# KINETICS OF OXIDATION OF BIS(ETHYLENEDIAMINE)-MERCAPTOACETATOCOBALT(III) AND CYSTEINATOBIS-(ETHYLENEDIAMINE)COBALT(III) IONS BY PEROXODISULPHATE IN AQUEOUS–NONAQUEOUS MIXED SOLVENTS

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The kinetics of oxidation in the first step was studied for coordination-bonded sulphur in the cysteinatobis(ethylenediamine)cobalt(III) and bis(ethylenediamine)mercaptoacetatocobalt(III) ions using peroxodisulphate as oxidant. The effect of the acid-base equilibria of the reactants was established based on the dependences of the rate constant and the thermodynamic activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on perchloric acid concentration. The effect of ionic strenght at various perchloric acid concentrations, was examined for the two complex ions. The combined effect of perchloric acid and sodium perchlorate was investigated in water–tert-butyl alcohol and water–ethylene glycol solutions. The transfer functions were calculated from the changes in the solubility of the reactants on passing from aqueous to the mixed aqueous–nonaqueous solutions, and the role of solvation during the oxidation of the complexes by peroxodisulphate was assessed based on the dependences of the transfer functions on the nonaqueous component content of the solvent system.

Cysteine and mercaptoacetic acid form chelate complexes with cobalt; cysteine is bonded to cobalt *via* sulphur and nitrogen, mercaptoacetic acid *via* sulphur and the oxygen of the carboxy group[1,2]. Unlike the bis(ethylenediamine)mercaptoacetato-cobalt(III) ion, the cysteinatobis(ethylenediamine)cobalt(III) ion involves a free carboxy group, which can protonate. The effect of the protonation equilibrium on the oxidation of $[CoCyS(en)_2]^+$ (CyS = cysteine) by hydrogen peroxide has been studied[3]; the reaction rate of the protonated species was found lower than that of the deprotonated species. The oxidation of the cysteinatobis(ethylenediamine)cobalt(III) ion by peroxodisulphate was partly studied previously[4]. The process occurs in two steps, the reaction rate for the first step being about two orders of magnitude higher than for the second step; the corresponding kinetics can be examined by suitably adjusting the oxidant-to-complex ion ratio. The oxidation of the ion in question by periodate was studied in detail in refs[5,6]. The periodate acid-base equilibrium was found to have a pronounced effect on the reaction rate and thermodynamic activation parameters, whereas the protonation equilibrium of the complex ions did not affect these characteristics appreciably. The reaction rate of the oxidation by peroxodisul-

phate was observed[4] to vary slightly with changing pH. In the work[4], the effect of the nonaqueous component on the reaction rate, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was examined in $0 \cdot 01 \text{M-HClO}_4$.

The aim of the present work was to investigate in detail the effect of the concentration of perchloric acid and of the ionic strength on the oxidation of the cysteinatobis(ethylenediamine)cobalt(III) and bis(ethylenediamine)mercaptoacetatocobalt(III) ions by peroxodisulphate, evaluate the effect of the acid-base equilibria on the reaction rate and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, examine the effect of tert-butyl alcohol and ethylene glycol at various concentrations of perchloric acid and various ionic strength values, and to analyze the trends in the reactivity with respect to changes in the chemical potentials of the reactants and of the activated complex occurring on changing the composition of solvent.

## EXPERIMENTAL

Cysteinatobis(ethylenediamine)cobalt(III) perchlorate was prepared as described[1]; for $C_7H_{21}N_5ClO_6SCo$ (397·7) calculated: 21·13% C, 5·32% H, 17·6% N; found: 21·0% C, 5·36% H, 17·6% N. Bis(ethylenediamine)mercaptoacetatocobalt(III) perchlorate was prepared similarly; for $C_6H_{18}N_4ClO_6SCo$ (368·5) calculated: 19·55% C, 4·88% H, 9·62% Cl; found: 19·3% C, 4·85% H, 10·14% Cl. Sodium peroxodisulphate (Serva, Heidelberg), perchloric acid (Carlo Erba, Milan), sodium perchlorate (Fluka, Buchs) and tert-butyl alcohol and ethylene glycol (Reanal, Budapest) were of reagent grade purity. The solvents were redistilled prior to use.

The kinetic measurements were performed on a Specol 210 digital spectrophotometer and Specol 10 interfaced to a K 200 recorder or a TEC A/D converter. The spectra were scanned on a Specord UV-VIS instrument (all Carl Zeiss, Jena). The reaction was monitored in 2 cm or 5 cm cells, thermostatted to within $\pm 0 \cdot 2$ K by means of a U 15c ultrathermostat (MLW-Prüfgerätewerk Medingen). The analytical wavelength was 371 nm, where the two ions oxidized in the first step exhibit their absorption maxima.

The reaction was monitored for a time of four halflives using a sufficient excess of oxidant. The reaction obeyed the first order patterns. The rate constants were evaluated by Guggenheim's method as averages of $4-6$ replicate measurements. The log $A = f(t)$ dependence was evaluated by the least squares method for each measurement. The temperature dependence of the rate constant was established by measurements at four temperatures within the $277 \cdot 8 - 298 \cdot 2$ K range, and used for determining the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values whose errors were assessed according to ref.[7].

