CHAPTER III

THERMODYNAMIC PROTON-LIGAND STABILITY CONSTANTS OF HYDROXAMIC ACIDS

ABSTRACT

The thermodynamic proton-ligand stability constants, pK_a, of the N-p-chlorophenyl-m-substituted benzohydroxamic acids have been determined in dioxan-water media [50-70% (v/v)] at 25±0.1°C. Empirical correction to pH meter readings in mixed aqueous media have been applied. The pK_a varies linearly with mole fraction of dioxan. Numerical equations expressing this linear relationship have been obtained using the method of least squares. The Hammett correlation function and the effect of substituents on ionization constants of hydroxamic acids is discussed.

THERMODYNAMIC PROTON-LIGAND STABILITY CONSTANTS OF HYDROXAMIC ACIDS

The physico-chemical properties of organic reagents are essential to understand their nature, reactivity and analytical applicability. Studies on the metal complexes and analytical applications of hydroxamic acids require a knowledge of their ionization constants. In recent years many analogous compounds have been prepared by introduction of various substituent groups in different positions in the hope of developing reagents with superior analytical properties.

In this portion of the investigation, proton-ligand stability constants (hereafter, termed as thermodynamic ionization constants, pK_a) of N-p-chlorophenyl-m-substituted benzohydroxamic acids have been determined in 50-70% (v/v) dioxan-water media at 25±0.1°C.

All these hydroxamic acids are insoluble in water. Hence a resource to the use of mixed aqueous solvent media has to be taken to obtain the desired constants. Water dioxan solutions were deliberately chosen for this study for several reasons. The thermodynamic significance of results obtained with pH meter in these solutions is well understood as a result of thorough investigations by Van Uitert et al. (1,2), Agrawal et al. (3-5) and others (6-8).

CALIBRATION OF GLASS ELECTRODE IN DIOXAN-WATER MEDIA

The use of mixed aqueous solvent necessitates the calibration of the glass electrode so that pH meter readings are valid for the system. Such calibration also affords a simple method for evaluation of thermodynamic data directly from the measurement.

Van Uitert and Haas (1,2) have established that the glass electrode can be calibrated to measure stoichiometric hydrogen ion concentration $[H^+]$ from the pH metric reading (hereafter referred to as B when obtained from aqueous mixed solutions) in aqueous dioxan media by the relation

$$- \log [H^+] = B + \log U_H \qquad (1)$$

where $$\log U_H = \log U_H^{\circ} + \log y_{\pm} \qquad (2)$$

or $$- \log [H^+] = B + \log U_H^{\circ} + \log y_{\pm} \qquad (3)$$

Here $y_{\pm}$ denotes the mean activity coefficient of HCl for the solvent composition, temperature and ionic strength for which $\log U_H$ has been determined and $\log U_H^{\circ}$ corresponds to the correction at zero ionic strength which is dependent on the composition and temperature of the solvent medium. Equation (1) is equally valid for water and water-dioxan mixtures (1-5).

CALCULATION OF THERMODYNAMIC IONIZATION CONSTANT

The thermodynamic dissociation constant K_a (aq) of hydroxamic acid, HA,

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

in an aqueous medium is given by equation (4) and (5),

$$K_a\ (aq) = \frac{[H^+]\ [A^-]}{[HA]} \quad \frac{y_{H^+} \cdot y_{A^-}}{y_{HA}} \qquad (4)$$

$$pK_a = -\log [H^+] + \log \frac{[HA]}{[A^-]} - 2 \log y_{\pm} \qquad (5)$$

where $y_{\pm}$ is the activity coefficient of a univalent ion ($y_{H^+} = y_{A^-} = y_{\pm}$) at a given temperature and medium and it is assumed that the activity coefficient of the unionized acid y_{HA} is unity. The final expression for calculating ionization constant in dioxan-water medium is obtained by substituting the value of hydrogen ion concentration from equation (3) in equation (5).

$$pK_a = B + \log U_H^{\circ} + \log \frac{[HA]}{[A^-]} + \log \frac{1}{y_{\pm}} \qquad (6)$$

The pK_a values thus obtained are termed as thermodynamic values as they include correction due to activity coefficients. The equation (6) can be written as

$$pK_a = B + \Delta$$

$$\text{where } \Delta = \log U_H^{\circ} + \log \frac{[HA]}{[A^-]} + \log \frac{1}{y_\pm} \qquad (7)$$

EXPERIMENTAL

CHEMICALS

All the chemicals used were of G.R. (E. Merck) and AnalaR (B.D.H.) grades unless otherwise stated.

SOLVENTS

Distilled water

Preparation of distilled water is described in Chapter II.

Dioxan

p-dioxan was purified by the procedure of Weissberger (9). It was refluxed over pellets of potassium hydroxide 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 point, which varied from 11.65° to 11.80° (uncorrected) against the reported range of 11.65° to 12.0° (10,11).

REAGENTS

Potassium hydroxide

Carbonate free potassium hydroxide was prepared according to the method described by Vogel (12) and diluted to 0.1 M with the desired composition of dioxan-aqueous mixture.

Hydroxamic acid

The preparation of the hydroxamic acids is described in Chapter II. They were purified by recrystallisation from proper mixtures of benzene-petroleum ether before each investigation.

Standard Buffers

They were prepared as per reference from Vogel (12).

APPARATUS

A radiometer pH meter PHM 84 equipped with a combined electrode was used for pH metric titrations. The pH meter was standardised at the desired temperature (25±0.1°C) with aqueous buffer solutions such as 0.05 M potassium acid phthalate (pH - 4.005 at 25°C) and 0.01 M borax (pH - 9.18 at 25°C). Standardisation was checked both before and after each titration.

TITRATION VESSEL

A titration vessel, with a capacity of 75 ml was specially fabricated for the pH titrations. Besides an inlet from the side for nitrogen gas, it had three necks, which accomodated the combined electrode and the microburette.

NITROGEN

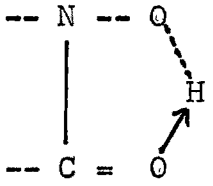
Nitrogen gas was passed through a series of bubblers containing a saturated alkaline solution of pyrogallol, 2N sulphuric acid, distilled water and finally the required solvent.

