

Solvent effects on the kinetics of oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate

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The kinetics of oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate was investigated as a function of ionic strength, concentration of perchloric acid, and temperature. Furthermore, the effect of the nonaqueous component of solvent on rate constant and activation parameters in the water—acetone and water—*tert*-butyl alcohol mixtures was estimated. The effect of solvent is discussed from the view-point of the change in solvation of the initial and transition state on going from water to a mixed solvent.

Исследована кинетика окисления иона цистеин-бис(этилендиамин)кобальта(III) периодатом в зависимости от ионной силы, концентрации хлористой кислоты и температуры. Затем было изучено влияние неводного компонента растворителя на константу скорости и активационные параметры в смеси вода—ацетон и вода—*трет*-бутиловый спирт. Влияние растворителя обсуждается с точки зрения изменения сольватации исходного и переходного состояний при переходе от воды к смешанному растворителю.

The oxidation of coordinatively bound cysteine in the cysteinato-bis(ethylenediamine)cobalt(III) ion by hydrogen peroxide was investigated earlier [1, 2]. Its mechanism was elucidated and the products of oxidation in the first and second step were determined in these studies. The reaction obeys the S_N2 mechanism involving the transfer of oxygen from the oxidizing agent to nucleophilic sulfur of the cysteine ligand. The cysteinesulfenato-bis(ethylenediamine)cobalt(III) ion is produced in the first step of oxidation while the cysteinesulfinato-bis(ethylenediamine)cobalt(III) is the product of the second step of oxidation. The influence of electrolytes and cosolvent on oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by peroxodisulfate was profoundly examined in paper [3]. On the basis of the change in reaction rate, activation parameters, and transfer functions of

reactants depending on concentration of the cosolvent, the effect of solvation on oxidation of the coordinatively bound cysteine was estimated.

In this study, we have been concerned with a more detailed investigation of the effect of nonaqueous component on the change in chemical potentials of the initial and transition state in media with varying concentration of perchloric acid. In respect of acid-base equilibria of both reactants, the effect of medium on the change in solvation of reactants in the protonated and deprotonated form has been appreciated.

The bonding of cysteine to the cobalt(III) ion has enabled us to investigate its oxidation up to the second step, which is not possible for the oxidation of free cysteine [4]. From this stand-point, the reaction may also serve as a model system for studying different biologically interesting ligands.

Experimental

Cysteinato-bis(ethylenediamine)cobalt(III) perchlorate was prepared according to [1]. Analysis: w_i (found): 21 % C, 5.35 % H, 17.6 % N; w_i (calculated): 21.15 % C, 5.30 % H, 17.60 % N. All chemicals used were anal. grade. Redistilled water was used for the preparation of solutions. The stock solutions were discarded after 5 h.

The reaction rate was investigated spectrophotometrically using Specol 10 (Zeiss, Jena) linked to a K 200 recorder (Zeiss, Jena). The measurements were carried out with 2 cm or 5 cm cells. The reaction mixture was thermostated within accuracy ± 0.1 K by means of a thermostat U 15 c. For studying the oxidation of $[\text{CoCySO}(\text{en})_2]\text{ClO}_4$ (CySO = cysteine, en = ethylenediamine) by periodate, the reaction mixture was prepared from the solutions of complex salt and periodate to which sodium perchlorate and perchloric acid were added for adjusting ionic strength and pH. The nonaqueous solvent was added in equal ratio into the solutions of both reactants in order to prevent variation of temperature during their mixing. Periodate was in 9-fold excess with respect to the complex ion. The course of the reaction was investigated for 3 half-lives by measuring the absorbance at $\lambda = 371$ nm where the absorption maximum of the product, *i.e.* cysteinesulfenato-bis(ethylenediamine)cobalt(III) ion ($\epsilon = 591 \text{ m}^2 \text{ mol}^{-1}$) appeared. The rate constant was calculated by the Guggenheim's method. The values given in tables are averages from six independent measurements. The temperature dependence of the rate constants in the range 276.9–298.2 K was used for calculating the thermodynamic activation parameters ΔH^\ddagger and ΔS^\ddagger . The errors in ΔH^\ddagger and ΔS^\ddagger were calculated according to the relations published in literature [5].

