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The Aquation of the *cis*-Bis(iminodiacetato)chromate(III) and *trans(fac)*-Bis(methyliminodiacetato)chromate(III) Ions in Acidic Aqueous Medium

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The aquation of the *cis*-bis(iminodiacetato)chromate(III) ion and the *trans(fac)*-bis(methyliminodiacetato)chromate(III) ion in acidic aqueous medium has been studied spectrophotometrically. The products of the aquation are the iminodiacetatotriaquochromium(III) cation and the methyliminodiacetatotriaquochromium(III) cation, respectively. In the reaction involving the *cis*-bis(iminodiacetato)chromate(III) ion, two distinct aquation steps were observed. The first observable step showed the rate law

$$-\frac{d[\text{complex}]}{dt} = k'[\text{H}_3\text{O}^+][\text{complex}]$$

The second step gave the rate law

$$-\frac{d[\text{intermediate}]}{dt} = (k'' + k'''[\text{H}_3\text{O}^+])[\text{intermediate}]$$

Values of k' , k'' , and k''' at 25.0° and ionic strength 0.9 are $7.08 \times 10^{-8} M^{-1} \text{sec}^{-1}$, $1.71 \times 10^{-4} \text{sec}^{-1}$, and $1.28 \times 10^{-4} M^{-1} \text{sec}^{-1}$, respectively. The activation parameters for k' , k'' , and k''' are $\Delta H^\ddagger = 15.3 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -17.0 \pm 1.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$; $\Delta H^\ddagger = 17.0 \pm 0.6 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -18.7 \pm 2.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$; and $\Delta H^\ddagger = 24.3 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 5.1 \pm 1.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively. In the aquation of the *trans(fac)*-bis(methyliminodiacetato)chromate(III) ion, an aquation step was observed with the rate law

$$-\frac{d[\text{complex}]}{dt} = (k'[\text{H}_3\text{O}^+] + k''[\text{H}_3\text{O}^+]^2)[\text{complex}]$$

Values of k' and k'' at 25.0° and ionic strength 0.9 are $1.88 \times 10^{-4} M^{-1} \text{sec}^{-1}$ and $5.74 \times 10^{-4} M^{-2} \text{sec}^{-1}$, respectively. The activation parameters for k' and k'' are $\Delta H^\ddagger = 17.0 \pm 0.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -18.6 \pm 1.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$; and $\Delta H^\ddagger = 15.6 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -21.2 \pm 0.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively. Reaction mechanisms for both systems, which are in agreement with the experimental data, are proposed.

The rate of release of bidentate ligands containing carboxyl or amine functional groups from the coordination sphere of chromium(III) has been rather systematically studied in acidic aqueous medium, where the ligand is oxalate,^{1,2} malonate,³ ethylenediamine,⁴ or glycine.⁵

We have extended these studies to the chromium(III) complexes formed with the tridentate ligands iminodiacetate ion (IDA, $\text{HN}(\text{CH}_2\text{COO}^-)_2$) and methyliminodiacetate ion (MIDA, $\text{CH}_3\text{N}(\text{CH}_2\text{COO}^-)_2$). Our immediate purpose was to compare the differences in the modes and rates of aquation of the respective *cis* and *trans* isomers in the two bis-tridentate complexes.

The *cis*-bis(iminodiacetato)chromate(III) and the *trans(fac)*-bis(methyliminodiacetato)chromate(III) ions have previously been synthesized and characterized.⁶ The *trans* isomer of the bis(iminodiacetato)chromate(III) ion could not be used for the study because of the apparent nonexistence of this isomer.

Experimental Section

Instruments.—All kinetic runs were made on a Beckman Model DU spectrophotometer, which was fitted with a constant-tem-

perature cell block in which matched 1-cm cells were used. A constant-temperature water bath and pump were utilized in circulating thermostated water through the block surrounding the sample and reference cells. The temperature within the block was maintained within $\pm 0.05^\circ$ of the desired value. Supplementary spectra were taken on a Cary Model 14 spectrophotometer or a Beckman Model DB spectrophotometer with recorder.

