		[HA]	[A^-]		
0.00	8.30	0.010	0.000	-	-
0.50	11.04	0.009	0.001	1.87	12.91
1.00	11.31	0.008	0.002	1.61	12.92
1.50	11.49	0.007	0.003	1.43	12.92
2.00	11.86	0.006	0.004	1.27	12.93
2.50	11.82	0.005	0.005	1.11	12.93
3.00	11.99	0.004	0.006	0.95	12.94
3.50	12.15	0.003	0.007	0.78	12.93
4.00	12.35	0.002	0.008	0.57	12.92
4.50	12.71	0.001	0.009	0.24	12.95

$$pK_a = B + \triangle, \text{ where } \triangle = \log U^{\circ}_{H} + \log \frac{[HA]}{[A^-]} + \log \frac{1}{y_{\pm}}$$

Results : Average $pK_a = 12.93 \pm 0.02$

TABLE 4

Thermodynamic ionization constants of substituted α-phenylcinnamohydroxamic acids in dioxan-water media at 25°C.

Compd No.	Cinnamohydroxamic acid	pK_a Mole fraction of dioxan, n_2		
		0.174	0.240	0.330
I	N-Phenyl-α-phenyl-p-methoxy-	11.10	11.85	12.85
II	N-p-Tolyl-α-phenyl-p-methoxy-	11.36	12.04	13.05
III	N-m-Tolyl-α-phenyl-p-methoxy-	11.30	12.00	12.96
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	10.72	11.40	12.40
V	N-Phenyl-α-phenyl-	10.75	11.60	12.70
VI	N-p-Tolyl-α-phenyl-	10.85	11.70	12.93
VII	N-m-Tolyl-α-phenyl-	10.80	11.65	12.85
VIII	N-p-Chlorophenyl-α-phenyl-	10.50	11.35	12.50
IX	N-phenyl-α-phenyl-3,4,5 trimethoxy-	11.05	11.80	12.80

TABLE 5

Thermodynamic ionization constants of substituted α-phenylcinnamohydroxamic acids in dioxan-water media at 35°C.

Compd No.	Cinnamohydroxamic acid	pK_a Mole fraction of dioxan, n_2		
		0.174	0.240	0.330
I	N-Phenyl-α-phenyl-p-methoxy-	10.87	11.60	12.60
II	N-p-Tolyl-α-phenyl-p-methoxy-	11.08	11.80	12.80
III	N-m-Tolyl-α-phenyl-p-methoxy-	11.05	11.70	12.75
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	10.45	11.15	12.15
V	N-Phenyl-α-phenyl-	10.50	11.35	12.48
VI	N-p-Tolyl-α-phenyl-	10.60	11.50	12.70
VII	N-m-Tolyl-α-phenyl-	10.55	11.40	12.60
VIII	N-p-Chlorophenyl-α-phenyl-	10.25	11.10	12.25
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	10.82	11.55	12.55

