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Kinetics of Complexation of Copper(I) Ions with Maleate and Fumarate in Aqueous Solutions. A Pulse Radiolytic Study

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Copper(I) ions form relatively stable complexes with organic compounds containing unsaturated carbon–carbon bonds.[1,2] These complexes have typical absorption bands in the near-uv region.[1,2] It seemed of interest to measure the kinetics of formation of such complexes. Thus, information concerning the rate of ligand exchange of copper(I) ions could be obtained. No data concerning the specific rate of ligand exchange of copper(I) have been reported to the best of our knowledge, though very high rates would seem reasonable for a monovalent d^{10} cation.

Results and Discussion

The pulse radiolytic technique was chosen for this study.[3] (The experimental procedure has been described elsewhere in detail.[4]) Nitrous oxide saturated solutions containing 1.0×10^{-2} *M* $CuSO_4$, 1.0 *M* methanol, and 1.0×10^{-5}–1.0×10^{-3} *M* of furmaric or maleic acid at pH 3.65 ± 0.05 were irradiated by 2.5×10^{19} eV/l. pulse. Reactions 1–10 might occur under

$$\mathrm{H_2O} \xrightarrow{e^-} \mathrm{e_{aq}}^-, \mathrm{H}, \mathrm{OH}, \mathrm{H_2}, \mathrm{H_2O_2} \qquad (1)$$

$$\mathrm{e_{aq}}^- + \mathrm{N_2O} + \mathrm{H_3O^+} \rightarrow \mathrm{OH} + \mathrm{N_2} \qquad k_2 = 8.7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{5} \qquad (2)$$

$$\mathrm{e_{aq}}^- + \mathrm{Cu_{aq}}^{2+} \rightarrow \mathrm{Cu_{aq}}^+ \qquad k_3 = 3.3 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{5} \qquad (3)$$

$$\mathrm{OH} + \mathrm{CH_3OH} \rightarrow \cdot\mathrm{CH_2OH} + \mathrm{H_2O} \qquad k_4 = 4.6 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{5} \qquad (4)$$

$$\mathrm{H} + \mathrm{CH_3OH} \rightarrow \cdot\mathrm{CH_2OH} + \mathrm{H_2} \qquad k_5 = 1.6 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{5} \qquad (5)$$

$$\mathrm{H} + \mathrm{Cu_{aq}}^{2+} \rightarrow \mathrm{Cu_{aq}}^+ + \mathrm{H_3O^+} \qquad k_6 = 5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{5} \qquad (6)$$

$$\cdot\mathrm{CH_2OH} + \mathrm{Cu_{aq}}^{2+} \rightarrow \mathrm{Cu_{aq}}^+ + \mathrm{CH_2O} \qquad k_7 = 1.1 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{6} \qquad (7)$$

$$\mathrm{Cu_{aq}}^+ + cis\text{- or } trans\text{-}\mathrm{HOOCCH{=}CHCOOH} \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} \underset{\mathrm{Cu}}{[\mathrm{HOOCCH{=}CHCOOH}]^+} \qquad (8)$$

$$\cdot\mathrm{H} + cis\text{- or } trans\text{-}\mathrm{HOOCCH{=}CHCOOH} \rightarrow \mathrm{HOOCCH_2\underset{\cdot}{C}HCOOH} \quad k_9 = 6 \times 10^8 \text{ and } 10^8\ M^{-1}\ \mathrm{sec}^{-1}\text{, respectively}^{7} \qquad (9)$$

$$\cdot\mathrm{CH_2OH} + \mathrm{HOCCH{=}CHCOOH} \rightarrow \mathrm{HOOCH(CH_2OH)\underset{\cdot}{C}HCOOH} \quad k_{10} = ? \qquad (10)$$

these conditions. (The yields of the radicals for eq 1 are[3] $G_{\mathrm{e_{aq}}^-} = 2.65$, $G_{\mathrm{OH}} = 2.65$, $G_{\mathrm{H}} = 0.6$, $G_{\mathrm{H_2O_2}} = 0.75$, and $G_{\mathrm{H_2}} = 0.45$ where *G* is defined as the number of molecules of product formed by absorption of 100 eV by the sample). Reaction 9 competes with reactions 6 and 5 for the hydrogen atoms, but even at the highest concentration of the unsaturated acid used, 1×10^{-3} *M*, less than 15% of the H atoms react via reaction 9. As the hydrogen atom yield is about 10% of the total radical yield, the maximal effect of reaction 9 is to decrease the Cu(I) concentration by 2%. Reaction 10 was found by blank experiments carried out in the absence of Cu^{2+} to be slow relative to reaction 7 and can be neglected.

