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Hydroxamic Acids and Their Metal Complexes

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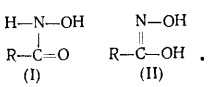
The chemical properties and thermodynamic characteristics of hydroxamic acids and their metal complexes are examined and Tables of proton-ligand and metal-ligand stability constants are presented. The influence of various factors on the dissociation of hydroxamic acids and their complexes is discussed.
The bibliography includes 123 references.

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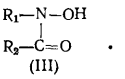
I. INTRODUCTION

Hydroxamic acids is the name given to *N*-acyl derivatives of hydroxylamine[1-3]:



(I) (II)

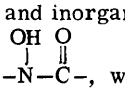
On the other hand, they can be regarded as *N*-hydroxy-derivatives of acid amides or as oximes of carboxylic acids[4]. The substitution of one or both hydrogen atoms in (I) or (II) by hydrocarbon or acyl groups yields compounds having the general formula



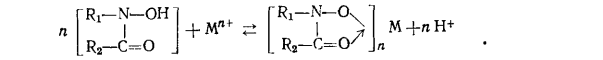
(III)

Here R_1 = H, phenyl, *o*-tolyl-, *m*-tolyl, *p*-tolyl, or *p*-chlorophenyl and R_2 consists of carboxylic or aliphatic acid derivatives.

Different terminologies are used for hydroxamic acids in the literature[1,3,5]. Thus in the publications of certain European workers a distinction is drawn between compounds designated above by odd and even numbers: the former are called "hydroxamic" acids and the latter are referred to as "hydroximic" acids. On the other hand, in certain American publications, including Chemical Abstracts[6-8], no such distinction is made and the general term "hydroxamic acids" is used for all compounds (I)-(III).

Hydroxamic acids are used in a wide variety of ways as reagents in organic and inorganic analysis. They contain the bidentate group , which meets all the requirements necessary for the formation of metal complexes.

Complexes are usually formed via the substitution of a hydrogen atom of hydroxylamine by a metal cation and ring closure via the carbonyl oxygen atom:



The formation of metal chelates via this mechanism has for a long time constituted the basis of a wide variety of analytical methods[9-25]. Because of the non-ionic nature of such metal complexes (or inner complexes), they can be extracted in all cases from aqueous solutions or suspensions with the aid of solvents immiscible with water, such as benzene, chloroform, carbon tetrachloride, higher alcohols, or dichlorobenzene; separation processes involving solvent extraction are based on this feature. If such inner complexes are very sparingly soluble in water, are fairly stable, and have a constant composition, they can be used in gravimetric methods.

The study of the possible analytical applications of hydroxamic acids requires the knowledge of their ionisation constants[26,27]. In the search for reagents with improved analytical properties, numerous analogous compounds have been synthesised in recent years by introducing various substituents in different positions. For such specific synthesis to be successful, it is desirable to know the physicochemical properties of the reagents and their metal complexes; this would lead to a better understanding of the causes of the selectivity and sensitivity of the corresponding analytical reactions.

II. PROTON-LIGAND STABILITY CONSTANTS OR IONISATION CONSTANTS (pK_a)

The thermodynamic dissociation constants K_a(aq) of hydroxamic acids HA (dissociation via the reaction $HA \rightarrow H^+ + A^-$) in an aqueous medium are defined by the

formula

$$K_a(\text{aq}) = \frac{[H^+]\cdot[A^-]}{[HA]}\cdot\frac{Y_{H^+}\cdot Y_{A^-}}{Y_{HA}}, \quad (1)$$

or

$$pK_a(\text{aq}) = \lg[H^+] + \lg\frac{[HA]}{[A]} + 2\lg\frac{1}{Y_\pm}, \quad (2)$$

where $Y_\pm$ is the activity coefficient of a univalent ion ($Y_{H^+} + Y_{A^-} = Y_\pm$) at a given temperature and in a given medium; it is assumed that the activity coefficient of the unionised acid Y_{HA} is unity.

If the medium is altered by the addition of water, then, according to Van Uitert and Hass, the stoichiometric hydrogen ion concentration $[H^+]$ can be obtained from instrumental readings (B) with the aid of the equation

$$\lg[H^+] = B + \lg U_H^0 - \lg\frac{1}{Y_\pm}. \quad (3)$$

The values of $\lg U_H^0$ have been determined experimentally[28] and are listed in Table 1 for the dioxan–water medium.

Table 1. The values of $\lg U_H^0$ for water–dioxan media of different composition.

Dioxan concentration		$\lg U_H^0$ at 25°C		$\lg U_H^0$ at 30°C			$\lg U_H^0$ at 35°C
vol.%	mole fraction	this work	Ref.96	this work	Ref.97	Ref.96	this work
0	0	0.00	0.00	0.00	0.00	0.00	0.00
10	0.023	0.01	0.01	0.01	—	0.03	0.01
20	0.050	0.02	0.04	0.02	0.02	0.06	0.02
30	0.083	0.04	0.06	0.05	0.05	0.10	0.06
40	0.123	0.08	0.11	0.09	0.09	0.16	0.10
45	0.147	0.12	0.16	0.13	0.13	0.20	0.14
50	0.174	0.20	0.22	0.22	0.22	0.26	0.24
60	0.240	0.40	0.44	0.39	0.40	—	0.42
70	0.330	0.80	0.85	0.80	0.80	—	0.83

We have from Eqns. (2) and (3)

$$pK_a = B + \lg U_H^0 + \lg\frac{[HA]}{[A^-]} + \lg\frac{1}{Y_\pm}, \quad (4)$$

or

$$pK_a = B + \Delta, \text{ where } \Delta = \lg U_H^0 + \lg\frac{[HA]}{[A]} + \lg\frac{1}{Y_\pm}. \quad (5)$$

The values of Δ are listed in Tables 2 and 3.

III. THERMODYNAMIC FUNCTIONS FOR IONIC EQUILIBRIA

The standard free energy ΔF° of the ionisation reaction $HA \rightleftharpoons H^+ + H^-$ can be determined from the equation

$$\Delta F^0 = 2.303RT\ pK_a, \quad (6)$$

which can be written in a simplified form:

$$\Delta F^0(298.2°) = 1.365pK_a \text{ (kcal)}; \quad (7)$$

$$\Delta F^0(308.2°) = 1.411\ pK_a \text{ (kcal)}. \quad (8)$$

The expression for the standard enthalpy of reaction ΔH° is obtained by integrating the van't Hoff equation for two temperatures T_1 and T_2:

$$\lg\frac{K_2}{K_1} = \frac{\Delta H^0(T_2 - T_1)}{4.576T_1T_2}. \quad (9)$$

Eqn. (9) is approximate, since ΔH° varies with temperature. However, for similar temperatures of the kind considered above (25° and 35°C), ΔH° can be assumed to be constant and Eqn. (9) can be written in the form

$$\Delta H^0 = 42.07\Delta pK_a \text{ (kcal)}, \quad (9a)$$

where

$$\Delta pK_a = pK_a(25°) - pK_a(35°).$$

Table 2. The values of Δ at 25°C.

[HA]	[A⁻]	Dioxan concentration, vol.% (mole fraction)								
		0 (0)	10 (0.023)	20 (0.050)	30 (0.083)	40 (0.123)	45 (0.147)	50 (0.174)	60 (0.240)	70 (0.330)
0.009	0.001	0.97	0.98	0.99	1.02	1.07	1.10	1.19	1.43	1.87
0.008	0.002	0.62	0.63	0.65	0.68	0.73	0.77	0.87	1.13	1.61
0.007	0.003	0.39	0.41	0.42	0.46	0.51	0.56	0.67	0.93	1.43
0.006	0.004	0.02	0.22	0.24	0.28	0.33	0.38	0.48	0.75	1.27
0.005	0.005	0.03	0.05	0.07	0.11	0.16	0.22	0.32	0.51	1.11
0.004	0.006	−0.14	−0.12	−0.10	−0.06	−0.01	0.05	0.15	0.42	0.95
0.003	0.007	−0.33	−0.31	−0.29	−0.25	−0.19	−0.14	−0.03	0.24	0.78
0.002	0.008	−0.56	−0.54	−0.52	−0.48	−0.42	−0.37	−0.26	0.02	0.57
0.001	0.009	−0.91	−0.89	−0.87	−0.83	−0.77	−0.71	−0.68	−0.32	0.24

Note. 0.01 M acid is titrated with 0.1 M alkali introduced in ten equal portions, each portion corresponding to the neutralisation of one tenth of an equivalent of the acid.

Table 3. The values of Δ at 35°C.

[HA]	[A⁻]	Dioxan concentration, vol.% (mole fraction)								
		0 (0)	10 (0.023)	20 (0.050)	30 (0.083)	40 (0.123)	45 (0.147)	50 (0.174)	60 (0.240)	70 (0.330)
0.009	0.001	0.97	0.98	0.99	1.04	1.09	1.13	1.25	1.47	1.92
0.008	0.002	0.62	0.63	0.65	0.70	0.75	0.80	0.93	1.16	1.65
0.007	0.003	0.39	0.41	0.42	0.48	0.53	0.59	0.71	0.95	1.47
0.006	0.004	0.21	0.22	0.24	0.29	0.35	0.41	0.53	0.77	1.30
0.005	0.005	0.03	0.05	0.07	0.13	0.19	0.24	0.36	0.61	0.15
0.004	0.006	−0.14	−0.12	−0.10	−0.05	0.02	0.08	0—20	0.45	0.99
0.003	0.007	−0.33	−0.32	−0.29	−0.23	−0.17	−0.11	0—02	0.27	0.82
0.002	0.008	−0.56	−0.55	−0.52	−0.46	−0.40	−0.34	−0.21	0.05	0.61
0.001	0.009	0.91	−0.90	−0.87	−0.81	−0.74	−0.68	−0.55	−0.29	0.27

Note. 0.01 M acid is titrated with 0.1 M alkali added in ten equal portions; each portion corresponds to the neutralisation of one tenth of an equivalent of the acid.

The standard entropy of reaction $-\Delta S^\circ$ is usually calculated from the Gibbs–Helmholtz equation

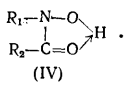
$$-\Delta S^0 = \frac{\Delta F^0 - \Delta H^0}{T}, \quad (10)$$

or

$$-\Delta S^0(25°) = 3.354\cdot10^{-3}(\Delta F^0 - \Delta H^0) \text{ (kcal)};$$
$$-\Delta S^0(35°) = 3.244\cdot10^{-3}(\Delta F^0 - \Delta H^0) \text{ (kcal)}.$$

IV. PROTON–LIGAND STABILITY CONSTANTS IN AN AQUEOUS MEDIUM

The ionisation constants of many substituted hydroxamic acids are listed in Table 4. These compounds are weak acids and, as has been observed for amides, the basicity of their nitrogen atom is also suppressed. In an aqueous medium and in dioxan–water mixtures the OH groups may be largely responsible for the acidity of hydroxamic acids. The suppression of the acid nature of these groups can then be accounted for by the intermolecular hydrogen bond formed by the compound. The formation of structure (IV) with intermolecular hydrogen bonds has been confirmed in several cases by infrared spectroscopy[30–33]:



(IV)

Table 4. Proton–ligand thermodynamic stability constants (in an aqueous medium at 25 °C).

Hydroxamic acid	pK_a	Hydroxamic acid	pK_a
Benzo-	8.91	Aceto-	9.46
p-Methylbenzo-	9.05	n-Butyro	9.50
p-Methoxybenzo-	9.15	Propeno	9.52
p-Fluorobenzo-	8.81	Phenyloaceto-	9.23
p-Chlorobenzo-	8.70	Salicyl	7.43
p-Bromobenzo-	insoluble	α-Naphtho-	7.75
p-Iodobenzo-	insoluble	Picolino-	8.85
p-Nitrobenzo-	8.13	Nicotino-	8.27
p-Aminobenzo-	9.42	Isonicotino-	7.94
p-Cyanobenzo-	8.26	Chloroaceto-	8.52
N-Phenylbenzo-	8.38	*N*-Phenylnicotino-	8.12
N-Phenyl-*o*-methenobenzo-	8.49	Phthalo-	9.60
N-Phenyl-*o*-methylbenzo-	8.39	Indole-3-aceto-	9.70
N-Phenyl-*o*-chlorobenzo-	8.16	Cyclohexano-	9.87
N-*m*-Tolyl-*m*-nitrobenzo-	8.33	L-Lacto-	9.46
N-*p*-Tolyl-*m*-nitrobenzo-	insoluble	*p*-Chlorophenoxyaceto-	8.86
N-*o*-Tolyl-*m*-nitrobenzo-	8.15	Formo-	8.77
N-*p*-Chlorophenyl-*m*-nitrobenzo-*	insoluble	Glycine-	7.81
o-Hydroxybenzo-	9.05	D-Lysine-	8.05
o-Aminobenzo-	9.29	L-Lysine	8.04
Phenylaceto-	9.33		

*All the substituted *N*-*p*-chlorophenylbenzohydroxamic acids, obtained from *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-benzoic acids, are insoluble in water.

