If the value of the activation entropy can be used as an indication of mechanism, as in an analogous system reported by Hunt and Taube,[24] trans exchange would be inferred to be a dissociative interchange, whereas cis exchange would be characterized as an interchange in which bond formation is comparable in importance to bond breaking. Relative values of ΔH^* are consistent with such a conclusion.

In the second coordination sphere of the polar acidopentaaquochromium(III) ion, it appears reasonable to assume a lesser degree of ordering of water molecules in the region surrounding the acido ligand and that water molecules would be unsuitably oriented to provide concerted assistance to the displacement of a cis-bound water from that direction. If that is the case, a statistical factor would favor the exchange of the water molecule in the trans position compared to a molecule in a cis position.

Registry No. Chloropentaaquochromium(III) perchlorate, 51052-36-9; bromopentaaquochromium(III) perchlorate, 51052-37-0; isothiocyanatopentaaquochromium(III) perchlorate, 27295-40-5.

(24) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **76**, 5960 (1954).

Contribution from the Department of Chemistry,
Dartmouth College, Hanover, New Hampshire 03755

Kinetics of the Spontaneous Ring-Closing and Aquation Reactions of Malonatopentaaquochromium(III)

M. V. OLSON* and C. E. BEHNKE

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The spontaneous dynamic behavior of malonatopentaaquochromium(III), a complex containing monodentate malonate, was investigated in the acidity range $0.1 \leqslant (H^+) \leqslant 1.0$ *M* at 25°. Experiments were carried out in which the concentrations of the monodentate species, the chelate complex malonatotetraaquochromium(III), and hexaaquochromium(III) were monitored chromatographically. The data were quantitatively consistent with a kinetic scheme in which the monodentate complex simultaneously undergoes irreversible aquation and reversible ring closing. The latter process, which is the faster of the two, approaches a steady state in which the monodentate and chelate complexes are very nearly at equilibrium; the acid-independent half-life for this transient phase of the reaction is 7 hr. Subsequent aquation of the steady-state mixture, in which the chelate predominates, is very slow. Substantial discrepancies between our results and those of earlier investigations are discussed.

Introduction

The kinetic inertness of chromium(III) complexes has made it possible to isolate and study many unusual, thermodynamically unstable species. We have investigated one such complex in detail, malonatopentaaquochromium(III). This complex, which contains a monodentate malonate ligand, was first reported by Huchital and Taube.[1]

Our involvement arose from an interest in its properties as an oxidizing agent; once we had prepared the complex, however, it became evident that the spontaneous dynamic behavior of our samples differed significantly from that described previously.[1-3] To resolve this discrepancy, we undertook a thorough kinetic study, the results of which are reported herein.

Experimental Section

Malonatotetraaquochromium(III). A 25-ml solution was prepared containing 1.0 *M* malonic acid, 0.25 *M* perchloric acid, and 0.25 *M* hexaaquochromium(III). It was thermostated at 40° for 5 days, diluted to 100 ml with water, and then charged onto an ion-exchange column with a bed volume of 50 ml (22-mm i.d.). The ion-exchange resin in this procedure, as well as all others described in this section, was specially cleaned[4] Bio-Rad AG50W-X2, 200–400 mesh resin in the hydrogen form. After charging was complete, the column was rinsed with 150 ml of 0.05 *M* perchloric acid to remove free malonic acid and anionic complexes. The main band of malonatotetraaquochromium(III) was then eluted with 0.50 *M* perchloric acid. A typical preparation yielded 30 ml of 5×10^{-2} *M* solution, collected from the central region of the 1+ band. The stock solution was stored at 0°.

Malonatopentaaquochromium(III). Three different preparations were used.

Method A. This procedure was a modified version of one described by Huchital and Taube.[1] It proved to be the simplest method of synthesizing substantial quantities of the complex. A 60-ml solution was prepared containing 0.10 *M* hexaaquoiron(III) (a stock solution of which had been made by dissolving iron wire in perchloric acid and oxidizing with hydrogen peroxide), 0.50 *M* malonic acid, and 0.06 *M* perchloric acid. It was then deaerated with argon and 30 ml of a solution containing 0.20 *M* chromium(II) (prepared by the zinc reduction of hexaaquochromium(III)) and 0.18 *M* perchloric acid was injected. The chromium(II)–iron(III) reaction occurred on mixing, after which the solution could be opened to the air. At this stage, 20 ml of 0.05 *M* sodium dichromate was added to oxidize the iron(II) to iron(III); if this step was omitted, the desired malonatopentaaquochromium(III) (2+ charge) was not easily separated from the large amounts of hexaaquoiron(II) present. The reaction mixture was then charged onto an ion-exchange column identical with that described above. After charging was complete, the column was rinsed with 200 ml of 0.10 *M* perchloric acid and then the malonatopentaaquochromium(III) was eluted with 0.50 *M* perchloric acid. Typically, 80 ml of the acid moved the 2+ band to the bottom of the column and its central portion could be collected in the next 25 ml. The resulting solution generally had a concentration of about 3.5×10^{-2} *M*.

Method B. A 20-ml 0.05 *M* malonatotriethylenetetraminecobalt(III) perchlorate solution (see below) was deaerated with argon and then 10 ml of a solution that was 0.10 *M* in chromium(II) and 0.60 *M* in perchloric acid was injected. The chromium(II)–cobalt(III) reaction appeared to be complete in about 1 min; after a few additional minutes, the reaction mixture was opened to the air. The chromatographic work-up, which followed the procedure described in method A (on a suitably reduced scale), typically produced 7 ml of 0.10 *M* product.

Method C. Malonatopentaaquochromium(III) could be recovered in small yield from the standard preparation of malonatotetraaquochromium(III), the recipe for which was described above. Elution was simply continued after the 1+ band had been collected with the perchloric acid concentration raised to 1.0 *M*; a small, but easily

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(1) D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

(2) M. J. Frank and D. H. Huchital, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 42.

