

KINETICS AND MECHANISMS OF THE REACTIONS BETWEEN
THE PENTAAMINE(DIMETHYLSULFOXIDE)COBALT(III)
COMPLEX AND THE REDUCING AGENTS CHROMIUM(II),
VANADIUM(II) AND EUROPIUM(II) IN AQUEOUS SOLUTION

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ABSTRACT: The electron transfer reactions between the complex $[\text{Co}(\text{NH}_3)_5\text{O}=\text{S}(\text{CH}_3)_2](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and the reducing agents Cr^{2+} , V^{2+} and Eu^{2+} in aqueous solution, $[\text{H}^+]$ in the range 0.20 - 1.00 M, $\mu = 1.50$ M (LiClO_4) were studied by conventional spectrophotometric technique. The measured rate constants at 35 °C are equal to $(3.4 \pm 0.1) \times 10^2$, (2.0 ± 0.3) and $(1.1 \pm 0.1) \text{ M}^{-1} \cdot \text{s}^{-1}$ for the reactions with Cr^{2+} , V^{2+} and Eu^{2+} , respectively. Based on the immediate product analysis, an outer-sphere mechanism was proposed for the reaction of Cr^{2+} . Using rate constants relationships based on Marcus Theory for outer-sphere electron transfer, outer-sphere mechanism were also proposed for the reactions where the reducing agents were V^{2+} and Eu^{2+} .

KEY-WORDS: Kinetics; mechanisms; electron transfer; cobalt complex; dimethyl sulfoxide.

INTRODUCTION

The sulfoxide ligands have two potential coordination sites, the oxygen and the sulfur atom. In the dimethyl sulfoxide (dmso) complex of pentaamminecobalt(III), the sulfoxide ligand is oxygen-bonded to the central cobalt ion¹, being the sulfur atom available, at least

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in principle, to coordination by other metallic center. This behaviour was observed in the reaction with the complex ion $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, where the formation of a binuclear complex of cobalt(III) and iron(II), bridged by the dimethyl sulfoxide ligand was observed².

The present work was initiated with the purpose of studying and characterizing the mechanism of the reactions of the complex $[\text{Co}(\text{NH}_3)_5\text{dmsO}](\text{ClO}_4)_3$ with the usual reducing agents Cr(II), V(II) and Eu(II) in aqueous solution. At least in the case of Cr(II) an inner-sphere electron transfer mechanism through the sulfoxide ligand was expected to be observed.

EXPERIMENTAL

The complex $[\text{Co}(\text{NH}_3)_5\text{dmsO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ was prepared and purified by the procedure described by MAC-COLL & BEYER¹. Solutions of the complex were prepared by dissolution of the adequate weight of the solid in solution of controlled ionic strength and acidity, and used immediately to minimize the influence of the aquation process.

Stock solution of chromium(III) perchlorate was prepared by reduction of potassium dichromate (Merck p.a.) by hydrogen peroxide 30% in excess of perchloric acid. The chromium content in the solution was determined spectrophotometrically at 372 nm, after oxidation of chromium by hydrogen peroxide in $\text{pH} > 9$ (HAUPT³).

Stock solution of vanadyl perchlorate was prepared by reacting vanadyl sulfate (Fisher p.a.) with barium perchlorate in presence of excess of perchloric acid, and removing the precipitated barium sulfate by vacuum filtration. The concentration of V(IV) in the resulting solution was determined by titration with standardized potassium permanganate solution⁴.

Stock solution of europium(III) perchlorate was prepared by dissolution of Eu_2O_3 (Sigma p.a.) in slight excess of perchloric acid. The concentration of Eu(III) in solution was determined by EDTA titration⁵.

The free acid concentrations in the stock solutions of chromium, vanadium and europium were determined by passing known volumes of each solution through an exchange column containing cationic, H^+ form, Dowex 50W-X4 resin, and titrating the resulting eluate with standard base. After subtracting the contribution arising from the metal ion present in solution the free acid concentration in solution was obtained.

Solutions of Cr(II), V(II) and Eu(II) were prepared in situ by reduction of the stock solutions of Cr^{3+} , VO^{2+} and Eu^{3+} , respectively, by zinc amalgam under argon atmosphere. Analysis of free dimethyl sulfoxide present in solution after the reaction between the sulfoxide cobalt complex and Cr^{2+} was over, was carried out by the method developed by TOMA *et alii*⁶, after the unreacted reducing agent was oxidized by bubbling air through the solution.

All oxygen sensitive solutions were manipulated by usual syringe techniques under argon atmosphere. The argon used was previously deoxygenated by bubbling in a solution of V^{2+} kept over zinc amalgam.

The ionic strength was maintained by using the adequate volumes of standard lithium perchlorate stock solution.

All the solutions were prepared using double distilled deionized water.

Kinetics Measurements

The kinetics of the reactions were followed by spectrophotometric technique, using a Cary 14 spectrophotometer, measuring the variation of the absorption of the solution in function of the time of reaction in convenient wavelengths.

