Ligand Effects on the Reactivity of $Cu^{I}L$ Complexes Towards $Cl_3CCO_2^-$

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The effect of the nature of the ligand L on the mechanism and kinetics of the reaction of $Cu^{I}L$ with $Cl_3CCO_2^-$ in aqueous solution is reported. The results demonstrate that the rate of the chlorine abstraction reaction, which is usually the rate-determining step in the process, is affected by: a) the redox potential of the $Cu^{II/I}L$ couple, b) the hybridization on Cu^{I} in the $Cu^{I}L$ complex, c) steric hindrance, d) electron density on the central Cu^{I} cation, at the binding site of the chlorine atom to be abstracted. Measurement of $\Delta V^{\neq}$ for the chlorine abstraction step indicates that this reaction proceeds by the inner-sphere mechanism, as expected. When the redox potential of the $Cu^{II/I}L$ couple is considerably cathodically shifted the transient complex $LCu^{II}{-}CCl_2CO_2^-$ is relatively long-lived.

Introduction

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 believed to be the rate-determining step of these processes. The addition of organic polyhalides to alkenes is a good example of such reactions.[3] The detailed mechanisms of these reactions have not been fully elucidated. Due to the low solubility of Cu^{I} halides and to the disproportionation of Cu^{+}_{aq} the concentration of Cu^{I} species in these systems is usually very low. In principle the addition of appropriate ligands for Cu^{I}, e.g. CH_3CN,[4] alkenes[5] and NH_3 [5] increases the concentration of the Cu^{I} species in the system and is therefore expected to increase the rate of the catalytic process. Tri- and tetradentate ligands, which stabilize Cu^{I}, were indeed shown to accelerate catalytic processes.[6−8] However, these ligands might also affect the reactivity of the Cu^{I} complexes due to one, or more, of the following reasons:

1. If the stability constant of the Cu^{I} complex with the ligand is larger than that of the corresponding Cu^{II} complex then the redox potential of the $Cu^{II/I}$ couple is shifted anodically, i.e. the Cu^{I} complex is a weaker reducing agent than Cu^{+}_{aq}, and vice versa.
2. Ligands can slow down the rate of Cu^{I} reactions due to steric effects.
3. Ligands might impose a coordination geometry, which affects the energy of the transition state thus affecting the rate of the reaction.

The effect of ligands that stabilize copper(I) on the rates and mechanisms of the catalytic processes was not studied in detail. The effect of fumarate on the reaction of Cu^{+}_{aq} with Cl_3CCOO^- (TCA) was recently[6] studied. The results demonstrate that the rate of reaction between Cu^{I}-($HOOCCH{=}CHCOO^-$) and Cl_3CCOO^- is very slow. Cl^- is a product of the reaction, its yield equals half the concentration of $Cu^{I}L$. The general reaction mechanism is:

$$Cu^{+}_{aq} + L \rightleftarrows Cu^{I}L \tag{1}$$

$$Cu^{I}L/Cu^{+}_{aq} + Cl_3CCOO^- \rightarrow (LCu^{II}Cl)/(CuCl)^+ + {}^{\cdot}CCl_2COO^- \tag{2}$$

$k_2 = 6.0 \pm 1.0\ \text{M}^{-1}\text{s}^{-1}$ for Cu^{+}_{aq} and $k_2 < 0.015\ \text{M}^{-1}\text{s}^{-1}$ for $Cu^{I}(HOOCCH{=}CHCOO^-)$

$$Cu^{I}L/Cu^{+}_{aq} + {}^{\cdot}CCl_2COO^- \rightarrow (LCu^{II}{-}CCl_2CO_2^-)^-/(Cu^{II}{-}CCl_2CO_2^-) \tag{3}$$

$$(LCu^{II}{-}CCl_2CO_2^-)^-/(Cu^{II}{-}CCl_2CO_2^-) + H_3O^+ \rightarrow Cu^{2+}_{aq} + HCCl_2COO^- + L \tag{4}$$

$$(Cu^{II}L)^+/Cu^{2+}_{aq} + {}^{\cdot}CCl_2COO^- \rightarrow (LCu^{III}{-}CCl_2CO_2^-)/(Cu^{III}{-}CCl_2CO_2^-)^+ \tag{5}$$

$$(LCu^{III}{-}CCl_2CO_2^-)/(Cu^{III}{-}CCl_2CO_2^-)^+ + Cu^{I}L/Cu^{+}_{aq} \rightarrow (LCu^{II}{-}CCl_2CO_2^-)^-/(Cu^{II}{-}CCl_2CO_2^-) + Cu^{II}L^+/Cu^{2+}_{aq} \tag{6}$$

