

Oxidation of bis(dimethylglyoximato)-bis(isothiocyanato)-cobaltate(III) with peroxydisulfate

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The kinetics of oxidation of one coordinatively bound NCS^- ligand in bis(dimethylglyoximato)-bis(isothiocyanato)cobaltate(III) ion with peroxydisulfate were investigated in 0.001—0.01 M- HClO_4 . The dissociation constant together with the thermodynamic parameters of dissociation of the complex as a weak acid were determined potentiometrically. The kinetic measurements lead to the conclusion that no cleavage of the $\text{Co}-\text{NCS}$ bond occurs in the rate-determining step.

В 0,001—0,01 М растворах HClO_4 исследована кинетика окисления пероксодисульфатом одной координационно связанной группы NCS^- в ионе бис(диметилглиоксимато)-бис(изотиоцианато)кобальта(III). Потенциометрически были определены константы диссоциации, а также термодинамические параметры диссоциации комплекса как слабой кислоты. Кинетические измерения позволили прийти к заключению, что в скорость определяющей стадии не происходит расщепление связи $\text{Co}-\text{NCS}$.

The cobalt(III) complexes with dimethylglyoxime ligand have been extensively studied in the past from the point of view of preparation, structure, and reactivity, due to interest in them in biochemistry and chemical catalysis [1—3]. The main difference between the similar complexes with ethylenediamine and dimethylglyoxime ligands consists in their different charges, the dimethylglyoximato complex ions of the type $[\text{Co}(\text{dmgH})_2\text{X}_2]^-$ ($\text{dmgH} = \text{C}_4\text{N}_2\text{O}_2\text{H}_7^-$, $\text{X}^- =$ anionic ligand) being charged negatively. The kinetic studies of the anionic Co(III) complexes of the above-mentioned type are rather rare [4—6]. The reactions of dimethylglyoximato complexes are influenced by the fast acid-base equilibria involving the complex ion as well as the coordinatively bound dimethylglyoxime itself [2, 6—8]. The kinetics of oxidation of NCS^- ligand in Co(III) complexes with various oxidants have been studied in detail in the case of $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ [9—11]. The oxidation of $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$ has not been reported till now.

The aim of the present work was to obtain the kinetic parameters of the oxidation of NCS^- ligand in the complex ion $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$ with

peroxodisulfate and by comparison of these data with those for the oxidation of other Co(III) complexes discuss the influence of the composition of coordination sphere on kinetics and mechanism of investigated reaction.

Experimental

[Co(dmgH)₂(NCS)₂]H was prepared by the literature method [12]. Potassium peroxodisulfate, anal. grade (Lachema, Brno) was the oxidant, all other reagents used were of reagent grade. Kinetic measurements were carried out using spectrophotometer Specord UV VIS (Zeiss, Jena), the reaction mixture was placed in a tempered cuvette. The temperature was maintained within ± 0.1 K. The pH of solutions as well as the dissociation constants of the complex was measured on a potentiometer OP 205/1 (Radelkis, Budapest), the value of pK'_A being evaluated from the titration data by means of a computer program ACBA [13, 14]. Carbonate-free sodium hydroxide was prepared by dissolution of metallic sodium in a redistilled water under inert atmosphere. Free hydrogen ion concentration was measured by a cell consisting of a glass electrode and a saturated calomel electrode. The concentration of titrated solutions of the complex was of the order of 10^{-2} mol dm⁻³. The computed values of dissociation constants are the mean from three independent measurements.

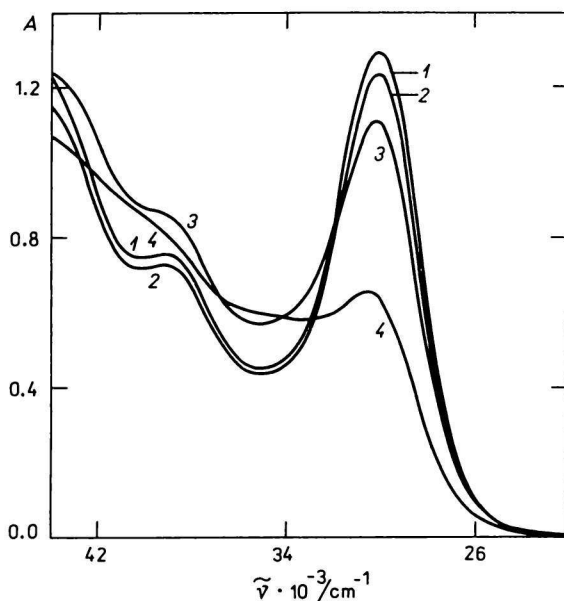


Fig. 1. Absorption spectrum of 5×10^{-5} M-[Co(dmgH)₂(NCS)₂]H in dependence on the acidity of solution. 1. pH = 3; 2. pH = 4; 3. pH = 5; 4. pH = 6.5; cell width 1.00 cm.