Therefore all the radicals formed under the experimental conditions reduce $\mathrm{Cu_{aq}}^{2+}$ to $\mathrm{Cu_{aq}}^+$, and $G(\mathrm{Cu_{aq}}^+) = 5.85$. (A somewhat higher yield is plausible due to the high solute concentrations.[8]) The formation of $\mathrm{Cu_{aq}}^+$ ends within less than 2 μsec.

The absorption spectra of the products formed by the pulse were measured 50 μsec after the pulse and were stable for several minutes. The spectra are shown in Figure 1 with $\lambda_{\max}$(copper(I) maleate) 345 ± 10 nm, $\epsilon_{\max}$ 2800 ± 500 M^{-1} cm^{-1}, and $\lambda_{\max}$(copper(I) fumarate) 335 ± 10 nm, $\epsilon_{\max}$ 3000 ± 500 M^{-1} cm^{-1}. (In Figure 1 the observed optical densities, OD, and the molar absorption coefficients, ϵ, calculated from OD, the pulse intensity, and the total radical yield are shown. The figures given above are higher by 10% due to the fact that in solutions containing 1×10^{-3} *M* unsaturated carboxylic acid 10% of the Cu(I) is uncomplexed; see below.) No stable products having absorption in the 300–500 nm range were observed when either $\mathrm{Cu_{aq}}^{2+}$ or the unsaturated carboxylic acid were omitted from the solution or when malonic acid was used instead of the unsaturated carboxylic acid. The observed spectra are similar to those reported in the literature for the same complexes at pH O.[2] The small shifts in $\lambda_{\max}$ and the larger $\epsilon_{\max}$ observed in this study are attributed to the partial acid dissociation of the carboxylic groups at pH 3.65.

The kinetics of formation of the absorption due to the Cu(I) complex always obeyed a pseudo-first-order rate law. The observed specific rates of reaction, *k*, are plotted against the unsaturated carboxylic acid concentration, *C*, in Figure 2. From the intercept and the slope of the straight lines obtained k_8 and k_{-8} can be calculated. ($k = k_8C + k_{-8}$ is predicted from the suggested mechanism.[9]) Thus for maleic acid $k_8 = (2.0 \pm 0.4) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, $k_{-8} = (1.8 \pm 0.4) \times 10^5\ \mathrm{sec}^{-1}$, and $K_8 = k_8/k_{-8} = (1.1 \pm 0.3) \times 10^4\ M^{-1}$ and for fumaric acid $k_8 = (1.7 \pm 0.4) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, $k_{-8} = (2.4 \pm 0.4) \times 10^5\ \mathrm{sec}^{-1}$, and $K_8 = (7.1 \pm 2.0) \times 10^3\ M^{-1}$ are obtained. The high specific rates of reaction 8 are in agreement with the expected rates of water exchange of $\mathrm{Cu_{aq}}^+$ ions.

The stability constants of the complexes were also calculated from the effect of the unsaturated carboxylic acid concentration on the yield of the complex as measured by the optical density

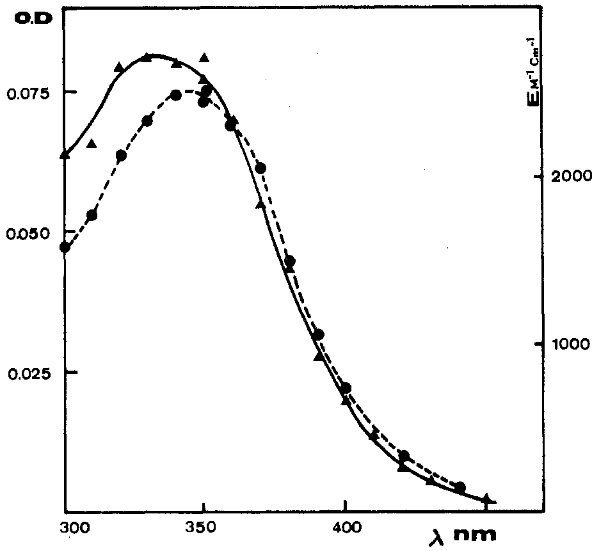

Figure 1. Absorption spectra of the complexes, measured 50 μsec after the pulse, with the solution composition of 1 × 10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol (N_2O saturation and pH 3.65 ± 0.05): ●, 1 × 10^{-3} *M* maleic acid; ▲, 1 × 10^{-3} *M* fumaric acid.

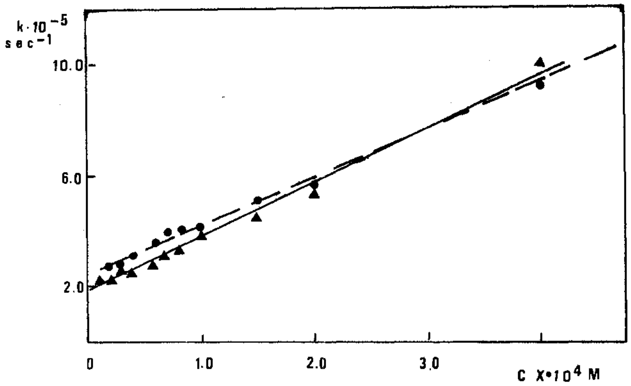

Figure 2. Dependence of the observed specific rates of reaction, *k*, on the unsaturated carboxylic acid concentration. Aqueous solutions containing 1 × 10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol (pH 3.65 ± 0.05 and N_2O saturation) at 22 ± 2° were used: ●, fumaric acid; ▲, maleic acid.