PROCEDURE

Into a 75-ml three necked titration cell having an inlet for nitrogen, the weighed amount of hydroxamic acid (corresponding to 0.01 M in a final volume of 50 ml), freshly distilled dioxan (as required for the desired composition) and double distilled water (as required for the desired composition) were added to yield the final composition of dioxan-water media under study. Due allowance for the contraction in volume on mixing of two solvents was made. The titration cell was thermostated at 25±0.1°C. Nitrogen, presaturated with the volume percentage dioxan-water media under study was bubbled through the solution. The electrode was placed in the cell. This solution was titrated against 0.1 M KOH also prepared in the required volume percentage dioxan-water media under study, taken in a burette (least count - 0.02 ml) adding the same in small aliquots (0.5 ml) and the pH was recorded.

RESULTS AND DISCUSSION

Hydroxamic acids are found to be the versatile analytical reagents (13-18). The acidity of the hydroxamic acids may be attributed essentially to the -OH group and basic character of nitrogen atom is suppressed as it is in amides. Hydroxamic acids are weak acids, though several times stronger than phenols. The suppression of acid character may be attributed to intramolecular hydrogen bonding as shown by infrared studies (19-21).

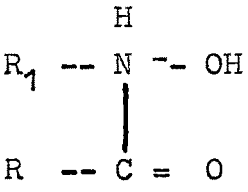


The acidic dissociation character of hydroxamic acids in ionizing solvents can be represented by the following equilibria.

$$H_2A^+ \rightleftharpoons HA + H^+$$

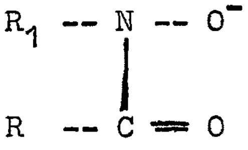
$$HA \rightleftharpoons A^- + H^+$$

and



Protonated species

Molecular species



Anion species

From the pH titrations performed here, it is inferred that the protonation of hydroxamic acids is relatively small.

The experimental observation for only three representative titrations are recorded in Tables 1-3. The values of pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids in 50-70% (v/v) dioxan-water media at 25±0.1°C are given in Table 4. The average pK_a generally falls within a spread of ±0.02 but not beyond ±0.03 in any case. The empiricals for different mole fractions of dioxan are given in Table 5.

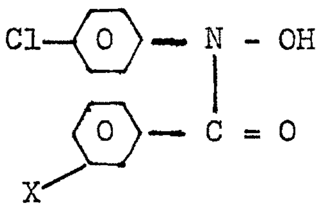
Medium Effect

In Figs. 1-2, the pK_a are plotted against mole fraction of dioxan, n_2, and a linear relationship is observed. The empirical values of pK_a indicate the maximum deviation from linearity of the order of about 0.5% in pK_a.

Generally 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 reason may be due to the fact that a linear relationship exists between the ionization constants (pK_a) of weak acids and mole fraction of dioxan (1-6,22-25). In case of water-alcohol system, hockey-stick shape curves are obtained (26).

TABLE 1

DETERMINATION OF pK_a of N-p-CHLOROPHENYL-m-METHOXYBENZOHYDROXAMIC ACID IN 50% (v/v) DIOXAN-WATER MEDIA

Structural Formula	Mol. Wt.	Temperature	Log U_H°
	277.7	25±0.1°C	0.20

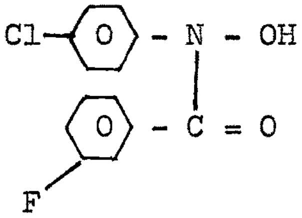
Concentration : 0.01 M at half neutralization. N-p-chlorophenyl-m-methoxybenzohydroxamic acid (0.13085 g) was dissolved in 23.75 ml of dioxan + 23.75 ml of water.

I	II	III		IV	V	VI	VII
Titrant 0.1000 M KOH		Stoichiometric concentration		$\frac{[HA]}{[A^-]}$	log of column IV	$\log\frac{1}{y_\pm}$	pK_a
		[HA]	$[A^-]$				
0.00	8.26	0.01	0.00	-	-	-	-
0.50	9.46	0.009	0.001	9/1	0.954	0.061	10.67
1.00	9.81	0.008	0.002	8/2	0.602	0.070	10.68
1.50	10.01	0.007	0.003	7/3	0.368	0.097	10.67
2.00	10.18	0.006	0.004	6/4	0.176	0.108	10.66
2.50	10.34	0.005	0.005	5/5	0.000	0.119	10.66
3.00	10.51	0.004	0.006	4/6	-0.176	0.127	10.65
3.50	10.70	0.003	0.007	3/7	-0.368	0.134	10.66
4.00	10.92	0.002	0.008	2/8	-0.602	0.142	10.66
4.50	11.27	0.001	0.009	1/9	-0.954	0.150	10.66

Results : Average pK_a = 10.66

TABLE 2

DETERMINATION OF pK_a OF N-p-CHLOROPHENYL-m-FLUOROBENZOHYDROXAMIC ACID IN 60% (v/v) DIOXAN-WATER MEDIA

Structural Formula	Mol. wt.	Temperature	log U_H°
	265.6	25±0.1°C	0.40

Concentration : 0.01 M at half neutralization. N-p-chlorophenyl-m-fluorobenzohydroxamic acid (0.13285g) was dissolved in 23.75 ml of dioxan + 23.75 ml of water.

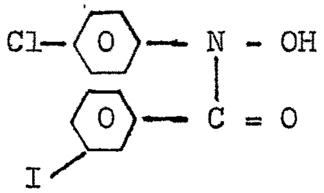
I Titrant 0.1000 M KOH	II B	III Δ	IV pK_a
0.00	8.46		
0.50	9.69	1.43	11.12
1.00	9.98	1.13	11.11
1.50	10.19	0.93	11.12
2.00	10.38	0.75	11.13
2.50	10.61	0.51	11.12
3.00	10.70	0.42	11.12
3.50	10.88	0.24	11.12
4.00	11.11	0.02	11.13
4.50	11.46	-0.32	11.14
5.00	11.77	-	-

Where $\Delta = \log \frac{[HA]}{[A^-]} + \log U_H^\circ + \log {}^1/y_\pm$

Results : Average pK_a = 11.12

TABLE 3

DETERMINATION OF pK_a OF N-p-CHLOROPHENYL-m-IODOBENZOHYDROXAMIC ACID IN 70% (v/v) DIOXAN-WATER MEDIA

Structural Formula	Mol. Wt.	Temperature	log U_H°
	373.5	25±0.1°C	0.80

Concentration : 0.01 M at half neutralization. N-p-chlorophenyl-m-iodobenzohydroxamic acid (0.18675 g) was dissolved in 23.75 ml of dioxan + 23.75 ml of water.

