Cation Catalysis of *trans–cis* Isomerization of Bis(oxalato)diaquochromate(III)

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The catalysis of the *trans–cis* isomerization of bis(oxalato)diaquochromate(III) by twelve different metal ions and by hydrogen ion has been studied. The catalytic reaction was found to be first order in cation concentration in all cases. The most effective catalytic agents for this reaction were the cerium(III) and lanthanum(III) ions. The catalytic effect of the divalent ions was in the order Cu > Ni > Zn > Co > Cd > Ca > Sr > Ba > Mg. Except for Mg these are in the same order as the formation constants of the monooxalato complexes of the metal ions. Activation parameters for the catalytic reactions have been determined. A "one-ended dissociation" mechanism is proposed for the catalytic reaction. This mechanism is in agreement with the measurements of this investigation and the chemistry of the oxalato complexes of chromium as reported by previous workers.

The kinetic investigation of the *trans–cis* isomerization of bis(oxalato)diaquochromate(III) was first done independently by Cunningham[1] and Hamm.[2] Later Schläfer, Gausmann, and Tausch[3] reported a 1.5-order hydrogen ion dependence for the hydrogen ion catalyzed *trans–cis* isomerization of this compound.

In view of the first-order hydrogen ion dependence of the reported kinetics of racemization of *cis*-bis(oxalato)diaquochromate(III) when hydrogen ion catalyzed,[4] there is some doubt whether the 1.5 order is correct for the *trans–cis* isomerization.

Schläfer and co-workers[3] have reported that the rate of the *trans–cis* isomerization was independent of added magnesium ion, whereas Besse and Johnson[5] have reported that the racemization of tris(oxalato)chromate(III) was dependent upon a large number of different cations, including magnesium.

A preliminary investigation in this laboratory of the effect of magnesium ion concentration on the rate of isomerization of the *trans*-bis(oxalato)diaquochromate(III) ion indicated that the increase in rate was first order in magnesium concentration. Because of the discrepancies of the findings on this system it was decided to investigate the catalytic effect of several different metal ions and to reinvestigate the effect of magnesium ion and hydrogen ion on the *trans–cis* isomerization of bis(oxalato)diaquochromate(III).

Experimental

trans-Potassium bis(oxalato)diaquochromate(III) was prepared by the method described by Werner,[6] air-dried, and analyzed as previously described.[2]

The stock solutions containing the investigated cations were prepared from the nitrate or perchlorate salts of the cations. These stock solutions were analyzed by complexometric titrations employing the disodium salt of ethylenediaminetetraacetic acid as the titrating agent.[7] Sodium perchlorate was prepared

by neutralizing reagent grade sodium carbonate with reagent grade perchloric acid and boiling the solution to expel all carbon dioxide. The solution was analyzed by evaporating to dryness a known volume of the solution and weighing the residue.

Solutions containing the investigated cations were prepared by adding the proper amount of cation stock solution, the proper amount of sodium perchlorate stock solution to bring the ionic strength to 1.0, enough perchloric acid to adjust the pH to about 3.0, and then diluting to volume with de-ionized water. A 100-ml. volume of the prepared solution was placed in each of the reaction flasks which were immersed in a constant temperature bath which was maintained within ±0.01° of the desired temperature. After the solution had come to the temperature of the bath, weighed samples of the pure finely ground *trans* complex were introduced into the flasks, agitation by means of a Teflon-coated stirring bar was performed until the solid was in solution, and the flasks were reinserted in the constant-temperature bath.

The pH of about 3 was chosen because at this point the hydrogen ion has no catalytic effect and at the same time the hydrolysis of the catalytic cations could be minimized.

The absorbance of these solutions was taken at the wave length 415 mμ by using the method of Guggenheim[8] as modified by King.[9] The concentration of the complex was about 0.016 M in all runs. The reference solution was allowed to react for several half-lives and then an identical sample of the *trans* complex was added to the reaction solution. A series of readings of the absorbance of the sample relative to the identical reference solution was taken with a Beckman Model DU spectrophotometer, fitted with a constant-temperature cell block, as a function of time. The log A_s was plotted against time and k_{obsd} was taken as 2.303 times the slope. In all cases these lines were straight with very little scatter.

