culated using eq 10 and are listed in Table IX as Δk_{isc} (calcd). As can be seen the agreement is quite good. In fact if the experimental values of k_{isc} for the Cl, Br, and I derivatives of free base or ZnTPP were used to calculate D directly from eq 9 the value obtained would have been close to k_{isc} of the unsubstituted derivative supporting the assumption of eq 10. Equation 11 indicates that it is the cross term $C\rho_x$ involving the product (ab) and the first power of ρ_x which accounts for the variation in $\Delta k_{\mathrm{isc}}/\rho_x^2$ for the para derivatives. For the ortho derivatives the constant a in eq 6 would be much larger than that of the para derivatives because the ortho substituent interacts more strongly with the porphin π system. Thus the first term in eq 9 would dominate the others even for the Cl derivative.

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(30) One of our referees, Dr. Martin Gouterman, has pointed out to us that the seemingly anomolously high fluorescence quantum yield of ZnOClTPP may be due to the fact that the terms involving the ortho halogen heavy effect and those involving the Zn heavy atom effect might enter into eq 5 with different sign. Since ortho-Cl substituents and Zn have spin-orbit effects of similar magnitude, as shown in Table IV, the ortho-Cl substituents might act to weaken the Zn effect. If this interpretation is correct it is probably the first observed case of counteracting heavy atom effect.

Kinetic and Equilibrium Studies on the Formation of Zinc(II)–Salicylaldehyde Schiff Bases Derived from Ethylenediamine and 1,3-Diaminopropane

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Abstract: The kinetic and equilibrium properties of Schiff bases derived from salicylaldehyde and either ethylenediamine or 1,3-diaminopropane in both the absence and presence of zinc(II) were studied over the pH range of 4.6 to 12.5 at 25.0°, 0.5 M ionic strength. Unprotonated, mono-, di-, and triprotonated sal$^-$-diamine adducts were found and their stabilities were established. The Zn(II)-Schiff base complexes have stabilities consistent with tridentate coordination of two nitrogen atoms and one oxygen atom. The rate law for diamine Schiff base formation was found to be similar to those found earlier for the reactions of amino acids with sal$^-$. Both unprotonated and monoprotonated diamines were found to be kinetically active. Coulombic effects account to a large extent for the reactivity differences exhibited by various amines toward sal$^-$; the cationic monoammonium ions show the largest rate constants and aminoacidate ions the smallest. Zn(II) promoted paths for Schiff base formation were found. The magnitudes of the rate constants are consistent with a mechanism which involves the preequilibrium formation of a mixed complex, (sal)Zn(diamine)$^+$.

The equilibrium and kinetic properties of Schiff bases and their metal ion complexes have received considerable attention owing to their relationship to vitamin B$_6$ chemistry. A quantitative study of the kinetic activity associated with metal ions in Schiff base formation was first reported from our laboratories in 1966 and 1967[2,3] but it was not until a few years later that the nature of the metal ion promoted step was more clearly recognized.[4] Metal ions were postulated to function by forming a mixed ligand complex with the amine donor and carbonyl compound in a preequilibrium step, followed by Schiff base formation in the primary, or secondary, coordination sphere of the metal ion,

$$\rangle\mathrm{C{=}O} + \mathrm{RNH_2} + \mathrm{M^{2+}} \underset{\mathrm{fast}}{\overset{\beta_{11}^{\ *}}{\rightleftharpoons}} (\rangle\mathrm{C{=}O})\mathrm{M(H_2NR)} \xrightarrow[k_{\mathrm{p}}]{\mathrm{slow}} \mathrm{M}(\rangle\mathrm{C{=}NR}) + \mathrm{H_2O} \quad \mathrm{(I)}$$

The observed third-order rate constant is the product, $\beta_{11}{}^*k_{\mathrm{p}}$.

The metal ion is considered to function by effectively reducing the condensation reaction from a second-order to a first-order process. The term *promnastic* (matchmaker) was applied to this effect.[4] A systematic variation in divalent metal ions revealed that Pb$^{\mathrm{II}}$, Cd$^{\mathrm{II}}$, Mn$^{\mathrm{II}}$, Mg$^{\mathrm{II}}$, and

Table I. Formation Constants for the Species Present in Salicylaldehyde–Diamine–Zn(II) Solutions (25°, $I = 0.5$)

Reaction	Log β
$\mathrm{sal^- + H^+ \rightleftarrows Hsal}$	8.22[a]
$\mathrm{sal^- + Zn^{2+} \rightleftarrows Znsal}$	2.87[a]
$\mathrm{2sal^- + Zn^{2+} \rightleftarrows Znsal_2}$	5.00[a]
$\mathrm{en + H^+ \rightleftarrows Hen^+}$	10.01
$\mathrm{en + 2H^+ \rightleftarrows H_2en^{2+}}$	17.36
$\mathrm{tn + H^+ \rightleftarrows Htn^+}$	10.40
$\mathrm{tn + 2H^+ \rightleftarrows H_2tn^{2+}}$	19.41
$\mathrm{sal^- + en \rightleftarrows sal{\cdot}en^-}$ [b]	1.34
$\mathrm{sal^- + en + H^+ \rightleftarrows Hsal{\cdot}en}$[b]	12.38
$\mathrm{sal^- + en + 2H^+ \rightleftarrows H_2sal{\cdot}en^+}$ [b]	21.21
$\mathrm{sal^- + en + 3H^+ \rightleftarrows H_3sal{\cdot}en^{2+}}$ [b]	26.08
$\mathrm{Zn^{2+} + en \rightleftarrows Znen^{2+}}$	6.01
$\mathrm{Zn^{2+} + 2en \rightleftarrows Znen_2{}^{2+}}$	11.19
$\mathrm{Zn^{2+} + 3en \rightleftarrows Znen_3{}^{2+}}$	13.15
$\mathrm{Zn^{2+} + sal^- + en \rightleftarrows Zn(sal{\cdot}en)^+}$ [b]	11.10
$\mathrm{Zn^{2+} + sal^- + 2en \rightleftarrows Zn(sal{\cdot}en)en^+}$ [b]	15.30
$\mathrm{sal^- + tn \rightleftarrows sal{\cdot}tn^-}$ [b]	1.91
$\mathrm{sal^- + tn + H^+ \rightleftarrows Hsal{\cdot}tn}$[b]	13.14
$\mathrm{sal^- + tn2H^+ \rightleftarrows H_2sal{\cdot}tn^+}$ [b]	22.39
$\mathrm{sal^- + tn + 3H^+ \rightleftarrows H_3sal{\cdot}tn^{2+}}$ [b]	27.35
$\mathrm{Zn^{2+} + tn \rightleftarrows Zntn^{2+}}$	5.41
$\mathrm{Zn^{2+} + 2tn \rightleftarrows Zntn_2{}^{2+}}$	9.73
$\mathrm{Zn^{2+} + sal^- + tn \rightleftarrows Zn(sal{\cdot}tn)^+}$ [b]	11.58

[a] Reference 3b. [b] H_2O molecules released in Schiff base formation have been omitted.

Zn^{II} were kinetically active, while Co^{II}, Ni^{II}, and Cu^{II}, with partially filled d orbitals, were inactive. The inactivity of the latter group of metal ions was ascribed to the rigid metal-ligand geometries imposed by the ligand field splitting of the 3d orbitals. Their inactivity also ruled out a mechanism in which polarization of the carbonyl group plays an important role.

The promnastic model was successful in quantitatively accounting for a 100-fold difference between the rates of the Zn^{II} promoted reactions of glycinate with pyruvate[2] (pyu^-) and salicylaldehyde[3,4] (sal^-). However, a study of the amine variation in salicylaldehyde reactions yielded ambiguous results. The rate constants for the Zn^{II} dependent reactions of ethylamine (eta), and β-alaninate (β-ala$^-$)[5] with sal^- were found to be practically identical with that found for glycinate (gly^-). This result could indicate that those factors which tend to increase $\beta_{11}{}^*$ produce a compensatory decrease in k_p, and vice versa. It could also indicate that amine coordination is not at all involved. With the hope of gaining more information, which would help to resolve the problem, this study of diamine behavior was undertaken. The diamines investigated were ethylenediamine (en) and 1,3-propanediamine (trimethylenediamine, tn).

