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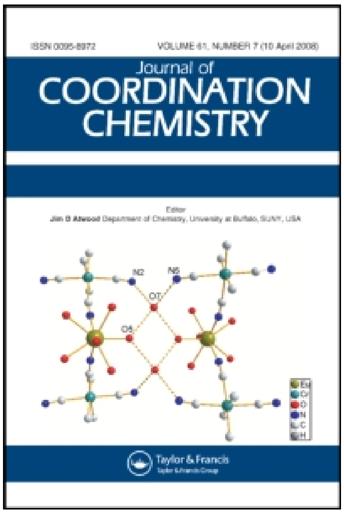

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THE CATALYSIS OF THE *trans-cis* ISOMERIZATION OF DIAQUOBIS(OXALATO)-CHROMATE(III) BY $Mg(NO_3)_2$ AND $MgSO_4$

DANIEL HUCHITAL and XIUCEN YANG[1]†

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The *trans-cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ was investigated using $Mg(NO_3)_2$ and $MgSO_4$ as catalysts at higher concentrations than reported in the literature. Linear behavior is observed between added catalyst concentration and rate until ca. 0.30M, after which the rate becomes much faster. The rate behavior over the entire range of added catalyst $MgSO_4$ is explained in terms of ion association. Both the free Mg^{2+} and the complex $MgSO_4$ catalyze the reaction. The catalytic rate constants obtained are $k_{Mg^{2+}} = 3.60 \times 10^{-3}$ M^{-1} s^{-1} and $k_{MgSO_4} = 8.00 \times 10^{-4}$ M^{-1} s^{-1}.

INTRODUCTION

Many transition metal and non-transition metal cations have been observed to catalyze the isomerization of the title complex, $Cr(C_2O_4)_2H_2O)_2^-$. Ashley and Hamm[2] reported that twelve different metal ions and hydrogen ion catalyzed the isomerization. Included in this study were the alkaline earth ions Mg^{2+} – Ba^{2+}, several first-row transition metal +2 ions and the tripositive species Al^{3+}, La^{3+}, and Ce^{3+}. Kelm, Stieger and Harris[3-4] extended this work to include the effect of the alkali metal ions, ammonium and alkylammonium ions, and multivalent ions.

The mechanism of the reaction has been proposed to involve attack of the catalyst on the chelated oxalate to form a five-coordinated intermediate with only one end of one oxalate bound to the chromium center. This "one-ended dissociation" mechanism could explain the experimental observations quite will. A log-log plot of k_2 vs β_1 for nine +2 metals supported the proposed mechanism. Only one cation studied by Ashley and Hamm, Mg^{2+}, did not fit the linear correlation above. In an effort to determine the reason for the divergent behavior of Mg^{2+}, we undertook a study of the catalysis by two magnesium salts, $Mg(NO_3)_2$ and $MgSO_4$. The results of this study are reported here.

EXPERIMENTAL SECTION

Material and Solutions

Sodium trans-diaquobis(oxalato)-chromate(III) was prepared by the method of Werner.[5] The purity was determined using methods reported in the literature.[6-8] Solutions of this compound used for kinetic runs were prepared directly by weighing the solid followed by addition of deionized distilled water and other reagents.

Solutions of sodium nitrate and sodium sulfate were prepared from Fisher A.C.S. reagent grade chemicals by weight after heating at 102°C for one hour. Solutions of magnesium nitrate hexahydrate and magnesium sulfate were prepared directly from the Fisher A.C.S. reagent grade chemicals by weight and analyzed by titration with the EDTA according to the procedure in Vogel.[9]

Kinetic Measurements

All kinetic measurements were obtained by using a Cary 15 spectrophotometer, the cell compartment of which was thermostatted at 25.0 ± 0.1°C. The reaction solutions were prepared as follows: a weighed amount of solid *trans* was placed in a flask followed by addition of water, sodium salt and magnesium salt solutions. All solutions for kinetic runs were prepared to be at pH = 3.0 using HNO_3 or H_2SO_4 and I = 1.50 M, and kept in a thermostatted Haake Model FK-2 temperature bath to reach

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reaction temperature. The reactions were followed at 416 nm, the wavelength maximum of the *cis* complex. First-order rate constants were obtained from slopes of plots of $\log(A_\infty - A_t)$ vs. time where A_t and A_∞ are the absorbancies at time t and after the reaction is complete.