The thermodynamic ionisation constants of *p*-substituted benzohydroxamic acids listed in Table 5 are satisfactorily correlated with the Hammett constants:

(V) (VI)

X = H, CH_3, OCH_3, F, Cl, Br, I, NO_2, NH_2, or CN .

Table 5 shows that the pK_a values found experimentally and calculated from the Hammett equation and by the method of least squares agree satisfactorily, the maximum difference amounting to 0.03 pK_a unit.

Plots of the pK_a of hydroxamic acids (V) against the pK_a of benzoic acids (VI) and against the constants σ are presented in Figs. 1 and 2 respectively. The plots are linear and the following equation can be fitted by least squares:

$$pK_a = 1.02X + 4.62, \quad (11)$$

where X is the pK_a of the substituted benzoic acid. Similarly the plot of the pK_a of *p*-substituted benzohydroxamic acids (V) against the Hammett function σ is linear and has a slope of 1.00, which agrees satisfactorily with experimental values. The relation between acidity and the effect of the substituent introduced into the benzene ring is expressed by the constant ρ, whose values, derived from different plots (Figs. 1 and 2), are the same.

Table 5. Thermodynamic ionisation constants and Hammett constants for substituted benzohydroxamic acids.

No.	Benzohydroxamic acid		σ	pK_a (calc. by Eqn.(11))*	pK_a (calc. by Hammett Eqn.)	ΔpK_a**	pK_a for benzoic acid
	X	pK_a (expt.)					
1	H	8.91	—	8.91	—	±0.00	4.21
2	CH_3	9.05	−0.170	9.05	9.08	±0.00	4.34
3	OCH_3	9.15	−0.268	9.18	9.18	−0.03	4.47
4	F	8.81	+0.062	8.84	8.85	−0.03	4.14
5	Cl	8.70	+0.227	8.69	8.69	+0.01	3.99
6	Br	insoluble	+0.232	8.70	8.68	—	4.00
7	I	insoluble	+0.276	8.63	8.63	—	—
8	NO_2	8.13	+0.778	8.13	8.13	±0.00	3.44
9	NH_2	9.42	−0.660	—	—	—	—
10	CN	8.26	+0.660	8.24	8.25	0.02	3.55

*Obtained by the method of least squares as the average of nine values: $pK_a = 1.02X + 4.62$.
**ΔpK_a is the difference between the values of pK_a obtained experimentally and found from Eqn. (11).

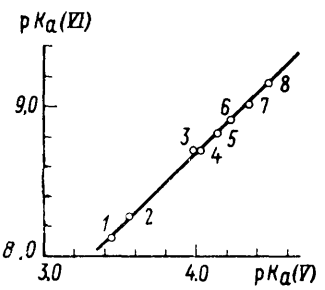


Figure 1. Relation between the pK_a values for benzoic acid (V) and benzohydroxamic acids (VI); substituent X: 1) NO_2; 2) CN; 3) Cl; 4) Br; 5) F; 6) H; 7) CH_3; 8) OCH_3.

The introduction of substituents into organic chelating compounds frequently alters their ability to form chelates and also influences other chemical and physical properties. Such changes in the acids have been studied on the basis of changes in their polarity, hydrogen bonding, and resonance and inductive effects.

In order to understand the relation between the molecular structure of hydroxamic acids and their pK_a values, it is necessary to investigate the pK_a of the initial carboxylic acids. All the hydroxamic acids (V) considered here were obtained from substituted benzoic acids (VI). Table 5 shows that the pK_a values for

hydroxamic acids form the same sequence as the pK_a for benzoic acids:

$$NH_2 > OCH_3 > CH_3 > F > Cl \simeq Br > NO_2 .$$

The introduction of the methyl group (X = CH_3), which has positive inductive and tautomeric effects, into (V) reduces the acidity. For the methoxy-group (X = OCH_3), which is an electronegative substituent[35], the positive tautomeric effect is much stronger than the inductive effect, which leads to a further decrease of acidity: $pK_a(OCH_3) > pK_a(CH_3)$. The strong influence of the nitro- and halogeno-substituents can be accounted for[36,37] by the mesomeric effect arising owing to the resonance between the benzenoid forms; in terms of this effect, halogens can be arranged in the sequence $F > Cl$; $Br > I$. Hydroxamic acids (Table 5) form the same sequence: compound 4 > compound 5; compound 6 > compound 7.

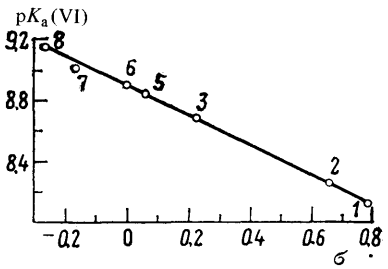


Figure 2. The Hammett relation for the pK_a values for benzohydroxamic acid; the significance of the circles is the same as in Fig. 1.

The nitro-group is a powerful *meta*-directing substituent with distinct electron-accepting properties, which increases the strength of benzoic acid, since pK_a(Hal) > $pK_a(NO_2)$; accordingly, the pK_a values for the compounds form the sequence 4–7 > 8 (Table 5).

V. PROTON–LIGAND STABILITY CONSTANTS IN MIXED AQUEOUS MEDIA

N-Arylhydroxamic acids are usually insoluble in water and readily dissolve in alcohol, dioxan, chloroform, etc. Their stability constants were therefore determined in dioxan–water mixtures of different compositions (10–70%) and were then extrapolated to the aqueous medium. The thermodynamic ionisation constants for certain hydroxamic acids are listed in Tables 6–8.

1. The Influence of Temperature

The ionisation constant of a weak acid is a function of temperature and usually has a maximum [K_a(max) or pK_a(min)] at approximately 25°C.[38] The data in Table 6 show that the pK_a for all hydroxamic acids in all solvents are lower at 35°C than at 25°C. The temperature corresponding to the maximum K_a can be found by determining pK_a at several temperatures, but it is evident that this temperature (T_{max}) must be higher than 25°C.

2. The Influence of the Medium

Agrawal and Tandon[39] observed that, with increase of the mole fraction of dioxan, the pK_a for hydroxamic acids also increases. This entails an intensification of the electrostatic interaction between the ions in a solvent with a low dielectric constant and facilitates the formation of molecular species. Gurney[40] and other workers[41,42] found that the change in standard free energy accompanying proton transfer ΔF°_{diss} can be represented by a sum of two components—electrostatic (ΔF°_{el}) and non-electrostatic (ΔF°_{nel}):

$$\Delta F^0_{diss} = \Delta F^0_{el} + \Delta F^0_{nel}, \qquad (12)$$

The electrostatic contribution to the free energy change can be estimated with the aid of the Born equation:

$$\Delta F^0_{el} = \frac{Ne^2}{2D}\left(\frac{1}{r^+} + \frac{1}{r^-}\right). \qquad (13)$$

For dilute solutions, D can be assumed equal to the dielectric constant of the solvent[43,44]; hence

$$pK_a = \frac{\Delta F^0_{nel}}{2.303RT} + \frac{Ne^2}{4.606RT}\left(\frac{1}{r^+} + \frac{1}{r^-}\right). \qquad (14)$$

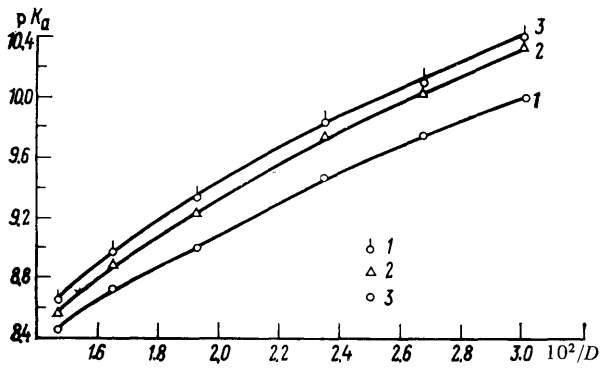


Figure 3. Dependence of pK_a on the dielectric constant (25°C): 1) *N*-*o*-tolylnitrobenzohydroxamic acid; 2) *N*-*m*-tolylnitrobenzohydroxamic acid; 3) *N*-*p*-tolylnitrobenzohydroxamic acid.

If it is assumed that ΔF°_{nel} is independent of the solvent, it is possible to plot pK_a against $1/D$. In certain cases, particularly for water-rich media, linear relations have been obtained[45–48], although deviations from linearity are not unusual either[49]. When such plots were constructed, it was observed that their curvature can vary. This is illustrated by typical curves in Fig. 3. Evidently non-electrostatic factors have a considerable influence on the dissociation of hydroxamic acids. Furthermore, a change in the dielectric constant and the consequent change in the shape and size of individual ions, hydrogen bonding, and other specific forms of solvent–solute interaction also have an appreciable influence on the dissociation of hydroxamic acids.