(3) M. J. Frank, Ph.D. Thesis, Seton Hall University, 1971.

(4) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

visible 2+ band moved down the column well ahead of hexaaquochromium(III). In a typical preparation, the main portion of the band would be collected in 20 ml with a concentration of 6×10^{-3} *M*.

Final Purification. Solutions from all three methods were frozen upon collection; a final chromatographic purification was always carried out immediately before their use. A water-jacketed, ice-cold column (17-mm i.d.) containing 5 ml of resin was used for this final step. In a typical separation, 15 ml of crude product solution with a concentration of 3.5×10^{-2} *M* was charged onto the column. On elution with 0.5 *M* perchloric acid, the main portion of the 2+ band could be collected in a 15-ml volume with a concentration of 1.7×10^{-2} *M*.

Triethylenetetraminecobalt(III) Perchlorate. We had hypothesized that malonatopentaaquochromium(III) would be the major product when chromium(II) was used to reduce malonate–oxidant complexes containing a chelating malonate. Under these circumstances, inner-sphere attack by chromium(II) is sterically constrained to occur at only one of the two carboxylate groups. This hypothesis draws recent support from Frank and Huchital's[2] preparation of malonatopentaaquochromium(III) by the chromium(II) reduction of tris(malonato)cobalt(III). Our own initial approach was to attempt to prepare malonatotetraamminecobalt(III)[5] or malonatobis(ethylenediamine)cobalt(III). These efforts yielded intractable product mixtures, leading us to turn to the synthesis of malonatotriethylenetetraminecobalt(III). This new, easily prepared complex provided the basis for the method B synthesis of malonatopentaaquochromium(III) described above. A 2.5-g sample (6.5 mmol) of $[\text{trienCoCO}_3]\text{ClO}_4\cdot\text{H}_2\text{O}$[6] was dissolved in 6.6 ml of 2.0 *M* perchloric acid (13 mmol). Once effervescence had ceased, 0.75 g of malonic acid (7.2 mmol) was dissolved in the cobalt(III) solution. The pH was adjusted to about 5 with 5.7 ml of 2.5 *M* sodium hydroxide (14 mmol). The solution was heated for 15 min on a steam bath; during this interval red solid began to form. The solution was cooled, and the solid was collected and washed with ethanol and ether. A typical yield was 2.1 g. The material moved as a homogeneous 1+ band on a cation-exchange column. The cobalt analysis (found 13.7%) corresponded to that expected for the monohydrate $[\text{trienC}\underline{\text{oO}_2\text{CCH}_2\text{CO}_2}]\text{ClO}_4\cdot\text{H}_2\text{O}$ (calculated 13.9%). Absorption maxima were at 357 nm (ϵ 148 M^{-1} cm^{-1}) and 407 mn (ϵ 197 M^{-1} cm^{-1}).

Chromatographic Analyses. An efficient, reproducible ion-exchange technique was devised for quantitatively analyzing chromium(III) solutions for the amounts of 1+, 2+, and 3+ charge types present. The procedure is described here in detail since essentially all of our quantitative observations depended on it. Semimicro chromatographic columns (7-mm i.d.) were employed which possessed a negligible dead volume beneath the resin bed. One milliliter of resin was measured out by water displacement, producing a column with a capacity of 1.4 ± 0.1 mequiv. An approximately 5-mm layer of 20–30 mesh sand was placed on top of the leveled resin to prevent disturbances when eluent solutions were added. The samples, which were always at nearly unit ionic strength, were charged in a 1.00-ml volume. The amount of chromium present in any particular fraction never exceeded 10^{-2} mmol, and it was usually arranged, in the largest fraction, to be at about half that level. The elution scheme, which involved a step concentration gradient, was as follows: 1+ fraction, 5.0 ml of 0.50 *M* perchloric acid plus charging effluent; 2+ fraction, 5.0 ml of 1.50 *M* perchloric acid; 3+ fraction, 5.0 ml of 3.00 *M* perchloric acid. The fractions were collected in 25-ml volumetric flasks and used directly for total chromium analysis by the chromate method.[3] Columns could be rinsed neutral directly after elution of the 3+ fraction and then reused indefinitely. The total amount of chromium eluted consistently balanced the amount charged within experimental error (*ca.* ±2%). With standard samples of malonatotetraaquochromium(III) (1+) and hexaaquochromium(III) (3+), 98–100% of the chromium appeared in the correct fraction. When a sample of freshly purified malonatopentaaquochromium(III) was charged, a typical analysis gave the following results: 2.8% 1+, 96.0% 2+, 1.2% 3+. The formation of 2–3% malonatotetraaquochromium(III) was expected since about 15 min elapses between the charging of the sample and the removal of the last of the 1+ fraction. From the observed rate constant for conversion of malonatopentaaquochromium(III) to malonatotetraaquochromium(III) in homogeneous solutions, it can be calculated that 2.1% conversion is expected in 15 min; ring closing, therefore, occurs at about the same rate on the resin as it does in solution. During kinetic runs, this small effect was corrected for by associating the time $t + 15$ min with an analysis made on an aliquot removed from its reaction mixture at time t.

