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Kinetics of Acid Hydrolysis of Resacetophenone Isoniazid Hydrazone in Presence & Absence of Molybdenum(VI) in Dimethylformamide†

(Mrs) M. C. S. SUBHA & S. BRAHMAJI RAO*
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003

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Kinetics of acid hydrolysis of resacetophenone isoniazid hydrazone alone and in presence of molybdenum(VI) in 10% (v/v) N,N-dimethylformamide have been studied at 30°C. The rate of hydrolysis increases with increase in [nitric acid], ionic strength and dielectric constant. The reaction is classified as *$A_{AC}2$* type involving two positive ions. The decrease in rate in the presence of molybdenum(VI) is attributed to the formation of metal complex having a bichelate ring structure.

RESACETOPHENONE isoniazid hydrazone (RPINH) has been extensively employed in our laboratories as a colorimetric reagent for many metal ions in acid media. RPINH in the absence and presence of Mo(VI) gives yellow colour in dil. nitric acid. While the yellow colour due to free reagent alone disappears rapidly, that in presence of Mo(VI) takes sometime to disappear. The colour change might be due to acid hydrolysis of the reagent in the free form or in the complexed form with the metal, the latter being hydrolysed at a lower rate. The role of metal ions in the hydrolysis of schiff bases has been investigated by different workers[1,2]. Eichhorn *et al.*[3] reports that the ease of hydrolysis is determined by the stability of the schiff base metal complex. With this background, RPINH-Mo(VI) system appeared attractive. The present paper describes the kinetics of the acid hydrolysis of RPINH in the presence and absence of Mo(VI) in dil. nitric acid medium.

Materials and Methods

All the chemicals used were of AR (BDH) or GR (E. Merck) quality. RPINH prepared by the literature procedure[4], was dissolved in N,N-dimethylformamide (E. Merck) and this stock solution was used after appropriate dilution. The reaction studied under pseudo-first order conditions with [reagent]<< [acid] was monitored spectrophotometrically following the decrease in absorbance of the substrate with time at 425 nm. At this wavelength absorbance of the reaction mixture is maximum and that of products negligible (Fig. 1).

Rate constants reported are average values from the replicate runs and are reproducible within ± 4%.

Results and Discussion

Hydrolysis of RPINH in the absence of Mo(VI)— The plot of log k versus pH was linear with a negative slope showing that the protonation of the substrate plays a significant role. The plot of log k versus $\sqrt{\mu}$ was also linear (Fig. 2) but with a positive slope, suggesting that the reaction is an ion-ion type involving ions of same sign. It was noticed that the rate decreased with increase of DMF percentage. The plot of log k versus 1/D was linear with a negative slope (Fig. 3) indicating that the reaction is between two positive ions[5].

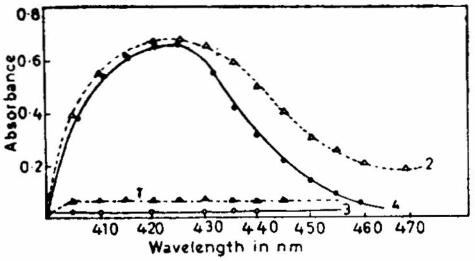

Fig. 1 — Absorption spectra of reagent in the absence and presence of molybdenum(VI) [1, after 3 hr in presence of Mo(VI); 2, immediately in presence of Mo(VI); 3, after 3 hr in absence of Mo(VI); 4, immediately in absence of Mo(VI)].

The rate decreased with increase in [substrate] in the range 0.2×10^{-3} to 3.0×10^{-3} M.

Activation parameters $\Delta S\ddagger$ and E_a were calculated from the rates determined at different temperatures and the values are $\Delta S\ddagger = -177.4$ J mol^{-1} K^{-1}, and $E_a = 35$ kJ mol^{-1}.

From the above observations it is concluded that the hydrolysis of RPINH in the absence of Mo(VI) proceeds by $A_{AC}2$ (positive ion-positive ion type) mechanism[6] involving positively charged protonated substrate and the hydronium ion.

According to Bruyneel *et al.*[7] the schiff bases undergo hydrolysis upto neutral pH as per reaction sequence shown in Scheme 1.

