Influence of medium on the kinetics of oxidation of the *cis*- and *trans*-bis(ethylenediamine)chloroisothiocyanatocobalt(III) ions by the cerium(IV) ions and peroxodisulfate

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The kinetics of oxidation of the *cis*- and *trans*-[Co(en)$_2$Cl(NCS)]$^+$ ions by the cerium(IV) ions and peroxodisulfate was investigated from the view-point of the influence of supporting electrolytes and nonaqueous component of solvent. The experimental results may be only partially interpreted on the basis of electrostatic theory. There are specific interionic interactions which manifest themselves significantly in the oxidation by the cerium(IV) ions. The relative permittivity is not regulating the course of reactions in mixed solvents. The reaction mixture was analyzed by ion-exchange technique and by means of resolution of pertinent absorption bands into Gaussian components.

Изучена кинетика окисления *цис*- и *транс*-[Co(en)$_2$Cl(NCS)]$^+$ ионов ионами Ce^{4+} и пероксидисульфатом с точки зрения влияния электролитов-носителей и неводного компонента растворителя. Результаты эксперимента можно лишь отчасти интерпретировать в рамках электростатической теории. В случае окисления ионами церия явно проявляются специфические межионные взаимодействия. При протекании реакций в смеси растворителей относительная проницаемость не служит решающим фактором. Реакционная смесь анализировалась на ионообменниках и разложением ее полос поглощения на Гауссовы составляющие.

The kinetics of oxidation of the coordinated isothiocyanate ion was formerly investigated for several cobalt(III) complexes by using peroxodisulfate, periodate, and hydrogen peroxide as oxidizing agents [1—11]. The cerium(IV) ions have not yet been used for studying these reactions. In some cases, the products of oxidation were analyzed in more detail and the experimental results were evaluated from the view-point of the theory of kinetic primary salt effect. Nevertheless, only qualitative agreement with the conclusions of electrostatic theory of ionic reactions in solution was thus obtained [7, 9—11]. The results of these investigations confirm the assumption that there are specific interactions between the ions present in

reaction systems which affect the kinetic parameters. These interactions are to be especially expected in case the reacting ions have like sign as it is in the reaction of the bis(ethylenediamine)chloroisothiocyanatocobalt(III) ions with the cerium(IV) ions. Further information about the character of interactions of reacting particles may be obtained by studying the influence of solvent and its composition. These facts were determining for the selection of investigated reactions and choice of experiments the aim of which was to obtain information about the influence of medium on the rate and activation parameters as well as the possibility of using them for the elucidation of properties of the activated complex.

Experimental

The complex salts *cis*-[Co(en)₂Cl(NCS)]Cl and *trans*-[Co(en)₂Cl(NCS)]SCN were prepared according to [12], other chemicals were anal. grade reagents. The absorption spectra were taken with a recording spectrophotometer Specord UV VIS (Zeiss, Jena) whereas the current kinetic measurements were performed with a spectrophotometer Spectromom 202 (MOM, Budapest). The reactions took place in a thermostatted reaction vessel (accuracy of thermostatting $\pm 0.1°$) from which the samples were taken in certain time intervals. The absorbance of these samples was measured immediately after sampling. The fractionation of the reaction mixtures obtained in the course of 10 reaction half-times was carried out on a column of ion exchanger Dowex 50WX8 (200—400 mesh) in H⁺ form, the dimensions of column being 7×1 cm. Hydrochloric acid of 1 mol dm⁻³ or 3 mol dm⁻³ was used as eluting agent. A solution with absorption maxima at 20 450 cm⁻¹ and 28 700 cm⁻¹ (488 nm and 348 nm) was obtained by elution of the *cis* isomer with 3 mol dm⁻³ HCl after reaction. Similarly, a solution with absorption maxima at 18 852 cm⁻¹ and 21 832 cm⁻¹ (530 nm and 458 nm) was obtained by separating the reaction mixture after reaction of the *trans* isomer.

