intramolecular electron transfer, are small, eq 10 reduces to

$$\lim_{k_1,k_3\to 0} k_f = K_1K_2k_3[\mathrm{Ti}^{3+}]/[\mathrm{H}^+] \qquad (15)$$

Linear dependence of redox rate on $[\mathrm{Ti}^{3+}]$ and inverse hydrogen ion dependence have been observed[4] for reduction of $(pd)_2Ru(fpd)$ by Ti(III). When k_3, the rate of intramolecular electron transfer, is small, eq 10 reduces to

$$\lim_{k_3\to 0} k_f = \frac{k_3K_1K_2[\mathrm{Ti}^{3+}]}{[\mathrm{H}^+] + K_1[\mathrm{Ti}^{3+}][\mathrm{H}^+] + K_1K_2[\mathrm{Ti}^{3+}]} \qquad (16)$$

which has the same form as the rate law determined for the Ti^{3+} reduction[5] of $Ru_2(OAc)_2(C_2O_4)_2^+$. Equation 16 is a special case of eq 10 that applies when the system is at or near[11] equilibrium.

Present understanding of Ru(III)-Ti(III) reactions can be summarized as follows. In reductions of $Ru^{III}X$ complexes by Ti(III), outer-sphere electron transfer prevails when X is NH_3, H_2O, Cl^-, pyridine, ethylenediamine, pentane-2,4-dionate, or sulfate. Some of these ligands have no open coordination position, but others, such as Cl^- and SO_4^{2-}, have residual coordinating ability. Lack of bridging effectiveness in these cases must have a different explanation. Insufficiency of interaction between electron-donor and electron-acceptor orbitals within the assembled binuclear intermediate must be invoked. This, in turn, seems due to inappropriate energy of ligand orbitals that have correct symmetry for mixing the electron-donor and electron-acceptor orbitals on the redox partners.

All known outer-sphere Ru(III)-Ti(III) redox reactions display $TiOH^{2+}$ paths, but reaction of Ti^{3+} with ruthenium(III) oxidants that lack electron-delocalizing ligands is not observed (such Ti^{3+} reactions are anomalously slow; this has been ascribed[1] to nonadiabaticity arising from lack of effective overlap between electron-donor and electron-acceptor orbitals). On the other hand, when X is a ligand such as oxalate, acetate, thiocyanate, or salicylate that has a coordination position to bind the reductant and also has a delocalized π-orbital system, inner-sphere electron transfer predominates and substitution on Ti^{3+} is rate-limiting. An extraordinarily unstable binuclear intermediate (as in the case of the thiosulfato complex reported here) can reduce observed rate constants even if electron transfer is rapid. When an oxidant-linked ligand has a vacant coordination site but there is a barrier to electron transfer, more complex rate behavior is observed, as required by eq 10. This occurs in the Ti^{3+} reductions of $(pd)_2Ru(fpd)$[4] and of $Ru_2(OAc)_2(C_2O_4)_2^+$.[5] The kinetics indicate that the formation constant of the binuclear complex between $(pd)_2Ru(fpd)$ and Ti^{3+} is small ($K_f \geq 1$ M^{-1}), whereas a relatively stable trinuclear complex (K_f = ca. 5×10^2 M^{-1}) is involved in reduction of $Ru_2(OAc)_2(C_2O_4)_2^+$. The differences in kinetic behavior observed can be understood on this basis.

The Ru(III)-Ti(III) couple exhibits a wide variety of kinetic patterns, but these differences in kinetic behavior follow understandable patterns.

Registry No. Ti^{3+}, 22541-75-9; $Ru(NH_3)_5SO_4^+$, 113322-96-6; $Ru(NH_3)_5S_2O_3^+$, 76790-96-0; $Ru(NH_3)_5NH_2SO_3^{2+}$, 51259-40-6.

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Volume Profiles as Mechanistic Information for the Trans ⇌ Cis Isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O, OH^-, NCS^-, NH_3, NO_2^-, Br^-, N_3^-$) and $Co(en)_2(OH)Y^{n+}$ ($Y = OH^-, NH_3$)

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Received February 26, 1987

Activation volumes (ΔV^*) and reaction volumes (ΔV) have been obtained for the title reactions. The magnitudes of ΔV are close to zero (-6 to +2 cm^3 mol^{-1}), and correlation exists between the ΔV for $Co(en)_2(H_2O)X^{n+}$ and the order of X in the spectrophotochemical series. Values of ΔV^* are in the range 5-8 cm^3 mol^{-1} for isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O$, OH^-, NCS^-, NH_3, N_3^-). These include three reactions ($X = H_2O$, OH^-, NCS^-) that are known to proceed with exchange of coordinated water with the solvent. By contrast, ΔV^* is conspicuously large (18 cm^3 mol^{-1}) for the isomerization of $Co(en)_2(OH)NH_3^{2+}$, which is known to proceed without exchanging OH^- or NH_3. We interpret the relatively small ΔV^* (2.1 cm^3 mol^{-1}) for the isomerization of $Co(en)_2(H_2O)Br^{2+}$ in light of the relative lability of the Br^- ligand. On this basis, we consider that isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O$, OH^-, NCS^-, NH_3, Br^-, N_3^-, SeO_3H^-, SeO_3^{2-}, CH_3COO^-, Cl^-) proceed through the $Co-OH_2$ bond dissociation by an interchange mechanism.