The solubilities of the reactants and potassium perchlorate were determined by a procedure as follows. A mixture of solvent and the substance investigated was stirred in a thermostatted vessel at 298·2 K, and the concentration of the dissolved fraction of the substance was determined after the equilibrium established (in $6-8$ hours). The concentrations of $[CoCyS(en)_2]ClO_4$ and $[Co(en)_2SCH_2COO]ClO_4$ were determined photometrically (the absorptivities remained unaffected by addition of the nonaqueous component to the solvent). The solubility of potassium perchlorate in water–ethylene glycol mixtures was determined gravimetrically; in water–tert-butyl alcohol the values are known[4]. The concentration of peroxodisulphate was determined iodometrically. The error in the solubility determination did not exceed $\pm 5\%$.

## RESULTS AND DISCUSSION

The first step of oxidation of the bis(ethylenediamine)mercaptoacetatocobalt(III) ion proceeds by pathway



$$ (A) $$
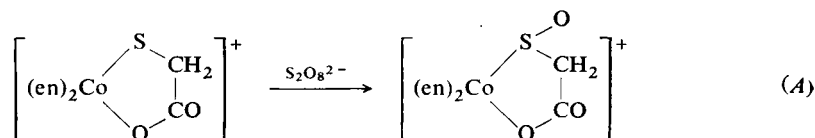
the oxidation of cysteinatobis(ethylenediamine)cobalt(III) ion is similar[4].

The experimental results show that the rate constants of the reactions in question obey the relation
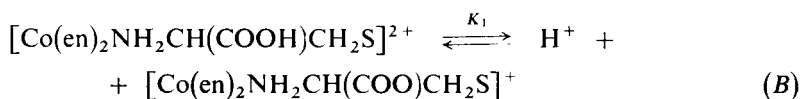
$$ -d[\text{complex}]/dt = k[S_2O_8^{2-}][\text{complex}], \tag{1} $$

where [complex] is the concentration of the complex ion. Owing to the excess of peroxodisulphate, Eq. (1) can be written as
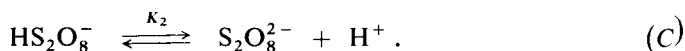
$$ -d[\text{complex}]/dt = k_{\text{obs}}[\text{complex}], \tag{2} $$

where $k_{\text{obs}} = k[S_2O_8^{2-}]$.

Of the two complexes studied, only the cysteinatobis(ethylenediamine)cobalt(III) ion occurs in an acid-base equilibrium[5],

$$ [Co(en)_2NH_2CH(COOH)CH_2S]^{2+} \xrightleftharpoons{K_1} H^+ + $$
$$ + [Co(en)_2NH_2CH(COO)CH_2S]^+ \tag{B} $$

with $K_1 = 3\cdot5 \cdot 10^{-3}$ mol $l^{-1}$ at 298·2 K. At the same time, the oxidant also occurs in an acid-base equilibrium,

$$ HS_2O_8^- \xrightleftharpoons{K_2} S_2O_8^{2-} + H^+. \tag{C} $$

Only approximate values of $K_2$, *viz.* 0·5 mol $l^{-1}$ and 0·14 mol $l^{-1}$, have been reported[8,9], both based on kinetic data. With regard to the $K_1$ and $K_2$ values, both of the acid-base equilibria will be significant within the HClO$_4$ concentration region used, $0\cdot001 - 0\cdot5$ mol $l^{-1}$. The rate constant and the thermodynamic activation parameters ($\Delta H^+$ and $\Delta S^+$) for the oxidation of the bis(ethylenediamine)mercapto-acetatocobalt(III) ion varied only slightly with the concentration of perchloric acid. For the cysteinatobis(ethylenediamine)cobalt(III) ion, the activation enthalpy increased and the rate constant decreased slightly with increasing HClO$_4$ concentration over the region of $0\cdot1 - 0\cdot5$ mol $l^{-1}$ (Table I). The slight change in the reaction rate is

associated with the protonation equilibrium of the oxidant. The increase in the activation enthalpy is presumably due to changes in the nucleophilic properties of the sulphur in the cysteine ligand, resulting from the protonation of the carboxy group. For the $[Co(en)_2SCH_2COO]^+$ ion, where the carboxy group cannot protonate because of its bonding to the central atom, no change in the activation enthalpy was observed. The protonation of the Co—S sulphur, which is assumed to occur in acid solutions particularly for sulphatocobalt(III) complexes ($c_{HClO_4} \approx 4$ mol $l^{-1}$), brings about[10] decomposition of the complex ion and formation of products containing Co(II); for the two reactions under study, however, spectroscopic evidence shows that this effect does not appear.

