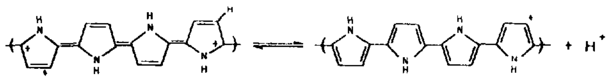
are summarized in Table 1. As can be seen from the table, the metal electrodes show the slopes of 50-52 mV/pH, which are about 14-11% lower than the expected value. The correlation coefficients of the linearity were better than 0.998 for all PPy modified electrodes.

The cause of the potential response has not been widely studied since Eq. (1) below was proposed. However, it is likely that the equilibrium of the acidic proton in the oxidized PPy in Eq. (1) leads to the appearance of a potential drop across the PPy layer. When the solution pH is changed, the dissociation equilibrium in Eq. (1) shifts. That is plausibly why the concentration of the charged PPy molecules and the associated potential drop changes. This dependence of the potential response on pH may be analogous to the dependence of the flat band potential of oxide semiconductors versus pH,[16] where hydroxyl groups on the surface dissociate in accordance with the ionization equation. The discrepancy in the Nernstian slope among metals appears to be caused by the morphology of PPy which changes depending on the surface conditions of an oxide-covered substrate. The morphology will affect the equilibrium in Eq. (1).



(1)

Table 1 also provides the response times averaged over the pH range studied. Response time is defined here as the time required for the voltage change to be less than 1 mV/60 sec. The response times of the PPy coated metal electrodes are longer than that of the glass electrode, implying most likely that it takes longer for the reaction in Eq. (1) to become equilibrated within PPy. This is attributed to the decrease in the electron transfer rate across the oxide layer which was formed prior to PPy. The variation in response times among metals reflects the difference in morphology of PPy on each substrate.

It is concluded that well-adhering polypyrrole layers are formed on stainless steel, Cr, Ta, Nb, and zircaloy electrodes in aqueous nitric acid. The PPy coated metal electrodes are utilizable as potentiometric sensors for hydronium ion.[10]

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Metal Ion Catalyzed Aquation of *cis*-bis(methylmalonato)diaquochromate(III)(1)

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Isomerization and aquation of chromium(III) oxalate and chromium(III) malonate have been extensively studied.[2~23] We[22,23] reported recently the results of catalytic effect of metal ions on the aquations of *cis*-bis(oxalato)diaquochromate (III), *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and *cis*-bis(malonato)-diaquochromate(III), *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2$ and suggested the ring-opening process as the rate determining step to account for the metal ion-catalyzed aquation pathway. We extend the study on the metal-ion catalysis of the aquation of chromium (III) methylmalonate complexes. We have chosen Cu(II), Al (III) and VO^{2+} ions as potential catalytic cations since this metal ions have large affinity toward dicarboxylate anions.

Experimentals

Reagents. Potassium *cis*-bis(methylmalonato)diaquochromate(III), $KCr(C_4H_4O_2)_2(H_2O)_2$ was prepared from postassium dichromate and methylmalonic acid as described by Palmer.[24] Chromium content was determined by conversion of chromium(III) complexes to CrO_4^{2-} with alkaline peroxide, followed by spectrophotometric analysis of the CrO_4^{2-} produced ($\varepsilon_{373} = 4815$).[25] The stock solutions of cations used as catalysts were prepared from the nitrate, sulfate or perchlorate salts of corresponding cations. The solutions were analyzed by complexometric titrations employing disodium salt of ethylenediaminetetraacetic acid as the titration agent.[26] 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. The absorbance measurements were done with a Shimadzu 250 UV-Visible spectrophotometer. 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 1.00 M and perchloric acid was used to adjust pH. Solutions reacting at 25 ℃ were kept in opaque, thermostated water bath, outside the spectrophotometer, except during periodic absorbance measurements.

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-A_∞) *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

Stoichiometry of the reaction. To confirm that only one methylmalonate ligand is lost from the metal ion-catalyzed aquation of $cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-$, 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, $Cr(C_4H_4O_4)(H_2O)_4^+$ 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 $NaClO_4$ and then eluted with 3 M $NaClO_4$ after monopositively charged species was completely removed from the resin. The 3 M $NaClO_4$ solution collected was free from chromium(III) and further aquation of $Cr(C_4H_4O_4)(H_2O)_4^+$ to $Cr(H_2O)_6^{+3}$ was confirmed not to occur and stoichiometry of aquation can be written by equation 1.

$$cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^- + M^{n+} \rightarrow Cr(C_4H_4O_4)(H_2O)_4^+ + M(C_4H_4O_4)(H_2O)_2^{(n-2)+} \qquad (1)$$

where $M^{n+} = Fe^{3+}$, Al^{3+} and VO^{2+}.

