SHORT REPORT

THE VOLUME OF ACTIVATION FOR AQUATION OF *TRANS*-CHLOROBIS-(DI-METHYLGLYOXIMATO) UREACOBALT (III) FROM HIGH PRESSURE SOLUTION KINETICS

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Summary

The first determination of a volume of activation ($\Delta V^{\ddagger}$) for the dissociation of a neutral ligand (urea) from a formally neutral octahedral complex (trans-chlorobis (dimethylglyoximato)-ureacobalt(III) in aqueous solution is reported. The measured $\Delta V^{\ddagger}$ of $+ 3.5 \pm 0.3$ cm^{3}mol^{-1} is consistent with a dissociative mechanism with stretching of the cobalt-urea (0) bond rather than complete ligand release in the transition state.

The application of volumes of activation ($\Delta V^{\ddagger}$) in the elucidation of inorganic reaction mechanisms has been reviewed previously[1]. For the simple case of dissociative release of a neutral ligand from an incompressible complex, the transition state occupies a larger volume than the precursor state, defined as the extra volume swept out by the dissociating ligand as it extends into the solvent, leading to a positive $\Delta V^{\ddagger}$. Interpretation of $\Delta V^{\ddagger}$ for reactions in which bond breaking or making of ionic ligands is involved are complicated by contributions to $\Delta V^{\ddagger}$ from changes in the electrostriction about the ion concomitant with bond making or breaking.
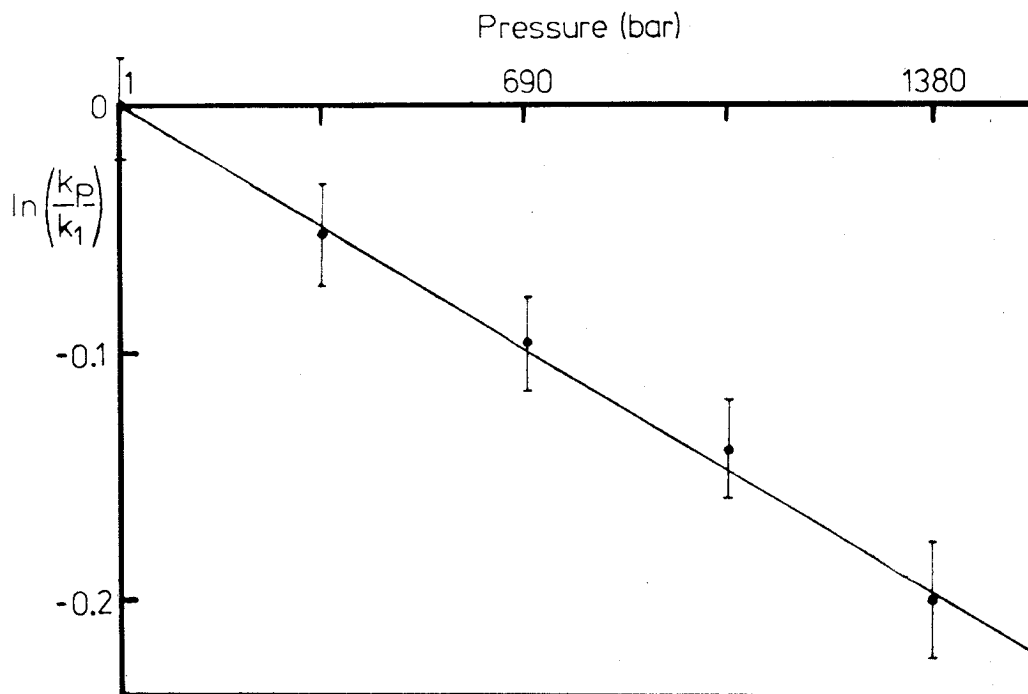
Fig. 1.　Pressure dependence of the rate of aquation of *trans*−[Co(DMG)$_2$(urea)Cl]
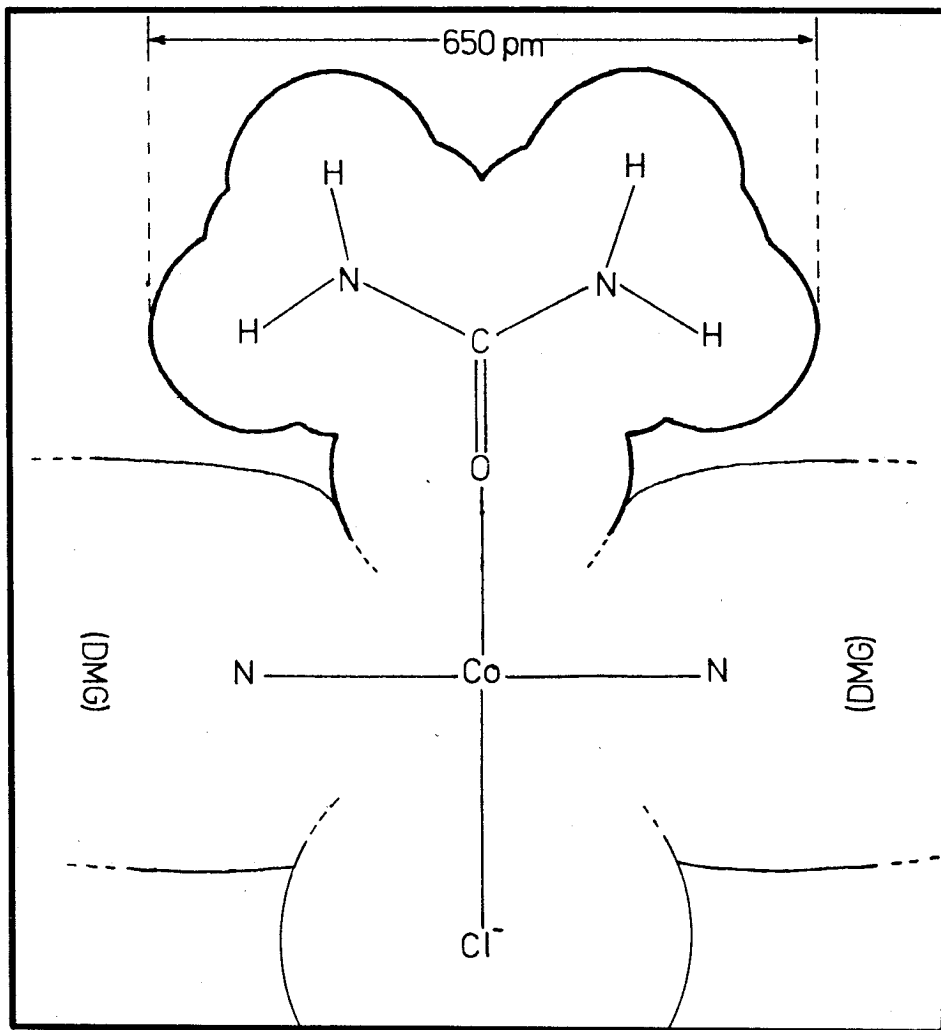
Fig. 2. Schematic diagram of the leaving group (urea) coordinated in the complex *trans*–[Co(DMG)$_2$(urea)Cl]. The urea molecule is of average thickness 260 pm.