Results and discussion

The absorption spectrum of the acid solution of $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]\text{H}$ ($\text{pH} \leq 5$) exhibits an intense band at $\tilde{\nu} = 30\,000\text{ cm}^{-1}$ which is practically unaffected by the changes of pH of solution. However, when pH is increased above 5 the significant changes of absorption spectrum are observed (Fig. 1). The complex as a weak acid is dissociated following the scheme



The values of dissociation constants at several temperatures and ionic strengths are listed in Table 1. The linear dependence of $\log K'_A$ on the function of ionic

Table 1

Dissociation constants of $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]\text{H}$ in dependence on temperature and ionic strength

T/K	$I/(\text{mol dm}^{-3})$	$10^2 \cdot K'_A$	T/K	$I/(\text{mol dm}^{-3})$	$10^2 \cdot K'_A$
289.28	0.014	1.62 ± 0.22	298.15	0.064	5.31 ± 0.81
289.28	0.114	2.65 ± 0.40	298.15	0.114	6.92 ± 0.70
289.28	0.214	3.18 ± 0.53	298.15	0.214	7.76 ± 1.1
289.28	0.314	3.40 ± 0.49	309.15	0.014	5.75 ± 0.91
289.28	0.414	4.47 ± 0.80	313.95	0.014	6.31 ± 0.94
298.15	0.014	3.09 ± 0.35	319.15	0.014	8.32 ± 1.24
298.15	0.034	3.80 ± 0.42			

strength $f(I) = I^{1/2}/(1 + I^{1/2})$ enabled the evaluation of K_A , *i.e.* the dissociation constant extrapolated to zero ionic strength. At 25°C (298.15 K) $K_A = (1.93 \pm 0.23) \times 10^{-2}$. The value of the enthalpy of dissociation, $\Delta H_{\text{diss}} = (44 \pm 6)\text{ kJ mol}^{-1}$, was evaluated from the dependence of K'_A on temperature at ionic strength 0.014 mol dm^{-3} . By means of K'_A the ratio of the dissociated and nondissociated form of the complex was determined, the reaction system contains 99 % of the dissociated form at $\text{pH} = 3$, and 92 % at $\text{pH} = 2$.

The kinetics of oxidation have been investigated by the measurements of absorbance changes at $\tilde{\nu} = 30\,000\text{ cm}^{-1}$ where the ligand band of the coordinatively bound isothiocyanate has a maximum. The absorbance diminishes in the course of reaction (Fig. 2). Rate equation (1) may be derived from experimental data obtained for the studied reaction

$$-\frac{d[[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-]}{dt} = k[[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-]_0[\text{S}_2\text{O}_8^{2-}]_0 \quad (1)$$

(Index 0 denotes the total concentrations of complex and oxidant, respectively.) Eqn (1) is valid, however, in a rather narrow interval of HClO_4 concentration

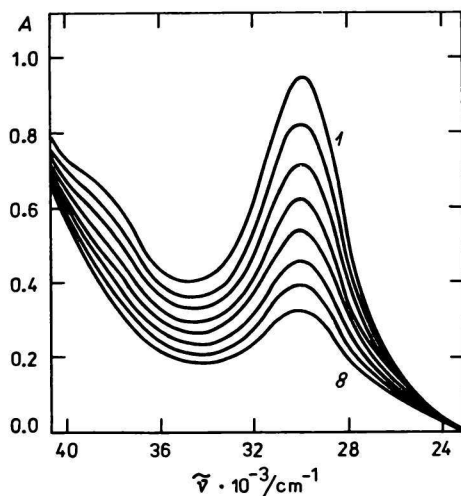


Fig. 2. Variation of absorbance of the reaction system with time. 5×10^{-5} M-[Co(dmgH)₂(NCS)₂]₂H, 5×10^{-3} M-K₂S₂O₈, 1×10^{-3} M-HClO₄, temperature 50 °C, cell width 1.00 cm. Time difference between the curves 1—8 was 20 min.

(0.001—0.01 mol dm⁻³). In this concentration range in the excess of oxidant with respect to the complex the reaction was of the first order. The Guggenheim method was used for calculation of the rate constant from the measured absorbance changes by means of the equation

$$\ln \Delta A = -kt + \text{const} \quad (2)$$

Table 2

Dependence of the rate constants of oxidation of [Co(dmgH)₂(NCS)₂]⁻ with peroxodisulfate on temperature, concentration of perchloric acid, and ionic strength;
 $c(\text{complex}) = 2.5 \times 10^{-5}$ mol dm⁻³, $c(\text{K}_2\text{S}_2\text{O}_8) = 2.5 \times 10^{-3}$ mol dm⁻³