RESULTS AND DISCUSSION

As shown by Kelm *et al.* and further reported by Kallen,[10] the rate law for the *trans-cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ is rate = $k_{obs}[trans]$, where k_{obs}, the observed first-order rate constant, is given by Eq. (1).

$$k_{obs} = k_{H_2O} + k_{M^+}[M^+] + k_{H^+}[H^+] \qquad (1)$$

This rate law refers to the reaction in the absence of metal ion catalysts, the rate constant terms in Eq (1) referring to the processes given by Eqs. (2)-(4).

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- \xrightarrow{k_{H_2O}} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- \qquad (2)$$

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- + M^+ \xrightarrow{k_{M^+}} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + M^+ \qquad (3)$$

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H^+ \xrightarrow{k_{H^+}} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H^+ \qquad (4)$$

In the presence of metal ion catalysts, a fourth term, $Kk_{Me^{n+}}[Me^{n+}]$, was assumed to be present. The observed rate constant was written as

$$k_{obs} = k_1 + k_2[Me^{n+}] \qquad (5)$$

where k_1 was the sum of the terms on the right side of Eq. (1). The overall reaction was fitted to the mechanism proposed by Kelm et al.,[3] viz.,

$$T \xrightarrow{k_1} C \qquad (6)$$

$$T + Me^{n+} \overset{K}{\rightleftharpoons} TIP \xrightarrow{k_{Me^{n+}}} C + Me^{n+} \qquad (7)$$

According to Eq. (5), a linear relation should be observed between k_{obs} and $[Me^{n+}]$ provided that the k_1 term did not vary significantly on changing the concentration of the metal catalyst. However, as done here, this could be checked by obtaining the k_1 term for each kinetic run by running the reaction at various concentrations of external salt (in the absence of Me^{n+} and at pH 3). The k_1 values obtained directly from a plot of k_{obs} versus external salt concentration, could then be subtracted from the observed rate constant in the presence of Me^{n+}, and the resultant values when plotted against $[Me^{n+}]$ would yield k_2 directly.

TABLE I

Rate data for the $Mg(NO_3)_2$ catalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$[a]

Mg^{II}(added), M	$10^4 k_{obs}$	$[NaNO_3]$, M	$10^4 k_1$	$10^4 k_c$[b]
0	6.06	1.50	6.09	0
0.04	6.44	1.38	6.12	0.32
0.08	6.64	1.26	6.07	0.57
0.12	7.05	1.14	6.02	1.03
0.16	7.30	1.02	5.96	1.34
0.20	7.74	0.90	5.89	1.85
0.24	8.12	0.78	5.82	2.30
0.28	8.46	0.66	5.73	2.73
0.32	8.67	0.54	5.62	3.05
0.36	9.18	0.42	5.47	3.71
0.40	9.76	0.30	5.30	4.46

[a] T = 25.0°C, I = 1.50 M, units of rate constants are sec^{-1}.
[b] $k_c = k_{obs} - k_1$

Tables I and II report data for the $Mg(NO_3)_2$ and $MgSO_4$ catalysis reactions. Each data set was performed at a constant ionic strength of 1.50 M. Each value of k_{obs} is the average of two kinetic runs, the reproducibility of which was usually within 3%. For each data set, a plot of k_c (= $k_{obs} - k_1$) versus added magnesium(II) was made. These are shown in Figure 1.

