CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SETON HALL UNIVERSITY,
SOUTH ORANGE, NEW JERSEY 07079

Kinetics and Mechanisms of Some Reactions Involving Chromium(III) Malonate Complexes[1]

BY MICHAEL J. FRANK AND DANIEL H. HUCHITAL*

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The kinetics of the acid-catalyzed aquation of *cis*-bis(malonato)diaquochromate(III) and the isomerization of *trans*-bis(malonato)diaquochromate(III) are reported. The rate laws (rate constants at 25° and $I = 1.0\ M$ follow in parentheses) are $-d[cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]/dt = k[cis\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-][H^+]$ ($k = 6.50 \times 10^{-5}\ M^{-1}\ sec^{-1}$) and $-d[trans\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-]/dt = [trans\text{-}Cr(C_3H_2O_4)_2(H_2O)_2^-](k_0 + k_1[H^+])$ ($k_0 = 1.78 \times 10^{-6}\ sec^{-1}$, $k_1 = 1.14 \times 10^{-5}\ M^{-1}\ sec^{-1}$). The mechanism for the aquation reaction involves a rapid protonation preequilibrium followed by rate-determining attack of water on the protonated intermediate. The ultimate reaction product of the acid-catalyzed trans–cis isomerization is $Cr(C_3H_2O_4)(H_2O)_4^+$. Rate and spectrophotometric data indicate that the monomalonate complex results from the trans–cis isomerization of the trans isomer followed by aquation of the cis isomer rather than direct aquation of the trans isomer.

Reactions of chromium(III) and cobalt(III) oxalate complexes have been studied extensively over the past two decades,[2] but except for a few cases, work on analogous malonate systems has remained essentially untouched. We report here the results of a study of the acid-catalyzed aquation of *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ and the trans–cis isomerization of $Cr(C_3H_2O_4)_2(H_2O)_2^-$. The investigation of the first reaction was prompted by the fact that the results of three previous investigations[3–5] differed considerably in the observed rate constants as well as in the rate expression, although the enthalpies of activation were nearly identical in all three cases. Furthermore, the rate of this reaction is important in interpreting the results of the acid-catalyzed trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$.

Experimental Section

Materials.—Sodium *cis*-bis(malonato)diaquochromate(III) was prepared according to the method of Chang.[6] *Anal.* Calcd for $Na[Cr(C_3H_2O_4)_2(H_2O)_2] \cdot 3H_2O$: Cr, 14.1; C, 19.5; H, 3.82. Found: Cr, 14.0; C, 19.4; H, 3.93.

Potassium *trans*-bis(malonato)diaquochromate(III) was prepared in a manner similar to that described by Chang.[6] After the reaction solution had been concentrated at 100 ml and cooled to room temperature, it was covered with a watch glass and stored overnight at 5°. The crystals which formed were removed with a spatula, washed with small amounts of water, 95% ethanol, and absolute ether, and air dried. This modification results in lower yields than those reported by Chang, but the crystals obtained are free of the cis isomer, as evidenced by the lower molar extinction coefficients than the literature values. *Anal.* Calcd for $K[Cr(C_3H_2O_4)_2(H_2O)_2] \cdot 3H_2O$: Cr, 13.5; C, 18.7; H, 3.66. Found: Cr, 13.4; C, 18.9; H, 3.79.

Chromium content was determined by conversion to CrO_4^{2-} with alkaline peroxide followed by spectrophotometric analysis of the CrO_4^{2-} produced (ϵ_{373} 4815).[7]

Kinetics Measurements.—The rates of reaction were determined spectrophotometrically using a Beckman DK-2 ratio-recording spectrophotometer. The reactions were followed for the most part at the wavelength maxima of the reactants. First-order or pseudo-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. For those runs performed in the absence of acid, A_∞ values corresponded to the absorbance of *cis*-bis(malonato)diaquochromate(III). For the acid-catalyzed trans-cis isomerization, A_∞ was taken to be that of the monomalonato complex.

Two methods of temperature control were used. For a reaction having a half-life greater than 5 hr the reaction vessel (a 1-, 2-, 5-, or 10-cm spectrophotometric cell) was kept in a constant-temperature bath and removed only long enough to take an absorbance reading. To minimize temperature variation, the cell holder of the DK-2 was brought to the same temperature as that of the bath prior to a reading. Reactions with half-lives less than 5 hr were run in the thermostated cell compartment of the spectrophotometer. In all cases temperature control was within ±0.1° of the desired temperature.