Solvent molecules form ordered electrostricted layers of significantly lower volume and compressibility than bulk solvent when in the vicinity of ions[1-3]. Reactions involving dissociation or association of ionic ligands, or even neutral ligands in ionic complexes, can involve a significant electrostrictive contribution to the observed $\Delta V^{\ddagger}$ which is difficult to assess separately, arising from movement of solvent molecules to regions of different electrostriction. Contributions to both $\Delta V^{\ddagger}$, and to a further activation parameter, the compressibility coefficient of activation ($\Delta \beta^{\ddagger}$) are possible[1].

The dissociation of a neutral ligand from a non-electrolyte complex in water with no added ionic species should minimize electrostatic contributions, allowing $\Delta V^{\ddagger}$ to be interpreted in terms of the volume difference between the activated and precursor states. We report the determination of $\Delta V^{\ddagger}$ for replacement of the neutral ligand urea ($H_2N-CO-NH_2$) by water from the neutral complex *trans*-chlorobis (dimethylglyoximato) urea cobalt (III). We believe this to be the first study of the effect of high pressure on the kinetics of aquation of a neutral ligand from a formally neutral octahedral complex.

The complex was prepared by the literature method[4]. The rate of aquation was determined spectrophotometrically by following the change in absorbance at 300 nm of a saturated (10^{-4}M) solution of complex in distilled water at 35°C over the pressure range 1 to 1380 bar. A special high pressure cell fitted into a Varian 635D spectrophotometer allowed the change in absorbance to be monitored under pressure. The aquation reaction is retarded by the application of pressure, with observed rates ($10^4 k_{obs}$, s^{-1}) of 3.48 ± 0.08 (1 bar), 3.30 ± 0.07 (345 bar), 3.16 ± 0.06 (690 bar), 3.03 ± 0.06 (1035 bar) and 2.85 ± 0.07 (1380 bar). The volume of activation for this reaction is $\Delta V^{\ddagger} = +3.5 \pm 0.3$ cm³mol⁻¹, determined graphically using the relationship[1]

$$- RT \, (\partial \ln(k_{obs})/\partial P)_T = \Delta V^{\ddagger} \qquad (1)$$

since a graph of $\ln(k_{obs})$ versus pressure is linear with a slope of $-\Delta V^{\ddagger}/RT$ (Fig. 1).

