Kinetics of Iron(III) Catalysed Aquation of Oxalatopentaamminecobalt(III) in Aqueous Methanol Media

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Received 29 October 1982; rrvised and accepted 20 April 1983

Rate and equilibrium data for the Fe(III)-catalysed aquation of oxalatopentaamminecobalt(III) in 10-50% (v/v) methanol/water media (I=0.3 M) are reported at 40°, 45° and 50°C. The first order rate constant of water substitution at Co(III) centre for the binuclear species, (NH₃)₅CoOCOCO₂Fe⁴⁺, is moderately sensitive to the solvent composition. The plot of rate constants for the binuclear complex versus solvent composition shows a maximum in 30% (v/v) methanol at 40°C. Activation enthalpy and entropy data also decrease to minimum values in 30% methanol. These results are compatible with differential solvation of the initial and transition states of the binuclear species. The mechanism of substitution of water for FeC₂O₄⁺ at the Co(III) centre is believed to be I_d

The kinetics of aquation of oxalatopentaaminecobalt(III) in aqueous medium in the presence of several non-reducing, substitution labile metal ions, M^{n+} (n=2 or 3), revealed that the binuclear species (NH₃)₅CoOCOCO₂M⁽ⁿ⁺¹⁾⁺, catalyse substitution of water for C₂O₄M⁽ⁿ⁻²⁾⁺ at the cobalt(III) centre¹. Of all the metal ions studied, Fe(III) was found to be the most effective catalyst. The catalyst metal ion was presumed to be chelated by the oxalate moiety in the binuclear species¹. A recent stopped flow kinetic study² for the formation/dissociation of (NH₃)₅CoOCOCO₂Fe⁴⁺ also supports the formation of the chelated binuclear Fe(III)-complex which may have structure (I).

$$\begin{bmatrix} (NH_3)_5 CO-O-C=0 & 4+ \\ O=C-O & Fe(OH_2)_4 \\ (1) \\ \end{bmatrix} \\ \begin{bmatrix} (NH_3)_5 CO-O-C=-C=-C & 0\\ O=C-O & Fe(OH_2)_4^+ \\ \end{bmatrix} \\ \begin{bmatrix} (NH_3)_5 CO-O-C=-C=-O & Fe(OH_2)_4 \\ O=C-O & Fe(OH_2)_4^+ \\ \end{bmatrix}$$

For the species (I) undergoing dissociative aquation at Co(III) centre (i.e. with rate-limiting Co-O bond breaking) the transition state will have to be represented by structure (II).

Considering the charge shift from Fe(III) to Co(III) centre in the transition state it is reasonable to expect that the solvation pattern of the ground state and the dissociatively active transition state of the binuclear species will be considerably different.

In recent years several studies have appeared on the solvent effects on the spontaneous and Hg(II) catalysed aquation of haloaminecobalt(III) and related complexes^{3 -9}. Attempts have been made to interpret the solvent effects on the rates of these reactions by

considering the solvation of the reactants and the products in the initial and the transition state of the aquation process^{9,10}. It was, therefore, considered worthwhile to investigate the solvent effect on the aquation kinetics of carboxylatopentaammine-cobalt(III) in the presence of metal ions. We present in this paper kinetic data on the Fe(III) catalysed aquation of oxalatopentaamminecobalt(III). The reaction has been investigated in methanol-water media (10-50 % v/v) at $I = 0.3 \text{ mol dm}^{-3}$ and 40-50°C.

Materials and Methods

[(NH₃)₅CoC₂O₄H](ClO₄)₂ was prepared by the published method¹¹. (Calc. for [(NH₃)₅CoC₂O₄H](ClO₄)₂: Co, 13.65. Found: Co, 13.58); λ_{max} 507 nm (ϵ , 73.0 dm³mol⁻¹cm⁻¹). Fe(III) perchlorate solution was prepared and estimated as reported earlier¹. Methanol (AR, BDH) was used to prepare solvent mixtures. HClO₄ (E. Merck) and NaClO₄ (Ridel) were used to adjust the acidity and ionic strength of the reaction medium respectively.

The kinetics of the aquation reaction was followed spectrophotometrically at 380 nm. Absorbances of prethermostated reaction mixtures, withdrawn at definite time intervals, were measured with a Beckman DU₂ spectrophotometer. The pseudo-first order rate constants (k_{obs}) were calculated from the slopes of the $log(A_{\infty} - A_t)$ versus time (t) plot where A_t and A_{∞} stand for the absorbances of the solution at time t and for 100% reaction respectively. All the runs were taken in duplicate and the mean k_{obs} values are collected in Table 1.

