# Solvent Effects on the Kinetics of Oxidation of Cysteinatobis(ethylenediamine)cobalt(III) Ion by Peroxodisulphate

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The kinetics of oxidation of cysteinatobis(ethylenediamine)cobalt(III) ion, [Co(CysOS)(en)$_2$]$^+$, by peroxodisulphate were investigated at different ionic strengths, adjusted with various electrolytes, and at different temperatures and concentrations of perchloric acid. Rate constants and activation parameters are also reported for this oxidation in mixtures containing up to 40% acetone, t-butyl alcohol, isopropyl alcohol, or acetonitrile. The solubilities of [Co(CysOS)(en)$_2$]ClO$_4$ and KClO$_4$ have been determined in water and aqueous acetone and aqueous t-butyl alcohol at 298.2 K. From these values, Gibbs free energies of transfer for [Co(CysOS)(en)$_2$]$^+$ and $S_2O_8{}^{2-}$ have been estimated. The solvent effects on the oxidation have been divided into their initial-state and transition-state components.

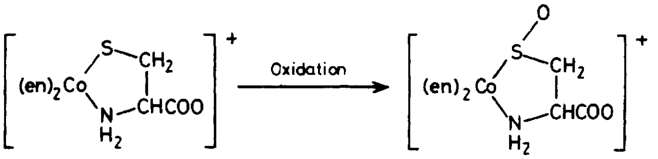
Previous studies [1,2] have dealt with the oxidation of cysteine in cysteinatobis(ethylenediamine)cobalt(III) by hydrogen peroxide. In the first step of the oxidation cysteinesulphenatobis(ethylenediamine)cobalt(III) ion is produced, and the product of the second step is cysteinesulphinatobis(ethylenediamine)cobalt(III) ion. In contrast, no formation of the corresponding cysteinesulphenate was observed during the oxidation of unco-ordinated cysteine.[3]

In studies of the effect of the medium on the oxidation of iron complexes with peroxodisulphate it was found [4,5] that changes in the solvation of the outer co-ordination spheres of the reactants as well as of the activated complex had a significant influence on the rate and activation parameters of the reactions. Similar effects would be expected on the kinetics of oxidation of cysteinatobis(ethylenediamine)-cobalt(III) ion with peroxodisulphate. The aim of this study was to elucidate the effects of a non-aqueous solvent component on the change in chemical potentials of the initial and transition states.

## Experimental

Cysteinatobis(ethylenediamine)cobalt(III) perchlorate was prepared by the literature method [2] (Found: C, 21.0; H, 5.35; N, 17.6%. Calc. for $C_7H_{21}ClCoN_5O_6S$: C, 21.15; H, 5.30; N, 17.6%). All chemicals were of p.a. grade; redistilled water was used for the preparation of solutions. Stock solutions were discarded after 5 h.

The kinetic measurements were carried out using a Specol 10 (Carl Zeiss Jena) spectrophotometer linked to a K 200 recorder (Carl Zeiss Jena). Cells of path length 2 cm were used and the temperature was kept to within $\pm 0.1$ K using a U 15 C thermostat. For the study of the oxidation of [Co(CysOS)(en)$_2$]ClO$_4$ (CysOS = cysteinate, en = ethylenediamine) with peroxodisulphate the reaction mixtures were prepared from separate solutions of the complex and peroxodisulphate to which HClO$_4$ and NaClO$_4$ had been added in order to adjust the pH and the ionic strength. The non-aqueous solvent was present in the same ratio in both the solutions so that no change in the temperature of the reaction mixture would occur during mixing. Peroxodisulphate was present in a nine-fold excess over the complex. The course of the reaction was followed for three half-lives by measuring the absorbance at 371 nm, the wavelength of maximum absorption of the product, *i.e.* cysteinesulphenatobis(ethylenediamine)cobalt(III) ion ($\varepsilon_{max.} = 591$ m$^2$ mol$^{-1}$). The rate constants were evaluated by Guggenheim's method, the values quoted being the averages from eight different runs.



Scheme 1.

