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Mechanism of Formation of Schiff Base Complexes. Part II. Reaction of Cu(bis-salicylaldehyde) with Primary Amines

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A kinetic study on the reaction between Cu(bis-salicylaldehyde) and primary amines is reported. Two stages were observed having different kinetic laws. The rate of the first stage is, in fact, slowed as $[CH_3O^-]$ *increases whereas the second stage is unaffected by the presence of methoxide. The observed effect of* CH_3O^-, *in the first stage, is interpreted considering a competition between methoxide and amine for the same site of attack on the carbonyl carbon of the* $[Cu(SA)(RNH_2)_2]^+$ *ion, whereas the second stage is attributed to a reaction of* SA^- *with* $RNH_2 \cdot Cu(SN)_2$ *(*SN^- *= salicylalaldiminato ion) complexes were always detected as final products.*

Introduction

Metal–Schiff-base complexes have been very well known for long time. Preparation methods include reactions both of salicylaldehyde complexes with primary amines or of Schiff bases with metal ions [1]. The mechanism of such reactions is of great importance in biochemistry. Several enzymes involved in aminoacid metabolism, notably aminotransferases and decarboxylases, require, in fact, pyridoxal phosphate as cofactor [2]. It was postulated independently by several authors [3, 4] that all such processes involve formation of a Schiff base between the aminoacid and the pyridoxal phosphate as the first stage.

Many of these enzymic reactions are also accelerated by the presence of a metal ion, an aminoacid and an analog of pyridoxal phosphate. Furthermore Schiff base formation, in the absence of metal ions, proceeds through the well known mechanism involving nucleophilic attack of an amine on a carbonyl compound to form a carbonilamine, which subsequently dehydrates. Both stages are reversible and subject to acid–base catalysis [5, 6].

The peculiarity of these systems prompted a great deal of research concerning both the factors affecting Schiff base formation and hydrolysis in solution [7] and the effect of a metal on the mechanism of these reactions [8].

In a previous paper we reported our results concerning reactions of primary amines with $Ni(SA)_2$ (SA^- = salicylaldehydato ion) or uncoordinated aldehydes [9].

This paper extends the earlier investigation to a mechanistic study of the reaction between $Cu(SA)_2$ and several primary amines such as n-butylamine, ethylamine and sec-butylamine in methanol at 25 °C and $\mu = 0.15$.

Experimental

$Cu(SA)_2$ and $Cu(SN)_2$ complexes (SA^- = salicylaldehydato ion, SN^- = salicylaldiminato ion) were prepared as reported in the literature [10, 11].

$Cu(SN)_2$ complexes were also prepared by using the same kinetic conditions. All amines were distilled before use and stored under argon in the dark.

Bis-μ-methoxo-bis(salicylaldehyde)copper(II), $[Cu(SA)(OCH_3)]_2$

300 mg of $Cu(SA)_2$ in 150 ml of CH_3OH react with a stoichiometric amount of CH_3ONa. A dark green compound precipitated, which was washed several times with CH_3OH. The I.R. spectrum of the compound shows a broad and intense band centered at 1630 cm^{-1} attributable to the $\nu C{=}O$ stretching and another one at 1050 cm^{-1} due to the $\nu O{-}C$ stretching of the $>OCH_3$ bridge. A molecular weight determination in CH_2Cl_2 gave a value of 450 (theor. 431.3). *Anal.* Found: C = 44.18%; H = 3.83%; O = 23.06%. Theor.: C = 44.1%; H = 3.72%; O = 22.25%.

The same compound was also obtained on leaving $Cu(SA)_2$ in methanol for several days.

Salicylaldehyde-bipyridyl-copper(II) Hexafluorophosphate, $[Cu(SA)Bipy]PF_6$

1 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 150 ml of CH_3OH containing 18% by volume of water reacts with 1

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*For Part 1 of this series see reference 9.

TABLE I. Values of Kinetic Constants for the First Stage of Reactions of $Cu(SA)_2$ with Primary Amines at 25 °C.

