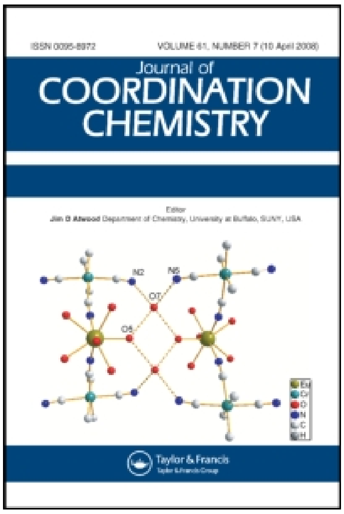

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Arup K. Basak[a]; D. Banerjea[ab]; R. W. Hay[c]; Chinmoy Chatterjee[de]
[a] Inorganic Chemistry Laboratories, University College of Science, Calcutta, India [b] Chemistry Department, University of Stirling, Stirling, Scotland, United Kingdom [c] Chemistry Department, University of Stirling, Stirling, Scotland [d] Department of Chemistry, Indian Institute of Technology, Powai, Bombay, India [e] Chemistry Department, University College, London, London

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KINETICS AND MECHANISM OF THE METAL ION CATALYSED AQUATION OF cis-DIAQUOBIS(MALONATO) CHROMATE(III) ION IN AQUEOUS-ACID MEDIA

ARUP K. BASAK† and D. BANERJEA

Inorganic Chemistry Laboratories, University College of Science, 92 Acharya P. C. Road, Calcutta 700009, India

R. W. HAY

Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland

and

CHINMOY CHATTERJEE‡

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

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The Cu(II), Ni(II), Co(II) and Zn(II) catalysed dissociation of the *cis*-diaquobis(malonato)chromate(III) ion has been studied kinetically in perchloric acid solution over a temperature range. Under these conditions $k_{obs} = k_H[H^+] + k_{cat}[M^{2+}]$ where k_{obs} is the observed first order rate constants and k_H and k_{cat} are the appropriate rate constants for the proton and metal ion catalysed pathways respectively. The metal ion exert marked catalytic effects with k_{cat} following the sequence Cu(II) > Ni(II) > Co(II) > Zn(II). A possible mechanism for the metal promoted reaction is proposed and the relevance of these results to the mechanism of the *trans* → *cis* isomerisation of $[Cr(mal)_2(H_2O)_2]^-$ considered.

INTRODUCTION

Although many investigations[1] have been made of various reactions of *cis*-diaquobis(oxalato)chromate(III). $[Cr(ox)_2(OH_2)_2]^-$, much less information is available on the analogous diaquobis(malonato)chromate(III), $[Cr(mal)_2(OH_2)_2]^-$. Some aquation,[2,3] anation[4] and isomerisation[1,5–7] reactions have been studied, and the behavior of the malonato complex appears to be somewhat different from that of the oxalato complex.

The acid catalysed aquation of several carboxylato complexes of chromium(III) have previously been studied by some of us.[2,8–11] It was concluded that aquation proceeds by a rapid pre equilibrium protonation followed by cleavage of the Cr(III)—O bond. In order to further test the generality of the Lewis acid catalysed aquation we have now studied the kinetics of the aquation of *cis*-$[Cr(mal)_2(OH_2)_2]^-$ to $[Cr(mal)(OH_2)_4]^+$ in the presence of several metal ions (Co(II), Ni(II), Cu(II) and Zn(II)). The acid catalysed aquation of the present complex has been reported previously.[2]

The present investigation should provide informations in the following points.

a) The complexing ability of the malonato ligands towards metal ions.

b) The catalytic coefficients (k_{cat}) for various metal ions in promoting the aquation of the Cr(III) carboxylato complexes.

c) Correlations between thermodynamic stabilities and chemical reactivities.

d) Reaction mechanisms for aquation in the presence of metal ions.

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†Author to whom correspondence should be sent. Present Address: Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland, United Kingdom.

‡Present Address: Chemistry Department, University College, London, London WC1 0AJ.

EXPERIMENTAL

Materials

A pure sample of potassium *cis*-diaquobis(malonato)-chromate(III) was prepared as previously described.[9] The purity was checked by analysis and by determination of the *d-d* spectrum (λ_{max} 418 ($\varepsilon = 42$) and 565 nm ($\varepsilon = 51$)).[9]

Stock solutions of the metal perchlorates were prepared by reaction of the corresponding metal carbonates with AR grade perchloric acid. The metal ion and free acid concentrations were determined by standard methods.[12] Sodium perchlorate was used to adjust the ionic strength.

