

Kinetics and Mechanism of Hydrolysis of Salicylidene-2-amino-1,3-pyrimidine Schiff Base in the Absence and Presence of Some Transition Metals

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The hydrolysis of salicylidene-2-amino-1,3-pyrimidine Schiff base is studied kinetically in a series of universal buffer (2.37-11.40) containing 0.2 mole fraction of ethanol at 30°C. Also, the effect of some transition metal ions (Cd(II), Mn(II), Fe(II), Co(II) and Ni(II)) on the hydrolysis rate of the Schiff base has been studied and discussed.

INTRODUCTION

The catalytic effect of metal ions has been recognised in a wide variety of reactions involving organic substrates. One important reaction of biological interest which merits mention in this connection is the hydrolysis of Schiff bases. A number of investigations have been devoted to exploring the effect of metal ions on the formation and hydrolysis¹⁻⁶ of such compounds. As a continuation of this work, a systematic study of the hydrolysis mechanism of salicylidene-2-amino-1, 3-pyrimidine in a series of universal buffer solutions and in the presence of some transition metal ions is reported.

EXPERIMENTAL

Chemicals of the purest available grade (A.R. products) were used in all experiments. The heterocyclic Schiff base was prepared as described before⁷. The compound was checked by elemental analysis and IR spectra. Universal buffer solutions were prepared according to the method described by Britton⁸.

To account for the difference in acidity, basicity, dielectric constant and ion activities in aqueous ethanol solutions relative to pure aqueous ones, the measured pH values of the former solutions were recorded as described by Qouhert⁹.

$$\text{pH}^* = \text{pH}(\text{R}) - \delta$$

where, pH* is the corrected reading and pH(R) is the pH-meter reading obtained in a partially aqueous medium where δ is a constant value.

Stock solutions (1×10^{-2} mole dm^{-3}) of Schiff base, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving the requisite amount of each in pure ethanol.

The rate of hydrolysis was followed spectrophotometrically by a Shimadzu UV-visible-240 digital spectrophotometer using 1 cm matched silica cells. The IR spectra was recorded on a Perkin-Elmer 599 A Spectrophotometer as KBr discs. The pH measurements were obtained using a MV 87 Digital Practronic pH-meter accurate to ± 0.005 units.

RESULTS AND DISCUSSION

Hydrolysis in Absence of Metal Ions

The hydrolysis of 1×10^{-3} mole dm^{-3} of salicylidene-2-amino-1, 3-pyrimidine was studied in a series of universal buffer solutions containing 0.2 mole fraction of ethanol of pH varying from 2.37 to 11.40 at 30°C. The observed first-order rate constants for hydrolysis are determined and plotted against pH values (Fig. 1).

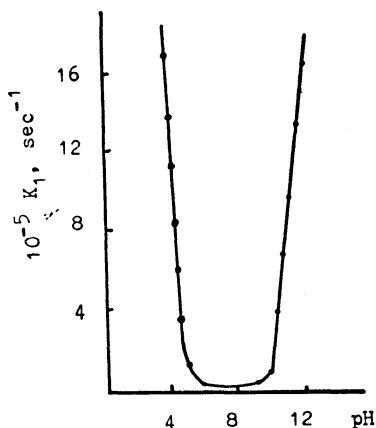


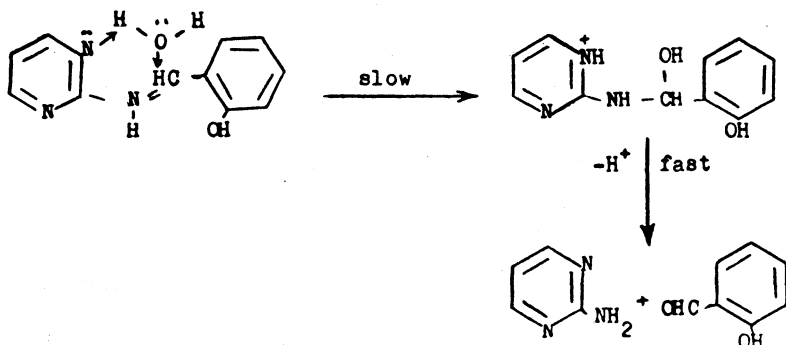
Fig. 1. Variation of the first-order rate constant (sec^{-1}) with pH for the hydrolysis of Schiff base

Examination of this figure reveals the following facts:

(i) Under more acidic medium $\text{pH} < 4$, the rate determining step of hydrolysis of Schiff base is suggested to be the decomposition of the protonated carbinolamine intermediate¹⁰⁻¹². So the hydrolysis rate is too rapid to be followed by the conventional methods.

