Effect of Stabilizing Ligands on the Rate of Reaction of Cu^IL with $CCl_3CO_2^-$ in Aqueous Solutions. 1. L = HOOCCH═CHCOO$^-$

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Copper(I) complexes catalyze a variety of organic reactions which are of synthetic and of industrial importance.[1−3] Many of these processes are initiated by halide abstraction from aryl or alkyl halides. The halide abstraction reaction by the Cu(I) catalyst is considered to be the rate-determining step of these processes. The additions of organic polyhalides to alkenes are a good example for such reactions.[3] The detailed mechanism of these reactions is not fully understood; especially, the effects of ligands that stabilize copper(I) on the rates and mechanisms of the catalytic processes have not been studied in detail. Such studies are also expected to enable improvements of the catalytic processes. It seemed therefore of interest to study the kinetics of halide abstraction from alkyl halides by Cu(I).

The system chosen was the reaction of Cu_{aq}^+ with Cl_3CCOO^-, TCA, in the presence of fumaric acid. The role of the fumaric acid is dual: (1) to form a stable complex with Cu(I)[4] and thus stabilize Cu(I) in aqueous solutions; (2) to simplify the spectrophotometric monitoring of the rate of reaction of the Cu(I) given that the Cu^I(fumaric acid) complex has a strong absorption band in the near UV.[4]

The technique used was pulse radiolysis. The experimental procedure has been described elsewhere in detail.[5] When N_2O-saturated aqueous solutions at pH 3.0 containing 5×10^{-2} $mol{\cdot}dm^{-3}$ $CuSO_4$, 1 $mol{\cdot}dm^{-3}$ CH_3OH, and $(0.1-5) \times 10^{-3}$ $mol{\cdot}dm^{-3}$ fumaric acid are irradiated, all the primary free radicals are transformed via reactions 1−4:

$$^{\bullet}OH/^{\bullet}H + CH_3OH \rightarrow {}^{\bullet}CH_2OH + H_2O/H_2 \qquad k_{OH} = 4.6 \times 10^8\ mol^{-1}{\cdot}dm^{-3}{\cdot}s^{-1},^{4}\ k_H = 1.6 \times 10^6\ mol^{-1}{\cdot}s^{-1\ 4} \quad (1)$$

$$^{\bullet}CH_2OH + Cu_{aq}^{2+} \rightarrow Cu_{aq}^{+} + CH_2O \qquad k = 1.1 \times 10^8\ mol^{-1}{\cdot}dm^3{\cdot}s^{-1\ 4} \quad (2)$$

$$e_{aq}^{-} + Cu_{aq}^{2+} \rightarrow Cu_{aq}^{+} \qquad k = 3.3 \times 10^{10}\ mol^{-1}{\cdot}dm^3{\cdot}s^{-1\ 4} \quad (3)$$

$$Cu_{aq}^{+} + HOOCCH{=}CHCOO^- \rightleftharpoons Cu^I(HOOCCH{=}CHCOO^-) \qquad k_4 = 1.7 \times 10^9\ mol^{-1}{\cdot}dm^3{\cdot}s^{-1},^{4}\quad k_{-4} = 2.4 \times 10^5\ mol^{-1}{\cdot}dm^3{\cdot}s^{-1}\ (pH\ 3.65)^4 \quad (4)$$