Introduction

Recently, activation volumes (ΔV^*) have been considered as useful mechanistic information for inorganic reactions.[2] Concerning the isomerization of a Co^{III} complex, Stranks and Vanderhoek followed the isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$

$$trans\text{-}Co(en)_2(H_2O)_2^{3+} \rightleftharpoons cis\text{-}Co(en)_2(H_2O)_2^{3+}$$

in acidic solution at high pressure up to 138 MPa and obtained ΔV^*.[3] They compared this magnitude of ΔV^* with that for the water-exchange reaction[4]

$$trans\text{-}Co(en)_2(H_2O)(H_2{}^{18}O)^{3+} + H_2O \rightarrow trans\text{-}Co(en)_2(H_2O)_2^{3+} + H_2{}^{18}O$$

They explained that the $\Delta V^* = 12.6\text{-}14.3$ cm^3 mol^{-1} of the isomerization corresponded to a dissociative water release in the transition state yielding a trigonal-bipyramidal configuration and that in contrast the $\Delta V^* = 5.9 \pm 0.2$ cm^3 mol^{-1} of the water exchange corresponded to a water release in the transition state by an interchange mechanism yielding a tetragonal-pyramidal configuration.[3,4] They emphasized that the mechanistic difference between the isomerization and the water exchange, as originally pointed out by Kruse and Taube, was revealed by these magnitudes of ΔV^*.[5] Subsequently, ΔV^* has been obtained for the following isomerizations:[6,7]

$$trans\text{-}Co(en)_2(H_2O)X^{n+} \rightleftharpoons cis\text{-}Co(en)_2(H_2O)X^{n+}$$

$$X = SeO_3H^-, SeO_3^{2-}, CH_3COO^-, Cl^-$$

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Table I. Dilatometrically Obtained ΔV° at 19.5 °C

reaction	ΔV°/cm^3 mol^{-1}
trans-$Co(en)_2(H_2O)OH^{2+} \rightleftharpoons$ *cis*-$Co(en)_2(H_2O)OH^{2+}$	−5.5 ± 0.4
trans-$Co(en)_2(H_2O)_2^{3+} \rightarrow$ *trans*-$Co(en)_2(H_2O)OH^{2+} + H^+$	3.0 ± 0.1
trans-$Co(en)_2(H_2O)OH^{2+} \rightarrow$ *trans*-$Co(en)_2(OH)_2^+ + H^+$	−5.9 ± 0.0

We have suggested that the ΔV^* values (5–8 cm^3 mol^{-1}) for these four reactions are comparable to the estimated value of activation volume $\Delta V^*_{\text{calcd}}$($D_P$ mechanism) = 2.7 cm^3 mol^{-1} for a dissociative release of water involving a tetragonal-pyramidal transition state (D_P mechanism). However, we could not understand the large ΔV^* for isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$ given by Stranks and Vanderhoek. The present work has been prompted by an interest in the ΔV^* of the following analogous isomerizations:

$$trans\text{-}Co(en)_2(H_2O)X^{n+} \rightleftharpoons cis\text{-}Co(en)_2(H_2O)X^{n+}$$

$$X = OH^-, NCS^-, NH_3, NO_2^-, Br^-, N_3^-$$

$$trans\text{-}Co(en)_2(OH)Y^{n+} \rightleftharpoons cis\text{-}Co(en)_2(OH)Y^{n+}$$

$$Y = OH^-, NH_3$$

Examination of ΔV^* in light of the available mechanistic evidence for certain of these reactions will further clarify the mechanistic implication of the ΔV^*. During the course of the present work, it has been found that isomerization velocity of *trans*-$Co(en)_2(H_2O)_2^{3+}$ is significantly dependent on the acidity of the solution. Therefore, the ΔV^* given for this reaction by Stranks and Vanderhoek turned out to be inaccurate because they ignored this acid dependence of the isomerization velocity in their calculation of ΔV^*.[3] We have taken this acid dependence into account and reinvestigated this reaction in a greater pressure range.

Experimental Section

Complexes were obtained according to a literature procedure, twice recrystallized, and identified by elemental analysis and UV absorption spectroscopy. UV absorptions, λ_{max}/nm (ϵ): *trans*-$[Co(en)_2(H_2O)Br]S_2O_6\cdot H_2O$[9] in water, 606 (35.3); *trans*-$[Co(en)_2(H_2O)NCS]Br_2\cdot 2H_2O$[10] in water, 537 (183); *trans*-$[Co(en)_2(OH)N_3][Co(en)_2(H_2O)N_3](ClO_4)_3$[11] in 0.01 M $HClO_4$, 551 (257), 500 (92.5); *trans*-$[Co(en)_2(H_2O)OH](ClO_4)_2$[11] in 0.1 M $HClO_4$, 551 (32), 435 (35), 347 (54.3); *trans*-$[Co(en)_2(H_2O)NH_3](NO_3)_3$[12] in water, 480 (46.4), 340 (50.7). Previously obtained *cis*-$[Co(en)_2(NO_2)Cl]Cl$ was used.[13]