From the dependence of the rate constants on temperature within the interval 6.8—24.8 °C the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated; the error in these parameters was calculated by a procedure described previously.[6]

The solubilities of [Co(CysOS)(en)$_2$]ClO$_4$ and KClO$_4$ in aqueous solution as well as in water–acetone and water–t-butyl alcohol mixtures were determined at 298.2 K, as was the solubility of $K_2S_2O_8$ in water and in water–t-butyl alcohol mixtures. After attainment of equilibrium between the solid phase and its solution, the concentration of $K_2S_2O_8$ was determined using iodometry, KClO$_4$ using gravimetry, and [Co(CysOS)(en)$_2$]ClO$_4$ at 483 nm using a Specord UV-VIS spectrophotometer (Carl Zeiss Jena) (the absorption coefficient, $\varepsilon = 12.6$ m$^2$ mol$^{-1}$, was not influenced by the addition of non-aqueous solvent).

## Results and Discussion

The oxidation of [Co(CysOS)(en)$_2$]ClO$_4$ with peroxodisulphate follows an analogous course to that of the oxidation with hydrogen peroxide [2] (Scheme 1).

On the basis of the obtained experimental data it is possible to derive the rate equation (1) for the present reaction, where

$$d[\mathrm{Co(CysOS)(en)_2}^+]/dt = k[\mathrm{S_2O_8}^{2-}][\mathrm{Co(CysOS)(en)_2}^+] \quad (1)$$

$[S_2O_8{}^{2-}]$ and [Co(CysOS)(en)$_2{}^+$] are the total concentrations of peroxodisulphate and complex. Because of the excess of peroxodisulphate, the observed rate constant, $k_{obs.}$, is $k[S_2O_8{}^{2-}]$. The subsequent oxidation of cysteinesulphenatobis(ethylenediamine)cobalt(III) is about 100 times slower and does not influence measurements of the first step. The rate constant $k_{obs.}$ was determined over the range $(0.8—8) \times 10^{-3}$ mol dm$^{-3}$ peroxodisulphate.

The effect of the ionic strength on the rate of oxidation of cysteinatobis(ethylenediamine)cobalt(III) ion was studied at 292.9 K within the range $I = 0.013—1.013$ mol dm$^{-3}$ (NaClO$_4$

**Table 1.** Dependence of the rate constant for oxidation of cysteinatobis(ethylenediamine)cobalt(III) by peroxodisulphate on ionic strength adjusted with various electrolytes; $[Co(CysOS)(en)_2{}^+] = 1.1 \times 10^{-4}$, $[Na_2S_2O_8] = 10^{-3}$, $[HClO_4] = 10^{-2}$, and $[HBr] = 10^{-2}$ mol dm$^{-3}$ (with $NBu_4Br$), 292.9 K

| $I$/ mol dm$^{-3}$ | $k$/dm$^3$ mol$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|
| | $NaClO_4$ | NaCl | $NBu_4Br$ |
| 0.013 | 54.7 ± 0.88 | 54.7 ± 0.90 | 54.7 ± 0.90 |
| 0.053 | 34.7 ± 0.03 | 31.1 ± 0.04 | 23.5 ± 0.59 |
| 0.093 | 27.5 ± 0.16 | 24.5 ± 0.09 | 16.5 ± 0.28 |
| 0.173 | 20.8 ± 0.13 | 18.4 ± 0.03 | 10.1 ± 0.22 |
| 0.253 | 15.7 ± 0.13 | 14.6 ± 0.47 | 7.6 ± 0.24 |
| 0.413 | 13.1 ± 0.10 | 12.6 ± 0.24 | 4.6 ± 0.07 |
| 0.513 | 9.9 ± 0.06 | 10.6 ± 0.20 | 4.1 ± 0.07 |
| 1.013 | 6.9 ± 0.05 | 9.1 ± 0.49 | — |
| | NaBr | LiCl | $Na_2SO_4$ |
| 0.513 | 9.7 ± 0.08 | 14.8 ± 0.34 | 11.7 ± 0.10 |

**Table 2.** Dependence of the rate constant of oxidation on ionic strength adjusted with $NaClO_4$ in media of $5 \times 10^{-1}$ and $1 \times 10^{-3}$ mol dm$^{-3}$ $HClO_4$; concentrations of $[Co(CysOS)(en)_2]ClO_4$ and $Na_2S_2O_8$ and temperature as in Table 1

| $[HClO_4] = 5 \times 10^{-1}$ mol dm$^{-3}$ | | $[HClO_4] = 10^{-3}$ mol dm$^{-3}$ | |
|---|---|---|---|
| $I$/ mol dm$^{-3}$ | $k$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | $I$/ mol dm$^{-3}$ | $k$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
| 0.503 | 11.0 ± 0.10 | 0.013 | 45.3 ± 0.97 |
| 0.703 | 9.41 ± 0.08 | 0.053 | 26.8 ± 0.79 |
| 1.003 | 7.35 ± 0.07 | 0.173 | 16.6 ± 0.50 |
| 1.303 | 5.97 ± 0.06 | 0.503 | 10.2 ± 0.21 |
| | | 1.013 | 7.5 ± 0.13 |

