

## Research Article

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# Kinetics of aquation of $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$ induced by Fe(III)

**Abstract:** The aquation reaction of the oxydiacetate cobalt(II) complex, namely  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (ODA = oxydiacetate), induced by the Fe(III) ions as the promoter has been studied spectrophotometrically (UV-Vis). Kinetic measurements were carried out in the 283.15 - 303.15 K temperature range and at a constant ionic strength of 1.0 M ( $\text{NaNO}_3$ ). The observed rate constants were computed by a program based on global analysis. Furthermore, the reaction activation parameters were determined using the Arrhenius and Eyring equations. The changes in the enthalpy, entropy as well as activation energy barriers were calculated in the range of 0.00125 M – 0.125 M of the Fe(III) ion concentration. Based on kinetic data a mechanism for the aquation of the  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  complex has been proposed.

**Keywords:** cobalt(II) complex, oxydiacetate, kinetics of aquation reaction

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## 1 Introduction

Knowledge of the mechanisms of substitution in coordination compounds is important to understand processes involving the activity of metalloenzymes, enzymes activated by metal ions or the transport of metal ions across the cell membrane [1-3]. Aquation reactions are a particular type of substitution which involves the exchange of labile ligands from a coordination sphere of the metal ion by water molecules [4]. The rate of such

reactions depends on the presence of other substances in the solution. For example, it has been found that Fe(III) ions, among others, accelerate the course of the oxalato ligand substitution reaction in chromium(III) complexes [5,6].

This contribution initiates a series of efforts confined to the study of aquation reactions of polycarboxylate metal complexes induced by metal ions. In this paper we present kinetic data, *i.e.*, the rate constants and the activation parameters of an aquation of the oxydiacetate cobalt(II) complex, namely  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (ODA = oxydiacetate) determined by UV-Vis measurements. Furthermore, a mechanism for the aquation reaction promoted by Fe(III) ions is proposed.

## 2 Experimental procedure

### 2.1 Reagents

$[\text{Co}(\text{ODA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  complex compound was synthesized according to the procedures described earlier [7]. The composition of the obtained compound was confirmed on the basis of elemental analysis (Vario EL analyzer Cube CHNS). The results obtained for carbon and hydrogen were as follows: %C 17.65, %H 4.83 while the theoretical values are: %C 17.45, %H 4.78. Other compounds such as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaNO}_3$  and  $\text{H}_2\text{ODA}$  (oxydiacetic acid) were purchased from Sigma-Aldrich.

### 2.2 Kinetic measurements

The progress of the aquation reaction of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$ , promoted by  $\text{Fe}^{3+}$  ions, was observed spectrophotometrically at 550 nm. This spectral range is not sensitive to absorptions of  $[\text{Fe}(\text{ODA})(\text{H}_2\text{O})_3]^+$ . The initial concentration of the  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  complex was  $4 \times 10^{-3}$  M and the concentration of  $\text{Fe}^{3+}$  was kept within the range of 0.00125 M – 0.125 M. The concentration of  $[\text{H}_3\text{O}]^+$

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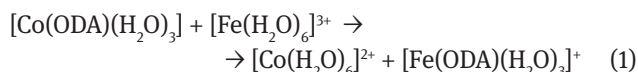
was kept constant at 0.15 M. The ionic strength of the solution was adjusted to 1.0 M ( $\text{Na}^+$ ,  $\text{NO}_3^-$ ).

## 2.3 Instrumentation and simulations

UV-Vis measurements were carried out using a Perkin Elmer Lambda 650 spectrophotometer equipped with a Temperature Control – Peltier System with a scan accuracy of 1 nm and a 1 nm slit width, at a scanning rate of  $120.00 \text{ nm min}^{-1}$ . The observed rate constants were computed using the “Glint” program based on a global analysis [8-11].