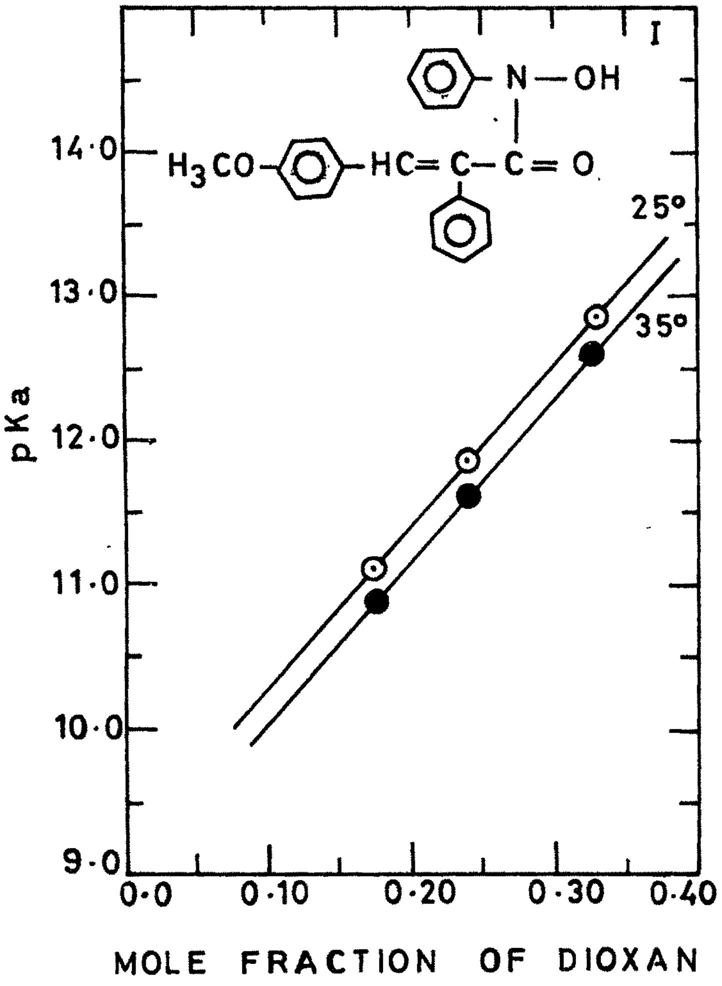


FIG. 1: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

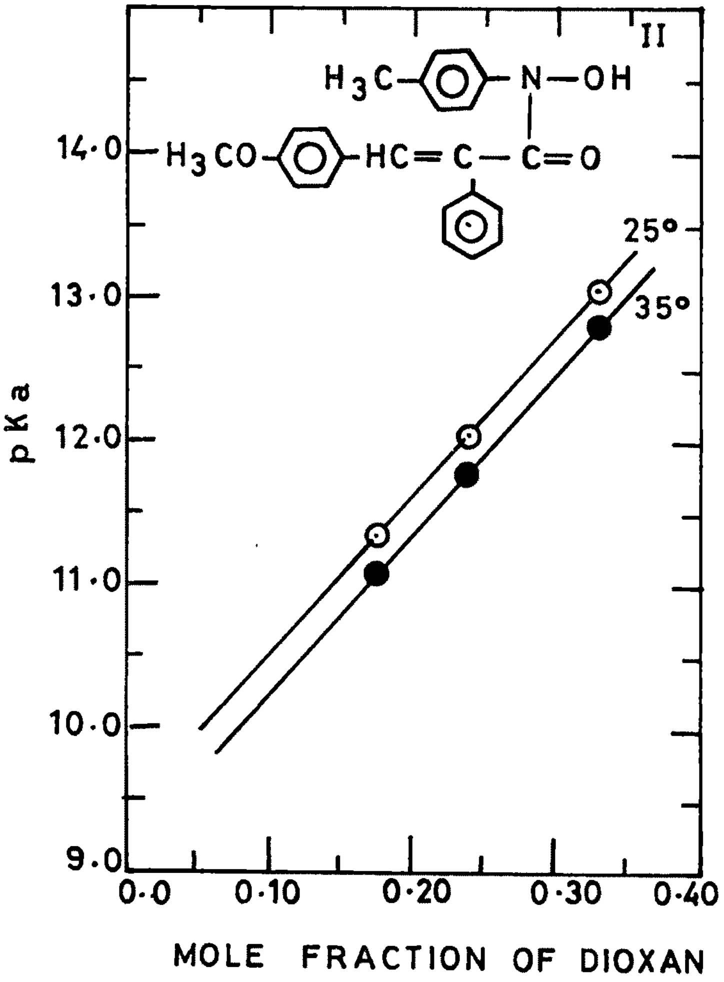


FIG. 2: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

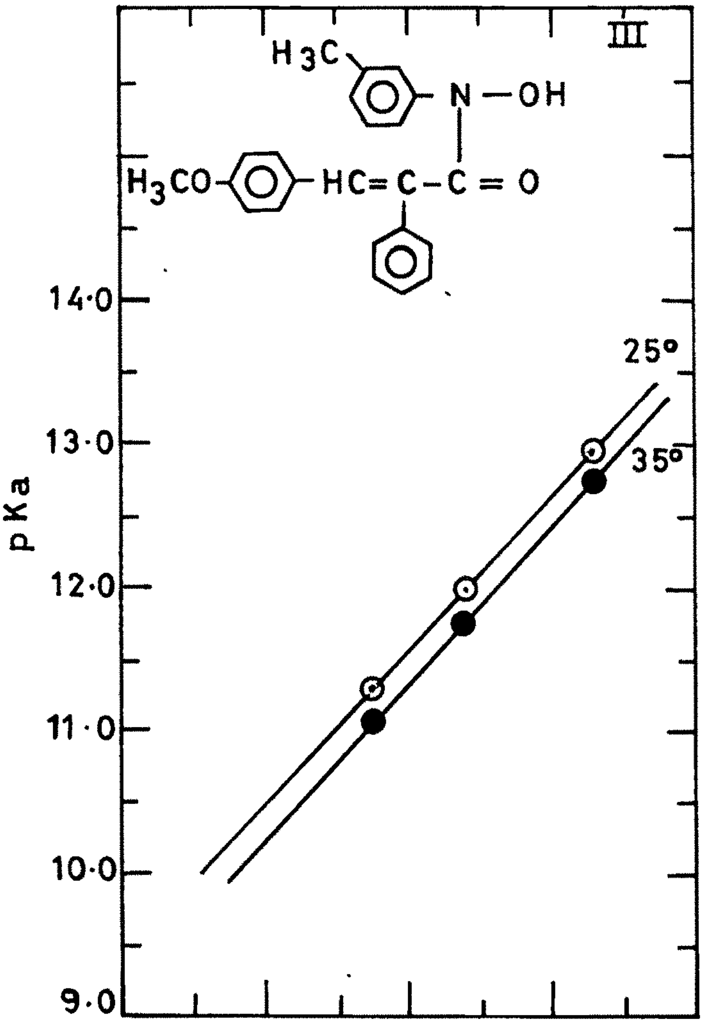


FIG. 3: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

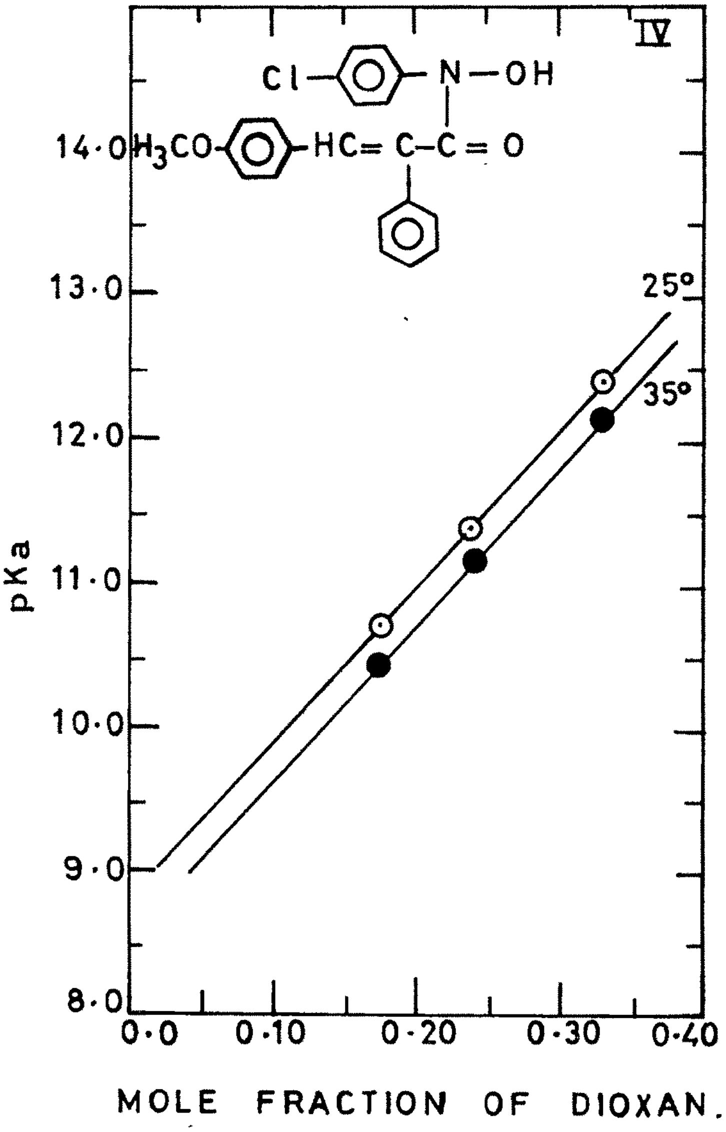


FIG. 4: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

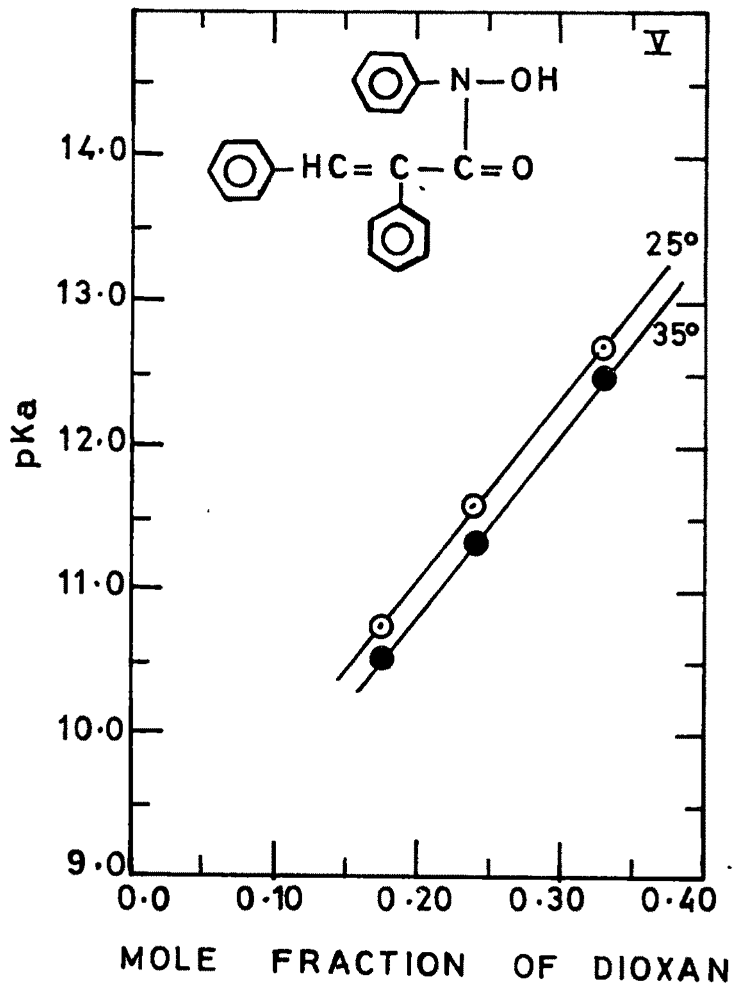


FIG. 5: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

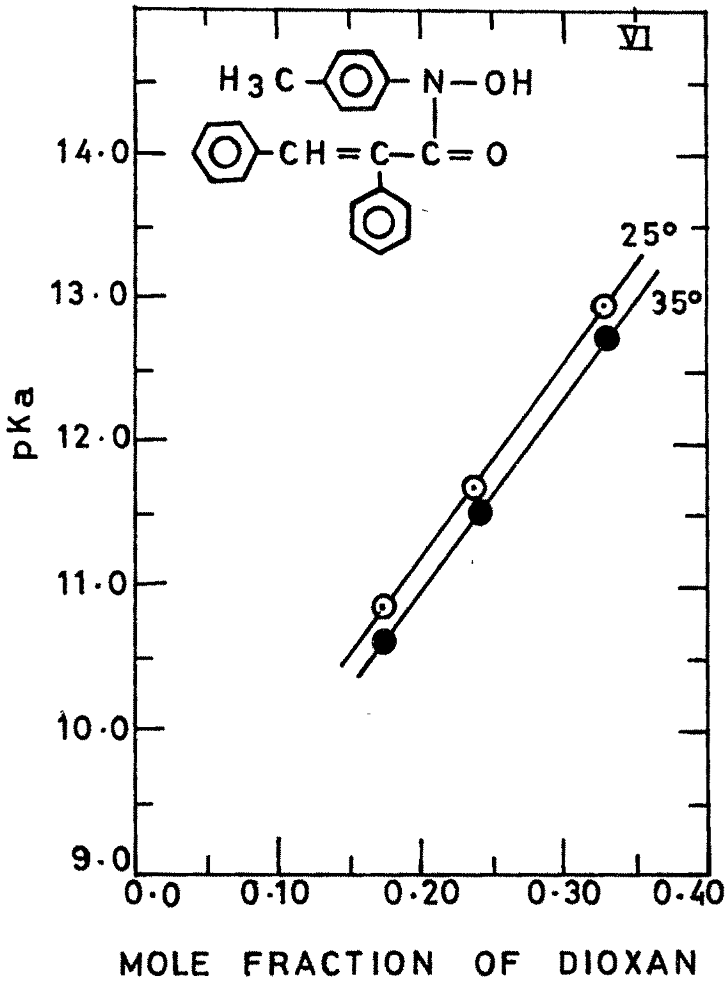


FIG. 6 : VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

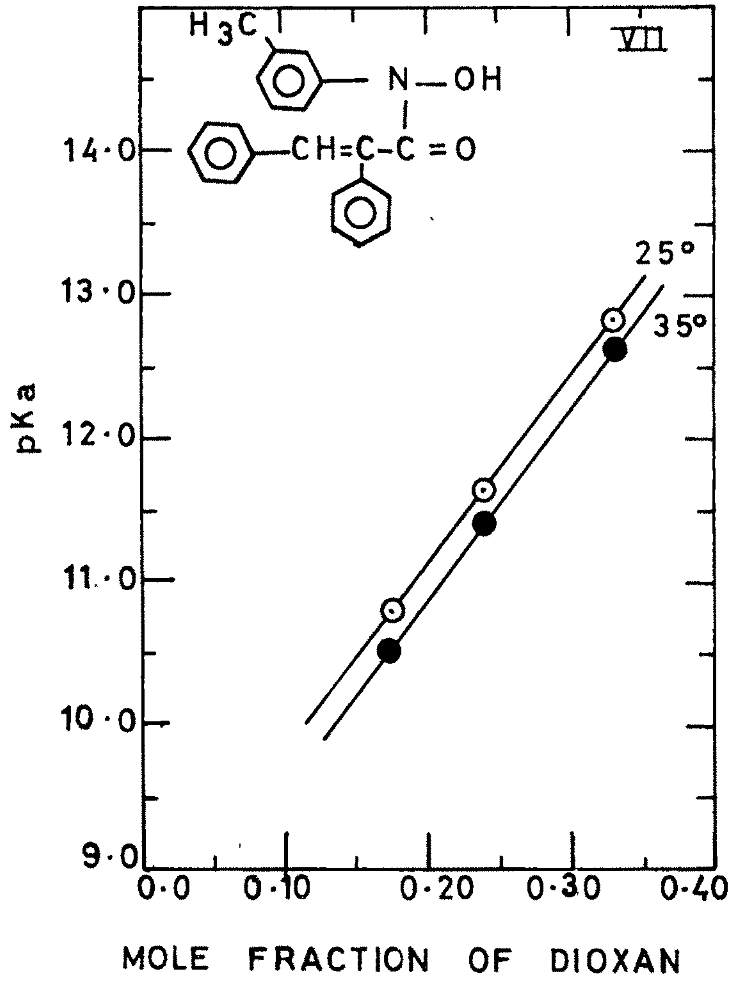


