

Kinetics of Acid & Ferric Ion Catalysed Aquation of Some Salicylatopentamminecobalt(III) Ions

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The kinetics of aquation of $N_5CoSalH^{2+}$ [$N_5 = (en)_2NH_3$, α -*cis*(trien)(NH_3) and tetren; $SalH^-$ = salicylate] are reported at $I = 1.0 \text{ mol dm}^{-3}$ and in the temperature range 65-85°C. Fe(III) catalyses the aquation of these substrates via the binuclear species, $N_5CoSalFe^{4+}$. The rates and activation parameters of aquation of the binuclear species of tetren-salicylato complex reveal that the rates of spontaneous, acid catalysed and Fe(III) catalysed aquation decrease with increase in steric crowding at the cobalt(III) centre.

Our earlier investigation¹ on the metal ion and acid catalysed aquation reactions of salicylatopentaamminecobalt(III) reveals that the catalyst metal ions associate with the cobalt(III) substrates resulting in the formation of binuclear species which act as the reactive substrate species in the metal ion catalysed paths. The rates of binuclear complexation of salicylatopentaamminecobalt(III) ions, $N_5CoSalH^{2+}$ [$N_5 = 5NH_3$, $(en)_2NH_3$, tetraethylenepentamine] with Fe(III) have been reported recently^{2a}. The present paper deals with the study of the equilibrium and kinetic behaviour of $N_5CoSalH^{2+}$ [$N_5 = \text{tetren}$ (tetraethylenepentamine), *trien*(NH_3), $(en)_2(NH_3)$] in aqueous acidic medium containing Fe(III) with a view to examining the effect of structural variation on the spontaneous, acid and metal ion catalysed aquation of the complexes.

Materials and Methods

The complexes, $[N_5CoSalH](ClO_4)_2$ [$N_5 = \text{tetren}$, *trien*(NH_3), $(en)_2(NH_3)$], were prepared as described earlier²⁻⁴. Cobalt analysis agreed within 0.1% of the calculated value. The UV-visible spectral data of the complexes were in good agreement with the literature data.

The acid hydrolysis of salicylato complexes in the presence and absence of Fe^{3+} has been studied in a medium of ionic strength = 1.0 mol dm^{-3} ($NaClO_4$). The catalytic effect of Fe(III) was examined at a fixed acidity and at different $[Fe(III)]$ and temperatures.

The acid and Fe(III) catalysed aquation reactions were studied spectrophotometrically under pseudo-first order conditions as described earlier¹.

Equilibrium studies

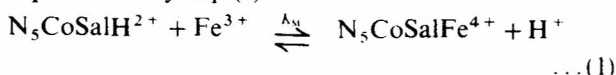
Complex formation between the salicylato complexes and Fe(III) was studied spectropho-

metrically at 540 nm. To a reaction mixture containing requisite amounts of sodium perchlorate, perchloric acid and ferric perchlorate was added a measured volume of the freshly prepared complex solution in distilled water and the total volume made up to 25 ml. Absorbances were measured at preset wavelengths at room temperature ($29.0 \pm 0.5^\circ C$) immediately after the reactants were mixed. Absorbance of the mixed solution remained unchanged upto 30 min after mixing the reactants indicating that equilibrium between the complex and ferric ion was rapidly established and that the metal ion catalysed hydrolysis reaction did not proceed to any appreciable extent during this period. The absorbances of solutions at equilibrium were used to calculate the equilibrium constants.