Results and discussion

The absorption spectra of the *cis*- and *trans*-bis(ethylenediamine)chloro-isothiocyanatocobalt(III), cerium(IV), and peroxodisulfate ions are shown in Fig. 1. In view of the absorption of individual components of reaction systems and the variation of absorption with time, the oxidation was investigated by measuring the decrease in absorbance at 19 800 cm⁻¹ (505 nm) for the cerium(IV) ions and at 36 000 cm⁻¹ (278 nm) for the peroxodisulfate ions. The oxidation by these two oxidizing agents is governed by the following rate equations

$$-\frac{d[Co(en)_2Cl(NCS)^+]}{dt} = k\,[Co(en)_2Cl(NCS)^+]\,[Ce^{4+}] \qquad (1)$$

$$-\frac{d[Co(en)_2Cl(NCS)^+]}{dt} = k\,[Co(en)_2Cl(NCS)^+]\,[S_2O_8^{2-}] \qquad (2)$$

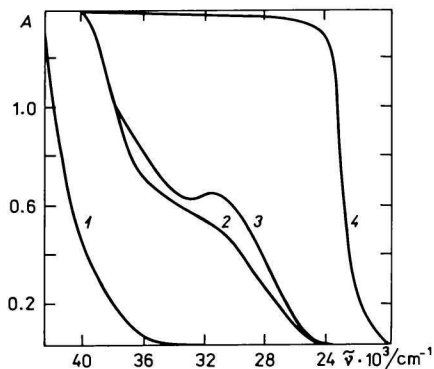*Fig. 1.* Absorption spectra of reactants in ultraviolet region.
1. 1.44×10^{-2} mol dm^{-3} Na$_2$S$_2$O$_8$; *2.* 3.5×10^{-4} mol dm^{-3} *cis*-[Co(en)$_2$Cl(NCS)]Cl; *3.* 3.5×10^{-4} mol dm^{-3} *trans*-[Co(en)$_2$Cl(NCS)]SCN; *4.* 6.0×10^{-2} mol dm^{-3} Ce(SO$_4$)$_2$. Cell width 1.00 cm.
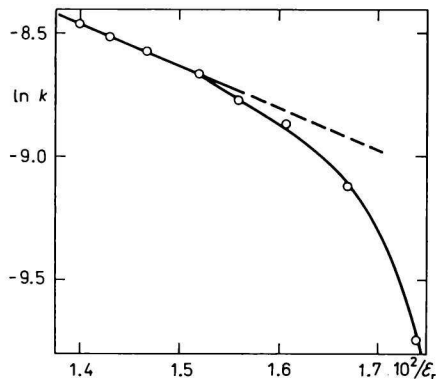
Fig. 2. Variation of the logarithm of rate constant for oxidation of the *cis*-[Co(en)$_2$-Cl(NCS)]$^+$ ion by peroxodisulfate with reciprocal value of relative permittivity in water—methyl alcohol mixtures.
3.5×10^{-4} mol dm^{-3} *cis*-[Co(en)$_2$Cl(NCS)]Cl, 1.44×10^{-2} mol dm^{-3} Na$_2$S$_2$O$_8$; temperature 313 K.

Eqns *(1)* and *(2)* are valid for the *cis* isomer as well as *trans* isomer of the investigated complex. The oxidizing agent was always in considerable excess with respect to the complex and the reactions were of the pseudo-first order. The rate constants were calculated from the measured changes in absorbance by the use of the *Guggenheim* method [13] and the constant time interval was not greater than the reaction half-time. The greatest relative error of rate constant was 6 % (error of the mean of independent measurements).

Influence of supporting electrolytes

The dependence of experimental rate constant for oxidation of the *cis*-[Co(en)$_2$Cl(NCS)]$^+$ ions by the cerium(IV) ions on the character and concentration of supporting electrolytes is presented in Table 1 while the analogous dependence for oxidation of the *trans*-[Co(en)$_2$Cl(NCS)]$^+$ ions is in Table 2. It results from these tables that the rate constant increased with electrolyte concentration in the presence of all investigated supporting electrolytes, which is consistent with its expected dependence on ionic strength in accordance with the theory of primary salt effect. Though the measured values are in agreement with eqn *(3)* and the dependence log $k = $ f(I) is linear, we cannot draw conclusions about the charge product of reacting ions because the ionic strength is too high ($I = 1.6$—2.2 mol dm^{-3})

$$\log k = \log k_0 + \frac{2Az_A z_B I^{1/2}}{1 + I^{1/2}} \qquad (3)$$

(A is the Debye—Hückel constant and $z_A z_B$ is the charge product of reacting ions.)