Kinetic Measurements

The aquation rates were monitored spectrophotometrically using a Carl-Zeiss Spectrophotometer. The Cu(II) catalysed reactions were studied at 420 nm and the other systems at 560 nm. Plots of $\log(A_t - A_\infty)$ were linear for at least three half lives. Values of k_{obs} (the first order rate constants) were evaluated from such plots or from Guggenheim plots.[13] The reference solution contained all the reagents except the complex and the pH of all the solutions was maintained constants (pH *ca* 1.5). Under the conditions of acidity employed the title complex only aquates[2] to $[Cr(mal)(OH_2)_4]^+$, and there is no hydrolysis of the metal ions.

RESULTS AND DISCUSSION

Plots of k_{obs} versus the metal ion concentrations (at constant hydrogen ion concentration) are linear with a positive intercept, (Figure 1). The rate expression thus takes the form

$$k_{obs} = k_H[H^+] + k_{cat}[M^{2+}] \qquad (1)$$

where k_H is the specific rate constant for the acid catalysed pathway and k_{cat} is the catalytic rate constant for the metal ion catalysed process. Values of k_{cat} and $k_H[H^+]$ were evaluated from the least square slope and intercept respectively of such plots, Table I. The rate constants were also determined over a range of temperature (30°C to 60°C) and the temperature dependence of the rate constants is summarised in Table II. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the acid catalysed pathway agree well with those reported earlier.[2]

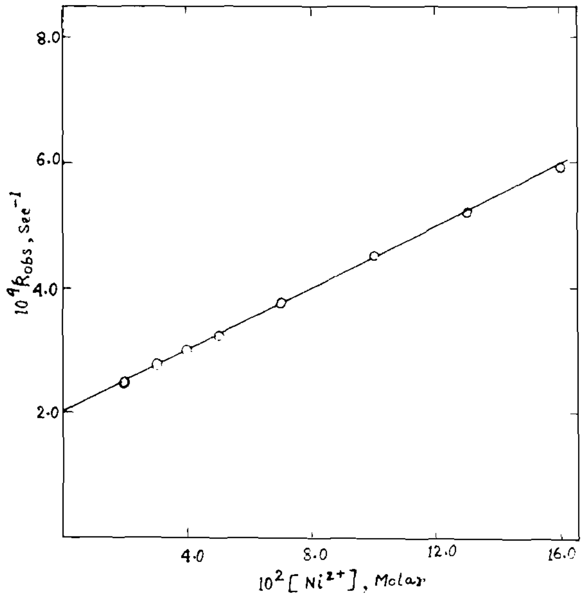


FIGURE 1 Nickel(II) catalysed aquation of *cis*-$[Cr(mal)_2(H_2O)_2]^-$ at 50°C, I = 2.0 M ($NaClO_4$) and $[HClO_4] = 5 \times 10^{-2}$ M.

TABLE I
First order rate constants (k_{obs}) for the metal ion catalysed aquation. [Complex] = 2×10^{-3}M; $[HClO_4] = 5 \times 10^{-2}$M; Temp., 50°C; I = 2.0 M ($NaClO_4$).

Metal Ions / Concentrations, M	$10^4 k_{obs}$, sec^{-1} [a]			
	Co(II)	Ni(II)	Cu(II)	Zn(II)
0.01	–	–	3.32	–
0.02	2.23	2.48	4.64	2.16
0.03	–	2.74	–	–
0.04	2.50	2.99	7.20	2.36
0.05	–	3.24	8.44	–
0.06	–	–	9.65	2.62
0.07	2.89	3.74	–	–
0.08	–	–	11.99	2.82
0.09	–	–	13.12	–
0.10	3.28	4.48	–	3.01
0.12	3.53	–	–	3.23
0.13	–	5.21	–	–
0.15	3.92	–	–	–
0.16	–	5.90	–	–

[a] k_{obs} values were evaluated by least squares. (σk_{obs}) = ±5%

The metal ions exert a substantial catalytic effect and a possible mechanism of the metal ion catalysed pathway is summarised in Figure 2. The reaction is presumed to involve a rapid pre-equilibrium step to form an ion pair or a binuclear bridge complex which then undergoes slow ring opening. Cleavage of the first Cr(III)—O malonate bond is probably rate determining. Tetranuclear bridged complexes of the type shown in (I) have recently been isolated[14] and characterised for M(II) = Ni(II) and Co(II), so that

TABLE II

Values of k_H and k_{cat} at different temperatures and the corresponding activation parameters. [Complex] = 2×10^{-3} M; $[HClO_4] = 5 \times 10^{-2}$ M; I = 2.0 M ($NaClO_4$).