These results indicate that carrying out catalytic processes in the absence of a large excess of alkenes is desired. It seemed of interest to extend this study to the effect of other ligands on this reaction. For this purpose the following ligands were chosen:

1. CH_3CN, which is often used as a solvent for the catalytic processes.

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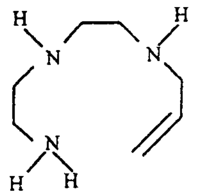
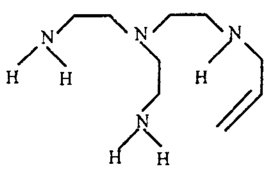
2. NH_3, a σ-donor ligand that shifts the redox potential of the Cu^{II}/Cu^{I} couple somewhat cathodically.

3. L^1 [7] and L^2,[8] ligands that were recently designed with the aim to stabilize Cu^I while cathodically shifting the redox potential of the Cu^{II}/Cu^{I} couple. It was therefore hoped that they will accelerate catalytic processes in which the Cu^I acts as a reducing agent in the rate determining step.



L^1



L^2

It was hoped that the choice of different types of ligands for this study might shed light on the factors affecting the rates of halide abstraction reactions by Cu^I complexes and thus enable the design of improved catalytic processes. In order to gain more insight on the detailed mechanism of the reaction of Cu^{+}_{aq} with $Cl_3CCO_2^-$ the volume of activation of this reaction was determined. The experimental conditions were identical to those used for the determination of the volume of activation for the reaction of Cu^{+}_{aq} with O_2,[9] i.e. He-saturated solutions containing 0.05 M $CuSO_4$, 1.0 M CH_3OH, 0.01 M Cl_3CCO_2Na, $1.0 \cdot 10^{-4}$ M $HOOCCH{=}CHCOO^-$ at pH = 3.0 were irradiated at different pressures.

Results and Discussion

In the following sections the effects of each ligand on the mechanism and kinetics of the reaction of Cu^I with CCl_3COO^- is described and discussed separately. Then the effects of the ligands are compared and general conclusions are derived.

CH_3CN

Acetonitrile forms the complexes $Cu(CH_3CN)_n^+$, n = 1−4, with Cu^I in aqueous solutions. In the concentration range of $(0.05-1.5) \cdot 10^{-1}$ M CH_3CN the main complexes present in the solutions are $Cu^I(CH_3CN)^+$ and $Cu^I(CH_3CN)_2^+$.

$$Cu^{+}_{aq} + CH_3CN \rightleftarrows Cu(CH_3CN)^+ \quad \log\beta_1 = 3.27^{[4a]} \tag{7a}$$

$$Cu^{+}_{aq} + 2\,CH_3CN \rightleftarrows Cu(CH_3CN)_2^+ \quad \log\beta_2 = 4.32^{[4b]} \tag{7b}$$

Since these complexes have no absorption bands in the near UV/Vis region, the effect of acetonitrile on the rate of the reaction of Cu^IL with $CCl_3CO_2^-$ was studied in the presence of low concentrations of fumaric acid. The Cu^I(fumaric acid) complex has a strong absorption band in the near UV region[10] and the ligand exchange reaction $Cu^{+}_{aq} + HOOCCH{=}CHCOO^- \rightleftarrows Cu^I(HO_2CCH{=}CHCO_2^-)$ is very fast.[11a] The addition of fumarate thus simplifies the use of spectrophotometry in order to follow the rate of reaction of Cu^I. The technique used was pulse radiolysis. When N_2O-saturated aqueous solutions at pH = 3.0 containing $5.0 \cdot 10^{-2}$ M $CuSO_4$, 1.0 M CH_3OH, $2.0 \cdot 10^{-4}$ M fumaric acid and $(0.05-1.5) \cdot 10^{-1}$ M CH_3CN are irradiated, all the primary radicals are transformed according reactions (7)−(11) to a mixture of Cu^{+}_{aq}, Cu^I(fumaric acid) and $Cu^I(CH_3CN)_n^+$.[6,12]

