Kinetics & Mechanism of Base Hydrolysis of Malonato & Succinato Complexes of Pentaamminecobalt(III) Ion

M. S. DASH

Department of Chemistry, B.J.B. College, Bhubaneswar 6

and

A. C. DASH*

Department of Chemistry, Utkal University, Bhubaneswar 4

The base hydrolysis reactions of malonato and succinato complexes of pentaamminecobalt(III) ion, $[(NH_3)_5CoCO_2(OH_2)_nCO_2]^+$ ($n = 1, 2$), have been investigated at 30°, 35° and 40° in a medium of $I = 0.3M$ (NaCl). At $[OH^-] = 0.02-0.2M$, the rate law for the reaction is given by $-d \ln [\text{complex}]/dt = k_1[OH^-]$. The values of the second order rate constant (in M^{-1} sec^{-1}) at 30° and the associated $\Delta H\ddagger$ (in kcal/mole), $\Delta S\ddagger$ (in e.u.) are $2.86(\pm 0.08) \times 10^{-4}$, $29.2(\pm 1.2)$, $22(\pm 4)$ for malonato complex and $1.18(\pm 0.04) \times 10^{-4}$, $34.2(\pm 3.5)$, $36(\pm 11)$ for succinato complex respectively. The rate and activation parameters have been compared with the analogous data for oxalato, maleato and fumarato complexes of pentaamminecobalt(III) cation. The results are in accord with the rate limiting Co-O bond fission of the ammine conjugate base $[(NH_2)(NH_3)_4CoCO_2(CH_2)_nCO_2]$.

EARLIER studies from this laboratory dealt with the kinetics of aquation of pentaamminecobalt(III) complexes of the dicarboxylic acids[1,2]. However, the kinetic data did not provide evidence in favour of the intramolecular acid catalysis due to the unbound carboxyl group in the aquation reactions of the complexes. It was, therefore, thought worthwhile to examine the effect of the unbound carboxylate function on the rate and mechanism of base hydrolysis of the dicarboxylic acid complexes of pentaamminecobalt(III) ion. The alkaline hydrolysis of oxalato, maleato and fumarato pentaamminecobalt(III) complexes[3,4] have been studied earlier. We report in this paper the kinetics of base hydrolysis of the malonato and succinato complexes of pentaamminecobalt(III).

Materials and Methods

All the chemicals used were of analar or extrapure quality. Solutions were prepared in distilled water from a copper still. The spectral measurements were made in a Beckman DU 2 spectrophotometer with 10 mm matched silica cells. The cobalt(III) complexes were prepared in acid form by the published method[2] and gave satisfactory elemental analysis. The malonato and succinato complexes show maxima (in nm) and corresponding molar absorbancy indices (in M^{-1} cm^{-1}) in $0.1M$ HClO$_4$ medium at 505(74.9), 350(58.2) and 505(68.2), 355 (54.8) respectively.

Rate measurements — The kinetics of base hydrolysis of the cobalt(III) complexes were investigated at 30°, 35° and 40° at an ionic strength of $0.3M$ adjusted with sodium chloride. The concentration of the complexes was varied in the range 7.6-9.9

$\times 10^{-4}M$. Reaction was initiated by adding 2 ml of a stock solution of the complex (at the reaction temperature) to the prethermostated reaction mixture. The rate of base hydrolysis was followed by withdrawing 5 ml of the reaction mixture at regular time intervals quenching the reaction by adding dil. hydrochloric acid to pH 1 and then measuring optical density at 260 nm at which the carboxylatopentaamminecobalt(III) complexes are the only significantly absorbing species. The reaction could be followed satisfactorily up to 40% completion beyond which the decomposition of hydroxopentaamminecobalt(III) ion to insoluble cobalt(III) oxide was significant and the reaction mixture even after acidification did not yield clear solution for the optical density measurement. The pseudo-first order rate constants (k_{obs}) were, therefore, calculated by the method of initial rates from the gradients of log D_t versus time plots where D_t stands for the optical density of the reaction mixture after acidification at time t. Each run at a given alkali concentration was repeated 3 to 5 times.