Results

Equilibrium constant (K_M)

The equilibrium existing in solution containing Fe(III) perchlorate, perchloric acid, sodium perchlorate and the cobalt(III) complex may be represented by Eq. (1)



The equilibrium constant of the binuclear complex may be defined as,

$$K_M = [N_5CoSalFe^{4+}][H^+]/([N_5CoSalH^{2+}][Fe^{3+}]) \quad \dots(2)$$

If A_2 and A_1 are the absorbances of solutions of the complex with and without Fe(III) and ϵ_1 and ϵ_2 are the extinction coefficients of $N_5CoSalH^{2+}$ and $N_5CoSalFe^{4+}$ respectively, then

$$A_1 = \epsilon_1 c_1 l \quad \dots(3)$$

$$A_2 = \epsilon_2 x l + \epsilon_1 (c_1 - x) l \quad \dots(4)$$

where $c_1 = [\text{complex}]_{\text{total}}$, $x = [N_5CoSalFe^{4+}]_{\text{total}}$ and

l is the cell path length. At constant ionic strength K_M is given by Eq. (5)

$$K_M = x[\text{H}^+] / ((c_1 - x)(c_2 - x)) \quad \dots (5)$$

where $c_2 = [\text{Fe}^{3+}]_{\text{total}}$. Combining Eqs (3), (4) and (5) and assuming $c_2 - x = c_2$ (since $c_2 \gg c_1$), it is possible to derive the relationship,

$$\frac{c_1}{A_2 - A_1} = \frac{1}{(\epsilon_2 - \epsilon_1)l} + \frac{1}{(\epsilon_2 - \epsilon_1)lK_M} \frac{[\text{H}^+]}{c_2} \quad \dots (6)$$

K_M was evaluated from the slope and intercept of $c_1/(A_2 - A_1)$ versus $[\text{H}^+]/c_2$ plot. The data are presented in Table 1.

Aquation of salicylato Co(III) complexes

The aquation of the salicylato Co(III) complexes was studied in HClO_4 solution over the acidity range 0.1-1.0 mol dm⁻³ at an ionic strength of 1.0 mol dm⁻³ adjusted with NaClO_4 , whenever necessary. The pseudo-first order rate constants at 75°C, 80°C and 85°C are given in Table 2. The plots of k_{obs} versus $[\text{H}^+]$ are linear with positive intercept. The rate expression, therefore, will have the form:

$$-\frac{d \ln [\text{Complex}]}{dt} = k_{\text{obs}} = k_0 + k_1 [\text{H}^+] \quad \dots (7)$$

The observed rate law (Eq. 7) is consistent with the following mechanism (Eqs 8 and 9):

Table 1—Equilibrium Constant of Formation of Binuclear Complexes, $\text{N}_5\text{CoSalFe}^{4+}$

$[I = 1.0 \text{ mol dm}^{-3}$; temp. = $29.0 \pm 0.5^\circ\text{C}$; $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$]

$10^4 [\text{Complex}]$ (mol dm ⁻³)	$[\text{Fe}^{3+}]$ (mol dm ⁻³)	A_1	A_2
$\text{N}_5 = (\text{trien})(\text{NH}_3)$; $\lambda = 540 \text{ nm}$			
4.47	0.0125	0.005	0.115
	0.015		0.133
	0.020		0.152
	0.030		0.220
	0.050		0.286
	0.075		0.350
	0.100		0.400
$K_M = 3.53 \pm 0.48$; $(1/(\epsilon_2 - \epsilon_1)l) \times 10^4 = 7.42 \pm 0.96$			
$\text{N}_5 = \text{tetren}$; $\lambda = 540 \text{ nm}$			
8.70	0.010	0.070	0.185
	0.0125		0.202
	0.015		0.230
	0.020		0.270
	0.030		0.380
	0.050		0.508
	0.075		0.620
	0.100		0.735

$K_M = 1.65 \pm 0.32$;

$(1/(\epsilon_2 - \epsilon_1)l) \times 10^4 = 5.95 \pm 1.13$

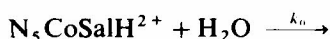
Table 2—Pseudo-first Order Rate Constants for Acid Hydrolysis of $\text{N}_5\text{CoSalH}^{2+}$ at $I = 1.0 \text{ mol dm}^{-3}$ and Different Temperatures

