Notes

Kinetics and Mechanisms of the Reactions Involving Bis(oxalato)diaquochromate(III) and Bis (malonato)diaquochromante(III) Ions[1]

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Isomerization and aquation reactions of chromium(III) oxalate and malonate complexes have been extensively studied and it is well known that these reactions are catalyzed by proton or some metal cations.[2-14] However, no systematic studies were made for the cation-catalysis on the aquation of these chromium(III) complexes. Recently, we[15] reported the results of catalytic effect of iron(III) on the aquation of *cis*-bis(malonato)diaquochromate(III), $Cr(C_3H_2O_4)(H_2O)_2^-$ and the ring-opening process is proposed as the rate determing step to account for the iron(III)-catalyzed aquation pathway. We extend the study on the metal-ion catalysis of the aquation of chromium(III) oxalate and malonate complexes. We have chosen Cu(II), Al(III) and VO^{2+} ions as potential catalytic cations since these metal ions have large affinity toward both oxalate and malonate anions.

Experimentals

Reagents. Potassium *cis*-bis(oxalato)diaquochromate(III), $KCr(C_2O_4)_2(H_2O)_2$ was prepared from postassium dichromate and oxalic acid as described by Palmer.[16] Potassium *cis*-bis (malonato)di-aquochromate(III), $KCr(C_3H_2O_4)_2(H_2O)_2$ was prepared by the method described previously.[15]

Chromium content was determined by conversion of chromium(III) complexes to CrO_4^{2-} with alkaline followed by spectrophotometric analysis of the CrO_4^{2-} produced ($\varepsilon_{373}=4815$).[17] The stock solutions of cations used as catalysts were prepared from aluminium nitrate, vanadium sulfate or copper perchlorate. The stock solutions were analyzed by complexometric titrations employing disodium salt of ethylenediaminetetraacetic acid as the titration agent.[18] Water used in all the reactions was doubly distilled and sodium perchlorate used was purchased from Fluka Co. and recrystallized before use.

Rate measurements. The rates of aquation were measured spectrophotometrically by observing the absorbance change at the wavelength maxima (560-562 nm) of the reactants. Solutions containing catalytic cations were prepared by adding the proper amount of cation stock solution. The proper amount of sodium perchlorate stock solution was used to bring the ionic strength to 1.0 M and perchloric acid was used to adjust pH to 3.0. Solutions reacting at 25℃, 35℃ and 45℃ were kept in opaque, themostated water bath, outside the spectrophotometer, except during periodic absorbance measurements.

Table 1. Spectral Data for the Chromium(III) Complexess Prepared in this Work

Complex	Absorption peaks (λ_{max}, nm)		Molar absorptivity ($cm^{-1}M^{-1}$)	
cis-$Cr(C_2O_4)_2^-$	416	562	68.5	51.0
$Cr(C_2O_4)(H_2O)_4^+$	418	556	40.1	34.8
cis-$Cr(C_3H_2O_4)_2^-$	417	565	40.6	50.8
$Cr(C_3H_2O_4)(H_2O)_4^+$	416	560	25.1	30.2
$Cr(H_2O)_6^{3+}$	417	589	15.0	14.0

The temperature was maintained with less than ±0.1℃ variation as measured by a calorimetric thermometer graduated in 0.01℃ units. Pseudo-first order rate constants were obtained from slopes of log $(A\text{-}A\infty)$ *vs.* time plots.

The reactions were followed at least five half times. The plots were linear for four or more half times for most experiments.

Result and Discussion

Spectrophotometric Data and Stoichiometry of the Reaction. The spectral data of the complexes considered in this work were obtained experimentally and are summarized in Table 1. These data were utilized to select the appropriate wavelength to monitor the reaction.

