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On the Mechanism of Formation of the Metal Complexes of Schiff Bases[1,2]

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The rate of formation of the complex of nickel and copper(II) with the salicylaldehyde–glycine Schiff base is studied for the cases in which one of the organic reactants is added to the metal complex of the other and for the case in which the metal is added to the premixed organic reactants. It is found that the formation of the Schiff base complex is greatly retarded by prior reaction of either nickel or copper with one of the Schiff base components. Nickel decreases the amount of Schiff base at equilibrium whereas copper increases it. Equilibrium is reached much more rapidly with nickel than with copper. When sarcosine is substituted for glycine, only the metal complex of sarcosine is produced. The data are given as evidence that any participation of metal ions in vitamin B_6 catalyzed reactions is important primarily in the steps following Schiff base formation.

Introduction

The metal complexes of Schiff bases lend themselves ideally to a study of the effect of metal ions upon the equilibrium between two small molecules and the larger molecule that may be produced from them. Metal ions form complexes with the small molecules, the amine and the aldehyde, and the larger molecule, the Schiff base. It has been demonstrated previously that metal ions can either stabilize or labilize the Schiff base double bond thermodynamically[4]; the kinetics and mechanism of the metal complex formation of Schiff bases, however, have not yet been investigated.

This mechanism is of importance in biochemistry, because the reactions catalyzed by vitamin B_6 have been postulated to proceed through the intermediate formation of Schiff bases from pyridoxal and amino acids.[5,9] Since most of these reactions have been carried out without enzyme, but in the presence of metal ions, by Metzler and Snell,[6–8] a mechanism for these reactions involving the metal complexes of these Schiff bases has been proposed.[9] This mechanism has been confirmed for the non-enzymatic reactions by spectrophotometric studies,[10] and some of the Schiff base complexes have been isolated in the solid state.[11,12]

In their formulation of a general mechanism for vitamin B_6 catalyzed reactions, Metzler, Ikawa and Snell[9] indicate that the metal ion could function to promote the formation of Schiff base, to maintain the planarity of the molecule and to serve as an electropositive group pulling the electrons in the same direction as the heterocyclic nitrogen atom.

The functional groups of the pyridoxal molecule that participate in the formation of the metal Schiff base complexes are also present in salicylaldehyde. The spectra of the metal complexes of salicylaldehyde–amino acid Schiff bases resemble those of the pyridoxal-amino acid Schiff bases.[2,7] It has been shown previously[2] that the thermodynamic stability of the salicylaldehyde–glycine Schiff base is enhanced by copper ion. The metal ion–salicylaldehyde–glycine system thus serves as the simplest model for the initial stages of the vitamin B_6 reactions.

The present investigation consists principally of kinetic studies designed to elucidate the mechanism of the reaction of salicylaldehyde with glycine in the presence of nickel or copper ions. The study was undertaken both for its fundamental concern with the participation of a metal ion in a reaction between two organic molecules and also for its relevance to vitamin B_6 reactions. The data indicate that Schiff base formation is perhaps not a basic function of the metal in such reactions, thus emphasizing the remaining two possibilities outlined by Metzler, Ikawa and Snell.

The method consisted of mixing salicylaldehyde, glycine and metal nitrates in equimolar concentrations and measuring the rate of the spectral changes in solution. Experiments also were conducted with sarcosine substituted for glycine.

Experimental

Solvent, Reagents and Solution.—In order to insure maximum simultaneous solubility of nickel nitrate or copper(II) nitrate, glycine and salicylaldehyde, a 50–50 mixture of water and dioxane was chosen as the solvent. The dioxane was purified,[13] other reagents were used without further purification.

The optimum concentration for spectrophotometric studies was found to be 0.075 M with respect to each component for the nickel system and 0.0125 M for the copper system. The solutions were prepared for measurement by mixing more concentrated stock solutions in equimolar ratios. The stock solutions were prepared by dissolving weighed quantities of reagents with solvent; the glycine and sarcosine solutions were neutralized with an equivalent amount of sodium hydroxide.

Rate Determinations.—The optical density measurements were made with the Beckman Model DU spectrophotometer, using 1 cm. matched Corex cells. The cell compartment was kept at the desired temperatures by circulating water from a constant temperature bath through thermo-

(1) Presented in part at the 131st National Meeting of the American Chemical Society, Miami, 1957, Abstracts, p. 52-C.

