Studies on the template synthesis, kinetics and mechanism of cadmium(II) complexes of schiff base derived from glycine and ninhydrin

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N-Diketohydrindylideneglycinatocadmium(II) (schiff base) has been synthesized from glycine-cadmium(II) interaction with ninhydrin and characterized by IR spectra. Kinetics of the reaction has been carried out spectrophotometrically under varying conditions of [ninhydrin], pH and (acetate ion] at different temperatures. During the course of reaction, formation of two different coloured products have been observed. The reaction follows a first order kinetics with respect to [glycine-cadmium(II)] and fractional order kinetics with respect to [ninhydrin] for the formation of both products. The reaction proceeds through the complexation of ninhydrin with glycine-cadmium(II) which is the feature of template mechanism (CLAM reaction). On the basis of observed data, probable structure and template mechanism have been proposed for the formation of two coloured products (Ama. = 375 and 510 nm). The values of k1', k2', K1, and K2, calculated from kinetic data are found to be 3.33 × 10⁻³S⁻¹, 13.4 and 14.2 respectively.

The most important template reaction is the formation of imine bonds (schiff base) used as ligand in the formation of metal complex. The glycine and ninhydrin reaction is an example of nucleophilic addition of amino group to carbonyl group and proceeds through the formation of Schiff base in the early stage and is too unstable for isolation. In the case of glycine-metal complexes, the lone pair of electrons of amino group are coordinated to the metal ion. Therefore, the coordinated nitrogen donor atom can be involved in chelate forming template reaction by virtue of nucleophilic addition to carbonyl group of ninhydrin. These reactions are now widely claimed but seldom proved and detailed mechanistic work has not been carried out on ninhydrin-glycine interaction.

and nothing is known about the schiff base complex derived from glycine-ninhydrin reaction with cadmium(II). Therefore, we planned to study the synthesis of cadmium(II) chelate of schiff base derived from glycine and ninhydrin with special interest in the investigation of kinetics and mechanism of the reaction and are reported in this note.

Experimental
Glycine, ninhydrin and cadmium nitrate (all BDH) were used as such. Solutions of glycine, ninhydrin and cadmium nitrate were prepared in sodium acetate-acetic acid buffer using Elco LI-120 digital pH-meter. IR spectra (KBr) were recorded on an IR-408 (Shimadzu). All the reagents used were of AR grade. Doubly distilled water was used throughout the studies.

The kinetics were followed at the desired temperature maintained at an accuracy of ±0.1°C. The reaction was initiated by adding the appropriate volume of ninhydrin solution in reaction vessel which has the equimolar (1.0 × 10⁻³ mol dm⁻³) solution of glycine and cadmium(II). Evaporation was prevented by using a double surface condenser. Efficient shaking of the reaction mixture was done by bubbling oxygen free nitrogen gas which also served to keep in inert atmosphere. Progress of the reaction was followed spectrophotometrically by pipetting aliquots of the reaction mixture at definite time intervals and the absorbance were measured at 375 and 510 nm. Rate constants were calculated over 80% completion of the reaction.

Preparation of cadmium(II) complex of schiff base derived from glycine and ninhydrin
The yellow coloured (schiff base) complex was prepared by the following general procedure as described elsewhere for the formation of other schiff base complexes. Glycine (0.05 mol) was dissolved in a minimum quantity of distilled water and to this was added cadmium nitrate (0.05 mol) in water (100 ml) at room temperature. Ninhydrin solution (0.05 mol in 150 ml of 95% ethanol) was added dropwise under constant stirring. A yellow colour developed immediately and after few minutes a heavy precipitate was observed. The mixture was allowed to stir at 313K for 1h. The yellowish orange (λ max = 375 nm) pro-
duct was then collected on a filter, washed several times with water, 95% ethanol, ether and then dried in vacuo over P₂O₅. The filtrate of the reaction mixture was refluxed for 1 h and the solution concentrated. The reddish coloured solid got separated on cooling when the reaction mixture was set aside for few hours. The chemical analysis for yellowish orange complex gave: [Found N, 3.98; C, 38.10; H, 2.30; Reqd for C₁₁H₅NO₃Cd N, 4.04; C, 38.15; H, 2.31%] and for reddish complex: [Found N, 3.12; C, 50.00; H, 2.08; Reqd for C₁₈H₁₀NO₃Cd: N, 3.24; C, 50.00; H, 2.31%] respectively.