$\frac{T}{\text{K}}$	$\frac{c(\text{HClO}_4)}{\text{mol dm}^{-3}}$	$\frac{I}{\text{mol dm}^{-3}}$	$\frac{k}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
317.65	0.001	0.0085	0.030 ± 0.003
323.15	0.001	0.0085	0.095 ± 0.001
323.15	0.001	0.2085	0.049 ± 0.006
323.15	0.005	0.2135	0.064 ± 0.006
323.15	0.010	0.2185	0.076 ± 0.012
323.15	0.001	0.0585	0.068 ± 0.004
323.15	0.001	0.0085	0.042 ± 0.001
327.65	0.001	0.0085	0.130 ± 0.018
333.15	0.001	0.0085	0.274 ± 0.068

Table 3

Activation parameters of oxidation of coordinatively bound thiocyanate ion

Reaction	Formal product of charge numbers $z_A z_B$	$\frac{\Delta H^*}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^*}{\text{J mol}^{-1} \text{K}^{-1}}$	Ref.
$[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+} + \text{S}_2\text{O}_8^{2-}$	-4	62.8	-74	[11]
$[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+} + \text{IO}_4^-$	-2	54.9	-86	[11]
$\text{cis-}[\text{CoCl}(\text{en})_2\text{NCS}]^+ + \text{IO}_4^-$	-1	59.7	-110	[16]
$\text{cis-}[\text{CoCl}(\text{en})_2\text{NCS}]^+ + \text{S}_2\text{O}_8^{2-}$	-2	58.5	-120	[16]
$\text{trans-}[\text{CoNH}_3(\text{en})_2\text{NCS}]^+ + \text{S}_2\text{O}_8^{2-}$	-2	55.2	-96	[17]
$\text{trans-}[\text{CoH}_2\text{O}(\text{en})_2\text{NCS}]^{2+} + \text{S}_2\text{O}_8^{2-}$	-4	60.1	-76	[18]
$\text{cis-}[\text{Co}(\text{en})_2(\text{NCS})\text{NO}_2]^+ + \text{S}_2\text{O}_8^{2-}$	-2	57.0	-82	[19]
$\text{NCS}^- (\text{free ion}) + \text{S}_2\text{O}_8^{2-}$	+2	48.9	-135	[20]

$\Delta A = A_t - A_{t+\tau}$, A_t being the absorbance in a time $t + \tau$. The constant time interval τ was chosen so that the measured absorbance A_t was a half of its initial value A_0 , i.e. $(A_t)_{\min} = A_0/2$. Such procedure enabled to measure the oxidation of one coordinated NCS^- ligand (the first step of the reaction). The dependence of the rate constant on temperature, concentration of perchloric acid, and on ionic strength (adjusted by sodium perchlorate) is shown in Table 2. The activation parameters evaluated from temperature dependence of the rate constant in 0.001 M- HClO_4 are: activation enthalpy $\Delta H^\ddagger = 113 \text{ kJ mol}^{-1}$, activation entropy $\Delta S^\ddagger = +75 \text{ J K}^{-1} \text{ mol}^{-1}$, and frequency factor $A = 5.146 \times 10^{14} \text{ s}^{-1}$. Positive value of activation entropy is at variance with the conclusions of the electrostatic theory of ionic reactions which claims a negative value of ΔS^\ddagger for a reaction between equally charged ions [15]. From the values in Table 2 it follows that also the dependence of the rate constant on ionic strength is not in accord with the theory, the rate constant diminishes with the increasing ionic strength. In Table 3 are listed the values of activation parameters of the oxidation of NCS^- ion in several Co(III) complexes as well as the values for the oxidation of free thiocyanate ion with peroxodisulfate. It can be seen from this table that only in the case of oxidation of free NCS^- the negative sign of the activation entropy is in accordance with the electrostatic theory. These results suggest that in the oxidation of coordinatively bound NCS^- ion the interionic electrostatic interactions play a less important role in the rate-determining step. The observed little influence of ionic strength on the reaction rate (Table 2) indicates the effect of an ion—dipole interaction.

The experimental value of the activation enthalpy is considerably larger than the values obtained for the oxidation of NCS^- ligand in other Co(III) complexes. The found value of ΔH^\ddagger corresponds to the cleavage of the Co—NCS bond in the rate-determining step, whereas in the reactions listed in Table 3 the metal—ligand bond is not broken. The aquation reactions with the cleavage of Co—NCS bond have the activation enthalpies (in kJ mol^{-1}): 112.9 (aquation of $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$), 125.5 (aquation of *trans*- $[\text{CoCl}(\text{en})_2\text{NCS}]^+$) (see Ref. [21]), and 132 (aquation of $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$) (see Ref. [6]).

The attempts to separate the reaction mixture after a sufficient reaction time, i.e. when no absorption in the ligand band of NCS^- could be observed, by ion-exchange techniques, proved the presence of a complex ion of the charge + 1. In the given experimental conditions the formation of the complex ion $[\text{Co}(\text{H}_2\text{O})_2(\text{dmgH})_2]^+$ is most probable one. At the same time the absorption bands of ammine and cyano complexes — the products of the oxidation of NCS^- ligand in the reactions occurring with the retention of metal—ligand bond, were not observed.

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