Experimental Section

Aqueous stock solutions of salicylaldehyde were prepared by weight from the redistilled reagent (Aldrich). Stock solutions of $ZnCl_2$ were prepared by dissolving a weighed amount of granular reagent grade Zn (Baker) in a slight excess of dilute HCl. The dihydrochloride salts of ethylenediamine (Sigma) and 1,3-diaminopropane (Aldrich) were twice recrystallized from water–enthanol mixtures. The dihydrochloride salt of *N,N*-dimethylethylenediamine (Aldrich) was prepared and standardized as described by Rosin.[6] All experiments were performed using doubly distilled, deionized, degassed water. Ionic strengths of all reaction mixtures were adjusted to 0.5 with KCl (Mallinckrodt) and the solutions were maintained at 25.0° in a thermostated bath. Hydrogen ion activity was measured using a Radiometer PHM26 pH meter directly after standardizing the glass electrode vs. NBS buffers. The equilibrium and rate constants which depend on hydrogen ion terms are reported here in units of hydrogen ion activity, that is, are "practical" constants.

A Durrum–Gibson stopped flow apparatus which was interfaced to a Nova minicomputer was employed for the fast rate experiments. Slow reaction rates were studied using a Cary 14 spectrophotometer and a Radiometer pH stat.

Equilibrium Studies. Potentiometric titrations were performed on the dihydrochloride salts of both ethylenediamine (H_2en^{2+}) and 1,3-diaminopropane (H_2tn^{2+}) to establish the respective pK_{a1} and pK_{a2} values. The binary zinc(II)–diamine complexes were also studied potentiometrically. Either Bjerrum $\bar{n}$ methods or nonlinear least-squares curve-fitting analyses[4] were employed in evaluating the formation constants. The values are given in Table I.

The formation constants of the protonated and unprotonated forms of the Schiff bases (sal·amine) and their Zn(II) complexes were evaluated using both potentiometric and spectrophotometric techniques. The reversible reaction of sal^- with en at pH 12.0, where the unprotonated adduct, $sal{\cdot}en^-$ is formed, was studied spectrophotometrically. The absorption intensity of the adduct band at its 349-nm maximum was measured in a series of solutions over which the en concentration was varied from 0.0080 to 0.160 *M* while the total salicylaldehyde was held constant at 2.0×10^{-4} *M*.

The adduct protonation reaction, $sal{\cdot}en^- + H^+ \rightleftarrows Hsal{\cdot}en$, was studied in a stopped flow apparatus by monitoring the increase in absorbance which occurred at 395 nm as the pH of solutions containing $sal{\cdot}en^-$ was rapidly decreased from pH 12.9 to lower values. It was necessary to perform these measurements rapidly because sal^- does not combine quantitatively with en at the concentration levels employed here and slow shifts in the total amount of adduct present accompany pH changes. Absorbance measurements were made within about 10 msec after solutions initially containing a total of 4.9×10^{-5} *M* sal^- and 0.1235 *M* en and preequilibrated at pH 12.9 were mixed with phosphate buffers in the stopped flow apparatus to give final solutions lying in the pH range 10.28–12.44. Because the sum of the concentrations of Hsal·en and $sal{\cdot}en^-$ remained constant in this set of experiments it was not necessary to know the individual extinction coefficients of $sal{\cdot}en^-$ and Hsal·en in order to obtain the protonation constant. The fraction of adduct present as Hsal·en in a solution at a given pH could be calculated from the absorbance using the equation

$$f_{\mathrm{Hsalen}} = (A_{\mathrm{pH}} - A_{\mathrm{salen}})/(A_{\mathrm{Hsalen}} - A_{\mathrm{salen}})$$

where A_{salen} and A_{Hsalen} are the respective absorbancies of solutions containing essentially only $sal{\cdot}en^-$ (pH 12.9) and Hsal·en (pH <10.3) at the same concentration. The protonation constant was then evaluated from a plot of pH vs. $-\log (f_{\mathrm{Hsalen}}/(1 - f_{\mathrm{Hsalen}}))$.

Interactions between Hsal and $enH_2{}^{2+}$ in acidic media were investigated potentiometrically using a Radiometer pH stat apparatus. A series of solutions were prepared containing total initial concentration of Hsal in the range $(0.22–1.1) \times 10^{-2}$ *M* and en·2HCl in the range $(0.40–5.3) \times 10^{-2}$ *M*, with the amine always being in excess of the aldehyde. A standard solution of sodium hydroxide was added to each reaction mixture from the Auto Buret of the apparatus to reach a pH at which reaction was observed. The pH range covered in this series of experiments was 4.6–6.4. The rate at which additional base was added to maintain each solution at its reaction pH (within 0.01–0.02 pH units) provided information regarding the reaction kinetics. The final equilibrium volume of NaOH was used to calculate the equilibrium constant for the formation of $H_2sal{\cdot}en^+$ according to the equation, $Hsal + H_2en^{2+} \rightleftarrows H_2sal{\cdot}en^+ + H^+$. The independence of the value of the equilibrium constant on reactant concentrations confirmed the assumed stoichiometry. After the appropriate conversion, the result is expressed in Table I as the constant for the overall reaction, $sal^- + en + 2H^+ \rightleftarrows H_2sal{\cdot}en^{2+}$. In the discussion below this constant is referred to as β_2.

Owing to the extensive hydrolysis of $H_3sal{\cdot}en^{2+}$ it was necessary to determine the protonation constant of $H_2sal{\cdot}en^+$ using the stopped flow apparatus in a manner analogous to that described above for the determination of the protonation constant of $sal{\cdot}en^-$. A solution containing 1.6×10^{-4} *M* total salicylaldehyde and 0.049 *M* total en was preequilibrated at pH 8.01 to form $H_2sal{\cdot}en^+$. Various portions of this solution were mixed with buffers in the stopped flow apparatus to give final solutions in the range pH 1.8–5.4, and the absorbance decrease at 395 nm, which accompanies the formation of $H_3sal{\cdot}en^{2+}$, was determined. In this way

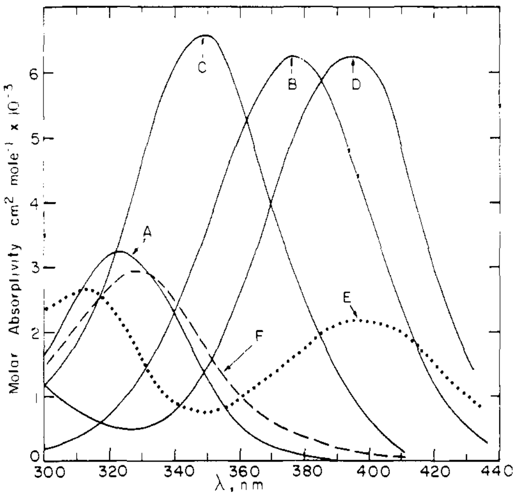


Figure 1. Overall molar absorbancies of the adducts formed between salicylaldehyde and ethylenediamine: A, Hsal; B, sal^-; C, $sal{\cdot}en^-$; D, Hsal·en; E, $H_2sal{\cdot}en^+$; F, $H_3sal{\cdot}en^{2+}$.

absorbance changes arising from protonation were measured before hydrolysis created interference. The protonation constant was evaluated graphically in a manner analogous to that described above.

The addition of Zn(II) to salicylaldehyde-ethylenediamine mixtures enhances absorption at 349 nm. Equilibrium values of absorbance at this wavelength were studied as a function of the concentrations of the components. Solution compositions covered the range of from 0.001 to 0.034 M total Zn(II), 0.005 to 0.035 M total en, and 1.1 to 12 × 10^{-5} M total sal in the pH range 5.75–10.54. The data were analyzed using a computer program, ABSFIT, which was developed in our laboratories to obtain least-squares values of equilibrium constants and extinction coefficients from absorbance-concentration data.