$[\text{H}^+]$ mol dm ⁻³	75.0 ± 0.1°C		80.0 ± 0.1°C		85.0 ± 0.1°C	
	Obs	Calc	Obs	Calc	Obs	Calc
$\text{N}_5 = (\text{trien})(\text{NH}_3)$						
0.1	0.61 ± 0.05	0.53	1.53 ± 0.01	1.47	2.03 ± 0.02	2.03
0.2	0.80 ± 0.01	0.87	1.86 ± 0.01	1.88	2.60 ± 0.01	2.66
0.4	1.53 ± 0.01	1.54	2.68 ± 0.02	2.71	4.00 ± 0.01	3.94
0.6	2.21 ± 0.02	2.21	3.47 ± 0.03	3.53	5.25 ± 0.02	5.21
0.8	2.88 ± 0.01	2.88	4.40 ± 0.06	4.36	6.50 ± 0.04	6.48
1.0	3.58 ± 0.05	3.56	5.21 ± 0.05	5.19	7.70 ± 0.05	7.75
$10^5 k_0 (\text{s}^{-1})$		0.20 ± 0.04		1.06 ± 0.04		1.40 ± 0.04
$10^5 k_1 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$		3.36 ± 0.07		4.13 ± 0.07		6.35 ± 0.07
$\text{N}_5 = \text{tetren}$						
0.1	0.25 ± 0.03	0.28	0.45 ± 0.02	0.49	0.95 ± 0.09	
0.2	0.40 ± 0.02	0.36	0.65 ± 0.10	0.60	1.28 ± 0.03	1.20
0.4	0.55 ± 0.05	0.52	0.80 ± 0.05	0.81	1.63 ± 0.02	1.61
0.6	0.64 ± 0.04	0.68	1.04 ± 0.03	1.03	1.92 ± 0.02	2.02
0.8	0.85 ± 0.01	0.85	1.27 ± 0.03	1.25	2.50 ± 0.10	2.44
1.00	1.02 ± 0.02	1.01	1.45 ± 0.05	1.47	2.85 ± 0.05	2.85
$10^5 k_0 (\text{s}^{-1})$		0.20 ± 0.03		0.38 ± 0.03		0.80 ± 0.06
$10^5 k_1 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$		0.81 ± 0.04		1.09 ± 0.05		2.06 ± 0.10

Table 3—Rates of Ferric Ion Catalysed Aquation of $N_5CoSalH^{2+}$
($I = 1.0 \text{ mol dm}^{-3}$; $[H^+] = 0.2 \text{ mol dm}^{-3}$)

$[Fe^{3+}]$ mol dm^{-3}	Temp. ^a °C	$10^5 k_2 (\text{s}^{-1})$		Temp. ^a °C	Obs	Calc
		Obs	Calc.			
$N_5 = \text{tetren}$						
0.01	70.0	0.70 ± 0.02	0.71	75.0	0.91 ± 0.02	0.92
0.02		1.00 ± 0.05	0.97		1.31 ± 0.02	1.25
0.03		1.18 ± 0.02	1.14		1.50 ± 0.01	1.48
0.05		1.32 ± 0.03	1.33		1.75 ± 0.05	1.78
0.075		1.43 ± 0.01	1.46		1.92 ± 0.01	2.00
0.10		1.50 ± 0.05	1.54		2.13 ± 0.02	2.14
$10^5 k_2 (\text{s}^{-1}) = 1.82 \pm 0.10$; $K_M = 5.52$				$10^5 k_2 (\text{s}^{-1}) = 2.76 \pm 0.10$; $K_M = 5.65$		
0.01	80.0	1.65 ± 0.03	1.68	85.0	2.25 ± 0.05	2.27
0.02		2.40 ± 0.02	2.25		3.00 ± 0.04	2.91
0.03		2.70 ± 0.01	2.62		3.50 ± 0.03	3.35
0.05		3.00 ± 0.02	3.07		3.90 ± 0.03	3.93
0.075		3.20 ± 0.04	3.38		4.15 ± 0.02	4.37
0.10		3.30 ± 0.05	3.56		4.50 ± 0.01	4.64
$10^5 k_2 (\text{s}^{-1}) = 4.33 \pm 0.20$; $K_M = 7.7$				$10^5 k_2 (\text{s}^{-1}) = 5.86 \pm 0.40$; $K_M = 5.50$		
		$N_5 = (\text{trien})(NH_3)$		$N_5 = (\text{en})_2 NH_3^b$		
0.01	85.0	3.25 ± 0.04	3.26	85.0	—	—
0.02		3.90 ± 0.02	3.79		5.02 ± 0.02	5.03
0.03		4.20 ± 0.02	4.24		5.60 ± 0.03	5.55
0.05		4.85 ± 0.01	4.92		6.20 ± 0.01	6.30
0.075		5.40 ± 0.05	5.54		6.90 ± 0.03	6.91
0.10		6.00 ± 0.03	6.00		7.40 ± 0.04	7.34
$10^5 k_2 (\text{s}^{-1}) = 8.85 \pm 0.95$; $K_M = 2.36$				$10^5 k_2 (\text{s}^{-1}) = 9.65 \pm 0.38$; $K_M = 3.20$		