The solubility of KIO_4 in water and water—acetone or water—*tert*-butyl alcohol mixtures was determined at 298.2 K. After attainment of equilibrium between the solid phase and its solution, the concentration of KIO_4 was determined iodometrically. The equilibrium constant for the acid-base equilibrium of $[\text{CoCySO}(\text{en})_2]\text{ClO}_4$ was determined potentiometrically according to literature [6].

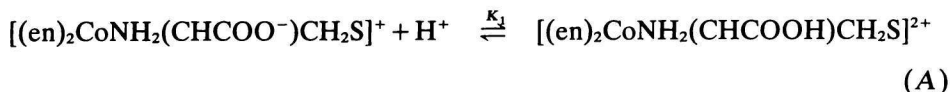
Results and discussion

On the basis of the obtained experimental data, we may write the following rate equation for the investigated reaction

$$d[\text{CoCySO}(\text{en})_2^+]/dt = k[\text{IO}_4^-][\text{CoCySO}(\text{en})_2^+] \quad (1)$$

where $[\text{IO}_4^-]$ and $[\text{CoCySO}(\text{en})_2^+]$ are total concentrations of periodate and complex ion, respectively. The subsequent oxidation of the cysteinesulfenato-bis(ethylenediamine)cobalt(III) ion is about hundred times slower and does not influence the measurements of the first step.

The effect of concentration of perchloric acid on rate constant and activation parameters was studied in the 1×10^{-3} — 5×10^{-1} mol dm⁻³ concentration range of HClO₄ (Table 1). According to literature [2], the complex ion participates in acid—base equilibrium (A)



the dissociation constant at 298.2 K being $K_1 = 3.5 \times 10^{-3}$ mol dm⁻³. Simultaneously, the oxidation agent is also in an acid—base equilibrium (B)



Table 1

Dependence of rate constant, activation enthalpy ΔH^\ddagger and activation entropy ΔS^\ddagger on perchloric acid concentration for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate $c([\text{CoCySO}(\text{en})_2]\text{ClO}_4) = 1.1 \times 10^{-4}$ mol dm⁻³, $c(\text{NaIO}_4) = 10^{-3}$ mol dm⁻³, $I = 0.501$ mol dm⁻³; $T = 298.2$ K

$\frac{c(\text{HClO}_4) \cdot 10^2}{\text{mol dm}^{-3}}$	$\frac{k}{\text{mol}^{-1} \text{s}^{-1} \text{dm}^3}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{J mol}^{-1} \text{K}^{-1}}$
50	18.5 ± 0.35	71.9 ± 1.1	20 ± 4
40	22.2 ± 0.60	—	—
30	28.0 ± 0.95	71.3 ± 1.6	20 ± 5
20	42.0 ± 0.86	66.8 ± 1.6	10 ± 5
10	66.4 ± 1.50	56.8 ± 2.3	- 19 ± 7
5	103.8 ± 2.60	52.2 ± 1.9	- 32 ± 6
1	161.8 ± 4.40	38.6 ± 1.6	- 67 ± 5
0.5	178.7 ± 3.75	29.2 ± 0.9	- 104 ± 4
0.3	190.0 ± 3.50	30.1 ± 1.1	- 100 ± 4
0.1	191.8 ± 3.80	29.7 ± 1.6	- 101 ± 5

the dissociation constant at 298.2 K being $K_2 = 2.3 \times 10^{-2} \text{ mol dm}^{-3}$ [7]. It results from the values of the dissociation constants K_1 and K_2 that the complex ion must be almost completely in the protonated form in the concentration range 5×10^{-2} — $5 \times 10^{-1} \text{ mol dm}^{-3}$ HClO_4 and the change in reaction rate in that interval may be attributed to the acid-base equilibrium of the oxidation agent. In this interval of HClO_4 concentrations, the dependence of the rate constant on HClO_4 concentration obeys eqn (2)