The interactions that exist in sal^-–tn solutions in the presence and absence of Zn(II) were, in general, investigated using experimental approaches similar to those described above but with certain exceptions. The formation constant of $sal{\cdot}tn^-$ was determined simultaneously with its protonation constant. A series of solutions containing 2 × 10^{-4} M sal^- and 0.008 to 0.5 M tn in the pH range 11.3–12.9 were prepared and values of the absorbance at 350 nm were measured. The data were analyzed using ABSFIT to obtain the two equilibrium constants.

The equillibrium constant for the reaction Hsal + H_2tn ⇄ $H_2sal{\cdot}tn^+$ + H^+ was determined potentiometrically, as described above for en, and also spectrophotometrically by determining absorbance changes at 395 mμ of sal–tn mixtures in the pH range 6.5–9.2. The values of the equilibrium constants obtained from the two types of measurements agreed within 15%.

Resolution of Absorption Spectra. The absorption spectra of the various adducts were obtained from solutions made up to contain accurately known concentrations of sal (at about 2 × 10^{-4} M) and diamine (0.004–0.2 M). In the case of en, solutions were preequilibrated at pH 2.0, 6.6, 10.26, and 12.00, while with the more basic tn molecule, values of pH 8.85, 11.48, and 12.30 were chosen. After calculating the equilibrium distributions which pertain to each reaction mixture, the extinction coefficients were resolved at various wavelengths by solving linear simultaneous equations. The spectra are shown plotted in Figure 1 for the en system and in Figure 2 for the tn system.

Formation of Zn-Sal-Diamine Complexes. Absorbance values of equilibrated solutions containing known amounts of Zn(II), salicylaldehyde, and diamine were determined at the wavelength of the maxima of the Schiff base complexes. This was found to be 349 nm for $Zn(sal{\cdot}en)^+$ and 345 nm for $Zn(sal{\cdot}tn)^+$.

For the en investigations, the concentrations employed lay in the range of (1.1–12) × 10^{-5} M sal, 0.001-0.035 M Zn(II) and 0.005-0.035 M en. The pH was varied from 5.75 to 10.54. For the tn systems the concentration of sal was held at 2.5 × 10^{-4} M while Zn(II) was varied from 0.0021 to 0.0049 M and tn was varied from 0.005 to 0.05 M in the pH range 6.3–9.4.

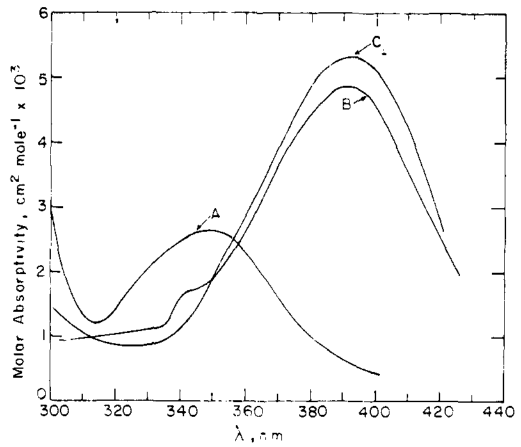


Figure 2. Overall molar absorbancies of the adducts formed between salicylaldehyde and 1,3-propanediamine: A, $sal{\cdot}tn^-$; B, Hsal·tn; C, $H_2sal{\cdot}tn^+$.

Rate Studies. In the stopped flow determinations, one of the two solutions to be mixed contained only sal^- (or Hsal) and KCl, while the second solution contained an excess of the diamine dihydrochloride, KCl, and varying, but known, amounts of NaOH, or HCl, to give the desired pH. When reaction mixtures containing Zn(II) were investigated, aliquots of the $ZnCl_2$ solution were initially added to the diamine solutions. Upon mixing the diamine and sal^- solutions, the reaction was followed by monitoring a wavelength where one of the reactants or products had a strong absorption band. The formation of protonated imines could be followed at 390–400 nm, the formation of Zn(II)-imines could be followed at 340–350 nm, and at pH >8 the disappearance of the 377-nm sal^- band could be followed. The total concentrations of the mixed solutions covered the ranges (4.6–24.7) × 10^{-5} M salicylaldehyde, 0.02–0.05 M diamine, and (1.3–5) × 10^{-3} M $ZnCl_2$. The pH values were adjusted to fall in the ranges pH 4.8–12.5 for the Zn(II)-free reactions and pH 5.6–10.5 for those containing Zn(II). The absorbance values were digitized using an analog to digital converter (10 bits in 10 μsec) at precisely determined time intervals and logged into the Nova computer memory. Between 5 and 12 replicate runs were obtained for each experiment. The exponential decay curves were processed in the manner described by Sharma and Leussing[7] to obtain values of the first-order relaxation constants, k_{obsd}. Values of pseudo-first-order forward rate constants, k_{fobsd} were calculated using the relationship, $k_{obsd} = k_{fobsd}(1 + (1/K_{cond}))$, where K_{cond} is the equilibrium ratio of total salicylaldehyde condensed as Schiff base to total uncondensed salicylaldehyde.

The kinetic data that were obtained with the pH stat apparatus were analyzed using the linear approximations which apply as a reaction system approaches equilibrium,[8] i.e., using relaxation techniques. This was necessary because the initial rates were too fast relative to the instrument time to be measured accurately. Rates close to equilibrium could be determined with little difficulty, however. Values of k_{obsd} obtained from the rate data (volume of NaOH vs. time) were resolved into forward and backward rate constants in a manner analogous to that described above for the stopped flow measurements. The rates were corrected for variations in the degree of protonation of reactants and producis as the pH was changed.

Results

At pH 12.0, when the concentration of en is progressively increased from 0 to 0.16 M in solutions that contain a constant total amount of sal^- (2 × 10^{-4} M) it is observed that the 377-nm band of sal^- decreases while an adduct band, 349 nm, increases. The existence of an isosbestic point at about 360 nm demonstrates that under these conditions sal^- and diamine react to give a product, or products, in which the sal^-:en combining ratio is constant. In agreement with a 1:1 reaction of the type,

$$\mathrm{sal^- + en \overset{\beta_{11}}{\rightleftharpoons} sal{\cdot}en^-}$$

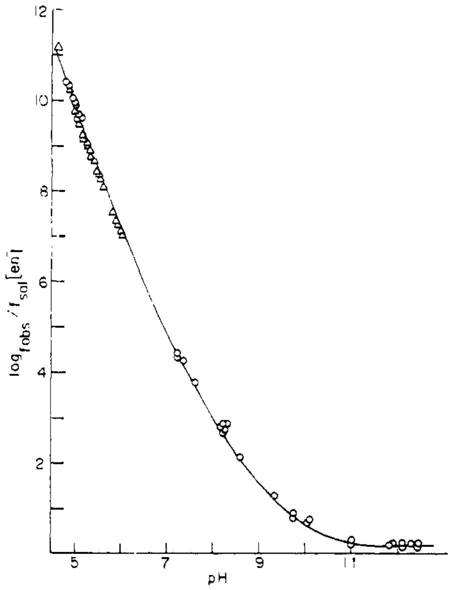


Figure 3. The logarithm of the observed first-order formation constant reduced by the en concentration and fraction of sal^- as a function of pH: △, pH stat results; ○, spectrophotometric results. The solid line is theoretical.

plots of $[sal]_{total}/A_\lambda$ vs. $(1 - \epsilon_{S\lambda}[sal]_{tot}/A_\lambda[en]^{-1})$ for two separate series of experiments were found to yield straight lines. A_λ represents the absorbance, measured at either 349 or 377 nm. From the slopes and intercepts of these plots values of 26.3 and 25.9 M^{-1} for the reaction constant were obtained. After correcting for the small amount of Hsal·en that is present under these conditions (see below) an average value of β_0 equal to 22.1 M^{-1} was obtained and is reported in Table I.