$$^{\cdot}OH/^{\cdot}H + CH_3OH \rightarrow {}^{\cdot}CH_2OH + H_2O/H_2 \quad k_{OH} = 4.6 \cdot 10^8\ \text{M}^{-1}\text{s}^{-1},^{[13]}\ k_H = 1.6 \cdot 10^6\ \text{M}^{-1}\text{s}^{-1\ [13]} \tag{8}$$

$$^{\cdot}CH_2OH + Cu^{2+}_{aq} \rightarrow Cu^{+}_{aq} + CH_2O + H_3O^+ \quad k = 1.6 \cdot 10^8\ \text{M}^{-1}\text{s}^{-1\ [10]} \tag{9}$$

$$e^{-}_{aq} + Cu^{2+}_{aq} \rightarrow Cu^{+}_{aq} \quad k = 3.3 \cdot 10^{10}\ \text{M}^{-1}\text{s}^{-1\ [13]} \tag{10}$$

$$Cu^{+}_{aq} + HOOCCH{=}CHCOO^- \rightleftarrows Cu^I(HOOCCH{=}CHCOO^-) \tag{11}$$

at pH = 3.65, $k_{11} = 1.7 \cdot 10^9\ \text{M}^{-1}\text{s}^{-1}$;[11] at pH =3.65, $k_{-11} = 2.4 \cdot 10^5\ \text{M}^{-1}\text{s}^{-1}$ [11]

This mixture reacts with the H_2O_2 formed by the pulse and the excess Cu^I is long-lived.[6,11] The mixture of Cu^{+}_{aq}, $Cu^I(HOOCCH{=}CHCOO^-)$ ($K = 8.7 \cdot 10^3\ \text{M}^{-1}$ at pH = 3.0 [11] and $Cu^I(CH_3CN)_n^+$ thus reaches equilibrium within less than 50 μs after the pulse.

The complex $Cu^I(HOOCCH{=}CHCOO^-)$ has an absorption band at λ_{max} = 346 nm.[11] When $(0.5-4.0) \cdot 10^{-2}$ M trichloroacetic acid is added to the solutions the disappearance of $Cu^I(HOOCCH{=}CHCOO^-)$ is observed within several hundreds of seconds.

The kinetics of this process were followed spectrophotometrically, using the M→L charge transfer band of the complex $Cu^I(HOOCCH{=}CHCOO^-)$. The kinetics obey a first-order rate law, 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 the trichloroacetate, Figure 1, and decreases with the increase in the acetonitrile concentration, Figure 2. In order to obtain an upper limit for the rate constant of the reaction between $Cu^I(CH_3CN)_2^+$ and Cl_3CCOO^-, the rate was measured in solutions containing high concentrations of acetonitrile [$(0.05-1.5) \cdot 10^{-1}$ M] in the presence of three different concentrations of fumarate ($2.0 \cdot 10^{-4}$, $6 \cdot 10^{-4}$ and $2 \cdot 10^{-3}$ M) at a constant concentration of Cl_3CCOO^- ($2.0 \cdot 10^{-2}$ M). The results are presented in Figure 2. The results demonstrate that the rate decreases as the concentration of acetonitrile is increased and seems to approach a limiting value, at [CH_3CN] = 0.15 M the same k_{obs} ($3.0 \cdot 10^{-3}$ s^{-1}) is measured for the three systems. In these systems at [CH_3CN] = 0.15 M, between 96.5% (for [fumarate] = $2.0 \cdot 10^{-3}$ M) and 99.5% (for [fumarate] = $2.0 \cdot 10^{-4}$ M) of the Cu^I is present in the form of the $Cu^I(CH_3CN)_2^+$,

$Cu^I(CH_3CN)_3^+$ and less than 0.2% Cu^+_{aq} in the latter system. The calculated rate of the reaction between $Cu^I(CH_3CN)_2^+$ and Cl_3CCOO^- is $k_{11} = 0.15$ M^{-1}s^{-1}, which is considerably higher than that which can be attributed to Cu^+_{aq} present in these solutions.