Dilatometry was carried out by using a Carlsberg dilatometer of capillary diameter 0.0448 cm, where temperature was controlled within ±0.001 °C.[14] Densimetry was carried out with a digital densimeter (Shibayama Scientific Co., Ltd., Model SS-D-200) equipped with a well-controlled (±0.002 °C) thermostat.[15]

Kinetics at normal pressure were carried out by following the optical density of solution contained in an ordinary thermostated (±0.1 °C) quartz cell of 1-cm path length. Kinetics at high pressure were performed by using a thermostated (±0.1 °C) high-pressure sapphire cell (Hawley and Chase type)[16] or a high-pressure reaction apparatus. With the latter, aliquots of the sample solution were removed at several reaction stages.[17] Reaction was followed spectrophotometrically at certain wavelengths during 2.5–3.0 half-lives. The isomerization rate constant k_{obsd} was calculated by applying a linear-regression program to a ln $|D_t - D_\infty|$ vs time plot, where D_t and D_∞ denote absorbances at reaction time t and at equilibrium. The value of D_∞ was estimated to give the best correlation coefficient.

Results

Dilatometric Result. A 15-cm^3 volume of solution containing 0.01 M *trans*-$[Co(en)_2(H_2O)OH](ClO_4)_2$ and 0.011 M NaOH was mixed with 3 cm^3 of 0.055 M $HClO_4$ or with 3 cm^3 of 0.110 M $HClO_4$ at 19.5 °C (M = mol dm^{-3}). After the mix, the meniscus height of the capillary changed according to the first-order rate law with a half-life of 3.1 or 1.5 min, respectively. The meniscus heights immediately after the mix and at equilibrium were calculated by a linear-regression program. Duplicate runs were performed. The volume change ascribable to the change of ionic strength during the mix was estimated as before.[14] The reaction volume at infinite dilution (ΔV°) was calculated therefrom, where ΔV° = 22.1 cm^3 mol^{-1} for $H^+ + OH^- = H_2O$ was used.[14] The results are given in Table I.

Table II. Densimetrically Obtained ΔV for Trans ⇌ Cis Isomerization at 25 °C

complex	solvent	μ^a/M	ΔV/cm^3 mol^{-1}
$Co(en)_2(OH)_2^+$	0.057 M NaOH	0.08	−3.2, −4.1
$Co(en)_2(OH)NH_3^{2+}$	0.015 M $NaNO_3$	0.06	−1.0, −2.0
$Co(en)_2(H_2O)NCS^{2+}$	0.02 M $HClO_4$	0.10	−0.8
		0.06	−0.8
$Co(en)_2(H_2O)NH_3^{3+}$	water	0.10	0.2
		0.08	0.6
$Co(en)_2(H_2O)Br^{2+}$	0.02 M $HClO_4$	0.11	−2.8, −2.8
$Co(en)_2(H_2O)N_3^{2+}$	0.01 M $HClO_4$	0.07	−2.1, −2.4

[a] Ionic strength of the solution.

Table III. Isomerization Rate Constant of *trans*-$Co(en)_2(H_2O)_2^{3+}$ at High Pressure (45 °C, μ = 1.05 M)

	10^4k_{obsd}/s^{-1}				
P/MPa	$[HClO_4]$ = 0.985 M	$[HClO_4]$ = 0.05 M	$[HClO_4]$ = 0.02 M	10^4k_0/s^{-1}	$10^6K_ak_1$/M^{-1} s^{-1}
2	1.63, 1.82	2.26, 2.76	4.46, 4.58	1.54	5.82
50	1.49, 1.34	2.49, 2.38	4.78, 3.43	1.35	5.50
100	1.38, 1.39	2.17, 2.72	3.30, 3.53	1.45	4.06
150	1.24, 1.22	1.77, 1.81	2.73, 2.71	1.19	3.05
200	1.08, 1.06	1.52, 1.48	2.30, 2.19	1.04	2.41

Densimetric Result. Generally, isomerization is slow enough at 25 °C. In these cases, density of a solution containing the trans complex (0.013–0.026 M) was measured after 15 min from the time of dissolution. This density value was regarded as the initial density (d_0) of isomerization. The solution was maintained at a certain temperature during an appropriate period while the isomerization proceeded to the equilibrium. The density (d_∞) of this solution was measured again at 25 °C. In the cases of $Co(en)_2(H_2O)Br^{2+}$ (0.023 M) and $Co(en)_2(H_2O)N_3^{2+}$ (0.02 M), solution density was followed at 25 °C from 15 to 120 min (ca. 1.5 half-lives of the isomerizations). The best values of d_0 and d_∞ were found by the linear-regression program. Reaction volume of isomerization $\Delta V = \bar{V}_{cis} - \bar{V}_{trans}$ was calculated by

$$\Delta V = \frac{1000}{\bar{m}\alpha}\left(\frac{1}{d_\infty} - \frac{1}{d_0}\right)$$

where $\bar{m}$ is the concentration in mol (kg of solution)$^{-1}$ units, α is the isomerization extent at equilibrium, and $\bar{V}_{cis}$ and $\bar{V}_{trans}$ represent the partial molal volumes of the cis and the trans isomers, respectively. Results of duplicate runs are given in Table II.