The protonation of sal·en$^-$ is evident as the pH is decreased below 12 by the disappearance of the 377-nm band and the appearance of a band at 395 nm. The stopped flow determinations of the 395-nm absorbance changes in the pH range 10.4–12.9 provided a measure of f_{Hsalen}, the fraction of total sal·en that is present as Hsal·en at a given pH. A plot of pH vs. $-\log (f_{Hsalen}/(1 - f_{Hsalen}))$, yielded a straight line of unit slope indicating the acquisition of a single proton. The intersection at the ordinate yielded a protonation constant, $K_{salen}{}^H$, of $10^{11.04}$ M^{-1} for the reaction $H^+ + sal{\cdot}en^- \rightleftarrows Hsal{\cdot}en$. The overall formation constant for the reaction

$$H^+ + sal^- + en \overset{\beta_1}{\rightleftarrows} Hsal{\cdot}en$$

was calculated from the relationship, $\beta_1 = \beta_0 K_{salen}{}^H$, and is given in Table I.

The second stepwise protonation constant for the reaction, $H^+ + Hsalen \rightleftarrows H_2salen^+$ was not determined directly but was evaluated from relationship, $K_{Hsalen}{}^H = \beta_2/\beta_1$. A value $10^{8.83}$ M^{-1} was obtained.

In a manner identical with that described above for the evaluation of $K_{salen}{}^H$ the third stepwise protonation constant, $K_{H_2salen}{}^H$, defined by the reaction, $H^+ + H_2sal{\cdot}en^+ \rightleftarrows H_3sal{\cdot}en^{2+}$, was calculated from the low pH stopped flow measurements to be $10^{4.87}$ M^{-1}. The overall formation constant, β_3, for the reaction $3H^+ + sal^- + en \rightleftarrows H_3sal{\cdot}en$, was calculated from the relationship, $\beta_3 = \beta_2 K_{H_2salen}{}^H$ and is, also, given in Table I.

In analyzing the equilibrium absorbance data obtained from the Zn(II)-sal$^-$-diamine mixtures the presence of uncomplexed sal-diamine adducts as well as binary Zn(II) sal$^-$ and diamine complexes must be taken into account.

Table II. Rate Constants for the Zn(II) Independent Paths for Schiff Base Formation (25°, $I = 0.5$)

$$d[\text{Schiff base}]_\Sigma/dt = \sum_{i=0}^{N} k_i{}^H[H^+]^i[sal^-][amine]$$

Amine	$k_0{}^H$, M^{-1} sec^{-1}	$k_1{}^H$, M^{-2} sec^{-1} ($\times 10^{-9}$)	$k_2{}^H$, M^{-3} sec^{-1} ($\times 10^{-15}$)	$k_3{}^H$, M^{-4} sec^{-1} ($\times 10^{-24}$)
en[a]	1.5	32.0	7,500	7.8
tn	2.1	29.0	32,000	100
eta[a]	1.0	2.5	1.6	
β-ala$^-$[a]	0.48	1.8	6.0	
gly$^-$[b]	0.18	0.67	6.9	

[a] Reference 5. [b] Reference 4.

Owing to this complexity it was necessary to use the computer program ABSFIT to analyze the data. The simplest model for the en system included only the formation of the additional comples Zn(sal·en)$^+$, and was found not to be able to reproduce the observations within the experimental accuracy. The further inclusion of a mixed complex, Zn(sal·en)(en)$^+$, which becomes important at high en and high pH, yielded a satisfactory model. To account for the behavior in the tn system it was sufficient to include only Zn(sal·tn)$^+$. The overall formation constants found for these complexes are given in Table I. The molar absorption spectra of these complexes were resolved from measurements taken on the equilibrium reaction mixtures and were found to be very similar to those found for sal·en$^-$ and sal·tn$^-$. Zn(sal·en)$^+$ has an absorption maximum at 349 nm with an extinction coefficient of 5.7×10^3 cm^2 mol^{-1} and Zn(sal·tn)$^+$ has an absorption maximum at 345 nm with the same extinction coefficient. The absorption spectrum of Zn(sal·en)(en)$^+$ was not resolved from high pH data but it appears to be identical with that of Zn(sal·en)$^+$. Experimentally, the extinction coefficients at 349 nm were found to be the same for these two complexes. Since the second en molecule is independently coordinated to the Zn(II) ion it should have little effect on the spectra.

Reaction Rates. Simple pH-rate profiles were found in plots of $k_{obsd}/[diamine]f_{sal}$ vs. pH, where [diamine] is the free diamine concentration and f_{sal} is the ratio $[sal^-]/([Hsal] + [sal^-])$. These results, shown in Figure 3 for the en system, indicate that the rate law for diamine Schiff base formation is the same as found earlier in the eta and aminoacidate studies.[4,5] The general rate law conforms to the expression,

$$d[\text{Schiff base}]/dt = \sum_{i=0}^{N} k_i{}^H[H^+]^i[RNH_2][sal^-]$$

The earlier studies in which monoamines were employed showed a maximum value of N equal to 2.0. With the diamines, a value of 3.0 was obtained as a result of the presence of a second highly basic group. The values of the $k_i{}^H$ which were numerically resolved from the data plotted in Figure 3 are given in Table II. For comparison purpose the values of rate constants previously found for the reactions of eta,[5] β-ala$^-$,[5] and gly$^-$[4] with sal$^-$ are also listed.

The values of k_{obsd} obtained for the rates of adduct formation in the presence of Zn(II) are presented in Table III. Analysis of the data reveals that the presence of Zn(II) in the reaction mixture gives rise to two additional terms in the rate law for Schiff base formation,

$$d(\text{Schiff base})/dt = \sum_{i=0}^{N} k_i{}^H[H^+]^i[sal^-][RNH_2] + (k_1{}^{Zn} + k_2{}^{Zn}[RNH_2])[sal^-][RNH_2]$$

The values of $k_1{}^{Zn}$ and $k_2{}^{Zn}$ which were found are given in Table IV. The theoretical values of the relaxation rate con-

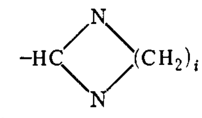
Table III. Observed and Calculated First-Order Relaxation Rate Constants for the Zn(II) Promoted Reaction of Salicylaldehyde and Ethylenediamine

Series	Total concentrations	pH	k_{obsd}, sec^{-1}	k_{calcd}, sec^{-1}
1	5.4×10^{-5} *M* sal, 0.025 *M* en, 0.00126 *M* Zn(II)	6.55	0.022	0.024
		6.87	0.034	0.035
		7.74	0.068	0.074
		8.66	0.079	0.080
		9.50	0.062	0.069
		9.70	0.059	0.065
		9.95	0.057	0.059
		10.55	0.046	0.048
2	4.6×10^{-5} *M* sal, 0.025 *M* en, 0.00378 *M* Zn(II)	6.64	0.021	0.027
		7.36	0.059	0.056
		7.76	0.064	0.067
		9.03	0.070	0.067
		9.55	0.050	0.058
		10.30	0.045	0.042
3	4.8×10^{-5} *M* sal, 0.0245 *M* en, 0.00504 *M* Zn(II)	6.68	0.031	0.029
		7.25	0.055	0.054
		7.49	0.052	0.059
		7.49	0.052	0.060
		7.49	0.061	0.060
		8.23	0.061	0.068
		8.23	0.072	0.068
		9.48	0.046	0.055
		10.39	0.033	0.038
		10.39	0.036	0.038
4	5.0×10^{-5} *M* sal, 0.025 *M* en, 0.00529 *M* Zn(II)	6.60	0.029	0.026
		7.41	0.067	0.058
		7.76	0.075	0.065
		8.16	0.077	0.069
		9.72	0.056	0.051
5	1.11×10^{-4} *M* sal, 0.025 *M* en, 0.00506 *M* Zn(II)	6.04	0.014	0.016
		6.13	0.015	0.016
		6.19	0.014	0.017
		6.24	0.015	0.017
		6.37	0.018	0.019
		6.45	0.019	0.021
		6.65	0.026	0.028
		6.71	0.029	0.030

stants which were calculated using these values are seen in Table III to be in good agreement with the experimental observations. Rate constants which have been found for the Zn(II) dependent paths in the monoamine-sal$^-$ reactions are also given in Table IV.

