3644 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 3644—3646 (1990) [Vol. 63, No. 12

Kinetics and Mechanism of Acid Hydrolysis of Bis(dicarboxylato)carbonatochromate(III) Complexes

C. S. T. Sai, N. R. Anipindi,* V. Subbiah,† and M. W. Pandit†
School of Chemistry, Andhra University, Visakhapatnam-530003, India
†Centre for Cellular and Molecular Biology, Hyderabad-500007, India

(Received October 19, 1989)

A study has been made of the acid-catalysed aquation reactions of three complex ions of the general formula $[\mathrm{Cr(XX)_2(CO_3)}]^{3-}$, where XX=oxalate, malonate, or methylmalonate, by stopped-flow spectrophotometry in the acid range 0.1—2.0 M (M=mol dm^{-3}) and 20—35 °C at an ionic strength of 2 M. Only the ring-opening reaction of the carbonate is observed, k=2.12, 3.28, and 4.02 M^{-1} s^{-1} at 25 °C respectively for oxalato, malonato, and methylmalonato complexes as the subsequent decarboxylation is too fast to measure. The observed trend was explained in terms of the basicity of the coordinated inert ligands.

Harris and co-workers have studied extensively the aquation of several anionic[1,2] and cationic[3] carbonato complexes of cobalt(III) and firmly established that the mechanism involves ring opening of the chelated carbonate catalyzed both by water and hydronium ion, followed by a rapid decarboxylation. A similar mechanism was suggested for the aquation of bis(oxalato)carbonatochromate(III).[4]

This paper now reports in detail the kinetic investigations of the acid-catalyzed aquation of bis(oxalato)carbonatochromate(III), bis(malonato)carbonatochromate(III), and bis(methylmalonato)carbonatochromate(III) and offers a possible explanation for the variation in the kinetic lability.

Experimental

Preparation of the Complexes: Potassium *cis*-bis(oxalato)diaquachromate(III) dihydrate was prepared by the method of Palmer.[5] The malonato and methylmalonato analogues as their trihydrates were prepared by the method of Chang.[6,7] The purity of the complexes was confirmed by microanalysis and UV-visible spectra agreed closely with those given in literature.[6–8]

The carbonato complexes were prepared according to the method of Kelm et al.[4] by gradually adding solid K_2CO_3 to a stirred solution containing 1 g of the aqua complex in 10 ml of water until a pH of 8.5 was attained. After stirring for ten minutes the solution was cooled in an ice bath and ethanol was added until a green precipitate (bluish green in the case of malonato and methylmalonato complexes) was formed. The crystals were filtered off and washed thoroughly with ethanol followed by ether. The purity of the complexes was checked by analysing the samples for carbon, hydrogen, chromium, and potassium.

All the other chemicals used were of reagent grade and distilled water redistilled twice with a little addition of NaOH and $KMnO_4$ was used for the preparation of all the solutions.

The UV-visible absorption spectra of these complexes were recorded using a Shimadzu UV-260 UV-visible recording spectrophotometer. The absorption maxima and the extinction coefficients of the carbonato complexes and their aquation products are tabulated (Table 1).

The infrared spectra of these carbonato complexes were obtained by means of the KBr disc technique with a Perkin-Elmer 1430 IR spectrophotometer. The C-O stretching frequencies of the bidentate carbonate for the Cr(III) complexes prepared appear at 1040 and 780 cm^{-1} for oxalato, 1030 and 760 cm^{-1} for malonato, and 1020 and 740 cm^{-1} for methylmalonato complexes which compare well with the reported C-O stretching frequencies of a series of carbonato cobalt(III) species[1–3] and bis(oxalato)carbonato chromate(III).[4] The C-O stretching frequency at 1593 cm^{-1} for CO_3^{2-} is masked by the strong band of the coordinated carboxylato group.