All the kinetics measurements were made under controlled temperature and pseudo-first order conditions, using at least ten times excess of the reducing agents over the concentration of the cobalt complex, except in the reaction with Eu^{2+} where it was used a minimum of four time excess. The kinetics curves were treated by a first-order equation and the observed rate constants were obtained from the slopes of the plots $\ln(A_t - A_{\text{inf}})$ vs. time of reaction, where A_t and A_{inf} are the absorbance at time t and infinite time, respectively. Each measurement represents the average of two independent determinations.

RESULTS AND DISCUSSION

The kinetics of the reactions of electron transfer between $[\text{Co}(\text{NH}_3)_5\text{dmsO}]^{3+}$ and the reducing agents Cr^{2+} , V^{2+} and Eu^{2+} were studied by monitoring the absorbance decrease at 260, 250 and 515 nm, respectively, under argon atmosphere. The observed rate constants of the reactions with Cr^{2+} , V^{2+} and Eu^{2+} are shown in the Tables 1, 2 and 3, respectively.

The second-order rate constants measured at 35°C are equal to $(3.4 \pm 0.1) \times 10^{-2}$, (2.0 ± 0.3) and $(1.1 \pm 0.1) \text{ M}^{-1} \text{ s}^{-1}$ for the reactions where the reducing agents are Cr^{2+} , V^{2+} and Eu^{2+} , respectively.

The data obtained for the reaction between the dmsO complex and Cr^{2+} indicate that the kinetics has a first order dependence in relation to each one of the reactants, and is independent of acid concentration in the range 0.2 - 1.0 M, obeying the rate law:

$$\frac{d[\text{Co}(\text{NH}_3)_5\text{dmsO}^{3+}]}{dt} = k_2[\text{Co}(\text{NH}_3)_5\text{dmsO}^{3+}][\text{Cr}^{2+}]$$

where $k_2 = (3.4 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 35.0°C.

TABLE 1 — Observed (k_{obsd}) and second order (k) rate constants of reduction of the complex ion $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+}$ by Cr^{2+} in aqueous solution

$[\text{Cr}^{2+}]$ ($\times 10^4 \text{ M}$)	$[\text{Co}(\text{NH}_3)_5\text{dmsso}^{3+}]$ ($\times 10^4 \text{ M}$)	$[\text{H}^+]$ (M)	T ($\pm 0.1^\circ\text{C}$)	k_{obsd} ($\times 10^4 \text{ s}^{-1}$)	k ($\times 10^2 \text{ M}^{-1} \text{ s}^{-1}$)
2.50	2.57	1.00	25.0	4.6	1.8
2.50	2.57	0.20	25.0	4.7	1.9
2.50	2.57	1.00	35.0	8.7	3.5
1.00	2.50	1.00	35.0	3.4	3.4*
1.00	5.02	1.00	35.0	3.4	3.4

$\mu = 1.50 \text{ M}$ lithium perchlorate.

TABLE 2 — Observed (k_{obsd}) and second order (k) rate constants of reduction of the complex ion $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+}$ by V^{2+} in aqueous solution

$[\text{V}^{2+}]$ ($\times 10^4 \text{ M}$)	k_{obsd} ($\times 10^3 \text{ s}^{-1}$)	k ($\text{M}^{-1} \text{ s}^{-1}$)
5.00	0.9	1.8
7.50	1.5	2.0
10.0	2.3	2.3

$T = 35.0 \pm 0.1^\circ\text{C}$; $[\text{Co}(\text{NH}_3)_5\text{dmsso}^{3+}] = 2.9 \times 10^{-5} \text{ M}$; $[\text{H}^+] = 1.00 \text{ M}$; $\mu = 1.50 \text{ M}$ lithium perchlorate.

TABLE 3 — Observed (k_{obsd}) and second order (k) rate constants of reduction of the complex ion $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+}$ by Eu^{2+} in aqueous solution

$[\text{Eu}^{2+}]$ ($\times 10^3 \text{ M}$)	k_{obsd} ($\times 10^3 \text{ s}^{-1}$)	k ($\text{M}^{-1} \text{ s}^{-1}$)
1.43	1.5	1.0
1.72	1.9	1.1
1.90	2.0	1.0
3.99	4.4	1.1

$T = 35.0 \pm 0.1^\circ\text{C}$; $[\text{Co}(\text{NH}_3)_5\text{dmsso}^{3+}] = 3.5 \times 10^{-4} \text{ M}$; $[\text{H}^+] = 1.00 \text{ M}$; $\mu = 1.50 \text{ M}$ lithium perchlorate.