The k_{obsd} values were determined for each cation at four different concentrations of the cation and also with no cation present. In some cases duplicate runs were performed and in these cases the usual finding was that the values would check within ±5% but in the worst cases the checks were within ±10%.

In the investigation of the catalytic effect of hydrogen ion, the solutions were prepared as above, using perchloric acid. The final concentration of hydrogen ion was determined by titration with standard sodium hydroxide.

Observation of the complete absorption spectra over the visible wave lengths gave indication that the product was the expected *cis* compound. In the case of calcium ion even at the highest concentration used there was no indication of a calcium oxalate precipitate at the end of the reaction. It was concluded from these observations that in the period of the rate measurements

(1) G. E. Cunningham, *Nature*, **169**, 1103 (1952).
(2) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 609 (1953).
(3) H. L. Schläfer, H. Gausmann, and W. Tausch, *Z. physik. Chem.*, **34**, 113 (1962).
(4) G. L. Welch and R. E. Hamm, *Inorg. Chem.*, **2**, 295 (1963).
(5) N. W. D. Besse and C. H. Johnson, *Trans. Faraday Soc.*, **31**, 1632 (1935).
(6) A. Werner, *Ann.*, **406**, 216 (1914).
(7) G. Schwarzenbach, "Complexometric Titrations," Methuen and Co. Ltd., London, 1957.

(8) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).
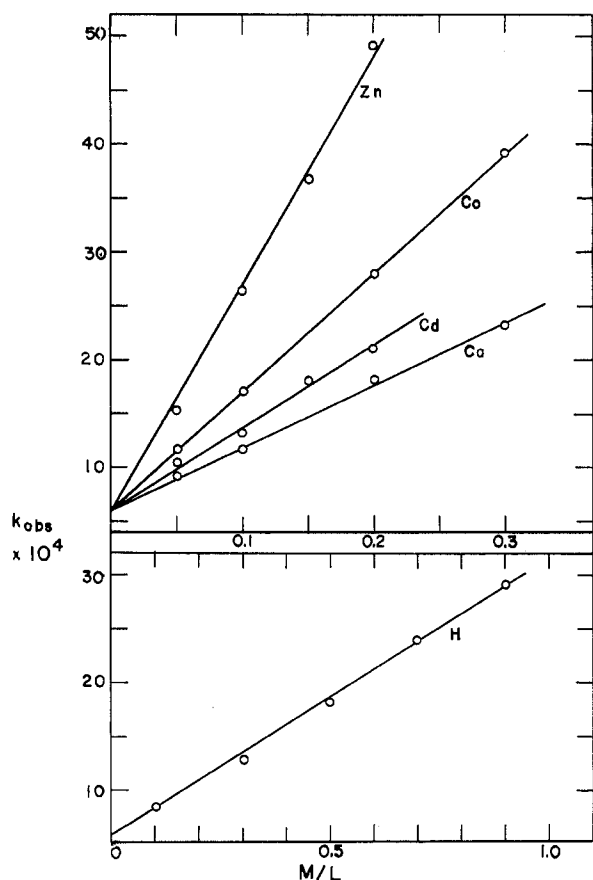(9) E. L. King, *J. Am. Chem. Soc.*, **74**, 563 (1952).

Figure 1.—Observed rate constants for the *trans–cis* isomerization of bis(oxalato)diaquochromate(III) as a function of cation concentration at total ionic strength 1.0.

TABLE I
trans–cis ISOMERIZATION OF BIS(OXALATO)DIAQUOCHROMATE(III) IN NITRATE AND PERCHLORATE MEDIUM AT IONIC STRENGTH 1.00

	$k_1 \times 10^4$ sec. $^{-1}$				ΔH^*, kcal.	ΔS^*, e.u.
	25°	35°	40°	45°		
NaNO$_3$	5.90^a		26.17^a			
NaClO$_4$	5.86^a	16.60^b	26.20^a	40.24^b	17.9 ± 1.2^c	−13 ± 4^c

^{a} The average of three runs. ^{b} The average of five runs. ^{c} Standard deviation.

the only important reaction occurring was the *trans–cis* isomerization.