Chemicals and Solutions.—All chemicals used were reagent grade or chemically pure. In analytical procedures only reagent grade chemicals were used. The chromium(III) complexes were prepared and analyzed as previously described.⁶

The stock solution of lithium perchlorate to be used in the kinetic runs was prepared by neutralizing analytical reagent grade lithium carbonate with 70% perchloric acid. Perchloric acid stock solution was prepared by diluting 70% analytical reagent grade perchloric acid to the desired volume. The water used was deionized and boiled to remove all carbon dioxide.

Analysis of Compounds and Solutions.—The lithium perchlorate stock solution was standardized by evaporating a known volume of the solution to dryness and weighing the anhydrous salt after heating to 170°. The perchloric acid stock solution was standardized by titrating against standardized carbonate-free sodium hydroxide solution.

Spectrophotometric Rate Determinations.—The rates of aquation of *cis*-bis(iminodiacetato)chromate(III) ion and *trans(fac)*-bis(methyliminodiacetato)chromate(III) ion in acidic aqueous medium were followed spectrophotometrically at selected wavelengths in the visible region. For the first species the wavelength 390 $m\mu$ was used and for the second species the wavelength 485 $m\mu$ was used. The wavelength 390 $m\mu$ was very close to the peak maxima for both the reactant and the product species. The wavelength 485 $m\mu$ was close to the peak maximum for the reactant but is on a shoulder for the product species. This

(1) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967), and references therein.

(2) D. Banerjee and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964).

(3) (a) J. C. Chang, *ibid.*, **30**, 945 (1968); (b) D. Banerjee and C. Chatterjee, *ibid.*, **29**, 2387 (1967).

(4) (a) H. L. Schläfer, O. Kling, L. Mahler, and H. P. Opitz, *Z. Physik. Chem.*, **24**, 307 (1960); (b) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749 (1968).

(5) T. W. Kallen, Ph.D. Thesis, Washington State University, 1968.

(6) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

position was chosen to minimize the effect of any decrease in absorbance due to the secondary aquation of the product.

"Infinite" absorption measurements for the *cis*-bis(iminodiacetato)chromate(III) aquation were made 12–24 hr after the reaction was begun depending upon the hydrogen ion concentration and temperature conditions. These readings were checked intermittently for constancy. For the *trans*-bis(methyliminodiacetato)chromate(III) species a calculated "infinite" absorbance was used. This was necessitated because of the slight decomposition of the product species in the 12–24-hr waiting period necessary before "infinite" absorption measurements could be made.

The procedure for a typical kinetic run for either of the two complexes is outlined as follows. Volumes of perchloric acid solution, lithium perchlorate solution, and water were measured into a 125-ml erlenmeyer reaction flask. The flask was then stoppered and allowed to come to the desired temperature in the water bath. A fresh stock solution of the complex ion was also made up and allowed to come to equilibrium. To initiate the reaction, 10.00 ml of the solution containing the complex ion was pipetted into the reaction flask. The resulting solution was stirred rapidly for approximately 30 sec, and then, using a 5-ml equilibrated syringe and needle, 3 ml of the solution was transferred to the dry, equilibrated 1-cm cell, and the change in absorbance was followed as a function of time. The reference cell contained water. All solutions and equipment were allowed at least 45 min to attain temperature equilibrium.

The ionic strength (μ) was held constant in all runs using perchloric acid–lithium perchlorate mixtures. A value of $\mu = 0.90$ was chosen for constant ionic strength except in those runs where the dependence of the rate constant with a change in ionic strength was investigated.

Characterization of Products and Intermediates.—The products of the two aquation reactions were isolated on a cation-exchange column containing Dowex 50W-X8 resin (100–200 mesh) in the sodium form. They were identified using their visible spectra and molar absorptivities.

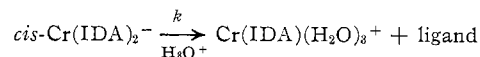
Intermediates for both aquation reactions were found using ion-exchange techniques. These species were characterized as regards to charge by studying their elution behavior on ion-exchange columns. The visible spectrum of the intermediate in the aquation of the *cis*-bis(iminodiacetato)chromate(III) ion was calculated in the following way. A 0.0050 *M cis*-Cr(IDA)₂[−] solution which was 0.50 *M* in HClO₄ and 0.40 *M* in LiClO₄ was allowed to react for 15 min at 25.0° and was then quenched at 0°. The visible spectrum of the mixture was then recorded. Since the concentrations of the reactant, intermediate, and product can be calculated at $t = 15$ min and since the molar absorptivities of the reactant and product are known, the molar absorptivities of the intermediate can easily be calculated. At $t = 15$ min the intermediate is present at its maximum concentration.