In recent years, considerable interest has been shown in aquation reactions of bis (dimethylglyoximato) complexes of cobalt(III)[5]. Although dissociative mechanisms have been most commonly observed for aquation reactions, there has been some conjecture over the mechanisms involved. Both dissociative mechanisms, as in the case of aquation of halogen ion from *trans*-[Co(DMG)$_2$(halogen)L] (DMG = dimethylglyoximato and L = semicarbazide or thiosemicarbazide)[6], and associative mechanisms, as in the case of aquation of urea from *trans*-[Co(DMG)$_2$(urea)X] ($X^- = Cl^-$, Br^-, I^- or NO_2^-)[4,7], have been proposed. The latter mechanistic assignment is supported by the negative entropy of activation observed for each reaction. Since such associative mechanisms are unusual for d^6 cobalt(III) complexes, the complex chosen for study is of particular interest. Mechanisms which are primarily associative have been found for a wide range of reactions to exhibit negative $\Delta V^{\ddagger}$ values, while reactions which are dissociative in character usually exhibit positive $\Delta V^{\ddagger}$ values[1]. The observation here of a positive $\Delta V^{\ddagger}$ of $+3.5$ cm³mol⁻¹ for aquation of *trans*-[Co(DMG)$_2$(urea)Cl] implies a transition state of greater volume than its precursor state, or a mechanism which is primarily dissociative in nature.

Using standard bond lengths, bond angles and van der Waals radii for the molecular components, it is possible to obtain a schematic representation of the leaving ligand urea as a relatively flat "sandwich" presenting a face to the solvent of about 650 pm maximum width and of average thickness 260 pm. A view of the model for coordinated urea in the complex under study is shown in Fig. 2. The experimental $\Delta V^{\ddagger}$ can then be considered to arise as a result of stretching of the Co-urea(0) bond causing the complex to sweep out an additional volume defined as the cross-sectional area of the urea molecules (650×250 pm^2) multiplied by the distance of extension (Δl). A stretching of the Co-urea(0) bond by $\Delta l = 35$ pm in the transition state will then account fully for the experimental volume of activation since $650 \times 260 \times 35 \times 10^{-30}$ (cm^3) $\times$ L(mol^{-1}) $= + 3.5$ cm^{3}mol^{-1}. This is equivalent to stretching of the Co-urea(0) bond by only about 18% in the transition state, provided the volume swept out by the rest of the molecules remains unchanged and assuming that the neutral complex is relatively incompressible. This calculated bond extension is less than the amount of extension required for complete dissociation, defined as the sum of the van der Waals radii for Co and 0 of approximately 355 pm, and is therefore most consistent with a dissociative interchange description of the aquation mechanism.

Solvation of the non-electrolyte at specific sites of low or high charge density at the periphery of the molecule are presumably occurring in solution, but these effectively should produce much less solvent electrostriction than is the case of a formally charged complex ion. It seems unlikely that the limited bond extension calculated from the model is sufficient to allow close approach of water molecules to the leaving site, and hence the mechanism involved is primarily dissociative. This is consistent with the mechanistic description for most cobalt(III) complexes.

The negative activation entropy ($\Delta S^{\ddagger}$) of -108 J K^{-1}mol^{-1} reported previously[4] is not indicative of a dissociative mechanism. The apparent relationship between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ recently proposed by Twigg[8] for a range of aquation reaction does not hold in this case. Motion of solvent molecules into or away from the severely electrostricted layers about ionic complexes cause changes in both freedom and volume of the system and thus contribute to both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. For the neutral complex studied in this report, solvent molecules in the vicinity of the complex should be less severely electrostricted than is the case for ionic complexes. Hence solvent motion in the second or third coordination spheres can contribute to $\Delta S^{\ddagger}$ but not markedly to $\Delta V^{\ddagger}$ since the motion does not involve movement between regions of markedly different solvent volume or compressibility for neutral complexes. For the neutral complex reported here, $\Delta V^{\ddagger}$ reflects primarily the process of ligand dissociation or the process of mechanistic significance, while $\Delta S^{\ddagger}$ is complicated by contributions from changes in solvation in forming the transition state which do not contribute to $\Delta V^{\ddagger}$. This suggests that the volume of activation is a superior mechanistic indicator compared with the entropy of activation in these systems. An extended study of activation volumes for a range of non-electrolyte complexes will allow a more detailed analysis.

References

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บทคัดย่อ

เราได้หาค่าปริมาตรกระตุ้น (volume of activation) ของปฏิกริยาแทนที่ของยูเรียโดยน้ำในสารประกอบเชิงซ้อน *trans*-chlorobis (dimethylglyoximato) urea-cobalt(III) ในสารละลายน้ำ พบว่าปริมาตรกระตุ้นมีค่าเท่ากับ + 3.5 ± 0.3 cm³mol⁻¹ ซึ่งทำให้ทราบว่ากลไกของปฏิกริยาเกิดจากการยืดของโคบอลท์-ยูเรียบอนด์ในสภาวะ transition (dissociative interchange mechanism)