Results and Discussion

A sampling of some of the results at 25° for various metal ions is shown plotted in Figure 1 and indicates that the increase in rate is first order in metal ion concentration. Similar results were obtained at temperatures of 25, 35, 40, and 45° for all twelve different metal ions. All of these data can be fitted by the equation

$$k_{obsd} = k_1 + k_2[M]$$

where k_1 is the specific rate constant in 1.0 M NaClO$_4$, k_2 is the second-order rate constant for the catalyzed rate process, and [M] is the concentration of the catalytically active ion. The same equation fits the data for hydrogen ion catalysis. This being true the complete rate expression is

$$\frac{d[trans]}{dt} = -(k_1 + k_2[M])[trans]$$

Since both nitrate and perchlorate salts were used, runs were made to establish that the rate of isomerization was independent of the two anions. Table I lists the values determined for these anions.

In Table II the data obtained for twelve different metal ions and hydrogen ion are shown. The activation parameters calculated for the particular cases in-

volved measurements at two additional temperatures in some cases.

The activation parameters for all of the ions except aluminum show no truly significant differences. The actual rates and activation parameters for aluminum were different than might be expected for a trivalent ion. The explanation may well be that at the pH that these experiments were run the aluminum ion is extensively hydrolyzed so that the actual effective catalytic species is not the aluminum ion, whereas for most of the other metal ions even though hydrolysis may interfere to some extent it is no where nearly so extensive.

The appearance of the lower half of Figure 1 shows that the reaction is first order with respect to hydrogen ion. Any attempt to plot k_{obsd} as a function of hydrogen ion concentration to the 1.5 power results in a definitely curved plot. It is believed by the present authors that Schläfer and co-workers obtained that result because they calculated the hydrogen ion concentrations from measurements with a glass electrode pH meter. Their hydrogen ion concentrations were probably subject to greater and greater positive error in pH as the pH decreased in the region between 0 and 1.

In Figure 2 the negative logarithm of k_2 is plotted against the logarithm of the formation constant (log β_1) of the metal ion oxalate for the reaction

$$M^{2+} + C_2O_4{}^{2-} = MC_2O_4$$
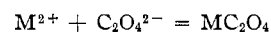
where the values were taken from Yatsimirskii and Vasil'ev[10] for the divalent metal ions studied. The values of β_1 are given at 18° with the exception of that for cadmium which is at 25°, but since only the general correlation is desired the plot is thought to be worthwhile. It is apparent that there is a good correlation between the first formation constant and the catalytic rate constant for these metal ions. Also plotted in this figure are the −log k_2 values found by Besse and Johnson[5] for the racemization of tris(oxalato)chromate(III) against log β_1. The same order is noted in the position of the particular metal ions. On each of these plots it is seen that Mg^{2+} is the one ion that is considerably divergent from the correlation, and one is forced to conclude that either the nature of the reaction for magnesium is quite different or there is a serious error either in k_2 or in β_1.

One may be able to attribute some part of the change in rate constant to change in activities as various cations are substituted for sodium ion while keeping the total ionic strength constant; however, it is extremely un-

(10) K. B. Yatsimirskii and V. P. Vasil'ev, "Instability Constants of Complex Compounds," Pergamon Press, New York, N. Y., 1960, pp. 161, 162.

Table II

Catalyzed *trans–cis* Isomerization of Bis(oxalato)diaquochromate(III) in $NaClO_4$ Medium at Total Ionic Strength 1.00

Cation	Highest concn., M	$k_2 \times 10^3$ M^{-1} sec.$^{-2}$				ΔH^*, kcal.	ΔS^*, e.u.
		$25°$	$35°$	$40°$	$45°$		
H^+	0.90	2.47					
Mg^{2+}	0.30	1.16	3.65	4.60	7.70	17.0 ± 1.0^a	-15 ± 3^a
Ba^{2+}	0.25	2.84	5.04	12.1	17.0	16.9 ± 2.0	-16 ± 7
Sr^{2+}	0.30	3.98	8.26	14.6	18.7	14.4 ± 1.2	-21 ± 4
Ca^{2+}	0.30	5.67	11.7	22.5	30.6	15.2 ± 1.2	-18 ± 4
Cd^{2+}	0.20	7.76	19.6	31.2	42.4	16.4 ± 0.7	-13 ± 2
Co^{2+}	0.30	11.1	25.9	42.2	62.0	15.7 ± 1.4	-15 ± 4
Zn^{2+}	0.20	21.0	48.8	93.0	115	16.0 ± 1.0	-12 ± 3
Ni^{2+}	0.20	20.5	59.3	108	124	16.1 ± 2.0	-12 ± 7
Cu^{2+}	0.07	47.4	113	166	338	16.9 ± 1.3	-10 ± 3
Al^{3+}	0.16	3.19	8.38	18.7	36.4	22.6 ± 1.8	$+6 \pm 6$
La^{3+}	0.12	106	269	486	582	15.9 ± 1.2	-9 ± 4
Ce^{3+}	0.007	161	333	551	697	13.9 ± 0.8	-15 ± 3