The yellowish orange complex (λ_max = 510 nm) is partially soluble in ethanol, methanol and chloroform. The complex is highly soluble in coordinating solvent (DMSO) but insoluble in common organic solvents. The melting point was found 608K and the complex was air stable. The reddish complex (λ_max = 510 nm) is soluble in methanol and chloroform. It is very unstable in aqueous solution which gives purple colour after the addition of water in methanol containing reddish complex. Similar observations were reported by Wieland et al. for the complex of cadmium(II) with the final product of glycine-ninhydrin reaction (purple colour). Lennard et al. studied the complexation of this product with cadmium(II) and reported the structure of the complex by X-ray method.

Results and discussion

The yellowish orange complex (I) was found to be non-conducting in DMSO. The composition of the complex has been determined by employing the Job's method of continuous variations and it was found that one mole of ninhydrin reacts with one mole of glycine-cadmium(II). The mode of coordination has been assigned by comparing the IR spectra of I with its ligands (ninhydrin and glycine). Ninhydrin shows vOH at 3300 and vC = O at 1750 and 1720 cm⁻¹ respectively. These frequencies of >C = O showed a negative shift with the complex suggesting its coordination to the metal ion. The IR spectrum of glycine exhibits vNH₂ at 3200-2700 and vCOO (as) at 1600 cm⁻¹. The complex shows a band at 1620 cm⁻¹ assigned to vCOO (as). A positive shift of 10-20 cm⁻¹ is observed in the antisymmetric stretching frequencies of the carboxylate group, the positive shift implying its coordination with cadmium(II). The IR frequencies corresponding to the −OH of ninhydrin and −NH₂ of glycine are absent in the spectra of complex. A new band is observed at 1570 cm⁻¹ in the spectra of complex, suggesting unequivocally, the coordination of nitrogen of C = N group. It could therefore be concluded that schiff base complex (I) behaves as a tridentate ONO donor involving a carbonyl oxygen and azomethine nitrogen in coordination (Scheme 1).

Preliminary kinetic studies showed that cadmium(II) formed a red coloured complex with purple colour-adduct (end product of glycine-ninhydrin reaction) giving only one peak (λ_max = 510 nm) at room temperature. It is a very fast reaction. If a solution containing an excess of ninhydrin was reacted with glycine-cadmium(II) solution at pH 5.0 and 303K, the appearance of yellow colour was observed with λ_max = 375 nm. As the temperature of the reaction mixture is increased, a new peak begins to develop at λ_max = 510 along with the peak at 375 nm. The peak at 510 nm was the same as that previously observed for the interaction of cadmium(II) amino acid with ninhydrin. On the basis of these observations, it was concluded that two coloured products (yellow and red) were formed during the interaction of ninhydrin with glycine-cadmium complex. The kinetics of the formation of these two coloured products was carried out at two different temperatures.

**Kinetics of formation of I [N-diketohydridylidenedglycinecadmium(II)]**

The ninhydrin concentration was always maintained at a large excess over the concentration of glycine-cadmium(II). The order of reaction with respect to glycine-cadmium(II) is found to be one as evidenced by the linear plot of log [glycine-cadmium] versus time. The order with respect to [ninhydrin] is fractional (0.54). Kinetic data for the formation of I are compiled in Table 1. The effect of pH was studied within a range of 3.8 to 5.0 at 303K in acetic acid-sodium acetate buffer beyond which no measurable reaction was possible due to precipitation of basic cadmium hydroxide. The stable products were formed in the range of pH 5.0. Therefore, the studies were limited upto pH


<table>
<thead>
<tr>
<th>pH</th>
<th>temp. = 353K.</th>
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<tr>
<td>5.0</td>
<td>pH = 5.0, temp. = 303K.</td>
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**Conditions for \((\text{obs})\)**:

\[
[A]_T = [A] + [C] \\
[A]_T = [A] + K[A][N] \\
d\text{d}[P]/dt = k_r K_n[C] [A]_T/K_1 + K_2[N] \\
\]

on rearranging Eq. (1),

\[
1/k_{(\text{obs})} = B_1/[\text{ninhydrin}] + B_2 \\
B_1 = 1/k_1, K_1, K_2 = 1/k_1 \\
\]

