Contribution from the Istituto di Chimica Generale
Università di Parma, I - 43100 Parma, Italy

The Protonation Constant of Oxamic Acid in Aqueous Solution and in Water-Tetrahydrofuran Mixture, at Different Temperatures and Ionic Strengths

A. Braibanti, E. Leporati, and F. Dallavalle

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The protonation constant of oxamic acid, H_2N—CO—COOH, was determined potentiometrically and resulted to be log $K_1 = 1.836$ in 0.1 M *KCl at 25.0 °C. No protonation or deprotonation is detectable in alkaline media. The calculation of the protonation constant has been carried out by a computer program based on the Sillén method. The estimated standard deviation of log K_1 has been determined from the statistical analysis of the distribution diagram of $\Delta p[H] = p[H_o] - p[H_c]$ against $p[H_o]$. This method can detect systematic errors affecting the data.*

Effects of (i) ionic strength (up to 2 M*), (ii) temperature (in the range $5 \div 30$ °C), (iii) solvent (in the mixture H_2O (40%)-tetrahydrofuran(THF) (60%)) on the equilibrium have been investigated. The effects of ionic strength and temperature are those typical for monocarboxylic acids. The protonation constant increases up to log $K_1 = 2.897$ in the mixture H_2O—THF. This variation is compared with the variations of log K_1 for other acids in water and in the same mixture; the possible influence of the dielectric constant of the solvent is considered. The coordinating power of oxamic acid toward divalent ions is very low and it is not enhanced by the changing of solvent.*

Introduction

The oxamic acid, H_2N—CO—COOH, presents a chain of atoms which might form pentatomic chelate rings whith N,O as donors like as those of hydrazine carboxilic acid[1] and glycine[2] provided that the amidic $-NH_2$ is able to cordinate to metallic atoms or, more likely, with O,O as donors like as those of oxalic acid. The protonation equilibrium of this compound has now been determined both in aqueous solutions and in a H_2O—THF mixture (THF = tetrahydrofuran). THF has been chosen as mixing solvent because it seems to have primarily an action deriving from its low dielectric constant and only in part from specific interactions with dissolved species.[3,4] The formation constants of this compound with divalent metals could not be determined because the titration curves do not change appreciably when divalent cations are added both in aqueous and mixed solvents.

Experimental Section

Reactants. Oxamic acid of reagent grade purity was converted into its potassium salt; this was recrystallized from water. Thiocarbohydrazide was prepared as described in a preceding paper.[5] All the remaining substances used were of reagent grade purity. Bidistilled boiled water has been used throughout.

Solutions. A stock solution of hydrogen chloride was prepared and its concentration (0.4903 *M*) determined titrimetrically both with potassium hydrogencarbonate and 2-amino-2-(hydroxymethyl)-1,3-propandiol. A stock solution of KOH (0.4425 *M*) was prepared by diluting concentrated KOH (BDH production) by CO_2-free water; the solution was stored in neutral Jena glass vessel and its concentration periodically checked against the standard solution of hydrochloric acid. Each solution to be titrated was prepared by subsequent addition of: 1) a weighed amount of potassium oxamate, 2) an exact volume of hydrochloric acid, 3) as much solid potassium chloride as required to keep the ionic strength at the chosen value and, 4) finally, water. The mixtures H_2O—THF contained 60% THF in volume, corresponding to 44.1% in weight and 23.6% in mole/litre. The initial volume of the solutions was 99.695±0.013 ml in each titration. The total volumes of the titrant solution, 3-4 ml, were subdivided by a microburette into 13-16 steps, measured with precision ±0.005 ml. Three, in a few cases two, titrations were performed for each constant to be determined.

Potentiometric Measurements. A potentiometer Metrohm E388 was employed with glass electrodes EA107 UX and EA107 T which were calibrated with respect to a HCl solution in KCl at the same ionic strength as the solutions to be measured. The reversibility of the glass electrode in the H_2O—THF mixture has been checked (Figure 1). Calomel electrode (KCl sat.) was used as reference. The reaction vessel was maintained at the chosen temperature within ±0.1 °C by circulation of thermostated water. The concentration ranges for each titration are quoted in Table I.

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(1) A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio and F. Bigoli, *Acta Cryst.*, *B25*, 100 (1969).
(2) H. C. Freeman, *Adv. in Protein Chemistry*, *22*, 259 (1967).
(3) C. Caullet, *Bull. Soc. Chim. France*, 3459 (1965).
(4) W Stroheimer, A. El Said Mahgoub and F. Gernert, *Z. Electrochem.*, *65*, 85 (1965).
(5) A. Braibanti, E. Leporati, F. Dallavalle and M. A. Pellinghelli, *Inorg. Chim. Acta*, *2*, 449 (1968).