Results

Spectrophotometric Data.—The highlights of the spectra of the chromium(III) ions considered in this work are presented in Table I. The values reported for *cis*- and *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ are for solutions at 1.0 M ionic strength ($LiClO_4$). The spectrum of the trans isomer was obtained in the same manner as that for the analogous oxalate complex.[8]

TABLE I

SPECTROPHOTOMETRIC FEATURES OF CHROMIUM(III) COMPLEXES

Complex	λ_{max},[a] nm	ϵ,[a] $M^{-1}\ cm^{-1}$	Ref
cis-$Cr(C_3H_2O_4)_2(H_2O)_2^-$	565 (566)	50.8 (49.9)	This work
	418 (417)	42.1 (41.4)	
trans-$Cr(C_3H_2O_4)_2(H_2O)_2^-$	555 (560)	17.6 (19.6)	This work
	401 (404)	20.3 (21.0)	
$Cr(C_3H_2O_4)(H_2O)_4^+$	559	31.4	*b*
	415	26.1	
$Cr(H_2O)_6^{3+}$	574	13.3	*c*
	408	15.8	

[a] Comparable literature[6] values are presented in parentheses. [b] D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965). [c] E. Deutsch and H. Taube, *ibid.*, **7**, 1532 (1968).

Rate Data. Acid-Catalyzed Aquation of *cis*-Bis(malonato)diaquochomate(III).—Kinetic results for the acid-catalyzed aquation of *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ are reported in Table II. A plot of the observed pseudo-first-order rate constant k_{obsd}, at 45°, *vs.* $[H^+]$ was linear. The dependence of k_{obsd} on $[H^+]$ follows the equation $k_{obsd} = k[H^+]$, where k is the second-order rate constant reported in column 5 of Table II and agrees with the rate expression obtained previously by Banerjea and Chatterjee[3] for this reaction. The activation parameters, determined by a least-squares com-

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(1) Presented in part before the Division of Inorganic Chemistry, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61**, 213 (1961).

(3) D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **29**, 2387 (1967).

(4) C. Furlani and E. Mantovani, *ibid.*, **31**, 1213 (1969).

(5) J. C. Chang, *ibid.*, **32**, 1402 (1970).

(6) J. C. Chang, *ibid.*, **30**, 945 (1968).

(7) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

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

TABLE II

RATE DATA FOR THE ACID-CATALYZED AQUATION OF *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$

Temp, °C	10^3[complex], *M*	$[H^+]$,[a] *M*	10^4k_{obsd},[b] sec^{-1}	10^4k,[b] $M^{-1}\ sec^{-1}$
25.0	2.03	1.00	0.650	0.650
30.0	2.15	1.00	1.20	1.20
37.0	2.13	1.00	2.85	2.85
45.0	2.04	0.20	1.45	7.25
	2.04	0.50	3.58	7.16
	2.03	0.80	5.85	7.31
	2.05	1.00	7.13	7.13
	5.04	1.00	7.24	7.24
				7.22 ± 0.06[d]

[a] Ionic strength maintained at *ca.* 1.0 using $LiClO_4$ as supporting electrolyte. [b] All values are the average of two runs. [c] $k = k_{obsd}/[H^+]$. [d] Average of 45° runs.

puter analysis of the rate data, are $\Delta H^* = 21.8 \pm 0.4$ kcal/mol and $\Delta S^* = -4.7 \pm 0.1$ cal/deg mol.

Trans–Cis Isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$.—The noncatalyzed trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ was studied in both 1.00 *M* $LiClO_4$ and 1.00 *M* $LiNO_3$ at pH 2.8. During the course of our investigation Ashley and Lane[9] reported the kinetics of the noncatalyzed trans–cis isomerization at pH 3 in 1.0 *M* $NaClO_4$. Kinetic results of our investigation are reported in Table III. The results of Ashley and Lane are reported for comparison purposes. The activation parameters obtained in our study are $\Delta H^* = 28.7 \pm 0.2$ kcal/mol and $\Delta S^* = 11.3 \pm 0.1$ cal/deg mol in $LiClO_4$ and $\Delta H^* = 29.1 \pm 0.9$ kcal/mol and $\Delta S^* = 13.0 \pm 0.3$ cal/deg mol in $LiNO_3$ as compared with $\Delta H^* = 30.5 \pm 0.5$ kcal/mol and $\Delta S^* = 17.6 \pm 1.4$ cal/deg mol in $NaClO_4$.[9]