Examination of the plots in Figure 1 reveals some interesting features. Both plots of k_c vs. added

TABLE II

Rate data for the $MgSO_4$ catalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$[a]

Mg^{II}(added), M	$10^4 k_{obs}$	$[Na_2SO_4]$, M	$10^4 k_1$	$10^4 k_c$[b]
0	6.94	0.500	6.92	0
0.02	6.91	0.473	6.81	0.10
0.04	6.94	0.447	6.70	0.24
0.08	7.11	0.393	6.46	0.65
0.12	7.20	0.340	6.22	0.98
0.16	7.38	0.287	6.00	1.38
0.20	7.52	0.233	5.76	1.76
0.24	7.56	0.180	5.53	2.03
0.28	7.87	0.127	5.28	2.59
0.32	8.19	0.073	4.99	3.20
0.36	8.54	0.020	4.65	3.89
0.375	8.67	0	4.46	4.21

[a] T = 25.0°C, I = 1.50 M, units of rate constants are sec^{-1}.
[b] $k_c = k_{obs} - k_1$

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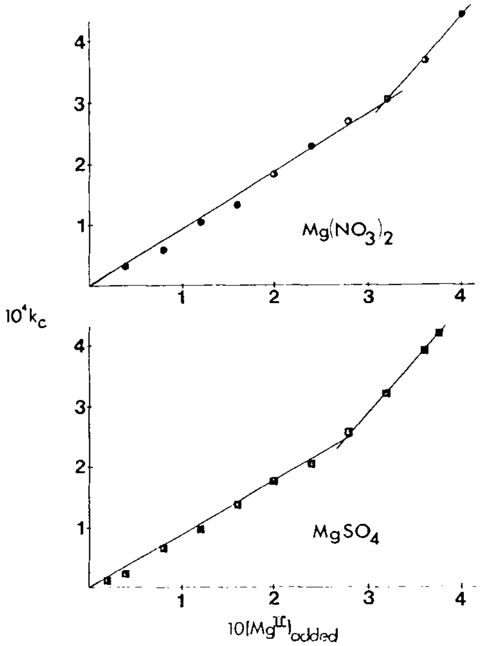

FIGURE 1 Plot of k_c (= $k_{obs} - k_1$) versus added magnesium(II) for the salts $Mg(NO_3)_2$ and $MgSO_4$.

magnesium are linear up to a concentration of ca. 0.30 M, after which the rate becomes much faster. The slopes of the linear portion at the lower magnesium concentrations are 1.02×10^{-3} and 9.4×10^{-3} $M^{-1}s^{-1}$. These values, obtained at an ionic strength of 1.50 M, compare well with a value of 1.16×10^{-3} $M^{-1}s^{-1}$ obtained by Ashley and Hamm[2] at a lower ionic strength. Because of ionic strength limitations, Ashley and Hamm's study of the magnesium catalysis did not extend beyond 0.30 M (added magnesium salt). Thus, they did not observe the increase in rate reported here.

We feel it is possible to rationalize the rate behavior over the entire range of added magnesium salts in terms of effect of ion association (complexation) between Mg^{2+} and the anion of the supporting electrolyte. Data on ion association is available for Mg^{2+} with sulfate ion.[12-13] These authors report that the log K_{IA} value for the association (Eq. 8) is 2.22[12] and 2.23 ± 0.07.[13] For the purposes of calculations, we chose a log K_{IA} = 2.22 or K_{IA} = 165 as reported by Atkinson and Petrucci.[12]

$$Mg^{2+}(aq) + SO_4^{2-}(aq) \xrightleftharpoons{K_{IA}} MgSO_4(aq) \qquad (8)$$

It is postulated that the observed first-order rate constant is composed of several terms when the reaction is run in the presence of added magnesium sulfate. This is given by Eq. (9). The first three terms in Eq. (9) refer to

$$k_{obs} = k_{H_2O} + k_{Na^+}[Na^+] + k_{H^+}[H^+] + k_{Mg^{2+}}[Mg^{2+}] + k_{MgSO_4}[MgSO_4] \qquad (9)$$

processes outlined above (Eqs. 2-4). The last two terms refer to the catalysis by free Mg^{2+} and complexed $MgSO_4$. The rate constants $k_{Mg^{2+}}$ and k_{MgSO_4} can be calculated. Eq. (9) can be written as

$$k_c = k_{Mg^{2+}}[Mg^{2+}] + k_{MgSO_4}k_{IA}[Mg^{2+}][SO_4^{2-}] \qquad (10)$$

