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Kinetics of the Anation of Diaquobis(ethylenediamine)cobalt(III) by Oxalic Acid in Aqueous Acidic Solution. Pressure and Medium Effects

R. VAN ELDIK

Institute for Physical Chemistry, University of Frankfurt, Robert Mayer Str. 11, 6000 Frankfurt/Main, F.R.G.

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The anation of cis-*diaquobis(ethylenediamine)cobalt(III) by oxalic acid has been reported in the literature to be catalyzed by nitrate ion. In this study the pressure dependence of the* k_{obs} versus *oxalic acid concentration plots was measured for the anation process in both perchlorate and nitrate reaction media at* $[H^+] = 2.0$ M. *The reported data at normal pressure are in good agreement with earlier findings. The volume of activation for the nitrate promoted anation process is interpreted in terms of a dissociative process in which a five-coordinate intermediate is formed. The discrimination ability of this intermediate to produce the diaquo or oxalato species, is independent of pressures up to 1500 bar.*

Introduction

The kinetics of the anation of diaquobis(ethylenediamine)cobalt(III) by oxalic acid and bioxalate ion in acidic aqueous solution [1] was recently reinvestigated [2] due to a discrepancy that existed between this and analogous systems reported in the literature [3–6]. In the original study Brown and Harris [1] reported kinetic evidence for strong ion-pair formation, as illustrated by the formation constants of 11 and 100 M^{-1} at 50 °C for the species *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4$ and *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot HC_2O_4^-$, respectively. This was in disagreement with later reported data [3–6] in which significantly smaller ion-pair formation constants were measured kinetically for very similar systems. In the reinvestigation [2] it was shown that the anation reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by $H_2C_2O_4$ and $HC_2O_4^-$ are strongly catalyzed by the presence of nitrate ion in solution, which resulted in abnormally high ion-pair formation constants as found by Brown and Harris [1]. It was further suggested that the catalyzed reaction proceeds *via* the formation of a five-coordinate intermediate, *viz.* $Co(en)_2(OH_2)^{3+}$, followed by the associative entrance of an oxalate molecule.

Stranks and Vanderhoek [7] studied the pressure dependence of this anation reaction under concentration and medium conditions similar to those of Brown and Harris [1]. Unfortunately, their interpretation of the obtained data was based on the mechanism proposed before [1], in which the strong curvature in the k_{obs} *versus* [total oxalate] plots was interpreted as evidence for ion-pair formation and not as resulting from catalysis by the nitrate reaction medium as reported recently [2]. Since the exact nature of the catalysis process is of great interest to us, the pressure dependence of the anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by oxalic acid was remeasured in both nitrate and perchlorate media. These data are discussed in reference to the data obtained in the earlier pressure dependence study [7] and the conclusions reached before [2–5, 8], which were based on kinetic measurements at normal pressure.

Experimental

The complex species *cis*-$Co(en)_2(OH_2)_2^{3+}$ and *cis*-$Co(en)_2(C_2O_4)^+$ were prepared and characterized as described before [2]. Spectra were recorded on a Zeiss DMR 10 spectrophotometer, and spectral changes during the anation reaction were measured on a Zeiss PMQ II instrument equipped with a thermostatted (±0.1 °C) high-pressure cell [9].

The reactions were studied in either 2 *M* $HClO_4$ or 2 *M* HNO_3. All chemicals used were of reagent grade, and doubly distilled water was used throughout the investigation. The reactions were monitored for at least 10 half-lives. The observed pseudo-first-order rate constants, k_{obs}, were calculated from plots of $\ln(A_\infty - A_t)$ *versus* t, where A_∞ and A_t are the absorbances at infinite time and time t, respectively. These plots were linear for at least 2 to 3 half-lives under all conditions.