As evident from Tables 1 and 2, the experimental rate constants have different values at equal ionic strengths adjusted by means of different electrolytes, which is the result of specific influence of anions in the reaction system (all used supporting electrolytes were in the form of sodium salts). The increase in rate constant with concentration of supporting electrolytes may be due to the formation of ion pairs while both reactants may associate, *i.e.* the complex cation as well as the cerium(IV) cation and the following equilibria are established in the solution

$$[Co(en)_2Cl(NCS)]^+ + X^- \rightleftharpoons [Co(en)_2Cl(NCS)]^+, X^- \qquad (4)$$

$$Ce^{4+} + X^- \rightleftharpoons Ce^{4+}, X^- \qquad (5)$$
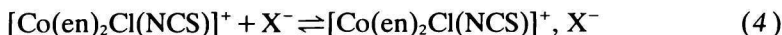
The ion pair of the reacting complex ion with univalent anion is an uncharged particle while the ion pair formed by association of the complex ion with the sulfate ion has negative charge. In either case, the Coulomb repulsive forces between reacting ions decrease or vanish owing to association. For this reason, we must take into account the fact that the charge of the cerium(IV) ion is also reduced by association. The different influence of supporting electrolytes on both isomers is also interesting. A comparison of the data in Table 1 and Table 2 leads to the conclusion that the influence of sodium chloride on reaction rate is lower for the *trans* isomer than for the *cis* isomer. This result as well as pertinent interpretation

Table 1

Rate constants for oxidation of the *cis*-$[Co(en)_2Cl(NCS)]^+$ ions by the cerium(IV) ions as a function of concentration of supporting electrolytes

$c_{complex} = 3 \times 10^{-3}$ mol dm^{-3}, $c_{Ce(SO_4)_2} = 6 \times 10^{-2}$ mol dm^{-3}, $c_{H_2SO_4} = 3 \times 10^{-1}$ mol dm^{-3}, temperature 303 K

c/mol dm^{-3}		$k \cdot 10^4$/s^{-1}	c/mol dm^{-3}		$k \cdot 10^4$/s^{-1}
	Na$_2$SO$_4$			NaCl	
0.05		4.90	0.30		7.59
0.10		6.25	0.50		10.5
0.15		7.76		NaClO$_4$	
0.20		9.44	0.05		4.12
	NaCl		0.10		4.27
0.05		4.27	0.15		4.79
0.10		4.95	0.20		4.90
0.15		5.50	0.30		5.75
0.20		6.61	0.50		7.08

Table 2

Rate constants for oxidation of the trans-$[Co(en)_2Cl(NCS)]^+$ ions by the cerium(IV) ions as a function of concentration of supporting electrolytes

$c_{complex} = 3 \times 10^{-3}$ mol dm^{-3}, $c_{Ce(SO_4)_2} = 6 \times 10^{-2}$ mol dm^{-3}, $c_{H_2SO_4} = 2 \times 10^{-1}$ mol dm^{-3},   temperature 303 K

c/mol dm^{-3}		$k \cdot 10^4/s^{-1}$	c/mol dm^{-3}		$k \cdot 10^4/s^{-1}$
	NaCl			NaNO$_3$	
0.05		3.18	0.10		3.23
0.10		3.54	0.20		3.41
0.20		4.20		Na$_2$SO$_4$	
	NaClO$_4$		0.20		0.99
0.20		2.79	—		—

is in harmony with the revelation concerning the influence of spatial configuration of the complex cation on the value of association constant with an anion [14, 15]. The temperature dependence of the rate constant of oxidation of the cis-$[Co(en)_2Cl(NCS)]^+$ ions by the cerium(IV) ions was investigated in the temperature interval 293—308 K whereas the rate constant of oxidation of the trans isomer was investigated in the region of 293—313 K. The relationships between rate constants and temperature were used for calculating the values of thermodynamic activation parameters. Thus it was obtained $\Delta H^{\ddagger} = 58.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -116$ J mol^{-1} K^{-1} for the cis isomer and $\Delta H^{\ddagger} = 63.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -104$ J mol^{-1} K^{-1} for the trans isomer. The ionic strength was equal in both cases, i.e. $I = 1.323$ mol dm^{-3}.

The influence of ionic strength and temperature on the rate constant of oxidation of the cis-$[Co(en)_2Cl(NCS)]^+$ ions by peroxodisulfate was thoroughly investigated earlier [8] and analogous results obtained with the trans isomer are given in Table 3. The dependence of rate constant on ionic strength was governed at all experimental temperatures by eqn (6) [16].

$$\log k_0' = \log k_0 + CI \qquad (6)$$

The values of constant C/dm^3 mol^{-1} were 0.2, 1.0, 1.1, and 1.3 for temperatures θ/K 308, 318, 323, and 328, respectively. The values of rate constants extrapolated to zero ionic strength were obtained from eqn (6) and the temperature dependence of these rate constants was used for calculating the extrapolated values of thermodynamic activation parameters, $\Delta H_0^{\ddagger} = 65.0$ kJ mol^{-1} and $\Delta S_0^{\ddagger} = -106$ J mol^{-1} K^{-1}.