Rearranging and dividing by $[Mg^{2+}]$ yields

$$\frac{k_c}{[Mg^{2+}]} = k_{Mg^{2+}} + k_{MgSO_4}K_{IA}[SO_4^{2-}] \qquad (11)$$

Thus, a plot of $k_c/[Mg^{2+}]$ versus $[SO_4^{2-}]$ should be linear with an intercept of $k_{Mg^{2+}}$ and a slope of $k_{MgSO_4}K_{IA}$. Such a plot was constructed using K_{IA} = 165 and calculating the concentrations of free Mg^{2+} and free SO_4^{2-} for each run in Table II. The plot, shown in Figure 2, is indeed linear except for the highest $[SO_4^{2-}]$ values. For each of these both the k_c and $[Mg^{2+}]$ values are quite small and subject to large errors. Thus, they are not taken into account in the analysis of the data. The intercept of the line in Figure 2 is 3.60×10^{-3} M^{-1} s^{-1}, representing the catalytic rate constant for magnesium ion. This value is more than three times larger than that obtained using Ashley and Hamm's technique,[2] and may well explain the poor fit of magnesium ion to their data. However, for a complete picture, the other alkaline earths should be reinvestigated.

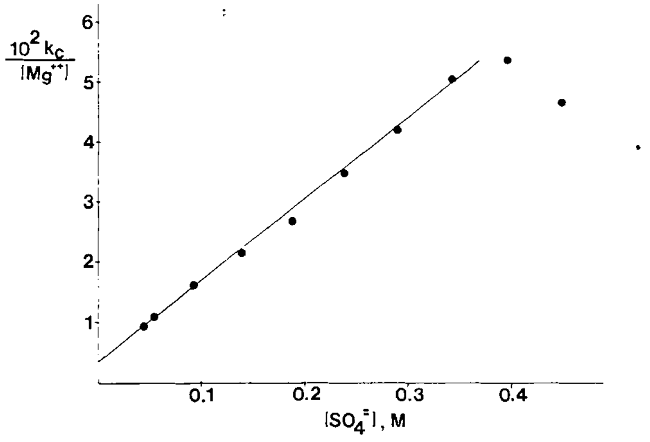

FIGURE 2 Plot of the left hand side of Eq. (11) versus $[SO_4^{-2}]$.

The slope of the line in Figure 2 represents the catalytic rate constant for the $MgSO_4$ complex. Using K_{IA} = 165, we can calculate a value of 8.00×10^{-4} M^{-1} s^{-1} as the catalytic rate constant for the $MgSO_4$ complex. In comparison with $k_{Mg^{2+}}$, this is a reasonable value considering both the charge difference and the nature of the catalysis as proposed in literature.[2]

REFERENCES

1. Visiting Chinese Scholar on leave from the Department of Medical Chemistry, Sichuan Medical College, Chengdu, Sichuan, PRC.
2. K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, 4, 1120 (1965).
3. H. Kelm, H. Stieger and G. M. Harris, *Ber. Bunsenges. Phys. Chem.*, 73, 939 (1969).
4. H. Kelm, H. Stieger and G. M. Harris, *F. Phys. Chem. (Franfurt am Main)*, 67, 98 (1969).
5. A. Werner, *Ann. Chem.*, 406, 216 (1914).
6. D. H. Huchital, *Inorg. Chem.*, 9, 486 (1970).
7. K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, 64, 346 (1968).
8. G. W. Haupt, *J. Res. Natl. Bur. Std.*, 48, 414 (1952).
9. A. I. Vogel, *A Textbook of Quantative Inorganic Analysis 3rd ed.*, Wiley, New York, N.Y. 1961, pp. 433–434.
10. T. W. Kallen, *Inorg. Chem.*, 15, 440 (1976).
11. The values of k_1 were obtained from curves of k_{obs} vs. [salt] for each of the two sodium salts used. The results were similar to those observed by Kelm *et al.* (Ref. 4).
12. G. Atkinson and S. Petrucci, *J. Phys. Chem.*, 70, 3122 (1966).
13. R. M. Izatt, D. Eatough, J. J. Christensen and C. H. Bartholomew, *J. Chem. Soc. (A)*, 47, (1969), and references therein.

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