FIG. 7: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

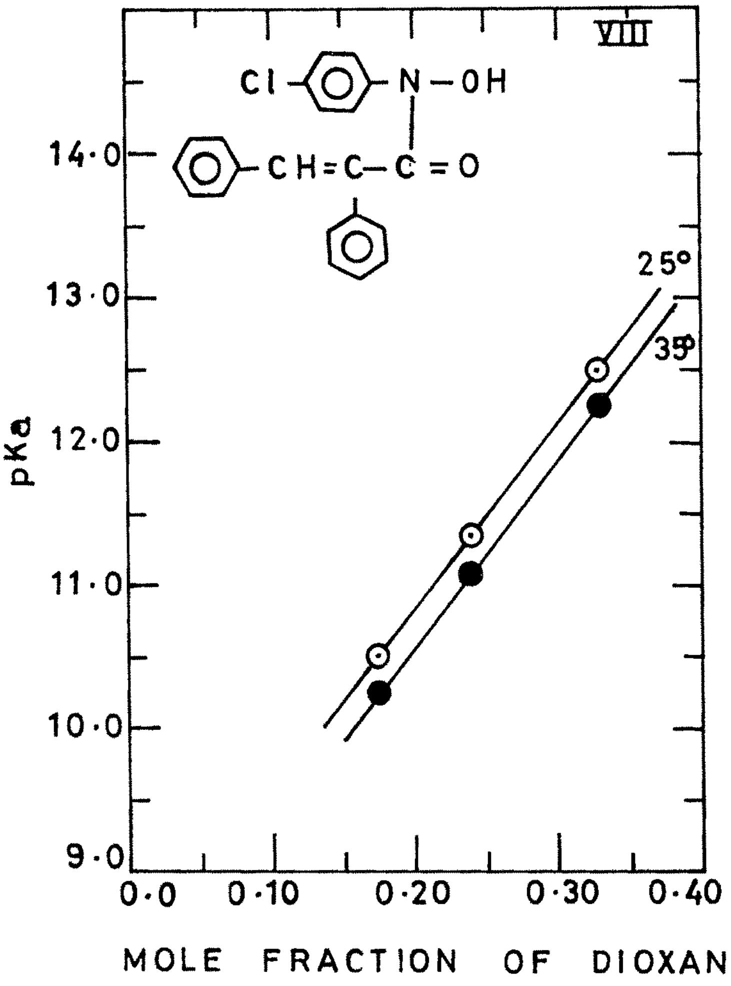


FIG. 8: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN

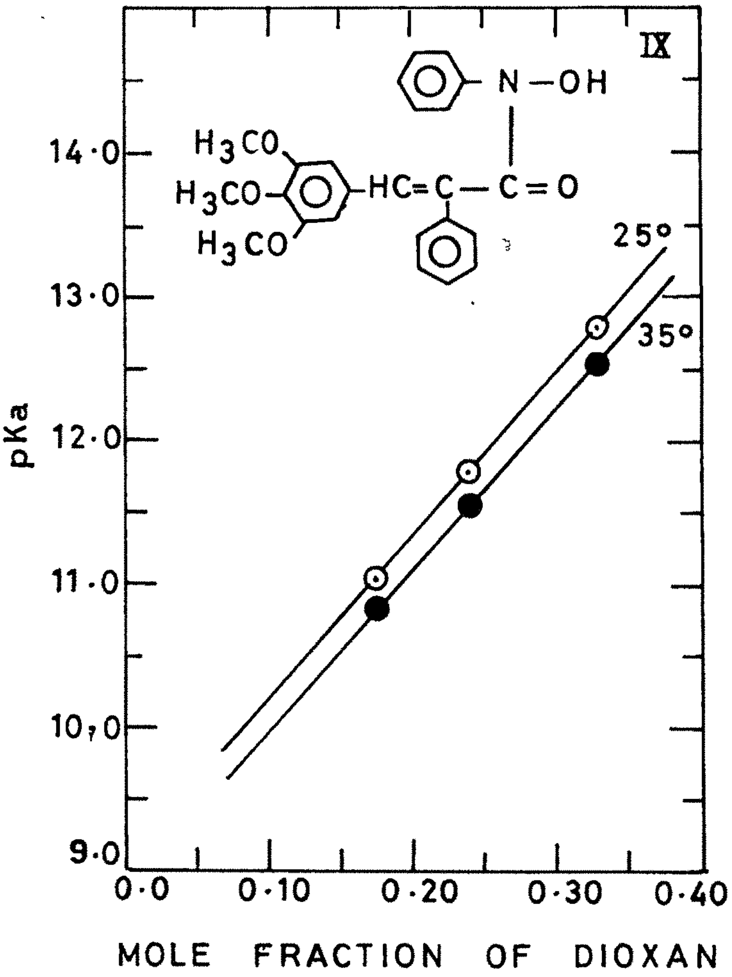


FIG 9: VARIATION OF pKa WITH MOLE FRACTION OF DIOXAN.

TABLE 6

Empirical correlation between pK_a and mole fraction of dioxan for substituted α-phenyl-cinnamohydroxamic acids at 25° and 35°C.

Compd No.	Cinnamohydroxamic acid	25°C $pK_a = mn_2 + c$			35°C $pK_a = mn_2 + c$		
		m	c	r	m	c	r
I	N-Phenyl-α-phenyl-p-methoxy-	11.22	9.15	1.00	11.09	8.94	1.00
II	N-p-Tolyl-α-phenyl-p-methoxy-	10.86	9.46	1.00	11.04	9.16	1.00
III	N-m-Tolyl-α-phenyl-p-methoxy-	10.64	9.45	1.00	10.91	9.14	1.00