(2) Taken in part from the M.S. thesis of Loys J. Nunez, Louisiana State University, 1955.

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(4) (a) G. L. Eichhorn and I. M. Trachtenberg, *J. Am. Chem. Soc.*, **76**, 5183 (1954). (b) G. L. Eichhorn and N. D. Marchand, *ibid.*, **78**, 2688 (1956).

(5) A. E. Braunshtein and M. M. Shemyakin, *Doklady Akad. Nauk, S.S.S.R.*, **85**, 1115 (1952).

(6) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

(7) D. E. Metzler and E. E. Snell, *J. Biol. Chem.*, **198**, 353 (1952).

(8) D. E. Metzler and E. E. Snell, *ibid.*, **198**, 363 (1952).

(9) D. E. Metzler, M. Ikawa and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 648 (1954).

(10) G. L. Eichhorn and J. W. Dawes, *ibid.*, 5663 (1954).

(11) J. Baddiley, *Nature*, **170**, 711 (1952).

(12) H. N. Christensen and S. Collins, *J. Biol. Chem.*, **220**, 279 (1956).

(13) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 368-369.

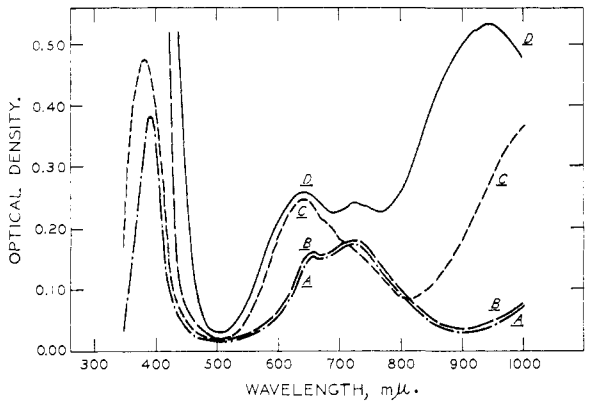


Fig. 1.—Absorption spectra of: (A) hydrated nickel ion; (B) nickel–salicylaldehyde; (C) nickel–glycine; (D) nickel–salicylaldehyde–glycine; 0.075 *M*.

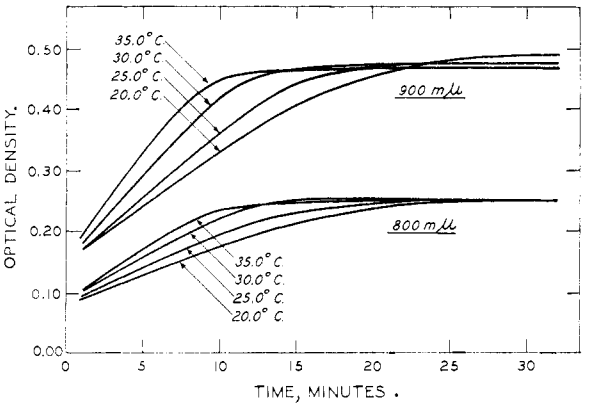


Fig. 2.—Rate of formation of nickel–salicylaldehyde–glycine; salicylaldehyde added to nickel–glycine, 0.075*M*

spacers surrounding it. Temperature variation did not exceed 0.05°.

A typical rate determination was carried out as follows: The Beckman cells and solvent blank were placed inside the cell compartment and constant temperature water was circulated through the thermospacers 1 hr. prior to the initiation of the reaction. Solutions of the component reagents were placed in small volumetric flasks and immersed in the constant temperature bath 0.5 hr. before the reaction was begun.

Reaction initiation consisted of pipetting one component into a mixture of the other two components. All volumetric measurements were made at the desired constant temperature. The time of initiation of the reaction was taken as that when half of the volume of the pipetted solution had dropped into the two-component mixture. The solution then was shaken vigorously, the empty sample cell quickly removed from the compartment, filled with the solution and replaced in the compartment. Measurement of optical density then was begun.