It results from the above data that the values of activation enthalpies and activation entropies are very near for a given isomer irrespective whether the cerium(IV) or peroxodisulfate ions have been used as oxidizing agent. In all cases,

Table 3

Rate constants for oxidation of the trans-[Co(en)$_2$Cl(NCS)]$^+$ ions by peroxodisulfate as a function of ionic strength[a] and temperature

$c_{complex} = 3.5 \times 10^{-4}$ mol dm^{-3}, $c_{Na_2S_2O_8} = 1.44 \times 10^{-2}$ mol dm^{-3}

T/K	I/mol dm^{-3}	$k \cdot 10^4$/s^{-1}	T/K	I/mol dm^{-3}	$k \cdot 10^4$/s^{-1}
308	0.043	0.88	323	0.073	3.02
308	0.093	0.67	323	0.093	2.83
308	0.143	0.56	323	0.193	2.56
318	0.043	2.13	328	0.043	4.32
318	0.093	1.95	328	0.093	4.00
318	0.143	1.93	328	0.143	3.81
318	0.193	1.68	328	0.193	3.63
323	0.043	3.12	—	—	—

a) Ionic strength was adjusted by adding sodium perchlorate.

the activation entropy has negative sign, which is in contradiction with the simple electrostatic theory as regards the oxidation by peroxodisulfate and in harmony with this theory as regards the oxidation by the cerium(IV) ions. The model of solid charged spheres [17] gives the subsequent eqn (7) for the activation entropy of a reaction between ions with charge numbers z_A, z_B in a medium with permittivity ε

$$\Delta S^+ = -\frac{N_A z_A z_B e^2 L}{4\pi\varepsilon d_{AB}} \qquad (7)$$

where N_A, e, L, and d_{AB} are the Avogadro constant, electron charge, Abegg constant, and the sum of radii of reacting ions, respectively. As it is valid $z_A z_B < 0$ for the reaction of the complex ions with the peroxodisulfate ions, the activation entropy ought to be positive. For the reaction of the complex ions with the cerium(IV) ions, it holds $z_A z_B > 0$ and eqn (7) can be used. It is evident that the calculated distance d_{AB} which may be in this case regarded as identical with the critical interionic distance must be significantly dependent on the value of product $z_A z_B$ used for calculation. For $z_A z_B = 4$, we obtain $d_{AB} = 0.28$ nm for oxidation of the cis isomer in aqueous medium at 300 K, which is a plausible value. This value of $z_A z_B$ is, however, little probable for the above-mentioned reasons. The real value of $z_A z_B$ may be considerably reduced by association of the cations reacting with the anions of reaction system. If we insert e.g. $z_A z_B = 2$ into eqn (7) (i.e. a reaction of the associate CeSO$_4^{2+}$ with the complex cation is assumed), we obtain $d_{AB} = 0.14$ nm, which is a too low value with respect to size of the reacting ions. The experimental value of activation entropy corresponds to an increased order in the activated complex and its near environment when compared with the initial state of system. As both reactants in the oxidation by the cerium(IV) ions have the charge

of equal sign, the activated complex must have a greater charge and higher electrostatic forces must be effective in its environment than those in the environment of the reacting ions themselves. This fact involves a greater degree of orientation of the water dipoles in the solvate sphere of the activated complex. In addition to an increased order due to the effect of a stronger electric field in vicinity· of the activated complex, a formation of complexes containing stronger bond between the cerium(IV) ions and isothiocyanate group of the complex ion like in other oxidation reactions involving the cerium(IV) ions, is also possible [18]. A greater degree of arrangement in the activated complex may be expected in the oxidation by peroxodisulfate with pertinent consequence, *i.e.* a negative value of activation entropy.

The results obtained by investigating the influence of supporting electrolytes on the kinetics of both these reactions examined at different temperatures confirm the experience that the specific interactions among the components of reaction system show themselves most explicitly in the values of activation parameters.

