

## Kinetics of the Solvolysis of the *cis*-Dichlorobis(1,2-diaminoethane)cobalt(III) Ion in Water and in Water–*t*-Butyl Alcohol Mixtures

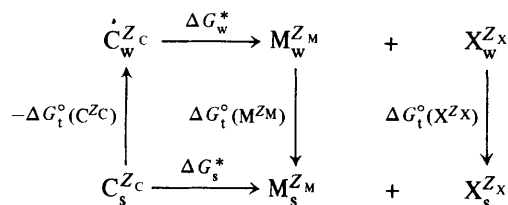
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The *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> cation is known to solvolyse with a transition state closely corresponding to the full dissociation of a Cl<sup>−</sup> ion leaving a pentacoordinated Co<sup>III</sup> cation. The kinetics of this solvolysis have been investigated in water with additions of *t*-butyl alcohol, which, as well as changing the dielectric constant of the mixtures, produces gradual changes in the solvent structure in a water-rich mixture. Curved plots of log(rate constant) *vs.* the reciprocal of the dielectric constant of the water–cosolvent mixtures suggest that changes in solvent structure have a differential effect on the initial and transition states for the solvolysis. The variations of both the enthalpy and the entropy of activation with solvent composition in water–*t*-butyl alcohol mixtures exhibit extrema which correlate well with the extrema in physical properties of the mixture influenced by changes in solvent structure. The application of a free-energy cycle to the loss of the Cl<sup>−</sup> ion for the solvolysis at 25 °C in the mixtures of water with a series of cosolvents shows that changes in solvent structure have a greater influence on the pentacoordinated Co<sup>III</sup> cation in the transition state than on the hexacoordinated Co<sup>III</sup> cation in the initial state.

It has long been accepted that the solvolysis in acidic conditions of many complexes of Co<sup>III</sup> ions, C<sup>Z<sub>c</sub></sup>, in aqueous mixtures proceeds by an I<sub>d</sub> mechanism with a long extension of the M<sup>Z<sub>M</sub></sup>...X<sup>Z<sub>X</sub></sup> bond in the transition state.<sup>1</sup> However, recent comparisons<sup>2</sup> of volume of activation Δ*V*<sup>\*</sup> with the overall volume change Δ*V*<sup>o</sup> for the solvolysis of complexes of the types [Co(NH<sub>3</sub>)<sub>5</sub>X]<sup>(3−Z<sub>X</sub>)<sup>2+</sup> and [CoN<sub>4</sub>X<sub>2</sub>]<sup>(3−2Z<sub>X</sub>)</sup> (where N<sub>4</sub> is a ligand or a set of ligands complexed to Co<sup>III</sup> through four nitrogen atoms) convincingly suggests<sup>3</sup> that for these complexes the extent of the dissociation M<sup>Z<sub>M</sub></sup>...X<sup>Z<sub>X</sub></sup> approximates very closely to 100% in the transition state. This view has been reinforced<sup>3</sup> by the conclusion<sup>4</sup> that the constancy of the ratio of stereochemical forms of the solvolytic products from complexes of the type [CoN<sub>4</sub>LX]<sup>Z<sub>c</sub></sup> with varying X<sup>Z<sub>X</sub></sup> over either *cis*- or *trans*-configurations in C<sup>Z<sub>c</sub></sup> indicates a common pentacoordinated Co<sup>III</sup> ion in the transition state for any particular ligand L. Such a full extension of the M<sup>Z<sub>M</sub></sup>...X<sup>Z<sub>X</sub></sup> bond in a dielectric continuum would require<sup>5</sup> a linear plot of log *k vs.* *D*<sup>−1</sup> for the solvolysis<sup>6–9</sup> (where *k* is the rate constant and *D* is the dielectric constant). This is rarely found<sup>5, 10–12</sup> and, even when observed for mixtures of water with some cosolvents,<sup>5</sup> it is transgressed<sup>3, 13</sup> by cosolvents such as propan-2-ol and *t*-butyl alcohol which, at low mole fractions, cause<sup>14</sup> considerable changes to the solvent structure of water. This non-linearity suggests<sup>5</sup> that there is an imbalance between the structural components of the free energy of transfer of C<sup>Z<sub>c</sub></sup> and of M<sup>Z<sub>M</sub></sup> + X<sup>Z<sub>X</sub></sup>.</sup>