Table 6. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	NH_2OH	C_6H_4NHOH	o-CH_3–C_6H_4NHOH	m-CH_3–C_6H_4NHOH	p-CH_3–C_6H_4NHOH
			Benzohydroxamic acid		
H^+	gl; 0.5; 20; Aq; k_1=8.88[102]	gl; 0.1; 30; Aq; k_1=8.15[25]	gl; *T*; 25; 20d; k_1=9.32[62]	gl; *T*; 25; 20d; k_1=9.38[61]	gl; *T*; 25; 20d; k_1=9.43[61]
H^+	gl; 1.0; 20; Aq; k_1=8.68[102]	pH; 0.2; 25; Aq; k_1=8.15[100]	gl; *T*; 35; 20d; k_1=9.20[61]	gl; *T*; 35; 20d; k_1=9.25[61]	gl; *T*; 35; 20d; k_1=9.26[61]
H^+	pH; 0.1; 30d; Aq; k_1=8.80[103]	pH; 0.005; 25; 30c; k_1=8.28[19]	gl; *T*; 35; 20d; k_1=9.79[61]	gl; *T*; 25; 30d; k_1=9.84[61]	gl; *T*; 25; 30d; k_1=9.85[61]
H^+	—; 0.1; 25; Aq; k_1=8.75[105]	sp; —; —; —; k_1=8.27[101]	gl; *T*; 35; 30d; k_1=9.65[61]	gl; *T*; 35; 30d; k_1=9.75[61]	gl; *T*; 35; 30d; k_1=9.78[61]
H^+	E; 0.1; 25; Aq; k_1=8.79[106]	pH; —; 25; 50d; k_1=10.45[111]	gl; *T*; 25; 40d; k_1=10.32[61]	gl; *T*; 25; 40d; k_1=10.38[61]	gl; *T*; 25; 40d; k_1=10.42[61]
H^+	—; —; —; Aq; k_1=8,07[107]	pH; 0.1; 25; Aq; k_1=8.14[99]	gl; *T*; 35; 40d; k_1=10.25[61]	gl; *T*; 35; 40d; k_1=10.34[61]	gl; *T*; 35; 40d; k_1=10.35[61]
H^+	pH; 1.0,25; Aq; k_1=8.97[108]	pH; 0.005; 25; 50d; k_1=11.04[110]	gl; *T*; 25; 50d; k_1=11.12[61]	gl; *T*; 25; 50d; k_1=11.12[61]	gl; *T*; 25; 50d; k_1=11.13[61]
H^+	gl; [illegible] Aq; k_1=8.80[19]	pH; 0.005; 35; 50d; k_1=10.96[110]	gl; *T*; 35; 50d; k_1=10.95[61]	gl; *T*; 35; 50d; k_1=11.07[61]	gl; *T*; 35; 50d; k_1=11.03[61]
H^+	gl; 0.005; 25; 30c; k_1=9.30[19]	pH; 0.1; 30; Aq; k_1=8.14[111]	—; 0.1; 30d; Aq; k_1=8.18[99]	—	—; 0.1; 30; Aq; k_1=8.27[99]
H^+	sp; —; —; —; k_1=8.78[101]	pH; —; —; 70a; k_1=1026[112]	—	—	—
H^+	gl; 0.1; —; 30; Aq; k_1=8.48[99]	gl; *T*; 25; 20d; k_1=9.23[61]	—	—	—
H^+	gl; *T*; 25; Aq; k_1=8.91[96]	gl; *T*; 35; 20d; k_1=9.13[61]	—	—	—
H^+	gl; *T*; 35; Aq; k_1=8.79[26]	gl; *T*; 25; 30d; k_1=9.76[61]	—	—	—
H^+	—; 0.1; 30; Aq; k_1=8.43[109]	gl; *T*; 35; 30d; k_1=9.63[61]	—	—	—
H^+	—	gl; *T*; 25; 40d; k_1=10.30[61]	—	—	—
H^+	—	gl; *T*; 35; 40d; k_1=10.20[61]	—	—	—
H^+		gl; *T*; 25; 50d; k_1=11.04[61]	—	—	—
H^+		gl; *T*; 35; 50d; k_1=10.96[61]	—	—	—
H^+		gl; *T*; 25; Aq; k_1=8.91[26]	—	—	—
H^+		gl; *T*; 25; Aq; k_1=8.79[26]	—	—	—
H^+		gl; *T*; 25; 10d; k_1	—	—	—
H^+		gl; *T*; 35; 10d; k_1	—	—	—
H^+		gl; *T*; 25; 45d; k_1	—	—	—
			m-Methylbenzohydroxamic acid		
Cu^{2+}	—	gl; *T*; 25; 45d; k_1=10.65[27]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 45d; k_1=10.62[27]	—	—	—
Cu^{2+}	—	gl; *T*; 25; 50d; k_1=11.08[4]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=11.04[27]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=10.35[59]; k_2=8.68	—	—	—
Zn^{2+}	—	gl; *T*; 35; 50d; k_1=8.63[59]; k_2=6.65	—	—	—
Ni^{2+}	—	gl; *T*; 35; 50d; k_1=7.77[59]; k_2=5.68	—	—	—
Mn^{2+}	—	gl; *T*; 35; 50d; k_1=6.80[59]; k_2=5.67	—	—	—
			p-Methylbenzohydroxamic acid		
H^+	—	gl; *T*; 25; 20d; k_1=9.35[61]	gl; *T*; 25; 20d; ins[61]	gl; *T*; 25; 20d; ins[61]	gl; *T*; 25; 20d; ins[61]
H^+	—	gl; *T*; 35; 20d; k_1=9.27[61]	gl; *T*; 35; 20d; ins[61]	gl; *T*; 35; 20d; ins[61]	gl; *T*; 35; 20d; ins[61]
H^+	—	gl; *T*; 25; 30d; k_1=9.84[61]	gl; *T*; 25; 30d; k_1=10.22[61]	gl; *T*; 25; 30d; k_1=9.96[61]	gl; *T*; 25; 30d; k_1=10.05[61]
H^+	—	gl; *T*; 35; 30d; k_1=9.75[61]	gl; *T*; 35; 30d; k_1=9.99[61]	gl; *T*; 35; 30d; k_1=9.88[61]	gl; *T*; 35; 30d; k_1=9.91[61]
H^+	—	gl; *T*; 25; 20d; k_1=10.49[61]	gl; *T*; 25; 40d; k_1=10.64[61]	gl; *T*; 25; 40d; k_1=10.57[61]	gl; *T*; 25; 40d; k_1=10.59[61]
H^+	—	gl; *T*; 35; 30d; k_1=10.33[61]	gl; *T*; 35; 40d; k_1=10.53[61]	gl; *T*; 35; 40d; k_1=10.46[61]	gl; *T*; 35; 40d; k_1=10.38[61]
H^+	—	gl; *T*; 25; 20d; k_1=11.13[61]	gl; *T*; 25; 50d; k_1=11.23[61]	gl; *T*; 25; 50d; k_1=11.32[61]	gl; *T*; 25; 50d; k_1=11.26[61]
H^+	—	gl; *T*; 35; 30d; k_1=10.98[61]	gl; *T*; 35; 50d; k_1=11.09[61]	gl; *T*; 35; 50d; k_1=11.10[61]	gl; *T*; 35; 50d; k_1=10.97[61]
H^+	—	gl; *T*; 35; 45d; k_1	—	—	—
H^+	—	gl; *T*; 25; 60d; k_1	—	—	—
H^+	—	gl; *T*; 35; 60d; k_1	—	—	—
H^+	—	gl; *T*; 25; 70d; k_1	—	—	—
H^+	—	gl; *T*; 35; 70d; k_1	—	—	—
Cu^{2+}	gl; *T*; 35; 50d; k_1=9.95[50]; k_2=8.12	gl; *T*; 25; 50d; k_1=10.30[111]	gl; *T*; 25; 50d; k_1=10.51[110]	gl; *T*; 25; 50d; k_1=10.52[110]; k_2=8.86	gl; *T*; 25; 50d; k_1=10.66[110]; k_2=8.87
Cu^{2+}	—	gl; *T*; 25; 50d; k_1=10.36[110]; k_2=8.78	gl; *T*; 35; 50d; k_1=10.40[110]; k_2=8.58		
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=10.29[110]; k_2=8.63		gl; *T*; 35; 50d; k_1=10.50[110]; k_2=8.76	gl; *T*; 35; 50d; k_1=10.52[110]; k_2=8.69
			o-Methoxybenzohydroxamic acid		
H^+	—	gl; *T*; 25; Aq; k_1=8.49[26]	—	—	—
H^+	—	gl; *T*; 35; Aq; k_1=8.48[26]	—	—	—
H^+	—	gl; *T*; 25; 10d; k_1=8.84[39]	—	—	—
H^+	—	gl; *T*; 35; 10d; k_1=8.74[39]	—	—	—
H^+	—	gl; *T*; 25; 20d; k_1=9.24[39]	—	—	—
H^+	—	gl; *T*; 35; 20d; k_1=9.21[39]	—	—	—
H^+	—	gl; *T*; 25; 30d; k_1=9.84[39]	—	—	—
H^+	—	gl; *T*; 35; 30d; k_1=9.70[39]	—	—	—
H^+	—	gl; *T*; 25; 40d; k_1=10.36[39]	—	—	—
H^+	—	gl; *T*; 35; 40d; k_1=10.27[39]	—	—	—
H^+	—	gl; *T*; 25; 45d; k_1=10.70[39]	—	—	—
H^+	—	gl; *T*; 35; 45d; k_1=10.66[39]	—	—	—

* The following notation is used in Table 6 (and also in Tables 7 and 8): a = acetone; Aq = aqueous medium; d = dioxan (20 denotes a 20% dioxan solution); dis = distribution method; e = methods of measurement differing from those enumerated below; gl = potentiometric method using a glass electrode; ins = insoluble; pH = potentiometric titration method; sp = spectrometric method; *T* = thermodynamic constant; $k_1 = \lg k_1$ = logarithm of stability constant; "–" data not presented in given study. The horizontal rows present the following data: method, ionic strength/thermodynamic constant, temperature, medium, stability constants, reference; for example: gl (method; *T* (thermodynamic constant); 25 (temperature); 20d (medium consisting of a 20% dioxan solution); k_1 = 10.49 (logarithm of stability constant); [61] (reference).

Table 7. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	NH_2OH	C_6H_5NHOH	o-CH_3 C_6H_4NHOH
		Benzohydroxamic acid	
Cu^{2+}		gl; *T*; 35; 50d; k_1 = 10.29[110] k_2 = 8.63	—
Fe^{3+}	B; 0.1; 20;Aq; k_1=11.06; k_2 = 9.37; k_3 = 7.40	sp; —; —; —; k_1 = 5.28	—
Fe^{3+}	dis; —; 25; —; k_1 =12.18	—	—
Mn^{3+}	gl; *T*; 35; 50d; k_1 = 5,97[58]; k_2 = 4.52	gl; *T*; 35; 50d; k_1 = 5.90[111]; k_2 = 10.80	gl; *T*; 25; 50d; k_1 = 6.39[110]; k_2 = 5.62
Ni^{3+}	gl; *T*; 35; 50d; k_1 = =7.18[58]; k_2 = 5.14	gl; *T*; 25; 50d; k_1 = 7.01[111]; k_2 = 5.91	—
Ni^{2+}	—	gl; *T*; 25; 50d; k_1 = 7.0[110]; k_2 = 5.91	—
Ni^{2+}	—	dis; 0.1; 25; —; k_1 = 6.10[112]; k_2 = 5.05	—
Th^{4+}	pH; —; 25;—; k_1=9.60[144]; k_2 = 9.21; k_3 = 8.95	dis; 0.1; —; —; k_1 = 10.40[113]; k_2 = 9.90; k_3 = 9.00; k_4 = 8.10	—
UO_2^{2+}	pH; 0.1; 25; —; k_1= =8.72[108]; B_2 = 16.77	pH; 0.1; 30; —; k_1 = 8.77[115]; k_2 = 8.21; B_2 = 16.98	pH; 0.1; 30; —; k_1 = 8.64[115]; gl; *T*; 35; 50d; k_1 = 10.20[117]; k_2 = 8.91
	pH; 0.1; 30; —; k_1 = 9.03[115]; k_2 = 8.91; B_2 = 17.94	gl; *T*; 35; 50d; k_1 = 70,59[116]; k_2 = 7.98	—
UO_2^{2+}	—	gl; *T*; 35; 50d; k_1 = 10.72[117]	—
U^{4+}	pH; —; 25; —; k_1 = = 9,89[114]; k_2 = 8.11; k_3 = 8.32; k_4 = 6.62	—	—
Zr^{4+}	dis; —; 25; —; k_1 = = 12.43[108]; B_2 = 24.08	—	—
La^{3+}	—	pH; 0.1; 25; —; k_1 = 7.28[118]; k_2 = 5.76	—
Pr^{3+}	—	pH; 0.1; 25; —; k_1 = 7.70[118]; k_2 = 6.20	—
Nd^{3+}	—	pH; 0.1; 25; —; k_1 = 7.88[118]; k_2 = 6.30	—
Sm^{3+}	—	pH; 0.1; 25; —; k_1 = 8.28[118]; k_2 = 6.35	—
Eu^{3+}	—	pH; 0.1; 25; —; k_1 = 8.45[118]; k_2 = 6.42	—
Cd^{3+}	—	pH; 0.1; 25; —; k_1 = 8.36[118]; k_2 = 6.32	—
Dy^{3+}	—	pH; 0.1; 25; —; k_1 = 8.60[118]; k_2 = 6.70	—
Er^{3+}	—	pH; 0.1; 25; —; k_1 = 8.75[118]; k_2 = 6.70	—
Yb^{3+}	—	pH; 0.1; 25; —; k_1 = 9.17[118]; k_2 = 6.95	—
Y^{4+}	—	pH; 0.1; 25; —; k_1 = 8.00[118]; k_2 = 6.32	—
Be^{2+}	—	gl; 0,1; 35; 50d; k_1 = 8.65[119]; k_2 = 7.20	—
Cu^{2+}	—	gl; *T*; 35; 50d; k_1 = =10.45[120]; k_2 = 8.90	—
Zn^{2+}	—	gl; *T*; 35; 50d; k_1 = = 8.16[120]; k_2 = 6.70	—
Ni^{2+}	—	gl; *T*; 35; 50d; k_1 = = 7.52[120]; k_2 = 6.01	—
Mn^{2+}	—	gl; *T*; 35; 50d; k_1 = = 6.33[120]; k = 5.99	—
		o-Methylbenozhydroxamic acid	
H^+	—	gl; *T*; 25; 20d; k_1 = 9.12[61]	gl; *T*; 25; 20d; ins[61]
H^+	—	gl; *T*; 35; 20d; k_1 = 9.02[61]	gl; *T*; 55; 20d; ins[61]
H^+	—	gl; *T*; 25; 30d; k_1 = 9.61[61]	gl; *T*; 25; 30d; k_1 = 9.87[61]
H^+	—	gl; *T*; 35; 30d; k_1 = 9.48[61]	gl; *T*; 35; 30d; k_1 = 9.68[61]
H^+	—	gl; *T*; 25; 40d; k_1 = 10.18[61]	gl; *T*; 25; 40d; k_1 = 10.45[61]
H^+	—	gl; *T*; 35; 40d; k_1 = 10.04[61]	gl; *T*; 35; 40d; k_1 = 10.35[61]
H^+	—	gl; *T*; 35; 40d; k_1 = 10.04[61]	gl; *T*; 35; 40d; k_1 = 10.33[61]
H^+	—	pl; *T*; 25; 50d; k_1 = 10.90[61]	gl; *T*; 25; 50d; k_1 = 11.13[61]
H^+	—	gl; *T*; 35; 50d; k_1 = 10.71[61]	gl; *T*; 35; 50d; k_1 = 11.02[61]
H^+	—	gl; *T*; 25; Ad; k_1 = 8.39[26]	—
H^+	—	gl; *T*; 35; Aq; k_1 = 8.32[26]	—
		m-Methylbenzohydroxamic acid	
H^+	—	gl; *T*; 25; Aq; k_1 = 8.58[26]	gl; *T*; 25; 20d; k_1 = 9.61[61]
H^+	—	gl; *T*; 35; Aq; k_1 = 8.53[62]	gl; *T*; 35; 20d; k_1 = 9.34[61]
H^+	—	gl; *T*; 25; 10d; k_1 = 8.91[26]	gl; *T*; 25; 30d; k_1 = 9.99[61]
H^+	—	gl; *T*; 35; 10d; k_1 = 8.88[27]	gl; *T*; 35; 30d; k_1 = 9.83[61]
H^+	—	gl; *T*; 25; 20d; k_1 = 9.29[27]	gl; *T*; 25; 40d; k_1 = 10.56[61]
H^+	—	gl; *T*; 35; 20d; k_1 = 9.26[27]	gl; *T*; 35; 40d; k_1 = 10.49[61]
H^+	—	gl; *T*; 25; 30d; k_1 = 9.76[27]	gl; *T*; 25; 50d; k_1 = 11.22[61]
H^+	—	gl; *T*; 35; 30d; k_1 = 9.74[27]	gl; *T*; 35; 50d; k_1 = 11.18[61]
H^+	—	gl; *T*; 25; 40d; k_1 = 10.30[27]	—
H^+	—	gl; *T*; 35; 40d; k_1 =10.23[27]	—