Table I. Initial concentrations and pH values for some titrations of oxamic acid in 0.1 *M* KCl

Temperature	Medium			
	H_2O		H_2O—THF	
°C	m*M*	p[H$_o$]	m*M*	p[H$_o$]
5	0.3705	2.597	0.4175	2.836
	0.4143	2.513	0.4837	2.760
	0.5192	2.457	0.5484	2.709
10	0.3707	2.512	0.3770	2.868
	0.4393	2.463	0.3815	2.864
	0.5518	2.396	0.5265	2.764
17	1.5136	2.076	0.4423	2.788
	1.7514	2.014	0.6184	2.693
20	1.5322	2.032	0.4532	2.779
	1.7636	1.996	0.5771	2.696
25	0.4419	2.787	1.5513	2.033
			1.7420	2.006
30	1.5415	2.017	0.5414	2.606

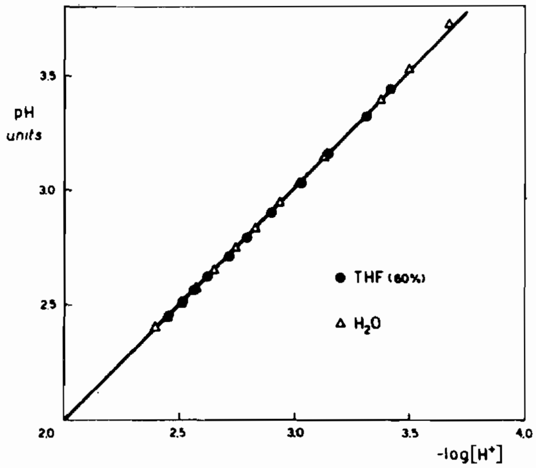

Figure 1. Electrode response against concentration [H$^+$] of hydrogen ions in H_2O and H_2O—THF mixture.

Results

The protonation constants have been calculated by the electronic computer ELEA 6001/S of Centro Calcolo Elettronico della Università di Parma, using a program prepared by Vacca, Arenare, and Paoletti.[6] The program, according to Sillén method,[7] calculates, by successive approximations for an acid H_pL_r:

$$[H] = T_H - \Sigma p\beta_{pr}[H]^p[L]^r \quad (1)$$

$$[L] = T_L - \Sigma r\beta_{pr}[H]^p[L]^r \quad (2)$$

where T_H and T_L are total concentrations of acid and ligand respectively. For the *n* experimental points, the minimum of the function

$$U = \sum_n (p[H_o]_n - p[H_c]_n)^2 \quad (3)$$

was sought for, being p[H$_o$] the observed quantity from the potentiometric measurements and p[H$_c$] the calculated quantity obtained from solution of the system formed by (1) and (2).

The constant β_{pr} written in logarithmic form is:

$$\log \beta_{pr} = pp[H] - r\log[L] + \log[H_pL_r] \quad (4)$$

and for a monoprotic and mononuclear acid ($p = 1$, $r = 1$) (4) is reduced to the well known expression

$$\log K_1 \equiv \log \beta_1 = p[H] + \log \frac{[HL]}{[L]} = p[H] + \log R \quad (5)$$

The variance in the determination of log K$_1$ is therefore[8]

$$\sigma^2(\log K_1) = \sigma^2(p[H]) + \sigma^2(\log R) \quad (6)$$

where $\sigma^2(\log R)$ depends upon the random errors in measurements of concentrations and volumes. The possible errors derive both from errors in volumes and concentrations and from error in potentiometric measurements. The composition of the errors according to (6) gives the standard deviation in log K$_1$. The value of (6) can be obtained by calculating $\sigma^2(\log K_1) = \frac{U}{n(n-1)}$ (7) following arguments described in a preceding paper.[9] An expression analogous to (5) can be obtained also for more complicated equilibria. In any case if only random errors affect the data, the actual distribution of $\Delta p[H]_n$ against $p[H_o]_n$ (or against other parameter of the titration) is normal (Figure 2). The latter distribution has been analysed according to statistical criteria.[10]

Table II. Protonation constants of oxamic acid in aqueous solutions at different ionic strengths (25°C)

μ(*M*)	log K$_1$	
KCl	observed	calculated*
0.034	1.915(1)	1.925
0.100	1.836(1)	1.820
0.500	1.711(2)	1.721
1.000	1.757(2)	1.760
1.500	1.808(2)	1.795
2.000	1.790(2)	1.796

* Calculated by equation (8).