Kinetic Results at Normal Pressure. *trans*-$[Co(en)_2(H_2O)OH](ClO_4)_2$ (0.01 M) was dissolved in aqueous $NaClO_4$–$HClO_4$ solution. Reaction was followed during 3–3.5 half-lives of isomerization, and the first-order rate constant k_{obsd} was calculated from the optical density at 492 nm. The resultant value of k_{obsd} (Figure 1) depends significantly on the $[H^+]$ of the solution and slightly on the ionic strength (μ) of the solution. At μ = 1.05 and 3.05 M a good linear correlation exists between k_{obsd} and $1/[H^+]$. Accordingly, isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$ proceeds through two routes.

$$k_{obsd} = k_0 + K_ak_1/[H^+] \qquad (1)$$

where k_0 and k_1 are the rate constants for isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$ and *trans*-$Co(en)_2(H_2O)OH^{2+}$, respectively, and K_a is the deprotonation constant of *trans*-$Co(en)_2(H_2O)_2^{3+}$. From the intercepts of lines at $1/[H^+]$ = 0, k_0 is obtained as 1.78 × 10^{-4}, 2.44 × 10^{-4}, and 3.70 × 10^{-4} s^{-1} at μ =

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Table IV. Isomerization Rate Constant $10^4k_{obsd}/s^{-1}$ at High Pressure

complex		$Co(en)_2(H_2O)OH^{2+}$	$Co(en)_2(OH)_2^+$	$Co(en)_2(OH)NH_3^{2+}$	$Co(en)_2(H_2O)NCS^{2+}$
C/M^c		0.01	0.013	0.01	0.003
solvent		water	0.057 M NaOH	0.0001 M NaOH	0.02 M $HClO_4$
$t/°C$		13.0	45.1	45.0	62.9
method		*a*	*b*	*b*, *f*	*b*
λ/nm^d		500	520	480	490
$K_{0.1}$		1.42^e	0.80^e	∞^g	4.26^h
P/MPa	5	5.82, 5.25, 5.91	1.89, 1.75	1.92, 1.82	1.63, 1.75, 1.72
	50	4.61, 4.98	1.51, 1.56	1.28, 1.44	1.56, 1.52, 1.54
	100	4.18, 4.04	1.15, 1.14	1.03, 1.01	1.32, 1.36, 1.29
	150	3.55, 3.44	0.888, 0.875	0.632, 0.686	1.13, 1.11, 1.10
	200	2.92, 2.86	0.736, 0.662	0.504, 0.506	1.01, 0.989, 1.06

complex		$Co(en)_2(H_2O)NH_3^{3+}$	$Co(en)_2(H_2O)NO_2^{2+j}$		$Co(en)_2(H_2O)Br^{2+}$	$Co(en)_2(H_2O)N_3^{2+}$
C/M^c		0.01	0.0005		0.004	0.002
solvent		0.2 M $HClO_4$	0.01 M $HClO_4$		0.01 M $HClO_4$	0.008 M $HClO_4$
$t/°C$		72.9	65.2		30.3	30.3
method		*b*	*b*		*a*	*a*
λ/nm^d		480	329		530	500
$K_{0.1}$		∞^i	0.45^k		3.76^l	1.94^l
P/MPa	5	0.548, 0.466	1.46, 1.39	5	3.91, 3.72, 4.01	3.26, 3.26, 3.19
	50	0.435, 0.482	1.20, 1.03	40	3.62, 3.68	2.72, 3.03
	100	0.387, 0.423	0.863, 0.904	80	3.58, 3.51	2.67, 2.67
	150	0.347, 0.361	0.758, 0.792	120	3.87, 3.54	2.26, 2.30
	200	0.301, 0.310	0.728, 0.640	160	3.22, 3.06	2.01, 1.96
				200		1.71, 1.73, 1.71

[a] High-pressure sapphire cell was used. [b] Aliquots were removed. [c] Concentration of the complex. [d] Reaction was followed at this wavelength. [e] At 25 °C and μ = 1.0 M ($NaNO_3$); ref 18. [f] Sample solution was acidified before spectrophotometry. [g] Reference 20. [h] In dilute solution at 62.6 °C; ref 10. [i] Reference 21. [j] Isomerization started from the cis isomer, which was derived by aquation of *cis*-$Co(en)_2(NO_2)Cl^+$. [k] In dilute solution at 90 °C; ref 22. [l] At 5 MPa and 30.3 °C in 0.01 M $HClO_4$; this work.

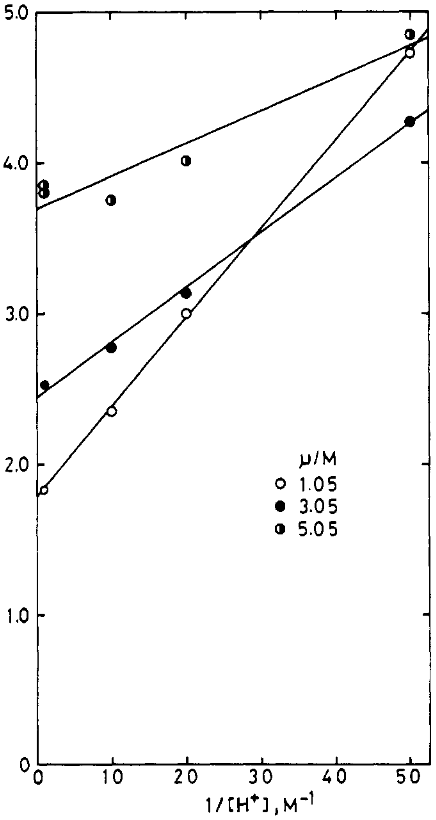

Figure 1. Acid-dependent isomerization velocity of *trans*-$Co(en)_2(H_2O)_2^{3+}$ at normal pressure and 45 °C.