**Table 3.** Dependence of the rate constant of oxidation on the concentration of perchloric acid; $[Co(CysOS)(en)_2{}^+] = 1.1 \times 10^{-4}$, $[Na_2S_2O_8] = 10^{-3}$, $I = 0.503$ mol dm$^{-3}$, 292.9 K

| 10[$HClO_4$]/ mol dm$^{-3}$ | $k$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^2$[$HClO_4$]/ mol dm$^{-3}$ | $k$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 5.0 | 10.5 ± 0.21 | 1.0 | 11.7 ± 0.12 |
| 3.0 | 11.0 ± 0.20 | 0.5 | 11.1 ± 0.28 |
| 2.0 | 11.4 ± 0.25 | 0.3 | 10.4 ± 0.31 |
| 1.0 | 11.6 ± 0.20 | 0.2 | 10.2 ± 0.18 |
| 0.5 | 11.6 ± 0.25 | 0.1 | 10.2 ± 0.21 |
| 0.2 | 11.8 ± 0.28 | | |

or NaCl) with $10^{-2}$ mol dm$^{-3}$ $HClO_4$ (Table 1). If tetrabutylammonium bromide was used for the adjustment of ionic strength, the salt effect was studied in $10^{-2}$ mol dm$^{-3}$ hydrobromic acid (Table 1) in order to avoid precipitation. The dependence $\log k = f[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})]$ for all electrolytes was linear with slopes $z_Az_B(NaCl) = z_Az_B(NaClO_4) = -2.1$ and $z_Az_B(NBu_4Br) = -3.6$ corresponding to a reaction of oppositely charged ions. The variation of the charge product on the type of electrolyte used to adjust the ionic strength was studied in detail. The rate constants at $I = 0.513$ mol dm$^{-3}$ with the electrolytes NaCl, $NaClO_4$, and NaBr are comparable. It follows that the rate constant is independent of the type of anion of the electrolyte used to adjust the ionic strength. On the other hand, when the ionic strength was adjusted with LiCl, KCl, NaCl, and $NBu_4Br$ the rate constant decreased in the sequence $Li^+ > Na^+$, $K^+ \gg NBu_4{}^+$, which suggests a specific effect of the cation probably connected with solvent-structure modification.

The product of the charge numbers of the reacting ions was also dependent on the concentration of perchloric acid in the medium. With respect to the acid–base equilibria expected for each reactant, the effect of the ionic strength (adjusted by $NaClO_4$) was studied at $5 \times 10^{-1}$ and $10^{-3}$ mol dm$^{-3}$ perchloric acid (Table 2). From the dependence $\log k = f[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})]$ the values of the charge product are $z_Az_B = -2.4$ and $-1.8$.

The effect of perchloric acid concentration on the rate of reaction was studied at 292.9 K and $I = 0.503$ mol dm$^{-3}$ in the range of $5 \times 10^{-1}$—$10^{-3}$ mol dm$^{-3}$ $HClO_4$ (Table 3). According to previous results,[1] the complex ion participates in the equilibrium (2) with an equilibrium constant of $K =$

$$[(en)_2CoNH_2(CHCOO^-)CH_2S]^+ + H^+ \rightleftharpoons [(en)_2CoNH_2(CHCOOH)CH_2S]^{2+} \quad (2)$$

$4 \times 10^{-3}$ dm$^3$ mol$^{-1}$ at 293 K. Within the concentration range $2 \times 10^{-1}$—$10^{-2}$ mol dm$^{-3}$ $HClO_4$ where the non-dissociated form of the complex ion prevails the rate constant changed only slightly; in the range $10^{-2}$—$10^{-3}$ mol dm$^{-3}$ $HClO_4$ the rate constant decreased by about 14%. At the concentration of $10^{-3}$ mol dm$^{-3}$ $HClO_4$ the presence of the dissociated form of the complex ion is expected, and its reactivity is apparently lower than that of the non-dissociated form. The decrease in rate constant with increasing concentration of perchloric acid is unexpected, since in the oxidation of cysteinatobis(ethylenediamine)cobalt(III) ion with hydrogen peroxide the dissociated form of the complex was found to be more reactive.[1] Similar results were obtained also during the oxidation of this complex with periodate.[7]