Rapid Scan Spectra.—In order to determine the nature of possible intermediates in the reaction between nickel, salicylaldehyde and either glycine or sarcosine, spectra of such solutions were obtained in approximately one minute intervals by using the maximum speed wave length scan on the Cary Model 14 recording spectrophotometer. As in the rate determinations, the third component was added to a previously mixed solution of the other two in a cuvette, which was placed immediately in the Cary cell compartment. The solutions were 0.150 *M*. A rapid scan spectrum was obtained from 1000 to 500 mμ, the wave length setting returned to 1000 mμ and a new spectrum recorded. This technique results in spectra of extremely low resolution, but it is, nevertheless, very well suited for the detection of large changes in spectra over short intervals of time.

Spectra of Solutions at Equilibrium.—These spectra (Fig. 1 and Fig. 8) were obtained at 25° on the Beckman DU spectrophotometer in 1 cm. matched Corex cells.

Ion Exchange Experiments.—Dowex 50 was regenerated with hydrochloric acid and converted into the sodium form with a solution of sodium chloride. The column was washed with distilled water and 10 ml. of solvent, and the solution of complex was allowed to pass through.

Results and Discussion

Spectra of the Nickel Complexes.—The spectra of solutions containing 0.075 *M* nickel nitrate and equimolar quantities of salicylaldehyde, glycine and both salicylaldehyde and glycine are contained in Figs. 1-B, C and D, respectively. The visible spectrum of the nickel–salicylaldehyde solution (1-B) is almost identical with that of the hydrated nickel ion, Fig. 1-A; little or no complex formation apparently takes place. In the presence of glycine the 650 mμ peak is greatly enhanced and the 725 mμ peak is reduced to an inflection; the optical density in the near infrared increases considerably. Curve C is taken as the spectrum of the nickel–glycine complex. In Curve D both the 650 and 725 maxima are in evidence, and a new peak is observed at 940 mμ. This peak is the same as that previously observed for the nickel–pyridoxal–alanine Schiff base.[10] In fact, the spectral relationships in the nickel–salicylaldehyde–glycine system are the same as those for nickel–pyridoxal–alanine; it may be concluded that the two Schiff base complexes have similar structures.

Reaction of Glycine with Nickel–Salicylaldehyde.—When glycine is added to a solution containing a mixture of nickel and salicylaldehyde, the initial optical densities observed at both 800 and 900 mμ are those of Fig. 1-C, and the final optical densities are those of Fig. 1-D. It may be concluded that the addition of glycine results in the very rapid formation of the nickel–glycine complex, which thereupon reacts further with salicylaldehyde to produce the Schiff base complex. The mechanism of the latter reaction thus does not depend upon whether glycine is added to nickel–salicylaldehyde or salicylaldehyde to nickel–glycine.

Reaction of Salicylaldehyde with Nickel–Glycine.—Curves for the changes in optical density at 800 and 900 mμ for solutions in which salicylaldehyde has been added to nickel–glycine are shown in Fig. 2. These curves do not fit any simple reaction order and suggest a consecutive reaction mechanism.

To determine the initial reaction order, kinetic data also were obtained at 0.0375 *M* concentration, at 25° and 800 and 900 mμ; the curves were plotted as in Fig. 2. Together with the 25° data at 0.075 *M* concentration from Fig. 2, these values were used to calculate the initial reaction order n from the initial slopes of the concentration *vs.* time curves at concentration c_1 (dc_1/dt) and c_2 (dc_2/dt), according to the equation[14]

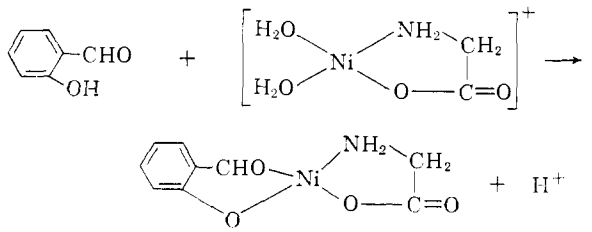
$$n = \frac{\log(-dc_1/dt) - \log(-dc_2/dt)}{\log c_1 - \log c_2}$$

Values for n calculated at 800 and 900 mμ were 2.02 and 1.95, respectively.[15] The initial reaction

(14) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 15.

