KINETICS OF OXIDATION OF THE BIS(ETHYLENEDIAMINE)-MERCAPTOACETATOCOBALT(III) AND CYSTEINATO-BIS(ETHYLENE-DIAMINE)COBALT(III) IONS BY HYDROGEN PEROXIDE IN MIXED AQUEOUS–NONAQUEOUS SOLUTIONS

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The kinetics of oxidation of the coordinatively bonded sulphur in the cysteinato-bis(ethylene-diamine)cobalt(III) and bis(ethylenediamine)mercaptoacetatocobalt(III) complexes by hydrogen peroxide to the sulphoxides was examined in $HClO_4$ solutions ($c(HClO_4) = 1-500$ mmol l^{-1}) with a view to obtaining data characterizing the effect of the acid-base equilibria of the reactants on the reaction rate. The reaction rate was found affected particularly by the acid-base equilibrium of the oxidant, which plays a role in strongly acid solutions. The oxidation was also studied in water–methyl alcohol, water–tert-butyl alcohol and water–ethylene glycol mixtures, and the effect of the mole fraction of the nonaqueous component on the rate constant and thermodynamic activation parameters was examined.

This study of the oxidation of the $[CoCyS(en)_2]^+$ (CyS = cysteine) and $[Co(en)_2SCH_2COO]^+$ ions by H_2O_2 is a continuation of our previous investigation of the oxidation of these complexes by peroxodisulphate[1,2] and periodate[3,4]. The effect of pH on the kinetics of oxidation of the former complex by H_2O_2 has been investigated by Herting and coworkers[5] who found the unprotonated complex species more reactive than the protonated species; in strongly acid solutions,however, the reaction rate increased due to the presence of the protonated form of H_2O_2. Using peroxodisulphate, on the other hand, the rate of oxidation of the two complexes is affected by the acid-base equilibrium of the oxidant to a much lesser extent[1,2].

The oxidation of coordinatively bound sulphur in investigated complexes with $S_2O_8^{2-}$ (refs[1,2]), IO_4^- (refs[3,4]) and H_2O_2 (ref.[5]) is an S_N2 nucleophilic substitution. While the solvent effect was examined from the viewpoint of the change of the water structure during the oxidation of $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ ions by $S_2O_8^{2-}$ and IO_4^-, during the oxidation these complexes by H_2O_2 the stabilisa-tion of activated complex by non-aqueous component would be expected similarly as in literature[6,7].

The aim of the present work was to examine in detail the effect of perchloric acid, ionic strength and co-solvent in mixed solutions on the oxidation of the

$[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ ions by hydrogen peroxide (during which sulphur is oxidized to sulphoxide), and to analyze the solvation effects based on the concentration dependences of the rate constant and the thermodynamic activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

EXPERIMENTAL

Synthesis of $[CoCyS(en)_2]ClO_4$ and $[Co(en)_2SCH_2COO]ClO_4$ and their analysis as well as the kinetic measurement procedure have been described[2]. All chemicals used were of reagent grade purity. The actual concentration of hydrogen peroxide of reagent grade purity (Chemapol, Prague) was determined iodometrically. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were determined from the temperature dependences of the rate constants over the region of 289—311 K and their errors were calculated following ref.[8]

RESULTS AND DISCUSSION

The experimental results gave evidence that the oxidation of the $[CoCyS(en)_2]^+$ ion by hydrogen peroxide obeys the relation

$$(1/[H_2O_2])(d[CoCyS(en)^+]/dt) = k_{SO}[CoCyS(en)_2^+] +$$
$$+ k_{2H^+}[CoCySH(en)_2^{2+}] + k_{3H^+}[CoCySH(en)_2^{2+}][H^+], \qquad (1)$$

where k_{SO}, k_{2H^+} and k_{3H^+} are the rate constants of oxidation of the unprotonated complex by H_2O_2, the protonated species by H_2O_2 and the protonated species by $H_3O_2^+$, respectively. In the $[CoCyS(en)_2]^+$ complex the cysteine free carboxylic group is protonated with an equilibrium constant $K_A = 3.5 \cdot 10^{-3}$ mol l^{-1} at 278 K (ref.[3]). The observed rate constant k_{obs} can be described by the relation

$$k_{obs} = (k_{SO}K_A + k_{2H^+}[H^+] + k_{3H^+}[H^+]^2)/(K_A + [H^+]). \qquad (2)$$