The full dissociation of complexes C<sup>Z<sub>c</sub></sup> into M<sup>Z<sub>M</sub></sup> and X<sup>Z<sub>X</sub></sup> in the transition state allows the application of a free-energy cycle<sup>5</sup> to the process initial state → transition state occurring in water (w) and in the mixture (s):



where  $\Delta G_t^{\circ}(i)$  is now the complete free energy of transfer of species  $i$  between  $w$  and  $s$ , covering the Born–Kirkwood effects and all other effects such as changes in solvent structure. Summing the free energies around the cycle and converting the free energies of activation into rate constants, eqn (1) applies:<sup>5</sup>

$$RT \ln \frac{k_w}{k_s} - \Delta G_t^{\circ}(X^{Z_X}) = \Delta G_t^{\circ}(M^{Z_M}) - \Delta G_t^{\circ}(C^{Z_c}). \quad (1)$$

For  $X^{Z_X} = Cl^-$  with  $Co^{III}$  complexes, it has been concluded that for a wide range of this type of complex for a range of co-solvents changes in solvent structure always have a greater influence on the pentacoordinated cation in the transition state than on the hexacoordinated cation  $C^{Z_c}$  in the initial state.<sup>3, 5, 10–13</sup> Extrema in the enthalpies and entropies of activation for these solvolyses with a range of cosolvents which modify the structure of water are found<sup>3, 5, 10–13</sup> to coincide with extrema in physical properties of the mixtures,<sup>14</sup> which are largely controlled by changes in solvent structure.

Rate constants are available at one temperature only for the solvolysis of  $cis-[Coen_2Cl_2]^+$  in water with added methanol,<sup>15, 16</sup> ethanol,<sup>15, 16</sup> acetone,<sup>15</sup> dioxan,<sup>15</sup> ethanonitrile,<sup>17</sup> ethylene carbonate<sup>18</sup> and propylene carbonate<sup>18</sup> and at a range of temperatures for methanol,<sup>19</sup> acetone,<sup>19</sup> dioxan,<sup>19</sup> sucrose<sup>20</sup> and ethylene glycol.<sup>20</sup> Plots of  $\log k_s$  vs.  $D_s^{-1}$  are curved in all cases,<sup>21</sup> suggesting<sup>5</sup> differential solvent structural effects for the initial and transition states. Values for transition-state parameters available are not extensive enough to compare with the variation in the physical properties of the mixtures for the solvolysis of this complex. To investigate this effect of solvent structure, we now report our kinetic investigation over a range of temperatures of the solvolysis of  $cis-[Coen_2Cl_2]^+$  in a range of mixtures of water and *t*-butyl alcohol, where the latter modifies the water structure at low mole fractions to a greater extent<sup>14</sup> than achieved with the cosolvents previously used with this complex.

## Experimental

Samples of  $cis-[Coen_2Cl_2]Cl$  were prepared by conversion from  $trans-[Coen_2Cl_2]Cl$  prepared as described previously<sup>12</sup> using the method<sup>22</sup> of Bailar for performing the  $trans \rightarrow cis$  conversion. This involves evaporation to dryness on a steam bath of a neutral aqueous solution of the  $trans$  complex and leaves the purple  $cis$  product contaminated with the green  $trans$  complex. To produce a pure sample of the  $cis$  complex, the evaporation was halted before dryness was attained and the syrupy mixture was then dried in a vacuum desiccator. The green  $trans$  complex remained in the surface layer which was first removed by washing in ice-cold water before the bulk product was washed with ice-cold water and dried. The  $cis$  complex exhibited spectral maxima at 225 and 533 nm with a shoulder at 398 nm. During the solvolysis the absorption at both peaks decreased, giving isosbestic points at 438 and 505 nm. Four methods were used to monitor the purity of the samples of the  $cis$  complex used. First, microanalysis showed 15.75% C, 5.67% H, 18.6% N and 36.0% Cl (theoretical: 15.82% C, 5.93% H, 18.46% N and 35.1% Cl). Secondly, only samples which showed sharp isosbestic points at 438 and 505 nm were used. Thirdly, only samples which provided linear plots of  $\log[(\text{absorbance})_t - (\text{absorbance})_{\infty}]$  vs. time over ten half-lives were used. Fourthly, the distinc-

**Table 1.** Values for the first-order rate constant  $k$  at 35 °C for the solvolysis of  $cis$ -[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in varying conditions