Malonic Acid Analyses. Malonic acid was determined by exhaustive oxidation with chromium(VI). A 2.00-ml sample containing $<1.4 \times 10^{-2}$ mmol of malonic acid was combined with 1.00 ml of 0.020 *M* potassium dichromate and 2.00 ml of concentrated sulfuric acid. After 2 hr in a boiling water bath, the reaction mixtures were cooled to room temperature, 2.0 ml of concentrated phosphoric acid was added, and the residual chromium(VI) was titrated with iron(II) to a diphenylaminesulfonate end point. The mean value and its standard deviation for six determinations of a 6.40×10^{-3} *M* malonic acid stock solution were $(6.40 \pm 0.02) \times 10^{-3}$ *M*, confirming that quantitative conversion of malonic acid to carbon dioxide was obtained. Blank solutions typically gave apparent malonic acid concentrations of $(1–2) \times 10^{-4}$ *M*, but unsurprisingly the most consistent results were obtained on known samples if no blank correction was applied.

Nonlinear Least-Squares Analysis of the Kinetic Data. The chemical symbols and rate constants used here are defined in the Results. Kinetic experiments starting with malonatopentaaquochromium(III) yielded three sets of data: $((\text{H}_2\text{O})_5\text{CrMH}^{2+})$, $((\text{H}_2\text{O})_4\text{CrM}^+)$, and $(\text{Cr}(\text{H}_2\text{O})_6{}^{3+})$ *vs.* time. We desired to find the values of the two adjustable parameters k_{12} (which also determined k_{21} *via* K_{eq}) and k_{23} that gave the best global representation of the three data sets. The following procedure was used. First, a least-squares fit of the $((\text{H}_2\text{O})_4\text{CrM}^+)$ curve was carried out with both k_{12} and k_{23} left adjustable; the resulting value of k_{12} was generally close to the globally optimum one, but the value of k_{23} was only approximate since the quality of these fits was relatively insensitive to k_{23}. The $(\text{Cr}(\text{H}_2\text{O})_6{}^{3+})$ curve was then fit by holding k_{12} fixed at the value obtained above, while k_{23} was varied. At this stage both k_{12} and k_{23} were always near their best global values; a fully consistent pair of estimates was obtained, however, by one or two new cycles of one-parameter fits of the $((\text{H}_2\text{O})_4\text{CrM}^+)$ and $(\text{Cr}(\text{H}_2\text{O})_6{}^{3+})$ data, varying k_{12} in the first case and k_{23} in the second. Finally, the $((\text{H}_2\text{O})_5\text{CrMH}^{2+})$ data were fit varying k_{12} while holding k_{23} at the value optimized by the above procedure. This last step produced a new value of k_{12} that could be compared to that obtained from the combined analysis of the $((\text{H}_2\text{O})_4\text{CrM}^+)$ and $(\text{Cr}(\text{H}_2\text{O})_6{}^{3+})$ data sets. The two different methods of estimating k_{12} differed by more than 2% in only one case; final globally optimum estimates of k_{12} were simply obtained by averaging the estimates obtained from the $((\text{H}_2\text{O})_4\text{CrM}^+)$ and $((\text{H}_2\text{O})_5\text{CrMH}^{2+})$ data sets.

Results

Spectra. Figure 1 displays the visible absorption spectra of malonatopentaaquochromium(III) (containing monodentate malonate), malonatotetraaquochromium(III) (containing chelating malonate), and hexaaquochromium(III) (henceforth referred to as $(\text{H}_2\text{O})_5\text{CrMH}^{2+}$, $(\text{H}_2\text{O})_4\text{CrM}^+$, and $\text{Cr}(\text{H}_2\text{O})_6{}^{3+}$, respectively). The complete spectra of the three complexes are presented to illustrate the limitations on spectrophotometry as a kinetic tool in this system. The usual starting complex in kinetic runs, $(\text{H}_2\text{O})_5\text{CrMH}^{2+}$, simultaneously undergoes ring closing to $(\text{H}_2\text{O})_4\text{CrM}^+$ and aquation to $\text{Cr}(\text{H}_2\text{O})_6{}^{3+}$. These two processes are associated with opposing, modest changes in extinction coefficient throughout the d–d spectral region; consequently, the observed net absorbance changes are quite small.

Our spectra for the two malonate complexes are in reasonable agreement with earlier reports, as indicated in Table I. Spectra of $(\text{H}_2\text{O})_5\text{CrMH}^{2+}$ were scanned within a few minutes of elution from an ion-exchange column that had been thermostated at 0°. There was no significant variation in spectra between samples prepared by the three different synthetic routes. Neither the spectrum of $(\text{H}_2\text{O})_4\text{CrM}^+$ nor that of $(\text{H}_2\text{O})_5\text{CrMH}^{2+}$ changes observably in the acidity range $0.1 < (\text{H}^+) < 1.0$ *M*.

Analyses of the Complexes. Analyses of $(\text{H}_2\text{O})_5\text{CrMH}^{2+}$ and $(\text{H}_2\text{O})_4\text{CrM}^+$ in solution were consistent with their formulation as two different 1:1 chromium(III)–malonate complexes. For $(\text{H}_2\text{O})_4\text{CrM}^+$, the mean value of the $(\text{H}_2\text{M})_{\text{tot}}/$

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(5) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, 2, 1204 (1963).

(6) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 787 (1967).

Table I. Spectra of the Chromium(III)-Malonate Complexes[a]

Complex	λ_{max}, nm	$\epsilon, M^{-1}\ cm^{-1}$	λ_{max}, nm	$\epsilon, M^{-1}\ cm^{-1}$	Ref
$(H_2O)_4Cr\underline{O_2CCH_2CO}_2{}^+$	412	25.2 ± 0.1	559	31.3 ± 0.0	This work[b]
	415	26.1	559	31.4	*d*
	416	27.2	559	32.4	*e*
	409	26	557	31	*f*
$(H_2O)_5CrO_2CCH_2CO_2H^{2+}$	410	23.7 ± 0.4	571	24.4 ± 0.3	This work[c]
	412	23.4	568	25.6	*d*

[a] Ambient temperatures; $0.1 < (H^+) < 1.0\ M$. [b] Extinction coefficients represent the mean values for three separately chromatographed samples; uncertainties are the standard deviations of the means. [c] As in *b*, but values are averaged for eight samples. [d] Reference 1. [e] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Amer. Chem. Soc.*, 80, 4469 (1958). [f] E. Mantovani and C. Furlani, *Z. Anorg. Allg. Chem.*, 364, 322 (1969).