Table 1. Observed and Calculated Rate Constants for Acid Catalyzed Aquation of $cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-$ at 1.00 M Ionic Strength and $[cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-] = 2.00\times10^{-3}$ M

$[H^+]$	Temp. (℃)	$k_{obsd}\times10^5$ (sec^{-1})	$k_{cald}\times10^5$ (sec^{-1})
0.10	25	0.47	0.48
0.25	25	1.15	1.15
0.60	25	2.86	2.72
0.75	25	3.28	3.39

Table 2. Observed and Calculated Rate Constants for M^{n+} Catalyzed Aquation of $cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-$ in Acidic Media (I=1.00 M and $[cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-] = 2.00\times10^{-3}$ M)

M^{n+}	$[M^{n+}]$ $\times10^2$	$[H^+]$	Temp. (℃)	$k\times10^5$ sec^{-1} Obsd.	Calcd.
	1.00	0.25	25	1.42	1.43
	3.00	0.25	25	1.88	1.87
Fe^{3+}	4.00	0.25	25	2.14	2.09
	9.00	0.25	25	3.09	3.19
	10.0	0.25	25	3.53	3.41
	5.00	0.001	25	0.22	0.24
VO^{2+}	7.50	0.001	25	0.29	0.28
	10.00	0.001	25	0.36	0.33
	12.50	0.001	25	0.40	0.42
	5.00	0.001	25	0.11	0.11
Al^{3+}	7.50	0.001	25	0.14	0.14
	10.00	0.001	25	0.18	0.17
	15.00	0.001	25	0.22	0.22

Kinetics. Before testing the metal ion effect on the aquation, we investigated acid catalyzed aquation as all the metal ion catalyzed aquation reactions are studied in acidic solution. Kinetic results for acid catalyzed aquation of $cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-$ are summarized in Table 1. A plot of the observed pseudo-first order rate constant k_{obs} at 25 ℃ *vs.* $[H^+]$ was linear. The dependence of k_{obs} on $[H^+]$ follows the equation $k_{obs} = k_o + k_1[H^+]$, while k_1 is the second-order rate constant. The k_o value for spontaneous pathway is calculated to be $(4.89\pm0.01)\times10^{-7}$ sec^{-1}. The mechanism of acid catalyzed aquation of *cis*-bis(methylmalonato)diaquochromate (III) parallels that of corresponding oxalate and malonate complexes, *i.e.*, a rapid protonation preequillibrium, followed by rate-determining attack of water on the protonated inter-

Table 3. Rate Parameters for the Aquation of *cis*-Bis(methyl-malonato)diaquochromate, $cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-$ ($[cis\text{-Cr}(C_4H_4O_4)_2(H_2O)_2^-] = 2.00\times10^{-3}$ M)

Forms of Rate Term	k_2 (25 ℃) $M^{-1}sec^{-1}\times10^5$
$k[Fe^{3+}][cis\text{-Cr}(C_4H_4O_4)_2^-]$	22.2± 0.5
$k[H^+][cis\text{-Cr}(C_4H_4O_4)_2^-]$	4.5± 0.1
$k[VO^{2+}][cis\text{-Cr}(C_4H_4O_4)_2^-]$	2.44± 0.02
$k[Al^{3+}][cis\text{-Cr}(C_4H_4O_4)_2^-]$	1.11± 0.03

Table 4. Rate Parameters for the Aquation of $cis\text{-Cr}(C_2O_4)_2^-$ $cis\text{-Cr}(C_3H_2O_4)_2^-$ and $cis\text{-Cr}(C_4H_4O_4)_2^-$

