Contribution from the Department of Physical and Inorganic Chemistry, University of Adelaide, Aldelaide 5000, Australia, and the Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Australia

Oxalate–Aquo Ligand Interchange Reactions of Aquobis(ethylenediamine)cobalt(III) Ions. Pressure Effects and Mechanisms.

D. R. STRANKS*[1] and N. VANDERHOEK

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The interchange reactions of both the ion pairs *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4$ and *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot HC_2O_4^-$ to yield $Co(en)_2C_2O_4^+$ exhibit a common volume of activation, $\Delta V^\ddagger = +4.8 \pm 0.2$ cm^3 mol^{-1}, with no detectable pressure dependence of $\Delta V^\ddagger$. The interchange reaction of $Co(en)_2(OH)OH_2^{2+}\cdot C_2O_4^{2-}$ to yield $Co(en)_2(OH)C_2O_4$ exhibits $\Delta V^\ddagger = +4.6 \pm 0.4$ cm^3 mol^{-1} (pressure independent), $\Delta H^\ddagger = 92.9 \pm 1.7$ kJ mol^{-1}, and $\Delta S^\ddagger = +(9.6 \pm 4.2)$ J K^{-1} mol^{-1}. These interchange reactions are all assigned a dissociative interchange, I_d, mechanism involving a stretched Co–OH_2 bond in the transition state. Ring closing $Co(en)_2(OH_2)C_2O_4^+$ to yield $Co(en)_2C_2O_4^+$ exhibits a zero volume of activation $\Delta V^\ddagger = 0 \pm 1.2$ cm^3 mol^{-1} and this reaction is assigned an I_a mechanism.

Introduction

The reaction of aquometal cations with anionic nucleophiles is frequently interpreted in terms of an ion-pair interchange mechanism.[2] The interchange mechanism is taken to be dissociative in character (I_d) if the rate coefficient for nucleophile entry into the primary coordination sphere from the secondary sphere is equal to, or slightly less than, the rate coefficient for aquo ligand exchange with solvent water. For an associative interchange mechanism, I_a, the rate coefficient for nucleophile entry should exceed the rate coefficient for water exchange. However, these rate comparisons can involve significant uncertainties since the rate coefficients are often measured independently in quite different electrolyte media and temperature extrapolations may be necessary. Moreover, rate coefficients, as composite quantities, are not reliable guides to finer details of reaction mechanisms.

Volumes of activation ($\Delta V_0^\ddagger$) and their pressure dependences ($\Delta\beta^\ddagger = -(\partial \Delta V^\ddagger/\partial P)_T$) for interchange reactions should reflect directly structural changes arising from the interchange process, thereby permitting more reliable mechanistic conclusions to be drawn. For a series of anation reactions of an aquometal cation, the volumes of activation for solvent exchange and for substitution by a variety of nucleophiles (after due allowance is made for ΔV° for precursor ion-pair formation) should be very similar if the interchange mechanism is truly I_d. Significant differences in volumes of activation should be observed for I_a mechanisms.

We have selected the diaquobis(ethylenediamine)cobalt(III) ion as the basis of a systematic evaluation of $\Delta V_0^\ddagger$ and $\Delta\beta^\ddagger$ values for interchange reactions since already these values are known for exchange[3] and isomerization[4] of the $Co(en)_2(OH_2)_2^{3+}$ cation. In this paper we report measurements of activation volume parameters for reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ and the more labile $Co(en)_2OH\cdot OH_2^{2+}$ with various protonated forms of oxalate.

Brown and Harris[5] have shown that the reaction paths shown in Scheme I are involved in acid solutions (pH 1 or less),

Scheme I. Reactions in Acidic Media

$$\begin{array}{l} cis\text{-}Co(en)_2(OH_2)_2^{3+} \\ \quad + \left\{ \begin{array}{ccc} H_2C_2O_4 & \overset{K_3}{\rightleftharpoons} & Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4 \\ \uparrow\downarrow K_1 & & \uparrow\downarrow K_2 \\ HC_2O_4^- & \overset{K_4}{\rightleftharpoons} & Co(en)_2(OH_2)_2^{3+}\cdot HC_2O_4^- \end{array} \right\} \xrightarrow{k_{an}'} \\ \qquad\qquad [Co(en)_2(OH_2)C_2O_4^+] \xrightarrow{\text{fast}} Co(en)_2C_2O_4^+ \quad (1) \end{array}$$

for which, under pseudo-first-order conditions with oxalate in great excess, we obtain eq 2, where h represents the stoichiometric hydrogen ion concentration and [Ox] represents the total concentration of oxalate in all of its protonated forms.