TABLE I

Dependence of the rate constant and thermodynamic activation parameters of oxidation of $[CoCyS(en)_2]ClO_4$ and $[Co(en)_2SCH_2COO]ClO_4$ by peroxodisulphate on the concentration of perchloric acid

| $c_{HClO_4}$ mmol $l^{-1}$ | $k$ l mol$^{-1}$ s$^{-1}$ | $\Delta H^{\ddagger}$ kJ mol$^{-1}$ | $\Delta S^{\ddagger}$ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| $c_{[CoCyS(en)_2]ClO_4} = 43{\cdot}2$ µmol $l^{-1}$, $c_{Na_2S_2O_8} = 0{\cdot}4$ mmol $l^{-1}$, $I = 0{\cdot}501$ mol $l^{-1}$, $T = 284{\cdot}9$ K | | | |
| 500 | $6{\cdot}10 \pm 0{\cdot}19$ | $44{\cdot}2 \pm 1{\cdot}8$ | $-74 \pm 5$ |
| 300 | $6{\cdot}46 \pm 0{\cdot}13$ | $42{\cdot}3 \pm 1{\cdot}2$ | $-80 \pm 5$ |
| 200 | $6{\cdot}70 \pm 0{\cdot}19$ | $41{\cdot}6 \pm 1{\cdot}2$ | $-82 \pm 5$ |
| 100 | $6{\cdot}97 \pm 0{\cdot}21$ | $39{\cdot}4 \pm 1{\cdot}6$ | $-90 \pm 4$ |
| 50 | $7{\cdot}16 \pm 0{\cdot}20$ | $40{\cdot}8 \pm 1{\cdot}3$ | $-85 \pm 5$ |
| 30 | $6{\cdot}94 \pm 0{\cdot}13$ | $37{\cdot}2 \pm 2{\cdot}0$ | $-97 \pm 7$ |
| 20 | $7{\cdot}04 \pm 0{\cdot}21$ | $38{\cdot}5 \pm 1{\cdot}9$ | $-93 \pm 6$ |
| 10 | $7{\cdot}03 \pm 0{\cdot}18$ | $37{\cdot}9 \pm 1{\cdot}5$ | $-95 \pm 4$ |
| 5 | $7{\cdot}08 \pm 0{\cdot}19$ | $36{\cdot}1 \pm 1{\cdot}8$ | $-102 \pm 4$ |
| 3 | $7{\cdot}25 \pm 0{\cdot}16$ | $34{\cdot}6 \pm 2{\cdot}0$ | $-110 \pm 6$ |
| 2 | $7{\cdot}01 \pm 0{\cdot}19$ | $33{\cdot}9 \pm 1{\cdot}5$ | $-110 \pm 3$ |
| 1 | $6{\cdot}88 \pm 0{\cdot}13$ | $32{\cdot}1 \pm 1{\cdot}5$ | $-116 \pm 3$ |
| $c_{[Co(en)_2SCH_2COO]ClO_4} = 58{\cdot}6$ µmol $l^{-1}$, $c_{Na_2S_2O_8} = 0{\cdot}768$ mmol $l^{-1}$, $I = 0{\cdot}102$ mol $l^{-1}$, $T = 298{\cdot}2$ K | | | |
| 100 | $51{\cdot}0 \pm 0{\cdot}8$ | $37{\cdot}4 \pm 1{\cdot}2$ | $-87 \pm 3$ |
| 50 | $54{\cdot}0 \pm 1{\cdot}5$ | $37{\cdot}1 \pm 1{\cdot}6$ | $-87 \pm 5$ |
| 30 | $54{\cdot}0 \pm 0{\cdot}9$ | $37{\cdot}9 \pm 1{\cdot}4$ | $-85 \pm 4$ |
| 10 | $54{\cdot}9 \pm 0{\cdot}8$ | $38{\cdot}3 \pm 1{\cdot}4$ | $-83 \pm 4$ |
| 5 | $48{\cdot}6 \pm 1{\cdot}1$ | $34{\cdot}1 \pm 1{\cdot}5$ | $-98 \pm 4$ |
| 3 | $50{\cdot}2 \pm 0{\cdot}8$ | $35{\cdot}3 \pm 1{\cdot}2$ | $-91 \pm 5$ |
| 1 | $48{\cdot}3 \pm 1{\cdot}7$ | $36{\cdot}3 \pm 1{\cdot}8$ | $-91 \pm 5$ |