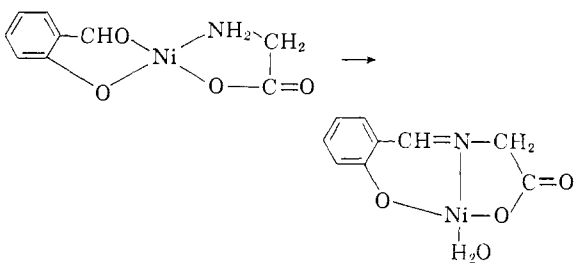
(15) At 0.075 *M* concentration, dc_1/dt at 800 and 900 mμ (in optical density/min.) was 0.01121 and 0.0219, respectively; at 0.0375 *M*

between salicylaldehyde and nickel–glycine thus appears to be second order. Since the curves of Fig. 2 do not continue to exhibit second order kinetics, it may be concluded that the initial reaction does not produce the final Schiff base complex but some complex intermediate; the initial process probably is



I

We may then suppose that the intermediate I decomposes in a second reaction to form the Schiff base complex



II

This second reaction would be expected to be first order with respect to the reaction product. The spectrum of this product II is known but not that of compound I; in such a case, first order plots may be obtained by plotting the logarithms of differences in optical density at times t and $t + \tau$ *vs.* t.[16] Such plots were made in Fig. 3 (using $\tau = -120$ sec.) from those portions of the curves in Fig. 2 which could be made to fit straight line plots; these portions presumably represent a stage in the process when the initial step is essentially complete, and only the second step is in operation. Rate constants were calculated from the 800 mμ curves of Fig. 3 by multiplying the slope by -2.303 and are reproduced in Table I.

TABLE I

RATE CONSTANTS FOR REACTION OF SALICYLALDEHYDE WITH NICKEL–GLYCINE

Temp., °C.	$k \times 10^3$, sec.$^{-1}$
20	2.23
25	2.92
30	4.98
35	5.75

The logarithms of the rate constants (in min.$^{-1}$) have been plotted *vs.* $1/T$°K. in Fig. 6-A; the activation energy (E) for this process calculated from the slope $= -E/2.303R$ is 12.0 kcal./mole;

concentration, dc_2/dt at 800 and 900 mμ was 0.00275 and 0.00567, respectively.

(16) G. L. Eichhorn and I. M. Trachtenberg, *J. Am. Chem. Soc.*, **76**, 4734 (1954).

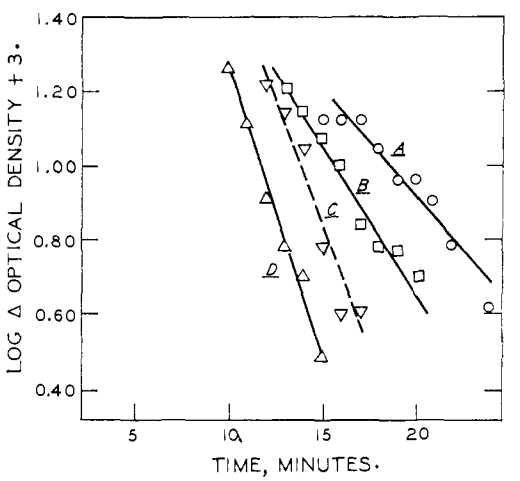


Fig. 3.—First order rate plots for latter part of curves from Fig. 2; 800 mμ: (A) 20.0°; (B) 25.0°; (C) 30.0°; (D) 35.0°.

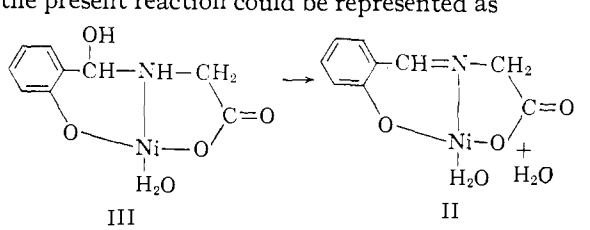
the activation entropy[17] from

$$\Delta S^* = R\left(\ln \frac{kh}{KT} + \frac{E}{RT} - 1\right)$$

is -32 e.u.

Reaction of Nickel with Salicylaldehyde–Glycine.—When nickel ion is added to a mixture of salicylaldehyde and glycine, the plots of optical density *vs.* time are very different from those observed when the glycine complex is originally present. Inspection of Fig. 4 reveals that a decrease, instead of an increase, in optical density now accompanies the reaction. Evidently the nickel–glycine complex is not produced initially under these conditions, but the nickel ion reacts with some substance in solution in such a manner as to produce higher absorption than that attributed to the Schiff base complex. The optical densities at both 800 and 900 mμ become those of a solution of the Schiff base complex at the conclusion of the reaction.