$$k_{\text{exp}} = (k(\text{IO}_4^-) K_2 + k(\text{HIO}_4)[\text{H}^+])/([\text{H}^+] + K_2) \quad (2)$$

where $k(\text{IO}_4^-)$ and $k(\text{HIO}_4)$ are the rate constants for the deprotonated and protonated form of the oxidation agent, respectively. If we express K_2 in eqn (2) by means of the equilibrium concentrations, the experimental rate constant is a linear function of the equilibrium concentration $[\text{IO}_4^-]_{\text{eq}}$ (eqn (3))

$$k_{\text{exp}} = k(\text{HIO}_4) + \{[\text{IO}_4^-]_{\text{eq}} (k(\text{IO}_4^-) - k(\text{HIO}_4))/c\} \quad (3)$$

where c is the total concentration of the oxidation agent. The rate constants $k(\text{IO}_4^-) = (317 \pm 27) \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ and $k(\text{HIO}_4) = (6.8 \pm 1.5) \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ were determined from the linear dependence $k_{\text{exp}} = f([\text{IO}_4^-]_{\text{eq}})$.

The deprotonated form of the oxidation agent must prevail in the 1×10^{-3} — $5 \times 10^{-3} \text{ mol dm}^{-3}$ concentration range of HClO_4 . In this interval, equilibrium (A) is predominantly in operation. A little conspicuous change in reaction rate in this interval indicates a small difference between reactivity of the protonated and deprotonated form of the complex ion. Owing to the narrow interval of perchloric acid concentration, it was possible to estimate only the ratio of rate constants for the reaction of the periodate ion with the deprotonated and protonated form of the complex ion ($k_{\text{deprot}}/k_{\text{prot}} = 1.1$ — 1.3). The dependence $k = f(\text{HClO}_4)$ is predominantly affected by the acid-base equilibrium of the oxidation agent. The smaller reactivity of HIO_4 is evidently due to electrostatic interactions the influence of which is lower if an uncharged particle enters into the rate-determining step.

The dependence of activation enthalpy ΔH^\ddagger and activation entropy ΔS^\ddagger changes most in that region of HClO_4 concentration where equilibrium (B) manifests itself. A similar dependence of ΔH^\ddagger and ΔS^\ddagger was obtained for oxidation of $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ by periodate [8]. The values of ΔH^\ddagger and ΔS^\ddagger involve the change of dissociation constants K_1 and K_2 with temperature.

The effect of ionic strength on oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion was investigated in the medium of $c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$ (Table 2) and $10^{-1} \text{ mol dm}^{-3}$. It results from the values of the dissociation constants K_1 and K_2 that the protonated forms of both reactants prevail in the medium of $c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$, i.e. the bivalent cation $[\text{CoCySOH}(\text{en})_2]^{2+}$ enters into reaction with an uncharged particle HIO_4 , owing to which the primary

Table 2

Dependence of rate constant on ionic strength for oxidation of the cysteinato-bis(ethylenediamine)-cobalt(III) ion by periodate

$$c([\text{CoCySO}(\text{en})_2]\text{ClO}_4) = 1.1 \times 10^{-4} \text{ mol dm}^{-3}, c(\text{NaIO}_4) = 10^{-3} \text{ mol dm}^{-3}, c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}; T = 278.8 \text{ K}$$

$\frac{I}{\text{mol dm}^{-3}}$	$\frac{k}{\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3}$	$\frac{I}{\text{mol dm}^{-3}}$	$\frac{k}{\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3}$
0.011	94.9 ± 3.5	0.251	60.0 ± 0.9
0.051	79.8 ± 3.0	0.411	56.0 ± 1.1
0.091	71.1 ± 2.0	1.011	48.0 ± 1.3
0.171	65.8 ± 1.0	—	—

salt effect should not appear. The rate constant has not practically changed in the 0.111—0.611 mol dm⁻³ range of ionic strength, which is in agreement with the above assumption. On the other hand, a negative primary salt effect has been observed in the medium of $c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$ because two ions with opposite charges react in this case. The relationship $\log \{k\} = f\{I\}^{1/2}/(\{I\}^{1/2} + 1)$ is linear, the slope being -0.77 . Because of protonation equilibria of both reactants, the slope found experimentally cannot be compared with the theoretical one.