Kinetics: The acid hydrolysis of $[\mathrm{Cr(XX)_2(CO_3)}]^{3-}$ (XX=oxalate, malonate, and methylmalonate) was investigated using a Hi-Tech stopped-flow spectrophotometer equipped with an Apple II data aquisition system. The reactions were monitored at 300, 260, and 250 nm for oxalato, malanato, and methylmalonato complexes respectively where the absorbance difference between the carbonato complexes and aquated products are maximum. The visible absorption spectra of the products correspond to the cis isomers of their diaquodicarboxylato complexes. The H$^+$ concentration was regulated with $HClO_4$ and the ionic strength was kept at 2 M using sodium perchlorate. The concentration of the complexes was maintained at 1.0×10^{-3} M throughout the course of investigation. The absorbance

Table 1. Absorption Maxima and Molar Extinction Coefficient Values of $[\mathrm{Cr(XX)_2(CO_3)}]^{3-}$, Their Aquation Products and *cis*-$\mathrm{Cr(XX)_2(H_2O)_2^-}$

XX	λ_{max}	ε_{max}	λ_{max}	ε_{max}	Ref.
	$\mathrm{Cr(XX)_2(CO_3)^{3-}}$				
Oxalate	416.8	107.4	580.0	74.0	This work
	413.3	102.0	578.6	72.0	4
Malonate	418.4	53.0	574.0	53.5	This work
Methylmalonate	422.0	66.0	578.8	70.0	This work
	Aquation Products of $\mathrm{Cr(XX)_2(CO_3)^{3-}}$				
Oxalate	413.5	65.0	560.2	50.0	
Malonate	415.3	41.8	566.1	47.8	
Methylmalonate	420.2	50.0	565.3	58.0	
	cis-$\mathrm{Cr(XX)_2(H_2O)_2^-}$				
Oxalate	415.0	64.5	560.0	50.6	8
Malonate	415.0	42.0	566.0	47.9	7
Methylmalonate	419.0	50.9	567.0	58.1	6

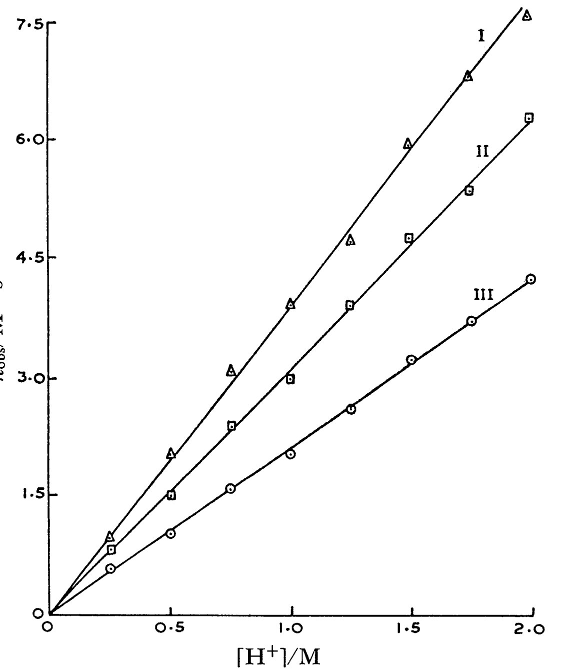


Fig. 1. Effect of $[H^+]$ on rate constant. $[Cr(XX)_2(CO_3)^{3-}]=1.0\times10^{-3}$ M, temp=25 °C, $\mu=2.0$ M, XX= methylmalonate(I); malonate(II); oxalate(III).

time-data were transferred to computer diskets and the rate constants were then computed using a standard least square program.

Results and Discussion

Preliminary studies were made of the rate of aquation at 25 °C for each of the three complexes at $[H^+]=1.0$ M with the complex ion concentration varied between the limits 1.0×10^{-3} and 5.0×10^{-3} M. The values of the rate constants were identical within ±5% confirming the expectation that the reaction is first-order in complex ion concentrations. In all the subsequent runs, this concentration was kept at 1.0×10^{-3} M.

Examples of the effect of hydrogen ion concentration on the rate of aquation are shown in Fig. 1. Each point in the graph represents the mean value of 10 runs. From these plots, it is seen that the rate of aquation of $[Cr(XX)_2(CO_3)]^{3-}$ can be expressed by a simple second-order equation:

$$-d[C]/dt=k_{obs}[C]=k_a[H^+][C] \tag{1}$$

where [C] is the concentration of the complex.

