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Kinetics and Mechanism of the Interaction of Iminodiacetate with *cis*-Tetraamminediaquacobalt(III) Ion in Acidic Media

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Kinetics of the reaction of iminodiacetate (Hida$^-$) with *cis*-tetraamminediaquacobalt(III) have been studied spectrophotometrically at pH 3.0—4.15, $[\text{iminodiacetate}]_T=0.03$—$0.4\ \text{mol dm}^{-3}$, $I=0.5\ \text{mol dm}^{-3}$ ($NaClO_4$), in the temperature range 30—50 °C. The reaction is governed by the rate law:

$$\text{rate} = \{k_{-1}+k_1[\text{iminodiacetate}]_T\}[\text{complex}],$$

where k_{-1} and k_1 denote the reverse aquation and anation rate constants respectively. At 40 °C the k_{-1} values increase with pH and show a limiting tendency at pH$\approx$4. The pH-anation rate profile indicates no reaction at pH$<$1.5 and in the range 3.5—3.9, k_1 remains constant. The pH dependence on rate is expressed as $k_1=k_AK_{AH}/([H^+]+K_{AH})$, where k_A is the anation rate arising from the aqua complex ion and Hida$^-$ species and K_{AH}, the dissociation constant for the iminodiacetic acid. The value of k_A at 40 °C$=(5\pm0.02)\times10^{-5}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$. The activation parameters, ΔH^* and ΔS^* for the anation step are $170\pm2\ \text{kJ mol}^{-1}$ and $239\pm3\ \text{JK}^{-1}\text{mol}^{-1}$. The reaction is believed to operate through the initial complexation at the carboxylate end followed by a fast intramolecular proton transfer with simultaneous ring closure to form a chelated product. The complexation probably takes place through a dissociative interchange (I_d) mechanism.

Mixed-ligand complex formation has several important biological implications because of the enhanced probability of bringing two different ligands together or of facilitating enzyme-substrate interaction through a bridging metal ion. Bulky ligands, especially those which form multimembered chelate rings, inhibit substitution reactions and usually tend to mask out the influence of bonding and charge on the substitution rates.[1] Unfortunately anation reactions involving such multidentate ligands and an inert metal centre are not explored much. Herein we report the kinetics of interaction of *cis*-tetraamminediaquacobalt(III) ion with iminodiacetate (Hida$^-$).

Experimental

Reagents. The *cis*-tetraamminediaquacobalt(III) perchlorate is prepared following literature method[2] and its purity is checked by spectral and elemental analyses.

The tetraammine(iminodiacetato)cobalt(III) perchlorate has been prepared for the first time by us using the following procedure.

0.44 g (0.15 mole) disodium iminodiacetate monohydrate is dissolved in miniumm volume of water. pH of the solution is adjusted with dilute $HClO_4$ (0.1 mol dm^{-3}) to $\approx$4.0 and the solution is heated on water bath. To this hot solution is added with stirring an aqueous hot solution of 0.86 g (0.125 mole) *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$. Total volume of the solution is kept at $\approx$15 cm^3. The mixture is heated on the water bath for about 30 min. Pink colored solid product separates out from the solution. It is then cooled. The solution is filtered, the solid is washed with a little cold water followed by cold ethanol and finally dried over fused $CaCl_2$. The purity of the complex is ascertained by elemental analyses: Calcd for $[Co(NH_3)_4(\text{Hida})](ClO_4)_2$: Co, 12.87; C, 10.48; H, 3.93; N, 15.29%. Found: Co, 12.73; C, 10.25; H, 3.79; N, 15.32%. Molar conductance (Λ_M at 25° (in water)) $=240\ \text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$.

Disodium iminodiacetate monohydrate (Fluka AG) is used as received. Recrystallized sodium perchlorate (E. Merck) is used for ionic strength adjustments. pH of the reacting solutions is maintained with dilute perchloric acid prepared from 70% $HClO_4$ (E. Merck).