Amine	$10^2[RNH_2]$	$10^2[CH_3O^-]$	$[ClO_4^-]$	$10^3\ k_{obs(1)}(sec^{-1})$	$1/k_{obs(1)}$
n-butylamine	0.79		0.15	30.6	
	1.58		0.15	46	
	3.95		0.15	90	
	11.7		0.15	190	
	0.56	3.75	0.112	3	
	2.8	3.75	0.112	22	
	5.6	3.75	0.112	43	
	11.3	3.75	0.112	78	
	2.8	0.375	0.146	55	18.18
	2.8	0.75	0.142	41	24.39
	2.8	1.5	0.135	33.6	29.76
	2.8	3.75	0.112	24	41.66
	8.7	0.25	0.147	138	7.24
	8.7	0.5	0.145	118	8.47
	8.7	1.0	0.14	110	9.1
	8.7	2.0	0.13	60	16.6
ethylamine	0.45		0.15	10.9	
	0.9		0.15	23.7	
	1.81		0.15	37	
	4.53		0.15	70	
	9.05		0.15	115	
	0.92	0.375	0.146	14.5	
	1.85	0.375	0.146	25	
	3.7	0.375	0.146	50	
	1.69	0.375	0.146	20.7	48.3
	1.69	0.75	0.142	16	62.5
	1.69	1.15	0.135	10	100
sec-butylamine	1.17		0.15	7.15	
	2.34		0.15	10.6	
	5.85		0.15	19.3	
	11.7		0.15	31.0	

mmol of CH_3ONa and 1 mmol of 2,2′-bipyridyl. By adding NH_4PF_6, [Cu(SA)Bipy]PF_6 precipitates. The compound behaves as 1:1 electrolyte in methanol and its I.R. spectrum shows a band at 1605 cm^{-1} (v.s.) due to $\nu C{=}O$ stretching and ring vibrations of bipyridyl and a very strong and broad band centered at 845 cm^{-1} due to the PF_6 ion. *Anal.* Found: C = 42.02%; H = 2.73%; N = 5.74%. Theor. C = 42.00%; H = 2.78%; N = 5.76%. On leaving the nitrate solution at –20 °C, [Cu(SA)Bipy]NO_3 can be obtained.

Kinetics

Separate solutions of the complex and reagents were prepared in methanol. The concentration of added CH_3O^- was determined by standard titrimetric methods before mixing it with amine solutions.

The ionic strength was maintained constant at the value of 0.15 *M*. The reagent solutions were separately brought to reaction temperature, then mixed in the thermostated cell of an OPTICA CF4R double beam recording spectrophotometer and the kinetics followed by observing absorption changes in the U.V. region of the spectrum. Any single kinetic run was carried out with a concentration of amine large enough to provide pseudo-first-order conditions.

All kinetics, carried out in the presence of added methoxide, were performed by adding to methanol solutions of $Cu(SA)_2$ solutions containing both CH_3O^- and amines.

For a two-stage reaction the expression relating to the absorbance may be written in the form:

$$A_t = a_1 e^{-k_{obs(1)}t} + a_2 e^{-k_{obs(2)}t} + A_\infty$$

where A_t is the total absorbance of the solution at different times, a_1 and a_2 are constants, A_∞ is the absorbance of the solution at the end of the reaction and $k_{obs(1)}$ and $k_{obs(2)}$ are pseudo-first-order rate constants respectively for the first and the second stage. Values of $k_{obs(2)}$ and of a_2 were then calculated respectively from slopes and intercepts of linear plots of $\lg(A_t - A_\infty)$ *versus* time for the last points of kinetics whereas values of $k_{obs(1)}$ were obtained

TABLE II. Values of Kinetic Constants for Reactions of $Cu(SA)_2$ with Primary Amines Performed in the Presence of $Cu(NO_3)_2$; ($[Cu(SA)_2]/[Cu(NO_3)_2] = 1$).

Amine	$10^2[RNH_2]$	$[ClO_4^-]$	10^3 $k_{obs(1)}$ (sec^{-1})
n-butylamine	1.2	0.15	30
	2.4	0.15	50
	3.5	0.15	72
	4.8	0.15	88
	8.5	0.15	140
	12.0	0.15	180
ethylamine	0.45	0.15	17.8
	0.9	0.15	28
	1.8	0.15	47
	4.53	0.15	80
	9.06	0.15	120
sec-butylamine	0.63	0.15	3.4
	1.26	0.15	6.0
	6.3	0.15	20.5
	12.6	0.15	32.2

from slopes of linear plots of $\lg\{A_t - (A_\infty + a_2e^{-k_{obs(2)}t})\}$ against time [12]. In any case the least-squares method was used.

