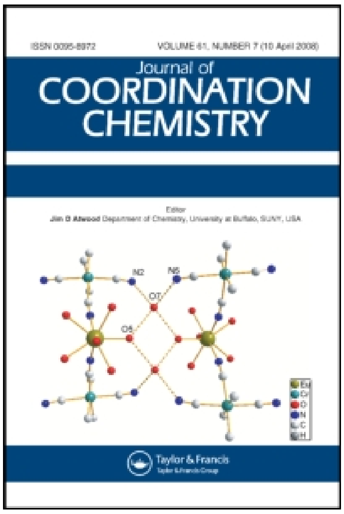

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THE EFFECT OF PRESSURE ON THE RATE OF ISOMERIZATION OF ACETATOAQUOBIS(ETHYLENE-DIAMINE)COBALT(III) PERCHLORATE

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The isomerization of *trans*-Co(en)$_2$(acet)(OH$_2$)$^{2+}$ (en = 1,2-diaminoethane; acet$^-$ = acetate anion) in aqueous acid is retarded upon the application of pressure. In 0.05 M HClO$_4$, a pressure-independent volume of activation ($\Delta V^{\neq}$) of +7.9 ± 0.3 cm^{3}mol^{-1} is obtained, together with $\Delta H^{\neq}$ = 117.1 ± 3.0 kJ mol^{-1} and $\Delta S^{\neq}$ = +61 ± 9 J K^{-1}mol^{-1}. In 0.05 M HClO$_4$ with added NaClO$_4$ (I = 1.0 M), $\Delta V^{\neq}$ = +6.5 ± 0.4 cm^{3}mol^{-1}, $\Delta H^{\neq}$ = 112.6 ± 2.4 kJ mol^{-1} and $\Delta S^{\neq}$ = +46 ± 7 J K^{-1}mol^{-1}. In 1.0 M HClO$_4$, $\Delta V^{\neq}$ = +5.6 ± 0.6 cm^{3}mol^{-1}, $\Delta H^{\neq}$ = 112.9 ± 2.8 kJ mol^{-1} and $\Delta S^{\neq}$ = +47 ± 8 J K^{-1}mol^{-1}. This data is most consistent with isomerization proceeding via dissociative aquo ligand release in a dissociative interchange (I_d) mechanism. Analogous I_d or D (dissociative) mechanisms have been assigned previously to isomerizations of several *trans*-Co(en)$_2$(X)(OH$_2$)$^{n+}$ complexes (X = OH$_2$, SeO$_3$H$^-$ or SeO$_3$$^{2-}$) on the basis of $\Delta V^{\neq}$ data, and the results for the X = acet$^-$ complex presented here support a general dissociative mechanism for complexes of this type.

INTRODUCTION

Isomerization reactions of inert octahedral transition metal complexes have been studied extensively in recent decades, and their kinetic behaviour has been reviewed previously.[1,2] In particular, *trans*→*cis* isomerization reactions of a range of bis(ethylenediamine)cobalt(III) complexes have been frequently reported,[1] and have been generally though not universally assigned dissociative type mechanisms. The acetatoaquobis(ethylenediamine)cobalt(III) cation has been studied on two occasions,[3,4] and apparently isomerization proceeds by a dissociative mechanism.

Recently, the application of volumes of activation ($\Delta V^{\neq}$) to the elucidation of reaction mechanisms, including isomerization reactions, from the effect of high pressure on rates of reaction in solution has been reviewed.[5] For isomerization of *trans*-Co(en)$_2$(OH$_2$)$_2$$^{3+}$, a $\Delta V^{\neq}$ of approximately +14 cm^{3}mol^{-1} with a non-zero compressibility coefficient of activation ($\Delta\beta^{\neq}$) has been reported.[6] Related complexes *trans*-Co(en)$_2$(SeO$_3$H)(OH$_2$)$^{2+}$ and *trans*-Co(en)$_2$(SeO$_3$)(OH$_2$)$^+$ exhibit $\Delta V^{\neq}$ of approximately +7 cm^{3}mol^{-1}, which are pressure independent ($\Delta\beta^{\neq}$ = 0).[7] The diaquo complex has been assigned a dissociative (D) mechanism in which a neutral water molecule is released into the bulk solvent in forming the transition state, while the selenite complexes have both been assigned dissociative interchange (I_d) mechanisms in which the neutral water ligand is released into the electrostricted first solvation sphere in the transition state. An I_d mechanism has also been proposed for isomerization of *trans*-Cr(mal)$_2$(OH$_2$)$_2$$^-$ (mal^{2-} = malonate dianion) on the basis of a pressure-independent $\Delta V^{\neq}$ of +8.9 cm^{3}mol^{-1}, whereas the analogous *trans*-Cr(ox)$_2$(OH$_2$)$_2$$^-$ (ox^{2-} = oxalate dianion) exhibits a $\Delta V^{\neq}$ of −16.6 cm^{3}mol^{-1} with a non-zero $\Delta\beta^{\neq}$, and evidently isomerizes by a distinctly different ring opening mechanism.[8]