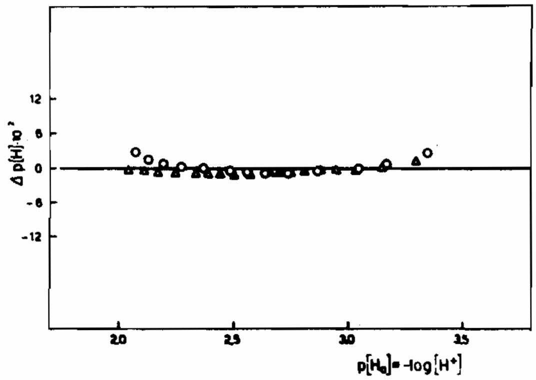

Figure 2. Normal distribution of points Δp[H] against p[H$_o$] for two typical titrations at the same temperature (17°C) and different acid concentrations.

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(6) A. Vacca, D. Arenare and P. Paoletti, *Inorg. Chem.*, *5*, 1384 (1966).

(7) L. G Sillén, *Acta Chem. Scand.*, *16*, 159 (1962), *18*, 1085 (1965).

(8) H. Cramèr, « The elements of probability theory », Almqvist and Wiksell, Stockholm (1954).

(9) A. Braibanti, F. Dallavalle and E. Leporati, *Inorg. Chim. Acta*, *4*, 459 (1969).

(10) C. J. Brookes, I. G. Betteley and S. M. Lokston, « Mathematics and Statistics for Chemists », John Wiley, London (1966).

Table III. Protonation constants of molecular and cation acids in H_2O and in H_2O–THF (60%) mixture at 25°C

Solvent	H_2O		H_2O–THF (60%)	
Compound	log K_1	ionic strength *M*	log K_1	ionic strength *M*
Molecular acid				
dichloroacetic ac.	1.480(12)		2.944	0.1 KCl
oxamic ac.	1.836	0.1 KCl	2.897	0.1 KCl
glycine (acid)	2.350(13)	0	2.996	0.1 KCl
chloroacetic ac.	2.861(12)	0.02–0.2	4.119	0.1 KCl
salicylic ac.	2.820(14,15)	0.17 $NaClO_4$	4.720	0.1 KCl
glycolic ac.	3.831(16)	0	4.522	0.1 KCl
benzoic ac.	4.010(17)	0.1 KCl	6.190	0.1 KCl
acetic ac.	4.559	0.1 KCl	5.863	0.1 KCl
Cation acid*				
tcaz H_2^{2+}	0.775(5)	0.1 KCl	0.938	0.1 KCl
tscaz H^+	1.743(5)	0.1 KCl	1.628	0.1 KCl
tcaz H^+	3.129(5)	0.1 KCl	2.653	0.1 KCl
scaz H^+	3.650(18)		3.362	0.1 KCl
py H^+	5.100(3)	1.0 $NaClO_4$	4.900	1.0 $NaClO_4$

* tcaz, thiocarbohydrazide; tscaz, thiosemicarbazide; scaz, semicarbazide; py, pyridine.

The equilibrium constants at different ionic strengths (Table II), determined at 25 °C, vary in a manner similar to that of acetic acid (Figure 3). The dependence on the ionic strength can be represented by the empirical relation calculated by least squares:

$$\log K = 2.1573 - 1.5600\mu^{1/2} + 1.7449\mu - 0.5817\mu^{3/2} \qquad (8)$$

with average error ±0.01. This relation is in fact comparable with a similar relation obtainable from data for acetic acid[11] in NaCl solutions:

$$\log K = 4.7458 - 0.8232\mu^{1/2} + 0.7106\mu - 0.1367\mu^{3/2} \qquad (9)$$

with average error ±0.006. The last measurements had been made by Harned and Hickey[11] in cells without transport and the difference in error gives a rough idea of the incidence of the fluctuations in junction potentials.

