

Reactions of Coordinated Ligands. I. Kinetics and Mechanism of Hydrolysis of N-Salicylideneaniline in the Presence of Metal Ions

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Abstract: The hydrolysis of N-salicylideneaniline Schiff base was studied in the presence and absence of Co(II), Ni(II), Cu(II), and Zn(II) ions in 10% ethanol-water medium. Proton-catalyzed addition of water at the aldimine linkage is suggested to be the rate-determining step for the hydrolysis of (1:1) metal chelates. The reactivity of the chelates was found to follow the reverse sequence of their stability constants. Zn(II) ion has been found to be the most effective catalyst in hydrolyzing the Schiff base.

The catalytic effect of metal ions has been recognized 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. Lately, a number of investigations have been devoted to exploring the effect of metal ions on the formation and hydrolysis¹⁻⁸ of such compounds. The present work was undertaken in order to (i) examine the kinetic course which the metal chelates of N-salicylideneaniline Schiff base follow during hydrolysis, (ii) find a correlation between the stability constants of the chelates and the rate constant of their hydrolysis, and (iii) correlate the catalytic efficiency of the metal ions with their electron-withdrawing ability from the chelate ring.

Experimental Section

Solutions of cobalt and zinc perchlorates were prepared from reagent grade metal carbonates and perchloric acid. Copper and nickel nitrate solutions were prepared from Analar samples. Metal ion contents of the solutions were estimated by standard procedures. Sodium perchlorate was used to maintain ionic strength. Propionate buffers were prepared from BDH reagent grade sodium hydroxide and propionic acid. All solutions were prepared in conductivity water.

N-Salicylideneaniline Schiff base was prepared by condensing salicylaldehyde with aniline in ethanol and was purified by recrystallization from the same solvent. It melted at 51.1° (lit.⁹ 51°).

The hydrolysis reaction was studied in 10% ethanol-water (v/v) medium. Dilute propionate buffers (the concentrations of sodium propionate and propionic acid were varied between 0.01 and 0.005 M and 0.01 and 0.0002 M, respectively) were used to control pH which varied from 5.37 to 6.86. pH measurements were made with a Marconi battery-operated pH meter, Model TF-511D. The glass electrode was standardized against phthalate (pH 4.01), acetate (pH 4.75), and phosphate (pH 6.86) buffers.

The concentration of Schiff base was varied between 4.2×10^{-5} and 1.8×10^{-4} M, and that of the metal ions was varied between 5.0×10^{-4} and 3.0×10^{-2} M. The rate of disappearance of the metal chelates as well as the Schiff base was followed spectro-

photometrically in a Hilger-Watt Uvispek spectrophotometer fitted with a thermostated cell block through which water from a thermostat was constantly circulated. Matched 3- and 1-cm quartz cells were used for optical density measurements.

Kinetics. A solution of sodium perchlorate, propionate buffer, absolute ethanol, and the metal perchlorate or nitrate in requisite amounts in conductivity water was allowed to equilibrate in the thermostat at $30.8 \pm 0.1^\circ$. The matched quartz cells were also allowed to equilibrate at the same temperature in the thermostated cell block.

After temperature equilibrium was attained, a known volume of the mixed solution was quickly transferred into the quartz cell. The reaction was initiated by rapidly injecting into the quartz cell a known volume of a freshly prepared solution of the Schiff base in absolute ethanol kept at $30.8 \pm 0.1^\circ$. In this way it was possible to record the first optical density reading at the preset wavelength within 20 sec of mixing the Schiff base. The reactions were studied under pseudo-first-order conditions and the rate constants were calculated from the $\log D_t - D_\infty$ vs. time plot. The rate constants were found to be reproducible within 10 and 20% when their magnitudes were of the order of 10^{-3} and 10^{-2} sec⁻¹, respectively. An identical procedure was adopted for following the hydrolysis of the Schiff base in the absence of metal ions.

