2298 © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54*, *2298—2301 (1981)* [Vol. 54, No. 8

The *trans-cis* Isomerization of Potassium Diaquabis(oxalato)chromate(III) in Various Organic Solvent-Water Mixtures

Kengo Uchida* and Yoshinobu Takinami

Department of Chemistry, Faculty of Science, Hirosaki University, Bunkyo-cho, Hirosaki 036

(Received October 31, 1980)

Kinetics of the *trans-cis* isomerization of $K[Cr(ox)_2(H_2O)_2]$ have been investigated in binary mixed solvents, including ethanol–, dioxane–, and acetone–water mixtures. The first-order rate constant decreases with an increase in the concentration of an organic solvent. A similar decrease by the addition of an organic solvent was observed in the presence of univalent and bivalent cations. These results are in contrast to those for the analogous malonato complex, and suggest that both dissociation and twist mechanisms are involved in the reaction.

Extensive investigations of the isomerization kinetics of *trans*-diaquabis(oxalato)chromate(III) ion have been reported.[1–12] A dissociation mechanism, where a bond rupture at Cr–oxalato is the rate determining step, has been reported and this has been supported by the catalytic effect of various cations,[1,3,11] while a twist mechanism has been suggested by Ashley and Lane.[13]

On the other hand, the studies on the influence of solvents are very few.[6] The authors have found that the rate of the isomerization of an analogous malonato complex increased with an increase of the concentration of organic solvents.[14] In this work, we have studied the effect of solvents on the rate of the isomerization. As the isomerization is catalyzed by some cations, the catalytic reaction is expected to be accelerated in organic solvents, because the reaction is ionic and depends on the relative permittivity of the solvent. Nevertheless, the reactions in the presence of univalent and bivalent cations are found to be retarded with increasing concentration of the organic solvent. We have also studied the reaction mechanism.

Experimental

Materials. Potassium *trans*-diaquabis(oxalato)chromate (III), *trans*-$K[Cr(ox)_2(H_2O)_2]\cdot 3H_2O$, was prepared by the standard method.[15] As considerable amount of by-products, $[Cr(ox)(H_2O)_4]^+$ and $[Cr(ox)_3]^{3-}$, were contained. The product was purified by using an ion exchange chromatography.[9] The absorption spectra ($\lambda_{max}=400$ nm ($\varepsilon_{max}=19.2$), 532 nm (19.0)) agreed well with those reported in the literature.[4,9] The stock solutions containing the investigated cations were prepared by dissolving the chlorides of the cations in redistilled water. The chlorides of a guaranteed reagent grade were recrystallized from distilled water. Organic solvents of a guaranteed reagent grade were purified by the usual methods,[16] and ultraspecial grade solvents were used without further purification.

Procedures. Experimental methods were described previously.[14] The rates of the reactions were determined spectrophotometrically at the wavelength of 415 nm at 25.0 °C. The concentration of the complex was 8.0×10^{-3} mol dm^{-3} in all cases. The pH value of the solution was not adjusted but remained constant at about 4.5 throughout the reactions.

Results and Discussion

In the absence of excess cations, the isomerization rates were determined in aqueous mixtures of ethanol, dioxane, acetone and *N*-methylacetamide. The isomerization obeys good first-order kinetics even after 90% reaction, and the rate constant, k_{obsd}, decreased with increasing concentration (mole fraction) of the organic solvents, contrary to the case of the analogous malonato

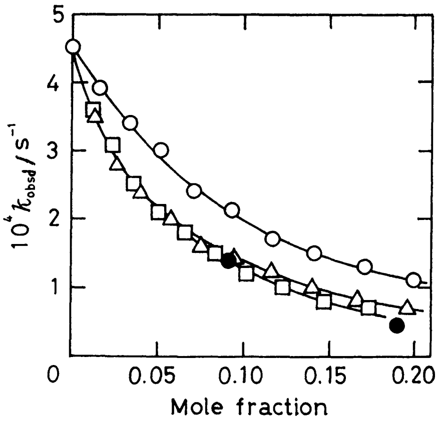

Fig. 1. Effects of the concentration of organic solvents on k_{obsd} in the absence of excess cation.
○: Ethanol, □: dioxane, △: acetone, ●: *N*-methylacetamide.

