318 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 318—320 (1983) [Vol. 56, No. 1

Metal Catalyzed Aquation of Tris(malonato)chromate(III)ion. Kinetics and Mechanistic Study[†]

Arup Kumar BASAK*,[††] and Chinmoy CHATTERJEE**,[†††]
Inorganic Chemistry Laboratories, University College of Science, Calcutta 700009, India
***Department of Chemistry, Indian Institute of Technology, Powaii, Bombay 400076, India*

(Received February 16, 1982)

Metal ion catalyzed aquation of tris(malonato)chromate(III) ion has been followed spectrophotometrically in perchloric acid solution ($[H^+]=0.05$ M) over a temperature range at an ionic strength of 2.0 M. Under these conditions $k_{obsd}=k_H[H^+]+k_M[M^{2+}]$ where k_{obsd} is the observed first order rate constants for the protons and the metal ion catalyzed pathways. Metal ions exert appreciable catalytic effect on the aquation of the complex with k_M following the sequence Cu(II)>Ni(II)>Co(II)>Zn(II)>Mn(II), which runs parallel to the metal monomalonato complex formation constants. A plausible mechanism for the metal promoted reactions is proposed.

Electrophillic catalysis by metal ions on the coordinated ligands receives much attention in recent years because of the vital role played by Lewis acids in biological processes. It is well known that the phosphate, carboxylate, amino and imidazolyl groups are important metal ion binding sites in biological systems.[1] Metal ions promoted hydrolysis of such coordinated ligands in metal complexes serves as a model for a better understanding of the mechanistic aspects of the biological processes. Bivalent metal ions are required by most enzymes which catalyze phosphate transfer reactions.[2] However the role of Zn(II) and Cu(II) in promoting the biologically important decarboxylation reactions of various acids,[3–5] amino acids and their esters[6] have recently been reviewed and in all cases promotions of hydrolytic reactions requires at least in aqueous solvents the involvement of the catalyzing metal ions and the potentially coordinating sites of the respective acids or esters.

The results of many investigations[7] have already been reported on various reactions of oxalato complexes of Cr(III), but much less informations is available on the analogous Cr(III)–malonato complex because of the inherent instability (kinetic and thermodynamic) of the six membered ring of the malonato system in comparison to the more stable (kinetic and thermodynamic) five membered ring of the oxalato complexes.

Some aquation;[8,9] anation,[10] and isomerization[7,11–13] reactions have been studied and the behavior of the malonato complex appears to be somewhat intriguing from that of the corresponding oxalato complex. In the acid assisted aquation of several carboxylato complexes of Cr(III) it was reported[8,14a–d] that aquation proceeds by a rapid preequilibrium protonation followed by cleavage of the Cr(III)–O bond. In continuation to our earlier studies[15,16] on the metal ion catalyzed aquation of Cr(III) complexes[15–18] it appears worthy of investigation to study the aquation of the title complex into cisdiaquabis(malonato)chromate(III) ion by bivalent metal ions of first transition series.

Here we are reporting the results of investigations on Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ion catalyzed aquation of $Cr(mal)_3{}^{3-}$ and the probable mechanism of the Lewis acid catalyzed aquations have been discussed.

The present investigation was undertaken with a view to examine the i) complexing ability of the chelated ligand towards the incoming metal ions and ii) effectiveness of various metal ions in promoting the hydrolysis of the coordinated malonato ligand to chromium(III).

Experimental

Materials and Method. Pure samples of potassium salt of tris and bis complex anions, $K_3[Cr(C_3H_2O_4)_3]\cdot 3H_2O$[19] and *cis*-$K[Cr(C_3H_2O_4)_2(OH_2)_2]$[10] were prepared by methods described in the literature. The purity of the compounds was checked by elemental analysis. Metal(II) perchlorate solutions were prepared by dissolving the corresponding carbonates with A.R. grade perchloric acid and after complete ceasession of the effervesence a slight excess of perchloric acid was added to check any possibility of hydrolysis. The metal ions and the free acid concentrations were determined by standard methods.[20] Other chemicals used were of reagent quality.

