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Pressure Effect on the Isomerization Velocities of β-[Co(edda)(tn)]$^+$ and β-[Co(edda)(en)]$^+$ in Solution

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The rates of the isomerization of β-[Co(edda)(tn)]$^+$ and β-[Co(edda)(en)]$^+$ to the α-isomers in a 0.2 M Na_2CO_3–0.2 M $NaHCO_3$ buffer solution have been measured under pressures of 1, 1000, 2000, and 3000 kg cm^{-2}. The activation volumes have been found to be 14.7 and 20.0 ml mol^{-1} respectively. It may be concluded that these reactions proceed through the SN1 CB mechanism.

The investigation of the pressure effect on a reaction velocity gives the value of the activation volume through the $\Delta V^{\neq} = -RT(\mathrm{d}\ln k/\mathrm{d}P)$ relation and, therefore, some information about the reaction mechanism.[1] Such investigations were carried out for several reactions of complex ions in solution, and the reaction mechanisms were deduced on the basis of the activation volume ($\Delta V^{\neq}$) and the total volume change (ΔV).[2] For an isomerization reaction, since the ligands of the reactant and of the resultant are identical, the total volume change can be assumed to be very small; hence, $\Delta V^{\neq}$ must be directly related to the reaction pathway.

Kuroda found that β-[Co(edda)(tn)]$^+$ and β-[Co(edda)(en)]$^+$ isomerize to the α-isomers in basic solutions, and proposed the Co–N bond rupture as the activation step.[3,4] In this study, the pressure dependence of the reaction rate was involved, and so the mechanism proposed by Kuroda was re-examined from the standpoint of the pressure effect.

Experimental

Materials. The α- and β-ethylenediamine-*N,N'*-diacetato(trimethylenediamine)cobalt(III) perchlorate, α- and β-[Co(edda)(tn)]ClO_4 (β-isomer is the monohydrate), were synthesized by the method developed by Kuroda and were identified by the agreement of the absorption spectra with those obtained by him.[3] The β-ethylenediamine-*N,N'*-diacetato(ethylenediamine)cobalt(III) perchlorate, β-[Co(edda)(en)]ClO_4, was provided by Kuroda.[5] Commercial reagent-grade chemicals were used. The water was distilled after an ion exchange.

Measurements. On the initiation of a reaction, about 20 mg of the complex salt and 10 ml of a 0.2 M Na_2CO_3–0.2 M $NaHCO_3$ buffer solution (pH=9.47 at 60 °C) at the reaction temperature were mixed in a beaker, and then 4 ml of the mixed solution was immediately poured into a glass syringe. The excess of the solution was quenched by putting the beaker in cold water, and the initial concentration was calculated from the absorption intensity of this quenched solution. The top of the syringe was sealed with a Teflon tape and was then set into liquid paraffin in a special steel cylinder, which had been maintained at the reaction temperature. The cylinder was set between the two plates of a press and pressurized rapidly. After a definite time, the pressure was released and the solution was quenched immediately. The absorption spectrum was measured subsequently.

The temperature of the cylinder block was controlled by circulating water from a thermostat and measured by a copper-constantan thermocouple, inserted in a hole of the cylinder block. It was maintained at 60±0.2 °C for the reaction of β-[Co(edda)(tn)]$^+$ and at 65±0.2 °C for that of the β-[Co(edda)(en)]$^+$.[6] The thermometer and the thermocouple were calibrated within ±0.1 °C by a standard thermometer made by the T. L. M. G. Co., Germany. The pressure value of the press was measured by means of a Bourdon gauge and controlled within ±2 kg cm^{-2}. The gauge was calibrated by a free piston gauge, and the pressure value was reproducible within ±1 kg cm^{-2}. The pressure generated in the cylinder was estimated from the piston-area ratio (22.56).

Results

Figure 1 illustrates the spectra of the initial solution of β-[Co(edda)(tn)]$^+$ and that after a definite reaction time. The three isosbestic points lie within ±4 nm from the positions obtained by Kuroda.[3] The concentration of each isomer was calculated from the absorption intensity at 503 nm, using the absorption coefficients of 153.8 and 64.8 l mol^{-1}cm^{-1} for the β- and the α-isomer respectively. A similar spectral change was observed for the reaction of β-[Co(edda)(en)]$^+$; the three isosbestic points lay within ±5 nm from the positions obtained by Kuroda.[4] The concentration of each isomer was calculated from the absorption intensity at 494 nm, using the absorption coefficient of 150.7 and 56.4 l mol^{-1} cm^{-1} for the β- and the α-isomers respectively.