These results could be explained in terms of the following mechanism which was proposed earlier for the acid hydrolysis of several anionic[1,2] and cationic[3] carbonatocobalt(III) complexes and for bis(oxalato)carbonatochromate(III)[4] and can be expressed as:

$$[Cr(XX)_2(CO_3)]^{3-}+H_3O^+ \xrightarrow{k_1} [Cr(XX)_2(HCO_3)(H_2O)]^{2-} \tag{2}$$

$$[Cr(XX)_2(HCO_3)(H_2O)]^{2-} \xrightarrow[\text{fast}]{k_2} [Cr(XX)_2(OH)(H_2O)]^{2-}+CO_2 \tag{3}$$

$$[Cr(XX)_2(OH)(H_2O)]^{2-} \underset{H^+}{\overset{K_1}{\rightleftarrows}} [Cr(XX)_2(H_2O)_2]^- \tag{4}$$

According to this reaction sequence the expected rate expression should be:

$$k_{obs}=k_1[H^+],\ \text{if}\ k_1[H^+]\ll k_2, \tag{5}$$

and

$$k_{obs}=k_2,\qquad \text{if}\ k_1[H^+]\gg k_2. \tag{6}$$

From the observed $[H^+]$ dependence, k_{obs} should equal to k_1. Table 2 gives the second order rate constants, k_1 determined from the slopes of the plots, $[H^+]$ vs. k_{obs} at three different temperatures together with the enthalpies and entropies of activation calculated from Eyring plots.

It is clear from the mechanism proposed above, that the k_{obs} values should increase linearly with $[H^+]$ and then level off to a constant value at high acidity i.e., $k_1[H^+]\gg k_2$. This constant value should represent the rate constant for decarboxylation of the aqua(hydrogencarbonato) species, k_2 in Eq. 3. This suggests that the rate of decarboxylation of the aqua(hydrogencarbonato) species is much faster than the rate of ring opening. Since the decarboxylation occurs by carbon-oxygen bond fission, the reactivity is not expected to depend on the nature of the central metal atom. Harris et al.[1,2] obtained a value of 55 s^{-1} for the decarboxylation of $[Co(nta)(HCO_3)(H_2O)]^-$ (nta=nitrilotriacetic acid) and $Co(edda)(HCO_3)(H_2O)$ (edda=ethylenediamine diacetic acid). Assuming this value for the decarboxylation of $[Cr(XX)_2(HCO_3)(H_2O)]^{2-}$ and from ring-opening rate constants, k_1 which are 2.12, 3.28, and 4.02 $M^{-1}\,s^{-1}$ respectively for oxalato, malonato, and methylmalonato complexes, the k_{obs} values for these complexes at 2 M $[H^+]$ are calculated. These values are 4.24, 6.56, and 8.04 s^{-1} for oxalato, malonato, and methylmalonato com-

Table 2. Rate Parameters for the Acid-Catalyzed Ring Opening of $[Cr(XX)_2(CO_3)]^{3-}$ $\mu=2.0$ M

Substrate	Temp	k_1	$\Delta H^{\neq}$	$-\Delta S^{\neq}$
	°C	$M^{-1}\,s^{-1}$	kcal M^{-1}	eu
$Cr(ox)_2(CO_3)^{3-}$	20	1.43±0.05		
	25	2.12±0.08	14.7±0.1	7.5±0.4
	30	3.56±0.10		
$Cr(mal)_2(CO_3)^{3-}$	25	3.28±0.06		
	30	4.68±0.11	10.1±0.2	22.2±0.5
	35	5.96±0.16		
$Cr(Mmal)_2(CO_3)^{3-}$	25	4.02±0.10		
	30	5.25±0.12	7.3±0.1	31.0±0.1
	35	7.30±0.21		

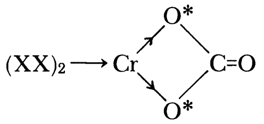
Table 3. Rate Parameters for the Acid-Catalyzed Ring Opening of Some Chromium(III) and Cobalt(III) Carbonato Complexes[a)]