Results

Equilibrium Constants. The zero-time spectra of N-salicylideneaniline indicates an absorption maximum at 430 m μ in the neutral region of pH. However, the absorbance of the Schiff base at the above wavelength was found to decrease with decrease in pH of the solution. Based on this, the extrapolated zero-time optical density of solutions (of the same total concentration of Schiff base) at different pH's was used to calculate the dissociation constant (K_{SH^+}) from the relationship

$$\frac{a}{D_0 - D} = \frac{1}{(E_1 - E_2)l} + \frac{K_{SH^+}}{(E_1 - E_2)l[H^+]} \quad (1)$$

where $a = [\text{Schiff base}]_{\text{total}}$, E_1 and E_2 are the extinction coefficients of the unprotonated and protonated Schiff base, respectively, l is the length of the light path in centimeters, D_0 is the optical density of the unprotonated Schiff base of concentration a , and D is that of the equilibrium mixture.

On representing the equilibrium between the metal ion and the Schiff base as



(where S and SM⁺ stand for unprotonated Schiff base and the (1:1) metal chelate, respectively), the equilibrium constant for the reaction is given by

- (1) G. L. Eichhorn and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 2905 (1953).
- (2) G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954).
- (3) G. L. Eichhorn and N. D. Marchand, *ibid.*, **78**, 2688 (1956).
- (4) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).
- (5) C. M. Harris, S. L. Lenzer, and R. L. Martin, *Aust. J. Chem.*, **14**, 420 (1961).
- (6) D. F. Martin and F. F. Cantwell, *J. Inorg. Nucl. Chem.*, **26**, 2219 (1964).
- (7) L. J. Nunez and G. L. Eichhorn, *J. Amer. Chem. Soc.*, **84**, 901 (1962).
- (8) D. L. Leussing and C. K. Stanfield, *ibid.*, **88**, 5726 (1966).
- (9) T. J. Lane and A. J. Kandathil, *J. Amer. Chem. Soc.*, **83**, 3782 (1961).

$$K_{SM^+} = \frac{[SM^+][H^+]}{[S][M^{2+}]} \quad (2)$$

If D is the optical density of the mixed solution (containing Schiff base and the metal ion) and E_3 and E_4 are the extinction coefficients of the metal ion and its chelate, respectively, then

$$D = E_1[S]_{free}l + E_2[SH^+]_{free}l + E_3[M^{2+}]_{free}l + E_4[SM^+]l \quad (3)$$

If D_2 is the optical density of the solution containing a fixed total concentration of the Schiff base b and D_3 is that of the solution containing metal ions only (D , D_2 , and D_3 being measured at the same pH), then eq 3 takes the form seen in eq 4, since $[M^{2+}]_{total} \gg [S]_{total}$.

$$D - D_2 - D_3 = (E_4 - E_1)[SM^+]l - \{(D_2 - E_1b)l - (E_1 - E_2)[SH^+]l\} \quad (4)$$

The Schiff base ($pK_{SH^+} = 4.76$) is expected to exist predominantly in the unprotonated form in the pH range 6.2–6.65 at which K_{SH^+} for the cobalt, nickel, and zinc chelates was determined. The equilibrium constant for the copper chelate was measured at pH 5.44 with $[Cu^{2+}]/[Schiff\ base] = 5, 10, 25, 30,$ and 50 , the total concentration of the Schiff base being $4.2 \times 10^{-5} M$. Under this condition it was observed that $D - D_2 - D_3 = D - D_2 > 2D_2$ and $\{(D_2 - E_1b)l - (E_1 - E_2)[SH^+]l\} \ll D_2$. In the case of the four metal ions, therefore, the concentration of the chelate is given by

$$[SM^+] = (D - D_2 - D_3)/(E_4 - E_1)l \quad (5)$$

Substituting the expression for $[SM^+]$ in eq 2 and taking into account the protonation equilibrium of the Schiff base, it is possible to get the relationship shown in eq 6.

$$\frac{b}{D - D_3 - D_2} = \frac{1}{(E_4 - E_1)l} + \frac{1}{(E_4 - E_1)l} \frac{[H^+] + K_{SH^+}}{K_{SH^+}(K_{SM^+})} \frac{[H^+]}{[M^{2+}]} \quad (6)$$

pK_{SH^+} and K_{SM^+} calculated from eq 1 and 6, respectively, are given in Table I.