TABLE III

RATE DATA FOR THE NONCATALYZED TRANS-CIS ISOMERIZATION OF *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ [a]

Temp, °C	Salt	10^6k_{obsd},[b] sec^{-1}	10^6k,[c] sec^{-1}
25.0	$LiClO_4$	1.78 ± 0.04	1.92
	$LiNO_3$	2.43 ± 0.03	
35.0	$LiClO_4$	8.92 ± 0.11	12.5
	$LiNO_3$	11.9 ± 0.2	
45.0	$LiClO_4$	39.8 ± 0.8	58
	$LiNO_3$	50.0 ± 1.4	

[a] $[Cr(C_3H_2O_4)_2(H_2O)_2^-]$ for all runs is 6.4×10^{-3}–1.0×10^{-2} *M*, pH is 2.8, and ionic strength is 1.0. [b] All values are the average (uncertainties are standard deviations) of four or more runs. [c] Extrapolated from data reported[9] between 40 and 70°.

The data in Table III show an approximately 30% increase in k_{obsd} for $LiNO_3$ solutions over those in $LiClO_4$ solutions. Some additional experiments were run at 35° in LiCl and a mixed $LiClO_4$–$LiNO_3$ solution, as well as one in pure water ($I \approx 0$), in an effort to understand this discrepancy in rate constants.[10] The results are $k_{obsd} = 8.97 \times 10^{-6}\ sec^{-1}$ (two runs) in 1.00 *M* LiCl and $8.25 \times 10^{-6}\ sec^{-1}$ (two runs) in pure water. In a solution 0.5 *M* $LiClO_4$–0.5 *M* $LiNO_3$ $k_{obsd} = 10.5 \times 10^{-6}\ sec^{-1}$ (two runs). These results suggest that nitrate ion may play an important role in the isomerization process. Kinetics results for the acid-catalyzed isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ are reported in Table IV. The results reported are for an acid concentration of 1.00 *M* ($HClO_4$). At acid concentrations above 0.2 *M* the only product observed is the malonatotetraaquochromium(III) complex. Thus, the overall result is aquation. At $[H^+] < 0.2\ M$ absorbance data indicate that some cis isomer forms which then aquates. The rate law for the isomerization reaction was assumed to be the same as that for the analogous oxalate system (*i.e.*, $k_{obsd} = k_0 + k_1[H^+]$, where k_0 is the rate constant for the isomerization in the absence of acid). The reasons for this assumption become apparent when one compares the rate of isomerization with the rate of aquation of this cis product (*cf.* Table II). Values of k_{obsd} for the isomerization at acid concentrations lower than 1.00 *M* are not very systematic due to variations in the formation and disappearance of the cis product. However, the absorbance data taken at $[H^+] = 0.05$–1.00 *M* will be used in the Discussion section in order to elucidate the reaction path. The activation parameters for the k_1 (acid-catalyzed) path are $\Delta H^* = 24.3 \pm 0.9$ kcal/mol and $\Delta S^* = 0.4 \pm 0.3$ cal/deg mol.

TABLE IV

RATE DATA FOR THE ACID-CATALYZED TRANS-CIS ISOMERIZATION OF *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ [a]

Temp, °C	10^5k_{obsd},[b] sec^{-1}	10^5k_1, $M^{-1}\ sec^{-1}$
25.0	1.32 ± 0.03	1.14 ± 0.03
35.0	5.07 ± 0.13	4.18 ± 0.13
45.0	20.0 ± 0.4	16.0 ± 0.4

[a] $[Cr(C_3H_2O_4)_2(H_2O)_2^-] = (2.0\text{–}8.0) \times 10^{-3}$ *M*; $[HClO_4] = 1.00$*M*. [b] All values are the average of two or more runs.

Discussion

Three studies on the acid-catalyzed aquation of *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ have appeared in the literature. The observed rate constants were reported to have the following dependencies on acid concentration: (a) $k_{obsd} = 2.33 \times 10^{-3}[H^+]$ (45°),[3] (b) $k_{obsd} = 3.2 \times 10^{-4} + 9.5 \times 10^{-3}[H^+]$ (50°),[4] and (c) $k_{obsd} = 4.2 \times 10^{-5} + 3.6 \times 10^{-4}[H^+]$ (45°).[5] Our value for k_{obsd} is $7.22 \times 10^{-4}[H^+]$ at 45°. It is quite difficult to explain the large variations in the observed rate constants, but it should be noted that in one of the investigations[3] the molar extinction coefficient was approximately 15% below the literature value, and in another study[4] the solid complex was never actually prepared. The most reliable rate constants therefore are those reported by Chang.[5] Chang's proposed mechanism, however, does not fit the data, as it requires that the rate of aquation show both a first-order and a second-order dependence on hydrogen ion concentration.