		$10^4\,k_{cat}$, $M^{-1}\,s^{-1}$			
Temp., °C	$10^3\,k_H$, $M^{-1}\,s^{-1}\,H^+$	Co(II)	Ni(II)	Cu(II)	Zn(II)
30	0.46	5.02	—	63.27	2.33
40	1.30	8.27	10.32	91.19	5.10
50	3.93	13.19	25.07	128.52	10.67
60	9.14	20.59	58.73	—	21.36
$\Delta H^‡$, kJ mol^{-1}	85.26	37.17	73.33	26.50	59.89
$\Delta S^‡$, Jk^{-1} mol^{-1}	−30.91	−188.37	−70.98	−202.3	−119.83
$\Delta G^‡_{323}$, kJ mol^{-1}	95.24	98.01	96.26	91.84	98.60

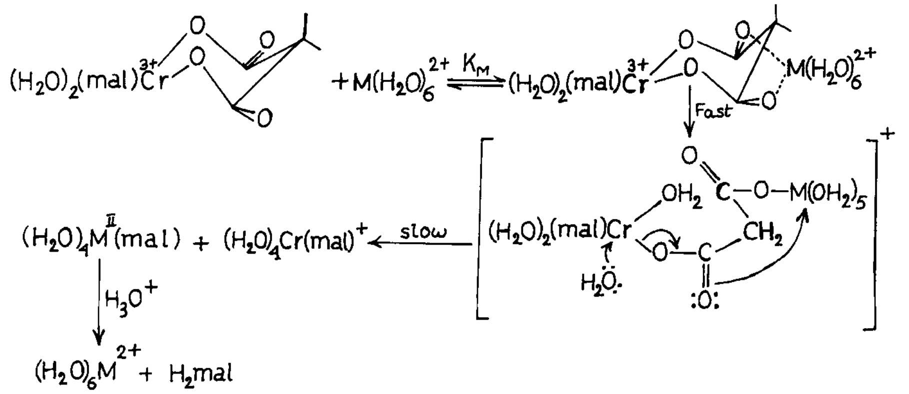
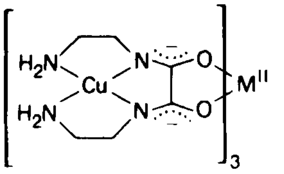


FIGURE 2 Possible Mechanism for the metal ion catalysed aquation of *cis*-$[Cr(mal)_2(H_2O)_2]^-$.



(I)

formation of a bridged complex may possibly occur in the present system. The kinetic scheme can be summarised,

$$\begin{tikzcd}
\mathrm{[Cr(mal)_2(H_2O)_2]^-} + M^{2+} \arrow[r, shift left, "K_M"] & \mathrm{[Cr(mal)_2(H_2O)_2^-} \cdot M^{2+}]^+ \arrow[l, shift left] \arrow[d, "k_M"', "\text{Slow}"] \\
 & \text{Products}
\end{tikzcd}$$

The catalytic rate constant k_{cat} is related to k_M by Eq. (2)

$$k_{cat} = k_M K_M/(1 + K_M[M^{2+}]) \tag{2}$$

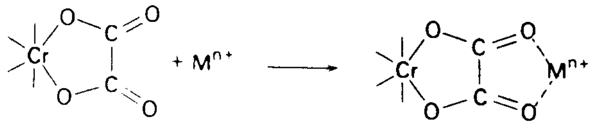
Under the conditions of the present experiments $K_M[M^{2+}] \ll 1$ so that Eq. (2) reduces to $k_{cat} = k_M \cdot K_M$. The activation parameters determined from the k_{cat} values thus involve both rate constants and equilibrium constants.

The k_{cat} values follow the sequence Cu(II) > Ni(II) > Co(II) > Zn(II). This series follows the formation constants of the monomalonato complexes (log K_1; 5.0(Cu^{2+}), 4.0(Ni^{2+}), 3.7(Co^{2+}) and 2.7(Zn^{2+})) at 25°C and I = 0.1 M[15], and probably mainly reflects the effects of K_M on k_{cat}. Studies of other metal ion catalysed processes[16] suggest that the k_M values will not vary by a factor of greater than 10 for the above series of metal ions.