In addition to the elemental analysis and conductance data, spectral measurements of the synthesized complex furnish further evidence regarding the mode of binding of the acid in the complex. It is well known that amino acids form chelated species with metal ions binding through carboxylato (O$^-$) and amino (N) groups. The position and intensities of the first and second bands of a freshly prepared solution (at pH$=$4.0, $I=0.5\ \text{mol dm}^{-3}$ ($NaClO_4$)) of the isolated complex (λ_{max}, 508 nm; $\varepsilon=90\pm1\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ and λ_{max}, 354 nm; $\varepsilon=60\pm1\ \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) corresponding to ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$ transitions match very well with those of tetraammine(amino acidato)cobalt(III) species.[3] For a tridentate ligand like *N*-methyliminodiacetate (mida^{2-}), Bailey *et al.*[4] have isolated an intermediate [Cr(mida)(Hmida)(H_2O)] during the anation studies of $[Cr(\text{mida})(H_2O)_3]^+$ with Hmida$^-$. In this intermediate Hmida$^-$ is coordinated as a bidentate ligand through nitrogen and one CO_2^- group and one carboxyl group (protonated) remains uncoordinated. The mode of bonding of Hida$^-$ in our complex follows the same fashion resulting in a 1 : 2 electrolyte. IR spectrum in KBr discs shows a strong absorption at 1630 cm^{-1} assignable to $[\nu_{COOM}+\delta_{d(NH_3)}]$. Free carboxyl stretching frequency generally encountered at $\approx$1700 cm^{-1} is probably masked by the presence of this strong band and does not appear. The presence of a sharp band at 555 cm^{-1} strongly indicates the occurance of ν(M–N(amino acid)) bonding.[5]

Measurements. The kinetics of the reaction have been followed with a Pye-Unicam SP8-150 spectrophotometer equipped with a thermostated cell compartment. pH of all the solutions has been measured with a Beckman pH meter (4500). The kinetic spectra has been recorded with a Hitachi 330 spectrophotometer. The spectral change observed during the reaction of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with iminodiacetate at pH 3.0—4.15 leads to an increase in the absorption maxima at 354$\pm$2 and 508$\pm$1 nm, and the rates of the reaction were followed by product absorption at 508 nm. Kinetics of the reaction were measured under pseudo-first-order conditions having $[\text{complex}]=2\times10^{-3}\ \text{mol dm}^{-3}$ and $[\text{iminodiacetate}]_T=0.03$—$0.4\ \text{mol dm}^{-3}$ in the pH region 3.0—4.15 at temperatures 30—50 °C. Examination of the

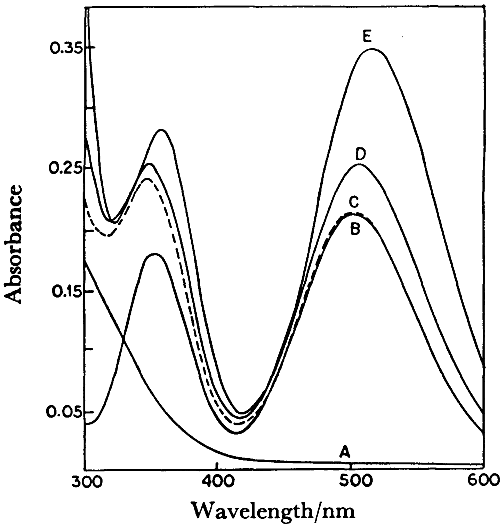


Fig. 1. Absorption spectra: (A) [iminodiacetate] = 0.4 mol dm^{-3}, pH = 4.00 ± 0.01, I = 0.5 mol dm^{-3}; (B) [Co(NH$_3$)$_4$(H$_2$O)$_2^{3+}$] = 4 × 10^{-3} mol dm^{-3}, pH = 4.00 ± 0.01; (C) [Co(NH$_3$)$_4$(H$_2$O)$_2^{3+}$] = 4 × 10^{-3} mol dm^{-3}, [iminodiacetate] = 0.4 mol dm^{-3}, pH = 4.00 ± 0.01, I = 0.5 mol dm^{-3} and temperature ≈ 15 °C (spectrum recorded within 2 min. of mixing); (D)→(E) Change in absorbance with time during the reaction in solution (C) by gradually raising the temperature to 40 °C; curve (E) actually denotes the infinite time spectrum of the reacting solution.

absorbances at infinite time (A_∞) for reacting solutions indicates an equilibrium for the anation process.[6] The approach to equilibrium first-order rate constants (k_{app}) are evaluated from the plots of $\log(A_\infty - A_t)$ *vs.* time (t). These plots are good straight lines for more than three half-lives of the reaction, free from any kinetic complications.