The effect of the ionic strength on the oxidation of $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ by peroxodisulphate was investigated over the concentration regions of $c_{HClO_4} = 0.001 - 0.3$ mol $l^{-1}$ and $0.001 - 0.1$ mol $l^{-1}$, respectively (Table II). At $c_{HClO_4} = 0.001$ mol $l^{-1}$ the reactants occur in their deprotonated forms. The plots of $\log k$ vs $I^{1/2}/(1 + I^{1/2})$ were linear for the two complexes, with slopes of $-1.96$ and $-1.48$, respectively (the theoretical value according to the Brønsted––Bjerrum theory is $-2.05$). At $c_{HClO_4} = 0.3$ or $0.1$ mol $l^{-1}$, more than 60% oxidant is in the $HS_2O_8^-$ form and the cysteinatobis(ethylenediamine)cobalt(III) ion occurs nearly completely (96%) in the protonated form. The $\log k$ vs $I^{1/2}/(1 + I^{1/2})$ plot at $c_{HClO_4} = 0.3$ mol $l^{-1}$ for this ion was linear, with a slope of $-2.72$. This increased value can be accounted for by an incomplete protonation of the peroxodisulphate. In addition to the reaction between the protonated $HS_2O_8^-$ species and the protonated $[Co(en)_2NH_2CH(COOH)CH_2S]^{2+}$ species, where the product of the charges is $z_A z_B = -2$, the reaction between the nonprotonated $S_2O_8^{2-}$ species and the protonated form of the complex ion, with $z_A z_B = -4$, also plays a role. For the bis-(ethylenediamine)mercaptoacetatocobalt(III) ion at $c_{HClO_4} = 0.1$ mol $l^{-1}$, the slope of the above-mentioned plot was $-1.56$, a value close to that observed at $c_{HClO_4} = 0.001$ mol $l^{-1}$. For the oxidant in the $HS_2O_8^-$ form the theoretical slope is $-1.02$.

TABLE II

Dependence of the rate constant of oxidation by $Na_2S_2O_8$ on the ionic strength adjusted with NaClO₄ for $[CoCyS(en)_2]ClO_4$ $(k_I)$ at $c_{[CoCyS(en)_2]ClO_4} = 43.2$ µmol $l^{-1}$, $c_{Na_2S_2O_8} = 0.4$ mmol . $l^{-1}$, and for $[Co(en)_2SCH_2COO]ClO_4$ $(k_{II})$ at $c_{[Co(en)_2SCH_2COO]ClO_4} = 58.6$ µmol $l^{-1}$, $c_{Na_2S_2O_8} = 0.768$ mmol $l^{-1}$; $c_{HClO_4} = 0.001$ $(A)$, $0.3$ $(B)$, $0.1$ mol $l^{-1}$ $(C)$; $T = 298.2$ K

| $I$ mol $l^{-1}$ | $k_I$ l mol$^{-1}$ s$^{-1}$ | | $k_{II}$ l mol$^{-1}$ s$^{-1}$ | |
| --- | --- | --- | --- | --- |
| | $A$ | $B$ | $A$ | $C$ |
| 0.004 | 59.7 ± 0.6 | — | 105.6 ± 3.1 | — |
| 0.014 | 49.5 ± 0.5 | — | 82.5 ± 2.1 | — |
| 0.054 | — | — | 59.4 ± 1.0 | — |
| 0.064 | 35.4 ± 0.3 | — | — | — |
| 0.104 | 23.4 ± 0.5 | — | 48.3 ± 1.4 | — |
| 0.304 | 14.3 ± 0.2 | 16.5 ± 0.2 | 34.3 ± 0.9 | 31.7 ± 0.9 |
| 0.404 | — | 12.6 ± 0.3 | — | — |
| 0.504 | 12.1 ± 0.3 | 11.4 ± 0.4 | 28.8 ± 0.9 | 25.1 ± 0.4 |
| 0.704 | 9.7 ± 0.4 | 9.2 ± 0.2 | 25.6 ± 0.5 | 23.0 ± 0.3 |
| 0.904 | — | 6.6 ± 0.2 | — | — |
| 1.004 | — | — | 22.1 ± 0.4 | 21.1 ± 0.6 |
| 1.104 | 8.1 ± 0.2 | 5.8 ± 0.1 | — | — |

The higher value observed indicates that the nonprotonated oxidant species again participates in the reaction. In addition to the acid-base equilibria, other effects, e.g., those associated with changes in the reactants' solvation sphere, can also occur, particularly at higher concentrations of the perchlorate ions. The specific effect of electrolytes on the oxidation of the cysteinatobis(ethylenediamine)cobalt(III) ion by peroxodisulphate has been examined in detail previously[4].

Of the solvents used, tert-butyl alcohol is among typical solvents for which $G^E > 0$ and $|TS^E| > |H^E|$, where $G^E$, $H^E$, and $S^E$ are the excess mixing thermodynamic functions. These solvents influence the hydrogen bonds between the water molecules, in dependence on concentration; at low mole fractions $(x_2)$ they favour the hydrogen bond formation and stabilize the water structure, up to a mole fraction $x_2^+$ $(x_2^+ = 0.04$ for tert-butyl alcohol) at which the maximum number of bonds are formed between the water molecules. Additional increase in the mole fraction of the nonaqueous component brings about disturbance of the water structure. Ethylene glycol, on the other hand, is among typical nonaqueous negative solvents $(G^E < 0$, $|TS^E| < < |H^E|)$, where the intercomponent interactions of the water molecules with the co-solvent molecules play a major role[11]. Tables III and IV give the dependences of the rate constants, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on the concentrations of tert-butyl alcohol and ethylene glycol in water at various concentrations of perchloric acid and ionic strengths. The different nature of the solvents manifested itself particularly in the dependences of the rate constants on the concentration of the co-solvent at $c_{HClO_4} = = 0.001$ mol l$^{-1}$. An addition of NaClO$_4$ induced similar changes in the $k = f(x_2)$ dependences as the same addition of HClO$_4$. This implies that it is the perchlorate ion concentration rather than the acid-base equilibria that exerts the major effect on the reaction rate.