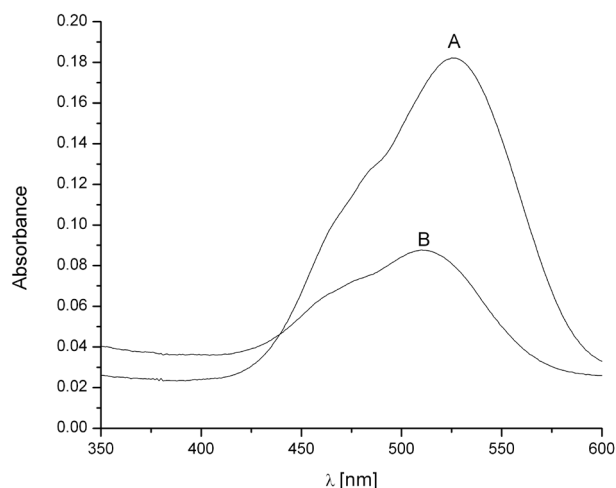
## 3 Results and discussion

In the solid state, the  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  complex exists as a polymer in which the ODA ligand displays the *mer*-conformation [12]. In solution, however, the cobalt(II) cation is probably hexacoordinated by three molecules of water and the tridentate ODA ligand can adopt both *mer*- and *fac*-coordination [13]. The  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  complex in aqueous solutions undergoes an aquation reaction induced by the  $\text{Fe}^{3+}$  ions, resulting in the substitution of the oxydiacetate anion by three water molecules (Eq. 1).



For all substrates and products of Reaction 1, the electronic spectra in the UV-Vis region were recorded. The spectra of the substrate  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  and the final product of the complete aquation product  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  are shown in Fig. 1. To prove that the final product of reaction is completely aquated, the spectrum of dissolved  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was also recorded and compared with that obtained for the final product of the aquation reaction of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$ . Both spectra were identical.

Based on the recorded spectra, the changes of absorbance in time were recorded in the region of the d-d low-energy bands at a wavelength  $\lambda = 550 \text{ nm}$ , where the largest differences in the absorbance between the substrate and product were observed. Furthermore, it was verified that the other species involved in the chemical reaction did not interfere with kinetic studies, since the absorption maximum for the  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$  substrate occurred at a wavelength  $\lambda = 305 \text{ nm}$ , while for the reaction product,  $[\text{Fe}(\text{ODA})(\text{H}_2\text{O})_3]^+$ , it occurred at  $\lambda = 440 \text{ nm}$ .



**Figure 1:** Electronic spectra of the reactant -  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  (A) and the final product  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (B) of the aquation reaction.

In order to determine the values of the observed reaction rate constants (Table 1), a global analysis method based on the model reaction  $A \rightarrow B$  was used. Very good agreement with the following first order reaction scheme was obtained:

$$\frac{-[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]}{dt} = k_{\text{obs}} \cdot [\text{Co}(\text{ODA})(\text{H}_2\text{O})_3] \quad (2)$$

Moreover, on the basis of the observed rate constants  $k_{\text{obs}}$ , a dependence of the rate constants on the concentration of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ions has been found. The pseudo-first-order rate constants depend linearly on the concentration of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  at all five temperatures studied, and the plots of  $k_{\text{obs}}$  versus  $c_{\text{Fe}^{3+}}$  have positive y-intercepts (Fig. 2). The results shown in Fig. 2 are consistent with the following equation:

$$k_{\text{obs}} = (k + k_1 K [\text{Fe}(\text{H}_2\text{O})_6]^{3+}) / (1 + K [\text{Fe}(\text{H}_2\text{O})_6]^{3+}) \quad (3)$$

where  $k$  represents the spontaneous reaction that takes place in the absence of the promoter,  $K$  is the precursor formation constant describing a fast pre-equilibrium step between the reactants and the dinuclear heterometallic intermediate and  $k_1$  denotes the interchange rate constant for a rate controlling step in which the intermediate undergoes decomposition to produce  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{ODA})(\text{H}_2\text{O})_3]^+$ .

However, only a limiting case of Eq. 3 is typically observed [14,15], since if  $1 \gg K[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , then Eq. 3 simplifies to Eq. 4:

$$k_{\text{obs}} = k + k_1 K [\text{Fe}(\text{H}_2\text{O})_6]^{3+} \quad (4)$$

**Table 1:** The promoter concentration (in the 0.00125 M – 0.125 M range of the Fe(III) ions) dependence of the observed rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) of the aquation reaction studied at five temperatures. The concentration of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3] = 4 \times 10^{-3}$  M,  $[\text{H}_3\text{O}^+] = \text{const} = 0.15$  M, ionic strength  $I = 1.0$  M. Standard deviation values are also given.