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	10.79	8.83	1.00	10.91	8.54	1.00
V	N-Phenyl-α-phenyl-	12.49	8.59	1.00	12.69	8.30	1.00
VI	N-p-Tolyl-α-phenyl-	13.49	8.49	1.00	13.46	8.26	1.00
VII	N-m-Tolyl-α-phenyl-	13.16	8.50	1.00	13.16	8.25	1.00
VIII.	N-p-Chlorophenyl-α-phenyl-	12.82	8.27	1.00	12.82	8.02	1.00
IX	N-Phenyl-α-phenyl-3,4,5-trimethoxy-	11.22	9.10	1.00	11.09	8.89	1.00

r = correlation coefficient.

TABLE 7

Thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ values for the ionization of substituted α-phenylcinnamohydroxamic acids at 25°C and 35°C.

Compd No.	Cinnamohydroxamic acid	Mole fraction of dioxan, n_2								
		0.174			0.240			0.330		
		$\Delta G°$	$\Delta H°$	$-\Delta S°$	$\Delta G°$	$\Delta H°$	$-\Delta S°$	$\Delta G°$	$\Delta H°$	$-\Delta S°$
I	N-Phenyl-α-phenyl-p-methoxy-	63.39 (64.18)	40.48	321.50 (321.68)	66.68 (68.49)	44.01	332.16 (332.27)	73.39 (74.39)	44.01	412.29 (412.35)
II.	N-p-Tolyl-α-phenyl-p-methoxy-	64.88 (65.42)	49.29	218.77 (218.93)	68.76 (69.67)	42.24	372.16 (372.31)	74.53 (75.57)	44.01	428.29 (428.36)
III	N-m-Tolyl-α-phenyl-p-methoxy-	64.53 (65.24)	44.01	287.96 (288.15)	68.53 (69.37)	44.01	344.09 (344.21)	74.01 (75.28)	36.96	519.92 (520.12)
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	61.22 (61.70)	47.53	192.11 (192.33)	65.11 (65.83)	44.01	296.10 (296.16)	70.82 (71.73)	44.01	376.22 (376.24)
V	N-Phenyl-α-phenyl-	61.39 (61.99)	44.01	243.89 (244.04)	66.25 (67.01)	44.01	312.09 (312.18)	72.53 (73.68)	38.72	474.46 (474.51)
VI	N-p-Tolyl-α-phenyl-	61.96 (62.58)	44.01	251.89 (252.05)	66.82 (67.90)	35.20	443.72 (443.84)	73.84 (74.98)	40.48	468.14 (468.27)
VII	N-m-Tolyl-α-phenyl-	61.88 (62.29)	44.01	250.77 (248.11)	66.53 (67.31)	44.01	316.02 (316.25)	73.39 (74.39)	44.01	412.29 (412.35)
VIII	N-p-Chlorophenyl-α-phenyl-	59.97 (60.52)	44.01	223.97 (224.09)	64.82 (65.53)	44.01	292.03 (292.09)	73.39 (72.32)	44.01	384.22 (384.25)
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	63.11 (63.88)	40.48	317.57 (317.61)	67.39 (68.19)	44.01	328.09 (328.20)	73.10 (74.10)	44.01	408.22 (408.41)