Results

Methanol solutions of $Cu(SN)_2$ and basic methanol solutions of $Cu(SA)_2$ follow the Lambert–Beer law in a wide range of the U.V. spectrum. $Cu(SA)_2$ reacts with all amines used according to the following reaction:

$$Cu(SA)_2 + 2RNH_2 \longrightarrow Cu(SN)_2 + 2H_2O \quad (1)$$

and two stages were observed.

The reaction [1] is more neat than that of $Ni(SA)_2$. In the latter case association of $Ni(SN)_2$ with RNH_2 can occur, at the end of the reaction, as the concentration of amine increases.

Kinetic calculations were performed at the wavelength showing the bigger absorption variation between the starting and the final spectrum.

Final spectra were always identical to those of authentic samples of $Cu(SN)_2$. Kinetic runs were also recorded in the presence of a 1:1 ratio of $[Cu(SA)_2]:[Cu(NO_3)_2]$ and a single stage was, in this case, detected.

Observed rate values, $k_{obs(1)}(sec^{-1})$, for the first stage of reactions of $Cu(SA)_2$ and primary amines, determined under various conditions, are reported in Table I.

Table II includes kinetic data relative to the reaction of $Cu(SA)_2$ with primary amines in the presence of $Cu(NO_3)_2$, $[Cu(SA)_2]/[Cu(NO_3)_2] = 1$. Figure 1 shows the dependence of $k_{obs(1)}(sec^{-1})$ values on $[RNH_2]$ in the absence of added CH_3O^- and with or without $Cu(NO_3)_2$.

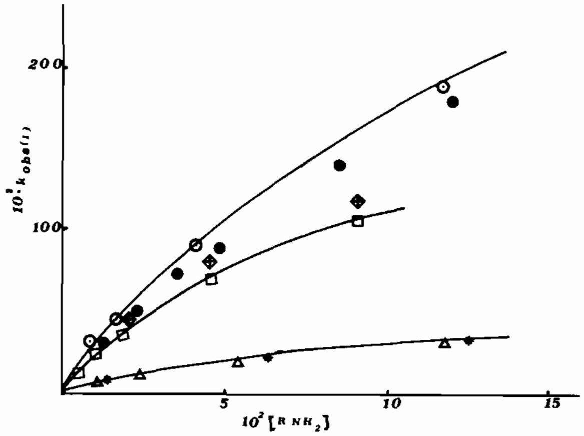


Figure 1. Plots of $k_{obs(1)}$ values against $[RNH_2]$ in the first stage of the reaction of $Cu(SA)_2$ alone or with $Cu(NO_3)_2$, ($[Cu(SA)_2]/[Cu(NO_3)_2] = 1$) with primary amines; ⊙ RNH_2 = n-butylamine; ● RNH_2 = n-butylamine, $[Cu(SA)_2]/[Cu(NO_3)_2] = 1$; □ RNH_2 = ethylamine; ◆ RNH_2 = ethylamine, $[Cu(SA)_2]/[Cu(NO_3)_2] = 1$; △ RNH_2 = sec-butylamine; ∗ RNH_2 = sec-butylamine, $[Cu(SA)_2]/[Cu(NO_3)_2] = 1$.

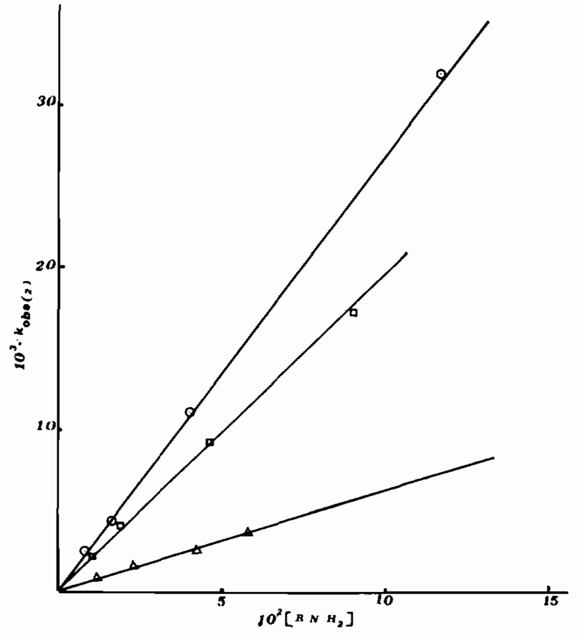


Figure 2. Linear plots of $k_{obs(2)}$ values against $[RNH_2]$ in the second stage of the reaction of $Cu(SA)_2$ with primary amines; ⊙ RNH_2 = n-butylamine; □ RNH_2 = ethylamine; △ RNH_2 = sec-butylamine.

