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Kinetics of Aquation of *Tris*(bromomalonato)chromate(III) Anion in Acidic Solution

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The aquation of tris*(bromomalonato)chromate(III) anion was studied at 25 °C and μ = 1.0* M. *The observed pseudo-first order rate constant (k_{obs}) was found to be dependent on the hydrogen ion concentration over the entire range of $[H^+]$: $k_{obs} = k_1[H^+]$. At 25 °C and μ = 1.0* M, *k_1 was found to be 3.9×10^{-4}* M^{-1} *sec^{-1}. Over the temperature range 25°–40 °C, E_a = 23.6 Kcal/mol. The product of aquation was found to be* cis*-di(aquo)*bis*(bromomalonato) chromate(III) and a mechanism for this aquation reaction is proposed.*

Introduction

The malonato and oxalato complexes of chromium(III) and cobalt(III) have been studied extensively in recent years [1–8]. The kinetics of aquation of *tris*(malonato)chromate(III) and *tris*(methylmalonato)chromate(III) have been reported [9–12]. In connection with our kinetic study of the aquation of *tris*(malonato)cobaltate(III) anion [13], the studies of the effect of substitution of one hydrogen atom of the methylenic group of malonate of chromium(III) by bromine on the rate of aquation are presented.

Unlike the *tris*(methylmalonato)chromate(III) which gave on aquation a *trans*-diaquo complex, the *tris*(bromomalonato)chromate(III) produced on aquation *cis*-di(aquo)*bis*(bromomalonato)chromate(III).

Experimental

Preparation of Chemicals

Potassium *tris*(bromomalonato)chromate(III) was made by our methods [16], which consist of brominating potassium *tris*(malonato)chromate(III) [14], using bromine in ether, N-bromosuccinimide in chloroform or by coordinating bromomalonic acid with chromium(III) in an analogous method for the preparation of potassium *tris*(malonato)chromate(III) [14]. *Anal.* Calc. for $K_3[Cr(C_3HBrO_4)_3]$ $3H_2O$: C, 14.0; H, 1.2; Cr, 6.8; Br, 31.2%. Found: C, 13.6; H, 1.2; Cr, 6.9; Br, 31.7%.

TABLE I. Visible Absorption Maxima of Cr(III) Malonato Complexes.

Complex[a]	Wavelength, nm	Ref.
$[Cr(mal)_3]^{3-}$	570, 420	9
cis-$[Cr(mal)_2(H_2O)_2]^-$	566, 417	9
trans-$[Cr(mal)_2(H_2O)_2]^-$	560, 404	9
$[Cr(M\ mal)_3]^{3-}$	574, 422	12
cis$[Cr(M\ mal)_2(H_2O)]^-$	565, 421	12
trans-$[Cr(M\ mal)_2(H_2O)_2]^-$	564, 417	12
$[Cr(Br\ mal)_3]^{3-}$	569, 418	present work
cis-$[Cr(Br\ mal)_2(H_2O)_2]^-$	565, 416	present work

[a]mal = malonate, M mal = methyl malonate, Br mal = bromomalonate.

Perchloric acid and sodium perchlorate of reagent grade were used.

Procedure

The rate of the reaction was determined by observing the change in absorbance with time at 569 nm where the *tris*(bromomalonato)chromate(III) shows high absorbance compared to the *cis*-di(aquo)-*bis*(bromomalonato)chromate(III). One ml of solution containing $HClO_4$–$NaClO_4$ mixture or $HClO_4$ alone was placed in an absorption silica-cell. The cell was then placed in the thermostated cell compartment to attain the required temperature. One ml of the complex solution was then added, the reaction mixture thoroughly mixed and the absorbance was measured as a function of time (Fig. 1).