| initial<br>concentration of<br>$cis$ -[Coen <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup><br>/mol dm <sup>-3</sup> | addition<br>to reaction<br>mixture           | $k/10^{-4} \text{ s}^{-1}$ |
|--|--|----------------------------|
| 0.010  | —  | 7.9                        |
| 0.010  | —  | 8.3                        |
| 0.010  | —  | 9.6                        |
| 0.010  | 0.005 mol dm <sup>-3</sup> HClO <sub>4</sub> | 8.8                        |
| 0.010  | 0.005 mol dm <sup>-3</sup> HClO <sub>4</sub> | 8.8                        |
| 0.010  | 0.020 mol dm <sup>-3</sup> HClO <sub>4</sub> | 8.5                        |
| 0.010  | 0.020 mol dm <sup>-3</sup> HClO <sub>4</sub> | 9.1                        |
| 0.010  | 0.0045 mol dm <sup>-3</sup> NaCl             | 8.6                        |
| 0.005  | 1.97 wt% Bu <sup>t</sup> OH                  | 7.4                        |
| 0.010  | 1.97 wt% Bu <sup>t</sup> OH                  | 7.4                        |
| 0.012  | 1.97 wt% Bu <sup>t</sup> OH                  | 7.5                        |

tive differences in the i.r. spectra of the *trans* and *cis* complexes were used.<sup>23</sup> Other materials were as described previously<sup>12</sup> and the spectrophotometers were the same as used in the earlier work on the solvolysis of the *trans* complex.<sup>12</sup>

## Results and Discussion

### Preliminary Observations

The form of the spectrum of  $cis$ -[Coen<sub>2</sub>Cl<sub>2</sub>]Cl in water was found to remain unchanged by the addition of *t*-butyl alcohol as cosolvent. Good linear plots of  $\log[(\text{absorbance})_t - (\text{absorbance})_\infty]$  *vs.* time *t* were always obtained with the samples of the *cis* complex used for the decrease in absorbance at 533 nm. An initial concentration of the *cis* complex of 0.01 mol dm<sup>-3</sup> was used, but table 1 shows that variations in this initial concentration have no effect on the value of the rate constant determined from the slopes of the plots. Table 1 also shows that the addition of HClO<sub>4</sub> or NaCl to the solution had no effect on the rate constant. However, the observation in table 1 that the first-order rate constant is more reproducible in acidic solutions in water than in neutral solutions proved to be general, so 0.02 mol dm<sup>-3</sup> HClO<sub>4</sub> was added to all solvolysing mixtures with or without *t*-butyl alcohol being added.

### Kinetics of Solvolysis in Water

Linear plots were obtained for plots of  $\log[(\text{absorbance})_t - (\text{absorbance})_\infty]$  *vs.* time for a range of temperatures and the values of the rate constants obtained from the slopes are given in table 2. Good agreement is obtained between repeated values for  $k$  at each temperature. A linear plot is obtained for  $\log k$  *vs.* the reciprocal of the absolute temperature. Values for the enthalpy, entropy and free energy of activation together with their standard deviations were obtained using all the individual values of  $k$  in the least-squares procedure with the aid of a computer.

The average values of  $k$  together with these values for  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are compared in table 3 with values obtained previously by other workers. The standard deviations in  $\Delta G^*$  at 25 °C in table 3 are dependent on the errors found for  $\Delta H^*$  over the whole temperature range and on those for  $\Delta S^*$  at 25 °C. Our values for  $k$  at 25 °C

**Table 2.** Individual values of the first-order rate constant  $k$  ( $10^{-4} \text{ s}^{-1}$ ) for the solvolysis of  $\text{cis}[\text{Coen}_2\text{Cl}_2]^+$  in  $0.02 \text{ mol dm}^{-3} \text{ HClO}_4$  with varying solvent composition and temperature