Forms of Rate Term	k(25 ℃)($M^{-1}sec^{-1}$)	Ref.
$k[H^+][cis\text{-Cr}(C_2O_4)_2^-]$	2.60×10^{-6}	10
$k[Fe^{3+}][cis\text{-Cr}(C_2O_4)_2^-]$	1.00×10^{-3}	10
$k[H^+][cis\text{-Cr}(C_3H_2O_4)_2^-]$	6.50×10^{-5}	9
$k[Fe^{3+}][cis\text{-Cr}(C_3H_2O_4)_2^-]$	5.56×10^{-5}	22
$k[H^+][cis\text{-Cr}(C_4H_4O_4)_2^-]$	$(4.5\pm0.1)\times10^{-5}$	this work
$k[Fe^{3+}][cis\text{-Cr}(C_4H_4O_4)_2^-]$	$(2.2\pm0.5)\times10^{-4}$	this work

$k = k_1$ for proton catalyzed pathways. $k = k_2$ for metal cation catalyzed pathways.

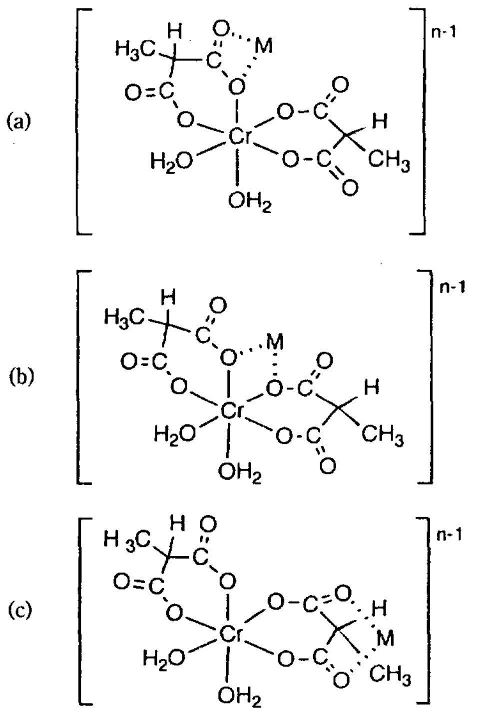

Figure 1. Possible structures of activated complexes in the transition state.

mediate.[9] The rate of acid-catalyzed aquation of cis-$Cr(C_4H_4O_4)_2(H_2O)_2^-$ is approximately 17 times greater than that of oxalate complex but is quite similar to that of malonate complexes. This may be due to the greater affinity of proton toward methylmalonate and malonate ligands, and/or the difference in chelate ring size. Reaction 1 was found to conform to the rate law given by equation 2.

$$-d[cis\text{-}Cr(C_4H_4O_4)_2(H_2O)_2^-]/dt = k_{obs}[cis\text{-}Cr(C_4H_4O_4)_2(H_2O)_2^-] \quad (2)$$

Since $[M^{n+}]$ and $[H^+]$ were always at least tenfold greater than $[cis\text{-}Cr(C_4H_4O_4)_2(H_2O)_2^-]$ and the reactions are carried at fixed pH condition, first order behavior was observed with $k_{obs}=k_0+k_1[H^+]+k_2[Mn^+]$, and k_2 varies for different metal ions in the order $Fe^{3+} \gg VO^{2+} > Al^{3+}$. Rate constants observed at various acidic condition and at different metal ion concentrations are summarized in Table 2. The second order rate constants, k_1 and k_2, determined by the least-square fitting procedures are listed in Tables 3 and 4. The mechanism of the aquation catalyzed by Fe^{3+}, VO^{2+}, and Al^{3+} seems to be quite similar to that of Fe^{3+}-catalyzed aquations of other chromium(III) dicarboxylate complexes previously reported,[10,22,23] and proton and metal ions are assumed to make a direct attack on the oxygen atom of methylmalonate bound to chromium (see Figure 1a or 1b). The role of proton and 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. Another mechanism was suggested by Basak *et al.*[14] and Casula *et al.*[11] previously. They suggested that the metal ion catalysis of chromium malonate complexes arises from chelation by the coordinated malonate as shown in Figure 1b, despite the presence of the backbone methylene group. It is quite certain that the rate of metal ion catalyzed aquation will be greatly reduced upon introduction of bulky methyl group on the methylenic linkage if the complex described by Figure 1c is the transition state intermediate in the rate determining step. However, the Fe^{3+} ion catalyzed aquation of $[cis\text{-}Cr(C_4H_4O_4)_2(H_2O)_2^-]$ is faster than that of $[cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]$ and the mechanism suggested by Basak *et al.*[14] is quite unlikely.

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