It is supposed that the present change of the rate constant is the result of the combined effects of perchloric acid on each reactant. Peroxodisulphate can exist in the forms $S_2O_8{}^{2-}$, $HS_2O_8{}^-$, or $SO_4{}^{\cdot -}$[8]. In previous studies on the oxidation of this cobalt complex with peroxodisulphate, no evidence for the ion radical was found.[9,10] From the measurements on the salt effect in $10^{-2}$ mol dm$^{-3}$ $HClO_4$ where the complex ion is expected to have a charge of 2+ according to the equilibrium constant $K$, the charge product of the reactants is $z_Az_B = -2.1$. Thus it may be assumed that the oxidant participates in the rate-determining step of the reaction as an univalent anion $HS_2O_8{}^-$ or in the form of an ion pair $M^+$, $S_2O_8{}^{2-}$ ($M^+$ = metal cation). In order to evaluate the association effect, potassium peroxodisulphate was used as the oxidant, the association constant for $K^+$, $S_2O_8{}^{2-}$ being 8.2 dm$^3$ mol$^{-1}$ at 298 K.[11] 1,4,7,10,13,16-Hexaoxacyclo-octadecane (18-crown-6), which is known for its ability to bind potassium ions ($K = 115.0$ dm$^3$ mol$^{-1}$ at 298 K),[12] was added to the reaction mixture. The results showed that a change in the concentration of the ion pair $K^+$, $S_2O_8{}^{2-}$ did not influence the reaction rate. Thus, in $10^{-2}$ mol dm$^{-3}$ $HClO_4$ the form $HS_2O_8{}^-$ of the oxidant is probably the most reactive one.

In $10^{-3}$ mol dm$^{-3}$ $HClO_4$ the dissociated form of the complex ion prevails and at the same time also greater dissociation of the peroxodisulphate ion can be expected. Thus the charge product of the reacting particles should again approach $-2$, *cf.* the experimental value of $-1.8$.

The effect of the co-solvent on the rate of oxidation was studied over the temperature interval 280.0—298.0 K. The values of the rate constants and activation parameters are shown in Table 4. With increasing concentration of the co-solvent in mixtures of water–t-butyl alcohol and water–isopropyl alcohol, the rate constant increased, but in mixtures of water–acetone and water–acetonitrile it decreased. This difference in behaviour is not connected with the classific-

**Table 4.** Dependence of the rate constant, activation enthalpy, $\Delta H^\ddagger$, and activation entropy, $\Delta S^\ddagger$, on the mole fraction of the non-aqueous solvent component. $[Co(CysOS)(en)_2^+] = 1.1 \times 10^{-4}$, $[Na_2S_2O_8] = 10^{-3}$, $[HClO_4] = 10^{-2}$ mol dm$^{-3}$, 297.9 K

| $x_2$ | $k$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $\Delta H^\ddagger$/kJ mol$^{-1}$ | $\Delta S^\ddagger$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| Acetone | | | |
| 0.000 | 50.5 ± 0.55 | 26.7 ± 1.7 | −122 ± 6 |
| 0.020 | 42.8 ± 1.38 | 23.3 ± 2.7 | −135 ± 9 |
| 0.044 | 35.9 ± 0.87 | 21.8 ± 1.2 | −141 ± 4 |
| 0.101 | 26.9 ± 0.80 | 31.9 ± 1.8 | −110 ± 6 |
| 0.176 | 22.2 ± 0.50 | 39.0 ± 1.5 | −87 ± 5 |
| 0.280 | 17.7 ± 0.26 | 41.9 ± 2.3 | −80 ± 8 |
| 0.460 | 12.2 ± 0.37 | 48.1 ± 2.0 | −62 ± 7 |
| t-Butyl alcohol | | | |
| 0.016 | 54.0 ± 1.58 | 16.8 ± 2.6 | −155 ± 9 |
| 0.034 | 59.2 ± 0.88 | 9.8 ± 2.0 | −177 ± 7 |
| 0.080 | 68.7 ± 1.30 | 20.0 ± 1.5 | −142 ± 5 |
| 0.142 | 97.5 ± 1.22 | 39.5 ± 2.2 | −73 ± 7 |
| 0.234 | 118.1 ± 3.00 | 48.0 ± 2.2 | −43 ± 7 |
| 0.382 | 87.1 ± 1.00 | 42.1 ± 1.9 | −66 ± 6 |
| Isopropyl alcohol | | | |
| 0.02 | 52.9 ± 1.45 | 24.4 ± 2.1 | −129 ± 7 |
| 0.042 | 51.5 ± 1.44 | 24.4 ± 2.3 | −129 ± 8 |
| 0.098 | 57.6 ± 1.17 | 23.1 ± 2.1 | −133 ± 7 |
| 0.172 | 70.7 ± 1.23 | 29.1 ± 2.4 | −111 ± 8 |
| 0.280 | 82.4 ± 1.11 | 35.9 ± 2.4 | −87 ± 8 |
| 0.467 | 66.8 ± 1.18 | 35.1 ± 2.3 | −91 ± 8 |
| Acetonitrile | | | |
| 0.029 | 32.0 ± 0.62 | 22.7 ± 1.1 | −139 ± 4 |
| 0.061 | 25.7 ± 0.38 | 29.0 ± 1.6 | −120 ± 5 |
| 0.137 | 20.5 ± 0.69 | 34.3 ± 2.5 | −104 ± 8 |
| 0.232 | 16.9 ± 0.15 | 35.5 ± 1.8 | −102 ± 6 |
| 0.364 | 16.4 ± 0.22 | 36.7 ± 1.4 | −98 ± 6 |
| 0.547 | 14.6 ± 0.13 | 34.4 ± 2.5 | −107 ± 8 |