I Titrant 0.1000 M KOH	II B	III Δ	IV pK_a
0.00	9.02		
0.50	10.21	1.87	12.08
1.00	10.48	1.61	12.09
1.50	10.66	1.43	12.09
2.00	10.83	1.27	12.10
2.50	10.99	1.11	12.10
3.00	11.16	0.95	12.11
3.50	11.32	0.78	12.10
4.00	11.54	0.57	12.11
4.50	11.88	0.24	12.12
5.00	12.01		

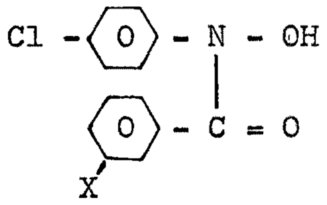
where $\Delta = \log \frac{[HA]}{[A^-]} + \log U_H^\circ + \log \frac{1}{y_\pm}$

Results : Average pK_a = 12.10

TABLE 4

THERMODYNAMIC IONIZATION CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN DIOXAN-WATER MEDIA AT 25°C

Structural Formula

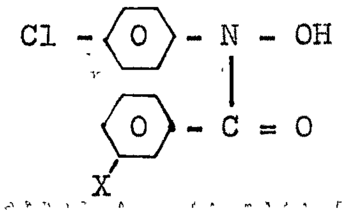


Compd. No.	Substituent X	pK_a		
		Mole fraction of dioxan, n_2		
		0.174	0.240	0.330
I	H	10.77	11.47	12.43
II	CH_3	10.88	11.54	12.45
III	OCH_3	10.66	11.36	12.32
IV	F	10.39	11.12	12.11
V	Cl	10.33	11.07	12.08
VI	Br	10.30	11.04	12.06
VII	I	10.36	11.10	12.10
VIII	NO_2	9.90	10.65	11.69

TABLE 5

EMPIRICAL CORRELATION BETWEEN pK_a AND MOLE FRACTION OF DIOXAN FOR N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS AT 25°C.

Structural Formula



Compd. No.	Substituent X	$pK_a = mn_2 + c$				
		Least square			Graphically	
		m	c	r	m	c
I	H	10.64	8.92	1.00	10.66	8.95
II	CH_3	10.07	9.13	1.00	10.00	9.15
III	OCH_3	10.64	8.81	1.00	10.72	8.80
IV	F	11.08	8.47	1.00	11.11	8.45
V	Cl	11.22	8.38	1.00	11.20	8.40
VI	Br	11.34	8.33	1.00	11.36	8.35
VII	I	11.15	8.42	1.00	11.11	8.40
VIII	NO_2	12.08	7.80	1.00	12.00	7.85

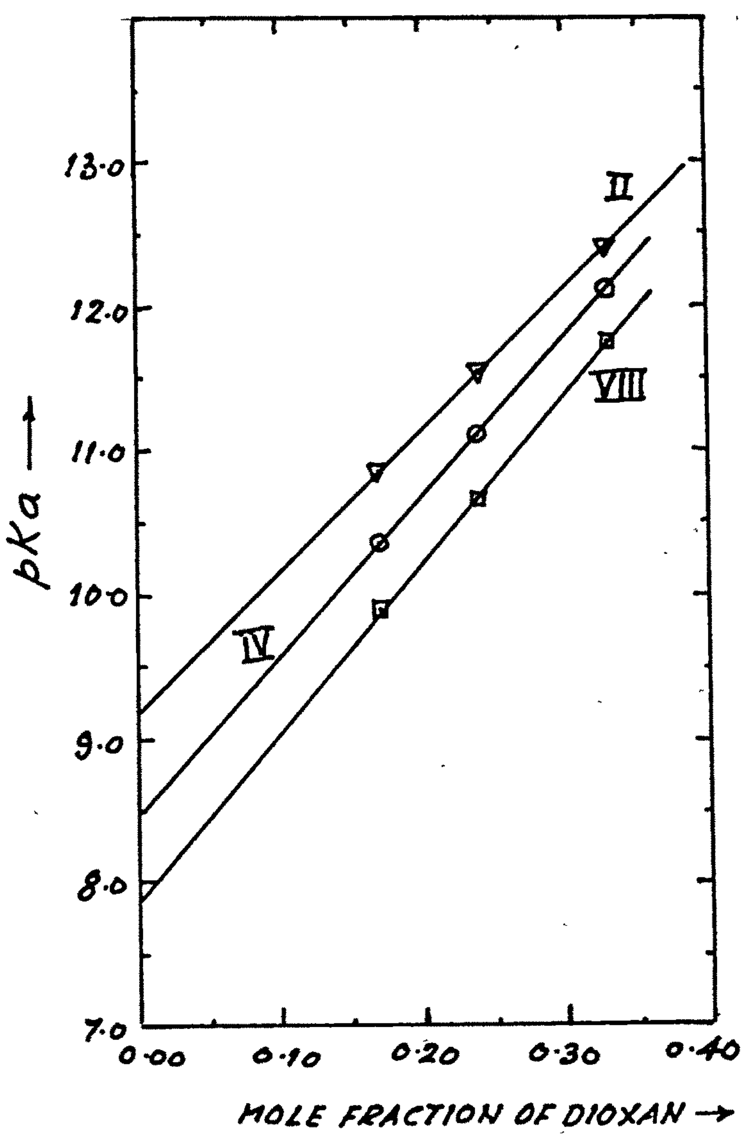


Fig. 1. Variation of pK_a vs Mole fraction of dioxan.