The presence of the unprotonated complex species is not assumed over the $HClO_4$ concentration region of 10—500 mmol l^{-1}, owing to which the $k_{SO}K_A$ term is eliminated from Eq. (2). Provided that $K_A \ll [H^+]$, the rate constants k_{2H^+} and k_{3H^+} are determined from the linear dependence $k = f([H^+])$, while k_{SO} is calculated using the region of $c(HClO_4) = 1-10$ mmol l^{-1}. The values obtained are $k_{SO} = 0.360$, $k_{2H^+} = 0.265$, $k_{3H^+} = 0.519$ l mol^{-1} s^{-1}. These values agree well with those reported in ref.[5], viz. $k_{SO} = 0.365$, $k_{2H^+} = 0.235$, and $k_{3H^+} = 0.544$ l mol^{-1}. s^{-1} at 293.5 K.

For the oxidation of $[Co(en)_2SCH_2COO]^+$ by hydrogen peroxide only the k_{SO} and k_{3H^+} values were determined inasmuch as the complex is not subject to acid-base equilibrium and Eq. (1) transforms into

$$k_{obs} = k_{SO} + k_{3H^+}[H^+]. \qquad (3)$$

The dependence of the rate constant on $c(HClO_4)$ (Table I) afforded the values of $k_{SO} = 0.841$ and $k_{3H^+} = 2.45 \ l \ mol^{-1} \ s^{-1}$ at 298.2 K. The thermodynamic activation parameters are $\Delta H_{SO}^{\ddagger} = (36.2 \pm 2.5) \ kJ \ mol^{-1}$, $\Delta H_{3H^+}^{\ddagger} = (44.0 \pm 2.5) \ kJ \cdot mol^{-1}$, $-\Delta S_{SO}^{\ddagger} = (125 \pm 8) \ J \ K^{-1} \ mol^{-1}$, $-\Delta S_{3H^+}^{\ddagger} = (90 \pm 8) \ J \ K^{-1} \ mol^{-1}$. The dependences of $k_{obs} = f(-\log c_{H^+})$ $(c_{H^+}$ in $mol \ l^{-1})$ for the two complexes are plotted in Fig. 1. The rate constant decrease over the region of $c(HClO_4) = 10^{-1}$ to

TABLE I

Dependence of rate constant and activation parameters of oxidation of $[Co(en)_2SCH_2COO]^+$ by H_2O_2 on the concentration of $HClO_4$; $I = 0.5$, $T = 298.2$ K, $c([Co(en)_2SCH_2COO]^+) = 0.244 \ mmol \ l^{-1}$, $c(H_2O_2) = 7.4 \ mol \ l^{-1}$

$c(HClO_4)$ $mmol \ l^{-1}$	k $l \ mol^{-1} \ s^{-1}$	$\Delta H^{\ddagger}$ $kJ \ mol^{-1}$	$-\Delta S^{\ddagger}$ $J \ K^{-1} \ mol^{-1}$
1	0.869 ± 0.017	38.1 ± 1.5	123 ± 5
3	0.871 ± 0.016	36.5 ± 1.7	123 ± 7
5	0.873 ± 0.017	36.5 ± 1.5	123 ± 5
10	0.874 ± 0.016	37.1 ± 1.3	121 ± 5
30	0.842 ± 0.019	37.2 ± 1.4	120 ± 5
50	0.930 ± 0.019	36.1 ± 1.2	124 ± 4
100	1.05 ± 0.021	39.4 ± 1.2	111 ± 4
300	1.52 ± 0.032	40.0 ± 1.3	107 ± 5
500	2.11 ± 0.060	41.5 ± 1.6	99 ± 6
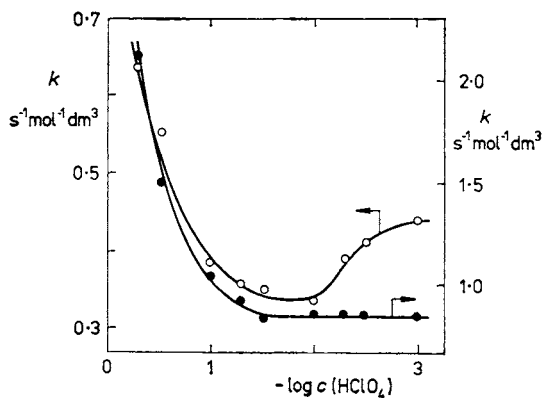
FIG. 1

Dependence of the rate of oxidation of the $[CoCyS(en)_2]^+$ (o) and $[Co(en)_2SCH_2COO]^+$ (●) ions by hydrogen peroxide on the concentration of perchloric acid at 198.1 K; $I = 0.5 \ mol \ l^{-1}$

10^{-2} mol l^{-1} is due to the acid-base equilibrium of the oxidant. The rate constant increase for $[CoCyS(en)_2]^+$ at $c(HClO_4) = 10^{-2} - 10^{-3}$ mol l^{-1} is associated with the protonation of the carboxy group of the cysteinate ligand; for the mercapto-acetate ligand, which is bonded to the central ion via the oxygen atom of the carboxy group, this value remains constant over the $c(HClO_4)$ region in question.