Discussion

In this study, 1:1 sal$^-$-diamine adducts, their mono-, di-, and triprotonated forms, and their Zn(II) complexes were found to exist in aqueous solutions. The equilibrium data which were obtained do not in themselves distinguish between possible isomeric forms or the number of water molecules involved in a reaction, so it is possible that the adducts found here exist as mixtures of imine, -HC=N-, carbinolamine, -HC(OH)NH, and cyclic imidazolidine (with en) or hexahydropyrimidine (with tn),



Gansow and Holm[9] presented ^{1}H NMR evidence for carbinolamine formation in alkaline *N*-pyridoxylidenealanine solutions, while Hilton and Leussing[10] demonstrated the reversible formation of a highly stable cyclic imidazolidene in glyoxylate-ethylenediamine solutions. Abbott and Martell[11] cite NMR evidence for cyclization in diamino acid-pyridoxal systems. In addition to these structures, various protomers are also possible.

From the spectroscopic data, various inferences regarding the microscopic distribution among these various species have been drawn. To assist the discussion the conclusions are anticipated and are presented in Schemes I and II. Microscopic equilibrium constants were resolved from

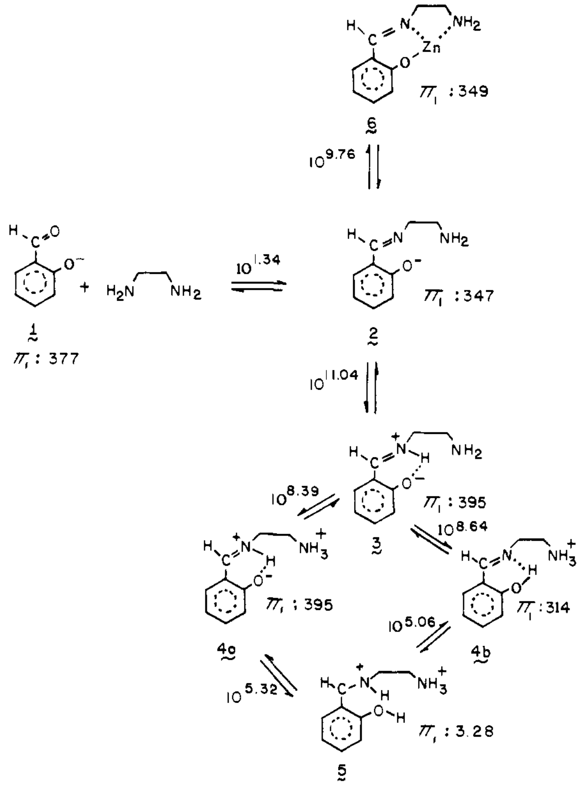
Table IV. Rate Constants for the Zn(II)-Dependent Pathways in Schiff Base Complex Formation

$$d[\text{Schiff base}]_\Sigma/dt = \sum_{i=0}^{N} k_i^{H}[H^+]^i[\text{sal}^-][\text{amine}] + (k_1^{Zn} + k_2^{Zn}[\text{amine}])[Zn^{2+}][\text{sal}^-][\text{amine}]$$

Amine	k_1^{Zn} (M^{-2} sec^{-1})	k_2^{Zn} (M^{-3} sec^{-1})	k_{p_1}[c] (sec^{-1})	k_{p_2}[d] (sec^{-1})	Log β_{11}^*	Log β_{12}^*
en	1.07×10^8	6.9×10^{11}	0.70	51.9	8.35	10.12
tn	4.9×10^7	2.9×10^{11}	0.98	~100	7.70	~9.5
eta[a]	8.0×10^4		0.75		5.03	
β-ala$^-$ [a]	6.5×10^4		0.026		6.41	
gly$^-$ [b]	5.9×10^4	1.2×10^9	0.0026	0.37	7.36	9.51

[a] Reference 5. [b] Reference 4. [c] $k_{p_1} = k_1^{Zn}/\beta_{11}^*$, see ref 4. [d] $k_{p_2} = k_2^{Zn}/\beta_{12}^*$, see ref 4.

Scheme I. Principle Equilibria in the sal$^-$–en System

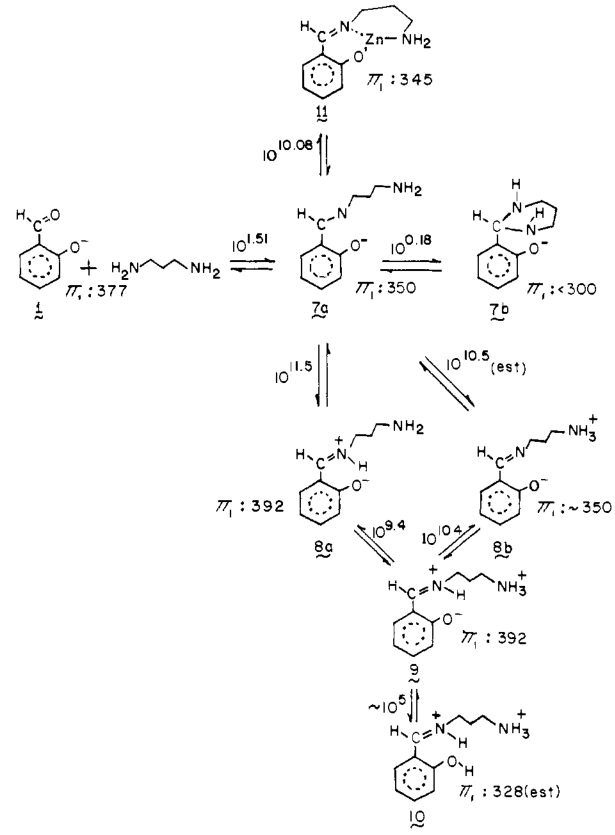


the overall constants given in Table I and are included as are, also, the assigned Schiff base π-π_1* transitions[12] (in nanometers) which are designated by the symbol π_1.

The molar absorption spectra shown in Figures 1 and 2 exhibit maxima which closely correspond to those previously found to be characteristic of Schiff bases formed between pyridoxal[12] or salicylaldehyde[3,5] and primary amines. Furthermore, the extinction coefficient found for the π_1 transition of a given species in this study in general agrees remarkably well with those previously found for the analogous monoamine Schiff bases. For example, the values found at the π_1 absorption maxima are 6.6×10^3 cm^2 mol^{-1} (357 nm) for sal·gly^{2-} and 5.6×10^3 cm^2 mol^{-1} (347 nm) for sal·en$^-$, **2**; 6.0×10^3 cm^2 mol^{-1} for Hsal·gly$^-$ and 6.3×10^3 cm^2 mol^{-1} for Hsal·en, **3** (both at 395 nm); and 5.8×10^3 cm^2 mol^{-1} (351 nm) for Zn(sal·gly) and 5.7×10^3 cm^2 mol^{-1} (349 nm) for Zn(sal·en)$^+$, **6**.

Since it is expected that an equilibrium distribution of an sal·amine adduct among imine, carbinolamine, and, if possible, a cyclic structure will vary to some extent depending on

Scheme II. Principle Equilibria in the sal$^-$–tn System



the nature of the amine moeity, degree of protonation, and complex formation, the relative invariance of these extinction coefficients together with their high values is interpreted here to indicate that, in these cases, forms other than the imine are present in negligible amounts. Unusually low extinction coefficients and/or the presence of more than one peak in the spectral region >300 nm are assumed to indicate the presence of structures other than the imine.

