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The *trans-cis* Isomerization of the Diaquabis(malonato)chromate(III) Ion in Various Organic Solvent-Water Mixtures

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(Received March 7, 1980)

The kinetics of the *trans-cis* isomerization of $[Cr(mal)_2(H_2O)_2]^-$ have been investigated in binary mixed solvents, including methanol–, ethanol–, dioxane–, and acetone–water mixtures. The first-order rate constant increases with a decrease in the volume percentage of the water, but is independent of the kind of organic solvent. The rate is not affected by the addition of any cation to an aqueous solution. These results are in contrast to those for the analogous oxalato complex, and are interpreted in terms of a dissociation mechanism in which the rate-determining step is the dissociation of the coordinating water molecule.

Many studies[1–14] have been made of various reactions of potassium diaquabis(oxalato)chromate(III), $K[Cr(ox)_2(H_2O)_2]$. Much less information is, though, available on the analogous complex of diaquabis(malonato)chromate(III). Some aquation,[15,16] anation,[17] and isomerization[8,18,19] have been investigated, though, and the behavior of the malonato complex seems to be rather different from that of the oxalato complex. For example, the isomerization of the malonato complex is much slower, but the aquation takes place more easily than that of the oxalato complex in an acid solution. With respect to the isomerization mechanism, Frank and Huchital[19] suggested a ring-opening mechanism and Casula *et al.*[8] proposed a primary dissociation of the water molecule.

In this work, we have studied the effects of mixed aqueous solvents, the addition of some kinds of salts, and the pH value of the solution on the *trans-cis* isomerization, and have proposed an aqua-ligand dissociation mechanism.

Experimental

Materials. Potassium *trans*-diaquabis(malonato)chromate(III), *trans*-$K[Cr(mal)_2(H_2O)_2]$, was prepared in a manner similar to that described by Chang.[20] The product was recrystallized twice from water. The other inorganic salts were of a guaranteed reagent grade and were recrystallized from water. Redistilled water and organic solvents of an ultraspecial grade or a guaranteed reagent grade were used as the solvents.

Procedures. The rates of the reactions were determined spectrophotometrically[8] at the wavelength of 565 nm using a Shimadzu double-beam spectrophotometer, UV 200S, with a temperature-controlled cell holder. The first-order rate constants, k, were obtained from the slopes of the plots of $\ln(A_\infty - A)$ *vs.* t, where A is the absorbance at time t and where A_∞ is the absorbance after the reaction is complete. These plots were straight, with very little scatter, in every case. The reaction cell was a quartz cell ($1 \times 1 \times 4.5$ cm) for a spectrophotometer with a branch. The concentration of the complex was 1.50×10^{-2} mol dm^{-3} in all cases. Most of the kinetic experiments were performed at 50 °C.

The pH values of the solution, which were not adjusted unless otherwise noted, were 4.4—4.6. When the pH value was varied, 0.1 mol dm^{-3} of NaOH or 0.05 mol dm^{-3} of HCl was added. The pH values were measured by means of a Hitachi-Horiba pH meter, M5, before and after the reaction. The pH values did not change during the reactions.

Results

Absorption Spectra. The wavelengths and the molar absorption coefficients, ε, of the absorption maxima of the complexes are collected in Table 1, where the subscript "eq" indicates the equilibrated mixture of the *trans*- and the *cis*-isomer after the reaction has stopped.

Table 1. Spectral data for some complex ions

Complex	λ_{1max}/nm[a]	λ_{2max}/nm[a]
trans-$[Cr(mal)_2(H_2O)_2]^-$	402(23.0)	556(18.6)
	401(20.3)[b]	555(17.6)[b]
	405(22)[c]	560(21)[c]
$[Cr(mal)_2(H_2O)_2]^-_{eq}$	418(40)	565(45.6)
cis-$[Cr(mal)_2(H_2O)_2]^-$	418(42.1)[b]	565(50.8)[b]
	415(41)[c]	565(51)[c]
trans-$[Cr(mal)_2(OH)(H_2O)]^{2-}$	414(38)	570(26)
	420(41)[c]	570(26)[c]
cis-$[Cr(mal)_2(OH)(H_2O)]^{2-}$	416(44)	574(39)
	425(48)[c]	575(43)[c]

a) Values in parentheses are the molar absorption coefficients (dm^3 mol^{-1} cm^{-1}). b) Ref. 19. c) Ref. 8.

Kinetics. When the *trans*-isomer is dissolved in water, *trans-cis* isomerization occurs and the reaction comes to an end at an equilibrium. The equilibrium lies close to the *cis*-form, and it has been reported[18] that 95% is of the *cis*-form at the equilibrium. The isomerization obeys good first-order kinetics even after 90% reaction, and a constant A_∞ value is always obtained. Aquation can be neglected in this work.