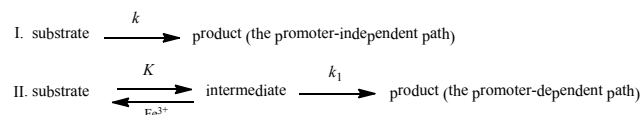
$c_{\text{Fe}^{3+}} [\text{M}]$	T [K]				
	283.15	288.15	293.15	298.15	303.15
$1.25 \times 10^{-3}$	$3.14 \times 10^{-4}$ $\pm 0.03 \times 10^{-4}$	$9.04 \times 10^{-4}$ $\pm 0.14 \times 10^{-4}$	$2.20 \times 10^{-3}$ $\pm 0.03 \times 10^{-3}$	$3.26 \times 10^{-3}$ $\pm 0.23 \times 10^{-3}$	$5.79 \times 10^{-3}$ $\pm 0.33 \times 10^{-3}$
$3.125 \times 10^{-2}$	$7.30 \times 10^{-4}$ $\pm 0.13 \times 10^{-4}$	$1.93 \times 10^{-3}$ $\pm 0.04 \times 10^{-3}$	$3.50 \times 10^{-3}$ $\pm 0.38 \times 10^{-3}$	$5.51 \times 10^{-3}$ $\pm 0.34 \times 10^{-3}$	$7.60 \times 10^{-3}$ $\pm 0.22 \times 10^{-3}$
$6.25 \times 10^{-2}$	$1.54 \times 10^{-3}$ $\pm 0.04 \times 10^{-3}$	$3.09 \times 10^{-3}$ $\pm 0.05 \times 10^{-3}$	$4.93 \times 10^{-3}$ $\pm 0.17 \times 10^{-3}$	$7.56 \times 10^{-3}$ $\pm 0.36 \times 10^{-3}$	$8.61 \times 10^{-3}$ $\pm 0.17 \times 10^{-3}$
$9.375 \times 10^{-2}$	$2.12 \times 10^{-3}$ $\pm 0.03 \times 10^{-3}$	$3.89 \times 10^{-3}$ $\pm 0.16 \times 10^{-3}$	$5.61 \times 10^{-3}$ $\pm 0.41 \times 10^{-3}$	$8.89 \times 10^{-3}$ $\pm 0.30 \times 10^{-3}$	$1.04 \times 10^{-2}$ $\pm 0.04 \times 10^{-2}$
$1.25 \times 10^{-1}$	$2.39 \times 10^{-3}$ $\pm 0.08 \times 10^{-3}$	$4.66 \times 10^{-3}$ $\pm 0.14 \times 10^{-3}$	$6.49 \times 10^{-3}$ $\pm 0.06 \times 10^{-3}$	$1.01 \times 10^{-2}$ $\pm 0.03 \times 10^{-2}$	$1.39 \times 10^{-2}$ $\pm 0.04 \times 10^{-2}$

**Table 2:** The values of the spontaneous reaction rate  $k$  ( $\text{s}^{-1}$ ) and the apparent second-order rate constant  $k_1' = k_1 \cdot K$  ( $\text{M}^{-1} \text{s}^{-1}$ ) for the aquation of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  at five temperatures studied. The concentration of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  equals  $4 \times 10^{-3}$  M,  $[\text{H}_3\text{O}^+] = 0.15$  M, ionic strength ( $\text{Na}^+$ ,  $\text{NO}_3^-$ ) = 1.0 M.

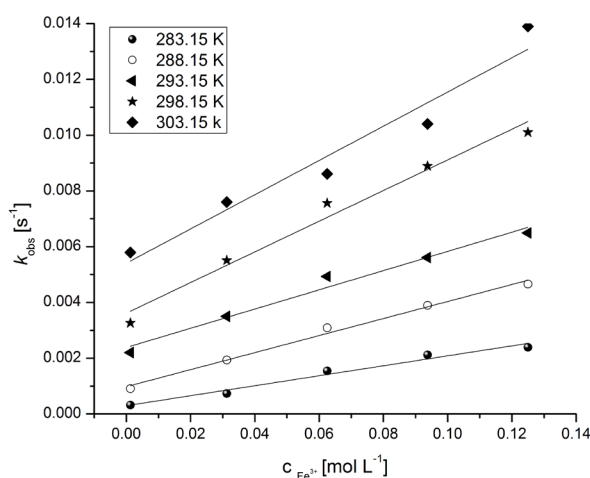
T [K]	$k \times 10^2 [\text{s}^{-1}]$	$k_1' \times 10^2 [\text{M}^{-1} \text{s}^{-1}]$
283.15	$0.03 \pm 0.01$	$1.79 \pm 0.16$
288.15	$0.10 \pm 0.01$	$3.05 \pm 0.16$
293.15	$0.24 \pm 0.02$	$3.45 \pm 0.29$
298.15	$0.36 \pm 0.04$	$5.46 \pm 0.47$
303.15	$0.54 \pm 0.06$	$6.14 \pm 0.79$