Table III lists observed rate constants $k_{obs(2)}$ (sec^{-1}) for the second stage of $Cu(SA)_2$ reactions. A linear dependence on the amine concentration is always observed as shown in Fig. 2.

TABLE III. Values of Kinetic Constants for the Second Stage of Reactions of $Cu(SA)_2$ with Primary Amines at 25 °C.

Amine	$10^2[RNH_2]$	$10^2[CH_3O^-]$	$[ClO_4^-]$	$10^3k_{obs(2)}(sec^{-1})$	$10^2k_{obs(2)}(sec^{-1})$
n-butylamine	0.79		0.15	2.4	
	1.58		0.15	4.37	
	3.95		0.15	11	26.6
	11.7		0.15	32	
	0.56	3.75	0.112	0.98	
	2.8	3.75	0.112	5.90	22
	5.6	3.75	0.112	12	
	11.2	3.75	0.112	24	
	2.8	0.375	0.146	7.3	
	2.8	0.750	0.142	7	
	2.8	1.5	0.135	6.4	
	2.8	3.75	0.112	6.4	
	8.7	0.25	0.147	17.8	
	8.7	0.5	0.145	18.2	
	8.7	1.00	0.14	18.5	
	8.7	2.00	0.13	18	
ethylamine	0.45		0.15	1.15	
	0.9		0.15	2.26	
	1.8		0.15	4.16	19.4
	4.56		0.15	9.2	
	9.1		0.15	17	
	0.9	0.375	0.146	1.5	
	1.8	0.375	0.146	3.7	18
	3.7	0.375	0.146	6.2	
	7.4	0.375	0.146	13	
	1.7	0.375	0.146	3.7	
	1.7	0.750	0.142	4	
	1.7	1.5	0.135	3.8	
sec-butylamine	1.17		0.15	0.90	
	2.34		0.15	1.59	6.2
	4.25		0.15	2.75	
	5.85		0.15	3.70	

Values of second order rate constants, $k_{O(2)}$, determined as slopes of plots in Fig. 2 are included in Table III. Whereas the second stage is practically unaffected by the presence of methoxide in solution, the rate of the first stage is slowed down as $[CH_3O^-]$ increases. Fig. 3 and Fig. 4 refer to the first stage and report respectively the linear dependence of $k_{obs(1)}$ on $[RNH_2]$ in the presence of a constant $[CH_3O^-]$ and plots of $1/k_{obs(1)}$ against the concentration of added methoxide at constant $[RNH_2]$.

These results indicate, for the first stage, an overall kinetic law of the form:

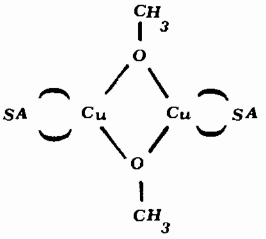
$$k_{obs(1)} = \frac{a[RNH_2]}{b[CH_3O^-] + c} \qquad (2)$$

and for the second stage:

$$k_{obs(2)} = k_{o(2)}[RNH_2] \qquad (3)$$

Discussion

By adding to a methanol solution of $Cu(SA)_2$, in equimolar amount, CH_3O^- we could isolate a new compound which, on the basis of elemental analysis and M.W. measurements, can be formulated as:



A possible pathway to the dimer may be the following:

$$\begin{tikzcd} Cu(SA)_2 \arrow[r, shift left] & \backslash Cu(SA)^+ / + SA^- \arrow[l, shift left] \arrow[d, "CH_3O^-"] \\ & -Cu(SA)(OCH_3) \arrow[d] \\ & \tfrac{1}{2}[Cu(SA)(OCH_3)]_2 \end{tikzcd} \quad (4)$$

By reacting $[Cu(SA)(OCH_3)]_2$ with primary amines, rate data obtained were completely different from those observed with $Cu(SA)_2$. It can, then, be deduced that the dimer is not involved, at least directly, in Schiff base formation starting from $Cu(SA)_2$ and primary amines.