As the complex does not dissolve in such organic solvents as methanol, ethanol, dioxane, and acetone, mixtures of the organic solvent and water were used as the solvents. In such mixtures, the kinetic behavior was very similar to that in an aqueous solution which contained no organic solvent. The k values increased with an increase in the concentration of the organic solvent in every case, as is shown in Fig. 1. The values at higher concentrations of the organic solvent could not be obtained because of the low solubility of the complex. It may be clear that the specificity of the solvents is very small, and the variation in k values can not be elucidated individually by the mole fraction of the organic solvents, the relative permittivity, or the

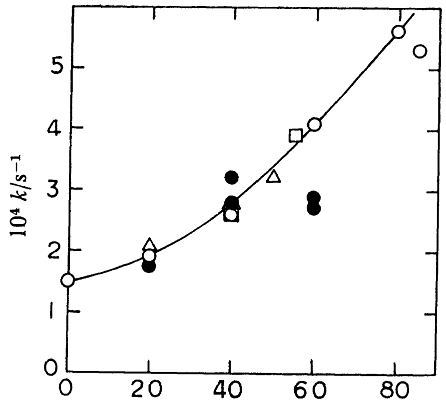


Fig. 1. Effect of concentration of organic solvent on the rate constant.

○: Methanol, ●: ethanol, □: dioxane, △: acetone.

viscosity of the solution. The k values seem to depend on only the volume percentage of the water, namely, the molarity of water, and to increase with a decrease in the molar concentration of the water. For example, the k values at 40 v/v% remain approximately constant ($(2.6$—$3.2) \times 10^{-4}$ s^{-1}) in every solvent. Some deviations do, however, occur near the limits of the solubility in the systems of alcohol and water. In these solvents, some structural effect due to a hydrogen bond between solvent molecules might play a special role.[21]

Effect of Added Salts on the k *Values.* *In an Aqueous Solution*: The effect of added salts on the k values was investigated. At first, several chlorides were added in order to examine the cationic effect. As the rate depends on the ionic strength, I, the concentration of the salts was adjusted to $I = 1.0$. The k values were 2.5×10^{-4}, 2.6×10^{-4}, 2.8×10^{-4}, and 2.4×10^{-4} s^{-1} for NaCl, $CaCl_2$, $SrCl_2$, and $LaCl_3$ respectively. Also, it is obvious that the values are approximately constant and independent of the kind of cation, in contrast to the case of the analogous oxalato complex, $[Cr(ox)_2(H_2O)_2]^-$.[4,11] As the reaction was not accelerated by the addition of a bivalent or tervalent cation, which has a great effect in the case of $[Cr(ox)_2(H_2O)_2]^-$, it is concluded that cations have no catalytic effect on the isomerization of the malonato complex.

On the other hand, Frank and Huchital[19] have found the accelerating effect of the nitrate ion. However, we found that this effect is general for the other anions and that the bivalent anion seems to be more effective. The effects of the concentration of the anions on the rate constants are shown in Fig. 2, where sodium salts are used. The sulfate ion has the greatest effect, and the order of the k values seems to be as follows:

$$SO_4^{2-} \gg I^- > NO_3^- > ClO_4^- \approx Br^- \geqslant Cl^-.$$

In Organic Solvent–Water Mixtures: A similar anionic effect was investigated in organic solvent–water mixtures. Ethanol of a protic solvent and acetone and dioxane of an aprotic solvent were used. The volume percentage of the organic solvent was adjusted to 50%, and sodium salts were used. As has been mentioned above, no solvent effect was observed in the absence of added salts, but a distinct solvent effect appeared in the presence of the added salts. The results are listed in Table 2. The order of k values is as follows:

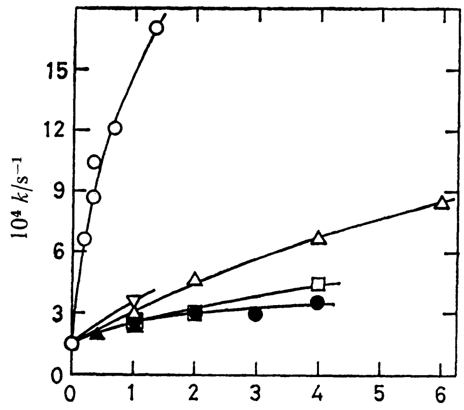


Fig. 2. Effect of concentration of various anion on the rate constant.