The effect of ionic strength was studied at $c(HClO_4) = 1, 10$, and 500 mmol l^{-1} with respect to the acid–base equilibria of reactants and to the charge numbers change of reactants; the rate constant was found independent of ionic strength for the two complexes studied, only a positive salt effect was observed for the cysteine complex at $c(HClO_4) = 500$ mmol l^{-1}, which is due to the fact that in this solution the reactants are present in the $[CoCySH(en)_2]^{2+}$ and $H_3O_2^+$ forms, respectively.

The mercaptoacetate complex *I* was found more reactive than the cysteinate complex *II*. At $c(HClO_4) = 1$ mmol l^{-1}, the ratio of the rate constants k_I/k_{II} is 1·76. This agrees rather closely with the values of 1·77 found for the oxidation by $S_2O_8^{2-}$ (ref.[2]) and 1·82 found for the oxidation by IO_4^- (refs[3,4]) at 298·2 K, which suggests that the difference in the reactivity of the two complexes is associated with the different nucleophilic properties of sulphur in the ligands oxidized rather than with the nature of oxidant: in the cysteinate complex, sulphur is nucleophilic to a lesser extent due to the inductive effect of the carboxy group.

In mixed solvents the mercaptoacetate-to-cysteinate rate constant ratio varied in different ways for the various oxidants used, which can be explained in terms of the different solvation of the latter. The dependences of the rate constants and of the ΔH^+ and ΔS^+ values on the concentration of the organic co-solvent for the oxidation of the $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ ions by hydrogen peroxide are given in Tables II and III, respectively. These dependences are different for the three co-solvents used. Whereas in the water–tert-butyl alcohol solutions the rate constants of oxidation of the two complexes by peroxodisulphate increase with increasing fraction of the organic co-solvent[2], the rate constants of oxidation by hydrogen peroxide in this system decrease or vary very slightly. Similar differences were observed for ethylene glycol as co-solvent. This may be related with the different change in the solvation spheres not only of oxidant but also of the activated complex. The increase in the rate constant for the oxidation by peroxodisulphate in the water––tert-butyl alcohol system is primarily due to the destabilization of the $S_2O_8^{2-}$ ion, as indicated by its transfer function values[9]. In view of the fact that hydrogen per-oxide is an unchanged species, it can be assumed that the nonaqueous component does not affect appreciably its solvation shell; in weakly acid solutions, change in the solvation of the activated complex can play a role. According to refs[6,7], solvent may form a part of the activated complex and stabilize it (Scheme 1). The extent of this stabilization is related with the protic properties of the solvent. The assumed stabilization according to Scheme 1 is reflected in the lowered ΔS_{so}^+ value in weakly acid solutions while in strongly acid solutions, where stabilization of this kind does

Dependence of rate constant and activation parameters of oxidation of $[CoCyS(en)_2]^+$ by H_2O_2 on the mole fraction (x_2) of nonaqueous co-solvent; $T = 298.2$ K, $c([CoCyS(en)_2]^+) =$ $= 0.226$ mmol l^{-1}, $c(H_2O_2) = 7.2$ mmol l^{-1}