The analysis of the free sulfoxide present in solution after the reaction is over, using initial concentrations of $[\text{Co}(\text{NH}_3)_5\text{dmsso}^{3+}]$ and $[\text{Cr}^{2+}]$ equal to $2.50 \times 10^{-4} \text{ M}$ and $1.00 \times 10^{-2} \text{ M}$, respectively, gave a result of $2.3 \times 10^{-5} \text{ M}$ of sulfoxide in the free state, compared to a total of $2.5 \times 10^{-5} \text{ M}$. This shows that within experimental error all the dmsso present in solution after the reaction is over is in the free state. Considering that the product ion Cr^{3+} is remarkably inert in solution⁷⁻⁹ (it exchanges its coordinated water molecules with a rate constant of $3 \times 10^{-6} \text{ s}^{-1}$) this result rules out the possibility that the reaction occurs through the binuclear cobalt-chromium complex bridged by the sulfoxide ligand, by an inner-sphere electron transfer mechanism. If this were the case the substitution inert product formed, $[\text{Cr}(\text{H}_2\text{O})_5\text{dmsso}]^{3+}$, would be detected in solution in the time of the experiment and no free dimethyl sulfoxide would be found. Based on these evidences, an outer-sphere electron transfer mechanism is proposed for the reaction¹⁰.

Two possible explanations can be given to the fact that the expected inner-sphere electron transfer mechanism is not operative in this reaction. One possibility is the existence of steric hindrance around the sulfoxide ligand, that would prevent the bonding of the reducing agent Cr^{2+} to the sulfur atom of the dimethyl sulfoxide. However, this possibility can be ruled out, since a binuclear complex with the sulfoxide acting as a bridging ligand is observed in the system² $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+} - [\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ where a greater steric hindrance is present. The second possibility is that Cr^{2+} , a hard acid, has low affinity for the sulfur atom of the sulfoxide ligand, a soft base. This would give a low stability constant for the binuclear precursor complex bridged by the sulfoxide ligand, and an outer-sphere mechanism would be favored over the inner-sphere mechanism. This would explain the formation of the binuclear complex in the case of $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, a softer acid than Cr^{2+} .

The assignment of the mechanism of the reactions between $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+}$ and V^{2+} and Eu^{2+} is not so straightforward as in the case of Cr^{2+} , since both reaction products are known to be substitution labile^{10,11}, and the assignment can not be based on the identification of the immediate products of the reactions. In these cases the relationship between rate constants of electron-transfer of the same reagent with different reducing agents proposed by LINCK¹²⁻¹⁴ was used to attribute the mechanism of the reactions. If all the reactions proceed through outer-sphere mechanisms the following relationships are expected for the rate constants of the reaction of the same reagent, in this case $[\text{Co}(\text{NH}_3)_5\text{dmsso}]^{3+}$, with the reducing agents^{12,13} V^{2+} and Eu^{2+} : $k_{\text{Cr}^{2+}} / k_{\text{V}^{2+}} = 0.021$ and $k_{\text{Eu}^{2+}} / k_{\text{V}^{2+}} = 0.35$.

Using these relationships, values of 1.6 and $0.7 \text{ M}^{-1} \text{ s}^{-1}$ are predicted for the rate constants of the reactions between the cobalt complex and V^{2+} and Eu^{2+} , compared to the experimental values of (2.0 ± 0.3) and $(1.0 \pm 0.1) \text{ M}^{-1} \text{ s}^{-1}$, respectively. So, within experimental error there is a reasonable agreement between the observed and predicted

values, and outer-sphere mechanisms can also be attributed to the electron transfer reactions between the cobalt complex and the reducing agents V^{2+} and Eu^{2+} .

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ANDRADE DE OLIVEIRA, et alii — Cinética e mecanismos das reações entre o complexo pentaamin(dimetilsulfóxido)cobalto(III) e os agentes redutores crômio(II), vanádio(II) e európio(II) em solução aquosa. *Ecl. Quím.*, São Paulo, 15: 9 – 15, 1990.

RESUMO: As reações de transferência de elétrons entre o complexo $[Co(NH_3)_5O = S(CH_3)_2(CIO_4)_3 \cdot 2H_2O$ e os agentes redutores Cr^{2+} , V^{2+} e Eu^{2+} foram estudadas em solução aquosa, $[H^+]$ na faixa 0,20 - 1,00 M, $\mu = 1,50$ M ($LiClO_4$), por técnica espectroscópica convencional. As constantes de velocidade medidas a 35,0 °C são iguais a $(3,4 \pm 0,1) \times 10^{-2}$, $(2,0 \pm 0,3)$ e $(1,1 \pm 0,1) M^{-1} \cdot s^{-1}$ para as reações com Cr^{2+} , V^{2+} e Eu^{2+} , respectivamente. Baseado na análise do produto imediato da reação, um mecanismo de esfera externa foi proposto para a reação com Cr^{2+} . Usando relações de constantes de velocidades baseadas na Teoria de Marcus para reações de transferência eletrônica de esfera externa, mecanismos de esfera externa foram também propostos para as reações onde os agentes redutores eram V^{2+} e Eu^{2+} .

UNITERMOS: Cinética; mecanismo; transferência eletrônica; complexo de cobalto; dimetilsulfóxido.

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