The usefulness of experimental volumes of activation in determining the mechanisms of reactions has prompted us to determine the effect of pressure on the rate of isomerization of the *trans*-Co(en)$_2$(acet)(OH$_2$)$^{2+}$ cation (en = 1,2-diaminoethane; acet$^-$ = acetate anion = CH$_3$COO$^-$). The possibility of using $\Delta V^{\neq}$ data to differentiate between D and I_d mechanisms by comparison with data previously reported for analogous complexes is also of interest. We report the results of our investigation in this paper.

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EXPERIMENTAL

Materials

The complex *trans*-$[Co(en)_2(acet)(OH_2)](ClO_4)_2 \cdot H_2O$ was prepared by the method reported by Dasgupta and Tobe.[4]

(*Anal.* Calculated for $C_6H_{23}CoN_4O_{12}Cl_2$: C, 15.2; H, 4.85; N, 11.8. Found: C, 15.4; H, 4.8; N, 11.9%).

Perchloric acid of the desired molarity was prepared from concentrated analytical grade $HClO_4$ by dilution with distilled water. Sodium perchlorate of analytical reagent grade was used without further purification. Standardized acid solutions 0.05 M and 1.0 M in $HClO_4$, and 0.05 M in $HClO_4$ with 0.95 M $NaClO_4$ added, were prepared for kinetic measurements.

Kinetic Measurements

The rate of isomerization at various high pressures was determined by monitoring absorbance changes at 490 nm using a Varian 635D spectrophotometer incorporating an optical high pressure cell in which the reaction solution, contained in an inner glass sample cuvette fitted with a teflon cap, was pressurized up to 1380 bar. Temperature within the high pressure cell block was maintained to within ±0.1°C by thermostated water circulation.

Rate constants (k_{isom}) were evaluated using least-squares analysis via the Guggenheim method. Volumes of activation were determined using the expression

$$(\delta \ln k_{isom}/\delta P)_T = -\Delta V^{\neq}/RT \qquad (1)$$

from plots of $ln(k_{isom})$ versus pressure (P). When the volume of activation itself exhibits a pressure dependence, a quadratic expression

$$\ln k_P = \ln k_O + bP + cP^2 \qquad (2)$$

adequately describes the curved shape of the $ln(k_P)$ versus pressure plots.[5] Absence of curvature in our data, determined by means of first, second and third order polynomial regressions on the data using a computer to determine the best fit, indicates that the compressibility coefficient of activation ($\Delta\beta^{\neq}$) is negligible in these reactions when determined over the pressure range employed.

The rate of isomerization at room pressure and various temperatures was determined by monitoring absorbance changes at 490 nm using a Cary 17 spectrophotometer fitted with a thermostated cell compartment in which the temperature was controlled to ±0.1°C by water circulation. Rate constants were evaluated as above, and activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) determined from $ln(k_{isom})$ versus 1/temperature analysis in the usual manner.

TABLE I
Pressure dependence of *trans*→*cis*-$Co(en)_2(acet)(OH_2)^{2+}$ isomerization[a]

Solvent	Pressure (bar)	$10^4 \cdot k_{isom}$ (sec^{-1})	No. runs
0.05 M $HClO_4$	1	5.60 (± 0.19)	3
	345	5.05 (± 0.16)	3
	690	4.54 (± 0.21)	5
	1035	4.02 (± 0.14)	3
	1380	3.67 (± 0.11)	4
0.05 M $HClO_4$	1	5.73 (± 0.12)	3
(I = 1.0 M, $NaClO_4$)	345	5.28 (± 0.16)	4
	690	4.75 (± 0.07)	3
	1035	4.40 (± 0.11)	3
	1380	4.05 (± 0.10)	2
1.0 M $HClO_4$	1	5.87 (± 0.14)	3
	345	5.46 (± 0.16)	3
	690	5.11 (± 0.09)	3
	1035	4.65 (± 0.14)	2
	1380	4.38 (± 0.12)	2

[a] Temperature = 45.2°C

RESULTS

Isomerization of *trans*→*cis*-$\mathrm{Co(en)_2(acet)(OH_2)^{2+}}$ proceeds with clean isosbestic points to an equilibrium mixture containing 75 ± 2% *cis* and 25 ± 2% *trans.*[4] The observed rate constant (k_{isom}) for the approach to equilibrium is the sum of the rate coefficients for the interconversions *trans*→*cis* (k_t) and *cis*→*trans* (k_c) and does not depend on the isomer initially chosen. The equilibrium quotient (K_{isom}) is invariant with temperature or pH.[4] We have detected no significant change in K_{isom} with pressure over the range employed, since the absorbance spectrum of an equilibrium mixture does not vary with applied pressure.