* For the significance of the notation, see footnote to Table 6.

Table 8. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	C_6H_5NHOH	Ion	C_6H_5NHOH
	o-Methoxybenzohydroxamic acid		*o*-Bromobenzohydroxamic acid
H^+	gl; *T*; 25; 50d; k_1 = 11.09[39]	H^+	gl; *T*; 25; 10d; k_1 = 8.45[39]
H^+	gl; *T*; 35; 50d; k_1 = 11.03[39]	H^+	gl; *T*; 35; 10d; k_1 = 8.34[39]
Cu^{2+}	gl; *T*; 35; 50d; k_1 = 10.35[71]; k_2 = 8.68	H^+	gl; *T*; 25; 20d; k_1 = 8.86[39]
Zn^{2+}	gl; *T*; 35; 50d; k_1 = 8.63[80]; k_2 = 6.65	H^+	gl; *T*; 35; 20d; k_1 = 8.76[39]
Co^{2+}	gl; *T*; 35; 50d; k_1 = 7.96[80]; k_2 = 6.60	H^+	gl; *T*; 25; 30d; k_1 = 9.36[39]
Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.77[80]; k_2 = 5.68	H^+	gl; *T*; 35; 30d; k_1 = 9.26[39]
Mn^{2+}	gl; *T*; 35; 50d; k_1 = 6.80[60]; k_2 = 6.67	H^+	gl; *T*; 35; 40d; k_1 = 9.96[39]
	m-Methoxybenzohydroxamic acid	H^+	gl; *T*; 35; 40d; k_1 = 9.84[39]
H^+	—	H^+	gl; *T*; 25; 45d; k_1 = 10.30[39]
UO_2^{2+}	gl; *T*; 35; 50d; k_1 = 10.59[116]; k_2 = 8.00	H^+	gl; *T*; 35; 45d; k_1 = 10.20[39]
	p-Methoxybenzohydroxamic acid	H^+	gl; *T*; 25; 50d; k_1 = 10.66[39]
H^+	—	H^+	gl; *T*; 35; 50d; k_1 = 10.58[39]
UO_2^{2+}	gl; 0.1; 35; k_1 = 8.68[111]; k_2 = 8.35	Cu^{2+}	gl; *T*; 35; 50d; k_1 = 9.90[60]; k_2 = 7.97
	o-Fluorobenzohydroxamic acid	Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.49[60]; k_2 = 5.87
H^+	gl; *T*; 35; Aq; k_1 = 8.10[26]		*o*-Iodobenzohydroxamic acid
H^+	gl; *T*; 25; 10d; k_1 = 8.51[39]	H^+	gl; *T*; 25; 10d; ins[39]
H^+	gl; *T*; 35; 10d; k_1 = 8.43[39]	H^+	gl; *T*; 35; 10d; ins[39]
H^+	gl; *T*; 25; 20d; k_1 = 8.92[39]	H^+	gl; *T*; 25; 20d; k_1 = 8.92[39]
H^+	gl; *T*; 35; 20d; k_1 = 8.83[39]	H^+	gl; *T*; 35; 20d; k_1 = 8.80[39]
H^+	gl; *T*; 25; 30d; k_1 = 9.42[39]	H^+	gl; *T*; 25; 30d; k_1 = 9.60[39]
H^+	gl; *T*; 35; 30d; k_1 = 9.32[39]	H^+	gl; *T*; 35; 30d; k_1 = 9.30[39]
H^+	gl; *T*; 25; 40d; k_1 = 10.00[39]	H^+	gl; *T*; 25; 40d; k_1 = 10.00[39]
H^+	gl; *T*; 35; 40d; k_1 = 9.82[39]	H^+	gl; *T*; 35; 40d; k_1 = 9.90[39]
H^+	gl; *T*; 25; 45d; k_1 = 10.34[39]	H^+	gl; *T*; 25; 45d; k_1 = 10.35[39]
H^+	gl; *T*; 35; 45d; k_1 = 10.26[39]	H^+	gl; *T*; 35; 45d; k_1 = 10.25[39]
H^+	gl; *T*; 35; 50d; k_1 = 10.74[39]	H^+	gl; *T*; 25; 50d; k_1 = 10.75[39]
H^+	gl; *T*; 35; 50d; k_1 = 10.67[39]	H^+	gl; *T*; 35; 50d; k_1 = 10.63[39]
Cu^{2+}	gl; *T*; 35; 50d; k_1 = 10.03[60]; k_2 = 8.06	Cu^{2+}	gl; *T*; 35; 50d; k_1 = 9.96[60]; k_2 = 8.12
Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.40[60]; k_2 = 5.69	Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.40[60]; k_2 = 6.64
Mn^{2+}	gl; *T*; 35; 50d; k_1 = 6.10[60]; k_2 = 4.68	Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.23[60]; k_2 = 5.30
Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.36[60]; k_2 = 5.54	Mn^{2+}	gl; *T*; 35; 50d; k_1 = 6.20[60]; k_2 = 4.68
	o-Chlorobenzohydroxamic acid		*o*-Nitrobenzohydroxamic acid
H^+	gl; *T*; 25; Aq; k_1 = 8.16[26]	H^+	gl; *T*; 25; 20d; k_1 = 8.87[39]
H^+	gl; *T*; 35; Aq; k_1 = 8.05[26]	H^+	gl; *T*; 35; 20d; k_1 = 8.78[39]
H^+	gl; *T*; 25; 10d; k_1 = 8.43[39]	H^+	gl; *T*; 25; 30d; k_1 = 9.39[39]
H^+	gl; *T*; 35; 10d; k_1 = 8.31[39]	H^+	gl; *T*; 35; 30d; k_1 = 9.29[39]
H^+	gl; *T*; 25; 20d; k_1 = 8.85[39]	H^+	gl; *T*; 25; 40d; k_1 = 10.01[39]
H^+	gl; *T*; 35; 20d; k_1 = 8.79[39]	H^+	gl; *T*; 35; 40d; k_1 = 9.95[39]
H^+	gl; *T*; 25; 30d; k_1 = 9.35[39]	H^+	gl; *T*; 25; 45d; k_1 = 10.37[39]
H^+	gl; *T*; 35; 30d; k_1 = 9.23[39]	H^+	gl; *T*; 35; 45d; k_1 = 10.29[39]
H^+	gl; *T*; 25; 40d; k_1 = 9.93[39]	H^+	gl; *T*; 25; 50d; k_1 = 10.80[39]
H^+	gl; *T*; 35; 40d; k_1 = 9.81[39]	H^+	gl; *T*; 35; 50d; k_1 = 10.69[39]
H^+	gl; *T*; 25; 45d; k_1 = 10.28[39]	Cu^{2+}	gl; *T*; 35; 50d; k_1 = 9.45[60]; k_2 = 7.49[60]
H^+	gl; *T*; 35; 45d; k_1 = 10.14[39]	Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.12[60]; k_2 = 5.44
H^+	gl; *T*; 25; 50d; k_1 = 10.67[39]	Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.07[60]; k_2 = 5.04
H^+	gl; *T*; 35; 50d; k_1 = 10.56[39]	Mn^{2+}	gl; *T*; 25; 50d; k_1 = 5.74[60]; k_2 = 4.38
Cu^{2+}	gl; *T*; 35; 50d; k_1 = 9.96[60]; k_2 = 8.04		3,5-Dinitrobenzohydroxamic acid
Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.52[60]; k_2 = 5.92	H^+	gl; *T*; 35; 50d; k_1 = 9.66[116]
Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.23[60]; k_2 = 5.45	UO_2^{2+}	gl; *T*; 35; 50s; k_1 = 9.75[116]; k_2 = 7.01
Mn^{2+}	gl; *T*; 35; 50d; k_1 = 6.04[60]; k_2 = 4.93		
	2-Furohydroxamic acid		*N*-Butyrohydroxamic acid
H^+	gl; *T*; 25; 50d; k_1 = 10.73[61]	H^+	gl; *T*; 25; 50d; k_1
UO_2^{2+}	gl; *T*; 25; 50d; k_1 = 9.73[61]; k_2 = 8.36	H^+	gl; *T*; 35; 50d; k_1
Cu^{2+}	gl; *T*; 25; 50d; k_1 = 8.95[61]; k_2 = 7.42	Cu^{2+}	gl; *T*; 25; 50d; k_1 = 10.64[121]; k_2 = 8.87
Zn^{2+}	gl; *T*; 25; 50d; k_1 = 6.63[61]; k_2 = 5.81	Cu^{2+}	gl; *T*; 35; 50d; k_1 = 10.75[122]; k_2 = 8.97
Ni^{2+}	gl; *T*; 25; 50d; k_1 = 5.99[61]; k_2 = 5.12	Zn^{2+}	gl; *T*; 25; 50d; k_1 = 7.85[123]; k_2 = 6.40
Mn^{2+}	gl; *T*; 25; 50d; k_1 = 5.13[61]; k_2 = 4.39	Zn^{2+}	gl; *T*; 35; 50d; k_1 = 7.79[135]; k_2 = 6.30
Co^{2+}	gl; *T*; 25; 50d; k_1 = 5.81[61]; k_2 = 4.86	Ni^{2+}	gl; *T*; 25; 50d; k_1 = 7.61[121]; k_2 = 5.69
		Ni^{2+}	gl; *T*; 35; 50d; k_1 = 7.46[122]; k_2 = 5.50
		Mn^{2+}	gl; *T*; 25; 50d; k_1 = 6 23[121]; k_2 = 4.53
		Mn^{2+}	gl; *T*; 35; 50d; k_1 = 6.22[122]; k_2 = 4.46
		UO_2^{2+}	gl; *T*; 35; 50d; k_1 = 11.26[122]; k^2 = 9.51
		UO_2^{2+}	gl; *T*; 35; 50d; k_1 = 10.84[116]; k_2 = 8.19

* For the significance of the notation, see footnote to Table 6.