The absence of a k_0 term (a least-squares analysis of the data yields $k_0 = 4 \times 10^{-7}\ sec^{-1}$ which is essentially zero within the errors of computation) is in agreement with the observation of Ashley and Lane[9] that in the trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ greater than 95% of the product is the cis isomer although at 50° the rate constant for isomerization of the trans isomer ($k = 1.07 \times 10^{-4}\ sec^{-1}$, pH 3) is only slightly larger than the rate constant for aquation of the cis isomer ($k = 0.85 \times 10^{-4}\ sec^{-1}$, the k_0 term at 50° from data in ref 5). The values of these two rate constants indicate that at 50° at least a considerable portion of the observed product of the isomerization in the absence of acid should be the monomalonate complex, $Cr(C_3H_2O_4)(H_2O)_4^+$. Since at least 95% of the

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

[10] Nitrate ion (as the sodium salt) appears to have no effect on the trans–cis isomerization rate for the oxalate system: K. R. Ashley and R. E. Hamm, *ibid.*, **4**, 1120 (1965).

isomerization product is the cis isomer, it is quite likely that the k_0 term reported in the literature is zero within the limits of experimental error.

The mechanism of aquation of the cis complex, we believe, parallels that of the corresponding oxalate complex, *i.e.*, a rapid protonation preequilibrium followed by rate-determining attack of water on the protonated intermediate. For both oxalate and malonate complexes, the values of the entropy of activation are compatible with processes in which the participation of a molecule of water in the rate-determining step is important. In the present study, the rate of aquation of the malonate complex was found to be approximately 20 times faster than that of the oxalate complex. This faster rate of aquation can be attributed to the greater basicity of the malonate ion, thus favoring the protonation preequilibrium step of the mechanism.

The possible mechanisms for the trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ are the same as those postulated for the analogous oxalate system[11] and are presented in Figure 1. The trigonal-twist mechanism[12] may be eliminated as a possible isomerization mechanism since the activation energy for this path has been estimated at 125 kcal/mol.[13] For the trans–cis isomerization of the trans oxalate complex, both mechanisms involving water exchange have been eliminated since at 25° the rate of the isomerization reaction is eighty times faster than the rate of water exchange.[11] Thus, for the trans–cis isomerization of the oxalate complex, only the ring-opening mechanism appears applicable.

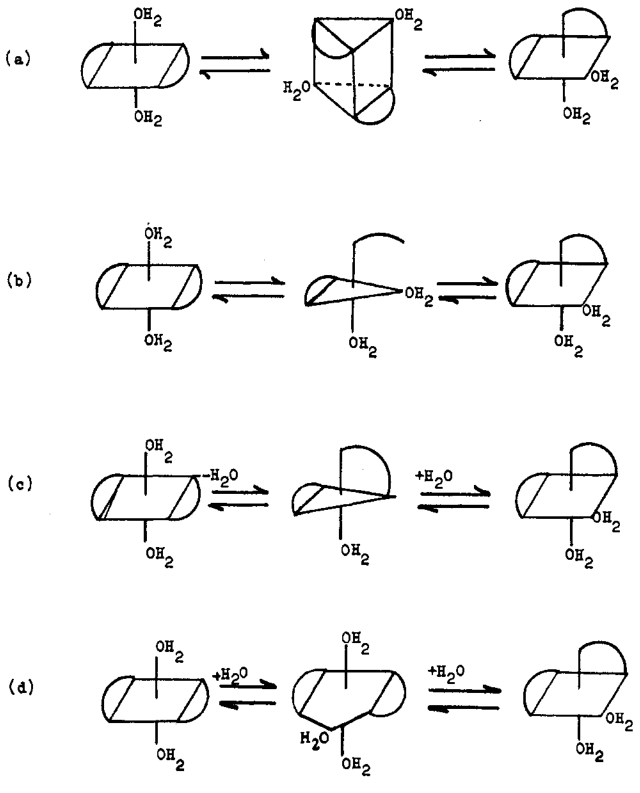

Figure 1.—Possible mechanisms for the trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$: (a) trigonal-twist mechanism; (b) ring-opening mechanism; (c) aquo ligand dissociation mechanism; (d) water-association mechanism.