| [t-butyl alcohol] |               | $T/^{\circ}\text{C}$ |      |      |      |      |      |
|-------------------|---------------|----------------------|------|------|------|------|------|
| wt%               | mole fraction | 25.0                 | 30.0 | 35.0 | 45.0 | 50.0 | 60.0 |
| 1.97              | 0.0049        | 1.94                 | 3.76 | 7.4  | 27.3 | —    | —    |
| 1.97              | 0.0049        | 2.05                 | 4.51 | 7.4  | 27.6 | —    | —    |
| 1.97              | 0.0049        | —                    | —    | 7.5  | —    | —    | —    |
| 3.95              | 0.0099        | 1.82                 | 4.00 | 7.8  | 24.7 | —    | —    |
| 3.95              | 0.0099        | 1.86                 | 4.23 | 7.8  | 27.9 | —    | —    |
| 3.95              | 0.0099        | —                    | —    | 8.3  | —    | —    | —    |
| 3.95              | 0.0099        | —                    | —    | 8.7  | —    | —    | —    |
| 7.99              | 0.0207        | 1.68                 | 3.31 | 5.7  | 21.5 | —    | —    |
| 7.99              | 0.0207        | 1.72                 | 3.93 | 5.8  | 23.4 | —    | —    |
| 7.99              | 0.0207        | —                    | —    | 5.9  | —    | —    | —    |
| 12.13             | 0.0325        | 1.51                 | 3.37 | 5.2  | 20.8 | —    | —    |
| 12.13             | 0.0325        | 1.54                 | 3.62 | 5.8  | 21.2 | —    | —    |
| 12.13             | 0.0325        | —                    | —    | 6.2  | —    | —    | —    |
| 12.13             | 0.0325        | —                    | —    | 6.4  | —    | —    | —    |
| 12.13             | 0.0325        | —                    | —    | 6.7  | —    | —    | —    |
| 16.35             | 0.0454        | 1.56                 | 3.03 | 5.9  | 19.5 | —    | —    |
| 16.35             | 0.0454        | 1.74                 | 3.25 | 6.0  | 19.5 | —    | —    |
| 20.68             | 0.0596        | 1.14                 | 2.95 | 5.5  | 16.9 | 29.5 | —    |
| 20.68             | 0.0596        | 1.25                 | 3.30 | 5.5  | 17.7 | —    | —    |
| 25.10             | 0.0753        | 1.24                 | 2.55 | 4.57 | 13.9 | 22.6 | —    |
| 25.10             | 0.0753        | 1.29                 | 2.76 | 4.97 | 14.0 | 23.4 | —    |
| 25.10             | 0.0753        | 1.51                 | —    | —    | —    | —    | —    |
| 34.22             | 0.113         | 1.19                 | 2.44 | 4.07 | 12.2 | 20.6 | —    |
| 34.22             | 0.113         | 1.28                 | 2.46 | 4.45 | 12.4 | 21.0 | —    |
| 34.22             | 0.113         | 1.32                 | —    | —    | —    | —    | —    |
| 39.01             | 0.135         | 1.35                 | 2.29 | 3.96 | 11.2 | 19.2 | —    |
| 39.01             | 0.135         | 1.41                 | 2.36 | 4.13 | 11.3 | 18.6 | —    |
| 43.88             | 0.160         | 1.23                 | 2.11 | 2.58 | 8.6  | 14.1 | 25.9 |
| 43.88             | 0.160         | 1.30                 | 2.24 | 3.46 | 8.8  | 14.3 | —    |

**Table 3.** Comparison of values for  $k$  ( $10^{-4} \text{ s}^{-1}$ ) and for the transition-state parameters from various sources for the solvolysis of  $\text{cis}[\text{Coen}_2\text{Cl}_2]^+$  in water

| $T/^{\circ}\text{C}$                          | values of $k$ and their origin |                                      |                       |                                     |                                     |                     |
|---|--------------------------------|--------------------------------------|-----------------------|-------------------------------------|-------------------------------------|---------------------|
|   | this work                      | Panasyuk <i>et al.</i> <sup>16</sup> | Mathieu <sup>24</sup> | Pearson <i>et al.</i> <sup>25</sup> | Baldwin <i>et al.</i> <sup>26</sup> | Brull <sup>27</sup> |
| 18.0  | —                              | —                                    | —                     | —                                   | —                                   | 0.73                |
| 20.0  | —                              | 1.30                                 | —                     | —                                   | —                                   | —                   |
| 25.0  | 2.50                           | 2.35                                 | 1.20                  | 2.50                                | 2.44                                | —                   |
| 30.0  | 4.83                           | 4.82                                 | 2.15                  | —                                   | —                                   | —                   |
| 35.0  | 9.0                            | 10.8                                 | 3.99                  | —                                   | —                                   | —                   |
| 40.0  | —                              | 26.8                                 | 6.9                   | —                                   | —                                   | —                   |
| 45.0  | 30.3                           | —                                    | 11.7                  | —                                   | —                                   | —                   |
| 50.0  | —                              | —                                    | 22.0                  | —                                   | —                                   | —                   |
| $\Delta H^*/\text{kJ mol}^{-1}$               | $95 \pm 2$                     | $113 \pm 7$                          | $89 \pm 2$            | —                                   | —                                   | —                   |
| $\Delta S^*/\text{J K}^{-1} \text{ mol}^{-1}$ | $4 \pm 4$                      | $65 \pm 22$                          | $20 \pm 5$            | —                                   | —                                   | —                   |
| $\Delta G^*/\text{kJ mol}^{-1}$               | $94 \pm 2$                     | $94 \pm 13$                          | $95 \pm 3$            | —                                   | —                                   | —                   |