Results and Discussion

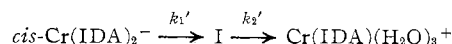
Aquation of the *cis*-Bis(iminodiacetato)chromate(III) Ion.—In aqueous solutions which are 0.1–1.0 *M* in hydrogen ion concentration the *cis*-bis(iminodiacetato)chromate(III) ion undergoes partial aquation to the iminodiacetatotriquo chromium(III) cation with the loss of one IDA ligand. The visible spectra of the aquation product and of Cr(IDA)(H₂O)₃⁺ which was prepared independently⁶ of the aquation reaction are identical for all practical purposes. The aquation product was isolated on a cation-exchange column and was shown by its elution behavior to exhibit a +1 charge. The product species appears to be quite stable at these hydrogen ion concentrations, the rate of further aquation being very slow.

The concentration of the *cis*-Cr(IDA)₂[−] ion was 0.0050 *M* in all kinetic runs except in those where the

concentration of complex was being varied. The hydrogen ion concentration was varied between 0.20 and 0.80 *M*, thus it was between 40 and 160 times as great as complex ion concentration. The reaction was assumed, therefore, to be taking place under pseudo-first-order conditions. The over-all aquation reaction is depicted as



Plots of $\log [A_t - A_\infty]$ vs. t were not linear until the later stages of the reaction, thus suggesting that a consecutive step type of mechanism would be in order. Assuming the reaction scheme to be



the following equation can be derived

$$A_t - A_\infty = a_1 e^{-k_1' t} + a_2 e^{-k_2' t}$$

where a_1 and a_2 are constants and are dependent upon the rate constants and molar absorptivities which describe the system. The linearity observed in the later stages of the plots can be explained if one rate constant is much larger than the other. The smaller rate constant can be obtained from the linear portion of the original plot. A plot of $\log \Delta(A_t - A_\infty)$ vs. t is linear for several half-lives allowing evaluation of the larger rate constant. Figure 1 is a plot of the results for a typical run.

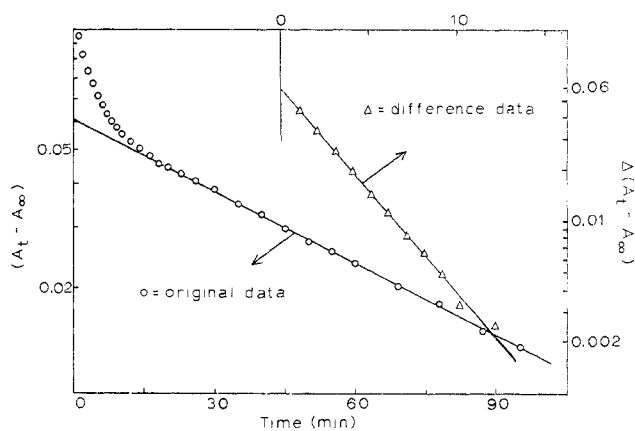


Figure 1.—Typical plot for the determination of the slow and fast rates of aquation of *cis*-bis(iminodiacetato)chromate(III).

A series of kinetic runs was performed at constant ionic strength but at various hydrogen ion concentrations in order to determine the effect of hydrogen ion on both the fast and slow observed pseudo-first-order rate constants. The series of runs was made over a temperature range of 15.5°.

The results of these runs for the fast rate constant, k_t , are depicted graphically in Figure 2. The rate constants were reproducible in most instances to 3% and in no case was the difference between duplicate determinations greater than 5%. The data indicate that the observed fast rate constant is first order in hydrogen ion and of the form $k_t = k'[\text{H}_3\text{O}^+]$.