x_2	k $l \, mol^{-1} \, s^{-1}$	$\Delta H^{\pm}$ $kJ \, mol^{-1}$	$-\Delta S^{\pm}$ $J \, K^{-1} \, mol^{-1}$
Water–methyl alcohol[a]			
0	0.433 ± 0.006	35.0 ± 1.4	135 ± 5
0.047	0.410 ± 0.004	34.2 ± 1.2	138 ± 4
0.100	0.393 ± 0.004	33.1 ± 1.2	142 ± 4
0.160	0.366 ± 0.005	32.3 ± 1.4	146 ± 5
0.229	0.310 ± 0.004	33.9 ± 1.2	142 ± 4
Water–methyl alcohol[b]			
0	0.526 ± 0.009	36.7 ± 1.3	129 ± 4
0.047	0.502 ± 0.009	35.3 ± 1.2	133 ± 4
0.100	0.484 ± 0.006	34.5 ± 1.1	136 ± 4
0.160	0.458 ± 0.008	34.5 ± 1.2	137 ± 4
0.229	0.395 ± 0.006	34.4 ± 1.2	138 ± 4
Water–methyl alcohol[c]			
0	0.514 ± 0.014	—	—
0.047	0.488 ± 0.008	—	—
0.100	0.459 ± 0.007	—	—
0.160	0.416 ± 0.007	—	—
0.229	0.367 ± 0.007	—	—
Water–tert-butyl alcohol[a]			
0.021	0.394 ± 0.005	32.9 ± 1.4	142 ± 5
0.046	0.373 ± 0.005	31.1 ± 1.3	149 ± 5
0.076	0.339 ± 0.006	33.3 ± 1.2	142 ± 4
0.113	0.328 ± 0.006	32.8 ± 1.8	141 ± 6
Water–tert-butyl alcohol[b]			
0.021	0.462 ± 0.006	35.5 ± 1.7	132 ± 6
0.046	0.439 ± 0.005	32.9 ± 1.2	141 ± 4
0.076	0.422 ± 0.006	32.5 ± 1.2	143 ± 4
0.113	0.427 ± 0.007	33.2 ± 1.6	140 ± 6

TABLE II

(Continued)

x_2	k $\mathrm{l\,mol^{-1}\,s^{-1}}$	$\Delta H^{\ddagger}$ $\mathrm{kJ\,mol^{-1}}$	$-\Delta S^{\ddagger}$ $\mathrm{J\,K^{-1}\,mol^{-1}}$
	Water–tert-butyl alcohol[c]		
0·021	0·465 ± 0·014	—	—
0·046	0·444 ± 0·007	—	—
0·076	0·427 ± 0·006	—	—
0·113	0·414 ± 0·006	—	—
	Water–ethylene glycol[a]		
0·035	0·403 ± 0·006	33·2 ± 1·2	140 ± 4
0·075	0·414 ± 0·008	31·4 ± 1·4	146 ± 5
0·121	0·427 ± 0·009	30·9 ± 1·3	148 ± 4
0·175	0·434 ± 0·007	30·1 ± 1·2	150 ± 4
	Water–ethylene glycol[b]		
0·035	0·526 ± 0·009	34·7 ± 1·4	134 ± 5
0·075	0·480 ± 0·009	33·7 ± 1·2	137 ± 4
0·121	0·504 ± 0·008	33·1 ± 1·4	139 ± 5
0·175	0·519 ± 0·008	31·0 ± 1·4	146 ± 5

[a] $c(\mathrm{HClO_4}) = 100\ \mathrm{mmol\,l^{-1}}$; [b] $c(\mathrm{HClO_4}) = 1\ \mathrm{mmol\,l^{-1}}$; [c] $c(\mathrm{HClO_4}) = 1\ \mathrm{mmol\,l^{-1}}$, $c(\mathrm{NaClO_4}) = 99\ \mathrm{mmol\,l^{-1}}$.

not operate, the $\Delta S^{\ddagger}_{3H^+}$ value is 35 J K^{-1} mol^{-1} higher. Of the organic solvents used, ethylene glycol displays the most pronounced protic properties, comparable to those of water[10].
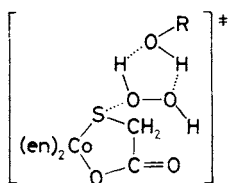
SCHEME 1

Structure of the activated complex for the oxidation of the $[\mathrm{Co(en)_2SCH_2COO}]^+$ ion by hydrogen peroxide in weakly acid solution

TABLE III

Dependence of rate constant and activation parameters of oxidation of $[Co(en)_2SCH_2COO]^+$ by H_2O_2 on the mole fraction (x_2) of nonoaqueous co-solvent; $T = 298.2$ K, $c([Co(en)_2SCH_2.COO]^+) = 0.244$ mmol l^{-1}, $c(H_2O_2) = 74$ mmol l^{-1}