Results and Discussion

The rate of aquation of the oxalato complex has been studied as a function of $[Fe^{3+}]_T$ in 10-50% (v/v)

	$[Fe^{3+}]_{T}$ (mol dm ⁻³)	10 ⁵ k at 40°C		10 ⁵ k at 45°C		10 ⁵ K at 50°C	
MeOH (%)		Obs (s ⁻¹)	Calc* (s ⁻¹)	Obs (s ⁻¹)	Calc* (s ⁻¹)	Obs (s ⁻¹)	Calc* (s ⁻¹)
10	0.005	3.10	3.00	5.55	5.46	8.40	8.30
	0.0075	3.60	3.70	7.00	7.00		
	0.01	4.05	4.21	7.77	8.16	13.90	14.30
	0.0125	4.50	4.57				
	0.015	5.00	4.85	9.10	9.79	18.38	18.70
	0.02	5.50	5.26	11.00	10.80	21.00	22.20
	0.025			12.80	11.60	25.00	25.00
	0.03					30.50	27.20
20	0.005	4.15	4.01	6.10	5.90	9.00	9.00
	0.0075	4.80	5.13	7.25	7.66		-
	0.01	5.70	5.96	8.40	9.00	15.30	15.10
	0.0125	6.40	6.62	10.23	10.00		
	0.015	8.10	7.13	12.00	10.90	20.00	19.50
	0.02				-	22.00	22.80
30	0.005	5.10	5.25	7.20	7.26	10.80	10.50
	0.006	6.40	6.08	8.50	8.39		
	0.0075	7.25	7.23	10.00	9.93	13.30	14.08
	0.01	8.71	8.92	12.00	12.16	16.50	16.90
	0.0125			_		19.20	19.30
	0.015			—		23.00	22.30
40	0.002	3.20	3.20	4.10	4.00	4.50	4.50
	0.003	4.48	4.48	5.10	5.60	6.63	6.53
	0.004	5.71	5.56	7.50	7.05	7.80	8.43
	0.005	6.66	6.51	8.50	8.30	11.12	10.20
	0.0075	8.00	8.42	11.00	11.00	14.00	14.20
50	0.002	3 50	3 50				

5.00

6.38

7.57

Table 1—Rate Data for Fe(III) Catalysed Aquation of Oxalatopentaamminecobalt(III) in Methanol-Water Media $\{[\text{Complex}]_T = (5.0 \pm 0.1) \times 10^{-4} \text{ mol dm}^{-3} (10-30\% \text{ MeOH}) \text{ or } (2.0 + 0.2) \times 10^{-4} \text{ mol dm}^{-3} (40-50\% \text{ MeOH}); I = 0.3 \text{ mol dm}^{-3}; [H^+]_T$

*Calculated by Eq. (1) using the values of the rate and equilibrium parameters given in Table 2.

5.10

6.40

7.40

0.003

0.004

0.005

methanol-water media at 40°, 45° and 50°C, $I = 0.3 \text{ mol dm}^{-3}$ (ClO₄⁻) and [H⁺]=0.1 mol dm⁻³. Independent studies also confirmed that aquation of the oxalate complex in methanol-water media in the absence of Fe(III) but under identical acidity, ionic strength and at the temperature range studied, is negligible. The various steps of the reaction may be represented as follows^{1,2}:

$$(\mathrm{NH}_{3})_{5}\mathrm{CoOCOCO}_{2}\mathrm{H}^{2} \stackrel{K_{1}}{\rightleftharpoons} (\mathrm{NH}_{3})_{5}\mathrm{CoOCOCO}_{2}^{+} + \mathrm{H}^{+}$$
$$(\mathrm{NH}_{3})_{5}\mathrm{CoOCOCO}_{2}^{+} + \mathrm{Fe}^{3} \stackrel{K_{2}}{\rightleftharpoons} (\mathrm{NH}_{3})_{5}\mathrm{CoOCOCO}_{2}\mathrm{Fe}^{4} +$$

$$(\mathrm{NH}_{3})_{5}\mathrm{CoOCOCO}_{2}\mathrm{Fe}^{4+} + \mathrm{H}_{2}\mathrm{O} \xrightarrow{k} \\ | (\mathrm{NH}_{3})_{5}\mathrm{CoOH}_{2}^{3+} + \mathrm{C}_{2}\mathrm{O}_{4}\mathrm{Fe}^{4+}$$

where K_1 is acid dissociation constant of the oxalato complex and K_2 , k are the stability constant and the rate constant of aquation of the binuclear species respectively. Under pseudo-first order conditions of constant $[Fe^{3+}]$ and $[H^+]$, the rate law of aquation is given by