ation of solvents into ' typically aqueous ' and ' typically non-aqueous ' since acetone and acetonitrile have similar influences on the rate constant where acetonitrile belongs to the latter group and acetone to the former. Typically aqueous solutions also include t-butyl alcohol and isopropyl alcohol.[13] According to electrostatic theory, the reaction rate should increase with decreasing relative permittivity in all solvents studied and the activation enthalpy should decrease as the reaction is between oppositely charged ions. However, the experimental results are inconsistent with these assumptions. The most remarkable changes in activation enthalpy were observed with water–t-butyl alcohol: when the mole fraction of t-butyl alcohol, $x_2$, was increased from 0 to 0.034, the value of $\Delta H^\ddagger$ decreased by a factor of three, but in the interval $x_2 = 0.034$—0.234 it increased to five times the lowest value. The lowest value of $\Delta H^\ddagger$ (9.8 ± 2.0 kJ mol$^{-1}$) was observed at a mole fraction $x_2^* \sim 0.04$, at which the co-solvent exerts its maximum water ' structure forming ' effect.[13] It is not possible to determine the minimum of the dependence of $\Delta H^\ddagger$ on f($x_2$) at the mole fraction $x_2^*$ in water–acetone and water–isopropyl acohol, at the given precision of measurement. At mole fractions of non-aqueous component higher than $x_2^*$, an increase in the value $\Delta H^\ddagger$ was observed like that in water–t-butyl alcohol. From the classification of acetonitrile as a typically non-aqueous solvent, a monotonous change in the activation enthalpy would be expected in water–acetonitrile.[13] This is inconsistent with our experimental results. At the mole fraction $x_2^*$, the water molecules are bound as clathrates and their ability to enter the reactant solvation spheres is reduced. Desolvated reactants are more reactive, however the total change in the reaction rate due to the addition of solvent will be the result of a change in solvation of not only the reactants but also of the activated complex.

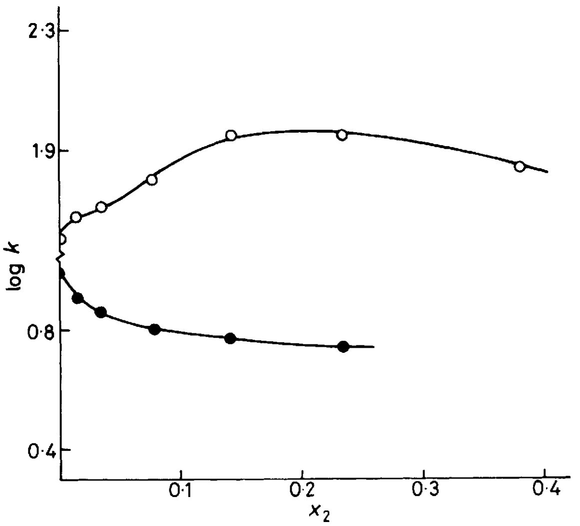


**Figure 1.** Dependence of logarithm of rate constant for oxidation of cysteinatobis(ethylenediamine)cobalt(III) by peroxodisulphate on mole fraction, $x_2$, of t-butyl alcohol; (○), t-butyl alcohol; (●), t-butyl alcohol and 0.5 mol dm$^{-3}$ $NaClO_4$. $[Co(CysOS)(en)_2^+] = 1.1 \times 10^{-4}$, $[Na_2S_2O_8] = 10^{-3}$, $[HClO_4] = 10^{-2}$ mol dm$^{-3}$, 292.9 K