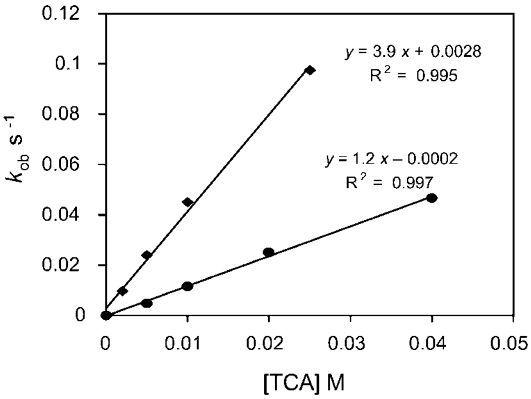


Figure 1. Dependence of the rate of the disappearance of Cu^I-($HOOCCH{=}CHCOO^-$) on [$Cl_3CCO_2^-$]; ■ N_2O saturated solutions, containing $5\cdot10^{-2}$ M $CuSO_4$, $2\cdot10^{-4}$ M fumaric acid, 1 M CH_3OH and $0.1-2.5\cdot10^{-2}$ Cl_3CCO_2H at pH = 3.0; • same solution but with 0.02 M CH_3CN

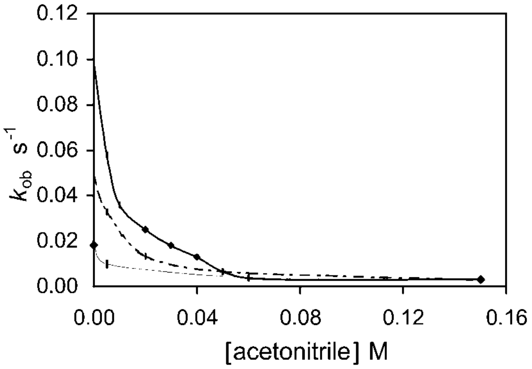


Figure 2. Dependence of the observed rate constant on [CH_3CN]; solution composition: N_2O saturated, containing $5\cdot10^{-2}$ M $CuSO_4$, $(0.2-2.0)\cdot10^{-4}$ M fumaric acid: ····· $2.0\cdot10^{-3}$ M, –·–·– $6.0\cdot10^{-4}$ M, —— $2.0\cdot10^{-4}$ M, 0–0.15 M CH_3CN, 1 M CH_3OH and $2.0\cdot10^{-2}$ Cl_3CCO_2H at pH = 3.0

$$Cu(CH_3CN)_n^+ + Cl_3CCOO^- \rightarrow {}^{\cdot}CCl_2CO_2^- + Cu(CH_3CN)_nCl^+ \quad (12)$$

As reaction (2) and/or (12) are the rate-determining steps the observed rate equals $2k_{12}$, therefore $k_{12} = 0.075 \pm 0.011$ M^{-1}s^{-1} for $Cu(CH_3CN)_2^+$. The reaction mechanism is analogous to reactions (1)–(6). Reaction (2) occurs via Cu^+_{aq} and/or via the $Cu^I(CH_3CN)_n^+$ reaction (12). The rate of reaction is independent of the concentration of all other components of the solution (i.e. of [$CuSO_4$], [CH_3OH]) and the pulse intensity. Analysis of the results presented in Figure 1, remembering that k [$Cu^I(HOOCCH{=}CHCO_2^-) + Cl_3CCO_2^-$] < 0.015 M^{-1}s^{-1} and k[$Cu^I(CH_3CN)^+_2 + Cl_3CCO_2^-$] = 0.075 M^{-1}s^{-1}, indicates that the contribution of Cu^+_{aq} to the observed rate is 0.24 s^{-1}, therefore a rate of 0.96 s^{-1} has to the attributed to the reaction of $Cu^I(CH_3CN)^+$ with $Cl_3CCO_2^-$.