Moreover, the influence of cosolvent on the rate constant of the investigated reaction was studied in the water—acetone, water—*tert*-butyl alcohol, water—*iso*-propyl alcohol, and water—acetonitrile mixtures (Fig. 1). A small change in rate constant was observed at low values of the mole fraction of cosolvent for all mixed solvents. The rate constant decreased in the water—acetone and water—acetonitrile mixtures with higher concentration of the nonaqueous component more remarkably than in the water—*tert*-butyl alcohol and water—*iso*-propyl alcohol mixtures. The different course of the dependences $\log \{k\} = f(x_2)$ for $x_2 > 0.1$ of individual solvents is not connected with the classification of solvents into typically aqueous and typically nonaqueous ones [8] since acetone, *tert*-butyl alcohol, and *iso*-propyl alcohol belong among typically aqueous and acetonitrile among typically nonaqueous solvents.

The dependence of rate constant on concentration of the cosolvent was investigated in more detail in the water—*tert*-butyl alcohol and water—acetone mixtures from the view-point of its effect on activation parameters of the reaction. The temperature dependence of rate constant for individual concentrations of the nonaqueous component was measured in the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$, $10^{-2} \text{ mol dm}^{-3}$, and $10^{-1} \text{ mol dm}^{-3}$ (Table 3). The activation enthalpy in both investigated mixtures decreased monotonously in the medium of

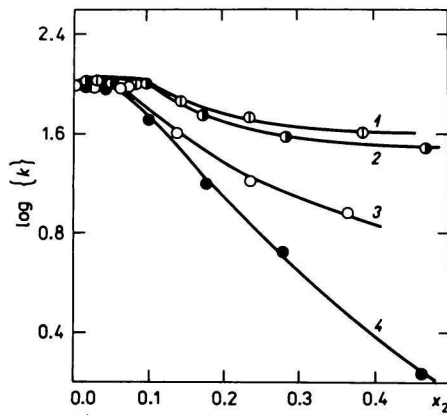


Fig. 1. Dependence of rate constant on concentration of the cosolvent for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate.

1. *tert*-Butyl alcohol; 2. isopropyl alcohol; 3. acetonitrile; 4. acetone.

$$c([\text{CoCySO}(\text{en})_2]\text{ClO}_4) = 1.1 \times 10^{-4} \text{ mol dm}^{-3}, c(\text{NaIO}_4) = 10^{-3} \text{ mol dm}^{-3}, c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}, T = 278.8 \text{ K}.$$

Table 3

Values of rate constants, activation enthalpies ΔH^\ddagger and activation entropies ΔS^\ddagger for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate in the water—acetone and water—*tert*-butyl alcohol mixtures at different concentrations of perchloric acid

$$c([\text{CoCySO}(\text{en})_2]\text{ClO}_4) = 1.1 \times 10^{-4} \text{ mol dm}^{-3}, c(\text{NaIO}_4) = 10^{-3} \text{ mol dm}^{-3}; T = 298.2 \text{ K}$$

	$\frac{k}{\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{J mol}^{-1} \text{ K}^{-1}}$
Acetone			
$c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$			
0	361.9 ± 16.5	40.0 ± 1.8	-70 ± 6
0.027	285.9 ± 9.0	33.3 ± 1.7	-94 ± 6
0.058	193.3 ± 7.2	33.0 ± 1.4	-98 ± 5
0.096	107.0 ± 5.5	32.1 ± 1.7	-106 ± 6
0.141	81.0 ± 2.9	41.9 ± 1.3	-76 ± 4
$c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$			
0	317.5 ± 3.2	38.6 ± 1.3	-67 ± 4
0.021	209.8 ± 3.4	31.4 ± 1.3	-93 ± 9
0.044	153.1 ± 3.4	19.5 ± 2.8	-136 ± 9
0.101	101.7 ± 1.8	20.9 ± 2.2	-136 ± 7
0.176	40.3 ± 0.9	29.5 ± 1.5	-114 ± 5
$c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$			
0	80.0 ± 2.2	74.8 ± 1.6	34 ± 5
0.027	92.5 ± 1.7	71.9 ± 2.0	26 ± 7