In order to elucidate the mechanism of reaction (1) we prefer to discuss, first of all, kinetic values relative to the second stage. Values of $k_{o(2)}$ are, indeed, very close to those previously determined for salicylaldehyde reactions [9]:

$$(k''_{o(n\text{-butylamine})} = 0.26\,M^{-1}\,sec^{-1};\ k''_{o(ethylamine)} = 0.19\,M^{-1}\,sec^{-1};\ k''_{o(s\text{-butylamine})} = 0.061\,M^{-1}\,sec^{-1})$$

Again, similarly to salicylaldehyde reactions, second-order rate constants, $k_{o(2)}$, are unaffected by the presence of CH_3O^- in solution. The second stage may then be due to Schiff base formation from SA^- and primary amines. Accordingly, when Cu^{2+} is added in equimolar amount, $([Cu^{2+}]/[Cu(SA)_2] = 1)$, to methanol solutions containing $Cu(SA)_2$ and primary amines, the second stage disappears.

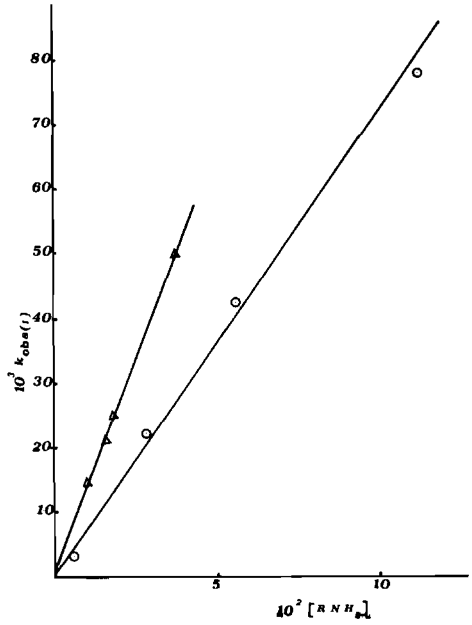


Figure 3. Linear plots of $k_{obs(1)}$ values against $[RNH_2]$ in the presence of a constant concentration of added CH_3O^- the first stage of the reaction of $Cu(SA)_2$ with primary amines. △ RNH_2 = n-butylamine, $[CH_3O^-] = 3.75 \times 10^{-2}$; ⊙ RHN_2 = ethylamine, $[CH_3O^-] = 3.75 \times 10^{-3}$.

The equilibrium constant for the reaction:

$$Cu^{2+} + SA^- \rightleftharpoons {>}Cu(SA)^+ \quad (5)$$

is 2.3×10^5 in water at 25 °C and $\mu = 0.5$ [13] and it should be expected that SA^- is largely complexed by Cu^{2+} contributing to the disappearance of the second stage. Taking into account, only as an order of magnitude, analytical constants relative to the systems:

$$\begin{aligned} &Cu^{2+} + SA^- \rightleftharpoons Cu(SA)^+ \\ &Cu^{2+} + 2\,SA^- \rightleftharpoons Cu(SA)_2 \end{aligned} \quad (6)$$

calculated in water at 25 °C and $\mu = 0.5$ ($\beta_1 = 2.3 \times 10^5$; $\beta_2 = 1.28 \times 10^{10}$) the monocationic species, $[Cu(SA)]^+$, should be present in appreciable concentration when Cu^{2+} and $Cu(SA)_2$ are dissolved in methanol solutions. Furthermore kinetic values relative to runs performed by reacting primary amines with $Cu(SA)_2$ and $Cu^{2+}([Cu^{2+}]/[Cu(SA)_2] = 1)$ fit those of the first stage of reaction 1 (Fig. 1) indicating that the same species is involved in the paths considered.