$$k_{obsd}' = \frac{k_{an}'(K_1K_4 + K_3h)[Ox]}{(K_1K_4 + K_3h)[Ox] + K_1 + h} \qquad (2)$$

The singly bonded oxalate species $Co(en)_2(OH_2)C_2O_4^+$ is a relatively short-lived intermediate which is not observed at higher temperatures (333 K) but it may be identified at lower temperatures and a higher pH values[6] (see Scheme III, later).

Around pH 7, different protonated forms react[5] through an ion-pair sequence shown in Scheme II. It is likely that the product $Co(en)_2(OH)\cdot C_2O_4$ is the cis isomer. The cis and trans isomers of $Co(en)_2(OH)OH_2^{2+}$ interconvert very rapidly[7] at 298 K (half-time 2.3 min) and both isomers may therefore react with oxalate anion. With oxalate in excess, the pseudo-first-order rate coefficient is given by eq 5.

Scheme II. Reactions in Neutral Media

$$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \rightleftharpoons Co(en)_2(OH)OH_2^{2+}\cdot C_2O_4^{2-} \quad K_5 \quad (3)$$

$$Co(en)_2(OH)OH_2^{2+}\cdot C_2O_4^{2-} \rightarrow Co(en)_2(OH)\cdot C_2O_4^{0} + H_2O \quad k_{an}'' \quad (4)$$

$$k_{obsd}'' = \frac{k_{an}''K_5[C_2O_4^{2-}]}{1 + K_5[C_2O_4^{2-}]} \qquad (5)$$

The neutral species $Co(en)_2(OH)C_2O_4$ can undergo a ring-closing reaction to form $Co(en)_2C_2O_4$ by intermediate formation of the corresponding aquo complex, according to Scheme III. The ring-closing reaction may also be considered to be an interchange reaction involving monodentate oxalate and aquo ligands. For this first-order reaction

Scheme III. Ring Closing at Intermediate pH

$$Co(en)_2(OH)C_2O_4 + H^+(aq) \rightleftharpoons Co(en)_2(OH_2)C_2O_4^+ \quad 1/K_6 \qquad (6)$$

$$Co(en)_2(OH_2)C_2O_4^+ \rightarrow Co(en)_2C_2O_4^+ + H_2O \quad k_{an}''' \qquad (7)$$

$$k_{obsd}''' = k_{an}'''h/K_6 \qquad (8)$$

We have studied the pressure dependences of all the reactions described by Schemes I–III and interpret the derived parameters in terms of the mechanisms of interchange between primary and secondary coordination spheres.

Experimental Section

Materials. Preparation of *cis*-$[Co(en)_2(OH_2)_2](NO_3)_3$. $[Co(en)_2CO_3]Cl$ was prepared by an established method.[8] A suspension of $[Co(en)_2CO_3]Cl$ (8 g) in water (60 cm^3) was shaken for 5 min with silver nitrate (3.7 g) in water (20 cm^3). The silver chloride was removed by filtration, ethanol was added to the filtrate, and the

$[Co(en)_2CO_3]NO_3$ which crystallized was washed with ethanol and dried; yield 60%. Solutions of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ were prepared directly from $[Co(en)_3CO_3]NO_3$ by the addition of nitric acid. Extinction coefficients compared well with the reported value,[9] namely, ϵ_{492} 80.9 M^{-1} cm^{-1}, and reactant solutions exhibited excellent kinetic characteristics.

cis-$[Co(en)_2(OH)OH_2](NO_3)_2$ was prepared from *trans*-$[Co(en)_2Cl_2]Cl$ by the method of Kruse and Taube.[10]

Trizma buffers were prepared from tris(hydroxymethyl)aminomethane (Sigma Chemical) and appropriate amounts of nitric acid. The pH of buffers, and all other solutions, was checked with a Radiometer TTT1 titrimeter with a scale expander, Model PHA 630T.