The kinetics are then described by the following equations:

$Cu^+_{aq} + L \rightleftarrows Cu^IL$
(L = fumarate)
$Cu^+_{aq} + n\ CH_3CN \rightleftarrows Cu^I(CH_3CN)^{n+}$

$$Cu^I(CH_3CN)^+ + TCA \xrightarrow{k_2} P$$

(TCA = trichloroacetate; P = products)
$d[P]/dt = k_2[Cu^I]_T[TCA]$
$K_1 = [Cu^IL]/[Cu^+_{aq}][L]$, $\beta_1 = [Cu^I(CH_3CN)^+]/[Cu^+_{aq}][CH_3CN]$, $\beta_2 = [Cu^I(CH_3CN)_2^+]/[Cu^+_{aq}][CH_3CN]^2$
$[Cu^I]_T = [Cu^+_{aq}] + [CuL] + [Cu^I(CH_3CN)^+] + [Cu^I(CH_3CN)_2^+]$

Inserting the known values of K_1, β_1, β_2, [L] and [CH_3CN], one obtains $k_2 = 0.62 \pm 0.012$ M^{-1}s^{-1} for $Cu^I(CH_3CN)^+$.

NH_3

In order to measure the rate of reaction between $Cu^I(NH_3)_2^+$ and Cl_3CCOO^-, Ar-saturated solutions containing $5.0\cdot10^{-4}$ M or $1.0\cdot10^{-3}$ M Cu^I and 1.0 M NH_3 were prepared. Under these conditions the Cu^I complex present in the solution is $Cu^I(NH_3)_2^+$ due to equilibrium (13).

$$Cu^+_{aq} + 2\,NH_3 \rightleftarrows Cu^I(NH_3)_2^+ \qquad \log \beta_2 = 10.4^{[14]} \quad (13)$$

These solutions were mixed in a fast-mixing cell with Ar-saturated solutions containing $(0.1-1.0)\cdot10^{-2}$ M Cl_3CCOO^-. Soon after the mixing, the formation of an absorption band at λ = 620 nm, typical for $Cu^{II}(NH_3)_4^{2+}$,[5] was observed. The kinetics of this process obey a first-order rate law, i.e. the reaction exhibits a first-order dependence on the concentration of Cu^I. The observed rate is propor-

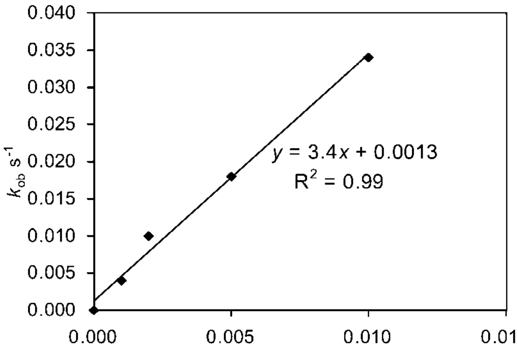


Figure 3. Dependence of the observed rate constant on [$Cl_3CCO_2^-$]; solution composition: Ar-saturated, containing $1.0\cdot10^{-3}$ M Cu^I, 1 M NH_3 and $(0.1-1.0)\cdot10^{-2}$ M $Cl_3CCO_2^-$ at pH = 11.0

tional to the concentration of the trichloroacetate, Figure 3. The kinetic equations that describe this system are as follows:

$$\begin{aligned}&Cu(NH_3)_2^+ + TCA \rightarrow P\\&\quad (P = \text{products})\\&\quad d[P]/dt = k_{14}[Cu(NH_3)_2^+][TCA],\ [TCA] >>\\&\quad [Cu(NH_3)_2^+],\ k_{obs} = k_{14}\,[TCA]\end{aligned} \qquad (14)$$

The rate constant is calculated from the slope of the line in Figure 3 as $k = 3.4 \pm 0.5$ $\text{M}^{-1}\text{s}^{-1}$. The yield of $Cu^{II}(NH_3)_4^{2+}$, measured in solutions containing an excess of Cu^I in comparison to Cl_3CCOO^-, is in agreement with the expected ratio $Cu^{II}(NH_3)_4^{2+}/TCA = 2$. These results are in agreement with the mechanism described in reactions (2)−(6). Equation (14a) is analogous to reaction (2).