Table I. Equilibrium Constants for the Chelates and the Dissociation Constant of the Schiff Base^a

Metal	$K_{SM^+} \times 10^4$	Wavelength of measurement, m μ
Co	1.10	370
Ni	11.80	380
Cu	478.4	380
Zn	0.46	370
$pK_{SH^+} = 4.76$ (3.83)		

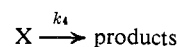
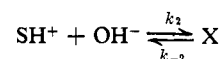
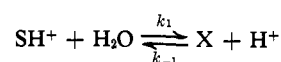
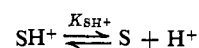
^a In 10% ethanol-water medium at $30.8 \pm 0.1^\circ$; $\mu = 0.2 M$.
^b T. J. Lane and A. J. Kandathil, *J. Amer. Chem. Soc.*, **83**, 3782 (1961).

Schiff bases capable of forming bicyclic chelate rings⁸ are known to be stabilized toward hydrolysis in the presence of metal ions under mild acidic conditions. However, bis(2-thiophenyl)ethylenediamine Schiff base,² which forms monocyclic chelates, is completely hydrolyzed in the presence of Cu(II) and Ni(II) ions. In the present study N-salicylideneaniline (which can form monocyclic chelate only) was also found to be completely hydrolyzed in the presence of metal ions.

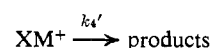
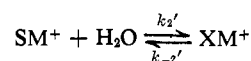
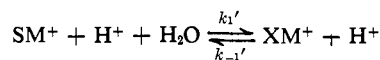
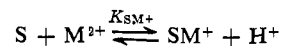
Discussion

The dissociation constants of N-salicylideneaniline (pK_{SH^+}) and its copper chelate (pK_d) have been determined by Lane and Kandathil⁹ at 25° in 50% dioxane-water medium by conventional potentiometric titration. The values reported by them are likely to be in error since no correction was made for the hydrolysis of the Schiff base and its copper chelate.¹⁰ The value for pK_{SH^+} (4.76) reported by us is surprisingly close to pK_a of aniline. As suggested by Cordes and Jencks¹¹ it is expected to be approximately 2 pH units lower than that of aniline, assuming that the hydroxy group behaves as a mere substituent. Dudek and Dudek¹² have reported that the Schiff base exists in keto-enol tautomeric equilibrium in methanol. The presence of such an equilibrium in the water-ethanol medium is expected to increase the pK_a of the Schiff base, and thus the observed pK_{SH^+} seems to be reasonable.

The hydrolysis of *o*-hydroxy Schiff bases up to the neutral region of pH involves the following paths.¹³



Assuming the additional metal ion-catalyzed paths¹⁴



and on making a steady-state approximation for the carbinolamine intermediates, the expression for the rate constant (k_{obsd}) takes the form seen in eq 7. In the ab-

$$k_{obsd} = \frac{\left\{ \frac{k_1 k_4 [H^+] + k_2 k_4 k_w}{k_{-1} [H^+] + k_{-2} + k_4} + (K_{SM^+})(K_{SH^+}) \times \frac{[M^{2+}]}{[H^+]} \frac{k_1' k_4' [H^+] + k_2' k_4'}{k_{-1}' [H^+] + k_{-2}' + k_4'} \right\}}{[H^+] + (K_{SH^+}) + (K_{SH^+})(K_{SM^+}) \frac{[M^{2+}]}{[H^+]}} \quad (7)$$

$$k_{obsd} = \frac{(k_1 k_4 [H^+] + k_2 k_4 k_w) / (k_{-1} [H^+] + k_{-2} + k_4)}{([H^+] + (K_{SH^+}))} \quad (8)$$

sence of metal ions eq 7 reduces to eq 8. The pH-rate profile observed in the hydrolysis of *o*-hydroxy-N-ben-

(10) K. K. Chatterjee, N. Farrier, and B. E. Douglas, *J. Amer. Chem. Soc.*, **85**, 2919 (1963).