1.05, 3.05, and 5.05, respectively.

Kinetic Results at High Pressure. Isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$ was followed at 492 nm by using the sapphire cell. Concentration of the complex was 0.01 M, and μ was adjusted to 1.05 M ($HClO_4$, $NaClO_4$). The dependence of k_{obsd} on $[H^+]$ was treated according to eq 1 at each pressure. Resultant values of k_0 and K_ak_1 are shown in Table III. Isomerization rate constants for the other complexes are summarized in Table IV. Generally, the reactions started from the trans isomer. The equilibrium constants $K_{0.1}$ at normal pressure (0.1 MPa) are also shown in Table IV. In every case, k_{obsd} decreases with increase of pressure, and a positive value for the activation volume can be expected.

Calculation of Activation Volume. Generally, isomerizations are reversible.

$$\text{trans} \underset{k_c}{\overset{k_t}{\rightleftharpoons}} \text{cis}$$

$$k = k_t + k_c \qquad (2)$$

$$K = k_t/k_c \qquad (3)$$

where k is the experimentally obtained first-order rate constant (k_0 in Table III or k_{obsd} in Table IV). The pressure dependence of K was estimated by

$$\ln K = -\frac{\Delta V}{RT}P + \ln K_{0.1}$$

where $K_{0.1}$ in Table IV, $K_{0.1}$ = 58 for $Co(en)_2(H_2O)_2^{3+}$ (1 M $NaNO_3$, 25 °C),[18] and ΔV in Table V were used. k_t and k_c at each pressure were calculated from eq 2 and 3. Activation volumes for the forward and the backward processes were calculated by

$$\Delta V^{\ddagger}_t = -RT\frac{d \ln k_t}{dP}$$

$$\Delta V^{\ddagger}_c = -RT\frac{d \ln k_c}{dP}$$

Isomerizations of $Co(en)_2(OH)NH_3^{2+}$ and $Co(en)_2(H_2O)NH_3^{3+}$ are irreversible ($k_{obsd} = k_t$). In these cases, activation volumes were calculated by

$$\Delta V^{\ddagger}_t = -RT\frac{d \ln k_{obsd}}{dP}$$

$$\Delta V^{\ddagger}_c = \Delta V^{\ddagger}_t - \Delta V$$

where ΔV in Table V was used. Linear correlation was assumed between $\ln k_t$, $\ln k_c$, or $\ln k_{obsd}$ and P.[19]

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Table V. Volume Profiles ($cm^3\ mol^{-1}$) for the Trans $\rightleftharpoons$ Cis Isomerizations[a]

<table>
<tr><th>complex</th><th>μ/M[b]</th><th>t/°C[b]</th><th>$\Delta V^{\ddagger}_t$</th><th>$\Delta V^{\ddagger}_c$</th><th>ΔV</th></tr>
<tr><td>$Co(en)_2(H_2O)_2^{3+}$</td><td>1.05</td><td>45</td><td>4.9 ± 1.3</td><td>5.8 ± 1.2</td><td>−1.0 ± 1.2[c]</td></tr>
<tr><td>$Co(en)_2(H_2O)SeO_3H^{2+}$ [d]</td><td></td><td></td><td colspan="2">7.2</td><td></td></tr>
<tr><td>$Co(en)_2(H_2O)SeO_3^{+}$ [d]</td><td></td><td></td><td colspan="2">7.3</td><td></td></tr>
<tr><td>$Co(en)_2(H_2O)CH_3COO^{2+}$ [d]</td><td>0.05</td><td>45</td><td colspan="2">7.9 ± 0.3</td><td>0</td></tr>
<tr><td>$Co(en)_2(H_2O)Cl^{2+}$ [e]</td><td>0.03</td><td>32</td><td>5.1 ± 0.3</td><td>8.0 ± 0.3</td><td>−2.9 ± 0.2</td></tr>
<tr><td>$Co(en)_2(H_2O)OH^{2+}$</td><td>0.03</td><td>13</td><td>6.1 ± 0.4</td><td>11.6 ± 0.4</td><td>−5.5 ± 0.4</td></tr>
<tr><td>$Co(en)_2(OH)_2^{+}$</td><td>0.07</td><td>45</td><td>11.4 ± 0.5</td><td>15.1 ± 0.5</td><td>−3.7 ± 0.5</td></tr>
<tr><td>$Co(en)_2(OH)NH_3^{2+}$</td><td>0.03</td><td>45</td><td>18.0 ± 0.6</td><td>19.5 ± 1.1</td><td>−1.5 ± 0.5</td></tr>
<tr><td>$Co(en)_2(H_2O)NCS^{2+}$</td><td>0.03</td><td>63</td><td>7.5 ± 0.3</td><td>8.3 ± 0.3</td><td>−0.8 ± 0.0</td></tr>
<tr><td>$Co(en)_2(H_2O)NH_3^{3+}$</td><td>0.26</td><td>73</td><td>7.4 ± 0.7</td><td>7.0 ± 0.9</td><td>0.4 ± 0.2</td></tr>
<tr><td>$Co(en)_2(H_2O)NO_2^{2+}$</td><td>0.01</td><td>65</td><td>11.4 ± 1.0</td><td>10.1 ± 1.0</td><td>1.5 ± 0.5[f]</td></tr>
<tr><td>$Co(en)_2(H_2O)Br^{2+}$</td><td>0.02</td><td>30</td><td>2.1 ± 0.7</td><td>4.9 ± 0.7</td><td>−2.8 ± 0.0</td></tr>
<tr><td>$Co(en)_2(H_2O)N_3^{2+}$</td><td>0.01</td><td>30</td><td>7.5 ± 0.3</td><td>9.8 ± 0.3</td><td>−2.3 ± 0.2</td></tr>
</table>