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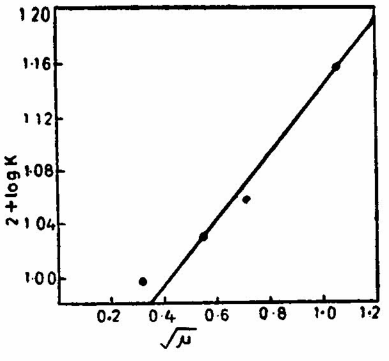


Fig. 2 — Plot of log k versus $\sqrt{\mu}$

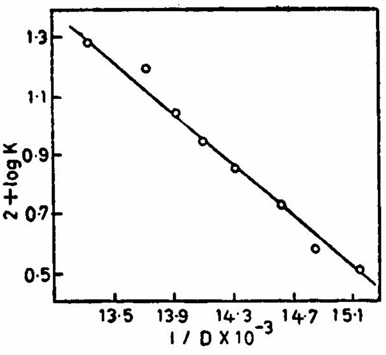


Fig. 3 — Plot of log k versus $1/D$

$$SH^+ \overset{K_{SH^+}}{\rightleftharpoons} S + H^+$$

$$SH^+ + H_2O \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} X + H^+$$

$$SH^+ + OH^- \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} X$$

$$X \xrightarrow{k_4} \text{Products}$$

Scheme 1

where S, SH^+ and X refer to substrate, protonated substrate and carbinolamine intermediate. Assuming a steady state approximation for the carbinolamine intermediate, the rate law takes the form

$$k_{obs} = \frac{(K_1 k_4 [H^+] + (K_2 k_4 K_W) K_{-1} [H^+] + K_{-2} + k_4)}{([H^+] + (K_{SH^+}))} \qquad ..(1)$$

In the acid range of study K_{-2} is negligible and k_4 and K_{SH+} will be considerably less than $[H^+]$. Hence Eq. (1) takes the form

$$k_{obs} = K_1 [H^+] + K_2 K_W \qquad ..(2)$$

or

$$\log k_{obs} = \log K_2 K_W + \log K_1 - pH \qquad (3)$$

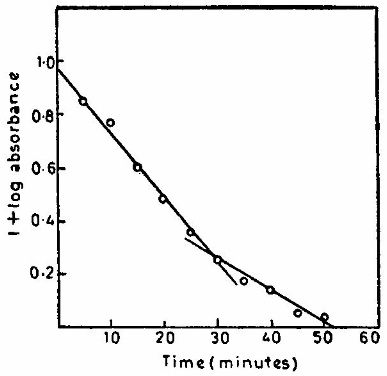


Fig. 4 — Plot of log (absorbance) versus time.

TABLE 1 — EFFECT OF [SUBSTRATE] ON THE RATE OF HYDROLYSIS

$[HNO_3] = 0.05$ M; solvent = 10%(v/v) aq. dimethylformamide; temp. = 30°C.

[RPINH] × $10^3 M$	$k \times 10^2$ min^{-1}	[RPINH] × $10^3 M$	$k \times 10^2$ min^{-1}
0.2	16.4	2.0	8.6
0.5	14.9	3.0	7.9
0.8	11.3		

TABLE 2 — EFFECT OF [MOLYBDENUM] ON THE RATE OF HYDROLYSIS

$[HNO_3] = 0.05$ M; [RPINH] = $1 \times 10^{-3} M$; solvent = 10% (v/v) aq. dimethylformamide; temp. = 30°C

[Mo(VI)] $10^5 M$	$k \times 10^2$ min^{-1}	[Mo(VI)] $10^5 M$	$k \times 10^2$ min^{-1}
0	106.6	6	1.4
2	2.5	8	1.1
4	1.9		

Thus the observed pH dependence on rate is justified by the mechanism proposed.

Hydrolysis of RPINH in the presence of Mo(VI) — It is observed that an initial rapid decrease of yellow colour of the reaction mixture is followed by the slow discharge of the yellow colour in presence of molybdenum. Log (absorbance) versus time plot (Fig. 4) shows two linear portions with different slopes. The first portion is due to the faster hydrolysis of the free RPINH and the second portion is attributed to the hydrolysis of the Mo(VI)—RPINH complex. The rates of hydrolysis of the complex at different [Mo(VI)] were computed from the slopes of the second linear portions and the values are given in Table 2.