To confirm that only one oxalate or malonate is lost from the metal ion-catalyzed $Cr(C_2O_4)_2(H_2O)_2^-$ or $Cr(C_3H_2O_4)_2(H_2O)_2^-$, spent reaction mixtures were separately passed through Dowex 50W-X8 ion-exchange resin. The column was first rinsed with 0.1 M $NaClO_4$ and the collected eluate, which contains mono-positively charged chromium species, $Cr(C_2O_4)(H_2O)_4^+$ or $Cr(C_3H_2O_4)(H_2O)_4^+$, was analyzed for chromium(III) contents. More than 90% of total chromium (III) was found to be in the form of mono-positively charged species after the reaction is over. Then the ion-exchange column was also rinsed with 1 M $HClO_4$ and then eluted with 3 M $HClO_4$ after mono-positively charged species was completely removed from the resin. The 3 M $HClO_4$ solution collected was free of chromium(III) and further aquation of $Cr(C_2O_4)(H_2O)_4^+$ or $Cr(C_3H_2O_4)(H_2O)_4^+$ to $Cr(H_2O)_6^{+3}$ was confirmed not to occur and stoichiometry of aquation can be written as Eq. (1).

$$Cr(AA)_2(H_2O)_2^- + M^{n+} \longrightarrow Cr(AA)(H_2O)_4^+ + M(AA)(H_2O)_4^{(n-2)+} \qquad (1)$$

where (AA) = bidentate $C_2O_4^{-2}$ or bidentate $C_3H_2O_4^{-2}$ and $M^{n+}=Cu^{2+}$, Al^{3+} and VO^{2+}.

Kinetics. Reaction 1 was found to conform to the rate law given by Eq. (2).

$$-d[Cr(AA)_2(H_2O)_2^-]/dt = k_{obs}[Cr(AA)_2)(H_2O)_2^-] \qquad (2)$$

Since $[M^{n+}]$ was always at least tenfold greater than $[Cr(AA)_2(H_2O)_2^-]$ and the reactions were carried out at fixed pH conditions to avoid the complication, first order behavior

Table 2. Observed and Calculated Rate Constants for Cu(II) Catalyzed Aquation of $Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_3H_2O_4)_2(H_2O)_2^-$ in Acidic Media (pH=3.0 and I=1.00 M)

Cr(III) complex	$[Cu^{2+}]$ $\times 10^2$	Temperature (℃)	$k\times 10^6$ sec^{-1}	
			obsd	calcd.
$Cr(C_2O_4)_2(H_2O)_2^-$	5.00	25	1.83	2.33
	10.0	25	5.58	4.58
	15.0	25	6.32	6.82
	5.00	35	9.14	9.14
	10.0	35	10.9	10.9
	15.0	35	16.1	16.1
	5.00	45	50.1	49.8
	7.50	45	57.2	57.8
	10.0	45	66.0	65.7
$Cr(C_3H_2O_4)_2(H_2O)_2^-$	4.00	25	0.630	0.560
	8.00	25	0.770	0.870
	16.0	25	1.52	1.49
	4.00	35	0.980	0.760
	8.00	35	1.54	1.88
	16.0	35	4.24	4.86
	4.00	45	3.77	3.27
	8.00	45	4.57	5.33
	16.0	45	9.70	9.45

Table 3. Observed and Calculated Rate Constants for VO^{2+} Catalyzed Aquation of $Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_3H_2O_4)_2(H_2O)_2^-$ in Acidic Media (pH=3.0 and I=1.00 M)

Cr(III) complex	$[VO^{2+}]$ $\times 10^2$	Temperature (℃)	$k\times 10^6$ sec^{-1}	
			obsd	calcd.
$Cr(C_2O_4)_2(H_2O)_2^-$	5.00	25	7.80	7.85
	10.0	25	9.35	9.25
	15.0	25	10.6	10.6
	5.00	35	13.9	13.5
	7.50	35	18.9	17.5
	10.0	35	21.6	21.4
	12.5	35	24.2	25.3
	5.00	45	41.7	43.0
	10.0	45	67.6	64.0
	15.0	45	83.7	85.0
$Cr(C_3H_2O_4)_2(H_2O)_2^-$	4.00	25	0.870	0.900
	8.00	25	1.88	1.84
	16.0	25	2.69	2.71
	4.00	35	0.900	0.910
	8.00	35	2.32	2.31
	16.0	35	5.11	5.11
	4.00	45	3.23	3.69
	8.00	45	7.86	7.17
	16.0	45	13.9	14.1