$$Cu(NH_3)_2^+ + ClCCOO_2^- \rightarrow {}^{\cdot}CCl_2CO_2^- + Cu(NH_3)_2Cl^+ \qquad (14a)$$

As reaction (14a) is the rate-determining step the observed rate equals $2k_{14}$, therefore $k_{14a} = 1.7 \pm 0.25$ $\text{M}^{-1}\text{s}^{-1}$.

L^1

L^1 forms a complex with Cu^I according to Equation (15).

$$\begin{aligned}&Cu^+_{aq} + L^1 \rightleftarrows (CuL^1)^+\\&\quad \log K = 11.94^{[7]}\end{aligned} \qquad (15)$$

In order to measure the rate of the reaction between $(CuL^1)^+$ and Cl_3CCOO^-, Ar-saturated solutions containing $1.0{\cdot}10^{-3}$ M $(CuL^1)^+$ at pH = 7.0 were prepared. These solutions were mixed in a fast-mixing cell with Ar-saturated solutions containing $(0.16-2.0){\cdot}10^{-1}$ M Cl_3CCOO^-. After mixing, the disappearance of the absorption band at λ = 236 nm, due to $[CuL^1]^+$,[7] is observed. The kinetics of this process obey a first-order rate law for the concentration of Cu^I. The observed rate is proportional to the concentration of trichloroacetate, Figure 4. The rate constant calculated from the slope of the line in Figure 4, $k = 0.27 \pm 0.04$ $\text{M}^{-1}\text{s}^{-1}$. The yield of $[CuL^1]^{2+}$, measured in solutions containing an excess of Cu^I, is in agreement with the expected ratio $[CuL^1]^{2+}/TCA = 2$. Thus, for each mol TCA two mol of $[CuL^1]^+$ are transformed into $[CuL^1]^{2+}$.

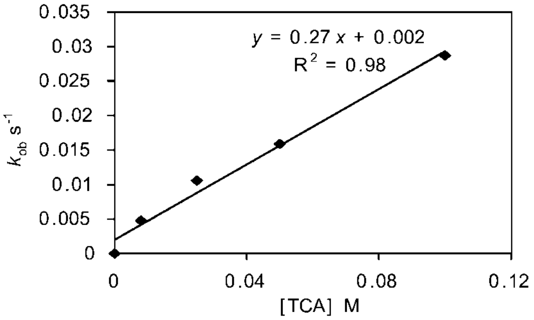


Figure 4. Dependence of the observed rate constant on $[Cl_3CCO_2^-]$; solution composition: Ar-saturated, containing $5.0{\cdot}10^{-4}$ M $(Cu^IL^1)^+$ and $(0.08-1.0){\cdot}10^{-1}$ M $Cl_3CCO_2^-$ at pH = 7.0

These results are in agreement with the mechanism described in reactions (2)−(6). Equation (16) is analogous to Equation (2).

$$(CuL^1)^+ + Cl_3CCOO^- \rightleftarrows {}^{\cdot}CCl_2CO_2^- + L^1Cu^{II}Cl^+ \qquad (16)$$

As reaction (16) is the rate-determining step the observed rate equals $2k_{16}$, therefore $k_{16} = 0.14 \pm 0.02$ $\text{M}^{-1}\text{s}^{-1}$.