$$\frac{-d \ln C_t}{dt} = k_{obs} = \frac{kK_1K_2[Fe^{3+}]/[H^+]}{1+K_1/[H^+]+K_1K_2[Fe^{3+}]/[H^+]}$$
...(1)

where $C_t = [\text{oxalato complex}]_T$. The acid dissociation constants, K_1 , at different temperatures and solvent compositions were obtained from our earlier work¹². The correction of $[\text{Fe}^{3+}]$ due to hydrolysis was considered negligible at the experimental acidity¹². The values of k and K_2 were calculated from the intercept and slope of the least square best line plot of k_{obs}^{-1} versus $[\text{Fe}^{3+}]^{-1}$ as it can be easily shown that Eq. (1) transforms to the form:

$$\frac{1}{k_{\rm obs}} = \frac{1}{k} + \left(\frac{1}{kK_2}\right) \frac{([{\rm H}^+] + K_1)}{K_1} \frac{1}{[{\rm Fe}^{3+}]} \qquad \dots (2)$$

Values of k and the associated activation perameters at different solvent compositions are summarised in Table 2.

In the present context it is worth examining the solvent effect on the Hg(II) catalysed aquation of haloaminecobalt(III) complexes. Unfortunately in most of such studies the haloaminecobalt(III) substrates used do not exhibit strong associative propensity for Hg(II), and the rate data have been collected in different solvent media of varying water-organic solvent compositions under second order conditions. Burgess and Price³ reported that the pseudo-first order rate constants for Hg(II) catalysed aquation of (NH₃)₅CoCl²⁺ and Rh(NH₃)₅Cl²⁺ increased with the addition of ethanol in aqueous-ethanol medium. The slopes of the Grunwald-Winstein plots of logarithms of rate constant against solvent Y-values (0-25% v/v, ethanol-water medium) turned out to be -0.35 for $(NH_3)_5CoCl^{2+}$ and -0.25 for $Rh(NH_3)Cl^{2+}$. Similarity in *m*-values was ascribed to similarity in the mechanism $(S_N 1 \text{ limit})$ and similar solvation requirements for the $(NH_3)_5 M^{n+} [M = Co(III)$ or Rh(III)] moieties. In another study of the mercury(II) induced aquation of trans-chloroammine-bis-(dimethylglyoximato)cobalt(III) complex Chan and Tan⁸ could determine the stability constant of the Clbridged binuclear complex, [Co(dmgh)(NH3)Cl- $Hg]^{2+}$ and its rate constant of aquation both in aqueous and aqueous ethanol (1:5.1) media. These data show that on changing the solvent from water to ethanol-water, the stability constant of the binuclear species increases 64-fold whereas the rate constant of aquation of such a species decreases only 5-fold. Combination of these two effects, however, is reflected as 4 to 8-fold increase in the apparent second order constant of Hg(II) catalysed aquation of this substrate. In a subsequent study Blandamer et al.9, have attempted to explain the solvent effect on the rate of Hg(II) catalysed aquation of chloroamine-metal complexes using a variety of aquo-organic solvent mixtures considering the initial state and transition state solvation effects of this reaction. They again used (NH₃)₅CoCl²⁺ and (trans) Co(en)₂Cl₂⁺ as substrates for which Hg(II) catalysed reactions are strictly second

order. As such the observed solvent effect on the second order rate constant could not be split into individual components for the initial equilibrium process to form the presumed binuclear complex, i.e. (NH₃)₅Co-Cl-Hg⁴⁺ and for its aquation. But one notes from their data in aqueous methanol media (10-40 %, v/v) that the second order rate constant for the Hg(II) catalysed aquation increases only slightly (from 0.095 to 0.112 dm³mol⁻¹s⁻¹ at 25°C). For oxalatopentaamminecobalt(III) the apparent second order rate constant for the Fe(III) catalysed aquation $(k_{app} = kK)$ increases with increasing methanol percentage. As for instance, k_{app} increases from 0.12 to 0.52 dm³ mol⁻¹s⁻¹ at 40°C ($I = 0.3 \text{ mol dm}^{-3}$) when MeOH is varied from 10 to 50%. It is, however, interesting to note that this effect is predominantly due to increase of the stability constant (K_2) of the binuclear species $(NH_3)_5 CoC_2 O_4 Fe^{4+}$ with increase in methanol content (see Table 2). The plot of aquation rate constants of the binuclear species against solvent Y-values¹³ shows a maximum in 30% MeOH at 40° and 45°C (see Fig. 1). However, at 50°C the rate constants appear to be virtually independent of solvent composition. It is worth noting that the first order rate constants of aquation of the binuclear complex at 40° and 45°C show a definite trend, i.e. these increase with methanol content (or decrease in water content) up to 30% MeOH. This argues against S_N 2 methanism (acyl cleavage) involving rate-controlling nucleophilic attack of water at the acyl carbon of the bridging carboxyl group followed by C-O bond fission.