By plotting the logarithms of the optical density changes at 900 mμ[18] (from Fig. 4), using $\tau = -1$ min., it is observed that this reaction follows first order kinetics from beginning to end (Fig. 5). Such a course can be interpreted by postulating a simple decomposition of some complex III of nickel ion with a species formed from salicylaldehyde and glycine into the Schiff base complex II. The addition product of glycine to the carbonyl double bond might be a reasonable structure for such an intermediate which would react with nickel ion to form III. If such is indeed the structure of III, the present reaction could be represented as



III II

(17) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

(18) The changes at 800 mμ were too small to permit accurate calculations.

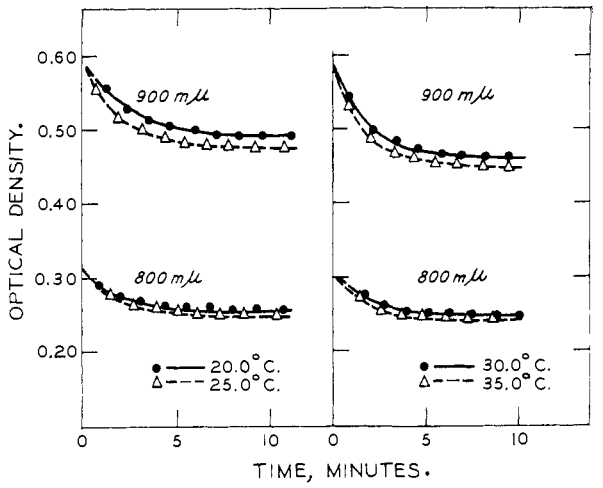


Fig. 4.—Rate of formation of nickel–salicylaldehyde–glycine: Ni^{+2} added to salicylaldehyde–glycine, 0.075 *M*.

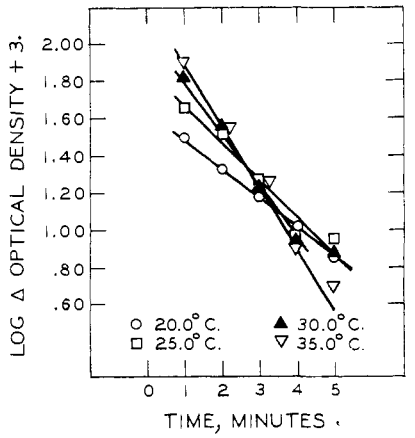


Fig. 5.—First order rate plots for curves from Fig. 5, 900 mμ.

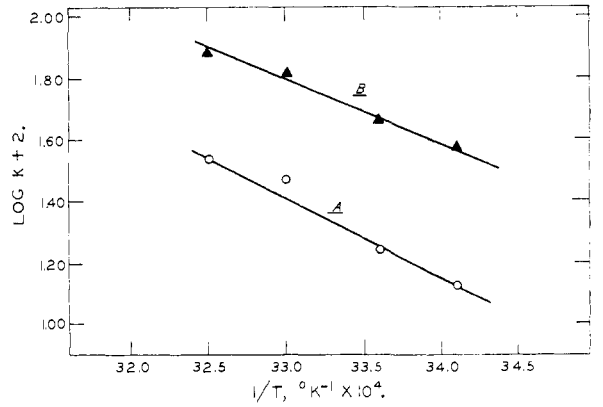


Fig. 6.—Plots for the determination of activation energy: (A) salicylaldehyde added to nickel–glycine, latter part of reaction, 800 mμ; (B) nickel added to salicylaldehyde–glycine, 900 mμ.

An alternative explanation of the data is that more of the nickel complex of the Schiff base is present at the beginning than at the end of the reaction.

Rate constants calculated from the data at 900 mμ[18] are reproduced in Table II.