Table 4. Observed and calculated rate constants for Al(III) catalyzed aquation of $Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_3H_2O_4)_2(H_2O)_2^-$ in acidic media (pH=3.0 and I=1.00 M)

Cr(III) complex	$[Al^{3+}]$ $\times 10^2$	Temperature (℃)	$k\times 10^6$ sec^{-1}	
			obsd	calcd.
$Cr(C_2O_4)_2(H_2O)_2^-$	5.00	25	4.46	4.80
	10.0	25	8.81	8.12
	15.0	25	11.1	11.4
	5.00	35	14.6	15.1
	10.0	35	19.4	19.4
	15.0	35	23.7	23.7
	5.00	45	47.0	75.9
	10.0	45	75.8	87.1
	15.0	45	105	98.2
$Cr(C_3H_2O_4)_2(H_2O)_2^-$	4.00	25	0.930	1.22
	5.60	25	1.65	1.46
	8.00	25	2.00	1.82
	12.0	25	2.38	2.42
	16.0	25	2.96	3.03
	4.00	35	1.18	1.08
	5.60	35	1.80	1.64
	8.00	35	2.30	2.50
	12.0	35	3.59	3.92
	16.0	35	5.60	5.34
	4.00	45	6.43	5.20
	5.60	45	7.03	7.26
	8.00	45	9.20	10.4
	12.0	45	14.8	15.5
	16.0	45	21.6	20.7

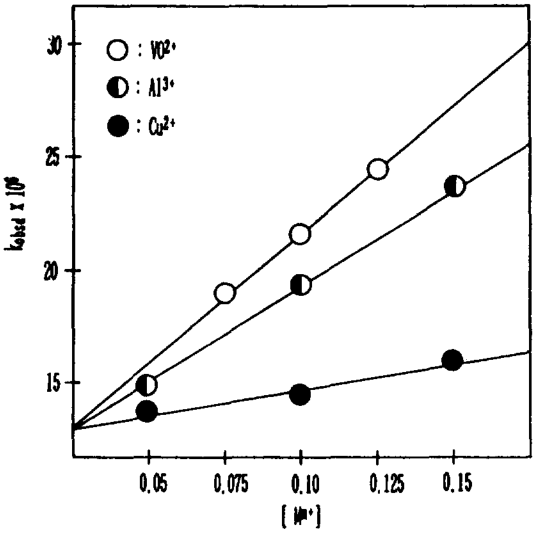

Figure 1. Observed rate constants for the meal ion catalyzed aquation of *cis*-bis(oxalato)diaquochramate(III) as a function of metal ion concentration at 35℃ and at total ionic strength 0.1 M.

was always observed with $k_{obs}=k_1[H^+]+k_2[M^{n+}]$. The k_1 $[H^+]$ term which reflects the contributions of proton-catalyzed pathway to the k_{obs} value remain constant as the reactions were carried out at $[H^+]=0.0010$ M. The measured rate constants for each experiments are summarized in Tables 2, 3 and 4. Metal ion dependencies of k_{obs} are shown