Results and Discussion

The experimental conditions of this investigation were chosen in such a way as to simplify the chemical system to a great extent. At an acid concentration of

TABLE I. Rate Data for the Anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by $H_2C_2O_4$ in Perchlorate Medium; [Co(III)] = 5×10^{-3} *M*, [H^+] = 2.0 *M*, Temp. = 70 °C, Wavelength = 353 nm.

[$H_2C_2O_4$] *M*	k_{obs}[a] × 10^4, sec^{-1}			
	P(bar) = 10	500	1000	1500
0.10	0.419	0.402	0.402	0.381
0.20	0.782	0.763	0.690	0.679
0.30	1.018	1.030	0.995	1.000
0.40	1.581	1.542	1.553	1.555
0.50	1.968	1.932	1.934	1.920

[a] Mean value of at least two kinetic runs; standard deviation ≤2%.

TABLE II. Rate Data for the Anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by $H_2C_2O_4$ in Nitrate Medium; [Co(III)] = 5×10^{-3} *M*, [H^+] = 2.0 *M*, Temp. = 60 °C, Wavelength = 353 nm.

[$H_2C_2O_4$] *M*	k_{obs}[a] × 10^4, sec^{-1}			
	P(bar) = 10	500	1000	1500
0.05	1.344	1.302	1.267	1.202
0.10	2.040	2.095	2.011	1.943
0.20	3.040	2.945	2.706	2.747
0.30	3.505	3.318	3.030	3.041
0.40	3.728	3.627	3.545	3.389
0.50	3.911	3.858	3.626	3.545

[a] Mean value of at least two kinetic runs; standard deviation ≤3%.

2 *M*, the bis(ethylenediamine)cobalt(III) complex is present as the *cis*-diaquo species [10, 11] and oxalic acid is the only oxalate species of importance [12]. Under such conditions [1, 2] the overall reaction is

$$\mathit{cis}\text{-Co(en)}_2(\mathrm{OH}_2)_2^{3+} + \mathrm{H_2C_2O_4} \xrightarrow{\text{slow}}$$

$$\mathit{cis}\text{-Co(en)}_2(\mathrm{OH}_2)(\mathrm{HC_2O_4})^{2+} + \mathrm{H_3O^+}$$

$$\text{fast}\big\downarrow$$

$$\mathit{cis}\text{-Co(en)}_2(\mathrm{C_2O_4})^{+} + \mathrm{H_3O^+}$$

in which the anation by oxalic acid is the rate-determining step, followed by a rapid ring-closing process. Such a simplification on the one hand, is of particular importance for the interpretation of the measured volume of activation. Contributions to $\Delta V^{\neq}$ that arise from the effect of pressure on the acid dissociation constants of axalic acid and the *cis*-diaquo species [7], as well as the equilibrium constants for *cis–trans* isomerization, can be assumed to be negligible. On the other hand, however, it is still possible to investigate the outlined discrepancy further since the anation reaction by oxalic acid clearly shows the nitrate catalysis effect [2].

It was reported [2] that similar isosbestic points and reaction products are obtained for the above reaction in both nitrate and perchlorate media. Since the reaction is significantly slower in perchlorate medium, it was studied at a higher temperature in order to obtain reasonable rate constants. The kinetic data as function of [oxalic acid] and pressure are summarized in Tables I and II for perchlorate and nitrate reaction media, respectively. Plots of k_{obs} *versus* [$H_2C_2O_4$] as a function of pressure for the reaction in perchlorate medium (Table I) are all within experimental error limits linear and do not exhibit any meaningful curvature. In the earlier study [2], slight curvature was observed in such plots (see Fig. 1 of ref. 2) for similar data at lower temperature and/or lower ionic strength, and ion-pair formation constants in the order of 0.8 M^{-1} were reported. However, it has been discussed in detail [13] that ion-pair formation constants decrease significantly on increasing the ionic strength as observed in this study. In addition, the present observations are in good agreement with those for closely related anation reactions [3–6] involving carboxylic acids as anating reagents.