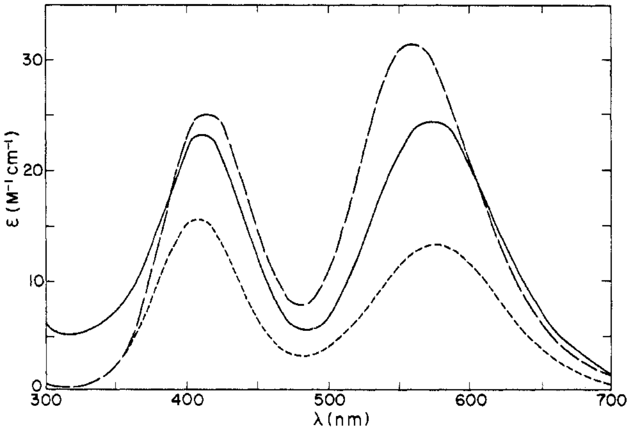

Figure 1. Visible absorption spectra of malonatotetraaquochromium(III) (– –), malonatopentaaquochromium(III) (—), and hexaaquochromium(III) (- - - -).

$(Cr)_{tot}$ ratio with its standard deviation was 1.04 ± 0.01 for four samples; a similar analysis of three $(H_2O)_5CrMH^{2+}$ samples (prepared by method B) gave the result 1.02 ± 0.01.

Kinetic Model. All kinetic data obtained on the chromium(III)-malonate system were consistent with the reaction scheme presented in eq 1 and 2. Consideration of the reverse reaction in eq 2 would undoubtedly be important under some circumstances. However, it proved to be negligible in our experiments, presumably because we worked at high acidities and never investigated solutions in which more than 10% of the chromium(III) was converted to $Cr(H_2O)_6{}^{3+}$. A set of approximate equilibrium constants for the chromium(III)-malonate system[7] also supports the conclusion that the anation of $Cr(H_2O)_6{}^{3+}$ by malonate should be negligible under our conditions. The rate constants k_{21}, k_{12}, and k_{23} are most conveniently defined as pseudo first order since all individual kinetic runs were carried out at essentially constant acidity. The differential rate law for the reaction network in eq 1 and 2 can be integrated in closed form by standard methods.[8] The results, presented in eq 3-5,

$$(H_2O)_5CrMH^{2+} \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} (H_2O)_4CrM^+ + H_3O^+ \tag{1}$$

$$(H_2O)_5CrMH^{2+} + H_3O^+ \xrightarrow{k_{23}} Cr(H_2O)_6{}^{3+} + H_2M \tag{2}$$

$$((H_2O)_4CrM^+) = \frac{((H_2O)_4CrM^+)_{t=0}}{\lambda_3 - \lambda_2}[(\lambda_3 - k_{12})e^{-\lambda_2 t} - (\lambda_2 - k_{12})e^{-\lambda_3 t}] + \frac{((H_2O)_5CrMH^{2+})_{t=0}k_{21}}{\lambda_3 - \lambda_2}[e^{-\lambda_2 t} - e^{-\lambda_3 t}] \tag{3}$$

$$((H_2O)_5CrMH^{2+}) = \frac{((H_2O)_4CrM^+)_{t=0}k_{12}}{\lambda_3 - \lambda_2}[e^{-\lambda_2 t} - e^{-\lambda_3 t}] + \frac{((H_2O)_5CrMH^{2+})_{t=0}}{\lambda_3 - \lambda_2}[(k_{12} - \lambda_2)e^{-\lambda_2 t} - (k_{12} - \lambda_3)e^{-\lambda_3 t}] \tag{4}$$

$$(Cr(H_2O)_6{}^{3+}) = ((H_2O)_4CrM^+)_{t=0}\left[1 - \frac{1}{\lambda_3 - \lambda_2}(\lambda_3 e^{-\lambda_2 t} - \lambda_2 e^{-\lambda_3 t})\right] + ((H_2O)_5CrMH^{2+})_{t=0} \times \left\{1 + \frac{k_{23}}{\lambda_3 - \lambda_2}\left[\frac{\lambda_2 - k_{12}}{\lambda_2}e^{-\lambda_2 t} - \frac{\lambda_3 - k_{12}}{\lambda_3}e^{-\lambda_3 t}\right]\right\} \tag{5}$$

$$\lambda_2 = {}^1/_2(p + q)$$

$$\lambda_3 = {}^1/_2(p - q)$$

$$p = k_{12} + k_{21} + k_{23}$$

$$q = (p^2 - 4k_{12}k_{23})^{1/2}$$

give the predicted time dependences for the concentrations of $(H_2O)_4CrM^+$, $(H_2O)_5CrMH^{2+}$, and $Cr(H_2O)_6{}^{3+}$; these equations apply to initial conditions in which either $(H_2O)_5CrMH^{2+}$ or $(H_2O)_4CrM^+$ is the starting material.

The detailed approach by which our kinetic data were fit to eq 3-5 is most easily described if we anticipate the principal results. Most experiments began with pure solutions of $(H_2O)_5CrMH^{2+}$; typical conditions were 25.0°, $(Cr)_{tot} \cong 5 \times 10^{-3}\ M$, $(ClO_4{}^-)_{tot} = 1.0\ M$, and $0.10 < (H^+) < 1.0\ M$. Under these circumstances, the following generalizations hold.