High-Pressure Procedures. All reactions were conducted in a high-pressure sampling vessel which permitted aliquot samples to be withdrawn while reactants were still pressurized. Reactants were mixed and then drawn into a Perspex (Lucite) syringe (80 or 150 cm^3) equipped with a floating Teflon plunger and a Pt–Ir outlet tube. The syringe was assembled inside the pressure vessel; the contents were pressurized and allowed to establish thermal and pressure equilibrium for 30 min before samples were withdrawn. The temperature of the assembly was regulated to within ±0.01 K, and in the pressure range 10–150 MPa,[11] pressures were maintained to ±0.5 MPa.

Kinetic Procedures. For reactions described by Scheme I, *cis*-$Co(en)_2(OH_2)_2^{3+}$ solutions were mixed with acidic oxalate solutions, aliquot samples were removed periodically into ice-chilled tubes, and optical absorbances were measured at 500 nm where ϵ is 80.9 (*cis*-$Co(en)_2((OH_2)_2^{3+}$) and 113 ($Co(en)_2C_2O_4^+$).

For reactions described by Scheme II, solutions of *cis*-$Co(en)_2(OH)OH_2^{2+}$ were mixed with solutions of sodium oxalate and sodium nitrate in Trizma buffers of the appropriate pH. Aliquot samples were passed through a Dowex 50W-X8, 20–50 mesh resin column in the Na^+ form to remove all cationic species. The effluent, containing $Co(en)_2OH{\cdot}C_2O_4$ as the only cobalt(III) species, was acidified and allowed to stand for 2 days for complete conversion to $Co(en)_2C_2O_4^+$. Optical absorptions were then measured at 500 nm.

Reactions described by Scheme III were followed by spectrophotometric analysis at 500 nm of the product $Co(en)_2C_2O_4^+$. Aliquot samples were passed through a Dowex 50W-X8 resin to remove the uncharged $Co(en)_2OH{\cdot}C_2O_4$ in the effluent. The resin was then acidified with dilute acid, and the $Co(en)_2C_2O_4^+$, eluted with 1 M sodium nitrate.

All reactions exhibited good first-order kinetic characteristics. Rate coefficients were evaluated from the linear variation of log $[(A_\infty - A_0)/(A_t - A_0)]$ with time where the absorbances A_t at time t were usually recorded over 2 half-times for the reaction and the infinite-time absorbance A_∞ was recorded after at least 6 half-times had elapsed.

Results

The anation rate coefficients k_{an}', k_{an}'', and k_{an}''', corresponding to Schemes I–III, respectively, were evaluated at different pressures. Possible pressure variations of the volumes of activation were tested by analyzing the data with the polynomial

$$\log (k_{an})_P = \log (k_{an})_0 + bP + cP^2 \tag{9}$$

where $\Delta V_0^{\ddagger} = -bRT$ and the compressibility coefficient of activation is $\Delta\beta^{\ddagger} = -(\partial\Delta V^{\ddagger}/\partial Vp)_T = 2cRT$. In all three reaction schemes, values of $\Delta\beta^{\ddagger}$ were not statistically different from zero and therefore volumes of activation were essentially pressure independent, as given by the relation

$$-RT(\partial \ln k_{an}/\partial P)_T = \Delta V^{\ddagger} \tag{10}$$

Oxalate Anation in Acidic Media (Scheme I). The values of k_{an}' were derived from sets of rate measurements at different oxalate concentrations and pressures. In all, 69 individual rate experiments were conducted. At each pressure, the value of k_{an}' was evaluated from the variation of $1/k_{obsd}'$ with $1/[Ox]$ using the reciprocal form of eq 2

$$1/k_{obsd}' = 1/k_{an}' + (K_1 + h)/k_{an}'(K_1K_4 + hK_3)[Ox] \tag{11}$$

Under all reaction conditions, excellent linear variations were observed with intercepts $1/k_{an}'$ and slopes $(K_1 + h)/k_{an}'(K_1K_4 + hK_3)$ as determined by a least-squares routine.