Results and Discussion

A close perusal of the kinetic spectra (Fig. 1) shows that curve (C) departs largely in the range 300—400 nm, though the visible region logically shows no progress in the reaction. The origin of the departure in the region mentioned is due to the absorbance of excess iminodiacetate (curve A) and if we subtract it from that in curve(C), there is practically no difference. This result suggests that no complex of significant stability is formed by association of the diaquacobalt(III) species and iminodiacetate at the time of mixing. The curve(E) shows that the absorbance maximum value at 354 nm is also little higher (*ca.* 15%) than that of the corresponding value of the isolated product under the same conditions (*vide supra*). This also originates from the residual absorbance of iminodiacetate.

At a constant pH, the rate of reaction is shown to be linearly dependent on total iminodiacetate concentration, [iminodiacetate]$_T$. Plots of k_{app} *vs.* [iminodiacetate]$_T$ are straight lines having appreciable intercepts (Fig. 2). The intercept should correspond to the reverse aquation path which has earlier been predicted from the inconcurrence of A_∞ values. With [iminodiacetate]$_T$ present in > ten fold excess over the complex, the rate law (1) is found to apply.

$$\text{Rate} = \{k_{-1} + k_1[\text{iminodiacetate}]_T\}[\text{complex}], \qquad (1)$$

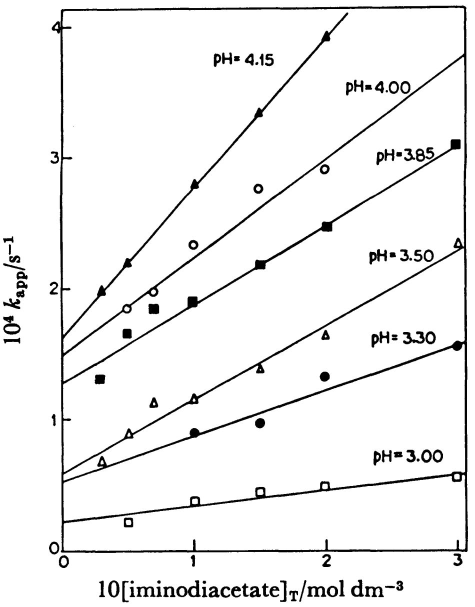


Fig. 2. Plots of k_{app} *vs.* [iminodiacetate]$_T$ at 40 °C, [complex] = 2 × 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} and pH = 3.0—4.15.

TABLE 1. KINETIC PARAMETERS OBTAINED IN THE ANATION REACTION OF *cis*-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ WITH IMINODIACETATE

Temp/°C	pH	$10^4 k_{-1}/s^{-1}$	$10^4 k_1$/mol^{-1} dm^3 s^{-1}
40	3.0	0.22 ± 0.01	1.24 ± 0.02
	3.3	0.53 ± 0.02	3.47 ± 0.02
	3.5	0.60 ± 0.02	5.60 ± 0.03
30	3.85	0.29 ± 0.01[a]	0.79 ± 0.01
35		0.56 ± 0.01[a]	4.41 ± 0.02
40		1.29 ± 0.03[a]	5.97 ± 0.03
50		3.81 ± 0.04[a]	68.70 ± 0.08
40	4.0	1.50 ± 0.01	7.49 ± 0.02
	4.15	1.62 ± 0.02	11.46 ± 0.06

a) Activation parameters obtained from the data corresponding to k_{-1} are $\Delta H^{\ddagger}_{-1} = 100 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger}_{-1} = -1 \pm 0.5$ JK^{-1} mol^{-1}.

where k_{-1} denotes the rate constant for the aquation path and k_1, the second order anation rate constant. The least-squares values of k_{-1} and k_1 obtained at different pH and temperatures are shown in Table 1. The k_{-1} values increase with pH and show a limiting tendency at pH ≃4. The pH-anation rate profile (Fig. 3) clearly indicates three important generalisations; (i) in the high acid region where pH < 1.5, there is no reaction, (ii) at pH > 3.5, Hida$^-$ is the only species in solution, (iii) at pH > 3.9, the reaction rate starts to increase. All three observations can be rationalized into the following derivations.

