

# Kinetics and mechanism of the redox reaction of the hexakis(hydroxylamine)cobalt(III) ions with the cerium(IV) ions

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The kinetics and mechanism of the redox reaction of the  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  ions with the Ce(IV) ions in sulfuric acid solution were studied polarographically. The reaction order with respect to either reactant was determined and the rate equation

$$v = k [\text{Ce(IV)}] [\text{Co}(\text{NH}_2\text{OH})_6^{3+}]^{0.6}$$

was put forward. On the basis of the dependence of the experimental rate constant on concentration of the hydroxonium ions and of hydrogensulfate ions, it was concluded that the reactive species of the Ce(IV) ions was  $\text{Ce}(\text{SO}_4)_2$ . The activation parameters, i.e. activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$ , were evaluated from the temperature dependence of the rate constant ( $\Delta H^\ddagger = 64.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -24 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The probable reaction mechanism was proposed. According to this mechanism, the reaction proceeds through the binuclear complex



the decay of which is the slowest and rate-determining step.

Полярграфически были изучены кинетика и механизм окислительно-восстановительной реакции ионов  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  и Ce(IV) в растворе серной кислоты. Были определены порядки реакции по отношению к обоим реактантам и сформулировано кинетическое уравнение

$$v = k [\text{Ce(IV)}] [\text{Co}(\text{NH}_2\text{OH})_6^{3+}]^{0.6}$$

На основании зависимости экспериментальной константы скорости от концентрации ионов гидроксония и гидросульфата было заключено, что реактивными частицами Ce(IV) являются молекулы  $\text{Ce}(\text{SO}_4)_2$ . На основании температурной зависимости константы скорости были определены параметры активации, энтальпия активации  $\Delta H^\ddagger =$

= 64,6 кДж моль<sup>-1</sup> и энтропия активации  $\Delta S^\ddagger = -24$  Дж моль<sup>-1</sup> К<sup>-1</sup>.  
Предложен вероятный механизм реакции с протеканием через двухядерный комплекс



распад которого является медленной и скорость определяющей ступенью.

Recently, an intensified attention was concentrated on the influence of coordination of the ligands on their reactivity and catalysis due to coordination. The redox reactions of bonded ligands and the role of coordination in redox reactivity are of particular importance [1, 2]. The kinetics of the redox reaction of free hydroxylamine with the Ce(IV) ions were described earlier [3]. Hydroxylamine as a ligand may be linked by a coordination bond through the nitrogen or oxygen atom. The study of infrared spectra of the hydroxylamine complexes with metal ions has led some authors [4, 5] to the conclusion that hydroxylamine in complexes with the Pd<sup>2+</sup>, Pt<sup>2+</sup>, Co<sup>3+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> ions is coordinated through the nitrogen atom whereas it is coordinated through the oxygen atom in complexes containing the Ca<sup>2+</sup>, Ba<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Mn<sup>2+</sup> ions. The coordination ought to induce the ligand to accept electrons more readily or to give them away less readily. The central atoms themselves frequently also take part in the redox process. Polarization of the ligand due to coordination may be manifested in two ways. In the first case, the central atom draws electrons from the ligand and this afterwards undergoes reduction. In the second case, the coordination of the ligand can lead to its reduction. For instance, the coordination of molecular oxygen in Fe(II) complexes results in its reduction [1]. The influence of coordination of the Co<sup>3+</sup> ions on kinetics of the oxidation by the Ce(IV) ions was studied for coordinated oxalates [6, 7] and coordinated *p*-hydroxymethyl benzoate [8].

The aim of this study is to investigate how much the coordination of hydroxylamine to the Co<sup>3+</sup> ion affects the fundamental kinetic parameters and mechanism of its oxidation by the Ce(IV) ions.

## Experimental

The execution of kinetic measurements and other experimental details were described in [3]. The synthesis of the [Co(NH<sub>2</sub>OH)<sub>6</sub>]Cl<sub>3</sub> complex was carried out in three steps. In the first step, we prepared the [Co(en)<sub>2</sub>CO<sub>3</sub>]Cl complex by oxidizing the Co<sup>2+</sup> ions by hydrogen peroxide in the presence of ethylenediamine and carbon dioxide [9]. In the second step, it was converted into the *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl complex which was transformed into [Co(NH<sub>2</sub>OH)<sub>6</sub>]Cl<sub>3</sub> in the third step according to [10].