(11) E. H. Cordes and W. P. Jencks, *ibid.*, **84**, 832 (1962).

(12) G. O. Dudek and E. P. Dudek, *ibid.*, **88**, 2406 (1966).

(13) W. Bruyneel, J. J. Charette, and E. de Hoffmann, *ibid.*, **88**, 3808 (1966).

(14) X, XM^+ , SM^+ , and S represent the carbinolamine, the coordinated carbinolamine, the Schiff base chelate, and the free Schiff base, respectively.

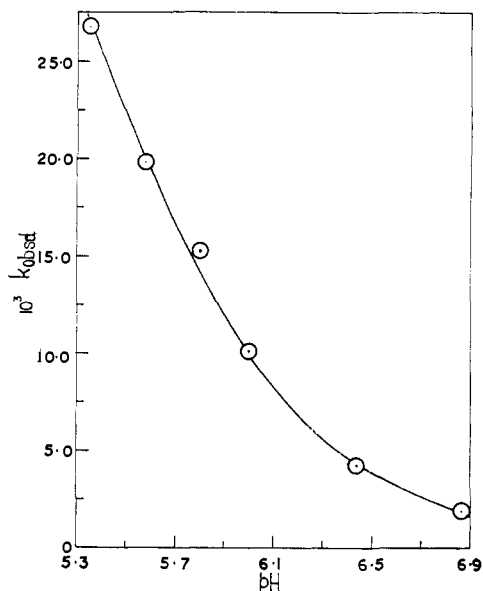


Figure 1. Plot of $10^3 k_{\text{obsd}}$ vs. pH for hydrolysis of N-salicylideneaniline in the absence of metal ions.

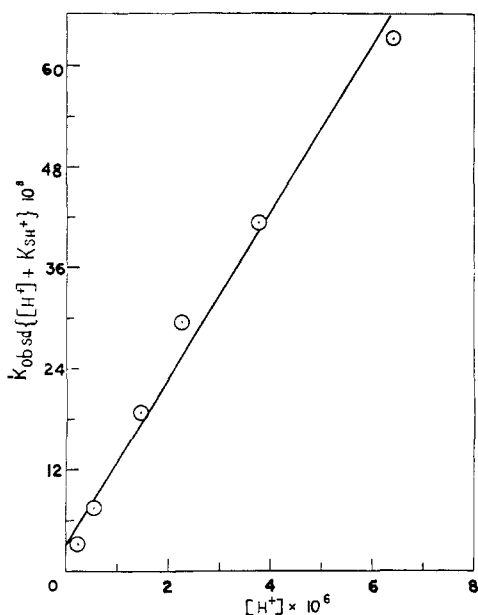


Figure 2. Plot of $10^3 k_{\text{obsd}}\{[H^+] + K_{\text{SH}^+}\}$ vs. $10^6 [H^+]$ for the hydrolysis of N-salicylideneaniline in the absence of metal ions.

ylidene-2-aminopropane¹³ indicates that (i) below pH 2 the decomposition of the carbinolamine is rate determining, and (ii) the attacks of water and hydroxide ion on the protonated Schiff base are the rate-determining steps in the region of pH 2–4 and 6–8, respectively.