$$\text{H}_2\text{ida} \overset{K_{AH}}{\rightleftharpoons} \text{Hida}^- + \text{H}^+, \qquad (2)$$

$$[\text{Co(III)}]_T + \text{Hida}^- \underset{k_{-1}}{\overset{k_A}{\rightleftharpoons}} \text{products}, \qquad (3)$$

$$k_1 = \frac{k_A K_{AH}}{[\text{H}^+] + K_{AH}}. \qquad (4)$$

The expression (4) is justified by the pH-anation rate

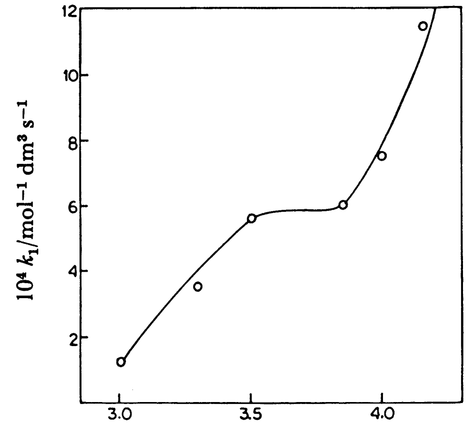


Fig. 3. pH-anation rate profile at 40 °C and $I=0.5$ mol dm^{-3}.

profile. At relatively high pH, $[\mathrm{H}^+] \ll K_{\mathrm{AH}}$ ($=3.55 \times 10^{-3}$ mol dm^{-3} at 40 °C[7]), the rate becomes acid-independent since $k_1 = k_{\mathrm{A}}$. At very low pH when $[\mathrm{H}^+] \gg K_{\mathrm{AH}}$, $k_1 = k_{\mathrm{A}} K_{\mathrm{AH}} [\mathrm{H}^+]^{-1}$. Thus a plot of k_1 *vs.* $[\mathrm{H}^+]^{-1}$ should produce strict linearity in the region of pH<2 having slope ($=k_{\mathrm{A}} K_{\mathrm{AH}}$) and $k_{\mathrm{A}} = (5.0 \pm 0.2) \times 10^{-5}$ mol^{-1} dm^3 s^{-1} at 40 °C obtained by extrapolation of the data to $[\mathrm{H}^+]^{-1}=0$, as we were unable to carry out experiments at pH <2 (the reaction rate becoming increasingly slow at lower pH). At pH >3.9 the increase in rate may be ascribed to the onset of protic equilibrium of the diaqua complex. The *cis*-labilisation phenomenon of coordinated-OH group is well documented in literature.[8–10]

The activation parameters obtained by analysing the kinetic data according to the Eyring equation are shown in Table 2. This also includes the comparable kinetic parameters for analogous systems. There is however not a large difference in the anation rates (k_1^x) of *cis*-$[\mathrm{Co(NH_3)_4(H_2O)_2}]^{3+}$ with NCS$^-$, Hsal$^-$, Hphthal$^-$, and Hida$^-$. If it is assumed that the mechanism is a dissociative interchange (I_d) type (Eqs. 5 and 6), the rate constant k_1 is a measure of $K_{\mathrm{IP}} k_i$.

$$[\mathrm{Co(NH_3)_4(H_2O)_2}]^{3+} + \mathrm{Hida}^- \overset{K_{\mathrm{IP}}}{\rightleftharpoons} [\mathrm{Co(NH_3)_4(H_2O)_2}^{3+}\mathrm{Hida}^-], \quad (5)$$

$$[\mathrm{Co(NH_3)_4(H_2O)_2}^{3+}\mathrm{Hida}^-] \xrightarrow{k_i} [\mathrm{Co(NH_3)_4(Hida)}]^{2+} + 2\mathrm{H_2O}. \quad (6)$$

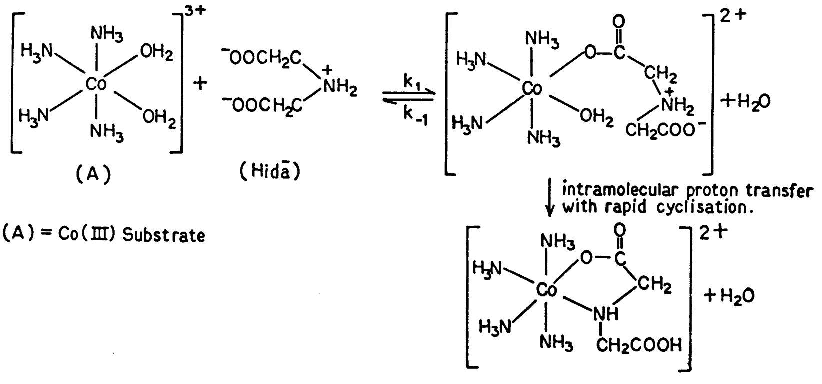
The relative small difference in the values of k_1^x (x$=$NCS$^-$, Hsal$^-$, Hphthal$^-$, and Hida$^-$) is thus indicative of a dissociative activation since the value of $K_{\mathrm{IP}} k_i$ are likely to remain fairly constant for similarly charged ligands. The activation parameters also support this mechanism. Assuming an I_d mechanism for any reaction, the activation parameters for the anation step imply more bond breaking than bond making in the transition state. If, however, the entering group is forming a bond in the transition state (associative in nature), stringent steric requirements have to be met and the entropy of activation would be relatively negative. The activation parameters obtained for the aquation step (Table 1) are in excellent agreement with those obtained for the aquation reaction of $[\mathrm{Co(NH_3)_4(NCS)(H_2O)}]^{2+}$ ($\Delta H^{*}=102 \pm 7$ kJ mol^{-1}, $\Delta S^{*}=3 \pm 5$ JK^{-1} mol) and of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ ($\Delta H^{*}=99.2$ kJ mol^{-1}, $\Delta S^{*}=-6.7$ JK^{-1}mol^{-1}).[12]