Results

The second order rate constants (k_1) obtained by dividing k_{obs} with the initial $[OH^-]$ are presented in Table 1.

pK_a of the free carboxyl group of H-malonato and H-succinato complexes is ~ 4 (ref. 2). As such both the complexes will exist as monopositive cations, $(NH_3)_5CoCO_2(CH_2)_nCO_2^+$, in the alkaline medium employed in the kinetic study. A perusal of the rate data presented in Table 1 indicates no systematic variation of the second order rate constant (k_1) with $[OH^-]$ in the range 0.02-0.2M. The rate law for base hydrolysis can be best repre-

TABLE 1 — RATE DATA FOR BASE HYDROLYSIS OF $(NH_3)_5CoL^{(3-n)+}$ AT $I = 0.3M$ (NaCl)

[OH⁻] M	10^4k_1 (for malonate²⁻) $(M^{-1}\ sec^{-1})$	10^4k_1 (for succinate²⁻) $(M^{-1}\ sec^{-1})$
	$30.0°(\pm0.1°)$	
0·02	2·84(±0·14)	—
0·05	3·05(±0·12)	1·37(±0·12)
0·10	2·92(±0·16)	1·18(±0·04)
0·20	2·73(±0·10)	1·12(±0·08)
	Av 2·86(±0·08)*	Av 1·18(±0·04)*
	$35.0°(\pm0.1°)$	
0·02	5·61(±0·25)	2·82(±0·31)
0·05	6·69(±0·10)	2·83(±0·22)
0·10	6·88(±0·10)	2·65(±0·30)
0·20	7·26(±0·58)	2·49(±0·31)
	Av 6·70(±0·19)*	Av 2·72(±0·08)*
	$40.0°(\pm0.1°)$	
0·02	13·0(±0·6)	7·06(±0·45)
0·05	13·6(±0·5)	7·75(±0·42)
0·10	15·0(±1·3)	7·79(±0·30)
0·20	15·4(±0·8)	9·30(±0·40)
	Av 13·8(±0·5)*	Av 7·99(±0·43)*

*Weighted mean value.

TABLE 2 — RATE AND ACTIVATION PARAMETERS FOR THE BASE HYDROLYSIS OF $(NH_3)_5CoL^{(3-n)+}$

L^{n-}	10^4k_1 (30°) $(M^{-1}\ sec^{-1})$	$\Delta H_{\ddagger}^{\ddagger}$ kcal/mole	$\Delta S_{\ddagger}^{\ddagger}$ e.u.	Ref.
Oxalate²⁻	6·2 (8·3)	31·7 (33·4)	32 (37)	(a)
Malonate²⁻	2·86±0·08	29·2±1·2	22±4	This work
Succinate²⁻	1·18±0·04	34·2±3·5	36±11	This work
Maleate²⁻	0·57, 0·76(b)	28·5	18·3	(a)
Fumarate⁻²	1·58, 2·11(b)	28·0	14·4	(a)

(a) $I = 1M$ (NaCl) (ref 4). Values given in parentheses refer to $I = 0.3M$ (NaClO₄) (ref. 3).

(b) Ionic strength corrected to $0.3M$ by the relationship: $k(I=0.3M)=k(I=1M) \times [k(I=0.3M)/k(I=1M)]_{oxalate}$.

sented as shown in Eq. (1)

$$-d\ \ln\ C_t/dt = k_{obs} = k_1[OH^-] \qquad ...(1)$$

where C_t is the total concentration of the complex at time t and k_1 is the second order rate constant for the reaction (2)

$$(NH_3)_5CoCO_2(CH_2)_nCO_2^+ + OH^- \xrightarrow{k_1} (NH_3)_5CoOH^{2+} + (CH_2)_n(CO_2^-)_2 \qquad ...(2)$$
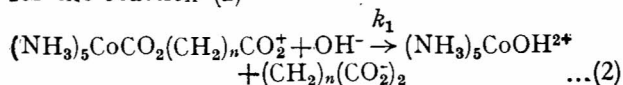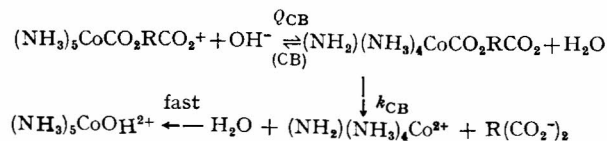
The rate law (1) has also been found to be valid in the base hydrolysis of maleato and fumarato complexes of pentaamminecobalt(III) cation at $(OH^-) \leq 1.0M$ (ref. 4) and also for the corresponding oxalato complex at $[OH^-] \leq 0.1M$ (ref. 3). The average values of k_1 given in Table 1 were obtained by the weighted least squares method. Weighting factor for k_1 was taken to be the reciprocal of its variance. The activation parameters were calculated from the least squares gradients and intercepts of $\ln\ (k/T)$ versus $1/T$ plots, the former being weighted as the reciprocal of its variance, which was calculated from the known variances of the average value of k_1 and T (Table 1). Calculations were performed by the least squares computer programmes adopted to an IBM 1130 computer. The values of activation parameters are given in Table 2.