○: SO_4^{2-}, ▽: I^-, △: NO_3^-, □: ClO_4^-, ●: Br^-, ▲: Cl^-.

$$\text{dioxane–}H_2O > \text{acetone–}H_2O > \text{ethanol–}H_2O.$$

Although the effect is not great, evidently some interaction between the anions and the organic solvents is present. The order of the catalytic effect by the anions also seems to change to $Cl^- > I^- > Br^-$, whereas the order is $Cl^- \leqslant Br^- < I^-$ in an aqueous solution containing no organic solvent.

pH Effect. The k values measured at various pH values are shown in Fig. 3. The rate increases rapidly above pH 5. All the spectra after the equilibrium is reached are very similar in the pH region of 3—6.

TABLE 2. EFFECT OF ADDED ANION ON k VALUES IN ORGANIC SOLVENT–WATER MIXTURES (50 v/v%, [anion] = 1.0 mol dm^{-3})

Solvent	$10^4\,k/s^{-1}$		
	Cl^-	Br^-	I^-
H_2O	2.5	2.7	3.7
Ethanol–H_2O	4.9	3.9	5.1
Acetone–H_2O	5.9	4.4	5.2
Dioxane–H_2O	6.1	4.9	6.1

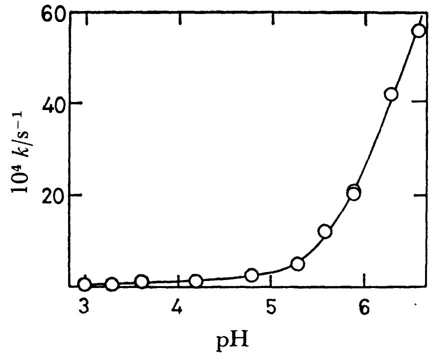


Fig. 3. Effect of pH on the rate constant.

Slight shifts of the absorption maxima can be seen above pH 6, but the molar absorption coefficients do not change so much. The spectral changes are probably due to the formation of a hydroxo complex of $[Cr(mal)_2(OH)(H_2O)]^{2-}$, spectral data of which are also shown in Table 1.

In the higher pH region, k values were obtained at 25.0 °C and $I=0.015$, because the rates were too fast to measure at 50.0 °C. The k values are $14.8\times10^{-4}\,s^{-1}$ at pH 8.3 and $15.9\times10^{-4}\,s^{-1}$ at pH 10.5.

Effect of the Temperature. The k values were measured at five different temperatures over the range from 307.2 K to 323.2 K. The activation parameters, listed in Table 3, were calculated from plots of $\ln k$ *vs.* $1/T$.

Table 3. Activation parameters

Solution	$\Delta H^{\neq}$/kJmol^{-1}	$\Delta S^{\neq}$/J mol^{-1}
Aqueous solution	116	42
Aqueous solution at pH 5.7	103	20
Aqueous solution containing Na_2SO_4	135	114
60%methanol–H_2O	163	195

Discussion

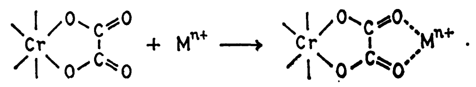
The rate of the isomerization of the malonato complex is much slower than that of the analogous oxalato complex. The orders of magnitude of the k values of the malonato and the oxalato complex are 10^{-6} and 10^{-4} s^{-1} respectively at 25 °C; the difference is about 100 times. The mechanism of the reaction has been studied for the oxalato complex,[6,8,22] and two main mechanisms have been proposed. At first, the added cation, such as Na^+, Ca^{2+}, or La^{3+}, forms an ion-pair, and a bond rupture takes place at a Cr–oxalato bond; then, the isomerization proceeds *via* a five-coordinated trigonal bipyramidal intermediate. Next is the twist mechanism, in which the rate is not affected by the cations and a proton.

In the malonato complex, the next four mechanisms could be considered in general: (a) a water-association mechanism, (b) a twist mechanism, (c) a ring-opening mechanism, and (d) an aqua-ligand dissociation mechanism.

Of these mechanisms, (a) can be eliminated because the k values increase with a decrease in the concentration of water and are independent of the kind of organic solvent, and it would be more difficult for solvent water to enter the complex when the concentration of the water decreases. Moreover, a seven-coordinated intermediate could hardly be considered, since the entropy of activation, $\Delta S^{\neq}$, is positive. If a water molecule coordinates to the Cr atom, $\Delta S^{\neq}$ would be negative because of the decrease in the degree of freedom.

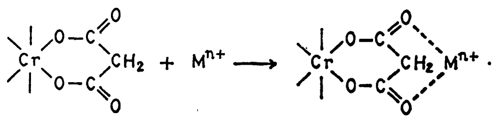
The twist mechanism (b) is also not reasonable, because the positive and great $\Delta S^{\neq}$ value, the anionic effect, and the increase in the k value with an increase in the volume percentage of the organic solvents could not be explained by this mechanism. Although the viscosity of the solvent may affect the twist, there is no close relation between the k value and the viscosity. However, it seems impossible to deny the possibility of this mechanism, since the oxalato complex may isomerize *via* a twist mechanism in the absence of any added salts.[22] A malonato chelate is larger and might be more easily distorted. Thus, the twist intermediate might be stabilized.