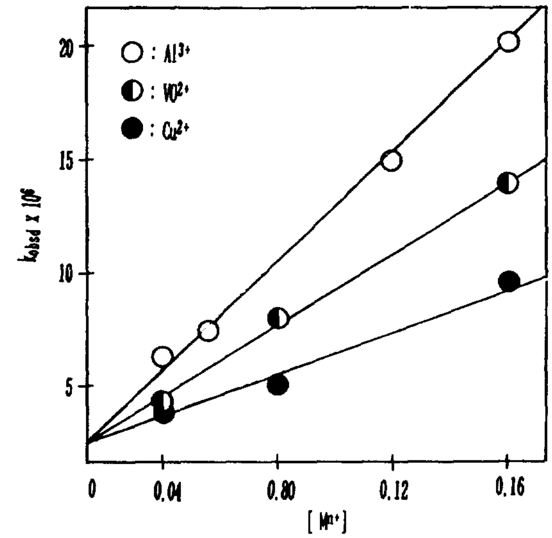

Figure 2. Observed rate constants for the meal ion catalyzed aquation of *cis*-bis(malonato)diaquochramate(III) as a function of metal ion concentration at 35℃ and at total ionic strength 1.0 M.

in Figures 1 and 2. Activation parameters are evaluated from the temperature dependency on the rate constants. The second-order rate constants, k_2 determined by the least-square fitting procedures are listed in Table 5. In the metal ion catalyzed aquation of $Cr(C_3H_2O_4)_2(H_2O)_2^-$, activation parameters are quite similar for three metal ions employed. The negative entropy of activation favors ring opening as the rate-determing step as it is suggested for the Fe^{3+} catalyzed aquation of $Cr(C_3H_2O_4)_2(H_2O)_2^-$.

In Figure 2, the negative logarithm of k_2 is plotted against the logarithm of the formation constant (log β_1) of the metal ion oxalate and malonate for the reaction 4

$$M^{n+} + AA^{-2} \rightleftarrows M(AA)^{(n-2)+} \qquad (4)$$

where the values were taken from the references.[20-25] The values of β_1 are given at different ionic strengths and or different temperature, but since only the general correlation is desired, the plot is considered to be worth while. There is a relatively good correlation between the first formation constant, β_1 and the catalytic rate constant, k_2 for the metal ions.

The VO^{2+} in the aquation of $Cr(C_2O_4)_2(H_2O_2)_2^-$ is the only ion that is considerably deviated from the correlation, and this may be due to either the nature of catalytic reaction for VO^{2+} is quite different from other metal ions or serious error.

Except for VO^{2+} in the aquation of $Cr(C_3H_2O_4)_2(H_2O)_2^-$, the catalytic effect of the metal ions are in the same order as the formation constants of the monooxalato- and monomalonato complexes (see Table 6, Figure 3).

The mechanism of the aquation catalyzed by Cu^{2+}, VO^{2+},

Table 5. Rate Parameters for the Aquation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$

Form of rate term	k_2 (35℃) $M^{-1}sec^{-1}$	$\Delta H^{\neq}$ (kcal·M^{-1})	$\Delta S^{\neq}$ (eu)	Reference
$k_2[Fe^{3+}][cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-]$	554×10^{-5}	24	9	6
$k_2[Al^{3+}][cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-]$	9.10×10^{-5}	20± 5	−12± 6	this work
$k_2[VO^{2+}][cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-]$	15.7×10^{-5}	25± 4	5± 1	this work
$k_2[Cu^{2+}][cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-]$	7.43×10^{-5}	23± 7	−1± 0.3	this work
$k_2[Fe^{3+}][cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]$	22.4×10^{-5}	23± 2	−2.6± 0.1	15
$k_2[Al^{3+}][cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]$	3.55×10^{-5}	20± 3	−15± 0.3	this work
$k_2[VO^{2+}][cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]$	3.50×10^{-5}	17± 3	−25± 0.3	this work
$k_2[Cu^{2+}][cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]$	2.81×10^{-5}	17± 3	−23± 0.4	this work

Table 6. Equilibrium Constants of the Reaction $M^{n+} + AA^{-2} = MAA^{(n-2)+}$ where AA is Malonate ion and Oxalate Ion