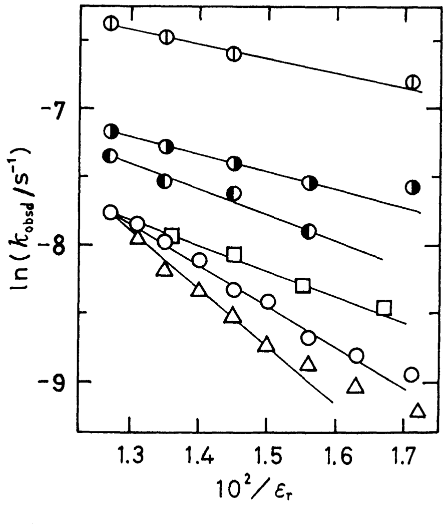

Fig. 2. Plots of $\ln(k_{obsd}/s^{-1})$ *vs.* the reciprocal of relative permittivity.
○: Ethanol, □: dioxane, △: acetone, ◐: $[Ca^{2+}]=0.0157$ mol dm^{-3} (ethanol), ◑: $[Ca^{2+}]=0.0314$ mol dm^{-3} (ethanol), ⦶: $[Sr^{2+}]=0.331$ mol dm^{-3} (ethanol).

complex.[14] The results are shown in Fig. 1. As the relative permittivity, ε_r, of the solvents increased, k_{obsd} increased smoothly except in the solution of *N*-methylacetamide and formamide. Plots of ln k_{obsd} *vs.* $1/\varepsilon_r$ were found to be linear, though deviations could be seen in the high concentrations of the organic solvents. The ε_r values were properly interpolated from known values.[17] The plots are shown in Fig. 2. Even if the ε_r value was the same, different k_{obsd} values were obtained in other solvents. Therefore k_{obsd} did not depend on the ε_r value only.

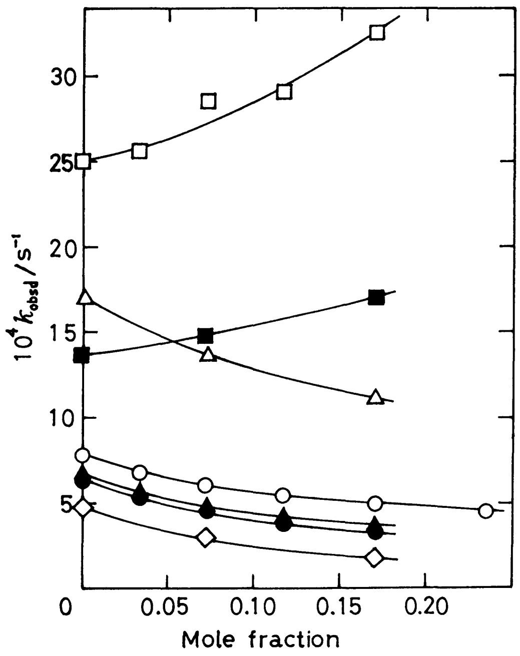

Fig. 3. Effects of the concentration of ethanol on k_{obsd} in the presence of some cations.
□: $[La^{3+}]=0.0040$ mol dm^{-3}, ■: $[La^{3+}]=0.0020$ mol dm^{-3}, △: $[Sr^{2+}]=0.331$ mol dm^{-3}, ▲: $[Sr^{2+}]=0.031$ mol dm^{-3}, ○: $[Ca^{2+}]=0.031$ mol dm^{-3}, ●: $[Ca^{2+}]=0.016$ mol dm^{-3}, ◇: $[K^+]=0.99$ mol dm^{-3}.