In one of the exceptions to "normal" behavior, the π_1 transition of sal·tn$^-$ is observed in Figure 2 to have an extinction coefficient at the maximum that is only about 45% of that of the "normal" value, but on conversion to either Zn(sal·tn)$^+$ or Hsal·tn, this π_1 transition regains "normal" intensity. Therefore, it appears that the low absorption intensity of sal·tn$^-$ is chemical in origin and an appreciable fraction exists as either the carbinolamine or the cyclic hexahydropyrimidine. The basicity of the condensing amine group does not appear to be a factor in producing the low π_1 intensity, because both eta$^-$ and β-ala^{2-} have similar basicities as tn but sal·eta$^-$ and sal·β-ala^{2-} show "normal" absorption behavior. It, therefore, seems to be the presence of the second highly basic nucleophile on the amine carbon chain which is associated with this effect, suggesting that **7a** cyclizes to give **7b**.

The nitrogen atoms of the gem-diimine group of **7b** have appreciably lower basicities and form weaker complexes than the imine nitrogen atom of **7a**.[10] Therefore, it is expected that either protonation or complexation with a metal ion will stabilize the Schiff base relative to the cyclic form and, thereby, induce an increase in the absorbance, as is observed.

Protonation of the imine nitrogen atom of *N*-salicylaldehydeamines and the related pyridoxal Schiff bases normally occurs in the relatively high pH range 11–12 owing to a substantial transfer of electron density from the phenolate oxygen atom via the π system to the imine nitrogen atom.[4,5,12-18] This reaction is accompanied by the appearance of an intense absorption band centered in the vicinity of 400 nm. In spectral studies on model compounds in partially aqueous media, Heinert and Martell[12] have experimentally demonstrated that protonation at the imine nitrogen atom of a Schiff base leads to a 30–40-nm shift of the π_1 band to longer wavelengths, while protonation at the phenolate oxygen atom leads to a shift of about 60 nm to shorter wavelengths. These results have been confirmed by molecular orbital calculations.[3b,19] The diamine Schiff bases also have a third site that may be protonated under somewhat alkaline conditions, the terminal nitrogen atom of the diamine chain. Protonation at this site is expected to have little direct effect on either the intensities of the π_1 transitions or their positions.

In Hsal·en the presence of a "normal" intense absorption maximum at 395 nm and a minimum at 320 nm indicates that this compound is present almost entirely in the form of the zwitterion, **3**. The slightly lower intensity of the 392 nm band of Hsal·tn and the appearance of a shoulder at 350 nm indicates the presence of about 10% of another structure in addition to the zwitterion, **8a**, Owing to the more basic character of the terminal amine nitrogen atom in tn compared to en, it is likely that it is the amine protonated isomer, **8b**, which is formed. **8b** is expected to have a spectrum similar to that of sal·tn$^-$, hence, the weak absorption band at 350 nm. The ratio of about 10:1 deduced from the band intensities for the ratio of the imminium to ammonium form is highly consistent with values given in Table I for the protonation constants of the imine nitrogen of the Schiff base, $10^{11.5}\ M^{-1}$, and the amine nitrogen of tn, $10^{10.4}\ M^{-1}$.

The second stepwise protonation constants of the diamine Schiff bases were found here to lie in the region of $10^9\ M^{-1}$. The absorption spectrum of H$_2$sal·tn$^+$ in Figure 2 shows "normal" behavior and closely resembles that of Hsal·tn and Hsal·gly$^-$. The 350-nm shoulder observed with Hsal·tn is seen to disappear while the intensity of the 395-nm band increases. Thus, H$_2$sal·tn$^+$ appears to be present almost completely as structure **9** in which both Schiff bases nitrogen atoms are protonated. On the other hand, the intensity of the 395-nm band of H$_2$sal·en$^+$ in Figure 1, is observed to have only one-third the "normal" value and a new band appears at 314 nm. The 395-nm band arises from the immimium-ammonium structure **4a**, and we have assigned the new band to the presence of the phenol-imine isomer **4b**. Precedent for this assignment has appeared in the literature. Christensen[20] observed similar spectral behavior with pyridoxal and pyridoxal phosphate Schiff bases derived from amines containing electronegative substitutents. He attributed the effect to the shift of a proton from the imine to the phenolate site as the result of a decrease in the basicity of the imine nitrogen atom. Heinert and Martell[12] have observed a similar pair of absorption bands in media of low dielectric constant where the zwitterion form of the protonated Schiff bases is destabilized with respect to the neutral phenol-imine structure. Cyclization to give an imidazolidine would seem to be ruled out by the observation that in Figure 4 the spectrum of H$_2$sal·enMe$_2$$^+$ (enMe$_2$ = *N′,N′*-dimethylethylenediamine) exhibits the same two peaks as that of H$_2$sal·en$^+$. It is unlikely that H$_2$sal·enMe$_2$$^+$ would show about the same tendency to cyclize as the en derivative.

In Figure 1 the spectrum of H$_3$sal·en^{2+} shows an absorption band having a maximum at 328 nm. The shift of the longer wavelength band of **4a** to shorter wavelengths by 67 nm on forming H$_3$sal·en^{2+} is consistent with phenolate group protonation, while the shift of the 314-nm band of **4b** by 14 nm to longer wavelengths is consistent with imine group protonation. The extinction coefficient at the maximum of the 328-nm band of $H_3sal{\cdot}en^{2+}$ (2.9×10^3 cm^2 mol^{-1}) is almost identical with that of the 323-nm maximum Hsal (3.2×10^3 cm^2 mol^{-1}). Thus, it appears unsafe to conclude that structures other than **5** are present, although the absorption intensity is relatively low for a Schiff base.

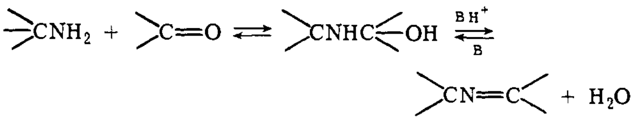
The equilibrium constants for the formation of the unprotonated diamine-sal$^-$ Schiff bases, **2** and **7a**, are $10^{1.34}$ and $10^{1.51}$ M^{-1}, respectively. These values are slightly higher than that found previously for the formation of the analogous ethylamine Schiff base, sal·eta$^-$, $10^{1.05}$ M^{-1}. Relative to Schiff base formation involving monoamines, the diamine constants are augmented by a statistical factor of 2.0 owing to the presence of two identical amine groups on one of the reactants. After correcting the microscopic constants of Schemes I and II for this statistical effect, the *Schiff* base formation constants found in this series of studies are ordered: sal·tn$^-$ ($10^{1.21}$ M^{-1}) > sal·eta$^-$ ($10^{1.05}$ M^{-1}) ~ sal·en$^-$ ($10^{1.04}$ M^{-1}) > sal·β-ala^{2-} ($10^{0.82}$ M^{-1}) > sal·gly^2 ($10^{0.45}$ M^{-1}). Thus, these diamines are approximately similar to ethylamine with respect to their affinities for sal$^-$. The order of basicities of the parent amines as measured by their protonation constants is eta ($10^{0.81}$ M^{-1}) > β-ala$^-$ ($10^{10.21}$ M^{-1}) > tn ($10^{10.10}$ M^{-1}) > en ($10^{9.71}$ M^{-1}) ~ gly$^-$ ($10^{9.70}$ M^{-1}), after the diamine protonation constants are similarly corrected for a statistical factor of 2.0. Basicity is, therefore, not the most important factor in determining the affinities of these amines for sal$^-$, but the order appears to be roughly neutral amine > long chain anion > short chain anion. From this it seems as if an electrostatic effect (repulsion between sal$^-$ and the amino acidate residues) is superimposed upon a weak chemical bond which differs only slightly in intrinsic strength from one amine to another.