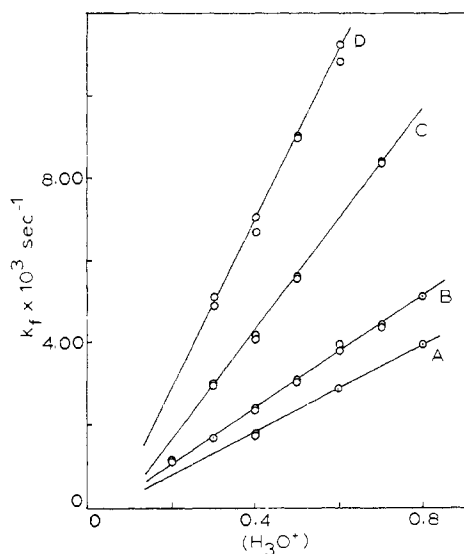


Figure 2.—Hydrogen ion dependence of the fast rate of aquation of *cis*-bis(iminodiacetato)chromate(III) at four temperatures: A, 22.5°; B, 25.0°; C, 32.0°; D, 38.0°.

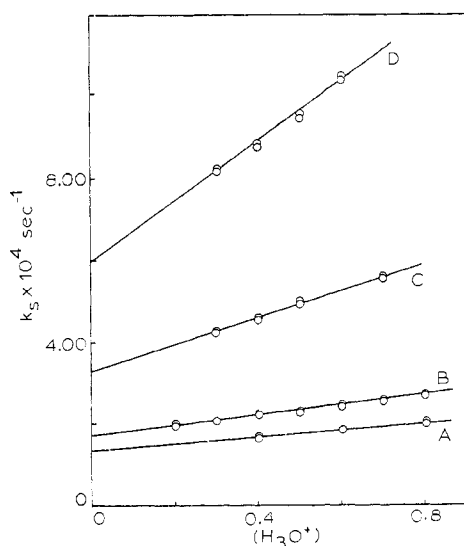


Figure 3.—Hydrogen ion dependence of the slow rate of aquation of *cis*-bis(iminodiacetato)chromate(III) at four temperatures: A, 22.5°; B, 25.0°; C, 32.0°; D, 38.0°.

The results of the runs for the slow rate constant are depicted graphically in Figure 3. In most cases, the rate constants were reproducible to within 2% except in one case where reproducibility within 8% was attained. The data indicate that the slow rate constant, k_s , is of the form $k_s = k'' + k'''[H_3O^+]$.

The values obtained for these rate constants for the four temperatures studied are given in Table I.

The data in Table I were treated using the absolute reaction rate theory of Eyring.⁷ For k' , k'' , and k''' , $\Delta H^\ddagger = 15.3 \pm 0.4$, 17.0 ± 0.6 , and 24.3 ± 0.4 kcal mol⁻¹, and $\Delta S^\ddagger = -17.0 \pm 1.5$, -18.7 ± 2.1 , and 5.1 ± 1.4 cal deg⁻¹ mol⁻¹, respectively.

(7) H. Eyring, *Chem. Rev.*, **17**, 65 (1935).

TABLE I
EFFECT OF TEMPERATURE ON THE REAL RATE CONSTANTS IN THE AQUATION OF *cis*-Cr(IDA)₂⁻

Temp, °C	Rate constants		
	10 ³ k', M ⁻¹ sec ⁻¹	10 ⁴ k'', sec ⁻¹	10 ⁴ k''', M ⁻¹ sec ⁻¹
22.5	5.48	1.34	0.875
25.0	7.08	1.71	1.28
32.0	13.1	3.36	3.20
38.0	21.3	5.98	7.38

Runs were made at complex ion concentrations of 0.0050 and 0.010 M in order to confirm first-order dependence on complex ion concentration. The fast and slow observed rate constants obtained at each concentration were identical within experimental error.

A series of runs was made at different ionic strengths, and these data are given in Table II. Although the ionic strength is far outside the area governed by the extended Debye-Hückel law, it is seen that the behavior is approximately that which would be expected for the mechanism which will be proposed.