It has been shown that the rates in aqueous solutions are accelerated by the addition of cations, M^{n+}.[1,3,11] A similar acceleration was observed in a mixture of an organic solvent and water. The effects of the solvents on k_{obsd} in the presence of cations are shown in Fig. 3 and Table 1. The k_{obsd} values decreased with increasing concentration of the organic solvents, whereas they increased in the presence of La^{3+} in most of the solvents except *N*-methylacetamide, whose ε_r value is larger than that of water. The k_{obsd} value was also given by

$$k_{obsd} = k_0 + k_M[M^{n+}], \qquad (1)$$

when the ionic strength of the solution was kept constant by the addition of potassium chloride. The results are shown in Fig. 4, where the dashed curves mean the k_{obsd} values when the ionic strength was not adjusted. The acceleration effect of K^+ could be neglected, compared with those of the bivalent and the tervalent cations. Some k_M values are listed in Table 2.

Generally a rate constant, k, for an ionic reaction is given by

Table 1. The k_{obsd} values in various solvents in the presence of some cations

Cation	[Cation]/mol dm^{-3}	$10^4\times k_{obsd}$/s^{-1}				
Vol% of organic solvent		0.0	20.0	30.0	40.0	50.0
(a) Mol% of dioxane		0.0	5.04		12.4	
Na^+	0.99	6.5	3.6		2.0	
K^+	0.99	5.6	2.9		1.5	
Sr^{2+}	0.331	17.0	11.9		9.3	
(b) Mol% of acetone		0.0	5.80		14.17	
Sr^{2+}	0.331	17.0	11.4		8.7	
(c) Mol% of formamide		0.0	10.15		23.20	
K^+	0.99	5.6	3.5		2.6	
Sr^{2+}	0.331	17.0	12.9		9.4	
(d) Mol% of *N*-methylacetamide		0.0		9.14		19.01
Sr^{2+}	0.331	17.0		9.5		7.5
La^{3+}	0.0153	46		20.2		15.2

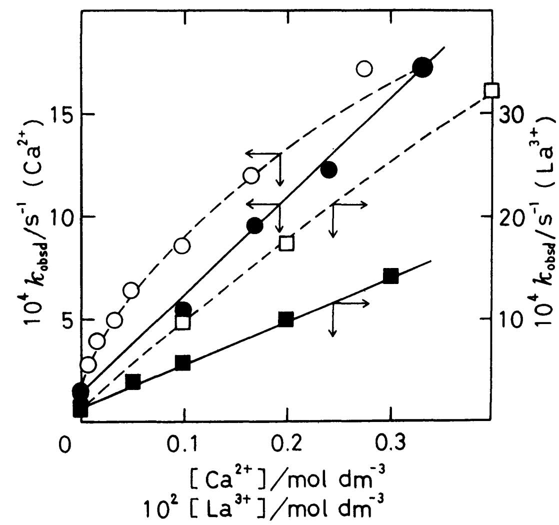

Fig. 4. Dependence of k_{obsd} upon the concentration of cations in 40 vol% ethanol–water.
○: Ca^{2+}, I is not adjusted, ●: Ca^{2+}, I is adjusted to 1.0 with KCl, □: La^{3+}, I is not adjusted, ■: La^{3+}, I is adjusted to 1.0 with KCl.

Table 2. The k_M values in various solvents ($I=1.0$)

Solvent	$10^4\times k_M$/s^{-1}				
	Na^+	K^+	Ca^{2+}	Sr^{2+}	La^{3+}
40% Ethanol–H_2O		0.4	46 121[a]	29 81[a]	7900[b] 7800[c]
40% Dioxane–H_2O	1.0	0.5	113[a]	26	
40% Acetone–H_2O				23	
40% Formamide–H_2O				21	
50% *N*-Methylacetamide–H_2O				22	970[a]
H_2O	2.0	1.1	105[a]	77[a]	4550[b] 5130[c]

a) $I=0.10$. b) $I=0.020$. c) $I=0.032$.

$$\ln k = \ln k^\circ - \frac{z_A z_B e^2}{d_{AB} \kappa T} \cdot \frac{1}{\varepsilon_r}, \tag{2}$$

where z_A and z_B are charge numbers of ion A and B, respectively, e is the elementary charge, d_{AB} the radius of an activated complex, κ the Bolzmann constant, T temperature, and k° the k value when ε_r is extrapolated to infinity.[18] Plots of $\ln k_{obsd}$ *vs.* $1/\varepsilon_r$ gave a straight line, as shown in Fig. 2. The slope of the plot should be positive when a complex anion reacts with a catalytic cation. However, the observed results were completely contrary to that expected from Eq. 2.