Table 3 (Continued)

	$\frac{k}{\text{mol}^{-1} \text{s}^{-1} \text{dm}^3}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{J mol}^{-1} \text{K}^{-1}}$
0.058	86.4 ± 1.5	59.7 ± 1.3	-16 ± 4
0.096	60.1 ± 2.2	50.8 ± 1.9	-49 ± 6
0.141	37.0 ± 0.9	43.7 ± 1.7	-76 ± 6
<i>tert</i> -Butyl alcohol			
$c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$			
0.021	364.0 ± 14.7	33.1 ± 1.6	-93 ± 6
0.046	301.7 ± 16.0	25.6 ± 1.8	-117 ± 6
0.076	220.7 ± 11.2	31.5 ± 2.0	-102 ± 7
0.113	174.7 ± 4.2	41.2 ± 1.8	-72 ± 6
$c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$			
0.016	343.2 ± 6.4	33.8 ± 2.2	-83 ± 7
0.034	321.4 ± 4.3	19.4 ± 1.2	-132 ± 4
0.078	222.6 ± 6.6	22.8 ± 1.6	-123 ± 6
0.142	138.9 ± 7.8	21.4 ± 3.3	-131 ± 11
$c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$			
0.021	110.9 ± 0.8	71.3 ± 0.7	25 ± 3
0.046	123.1 ± 4.1	67.6 ± 1.5	14 ± 5
0.076	107.9 ± 5.5	54.1 ± 2.0	-33 ± 7
0.113	89.0 ± 2.5	50.7 ± 1.3	-46 ± 4

$c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$. A minimum in the dependence $\Delta H^\ddagger = f(x_2)$ was observed in the medium of $c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$ and $10^{-3} \text{ mol dm}^{-3}$. At higher concentrations of the cosolvent, the activation enthalpy increased more remarkably in the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$ than in the medium of $c(\text{HClO}_4) = 10^{-2} \text{ mol dm}^{-3}$. The minimum in the dependence $\Delta H^\ddagger = f(x_2)$ for the water—*tert*-butyl alcohol mixture is at $x_2^* \approx 0.04$ and for the water—acetone mixture at $x_2^* \approx 0.06$, which is consistent with our knowledge of the influence of these cosolvents on water structure [9]. An addition of cosolvent may result in build up of the water structure which has been attributed to the formation of clathrates of type II with participation of the cosolvent. Further addition of the cosolvent produces a breakdown of the clathrates [10]. A similar character of the dependence $\Delta H^\ddagger = f(x_2)$ as observed in the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$ and $10^{-2} \text{ mol dm}^{-3}$ was found by investigating many other reactions [9].

The variation of activation parameters due to the transfer from water to mixed medium is mainly caused by a change in solvation of the reactants and activated complex as well. Some information about the change in solvation may be obtained from transfer functions (calculated from solubilities) and change in the Gibbs energy $\delta_m \Delta G^\ddagger$ (Table 4). The change in chemical potential of the dissolved substance due to a change in its solvation on going from water to mixed solvent reflects the degree of its stabilization in a given solvent [11]. The solubility of a salt

Table 4

Solubility of KIO_4 and $[\text{CoCySO}(\text{en})_2]\text{ClO}_4$, Gibbs transfer energies $\delta_m\mu(\text{HIO}_4)$, $\delta_m\mu(\text{IO}_4^-)$, $\delta_m\mu([\text{CoCySO}(\text{en})_2]^+)$, $\delta_m\mu([\text{CoCySOH}(\text{en})_2]^{2+})$ in the water—acetone (a) and water—*tert*-butyl alcohol (b) mixtures at 298.2 K