Table I. Variation with Pressure of k_{obsd}' for the Overall Reaction (Scheme I) in Acid Medium at 60.0 °C, $[HNO_3] = 0.5$ M, and Ionic Strength 2.0 M ($NaNO_3$)

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + \begin{cases} H_2C_2O_4 \rightarrow Co(en)_2C_2O_4^+ \\ HC_2O_4^- \end{cases}$$

Applied pressure, MPa	[Ox], M	$10^5k_{obsd}'$, s^{-1}	No. of runs
0.10	0.015	9.18 ± 0.15 (9.03)[a]	4
	0.020	11.37 ± 0.17 (10.9)	4
	0.030	14.18 ± 0.26 (14.0)	5
	0.060	20.90 ± 0.38 (21.2)	4
55.2	0.015	7.88 ± 0.21	4
	0.020	9.90 ± 0.21	4
	0.030	12.28 ± 0.26	4
	0.060	18.62 ± 0.30	4
103.4	0.015	7.10 ± 0.09	5
	0.020	9.16 ± 0.22	4
	0.030	10.95 ± 0.15	4
	0.060	16.80 ± 0.41	4
151.7	0.015	6.39 ± 0.20	6
	0.020	8.06 ± 0.16	5
	0.030	9.96 ± 0.24	5
	0.060	15.04 ± 0.33	3

[a] Parenthesized values reported by Brown and Harris.[5]

Table II. Variation of k_{an}' and $K_{IP}^{-1} = (K_1 + h)/(K_1K_4 + hK_3)$ with Pressure for Reaction Scheme I at 60.0 °C, $[HNO_3] = 0.5$ M, and Ionic Strength 2.0 M ($NaNO_3$)

Applied pressure, MPa	$10^5k_{an}'$, s^{-1}	K_{IP}
0.10	34.9 ± 1.2	23.8 ± 1.2
55.2	32.1 ± 1.5	21.8 ± 1.4
103.4	28.8 ± 2.2	22.1 ± 2.5
151.7	26.9 ± 1.5	20.6 ± 1.7

Table I lists the sets of rate data determined at four different pressures, each at four different oxalate concentrations. The standard deviation of each mean value of k_{obsd}' was usually ±2% based on at least four runs at each oxalate concentration. At 0.10 MPa (1 atm) the present values of k_{obsd}' agree within experimental error with those previously reported by Brown and Harris.[5]

Table II lists the deduced values of k_{an}' and the composite equilibrium quotient $K_{IP}^{-1} = (K_1 + h)/(K_1K_4 + hK_3)$. Since the values of k_{an}' and K_{IP} must be deduced by extrapolation, the concomitant errors are greater than those in the individual values of k_{obsd}' but there is a clear decrease in both K_{an}' and K_{IP} with pressure. A least-squares analysis yields the values $\Delta V_{an}'^{\ddagger} = +4.8 \pm 0.2$ cm^3 mol^{-1} (with $\Delta\beta^{\ddagger} \leq 0.01$ cm^3 mol^{-1} MPa^{-1}) and $\Delta V_{IP} = +2.3 \pm 0.6$ cm^3 mol^{-1}.

The composite quotient K_{IP} may be simplified, since under the reaction conditions employed $h > K_1$ and $K_1K_4 > hK_3$;[5] thus to a reasonable approximation $K_{IP}^{-1} \approx h/K_1K_4$ and $\Delta V_{IP} \approx (\Delta V_1 + \Delta V_4)$. Since $\Delta V_1 = -12$ cm^3 mol^{-1}, then $\Delta V_4 \approx +10$ cm^3 mol^{-1}. It is emphasized that these approximations have no bearing on the mechanistic conclusions drawn later, but the positive value of ΔV_4 is consistent with outer-sphere ion pairing between $Co(en)_2(OH_2)_2^{3+}$ and $HC_2O_4^-$.