**Table 4.** Values for the enthalpy, entropy and free energy of activation for the solvolysis of *cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in water–*t*-butyl alcohol mixtures

| t-butyl alcohol |               | $\Delta H^*$<br>/kJ mol <sup>-1</sup> | $\Delta S^*$ at 25 °C<br>/J K <sup>-1</sup> mol <sup>-1</sup> | $\Delta G^*$ at 25 °C<br>/kJ mol <sup>-1</sup> |
|-----------------|---------------|---------------------------------------|---|--|
| wt %            | mole fraction |                                       |   |  |
| —               | —             | 95 ± 3                                | 4 ± 4   | 94 ± 2   |
| 1.97            | 0.0049        | 100 ± 3                               | 19 ± 9  | 94 ± 6   |
| 3.95            | 0.0099        | 102 ± 4                               | 26 ± 13   | 94 ± 8   |
| 7.99            | 0.0207        | 98 ± 5                                | 10 ± 16   | 95 ± 10  |
| 12.13           | 0.0325        | 99 ± 4                                | 15 ± 14   | 95 ± 8   |
| 16.35           | 0.0454        | 95 ± 2                                | 1 ± 7   | 95 ± 4   |
| 20.68           | 0.0596        | 98 ± 5                                | 10 ± 15   | 95 ± 9   |
| 25.10           | 0.0753        | 89 ± 3                                | –21 ± 8   | 95 ± 5   |
| 34.22           | 0.113         | 87 ± 2                                | –28 ± 4   | 95 ± 3   |
| 39.01           | 0.135         | 81 ± 2                                | –46 ± 5   | 95 ± 3   |
| 43.88           | 0.160         | 74 ± 4                                | –72 ± 13  | 95 ± 8   |

agree well with those of Panasyuk *et al.*,<sup>16</sup> Pearson *et al.*<sup>24</sup> and Baldwin *et al.*,<sup>25</sup> which all differ from the value of Mathieu.<sup>26</sup> Our value for  $\Delta H^*$  agrees better with that obtained from Mathieu's results<sup>24</sup> than with that obtained from the results of Panasyuk *et al.*<sup>16</sup> However, we find that the plot of  $\log k$  *vs.*  $T^{-1}$  is curved using the data of Panasyuk *et al.*<sup>16</sup> and linear using the data of Mathieu.<sup>24</sup> The value for  $k$  at 18 °C of Brull<sup>27</sup> fits well on the linear plot of  $\log k$  *vs.*  $T^{-1}$  using our data in the temperature range 25–45 °C.

### Kinetics of the Solvolysis in Water–*t*-Butyl Alcohol Mixtures

Linear plots of  $\log[(\text{absorbance})_t - (\text{absorbance})_\infty]$  against time  $t$  were obtained in water–*t*-butyl alcohol mixtures ranging from 1.97 to 43.88 wt% *t*-butyl alcohol covering 25, 30, 35 and 45 °C up to 43.88 wt% *t*-butyl alcohol with additional results at 50 °C in the range 16.35 to 43.88 wt% *t*-butyl alcohol and one additional result at 60 °C for 43.88 wt% *t*-butyl alcohol. The values of  $k$  obtained from the slopes are given in table 2. Linear plots were obtained for  $\log k$  *vs.*  $T^{-1}$  for each mixture. Values for the enthalpy, entropy and free energy of activation were obtained with their standard deviations by the application of the least-squares procedure to all the individual values of  $k$  at each concentration of *t*-butyl alcohol in table 2. These values for  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are given in table 4, which also includes our values in water. As before, the standard deviations in  $\Delta G^*$  at 25 °C are dependent on the standard errors in  $\Delta H^*$  and  $\Delta S^*$  found from all the data at that composition.

### Influence of Solvent Structure on the Solvolysis

A plot of  $\log k$  *vs.*  $D_s^{-1}$  at 25 °C is a curve, suggesting<sup>5</sup> for water–*t*-butyl alcohol mixtures that differential changes in  $\Delta G_t^\circ(C^Z_C)$  for the initial state and in  $\Delta G_t^\circ(M^Z_M) + \Delta G_t^\circ(X^Z_X)$  for the transition state exist with varying composition of the water–*t*-butyl alcohol mixtures. Values for  $D_s$  at 25 °C were interpolated from the data<sup>28</sup> of Broadway and Kay and of Brown and Ives. Similarly, a plot of  $\log k$  at 25 °C *vs.* the values<sup>12</sup> for the Grunwald–Winstein  $Y$  factor is curved.

