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KINETICS OF ANATION OF *CIS*-DIAQUO-BIS-(1,3-DIAMINOPROPANE) COBALT(III) BY OXALATE

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The kinetics of anation of *cis*-diaquobis(1,3-diaminopropane) cobalt(III) by oxalic acid and bioxalate anion have been studied at 35°, 40° and 45°C, I = 1.0 M(NaClO₄). The observed rate law for the formation of Co(tmd)₂C₂O₄⁺,

$$-\frac{d \ln[\text{Co(III)}]_T}{dt} = k_{\text{obs}} = \frac{k_1 Q_1 [\text{H}_2\text{C}_2\text{O}_4] + k_2 Q_2 [\text{HC}_2\text{O}_4^-]}{1 + Q_1 [\text{H}_2\text{C}_2\text{O}_4] + Q_2 [\text{HC}_2\text{O}_4^-]}$$

is valid in the range of [Ox]_T = 0.03–0.50 M, pH = 0.3–2.03. The anation rate constants, k₁ and k₂, for *cis*-{Co(tmd)₂(OH₂)₂³⁺, H₂C₂O₄} and *cis*-{Co(tmd)₂(OH₂)₂³⁺, HC₂O₄⁻} ion pairs respectively are found to be virtually the same (k₁ = 10.7 × 10⁻⁴ sec⁻¹ and k₂ = 11.0 × 10⁻⁴ sec⁻¹ at 40°C). Temperature independent oxalic acid and bioxalate ion-pair association constants (Q₁ and Q₂) are 1.7(±0.3)M⁻¹ and 11.5(±0.7)M⁻¹, respectively. The activation enthalpy and entropy for k₁ and k₂ paths are 122.6 kJ mol⁻¹, 89.5 JK⁻¹ mol⁻¹ and 103.8 kJ mol⁻¹, 29.3 JK⁻¹ mol⁻¹, respectively. The anation of *cis*-{Co(tmd)₂(OH₂)₂³⁺, X} ion pairs (X = H₂C₂O₄ or HC₂O₄⁻) is believed to involve Id mechanism. The reaction is catalysed by NO₃⁻.

INTRODUCTION

The anation of *cis*-diaquobis-(ethylenediamine)cobalt(III) cation by oxalic acid and bioxalate anion has been studied by Harris and coworkers^{1,2} and by Stranks and Vanderhoek.³ From rate measurements in NO₃⁻-ClO₄⁻-media, Eldik and Harris² recently reported that NO₃⁻ catalysed the reaction; they presumed the formation of a reactive five coordinate intermediate, Co(en)₂OH₂³⁺. However, these groups of workers agreed that the anation of *cis*-diaquobis-(ethylenediamine)cobalt(III) cation by both oxalic acid and bioxalate anion involves outer sphere ion association equilibria between the reacting species followed by a rate determining outer sphere–inner sphere interconversion reaction virtually at the same rate by a dissociative interchange (Id) mechanism. The anation of the β-*cis*-Co(trien)(OH₂)₂³⁺ cation (trien = triethylenetetramine) by oxalate species has been studied by us.⁴ It was also observed that both the ion pairs, β-*cis*-{Co(trien)(OH₂)₂³⁺, H₂C₂O₄} and β-*cis*-{Co(trien)(OH₂)₂³⁺, HC₂O₄⁻} undergo anation virtually at the same rate. The anation reaction was believed to involve the Id mechanism. In continuation with the above work this paper reports the kinetics of anation of *cis*-diaquobis-(1,3-diaminopropane)cobalt(III) by oxalic acid and bioxalate anion. Our aim was to examine the effect of changing the chelate ring size on the rate and mechanism of the anation reaction of such *cis*-diaquo cations, *cis*-CoN₄(OH)₂³⁺, by oxalate species.