(1) With a half-life of *ca.* 7 hr the reaction in eq 1 approaches a steady state in which $(H_2O)_4CrM^+$ and $(H_2O)_5CrMH^{2+}$ are very nearly at equilibrium. The steady-state ratio of $(H_2O)_4CrM^+$ to $(H_2O)_5CrMH^{2+}$ varies from *ca.* 10 at 1 *M* acid to *ca.* 10^2 at 0.1 *M* acid.

(2) During the first few half-lives for this process, the reaction in eq 2 accounts for the conversion of 5-10% of the total chromium to $Cr(H_2O)_6{}^{3+}$.

(3) Once the steady-state ratio of $(H_2O)_4CrM^+$ to $(H_2O)_5CrMH^{2+}$ is established, further production of $Cr(H_2O)_6{}^{3+}$ proceeds with a half-life of weeks at 1 *M* H^+ and even slower rates at lower acidities.

Formal Equilibrium Constant for Ring Closing. Equations 3-5 contain the three unknown parameters k_{12}, k_{21}, and k_{23}. In order to reduce the number of fitting parameters to 2, the formal equilibrium constant for the reaction in eq 1 was measured. Samples at varying acidity were thermostated until the steady state was established and then analyzed chromatographically for $(H_2O)_4CrM^+$ and $(H_2O)_5CrMH^{2+}$. In order to provide as stringent a test as possible for both the proposed model and for the experimental method, the steady state was approached starting from both pure $(H_2O)_4CrM^+$ and pure $(H_2O)_5CrMH^{2+}$.

The formal equilibrium constant for the reaction in eq 1 is

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(7) E. Mantovani and C. Furlani, *Z. Anorg. Allg. Chem.*, 364, 332 (1969).

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism." 2nd ed, Wiley, New York, N. Y., 1961, pp 173-177.

defined by eq 6 in which the quantities in parentheses are

$$K_{\text{eq}} = \frac{((H_2O)_4CrM^+)_{\text{eq}}(H^+)}{((H_2O)_5CrMH^{2+})_{\text{eq}}} \tag{6}$$

equilibrium concentrations. In terms of the pseudo-first-order rate constants in eq 1, $K_{\text{eq}} = k_{21}(H^+)/k_{12}$. It is convenient to define a quantity R by a relationship analogous to eq 6, but with the equilibrium concentrations replaced by steady-state values. The defining feature of the steady state is that R is independent of time, the rigorous criterion being that $e^{-\lambda_2 t} \cong 0$ in eq 3-5; for practical purposes, this condition can be met by using the approximation $\lambda_2 \cong k_{12} + k_{21}$ and allowing about 10 half-lives for the decay of $e^{-\lambda_2 t}$. Table II summarizes the results of measurements of R that were carried out in this way.

The data support the conclusion that the same steady-state ratio of $(H_2O)_4CrM^+$ to $(H_2O)_5CrMH^{2+}$ is established regardless of the direction from which the steady state is approached. The quantity R also shows no significant trend with acidity. The measurements should be interpreted with a recognition that they become less reliable at low acidity. At $(H^+) = 0.4\ M$, for instance, the steady-state ratio of $((H_2O)_4CrM^+)$ to $((H_2O)_5CrMH^{2+})$ is nearly 20; therefore, small absolute errors in measuring $((H_2O)_5CrMH^{2+})$ result in large errors in R. Furthermore, values of R measured under these conditions are suspect of being systematically low since any tailing of the very large $(H_2O)_4CrM^+$ band into the small $(H_2O)_5CrMH^{2+}$ fraction gives low results. For instance, at $(H^+) = 0.40\ M$, assuming that the true value of R is 8.0 M, tailing of just 1% of the 1+ band into the 2+ fraction would lead to an observed value of 6.7 M. For these reasons the measurements were not extended to still lower hydrogen ion concentrations. Also, for purposes of calculating K_{eq}, the best value of R was taken as the average of the eight measurements (four sets of duplicates) at $(H^+) = 0.80$ and 1.0 M. The mean value of these measurements and its standard deviation are 8.1 ± 0.3 M.

Combination of eq 3 and 4 leads to eq 7 for R. Anticipat-

$$R = \frac{(\lambda_{12} - k_{12})(H^+)}{k_{12}} \tag{7}$$

ing the relative magnitudes of k_{12}, k_{21}, and k_{23} that were obtained from the kinetic study (*i.e.*, $k_{12} + k_{21} \gg k_{23}$), the approximation in eq 8 can be derived. This form is more

$$K_{\text{eq}} = R - \frac{k_{23}(H^+)}{k_{12}} - \frac{k_{23}(H^+)}{k_{12} + k_{21} + k_{23}} \tag{8}$$

useful than eq 7 since it allows the calculation of K_{eq} by applying a simple additive correction to R. If the last term, which is almost negligible under our conditions, is omitted, eq 8 reduces to the result obtained from the classical steady-state approximation $d((H_2O)_5CrMH^{2+})/dt = 0$.

Since the best estimate of R was obtained from measurements at hydrogen ion concentrations of 0.80 and 1.0 M, values of k_{12}, k_{21}, and k_{23} in the same acidity range will be used in calculating K_{eq} from R. Values of the rate constants were taken from Table III, which is discussed below. If the average parameters from the three kinetic runs at $(H^+) = 1.0\ M$ are employed, the difference $R - K_{\text{eq}}$ is calculated to be 0.52 M. The single experiment at $(H^+) = 0.70\ M$ gives a value of 0.59 M. A reasonable value for the best estimate of K_{eq}, therefore, is 7.5 ± 0.4 M.

Obviously the calculation of K_{eq} has a small circular component since the rate constants employed were derived from the kinetic data by a curve-fitting procedure that made use of the final value of K_{eq}. Our approach, however, yields a set of parameters K_{eq}, k_{12}, k_{21}, and k_{23} that are internally consistent and represent the best overall fit to both the steady-state analyses and the kinetic data. In reality, the difference between R (directly measured) and K_{eq} (derived) is so small that the derivation of K_{eq} from R and the treatment of the kinetic data are only weakly coupled.