Results and Discussion

The product of aquation of *tris*(bromomalonato)-chromate(III) anion was found to be *cis*-di(aquo) *bis*-

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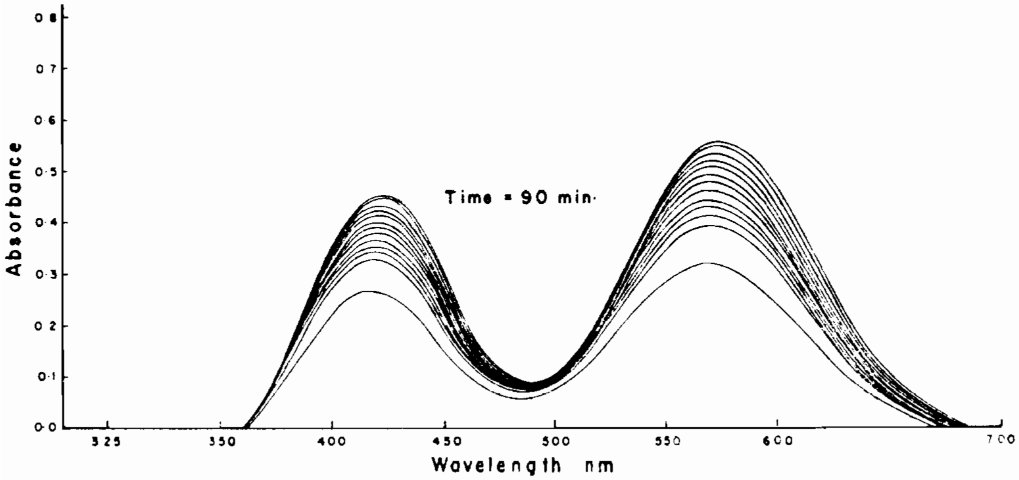

Figure 1. Changes of the UV–visible absorption spectrum of $[Cr(Br\ mal)_3]^{3-}$ with time (μ = 1.0 *M*, $[H^+]$ = 0.5 *M*, temp. = 25 °C).

TABLE II. Pseudo-first Order Rate Constants for the Aquation of $[Cr(Br\ mal)_3]^{3-}$.[a]

$[Cr(Br\ mal)_3)^{3-}] \times 10^3$ *M*	$k_{obs} \times 10^4\ sec^{-1}$
8.0	1.96
6.0	1.88
5.0	1.99
4.0	1.96

[a] $[H^+]$ = 0.5 *M*; μ = 1.0 *M* ($NaClO_4$), temp. 25 °C.

(bromomalonato)chromate(III), instead of the *trans* isomer as in the aquation of *tris*(methylmalonato)-chromate(III). This was confirmed by comparing the visible absorption spectra of *di*(aquo)*bis*(bromomalonato) chromate (the product) with the visible absorption spectra of *cis* and *trans*-di(aquo)*bis*-(malonato)chromate(III) and related complexes (Table I).

The fact that the visible absorption spectrum of *tris*(bromomalonato)chromate(III) is rather similar to the visible absorption spectrum of *tris*(malonato) chromate(III) and because the product of aquation, *i.e.* di(aquo)*bis*(malonato)chromate(III), shows two visible absorption maxima at 565 nm and 416 nm slightly shifted to a shorter wavelength, these are in support of *cis* configuration. If the product of aquation is the *trans* isomer then a larger shift in the positions of the visible absorption maxima would have occurred.

Rate of Aquation of Tris*(bromomalonato)chromate(III)*

The rate of aquation of $[Cr(Br\ mal)_3]^{3-}$ was followed spectrophotometrically at 569 nm up to 90% of the reaction. The rate plots gave straight lines. The values of the observed rate constants are summarized in Table II.