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EXPERIMENTAL

Trans-dichlorobis-(1,3-diaminopropane)cobalt(III) perchlorate was prepared by the reported method.⁵ Carbonatobis-(1,3-diaminopropane)cobalt(III) perchlorate was prepared from *trans*-dichlorobis-(1,3-diaminopropane)cobalt(III) perchlorate by closely following the method reported in the literature.⁶ The perchlorate salt of the carbonato complex was recrystallized a number of times from sodium perchlorate solution until it was free of chloride. The purity of the sample was checked by analysing its cobalt content. Anal: Calcd. for $[\text{Co}(\text{tmd})_2\text{CO}_3]\text{ClO}_4$: Co 16.07%. Found: Co 15.85%. The visible spectral parameters of the complex were found to be as follows; λ/nm (max)(ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 360(132), 520(109). For the kinetic runs *cis*- $[\text{Co}(\text{tmd})_2(\text{OH}_2)_2](\text{ClO}_4)_3$ was generated by adding a calculated amount of standard perchloric acid to a weighed amount of $[\text{Co}(\text{tmd})_2\text{CO}_3]\text{ClO}_4$. The spectral parameters of the diaquo complex in aqueous solution (0.10 M in HClO_4) were found to be as follows: λ_{max} (nm)(ϵ , $\text{M}^{-1} \text{cm}^{-1}$); 362(67.7), 505(55.2). All other reagents were of 'extrapure' or 'AnalaR' grade. Electronic spectra were measured with a Beckman DU spectrophotometer.

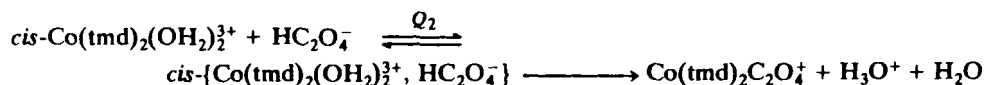
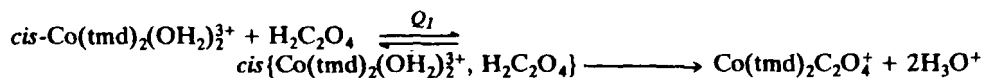
KINETICS

The kinetics of formation of $\text{Co}(\text{tmd})_2\text{C}_2\text{O}_4^+$ was followed spectrophotometrically at 510 nm, where extinction coefficients of the *cis*- $\text{Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ and $\text{Co}(\text{tmd})_2\text{C}_2\text{O}_4^+$ were 54.6 and 83.0 $\text{M}^{-1} \text{cm}^{-1}$, respectively. The details of the experimental procedure have been described earlier.⁴ The observed pseudo-first order rate constant was calculated from the slope of the linear plot of $\log(A_\infty - A_t)$ vs. time (sec), where A_∞ and A_t stand for the absorbance at the completion of the reaction and at any time t , respectively. A_∞ values agreed satisfactorily with the value calculated from the known extinction coefficient of $\text{Co}(\text{tmd})_2\text{C}_2\text{O}_4^+$. k_{obs} values reported are the average of at least duplicate runs which agreed within $\pm 3\%$.

RESULTS AND DISCUSSION

Observed pseudo first-order rate constants, k_{obs} , for the anation of *cis*- $\text{Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ by both oxalic acid and bioxalate anion have been collected in Table I. The rate data for the anation of *cis*- $\text{Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ by oxalic acid at $[\text{H}_2\text{C}_2\text{O}_4]_{\text{T}} = 0.20 \text{ M}$, $[\text{H}^+] = 0.50 \text{ M}$, $[\text{ClO}_4^-]_{\text{T}} = 0.995 - 0.025 \text{ M}$ and $[\text{NO}_3^-]_{\text{T}} = 0.00 - 0.93 \text{ M}$ (40°C) have been collected in Table II.