The suggested mechanism for the reaction in perchlorate medium consists of the reactions [1, 2]

TABLE III. Values of k_1Q_1 as Function of Pressure.

Pressure (bar)	$k_1Q_1{}^a \times 10^4$ M^{-1} sec^{-1}	$(k_1Q_1)_{corr}{}^b \times 10^4$ M^{-1} sec^{-1}
10	3.87 ± 0.18	3.87 ± 0.18
500	3.81 ± 0.14	3.73 ± 0.14
1000	3.84 ± 0.19	3.69 ± 0.18
1500	3.84 ± 0.18	3.64 ± 0.17
$\Delta V^{\neq}$, cm^3 mol^{-1}		+1.10 ± 0.24

[a] Calculated from a least squares fit of the data in Table I, adding one zero point to each set of data. [b] Corrected for the compressibility of the solvent.

$$\begin{tikzcd} cis\text{-}Co(en)_2(OH_2)_2^{3+} + H_2C_2O_4 \arrow[r, shift left, "Q_1"] & \arrow[l, shift left] \{cis\text{-}Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4\} \arrow[d, "k_1"] \\ & cis\text{-}Co(en)_2(C_2O_4)^+ + 2H_3O^+ \end{tikzcd} \qquad (1)$$

for which $k_{obs} = k_1Q_1[H_2C_2O_4]/\{1 + Q_1[H_2C_2O_4]\}$ Since no meaningful kinetic evidence for the participation of ion-pairs was found, it follows that Q_1 is rather small such that $1 + Q_1[H_2C_2O_4] \cong 1$ and $k_{obs} = k_1Q_1[H_2C_2O_4]$.

The values of k_1Q_1 are summarized in Table III and it can be seen that they do not exhibit any pressure dependence. The value at 10 bar is in close agreement with the value (5.3 ± 1.5) × 10^{-4} M^{-1} sec^{-1} reported [2] at normal pressure and $[H^+] = 1.0$ *M*. If we consider the reaction to be a second-order process with rate constant k_1Q_1, the latter should be corrected for the compressibility of the solvent [14]. It follows from Table III that $(k_1Q_1)_{corr}$ decreases slightly with increasing pressure, such that $\Delta V^{\neq} = +1.1 \pm 0.2$ cm^3 mol^{-1}. The sign and magnitude of this value is considered as evidence for an I_d mechanism when interpreted as discussed in detail before [13]. It is, furthermore, in close agreement with the values +1.4 ± 0.8 and +2.3 ± 1.8 cm^3 mol^{-1} reported [13] for the anation of $Co(NH_3)_5OH_2^{3+}$ by Cl^- and SO_4^{2-}, respectively, for which also no kinetic evidence for the participation of ion-pairs at an ionic strength of 2.0 *M* could be found.

A comparison of the data in Tables I and II confirms the substantial difference in k_{obs} for the two media, especially when the 10 °C temperature difference is taken into account. Furthermore, plots of k_{obs} *versus* $[H_2C_2O_4]$ for the anation reaction in nitrate medium (Table II) are strongly curved, in agreement with similar observations reported before [1, 2, 7]. If this curvature is interpreted as evidence for ion-pair formation, the appropriate fit of the data [1, 2] results in ion-pair formation constants between 7.2 and 7.9 M^{-1} for pressures up to 1500 bar and at 60 °C. These values are in good agreement with that reported by Brown and Harris [1] for the anation by oxalic acid at normal pressure, *viz.* 7 M^{-1} at 60 °C. In addition these values are much larger than that found for the reaction in perchlorate medium in the present and earlier [2] study. However, it was shown [2] that the observed curvature in the k_{obs} *versus* $[H_2C_2O_4]$ plots is a result of a nitrate catalysis effect for which the following mechanism was suggested:

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \xrightarrow{k_2} Co(en)_2(OH_2)^{3+} + NO_3^- + H_2O \qquad (2)$$

$$\begin{tikzcd} Co(en)_2(OH_2)^{3+} + NO_3^- \arrow[r, "k_3"] & cis\text{-}Co(en)_2(OH_2)(NO_3)^{2+} \arrow[d, "fast"', "+H_2O"] \\ & cis\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \end{tikzcd} \qquad (3)$$

$$\begin{tikzcd} Co(en)_2(OH_2)^{3+} + H_2C_2O_4 \arrow[r, "k_4"] & cis\text{-}Co(en)_2(OH_2)(HC_2O_4)^{2+} + H^+ \arrow[d, "fast"', "ring\ closure"] \\ & cis\text{-}Co(en)_2(C_2O_4)^+ + H_3O^+ \end{tikzcd} \qquad (4)$$

In this mechanism a five-coordinate intermediate $Co(en)_2(OH_2)^{3+}$ is produced, which can either react with NO_3^- followed by a rapid aquation step, or react with $H_2C_2O_4$ followed by a rapid ring-closing step.

For the nitrate promoted process [2]

$$k_{obs} = \frac{k_2k_4[NO_3^-][H_2C_2O_4]}{k_3[NO_3^-] + k_4[H_2C_2O_4]} \qquad (5)$$

TABLE IV. Values of k_2 and k_4/k_3 as Function of Pressure.

Pressure (bar)	$k_2{}^a \times 10^4$ M^{-1} sec^{-1}	$(k_2)_{corr}{}^b \times 10^4$ M^{-1} sec^{-1}	$(k_4/k_3)^a$
10	2.08 ± 0.07	2.08 ± 0.07	17.7 ± 1.1
500	2.03 ± 0.06	1.98 ± 0.06	17.9 ± 1.0
1000	1.83 ± 0.05	1.76 ± 0.05	19.8 ± 1.2
1500	1.85 ± 0.07	1.75 ± 0.06	18.1 ± 1.3
$\Delta\bar{V}^{\neq}$, cm^3 mol^{-1}	–	+3.50 ± 0.78	–

[a] Calculated from a least squares fit of the data in Table II according to eqn. (7); see Fig. 1. [b] Corrected for the compressibility of the solvent.

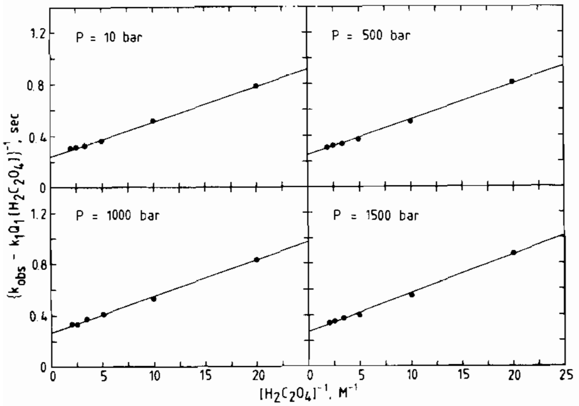

Fig. 1. $\{k_{obs} - k_1Q_1[H_2C_2O_4]\}^{-1}$ *versus* $[H_2C_2O_4]^{-1}$ for the data in Table II according to eqn. (7).

which, when combined with the rate law for the uncatalyzed (background) reaction, yields the overall expression

$$k_{obs} = k_1Q_1[H_2C_2O_4] + \frac{k_2k_4[NO_3^-][H_2C_2O_4]}{k_3[NO_3^-] + k_4[H_2C_2O_4]} \quad (6)$$

Equation (6) can be rewritten in the form

$$\{k_{obs} - k_1Q_1[H_2C_2O_4]\}^{-1} = k_3\{k_2k_4[H_2C_2O_4]\}^{-1} + \{k_2[NO_3^-]\}^{-1} \quad (7)$$