(a) $\pm 0.1^\circ\text{C}$, (b) $k_{\text{obs}} = (3.5 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$ at $[Fe^{3+}] = 0$, $[H^+] = 0.2 \text{ mol dm}^{-3}$.



where k_0 and k_1 represent the rate constants for the uncatalysed and acid catalysed paths of aquation of the complexes respectively.

Effect of ferric ion on the aquation rate

The aquation reactions of $N_5CoSalH^{2+}$ ($N_5 = \text{tetren, trien}(NH_3), (\text{en})_2NH_3$) have been studied in the presence of $Fe(III)$ ion at $I = 1.0 \text{ mol dm}^{-3}$. The data collected in Table 3 indicate that the ferric ion catalyses the hydrolysis of the $Co(III)$ complexes. A rapid and reversible equilibrium between the $Co(III)$ complex and ferric ion is presumed to be followed by the rate-determining loss of the $Fe(III)$ -salicylato complex from the binuclear complex as indicated in Eq. (10).



Combining Eqs (1), (8), (9) and (10), we get relationship (11) for the pseudo-first order rate constants (k_{obs}) of aquation of the complexes in the presence of $Fe(III)$ ion.

$$k_{\text{obs}} = \frac{k_0 + k_1[H^+] + k_2 K_M [Fe^{3+}]/[H^+]}{1 + K_M [Fe^{3+}]/[H^+]} \quad \dots(11)$$

On rearranging, Eq. (11) can easily be transformed to Eq. (12).

$$\frac{1}{k_{\text{obs}} - k'_{\text{obs}}} = \frac{1}{k_2 - k'_{\text{obs}}} + \frac{1}{(k_2 - k'_{\text{obs}}) K_M} \frac{[H^+]}{[Fe^{3+}]} \quad \dots(12)$$

$$(k'_{\text{obs}} = k_0 + k_1[H^+] \text{ at } [Fe^{3+}] = 0).$$

The values of K_M and k_2 (Table 3) have been calculated from the intercept and slope of $1/(k_{\text{obs}} - k'_{\text{obs}})$ versus $[H^+]/[Fe^{3+}]$ plot respectively. The activation parameters for k_0 , k_1 and k_2 paths of aquation of salicylato $Co(III)$ complexes, calculated using equations based on transition state theory are presented in Table 4.

Discussion

Examination of the k_0 data in Table 4 reveals that the rates of spontaneous aquation of the complexes

Table 4—Comparison of Rates and Activation Parameters of Spontaneous, Acid and Fe(III) Catalysed Aquation Reactions of Some Salicylatopentaminecobalt(III) Complexes, $[N_5CoSalH^{2+}]$.