3. The Mole Fraction of Dioxan

When the mole fraction of dioxan is altered, an appreciable change in the pK_a is observed for all hydroxamic acids. The difference between the pK_a in water (n_2 = 0) and in a 70% dioxan–water mixture (n_2 = 0.33) is more than 4 pK_a units. The plot of the pK_a for hydroxamic acids against dioxan concentration is linear (Fig. 4). The

experimental values of the pK_a for almost all hydroxamic acids deviate from linearity by not more than 0.05 of a pK_a unit (i.e. by approximately 0.5%).

It is of interest to determine the accuracy of the pK_a values obtained by extrapolation to zero dioxan concentration (i.e. for $n_2 = 0$). In the case of hydroxamic acids for which data can be obtained in an aqueous medium it is possible to compare the extrapolated and experimental values. Table 9 shows that the agreement between them is satisfactory.

It is noteworthy that the validity of the extrapolation depends greatly on the availability of pK_a data in the region of low dioxan concentrations. The insolubility of the hydroxamic acid in 10 and 20% dioxan can hinder the extrapolation.

Table 9. Ionisation constants of hydroxamic acids in an aqueous medium.

Hydroxamic acid	Values obtained by extrapolation		Values obtained experimentally[a]		$T_pK = mn_2 + C$ (at 25°C)				$T_pK = mn_2 + C$ (at 35°C)			
	25°	35°	25°	35°	graphical method		least squares method		graphical method		least squares method	
					m	C	m	C	m	C	m	C
Benzo-	8.92	8.80	8.91[b]	8.70	10.05	8.92	10.10	8.92	10.00	8.80	10.10	8.79
N-Phenylbenzo-	8.55	8.45	8.38[c]	8.44	14.50[f]	8.55	14.95	8.46	14.51[d]	8.45	14.95	8.36
N-Phenyl-*o*-methoxybenzo-	8.52	8.46	8.49	8.48	14.85	8.52	14.90	8.52	14.86	8.46	14.90	8.45
N-Phenyl-*o*-methylbenzo-	8.44	8.28	8.39[d]	8.32	14.05	8.44	14.09	8.44	14.60	8.28	14.60	8.28
N-Phenyl-*o*-fluorobenzo-	8.18	8.10	—	8.10	14.80	8.18	14.75	8.18	14.78	8.10	14.75	8.09
N-Phenyl-*o*-chlorobenzo-	8.14	8.03	8.16[e]	8.05	14.70	8.14	14.65	8.12	14.66	8.03	14.65	8.01
N-Phenyl-*o*-bromobenzo-	8.14	8.01	—	—	14.85	8.14	14.80	8.12	14.90	8.01	14.85	8.01
N-Phenyl-*o*-iodobenzo-	8.18	8.09	—	—	14.82	8.18	14.85	8.17	14.85	8.09	14.85	8.07
N-Phenyl-*o*-nitrobenzo-	8.08	8.04	—	—	15.35	8.08	15.35	8.11	15.35	8.04	15.35	8.03
N-Phenyl-*m*-methylbenzo-	8.59	8.56	—	8.53	14.53	8.59	14.20	8.58	13.92	8.56	14.20	8.54

[a] This work.

[b] Priyadarshi[19] quotes pK_c values of 8.75 in 0.1 M KCl and 8.80; the calculated values of T_pK are 8.85 and 8.84 respectively.

[c] Taken from Priyadarshi[19].

[d] Taken from Shukla and Tandon[61].

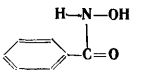
[e] According to the data of Dutta and Seshadari[99], pK_c = 8.08 at I = 0.1 M and 30°C; the calculated value is T_pK = 8.19.

[f] According to Dutta and Seshadari[99], pK_c = 7.60 at I = 0.1 M and 30°C; the calculated value is T_pK = 7.71.

4. Thermodynamic Functions

The pK_a values can be determined to within 0.02–0.03, whence the error of the determination of ΔF° is estimated as 0.03–0.04 kcal. The temperature coefficient method, normally employed for the calculation of ΔH°, can lead to a large error, because (1) the enthalpy of ionisation of acids is low and (2) the pK_a values have not been determined at many temperatures, which necessitates a more accurate graphical method for their estimation[50]. Eqn.(9a) shows that an error of 0.01 of a pK_a unit leads to an error in ΔH° of 0.42 kcal; the error in the determination of pK_a depends on the mutual cancelling or addition of errors in the pK_a values determined at two temperatures. Owing to the inherent deficiencies of the method, it is impossible to observe any definite tendencies in the variation of ΔH° as the medium is altered. This is illustrated by the data in Table 10 for benzohydroxamic acid (columns 4 and 5). It follows from the foregoing that ΔH° is best determined with the aid of the more accurate calorimetric method.

Table 10. The pK_a values for benzohydroxamic acid (BHA) calculated with the aid of thermodynamic functions*



Dioxan concn. vol.%	pK_a 25°	pK_a 35°	ΔpK_a	ΔH°
0	8.91	8.79	0.12	5.1
10	9.17	9.02	0.15	6.3
20	9.45	9.29	0.16	6.7
30	9.79	9.64	0.15	6.3
40	10.14	10.03	0.11	4.6
45	10.41	10.26	0.15	6.3
50	10.69	10.57	0.12	5.1
60	11.34	11.21	0.13	5.5
70	12.25	12.12	0.12	5.1

*Here $\Delta pK_a = pK_a(25^\circ) - pK_a(35^\circ)$; $pK_a(25^\circ) = 10.10n_2 + 8.92$; $r = 0.999$; $pK_a(35^\circ) = 10.10n_2 + 8.79$; $r = 0.999$ (r = correlation coefficient).

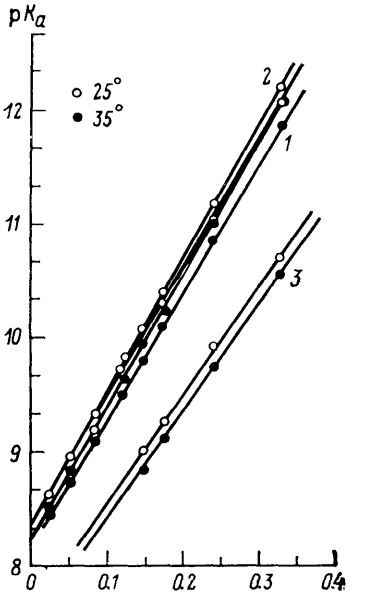


Figure 4. Dependence of pK_a on the mole fraction of dioxan: 1) *N*-phenylbenzohydroxamic acid; 2) *N*-*o*-tolyl-*m*-nitrobenzohydroxamic acid; 3) *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid.

Despite the relatively large errors in the values of ΔH° calculated by the temperature coefficient method, these data are very important, because they permit many important conclusions. At any rate, there is no doubt about the positive values of ΔH° found for all hydroxamic

acids in all solvents. This means that the ionisation reaction is endothermic below 25°C and becomes exothermic only above T_{max}. Furthermore, there is no doubt that the changes in ΔH° when the medium is altered are relatively small and are within the limits of experimental error. This is why the slopes of the linear plots of pK_a against n_2 are the same or almost the same at two temperatures for individual hydroxamic acids (Tables 6–8).

In the light of the foregoing, it would be correct to assume that ΔH° is to a first approximation independent of the medium, at least in the range of dioxan mole fractions 0–0.33.

Table 11. The free energies, enthalpies, and entropies of ionisation of hydroxamic acids*.

Thermodynamic functions	Dioxan concentration, vol.%						
	0	10	20	30	40	45	50
	X=OCH$_3$						
ΔF°	(11.62)	12.60	12.61	13.39	14.14	14.60	15.13
	(11.91)	12.38	12.99	13.68	14.48	15.03	15.55
(ΔH° 2.9) or $-\Delta S^\circ$	(29.1)	30.6	32.4	35.0	37.6	39.1	40.9
	(29.1)	30.6	32.6	34.9	37.4	39.2	40.9
	X=CH$_3$						
ΔF°	(11.52)	—	12.45	13.11	13.89	—	14.87
	(11.68)	12.10	12.78	13.32	14.27	14.67	15.26
(ΔH° 6.7) or $-\Delta S^\circ$	(16.1)	—	19.2	21.4	24.0	—	27.3
	(16.1)	17.4	19.6	21.4	24.5	25.7	27.7
	X=H						
	11.42	12 08	12.60	14.00	—	15.06	—
	11.69	12.32	12.87	13.58	14.38	—	15.67
(ΔH° 4.2) or $-\Delta S^\circ$	24.2	26.4	28.1	30.6	32.8	—	36.4
	24.3	26.3	28.1	30.4	33.0	—	36.5
	X=F						
ΔF°	(11.16)	11.61	12.17	12.85	13.65	14.12	14.65
	(11.40)	11.89	12.46	13.14	13.95	14.46	36.4
(ΔH° 2.8) or $-\Delta S^\circ$	(24.7)	26.2	28.1	30.4	33.1	34.6	36.4
	(24.7)	26.2	28.1	30.3	33.0	34.6	36.5
	X=Cl						
ΔF°	(11.08)	11.50	12.07	12.76	13.55	14.03	14.55
	(11.29)	11.72	12.39	13.01	13.83	14.30	14.89
(ΔH° 4.6) or $-\Delta S^\circ$	(21.6)	23.0	25.0	27.3	29.9	31.5	33.3
	(21.6)	23.0	25.2	27.2	29.9	31.4	33.3
	X=Br						
ΔF°	(11.08)	11.53	12.09	12.77	13 59	14.05	14.54
	(11.29)	11.75	12.35	15.05	13.88	14.38	14.92
(ΔH° 4.6) or $-\Delta S^\circ$	(21.6)	23.1	25.0	27.3	30.0	31.6	33.2
	(21.6)	23.1	25.0	27.3	30.0	31.6	33.4
	X=I						
ΔF°	(11.34)	insoluble	12.17	12.84	13.64	14.12	14.67
	(11.38)	insoluble	12.41	13.11	13.96	14.45	14.98
(ΔH° 4.2) or $-\Delta S^\circ$	(23.2)	insoluble	26.7	28.9	31.6	33.2	35.0
	(23.3)	insoluble	26.6	28.9	31.6	33.2	34.9
	X=NO$_2$						
ΔF°	(11.06)	insoluble	12.10	12.81	13.66	14.15	14.73
	(11.32)	insoluble	12.38	13.10	14.03	14.51	15.07
(ΔH° 3.4) or $-\Delta S^\circ$	(25.8)	insoluble	29.3	31.6	34.5	36.2	38.1
	(25.8)	insoluble	29.2	31.6	34.6	36.1	38.0
	Benzohydroxamic acid						
ΔF°	(12.15)	12.61	12.89	13.36	13.83	14.20	14.58
	12.40	12.72	13.10	13.59	14.14	14.46	14.90
(ΔH° 5.5) or $-\Delta S^\circ$	22.4	23.6	24.9	26.5	28.0	29.3	30.6
	22.5	23.5	24.8	26.3	28.1	29.2	30.5

*Here ΔF° and ΔH° are expressed in kcal mole^{-1} and ΔS° is expressed in cal mole^{-1} K^{-1}; the first value refers to 25°C and the second to 35°C. The values given in brackets have been obtained by extrapolation.

On this hypothesis, the values of ΔH° were calculated for different hydroxamic acids; they are equal to the difference between the intercepts made by the parallel lines on the pK_a axis multiplied by 42.07. The values of ΔH° calculated in this way are listed in Table 10, while the values calculated for each dioxan concentration have been deliberately omitted for reasons stated previously.

The errors in the determination of ΔF° and ΔH° are reflected in the values of ΔS°. Taking into account the considerations described in the preceding paragraphs, the values of ΔS° listed in Table 11 were calculated on the assumption that ΔH° is independent of solvent composition. It must be emphasised that ΔH° should change when the medium is altered. However, in the present study the influence of this factor was not observed and the simplifying assumption was made that ΔH° is independent of medium composition.