It is seen that k_{obs} increases with $[\text{H}_2\text{C}_2\text{O}_4]$ and $[\text{HC}_2\text{O}_4^-]$. However, $k_{\text{obs}}/[\text{H}_2\text{C}_2\text{O}_4]$ (at $[\text{H}^+] = 0.5 \text{ M}$, $[\text{HC}_2\text{O}_4^-] \approx 0.0$) and $k_{\text{obs}}/[\text{HC}_2\text{O}_4^-]$ at given $[\text{H}_2\text{C}_2\text{O}_4]$ decreases with $[\text{H}_2\text{C}_2\text{O}_4]$ and $[\text{HC}_2\text{O}_4^-]$, respectively. Such an observation is reconciled with the fact that the rate determining step in the anation reaction is preceded by reactant association. Keeping this in view the following reaction scheme may be suggested.



The rate law for such a scheme is given as

$$-\frac{d \ln[\text{Co(III)}]_{\text{T}}}{dt} = k_{\text{obs}} = \frac{k_1 Q_1 [\text{H}_2\text{C}_2\text{O}_4] + k_2 Q_2 [\text{HC}_2\text{O}_4^-]}{1 + Q_1 [\text{H}_2\text{C}_2\text{O}_4] + Q_2 [\text{HC}_2\text{O}_4^-]} \quad (1)$$

TABLE I
Pseudo first order rate constant for the anation of $\text{cis-Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ by oxalic acid and bioxalate anion

$\text{cis-Co}(\text{tmd})_2(\text{OH}_2)_2^{3+} = 5.0 \times 10^{-3}\text{M}, I = 1.0\text{M}(\text{NaClO}_4)$					
$[\text{H}_2\text{C}_2\text{O}_4][\text{NaHC}_2\text{O}_4][\text{H}^+]^a$			$10^4 k_{\text{obs}}, \text{sec}^{-1}$		
(M)	(M)	(M)	35°C	40°C	45°C
0.10		0.50	0.82	1.65	3.90
0.20		0.50	1.50	2.63	5.45
0.30		0.50	1.80	3.85	7.13
0.40		0.50	2.08	4.50	8.20
0.50		0.50	2.50	5.10	9.84
0.01	0.02	0.047	1.06	2.21	4.32
0.01	0.04	0.023	1.55	3.32	6.76
0.01	0.06	0.015	2.17	4.53	8.80
0.01	0.08	0.012	2.66	5.17	10.22
0.01	0.10	0.009	3.07	5.92	12.01
$10^4 k_1, \text{sec}^{-1}$			4.93	10.75	22.73
$10^4 k_2, \text{sec}^{-1}$			5.45	11.03	20.43
Q_1, M^{-1}			1.7(±0.3)	1.7(±0.3)	1.7(±0.3)
Q_2, M^{-1}			11.5(±0.7)	11.5(±0.7)	11.5(±0.7)

^aValues of $[\text{H}^+]$ for $\text{H}_2\text{C}_2\text{O}_4/\text{NaHC}_2\text{O}_4$ buffer medium were calculated using $\text{p}K_1(\text{H}_2\text{C}_2\text{O}_4) = 1.03$; $[\text{H}^+]$ was taken to be $[\text{HClO}_4]$ at 0.5 M.

When the anation is carried out at $[\text{H}^+] = 0.5\text{M}$, oxalic acid may be assumed to be the only anating species. Eq. (1) then reduces to

$$k_{\text{obs}} = \frac{k_1 Q_1 [\text{H}_2\text{C}_2\text{O}_4]}{1 + Q_1 [\text{H}_2\text{C}_2\text{O}_4]} \quad (2)$$

which can be rearranged to

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1 Q_1} \times \frac{1}{[\text{H}_2\text{C}_2\text{O}_4]} + \frac{1}{k_1} \quad (3)$$

A linear plot of k_{obs}^{-1} vs $[\text{H}_2\text{C}_2\text{O}_4]^{-1}$ (Figure 1) provides validity for Eq. (3). From the intercepts and slopes of such linear plots, k_1 and Q_1 could be calculated and these values are