N_5	Constant at 85°C		ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹
5NH ₃ ^(a)	$10^5 k_0 (s^{-1})$	5.89	160.3 ± 16.7	121 ± 50.2
	$10^5 k_1 (dm^3 mol^{-1} s^{-1})$	18.7	112.6 ± 4.2	-2.5 ± 12.5
	$10^5 k_2 (s^{-1})$	50.0	145.2 ± 38.9	96.2 ± 117.1
(en) ₂ NH ₃ ^(b)	$10^5 k_0 (s^{-1})$	3.19	96.6 ± 8.3	-12.5 ± 25.0
	$10^5 k_1 (dm^3 mol^{-1} s^{-1})$	4.01	119.7 ± 8.3	29.3 ± 25.0
	$10^5 k_2 (s^{-1})$	9.65 ± 0.38	—	—
(trien)NH ₃	$10^5 k_0 (s^{-1})$	1.40 ± 0.04	—	—
	$10^5 k_1 (dm^3 mol^{-1} s^{-1})$	6.35 ± 0.07	64.4 ± 16.3	-146.9 ± 46.4
	$10^5 k_2 (s^{-1})$	8.85 ± 0.95	—	—
(tetren)	$10^5 k_0 (s^{-1})$	0.80 ± 0.06	141.0 ± 7.1	50.2 ± 20.9
	$10^5 k_1 (dm^3 mol^{-1} s^{-1})$	2.06 ± 0.10	93.3 ± 26.8	-75.3 ± 75.3
	$10^5 k_2 (s^{-1})$	5.86 ± 0.39	77.4 ± 4.2	-115.4 ± 12.5

(a) $I = 0.6 \text{ mol dm}^{-3}$ (ClO₄⁻); (b) $I = 2.0 \text{ mol dm}^{-3}$ (ClO₄⁻) for k_0 and k_1 paths (ref. 5).

decrease in the sequence: (en)₂NH₃ > trien(NH₃) > tetren. Similar behaviour is also observed in the acid catalysed path. The divergence of the ethylenediamine complex from such a correlation may be attributed to the ionic strength effect.

It is reasonable to believe that the cobalt(III) centre is increasingly protected from solvation by water due to the hydrophobic carbon skeleton of the multidentate amine ligand. Fe(III) ion catalysed aquation of (trien)(NH₃)Co(III) salicylato and (en)₂(NH₃)Co(III) salicylato complexes was studied at only one temperature for the sake of comparison of the rate data. The aquation rate constants of the binuclear species, given in Table 3, also decrease in the sequence: (en)₂NH₃ > (trien)NH₃ > tetren. But it is interesting to see that (k_0/k_2) values decrease in the order: tetren ≥ (trien)NH₃ > (en)₂NH₃ at 85°C (see Table 4). Thus the catalytic effect of Fe³⁺ becomes more prominent with increase in steric crowding at cobalt(III) centre. Similar effect was also observed for the rate of dissociation of Fe³⁺ from the binuclear species, N₅CoSalFe⁴⁺ (N₅ = 5NH₃, (en)₂NH₃ and tetren)^{2a}. This fact is reconciled with increasing electrostatic

repulsion between Co(III) centre and the leaving group, FeSal⁺ in the transition state as the hydrophobicity of the groups attached to the cobalt(III) centre increases. This agrees with the dissociative mode of spontaneous aquation (Co—O bond cleavage as the rate-limiting step) of the salicylato complexes and also the corresponding binuclear species, N₅CoSalFe⁴⁺. For the tetren complex significantly lower value of the activation enthalpy for the aquation of the binuclear species (k_2 -path) as compared to that of the spontaneous aquation path is observed. But this is again partly offset by the relatively lower value of ΔS^\ddagger (see Table 4). The negative value of ΔS^\ddagger for the binuclear species depicts the solvation requirement of the transition state of the Fe(III) catalysed path.

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