From a detailed analysis of kinetic data, Jordan[13] has suggested that the initial complexing of a metal

TABLE 2. ANATION RATE CONSTANTS[a] AND ACTIVATION PARAMETERS

Nucleophile	$10^4 k_1^x$/mol^{-1} dm^3 s^{-1}	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/JK^{-1} mol^{-1}	Ref.
NCS$^-$	2.44±0.07[b]	143±2	141±5	8
Hsal$^-$	7.5 ±0.01	138±3	135±4	9
Hphthal$^-$	14.1 ±0.02[c]	116±2	70±4	11
Hida$^-$	5.60±0.03	170±2	239±3	This work

a) All at temp 40 °C and ionic strength$=0.5$ mol dm^{-3}. b) Represents k_1 value at pH$=2.0$ where no contribution from aquahydroxocobalt(III) is present, since an unusual *cis*-labilisation for the hydroxo group even at pH>2.4 has been encountered in this reaction. c) At pH 3.5 no contribution for phthal^{2-} is observed and the rate-law is fully described by an equation analogous to (1).



Scheme 1.

ion by a simple amino acid ($^{-}$O–N) occurs at the carboxylato group and chelate ring closure is an important kinetic factor specially for those amino acids with $pK_1>8$ even in a less labile system like nickel(II). With an inert metal centre, it is generally believed[14] that the initial complexing is the rate determining step followed by a rapid cyclization to form the chelated species. All these considerations lead us to the postulation of a total reaction as in Scheme 1.

References

1) V. S. Sharma and D. L. Leussing, "Metal Ions in Biological Systems," ed by H. Siegel, Marcell Dekker, Inc., New York (1973), Vol. 2, p. 127.

2) J. Springborg and C. E. Schaffer, *Inorg. Synth.*, **18**, 83 (1978).

3) W. U. Malik, R. Bembi, and Sushila, *J. Inorg. Nucl. Chem.*, **39**, 345 (1977).

4) A. A. T. Bailey, S. Dutta-Chaudhuri, C. J. O'Connor, and A. L. Odell, *J. Chem. Soc., Dalton Trans.*, **1976**, 2103.

5) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley, New York (1977), p. 308.

6) The higher the incoming ligand concentration, the more complete the reaction becomes. At $[\text{iminodiacetate}]_T \geq 0.15$ mol dm^{-3}, the A_∞ values become almost equal to the absorbance maximum of the isolated tetraammine(iminodiacetato)cobalt(III) product. The percentage of equilibrium reaction varies from *ca.* 85—95 in the range of $[\text{iminodiacetate}]_T$, 0.03—0.40 mol dm^{-3}.

7) This value has been obtained by extrapolation of the corresponding parameter at other temperatures (S. Chaberek Jr. and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952)).

8) M. C. Ghosh and P. Banerjee, *J. Coord. Chem.*, **13**, 237 (1984).

9) M. C. Ghosh, P. Bhattacharya, and P. Banerjee, *Transition Met. Chem.*, **9**, 68 (1984).

10) S. Balt, *Recl. Trav. Chim. Pays-Bas*, **91**, 1026 (1972).

11) P. Bhattacharya and P. Banerjee, unpublished results.

12) A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954).

13) R. H. Voss and R. B. Jordan, *J. Am. Chem. Soc.*, **98**, 2173 (1976).

14) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston (1974), p. 196.