For [Co(NH<sub>2</sub>OH)<sub>6</sub>]Cl<sub>3</sub> calculated: 4.99% H, 23.12% N; found: 4.89% H, 22.86% N.

## Results

The oxidation of the  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  ions by the Ce(IV) ions in 3 M- $\text{H}_2\text{SO}_4$  is a reaction of the first order with respect to the Ce(IV) ions. The plot of  $\log(I/I_0)$  against time value is linear in the course of the first two half-lives of the reaction even if the reductant is not present in excess (Fig. 1).  $I_0$  is the value of the limiting

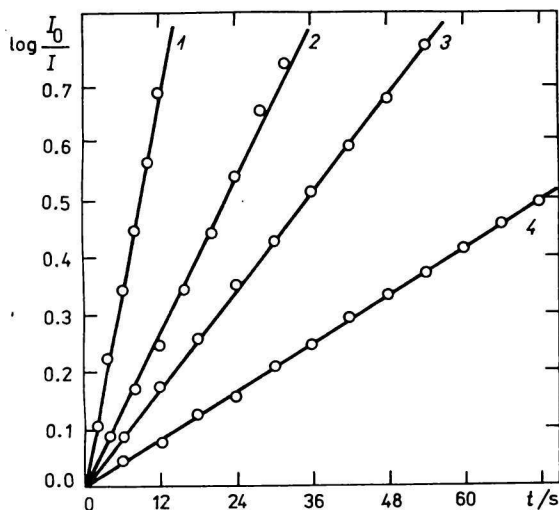


Fig. 1. Evidence for a first-order reaction with respect to Ce(IV).

3 M- $\text{H}_2\text{SO}_4$ ;  $4 \times 10^{-3}$  M-Ce $(\text{SO}_4)_2$ .

1.  $3 \times 10^{-2}$  M- $\text{Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ; 2.  $7.5 \times 10^{-3}$  M- $\text{Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ; 3.  $3.5 \times 10^{-3}$  M- $\text{Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ;
4.  $5 \times 10^{-4}$  M- $\text{Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ; temperature 20°C.

diffusion current of the Ce(IV) ions at the outset of the reaction while  $I$  is its value at a given time moment. The cathodic wave of the  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  ions with the half-wave potential  $E_{1/2} = -0.66$  V against a 3 M- $\text{Hg}_2\text{SO}_4$  electrode decreases during the reaction. The experimental value of rate constant ( $\text{s}^{-1}$ ) nonlinearly increases with concentration of the Co(III) complex (Fig. 2). It was ascertained by logarithmic analysis that the reaction order was equal to  $\beta = 0.6$ . The experimental rate constant decreases with increasing concentration of the  $\text{H}_3\text{O}^+$  ions (Fig. 3). The rate equation may be expressed in the following form

$$\frac{-d[\text{Ce(IV)}]}{dt} = \left( k_0 + \frac{k'}{[\text{H}_3\text{O}^+]} \right) [\text{Ce(IV)}] [\text{Co}(\text{NH}_2\text{OH})_6^{3+}]^{0.6} \quad (1)$$

where  $k_0 = 1.8 \text{ s}^{-1}$  and  $k' = 2.3 \text{ s}^{-1}$  at 20°C. The experimental rate constant at constant concentration of the  $\text{H}_3\text{O}^+$  ions and constant concentration of the  $\text{HSO}_4^-$

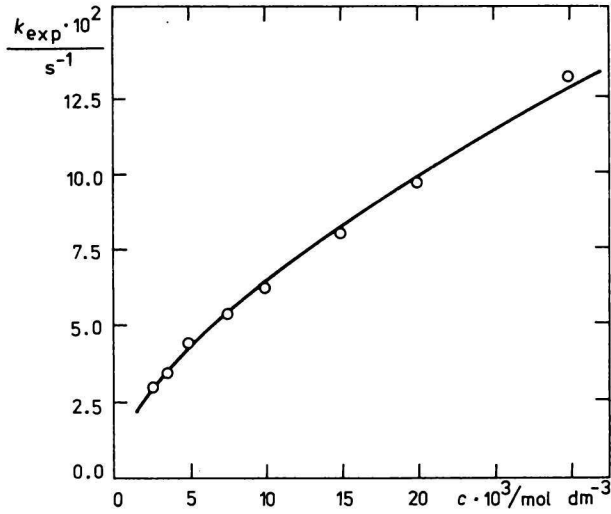


Fig. 2. Variation of the experimental rate constant with concentration of the Co(III) complex.  $3 \text{ M-H}_2\text{SO}_4$ ;  $4 \times 10^{-3} \text{ M-Ce(SO}_4)_2$ ; temperature  $20^\circ\text{C}$ .