TABLE II
Temperature dependence of *trans*→*cis*-$\mathrm{Co(en)_2(acet)(OH_2)^{2+}}$ isomerization

Solvent	Temperature (°C)	$10^4 \cdot k_{\mathrm{isom}}(\mathrm{sec^{-1}})^a$
0.05 M $\mathrm{HClO_4}$	36.4	1.46 (±0.03)
	41.0	3.06 (±0.08)
	46.0	6.61 (±0.06)
	50.7	12.07 (±0.18)
	55.6	22.11 (±0.57)
0.05 M $\mathrm{HClO_4}$ (I = 1.0 M, $\mathrm{NaClO_4}$)	35.4	1.27 (±0.02)
	40.8	2.96 (±0.03)
	45.8	5.81 (±0.14)
	49.2	8.60 (±0.24)
	54.1	17.12 (±0.20)
1.0 M $\mathrm{HClO_4}$	35.2	1.30 (±0.03)
	40.8	3.26 (±0.11)
	45.5	5.98 (±0.05)
	50.6	11.83 (±0.21)
	55.0	20.11 (±0.42)

[a] Average of three independent runs

The effect of pressure on k_{isom} between 1 and 1380 bar has been measured in 0.05 M $\mathrm{HClO_4}$ at different electrolyte concentrations (0.05 M and 1.0 M) and in 1.0 M $\mathrm{HClO_4}$, using a complex concentration of 0.005 M. In each case k_{isom} is retarded upon the application of pressure. The results are summarized in Table I. The variation of $\ln(k_{\mathrm{isom}})$ with pressure is essentially linear, which implies that the volume of activation is pressure independent ($\Delta\beta^{\neq} = 0$). Determined $\Delta V^{\neq}$ values are included in Table III.

The temperature dependence of k_{isom} in the same solvent systems was evaluated between 35° and 55°C at five different temperatures. The results are summarized in Table II. Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) derived from this data are included in Table III. The earlier work of Dasgupta and Tobe reported $\Delta H^{\neq} = 119.2 \pm 1.7$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^{\neq} = +65 \pm 7$ J $\mathrm{K^{-1} mol^{-1}}$ in 0.01 M $\mathrm{HClO_4}$[4], while Caruchio and Ortaggi have also reported $\Delta H^{\neq} = 112.6$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^{\neq} = +46$ J $\mathrm{K^{-1} mol^{-1}}$ for the same reaction.[3] We observe no statistical difference in our activation parameters determined in 1.0 M $\mathrm{HClO_4}$ and 0.05 M $\mathrm{HClO_4}$ of ionic strength 1.0 M ($\mathrm{NaClO_4}$), consistent with no acid catalysis. Values in the low ionic strength 0.05 M $\mathrm{HClO_4}$ are slightly different, however.

DISCUSSION

Previously, it has been argued that a positive $\Delta V^{\neq}$ is evidence for a dissociative type mechanism,[5,9] though this case can only be argued firmly when the leaving group is a neutral molecule. When the leaving ligand in a dissociative mechanism is a charged molecule, electrostriction about the new charge centre may be the dominant effect, leading to an appreciable negative $\Delta V^{\neq}$. Examples of activation volumes for isomerization via dissociative

TABLE III
Activation parameters for *trans*→*cis*-$\mathrm{Co(en)_2(acet)(OH_2)^{2+}}$ isomerization

Solvent	$\Delta H^{\neq}$ (kJ $\mathrm{mol^{-1}}$)	$\Delta S^{\neq}$ (J $\mathrm{K^{-1} mol^{-1}}$)	$\Delta V^{\neq}$ ($\mathrm{cm^3 mol^{-1}}$)
0.05 M $\mathrm{HClO_4}$	117.1 (±3.0)	+61 (±9)	+7.9 (±0.3)
0.05 M $\mathrm{HClO_4}$ (I = 1.0 M, $\mathrm{NaClO_4}$)	112.6 (±2.4)	+46 (±7)	+6.5 (±0.4)
1.0 M $\mathrm{HClO_4}$	112.9 (±2.8)	+47 (±8)	+5.6 (±0.6)

mechanisms involving release of either neutral or charged ligands in forming the transition state have been presented recently for *trans→cis* isomerization of $Cr(mal)_2(OH_2)_2^-$ and $Cr(ox)_2(OH_2)_2^-$ (mal^{2-} = malonate dianion; ox^{2-} = oxalate dianion), which exhibit $\Delta V^{\neq}$ of +8.9 and −16.6 $cm^3 mol^{-1}$ respectively.[8]