These reactions have been known to be opposing first-order reversible reactions with respect to the

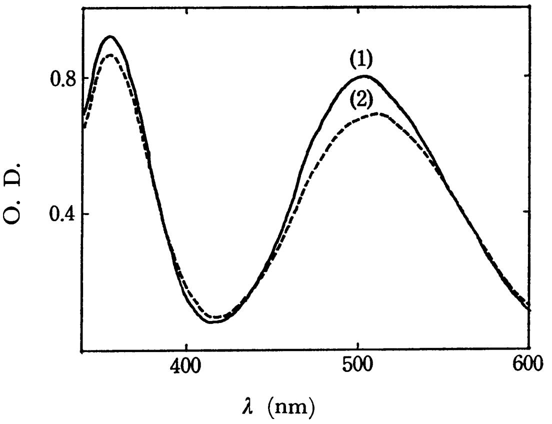

Fig. 1. Change of the absorption spectrum of β-[Co(edda)(tn)]$^+$ in 0.2 M Na_2CO_3–0.2 M $NaHCO_3$ solution.
1: Initial, 2: after reaction for 383 min at 58.6 °C and 3000 kg cm^{-2}.

complex ions at normal pressure.[3,4] This was ascertained to be also true under high pressures, and the rate constants were calculated from the following equations:

$$\beta\text{-[Co(edda)(tn or en)]}^+ \rightleftarrows \alpha\text{-[Co(edda)(tn or en)]}^+$$

$$k_1 = \frac{1}{(1+1/K)t}\ln\frac{m}{m-x},\quad K = \frac{k_1}{k_{-1}},\quad m = \frac{k_1b-k_{-1}a}{k_1+k_{-1}}$$

where

k_1, k_{-1}: rate constants of the forward and the backward reactions; K: the equilibrium constant; t: the reaction time at a high pressure; a, b: the concentrations of the α-isomer and of the β-isomer at the biginning of the pressurization, and x: the concentration isomerized during time t

Kuroda has reported, for the β-[Co(edda)(tn)]$^+$ solution, that, at equilibrium, 88.3—89.5% of the initial β-isomer isomerizes to the α-isomer, irrespective of the reaction temperature and the pH value of the solution.[3] For this complex ion in the 0.2 M Na_2CO_3–0.2 M $NaHCO_3$ solution, an 89% isomerization was found after 11 half-lives at 1000 kg cm^{-2} and 68.6 °C. $K=7.93$, which corresponds to an 88.8% (average value) isomerization, was used throughout the calculations at each pressure. For β-[Co(edda)(en)]$^+$ in the 0.2 M Na_2CO_3–0.2 M $NaHCO_3$ solution at 68.6 °C, a 95.3% isomerization was found after 9 half-lives at normal pressure and a 93.3% isomerization after 8 half-lives at 1000 kg cm^{-2}. The k_1 value is not very much influenced by the small variations in K value, and so $K=20.3$, which corresponds to a 95.3% isomerization, was used throughout the calculations for this complex. a and b were estimated from the initial concentration and a consideration of the progress of the reaction during the time from the mixing to the attainment of a high pressure. It took about 3 min. Similarly, for the estimation of x, the progress during the time from the release of the pressure to the quenching was taken into account. It took about 2 min.

The rate constants at each pressure are summarized in Table 1. The real reaction temperature in the syringe was slightly lower than the block temperature because of the heat loss through the cylinder bottom and the piston. For the estimation of the temperature difference, the rate constants at a normal pressure in Table 1 were compared with those obtained in a flask in an ordinary thermostat controlled at 60 °C for β-[Co(edda)(tn)]$^+$ ($k_1=6.20\times10^{-3}$ m^{-1}) and at 65 °C for β-[Co(edda)(en)]$^+$ ($k_1=10.0\times10^{-3}$ m^{-1}). Taking the activation energies into account, the temperature difference was estimated to be 1.4 °C. The rate constants were fitted to the formula: $\ln(k_{1\text{p}}/k_{10})=cP+dP^2$, by the least-mean-square method, where $k_{1\text{p}}$ and k_{10} represent the rate constants at a high pressure and at zero pressure respectively.[1] The relationships are shown in Fig. 2. The activation volumes at zero pressure were calculated from the $\Delta V^{\neq}=-RTc$ relation as 19.9 ml mol^{-1} for β-[Co(edda)(tn)]$^+$ and as 25.2 ml mol^{-1} for β-[Co(edda)(en)]$^+$.