$\varphi/\text{vol. } \%$	$\frac{S(\text{KIO}_4) \cdot 10^2}{\text{mol dm}^{-3}}$		$\frac{\delta_m\mu(\text{IO}_4^-)}{\text{kJ mol}^{-1}}$		$\frac{\delta_m\mu(\text{HIO}_4)}{\text{kJ mol}^{-1}}$	
	a	b*	a	b	a	b
0	2.26	2.26	—	—	-0.6	0.7
10	2.13	1.63	2.1	2.9	-1.3	0.9
20	2.10	1.43	3.9	6.7	-2.0	-0.5
30	2.18	1.41	5.4	7.8	-2.0	-0.5
40	2.38	1.29	6.9	6.5	-3.0	-1.7

$\varphi/\text{vol. } \%$	$\frac{S([\text{CoCySO}(\text{en})_2]\text{ClO}_4) \cdot 10^2}{\text{mol dm}^{-3}}$		$\frac{\delta_m\mu([\text{CoCySO}(\text{en})_2]^+)}{\text{kJ mol}^{-1}}$		$\frac{\delta_m\mu([\text{CoCySOH}(\text{en})_2]^{2+})}{\text{kJ mol}^{-1}}$	
	a	b	a	b	a	b
0	0.96	0.96	—	—	—	—
10	0.93	0.77	-1.7	-2.2	-4.4	-4.4
20	0.93	0.58	-3.6	-5.6	-8.8	-10.7
30	0.95	0.51	-4.6	-7.0	-13.0	-14.9
40	0.99	0.45	-6.4	-6.0	-16.3	-14.4

* Ref. [8].

in water $s(w)$ and mixed solvent $s(x)$ is related to the difference in chemical potential $\delta_m\mu(\text{salt})$ according to eqn (4) where $\gamma_{\pm}(w)$ and $\gamma_{\pm}(x)$ are molar activity coefficients

$$\delta_m\mu(\text{salt}) = \mu(\text{salt}, x) - \mu(\text{salt}, w) = nRT \ln (s(w)\gamma_{\pm}(w)/s(x)\gamma_{\pm}(x)) \quad (4)$$

for $[\text{CoCySO}(\text{en})_2]\text{ClO}_4$ and KIO_4 , $n = 2$.

The change in chemical potential $\delta_m\mu(\text{salt})$ was calculated on the assumption that $\gamma_{\pm}(w)/\gamma_{\pm}(x) \approx 1$. Provided the values of solubility are small, this assumption may be admitted like in papers [3, 12]. The transfer function of the periodate ion was calculated from the difference between the transfer functions of the salt and potassium ion according to eqn (5)

$$\delta_m\mu(\text{KIO}_4) = \delta_m\mu(\text{IO}_4^-) + \delta_m\mu(\text{K}^+) \quad (5)$$

The transfer function $\delta_m\mu(\text{HIO}_4)$ was obtained as the sum of $\delta_m\mu(\text{IO}_4^-)$ and $\delta_m\mu(\text{H}^+)$. The values of $\delta_m\mu(\text{K}^+)$ and $\delta_m\mu(\text{H}^+)$ are known from literature for the water—acetone [13] and water—*tert*-butyl alcohol [14] mixtures. The transfer function of the protonated form of the complex ion was calculated in a similar way. The kinetic data were used for calculating the change in the Gibbs energy $\delta_m\Delta G^+$ which is, according to eqn (6), equal to the difference between the solvation effects

of the transition state $\delta_m\mu^\ddagger$ and initial state $\delta_m\mu_i$.

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - [\delta_m\mu(\text{complex}) + \delta_m\mu(\text{ox})] \quad (6)$$

where (complex) = $[\text{CoCySO}(\text{en})_2]^+$ and $[\text{CoCySOH}(\text{en})_2]^{2+}$, (ox) = IO_4^- and HIO_4 . The dependence of the transfer functions on concentration of the cosolvent is represented in Figs. 2—5.