a Standard deviation.
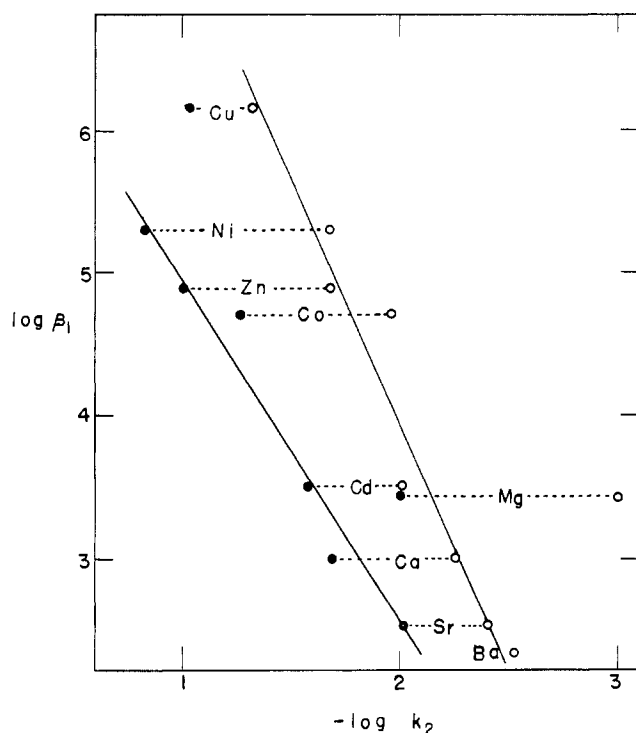
Figure 2.—Negative logarithm of k_2 against formation constant for metal ion oxalate complexes: O, *trans–cis* isomerization of bis(oxalato)diaquochromate; ●, racemization of tris(oxalato)-chromate (data of Besse and Johnson).

chromate(III) no measurable exchange with oxygen in the solvent water occurs. The same workers report that in the presence of free acid all twelve oxygens of the oxalate exchange with oxygen of the solvent at a rate proportional to the acid concentration, but at a rate faster than the exchange of chelated oxalate with unbound oxalate. These facts were explained by a "one-ended dissociation" mechanism for oxygen-18 exchange. It was also reported[12] that at pH 1.0 there is no direct oxalate exchange between free oxalate and bis(oxalato)diaquochromate(III) ion. From this last observation one must conclude that aquation of bis-(oxalato)diaquochromate(III) does not occur.

A "one-ended dissociation" mechanism is consistent with the experimental observations made. In this mechanism a direct attack of the cation on the chelated oxalate forms a five-coordinated intermediate with only one end of the oxalate bound to the chromium. Subsequently the released end of the oxalate becomes rebound to the chromium with simultaneous release of the cation. This mechanism is essentially identical with the one previously proposed[2] for the hydrogen ion catalysis of the racemization of *cis*-bis(oxalato)-diaquochromate(III). It is expected that the cations studied in this investigation would also catalyze that reaction.

Because of the observation of absence of oxygen-18 exchange in aqueous solutions of tris(oxalato)chromate(III),[13] it would be interesting to measure this exchange in the presence of catalytic metal ions in these solutions. The expected result is that oxygen exchange would be catalyzed by the presence of certain metal ions.

likely that any large part of the very great increase in rates is due to this effect, particularly when one looks only at the series of divalent cations.

It has been reported[11,12] that the exchange of oxalate with tris(oxalato)chromate(III) ion is faster between pH 0 and 2 than in the pH range above 2. It also has been reported[13] that in a 0.02 M solution of tris(oxalato)-

(11) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).
(12) K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).
(13) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. O'Dell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).