Complex	k_1	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Average pK_a	Ref.
	$M^{-1}s^{-1}$	kcal M^{-1}	eu		
$Co(nta)(CO_3)^{2-}$	47	18.6	+11	4.7	1
cis-$Co(edda)(CO_3)^-$	118	12.0	− 8	5.9	2
trans-$Co(edda)(CO_3)^-$	2.4	10.8	−20	5.9	2
$Co(trien)(CO_3)^+$	5.2	15.0	− 5	7.3	3
$Co(trien)(CO_3)^+$	0.2	17.0	− 5	7.3	3
$Co(en)_2(CO_3)^+$	0.6	13.8	− 7	8.0	3
$Co(tren)(CO_3)^+$	2.0	11.1	−20	9.5	4
$Cr(ox)_2(CO_3)^{3-}$	2.1	14.7	− 8	2.8[b)]	This work
$Cr(mal)_2(CO_3)^{3-}$	3.3	10.1	−22	4.3[b)]	This work
$Cr(Mmal)_2(CO_3)^{3-}$	4.0	7.3	−31	4.5[b)]	This work
$Cr(ox)_2(CO_3)^{3-}$	2.0	14.7	− 8	—	5

a) en : Ethylenediamine, trien : Triethylenetetramine, edda : Ethylenediaminediacetato (2−), nta : Nitrilotriacetato (3−), tren : Tris(2-aminoethyl)amine. b) Ref. 9.

plexes, respectively. Thus at the highest acid concentration of 2 M [H^+] studied, the k_2 values are nearly 14, 8, and 7 times greater than k_1, which satisfies our experimental observation that the second step of the aquation process is very fast.

It is of interest to compare the rate parameters for the acid-catalyzed ring-opening processes of $[Cr(XX)_2(CO_3)]^{3-}$ with those of various anionic and cationic carbonatocobalt(III) complexes since the rates of aquation of cobalt (III) complexes do not differ very much from those of chromium(III) complexes. Table 3 gives the rate parameters for the aquation of several cobalt(III)- and chromium(III)-carbonato complexes. It is clear from the table that with cobalt(III) complexes, neither do considerations of overall charge on the complex nor ligand basicity afford clear cut correlation of reactivities. It was suggested that the relative magnitudes of the rate constants for the acid-catalyzed ring opening of chelated carbonato complexes include a stereochemical component.[2)] The influence of the electronic structure of the inert ligand, at least as evidenced by the type of pK_a data quoted is not yet clearly delineated for this type of reactions. However, with chromium(III)-carbonato complexes, the present studies revealed that there is a good correlation between the rate of ring-opening and average pK_a's of the inert ligands. The increase in basicity of the inert ligands from oxalate to methylmalonate increases the negative charge on the central chromium atom by inductive effect which in turn increases the basicity of O*. This will weaken the Cr–O bond and also facilitates hydrogen bonding in the transition state.



XX=oxalate, malonate, or methylmalonate.

The $\Delta H^{\neq}$ values presented in the table clearly reflect the explanation given for the observed trend in the rate constants. It is interesting to note that a similar trend in the rate constants was observed in the aquation of $[Cr(XX)_3]^{3-}$(XX=oxalate, malonate, and methylmalonate) and was explained in terms of the basicity of dicarboxylato ligand.[10)] Hence the present studies reveal that the rate of ring-opening depends on the electronic structure of the inert ligand.

References

1) T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **13**, 1275 (1974).

2) T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **14**, 2573 (1975).

3) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **93**, 91 (1971).

4) D. A. Palmer, T. P. Dasgupta, and H. Kelm, *Inorg. Chem.*, **17**, 1173 (1978).

5) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London (1954), p. 387.

6) J. C. Chang, *J. Inorg. Nucl. Chem.*, **35**, 2417 (1973).

7) J. C. Chang, *J. Inorg. Nucl. Chem.*, **34**, 221 (1972).

8) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).

9) A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York (1977).

10) J. C. Chang, *J. Inorg. Nucl. Chem.*, **30**, 945 (1968).