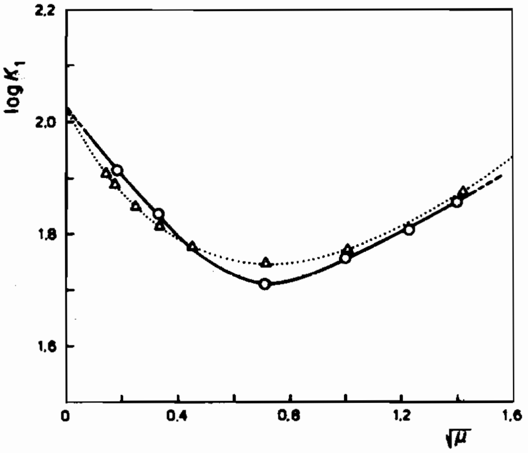

Figure 3. Dependence of the formation constant on ionic strength μ for oxamic (○) and acetic (△) acid at 25°C. For acetic acid values (log K_1—2.025) are plotted.

The protonation constants of oxamic and other acids have been determined in a mixture water-tetrahydrofuran of low dielectric constant (~36) and compared with constants in aqueous solutions quoted in literature (Table III).

According to the Born theory,[19] with radii, $r_{H_3O^+} = 1.4$ Å of hydronium ion and $r_{A^-} \sim 2.7$ Å of anion, one obtains $\Delta(\log K)_{calc.} = 0.83$, *i.e.* the increment can be due mainly to the influence of the dielectric constant. Effect of comparable intensity and nature are exerted by the medium on the complexes as shown by the comparison of the $\bar{n}$ formation function in H_2O and H_2O–THF mixture. The influence of the dielectric constant is illustrated also by the plot of log $K_{H_2O\text{-}THF}$ against log K_{H_2O} for several acids (Figure 4). For the cation acids the constants are practically the same in both solvents, in accordance with the theory (*cfr.* Charlot and Tremillon).[20] For other acids the protonation constant increases with respect to the value in H_2O but

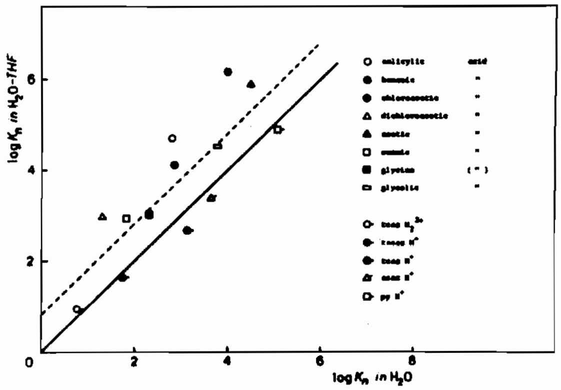

Figure 4. Comparison of log K_n in H_2O and in H_2O—THF mixture. Full line indicates no change; dotted line calculated according to Born.[19]

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(11) H. S Harned and F. C. Hickey, *J. Am. Chem. Soc.*, *59*, 1284 (1937).

(12) R. A. Day Jr. and R. W. Stoughton, *J. Am. Chem. Soc.*, *72*, 5662 (1950).

(13) B. B. Owen, *J. Am. Chem. Soc.*, *56*, 24 (1934).

(14) B. Kok-Bernstrom, *Acta Chem. Scand.*, *10*, 163 (1956).

(15) B. Hok, *Svenk Kem. Tidskr.*, *65*, 106 (1953).

(16) L. F. Nims, *J. Am. Chem. Soc.*, *58*, 987 (1936).

(17) M Yasuda, K. Yamasaki, and H. Ohtaki, *Bull. Chem. Soc. Japan*, *33*, 1067 (1960).

(18) N. F. Hall, *J. Am. Chem. Soc.*, *52*, 5115 (1930).

(19) R W. Gurney, « Ionic Process in Solution », Dover Publications, New York (1953).

(20) G. Charlot and B. Trémillon, « Les réactions chimiques dans les solvents et les sels fondus » Gauthier-Villars, Paris (1963).

Table IV. Protonation constants of oxamic and acetic acid in H_2O and in H_2O—THF (60%) mixture at different temperatures. Ionic strength, $\mu = 0.1\,M$ KCl

Acid	H_2N—CO—COOH		CH_3COOH	
Solvent	H_2O	H_2O—THF	H_2O	H_2O—THF
t°C	log $K_1(\sigma)$	log $K_1(\sigma)$	log $K_1(\sigma)$	log $K_1(\sigma)$
5	2.070(2)	2.973(3)	—	5.857(3)
10	1.935(2)	3.013(3)	4.569(2)	5.866(3)
17	1.893(2)	2.948(8)	4.562(4)*	5.929(3)*
20	1.869(1)	2.915(7)	4.540(6)	5.895(7)
25	1.836(1)	2.897(6)	4.559(2)	5.863(5)
30	1.809(1)	2.842(4)	4.560(1)	5.839(8)

* At 15°C.