Indeed the dependence of $k_{obs(1)}(sec^{-1})$ values on $[CH_3O^-]$, shown in Fig. 4, suggests an interaction of methoxide with a salicylaldehydato–copper(II) complex and we propose the following equilibria in order to explain the experimental results:

$$\begin{aligned} &[Cu^{2+} + Cu(SA)_2 \xrightleftharpoons{RNH_2} \\ &\quad 2[Cu(SA)(RNH_2)_2]^+ \xrightleftharpoons{CH_3O^-} \\ &\qquad 2[Cu(SA)(OCH_3)(RNH_2)_n] + x\,RNH_2 \end{aligned} \quad (7)$$

or in the absence of Cu^{2+}:

$$\begin{tikzcd} Cu(SA)_2 \arrow[r, shift left, "RNH_2"] & {[Cu(SA)(RNH_2)_2]^+ + SA^-} \arrow[l, shift left] \arrow[d, "CH_3O^-"'] \\ & {[Cu(SA)(OCH_3)(RNH_2)_n] + x\,RNH_2} \end{tikzcd} \quad (8)$$

Coordination of amines to Cu^{2+} is quite straightforward considering the high affinity of ammonia to bind copper(II) [14] and contributes to shift equilibria (7) and (8) towards the right. Accordingly, when a ten-fold excess of n-butylamine is added to a 1.5×10^{-3} *M* methanol solution of $Cu(SA)_2$ at 20 °C the conductivity immediately jumps from 26.3×10^{-6} ohm^{-1} to 194×10^{-6} ohm^{-1} and then slowly

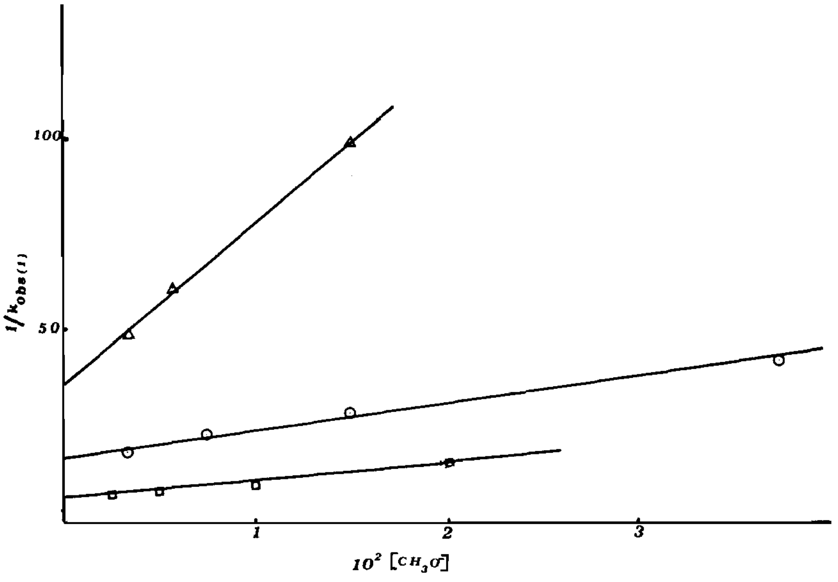


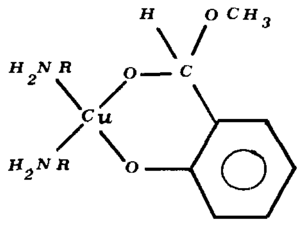
Figure 4. Linear plots of $1/k_{obs(1)}$ values against $[CH_3O^-]$ at constant $[RNH_2]$ in the first stage of the reaction of $Cu(SA)_2$ with amines; ⊙RNH_2 = n-butylamine, $[RNH_2] = 2.8 \times 10^{-2}$; □$RNH_2$ = n-butylamine, $[RNH_2] = 8.7 \times 10^{-2}$; △ RNH_2 = ethylamine, $[RNH_2] = 1.69 \times 10^{-2}$.

decays owing to $Cu(SN)_2$ formation. This is a clear indication that ionic species are formed, in a fast step, when RNH_2 is added to $Cu(SA)_2$.

The value of n may be 1 or 2 and that of x 1 or 0 respectively depending on the site of attack of CH_3O^-: the coordinating metal, as pathway 4 suggests, or also the carbonyl group.

Interestingly we note that the νCO stretching frequency for $Cu(SA)_2$ (1608 cm^{-1}) is lower than that observed for $Ni(SA)_2$ (1652 cm^{-1}), indicating a more ionic type of linkage in the first case [15]. Although we can exclude that the dimer $[Cu(SA)(OCH_3)]_2$ is involved in our kinetic reactions, its precursor $-CuSA(OCH_3)$, however, may be stabilized in solution by coordination with RNH_2. Therefore two structures are possible for $Cu(SA)(OCH_3)(RNH_2)_n$.