The usual tendency towards an increase of ΔS° with increasing content of dioxan in the solvent was noted. This tendency appears to be reliable and is observed also in the calculation of ΔS° from calorimetric values of ΔH°. If the acid ionises in two media—in water and in dioxan–water mixtures—the equations can be formulated as follows:

$$HA\,(aq) \rightleftarrows H^+\,(aq) + A^-\,(aq),$$
$$\Delta F^0\,(aq) = 2.303RT\,p K_a\,(aq). \qquad (15)$$

For mixed media, we have

$$HA \rightleftarrows H^+ + A^-,$$
$$\Delta F^0 = 2.303RT\,p K_a. \qquad (16)$$

Hence we have for the transfer reaction

$$HA + H^+\,(aq) + A^-\,(aq) \rightleftarrows HA\,(aq) + H^+ + A^-,$$
$$\Delta F^0 - \Delta F^0\,(aq) = 2.303RT\,(p K_a - p K_a\,(aq)) = 2.303RT\Delta p K_a. \qquad (17)$$

Thus, as shown above, the free energy ΔF° of the transfer reaction is proportional to the difference between the pK_a values in the aqueous and aqueous dioxan media. Hence it is readily seen that, since ΔH° is independent of the medium and is consquently zero for the transfer reaction, the changes in ΔF° are due to the changes in ΔS°. This can be illustrated in relation to benzohydroxamic acid for which ΔF°(aq) = 12.15 kcal mole^{-1} and $\Delta F^\circ(n_2 = 0.174)$ = 14.58 kcal mole^{-1}. Thus the transfer reaction entails a change in ΔF° by 2.43 kcal mole^{-1} due to the change in ΔS by 30.6 – 22.4 = –8.2 cal mole^{-1} K^{-1}.

VI. METAL–LIGAND STABILITY CONSTANTS

The stepwise formation of the hydroxamic acid complex (a 1 : 2 complex) can be represented as follows:

$$M^{n+} + HA \rightleftarrows MA^{(n-1)+} + H^+, \qquad (18)$$
$$MA^{(n-1)+} + HA \rightleftarrows MA_2^{(n-2)+} + H^+. \qquad (19)$$

The corresponding stability constants are defined in the following way:

$$k_1 = \frac{\{MA^{(n-1)+}\}}{\{M^{n+}\}\{A^-\}} = \frac{[MA^{(n-1)+}]}{[M^{n+}]\cdot[A^-]} \cdot \frac{Y_{MA}}{Y_{M+}\cdot Y_{A^-}} = k_1 \cdot \frac{Y_{MA}}{Y_M \cdot Y_A}; \qquad (20)$$

$$k_2 = \frac{\{MA_2^{(n-2)+}\}}{\{MA^{(n-1)+}\}\cdot\{A^-\}} = \frac{[MA_2^{(n-2)+}]}{[MA^{(n-1)+}][A^-]} \cdot \frac{Y_{MA_2}}{Y_{MA^+}Y_{A^-}} = k_2 \frac{Y_{MA_2}}{Y_{MA^+}Y_{A^-}}, \qquad (21)$$

where the symbols in curved brackets represent activities, Y are activity coefficients, and the symbols in square brackets are concentrations. The expressions for the constants K_1 and K_2 can be formulated thus:

$$\lg K_1 = \lg k_1 + 4\lg\frac{1}{Y_\pm}, \qquad (22)$$

$$\lg K_2 = \lg k_2 + 2\lg\frac{1}{Y_\pm}. \qquad (23)$$

where K_1 and K_2 are the thermodynamic stability constants and k_1 and k_2 are the molar contributions to the reversible reactions (18) and (19) respectively. Eqns. (22) and (23) can be obtained on the assumption that the activity coefficients of neutral species are unity and those of univalent negative and positive ions are approximately equal to the mean activity coefficient $Y_\pm$ of hydrochloric acid. In the limiting case where the Debye–Hückel law is applicable, we have $\lg Y_M^{2+} = 4 \lg Y_\pm$ (1 : 1).

In the study of equilibrium solutions it is customary to carry out measurements of concentration coefficients in media containing supporting salts at constant and high concentrations, which ensures a fixed ionic strength of the solution, so that the activity coefficients remain constant. Thus the concentration coefficients can be regarded as conventional constants applicable to solutions with the same supporting salt compositions as those used in the measurement of these constants.

There are three ways of obtaining experimental data for the calculation of thermodynamic constants: (1) experiments are performed in solutions which are sufficiently dilute for the concentrations to be set equal to the activities; (2) experiments are performed at different ionic strengths and the concentration coefficients are extrapolated to zero ionic strength; (3) corrections are applied for activity coefficients on the basis of the Debye–Hückel theory.

VII. DETERMINATION OF STABILITY CONSTANTS

Hydroxamic acids are weak acids and, when a complex is formed, there is competition between protons and metal ions for the ligand; the stability constant can be obtained by measuring the pH. pH measurements for the determination of stability constants are carried out by one or both methods presented below: (a) pH is measured as a function of ligand concentration; (b) pH is measured as a function of the amount of added acid (or base) at a constant metal ion and ligand concentration. In the second case the concentration of the free ligand, in excess relative to the amount required for complex formation, can be varied within wider limits than in the first case.

The stability constants can be calculated by the Bjerrum method[51] as developed by Calvin and Wilson[52]. The Bjerrum method has been examined theoretically by several workers[53–56].

The formation function $\bar{n}$, equal to the average number of coordinated groups per metal ion, is given by

$$\bar{n} = \frac{[MA] + 2[MA_2] + \ldots + N[MA_N]}{[M] + [MA] + [MA_2] + \ldots + [MA_N]} . \quad (24)$$

Using the expressions for the stability constant, it can be shown that $\bar{n}$ is a function of the free ligand concentration.

The values of $\bar{n}$ can be calculated in two ways. In the first procedure two titrations are carried out: initially, at a high concentration of added electrolyte the ligand is titrated with a standard solution of alkali, the pH change after each successive addition of alkali is noted, and the corresponding curve is plotted. One then titrates with alkali a mixture of the metal ions and the ligand in the presence of the same electrolyte and a plot is again constructed. The second titration curve lies significantly below the curve for the ligand alone; the decrease in pH shows that complex formation leads to neutralisation of the solution. The distance between the two titration curves in the horizontal direction yields the total number of ligand linkages and its division by the total concentration of metal ions makes it possible to obtain $\bar{n}$.

In the second case the free ligand concentration is calculated from the principle of electroneutrality. Substitution of this concentration in Eqn. (5) gives $\bar{n}$:

$$\bar{n} = \frac{A^0 - [A^-]}{M^0} , \quad (25)$$

where $[A^-] = 1 + [H^+]/k_1 + [H^+]^2/k_1k_2 + \ldots + [H^+]^n/k_1k_2 \ldots k_n$ and A^0 and M^0 are the total ligand and metal ion concentrations respectively.

The free ligand concentration can be determined as follows: the concentration of undissociated acid is equal to the difference between the total acid concentration ions and the concentration of acid which has reacted and dissociated:

$$[HA] = A^0 - C_{OH} - [H^+] - [OH^-]. \quad (26)$$

We have from Eqn. (1)

$$K_a = \frac{1}{q_H} \cdot Y_\pm^2,$$

where

$$q_H = [HA]/[H^+]\,[A^-]$$

or

$$\lg q_H = \mathrm{p}K_a - 2 \lg \frac{1}{Y_\pm} .$$

On substituting the expression for [HA] in Eqn. (26), we obtain

$$[A^-] = \frac{A^0 - C_{OH} - [H^+] - [OH^-]}{q_H [H^+]} . \quad (27)$$

The stability constants are calculated for different values of $\bar{n}$ and the corresponding values of $[A^-]$ by solving a system of N equations. Block and McIntyre[57] obtained equations for different values of N; thus the expressions for $N = 2$ are

$$k_1 = \frac{\bar{n}\,J_2' - \bar{n}J_2}{J_1\,J_2' - J_2'\,J_2} , \quad (28)$$

$$k_2 = \frac{\bar{n}'J_1 - \bar{n}J_1'}{\bar{n}J_2 - \bar{n}'J_2} \quad (29)$$

where

$$J_n = (n - \bar{n})[A^-]^n, \quad (30)$$

$$J_n' = (n' - \bar{n}')[A^-]'^n . \quad (31)$$

This method has been used by the majority of workers who have investigated the metal complexes of hydroxamic acids[58–62].

If $K_1 \gg K_2$, it is possible to obtain a plot of $\bar{n}$ against $[A^-]$ and find from the latter the stability constants at half-integral values of $\bar{n}$:[63]

$$\bar{n} = 1/2,\ k_1 = 1/[A^-]; \quad (32)$$

$$\bar{n} = 3/2,\ k_2 = 1/[A^-]; \quad (33)$$

$$\bar{n} = 1,\ \sqrt{k_1k_2} = k = 1/[A^-]. \quad (34)$$

Other methods for the calculation of the constants have been summarised by Beck[53]. The most important is the method according to which the relation between $\bar{n}$ and $[A^-]$ is transformed in such a way that the plot of $\bar{n}/(1 - \bar{n})[A^-]$ against $(2 - \bar{n})[A^-]/(1 - \bar{n})$ is represented by a straight line which makes an intercept on the ordinate axis equal to k_1 and which has a slope equal to k_1k_2.

Agrawal et al.[64] developed a computer program based on the method of least squares and using all experimental data.

VIII. LINEAR FREE ENERGY RELATIONS

The standard free energy of reaction ΔF° can be represented as a function of a large number of independent variables w, x, y, and z, whereupon ΔF° is described by the equation

$$d(\Delta F^0) = (\partial \Delta F^0/\partial w)_{x,y,z}\, dw + (\partial \Delta F^0/\partial x)_{w,y,z}\, dx + \ldots \quad (35)$$

An expression whereby the standard free energies of related reactions can be compared has been obtained from Eqn. (35) by regarding $d(\Delta F^\circ)$ as a function of independent variables. Wells[65] used this approximation to derive empirical equations of the Hammett type. Equations involving the metal complex stabilisation factor have also been obtained[66] by regarding the free energy of formation of the complex as a function of a single variable. However, Nieboer and McBryde[67] believe that the standard free energy of formation of metal complexes in a series of reactions is a function of two variables; their reasoning is examined below.

We assume that only a 1 : 1 complex is formed and the following equations are formulated:

$$M + A \overset{K_{MA}}{\rightleftarrows} MA \ , \quad (36)$$

$$M_s + A_o \overset{K_{M_sA_o}}{\rightleftarrows} M_sA_o \ . \quad (37)$$

$$\Phi = \lg (K_{MA}/K_{M_sA_o}), \quad (38)$$

$$M_s + A \overset{K_{M_sA}}{\rightleftarrows} M_sA \ , \quad (39)$$

$$\sigma = \lg (K_{M_sA}/K_{M_sA_o}) \ , \quad (40)$$

$$M + A_o \overset{K_{MA_o}}{\rightleftarrows} MA_o \ , \quad (41)$$

$$\theta = \lg (K_{MA}/K_{M_sA_o}) \ . \quad (42)$$

The subscripts s and o refer respectively to the metal and the ligand chosen as reference standards. Furthermore, it is readily seen that σ and θ are logarithms of the equilibrium constants for the following substitution reactions:

$$M_sA_o + A \rightleftarrows M_sA + A_o \ , \quad (43)$$

$$\sigma = \lg K_A \ , \quad (44)$$

$$M_sA_o + M \rightleftarrows MA_o + M_s \ , \quad (45)$$

$$\theta = \lg K_M \ . \quad (46)$$

We assume that Φ is a function of the dependent variables σ and θ and Eqns. (39) and (41) therefore represent series of reactions to be compared. A series of ligands react with the standard or reference metal M_S via reaction (39). It is next assumed that the parameter σ depends only on the nature of the ligand, which is equivalent to a ligand-dependent contribution to Φ. Eqn. (39) now describes a ligand-dependent standard reaction series and Eqn. (41) represents a metal-dependent standard reaction series. In Eqn. (41) the only variable factor is the metal ion M, and A_O is the standard or reference ligand. The assumption is made that the parameter θ depends only on the nature of the metal ion and that a metal-dependent contribution to Φ corresponds to it. Having made these assumptions, we shall subject them to a critical examination.