II N-p-chlorophenyl-m-methylbenzohydroxamic acid
IV N-p-chlorophenyl-m-fluorobenzohydroxamic acid
VIII N-p-chlorophenyl-m-nitrobenzohydroxamic acid

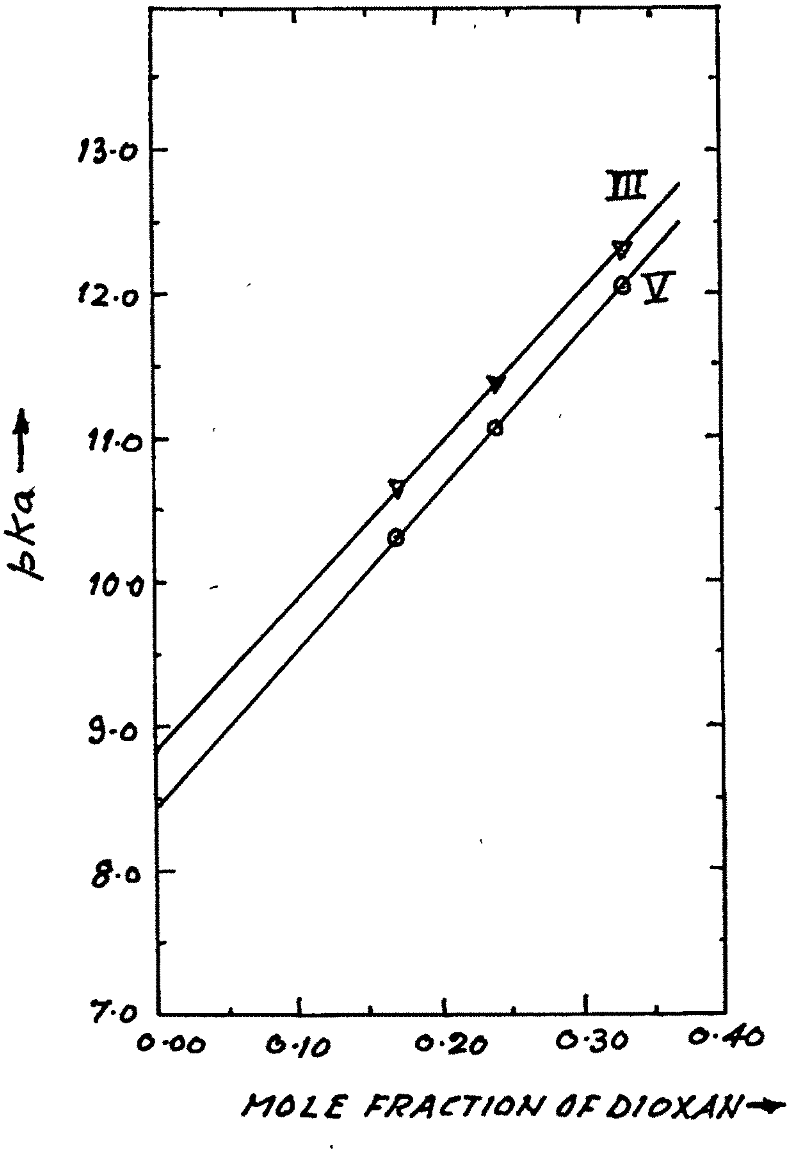


Fig. 2. Variation of pK_a vs Mole fraction of dioxan.

III N-p-chlorophenyl-m-methoxybenzohydroxamic acid.
V N-p-chlorophenyl-m-chlorobenzohydroxamic acid.

The effect of solvent on the Gibbs energy for the dissociation of a weak acid has sometimes been ascribed to a change in the electrostatic self energy of the ions. Gurney (27) and others (28,29), have pointed out that the standard free energy change of proton transfer may be considered in two parts, electrostatic (ΔG°_{el}) and non electrostatic (ΔG°_{non}). The simplest expression for electrostatic energy of a mole of univalent ions is that of Born (30).

$$\Delta G^{\circ}_{el} = \frac{Ne^2}{2} \quad \frac{1}{Dr_s} \qquad (8)$$

where N is the Avogadro number, e is the electronic charge, D is the dielectric constant of the medium and r_s the radius of the (spherical) ion.

In the dissociation of a weak acid in the mixture of the solvents of a charge type $HA \rightleftharpoons H^+ + A^-$, the electrostatic forces between the cation and anions are increased and formation of molecular species is facilitated (24). The change in the energy on the transfer from water to 70 percent dioxan is then

$$\Delta G^{\circ}_{el} = \left(\frac{Ne^2}{2} \frac{1}{D_s} - \frac{1}{D_w}\right)\left(\frac{1}{r_+} - \frac{1}{r_-}\right) \qquad (9)$$

where D_s is the dielectric constant of dioxan-water percent and D_w is that of water (78.36 at 25°C).

Further on substitution of $\Delta G^{\circ}_{diss} = 2.303\ RTpK_a$ becomes

$$pK_a = \frac{\Delta G^{\circ}_{non}}{2.303\ RT} + \frac{Ne^2}{4.606\ RT}\left(\frac{1}{D_s} - \frac{1}{D_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \quad (10)$$

When the pK_a of hydroxamic acids are plotted against 1/D (Fig. 3) it is observed that the plots possess the distinct curvature. This suggests non electrical forces which could include geometrical factors,hydrogen bonding and solvent solute interactions, influencing the dissociation process.

Agrawal et al. observed (4,5, 31-35) that the pK_a of hydroxamic acids are increasing with the increase in dioxan content (mole fraction of dioxan, n_2) due to 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. For all hydroxamic acids,the change in pK_a with mole fraction of dioxan is of considerable magnitude. When the pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids are plotted against the mole fraction of dioxan, linear relationships are observed (Figs. 1-2). The experimental values of pK_a for almost all hydroxamic acids indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% pK_a.