The observed trend in rate can be more realistically accommodated by the difference in solvation pattern of the initial and $S_N 1$ (limit) transition state for the aquation process of the binuclear species. This is further supported by the analysis of ΔH^{\ddagger} data (Table 3).

The activation free energy (ΔG^{\ddagger}) appears to be almost independent of solvent. But on splitting it into ΔH^{\ddagger} and ΔS^{\ddagger} (see Fig. 2) the solvent dependence is evident. It appears that both ΔH^{\ddagger} and ΔS^{\ddagger} decrease to

	МеОН (%)	40°C		43	5°C	50°C	
		$\frac{10^4 k}{(s^{-1})}$	$K_{2^{*}}^{*}$ (dm ³ mol ⁻¹)	$\frac{10^4 k}{(s^{-1})}$	$\frac{K_2^*}{(\mathrm{dm}^3 \mathrm{mol}^{-1})}$	$\frac{10^4 k}{(s^{-1})}$	K [*] ₂ (dm ³ mol ⁻¹)
	10	0.70 ± 0.04	1776 ± 112	1.60 ± 0.10	1202 ± 97	5.0±0.50	472±47
	20	1.20 ± 0.20	1674 ± 331	1.90 ± 0.40	1455 ± 276	4.7 ± 0.40	780 ± 57
	30	3.00 ± 1.30	805 ± 360	3.70 ± 0.7	912±169	4.4 ± 0.80	1200 ± 220
	40	2.00 ± 0.20	2038 ± 232	3.00 ± 1.20	1652 ± 646	6.7 ± 3.60	776 ± 420
	50	3.20 ± 0.60	1618 ± 281				

*Based on temperature independent values of $10^{3}K_{1}$ (mol dm⁻³) = 9.3, 6.6, 5.6, 4.85, 3.93, at 10, 20, 30, 40 and 50 % MeOH respectively (ref. 12).



Fig. 1—Plot of log k versus Y for the aquation of (NH₃)₅CoO₂CCO₂Fe⁴⁺ [I-40°, II-45° and III-50°C]

minimum values in 30 % MeOH, corresponding to the maximum in the rate profile at 40-45°C. The highly negative value of ΔS^{\ddagger} and low positive value of ΔH^{\ddagger} in 30% MeOH probably reflect greater stability of the transition state in relation to the ground state due to solvation interaction with the medium. A near constancy of ΔG^{\ddagger} , and strong dependence of ΔH^{\ddagger} and ΔS^{\ddagger} on solvent composition clearly indicates that both enthalpy and entropy effects are mutually compensatory. This could be an indication of constancy of the mechanism (mostly $S_{\mathbb{N}}1$ limit) over the solvent composition range studied. Similar observation has been made by Holba *et al.*¹⁴ in the aquation of *cis*-[CoNH₃Br(en)₂]²⁺ in aquo-organic solvent mixtures.

At this stage it appears relevant to mention about the solvated Fe³⁺ species involved in the process. Absorbance measurements of Fe(III) perchlorate solution in methanol/water media indicate that absorbance of Fe³⁺ at 380 nm is strongly sensitive to methanol content of the medium. This, infact, causes serious problem in the choice of the range of $[Fe^{3+}]$ in the aquation study. Similar observation has also been reported by Kunimura et al.¹⁵. Although there is evidence that the aquo ligands in the coordination sphere of Fe³⁺ are partially replaced by MeOH, our kinetic data, however, do not differentiate between catalytic behaviour of $Fe(OH_2)_6^{3+}$ the and $Fe(OH_2)_m(MeOH)_{6-m}^3$



Fig. 2—Plot showing the sensitivity of the activation parameters to the solvent composition [Units; kJ mol⁻¹ for ΔH^{+}_{\pm} , ΔG^{+}_{\pm} and JK⁻¹mol⁻¹ for ΔS^{+}_{\pm}]

Table 3—Activation Parameter Data (40°C)							
MeOH (%)	$\Delta G^{\ddagger}_{\rm kJ \ mol^{-1}}$	$\Delta H\ddagger (kJ \text{ mol}^{-1})$	$\frac{\Delta S^{\ddagger}}{\mathrm{JK}^{-1} \mathrm{mol}^{-1}})$				
10	101.7	156.1 ± 43.1	171.6 ± 134				
20	100.3	114.7 ± 31.4	46.0 ± 96.2				
30	97.95	29.3 ± 7.1	-217.6 ± 23				
40	99.0	82.4 ± 16.7	-54.0 ± 50				
50	97.8	—	—				

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