Complex		Cr(%)	C(%)	H(%)
$K_3[Cr(C_3H_2O_4)_3]\cdot 3H_2O$	Calcd	9.82	20.42	2.27
	Found	9.90	20.31	2.40
cis-$K[Cr(C_3H_2O_4)_2(OH_2)_2]$	Calcd	15.71	21.76	2.42
	Found	15.66	21.60	2.51

Experimental procedures are the same as described elsewhere.[16] Plots of $\log\{(A_0-A_t)/(A_t-A_\infty)\}$ *versus* time (t) were linear for at least three to four half lives and passing through the origin, where A_∞ is the absorbance of diaqua species and A_t are that at different time interval. The preliminary spectral observations of the reacting solutions after digesting for at least ten half lives agrees well with spectra of the corresponding cis-diaqua product which further indicates that the reaction is free of any undue complication, which may arise from the subsequent aquation of diaqua to tetraaqua products.

Results and Discussion

At a constant hydrogen ion concentration the pseudo first order rate constant, k_{obsd}, is found to increase

---

[†] Presented at the XXIst ICCC at Toulouse, France 1980.

[††] Present address: Institut für Anorganische Chemie, Universitat Basel, Spitalstrasse 51, CH 4056, Basel, Switzerland.

[†††] Present address: Chemistry Department, University College, London, England.

with increasing metal ion concentration and at a fixed metal ion concentration, k_{obsd}, also increases with increase in the acidity of the medium.

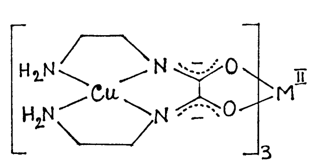
Detailed analysis of the results indicates that the dissociation of the title complex follows a two term rate law:

$$k_{obsd} = k_1[H^+] + k_2[M^{2+}], \qquad (1)$$

where k_1 represents the specific rate constants for the acid catalyzed pathway and k_2 is the catalytic rate constant for the metal-ion-catalyzed process. Using the least squares method, values of $k_1[H^+]$ and k_2 have been evaluated from the linear plot of k_{obsd} *versus* $[M^{2+}]$ (*cf.* Fig. 1). The present k_1 values agree well with that reported earlier.[14b)] Values of k_{obsd} at 40 °C for all the metal ions are given in Table 1. Values of k_1 and k_2 corresponding to H^+ ion and different metal ions catalyzed path and the corresponding activation parameters are given in Table 2.

The metal ions exert a substantial catalytic effect and a possible mechanism for the metal ion catalyzed pathway is summarized in Fig. 2.

The mechanistic feature of the above mentioned process is thought to involve a rapid pre-equilibrium step to form an ion pair or a binuclear bridged complex followed by the cleavage of the first Cr(III)–O malonate bond in a slow rate determining step. Very recently Kida *et al.*[21)] isolated and characterised some tetranuclear bridged complexes of **1** where M^{II}=Co(II),Ni(II). From this it appears that the electron rich carbonyl oxygen can form bonds with catalyzing aquo metal ion centre in the transition state which enhances the ring opening of the malonate ligand as shown in Fig. 2. In view of the above findings the



1

Table 1. Metal(II) catalyzed aquation of tris(malonato)chromate(III) ion at 40 °C and at ionic strength 2.0 M
[Complex]: 2×10^{-3} M; [HClO$_4$]: 5×10^{-2} M

$10^2[M^{2+}]$ mol dm^{-3}	$10^3 k_{obsd}$/min^{-1}				
	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
2.0	13.94	14.21	14.43	14.84	14.06
4.0	—	15.42	16.42	16.78	—
5.0	15.35	—	—	—	15.81
6.0	—	17.18	18.02	18.61	—
8.0	—	—	19.76	20.64	17.73
9.0	—	18.72	—	—	—
10.0	17.46	—	21.56	22.26	18.87
12.0	18.55	20.84	22.87	24.42	—
14.0	—	—	—	—	20.63
15.0	19.83	—	—	—	—
18.0	—	—	—	—	22.97