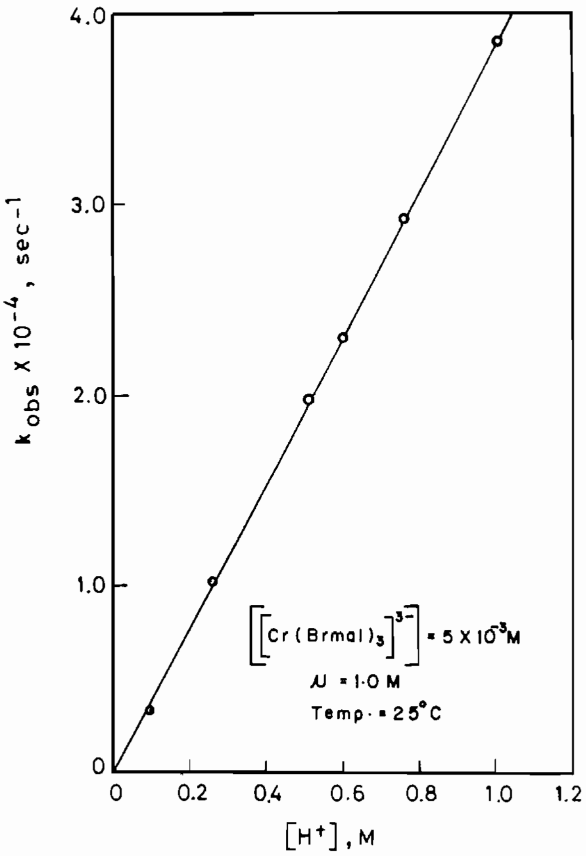

Figure 2. Effect of hydrogen ion concentration on rate constants.

That the reaction was pseudo-first order was shown by the nearly constant rate with 2-fold changes in the initial concentration of $[Cr(Br\ mal)_3]^{3-}$. The rate of aquation can be represented by equation (1):

TABLE III. Variation of k_{obs} with Ionic Strength.^{a}

Ionic Strength, *M*	$k_{obs} \times 10^4$ sec^{-1}
1.50	1.77
1.00	1.88
0.75	2.03
0.50	2.30

^{a}[$(Cr(Br\ mal)_3)^{3-}$] = 5×10^{-3} *M*; [H^+] = 0.5 *M*; temp. = 25 °C.

$$\text{rate} = k_{obs}[(Cr\,(Br\ mal)_3)^{3-}] \qquad (1)$$

where k_{obs} is the pseudo-first order rate constant under the same conditions ([H^+] = 0.5 *M*; μ = 1.0 *M*, temperature 25 °C). The observed rate constants increased with increasing hydrogen ion concentration from 0.25 *M* to 1.0 *M* at constant ionic strength and the acid dependence of k_{obs} follows the equation:

$$k_{obs} = k_1[H^+] \qquad (2)$$

A plot of k_{obs} *vs.* [H^+] is shown in Fig. 2. At 25 °C, k_1 was found to be 3.9×10^{-4} M^{-1} sec^{-1}. From the plot of the k_{obs} *vs.* [H^+] it is seen that the rate of aquation of $[Cr(Br\ mal)_3]^{3-}$ can be expressed by equation 3.

$$\frac{-d[C]}{dt} = k_{obs}[C] = k_1[H^+][C] \qquad (3)$$

where [C] is the concentration of $[Cr(Br\ mal)_3]^{3-}$.

The ionic strength affected the rate of aquation and it was found that k_{obs} decreases with increasing ionic strength. The values of k_{obs} at various ionic strengths are shown in Table III.

The influence of temperature on the rate of the reaction was studied. The temperature range was between 25 and 40 °C at constant hydrogen ion concentration 0.5 *M*, 5×10^{-3} *M* of [$(Cr(Br\ mal)_3)^{3-}$] and ionic strength 1.0 *M*. The results indicate that the rate constant is approximately doubled for each 5 °C rise in temperature (Table IV).

The Arrhenius activation energy E_a for the aquation of $[Cr(Br\ mal)_3]^{3-}$, over the temperature range 25–40 °C, was obtained from a plot of log k_{obs} *vs.* 1/T using the values of k_{obs} under the conditions of [H^+] = 0.5 *M*, μ = 1.0 *M*. A straight line plot was obtained from which E_a was found to be 23.6 Kcal mol^{-1}. The activation energy E_a is almost the same as that for the aquation of $[Cr(mal)_3]^{3-}$ [9], but is slightly higher than that for the aquation of $[Cr(M\ mal)_3]^{3-}$ and that for the aquation of $[Cr(Ox)_3]^{3-}$ [6, 12]. This is in agreement with our results that substitution of one hydrogen atom of the methylenic group of the malonate of chromium(III) by bromine has no effect on the rate of aquation (Table V).