A range of physical properties of water–*t*-butyl alcohol mixtures show that structure in the solvent is enhanced when *t*-butyl alcohol is added to water at low mole fractions  $x_2$  of the former. Positive values are found<sup>29</sup> for the structural contribution to the temperature of maximum density,  $\Delta T^{\text{st}}$ , deep sharp minimum of the relative partial

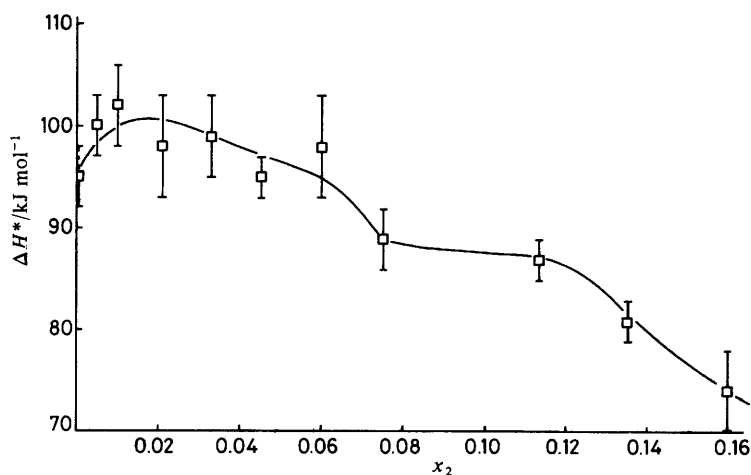


Fig. 1. Plot of the enthalpy of activation for the solvolysis of *cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in water–t-butyl alcohol mixtures vs. mole fraction of t-butyl alcohol.

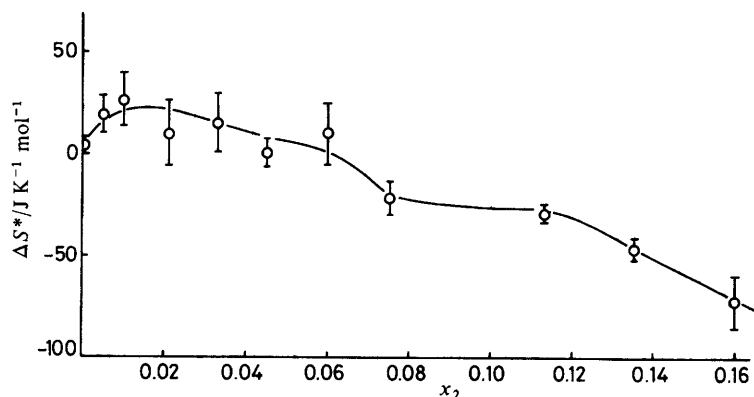
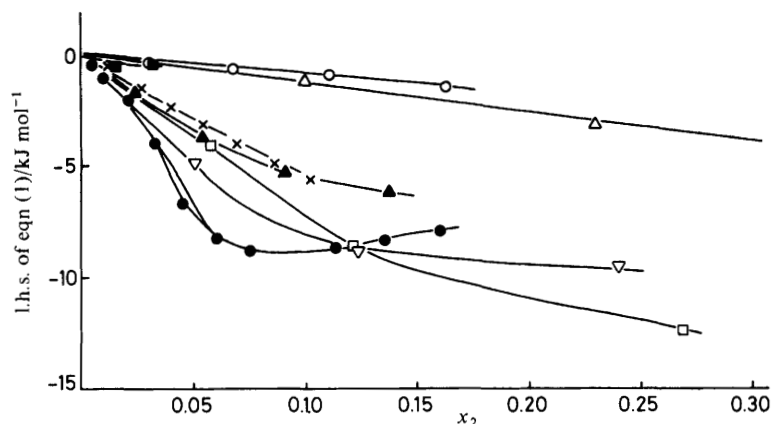


Fig. 2. Plot of the entropy of activation at 25 °C for the solvolysis of *cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in water–t-butyl alcohol mixtures vs. mole fraction of t-butyl alcohol.

molar volume of t-butyl alcohol,  $\bar{V}_2 - V_2^\circ$ , is found in the mixtures at  $x_2 \approx 0.025$ ,<sup>30, 31</sup> a minimum in the excess enthalpy of mixing,  $\Delta H^E$ , at  $x_2 \approx 0.25$ ,<sup>31</sup> maximum in the viscosity  $\eta$  of the mixtures at  $x_2 \approx 0.3$ ,<sup>31</sup> and a sharp, high maximum in the ultrasonic absorption at  $x_2 \approx 0.1$ .<sup>32</sup> Fig. 1 and 2 show plots of  $\Delta H^*$  and  $\Delta S^*$  vs. solvent composition and these are similar to the variations of  $\Delta H^*$  and  $\Delta S^*$  for the solvolysis of *trans*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in water–t-butyl alcohol mixtures. Both show a maximum in  $\Delta H^*$  and  $\Delta S^*$  in the region  $x_2 \approx 0.02$ – $0.03$  and a plateau in the region of  $x_2 \approx 0.10$ . The first of these extrema corresponds to the minimum in  $\bar{V}_2 - V_2^\circ$  which is associated<sup>33</sup> with the situation where the branched alkyl chains excluded from the ‘flickering icebergs’ of structured water<sup>34</sup> exert maximum structure formation within the latter. The second extremum corresponds with the maximum in the ultrasonic absorption, which has been ascribed<sup>33</sup> to the onset of the breakdown of the ‘iceberg-like’ structures of water. A plot of  $\Delta H^*$  vs.  $\Delta S^*$  is linear.