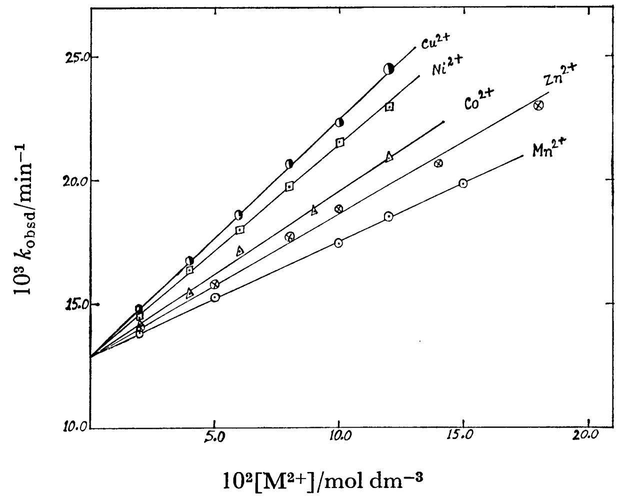


Fig. 1. Dependence of k_{obsd} on the metal ion concentrations at 40 °C, I=2.0 M (NaClO$_4$).

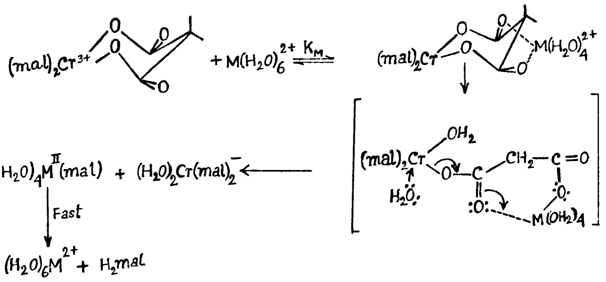


Fig. 2. Probable mechanism for the metal ion catalyzed aquation of $[Cr(mal)_3]^{3-}$ ion.

Table 2. Values of k_{cat} for proton and different metal ion catalyzed paths at different temperatures and the corresponding activation parameters at μ=2.0 M
Acid: 5×10^{-2} M; Complex 2×10^{-3} M

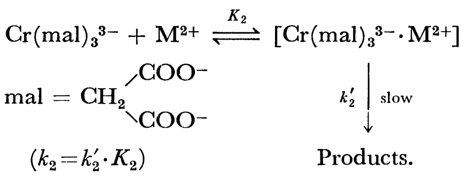
Temperature K		$10^3 k_{cat}$$^{a)}$/s^{-1} M^{-1}					
	Ions	H^+	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
303		1.06	0.17	0.47	0.54	0.67	0.35
308		2.15	0.42	0.75	0.94	1.08	0.63
313		4.28	0.79	1.12	1.43	1.63	0.99
ΔH^*/kJ mol^{-1} $^{b)}$		109.2	118.9	67.2	73.5	67.6	80.2
ΔS^*/J K mol^{-1} $^{c)}$		+55.0	+72.7	−89.5	−67.6	−86.1	−50.0

a) $\sigma(k_{cat}) = \pm5\%$. b) $\sigma(\Delta H^*) = \pm2.5$ kJ mol^{-1}. c) $\sigma(\Delta S^*) = \pm5.5$ J K mol^{-1}. N.B. For H^+, k_{cat} stands for k_1 and for other metal ions it represents k_2.

formation of a bridged complex is quite probable in the transition state of the metal catalyzed pathway for the present system.

The kinetic scheme for the aquation of the title complex are as follows.

a) Acid catalyzed pathway was discussed earlier.[14b)]
b) Metal ion assisted pathway:



$$\mathrm{Cr(mal)_3^{3-}} + \mathrm{M^{2+}} \overset{K_2}{\rightleftharpoons} [\mathrm{Cr(mal)_3^{3-}\cdot M^{2+}}] \xrightarrow[\text{slow}]{k_2'} \text{Products.}$$

$$\text{mal} = \mathrm{CH_2(COO^-)_2} \qquad (k_2 = k_2'\cdot K_2)$$

The catalytic rate constants k_2 is related to K_2 and k'_2 by the relation

$$k_2 = \frac{k_2'\cdot K_2}{1+K_2[\mathrm{M^{2+}}]}. \tag{2}$$

Under the present experimental conditions $K_2[\mathrm{M^{2+}}] \ll 1$ as evident from the linearity of the plot of k_{obsd} *vs.* $[\mathrm{M^{2+}}]$ even at highest metal ion concentrations. Hence Eq. 2 reduces to