A mechanism for the reaction is proposed as follows.

TABLE IV. Variation of k_{obs} with Temperature.^{a}

Temp. (°C)	$k_{obs} \times 10^4$ sec^{-1}
25	1.99
30	3.15
35	6.14
40	11.52

^{a}[H^+] = 0.5 *M*, $\bar{\mu}$ = 1.0*M*, [$(Cr(Br\ mal)_3)^{3-}$] = 5×10^{-3} *M*.

The first step (4) is a slow protonation of one of the coordinated bromomalonate groups so that one end of it is replaced by a water molecule:

$$[Cr(Br\ mal)_3]^{3-} + H^+ \underset{k_{-1}}{\overset{k_1[H_2O]}{\rightleftharpoons}} [Cr(Br\ mal)_2(BrH\ mal)(H_2O)]^{-2} \qquad (4)$$

In the second step (5), a second water molecule replaces the other end of the protonated bromomalonate group, resulting in the diaquo complex and the release of BrH mal^{-1} ion:

$$[Cr(Br\ mal)_2(BrH\ mal)(H_2O)]^{2-} \xrightarrow[\text{fast}]{k_2[H_2O]} [Cr(Br\ mal)_2(H_2O)_2]^- + BrH\ mal^- \qquad (5)$$

Using the steady-state concentration of the intermediate, such a mechanism gives the rate equation:

$$\frac{-d[C]}{dt} = \frac{k_1k_2[C][H^+]}{k_{-1} + k_2} \qquad (6)$$

Since the second step of the mechanism is the fast step, $k_2 \gg k_{-1}$ and (6) is reduced to (3).

This mechanism is similar to that proposed by Chang [9] for the aquation of *tris*(malonato)chromate(III).

The above mechanism is typical of many organic reactions which are first order in hydrogen-ion concentration [15]. However, since the second step of the mechanism is a fast step and since BrH mal$^-$ anion is still a fairly strong base, the second step of the mechanism might also involve a proton:

$$[Cr(Br\ mal)_2(BrH\ mal)(H_2O)]^{-2} + H^+ \xrightarrow{k_2'[H_2O]} [Cr(Br\ mal)_2(H_2O)_2]^- + BrH_2\ mal \qquad (7)$$

Using the steady-state concentration of the intermediate, the rate equation becomes

$$\frac{-d[C]}{dt} = \frac{k_1k_2'[C][H^+]^2}{k_{-1} + k_2'[H^+]} \qquad (8)$$

Since $k_2'[H^+] \gg k_{-1}$ because step (7) is fast, (8) is again reduced to (3). Both steps (4) and (7) agree

TABLE V. Pseudo-first Order rate Constants for the Aquation of Cr(III) Malonato and Oxalato Complexes.[a]

Complex	$k_{obs} \times 10^4$ sec^{-1}	Refs.
$[Cr(Ox)_3]^{3-}$	0.40	6, 8
$[Cr(mal)_3]^{3-}$	3.48	9
$[Cr(Br\ mal)_3]^{3-}$	3.84	present work
$[Cr(M\ mal)_3]^{3-}$	6.88	12

[a] $[H^+] = 1.0 M$, $\mu = 1.0 M$, t = 25.0 °C.

with the observed dependence of k_{obs} on ionic strength because these steps are reactions between ions of opposite charges. However, such a mechanism has been given for the aquation of *tris*(malonato)-chromate(III) [6–8].

In conclusion, under similar conditions the rate of aquation of *tris*(bromomalonato)chromate(III) is similar to that of aquation of *tris*(malonato)chromate(III) [9, 10]. This might be due to the low inductive effect of bromide. On the other hand, the rate of aquation of *tris*(methylmalonato) chromate(III) is slightly higher than that of *tris*(malonato)chromate(III) [12] (Table V). This was explained by the base strength of the ligands: methylmalonate ion is more basic than malonate ion, due to the positive inductive effect of the methyl group which increases the protonation of the methylmalonate ion.

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