Kuroda measured the rate constants at 65 °C at different OH$^-$ ion concentrations. His results show that k_1 is linearly dependent on [OH$^-$] for β-[Co(edda)(tn)]$^+$ and that k_1 is expressed as $k_1=k'_1[\text{OH}^-]+k_0$, where k_0 is a parameter.[3] For this complex, k_1 was also measured in the 0.08 M Na_2CO_3–0.32 M $NaHCO_3$ solution (pH=8.90 at 60 °C) at 58.6 °C; it was found to be 2.06×10^{-3}, 1.10×10^{-3}, and 0.46×10^{-3} m^{-1} at 1, 1000, and 2000 kg cm^{-2} respectively. Assuming a linear relationship between k_1 and [OH$^-$], the k_0 value was obtained to be 1.01×10^{-3}, 0.64×10^{-3}, and 0.15×10^{-3} m^{-1} at 1, 1000, and 2000 kg cm^{-2} respectively. This pressure dependence of k_0 is approximately equal to that of k_1, at least in the lower pressure range (≤1000 kg cm^{-2}); therefore, the pressure dependence of $k'_1[\text{OH}^-]$ may be taken as equal to that of k_1. For β-[Co(edda)(en)]$^+$, k_1 is approximately proportional to [OH$^-$] and may be expressed as $k_1=k'_1[\text{OH}^-]$ for a relatively small range of [OH$^-$].[4]

The OH$^-$ ion concentration in this buffer solution is given by: $[\text{OH}^-]=K_\text{w}[\text{CO}_3{}^{2-}]/K_2[\text{HCO}_3{}^-]$, where

Table 1. Rate constants for the isomerization of β-[Co(edda)(tn)]$^+$ and β-[Co(edda)(en)]$^+$ in 0.2 M Na_2CO_3-0.2 M $NaHCO_3$ solution[a)]

	β-[Co(edda)(tn)]$^+$ at 58.6 °C			
P (kg cm^{-2})	1	1000	2000	3000
	4.82(116)	2.54(366)	1.20(480)	0.62(383)
$k_1/10^{-3}$ m^{-1}	5.06(99)	2.36(184)	1.46(362)	0.68(191)
	4.87(88)	2.19(126)	1.25(261)	
average	4.92	2.36	1.30	0.65
	β-[Co(edda)(en)]$^+$ at 63.6 °C			
P (kg cm^{-2})	1	1000	2000	3000
	7.75(132)	3.49(242)	1.43(410)	0.84(410)
$k_1/10^{-3}$ m^{-1}	7.54(60)	3.61(131)	1.42(264)	0.75(340)
			1.44(121)	
average	7.65	3.55	1.43	0.80

a) The figure in the parentheses denotes the pressure duration in min,

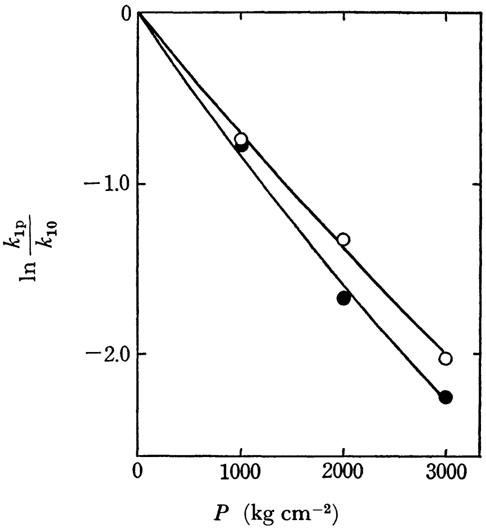

Fig. 2. The relation between $\ln(k_{1\text{p}}/k_{10})$ and P (kg cm^{-2}).
○: For β-[Co(edda)(tn)]$^+$, $c=-7.09\times10^{-4}$, $d=1.26\times10^{-8}$.
●: For β-[Co(edda)(en)]$^+$, $c=-8,84\times10^{-4}$, $d=4,11\times10^{-8}$,

K_w is the ionic product of water and where K_2 is the 2nd dissociation constant of carbonic acid.[7] When the buffer concentration is sufficiently high, as in this case, the pressure-induced change in pH does not significantly alter the $[CO_3^{2-}]/[HCO_3^-]$ ratio term.[8] Hence,

$$-RT\frac{\mathrm{d}\ln k_1}{\mathrm{d}P} = -RT\left[\frac{\mathrm{d}\ln k_1'}{\mathrm{d}P}+\frac{\mathrm{d}\ln[\mathrm{OH}^-]}{\mathrm{d}P}\right]$$

$$= -RT\left[\frac{\mathrm{d}\ln k_1'}{\mathrm{d}P}+\frac{\mathrm{d}\ln K_w}{\mathrm{d}P}-\frac{\mathrm{d}\ln K_2}{\mathrm{d}P}\right]$$