Discussion

The rate and activation parameters for the base hydrolysis of oxalato, malonato, succinato, maleato and fumarato complexes of pentaamminecobalt (III) ion have been collected in Table 2 for the sake of comparison. The rate data for the latter two complexes (at $I = 1M$ NaCl) have been corrected to $I = 0.3M$ by considering the retarding influence of ionic strength on the rate of base hydrolysis of the oxalato complex (see Table 2). This method of ionic strength correction of the rate constant is

reasonable as the rate influencing effect of Cl⁻ relative to that of ClO₄⁻ in the base hydrolysis reaction is expected to be negligible[3]. The order of reactivities of the complexes as evidenced from the values of k_1 at 30° is oxalate > malonate > fumarate > succinate > maleate. The rate decreases as the carbon chain intervening the free and the cobalt (III)-bound carboxylate groups increases. This is in accord with the fact that the electron withdrawing effect of the unbound carboxylate anion influences the rate. The reactivity sequence fumarate > succinate > maleate also indicates that the orientation of the free carboxylate anion with respect to the cobalt (III)-bound carboxylate group has some effect on the base hydrolysis rates. Tracer studies have indicated that oxalatopentaamminecobalt(III) undergoes base hydrolysis via both Co-O and C-O bond fission, the latter arising out of a third order process[4,5]. The former mechanism, however, operates predominantly at $[OH^-] \leq 0.1M$ (ref. 3, 4). The conjugate base mechanism with rate limiting Co-O bond breaking also applies to the base hydrolysis of maleato and fumarato complexes under consideration[4].

The conjugate base mechanism may be depicted as shown in Scheme 1.

$$(NH_3)_5CoCO_2RCO_2^+ + OH^- \underset{(CB)}{\overset{Q_{CB}}{\rightleftharpoons}} (NH_2)(NH_3)_4CoCO_2RCO_2 + H_2O$$

$$\downarrow k_{CB}$$

$$(NH_3)_5CoOH^{2+} \xleftarrow{fast} H_2O + (NH_2)(NH_3)_4Co^{2+} + R(CO_2^-)_2$$

Scheme 1

For all dicarboxylic acid complexes under consideration (see Table 2) a constant value of Q_{CB} appears reasonable. The sensitivity of k_1 to the nature of the leaving group would then indicate how both electronic and steric effects of the latter affect the reactivities of the conjugate bases (since $k_1 = k_{CB} \times Q_{CB}$). The charge of the leaving groups remaining same it is the Co-O bond weakening effect of the unbound carboxylate group which will govern the reactivity sequence of the conjugate bases of oxalato, malonato, and succinato complexes. The observed reactivity sequence oxalate > malonate

> succinate supports this fact. The dissociative transition state of the reactive conjugate base may be visualized to be an ion-paired complex, $[(NH_2)(NH_3)_4Co^{2+}...(^-O_2C)_2R]$ and as such k_{CB} (and hence k_1) will decrease as the electrostatic interaction between the leaving group and the cobalt(III) centre will increase when the group R is varied. The *cis* and *trans* conformations of the carboxylate anions in maleato and fumarato complexes, restriction to rotation of the carboxylate groups about $C=C$ bond in these complexes and absence of such factors in the succinato complex indicate that the electrostatic interaction between the carboxylate anions and the cobalt(III) centre in the transition state will decrease in the order maleate > succinate > fumarate. The reverse order of reactivities (i.e. fumarate > succinate > maleate) observed for these complexes thus lends support in favour of the dissociative transition state of the conjugate bases.

The activation enthalpies for oxalato (Co-O fission path), malonato, and succinato complexes are very much alike and are slightly higher in magnitude than for fumarato and maleato complexes (Table 2). The activation entropies are large positive.

$\Delta S^{\ddagger}$, however, decreases in the order oxalate > malonate $\sim$ succinate > maleate > fumarate. Much significance cannot be attached to the activation parameter data without knowing the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the conjugate base equilibria. But it is worth noting that the base hydrolysis reaction of the complexes under consideration (Table 2), like that of several other $(NH_3)_5CoX^{2+}$ complexes[6], are both enthalpy and entropy controlled. The effect of higher activation enthalpy is counterbalanced by large positive $\Delta S^{\ddagger}$ factor. Such a compensatory effect may be diagnostic of a common rate limiting step[2,7].

References

1. DASH, A. C. & NANDA, R. K., *Inorg. Chem.*, 13 (1974), 655.
2. DASH, A. C. & NANDA, R. K., *J. inorg. nucl. Chem.*, 38 (1976), 119.
3. DASH, A. C. & NANDA, R. K., *J. Indian chem. Soc.*, 52 (1975), 298.
4. ANGERMAN, N. S. & JORDAN, R. B., *Inorg. Chem.*, 6 (1967), 1376.
5. JORDAN, R. B. & TAUBE, H., *J. Am. chem. Soc.*, 86 (1964), 3891.
6. BASOLO, F. & PEARSON, R. G., *Mechanisms of inorganic reactions* (Wiley, New York), 1967, 180.
7. LEFFLER, J. E., *J. org. Chem.*, 20 (1955), 1202.