In this equation k_1Q_1 is independent of pressure (Table III) and has a value of 1.3 × 10^{-4} M^{-1} sec^{-1} at 60 °C as extrapolated from the data in Table III and the activation parameters determined before [2]. Plots of $\{k_{obs} - k_1Q_1[H_2C_2O_4]\}^{-1}$ *versus* $[H_2C_2O_4]^{-1}$ as a function of pressure for the data in Table II, are all linear (Fig. 1) and confirm the validness of the suggested mechanism. From the intercept and slope of these plots, k_2 and k_4/k_3 were calculated as function of pressure (Table IV) since $[NO_3^-]$ was kept constant at 2.0 *M*. Reactions (2) to (4) are all second-order processes with the result that the rate constants k_2, k_3 and k_4 must be corrected for the compressibility of the solvent [14]. This, however, has no effect on the ratio of two such rate constants (*i.e.* k_4/k_3). From the pressure dependence of $(k_2)_{corr}$ an activation volume of +3.5 ± 0.8 cm^3 mol^{-1} was estimated.

In general, $\Delta\bar{V}^{\neq}$ consists of two components [15–17]: an intrinsic part, $\Delta V^{\neq}_{intr}$, due to alterations in bond lengths and angles during the formation of the transition state, and a solvation part, $\Delta V^{\neq}_{solv}$, resulting from variations in solvation. Since no charges are quenched or created to any significant extent in reaction (2), no major changes in solvation are expected, such that $\Delta V^{\neq}_{solv} \cong 0$. This is in agreement with the pressure independence of $\Delta\bar{V}^{\neq}$, and it follows that $\Delta\bar{V}^{\neq} \cong \Delta V^{\neq}_{intr}$. On this basis the positive activation volume for k_2 (Table IV) can be interpreted as indication that partial bond cleavage occurs during the activation process. In addition, this value is close to that reported for aquo exchange [18] on $Co(en)_2(OH_2)_2^{3+}$, *viz.* $\Delta\bar{V}^{\neq}$ = +5.9 ± 0.2 cm^3 mol^{-1} at 35 °C, which was interpreted as evidence for a dissociative interchange mechanism involving the formation of a five-coordinate tetragonal-pyramidal intermediate [18]. It is, therefore, concluded that the $\Delta\bar{V}^{\neq}$ data for k_2 confirms the dissociative nature of reaction (2).

The ratio k_4/k_3 is within experimental error limits independent of pressure and has an average value of 18.4 ± 1.0. This means that the reaction of the five-coordinate intermediate with $H_2C_2O_4$ is approx. 20 times faster than the reaction with NO_3^- at 60 °C. This ratio is smaller than that found previously [2] at 50 °C, *viz.* k_4/k_3 = 48 ± 20. The pressure independence of k_4/k_3 illustrates that both processes exhibit similar pressure dependencies, or in other words, that reactions (3) and (4) probably proceed according to similar mechanisms. This is within reasonable expectation since both steps involve metal-ligand bond formation accompanied by either charge neutralization (reaction with NO_3^-) or charge separation (reaction with $H_2C_2O_4$).

In conclusion, it is appropriate to point out that the data reported and conclusions drawn in this study, are in good agreement with that reported before [1, 2, 7]. In general, the values of $\Delta\bar{V}^{\neq}$ support the nature of the suggested mechanisms, but are such that they do not allow detailed interpretation. One would expect $\Delta\bar{V}^{\neq}$ to be larger for a purely dissociative step as in reaction (2), indicating a possible counter effect of secondary bond formation with the nitrate ion. Furthermore, since k_3 and k_4 could not be separated, and $\Delta\bar{V}^{\neq}$ for reactions (3) and (4) could, therefore, not be determined, no further information concerning the intimate mechanism involved in these reactions could be reported. It follows that the mechanistic detail of the nitrate promoted anation reactions of *cis*-diaquobis(ethylenediamine)cobalt(III) has, despite various attempts, not been clarified unequivocally.

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