Metal ion	Ligand	Temp.	Logarithm of equilibrium constants	Medium	Reference
Fe^{3+}	oxalate	25	$\beta_1 = 7.56$	0.50 M ($NaClO_4$)	20
Al^{3+}	oxalate	25	$\beta_1 = 4.85$	0.10 M ($KClO_4$)	21
VO^{2+}	oxalate	25	$\beta_1 = 6.48$	0.10 M ($NaClO_4$)	21
Cu^{2+}	oxalate	25	$\beta_1 = 4.49$	0.10 M ($NaClO_4$)	22
Cr^{3+}	oxalate	25	$\beta_1 = 5.34$ $\beta_2 = 5.17$	0.10 M ($NaClO_4$)	23
Fe^{3+}	malonate	25	$\beta_1 = 7.46$	0.50 M ($LiClO_4$)	24
Al^{3+}	malonate	25	$\beta_1 = 5.24$	1.0 M ($NaClO_4$)	21
VO^{2+}	malonate	25	$\beta_1 = 5.23$	1.0 M ($NaClO_4$)	21
Cu^{2+}	malonate	25	$\beta_1 = 5.04$	1.0 M ($NaClO_4$)	22
Cr^{3+}	malonate	25	$\beta_1 = 7.06$ $\beta_2 = 5.79$	0.10 M ($NaClO_4$)	25

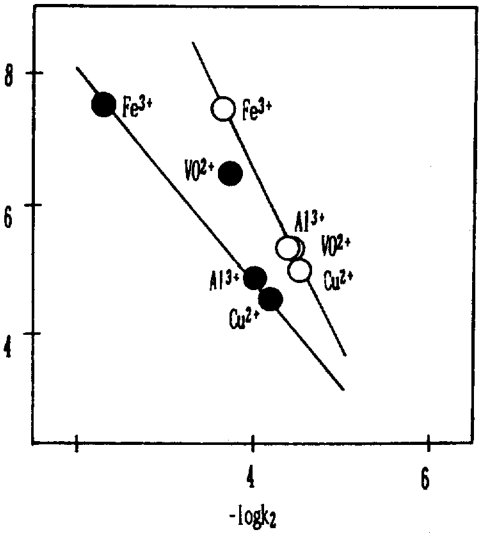

Figure 3. Negative logarithm of k_2 aganist logarithm of first formation constant for metal ion oxalate (●) and malonate complexes (○).

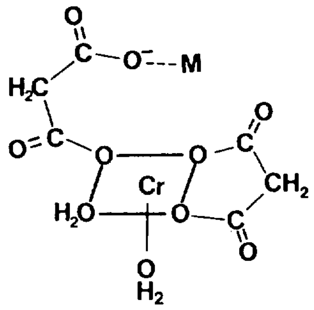

Figure 4. Proposed activated complex in the metal ion catalyzed aquation pathway of $Cr(C_3H_2O_4)_2(H_2O)_2^-$.

and Al^{3+} seems to be quite similar to that of Fe^{3+}-catalyzed aquation previously reported.[15] In previous studies[7,15] of acid catalyzed and Fe^{3+}-catalyzed aquations of these complexes, proton or Fe^{3+} are assumed to make a direct attack on the oxygen atom of oxalate or malonate,[15] forming five coordinated intermediate with only one end of oxalate or malonate bound to chromium (see Figure 4). The role of metal ions is either to help to break the first chromium-oxygen bond and then to help to break the second one or simply to help chelate ring opening.

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Carbonylation of Bromobenzenes having Aldehyde or Protected Aldehyde Groups Catalyzed by Cobalt Carbonyl(I)

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The metal-catalyzed carbonylation of aryl halides is being currently used for many chemicals.[1] Mainly of these, the carbonylation of aryl halides catalyzed by cobalt carbonyl species is successful under mild conditions (room temperature and one atmospheric pressure of carbon monoxide). Many applications were reported by us on the carbonylation of benzal halides (X=Cl, Br),[2-5] halo(halomethyl)benzenes,[6-8]