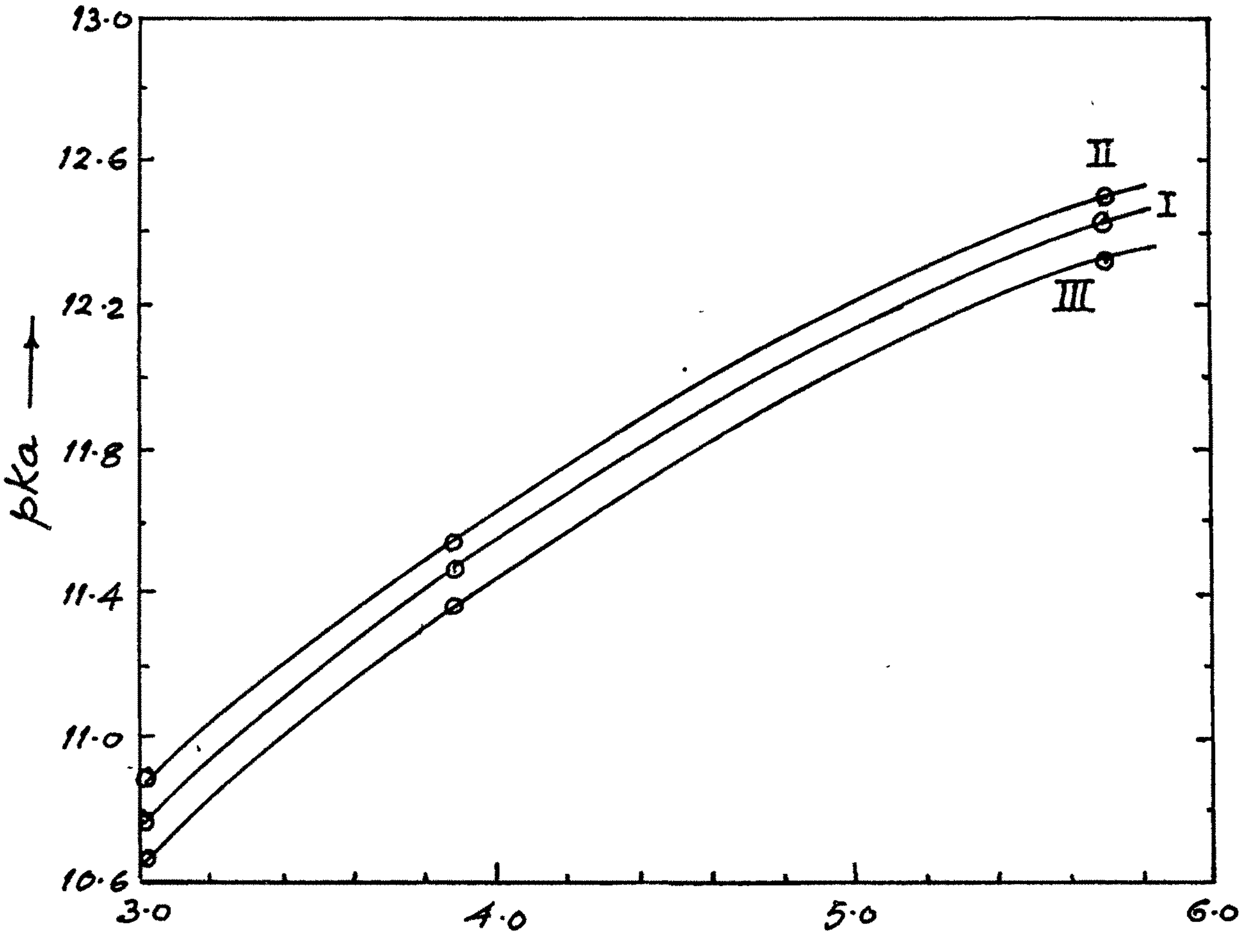


Fig. 3. Plots of pK$_a$'s of N-p-chlorophenyl-m-substituted benzohydroxamic acids vs 100/D at 25°C.

Hammett correlation

Hammett (36) and Jaffe (37) correlated the effect of substitution on the reactivity of benzene derivatives. Agrawal et al. (38-40) have made an attempt to correlate the pK_a of substituted benzohydroxamic acid with benzoic acid and obtained a good agreement between the two sets of values. In the present investigation a correlation is established between the pK_a values of N-p-chlorophenyl-m-substituted benzohydroxamic acids with Hammett equation (11).

$$\log \frac{K}{K_o} = \rho\sigma \qquad (11)$$

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

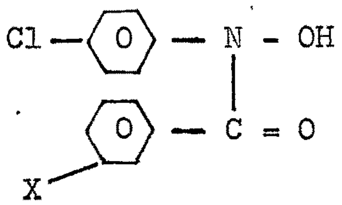
The pK_a in Table 6 indicate that the experimental values (extrapolated), values calculated by Hammett equation and least squares are in good agreement.

A plot of pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids against the pK_a of respective benzoic acids is linear (Figs. 4-7) in aqueous (extrapolated) and 50-70% dioxan-water media and is in agreement with the experimental values (Tables 6-9). The dependence of the acidity on substitution on benzene nucleus was followed by the same

TABLE 6

HAMMETT pK_a OF THE N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN AQUEOUS MEDIA AT 25°C

Structural formula



Compd. No.	Substituent X	pK_a^{i}	pK_a^{j}	σ	pK_a^{k} Hammett $\rho=1.6$	pK_a Benzoic acid
I	H	8.95	8.92	0.0	8.92	4.18
II	CH_3	9.15	9.13	- 0.07	9.03	4.27
III	OCH_3	8.80	8.81	+ 0.12	8.73	4.09
IV	F	8.45	8.47	+ 0.34	8.38	3.87
V	Cl	8.40	8.38	+ 0.37	8.33	3.83
VI	Br	8.35	8.33	+ 0.39	8.30	3.81
VII	I	8.40	8.42	+ 0.35	8.36	3.85
VIII	NO_2	7.85	7.80	+ 0.71	7.78	3.49

i = pK_a in aqueous media, extrapolated values (graphically).

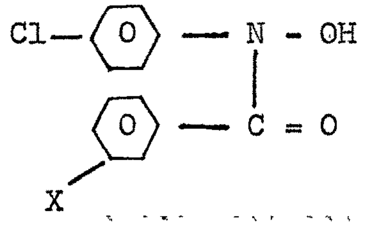
j = pK_a in aqueous media,by least square.

k = pK_a obtained from Hammett σ function ($\log K - \log K_0 = \rho\sigma$)

TABLE 7

HAMMETT pK_a OF THE N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 50% (v/v) DIOXAN-WATER MEDIA AT 25°C

Structural formula



Compd. No.	Substituent X	Mole fraction of dioxan, n_2		
		pK_a Experimental	σ	pK_a^a Hammett $\rho = 1.28$
I	H	10.77	0.00	10.77
II	CH_3	10.88	-0.07	10.85
III	OCH_3	10.66	+0.12	10.62
IV	F	10.39	+0.34	10.34
V	Cl	10.33	+0.37	10.30
VI	Br	10.30	+0.39	10.28
VII	I	10.36	+0.35	10.33
VIII	NO_2	9.90	+0.71	9.87

$n_2 = 0.174$

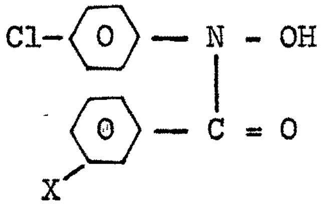
pK_a^a = pK_a obtained from Hammett σ function