Table II. Measurements of the Quantity $R = ((H_2O)_4CrM^+)(H^+)/((H_2O)_5CrMH^{2+})$ under Steady-State Conditions[a]

	R, M	
$(H^+), M$	*b*	*c*
0.40	6.0 ± 1.0	7.3 ± 1.4
0.60	7.0 ± 0.7	8.0 ± 0.8
0.80	7.7 ± 1.0	8.4 ± 0.0
1.0	8.3 ± 0.4	7.9 ± 0.6

[a] Experimental conditions were 25.0°, $(ClO_4^-)_{\text{tot}} = 1.00\ M$. The cited uncertainties reflect the spread about the mean of duplicate determinations of R on the same solution. [b] Measured on equilibrium mixtures obtained by thermostating samples for 72 hr which initially contained $(Cr)_{\text{tot}} = ((H_2O)_5CrMH^{2+}) = 6.3 \times 10^{-3}\ M$. The $(H_2O)_5CrMH^{2+}$ was prepared by method B. [c] Measured on equilibrium mixtures obtained by thermostating samples for 75 hr which initially contained $(Cr)_{\text{tot}} = ((H_2O)_4CrM^+) = 6.0 \times 10^{-3}\ M$.

Table III. Results of Kinetic Runs in Which the Steady State Was Approached Starting from $(H_2O)_5CrMH^{2+}$ [a]

Run no.	(H^+), M	$10^6 \cdot k_{12}$,[b] sec^{-1}	$10^5 \cdot k_{21}$,[b] sec^{-1}	$10^6 \cdot k_{23}$, sec^{-1}	$10^5 k$,[f] sec^{-1}	$10^5 \cdot (k_{12} + k_{21})$,[g] sec^{-1}
1[c]	1.0	3.08	2.30	1.58	2.7	2.51
2[d]	1.0	3.11	2.33	1.48	2.7	2.64
3[e]	1.0	3.19	2.39	1.39	2.5	2.43
4	0.7	2.09	2.24	1.65	3.1	2.31
5	0.5	1.49	2.23	1.17	2.5	2.38
6	0.3	0.876	2.19	1.39	2.7	2.28
7	0.1	0.306	2.30	1.28	2.4	2.33

[a] Experimental conditions were 25.0°, $(ClO_4^-)_{\text{tot}} = 1.00\ M$, and $4.0 \times 10^{-3} < (Cr)_{\text{tot}} < 5.6 \times 10^{-3}\ M$. [b] The constants k_{12} and k_{21} are constrained by the method of data reduction to obey the relationship $k_{21} = k_{12}K_{\text{eq}}/(H^+)$ with $K_{\text{eq}} = 7.5\ M$; see text. [c] Method A used to prepare $(H_2O)_5CrMH^{2+}$ unless otherwise noted. [d] Method B used to prepare $(H_2O)_5CrMH^{2+}$. [e] Method C used to prepare $(H_2O)_5CrMH^{2+}$. [f] Defined by eq 9 and calculated from the absorbance measurements. [g] Calculated by summing columns 3 and 4.

Kinetic Measurements on the Approach to the Steady State. The success with which R was measured chromatographically encouraged us to use the same technique to study the dynamics by which the steady state is approached. Solutions of pure $(H_2O)_5CrMH^{2+}$ were prepared and aliquots analyzed for $(H_2O)_4CrM^+$, $(H_2O)_5CrMH^{2+}$, and $Cr(H_2O)_6^{3+}$ at appropriate times. The resulting data were fit to eq 3-5 using a standard nonlinear least-squares program following the procedure described in the Experimental Section. Figure 2 shows the data from a typical experiment together with the best fits to eq 3-5 while Table III gives the derived rate constants for all runs.

Runs 1-3 provide convincing evidence that the three methods used to prepare $(H_2O)_5CrMH^{2+}$ produce kinetically indistinguishable samples. For the whole set of runs, the values of k_{21}, the constant for the ring-closing step, show good precision with no observable acid dependence; the mean value of k_{21} with its standard deviation is $(2.28 \pm 0.03) \times 10^{-5}$ sec^{-1}. It is worth noting that since ring closing is the dominant process under observation, the optimized values of k_{21} are relatively insensitive to the value of K_{eq} used in the data analysis. The optimized k_{12} values, on the other hand, have

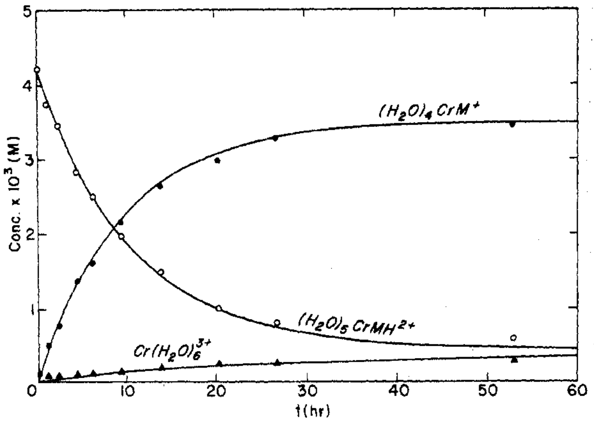


Figure 2. Concentration-time profiles for a typical kinetic run (no. 1, Table III) starting with malonatopentaaquochromium(III).