For isomerization of *trans*-$Co(en)_2(acet)(OH_2)^{2+}$, it is possible to consider dissociative mechanisms involving release of the acetate anion or of coordinated water in forming a transition state intermediate of lower coordination number. Dissociation of chelated ethylenediamine is not a likely mechanism. Release of $acet^-$ would be analogous to the one-ended release of ox^{2-} in $Cr(ox)_2(OH_2)_2^-$ previously studied, for which a negative $\Delta V^{\neq}$ is predicted and observed.[8] Release of OH_2 is the favoured mechanism, since isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ and of *trans*-$Co(en)_2(X)(OH_2)^{n+}$ (X = SeO_3H^- or SeO_3^{2-}) proceed by dissociative aquo release, with positive $\Delta V^{\neq}$ values predicted and observed.[6,7] Of other possible mechanisms, associative type mechanisms generally involve negative $\Delta V^{\neq}$ values,[5] while a twist mechanism should exhibit a near-zero $\Delta V^{\neq}$ since forming the transition state principally involves changes in bond angles and not bond lengths.[10]

Of all these mechanistic possibilities, a mechanism of dissociative aquo ligand release is most consistent with positive $\Delta V^{\neq}$ of between +5.6 and +7.9 $cm^3 mol^{-1}$ observed for *trans→cis*-$Co(en)_2(acet)(OH_2)^{2+}$ isomerization. The reaction is uncomplicated by changes in solvent electrostriction since it involves only the exchange of neutral water with no change in formal charge of the initial complex ion. Analogous mechanisms apply for isomerization of *trans*-$Co(en)_2(X)(OH_2)^{n+}$ (X = OH_2, SeO_3H^- or SeO_3^{2-})[6,7] and of *trans*-$Cr(mal)_2(OH_2)_2^-$.[8]

Two limiting dissociative mechanisms can be considered, namely dissociative (D) and dissociative interchange (I_d). For aquo release, the former can be considered to involve complete transfer of an aquo ligand to the bulk solvent in forming the transition intermediate of lower coordination number, while the latter can best be visualized in terms of transfer of an aquo ligand to the immediate electrostricted hydration sphere of the complex ion. Water in the bulk solvent region exhibits a partial molar volume of approximately 18 $cm^3 mol^{-1}$ with a compressibility coefficient (β) of 0.84 $cm^3 mol^{-1} kbar^{-1}$.[5] In the first hydration sphere about an ion, water has been estimated[5,6] to have an appreciably smaller partial molar volume of 15 $cm^3 mol^{-1}$ together with a compressibility as low as 0.06 $cm^3 mol^{-1} kbar^{-1}$, due to electrostatic compression. These latter parameters will be comparable to those of an aquo ligand within the coordination sphere of a complex ion, so that for an I_d mechanism aquo ligand release will lead to a compressibility coefficient of activation ($\Delta\beta^{\neq}$) = (β(hydration sphere) − β(coordination sphere)) which will approach zero. For a D mechanism, however, $\Delta\beta^{\neq}$ = (β(bulk water) − β(coordination sphere)) will be approximately 0.8 $cm^3 mol^{-1} kbar^{-1}$.

By assuming that a five-coordinate species sweeps out the same volume as its six-coordinate precursor, a D mechanism will yield $\Delta V^{\neq} \simeq +18$ $cm^3 mol^{-1}$ as an upper limit, corresponding to complete release of an aquo ligand into the bulk solvent. An I_d mechanism will similarly yield $\Delta V^{\neq} \simeq +15$ $cm^3 mol^{-1}$ as an upper limit. Lower values of $\Delta V^{\neq}$ experimentally may imply substantial bond stretching rather than complete dissociative release for an I_d mechanism, although no detailed argument can be presented since secondary contributions to $\Delta V^{\neq}$ from solvation changes or general bond length changes for the transition intermediate cannot be readily estimated. Generally, however, it could be expected than an I_d mechanism may be characterized by a smaller $\Delta V^{\neq}$ than that expected for a D mechanism, together with $\Delta\beta^{\neq} \simeq 0$ $cm^3 mol^{-1} kbar^{-1}$ for an I_d compared with $\Delta\beta^{\neq} \geqslant 0.8$ $cm^3 mol^{-1} kbar^{-1}$ for a D mechanism.