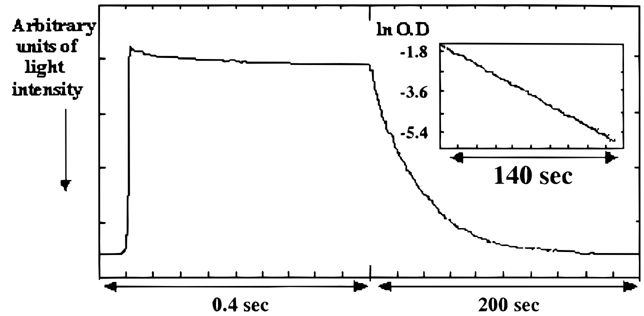

Figure 1. Computer output of light intensity vs time. Solution composition: N_2O saturated, containing 5×10^{-2} $mol{\cdot}dm^{-3}$ $CuSO_4$, 1×10^{-3} $mol{\cdot}dm^{-3}$ fumaric acid, 1 M CH_3OH, and 2.5×10^{-2} $mol{\cdot}dm^{-3}$ Cl_3CCO_2H at pH 3.0, measured at 350 nm; $[Cu^I]_0 = 10$ $\mu mol{\cdot}dm^{-3}$. Inset: Kinetics of disappearance of the complex Cu^I(HOOCCH═CHCOO$^-$), a fit to a first-order rate law.

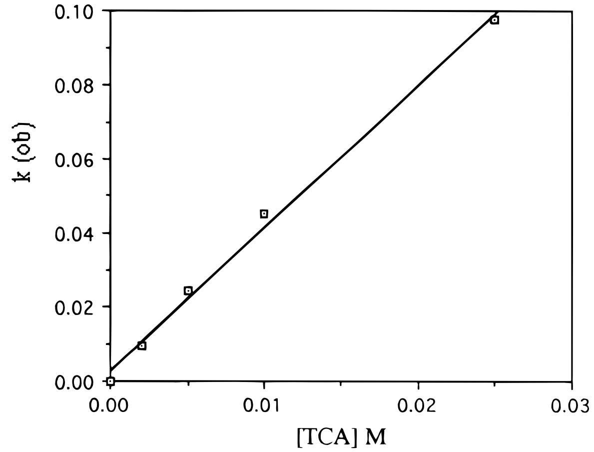

Figure 2. Dependence of the rate of the decomposition of Cu^I(HOOCCH═CHCOO$^-$) on $[Cl_3CCO_2^-]$. Solution composition: N_2O saturated, containing 5×10^{-2} $mol{\cdot}dm^{-3}$ $CuSO_4$, 2×10^{-4} $mol{\cdot}dm^{-3}$ fumaric acid, 1 M CH_3OH, and $(0.1-2.5) \times 10^{-2}$ $mol{\cdot}dm^{-3}$ Cl_3CCO_2H at pH 3.0.

A mixture of Cu_{aq}^+ and Cu^I(fumaric acid) results.[4] A small portion of this mixture reacts with the H_2O_2 formed by the pulse, but the excess Cu(I) survives.[4] The mixture of Cu_{aq}^+ and Cu^I(HOOCCH═CHCOO$^-$) ($K = 8.7 \times 10^3$ $mol^{-1}{\cdot}dm^3$ at pH 3.0)[4] thus reaches equilibrium according to eq 4 within less than 50 μs after the pulse. The complex has an absorption band with λ_{max} at 346 nm.[4] When $(0.2-2.5) \times 10^{-2}$ $mol{\cdot}dm^{-3}$ trichloroacetic acid is added to the solutions, the disappearance of Cu^I(HOOCCH═CHCOO$^-$) occurs within several hundred seconds, as shown in Figure 1.

The kinetics of this decomposition were followed spectrophotometrically, using the M → L charge transfer band of the complex Cu^I(HOOCCH═CHCOO$^-$). The kinetics of this process obeys a first-order rate law (Figure 1); *i.e.*, the reaction exhibits a first-order dependence on the concentration of Cu(I). The observed rate of this process is proportional to the concentration of trichloroacetate ions, Figure 2, and inversely proportional to the fumaric acid concentration, Figure 3. The rate is independent of the concentration of all other components of the solution (*i.e.* of $[CuSO_4]$, $[CH_3OH]$, and the pulse intensity).