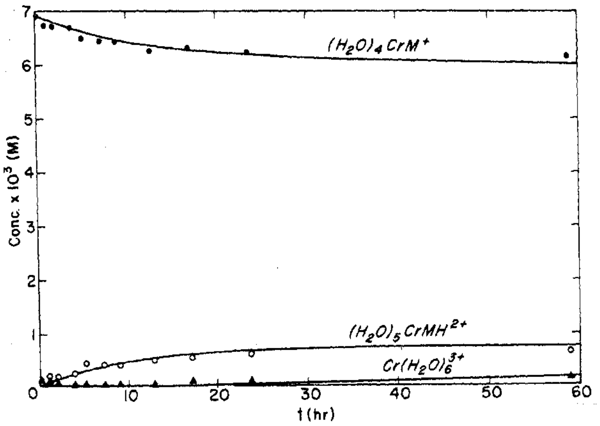


Figure 3. Concentration-time profiles for a kinetic run at $(H^+) = 1.0$ *M* starting with malonatotetraaquochromium(III).

nearly unit correlation with the choice of K_{eq}.

Not surprisingly, the values of k_{23} show considerably greater scatter than those for k_{21}. The range of values is $(1.17\text{-}1.65) \times 10^{-6}$ sec^{-1}; the mean value with its standard deviation is $(1.42 \pm 0.06) \times 10^{-6}$ sec^{-1}. Although a small component of k_{23} that is first-order in (H^+) cannot be precluded, no statistically significant acid dependence is present.

Experiments starting with $(H_2O)_5CrMH^{2+}$ have the advantage that the initial and steady-state conditions differ greatly from one another. One kinetic experiment was carried out, however, starting with pure $(H_2O)_4CrM^+$; a hydrogen ion concentration of 1.0 *M* was selected to maximize the expected concentration changes. Figure 3 shows the observed results. The theoretical curves were plotted using $k_{21} = 2.28 \times 10^{-5}$ sec^{-1} and $k_{23} = 1.42 \times 10^{-6}$ sec^{-1}, the average values for runs 1-7. The good fits obtained provide further support for the experimental method, the proposed kinetic scheme, and the specific rate constants in Table III.

Absorbance measurements were made concurrently with the chromatographic analyses during all kinetic runs. Although these measurements contain less information than the chromatographic data, they provide an independent check on the derived rate constants. Figure 4 shows a typical absorbance-time profile. The wavelength 550 nm was chosen to maximize the difference in extinction coefficient between $(H_2O)_4CrM^+$ and $(H_2O)_5CrMH^{2+}$.

The solid line is a calculated curve obtained by carrying out a least-squares fit of the data to eq 9. The parameters A_0, A_∞,

$$A = A_\infty - (A_\infty - A_0)e^{-kt} \quad (9)$$

and k were left adjustable in the curve-fitting procedure. This method of evaluating k is essentially equivalent to finding the slope of a plot of ln $(A_\infty - A_0)$ *vs.* time; it has the advantage, however, that the weighting of points at long times is not exaggerated. The rate constant k in eq 9 has no exact interpretation in our kinetic scheme. Equation 9 is expected to be obeyed, however, as long as $k_{12} + k_{21} \gg k_{23}$, in which case $k \cong k_{12} + k_{21}$. Since $(k_{12} + k_{21})/k_{23}$ is in the range *ca.* 15-20 under our conditions, the identification of k with $k_{12} + k_{21}$ is a good approximation. Comparison of the last two columns in Table III shows that although the precision of k is not as good as that for the sum $k_{12} + k_{21}$, there is good overall consistency between the spectrophotometric and chromatographic results.

Discussion

Limited comparison is possible between our results and those of two previous kinetic studies.[1,2] In both earlier investigations, only absorbance measurements were made; the first-order rate constants k_{obsd} were obtained from the slopes of plots of ln $(A_\infty - A)$ *vs.* t with A_∞ chosen as the value observed at the broad absorbance maximum that occurs when steady-state conditions are first established. As mentioned earlier, this method is equivalent to the use of eq 9, and the resulting values of k_{obsd} are directly comparable to our values for k (Table III). Huchital and Taube[1] reported the rate law $k_{obsd} = 4.0 \times 10^{-6}$ sec^{-1} + $[2.2 \times 10^{-5}\ M^{-1}$ sec$^{-1}](H^+)$ for the acidity range $0.10 \leqslant (H^+) \leqslant 1.0\ M$. This expression conflicts with our finding that k is independent of the hydrogen ion concentration, although the two sets of results agree when $(H^+) = 1.0\ M$. Frank and Huchital,[2] on the other hand, recently found results in the range $k_{obsd} = (5.2 \pm 0.3) \times 10^{-5}$ sec^{-1} when $0.10 \leqslant (H^+) \leqslant 0.30\ M$. Although they observed no significant acid dependence at these acidities, their values for k_{obsd} are about twice as high as our values for k. Their estimate of K_{eq} (4.0 *M*), measured spectrophotometrically, also differs substantially from ours.

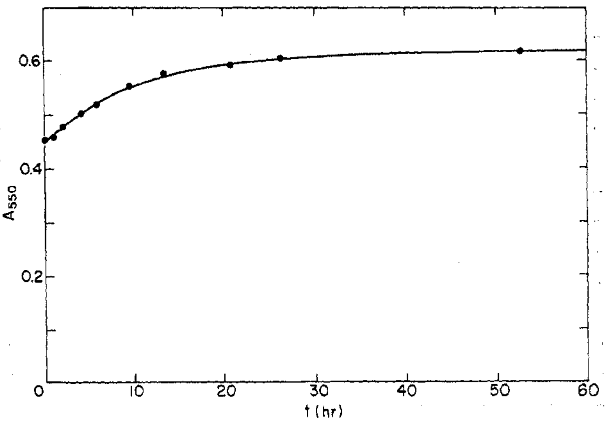


Figure 4. Absorbance-time profile for a typical kinetic run (no. 1, Table III) starting with malonatopentaaquochromium(III); $(Cr)_{tot} = 4.3 \times 10^{-3}$ *M*, $l = 5$ cm.