The changes in Φ caused by the increase in $d\sigma$ and $d\theta$ can be expressed in a differential form by the formula

$$d\Phi = (\partial\Phi/\partial\sigma)_\theta\, d\sigma + (\partial\Phi/\partial\theta)_\sigma\, d\theta \ . \quad (47)$$

We denote $(\partial\Phi/\partial\sigma)_\theta$ by B and $(\partial\Phi/\partial\theta)_\sigma$ by C. Since $K_{M_SA_O}$ does not vary for any reaction series, it follows that $d \lg K_{M_SA_O} = 0$. Consequently, $d\Phi = d \lg K_{MA}$, $d\sigma = d \lg K_{M_SA}$, and $d\theta = d \lg K_{MA_O}$ and the quantities B and C can be expressed as follows:

$$B = (\lg K_{MA}/\lg K_{M_sA}), \quad (48)$$

$$C = (\lg K_{MA}/\lg K_{MA_o}). \quad (49)$$

MA can be obtained from M_S and A_O in two ways:

$$(1)\ M_sA_o \rightarrow MA_o \rightarrow MA \ ;$$
$$(2)\ M_sA_o \rightarrow M_sA \rightarrow MA \ .$$

In the first procedure integration of Eqn. (47) leads to the expression

$$\Phi = B\sigma + \theta \quad (50)$$

and in the second we have

$$\Phi = \sigma + C\theta. \quad (51)$$

In order that Φ is a function of σ only, it must not depend on θ or it must depend on the ligand alone. Putting

$$\Phi' = \lg (K_{MA}/K_{MA_o}), \quad (52)$$

we obtain

$$\Phi' = \Phi - \theta = B\sigma. \quad (53)$$

When $M_S = H^+$, Eqn. (53) is a Hammett type equation, although the quantity σ involved in it is not equal to the Hammett factor. If Φ, σ, and θ are expressed in terms of the corresponding equilibrium constants, then Eqn. (53) can be written in the following form:

$$\lg K_{MA} = B \lg K_{M_sA} + [\lg K_{MA_o} - B \lg K_{M_sA_o}]. \quad (54)$$

Eqns. (53) and (54) describe the substitution effect. With their aid, it is possible to compare the stabilities of the complexes of two metals (M and M_S) for a series of related ligands A. The series of ligands A (hydroxamic acids) usually consists of the initial reagent and its substituted derivatives. Hence σ is a measure of the effect of substitution of the ligand in the ligand-dependent standard reaction series and Φ' is a measure of this effect in the test reaction.

In order that Φ is a function of θ alone, it must depend solely on the metal ion. Defining a new variable Φ'', i.e.

$$\Phi'' = \lg (K_{MA}/K_{M_sA}), \quad (55)$$

we obtain

$$\Phi'' = \Phi - \sigma = C\theta. \quad (56)$$

Substitution of the corresponding values in Eqn. (56) leads to the expression

$$\lg K_{MA} = C \lg K_{MA_o} + [\lg K_{M_sA} - C \lg K_{M_sA_o}]. \quad (57)$$

With the aid of Eqns. (56) and (57), it is possible to compare the stabilities of the complexes of two ligands (A and A_O) with a series of metal ions M and to describe a quasi-substitution effect. The parameters Φ and Φ'' are a measure of the quasi-substitution effect in the metal-dependent standard reaction series and in the test reaction respectively.

The results of the tests of Eqns. (54) and (57) (Fig. 5) with the aid of data for the reactions of *ortho*-substituted *N*-phenylbenzohydroxamic acids with certain metal ions are summarised in Table 12. The existence of two fundamentally different types of behaviour has been noted[67]. In the first case there is a simultaneous dependence of B on the metal ions and of C on the ligands, and in the second case all the values of B and C are unity regardless of the nature of the metal ion and the ligand. The cause of these differences is still obscure.

Table 12. The values of B for *N*-phenylbenzohydroxamic acids.

Ion	B	r	C. I., %	$-\theta$ *
H^+	1.00	1.00	100	0.00
Cu^{2+}	0.90	1.28	99.3	0.67
Zn^{2+}	0.62	0.99	99.9	3.25
Ni^{2+}	0.56	1.11	99.2	3.76

* Here $\theta = \lg K_{MA} - pK_0$; $M_S = H^+$; A_0 = phenylbenzohydroxamic acid.

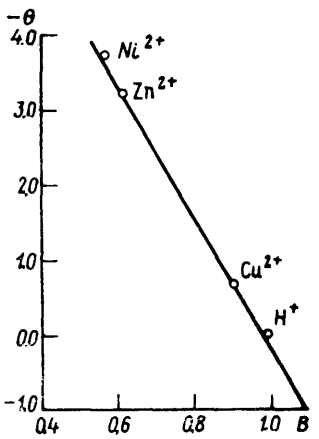


Figure 5. Test of the accuracy for a series of *N*-phenylbenzohydroxamic acids.

IX. THE SOLVENT EFFECT

The stability constants of metal complexes increase with increasing dioxan content. Since the dielectric constant of the medium decreases under these conditions, the ion–ion interaction between the metal ion and the oxygen anion of the ligand intensifies to a greater extent than the ion–dipole interaction between the metal ion and solvent molecules. The plot of $\lg k_1$ against the mole fraction of dioxan for copper(II), zinc(II), nickel(II), and manganese(II) is linear (Fig. 6). According to Irving and Rossotti[68], the dependence of the stability constants of metal complexes of hydroxamic acids in 60% dioxan solution on the stability constants of the metal ions at other dioxan concentrations (50 and 70%) is also linear and the slope of the straight lines is unity (Fig. 6). The same type of dependence has been found in many instances by Van Uitert et al.[69]

X. CORRELATION BETWEEN IONISATION CONSTANTS AND THE STABILITY OF THE COMPLEX

Approximately linear relations between the logarithms of the stability constants of a series of complexes of the same metal ion with a series of closely related ligands have been noted in several studies[68-74]. On this basis, it was expected that more basic ligands should give rise to more stable complexes.

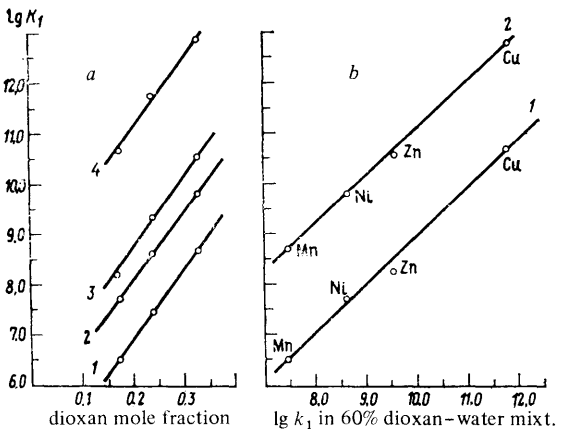


Figure 6. *a*) Dependence of $\lg K_1$ on dioxan concentration [1) Mn^{2+}; 2) Ni^{2+}; 3) Zn^{2+}; 4) Cu^{2+}]; *b*) dependence of $\lg K_1$ in a 60% dioxan–water mixture on $\lg K_1$ in 50% (line *1*) and 70% (line *2*) dioxan–water mixtures (*N*-*m*-tolyl-*m*-methylbenzohydroxamic acid).

If the hydrogen ion is adopted as the standard ion, Eqns. (54) and (57) can be formulated as follows:

$$\lg K_{MA} = B_p K + [\lg K_{MA} - B\, pK_0], \quad (58)$$

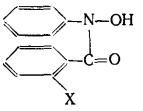
$$\lg K_{MA} = C \lg K_{MA_0} + [pK - C_p K_0]. \quad (59)$$

Eqn. (58) refers to those cases where the stability constants of complexes of one metal ion with a series of ligands substituted in the same position are considered. Eqn. (59) makes it possible to compare the stability constants of complexes of two closely related ligands with a series of metal ions. It has been shown[75] that there is a linear relation between the stability constants and the pK values for copper complexes of *N*-arylhydroxamic acids:

$$\lg K_1 = 0{,}73\, pK_a + \text{const}. \quad (60)$$

The slope of this straight line is less than unity, which shows that copper(II) has the properties of a π-donor. Agrawal and Tandon[63] showed that the slope of this straight line depends on the nature of the metal ion.

However, in the case of *ortho*-substituted hydroxamic acids (VII) a linear relation between pK_a and $\lg K_1$ was not observed for any metal ion:



(VII)

X=H, CH_3, CH_3O, F, Cl, Br, I, or NO_2 .

Fig. 7 presents typical curves for Cu^{2+}, Zn^{2+}, Ni^{2+}, and Mn^{2+}; evidently the deviations from the straight line are considerable for at least two ligands. The absence of a linear relation can probably be caused by the steric hindrance arising owing to the presence of *ortho*-substituents; electronic effects can also play a role. Such deviations from linearity, due to the perturbing influence of steric hindrance, have been demonstrated for certain types of ligands[68].

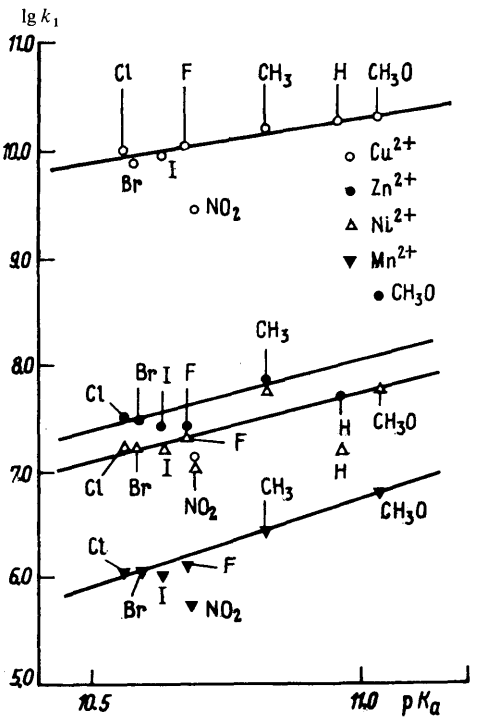


Figure 7. Dependence of $\lg K_1$ on pK_a for *ortho*-substituted *N*-phenylbenzohydroxamic acid derivatives.

The absence of a correlation between pK_a and $\lg K_1$ has been discussed from the standpoint of thermodynamics[73]. The authors established that the linearity of the relation between $\lg K_H(pK_a)$ and $\lg K_{MA}(\lg K_1)$ is not a general property owing to the differences between the ways in which π-donor (or π-acceptor) properties affect pK_a and $\lg K_1$. For beryllium complexes of *para*-substituted hydroxamic acids, the system of linear equations is of the form[76]

$$\lg K_1 = 1.44\, pK_a - 6.99. \qquad (60a)$$

Eqn. (60) has not so far been tested against the stability constants of hydroxamic acids.

XI. THE SEQUENCE OF STABILITY CONSTANTS

The sequence of the stabilities of the copper(II), zinc(II), nickel(II), and manganese(II) complexes of hydroxamic acids can be accounted for by inspecting the ionic radii or the electronegativities determined in terms of the ionisation potentials and ligand field stabilisation energies. The usual stability series for the bivalent ions of 3*d* transition metals, quoted by Maley and Mellor[77] and later by Irving and Williams[78], is

$$Mn^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}.$$

The stability constants of hydroxamic acid complexes can be arranged in the sequence:

$$Mn^{+2} < Ni^{+2} < Zn^{2+} < Cu^{2+}.$$

The dependence of $\lg K_1$ on the atomic number, ΔF°, and ΔH° follows from the above sequence.

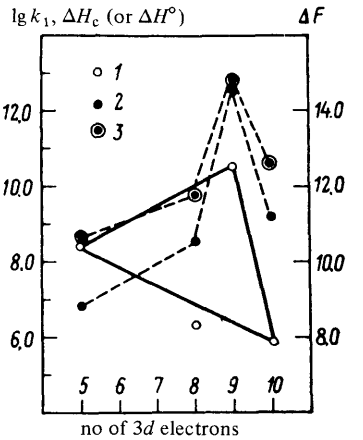


Figure 8. The values of ΔH_C (*1*), ΔF° (*2*), and $\lg K_1$ (*3*) (for *N*-*m*-tolyl-*p*-methylbenzohydroxamic acid) at 25°C in 70% dioxan–water mixtures.