It is seen from Table 2 that the rate decreases with increase in [Mo(VI)] indicating that the hydrolysis of the metal complexed substrate is inversely related to its concentration. Similar inverse relation between the rate and substrate concentration is observed in the hydrolysis of uncomplexed RPINH (cf. Table 1) also. This observation is attributed to a decrease

TABLE 3 — EFFECT OF [RPINH] ON RATE OF HYDROLYSIS

Temp. = 30°C; $[HNO_3]$ = 0.05 *M*; solvent = 10% (v/v) aq dimethylformamide

[RPINH] 10^3M	$k \times 10^2$ min^{-1}	[RPINH] 10^3M	$k \times 10^2$ min^{-1}
[Mo(VI)] = $8 \times 10\ ^{5}M$		[Mo(VI)] = $6 \times 10^{-5}M$	
1.0	1.1	1.00	1.4
0.8	1.0	0.75	1.3
0.6	1.0	0.50	1.3
0.4	0.9	0.25	1.3

in the concentration of the active protonated species with increase in [substrate] in view of the limited availability of hydrogen ions.

The rates of hydrolysis in presence of different concentrations of RPINH and 0.05 *M* HNO_3 was carried out keeping the concentration of molybdenum at $8 \times 10^{-5}M$ or $6 \times 10^{-5} M$. The results, presented in Table 3 show that the rate is independent of free [RPINH] at any [Mo(VI)] confirming that the second linear portion conforms to the hydrolysis of complexed RPINH.

The dependence of the rate on the [acid] was studied at fixed [RPINH] ($=1 \times 10^{-3}$ *M*) and [molybdenum]$=1 \times 10^{-4}$ *M*). Plot of log *k* versus *p*H is linear with a negative slope, suggesting the participation of protonated species.

The activation parameters for the hydrolytic reactions in the presence of Mo(VI) have been calculated from the rates measured at different temperatures. $\Delta S^{\ddagger}$ and E_a are —98.7 J mol^{-1} K^{-1} and 58 kJ mol^{-1} respectively. The higher activation energy accounts for the lower rate.

The observations made indicate that the mechanism suggested by Bruyneel *et al.*[7] for the hydrolysis of schiff bases in the presence of metal ions holds good for the present system also (see Scheme 2).

$$S + M^{+n} \xrightleftharpoons{K_{SM^{(n-1)+}}} SM^{(n-1)+} + H^+$$

$$SM^{(n-1)+} + H^+ + H_2O \xrightleftharpoons[K'_{-1}]{K'_1} XM^{(n-1)+} + H^+$$

$$SM^{(n-1)+} + H_2O \xrightleftharpoons[K'_{-2}]{K'_2} XM^{(n-1)+}$$

$$XM^{(n-1)+} \xrightarrow{k'_4} \text{Products}$$

Scheme 2

The rate law based on Scheme 2 is given by Eq. (4)

$$k_{app} = \frac{K'_1k'_4[H^+] + K'_2k'_4}{K'_{-1}[H^+] + K'_{-2} + k'_4} \quad ..(4)$$

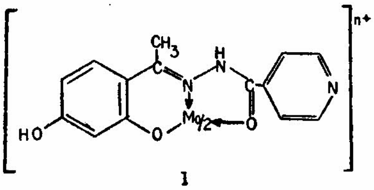
Equation (4) reduces to Eq. (5)

$$k_{app} = k'_1 [H^+] \quad ..(5)$$

assuming $K_1'k'_4 [H^+] >> K'_2k'_4$ and $k'_4 >> K'_{-1} [H^+] + K'_{-2}$

The experimental results obtained on the effect of *p*H, thus confirm the mechanism proposed.

The decrease in the rate of hydrolysis of the Mo(VI)—RPINH complex is attributed to the bichelate ring structure (I) of the complex. The structure (I) has been arrived at on the basis of 1:2 (metal-ligand) stoichiometry of the complex determined by Job's method.



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