The changes in the thermodynamic activation parameters in dependence on the concentration of the co-solvent were within the limits of accuracy of their determination, only for the cysteinatobis(ethylenediamine)cobalt(III) ion in the water–tert-butyl alcohol system at $c_{HClO_4} = 0.001$ mol l$^{-1}$ a pronounced minimum of the $\Delta H^{\ddagger} = f(x_2)$ dependence was observed at $x_2 \approx x_2^+$. A similar dependence has been measured before[4] at $c_{HClO_4} = 0.01$ mol l$^{-1}$. In solutions with $c_{NaClO_4} = 0.1$ mol l$^{-1}$ or with $c_{HClO_4} = 0.1$ mol l$^{-1}$ the minimum mentioned was not observed. This suggests that at lower concentrations of perchlorate ions, the effect of the co-solvent on the structure of water will play the major role, whereas at higher concentrations of HClO$_4$ or NaClO$_4$ the effect of the perchlorate ions will be appreciable. According to published data[12], tert-butyl alcohol forms clathrates which contain vacancies in their structure. Whereas occupation of the vacancies by small atoms may not disturb the solvent structure, disturbances can occur with bulky ions such as the perchlorate anion. The maximum of this effect was observed at $x_2 \approx 0.05$.

Additional information about the solvent effect on the reaction rate can be extracted from the dependences of the transfer functions of reactants and of the change

TABLE III

Dependence of the rate constant and thermodynamic activation parameters of oxidation of the $\{CoCyS(en)_2\}^+$ ion by $Na_2S_2O_8$ on the mole fraction of tert-butyl alcohol or ethylene glycol $(x_2)$ in water at 298·2 K; $c_{[CoCyS(en)_2]^+} = 43\cdot2\ \mu mol\ l^{-1}$, $c_{S_2O_8{}^{2-}} = 0\cdot4\ mmol\ l^{-1}$

| $x_2$ | $k$ $l\ mol^{-1}\ s^{-1}$ | $\Delta H^{\ne}$ $kJ\ mol^{-1}$ | $\Delta S^{\ne}$ $J\ K^{-1}\ mol^{-1}$ |
|---|---|---|---|
| | tert-Butyl alcohol $c_{HClO_4} = 0\cdot3\ mol\ l^{-1}$ | | |
| 0 | 16·5 ± 0·2 | 38·4 ± 1·0 | −94 ± 4 |
| 0·121 | 14·7 ± 0·5 | 36·9 ± 1·4 | −102 ± 4 |
| 0·046 | 13·1 ± 0·3 | 34·0 ± 1·4 | −109 ± 5 |
| 0·076 | 12·2 ± 0·4 | 33·4 ± 1·3 | −112 ± 5 |
| 0·113 | 11·9 ± 0·3 | 35·1 ± 1·7 | −106 ± 6 |
| | $c_{HClO_4} = 0\cdot001\ mol\ l^{-1}$ | | |
| 0 | 59·7 ± 0·6 | 38·8 ± 1·1 | −78 ± 4 |
| 0·021 | 68·5 ± 1·2 | 38·1 ± 1·1 | −79 ± 4 |
| 0·046 | 73·0 ± 1·3 | 31·7 ± 1·0 | −101 ± 4 |
| 0·076 | 86·0 ± 1·1 | 40·2 ± 1·1 | −70 ± 4 |
| 0·113 | 111·1 ± 3·3 | 43·2 ± 1·8 | −58 ± 6 |
| | $c_{HClO_4} = 0\cdot001\ mol\ l^{-1}$, $c_{NaClO_4} = 0\cdot3\ mol\ l^{-1}$ | | |
| 0 | 14·3 ± 0·3 | 36·0 ± 1·0 | −103 ± 4 |
| 0·021 | 14·0 ± 0·3 | 35·0 ± 1·0 | −106 ± 4 |
| 0·046 | 12·8 ± 0·3 | 37·1 ± 1·0 | −99 ± 4 |
| 0·076 | 12·2 ± 0·2 | 38·1 ± 1·5 | −96 ± 6 |
| 0·113 | 12·5 ± 0·2 | 36·7 ± 1·4 | −101 ± 6 |
| | Ethylene glycol $c_{HClO_4} = 0\cdot3\ mol\ l^{-1}$ | | |
| 0·035 | 16·3 ± 0·3 | 41·4 ± 1·0 | −83 ± 4 |
| 0·075 | 14·7 ± 0·4 | 40·7 ± 1·3 | −84 ± 5 |
| 0·121 | 13·7 ± 0·4 | 42·3 ± 1·2 | −81 ± 5 |
| 0·175 | 12·7 ± 0·2 | 40·6 ± 1·0 | −88 ± 4 |
| | $c_{HClO_4} = 0\cdot001\ mol\ l^{-1}$ | | |
| 0·035 | 71·9 ± 1·9 | 43·4 ± 1·4 | −64 ± 6 |
| 0·075 | 72·8 ± 4·3 | 43·8 ± 2·0 | −63 ± 8 |
| 0·121 | 80·1 ± 1·9 | 44·8 ± 1·3 | −58 ± 5 |
| 0·175 | 63·9 ± 1·4 | 39·8 ± 1·1 | −77 ± 5 |
| | $c_{HClO_4} = 0\cdot001\ mol\ l^{-1}$, $c_{NaClO_4} = 0\cdot3\ mol\ l^{-1}$ | | |
| 0·035 | 13·7 ± 0·2 | 39·4 ± 1·0 | −91 ± 4 |
| 0·075 | 12·9 ± 0·4 | 38·3 ± 1·3 | −95 ± 5 |
| 0·121 | 12·1 ± 0·2 | 41·8 ± 1·0 | −84 ± 4 |
| 0·175 | 10·4 ± 0·3 | 40·4 ± 1·2 | −90 ± 5 |