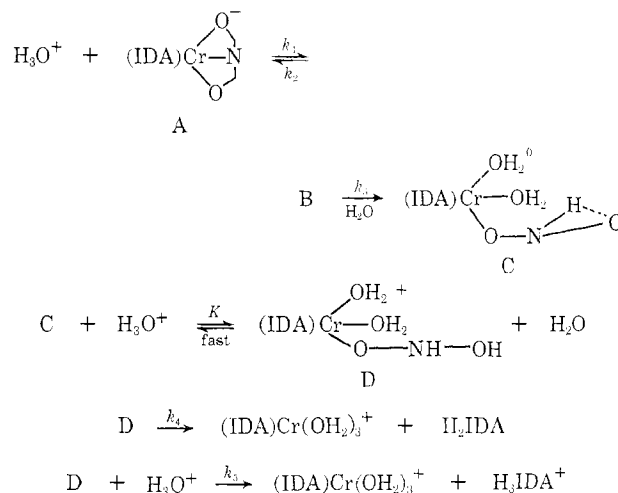
TABLE II
EFFECT OF IONIC STRENGTH ON THE OBSERVED RATE CONSTANTS IN THE AQUATION OF *cis*-Cr(IDA)₂⁻

Rate constants	Ionic strength ^a			
	0.65	0.90	1.67	2.20
10 ³ k _f , sec ⁻¹	4.17	3.91	3.38	3.25
10 ⁴ k _s , sec ⁻¹	2.38	2.46	2.76	2.70

^a [H₃O⁺] = 0.60 M; temperature 25.0°.

In order to determine the ordering of the fast and slow steps in the process, the spectrum of the intermediate, I, was calculated first assigning the fast rate to the first step and the slow rate to the second step and then repeating the calculation making the assignments in the other order. In the first set of assignments a very normal chromium(III) spectrum was attained, but in the second set of assignments a spectrum was obtained which generated negative values for molar absorptivities at some wavelengths. Based on these results the assignments are: $k_1' = k_f$ and $k_2' = k_s$.

A mechanism which is in agreement with the experimental data for the aquation of the *cis*-bis(iminodiacetato)chromate(III) ion in acidic aqueous medium is



From the mechanism and by assuming a steady state on B the following equations can be derived

$$-\frac{d[A]}{dt} = \frac{k_1 k_3}{k_2 + k_3} [H_3O^+] [A], \quad k_t = \frac{k_1 k_3}{k_2 + k_3} [H_3O^+]$$

$$-\frac{d[D]}{dt} = (k_4 + k_5 [H_3O^+]) [D], \quad k_s = k_4 + k_5 [H_3O^+]$$

According to the mechanism, the intermediates C and D have only one nitrogen coordinated to chromium(III).⁸ This would indicate that the peak positions for the visible spectrum of the intermediate should be almost identical with the peak positions for the product. This is expected because of the different crystal field splitting capabilities exhibited by the amino nitrogen and aquo coordinating groups in the spectrochemical series. One might expect that the molar absorptivities for the intermediate would be greater than those for the product, but the peak positions should be very similar.

Table III compares the visible spectra of the *cis*-Cr(IDA)₂⁻ ion, the intermediate, and the Cr(IDA)(H₂O)₃⁺ ion. It is easily seen that the peak positions of the intermediate and the product are essentially identical, thus supporting the proposal that only one nitrogen is coordinated to chromium(III).

TABLE III
VISIBLE ABSORPTION SPECTRA OF THE VARIOUS
CHROMIUM (III) COMPLEXES

<i>cis</i> -Cr(IDA) ₂ ⁻ ^a	391 ^b (79), ^c 442 (26, min), 519 (76)
Intermediate	394 (64), 461 (15, min), 543 (76)
Cr(IDA)(H ₂ O) ₃ ⁺ ^a	393 (50), 460 (13, min), 544 (60)

^a Reference 6. ^b Wavelength (mμ). ^c Molar absorptivity (M⁻¹ cm⁻¹).