The differential effect of the changes in solvent structure with varying solvent composition between the initial and the transition states can be further explored by applying the free-energy cycle discussed earlier using eqn (1). Values for  $k_w$  and  $k_s$  at 25 °C are available in table 2 and the values for  $\Delta G_i^\circ(\text{Cl}^-)$  can be interpolated from the





**Fig. 3.** Plot of the left-hand side of eqn (1) at 25 °C vs. mole fraction of cosolvent for the solvolysis of  $\text{cis}[\text{Coen}_2\text{Cl}_2]^+$  in mixtures of water with the following cosolvents: t-butyl alcohol (●), acetone (□), methanol (△), dioxan (▽), ethylene glycol (○), ethanoneitrile (×), ethylene carbonate (▲) and propylene carbonate (■).

published data.<sup>35</sup> The left-hand side of eqn (1) plotted against the mole fraction of t-butyl alcohol in fig. 3 is found to be negative for water–t-butyl alcohol mixtures. As  $\Delta G_t^\circ(i)$  for  $i = \text{a cation}$  are negative<sup>35</sup> in water–t-butyl alcohol mixtures at low  $x_2$ , and, indeed,  $\Delta G_t^\circ(i)$  for  $i = \text{a cation}$  are generally negative<sup>36</sup> for mixtures of water with a cosolvent at low mole fractions of cosolvent, it is concluded that  $-\Delta G_t^\circ(\text{Coen}_2\text{Cl}^{2+}) > -\Delta G_t^\circ(\text{Coen}_2\text{Cl}^+)$ ; the effect of changes of solvent structure on the pentacoordinated  $\text{Co}^{\text{III}}$  cation in the transition state dominate that on the hexacoordinated  $\text{Co}^{\text{III}}$  cation in the initial state. This resembles the situation found in the solvolysis of a range of  $\text{Co}^{\text{III}}$  complexes in mixtures of water with a range of cosolvents.<sup>3, 5, 10–13</sup> This corresponds well with the usual finding<sup>35, 36</sup> for  $\Delta G_t^\circ(i)$  for cations of similar size: viz.  $-\Delta G_t^\circ(\text{M}^{2+}) > -\Delta G_t^\circ(\text{M}^+)$ . Also plotted against solvent composition in fig. 3 are the values of the left-hand side of eqn (1) for the solvolysis of  $\text{cis}[\text{Coen}_2\text{Cl}_2]^+$  at 25 °C in mixtures of water with a range of cosolvents, calculated using the values of  $k_s$  available in the literature<sup>16, 18–20</sup> and the known values for  $\Delta G_t^\circ(\text{Cl}^-)$  in these mixtures.<sup>36</sup> Although the extent of the difference between  $\Delta G_t^\circ(\text{Coen}_2\text{Cl}^{2+})$  and  $\Delta G_t^\circ(\text{Coen}_2\text{Cl}_2^+)$  varies with the identity of the cosolvent,  $-\Delta G_t^\circ(\text{Coen}_2\text{Cl}^{2+})$  is always greater than  $-\Delta G_t^\circ(\text{Coen}_2\text{Cl}_2^+)$ , i.e. the effect of changes in the solvent structure dominates the cation in the transition state over the cation in the initial state, as found generally for the  $\text{Co}^{\text{III}}$  complexes of this type.<sup>3, 5, 10–13</sup>

## References

- 1 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (Wiley, New York, 2nd edn, 1967), chap. 3.
- 2 W. E. Jones, L. R. Carey and J. W. Swaddle, *Can. J. Chem.*, 1972, **56**, 2739; G. A. Lawrance, *Inorg. Chim. Acta*, 1980, **45**, L275; G. A. Lawrance and S. Suvachittanont, *Aust. J. Chem.*, 1980, **33**, 277; D. A. Palmer and H. Kelm, *Inorg. Chem.*, 1977, **16**, 3139; *Coord. Chem. Rev.*, 1981, **36**, 89; G. Daffner, D. A. Palmer and A. Kelm, *Inorg. Chim. Acta*, 1982, **61**, 57.
- 3 A. E. Eid and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1401.
- 4 W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 1348; W. G. Jackson and C. M. Begbie, *Inorg. Chim. Acta*, 1982, **69**, 115.
- 5 C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1851.
- 6 K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, 1956, **52**, 200; K. J. Laidler, *Suomen Kemistil. A*, 1960, **33**, 44; *Chemical Kinetics* (McGraw-Hill, New York, 2nd edn, 1965), chap. 5.