TABLE IV

Dependence of the rate constant and thermodynamic activation parameters of oxidation of the $[Co(en)_2SCH_2COO]^+$ ion by $Na_2S_2O_8$ on the mole fraction of tert-butyl alcohol or ethylene glycol $(x_2)$ in water at 298·2 K; $c_{[Co(en)_2SCH_2COO]^+} = 58·6\ \mu mol\ l^{-1}$, $c_{S_2O_8^{2-}} = 0·786\ mmol\ l^{-1}$

| $x_2$ | $\dfrac{k}{l\ mol^{-1}\ s^{-1}}$ | $\dfrac{\Delta H^{\ddagger}}{kJ\ mol^{-1}}$ | $\dfrac{\Delta S^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$ |
|---|---|---|---|
| | tert-Butyl alcohol $c_{HClO_4} = 0·1\ mol\ l^{-1}$ | | |
| 0 | 51·0 ± 0·5 | 37·3 ± 1·0 | −86 ± 4 |
| 0·021 | 53·3 ± 0·7 | 38·2 ± 1·7 | −84 ± 4 |
| 0·046 | 51·3 ± 1·5 | 36·7 ± 1·4 | −89 ± 4 |
| 0·076 | 54·5 ± 0·9 | 39·4 ± 1·0 | −79 ± 5 |
| 0·113 | 57·3 ± 0·9 | 37·1 ± 1·2 | −87 ± 5 |
| | $c_{HClO_4} = 0·001\ mol\ l^{-1}$ | | |
| 0 | 105·6 ± 3·1 | 40·2 ± 1·3 | −71 ± 6 |
| 0·021 | 105·4 ± 2·5 | 37·2 ± 1·5 | −81 ± 6 |
| 0·046 | 104·9 ± 3·2 | 37·0 ± 1·4 | −82 ± 6 |
| 0·076 | 121·0 ± 2·0 | 39·9 ± 1·0 | −71 ± 4 |
| 0·113 | 142·7 ± 1·7 | 42·2 ± 1·3 | −62 ± 6 |
| | $c_{HClO_4} = 0·001\ mol\ l^{-1}$, $c_{NaClO_4} = 0·1\ mol\ l^{-1}$ | | |
| 0 | 48·3 ± 1·4 | 36·2 ± 1·1 | −91 ± 4 |
| 0·021 | 47·9 ± 1·6 | 36·7 ± 1·4 | −90 ± 6 |
| 0·046 | 44·3 ± 1·1 | 34·2 ± 1·7 | −99 ± 7 |
| 0·076 | 44·6 ± 0·7 | 35·1 ± 1·1 | −96 ± 5 |
| 0·113 | 46·0 ± 1·1 | 34·6 ± 1·4 | −97 ± 6 |
| | Ethylene glycol $c_{HClO_4} = 0·1\ mol\ l^{-1}$ | | |
| 0·035 | 52·2 ± 1·0 | 37·0 ± 1·0 | −88 ± 4 |
| 0·075 | 46·2 ± 2·4 | 34·7 ± 1·0 | −97 ± 4 |
| 0·121 | 43·8 ± 1·5 | 37·5 ± 1·9 | −88 ± 7 |
| 0·175 | 36·8 ± 1·2 | 35·6 ± 1·4 | −96 ± 6 |
| | $c_{HClO_4} = 0·001\ mol\ l^{-1}$ | | |
| 0·035 | 89·4 ± 4·0 | 33·2 ± 1·7 | −96 ± 7 |
| 0·075 | 93·1 ± 3·7 | 36·3 ± 1·7 | −85 ± 7 |
| 0·121 | 98·0 ± 4·9 | 37·5 ± 1·8 | −81 ± 8 |
| 0·175 | 78·5 ± 3·4 | 36·3 ± 1·6 | −87 ± 7 |
| | $c_{HClO_4} = 0·001\ mol\ l^{-1}$, $c_{NaClO_4} = 0·1\ mol\ l^{-1}$ | | |
| 0·035 | 45·6 ± 1·5 | 35·8 ± 1·2 | −93 ± 5 |
| 0·075 | 43·6 ± 0·6 | 37·2 ± 1·0 | −89 ± 4 |
| 0·121 | 39·2 ± 0·8 | 37·3 ± 1·0 | −89 ± 4 |
| 0·175 | 35·0 ± 0·6 | 37·8 ± 1·1 | −89 ± 5 |