In view of the similarity in the pH-rate profile (Figure 1) of N-salicylideneaniline with that of *o*-hydroxy-N-benzylidene-2-aminopropane¹³ in the pH range studied (5.37–6.86), it appears reasonable to assume that $k_4 > k_{-1}[H^+] + k_{-2}$. On the basis of such an assumption, eq 8 reduces to the form

$$k_{\text{obsd}} = (k_1[H^+] + k_2k_w)/([H^+] + K_{\text{SH}^+}) \quad (9)$$

The values of k_1 and k_2 (based on $k_w = 3.0 \times 10^{-14}$ at $\mu = 0.2 M$ and 30°) obtained from the slope and intercept of $k_{\text{obsd}}\{[H^+] + K_{\text{SH}^+}\}$ vs. $[H^+]$ plot (Figure 2)

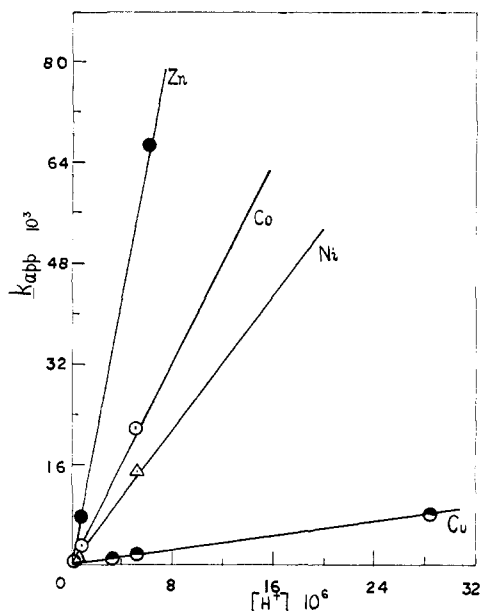


Figure 3. Plot of $10^3 k_{\text{app}}$ vs. $10^6 [H^+]$ for the hydrolysis of metal chelates: ●, Zn; ○, Co; △, Ni; and ●, Cu.

are found to be 0.108 min^{-1} (after correction for molar concentration of water) and $6.0 \times 10^7 M^{-1} \text{ min}^{-1}$, respectively. It is interesting to see that the rate constants for the hydrolysis of N-salicylideneaniline are of the same order of magnitude as those for *o*-hydroxy-N-benzylidene-2-aminopropane ($k_1 = 0.125 \text{ min}^{-1}$, $k_2 = 7.2 \times 10^7 \text{ min}^{-1} M^{-1}$).¹³ However, the smaller values of the rate constants for the former indicate greater hydrolytic stability of the *o*-hydroxy Schiff bases derived from aromatic amines compared to their aliphatic analogs.

The apparent rate constants for the hydrolysis of the Schiff base chelates

$$k_{\text{app}} = \frac{k_1'k_4'[H^+] + k_2'k_4'}{k_{-1}'[H^+] + k_{-2}' + k_4'} \quad (10)$$

were evaluated by plotting $k_{\text{obsd}}\{[H^+] + (K_{\text{SH}^+}) + (K_{\text{SH}^+})(K_{\text{SM}^+})([M^{2+}]/[H^+])\}$ vs. $(K_{\text{SM}^+})(K_{\text{SH}^+})([M^{2+}]/[H^+])$ (eq 7). Similar plots in the copper system ($[Cu^{2+}]/[\text{Schiff base}] > 25$) at pH 5.44 and 5.64 resulted in zero intercept which is reconciled with the hydrolysis of the chelate alone.