L^2

L^2 forms a complex with Cu^I according to Equation (17).[8]

$$\begin{aligned}&Cu^+_{aq} + L^2 \rightleftarrows [CuL^2]^+\\&\quad \log K = 13.40\end{aligned} \qquad (17)$$

In order to measure the rate of the reaction between $(CuL^2)^+$ and Cl_3CCOO^-, the stopped-flow technique was used. Ar-saturated solutions containing $8.0{\cdot}10^{-4}$ M $(CuL^2)^+$ at pH = 6.5 were mixed with Ar-saturated solutions containing $(0.5-2.0){\cdot}10^{-1}$ M Cl_3CCOO^- and 0.5 M $NaClO_4$ at the same pH. After the mixing, two processes were observed (Figure 5). The first process, the formation of an absorption band at λ = 350 nm, occurs within a few seconds. The second process, the disappearance of the absorption band formed in the first process, occurs within several tens of seconds. The kinetics of the first process obey a first-order rate law in the concentration of Cu^I. The observed rate is proportional to the concentration of trichloroacetate (Table 1). The kinetics of the second process obey a first-order rate law and do not depend on the composition of the solutions, within the experimental error.

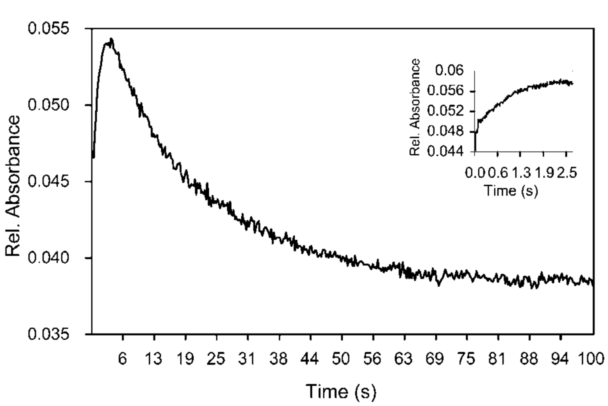


Figure 5. Computer output of the absorbance vs. time; experimental conditions: Ar-saturated solutions containing $8.0{\cdot}10^{-4}$ M $(CuL^2)^+$ at pH = 6.5 were mixed with Ar-saturated solutions containing 0.02 M $Cl_3CCO_2^-$ and 0.5 M $NaClO_4$ at the same pH measured at λ = 350 nm

Table 1. Observed rate constants in the L^2 system under different conditions; k_1: the observed rate constants of the first process (error limits ± 0.10); k_2: the observed rate constants of the second process (error limits ± 0.01)

	$[Cu^{I}L^2]^+$ $4.0 \cdot 10^{-4}$ M		$[Cu^{I}L^2]^+$ $4.0 \cdot 10^{-4}$ M $[Cu^{II}L^2]^{2+}$ $2.5 \cdot 10^{-4}$ M		$[Cu^{I}L^2]^+$ $4.0 \cdot 10^{-4}$ M $[Cu^{II}L^2]^{2+}$ $2.0 \cdot 10^{-3}$ M	
[TCA]	k_1 [s^{-1}]	k_2 [s^{-1}]	k_1 [s^{-1}]	k_2 [s^{-1}]	k_1 [s^{-1}]	k_2 [s^{-1}]
0.025	0.37	0.02	1.4	0.03	0.44	0.03
0.050	0.70	0.03	1.9	0.05	0.74	0.04
0.10	1.4	0.05	3.4	0.07	1.5	0.06

The effect of $[CuL^2]^{2+}$ on the rate of the processes was measured. Ar-saturated solutions containing $8.0 \cdot 10^{-4}$ M $[CuL^2]^+$ and $(0.5-4.0) \cdot 10^{-3}$ M $[CuL^2]^{2+}$ at pH = 6.5 were mixed with Ar-saturated solutions containing $(0.5-2.0) \cdot 10^{-1}$ M Cl_3CCOO^- and 0.5 M $NaClO_4$ at the same pH. The results are summed up in Table 1. The results show that the presence of $[CuL^2]^{2+}$ in similar concentrations as to those of $[CuL^2]^+$ accelerates the rate of the first process. However, in the presence of an excess of $[CuL^2]^{2+}$, in comparison to $[CuL^2]^+$, the rate of the first process is similar to that obtained in the absence of $[CuL^2]^{2+}$. The rate constant of the second process is independent of $[CuL^2]^{2+}$ within the experimental accuracy. The yield of Cl^- was determined and equals half the concentration of Cu^{I}. The yield of Cl^- is independent of the concentration of $[CuL^2]^{2+}$.