According to the Brϕnsted-Bjerrum theory, the logarithm of the ionic reaction rate constant, k_M, is generally given for a dilute solution by

$$\ln k_M = \ln k_{M,O} + 2Q z_A z_B \varepsilon^{-3/2} I^{1/2}, \tag{3}$$

where $k_{M,O}$ is the k_M value when ionic strength, I, is zero, and Q is given by

$$Q = (2\pi L)^{1/2} e^3/(1000)^{1/2}(\kappa T)^{3/2}, \tag{4}$$

where L is the Avogadro constant.[18] The $k_{M,O}$ value may be obtained from the plot of $\ln k_M$ *vs.* $I^{1/2}$. Strictly speaking, however, this method was not applicable when some cations were added to change the ionic strength of the solution, because the acceleration effect of these cations could not be neglected completely, especially in the study of the effect of a univalent cation. The k_M value decreased with increasing ionic strength. Therefore, the $k_{M,O}$ values were evaluated from Eq. 3 by subtracting the calculated second term of the right side of the equation from $\ln k_M$.

The plots of $\ln k_{M,O}$ *vs.* $1/\varepsilon_r$ were linear, as shown in Fig. 5, and the slope became positive when the bivalent and the tervalent cations were added. As the concentration of the organic solvent increased, k_0 in Eq. 1 decreased rapidly and k_M also decreased as the second term of the right side of Eq. 3 decreased, while $k_{M,O}$ increased. Consequently, in the presence of bivalent cations, k_{obsd} apparently decreased as ε_r decreased. On the other hand, the increase in $k_{M,O}$ in the presence of La^{3+}, was very large and k_{obsd} did not decrease with the concentration of the organic solvent. When the univalent cation was added, $k_{M,O}$ was small, and unfortunately the relationship between $\ln k_M$ and $1/\varepsilon_r$ was not clear. The radius of the activated complex, d_{AB}, may be obtained from the slopes of the plots in Fig. 5 and the values of 1.5 nm for Sr^{2+}: 1.4 nm for Ca^{2+} and 1.0 nm for La^{3+} were obtained tentatively. The values were slightly greater than those expected for the free ions. The ion of La^{3+} has a large charge and might come closer to the complex than the bivalent cations.

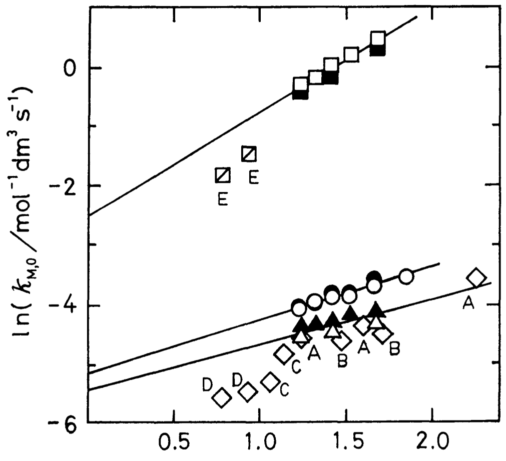

Fig. 5. Plots of $\ln(k_{M,O}/\mathrm{mol^{-1}\,dm^3\,s^{-1}})$ *vs.* the reciprocal of relative permittivity in ethanol–water system except A—E.
○: $[Ca^{2+}]=0.031\ \mathrm{mol\,dm^{-3}}$, ●: $[Ca^{2+}]=0.016\ \mathrm{mol\,dm^{-3}}$, △: $[Sr^{2+}]=0.33\ \mathrm{mol\,dm^{-3}}$, ▲: $[Sr^{2+}]=0.031\ \mathrm{mol\,dm^{-3}}$, ◇: $[Sr^{2+}]=0.33\ \mathrm{mol\,dm^{-3}}$; A: dioxane–$H_2O$, B: acetone–$H_2O$, C: formamide–$H_2O$, D: *N*-methylacetamide–H_2O, □: $[La^{3+}]=0.0040\ \mathrm{mol\,dm^{-3}}$, ■: $[La^{3+}]=0.0020\ \mathrm{mol\,dm^{-3}}$, ▨: $[La^{3+}]=0.015\ \mathrm{mol\,dm^{-3}}$ in *N*-methylacetamide–H_2O; E.