Table I. Stability Constants of Copper(I) with Maleic and Fumaric Acids[a]

	Maleic acid		Fumaric acid	
[C], *M*	OD	$10^{-4}K_8, M^{-1}$	OD	$10^{-3}K_8, M^{-1}$
1.0 × 10^{-5}	0.0100	1.3	0.0089	10.0
2.0 × 10^{-5}	0.0200	1.5	0.0147	9.6
3.0 × 10^{-5}	0.0240	1.5	0.0200	9.5
4.0 × 10^{-5}	0.0306	1.4	0.0262	10.0
6.0 × 10^{-5}	0.0401	1.4	0.0333	9.5
7.0 × 10^{-5}			0.0345	8.5
8.0 × 10^{-5}	0.0438	1.3	0.0378	8.8
1.0 × 10^{-4}	0.0481	1.2	0.0414	8.3
1.5 × 10^{-4}	0.0543	1.2	0.0488	7.9
2.0 × 10^{-4}	0.0621	1.3	0.0567	7.9
4.0 × 10^{-4}	0.0677	0.9	0.0718	9.1
7.0 × 10^{-4}	0.0759	1.1	0.0783	8.5
		Av 1.3		Av 9.0

[a] All solutions were N_2O saturated and contained 1 × 10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol at pH 3.65 ± 0.05; OD measurements were taken at 350 nm, 50 μsec after the end of the pulse. Accuracy of K_8 is ±20%. [C] is the concentration of the unsaturated carboxylic acid, at 22 ± 2° and $\mu = 0.04$.

at 350 nm. The results are summarized in Table I. [The calculation was carried out by assuming the value obtained for K_8 in the kinetic runs, and calculating the optical density for a solution in which 100% of the Cu(I) formed appears in the complex, OD_T, from K_8 and the measured OD in solutions for which $C = 7 \times 10^{-4}$ *M*, using the equation $OD_T = OD(1 + K_8C)/K_8C$. Using the value of OD_T K_8 was calculated for all other concentrations by applying the equation

$$K_8 = \frac{OD}{OD_T - OD}\,\frac{1}{C}$$

The average of these values of K_8 was used for a new calculation until a self-consistent value was obtained.] The average values for K_8 thus obtained, (1.3 ± 0.2) × 10^4 and (9.0 ± 2.0) × 10^3 M^{-1}, for maleic and fumaric acid, respectively, are in good agreement with those obtained from the kinetic study.

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Registry No. Copper(I) fumarate, 54964-69-1; copper(I) maleate, 55028-63-2.

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(9) The reviewers have requested the derivation of the rate law. The reaction studied can be summed up as

$$A + B \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} C$$

where $[C]_{t=0} = 0$, $[A]_{t=0} = A^0$, and $[B] >> A^0$. Therefore $d[C]/dt = -d[A]/dt = k_8[A][B] - k_{-8}[C] = k_8[A][B] - k_{-8}(A^0 - [A]) = (k_8[B] + k_{-8})[A] - k_{-8}A^0$. Integration of this equation yields $-\ln\{(k_8[B] + k_{-8})[A] - k_{-8}A^0\} = (k_8[B] + k_{-8})t$ + constant. If the equilibrium concentrations are A^∞ and C^∞, respectively, then $k_8A^\infty[B] = k_{-8}C^\infty = k_{-8}(A^0 - A^\infty)$; $k_{-8}A^0 = (k_8[B] + k_{-8})A^\infty$. Therefore $-\ln\{(k_8[B] + k_{-8})[A] - (k_8[B] + k_{-8})A^\infty\} = (k_8[B] + k_{-8})t$ + constant *or* $-\ln([A] - A^\infty) = (k_8[B] + k_{-8})t$ + constant. Thus the observed rate constant k equals $k_8[B] + k_{-8}$.

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Crown Ethers in Inorganic Chemistry. Preparation and Characterization of the Group 6 Pentacarbonyl Hydroxides and Fluorides

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Crown ethers have been employed recently in organic chemistry to dissolve inorganic salts in nonpolar media and to thereby promote reactions that would either occur only slowly or not at all.[2-5] As yet, we know of no reports of their use *as an aid* in the synthesis of transition metal complexes. Depending upon the ring size of the crown ether, different cationic species may be complexed with varying degrees of efficiency.[2,3] Also, increasing the size and number of organic