Kinetics of Acid-catalysed Hydrolysis of Hexanohydroxamic Acid

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Kinetics of the acid-catalysed hydrolysis of hexanohydroxamic acid has been investigated in hydrochloric, perchloric and sulphuric acids. The effect of catalysts, temperature, ionic strength and solvent isotope effect have been investigated and the results show that the hydrolysis occurs by an A_{AC}^2 mechanism giving hexanoic acid and hydroxylamine. The variation of reaction rate with [acid] has been satisfactorily explained by a two-parameter equation.

THE acid-catalysed hydrolysis of some aromatic[1-6] and few aliphatic[7-9] hydroxamic acids have been studied. Though the hydrolysis of hexanohydroxamic acid was studied[10] in dil. aq. HNO_3, no kinetic study of the reaction has been studied. A detailed kinetic study of hydrolysis of hexanohydroxamic acid in aq. mineral acids has now been undertaken and a mechanism consistent with the results has been proposed.

Materials and Methods

Hexanohydroxamic acid (K & K Labs, USA) was recrystallized from benzene, m.p. 62° (lit.[10] 61·5-63·5°). HCl, $HClO_4$, H_2SO_4 used were of AR quality. A 1% solution of $FeCl_3.6H_2O$ (BDH, AR) was prepared in distilled water containing $0·1M$ HCl.D_2O (isotopic purity 99·4%) was precured from BARC, Bombay. All other chemicals used were of AR grade.

Kinetic measurement — All kinetic measurements were carried out at $40° \pm 0.05°$. The hydrolysis rates were determined from the rate of disappearance of the hydroxamic acid. Aliquots of the reaction mixture were withdrawn at regular time intervals and the concentration of hexanohydroxamic acid determined colorimetrically[1] at 520 nm. The rate constants were calculated using the integrated rate equation for first order reactions. Initial concentration of hexanohydroxamic acid in all kinetic run was $0·012M$.

Results and Discussion

The hydrolysis was found to be first order with respect to both substrate and HCl. But in the presence of excess hydronium ions, pseudo-first order rates were ensured.

Effect of varying [acid] on reaction rate — The hydrolysis rates were studied in aq. HCl, $HClO_4$ and H_2SO_4 at 40° in the range 1 to $8M$. The rates were found to increase with increase in [acid] and attained optimum value at $5M$ HCl, $3M$ $HClO_4$ and $3M$ H_2SO_4 and then tended to decrease (Table 1). Rate maxima is also observed for acid-catalysed hydrolysis of benzohydroxamic acid and its derivatives[2,3]. It can be presumed in analogy with amides[11] that the protonation of hexanohydroxamic

is complete at $5M$ HCl, $3M$ $HClO_4$ and $3M$ H_2SO_4. Activity of water goes on decreasing with increase in [acid]. Above the optimum rate, decrease in activity of water outweighs the protonated species and so the rate of hydrolysis goes on decreasing at higher acid concentration.

Effect of varying temperature on reaction rate — The hydrolysis of hexanohydroxamic acid was studied in $1·0M$ HCl in the temperature range 35-55° (Table 2). The rate constants $(k \times 10^4)$: 0·45, 0·71, 1·13 and 1·77 sec^{-1} at 35°, 40°, 45° and 50° respectively are average of duplicate runs and the average deviation from the mean is less than 3%. The values of activation parameters fall in the range typical of a reaction proceeding by A_2-mechanism. The entropy of activation is negative and falls in the range −15 to −30 e.u., characteristic of bimolecular mechanism[12]. The values of $\Delta E\ddagger$, $\Delta H\ddagger$ and frequency factor A are $18·3 \pm 0·3$ kcal mol^{-1}, $17·5 \pm 0·1$ kcal mol^{-1} and $3·1 \times 10^8$ sec^{-1} respectively.

Zucker and Hammett[13] treated quantitatively acidity dependence rates and grouped reactions into two categories depending on whether the logarithm of the pseudo-first order rate constants were linear either with H_0 (A_1-mechanism; rate determining unimolecular decomposition of protonated species) or with log C_{H^+} (A_2-mechanism; rate determining attack on protonated substrate by a water molecule). We observed that plot of log k_1 against $−H_0$ was not linear. However the plot of log k_1 against log (C_{H^+}) was linear up to $4M$ HCl with approximate unit slope (0·92) indicating that a bimolecular mechanism operates.

Bunnett[14] found empirically that for a large number of reactions, plots of (log k_1+H_0) versus the logarithm of the activity of water‘ (log a_{H_2O}) were linear or very nearly linear and classified the reactions into three categories according to slopes (w values) of the above plots. The present data gave a value of $w = 7·3$ in HCl. This value suggested that water played the role of a proton transfer agent ($w > +3·3$). From w value we can say that the transition state is more polar than the substrate[14]. The large +ve value of w have been observed (+6·1 in

TABLE 1 — EFFECT OF VARYING [ACID] ON THE RATE CONSTANT

[Acid] (M)	k_1 10^4 sec^{-1} in		
	HCl*	HClO$_4$	H$_2$SO$_4$
1·0	0·71 (0·69)	0·68	0·77
2·0	1·41 (1·28)	1·10	1·46
3·0	1·90 (1·74)	1·30	2·17
4·0	2·02 (2·04)	1·10	1·67
5·0	2·16 (2·12)	0·90	1·46
6·0	1·97 (1·90)	0·65	1·05
7·0	1·74 (1·81)	0·47	0·61
8·0	1·31 (1·49)	0·27	0·28

*Values calculated with the help of Eq. 2 are given in parentheses.