[a] Obtained in this work unless otherwise indicated. [b] Condition for activation volume. [c] At 25 °C and μ = 0.1–0.2 M; ref 7. [d] Reference 6. [e] ΔV at 32 °C and μ = 0.11 M; ref 7. [f] At 10 °C and μ = 0.03–0.09 M; ref 7.

Discussion

As can be seen in Table V, the magnitude of ΔV ranges from −6 to +2 $cm^3\ mol^{-1}$. These nearly zero magnitudes of ΔV are understandable when one considers that no substitution occurs in these reactions. It should be noteworthy that correlation exists between the magnitude of ΔV (given in Table V) for isomerization of $Co(en)_2(H_2O)X^{n+}$ and the order of X in the spectrophotochemical series.[23] The order is given as follows [$\Delta V/cm^3\ mol^{-1}$, $10^{13}\nu_{max}/s^{-1}$ of *trans*-$Co(en)_2(H_2O)X^{n+}$, X]: 1.5, 64.8, NO_2^-; 0.4, 62.5, NH_3; −0.8, 55.9, NCS^-; −1.0, 54.4, H_2O; −2.3, 54.4, N_3^-; −2.9, 51.0, Cl^-; −2.8, 49.5, Br^-. ΔV becomes larger when X is changed to cause a stronger crystal field.

On the other hand, the activation volumes are all positive and in the range 2–20 $cm^3\ mol^{-1}$. In most cases, the $\Delta V^{\ddagger}$'s are below 8 $cm^3\ mol^{-1}$, and in a few cases they exceed 10 $cm^3\ mol^{-1}$. In the interpretation of $\Delta V^{\ddagger}$, we consider that the effects of μ and temperature on the magnitude of $\Delta V^{\ddagger}$ are minor.[6,7] Most interestingly, $\Delta V^{\ddagger}_t$ is small (4.9–7.5 $cm^3\ mol^{-1}$) for isomerizations of $Co(en)_2(H_2O)X^{n+}$ (X = H_2O, OH^-, NCS^-). These three reactions are known to proceed through Co–OH_2 bond dissociation because during isomerization one molecule of water is brought into exchange with the solvent.[5,24] By contrast, $\Delta V^{\ddagger}_t$ is conspicuously large (18 $cm^3\ mol^{-1}$) for the isomerization of $Co(en)_2(OH)NH_3^{2+}$, during which the coordinated oxygen does not exchange with the solvent.[20] Isomerizations of $Co(en)_2(H_2O)X^{n+}$ with X = SeO_3H^-, SeO_3^{2-}, CH_3COO^-, Cl^-, NH_3, or N_3^- will also proceed through the Co–OH_2 bond dissociation path because their magnitudes of $\Delta V^{\ddagger}_t$ are quite similar to the magnitudes of those with X = H_2O, OH^-, NCS^-. In the isomerization of $Co(en)_2(H_2O)Br^{2+}$, $\Delta V^{\ddagger}_t$ is slightly below the range. This small $\Delta V^{\ddagger}_t$ for $Co(en)_2(H_2O)Br^{2+}$ is not caused by simultaneous Br^- liberation from the complex. The latter reaction should have a negative activation volume ca. −5 $cm^3\ mol^{-1}$.[17] It has been pointed out that the spectral change of *trans*-$Co(en)_2(H_2O)Br^{2+}$ in dilute acid maintains isosbestic points during 4–5 half-lives of the isomerization.[25] This observation has been confirmed by us in the present work. So, the aquation of $Co(en)_2(H_2O)Br^{2+}$ is slow enough not to interfere with the course of the isomerization. We have calculated k_{obsd} for $Co(en)_2(H_2O)Br^{2+}$ utilizing the spectral data during 3 half-lives of isomerization (Table IV). In this connection, we have recalculated k_{obsd} utilizing the data only for the initial 1.4 half-lives. The resultant $\Delta V^{\ddagger}_t$ = 1.4 ± 0.7 $cm^3\ mol^{-1}$ coincided within the error limit with the $\Delta V^{\ddagger}_t$ = 2.1 ± 0.7 $cm^3\ mol^{-1}$ given in Table V. This more or less low $\Delta V^{\ddagger}_t$ for $Co(en)_2(H_2O)Br^{2+}$ must also correspond to the Co–OH_2 bond dissociation path, since this reaction probably proceeds through the same mechanism as the isomerization of $Co(en)_2(H_2O)Cl^{2+}$.