Electron delocalization appears to influence the magnitude of the inductive effect of the imminium group on the basicity of the terminal amine group of the Schiff base; the amine group protonation constants of **3** and **7a** are $10^{8.39}$ and $10^{9.4}$ M^{-1}, respectively, compared to the analogous values $10^{7.35}$ and $10^{9.01}$ M^{-1} for Hen$^+$ and Htn$^+$. In the reverse direction, the inductive effect of the positive charge of the ammonium group on the basicity of the imine nitrogen, is sufficient in $H_2sal{\cdot}en^+$ to cause a partial transfer of the proton from the imine group to the phenolate oxygen atom, resulting in a mixture of structures **4a** and **4b**. In $H_2sal{\cdot}tn^{2+}$ the greater length of the carbon chain diminished this effect so that the phenol form is not observed.

The constant for the phenolate group protonation of $H_2sal{\cdot}en^+$, **4a** → **5**, is about $10^{5.32}$ M^{-1}. This is close to the value $10^{4.95}$ M^{-1} reported elsewhere[21] for the protonation of the phenolate oxygen atom of the imminium form of salicylaldehyde Schiff bases. The third protonation constant of the propanediamine-sal$^-$ Schiff base was not measured but is, also, likely to be about 10^5 M^{-1}.

The formation constants in Table I show that Zn(II) forms an appreciably more stable binary complex with free en than it does with free tn. In contrast, with the diamine Schiff bases, sal·tn$^-$ forms the more stable Zn(II) complex. Ring strain, introduced by the 120° bond angle of the imine group, is less in the six-membered chelate ring of Zn(sal·tn)$^+$, **11**, than in the five-membered chelate ring of Zn(sal·en)$^+$, **6**. Relief of this strain more than compensates for the less favorable entropy of forming six-membered rings. A complex, Zn(sal·en)(en)$^+$, with an independently bound en molecule was, also, uncovered. The analogous tn complex was not observed in these studies owing to the weak binding of free tn to Zn(II).

Schiff base condensation reactions proceed through the formation of an intermediate carbinolamine,[22]



In acid media with bases of the strength of hydroxylamine or stronger, the first step is generally rate limiting but in basic media tends to be fast with respect to dehydration.[22] The dehydration step shows general acid catalysis ($\alpha \sim 0.75$).[22] The cross-over pH from the first to second rate limiting step increases as the ease of protonation and expelling an OH$^-$ from the intermediate increases, i.e., as the electron donating ability of substituents on the moiety originating with the carbonyl compound increases.[22] With aromatic aldehydes which possess an oxy atom ortho to the carbonyl group, only a monophasic reaction has been observed[4,5,23] implying that one step is much faster than the other. Evidence has been cited that the first step is rate limiting.[4,5,23]

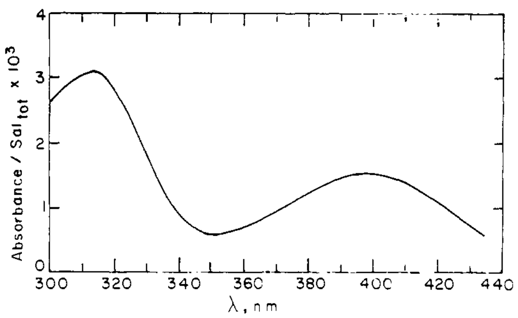


Figure 4. The overall molar absorbance of the adduct formed between salicylaldehyde and *N,N*-dimethylethylenediamine at pH 6.93: $[sal]_{tot} = 2.55 \times 10^{-4}$ *M*, $[Me_2en]_{tot} = 0.40$ *M*, 1.00-cm cell.

For the reaction

$$sal^- + amine \underset{}{\overset{k_0}{\rightleftharpoons}} sal{\cdot}amine^-$$

it is seen in Table II that the diamine rate constants have similar values as that found earlier for eta. After correcting the diamine values for the statistical factor of 2.0, the tn and eta values become essentially identical, while the en value is slightly smaller. In those amine addition and elimination reactions which are subject to base catalysis, diamines tend to show greatly enhanced rate constants compared to monoamines owing to internal base catalysis.[24,25] No such diamine effect is observed in these reactions, consistent with the postulate that dehydration is fast compared to addition.

The diamine rate constants for those paths which exhibit a proton dependence are seen in Table II to be much larger than the corresponding monoamine constants. It appears that the proton dependent diamine terms arise from paths involving the reactions of *monoprotonated* diamines with sal$^-$ and Hsal, while the monoamine paths involve the reactions of the *free* amines with Hsal. The difference merely arises from the fact that under the pH conditions where the proton dependent paths become important, the concentration levels of the monoprotonated diamines are usually higher than those of the free diamines. The reduced rate constants which have been derived for these proposed reaction paths by dividing the values in Table II by the appropriate reactant protonation constants are presented in Table V.

It is seen in Table V that the diamine rate constants reduced from the k_1 of Table II by assuming the reaction paths, $sal^- + H_2N(CH_2)_iNH_3{}^+ \rightarrow$ products, fall in the range of group I values, which are reactions of the free amines with sal$^-$. Similarly, the diamine k_2 and k_3 can be considered to arise from the solvent catalyzed (group II)

Table V. Reduced Rate Constants for Schiff Base Formation

Reaction path	k_f, M^{-1} sec^{-1} or M^{-2} sec^{-1}
Group I. Reactions Involving sal$^-$	
sal$^-$ + eta	1.0
sal$^-$ + gly$^-$	0.18
sal$^-$ + β-ala$^-$	0.48
sal$^-$ + en	1.5 (0.75)[a]
sal$^-$ + tn	2.1 (1.05)[a]
sal$^-$ + Hen$^+$	3.0
sal$^-$ + Htn$^+$	1.2
Group II. Reactions Involving Hsal	
Hsal + eta	13
Hsal + gly$^-$	4.0
Hsal + β-ala$^-$	11
Hsal + Hen$^+$	4.4
Hsal + Htn$^+$	7.7
Group III. Proton Catalyzed Reactions Involving Hsal	
Hsal + eta + H$^+$	9.6×10^6
Hsal + gly$^-$ + H$^+$	42×10^6
Hsal + β-ala$^-$ + H$^+$	36×10^6
Hsal + Hen$^+$ + H$^+$	4.6×10^6
Hsal + Htn$^+$ + H$^+$	24×10^6

[a] Corrected by a statistical factor of 2.0.

and proton catalyzed (group III) reactions of the monoprotonated diamines with Hsal, Hsal + $H_2N(CH_2)_iNH_3^+ \rightarrow$ products. Reduced second- and third-order rate constants similar in magnitude to the corresponding reduced monoamine constants are thereby obtained. See Table V. The results of this interpretation suggest that the two types of systems are highly similar, with en, Hen$^+$, tn, and Htn$^+$ showing roughly the same reactivity toward sal$^-$ and Hsal as eta, gly$^-$, and β-ala$^-$.

Coulombic effects appear to exert a measurable influence on the values of the reduced Schiff base formation rate constants, just as they influenced the Schiff base equilibrium constants. Considering the group I reactions, which involve negatively charged sal$^-$, the constants in Table V are seen to decrease in the order enH$^+$ > tnH$^+$ > eta > β-ala$^-$ > gly$^-$. This is the same order as short chain cation > long chain cation > neutral molecule > long chain anion > short chain anion. Furthermore, the rate constants for the group II paths, which involve neutral Hsal, are seen to be much less dependent on the electrical charge of the amine, with the reactions involving the strongest bases, eta and β-ala$^-$, showing the highest rate constants. Finally, the proton catalyzed reactions of group III give rise to either a positively charged or neutral activated complex, and it is seen that the fatest rate is exhibited by the smallest anion, gly$^-$, while the slowest rate is exhibited by smallest cation, enH$^+$. The intermediate ordering of reactivities in this last group is more ambiguous, however. Similar electrostatic effects in the reactions of the monocations of diamines have been observed by Kirby and Jencks[26] and by Schwartz.[27] Thus, coulombic interactions appear to be important in determining reactivity orders in these types of reactions but are not the sole factor.