in the Gibbs energy $\delta_m \Delta G^{\pm}$ on the concentration of the co-solvent. The transfer functions are a measure of the stabilization or destabilization of the substance during its transfer from a reference medium (water) to the medium of interest. The change in the Gibbs energy for the transfer from water to the given medium is the difference between the transfer functions of the transition state and the initial state,

$$\delta_m \Delta G^{\pm} = \delta_m \mu^{\pm} - \delta_m \mu_i , \qquad (3)$$

where $\delta_m \mu_i$ is the sum of the transfer functions of the reactants $(\delta_m \mu_{S_2O_8^{2-}} + \delta_m \mu_{complex})$. At the same time, $\delta_m \Delta G^{\pm}$ can be related to the rate constants in water $(k_{H_2O})$ and in the medium under study $(k_{x_2})$ as

$$\delta_m \Delta G^{\pm} = RT \ln (k_{H_2O}/k_{x_2}) . \qquad (4)$$

Eqs (3) and (4) can serve to calculate the transfer function of the activated complex.

The transfer functions of $S_2O_8^{2-}$ and $[CoCyS(en)_2]^+$ for a water–tert-butyl alcohol mixture have been calculated[4] based on the solubilities; the remaining transfer functions used were calculated from the solubilities $S_{H_2O}$ and $S_{x_2}$ by means of the relation

$$\delta_m \mu_{salt} = nRT \ln (S_{H_2O}/S_{x_2}) (\gamma_{H_2O}/\gamma_{x_2}) , \qquad (5)$$

where the $\gamma$'s are the respective mean molar activity coefficients of the salt; $n$ is 3 for $K_2S_2O_8$ and 2 for the complex perchlorates. With regard to the relatively low solubilities (Table V), the $\gamma_{H_2O}/\gamma_{x_2}$ ratio can be approximated by unity, similarly as in papers[4,13]. The transfer functions of $S_2O_8^{2-}$ and $ClO_4^-$ in the water–ethylene glycol system were calculated as the differences between the transfer functions of potassium peroxodisulphate and potassium perchlorate, respectively, and the transfer function of the potassium ion published in ref.[14] For the water–tert-butyl alcohol system, the transfer function of the perchlorate ion is known[4]. The transfer functions of $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ ions were obtained by subtracting the transfer function of the perchlorate ion from the transfer functions of the respective complex perchlorates. The values are summarized in Table VI. The transfer functions of the salts are accurate to within $\pm 0.2$ kJ mol$^{-1}$. The error in $\delta_m \mu_{salt}$ was calculated similarly as for $\Delta H^{\pm}$. The error in the determination of the transfer functions of the ions, resulting from the experiment, did not exceed $\pm 1$ kJ mol$^{-1}$, the overall error, however, depends also on the accuracy of the transfer function of the potassium ion[14].

The transfer functions indicate that in the water–tert-butyl alcohol mixture, the two complex ions are stabilized to approximately the same extent. In the water–ethylene glycol mixture the transfer functions change only slightly, which implies

that no substantial change in the solvation sphere of the $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ ions takes place in this solvent mixture. Similarly small

TABLE V

Solubilities $S$ (mmol $l^{-1}$) of the reactants in water–ethylene glycol and, for $[Co(en)_2SCH_2COO]$. $.ClO_4$, also in water–tert-butyl alcohol mixtures at 298·2 K

| $\varphi^a$ vol. % | $[Co(en)_2SCH_2COO]ClO_4$ | | $[CoCyS(en)_2]ClO_4$ | $K_2S_2O_8$ | $KClO_4$ |
|---|---|---|---|---|---|
| | ethylene glycol | tert-butyl alcohol | | | |
| 0 | 34·4 | 34·4 | 9·6 | 192 | 151 |
| 10 | 30·3 | 27·2 | 10·0 | 146 | 146 |
| 20 | 25·9 | 23·3 | 10·6 | 134 | 138 |
| 30 | 23·1 | 19·7 | 8·4 | 93 | 124 |
| 40 | 21·4 | 17·5 | 7·8 | 78 | 131 |

[a] Concentration of the nonaqueous component in the solvent system.