According to Eq. (2), the plots of \(1/k_{(\text{obs})}\) versus \(1/[\text{ninhydrin}]\) should be linear. This has been found to be the case, thus supporting the proposed mechanism. \(B_1\) and \(B_2\) are the gradients and intercepts of the plots. Fractional order in the \([\text{ninhydrin}]\) and a definite intercept in the \(1/k_{(\text{obs})}\) against \(1/[\text{ninhydrin}]\) plot, suggest that the condensation of coordinated amino group to coordinated carbonyl group is the rate determining step. From the intercepts and gradients, the values of \(k_1\) and \(K_2\) have been calculated and found to be \(3.3 \times 10^{-3}\) and \(13.4\) respectively. These values further indicate that \(k_1\) is the rate determining step and confirms the proposed mechanism. Substituting the values of \(k_1\) and \(K_2\) in the rate Eq. (1), the rate constants have been calculated in various kinetic runs and compared with the values determined experimentally (Table 1). The close agreement between the observed and calculated values provides supporting evidence for the proposed mechanism and also for Eq. (1).

The metal ions catalyzed and retarded the hydrolysis of Schiff bases. The carbon-nitrogen double bonds of Schiff bases are susceptible both to hydrolytic cleavage and the coordination with metal ions. Schiff bases capable of forming bicyclic chelate rings are known to be stabilized towards hydrolysis in the presence of metal ions under mild acidic conditions. However, the Schiff bases which forms monomeric chelates are completely hydrolyzed in the presence of metal ions. In the interaction of glycine with ninhydrin, the reaction proceeds through the formation of Schiff base (I). This reaction acts as a potential tridentate ligand containing ONO donor atoms and forms the bicyclic chelate ring with cadmium(II). The presence of cadmium(II) inhibits the cleavage of \(-\text{COO}\) group by reducing the escaping tendency of \(-\text{COO}\) group and by enhancing the electrophilic character of \(>\text{C}=\text{O}\) group, whereas the decarboxylation of uncomplexed Schiff bases is very fast. The role of cadmium(II) in this reaction is to stabilize(I) towards decarboxylation and hydrolysis.
Kinetics of the formation of red coloured product (II)

The kinetic studies of the formation of this complex was carried out under same conditions as for (I). The results are given in Table 1. The reaction is fractional order with respect to [ninhydrin] and optimum pH of stable product was found in the vicinity of pH 5.0. [Acetate ion] had no significant effect on the rate constants. Formation of II was observed at temperature higher than 323K along with the peak at 375 nm.

Due to the labile nature of glycine-cadmium(II) complex, glycine reacts with ninhydrin in the usual way to give 2-aminodanedione which further reacts with cadmium(II) and ninhydrin to form II through the template reaction path (CLAM reaction). The proposed mechanism is given in Scheme 2. The following kinetic rate equation has been derived:

\[ k_{2(\text{obs})} = k_2 K'\text{[ninhydrin]} / (1 + K'\text{[ninhydrin]}) \quad (3) \]

Rearrangement of Eq. (3) gives,

\[ 1/k_{2(\text{obs})} = C_1 / \text{[ninhydrin]} + C_2 \quad (4) \]

where \( C_1 = 1/k_2 K' \) and \( C_2 = 1/k_2 \)

Thus a plot of \( 1/k_{2(\text{obs})} \) against \( 1/\text{[ninhydrin]} \) should give a straight line. \( C_1 \) and \( C_2 \) were calculated from the intercepts and slope of plots. The values of \( k_2 \) and \( K' \) were found to be \( 6.2 \times 10^{-2}s^{-1} \) and 14.2 respectively. The rate constant (kcal) have been calculated by substituting the values of \( k_2 \) and \( K' \) in Eq. (4) and confirms the validity of rate equation and proposed mechanism. During the studies of red colour formation, it was also observed that intensity of peak at 375 nm was increased with time and it was confirmed that the reaction of glycine and ninhydrin proceeds through the formation of schiff base in the early stage of the reaction.

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References