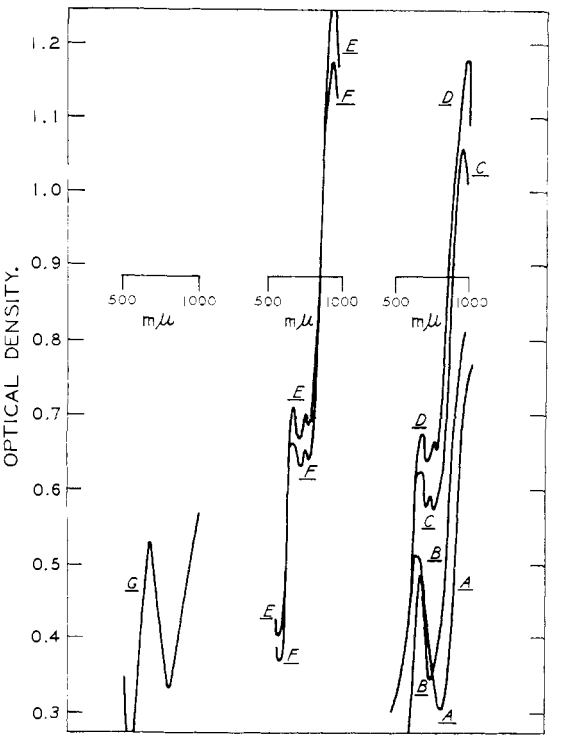


Fig. 7.—Rapid scan spectra, 0.150 *M*: glycine added to nickel–salicylaldehyde: (A) 15 sec.; (B) 1 min. 15 sec.; (C) 7 min.; (D) 12 min. Ni^{+2} added to salicylaldehyde–glycine: (E) 15 sec.; (F) 5 min. Sarcosine added to nickel–salicylaldehyde, or Ni^{+2} added to sarcosine salicylaldehyde; (G) no change with time.

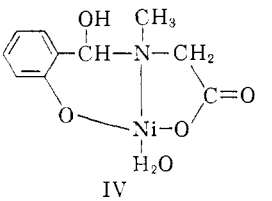
The activation energy calculated from the slope of the log *k vs.* $1/T$°K. plot of Fig. 6-B is 9.7 kcal./mole, and the activation entropy is −38.2 e.u.

TABLE II

RATE CONSTANTS FOR REACTION OF NICKEL WITH SALICYLALDEHYDE–GLYCINE

Temp., °C.	$k \times 10^3$, sec.$^{-1}$
20	6.22
25	7.68
30	10.87
35	12.77

The Test for the Intermediate.—Since only primary amines are capable of reacting with aldehydes to form Schiff bases, no Schiff base can be expected from a reaction of sarcosine, instead of glycine, with salicylaldehyde. However, if intermediate III is capable of existence, the formation of a similar compound IV from sarcosine might be anticipated.



IV

The production of compound IV should be accompanied by a spectrum similar to that of III,

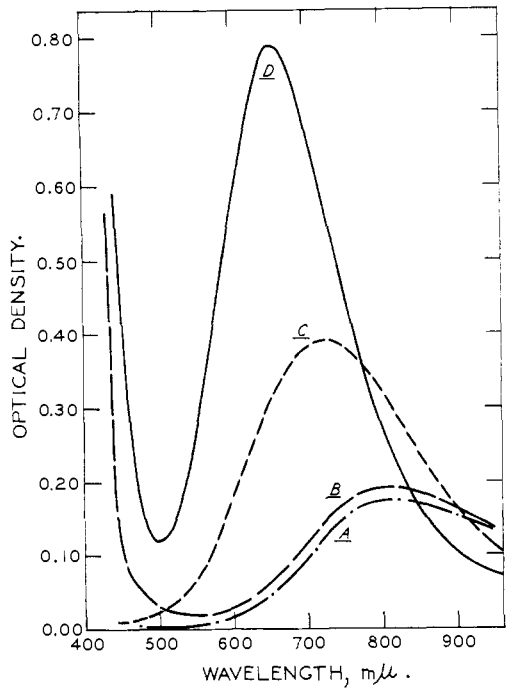


Fig. 8.—Absorption spectra of: (A) hydrated copper(II) ion; (B) copper–salicylaldehyde; (C) copper glycine; (D) copper–salicylaldehyde–glycine, 0.0125 *M*.

which unlike III would not decompose to yield a spectrum resembling that of II. The rapidly scanned spectra of nickel–sarcosine–salicylaldehyde solutions are compared with those of nickel–glycine–salicylaldehyde in Fig. 7. In the former system, no change occurs in the spectrum at all whether salicylaldehyde is added to nickel sarcosine or nickel is added to sarcosine–salicylaldehyde (Fig. 7-G). The spectrum remains that of the nickel–sarcosine complex, which resembles that of nickel–glycine.[19] It appears, therefore, that the only complex observed in this system is that of nickel–sarcosine and that no complexes analogous to either II or III are detected. It certainly can be concluded that the "intermediate" formed in the nickel plus glycine–salicylaldehyde reaction does not exist with sarcosine.