TABLE VI

Transfer functions $\delta_m\mu$ (kJ mol$^{-1}$) of $[CoCyS(en)_2]^+$ (*I*), $[CoCySH(en)_2]^{2+}$ (*II*), $[Co(en)_2SCH_2COO]^+$ (*III*), $S_2O_8^{2-}$ (*IV*), and $HS_2O_8^-$ (*V*) from water to water–tert-butyl alcohol and water–ethylene glycol mixed solvents at 298·2 K

| $\varphi^a$ vol. % | $\delta_m\mu_I$ | $\delta_m\mu_{II}$ | $\delta_m\mu_{III}$ | $\delta_m\mu_{IV}$ | $\delta_m\mu_V$ |
|---|---|---|---|---|---|
| | | tert-Butyl alcohol | | | |
| 10 | −2·2 | −4·4 | −1·7 | 5·3 | 3·3 |
| 20 | −5·6 | −10·7 | −5·2 | 15·2 | 9·7 |
| 30 | −7·0 | −14·9 | −6·6 | 20·7 | 12·5 |
| 40 | −6·0 | −14·4 | −4·8 | 22·2 | 13·3 |
| | | Ethylene glycol | | | |
| 10 | −0·4 | −0·6 | 0·4 | 2·1 | 1·9 |
| 20 | −1·0 | −1·5 | 0·9 | 2·8 | 2·3 |
| 30 | −0·4 | −1·4 | 0·9 | 5·7 | 4·6 |
| 40 | 0·1 | −1·7 | 1·5 | 7·0 | 5·5 |

[a] Concentration of the nonaqueous component in the solvent system.

changes in the transfer function of the latter ion have been observed in water–methyl alcohol mixtures[15]. The peroxodisulphate ion is destabilized in both solvents. A more pronounced change in the transfer function of the peroxodisulphate ion was again observed in the water–tert-butyl alcohol mixture. Figs 1 and 2 demonstrate that in both solvents at $c_{HClO_4} = 0.001$ mol $l^{-1}$ the initial state for the oxidation of the bis(ethylenediamine)mercaptoacetatocobalt(III) ion by peroxodisulphate is destabilized $(\delta_m \mu_i > 0)$, the destabilization being contributed to mainly by the oxidant. In view of the small change in $\delta_m \Delta G^{\neq}$ the activated complex can be supposed to be destabilized to a similar extent as the initial state. The course of the transfer functions for the oxidation of the cysteinatobis(ethylenediamine)cobalt(III) ion was similar as in Figs 1 and 2.

At $c_{HClO_4} = 0.1$ or $0.3$ mol $l^{-1}$ the protonated forms of the reactants predominate (the transfer functions $\delta_m \mu_{H^+}$ for the water–tert-butyl alcohol and water–ethylene glycol mixtures see in refs[16,14], respectively); the initial state is destabilized to a lesser extent than at $c_{HClO_4} = 0.001$ mol $l^{-1}$. In the water–tert-butyl alcohol mixture, the initial state for the oxidation of the cysteinatobis(ethylenediamine)cobalt(III) ion was stabilized.
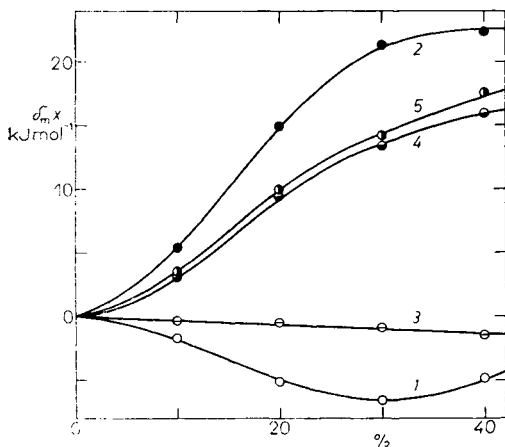


FIG. 1

Analysis of the solvent effect on the oxidation of $[Co(en)_2SCH_2COO]^+$ by peroxodisulphate in water–tert-butyl alcohol mixture at $c_{HClO_4} = 0.001$ mol $l^{-1}$ and $T = 298.2$ K. 1 $\delta_m \mu_{[Co(en)_2SCH_2COO]^+}$, 2 $\delta_m \mu_{S_2O_8^{2-}}$, 3 $\delta_m \Delta G^{\neq}$, 4 $\delta_m \mu^{\neq}$, 5 $\delta_m \mu_i$; abcissa-vol. %
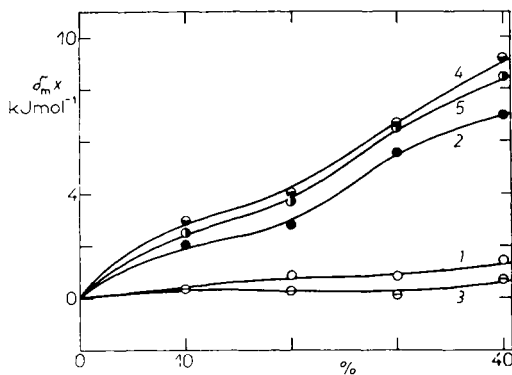
FIG. 2

Analysis of the solvent effect on the oxidation of $[Co(en)_2SCH_2COO]^+$ by peroxodisulphate in water–ethylene glycol mixture at $c_{HClO_4} = 0.001$ mol $l^{-1}$ and $T = 298.2$ K. Symbols as in Fig. 1

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Translated by P. Adámek.