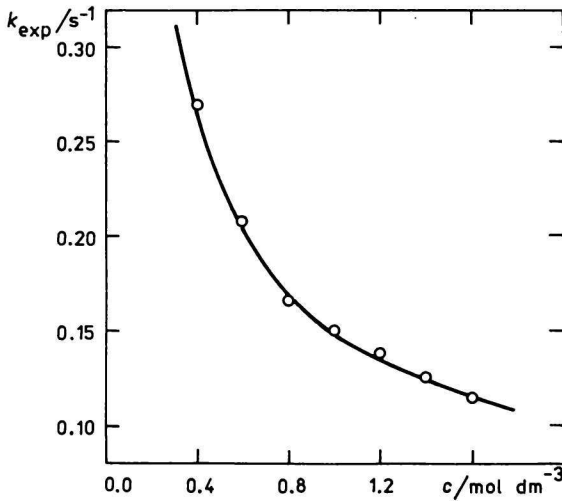


Fig. 3. Variation of the experimental rate constant with concentration of the  $\text{H}_3\text{O}^+$  ions.  $4 \times 10^{-3} \text{ M-Ce(SO}_4)_2$ ;  $4 \times 10^{-3} \text{ M-Co(NH}_2\text{OH)}_6\text{Cl}_3$ ;  $I_c = 3 \text{ mol dm}^{-3}$ ;  $6 \times 10^{-1} \text{ M-Na}_2\text{SO}_4$ ; temperature  $20^\circ\text{C}$ .

ions decreases with increasing ionic strength. The plot of  $\log k_{\text{exp}}/s^{-1}$  against  $I_c'^{1/2}/(1 + I_c'^{1/2})$  is linear in the interval of values of relative ionic strength from  $I_c' = 3.0$  to  $I_c' = 3.6$ , the slope being 1.5. The experimental rate constant also decreases with increasing concentration of the  $\text{HSO}_4^-$  ions at constant ionic strength and constant concentration of the  $\text{H}_3\text{O}^+$  ions (Table 1). A special attention was given to the temperature dependence of the rate constant (Fig. 4) from which the activation parameters, *i.e.* activation enthalpy and activation entropy, were calculated by means of the Eyring equation. Thus it was found  $\Delta H^\ddagger = 64.6 \text{ kJ mol}^{-1}$  and

Table 1

Variation of the experimental rate constant with concentration of the  $\text{HSO}_4^-$  ions  
 $4 \times 10^{-3} \text{ M-Ce}(\text{SO}_4)_2$ ;  $4 \times 10^{-3} \text{ M-Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ;  $I = 3 \text{ mol dm}^{-3}$ ;  $\text{H}_3\text{O}^+ = 3 \text{ M}$ ; temperature  $20^\circ\text{C}$

$\text{HSO}_4^-/\text{mol dm}^{-3}$	$10^2 \cdot k_{\text{exp}}/s^{-1}$
0.5	8.5
1.0	7.0
1.5	6.3
2.0	5.5
2.5	4.6
3.0	4.2

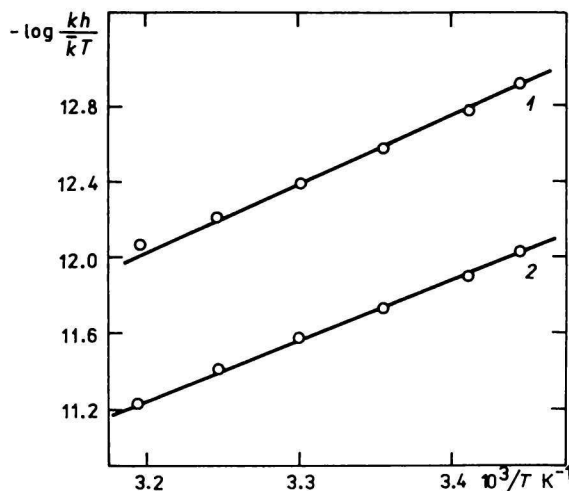


Fig. 4. Temperature dependence of the rate constant.  
 3 M- $\text{H}_2\text{SO}_4$ ;  $4 \times 10^{-3} \text{ M-Ce}(\text{SO}_4)_2$ .  
 1.  $4 \times 10^{-3} \text{ M-Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ ; 2.  $4 \times 10^{-3} \text{ M-NH}_2\text{OH} \cdot 1/2\text{H}_2\text{SO}_4$ .