Indeed equation (2) may be reasonably accounted considering a competition between CH_3O^- and amine for the same site of attack on the carbonyl carbon of the salicylaldehydato coordinated group so that the value of n may be two and an attack of methoxide on the carbonyl group should occur:



In order to confirm this hypothesis we prepared a new compound, $[Cu(SA)(Bipy)]PF_6$ (Bipy = 2,2'-bipyridyl)(E) structurally similar to $[Cu(SA)(RNH_2)_2]^+$.

By reacting $[Cu(SA)(Bipy)]PF_6$ with amines both in the presence and in the absence of added CH_3O^- we observed a kinetic behaviour of (E) very similar to that of the first stage of reaction (1) [16].

Taking into account all these observations a possible mechanism for the first stage is shown in the scheme on page 195.

Since no intermediate was observed during the first stage of reaction (1) we can apply to the carbinolamine derivative (C) the steady step approximation and the following kinetic expression may be derived:

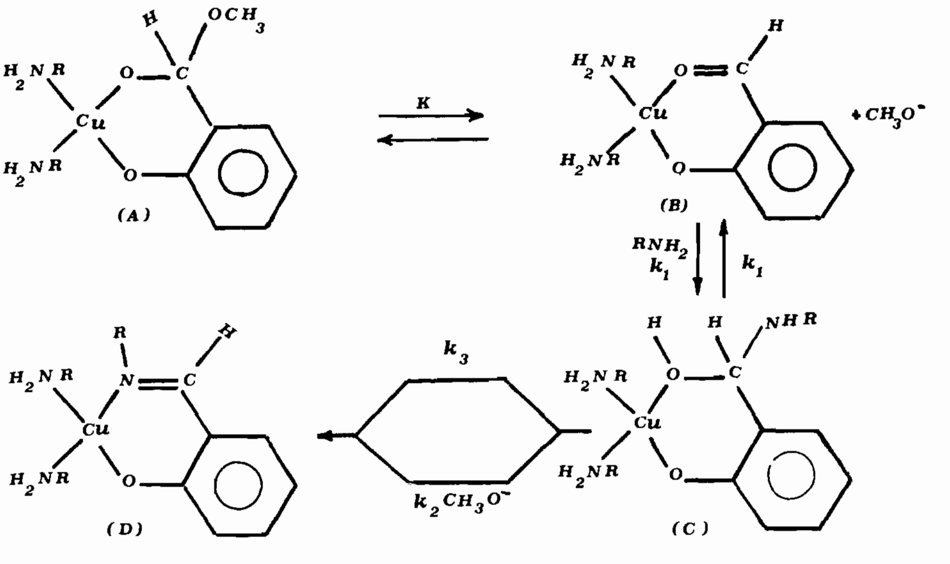
$$\frac{1}{[\text{complex}]_o}\frac{dD}{dt} = k_{obs} = \tag{9}$$

$$\frac{\{k_2[CH_3O^-] + k_3\}\,Kk_1\,[RNH_2]}{([CH_3O^-] + K)\,\{k_{-1} + k_3 + k_2[CH_3O^-]\}}$$

Eq. (9), if $k_2[CH_3O^-] \gg k_3$ and if $[CH_3O^-] \gg K$, reduces to:

$$k_{obs} = \frac{k_2 k_1 K [RNH_2]}{k_{-1} + k_2 [CH_3O^-]} \tag{10}$$

Eq. 10 is identical to kinetic law (2) if $k_2k_1\,K = a$, $k_{-1} = b$, $k_2 = c$. The assumption that $[CH_3O^-] \gg K$ allows the interesting observation that equilibrium A ⇌ B must be shifted towards A. This also implies that the main species of equilibrium (7) is $[Cu(SA)(OCH_3)(RNH_2)_n]$ and those of equilibrium (8) are $[Cu(SA)(OCH_3)(RNH_2)_n]$ and SA^- at least in the presence of added CH_3O^-.



Scheme. Proposed mechanism for the first stage of reaction (1) (All charges on the complexes have been omitted.)