In the monoamine investigations it was found that the rate constants for Schiff base formation via Zn(II) dependent paths are more, or less, independent on the nature of the amine. In striking contrast the rate constants for the Zn(II) dependent diamine paths are about a factor of 10^3 greater than those found earlier. The preequilibrium step shown in mechanism I accounts for a major portion of this large difference. Diamines have a much higher affinity for Zn(II) than the monoamines. Another important fact in support of mechanism I is that Zn(II) mediated paths which involve the reaction of the monoprotonated diamines, enH$^+$ and tnH$^+$, were not observed. If the reaction mechanism involved the external attack of diamine on complexed sal$^-$, Znsal$^+$, it is then expected that reaction paths involving enH$^+$ and tnH$^+$ would be observed, just as in the absence of metal ion. Such reactions would be highly favored under the experimental conditions employed in this work, with the ratios of free monocation to free unprotonated diamine having been as high as 10^5:1, in some cases. The absence of such paths together with the kinetic inactivities of Co^{2+}, Ni^{2+}, and Cu^{2+}, indicates that activation of sal$^-$ via metal ion polarization is not an important contribution to the reaction mechanism.

Assuming reaction mechanism I, the observed overall third- and fourth-order rate constants, k_1^{Zn} and k_2^{Zn} of Table IV, were reduced by the preequilibrium mixed ligand complex formation constants of (sal)Zn(diamine)$^+$ and (sal)Zn(diamine)$_2^+$ to give the first-order promanstic constants, k_{p1} and k_{p2}, which are also listed in Table IV. Within the accuracy of the calculations, the values of k_{p1} are seen to be about equal for the eta, en, and tn reactions, while the amino acids, β-ala$^-$ and gly$^-$, have much smaller values. This is consistent with an assumption of the promnastic mechanism that the coordinated ligands of the mixed complex must have sufficient freedom to react within the primary or secondary coordination sphere of the metal ion. The sp^2 hybridization of the amino acid carboxylate carbon atom reduces the ligand flexibility and thereby tends to inhibit the reaction. In accordance with this view, the smaller gly$^-$ ion shows a lower reactivity than the more flexible and larger β-ala$^-$ ion.

Finally, while the promnastic model accounts satisfactorily for the observed differences in rate constants produced by variations in metal ion, carboxyl compound, and amine, it should be noted that the effect is relatively small, especially when compared with the full potential of such a mechanism. By reducing the order of the reaction through a fast preequilibrium step a rate enhancement up to a factor of 10^8 is possible.[28] The relatively small values of k_{p1} and k_{p2} found in these investigations show that the normal metal ion–ligand interactions which are involved in coordination drastically reduce the ligand reactivities. In metalloenzyme systems it appears that entatic distortion[29] is one way by which such coordination inhibition is circumvented.

References and Notes

(1) We gratefully acknowledge support of this research by the National Science Foundation.
(2) (a) D. L. Leussing and C. K. Stanfield, *J. Am. Chem. Soc.*, **88**, 5726 (1966); but see, (b) L. Anderson and D. L. Leussing, *ibid.*, **91**, 4698 (1969).
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Reversible Adsorption of Oxygen on Silica Gel Modified by Imidazole-Attached Iron Tetraphenylporphyrin

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Abstract: Oxygen adsorbs reversibly on an iron(II) porphyrin attached to the imidazole groups of a silica gel containing 3-imidazolylpropyl groups bonded to surface atoms of silicon. The chemisorption of oxygen is weak at 0°, rather strong at −78°, and irreversible at −127°. Each iron atom can adsorb one molecule of oxygen, a result in accord with formation of a monoadduct of the type $Fe\text{-}O_2$. Similarly, carbon monoxide is reversibly adsorbed by the activated modified gel giving the adduct Fe-CO. Worthy of note is the fact that the adsorbent is stable in oxygen at room temperature, presumably because the attachment of iron porphyrin to the rigid support prevents the dimerization to form $Fe^{III}\text{-}O\text{-}Fe^{III}$ which usually takes place.

One of the major difficulties encountered in attempts to prepare monomeric iron-oxygen adducts, particularly adducts of iron porphyrins, is preventing the conversion of the adduct to the μ-oxo dimer

$$\mathrm{Fe(II)} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe\text{-}O_2} \xrightarrow{\mathrm{Fe(II)}} \mathrm{Fe^{III}\text{-}O\text{-}Fe^{III}}$$

Considerable recent work has been aimed at overcoming this problem, and two approaches have been successful. In the first, the reactions are carried out at a temperature so low that the reactions leading to dimerization are very slow but high enough so that the formation of adduct proceeds readily.[1,2] Such a temperature is about −78°. In the second, porphyrins have been substituted in a fashion that inhibits dimerization. By this means reversible reaction between oxygen and Fe(II) porphyrins in solution has been achieved at room temperature.[3,4]

An additional approach would be to attach the iron complex to the surface of a solid so that two iron atoms could not approach each other in such a manner as to lead to dimerization. Wang[5] reported spectral evidence that oxygen binds reversibly to 1-(2-phenylethyl)imidazoleheme diethyl ester embedded in a matrix of an amorphous mixture of polystyrene and 1-(2-phenylethyl)imidazole. However, Collman and Reed[6] reported that cross-linked polystyrene containing imidazole ligands was a support not rigid enough to prevent dimerization and that, upon treatment with oxygen, μ-oxo dimer was extracted by benzene from tetraphenylporphyriniron(II) attached to the modified polystyrene.

Attachment of an iron porphyrin to a rigid support should better inhibit dimerization. We had prepared a number of modified silica gels for use as selective adsorbents and catalysts.[7,8] One of these[7] contained surface 3-imidazolylpropyl groups

to which it should be possible to attach iron(II) porphyrins. This has been done and it has led to the preparation of an adsorbent to which oxygen binds reversibly and which is stable in oxygen even at room temperatures.

Experimental Section

Surface Modification. The imidazolylpropyl gel was prepared as previously described.[7] Ten grams of 60–80 mesh Davison grade 59 silica gel (a wide-pore gel with a nominal pore diameter of 14 nm, a specific area of 340 m^2, and a pore volume of 1.1 cm^3/g) was dried in the oven at 150° and refluxed in *m*-xylene with 2 g of imidazole and 3 g of redistilled 3-chloropropyltrimethoxysilane. Different coverages were obtained by varying the time of reflux from 45 min to 9 hr. The product was washed consecutively in the absence of moisture with benzene and acetone to produce a modified imidazolyl hydrochloride gel. The gel was dehydrochlorinated by treatment with ethylene oxide[9] at 0°, washed with acetone, and dried at 150°. Coverages calculated from C, H, N microanalysis by Miss H. Beck ranged between 1.30 and 1.60 molecules/nm^2 (1.29–1.45 mmol of N/g).

Characterization. The ir spectrum of the modified gel was recorded on a Beckman IR-5 spectrometer in the region 4000–800 cm^{-1} using the KBr disk technique. A silica-KBr disk was used as the reference. Absorption bands were observed at 3140 (w), 1570 (w), 1550 (w), 1220 (s), 1040 (s), and 930 (m) cm^{-1} which can be assigned to vibrations involving the imidazole group,[10] and at 2960 (w) cm^{-1} which corresponds to C–H stretching in the propyl groups.[11] These results accord with the presence of imidazole and of propyl groups on the surface.

Preparation of Adsorbents. All preparations of the iron complexes and absorbents were carried out in Schlenk-type glassware[12a] under an atmosphere of thoroughly deoxygenated and dried nitrogen. All solvents were saturated with nitrogen and transferred by syringe techniques.[12b]

The iron complexes,[13] $Fe(TPP)(py)_2$[14] and $Fe(TPP)(pip)_2$.[15] were prepared by literature methods and were characterized by satisfactory C, H, N analyses and by their visible spectra.[14]

A typical adsorbent was prepared by adding 30 cm^3 of solvent to a 100-cm^3 Airless-Ware flask containing 50–60 mg of the iron complex and 1 g of the modified silica gel. Benzene or methylene chloride was the solvent for $Fe(TPP)(py)_2$, and 1% piperidine-methylene chloride (v/v) for $Fe(TPP)(pip)_2$. The mixture was