$$k_2 = k_2'\cdot K_2.$$

The activation parameters corresponding to k_2 values involve both rate constants and equilibrium constants. The overall rate constants for the metal catalyzed process follows the sequence $\mathrm{Cu^{2+}} > \mathrm{Ni^{2+}} > \mathrm{Co^{2+}} > \mathrm{Zn^{2+}} > \mathrm{Mn^{2+}}$, which follows the Irving-Williams natural order of stability,[22)] of the catalyzing metal monomalonato complex. The activation parameters clearly reveal that the metal ion catalyzed aquations with lowest activation enthalpies have more negative entropies of activation whereas for reactions of high enthalpy of activation have positive entropy of activation. The parrallel increase of both ΔH^* and ΔS^* clearly suggests the applicability of kinetic compensation law.[23)] Further a linear correlation between $\log k_2$ and $\log K_\mathrm{M}$ (K_M=the formation constants of the monomalonato complexes) clearly reflects the dominating effect of K_2 on the metal catalyzed pathway.

We thankfully acknowledge the assistance offered by Professor D. Banerjea, Calcutta University, India regarding laboratory facilities and other critical suggestions in writting the paper.

References

1) H. Sigel and D. B. McCormick, *Acc. Chem. Res.*, **3**, 201 (1970).

2) R. M. Bock, "The Enzymes," ed by P. D. Beyer, M. Lardy, and K. Myrback, 2nd ed, Academic Press, N.Y. (1960), Vol. 2, p. 22.

3) W. D. Covey and D. L. Leussing, *J. Am. Chem. Soc.*, **96**, 3860 (1960).

4) D. L. Leussing and N. V. Raghavan, *J. Am. Chem. Soc.*, **96**, 7147 (1974).

5) N. V. Raghavan and D. L. Leussing, *J. Am. Chem. Soc.*, **99**, 2188 (1977).

6) R. W. Hay, "Metal Ions in Biological Systems," ed by H. Sigel, Marcel Dekker, Basle (1977), Vol. 5.

7) K. Uchita and Y. Takinami, *Bull. Chem. Soc. Jpn.*, **53**, 3522 (1980).

8) D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **29**, 2387 (1967).

9) C. Furlani and E. Mantovani, *J. Inorg. Nucl. Chem.*, **31**, 1213 (1969).

10) R. E. Hamm and R. H. Perkins, *J. Am. Chem. Soc.*, **77**, 2083 (1955).

11) M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **11**, 1062 (1972).

12) K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).

13) M. J. Frank and D. H. Huchital, *Inorg. Chem.*, **11**, 776 (1972).

14) a) D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965); b) D. Banerjea and C. Chatterjee, *ibid.*, **30**, 3354 (1968); c) D. Banerjea and M. S. Mohan, *ibid.*, **26**, 613 (1964); d) J. C. Chang, *ibid.*, **30**, 945 (1968).

15) R. N. Banerjee and D. Banerjea, *J. Ind. Chem. Soc.*, **55**, 969 (1978).

16) A. K. Basak, D. Banerjea, R. W. Hay, and C. Chatterjee, *J. Coord. Chem.*, **11**, 195 (1981).

17) D. Banerjea, *J. Ind. Chem. Soc.*, **54**, 44 (1977).

18) L. Goswami, S. Sarkar, and D. Banerjea, *Z. Anorg. Allg. Chem.*, **435**, 301 (1977).

19) H. T. S. Britton and M. E. D. Jarrett, *J. Chem. Soc.*, **1935**, 1728.

20) A. I. Vogel, "Text Book of Quantitative Analysis," 4th ed, Longmans, London (1978).

21) H. Okawa, Y. Kawahara, M. Mikuriya, and S. Kida, *Bull. Chem. Soc. Jpn.*, **53**, 549 (1980).

22) H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

23) R. Romeo, M. L. Tobe, and M. Trozzi, *Inorg. Chim. Acta*, **11**, 231 (1974).