The pressure dependence of K_w has been measured by Hamann, and that of K_2, by Distèche and Distèche.[9,10] From their measurements, the ΔV value for $H_2O=H^+ + OH^-$ was calculated to be -20.4 ml mol^{-1} at 25 °C, and that for $HCO_3^- = H^+ + CO_3^{2-}$, to be -25.6 ml mol^{-1} at 22 °C. Thus, $\Delta V^{\neq 1} = -RT\mathrm{d}\ln k_1'/\mathrm{d}P$ can be calculated; 14.7 ml mol^{-1} and 20.0 ml mol^{-1} were obtained for β-[Co(edda)(tn)]$^+$ and β-[Co(edda)(en)]$^+$ respectively.

Discussion

Two reaction mechanisms are conceivable in view of the k_1 dependence on [OH$^-$]. One is the associative (SN2) mechanism, and the other is the dissociative (SN1 CB) mechanism. In the associative case, the rate-determining process is the association of the β-isomer with an OH$^-$ ion to form a seven-coordinated intermediate:

$$\beta\text{-[Co(edda)(tn or en)]}^+ + \mathrm{OH}^-$$
$$\rightarrow \beta\text{-[Co(edda)(tn or en)(OH)]}$$

An analogous case would be the substitution reaction of [Pt(dien)X]$^+$ by Y$^-$ (X$^-$=Cl$^-$, Br$^-$, I$^-$, N$_3^-$; Y$^-$=N$_3^-$, NO$_2^-$, I$^-$, SCN$^-$) through the five-coordinated neutral intermediate; activation volumes of -5—-12 ml mol^{-1} were obtained for these reactions.[11] Therefore, negative values of $\Delta V^{\neq\prime}$ may be expected in the associative case.

The activation volume would result partly from the intrinsic volume change accompanying the bond formation, and partly from the release of the solvated water molecules owing to the neutralization of the ionic charges of reactant ions, *i.e.*, the electrostrictive volume change. The electrostrictive part for the complex ion may be interpreted by means of Born's equation, which is considered to be valid for a large ion.[12] It amounts to 2 ml mol^{-1}, since the radius of the complex ion may be estimated as 3 Å from the Co–O and Co–N bond distances and the molecular extensions.[13,14] For the OH$^-$ ion, the crystal radius is 1.38 Å, and the absolute partial molal volume, $\bar{V}_{OH^-}$, may be estimated as 1.5 ml mol^{-1} at 60 °C, taking a reasonable average value of $\bar{V}_{H^+}$ (-6.2 ml mol^{-1}) from several reported values.[15] For a singly charged ion of this crystal radius in water, the disordered or the void space volume, $\bar{V}_{disord}$, and the electrostrictive volume, $\bar{V}_{elect}$, have been semiempirically estimated as 9±3 ml mol^{-1} and 7±3 ml mol^{-1} respectively.[15]

The activation process of the substitution reaction of [Pd(Et$_4$dien)X]$^+$ by Y$^-$ (X$^-$=Cl$^-$, Br$^-$, I$^-$; Y$^-$=Br$^-$, I$^-$, N$_3^-$) is considered to be the incorporation of a water molecule into the complex ion; activation volumes of -14—-10 ml mol^{-1} were obtained.[11] A water molecule has the same crystal radius as the OH$^-$ ion, and the arrangement of the solvent molecules around them must be similar. Therefore, the intrinsic change caused by OH$^-$-ion incorporation would be of a nature analogous to that of a H$_2$O incorporation, and it may be assumed that

$$\Delta V(\mathrm{H_2O\ incorporation})/$$
$$\Delta V_{int}(\mathrm{OH^-\ incorporation}) = \bar{V}_{H_2O}/\bar{V}_{OH^-int}.$$

$\bar{V}_{H_2O}$ may be taken as 18.3 ml mol^{-1} at 60 °C from the water density.