(ii) In acidic medium at $\text{pH} < 6.5$, the rate determining step of the hydrolysis reaction is the addition of water on the protonated Schiff base^{10, 13-15}. Thus, in this medium the Schiff base is present mainly in their conjugate acid and the hydrolysis rate starts to increase with increasing acidity.

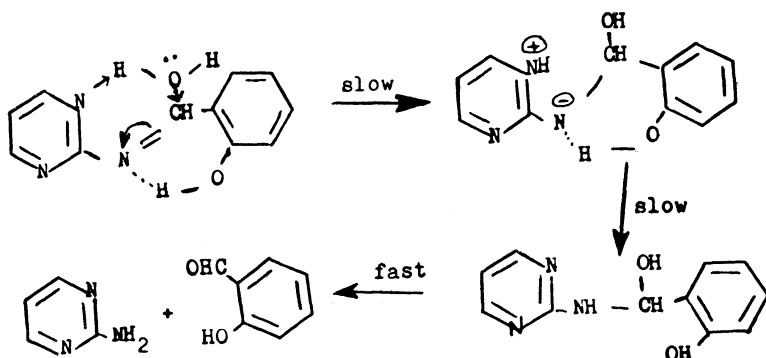
The suggested mechanism can be represented as below:



From the above mechanism, it is clear that the Schiff base is capable of forming a mono six-membered ring; so the carbinolamine intermediate is formed in a slow step and it is suggested to be the rate determining step.

(iii) In the pH range 6.5–9.5, no measurable hydrolysis rate is observed. This can be interpreted on the principle that, in this pH range, a transition in rate determining step occurs from the attack of water on the protonated Schiff base to water attack on the free Schiff base⁶.

The suggested mechanism is represented as follows:



This mechanism shows the formation of two six-membered rings, one as a result of the interaction of the added water molecule with the Schiff base and the other between imine nitrogen atom and the ortho-hydroxy group. For this reason, the carbinolamine intermediate is expected to be more stable and the hydrolysis rate is very slow.

(iv) At alkaline pH (>9.5), the hydrolysis rate increases as the pH of the medium is increased and the rate limiting step is expected to be the attack of OH^- on the free Schiff base. Accordingly, an increase in the OH^- will result in an increase in Schiff base hydrolysis rate.

Hydrolysis in Presence of Metal Ions

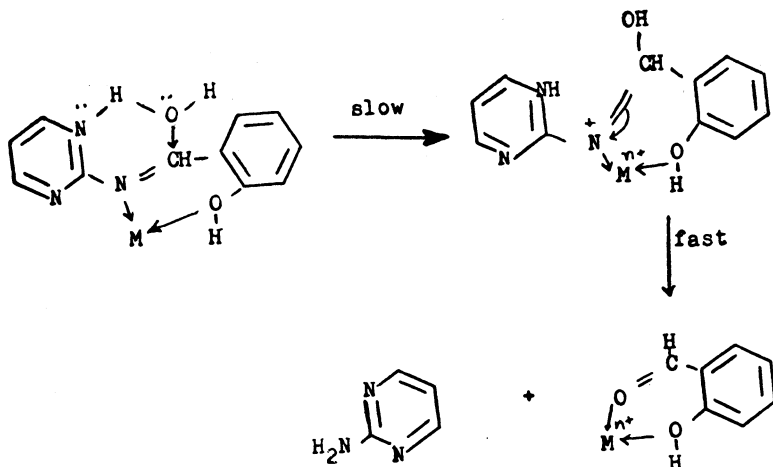
The hydrolysis of 1×10^{-3} mole dm^{-3} of salicylidene-2-amino-1, 3-pyrimidine is followed kinetically in neutral medium ($\text{pH} \cong 7.0$) of 0.2 mole fraction of ethanol in presence of different concentrations of divalent transition metal ions, viz., Cd(II), Mn(II), Fe(II), Co(II) and Ni(II), ($0.1-1 \times 10^{-3}$) at 30°C . These metal ions are chosen due to their interesting character in forming complexes with *o*-hydroxy Schiff bases^{16, 17}. The first order hydrolysis rate constant at each metal ion concentration was calculated and the results obtained are listed in Table 1. Examination of these results reveals that the presence of metal ion accelerates the hydrolysis rate and the rate increases along the sequence Cd(II)→Mn(II)→Fe(II)→Co(II)→Ni(II). These observations can be explained as follows:

TABLE 1

FIRST-ORDER RATE CONSTANT VALUES FOR THE HYDROLYSIS OF 1×10^{-3} mol dm^{-3} OF SCHIFF BASE IN 0.2 M.F. OF ETHANOL IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF METAL IONS AT 30°C

$[\text{M}^{n+}] \times 10^{-3}$ mole dm^{-3}	First-order rate constant $\times 10^{-4} \text{ sec}^{-1}$				
	Cd(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)
0.0	First-order rate constant (K) = $1.25 \times 10^{-5} \text{ sec}^{-1}$				
0.1	1.02	2.42	3.41	5.15	5.31
0.3	1.95	3.05	4.11	5.91	6.09
0.5	2.83	3.95	4.87	6.38	6.88
0.7	3.40	4.62	5.53	6.99	7.34
0.9	3.99	5.12	6.01	7.52	7.99
1.0	4.32	5.70	6.40	7.91	8.23

The Schiff base under study has a high tendency to coordinate to the metal ion as a bidentate ligand, through the imine nitrogen and phenolic oxygen atoms^{18, 19}, one might expect that, in the presence of a metal ion the substrate exists mainly in a metal complex form. Accordingly, the azomethine carbon atom is expected to carry high positive charge relative to that in absence of metal ion. This results in a higher nucleophilic attack by water on this carbon atom. Furthermore, the decomposition of carbinolamine intermediate in a metal complex form is expected to occur faster than that in the free one and the high tendency of the hydrolysis product salicylaldehyde to coordinate to metal ion will result in high Schiff base hydrolysis rate in the presence of metal ion. The hydrolysis mechanism in the presence of metal ion can be represented as below:



The results show that the hydrolysis rate follows the same sequence of the ionic radius of the metal ion. This behaviour may be attributed to the degree of stability of the hydrolyzed chelated carbinolamine intermediate⁶, where the stability of the carbinolamine complex will be delay the last step of the suggested mechanism (the decomposition of the carbinolamine).

REFERENCES

1. D. F. Martin and F. F. Cantwell, *J. Inorg. Nucl. Chem.*, **26**, 2219 (1964).
2. A. C. Dash and R. K. Nanda, *J. Am. Chem. Soc.*, **91**, 25 (1969).
3. C. V. McDonnell, Jr., M. S. Michailidis and R. B. Martin, *J. Phys. Chem.*, **74**, 1 (1970).
4. L. F. Lindoy, *Quart. Rev.*, **25**, 379 (1971).
5. R. W. Hay and K. B. Nolan, *J. Chem. Soc., Dalton Trans.*, 548 (1976).
6. F. A. Adam, M. T. El-Haty and S. A. El-Gyar, *J. Indian Chem. Soc.*, **65**, 651 (1988).
7. L. P. Kyrides, F. B. Zienty and R. W. Stephenson, Monsanto Chemical Co., U.S., **2**, 420 (May 13, 1947).
8. H. T. S. Britton, *Hydrogen Ions*, Chapman and Hall, London, p. 364 (1958).
9. G. Qouhert, *Bull. Soc. Chem. Fr.*, 1412 (1967).
10. J. J. Charette and E. De Hoffmann, *J. Org. Chem.*, **44**, 13 (1979).
11. D. Pitea, G. Favini and D. Grasso, *J. Chem. Soc. Perkin*, **II**, 1595 (1974).
12. R. Herscovitch, J. J. Charette and E. De Hoffmann, *J. Am. Chem. Soc.*, **95**, 5135 (1973); **96**, 4954 (1974).
13. R. L. Reeves, *J. Am. Chem. Soc.*, **30**, 9129 (1965).
14. S. Patai, *The Chemistry of the Carbon Nitrogen Double Bond*, Wiley, New York, p. 468 (1970).

15. A. C. Dash, B. Dash and P. K. Mahapatra, *J. Chem. Soc., Dalton Trans.*, 1503 (1983).
16. B. E. Leach and D. L. Leussing, *J. Am. Chem. Soc.*, **93**, 3377 (1971).
17. F. A. Adam, *J. Chin. Chem. Soc.*, **34**, 111 (1987).
18. M. T. El-Haty and F. A. Adam, *Bull. Soc. Chim. France*, 284 (1983).
19. M. T. El-Haty, F. A. Adam and N. A. Abdalla, *J. Chin. Chem. Soc.*, **31**, 49 (1984).

[Received : 14 December 1989; Accepted : 1 February 1990]

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