$(\log K - \log K_0 = \rho\sigma)$

TABLE 8

HAMMETT pK_a OF THE N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 60% (v/v) DIOXAN-WATER MEDIA AT 25°C

Structural formula



Compd. No.	Substituent X	Mole fraction of dioxan, n_2		
		pK_a Experimental	σ	pK_a^b Hammett $\rho = 1.16$
I	H	11.47	0.00	11.47
II	CH_3	11.54	- 0.07	11.55
III	OCH_3	11.36	+ 0.12	11.34
IV	F	11.12	+ 0.34	11.08
V	Cl	11.07	+ 0.37	11.05
VI	Br	11.04	+ 0.39	11.02
VII	I	11.10	+ 0.35	11.06
VIII	NO_2	10.65	+ 0.71	10.65

$n_2 = 0.240$

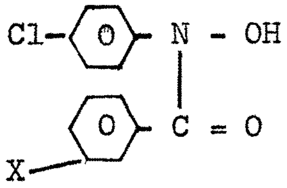
pK_a^b = pK_a obtained from Hammett σ function

$(\log K - \log K_0 = \rho\sigma)$

TABLE 9

HAMMETT pK_a OF THE N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 70% (v/v) DIOXAN-WATER MEDIA AT 25°C

Structural Formula



Compd. No.	Substituent X	Mole fraction of dioxan, n_2		
		pK_a Experimental	σ	pK_a^c Hammett $\rho = 0.92$
I	H	12.43	0.00	12.43
II	CH_3	12.45	- 0.07	12.50
III	OCH_3	12.32	+ 0.12	12.31
IV	F	12.11	+ 0.34	12.08
V	Cl	12.08	+ 0.37	12.05
VI	Br	12.06	+ 0.39	12.03
VII	I	12.10	+ 0.35	12.07
VIII	NO_2	11.78	+ 0.71	11.78

$n_2 = 0.330$

$pK_a^c = pK_a$ obtained from Hammett σ function

$(\log K - \log K_0 = \rho\sigma)$

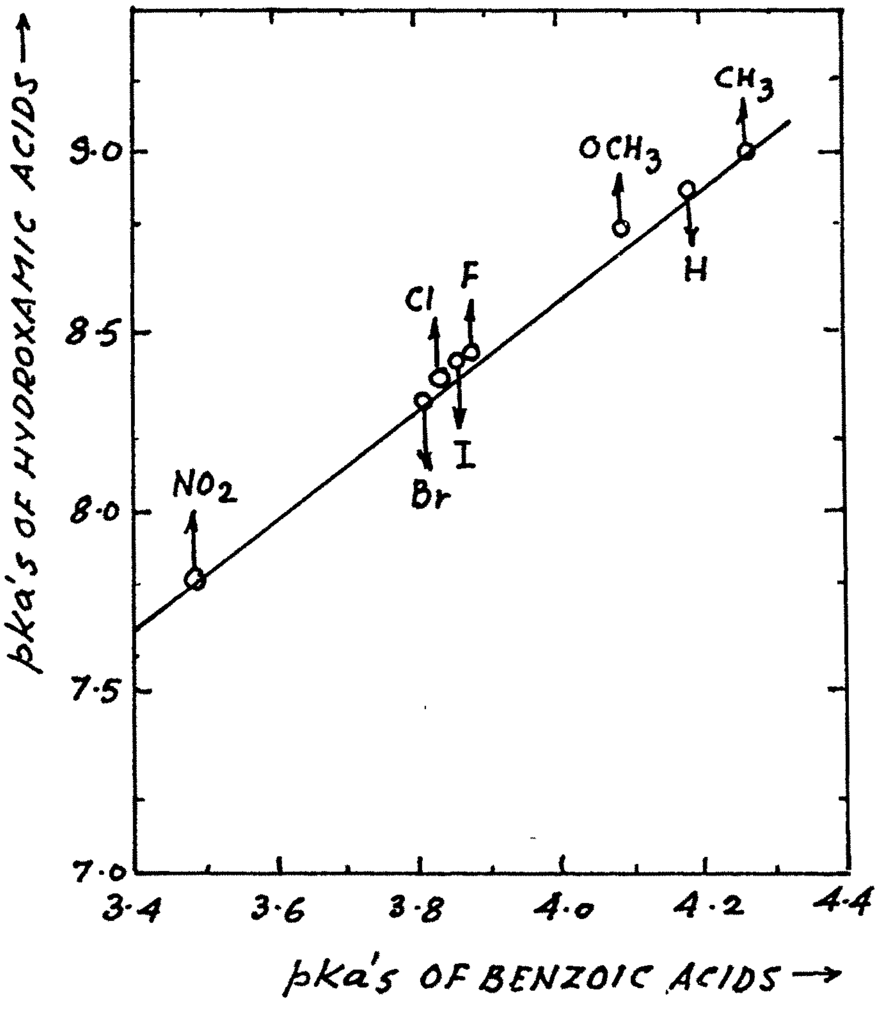


Fig. 4. Plot of pK_a's of N-p-chlorophenyl-m-substituted benzohydroxamic acids vs pK_a's of benzoic acids at 25°C.