In this situation, the upper limit of the activation volume in the associative case is obtained by assuming the highest value for $\bar{V}_{OH^-elect}$, or the highest value for $\bar{V}_{OH^-disord}$, to give the $\bar{V}_{OH^-} = 1.5$ ml mol^{-1};

$$\bar{V}_{OH^-int} = \bar{V}_{OH^-cryst} + \bar{V}_{OH^-disord} = 6.6 + 12 = 18.6\ \mathrm{ml\ mol^{-1}},$$
$$\bar{V}_{OH^-elect} = \bar{V}_{OH^-int} - \bar{V}_{OH^-} = 18.6 - 1.5 = 17.1\ \mathrm{ml\ mol^{-1}}.$$

Then the upper limit may be given by $(-10\times 18.6/18.3)+2+17.1=8.9$ ml mol^{-1}. This is still considerably smaller than the obtained values of $\Delta V^{\neq\prime}$, so the possibility of the associative mechanism can be excluded.

For the SN1 CB mechanism, by analogy with the base hydrolysis of [Co(NH$_3$)$_5$X]$^{2+}$ (X$^-$=Cl$^-$, Br$^-$, NO$_3^-$), the reaction series may be written as:

$$\beta\text{-[Co(edda)(H}_2\text{N-R-NH}_2)]^+ + \mathrm{OH}^-$$
$$\rightleftharpoons \beta\text{-[Co(edda)(HN-R-NH}_2)] + \mathrm{H_2O}$$
$$\beta\text{-[Co(edda)(HN-R-NH}_2)] \rightarrow \alpha\text{-[Co(edda)(HN-R-NH}_2)]$$
$$\alpha\text{-[Co(edda)(HN-R-NH}_2)] + \mathrm{H_2O}$$
$$\rightleftharpoons \alpha\text{-[Co(edda)(H}_2\text{N-R-NH}_2)]^+ + \mathrm{OH}^-,$$

where the 1st and 3rd steps are assumed to be rapid and where the 2nd is assumed to be the rate-determining process.[16] Hence, $k'_1 = k''_1 K_{pre}$, where k''_1 is the rate constant of the 2nd step and where K_{pre} is the equilibrium constant of the 1st step. Thus,

$$-RT\frac{\mathrm{d}\ln k_1'}{\mathrm{d}P} = -RT\left[\frac{\mathrm{d}\ln k_1''}{\mathrm{d}P}+\frac{\mathrm{d}\ln K_{pre}}{\mathrm{d}P}\right],$$

$$\text{or } \Delta V^{\neq\prime} = \Delta V^{\neq\prime\prime} + \Delta V_{pre}$$

The volume change accompanying the pre-equilibrium (ΔV_{pre}) may be estimated as $\Delta V_{pre} = \bar{V}_{H_2O} - \bar{V}_{OH^-} + \Delta V_{el}$, where ΔV_{el} is the partial molal volume difference between the conjugate base form and the acid form of the β-isomer. ΔV_{el} may be estimated as 2 ml mol^{-1} from Born's equation.[12] Hence, ΔV_{pre} amounts to 18.8 ml mol^{-1} at 60 °C. Then, $\Delta V^{\neq\prime\prime}$, which is attributed to the activation of the rate-determining process, is -4.1 mol ml^{-1} and 1.2 ml mol^{-1} for β-[Co(edda)(tn)]$^+$ and for β-[Co(edda)(en)]$^+$ respectively. These magnitudes of $\Delta V^{\neq\prime\prime}$ are comparable with that expected from a bond rupture and the resulting solvations, and the SN1 CB mechanism seems reasonable.[17–19]

The activation energy and activation entropy were measured for these reactions by Kuroda; the values of 36.0 kcal mol^{-1} and 29.7 e.u. for β-[Co(edda)(tn)]$^+$ and of 42.1 kcal mol^{-1} and 46.5 e.u. for β-[Co(edda)(en)]$^+$ were obtained.[3] The large positive values of the activation entropies are in accordance with the qualitative proportionality relation between the activation volume and the activation entropy.[20] The energy and entropy changes for the pre-equilibrium must be approximately equal for these two complexes, and the differences in the activation energy and in the activation entropy should be attributed to the activation of the rate-determining process.

Following the proposal by Kuroda that the activation of the rate-determining process is the Co–N bond rupture of *tn* or *en*,[3,4] the obtained magnitudes of $\Delta V^{\neq\prime\prime}$ may be interpreted as follows. For β-[Co(edda)(tn)]$^+$, the long trimethylenediamine chain was rather loosely attached in the complex and could move rather freely in its initial state. Hence, the intrinsic volume change resulting from the bond rupture was rather small, and the negative contribution owing to the solvation to the unoccupied site of the intermediate ion and to the partly liberated polar R–NH_2 group was the dominant factor. In contrast, for β-[Co(edda)(en)]$^+$, the ethylenediamine chain is rather firmly and compactly attached in the complex; hence, the Co–N bond rupture results in a rather large intrinsic volume change, which compensates for the solvation effects.

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