The structure of water is influenced not only by other solvents but also by any electrolyte added. Therefore, the combined effect of the added non-aqueous component t-butyl alcohol and 0.5 mol dm$^{-3}$ of sodium perchlorate on the oxidation rate of cysteinatobis(ethylenediamine)cobalt(III) with peroxodisulphate was studied at 292.9 K (Figure 1). The addition of t-butyl alcohol to the water may result in a build up of the water structure, which has often been attributed to the formation of fluctuating structures of the clathrate type II about the co-solvent molecules. Mixed clathrates such as $Bu^tOH{\cdot}17H_2O{\cdot}2H_2S$ have been described in the literature;[14] in type II clathrates there are two small holes in addition to a large one for 17 water molecules. Therefore in the liquid state the small solute ions or molecules could fill the vacant holes of the clathrate structure in such a way that there would be no need to break the structure. On the other hand, large ions, *e.g.* the perchlorate ion, would cause significant breakage in the structure of water and the maximum of this endothermic effect can be expected at a mole fraction of t-butyl alcohol, $x_2$, of 0.055.[14]

The change in the rate constant in the t-butyl alcohol mole fraction range 0—0.055 is approximately four times higher than that in the interval from 0.055 to 0.234. In the former range t-butyl alcohol is expected to exert a water structure forming effect and the sodium perchlorate a structure breaking effect, while in the latter both exhibit a structure breaking action. For example, at $x_2 = 0.034$, according to Brönsted–Bjerrum theory (provided that the distance of closest approach $a = 0.3$ nm and the product $z_Az_B = -2$) an increase in the ionic strength due to the addition of $NaClO_4$ would be expected to result in a change of rate constant, [log $k$($Bu^tOH$) − log $k$($Bu^tOH + NaClO_4$)], of 0.99, whereas the experimental value is 0.85. On the other hand at $x_2 = 0.234$ the expected value calculated in this manner is 2.8 compared with the experimental value of 1.2. Thus it is

**Table 5.** Solubilities (mol dm$^{-3}$) of [Co(CysOS)(en)$_2$]ClO$_4$, KClO$_4$, and K$_2$S$_2$O$_8$ in water and in aqueous-acetone (a) and aqueous-t-butyl alcohol (b) mixtures at 298.2 K

| Percentage of organic component | $10^2S$\{[Co(CysOS)(en)$_2$]ClO$_4$\} | | $10S$(KClO$_4$) | | $10S$(K$_2$S$_2$O$_8$) |
|---|---|---|---|---|---|
| | (a) | (b) | (a) | (b) | (b) |
| water | 0.96 | 0.96 | 1.51 | 1.51 | 1.92 |
| 10 | 0.93 | 0.77 | 1.48 | 1.13 | — |
| 20 | 0.93 | 0.58 | 1.54 | 0.94 | 0.83 |
| 30 | 0.95 | 0.51 | 1.66 | 0.80 | 0.52 |
| 40 | 0.99 | 0.45 | 1.80 | — | 0.36 |
| 50 | — | — | — | 0.57 | 0.23 |

**Table 6.** Gibbs free energies of transfer, $\delta_m\mu^\ominus$/kJ mol$^{-1}$, for ClO$_4^-$, [Co(CysOS)(en)$_2$]$^+$, and S$_2$O$_8^{2-}$ ions from water to water-acetone (a) and water-t-butyl alcohol (b) mixtures at 298.2 K

| Percentage of organic component | $\delta_m\mu^\ominus$(ClO$_4^-$) | | $\delta_m\mu^\ominus$\{[Co(CysOS)(en)$_2$]$^+$\} | | $\delta_m\mu^\ominus$(S$_2$O$_8^{2-}$) | |
|---|---|---|---|---|---|---|
| | (a) | (b) | (a) | (b) | (a) * | (b) |
| 10 | 1.9 | 2.7 | −1.7 | −2.2 | 4.7 | 5.3 |
| 20 | 3.8 | 6.8 | −3.6 | −5.6 | 10.1 | 15.2 |
| 30 | 4.7 | 8.6 | −4.6 | −7.0 | 15.2 | 20.7 |
| 40 | 6.3 | 8.1 | −6.4 | −6.0 | 19.8 | 22.2 |

* From ref. 15.

obvious in the latter case that specific interactions other than electrostatic ones between the solvent and the electrolyte are involved.