Eq. 4 consists of two parts - the first term is independent while the second term is dependent on the concentration of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ions. The factor  $k_1 K$  cannot be separated into two independent constants ( $k_1$  and  $K$ ) due to the linear dependence presented in Fig. 2. The values of  $k$  and  $k_1 K$  for all temperatures studied are listed in Table 2.

Based on the analysis of the kinetic relationships (Eqs. 2, 3 and 4), it can be suggested that the investigated reaction proceeds in two parallel paths (Scheme 1):



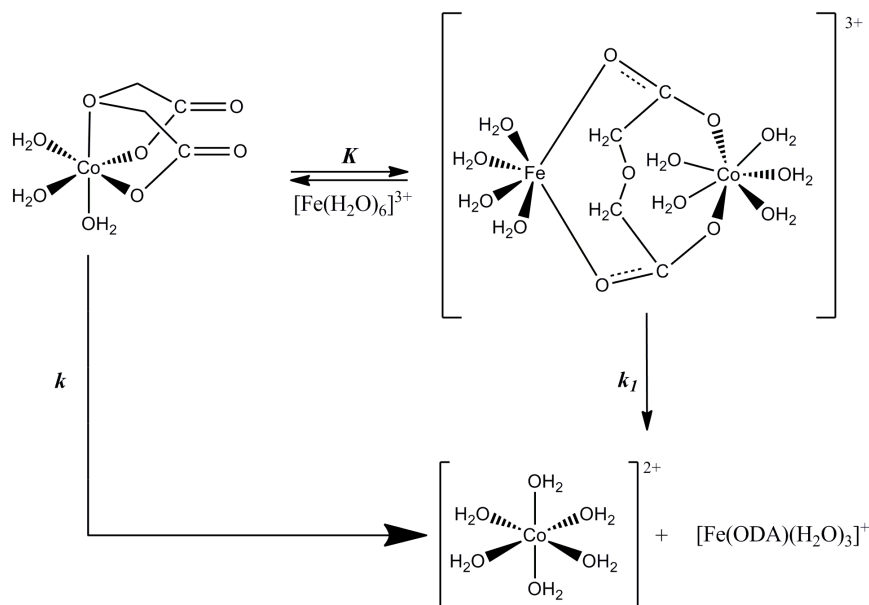
In the first path the aquation of the complex is independent on the concentration of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ions. In the second path, a fast reversible reaction takes place. A binuclear intermediate complex is formed by the interaction of the  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  complex via the two carboxylate oxygen atoms of the ODA ligand with the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion. The formation of the intermediate species precedes the dissociation of two water molecules from the



**Figure 2:** The dependence of the observed rate constants  $k_{\text{obs}}$  for the aquation reaction at five temperatures. The concentration of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3] = 4 \times 10^{-3}$  M,  $[\text{H}_3\text{O}^+] = \text{const} = 0.15$  M, ionic strength ( $\text{Na}^+$ ,  $\text{NO}_3^-$ )  $I = 1.0$  M.

coordination sphere of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and the substitution of the ethereal oxygen then follows. This assumption can be supported by comparing the donor-acceptor bond lengths in the oxydiacetate cobalt(II) complex. In the solid state, the bonds between the terminal chelating oxygens and cobalt(II) are shorter than that the ethereal oxygen bond [16]. For this reason the Co-O(ethereal) bond is probably less stable and breaks first, creating a new bond to the iron(III) ion. Then, the intermediate complex decomposes during the rate controlling step, producing,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{ODA})(\text{H}_2\text{O})_3]^+$ .

An attempt was made to detect spectrophotometrically the intermediate dual-core complex. For this purpose, the additivity of spectra of individual reactants and their



**Scheme 1:** The proposed mechanism of the substitution reaction of the oxydiacetate anion in  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  induced by  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

mixtures was tested. It has been found that there are no deviations from the additivity in the analyzed spectra, which might indicate a very low concentration of the intermediate in the reaction system, and, consequently, a very low value of the equilibrium constant of the reaction. The low value of the equilibrium constant  $K$  is consistent with the linear relationship between rate constants and the concentration of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , as shown in Fig. 2.