$\Delta G°$ and $\Delta H°$ are in kj mol^{-1} and $-\Delta S°$ is in j $mol^{-1} k^{-1}$.
The values given in parentheses are at 35°C.

Medium effects

Most of the hydroxamic acids have lower solubility in water consequently the equilibrium studies have been made in mixed solvent systems. Of the various solvent systems chosen the mixture of water and dioxan appears to be the most convenient.

The equilibrium of hydroxamic acid (HA) when dissolved in the solvent (SH) can be represented

$$HA + SH \rightleftharpoons SH_2^+ + A^Z \qquad (1)$$

The ionization equilibrium of an acid or of a base is affected by the solvent change, not only because of the acidity or basicity of the solvent but also of its dielectric constant and the ability of the solvent to solvate the various species. The electrostatic work necessary to charge an isolated species HA, which is assumed to be spherical with radius r_{HA} and charge $Z_{HA}.e$, in a medium of dielectric constant D, is given by the Born equation (18).

$$\triangle G_{electrostatic} = \frac{N_A.Z_{HA}^2.e^2}{2\,\varepsilon r_{HA}} \qquad (2)$$

(e = electronic charge; N_A = Avogadro constant)

Application of this eq.(2) to acid-base reaction (1) leads to a net change in free energy per mol as shown in eq (2), if only pure electrostatic interactions are considered (19).

$$\triangle G_{\text{electrostatic}} = \frac{N_A \cdot e^2}{2\varepsilon}\left(\frac{1}{r_{SH_2^+}} + \frac{z_A^2}{r_A} - \frac{z^2_{HA}}{r_{HA}}\right) \qquad (3)$$

Thus the free energy difference $\triangle\triangle G$ for the ionization of a mol of HA in solvent 1 and solvent 2 with dielectric constant ε_1 and ε_2, respectively, provided that the radii of the reactants are the same in the both solvents, is given by eq.(4)

$$\triangle\triangle G = (\triangle G_{\text{electrostatic}})_2 - (\triangle G_{\text{electrostatic}})_1$$

$$= \frac{N_A e^2}{2}\left(\frac{1}{r_{SH_2^+}} + \frac{z_A^2}{r_A} - \frac{z_{HA}^2}{r_{HA}}\right)\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) \qquad (4)$$

Since the free energy of reaction $\triangle G$ is related to the equilibrium constant K_a

$$\triangle G = - RT \ln K \qquad (5)$$

Then according to eq.(4), eq.(5) can be written as

$$\frac{(K_a)_2}{(K_a)_1} = \frac{N_A \cdot e^2}{2\ RT}\left(\frac{1}{r_{SH_2^+}} + \frac{z_A^2}{r_A} - \frac{z_{HA}^2}{r_{HA}}\right)\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) \qquad (6)$$

Under these conditions, eq.(6) predicts that the logarithm of the ionization constant K_a of HA should be inversely proportional to the dielectric constant of the solvent in which the HA is dissolved. In several cases nearly linear relationships have been reported (20-22), while instances of failure from linearity too have not been uncommon (23). When pK_a of hydroxamic acids are plotted against 1/D, it is observed that fairly a linear relationship is observed.

Mole fraction of dioxan

Agrawal et al. observed that the pK_a of hydroxamic acids increases with the increase in mole fraction of dioxan (n_2) (1,4,24-30). This is because a solvent of low dielectric constant increases the electrostatic forces between the ions and thereby facilitates the formation of molecular species. The pK_a of hydroxamic acids studied here are plotted against the mole fraction of dioxan, a linear relationship is observed, Figs. 1-9. The experimental values of pK_a for almost all hydroxamic acids indicate a maximum deviation of 0.05 or about 0.5% in pK_a from linearity. Linear equations between pK_a and n_2 and respective correlation coefficients, r, given in Table 6 have been calculated by method of least square. Interpolation of pK_a by these equations is more convenient than by the graphs, while the accuracy is almost of the same order.

Thermodynamic functions

The data on $\Delta G°$, $\Delta H°$ and $-\Delta S°$ are given in Table 7. The pK_as have been determined with the precision of ±0.02 to 0.03 and hence $\Delta G°$ is estimated between ±0.13 and ±0.17 KJ.