That the trans–cis isomerization of the trans malonate complex may proceed by any of the last three mechanisms can be demonstrated by use of available rate data. The rate constants for water exchange of $Cr(H_2O)_6^{3+}$ and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ have been determined[11,14] at 25° to be 2.9×10^{-5} sec^{-1} and 7.8×10^{-6} sec^{-1}, respectively. It is not unreasonable to assume that the rate constant for water exchange of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ is approximately 10^{-6}–10^{-5} sec^{-1}. Hence, both mechanisms involving water exchange are possible according to the rate data. The positive ΔS^* value for the isomerization of the malonate complex would eliminate the water association mechanism since one would expect a negative entropy of activation upon formation of a seven-membered activated complex. Therefore, only the water-dissociation mechanism of the two water-exchange mechanisms appears to apply to the present case.

A comparison of the second formation constants of *cis*-bis(oxalato)diaquochromate(III) and *cis*-bis(malonato)diaquochromate(III) shows that the formation constant of the malonate complex is 4 times larger than that of the oxalate complex[15] under identical conditions. This indicates that malonate forms a more stable complex with chromium(III) than does oxalate. Since ring opening appears to be the rate-determining step for the isomerization of the trans oxalate complex and since the rate constant for this reaction at 25° is 6.24×10^{-4} sec^{-1},[8] the rate constant for malonate ring opening is expected to be lower than that obtained for oxalate ring opening. The rate constant for the trans–cis isomerization of the malonate complex at 25° is indeed less than that of the oxalate complex. The trans–cis isomerization of *trans*-bis(malonato)diaquochromate(III) could therefore proceed through the ring-opening mechanism or possibly a combination of the ring-opening and water-dissociation mechanisms. The positive entropy of activation favors ring opening as the rate-determining step.

In attempting to arrive at an understanding of the role which the anions play, it is difficult to separate salt effects, which imply a general ion atmosphere effect exerted by the anions, from chemical effects, which imply a well-defined participation by the anion in the activated complex, since the experiments were performed in solutions at high salt concentrations. An argument favoring the chemical interpretation is the result of the experiment carried out at 35° in a 1:1 mixture of lithium perchlorate–lithium nitrate. The observed rate constant is exactly what one would predict for a linear dependence of the rate constant on nitrate concentration based on the rate constants obtained in 1.00 *M* $LiClO_4$ and $LiNO_3$. A possible mode of action for the negative ion is that water in its hydration sphere is replaced by a water molecule oriented about the chromium(III) ion in the first hydration sphere, and the increased negative charge on the complex results in an overall rate increase for the isomerization reaction. It is extremely interesting that the order of effectiveness of the anions in promoting the trans–cis isomerization is the same order found by Plane and Taube[16] for pro-

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[11] H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsenges. Phys. Chem.*, **74**, 262 (1970).

[12] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[13] R. E. Hamm, R. Kollrack, G. L. Welch, and R. H. Perkins, *J. Amer. Chem. Soc.*, **83**, 340 (1961).

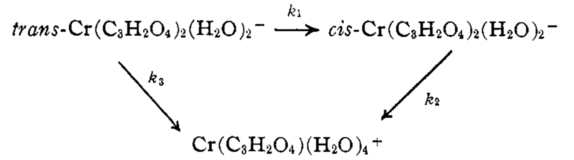
[14] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

[15] H. Muro and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, **39**, 1589 (1966).

[16] R. A. Plane and H. Taube, *J. Chem. Phys.*, **56**, 33 (1952).

moting the exchange of water between hexaaquochromium(III) and solvent. It is highly unlikely that the modes of action of the anions are the same in both cases since one involves a positively charged complex and the other a negatively charged species. The present study clearly indicates that nitrate only affects the entropy of activation for the isomerization reaction and the positive trend in this parameter is in complete agreement with the rationale presented above for the mode of action of the anions. Further investigations on similar systems are currently being studied.[17]

Since the observed product of the trans–cis isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ is the monomalonate complex of chromium(III), it was of interest to learn whether this is due to direct aquation of the trans isomer or results from the trans–cis isomerization of the trans isomer followed by aquation of the cis isomer which is formed.