$\Delta S^\ddagger = -24 \text{ J mol}^{-1} \text{ K}^{-1}$ . The value of the activation enthalpy when compared with the corresponding value of the redox reaction of free hydroxylamine is by  $8.3 \text{ kJ mol}^{-1}$  higher. On the other hand, the value of the activation entropy is by  $12 \text{ J mol}^{-1} \text{ K}^{-1}$  lower than the corresponding value of the redox reaction of free hydroxylamine [3].

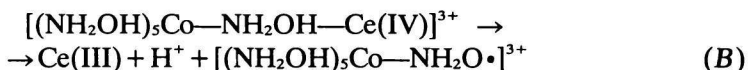
The stoichiometry determined by polarometric titration corresponds to the consumption of 22–24 Ce(IV) ions for a  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  ion, *i.e.* to the consumption of 4 Ce(IV) ions for a molecule of hydroxylamine.

### Discussion

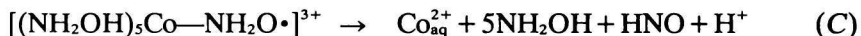
The decrease in concentration of Ce(IV) during the redox reaction of  $\text{Co}(\text{NH}_2\text{OH})_6^{3+}$  with the Ce(IV) ions which is governed by the first-order kinetics even at comparable concentrations of both reactants may be explained by the assumption that an intermediary binuclear complex arises in the following step of reaction



and the decay of this complex due to reduction of the Ce(IV) ion to the Ce(III) ion is the slow and rate-determining step



The coordinated  $\text{NH}_2\text{O}\cdot$  radical is very likely to be oxidized in the subsequent step by the central Co(III) ion, which is indicated by a decrease in cathodic wave of the Co(III) complex. The complex inert with respect to substitution is transformed into an unstable complex owing to which it decays according to the following equation



In the following steps, other Ce(IV) ions are consumed for oxidation of the free  $\text{NH}_2\text{OH}$  molecules and oxidation of the HNO molecules

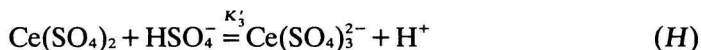
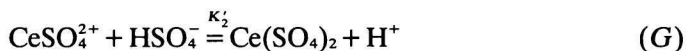
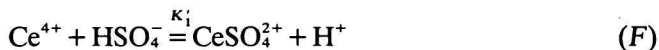


Of course, these molecules also decay in the step



The fractional partial reaction order with respect to the Co(III) complex may be explained by the assumption that the Ce(IV) ions also react with the liberated molecules of hydroxylamine but the rate of this reaction is different from the rate of the reaction with the Co(III) complex. The reaction stoichiometry is consistent with

the proposed mechanism. The decrease in experimental rate constant with increasing concentration of the  $\text{H}_3\text{O}^+$  ions and  $\text{HSO}_4^-$  ions is due to a shift in equilibria of individual Ce(IV) complexes [11]



It may be assumed that the reactive particles are  $\text{Ce}(\text{SO}_4)_2$  the equilibrium concentration of which decreases with increasing concentration of the  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$  ions in a certain concentration interval. Thus a decrease in equilibrium concentration of the  $\text{Ce}(\text{SO}_4)_2$  brings about a decrease in reaction rate. This conclusion is also supported by relatively small influence of ionic strength on the reaction rate.

The coordination of hydroxylamine to the  $\text{Co}^{3+}$  ion results in an increase of activation enthalpy by  $8.3 \text{ kJ mol}^{-1}$ . That is evidently a consequence of polarization of the molecules of hydroxylamine by the Co(III) ions owing to which a coordinated molecule is less disposed to deliver the first electron to the Ce(IV) ion than a molecule of free hydroxylamine.

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