The temperature coefficient method is used here for the computation of $\Delta H°$. It is apparent from equation (XIII) that error of 0.01 in pK_a 0.01 in pK_a causes an error of 1.76 KJ in $\Delta H°$ while the magnitude of error in pK_a depends on the cancellation or addition of errors of an individual set of pK_a determined at two temperatures.

It is observed that there is a general tendency of increase in magnitude of $\Delta S°$ with increase in dioxan content of the solvent medium.

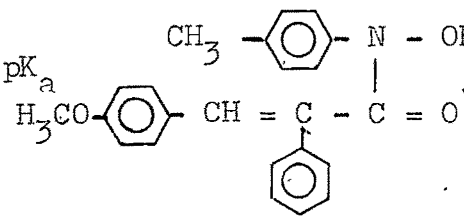
SUBSTITUENT EFFECTS ON pK_a VALUES

The hydroxamic acids under study can be classified in the following groups.

Category I	Compounds with p-methoxy substitution in C-phenyl ring (e.g. α -phenyl-p-methoxy cinnamo-) with methyl or Cl substitution in N-phenyl ring.
Category II	Compounds with α-phenyl in C-phenyl ring with methyl or Cl substitution in N-phenyl ring.

An examination of the pK_a values of categories I and II reveal that the order of acid strength of methyl and chloro-substitution in N-phenyl ring follow the order

Cat I pK_a



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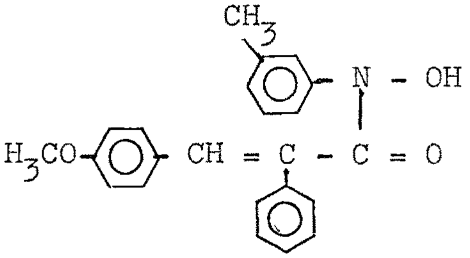

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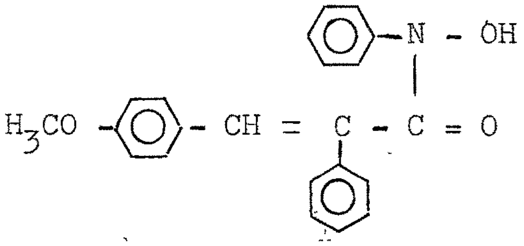
Compd No. II III



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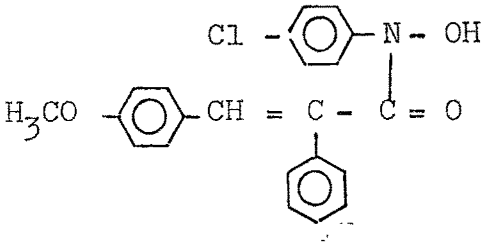
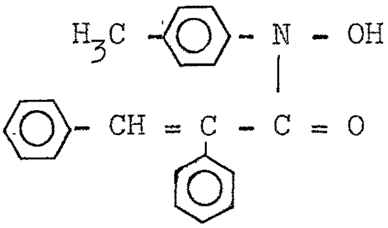


Compd No. I IV

Electronic substituents, such as methyl group in the meta and p-position weaken the aromatic acids whereas chloro group strengthen the acid. Acid weakening of meta and para isomers is generally explained by the positive inductive (electron repelling) effect. The high acid strength of the compound IV having chloro substituent is due to the mesomeric effect arising from the resonance of the benzenoid forms (31,32).

Substitution of methyl group in N-phenyl ring causes a gradual acid weakening. The similar trend of acid weakening is obtained with α-phenyl cinnamo hydroxamic acids category II.

Cat. II pK$_a$



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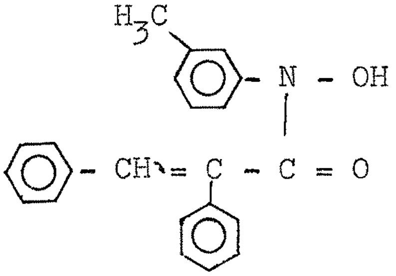

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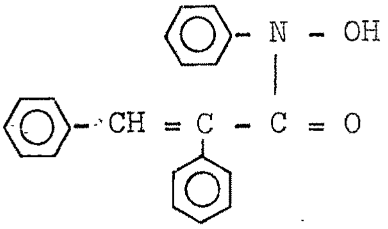

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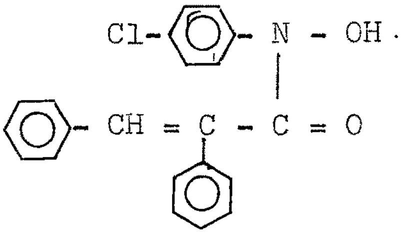

Compd.No. V VIII

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