The pathway (k_1, k_2) in which the trans isomer proceeds to the mono complex exclusively through the cis isomer is treated mathematically by Frost and Pearson.[18] For our system the rate constants were taken to be $k_1 = 0.4 \times 10^{-4} + 1.6 \times 10^{-4}[H^+]$ and $k_2 = 7.22 \times 10^{-4}[H^+]$, both for a temperature of 45°. The series-first-order equations were then solved at each of six acid concentrations for the maximum per cent cis isomer ($\beta_{max} = [cis]_{max}/[trans]_0$) as well as the per cent trans isomer (α) and per cent mono complex (γ) corresponding to β_{max}. Having determined these values at τ_{max} (related to the time required for β to reach its maximum), we can calculate the apparent molar extinction coefficient of the solution by using the equation $\epsilon_{app} = \alpha(\epsilon_{trans}) + \beta(\epsilon_{cis}) + \gamma(\epsilon_{mono})$, where ϵ_{app} should have its maximum value at $[cis]_{max}$. Table V presents the results of such a calculation. The results clearly indicate that at $[H^+] = 0.05$ and $0.10\ M$ the apparent molar extinction coefficients should exceed that for the mono complex alone. The absorbance data at these acid concentrations were used to determine the experimental apparent molar extinction coefficients. At $[H^+] = 0.10\ M$, ϵ_{app}(exptl) $= 31.6\ M^{-1}\ cm^{-1}$, and at $[H^+] = 0.05\ M$, ϵ_{app}(exptl) $= 36.0\ M^{-1}\ cm^{-1}$, both in excellent agreement with the calculated values. This strongly argues that the trans isomer proceeds to the monomalonate complex exclusively through the cis isomer.

TABLE V

CALCULATED APPARENT MOLAR EXTINCTION COEFFICIENTS FOR THE ACID-CATALYZED ISOMERIZATION OF *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ AS A FUNCTION OF ACID CONCENTRATION[a]

$[H^+]$, M	10^4k_1,[b] sec^{-1}	10^4k_2,[c] sec^{-1}	α	β_{max}	γ	ϵ_{app} (calcd)[d]	ϵ_{app} (exptl)
1.00	2.00	7.22	0.610	0.170	0.220	26.2	. . .
0.80	1.68	5.76	0.602	0.176	0.212	26.1	26.2
0.50	1.20	3.61	0.577	0.193	0.240	27.4	27.1
0.20	0.72	1.44	0.500	0.250	0.250	29.3	29.5
0.10	0.56	0.72	0.414	0.325	0.261	31.9	31.6
0.05	0.48	0.36	0.371	0.421	0.262	35.4	36.0

[a] Temperature 45°; λ 560 nm. [b] $k_1 = 0.4 \times 10^{-4} + 1.6 \times 10^{-4}[H^+]$. [c] $k_2 = 7.22 \times 10^{-4}[H^+]$. [d] At 560 nm, $\epsilon_{trans} = 17.5\ M^{-1}\ cm^{-1}$, $\epsilon_{cis} = 50.7\ M^{-1}\ cm^{-1}$, and $\epsilon_{mono} = 31.2\ M^{-1}\ cm^{-1}$.

No definitive statement can be made presently with regard to the origin of the catalytic effect of acid on the trans–cis isomerization; however, the presence of acid is expected to facilitate ring opening which is postulated as the rate-determining step for the isomerization reaction. The lower entropy of activation is surprising but is consistent with the participation of a cation in the rate-determining step.[10]

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[17] Preliminary results indicate that free oxalate anion increases the rate of isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$: K. R. Dekker, F. C. Maenpa, and D. H. Huchital, work in progress.

[18] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 166–169.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Electrochemical Studies of the Interactions of Riboflavin and of Its Reduction Products with Metal Ions in Dimethyl Sulfoxide

BY DONALD T. SAWYER* AND RICHARD L. McCREERY

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The nonaqueous electrochemistry of riboflavin and its metal ion interactions has been studied at a platinum electrode in dimethyl sulfoxide. Cyclic voltammetry, chronopotentiometry, and controlled-potential electrolysis have been used to establish that riboflavin is reduced in neutral solutions by two one-electron steps with a stable anion radical produced by the first of these; under acidic conditions it is reduced by a single two-electron process. The interactions of the riboflavin radical anion with iron(II), nickel(II), yttrium(III), lanthanum(III), thorium(IV), calcium(II), and sodium(I) ions have been investigated and the relative stabilities of the resulting complexes have been determined. Disproportionation of the radical anion appears to be promoted by the higher valent metal ions.

Introduction

The flavoproteins, which represent an important class of enzymes for biological oxidations, contain flavin mononucleotide (FMN) and flavin–adenine dinucleotide (FAD) as prosthetic groups with the isoalloxazine ring system (I) acting as the electron-transfer (or dehydrogenation) catalyst. In addition to FMN and FAD a number of flavoproteins also contain metal