TABLE II
Observed pseudofirst order rate constant for the anation of $\text{cis-Co}(\text{tmd})_2(\text{OH}_2)_2(\text{ClO}_4)_3$ by Oxalic acid in $\text{ClO}_4^-/\text{NO}_3^-$ media

$[\text{Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}] = 5.0 \times 10^{-3}\text{M}, [\text{H}_2\text{C}_2\text{O}_4] = 0.20\text{M}, [\text{H}^+] = 0.50\text{M}, I = 1.0\text{M}, \text{Temp.} = 40^\circ\text{C}.$

$[\text{ClO}_4^-]_T$	$[\text{NO}_3^-]_T$	$10^4 k_{\text{obs}}, \text{sec}^{-1}$
0.955	0.00	2.63
0.755	0.20	5.44
0.555	0.40	6.62
0.355	0.60	7.12
0.155	0.80	7.91
0.025	0.93	9.49

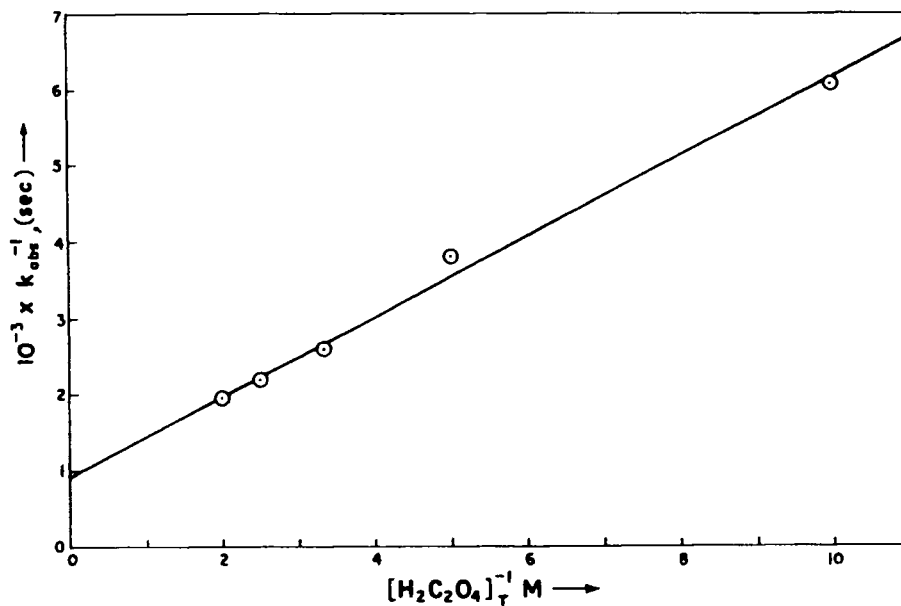


FIGURE 1

collected in Table I. To calculate k_2 and Q_2 , Eq. (1) can be rearranged to

$$Y = \frac{k_{\text{obs}}(1 + Q_1[\text{H}_2\text{C}_2\text{O}_4]) - k_1 Q_1[\text{H}_2\text{C}_2\text{O}_4]}{[\text{HC}_2\text{O}_4^-]} = k_2 Q_2 - Q_2 k_{\text{obs}} \quad (4)$$

The rate constant (k_2) and the association constant (Q_2) of the bioxalate ion pair, $\text{cis}\{\text{Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}, \text{HC}_2\text{O}_4^-\}$ were calculated from the slope and intercept of the Y vs. k_{obs} plot utilising the rate data at $[\text{H}^+]_{\text{Calcd}} = 9.33 \times 10^{-3} - 4.67 \times 10^{-2} \text{ M}$. These values are incorporated in Table I. It is seen that the values of k_1 and k_2 at any temperature (35–45°C) are more or less the same. This is in keeping with earlier findings on the anation of $\text{cis-Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ and $\beta\text{-cis-Co}(\text{trien})(\text{OH}_2)_2^{3+}$ by oxalic acid and bioxalate anion. The ion pair association constants (Q_1 and Q_2) and kinetically temperature independent in the range studied. Activation enthalpies and entropies, ΔH^\ddagger and ΔS^\ddagger , were calculated from the relationship