The sequence of the stability constants is the same also in the case of $\lg K_1$ ($\lg K_2$ or $\lg \beta_2$) for hydroxamic acids and bivalent ions of 3*d* transition metals (Fig. 8). Beyond manganese, the constants increase with increasing atomic number, reaching a maximum for $3d^9$ [copper(II)] and then decrease for $3d^{10}$ [zinc(II)]:

$$Mn\,(II) < Ni\,(II) < Cu\,(II) > Zn\,(II)\ .$$

One may note the unusually high stabilities for $3d^9$ [copper(II)], while the stability of $3d^8$ [nickel(II)] is minimal. There is also a correction for the crystal field, which is a maximum for copper and falls rapidly to zero for zinc[79,80]. It is also seen that the stability constants

for zinc(II) are higher than for nickel(II), while those for copper(II) are appreciably higher.

The relative decrease in the stability of nickel(II) chelates may be due to steric hindrance, which prevents the formation of a square planar structure. The same picture was observed also for nickel chelates with other ligands[81,82]. The hydrolysis constants for zinc are lower than those for nickel, which implies a greater affinity of the Zn^{2+} ion for OH groups. Hydroxamic acids containing the –C(O)–N–OH functional group resemble acids with an OH group, because both these groups have a negatively charged oxygen atom. One may expect that, on formation of a bond, the smaller ion (i.e. Zn^{2+}) [83] would give rise to more stable complexes than Ni^{2+}, which is indeed the case.

XII. IONIC CHARGES AND RADII

The stability constants of the metal complexes of hydroxamic acids available at present as a rule increase with increasing ionic potential (i.e. with the charge/radius ratio).

It has been shown[42] that the energy of solution of gaseous ions should be expressed by Eqn. (13) (if it is assumed that they are spherical). Since K is directly related to energy, presumably the ratio of the spherical charge to the radius or to the reciprocal of the radius or the ratio of the charge to the radius should be directly proportional to the stability of the metal chelates with the same ligand. The plot of the stabilities of various metal chelates ($\lg K_1$) against the reciprocals of the ionic radii is linear for all known hydroxamic acids.

XIII. THE IONISATION POTENTIAL AND ELECTRONEGATIVITY

A number of attempts have been made to correlate the stability constants of a series of hydroxamic acid complexes and the ionisation potentials of metals[58–60,63,84,85]. Approximately linear relations have been observed. Other parameters have also been proposed in the literature for correlations. For example, linear relations between $\lg K_1$ and the electronegativities of metal ions X_M (on the Pauling scale) were obtained for the first time by Fernelius and coworkers[86–88] for a series of complexes of a large number of cations with the usual ligands. Normally, individual linear correlations were obtained for univalent, bivalent, and tervalent central metal ions. However, Van Uitert and Fernelius[87] found that a single correlation can be obtained for benzoylmethanates by plotting $\lg K_1$ against the product of X_M and a quantity which was initially referred to as the bond strength and was later identified as the ionic charge z.

In order to characterise individual metal ions, Craig and Nyholm[89] proposed the parameter $R = \Sigma I_M(r_M + r_L)/z^2$, where ΣI_M is the sum of the ionisation energies of the metals up to a charge z and r_M and r_L are the ionic radii of the metal and the ligand respectively. A numerical correlation index Q has been introduced[90]:

$$Q = (a\delta z X_M + b X_M^2)/(a + b) , \qquad (61)$$

where X_M is the Albert electronegativity[57] of the metal ion, a and b are integral weight coefficients (0, 1, 2, ...), and δ is a parameter calculated with the aid of Slater atomic shielding constants[92] and designed to compensate the marked increase of the electronegativities of certain elements due to the small size of their atoms or the marked covalent nature of their bonds. For certain metal ions, the set of parameters a, b, and δ depends on the type of ligand with which the metal forms a complex. Nieborer and McBryde[90] obtained linear relations between $\lg K_1$ and Q for complexes of different metals with more than thirty ligands.

Fig. 9 presents plots of the stability constants of metal complexes of hydroxamic acids against the ionisation potentials of the metal ions. Evidently straight lines were obtained in all cases. The points corresponding to the copper(II) complexes of all the ligands do not fit on these lines and are always above them. The high stability constants of the copper complexes can be accounted for[58–60] by the unusual electronic configuration of the Cu^{2+} ion, for which there is a possibility of additional stabilisation of the complexes due to the tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect. For the Cu^{2+} ion with its d^9 configuration, this distortion is manifested to an appreciable degree.

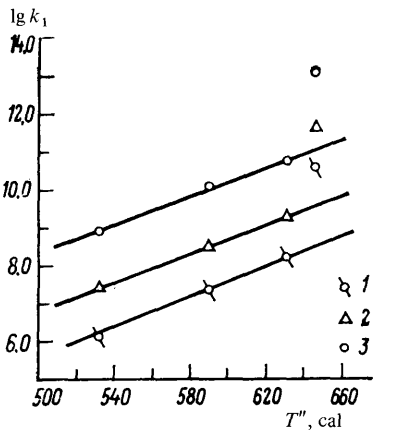


Figure 9. Dependence of $\lg K_1$ (for *N*-*p*-tolyl-*p*-methylbenzohydroxamic acid) on the field ionisation potential I'' in dioxan–water mixtures with different percentages of dioxan: 1) 50; 2) 60; 3) 70.

XIV. THE LIGAND FIELD STABILISATION ENERGY

The stability constants of complexes are related to the free energy change and hence to the temperature-independent heat of reaction:

$$RT \ln K = \Delta F^0 = \Delta H^0 - T\Delta S^0 .$$

These quantities are presented in Fig. 8 and in Tables 13 and 14. The values of $\Delta H_c(\Delta H^\circ)$ for bivalent ions of 3*d* transition metals fit on a curve with a maximum. The latter can be interpreted, as was done above, from the standpoint of ionisation potentials whose curve has a similar shape. The lower line in Fig. 8 represents the same values but with a correction for the orbital stabilisation energy obtained by applying the ligand field theory to the complexes. The curves indicate a constant increase of ΔH_c with increase of the atomic number.

According to the ligand field theory, the thermodynamic properties of metal chelate compounds vary as a function of the inner shells of the transition metal ions and the splitting of the orbitals in the ligand field leads to the stabilisation of the inner electrons compared with the energy which they would have had in the absence of the ligand field[93]. The contraction energy E_r has been determined[94] for a series of transition metals (Mn–Zn) as the heats of the reaction

$$Zn^{2+}_{(g)} + MnA^{2+}_{(nag)} \rightarrow ZnA^{2+}_{(nag)} + Mn^{2+}_{(g)}. \quad (62)$$

E_r can be calculated from the equation

$$E_r = -[\Delta H_H(Zn^{2+}) + \Delta H_c(Zn^{2+})] + [\Delta H_H(Mn^{2+}) + \Delta H_c(Mn^{2+})], \quad (63)$$

where $\Delta H_H(M^{2+})$ is the heat of hydration of the transition metal ion, i.e. the heat of the reaction $M^{2+}_{(g)} = M^{2+}_{(aq)}$, $\Delta H_c(\Delta H^\circ)$ the heat of formation of the complex, and E_r the contraction energy for the series from Mn to Zn ($3d^5$–$3d^{10}$).

Table 13. Free energies, enthalpies, and entropies of formation of complexes of $3d$ transition metal ions and N-m-tolyl-p-methylbenzohydroxamic acid*.

Thermodynamic functions	Dioxan concentration, vol.%								
	50			60			70		
	lg K_1	lg K_2	lg B_2	lg K_1	lg K_2	lg B_2	lg K_1	lg K_2	lg B_2
				Mn^{2+}					
ΔF°	8.87	7.25	16.13	10.17	9.12	19.29	11.81	9.39	21.20
	9.03	7.34	16.37	10.37	9.28	19.65	12.06	2.57	21.63
ΔH°	4.20	4.20	8.40	4.20	2.52	8.40	4.20	2.52	8.40
$-\Delta S^\circ$	15.66	10.16	25.93	20.02	22.14	39.88	25.52	23.04	42.93
	15.69	10.19	25.72	20.02	22.25	36.50	25.50	22.87	42.92
				Ni^{2+}					
ΔF°	10.52	9.02	19.59	11.74	9.15	20.89	13.38	10.78	24.16
	10.74	9.30	20.04	12.01	9.37	21.38	13.69	11.06	24.74
ΔH°	4.20	2.52	6.31	4.20	2.52	6.31	4.20	2.52	6.31
$-\Delta S^\circ$	21.20	25.36	44.54	25.29	22.20	48.90	30.79	27.70	53.16
	21.22	21.99	44.54	25.34	22.22	48.89	30.78	27.70	59.82
				Cu^{2+}					
ΔF°	14.56	12.08	26.70	16.01	15.45	29.56	17.54	15.08	32.62
	14.92	12.26	27.19	16.42	13.67	30.09	16.59	15.37	31.96
ΔH°	3.79	6.72	10.51	3.79	6.72	10.52	3.79	6.72	10.51
$-\Delta S^\circ$	36.12	17.94	54.30	40.99	22.57	63.76	46.18	28.04	74.12
	35.03	17.94	54.11	40.97	22.55	63.51	41.52	28.06	69.58
				Zn^{2+}					
ΔF°	11.19	9.17	20.37	12.71	10.69	23.40	14.34	12.33	26.67
	11.51	9.34	20.85	13.08	10.91	23.99	14.77	12.60	27.37
ΔH°	1.68	4.20	5.89	1.68	4.20	5.89	1.68	4.20	5.89
$-\Delta S^\circ$	31.86	20.02	48.57	36.99	21.77	58.72	42.46	27.27	69.70
	31.89	16.67	48.53	26.98	21.77	58.72	42.46	27.25	69.68

*Here ΔF° and ΔH° are expressed in kcal mole^{-1} and ΔS° is expressed in cal mole^{-1} K^{-1}; the first value refers to 25 °C and the second to 35 °C.

The ligand field stabilisation energy δH for complexes of $3d^n$ transition metal ions M^{2+} can be obtained knowing the enthalpy if one assumes that all the complexes of metal ions ranging from Mn^{2+} to Zn^{2+} have the same symmetry, namely octahedral or tetrahedral[94]. Then

$$\delta H_i(M^{2+}) = \Delta H_c(M^{2+}) - \left(\frac{n-5}{5}\right)E_r - \Delta H_c(Mn^{2+}) - \Delta H_H(M^{2+}),$$

where n is the number of d electrons.

A plot of $\Delta H_H + \Delta H_c$ against the number of $3d$ electrons in the metal ion for complexes of p-methyl-N-m-tolylbenzohydroxamic acid is presented in Fig. 9. The hydration energies ΔH_H were taken from George and McClure[94]. The stabilisation energy of the complexes δH was calculated as the difference between the true value and the corresponding value obtained from the interpolation curve. The stabilisation energy thus increases from $3d^5$ to $3d^8$ and falls for the $3d^{10}$ ion, following the sequence of increasing field stabilisation energy—it is higher for Ni^{2+} than for Cu^{2+}.[95]

Table 14. The ligand field stabilisation energies for bivalent metal ions (N-m-tolyl-p-methylbenzohydroxamic acid)*.

Transition metal	$3d^n$	ΔH_H	ΔH_c	$\Delta H_H + \Delta H_c$	$(n-5)/5$	δH
Mn(II)	$3d^5$	654.0	8.40	662.40	0	
Ni(II)	$3d^8$	716.0	6.31	722.31	26.75	33.30
Cu(II)	$3d^9$	716.9	10.51	727.41	35.67	29.25
Zn(II)	$3d^{10}$	701.1	5.89	706.99	—	

*The contraction energy for the series from Mn to Zn is E_r(Mn–Zn) = 44.59.

Since the ability of the metal ion to interact with the ligand is proportional to the number of vacant sites, the ratio of the successive stability constants is to some extent determined by statistical factors[51]. For anionic ligands, the Coulombic attraction to Mn^{2+} is greater than for MA^+. The quantity lgK_1 – lgK_2 itself is usually positive[96]. The study of hydroxamic acid complexes established that the difference lgK_1 – lgK_2 is greater than zero for all the systems and lies in the range from 1 to 2.5 (in terms of logarithmic units).

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