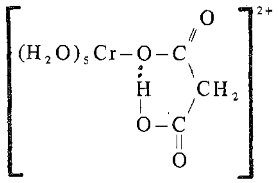
We can offer no detailed rationalization for the discrepancies between the three sets of results. It may be significant, however, that in both previous studies the $(H_2O)_5CrMH^+$ was generated *in situ* by various redox reactions and then studied directly. Since the absorbance changes in the chromium(III)-malonate system are inherently quite small, even minor accompanying changes due to other metastable redox products could seriously interfere.

Regardless of the reasons for the confusing history of work on this system, we have strong confidence in the results reported here. Our measurements were made on purified samples of $(H_2O)_5CrMH^{2+}$ synthesized by three different routes; two independent methods were used to follow the kinetics, and steady-state mixtures of $(H_2O)_5CrMH^{2+}$ and $(H_2O)_4CrM^+$ were approached starting with pure solutions of each complex.

Our results are consistent with a simple picture for the ring-closing reaction. The lack of any acid dependence for the k_{21} step suggests an activated complex in which the unbound carboxylic acid group is undissociated. Presumably, the primary energetic requirement for the ring-closing step is the dissociative loss of a cis water molecule from the metal center. In a series of chromium(III) complexes with 2+ charges, Baldwin and Bracken[9] have measured rates about 10 times slower than k_{21} for the exchange of cis water molecules with solvent waters. This factor of 10 can presumably be accounted for by invoking some entering group participation in the transition state for ring closing. There is considerable evidence that the energetics of chromium(III) substitution reactions, although dominantly dissociative, do have an associative component as well.[10-12] Mechanisms in which the ring-closing process involves carbon–oxygen rather than chromium–oxygen bond cleavage are rendered unlikely by the observation that k_{21} has no acid dependence. Oxygen exchange between simple carboxylic acids and solvent waters proceeds dominantly by a first-order acid path when $(H^+) = 1\,M$;[13] it is reasonable to expect that the rate of ring closing would follow a similar pattern if its mechanism were analogous.[1]

Huchital and Frank[2] reported considerable increases in the rate of ring closing at hydrogen ion concentrations below 0.1 *M*. This effect is expected since the energy of the activated complex could be lowered by the loss of a proton either from a coordinated water molecule (in a conjugate-base mechanism) or from the entering carboxylic acid group.[10,11] Our results simply establish that these processes are unimportant when $(H^+) \geq 0.1\,M$.

The most striking feature of the k_{23} data is the lack of any appreciable acid dependence. As a comparison, the aquation rate of acetatopentaaquochromium(III) increases by a factor of 7 when the acidity is increased from 0.1 to 1.0 *M*.[4] An upper limit to the corresponding increase for malonatopentaaquochromium(III) is about 20%, and there may well be no increase at all. This effect can be reasonably explained by invoking intramolecular general acid catalysis of aquation in the malonate case. The free carboxylic acid group is well situated to participate in a transition state such as



Analogous effects are known in the hydrolysis of maleate and phthalate half-esters;[14] the rates of these processes are also insensitive to the ambient acid concentration, in sharp contrast to monofunctional models.

Our values for K_{eq} and k_{23} can be used to predict the rate at which $(H_2O)_4CrM^+$ solutions would be observed to undergo aquation in a standard spectrophotometric experiment that took no explicit account of the monodentate intermediate. To the approximation that k_{23} is independent of acid, the observed pseudo-first-order rate constant for $(H_2O)_4 \cdot CrM^+$ aquation should be strictly first-order in (H^+), as shown in eq 10. Even in 1 *M* acid the predicted half-life is 44 days,

$$k_{obsd}((H_2O)_4CrM^+ \rightarrow Cr(H_2O)_6{}^{3+}) = k_{23}(H^+)/R = [1.8 \times 10^{-7}\ M^{-1}\ sec^{-1}](H^+) \qquad (10)$$

but we can compare this prediction with results extrapolated from two investigations of $(H_2O)_4CrM^+$ aquation at elevated temperatures. Extrapolation of Mantovani and Furlani's[7] data at $I = 2.0\,M$ from the temperature range 47–67° gives the result $k_{obsd} = 3 \times 10^{-6}\ sec^{-1} + [1.2 \times 10^{-5}\ M^{-1}\ sec^{-1}] \cdot (H^+)$ at 25°. Clearly, the drastic discrepancy with our data cannot be rationalized on the basis of errors in extrapolation or the difference in ionic strength. Banerjea and Chaudhuri[15] have independently published results which are more nearly compatible with ours at the single common acidity of 1 *M*. Extrapolation from the temperature range 60–90° gives $k_{obsd} = 6 \times 10^{-8}\ sec^{-1}$ at 25°. Particularly since the effective activation energy of related processes has been observed, in at least one case, to increase with temperature,[4] this result is not necessarily irreconcilable with our measurements. The far greater lability of Mantovani and Furlani's material casts doubt on the composition of their solutions and possibly on the innocuousness of nitrate as a supporting electrolyte, as well. Their samples were prepared *in situ* from hexaaquochromium(III) and malonic acid. In working with substitution-inert complexes that are not easily purified as solids, an apt lesson from the history of the chromium(III)-malonate system would appear to be that careful chromatographic isolation is an indispensable prerequisite to a kinetic study.

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Registry No. $(H_2O)_4CrO_2CCH_2CO_2{}^+$, 23153-91-5; $(H_2O)_5CrO_2CCH_2CO_2H^{2+}$, 45095-55-4; [trienCoO$_2CCH_2CO_2$]ClO$_4$, 51016-53-6; [trienCoCO$_3$]ClO$_4$, 14023-67-7.

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