Examination of the spectra of solutions in which salicylaldehyde has been added to nickel–glycine reveals a gradual change from the characteristics of nickel–glycine (Fig. 7-A) to those of the Schiff base complex (Fig. 7-D). When nickel is added to salicylaldehyde–glycine (Fig. 7-E), the generalized decrease in optical density (Fig. 7-F), most marked at 940 mμ, is not accompanied by any other change in the characteristics of the spectrum.

These results are difficult to reconcile with the existence of an intermediate III. They indicate, on the other hand, that nickel reacts with a preformed Schiff base to form a Schiff base complex and that a small portion of these molecules of Schiff base complex decompose into nickel–glycine

(19) H. N. Christensen and T. R. Riggs, *J. Biol. Chem.*, **220**, 265 (1956), have obtained evidence from titration curves that some interaction does occur between nickel sarcosine and pyridoxal; they also determined the spectrum of the resulting substance and found that it does not differ significantly from that of nickel sarcosine.

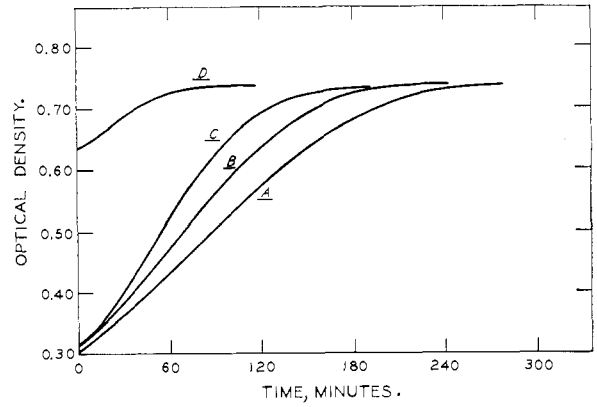


Fig. 9.—Rate of formation of copper–salicylaldehyde–glycine, 0.0125 *M*, 650 mμ. Salicylaldehyde added to copper–glycine: (A) 45.0°; (B) 50.0°; (C) 55.0°. Cu^{+2} added to salicylaldehyde–glycine: (D) 50.0°.

and salicylaldehyde until equilibrium is attained. Such a decomposition would follow first-order kinetics.

This conclusion is strengthened by a study of the behavior of the complexes with ion exchangers. Since 1:1 complexes of nickel with either salicylaldehyde alone or glycine alone have a positive charge, they should be absorbed on a cation exchanger, but the neutral Schiff base complex should pass through the column. None of the complexes should adhere to an anion exchanger.

When either nickel–salicylaldehyde or nickel–glycine was passed through a column of the sodium salt of the cation exchanger Dowex 50, the effluent was colorless, and a sharp green ring remained on the column. Both complexes therefore must be completely in the charged form. When a solution of the Schiff base complex product was passed through a similar column, a ring again was produced on the column, but in this case the effluent was also green; this effluent then could be run repeatedly through cationic or anionic exchange columns (Dowex 1) without any visible absorption. The product of the reaction of nickel, salicylaldehyde and glycine, therefore, contains both a neutral complex and a positively charged complex, consistent with the presence of the Schiff base complex in equilibrium with nickel–glycine.

The curves of Fig. 4 thus represent the decomposition of a portion of the Schiff base complex to nickel–glycine. The values obtained for the activation energy and entropy are of similar magnitude to those previously determined for the decomposition of the nickel complex of the thiophenaldehyde–ethylenediamine Schiff base.[1,20]

It is therefore apparent that nickel ion is not a favorable agent for bringing salicylaldehyde and glycine together, since nickel actually brings about

(20) It is possible to make an approximate evaluation of the equilibrium constant

$$K = \frac{[\text{Ni–Schiff base}]}{[\text{Ni–glycine}]\,[\text{salicylaldehyde}]}$$

from the data in Fig. 4 by taking the optical density at zero time (0.58 for 900 mμ) as the optical density of a 0.075 *M* solution containing only the Schiff base complex. The optical density of nickel–glycine is taken as 0.18 at 900 mμ from Fig. 1; from the optical density at equilibrium (0.47), *K* is calculated as 10 ± 2.

a partial decomposition of Schiff base. Possibly a higher activation energy is required to convert compound I to II than that for the Schiff base formation in the absence of metal, since the former requires splitting a nickel–oxygen bond that does not occur in the latter case.