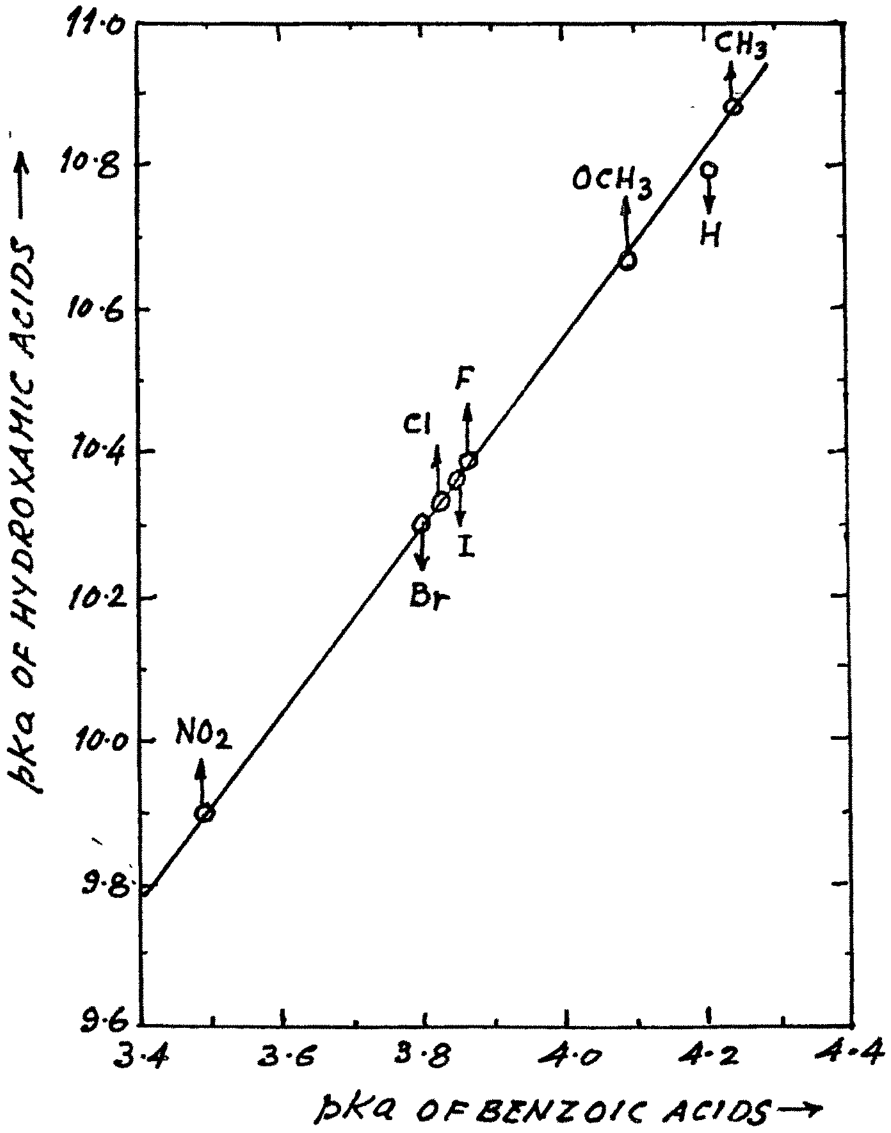


Fig. 5. Plot of pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids vs pK_a of benzoic acids in 50% (v/v) Dioxan-water media at 25±0.1°C.

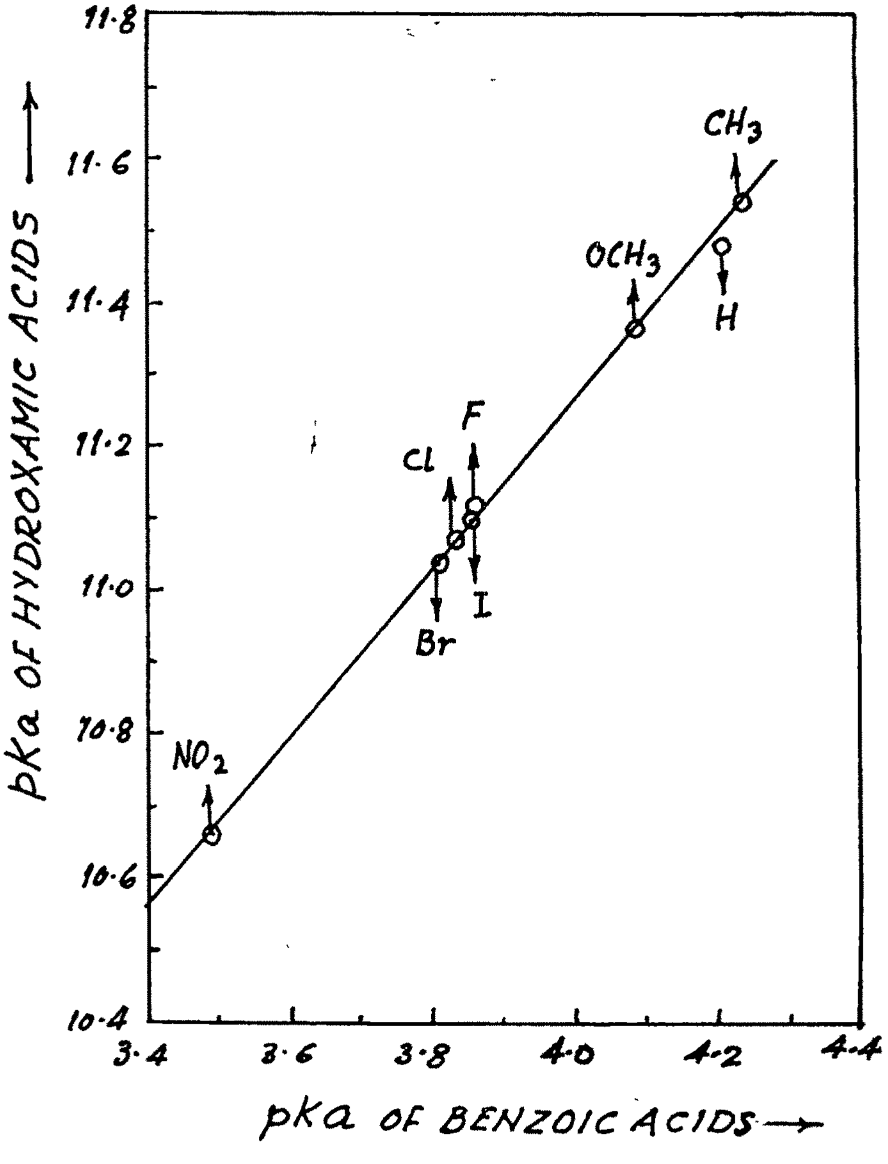


Fig. 6. Plot of pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids vs pK_a of benzoic acids in 60% (v/v) Dioxan-Water media at 25±0.1°C.