Although much work has supported a dissociation mechanism, a twist mechanism can not be excluded, since the activation parameters are more suitable for the twist mechanism,[13] and the ligand water is not liberated easily.[19] Then the reaction may involve two mechanisms. One is independent of ionic effects and would be the twist mechanism, the rate constant of which is k_0. Another is dependent on the cations and the dissociation mechanism would be predominant, the rate constant of which is k_M. When $\ln k_{obsd}$ was plotted *vs.* $1/\varepsilon_r$, without dividing k_{odsd} into k_0 and k_M, some linear plots of negative slope were obtained, as shown in Fig. 2, but the positive slopes, which are expected for reactions between ions of the opposite sign, were not obtained. With an increase in the concentration of the organic solvent, the k_0 value decreased, but on the other hand the $k_{M,O}$ value increased. These results suggest the existence of two different mechanisms. If the intermediate with a unidentate oxalato ligand formed by the dissociation is stabilized with an increase in the ε_r value of solvent, it is unreasonable that k_{obsd} becomes small in *N*-methylacetamide–water system. The ε_r value of *N*-methylacetamide is 182 and is much larger than that of water.[17] Kelm *et al.*[6] explained this decrease in terms of Grundwald-Winstein's Y-parameter. The rapid decrease of k_0 with an increase in the concentration of the organic solvent could be elucidated by such a solvent effect.

The authors wish to thank Professor Taro Isobe for useful suggestions during this work.

References

1) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).

2) H. Kelm, H. Stieger, and G. M. Harris, *Ber. Bunsenges. Phys. Chem.*, **73**, 939 (1969).

3) H. Kelm, H. Stieger, and G. M. Harris, *Z. Phys. Chem.* (*Frankfurt am Main*), **67**, 98 (1969).

4) D. H. Huchital, *Inorg. Chem.*, **9**, 486 (1970).

5) M. W. Rophael and M. A. Malati, *J. Chem. Soc.*, *A*, **1971**, 1903.

6) H. Kelm, H. Stieger, and G. M. Harris, *Chem. Ber.*, **104**, 2743 (1971).

7) M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **11**, 1062 (1972).

8) M. W. Rophael and M. A. Malati, *J. Inorg. Nucl. Chem.*, **36**, 1355 (1974).

9) M. B. Davies and J. W. Lethbridge, *J. Inorg. Nucl. Chem.*, **37**, 141 (1975).

10) Y. Harada and K. Uchida, *Sci. Rep. Hirosaki Univ.*, **23**, 68 (1976).

11) L. Goswami, S. Sarkar, and D. Banerjea, *Z. Anorg. Allg. Chem.*, **435**, 301 (1977).

12) P. L. Kendall, G. A. Lawrance, and D. R. Stranks, *Inorg. Chem.*, **17**, 1166 (1978).

13) K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).

14) K. Uchida and Y. Takinami, *Bull. Chem. Soc. Jpn.*, **53**, 3522 (1980).

15) M. Nakahara, "Mukikagōbutsu No Gōsei," in "Shin-Jikkenkagaku-kōza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), Vol. 8, Part 3, p. 1102; A. Werner, *Ann.*, **406**, 286 (1914).

16) J. A. Riddic and W. B. Bunger, "Organic Solvents," in "Techniques of Chemistry," 3rd ed, ed by A. Weissberger, Wiley-Interscience, New York (1970), Vol. 2, p. 724.

17) G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932); "Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 6 Aufl. Springer-Verlag, Berlin (1959), Vol. II-6-I, pp. 614—753.

18) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York (1965), Chap. 5.

19) J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc., A*, **1968**, 1413.