Reaction between Copper(II), Salicylaldehyde and Glycine.—The reactions between glycine and salicylaldehyde with copper(II) ion proved to be not so favorable for quantitative studies as those with nickel. Fig. 8-A, B, C and D are the spectra of copper ion and the copper complexes of salicylaldehyde, glycine and salicylaldehyde–glycine, respectively. The lower three curves of Fig. 9 represent the changes in optical density with time for the addition of salicylaldehyde to copper–glycine. As in the nickel system, there is a transition from the glycine complex spectrum to the Schiff base complex spectrum.

The upper curve of Fig. 9 represents the optical density changes for the addition of copper(II) to salicylaldehyde–glycine. The initial optical density in this case, again as in the nickel system, is not that of the glycine complex but fairly close to the absorption of the Schiff base complex. Again the attainment of equilibrium is much faster when the Schiff base components are mixed initially than when the metal is permitted first to react with one of them. In fact, the initial optical density is equivalent to that obtained after more than 1.5 hr. when salicylaldehyde is added to copper–glycine.

The behavior of copper differs from that of nickel in two respects: (1) copper increases the amount of Schiff base present at equilibrium, and (2) all of the reactions are very much slower than those with nickel, as a comparison of Figs. 2 and 4 with Fig. 9 will demonstrate.

Conclusions

These experiments demonstrate that the nature of the participation of metal ions in Schiff base formation is determined by the order in which the reactants are mixed; equilibrium is achieved most rapidly when the metal ion is added last. It is noteworthy that the thermodynamic stabilization of the product of a reaction by a metal ion can be accompanied by a retardation of the reaction with the metal.

The instantaneous production of the spectrum characteristic of nickel Schiff base complexes upon the addition of nickel to the Schiff base components indicates that the Schiff base is formed in solution without the aid of metal. The addition of either copper or nickel ions to the premixed organic reagents results in the immediate formation of Schiff base complex in concentrations not very different from those at equilibrium; further progress toward equilibrium produces somewhat more Schiff base with copper and less with nickel. The prior formation of a metal complex with glycine results in drastic retardation of Schiff base formation both with nickel and with copper. It is concluded that, even when the metal thermodynamically favors Schiff base formation, as is the case with copper, the metal tends to prevent rapid attainment of equilibrium.

Ikawa and Snell[21] and Christensen and Riggs[19] have found that salicylaldehyde does not participate in transamination and the other vitamin B_6-catalyzed reactions. Salicylaldehyde is therefore not analogous to pyridoxal in the molecular rearrangements that follow Schiff base formation, since these rearrangements require either the pyridoxal nitrogen or another electron-attracting group.[9,19] However, all of the ligands that bind metal in the pyridoxal-amino acid Schiff bases are also present when salicylaldehyde is substituted for pyridoxal. The conclusions drawn from the salicylaldehyde system are therefore also applicable to pyridoxal Schiff base formation. Since this reaction is retarded by metal ions, it would appear that the effect of metal ions on the vitamin B_6-catalyzed reactions occurs after, and not before, Schiff base formation.

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(21) M. Ikawa and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 653 (1954).

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The Voltammetric Characteristics and Mechanism of Electroöxidation of Hydrazine

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The oxidation of hydrazine at a mercury or oxide-coated platinum electrode yields nitrogen as the principal product. Under some conditions, however, ammonia also is formed as a result of the dimerization of diimide. A mechanism for the process is suggested: though generally similar to the accepted mechanism for the reaction of hydrazine with a two-electron chemical oxidizing agent, it also serves to explain the effects of such variables as *p*H and chloride-ion concentration on the extent of the dimerization reaction.

Introduction

Many electro-reductions and -oxidations, especially of organic substances, proceed *via* free-radical intermediates whose dimerizations exert marked effects on the products, yields and apparent *n*-values obtained by controlled-potential electrolysis

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