Oxalate Anation in Neutral Media (Scheme II). The pressure and temperature dependences of k_{an}'' and the ion-pair constant K_5 (eq 3) were deduced from the variation of the first-order rate coefficient k_{obsd}'' with oxalate concentration according to the reciprocal form of (5)

$$1/k_{obsd}'' = 1/k_{an}'' + 1/k_{an}''K_5[C_2O_4^{2-}] \tag{12}$$

Chan and Harris[6] reported complications in their rate measurements but these were overcome in these studies by the use of Trizma base buffer. Under all conditions of temperature and pressure, excellent linear variations of $1/k_{obsd}''$ with

Table III. Temperature Variation of k_{obsd}'' for the Overall Reaction (Scheme II) at Ionic Strength 0.37 M ($NaNO_3$) and pH (Trizma Buffer, 25 °C) 7.30

$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \rightarrow Co(en)_2OHC_2O_4^0 + OH_2$

Temp, °C	$[C_2O_4^{2-}]$, M	$10^4 k_{obsd}''$, s^{-1}	No. of runs
20	0.030	0.55 ± 0.01	3
	0.040	0.69 ± 0.01	3
	0.060	0.97 ± 0.02	3
25	0.020	0.87 ± 0.02	3
	0.030	1.24 ± 0.02	4
	0.040	1.58 ± 0.03	4
	0.060	2.12 ± 0.04	3
30	0.020	1.17 ± 0.01	4
	0.030	1.66 ± 0.03	3
	0.040	2.17 ± 0.05	3
	0.060	3.05 ± 0.06	4
35	0.020	1.57 ± 0.02	4
	0.030	2.18 ± 0.04	3
	0.040	2.94 ± 0.04	3
	0.060	4.34 ± 0.08	4

Table IV. Variation of k_{an}'' and K_5 with Temperature for Reaction Scheme II

Temp, °C	pH	f[a]	$10^4 k_{an}''$, s^{-1}	$10^4 k_{an}''$ (cor), s^{-1}	K_5, M^{-1}	K_5(cor), M^{-1}
20	7.40	0.82	3.97	$4.9 \pm 0.1_4$	5.3	6.5 ± 0.5
25	7.30	0.83	7.84	$9.4 \pm 0.1_8$	6.2	7.5 ± 0.4
30	7.20	0.84	15.0	$17.9 \pm 0.7_5$	4.2	4.9 ± 0.4
35	7.10	0.85	28.3	33.2 ± 2.0	2.9	3.4 ± 0.8

[a] Fraction existing as $Co(en)_2(OH)OH_2^{2+}$ at stated pH.

Table V. Variation of k_{obsd}'' with Pressure for the Overall Reaction (Scheme II) at 30 °C and Ionic Strength 0.32 M ($NaNO_3$)

$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \rightarrow Co(en)_2(OH)C_2O_4^0 + H_2O$

Applied pressure, MPa	$[C_2O_4^{2-}]$, M	$10^4 k_{obsd}''$, s^{-1}	Applied pressure, MPa	$[C_2O_4^{2-}]$, M	$10^4 k_{obsd}''$, s^{-1}
0.10	0.020	1.17 ± 0.03	103.4	0.020	0.93 ± 0.03
	0.030	1.66 ± 0.04		0.030	1.36 ± 0.02
	0.040	2.17 ± 0.04		0.040	1.74 ± 0.04
	0.060	3.05 ± 0.06		0.060	2.41 ± 0.04
51.70	0.020	1.06 ± 0.02	155.1	0.020	0.82 ± 0.02
	0.030	1.54 ± 0.02		0.030	1.17 ± 0.03
	0.040	1.99 ± 0.04		0.040	1.53 ± 0.03
	0.060	2.73 ± 0.05		0.060	2.15 ± 0.04

Table VI. Variation of k_{an}'' and K_5 with Pressure for Reaction Scheme II

Pressure, MPa	pH	f[a]	10^4-k_{an}'', s^{-1}	10^4-k_{an}''(cor), s^{-1}	K_5, M^{-1}	K_5 (cor), M^{-1}
0.10	7.2	0.85	15.0	17.6 ± 0.8	4.2	4.9 ± 0.4
51.7	7.2	0.85	13.8	16.2 ± 0.6	4.1	4.8 ± 0.3
103.4	7.1	0.85	12.4	14.6 ± 0.6	4.0	4.7 ± 0.3
155.1	7.1	0.85	11.2	13.2 ± 0.5	3.9	4.6 ± 0.3

[a] Fraction existing as $Co(en)_2(OH)OH_2^{2+}$ at stated pH.