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \left(\frac{\Delta S^\ddagger}{R} + \ln \frac{k'}{h} \right)$$

where k' and h are Boltzman constant and Planck's constant, respectively. Values of ΔH^\ddagger and ΔS^\ddagger are collected in Table III. Comparing the activation parameter data for the anation reaction of $\text{cis-Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ by oxalic acid and bioxalate anion with those of some other aquoamine systems (see Table III) it is reasonable to assume that oxalate ($\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^-) anation of $\text{cis-Co}(\text{tmd})_2(\text{OH}_2)_2^{3+}$ proceeds through Id mechanism.

It is seen that the anation rate constant for the diaquobis(1,3-diaminopropane)cobalt(III) system is about 100 times higher than that for diaquobis(ethylenediamine)cobalt(III) complex. This could be due to the fact that the formation of the five coordinate intermediate in the transition state is more favourable in case of the 1,3-diaminopropane complex compared to its ethylenediamine analogue. Six membered ring formation with the cobalt(III) centre by 1,3-diaminopropane is known to result in considerable steric strain which is relieved by

TABLE III
Comparative listing of the rate and activation parameters for the anation of aquoamine cobalt(III) cations by oxalate species

Complex	Anation species	$10^5 k$ (40°C) s^{-1}	ΔH^\ddagger $kJ mol^{-1}$	ΔS^\ddagger $J k^{-1} mol^{-1}$	Ref.
<i>cis</i> -Co(en) ₂ (OH ₂) ₂ ³⁺	H ₂ C ₂ O ₄	4.1	103.8 ± 2.1	6.3 ± 6.3	1
	HC ₂ O ₄ ⁻	1.6 ^a	114.6 ± 5.4 ^a	28.0 ± 15.9 ^a	2
		1.4 ^b	113.0 ± 3.3 ^b	23.0 ± 10.5 ^b	2
<i>cis</i> -Co(tmd) ₂ (OH ₂) ₂ ³⁺	H ₂ C ₂ O ₄	107.3	122.6	89.5	This work
	HC ₂ O ₄ ⁻	110.0	103.8	29.3	This work
β - <i>cis</i> -Co(trien)(OH ₂) ₂ ³⁺	H ₂ C ₂ O ₄ HC ₂ O ₄ ⁻	6.7	102.5	3.3	4
<i>cis</i> -Co(en) ₂ (NH ₃)OH ₂ ³⁺	H ₂ C ₂ O ₄	0.54 ^c	95.8 ± 13.8	-37.6 ± 41.8	8
	HC ₂ O ₄ ⁻	1.76	108.8 ± 2.1	12.6 ± 8.4	8
(NH ₃) ₅ CoOH ₂ ³⁺	H ₂ C ₂ O ₄	2.03 ^c	57.3 ± 0.8	-150.6 ± 4.2	9
	HC ₂ O ₄ ⁻	1.94	93.7 ± 9.2	-37.6 ± 29.3	10

^aData for H₂C₂O₄; ^bData for HC₂O₄⁻; ^cUnit: s⁻¹ M⁻¹.

expansion of its bite angle with the cobalt(III) centre on formation of the five coordinate intermediate.⁷ The higher rate constant for the anation of the diaquo *bis*-(1,3-diaminopropane) cobalt(III) complex thus provides an indirect confirmation of this reaction proceeding by the Id mechanism.

When the anation reaction is carried out in ClO₄⁻/NO₃⁻ media at 40°C, [H₂C₂O₄] = 0.2 M, [H⁺] = 0.50 M, I = 1.0 M, about four fold increase in *k*_{obs} values is noticed for NO₃⁻ variation in the range 0.00 to 0.93 M (see Table II). This suggests that the reaction is catalysed by NO₃⁻.

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