x_2	k $l\,mol^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$ $kJ\,mol^{-1}$	$-\Delta S^{\ddagger}$ $J\,K^{-1}\,mol^{-1}$
Water–methyl alcohol[a]			
0	1.08 ± 0.011	39.8 ± 1.6	111 ± 5
0.047	1.12 ± 0.020	38.9 ± 1.4	114 ± 5
0.100	1.33 ± 0.021	35.0 ± 1.4	127 ± 5
0.160	1.23 ± 0.015	34.5 ± 1.3	128 ± 4
0.229	1.09 ± 0.002	35.6 ± 1.4	125 ± 5
Water–methyl alcohol[b]			
0	0.926 ± 0.012	38.2 ± 1.2	118 ± 4
0.047	0.924 ± 0.014	36.3 ± 1.3	124 ± 5
0.100	0.905 ± 0.012	34.4 ± 1.1	131 ± 4
0.160	0.865 ± 0.013	34.5 ± 1.1	131 ± 4
0.229	0.804 ± 0.011	34.4 ± 1.2	132 ± 4
Water–methyl alcohol[c]			
0	0.934 ± 0.012	—	—
0.047	0.927 ± 0.011	—	—
0.100	0.907 ± 0.016	—	—
0.160	0.865 ± 0.015	—	—
0.229	0.791 ± 0.014	—	—
Water–tert-butyl alcohol[a]			
0.021	1.03 ± 0.013	35.9 ± 1.2	124 ± 4
0.046	1.02 ± 0.020	33.1 ± 1.5	133 ± 5
0.076	1.01 ± 0.015	34.7 ± 1.4	128 ± 5
0.113	1.02 ± 0.020	36.0 ± 1.7	123 ± 6
Water–tert-butyl alcohol[b]			
0.021	0.819 ± 0.012	35.7 ± 1.7	126 ± 6
0.046	0.793 ± 0.011	32.5 ± 1.6	137 ± 6
0.076	0.770 ± 0.009	33.8 ± 1.5	133 ± 5
0.113	0.760 ± 0.015	34.4 ± 1.5	131 ± 5

TABLE III
(Continued)

x_2	k $1\ mol^{-1}\ s^{-1}$	$\Delta H^{\neq}$ $kJ\ mol^{-1}$	$-\Delta S^{\neq}$ $J\ K^{-1}\ mol^{-1}$
	Water–tert-butyl alcohol[c]		
0·021	0·839 ± 0·012	—	—
0·046	0·813 ± 0·015	—	—
0·076	0·786 ± 0·013	—	—
0·113	0·789 ± 0·012	—	—
	Water–ethylene glycol[a]		
0·035	1·09 ± 0·021	36·7 ± 1·6	120 ± 5
0·075	1·18 ± 0·015	34·4 ± 1·5	128 ± 5
0·121	1·29 ± 0·022	34·2 ± 1·4	127 ± 5
0·175	1·35 ± 0·021	32·3 ± 1·5	133 ± 5
	Water–ethylene glycol[b]		
0·035	0·893 ± 0·020	35·9 ± 1·8	125 ± 6
0·075	0·939 ± 0·025	31·2 ± 1·6	140 ± 5
0·121	0·984 ± 0·019	31·6 ± 1·9	138 ± 6
0·175	1·02 ± 0·020	31·4 ± 1·7	138 ± 6
	Water–ethylene glycol[c]		
0·075	0·963 ± 0·024	—	—
0·175	1·04 ± 0·021	—	—

[a] $c(HClO_4) = 100\ mmol\ l^{-1}$; [b] $c(HClO_4) = 1\ mmol\ l^{-1}$; [c] $c(HClO_4) = 1\ mmol\ l^{-1}$, $c(NaClO_4) = 99\ mmol\ l^{-1}$.

The changes in the rate constants of oxidation by hydrogen peroxide on passing from water to the water–tert-butyl alcohol mixture are roughly identical for the $[CoCyS(en)_2]^+$ and $[Co(en)_2SCH_2COO]^+$ complexes in weakly acid solutions, which can be accounted for by the nearly identical values of the transfer functions $\delta_m\mu^\theta([complex]^+)$ (ref.[2]). In strongly acid water–tert-butyl alcohol mixtures the protonated form of the cysteine complex is better stabilized, which results in a decrease in the reaction rate[2]. In the water–ethylene glycol mixture the cysteine complex is stabilized somewhat better than the mercaptoacetate complex whose transfer function acquires a positive value. The increase in the reaction rate for the latter complex

can be explained in terms of its destabilization. The more marked decrease in the reaction rate for the oxidation of the cysteine complex in the water–methyl alcohol mixture can be explained similarly.

The decrease in the activation enthalpy on passing from water to the water– –ethylene glycol system is due to the lowering energy barrier resulting from the stabilization of the activated complex. In the water–tert-butyl alcohol mixture, the ΔH^+ value is lowest at the alcohol mole fraction $x_2 = x_2^*$, which indicates that the change in the solvent structure with the addition of co-solvent[11] manifests itself similarly as in ref.[1]

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