Table VII. Variation of k_{obsd}''' and k_{an}''' with Pressure for the Overall Reaction (Scheme III) at 50.0 °C and Ionic Strength 0.37 M ($NaNO_3$)

$Co(en)_2(OH)C_2O_4 + H^+(aq) \rightarrow Co(en)_2C_2O_4^+ + H_2O$

Pressure, MPa	$10^5 k_{obsd}'''$, s^{-1}	No. of runs	pH (cor)	h/K_6 (eq 8)	10^3-k_{an}''',[b] s^{-1}
0.10	6.28 ± 0.10[a]	4	7.80	0.0501	1.25
0.10	6.36 ± 0.12	6	7.80	0.0501	1.27
34.5	6.64 ± 0.10	6	7.78	0.0513	1.29
68.9	6.68 ± 0.13	6	7.77	0.0506	1.32
103.4	6.56 ± 0.08	6	7.75	0.0514	1.28
137.9	6.24 ± 0.10	6	7.74	0.0512	1.22

[a] Measurements with optical vessel with glass surfaces; all others with sampling vessel with Perspex surfaces. [b] Values of k_{an}''' subject to random errors of ±0.02.

$1/[C_2O_4^{2-}]$ were observed yielding intercepts $1/k_{an}''$ and slopes equal to $1/k_{an}''K_5$. Mean values of k_{obsd}'' were reproducible to within ±2%.

Table III lists sets of rate data determined at four different oxalate concentrations at four temperatures between 293 and 308 K; 51 runs in all were conducted.

Values of k_{an}'' and K_5, calculated by a least-squares routine, are listed in Table IV together with corrected values k_{an}''(cor) and K_5(cor), derived by dividing k_{an}'' and K_5 by f, the fraction of the aquobis(ethylenediamine)cobalt(III) ions which are in the reactive form[6] $Co(en)_2(OH)OH_2^{2+}$ at the specified pH. At 298 K the value of $k_{an}''(\text{cor}) = (9.4 \pm 0.2) \times 10^{-4}\ s^{-1}$ is in good agreement with the mean value reported by Chan and Harris,[6] namely, $(9.4 \pm 0.5) \times 10^{-4}\ s^{-1}$. The temperature variation of k_{an}''(cor) and K_5(cor) yields $\Delta H_{an}''^{\ddagger} = 92.9 \pm 1.7$ kJ mol^{-1}, $\Delta S_{an}''^{\ddagger} = +9.6 \pm 4.2$ J K^{-1} mol^{-1}, and $\Delta H_5 = -34 \pm 17$ kJ mol^{-1}.

Table V lists analogous sets of data for the variation of k_{obsd}'' at four different oxalate concentrations, each at four different pressures. Each value of k_{obsd}'' represents the mean of two or three individual runs.

Table VI lists values of k_{an}''(cor) and K_5(cor) deduced as before. In the case of the pressure variations, allowance must be made for the pressure variation of the acidity constant for Trizma base. Distèche[12] has measured the molal volume change for the reaction

$$TH^+ + H_2O \rightleftarrows T + H_3O^+$$

to be -2.5 cm^3 mol^{-1} so that the pH of a Trizma-buffered solution falls by 0.023 pH unit for an increase of 51.7 MPa pressure.

The pressure variation of k_{an}''(cor) yields the value $\Delta V''^{\ddagger} = +4.6 \pm 0.4$ cm^3 mol^{-1} with $\Delta\beta^{\ddagger} \leq 0.01$ cm^3 mol^{-1} MPa^{-1}. The ion-pair constant K_5(cor) exhibits only a slight pressure variation which is within the experimental uncertainties and $\Delta V_5 = -1.0 \pm 1.5$ cm^3 mol^{-1}.

Oxalate Ring-Closing Reaction (Scheme III). The monodentate oxalate complex $Co(en)_2(OH)C_2O_4$ was prepared in situ and allowed to undergo the ring-closing reaction in Trizma buffers at pH 7–8.0 (0.1 MPa), at 323 K, and at an ionic strength of 0.37 M $NaNO_3$. The mean value of rate coefficients at each pressure was subject to a variance of ±3% and within the experimental uncertainties there was no detectable difference in rates measured in glass and Perspex reaction vessels.