The results clearly point of that the rate of reaction between Cu^I(HOOCCH═CHCOO$^-$) and Cl_3CCOO^- is considerably

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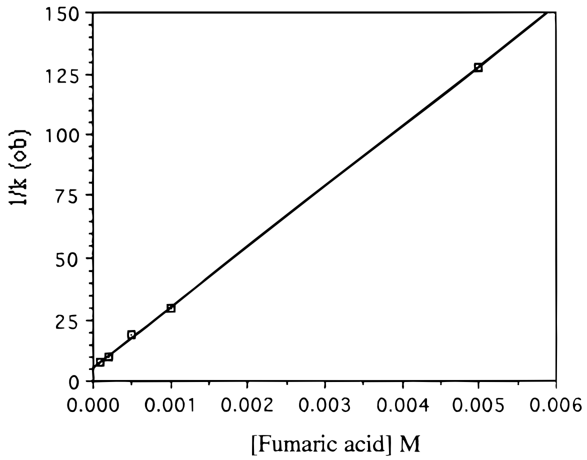

Figure 3. Dependence of the rate of the decomposition of $Cu^I(HOOCCH{=}CHCOO^-)$ on the fumaric acid concentration. Solution composition: N_2O saturated, containing 5×10^{-2} mol·dm^{-3} $CuSO_4$, $(0.1-5) \times 10^{-3}$ mol·dm^{-3} fumaric acid, 1 M CH_3OH, and 2.5×10^{-2} mol·dm^{-3} Cl_3CCO_2H at pH 3.0.

lower than that of the reaction between Cu_{aq}^+ and Cl_3CCOO^-. It was therefore decided to analyze the result by assuming that the reaction between the complex and TCA does not contribute to the observed kinetics. The kinetics are then described by the following equations:

$$Cu_{aq}^{+} + L \overset{K_1}{\rightleftharpoons} Cu^{I}L \qquad L = \text{fumarate}$$

$$Cu_{aq}^{+} + TCA \xrightarrow{k_2} P \qquad TCA = \text{trichloroacetate}, \quad P = \text{products}$$

$$K_1 = \frac{[Cu^IL]}{[Cu_{aq}^{+}][L]} \qquad [Cu(I)]_T = [Cu_{aq}^{+}] + [Cu^IL]$$

$$\frac{dP}{dt} = k_2[Cu_{aq}^{+}][TCA]$$

$$\frac{dP}{dt} = k_2\frac{[Cu(I)]_T}{1 + K_1[L]}[TCA] \quad [TCA] \gg [Cu(I)]_T$$

$$k_{ob} = \frac{k_2}{1 + K_1[L]}[TCA] \qquad [L] = \text{constant}$$

$$\frac{1}{k_{ob}} = \frac{1}{k_2[TCA]} + \frac{K_1}{k_2[TCA]}[L] \qquad [TCA] = \text{constant}$$

Indeed when k_2 is calculated from the slopes of the lines in Figure 2 and 3, as K_1 and [L] in Figure 2 and K_1 and [TCA] in Figure 3 are known, one obtains $k_2 = 10.3 \pm 2.0$ mol^{-1}·dm^3·s^{-1} and $k_2 = 13.5 \pm 2.0$ mol^{-1}·dm^3·s^{-1}, respectively. A calculation points out that $k(Cu_{aq}^+ + TCA)/k(Cu^IL + TCA) \geq 35$, as otherwise the line in Figure 3 would deviate significantly from linearity.

The reaction of Cu_{aq}^+ with TCA, reaction 5, yields the $^{\bullet}CCl_2CO_2^-$ radical which clearly is highly reactive. As all aliphatic radicals react with Cu_{aq}^+ and Cu_{aq}^{2+},[6,7] reactions 6 and 7 have to be considered as the next step. Reaction 6 is expected to be followed by reaction 8 in analogy to the mechanism of decompositions of $Cu^{II}{-}CH_2CO_2^-$ and $Cu^{II}{-}CH(CH_3)CO_2^-$.[7] If this is the mechanism, then the yield of Cl^- should be half the yield of Cu(I).