Information on changes of solvation can be obtained from the dependence of the transfer function $\delta_m\mu^\ominus$ (calculated from solubilities) on the non-aqueous component.[4,5] The solubilities of [Co(CysOS)(en)$_2$]ClO$_4$, KClO$_4$, and K$_2$S$_2$O$_8$ in up to 40% by volume of t-butyl alcohol and acetone-water mixtures are reported in Table 5. The solubilities of the salts in water, $S$(w), and in the solvent mixture, $S$(x), are related to the difference in standard-state chemical potentials, $\delta\mu^\ominus$(salt), by equation (3) where $\gamma_\mp$ represents the corresponding molar activity coefficient; for K$_2$S$_2$O$_8$, $n = 3$ and for [Co(CysOS)(en)$_2$]ClO$_4$ and KClO$_4$, $n = 2$.

$$\begin{aligned}\delta\mu^\ominus(\text{salt}) &= \mu^\ominus(\text{salt, x}) - \mu^\ominus(\text{salt, w}) \quad (3)\\ &= nRT\ln S(\text{w})\gamma_\mp(\text{w})/S(\text{x})\gamma_\mp(\text{x})\end{aligned}$$

The quantity $\delta_m\mu^\ominus$ (salt) on the molar scale has been calculated assuming $\gamma_\mp(\text{w})/\gamma_\mp(\text{x}) \approx 1$. The same assumption has been made for the transfer function of peroxodisulphate from water into acetone-water mixtures.[15] The quantity $\delta_m\mu^\ominus$(salt) is related to the corresponding values for the individual ions, *e.g.* for the potassium and peroxodisulphate ions, as in equation (4).

$$\delta_m\mu^\ominus(\text{K}_2\text{S}_2\text{O}_8) = 2\delta_m\mu^\ominus(\text{K}^+) + \delta_m\mu^\ominus(\text{S}_2\text{O}_8{}^{2-}) \quad (4)$$

Hence Gibbs free energies of transfer for peroxodisulphate and perchlorate anion can be calculated using published estimates of the corresponding values for K$^+$ in aqueous acetone [15] and aqueous t-butyl alcohol.[16] From the difference in the values of $\delta_m\mu^\ominus$\{[Co(CysOS)(en)$_2$]ClO$_4$\} and $\delta_m\mu^\ominus$(ClO$_4^-$) the value of $\delta_m\mu^\ominus$\{[Co(CysOS)(en)$_2$]$^+$\} has been calculated. The values of $\delta_m\mu^\ominus$(S$_2$O$_8^{2-}$), $\delta_m\mu^\ominus$(ClO$_4^-$), and $\delta_m\mu^\ominus$\{[Co(CysOS)(en)$_2$]$^+$\} at 298.2 K are set out in Table 6. From the kinetic data it is possible to calculate values for $\delta_m\Delta G^\ddagger$, the change in activation barrier on going from water to the mixed solvent [equation (5)]. The division of the solvent

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - [\delta_m\mu^\ominus\{[\text{Co(CysOS)(en)}_2]^+\} + \delta_m\mu^\ominus(\text{S}_2\text{O}_8{}^{2-})] \quad (5)$$

effects into those upon the initial and transition states is illustrated in Figures 2 and 3.