Solvent effect

The deficiency of the simple electrostatic theory to interpret the obtained experimental results is also disclosed by the measurements of the kinetic parameters of oxidation of both complexes by peroxodisulfate in mixed aqueous—nonaqueous media (Tables 4 and 5). Eqn (8) expressing the relation between the rate

Table 4

Rate constants for oxidation of the cis-[Co(en)$_2$Cl(NCS)]$^+$ ions by peroxodisulfate as a function of mole fraction x_2 of nonaqueous component of solvent

$c_{complex} = 3.5 \times 10^{-4}$ mol dm^{-3}, $c_{Na_2S_2O_8} = 1.44 \times 10^{-2}$ mol dm^{-3}, temperature 313 K

x_2	$k \cdot 10^4/s^{-1}$	x_2	$k \cdot 10^4/s^{-1}$
Methyl alcohol		Isopropyl alcohol	
0.023	2.13	0.091	1.44
0.047	2.01	0.135	1.18
0.073	1.91	0.189	0.68
0.100	1.73	tert-Butyl alcohol	
0.129	1.55	0.10	2.03
0.160	1.41	0.021	1.70
0.193	1.08	0.032	1.50
0.229	0.61	0.045	1.42
Isopropyl alcohol		0.075	1.32
0.025	2.06	0.112	1.24
0.055	1.90	0.159	0.97

Table 5

Rate constants for oxidation of the trans-[Co(en)$_2$Cl(NCS)]$^+$ ions by peroxodisulfate as a function of mole fraction x_2 of nonaqueous component of solvent
$c_{complex} = 3.5 \times 10^{-4}$ mol dm^{-3}, $c_{Na_2S_2O_8} = 1.44 \times 10^{-2}$ mol dm^{-3}, temperature 323 K

x_2	$k \cdot 10^4/s^{-1}$	x_2	$k \cdot 10^4/s^{-1}$
Isopropyl alcohol		tert-Butyl alcohol	
0.0097	2.78	0.0204	2.53
0.0200	2.59	0.0395	1.77
0.0309	2.80	0.0617	2.26
0.0398	2.90	0.0809	2.37
0.0621	2.97	0.1030	2.48
0.0836	2.90	0.1473	2.50

constant and relative permittivity of solvent is to a certain extent consistent only with oxidation of the cis isomer in the medium water—methyl alcohol (k is the Boltzmann constant, r_0 is the critical interionic distance and other symbols have equal meaning as in preceding equations).

$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{4\pi\varepsilon_0\varepsilon_r kTr_0} \qquad (8)$$

It results from Fig. 2 that the function $\ln k = f(1/\varepsilon_r)$ is linear and in harmony with eqn (8) only for higher values ε_r, i.e. for low concentrations of methyl alcohol. The specific influence of cosolvent evidently manifests itself at higher concentrations and the relationship loses its validity. The linear section in Fig. 2 enables us to calculate the critical interionic distance r_0 for which we obtain 0.64 nm, i.e. a plausible value with respect to the size of the reacting ions. As for the trans isomer, the plots $k = f(x_2)$ go through a minimum at low content of isopropyl alcohol or tert-butyl alcohol ($x_2 = 0.020$ or $x_2 = 0.039$; Table 5). This fact may be due to a change in cluster structure of water which takes place at low concentrations of nonaqueous cosolvents [19]. An addition of isopropyl alcohol or tert-butyl alcohol produces a change in activation enthalpy while the activation entropy remains constant in the range of experimental error (with one exception), as obvious from Table 6. The results obtained by studying the influence of medium on the kinetic parameters of oxidation of the isothiocyanato ligand in both isomers confirm again the fact that the inconsistency of experimental quantities with theoretical prediction is closely related with mechanism of the reactions. As for the oxidation by peroxodisulfate, it is evidently the reaction of the ion-radical $SO_4^{-\cdot}$ [20], which is indicated by a small value of the charge product of the reacting ions ($z_A z_{B\,exp} = -0.64$ at 323 K and $z_A z_{B\,exp} = -0.59$ at 318 K) calculated on the basis of data in Table 3 from the slope of linear section of the plot $\log k = f(I)$ by means of eqn (3). The radical mechanism is also indicated by the results of some

Table 6

Thermodynamic activation parameters for oxidation of the *cis*- and *trans*-[Co(en)$_2$Cl(NCS)]$^+$ ions by peroxodisulfate as a function of mole fraction x_2 of nonaqueous component of solvent