Reaction 7 is expected to be followed by reactions 9 (which is analogous to the mechanism of decomposition of $Cu^{III}{-}CH_2CO_2^-$ and $Cu^{III}{-}CH(CH_3)CO_2^-$ [6]) and 10.

$$Cu_{aq}^{+} + Cl_3CCOO^- \xrightarrow{k_2} (CuCl)^+ + {}^{\bullet}CCl_2COO^- \tag{5}$$

$$Cu_{aq}^{+} + {}^{\bullet}CCl_2CCO^- \rightarrow (Cu^{II}{-}CCl_2COO^-) \tag{6}$$

$$Cu_{aq}^{2+} + {}^{\bullet}CCl_2COO^- \rightarrow (Cu^{III}{-}CCl_2COO^-)^+ \tag{7}$$

$$(Cu^{II}{-}CCl_2COO^-) + H_3O^+ \rightarrow Cu_{aq}^{2+} + HCCl_2COO^- \tag{8}$$

$$(Cu^{III}{-}CCl_2COO^-)^+ \rightarrow Cu_{aq}^{+} + HOCCl_2COO^- \tag{9}$$

$$HOCCl_2COO^- + H_2O \rightarrow HOOCCOO^- + 2HCl \tag{10}$$

$$(Cu^{III}{-}CCl_2COO^-)^+ + Cu_{aq}^{+} \rightarrow (Cu^{II}{-}CCl_2COO^-) + Cu_{aq}^{2+} \tag{11}$$

This mechanism would predict a long chain reaction, as Cu_{aq}^+ is re-formed in reaction 10, and therefore a very high Cl^- yield. Therefore Cl^- was determine by ion chromatography. Cl^- is indeed a product of the process. Its yield equals half the yield of Cu(I), thus suggesting that the follow up reactions are (6) and (8).

However as $k(Cu_{aq}^{2+} + {}^{\bullet}CH_2CO_2^-) = 6.4 \times 10^8$ mol^{-1}·dm^3·s^{-1},[6] reaction 8 is also expected to be fast. Since under our experimental conditions $[Cu_{aq}^{2+}]/[Cu_{aq}^{+}]_T > 2.5 \times 10^3$, even if k_6 is diffusion controlled as expected,[7] $k_7[Cu_{aq}^{2+}] \gg k_6[Cu(I)]_T$. Therefore an alternative explanation to the lower yield of Cl^- has to be given. Reaction 9 is expected to be slow, in analogy to the rate of decomposition of $Cu^{III}{-}CH_2CO_2^-$,[6] so it is plausible that reaction 11 might occur. Reaction 11 was imitated by producing the transient complex $(Cu^{III}{-}CH_2COO^-)^+$ in the presence of Cu_{aq}^+ and measuring the kinetics of decomposition of this transient complex; indeed, Cu_{aq}^+ produces a significant acceleration. Thus the results are in accord with the observed process consisting of reaction 5 which is either followed by reactions 6 and 8 or by reactions 7 and 11.

The ratio of the process occurring via these two routes depends on the ratio $[Cu_{aq}^{+}]/[Cu_{aq}^{2+}]$. The final products are independent of the route occurring. Since reaction 5 is rate determining, the observed rate constant equals $2k_2$; therefore, $k_2 = 6.0 \pm 1.0$ mol^{-1}·dm^3·s^{-1}.

The source of the effect of fumaric acid on the rate of reaction has not been elucidated. In principle it might be due to the effect of furmaric acid on the redox potential of Cu(I) and/or on the electron density in the orbitals with σ and π symmetry of the Cu(I). In order to get a better understanding of the relative contributions of these effects on the reaction rate constant, experiments to check whether other ligands, *e.g.* CH_3CN, NH_3, and CO, have similar effects are in progress.

Conclusions

The observation that the $Cu^I(HOOCCH{=}CHCOO^-)$ complex reacts considerably slower than Cu_{aq}^+ with Cl_3CCOO^- suggests

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that it would be advantageous to work in the catalytic systems, which are all carried out in organic solvents, in the absence of a large excess of alkenes.

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