- 7 E. A. Moelwyn-Hughes, *Proc. R. Soc. London, Ser. A*, 1936, **155**, 308; 1936, **157**, 667; *The Kinetics of Reactions in Solution* (Oxford University Press, London, 2nd edn, 1947), chap. 4, 5 and 7; *Physical Chemistry* (Pergamon Press, Oxford, 2nd edn, 1961), chap. 7–9 and 24.
- 8 E. S. Amis, *Kinetics of Chemical Change in Solution* (Macmillan, New York, 1949), chap. 5 and 9; *Solvent Effects on Reaction Rates and Mechanisms* (Academic Press, New York, 1966), chap. 1–3.
- 9 K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, 1940, **39**, 303; S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941), chap. 8.
- 10 C. N. Elgy and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1980, 2405; 1982, 1617; *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2367; 1985, **81**, 2145.
- 11 I. M. Sidahmed and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1983, 1035; 1984, 1969.
- 12 G. S. Groves and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 619; 1985, **81**, 2475; *Trans. Metal Chem.*, 1986, **11**, 20; *Int. J. Chem. Kinet.*, 1986, **18**, 529.
- 13 A. E. Eid and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1621; 1983, **79**, 253; 1986, **82**, 1643; *Trans. Metal Chem.*, 1985, **10**, 223; *Int. J. Chem. Kinet.*, 1986, **18**, 215.
- 14 F. Franks and D. J. G. Ives, *Q. Rev. Chem. Soc.*, 1966, **20**, 1.
- 15 J. Burgess, *J. Chem. Soc. A*, 1970, 2703.
- 16 V. D. Panasyuk, V. P. Solomko and L. G. Reiter, *Russ. J. Inorg. Chem.*, 1961, **6**, 1035.
- 17 J. Burgess, *J. Chem. Soc. A*, 1970, 2351.
- 18 M. J. Blandamer, J. Burgess, S. J. Hamshire, F. M. Mekhail, *Trans. Metal Chem.*, 1979, **4**, 77.
- 19 V. D. Panasyuk and E. R. Falendysh, *Dopov. Akad. Nauk Ukr. RSR*, 1964, **26**, 741.
- 20 V. D. Panasyuk and A. V. Arkharov, *Ukr. Khim. Zh.*, 1967, **32**, 716.
- 21 G. S. Groves, *Ph.D. Thesis* (Univ. of Birmingham, 1983).
- 22 J. C. Bailar Jr, *Inorg. Synth.*, 1946, **2**, 222.
- 23 R. W. Hay and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 556; M. E. Baldwin, *J. Chem. Soc.*, 1960, 4369; M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 1521.
- 24 R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, 1955, **59**, 304.
- 25 M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637.
- 26 J. P. Mathieu, *Bull. Soc. Chim. Fr.*, 1936, **3**, 2152.
- 27 J. Brull, *C.R. Seances Acad. Sci.*, 1936, **202**, 1584.
- 28 T. L. Broadway and R. L. Kay, *J. Phys. Chem.*, 1970, **70**, 3802; A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1962, 1608.
- 29 G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn*, 1962, **35**, 646.
- 30 K. Nakanishi, *Bull. Chem. Soc. Jpn*, 1960, **33**, 793.
- 31 J. Kenttämää, E. Tommila and M. Martti, *Ann. Acad. Sci. Fenn.*, 1959, 93.
- 32 M. J. Blandamer, *Introduction to Chemical Ultrasonics* (Academic Press, London, 1973), chap. 11.
- 33 C. F. Wells, *Trans. Faraday Soc.*, 1970, **66**, 204; *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 694.
- 34 H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507; H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133; G. Nemethy and H. A. Sheraga, *J. Chem. Phys.*, 1962, **36**, 3382, 3401; G. Nemethy, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 195; W. Laiden and G. Nemethy, *J. Phys. Chem.*, 1970, **74**, 3501.
- 35 C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 601; *Aust. J. Chem.*, 1983, **36**, 1739.
- 36 C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 984; 1974, **70**, 694; 1975, **71**, 1868; 1978, **81**, 1569; 1981, **77**, 1515; 1984, **80**, 2445; *Adv. Chem. Ser.*, 1979, **177**, 53; *Thermochim. Acta*, 1982, **53**, 67; G. S. Groves and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1985, 3091; I. M. Sidahmed and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2577; G. S. Groves and K. H. Halawani, I. M. Sidahmed and C. F. Wells, unpublished results.