In our previous report, it has been shown that the $\Delta V^{\ddagger}_t$ of these reactions proceeding through Co–OH_2 bond dissociation is comparable to $\Delta V^{\ddagger}$(D_P mechanism) = 2.7 $cm^3\ mol^{-1}$.[7] On this basis we have suggested that the Co–OH_2 bond dissociation will occur by the D_P mechanism. However, if we reexamine this problem in conjunction with our recent findings and with the present results, an interchange (I) mechanism might be more plausible. Recently, we have found that the $\Delta V^{\ddagger}$'s for the aquations of *trans*- and *cis*-$Co(en)_2NH_3Cl^{2+}$ and *trans*- and *cis*-$Co(en)_2NH_3Br^{2+}$ are slightly larger than those for the aquations of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$.[26] We interpret that this difference (2 ± 1 $cm^3\ mol^{-1}$) is caused by some expansion of the $(en)_2$ chelate rings in the transition state of the I mechanism. When isomerization with Co–OH_2 bond dissociation proceeds by the I mechanism, one may estimate the activation volume $\Delta V^{\ddagger}_{calcd}$(I) by analogy to the aquation reaction with the neutral leaving ligand N:

$$Co(NH_3)_5N^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + N \qquad (4)$$

With 11 neutral ligands involving H_2O, the $\Delta V^{\ddagger}$'s of reaction 4 have been experimentally obtained at 25 °C as $\Delta V^{\ddagger}_{exptl}(4)$ = −1.7 to +3.8 $cm^3\ mol^{-1}$ (average 1.5 ± 1.0 $cm^3\ mol^{-1}$). Volume profiles of reaction 4 have been consistent with the I mechanism, where the leaving N and entering H_2O participate almost equally in the transition state.[8] When Co–OH_2 bond dissociation in $Co(en)_2(H_2O)X^{n+}$ occurs by the I mechanism, volume increase of 2 ± 1 $cm^3\ mol^{-1}$ might arise owing to the expansion of the chelate rings in the transition state.[26] Then, one can predict that $\Delta V^{\ddagger}_{calcd}(I) = \Delta V^{\ddagger}_{exptl}(4) + (2.0 \pm 1.0) = 3.5 \pm 2.0$ $cm^3\ mol^{-1}$. This magnitude of $\Delta V^{\ddagger}_{calcd}$(I) is compatible with the experimental mean $\Delta V^{\ddagger}_t(Co\text{–}OH_2)$ = 6.3 ± 1.4 $cm^3\ mol^{-1}$ for isomerizations proceeding through Co–OH_2 bond dissociation. The order of lability of the X ligand in $Co(en)_2(H_2O)X^{n+}$ will be $H_2O \sim Br^- > Cl^- > CH_3COO^- > N_3^- > NCS^- > NH_3 > OH^-$.[24] In the I mechanism, crowding would occur around Co^{III} owing to the attack by a water molecule. When the complex contains the relatively labile Br^- or Cl^- ligand, this crowding will be relaxed partly by the elongation of the Co–Br or Co–Cl bond. This elongation should give rise to a charge separation or dipole moment on the complex, which contributes a negative electrostrictive component to the activation volume.[2,14] On the other hand, when the anionic ligand in the complex is firmly bound to the Co^{III} center, this elongation of the Co^{III}–X bond will not occur and the crowding must be relaxed by additional expansion of the $(en)_2$ chelate rings. The latter event contributes an additional positive component to

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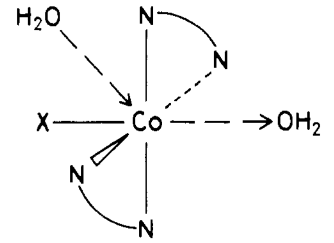

Figure 2. Probable configuration of the transition state for isomerization with H_2O exchange. N⌒N represents an ethylenediamine molecule, and H_2O - - -→ etc. represent weak coordination bonds between an entering water and the Co^{III} and between a leaving water and the Co^{III}.

the activation volume. In this consideration, we do not take account of the relatively small $\Delta V^{\ddagger}_t$ for isomerization of $Co(en)_2(H_2O)_2^{3+}$ because it is obtained at high ionic strength. Accordingly, the relatively small magnitudes of $\Delta V^{\ddagger}_t$ for isomerizations of $Co(en)_2(H_2O)Cl^{2+}$ and $Co(en)_2(H_2O)Br^{2+}$ can be explained consistently with the I mechanism. On these bases, we prefer the I mechanism as depicted in Figure 2 rather than the D_P mechanism. Our value of $\Delta V^{\ddagger}_t = 4.9 \pm 1.3$ cm^3 mol^{-1} for isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$ coincides within the error limit of the $\Delta V^{\ddagger} = 5.9 \pm 0.2$ cm^3 mol^{-1} for water exchange of the same complex at $\mu = 2.0$ M and 35 °C.[4] Thus, the configurational difference between the transition states of isomerization and water exchange is not reflected in their magnitudes of $\Delta V^{\ddagger}$.[5] This mechanistic difference concerns the attacking site by a water molecule, as pointed out by Martin and Tobe.[20] In isomerization, the entering H_2O will attack the complex at a site opposite to the leaving H_2O (Figure 2), whereas in water exchange it will attack at a site adjacent to the leaving H_2O. We have some ground to consider that this difference of the attacking position does not cause an essential difference in the magnitude of $\Delta V^{\ddagger}$.[27]