Furthermore the CH_3O^- attack on the carbonyl carbon atom should be fast with respect to that of amines because of the higher basicity of methoxide.

The final product of the first stage is postulated to be $[(RNH_2)_2Cu(SN)]^+$. Indeed when we performed an experiment using $Cu(SA)_2$ and $Cu(NO_3)_2$, in equimolar amount, and an excess of n-butylamine (1:10), the colour of the methanol solution faded from deep yellow to deep green and by adding $NaBPh_4$ and water we isolated a new compound which shows a broad band centered at 3200 cm^{-1}, attributable to ν_{N-H} stretchings of coordinated amines, a broad and intense band centered at 1600 cm^{-1} attributable to the $\nu_{C=N}$ stretching of a coordinated salicylaldiminato group and very strong bands at 710 cm^{-1} and 740 cm^{-1} due to out-of-plane aromatic hydrogen bending of the BPh_4 group. The last bands are not present, in fact, in the I.R. spectrum of $Cu(SN)_2$. The compound may be formulated as $[Cu(SN)(n\text{-butylamine})_2]BPh_4$, behaves as 1:1 electrolyte in a methanol solution and during the time decomposes.

Taking into account our previous observations, the second stage may be only due to the reaction:

$$SA^- + RNH_2 \longrightarrow SN^- + H_2O$$

and, since no other stage was experimentally observed, SN^- should react fast with the final product of the first stage giving $Cu(SN)_2$:

$$\left[\begin{matrix} H_2NR \\ \quad \diagdown Cu(SN) \\ \quad \diagup \\ H_2NR \end{matrix}\right]^+ + SN^- \xrightarrow{\text{fast}} Cu(SN)_2 + 2RNH_2 \qquad (11)$$

The high nucleophilicity of SN^- and the stability of $Cu(SN)_2$ complexes account for reaction (11).

Plots in Fig. 4 allow also an interpretation of the dependence of $k_{obs(1)}(sec^{-1})$ values on $[RNH_2]$ in Fig. 1. All amines used are in fact basic [14] enough to account for the following reaction:

$$RNH_2 + CH_3OH \rightleftharpoons RNH_3^+ + CH_3O^-$$

CH_3O^-, of course, depends on $\sqrt{[RNH_2]}$ so that according to eq. (9), plots in Fig. 1 must flatten as $[RNH_2]$ increases.

It may be that all simplifications introduced to derive eq. (10) are not possible in this case since the methoxide concentration is not so high to allow them.

There are, now, in the literature interesting results concerning the effect of metal ions on the rates of formation of Schiff bases from salicylaldehyde and aminoacids or primary amines [8, 17]. It has been found that several polarizing metal ions such as Cu^{2+}, and Ni^{2+} are kinetically inactive in these reactions whereas others, such as Cd^{2+}, Pb^{2+}, Mn^{2+}, Mg^{2+} and Zn^{2+} favour these processes. In order to explain the observed behaviour the promnastic effect was postulated [8]. It was proposed that the presence of the metal ion principally serves to lower the order of the reaction from the second to a first order, the reaction occurring within a mixed complex in which the reactants are loosely bound to the metal [8].

All evidences, here presented, allow the conclusion that $[(RNH_2)_2Cu(SA)]^+$ is a reactive species; however the dependence of the rate on $[RNH_2]$, shown in Fig. 1 and in Fig. 3, would suggest that an external attack of primary amines is involved in the first stage reaction. Ligand-field forces, which are present in Cu(II) ions owing to unfilled *d* orbitals, cause the ligands to be bounded to well defined coordination site and to be prevented from reacting.

The comparison between the reactivity of $Ni(SA)_2$ and that of $Cu(SA)_2$ in methanol towards primary amines deserves also some comments. It is already known that $Cu(SA)_2$ is more stable than $Ni(SA)_2$ [13]; therefore the different reactivity of the Ni(II) complex, which reacts as bis-chelated compound [9], may be attributed to the higher affinity of salicylaldehydato–copper(II) complexes towards CH_3O^- and amines as shown by equilibria (7) and (8).

Finally we observe that the order of reactivity is always, in the first and in the second stage, n-butylamine ≅ ethylamine ≫ sec-butylamine, confirming that the steric hindrance of amines is a very important factor in these reactions.

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