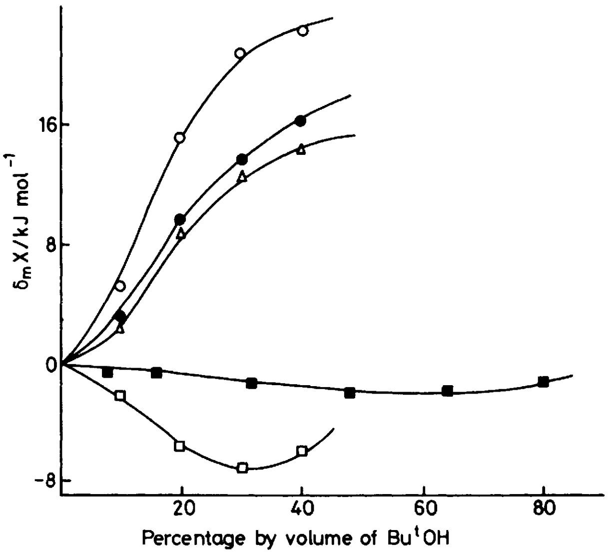


**Figure 2.** Analysis of solvent effects in water-t-butyl alcohol mixtures at 298.2 K; (○), $\delta_m\mu^\ominus$(S$_2$O$_8^{2-}$); (□), $\delta_m\mu^\ominus$\{[Co(CysOS)(en)$_2$]$^+$\}; (●), the transfer function for the initial state, $\delta_m\mu_i$; (■), the Gibbs free energy of activation, $\delta_m\Delta G^\ddagger$; (△), the transfer function for the transition state, $\delta_m\mu^\ddagger$

The transfer functions of the reactants in both mixtures have approximately the same course. The complex ion is stabilized when transferred from water to the aqueous-non-aqueous media, which may be due to the interaction of its hydrophobic part with the non-aqueous component of the solvent. Similar behaviour was found for *cis*-[Co(NH$_3$)Br(en)$_2$]$^{2+}$ and *cis*-[Co(H$_2$O)Br(en)$_2$]$^{2+}$,[17] which suggests that the non-aqueous component will solvate primarily ethylenediamine. In case of the above two complexes a greater change in the transfer function was observed with increasing concentration of t-butyl alcohol when compared with the present cysteinato-

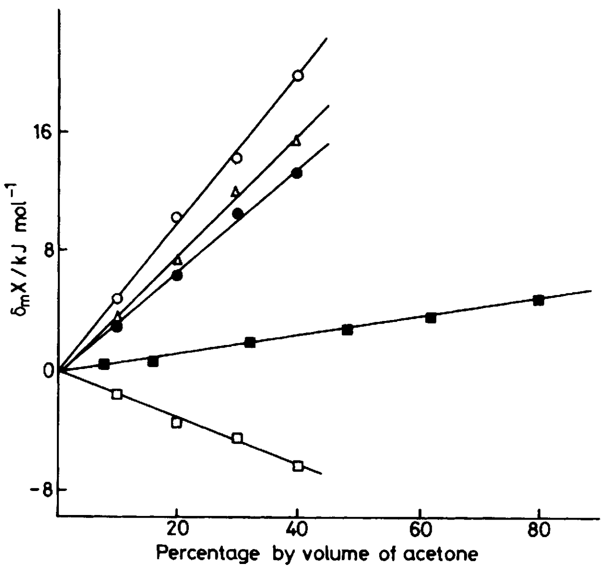


**Figure 3.** Analysis of solvent effects in water–acetone mixtures at 298.2 K. Symbols as in Figure 2

complex. Thus it is possible to assume a small solvation of cysteine by the non-aqueous component of the solvent. Peroxodisulphate ion was significantly destabilized in both media studied, resulting in positive values for the transfer functions of the initial state, $\delta_m\mu_i$. Comparing the transfer functions of the initial and transition states, $\delta_m\mu_i$ and $\delta_m\mu^\ddagger$, for the individual solvents it is seen that the change of solvation of the initial and the transition states is similar and results in a relatively small change in $\delta_m\Delta G^\ddagger$. The decrease in the rate constant with increasing concentration of acetone reflects a lower destabilization of the initial state in comparison with the transition state. In the case of t-butyl alcohol the opposite trend was observed, resulting in an increased reaction rate. The same signs and trends in the transfer functions, $\delta_mX^\ddagger$, with the concentration of the non-aqueous component are found if the transfer Gibbs free energies are estimated by taking account of activity-coefficient corrections and single-ion assumptions. The molar activity coefficients of $K_2S_2O_8$ and $[Co(CysOS)(en)_2]ClO_4$ in equation (3) were calculated from equation (6),[18] as in other studies,[19,20] where $I$ represents the ionic strength and $z_Az_B$ the charge product.

$$-\log\gamma_{\mp} = z_Az_BA[I^{\frac{1}{2}}(1 + I^{\frac{1}{2}}) - 0.3\,I] \qquad (6)$$

The reaction studied is a nucleophilic substitution, $S_N2$, with transfer of oxygen to the sulphur of the cysteine ligand. The negative values of the activation entropy are due to the reorganization of the solvation spheres.

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