In addition, using the Arrhenius and Eyring equations [17,18], the reaction activation parameters were determined for the spontaneous and the  $\text{Fe}(\text{III})$  ion-induced steps of the reaction (Table 3). In contrast to the process in which the  $\text{Fe}^{3+}$  ion acts as a promoter of the reaction, the activation energy is over two times higher for the spontaneous aquation step. The differences in both values of the activation energy and the rate constants ( $k$  and  $k_1'$ ) of these two steps are in an agreement with the empirical Arrhenius equation describing the relationship between the rate constant and the activation energy (the higher the activation energy, the lower the rate constant). The activation enthalpy ( $\Delta H^\ddagger$ ) for the spontaneous reaction is also *ca.* two times higher. Thus, the absolute value of the free energy ( $\Delta G^\ddagger$ ) of activation resulting in the formation of the transition complex tends to be higher and, consequently, the rate of aquation of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  in the absence of the  $\text{Fe}^{3+}$  ion is slower. It is also worth noting that the change in the activation entropy in the presence of the  $\text{Fe}^{3+}$  ion is negative (Table 3). Since the slope of the plots in Fig. 2 represents  $k_1K$ , the experimental value of  $\Delta S^\ddagger$  can be expressed as  $\Delta S^\ddagger(k_1K) = \Delta S^\ddagger(k_1) + \Delta S^\circ(K)$ . Thus, the

**Table 3:** Activation parameters for the aquation of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$ .

Rate constant	$\Delta H^\ddagger$ [kJ mol <sup>-1</sup> ]	$\Delta S^\ddagger$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$E_a$ [kJ mol <sup>-1</sup> ]
$k_1' = k_1 \cdot K$	$41 \pm 5$	$-132 \pm 17$	$44 \pm 5$
$k$	$99 \pm 14$	$98 \pm 56$	$101 \pm 14$

very negative value of  $\Delta S^\ddagger$  can be ascribed to the formation of a more rigid structure of the activated complex in the region of the transition state (fewer degrees of freedom); hence  $\Delta S^\circ(K)$  is lower than the entropy of the substrates in the ground state. On the other hand, the positive value for  $\Delta S^\ddagger(k)$  can point to a dissociative interchange mechanism for the spontaneous reaction.

## 4 Conclusions

The rate of aquation of  $[\text{Co}(\text{ODA})(\text{H}_2\text{O})_3]$  has been determined spectrophotometrically at 550 nm. The reaction was studied in the presence of the  $\text{Fe}^{3+}$  ion as a promoter. It has been found that the values of the observed rate constants  $k_{\text{obs}}$  increase proportionally with the concentration of the promoter over the entire range of temperatures studied (283.15 - 303.15 K). Based on kinetic data, it has been suggested that the reaction studied proceeds in two parallel paths. The first path is the promoter-independent ( $k$ ) and is likely to proceed according to a dissociative interchange mechanism.

The second path consists of two steps. The first one is fast and reversible ( $K$ ). It depends on the concentration of iron(III) and results in the formation of a binuclear intermediate complex. In the second, rate-controlling step, the decomposition of the intermediate takes place ( $k_1$ ), resulting in the formation of the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{ODA})(\text{H}_2\text{O})_3]^+$  species. The activation energy and the activation enthalpy calculated based on the Arrhenius and Eyring equations are higher for the spontaneous, iron(III)-independent path of the reaction. These findings confirm that the aquation of the complex is driven by the presence of the promoter in the system under study. The transition state in the case of the fast step is more ordered in comparison to the state of the substrates, probably due to a more rigid structure of the activated complex. It leads to the reduction of the degrees of freedom of translation, rotation or vibration of the activated complex in comparison to the degrees of freedom of the substrates. However, the  $\Delta H^\ddagger$  for this path is *ca.* two times lower than that of the promoter-independent path of the aquation and overcompensates the negative value of  $\Delta S^\ddagger$ . Thus, the change in the free energy of activation ( $\Delta G^\ddagger$ ) is lower for the iron(III)-dependent path of reaction. The aquation rate of the complex under study is mainly governed by the dissociation of the intermediate binuclear complex.

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