Mechanism (c) could be removed since the isomerization is not catalyzed by cations in the case of the malonato complex. On the other hand, in the oxalato complex the apparent rate constants are $5.5\times10^{-4}\,s^{-1}$ and $1.3\times10^{-2}\,s^{-1}$ in the presence of Na^+ and La^{3+} respectively,[11] these values differ by about 24 times. From these results, it seems that the cation may not play an important part in breaking the Cr–malonato bond, contrary to the case of the oxalato complex. Frank and Huchital[19] suggested the ring-opening mechanism because of the positive $\Delta S^{\neq}$, the analogy to the oxalato complex, and the stability of the malonato complex referred to the second formation constants of the *cis*-oxalato and the *cis*-malonato complexes. However, they did not neglect the dissociation mechanism and proposed a combination of the ring-opening and water-dissociation mechanisms. However, Banerjea and Chatterjee[15] reported that the rate of the dissociation (aquation) of the *cis*-malonato complex in an aqueous acidic solution is about 70 times faster than that of the oxalato complex, and that the former is much more labile. If the malonato chelate is labile, the other mechanism should be proposed because the k value of the malonato is about 100 times smaller than that of the oxalato complex. An ion-pair formation would be important in the catalytic effect by cations in the oxalato complex, which is given by:



(1)

In the malonato complex, however, the methylene group seems to prevent the ion-pair formation, as given by:



(2)

Mechanism (d) seems to be most plausible. In the mechanism accompanying a dissociation of a ligand water molecule, $\Delta S^{\neq}$ would have a large positive value. Then, a five-coordinated intermediate may be formed after the dissociation. Moreover, the k value may increase with the decrease in the concentration of water, since the ligand water molecule could be removed more easily when the concentration of the water decreases. After the release of the water molecule, the chance of the recombination of the intermediate complex and a water molecule may decrease, while the possibility of the isomerization may increase as the concentration of the organic solvent increases. Although the organic solvent molecule may coordinate to the intermediate, the bond may be weak, and so the isomerization would take place easily. Consequently, the isomerization could be accelerated. A catalytic effect by a nitrate ion has been found,[19] but a sulfate ion has an even more remarkable effect. A bivalent anion coming close to the ligand water molecule may assist the release of the water molecule effectively. The effects of univalent anions are less significant, and the difference in the effects in organic solvents could not be elucidated clearly. Hunt *et al.*[23] reported that the rate constant of the exchange of a water molecule, k_{ex}, is 7×10^{-7} s^{-1} and that the activation energy, E_a, is 112 kJ mol^{-1} [24] for $[Cr(H_2O)_6]^{3+}$ at 25 °C, while k_{ex} is less than 10^{-6} s^{-1} for *cis*-$[Cr(ox)_2(H_2O)_2]^-$.[3] It may tentatively be assumed from these values that the k_{ex} is 10^{-6}—10^{-7} s^{-1} for $[Cr(mal)_2(H_2O)_2]^-$. The observed k is 1.5×10^{-6} s^{-1}, and E_a is 119 kJ mol^{-1}, for the malonato complex in an aqueous solution. The similarity of these values may also support the theory that the rate-determining step is the dissociation of the ligand water molecule.

In the higher pH region, $[Cr(mal)_2(OH)(H_2O)]^{2-}$ is formed and the k values become larger. These values at 25 °C, which are very close to the values obtained by Casula *et al.*,[8] can be reduced to k=0.040 s^{-1} at pH 8.3 and k=0.043 s^{-1} at pH 10.5 at 50 °C by using the activation parameters. The two values are approximately the same as the rate constant for the hydroxo complex. In general, a hydroxo complex is more labile than a conjugate acid complex, as well as a cobalt(III) complex, since the charge of the central metal atom decreases partially upon the addition of a negative OH group and the bond of $Cr-OH_2$ becomes weak. The rate constant of the *trans-cis* isomerization of $[CrCl(en)_2(H_2O)]^{2+}$ is less than 6×10^{-6} s^{-1} at 35.0 °C.[25] If the isomerization occurs *via* water exchange, the rate might be expected to be similar for the malonato complex. The isomerization rate constant of the conjugate base, $[CrCl(OH)(en)_2]^+$, is less than 6×10^{-5} s^{-1}.[26] This value is not large, but it may be a little larger than that of $[CrCl(en)_2(H_2O)]^{2+}$.

The authors are sincerely grateful to Professor Taro Isobe for his continuing interest and encouragement.

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