Table VII lists the variation of k_{obsd}''' and k_{an}''' with pressure. The true volume of activation for the ring-closing reaction must be deduced from the pressure dependence of k_{an}''' and in deducing k_{an}''' from k_{obsd}''' (eq 8) due allowance must be made for the pressure dependences of both the hydrogen ion concentration in Trizma buffers and the acidity constant of $Co(en)_2(OH_2)C_2O_4^+$. The slight fall in pH at different pressures[12] using the same buffer ratio established at 0.1 MPa is listed in Table VII. Chan and Harris[6] measured the pK_a of $Co(en)_2(OH_2)C_2O_4^+$ as 6.7 at 298 K and assumed pK_a = 6.5 at 323 K. We have assumed a partial molar volume change for the acidity of $Co(en)_2(OH_2)C_2O_4^+$ of $\Delta\bar{V} = -2.3$ cm^3 mol^{-1}, a value we have observed for the $Co(NH_3)_5OH_2^{3+}$ cation.[13] For other aquometal cations we find[13] that $\Delta\bar{V} = -1.2 \pm 0.5$ cm^3 mol^{-1} ($Fe(OH_2)_6^{3+}$), $\Delta\bar{V} = -3.2 \pm 0.9$ cm^3 mol^{-1} (Tl^{3+}(aq)), and $\Delta\bar{V} = -3.8 \pm 0.7$ cm^3 mol^{-1} ($Cr(OH_2)_6^{3+}$) have been reported.[14] The value assumed for $Co(en)_2(OH_2)C_2O_4^+$ probably introduces a systematic uncertainty of about 1.2 cm^3 mol^{-1} into the final $\Delta V^{\ddagger}$ value for k_{an}'''.

The deduced values of k_{an}''' show no statistically significant variation with pressure and we set $\Delta V^{\ddagger} = 0 \pm 1.2$ cm^3 mol^{-1}.

Discussion

The interchange of oxalate with an aquo ligand within the ion pairs *cis*-$Co(en)_2(OH_2)_2^{3+}$,$H_2C_2O_4/HC_2O_4^-$ and $Co(en)_2(OH)OH_2^{2+}$,$C_2O_4^{2-}$ involves virtually identical volumes of activation (+4.8 ± 0.2 and +4.6 ± 0.4 cm^3 mol^{-1}) and this common $\Delta V^{\ddagger}$ value is very similar to that observed[3] for exchange of solvent water with *trans*-$Co(en)_2(OH_2)_2^{3+}$ (+5.9 ± 0.2). Furthermore values of $\Delta\beta^{\ddagger}$ for all three reactions are virtually zero, suggesting that there is no significant movement of solvent in or out of the secondary hydration spheres of the substrate cations or the oxalate in its three possible protonic forms. These observations suggest that all three reactions involve dissociative interchange of an aquo ligand as the prime feature of an I_d mechanism. Water and oxalate may compete for reaction with the intermediate so generated. This interchange mechanism is in striking contrast with the D mechanism for isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ with a much larger positive $\Delta V^{\ddagger} = +13.2$ cm^3 mol^{-1} and with extensive desolvation attending the stereochemical change, as indicated by $\Delta\beta^{\ddagger} = 0.10$ cm^3 mol^{-1} MPa^{-1}.

A number of authors [15-18] have now shown that the measured volume of activation for a dissociative reaction may be used to obtain a crude estimate of the extent to which a bond must be stretched, Δl, to generate the transition state. The leaving group, which is assigned a radius r, is assumed to create a cylindrical hole equivalent to the volume of activation, $\Delta V^{\ddagger} = \pi r^2 \Delta l$. This approach attributes the total volume change in forming the transition state to stretching of the one critical coordinate; secondary contributions from concomitant contractions in other regions of the substrate molecule and from changes in solvent electrostriction, due to a change in radius and possible charge separation, are ignored. In the case of the I_d mechanism for an aquometal ion, these secondary contributions are unlikely to be important since the remaining ligands are already close-packed in the ground state[18] and the aquo leaving group is uncharged. The radius to be assigned to an aquo ligand is uncertain. A lower estimate (145 pm) would be given by half the sum of the O–O bond distance in liquid water[19] but this assumes that the aquo ligand fits neatly into the surrounding hydrogen-bonded bulk water structure. This radius suggests that the Co–O bond, normally 200 pm in the ground state, would be stretched 121 pm to generate a volume of 4.8 cm^3 mol^{-1}. An upper limit to the radius (162 pm) may be derived for a tetrahedral molecule using the known O–H bond length and the van der Waals radius of hydrogen. This radius would entail a Co–O bond stretch of 97 pm. Both estimates indicate a substantial stretching of the Co–O bond and a similar estimate has been given[18] for substitution of aquated Ni^{2+} and Co^{2+} cations.