We observe that isomerization of *trans*-$Co(en)_2(acet)(OH_2)^{2+}$ in 0.05 M $HClO_4$ proceeds with $\Delta V^{\neq} = +7.9$ $cm^3 mol^{-1}$ and $\Delta\beta^{\neq} = 0$ $cm^3 mol^{-1} kbar^{-1}$. By comparison, *trans*-$Co(en)_2(OH_2)_2^{3+}$ isomerizes with $\Delta V^{\neq} = +14.2$ $cm^3 mol^{-1}$ and $\Delta\beta^{\neq} = 1.0$ $cm^3 mol^{-1} kbar^{-1}$ in the same solvent.[6] The latter complex has been assigned a D mechanism. The smaller, pressure-independent $\Delta V^{\neq}$ observed for the acetatoaquo complex is most consistent with an I_d rather than a D mechanism. The complexes *trans*-$Co(en)_2(X)(OH_2)^{n+}$ (X = SeO_3H^- or SeO_3^{2-}) have also been assigned I_d mechanisms,[7] and exhibit similar pressure-independent $\Delta V^{\neq}$ values (Table IV). At least for these related complexes, it would appear that a qualitative differentiation between D and I_d mechanisms can be made on the basis of $\Delta V^{\neq}$ and $\Delta\beta^{\neq}$ data.

Further, it can be seen (Table IV) that generally a higher $\Delta V^{\neq}$ value is associated with a higher $\Delta S^{\neq}$, which is consistent with an expected correlation of these parameters recently presented by Twigg.[11] It is apparent from the data in Table IV, however, that for the three complexes assigned I_d mechanisms,

TABLE IV

Activation parameters for isomerization reactions of $Co(en)_2(X)(OH_2)^{n+}$ complexes

Complex	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})	$\Delta\beta^{\neq}$ (cm^3 mol^{-1} $kbar^{-1}$)	Reference
trans-$Co(en)_2(OH_2)_2^{3+}$	131.4[a]	+103	+14.2	+1	6
	121.7[b]	+ 64	+12.6	+8	6
trans-$Co(en)_2(SeO_3H)(OH_2)^{2+}$	95.4	+ 1.5	+ 7.2	0	7
trans-$Co(en)_2(acet)(OH_2)^{2+}$	117.1[a]	+ 61	+ 7.9	0	c
	112.9[b]	+ 47	+ 5.6	0	c
trans-$Co(en)_2(SeO_3)(OH_2)^{+}$	105.4	+ 19	+ 7.3	0	7

[a] 0.05 M $HClO_4$

[b] 1.0 M $HClO_4$

[c] This work

$\Delta V^{\neq}$ is fairly constant at about +7.5 $cm^3 mol^{-1}$, while variation of $\Delta S^{\neq}$ from +1.5 to +61 J $K^{-1} mol^{-1}$ is observed. It is likely that certain rotational and translational effects associated with aquo ligand release and possible rearrangements in the electrostricted layer, together with contributions from enhanced flexibility of en chelate rings on forming the transition intermediate, may contribute to $\Delta S^{\neq}$ but not $\Delta V^{\neq}$. No contribution to $\Delta V^{\neq}$ will occur unless there are partial molar volume changes attributable to these effects, and hence $\Delta V^{\neq}$ may generally allow mechanistic information to be assessed with more certainty than can be inferred from $\Delta S^{\neq}$ data alone.

The rate of isomerization is not appreciably dependent on acidity, and activation parameters determined in 1.0 M $HClO_4$ and in 0.05 M $HClO_4$ (I = 1.0 M, $NaClO_4$) are the same within statistical errors. Some variation in activation parameters can be observed in the lower ionic strength acid solution, as exemplified by a change of $\Delta V^{\neq}$ from +6.5 ± 0.4 $cm^3 mol^{-1}$ in 0.05 M $HClO_4$ (I = 1.0 M) to +7.9 ± 0.3 $cm^3 mol^{-1}$ in only 0.05 M $HClO_4$. It is apparent that release of an aquo ligand requires cooperative displacement of other solvent molecules in the vicinity of the cation, while movement of en chelate rings about the cobalt centre is necessary for stereochemical change, possibly via a trigonal bipyramidal intermediate. Possible effects of variation in solvent structure as a result of change in electrolyte concentration has been discussed previously.[6] The minor variation in $\Delta V^{\neq}$ with ionic strength and acidity, together with no measurable variation in $\Delta\beta^{\neq}$, suggests that the volume of activation is a measure principally of aquo ligand release uncomplicated by marked solvation contributions in this case.

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