The proposed mechanism also dictates the charge of the intermediate. In acidic solution the intermediate should have a +1 charge, whereas in very slightly acidic solutions (pH 4–5) the intermediate should exhibit a zero charge. Allowing the aquation to continue until maximum concentration of the intermediate is attained, then quenching at 0°, diluting the mixture appropriately, and then charging a cation column at 2° containing Dowex 50W-X8 (100–200 mesh) resin in the sodium form, it was observed that approximately 90–95% of the colored material was held by the column. The colored material which ran through the column was unreacted *cis*-Cr(IDA)₂⁻ ion. In acidic solution, the intermediate has been shown to have a positive charge. Elution behavior with 0.1 M NaClO₄ indicated that the intermediate was exhibiting a charge of +1. It was found, after washing the column with water, rapidly removing the resin containing the intermediate, removing the intermediate from the resin using 1 M NaClO₄ solution, and reacidifying the solution, that the intermediate had the approximate visible spectrum which had been calculated for it, and its decomposition into products was

qualitatively observed using a Beckman DB spectrophotometer. Running the same experiment only bringing the solution to a pH of 4–5 with sodium hydroxide solution before charging the cation column showed only a small amount of retention of the purple species by the cation column, thus supporting the existence of a zero-charged intermediate at pH 4–5. Elution of the column at 2° containing the protonated intermediate with 0.1 M NaClO₄ solution produced two bands on the column, one being the intermediate band (top) and the other being the product band. It was noticed during the elution with the neutral eluent that the intermediate band bled considerably until an actual band no longer existed, again supporting the existence of a +1-charged-zero-charged intermediate equilibrium. Columns charged with solutions which were allowed to aquate freely for 12–15 half-lives before introduction onto a cation-exchange column showed only one +1-charged band on elution, the band being the product species.

Since all of the studies involving aquation of oxalate complexes of chromium(III) in acidic media^{1,2} postulate a monodentate oxalate intermediate, one might propose that B has one iminodiacetate ion acting as a tridentate ligand and the other acting as a bidentate ligand with a carboxyl group not coordinated. It is also possible that B has one iminodiacetate ion functioning as a bidentate ligand bonded through the two carboxyl groups with the nitrogen uncoordinated. This would not imply direct proton attack upon a nitrogen since the mechanism could involve proton attack at a carboxyl group followed by a rearrangement involving loss of the nitrogen group.

Aquation of the *trans*(*fac*)-Bis(methyliminodiacetato)chromate(III) Ion.—In a fashion similar to that of the *cis*-bis(iminodiacetato)chromate(III) system, the *trans*(*fac*)-bis(methyliminodiacetato)chromate(III) ion undergoes partial aquation to the methyliminodiacetatotriaquochromium(III) cation in aqueous solutions which are 0.1–1.0 M in hydrogen ion concentration. The visible spectrum of the aquation product is identical with the spectrum obtained from a sample of methyliminodiacetatotriaquochromium(III) cation prepared and characterized independently of the aquation reaction. The aquation product was isolated on a cation-exchange column, and its elution behavior showed it to possess a +1 charge.

For all runs the concentration of the *trans*(*fac*)-Cr(MIDA)₂⁻ ion was 0.0050 M except when the dependence of the rate constant on complex concentration was being determined. The hydrogen ion concentration was varied between 0.20 and 0.80 M using perchloric acid, giving pseudo-first-order conditions. The reaction was studied over a 14° temperature range.

Plots of log [A_t - A_∞] vs. t were linear implying that only a single kinetic step was being observed. Some reactions were followed for a period of 4 half-lives with no deviation from linearity being noted. All reactions were followed for at least 2 half-lives.

The effect of hydrogen ion concentration on the

(8) D is probably the only appreciable species present because of the large hydrogen ion concentration and the probable lower limit of 10 on K.

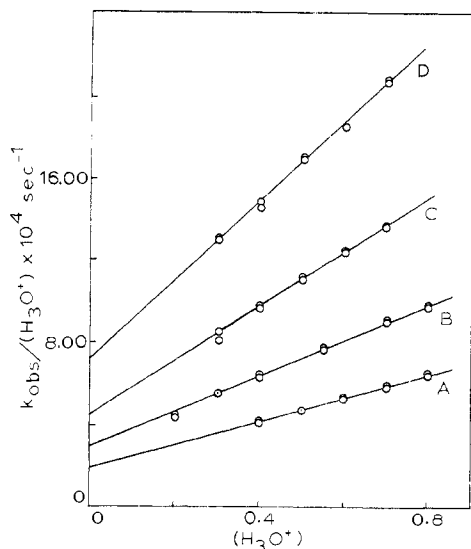


Figure 4.—Plot of $k_{\text{obsd}}/[\text{H}_3\text{O}^+]$ vs. $[\text{H}_3\text{O}^+]$ for the aquation of *trans(fac)*-bis(methyliminodiacetato)chromate(III) at four temperatures: A, 25.0°; B, 30.0°; C, 34.0°; D, 39.0°.