The virtually identical volumes of activation for substitution of the substrate $Co(en)_2(OH_2)_2^{3+}$ and $Co(en)_2(OH)(OH_2)^{2+}$ ions suggest that the degree of bond stretching to form the transition state is the same even though the latter ion is 250 times more labile[20] at 298 K than the former. The source of this lability, which is attributed to the influence of the hydroxo ligand, resides in the relative $\Delta H^{\ddagger}$ values. For oxalate interchange[5] on $Co(en)_2(OH_2)_2^{3+}$, $\Delta H^{\ddagger} = 103.8 \pm 2.1$ kJ mol^{-1}, while for interchange on $Co(en)_2(OH)(OH_2)^{2+}$ this study shows that $\Delta H^{\ddagger} = 92.9 \pm 1.7$ kJ mol^{-1}.

The I_d mechanism for oxalate–aquo interchange is supported by other lines of evidence. The rate of water exchange in *cis*-$Co(en)_2(OH_2)_2^{3+}$ is 4 times that of oxalate interchange in *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4$.[20] The positive entropy of activation for oxalate interchange[5] ($\Delta S^{\ddagger} = +6.3 \pm 6.3$ J K^{-1} mol^{-1}) is consistent with some aquo dissociation although for exchange of water $\Delta S^{\ddagger} = +63$ J K^{-1} mol^{-1}. Likewise in the more labile $Co(en)_2(OH)OH_2^{2+}$ cation, the rate of water exchange is twice that of oxalate interchange in $Co(en)_2(OH)OH_2^{2+}\cdot C_2O_4^{2-}$ which is shown by this study to exhibit $\Delta S^{\ddagger} = +9.6 \pm 4.2$ J K^{-1} mol^{-1}, again consistent with dissociative interchange of the aquo ligand. Nevertheless the $\Delta V^{\ddagger}$ values, with smaller relative errors, yield more clear-cut evidence for the I_d mechanism. Such an I_d mechanism can now be proposed with rather more confidence for the $Fe(OH_2)_6^{3+} + NCS^-$ reaction[21] ($\Delta V^{\ddagger} = +5$ cm^3 mol^{-1}) and reactions of Co^{2+}(aq), Ni^{2+}(aq), Cu^{2+}(aq), and Zn^{2+}(aq) with glycinate, ammonia, and PADA, all of which exhibit[22] values in the region of +4 to +8 cm^3 mol^{-1}. On the other hand, the value $\Delta V^{\ddagger} = -2.2 \pm 1$ cm^3 mol^{-1} [23] for the reaction of $Cr(OH_2)_6^{3+} + HC_2O_4^-$ is likely to be I_a in character.

Ring closing of $Co(en)_2OH_2\cdot C_2O_4^+$ to form $Co(en)_2C_2O_4^+$ exhibits $\Delta V^{\ddagger} = 0 \pm 1.2$ cm^3 mol^{-1}, in contrast to the other oxalate–aquo interchange reactions. It would seem likely that if stretching of the Co–OH_2 bond occurs in forming the transition state, then this volume increase is being offset by a net volume decrease as the monodentate oxalate swings in to take up the second coordination site. An additional positive volume contribution could be made by partial desolvation of the carboxylate group in the transition state. Overall the mechanism probably involves a significant degree of associative character and this would be described as I_a. The negative entropy of activation ($\Delta S^{\ddagger} = -27 \pm 4$ J K^{-1} mol^{-1}) may reflect losses of internal degrees of freedom within the incipient oxalate bidentate which are not reflected in corresponding structural contributions to the zero volume of activation. The negative $\Delta S^{\ddagger}$ value argues against significant desolvation of the carboxylate in the transition state.

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Registry No. *cis*-$Co(en)_2(OH_2)_2^{3+}$, 21247-59-6; $H_2C_2O_4$, 144-62-7; $Co(en)_2(OH)C_2O_4$, 59982-23-9; $[Co(en)_2CO_3]Cl$, 15842-50-9.

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