The large magnitude of $\Delta V^{\ddagger}_t = 18.0$ cm^3 mol^{-1} for $Co(en)_2(OH)NH_3^{2+}$ is compatible with the idea that twisting occurs in an expanded state of the complex. When a sphere with a radius (r) of 4 Å expands by $\Delta r = 0.17$ Å, a volume increase of 20 cm^3 mol^{-1} can be expected. However, this magnitude of $\Delta V^{\ddagger}_t = 18.0$ cm^3 mol^{-1} is also compatible with an alternative I mechanism, whereby $Co-NH_2R$ bond dissociation occurs by stimulation of an attacking water molecule and approximately half of an ethylenediamine chain is freed in the transition state.[20] The partial molal volume of ethylenediamine $\bar{V}$(en) is 62.6 cm^3 mol^{-1} at 25 °C.[28] $\Delta V^{\ddagger}_t$ for $Co(en)_2(OH)NH_3^{2+}$ is larger by 12 cm^3 mol^{-1} than the $\Delta V^{\ddagger}_t(Co-OH_2) = 6.3 \pm 1.4$ cm^3 mol^{-1}. This difference is close to the difference between $0.5\bar{V}$(en) and $\bar{V}(H_2O) = 18.0$ cm^3 mol^{-1}, $0.5\bar{V}(en) - \bar{V}(H_2O) = 13.3$ cm^3 mol^{-1}. The $\Delta V^{\ddagger}_t = 11.4$ cm^3 mol^{-1} for $Co(en)_2(OH)_2^{+}$ is intermediate between the $\Delta V^{\ddagger}_t(Co-OH_2)$ and the $\Delta V^{\ddagger}_t = 18.0$ cm^3 mol^{-1} for $Co(en)_2(OH)NH_3^{2+}$. This result corresponds to the fact that only a fraction of one oxygen per ion exchanges for each act of isomerization of $Co(en)_2(OH)_2^{+}$.[5] The fairly large $\Delta V^{\ddagger}_t$ for $Co(en)_2(H_2O)NO_2^{2+}$ suggests that $Co-NH_2R$ bond dissociation takes some part in the transition state of this reaction. But, at our present state of knowledge, it seems difficult to specify one of the two possible paths proposed by Hughes.[29]

Registry No. $Co(en)_2(H_2O)_2^{3+}$, 19314-32-0; $Co(en)_2(H_2O)OH^{2+}$, 24458-51-3; $Co(en)_2(OH)_2^{+}$, 21772-94-1; $Co(en)_2(OH)NH_3^{2+}$, 38246-62-7; $Co(en)_2(H_2O)NCS^{2+}$, 24913-06-2; $Co(en)_2(H_2O)NH_3^{3+}$, 21199-56-4; $Co(en)_2(H_2O)NO_2^{2+}$, 24913-08-4; $Co(en)_2(H_2O)Br^{2+}$, 24913-01-7; $Co(en)_2(H_2O)N_3^{2+}$, 29770-07-8.

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Photoaquation Reactions of Chromium(III) Polypyridine Complexes Induced by Sequential Biphotonic Irradiations

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Received June 3, 1987

The long-lived, low-lying doublet states of Cr(III) polypyridine complexes have been generated and irradiated by using sequential biphotonic techniques. The detection of products and the time-resolved spectroscopy of the processes have shown that biphotonic irradiation induces a ligand photolabilization independent of acid concentration. Such a reaction cannot be associated with the photolabilization induced in monophotonic irradiations with low light intensities and has been related to processes initiated in upper excited states.

Introduction

Photochemical ligand labilization in Cr(III) complexes with polypyridine ligands has been extensively investigated.[1,3] These compounds have long-lived, low-lying doublet states, labeled ^2E and $^2T_1$ in an octahedral microsymmetry, whose intrinsic processes, relaxation to the ground state and ligand labilization, are medium-determined.[1-3] The sequential biphotonic technique proved to be very useful in our studies of the photochemistry of phthalocyanine radicals.[4-6] In this regard, one can use this technique with Cr(III) complexes in order to promote the population of upper doublet sttes by using the thermally equilibrated ($^2T_1$, ^2E) states as receptors of a second photon. If the relaxation from the upper states to the lowest quartet and/or doublet states is too fast and competition with chemical reactions is insignificant, no difference between monophotonic and sequential biphotonic excitations are expected. However, the differences must be appreciable if upper states present intrinsic reactivities and such states do not achieve significant populations in monophotonic excitations.

Experimental Section

Photochemical Procedures. The flash photolysis apparatus has been previously described and is based on the synchronous triggering of two flash-pumped dye lasers.[5] Each experiment involves the generation of the long-lived, lowest lying doublet states of the Cr(III) complexes by

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