In the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$ the reactants are predominantly in the deprotonated form and the values of their transfer functions (Table 4) indicate destabilization of the periodate ion, while the complex ion is stabilized. The degree of stabilization of the complex and destabilization of the oxidation agent is comparable for both reactants, from which a small change $\delta_m\mu_i$ results. The change $\delta_m\Delta G^\ddagger$ is given by the change in transfer function of the activated complex which is destabilized. From the plots $\delta_m\mu_i$ and $\delta_m\mu^\ddagger$ in Figs. 2 and 3, we may see that a change in solvation of the initial state and activated complex manifests itself mainly at higher concentrations of the cosolvent. A shift in equilibrium of the reactants in favour of the protonated form due to increasing concentration of the cosolvent may appear in this medium. The course of the dependence $\Delta H^\ddagger = f(x_2)$ suggests that this effect is not operative in a decisive manner.

The reactants prevalingly occur in the medium of $c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$ in the protonated form. The transfer function of periodic acid changes very little when compared with the transfer function of the complex ion. The complex ion is fairly

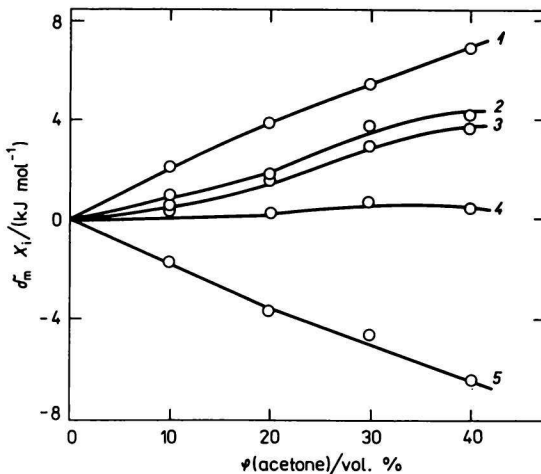


Fig. 2. Effect of solvent on reactivity of the initial and transition state for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate in the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$ and water—acetone mixture at 298.2 K.

1. $\delta_m\mu(\text{IO}_4^-)$; 2. $\delta_m\mu^\ddagger$; 3. $\delta_m\Delta G^\ddagger$; 4. $\delta_m\mu_i$; 5. $\delta_m\mu([\text{CoCySO}(\text{en})_2]^+)$.

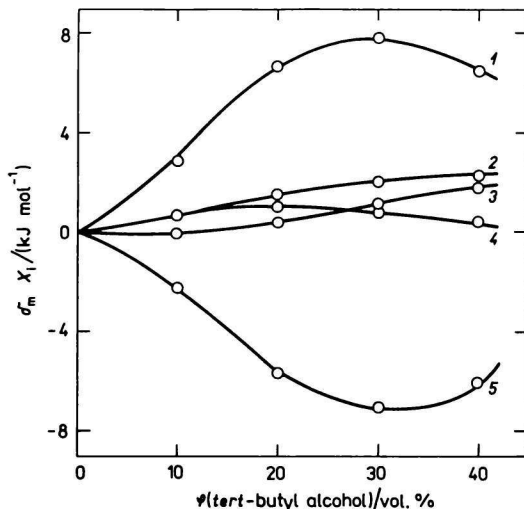


Fig. 3. Effect of solvent on reactivity of the initial and transition state for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate in the medium of $c(\text{HClO}_4) = 10^{-3} \text{ mol dm}^{-3}$ and water—*tert*-butyl alcohol mixture at 298.2 K.
 1. $\delta_m \mu(\text{IO}_4^-)$; 2. $\delta_m \mu^+$; 3. $\delta_m \Delta G^+$; 4. $\delta_m \mu_i$; 5. $\delta_m \mu([\text{CoCySO}(\text{en})_2]^+)$.