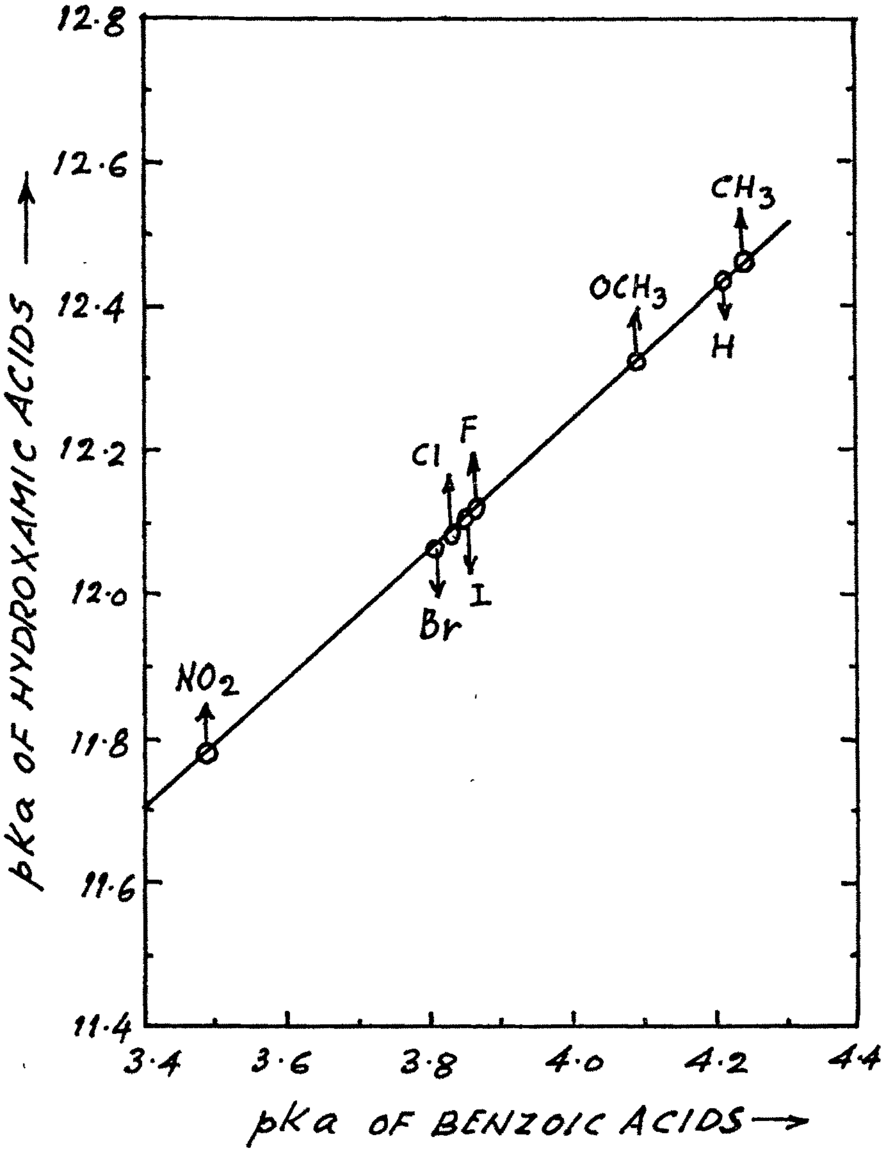


Fig. 7. Plot of pK_a of N-p-chlorophenyl-m-substituted benzohydroxamic acids vs pK_a of benzoic acids in 70% (v/v) Dioxan-Water media at 25±0.1°C.

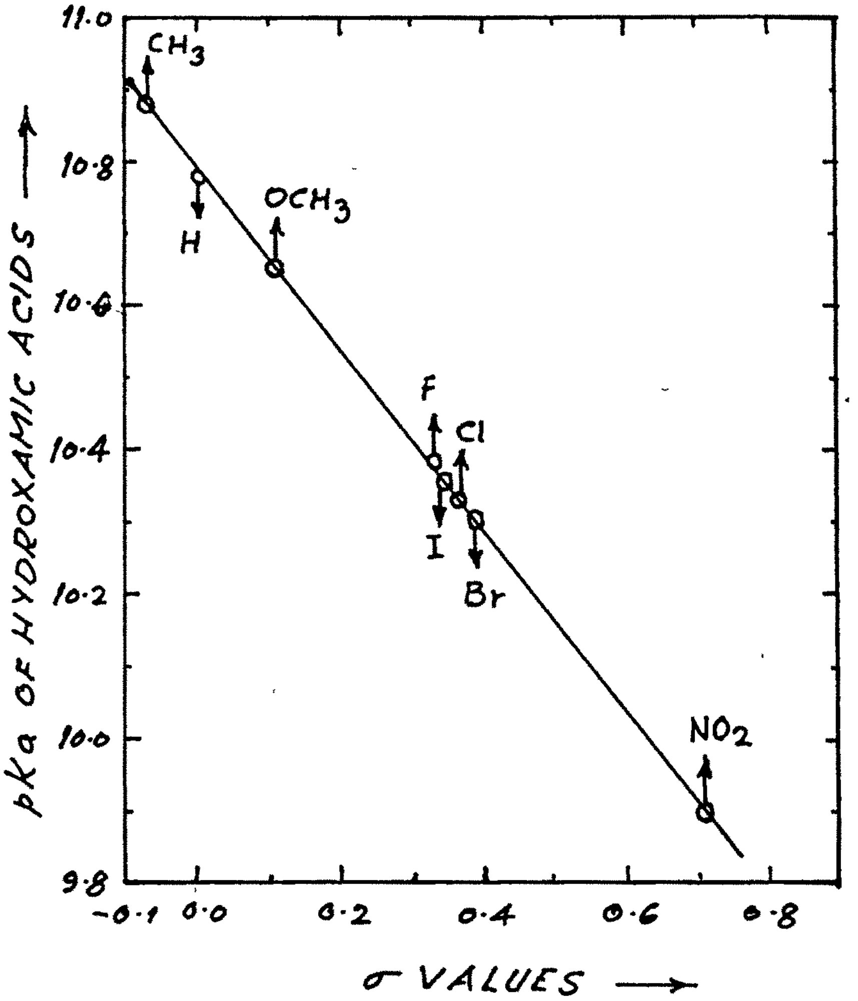


Fig. 8. Hammett's σ plots at 25°C.

reaction constant, ρ , obtained by two different plots (Figs. 4-7 and 8).

Substituent effect

In order to understand the relation between the molecular structure of hydroxamic acids and their pK_a, it is convenient to examine the parent carboxylic acids.

The hydroxamic acids under study are derived from m-substituted benzoic acids and follow the order of pK_a of the benzoic acids, in all mole fractions of dioxan, thus

pK_a of benzoic acids $CH_3 > H > CH_3O > F > I > Cl > Br > NO_2$

pK_a of hydroxamic acids $CH_3 > H > CH_3O > F > I > Cl > Br > NO_2$.

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