Table V. Thermodynamic functions of oxamic and acetic acid at 25°C

Reaction: $R—COO^- + H^+ \longrightarrow R—COOH$

Solvent	H_2O		H_2O—THF	
	$\Delta H(\sigma)$ kcal $mole^{-1}$	$\Delta S(\sigma)$ cal deg^{-1} $mole^{-1}$	$\Delta H(\sigma)$ kcal $mole^{-1}$	$\Delta S(\sigma)$ cal deg^{-1} $mole^{-1}$
ox	−3.3(0.5)	2.1(1.6)	−2.1(0.6)	6.1(2.0)
acet	0.3(0.3)	21.9(1.0)	−0 3(0.4)	25.4(1.4)
$\Delta X_{ox}—\Delta X_{acetic}$	−3.6(0.6)	−19.8(1.9)	−1.8(0.7)	−19.3(2.4)

the points are somewhat scattered due to specific interactions of the acid with the solvent, and in fact the increments observed in the mixture H_2O—THF are smaller in those acids having groups capable to form hydrogen bonds with the solvent. The behaviour of the oxamic acid is approximately on the same line as glycolic acid.

The effect of the temperature on the equilibrium constant of oxamic acid has been determined in the range 5÷30 °C for both aqueous and H_2O—THF solutions. All the solutions were 0.1 *M* in KCl (Table IV). The Pitzer[21] equation

$$\log K_T = \frac{A}{T} - B + 20 \log T \qquad (10)$$

fits the data at different temperatures, with the following constants for oxamic acid: $A_{H_2O} = 3315.1$, $B_{H_2O} = -58.8$ and $A_{H_2O\text{-}THF} = 3049.8$, $B_{H_2O\text{-}THF} = -56.8$ and for acetic acid: $A_{H_2O} = 2522.3$, $B_{H_2O} = -53.4$ and $A_{H_2O\text{-}THF} = 2657.9$, $B_{H_2O\text{-}THF} = -52.5$. The discrepancies between the observed values and those calculated by (10) give the following standard deviations:

oxamic acid, in H_2O, $\sigma(\log K_T) = 0.011$,

in H_2O—THF, $\sigma(\log K_T) = 0.014$

acetic acid, in H_2O, $\sigma(\log K_T) = 0.006$,

in H_2O—THF, $\sigma(\log K_T) = 0.0095$

From the value of log K_T and by differentiating (10) with respect to T, the thermodynamic functions at 25 °C, with standard deviations in parenthesis, can be calculated (Table V).

The thermodynamic functions, namely enthalpy and entropy change, however, are not able to throw some light on the different behaviour of acids more or less capable to form hydrogen bond, say, for example acetic and oxamic acid. Neither the values $\Delta H_{ox}—\Delta H_{acet}$ in H_2O and H_2O—THF, nor the values $\Delta S_{ox}—\Delta S_{acet}$ (*cfr.* Table V) differ at a statistically significant level because P (probability) <90% as calculated from

$$t = \frac{\Delta H_2—\Delta H_1}{(\sigma_1^2 + \sigma_2^2)^{1/2}}\,.$$

It can be mentionated, however, that the entropy change $\Delta S_{ox}—\Delta S_{acet}$ is rather high when compared with the values quoted by Bell,[22] but follows the same trend of those values, in the sense that $\Delta S_{ox}—\Delta S_{acet}$ increases as log K decreases.

Conclusion

The examination of the potentiometric data for solutions of oxamic acid, H_2N—CO—COOH, in H_2O shows that this acid is monoprotic, with log $K_1 = 1.836$ at 25°C in 0.1 *M* KCl. The influence of the ionic strength on the equilibrium constant confirms that the acid is molecular, monoprotic such as acetic acid. When the equilibrium is measured in H_2O—THF solutions, the equilibrium constant is increased in accordance with the diminution of the dielectric constant of the medium. The small differences, when passing from H_2O to H_2O—THF solutions, in the behaviour of acetic and oxamic acid, cannot be explained in terms of enthalpy or entropy change because the differences observed in these quantities are not statistically significant.

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(21) K. S. Pitzer, *J. Am. Chem. Soc.*, *59*, 2365 (1937).

(22) R. P. Bell, « The Proton in Chemistry » Methuen, London (1959).