Cosolvent	x_2	$\Delta H^+/\text{kJ mol}^{-1}$	$\Delta S^+/\text{J mol}^{-1}\text{K}^{-1}$
		cis-[Co(en)$_2$Cl(NCS)]$^+$ + S$_2$O$_8^{2-}$	
—	0	47.5	−278
Isopropyl alcohol	0.0398	56.8	−255
tert-Butyl alcohol	0.0395	71.8	−276
tert-Butyl alcohol	0.1030	71.3	−279
		trans-[Co(en)$_2$Cl(NCS)]$^+$ + S$_2$O$_8^{2-}$	
—	0	63.2	−279
Isopropyl alcohol	0.0200	70.6	−282
Isopropyl alcohol	0.0621	67.5	−280
tert-Butyl alcohol	0.0395	66.4	−281
tert-Butyl alcohol	0.1473	61.3	−279

measurements revealing a short induction period in the course of which the radicals SO$_4^{-\cdot}$ are likely to arise by homolysis of the S$_2$O$_8^{2-}$ ions [20]. The concentration of the HS$_2$O$_8^-$ ions, the reaction of which with the oxidized substrate is assumed in acid medium [10, 11], is negligible under conditions of this study.

Analysis of reaction products

The fact that peroxodisulfate does not absorb in the region of *d—d* bands of the investigated complexes made possible to analyze the changing reaction mixture in the presence of this oxidizing agent from the view-point of oxidation products. Even the shape of the absorption curves recorded in the course of reaction (Fig. 3) shows that the reaction mixture consisted of several substances which absorbed in the measured region. The recorded bands were resolved by means of a mathematical method [21, 22] which enabled us to obtain the pure Gaussian components (dashed lines in Fig. 3). The results obtained by fractionation of the reaction mixture on a column of ion exchanger reveal the prevailing presence of the complex ion *cis*-[Co(en)$_2$(NH$_3$)Cl]$^+$ the absorption maxima of which are at 22 400 cm^{-1} and 28 400 cm^{-1} (446 nm and 352 nm) [23]. The complex ion *trans*-[Co(en)$_2$(NH$_3$)Cl]$^+$ has the absorption maxima at 19 100 cm^{-1} and 21 900 cm^{-1} (524 nm and 547 nm) [23]. The spectral data of the fraction of the reaction mixture obtained by elution with 3 mol dm^{-3} HCl after reaction of the *trans* isomer are very near to the above values. As for other probable oxidation products, we must mention the complex ions [Co(en)$_2$(NCS)CN]$^+$ which may arise by peroxodisulfate oxidation as it was ascertained for the oxidation of the pentaammineisothiocyanatocobalt(III) ions [2, 4]. The presence of cyano complex-
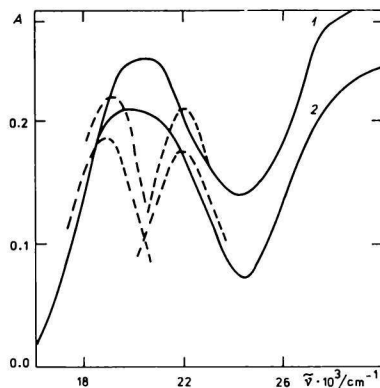
Fig. 3. Absorbance of the mixture containing the *cis*- and *trans*-bis(ethylenediamine)chloro-
isothiocyanatocobalt(III) ions and peroxodisulfate as a function of wavelength.
1. cis-$[Co(en)_2Cl(NCS)]^+ + S_2O_8^{2-}$, 105 min from the beginning of the reaction;
2. trans-$[Co(en)_2Cl(NCS)]^+ + S_2O_8^{2-}$, 240 min from the beginning of the reaction.
Concentration of complexes 4.5×10^{-3} mol dm^{-3}, concentration of peroxodisulfate 6.0×10^{-2} mol dm^{-3}, cell width 4.00 cm, temperature 323 K. The dashed lines represent the Gaussian components of absorption bands.

es is also indicated by existence of the eluate obtained by washing the column of ion exchanger with 1 mol dm^{-3} HCl which absorbed in the region of d—d bands of the investigated complex. Because of equal charge of the original complex ion and the formed cyano complex, the fraction obtained by elution with 1 mol dm^{-3} HCl was a mixture of both substances and was not further analyzed.

At the conclusion, we may state that an addition of supporting electrolytes into the reaction system as well as a change in composition of the solvent affects the kinetics of the investigated reactions in a complicated manner. The interpretation of experiments especially necessitates to take into account a decrease in charge of the reactants due to ion association and change in cluster structure of water produced by the presence of nonaqueous cosolvent in mixed media.

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