It is evident that the rate constants, k_{app} (given in Table II), are pH dependent in all cases and the plots of

Table II. Rate Constants for Hydrolysis of Metal Chelates^a

Metal	pH	$k_{\text{app}}, \text{sec}^{-1} \times 10^3$	$k_1', \text{sec}^{-1} \times 10^{-3}$
Co	5.45 ± 0.02	21.59	3.8
	6.20 ± 0.03	2.24	
	6.66 ± 0.02	1.22	
Ni	5.44 ± 0.02	15.10	2.4
	6.44 ± 0.02	0.94	
Cu	4.70 ± 0.04	8.38	0.29
	5.44 ± 0.02	1.36	
Zn	5.64 ± 0.02	0.83	10.6
	6.27 ± 0.03	7.77	

^a At $30.8 \pm 0.1^\circ$; $\mu = 0.2 M$.

k_{app} vs. $[H^+]$ (Figure 3) are linear with a vanishing intercept. This indicates that the rate-determining step for

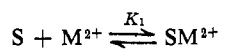
hydrolysis of metal chelates involves proton-catalyzed addition of water at the aldimine linkage in the range of pH at which the present investigation was carried out. On the basis of such a mechanism, k_{app} (eq 10) reduces to

$$k_{app} = k_1[H^+] \quad (11)$$

assuming $k_1'k_4'[H^+] \gg k_2'k_4'$ and $k_4' \gg k_{-1}[H^+] + k_{-2}'$. The rate constants (k_1') estimated from the above relationship have been collected in Table II.

Arranging the chelates (SM^+) in increasing order of their formation constants and hence in increasing order of thermodynamic stability as $CuS^+ > NiS^+ > CoS^+ > ZnS^+$, their kinetic lability (toward hydrolysis) follows the sequence: $ZnS^+ > CoS^+ > NiS^+ > CuS^+$. It has also been observed in the case of copper(II) and nickel(II) ion-catalyzed hydrolysis of bis(2-thiophenyl)ethylenediamine² that the latter ion exerts greater catalytic effect than copper from the consideration of observed rate constants. Although the Schiff base involved in the present study is not structurally similar to bis(2-thiophenyl)ethylenediamine, identical results obtained in both cases indicate a general reactivity sequence of Schiff base chelates toward hydrolytic degradation. Further, a linear correlation between $\log k_1'$ and $\log K_{SM^+}$ (Figure 4) is found to be satisfied in the present investigation.

Representing the equilibria between the Schiff base and the metal ions as



the equilibrium constant K_{SM^+} can be expressed as $K_{SM^+} = K_1K_2$. It is expected that both K_1 and K_2 will

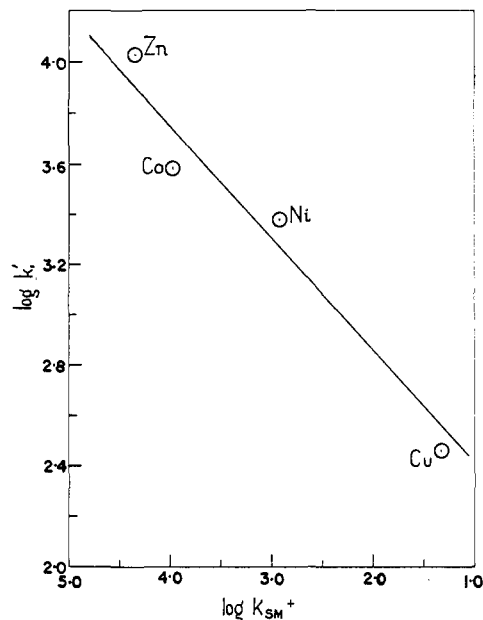


Figure 4. Plot of $\log k_1'$ vs. $\log K_{SM^+}$.

follow the sequence observed for K_{SM^+} . This means that the order in which the metal ions increase the acidity of the coordinated Schiff base (SM^{2+} species), which is a measure of their electron-withdrawing tendencies, is given by $Cu(II) > Ni(II) > Co(II) > Zn(II)$. From the k_1' values, the stabilizing influence of metal ions on the aldimine linkage is also seen to decrease in the sequence $Cu(II) > Ni(II) > Co(II) > Zn(II)$. Thus it is evident that the catalytic efficiencies of the metal ions concerned in the hydrolysis of N-salicylidene-aniline Schiff base are inversely related to their electron-withdrawing abilities from the reaction center.