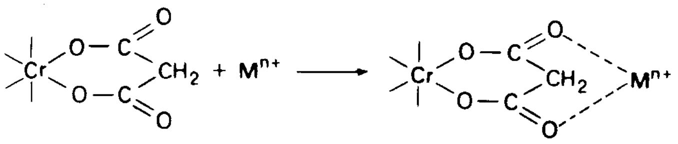
Further studies are planned using high metal $[Cr(mal)_2(H_2O)_2]^-$ ratios which might allow values of k_M and K_M to be directly determined. Under the conditions of the present experiments less than 10% of *cis*-$[Cr(mal)_2(H_2O)_2]^-$ is present as the ion pair or the binuclear complex, since there is a linear dependence of k_{obs} on the concentration of the catalysing metal ions.

Similar metal ion dependence on the rate of aquation of *cis*-$[Cr(ox)_2(H_2O)_2]^-$ has also been reported.[17]

The present results have some bearing on the *trans* → *cis* isomerisation of $[Cr(mal_2(H_2O)_2]^-$. When the *trans*-isomer is dissolved in water the complex isomerises to the *cis*-isomer and there is some 95% of the *cis* isomer at equilibrium. Frank and Huchital[7] have suggested that isomerisation occurs by ring opening, and Casula *et al.*[5] have proposed that the reaction proceeds by dissociation of a water molecule. The kinetics of the isomerisation of *trans*-$[Cr(mal)_2(H_2O)_2]^-$ have recently been studied in detail by Uchida and Takinami.[1] Catalysis by NaCl, $CaCl_2$, $SrCl_2$ and $LaCl_3$ was not observed, although marked catalysis by La(III) occurs in the corresponding oxalato complex.[18] Uchida and Takinami[1] therefore concluded that ion pair formation of the type II is important in the oxalato system, but that the methylene group in the malonato complex prevents ion pair formation of the type III as follows.



(II)



(III)

These considerations were used to support the view that isomerisation occurs by a dissociative mechanism in which the rate determining step was the dissociation of a coordinated water molecule. The present results do, however, establish that under present experimental conditions ion pair formation occurs between $[Cr(mal)_2(H_2O)_2]^-$ and Cu(II), Ni(II), Co(II) and Zn(II), and that such ion pairing leads to the Cr—O bond cleavage, which would lead to isomerisation in the five coordinated intermediate. The effect of transition metal ions on the isomerisation rate of *trans*-$[Cr(mal)_2(H_2O)_2]^-$ thus requires detailed examination.

REFERENCES

1. K. Uchida and Y. Takinami, *Bull. Chem. Soc. Japan*, **53**, 3522 (1980) and references cited therein.
2. D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **29**, 2387 (1967).
3. C. Furlani and E. Mantovani, *J. Inorg. Nucl. Chem.*, **31**, 1213 (1969).
4. R. E. Hamm and R. H. Perkins, *J. Amer. Chem. Soc.*, **77**, 2083 (1955).
5. M. Casula, G. Illuminati and G. Ortaggi, *Inorg. Chem.*, **11**, 1062 (1972).
6. K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).
7. M. J. Frank and K. H. Huchital, *Inorg. Chem.*, **11**, 776 (1972).
8. D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).
9. D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **30**, 3354 (1968).
10. D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964).
11. D. Banerjea and S. Duttachaudhury., *J. Inorg. Nucl. Chem.*, **32**, 2985 (1970).
12. A. I. Vogel, *Text Book of Quantitative Inorganic Analysis*, 4th Edn., Longmans, London, 1978.
13. E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).
14. H. Okawa, Y. Kawahara, M. Mikuriya and S. Kida, *Bull. Chem. Soc. Japan*, **53**, 549 (1980).
15. *Stability Constants of Metal Ion Complexes* L. G. Sillen and A. E. Martell, Chemical Society, London, 1964.
16. See for example R. W. Hay and P. J. Morris, in *Metal Ions in Biological Systems*. H. Sigel (Ed.), Marcel Dekker, New York 1976 vol. 5.
17. L. Goswami, S. Sarkar and D. Banerjea, *Z. anorg. allgm. Chem.*, **435**, 301 (1977).
18. Y. Harada and K. Uchida, *Sci. Rep., Hirosaki Univ.*, **23**, 68 (1976).