TABLE 2 — VARIATION OF RATE CONSTANT AT DIFFERENT [HCl] AND IONIC STRENGTHS

[Ionic strength maintained by adding NaCl; temp. 40°]

| [HCl] M	k_1 10^4 sec^{-1} at μ			
	ml	1·0M	2·0M	3·0M
0·10	0·07	0·09	—	—
0·25	0·18	0·21	0·23	—
0·50	0·36	0·41	0·45	0·50
0·75	0·51	0·58	0·62	0·69
1·00	0·71	—	0·81	0·90
1·00	1·28*	—	—	—
1·50	1·11	—	1·19	1·23
1·70	1·29	—	—	1·43
2·00	1·41	—	—	1·62
3·00	1·90	—	—	—

*In D$_2$O medium.

Scheme 1

HCl and +8·9 in HClO$_4$) for acid-catalysed hydrolysis of N-phenyl-n-butyrohydroxamic acid[6].

Bunnett and Olsen[15] suggested that the slopes (ϕ) of the plot of (log $k_1 + H_0$) versus ($H_0 + $log H$^+$) can be used as a criterion postulating for a reaction mechanism. The (ϕ) values obtained for hydrolysis of hexanohydroxamic acid are 1·35 in HCl, 1·25 in HClO$_4$ and 1·2 in H$_2$SO$_4$ which fall clearly in the third category implying that water acts as proton transfer agent ($\phi > 0.56$). The ϕ value observed for benzohydroxamic acid and its some p-substituted derivatives have been reported[2] to lie in the range 0·84 to 1·1.

Bunnett and coworkers[16] suggested that for A_1-reactions the catalytic effect of added acids followed the order: HClO$_4$ > HCl > H$_2$SO$_4$, while for A_2-reactions the order was H$_2$SO$_4$ > HCl > HClO$_4$. Thus higher rate in H$_2$SO$_4$ (> HCl > HClO$_4$) provides support for a bimolecular mechanism.

Solvent isotope effect — The hydrolysis of hexanohydroxamic acid in H$_2$O and D$_2$O using 1·0M HCl at 40° showed that the hydrolysis occurs 1·8 times faster in D$_2$O than in H$_2$O (Table 2). Higher rate in D$_2$O is suggestive of a rapid transfer of proton to the substrate in the reaction and pre-equilibrium step therefore is not the rate determining step[17]. As suggested for amide hydrolysis[18,19] seat of protonation in hydroxamic acids may be assumed to be the oxygen atom[2].
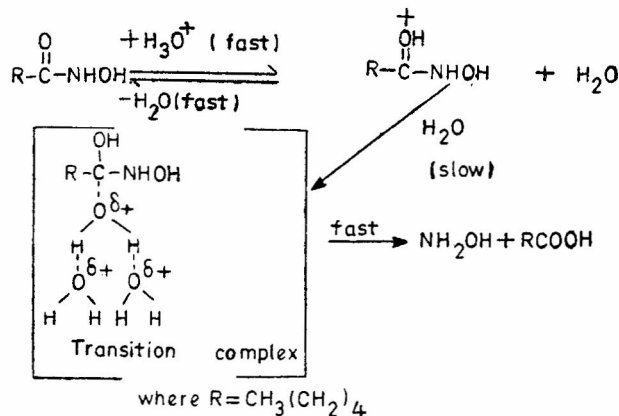
Effect of ionic strength — The hydrolysis of hexanohydroxamic acid studied at varying [HCl] and ionic strengths [1·0, 2·0, 3·0M (NaCl)], showed only slight increase in the rate constant (15-20%) with increasing ionic strength (Table 2). From the plots of rate constants against acidity at different ionic strengths, it can be concluded that: (i) at each ionic strength the reaction can be represented by Eq. (1)

$$k = k_{H^+}.C_{H^+} \qquad ...(1)$$

where k and K_{H^+} are the observed and specific rate constants respectively; (ii) since the slopes (k_{H^+}) of the curves increase with increase in ionic strength, the reaction is presumed to exhibit positive salt effect. The linearity of the plots with positive slopes indicates an acid-catalysed reaction[20]; (iii) the reaction due to neutral species is absent as the plots pass through the origin[21].

These results favour the reaction proceeding via the protonated species only. The rate data may be represented by a modified form of the Bronsted-Bjerrum equation[22].

$$k = k_{H_0^+}.C_{H^+}e^{b.\mu}(a_{H_2O})^n \qquad ...(2)$$

where a_{H_2O} is the activity of water[23], n is the number of water molecules and μ the ionic strength.

The values of k_{H^+} at $\mu = 1.0$, 2·0 and 3·0 are 0·72, 0·77 and 0·81 respectively. The values $k_{H_0^+}$ and b are obtained from the linear plot of log k_{H^+} versus μ. The gradient gives b while the intercept at zero ionic strength, gives $k_{H_0^+}$. The value of b is found to be 0·015 and that of $k_{H_0^+}$ is $0.72 \times 10^4 M^{-1}$ sec^{-1}.

Mechanism of hydrolysis — The above results indicate that water molecules are involved in the rate determining step. The number of water molecules actually involved can be obtained by the method proposed by Yates and McClelland[24].

The new acidity function H_s ($= MH_0$) can be obtained from protonation of some p-substituted benzohydroxamic acids[2]. The value of M was in the range 0·58 to 0·68. The average value of M is taken as 0·60.

The plot of (log $k_1 + H_s$) versus log a_{H_2O} was linear with slope $= 3.1$, indicating that 3 water molecules are involved in the formation of transition complex during the hydrolysis of hexanohydroxamic acid. On the basis of above results the probable mechanism (Scheme 1) appears to involve reversible rapid

protonation of hexanohydroxamic acid followed by a slow reaction of water with the protonated form, leading to the transition complex[25] and subsequent hydrolysis giving the products, hexanoic acid and hydroxylamine.

Acknowledgement

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