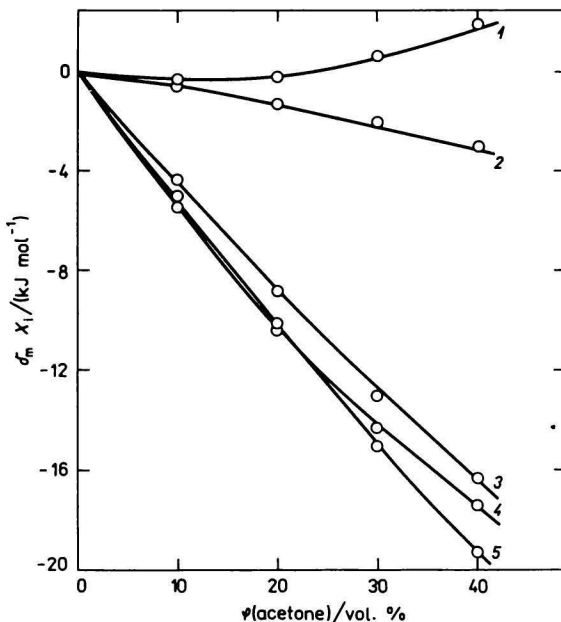


Fig. 4. Effect of solvent on reactivity of the initial and transition state for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate in the medium of $c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$ and water—acetone mixture at 298.2 K.
 1. $\delta_m \Delta G^+$; 2. $\delta_m \mu(\text{HIO}_4)$; 3. $\delta_m \mu([\text{CoCySOH}(\text{en})_2]^{2+})$; 4. $\delta_m \mu^+$; 5. $\delta_m \mu_i$.

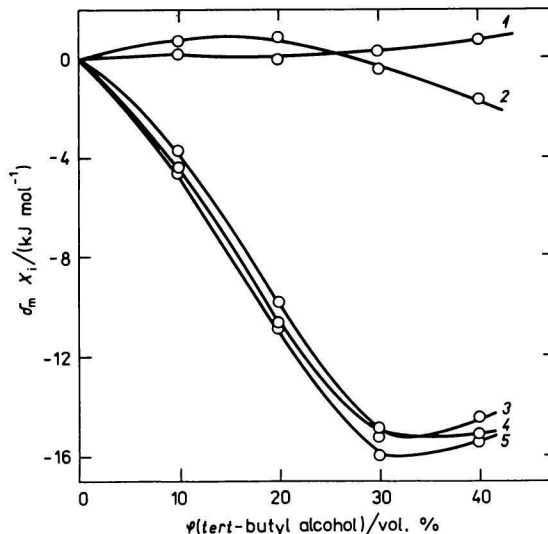


Fig. 5. Effect of solvent on reactivity of the initial and transition state for oxidation of the cysteinato-bis(ethylenediamine)cobalt(III) ion by periodate in the medium of $c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$ and water—*tert*-butyl alcohol mixture at 298.2 K.

1. $\delta_m \Delta G^\ddagger$; 2. $\delta_m \mu(\text{HIO}_4)$; 3. $\delta_m \mu([\text{CoCySOH}(\text{en})_2]^{2+})$; 4. $\delta_m \mu^\ddagger$; 5. $\delta_m \mu_i$.

stabilized in both media. The changes $\delta_m \mu_i$ and $\delta_m \mu^\ddagger$ are comparable in the whole interval of concentration of the cosolvent (Figs. 4 and 5), owing to which the change in the Gibbs energy $\delta_m \Delta G^\ddagger$ is small. A remarkable decrease in ΔH^\ddagger and ΔS^\ddagger with concentration of the cosolvent may be due to a change in structure of the solvation shell of the complex ion produced by solvation of the carboxyl group of the cysteine ligand. A similar course of the dependence of ΔH^\ddagger and ΔS^\ddagger on concentration of *tert*-butyl alcohol in the medium of $c(\text{HClO}_4) = 10^{-1} \text{ mol dm}^{-3}$ was also observed for oxidation of the cysteinesulfenato-bis(ethylenediamine)cobalt(III) ion by periodate where the complex ion undergoes acid-base equilibrium [15]. The oxidation of the pentamine-isothiocyanatocobalt(III) ion, which does not participate in an acid-base equilibrium, by periodate gives rise to a minimum in the dependence $\Delta H^\ddagger = f(x_2)$ for the water—*tert*-butyl alcohol mixture in the medium of $c(\text{HClO}_4) = 3 \times 10^{-1} \text{ mol dm}^{-3}$ at $x_2 = x_2^*$, which supports the above assumption.

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