observed rate constant was determined. Plots of k_{obsd} vs. $[\text{H}_3\text{O}^+]$ were curved; however, if k_{obsd} is of the form $k_{\text{obsd}} = k'[\text{H}_3\text{O}^+] + k''[\text{H}_3\text{O}^+]^2$, a plot of $k_{\text{obsd}}/[\text{H}_3\text{O}^+]$ vs. $[\text{H}_3\text{O}^+]$ should be linear and allow evaluation of k' and k'' . Figure 4 shows such linear plots. Values of k_{obsd} were reproducible in most instances to within 2% in duplicate runs, the greatest deviation being 5%. The values of k' and k'' obtained at four different temperatures are given in Table IV.

TABLE IV
EFFECT OF TEMPERATURE ON THE REAL RATE CONSTANTS IN THE
AQUATION OF *trans(fac)*-Cr(MIDA)₂⁻

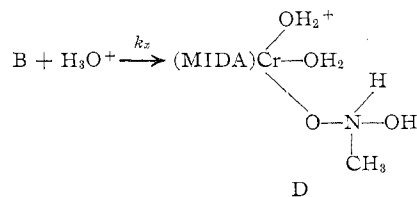
Temp, °C	Rate constants	
	$10^4 k', M^{-1} \text{sec}^{-1}$	$10^4 k'', M^{-2} \text{sec}^{-1}$
25.0	1.88	5.74
30.0	2.98	8.54
34.0	4.49	13.2
39.0	7.19	19.3

Activation parameter plots were made to determine ΔH^\ddagger and ΔS^\ddagger for k' and k'' . For k' , $\Delta H^\ddagger = 17.0 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -18.6 \pm 1.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$. For k'' , $\Delta H^\ddagger = 15.6 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -21.2 \pm 0.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$.

The rate constants obtained from runs made at 0.0050 and 0.010 *M* complex concentrations were identical within experimental error indicating first-order dependence on complex ion concentration. The acid concentration was 0.55 *M* in each case, and the runs were made at 30.0°.

A search for intermediates in the aquation was initiated in order to determine which of three possible steps was being observed. The reaction was allowed to proceed for a time and was then quenched and charged onto a cation-exchange column which was cooled to 2°. After washing, elution of the purple positively charged species with 0.1 *M* NaClO₄ showed that two bands were present and that each was exhibiting a +1 charge. In a manner similar to the previous system, one of the bands bled profusely upon elution, until it had disappeared. The remaining lower band was identified as the product species. This evidence supports the existence of an intermediate similar to the one found in the *cis*-Cr(IDA)₂⁻ system. Performing the same experiment, except removing the resin from the column after washing, and observing the spectrum of the intermediate and product mixture as previously described showed that the intermediate had peak absorption positions approximately the same as the product species. Also in qualitatively watching the decay of the intermediate, it was observed that the intermediate had molar absorptivities which were slightly larger than those of the product species. The step from intermediate to product was probably not observed because the reaction was followed at a wavelength which was essentially an isosbestic point for the intermediate and product.

A mechanism which is in agreement with the experimental data can be proposed which is similar to that previously proposed for the *cis*-Cr(IDA)₂⁻ ion and involves the additional reaction



This total mechanism, if treated assuming a steady state in B and neglecting the reaction involving k_3 , gives a rate equation which reduces to

$$-\frac{d[\text{A}]}{dt} = (k'[\text{H}_3\text{O}^+] + k''[\text{H}_3\text{O}^+]^2)[\text{Cr}(\text{MIDA})_2^-]$$

In comparing the k' values for the *cis*-Cr(IDA)₂⁻ ion and the *trans(fac)*-Cr(MIDA)₂⁻ ion it is noted that the *cis* complex appears to be more labile than the *trans* complex. This is also evident in comparing the ΔH^\ddagger values for k' in the two systems.

Acknowledgment.—J. A. W. wishes to thank the National Science Foundation and the Dow Chemical Co. for summer research fellowships which assisted in this investigation.