Based on these results and on the assumption that the absorption band at $\lambda = 350$ nm is due to the formation of the transient complex $L^2Cu^{II}-CCl_2CO_2^-$ (complexes with $Cu^{II}-C$ σ-bonds are known to absorb in this wavelength region[15]) it is reasonable to propose that the following reactions and kinetic equations describe the system:

$$\mathrm{Cu(I)L + RX} \xrightarrow{k_{\mathrm{I}}} \mathrm{Cu(II)L + {}^{\cdot}R + X^-} \qquad \text{(I)}$$

$$\mathrm{(L - L^2,\ X - Cl^-,\ RX - ClC(Cl)_2CO_2^-)}$$

$$\mathrm{{}^{\cdot}R + Cu(I)L} \xrightarrow{k_{\mathrm{II}}} \mathrm{LCu(II)\text{-}R} \qquad \text{(II)}$$

$$\mathrm{{}^{\cdot}R + LCu(II)\text{-}R} \xrightarrow{k_{\mathrm{III}}} \mathrm{Cu(I)L + R_2} \qquad \text{(III)}$$

$$\mathrm{{}^{\cdot}R + Cu(II)L} \xrightarrow{k_{\mathrm{IV}}} \mathrm{LCu(III)\text{-}R} \qquad \text{(IV)}$$

$$\mathrm{Cu(I)L + LCu(III)\text{-}R} \xrightarrow{\text{fast}} \mathrm{LCu(II)\text{-}R + Cu(II)L} \qquad \text{(V)}$$

$$\mathrm{LCu(II)\text{-}R + H_3O^+} \xrightarrow[\text{very slow}]{k_{\mathrm{VI}}} \mathrm{Cu(II)L + RH} \qquad \text{(VI)}$$

$$k_{\mathrm{VI}} = 0.04 \pm 0.02\ \mathrm{s^{-1}}$$

$$\mathrm{d[LCu(II)\text{-}R]/d}t =$$

$$k_{\mathrm{II}}[\mathrm{{}^{\cdot}R}][\mathrm{Cu(I)L}] - k_{\mathrm{III}}[\mathrm{{}^{\cdot}R}][\mathrm{LCu(II)\text{-}R}] + k_{\mathrm{IV}}[\mathrm{{}^{\cdot}R}][\mathrm{Cu(II)L}]$$

Applying the steady-state assumption for $[{}^{\cdot}R]$:

$$d[\cdot R]/dt = k_{I}[Cu^{I}L][RX] + (k_{II}[Cu^{I}L] + k_{III}[LCu^{II}-R] + k_{IV}[Cu^{II}L])[{}^{\cdot}R] = 0$$

$$[{}^{\cdot}R] = k_{I}[Cu^{I}L][RX]/(k_{II}[Cu^{I}L] + k_{III}[LCu^{II}-R] + k_{IV}[Cu^{II}L])$$

$$d[Cu^{II}-R]/dt = (k_{II}[Cu^{I}L] - k_{III}[Cu^{II}-R] + k_{IV}[Cu^{II}L])k_{I}[Cu^{I}L][RX]/(k_{II}[Cu^{I}L] + k_{III}[LCu^{II}-R] + k_{IV}[Cu^{II}L])$$

The latter rate law is in agreement with the experimental observations:

a) At low $[Cu^{II}L]$ the contribution of k_{IV} $[Cu^{II}L]$ to the nominator is larger than to the denominator as $(k_{II}[Cu^{I}L] + k_{III}[LCu^{II}-R]) > (k_{II}[Cu^{I}L] - k_{III}[LCu^{III}-R])$. It should be noted that $[Cu^{II}L]$ is always > 0 as it is formed in reaction (I).

b) At high $[Cu^{II}L]$, i.e. when $k_{IV}[Cu^{II}L] >> (k_{II}[Cu^{I}L] + k_{III}[LCu^{II}-R)$ the rate law is reduced to $d[Cu^{II}-R]/dt = k_{I}[Cu^{I}L][RX]$ and therefore it is concluded that the large error limit is due to the observation that $k_{IV}[Cu^{II}L]$ is still not large enough and that $[Cu^{II}L] > 0$ even when no $Cu^{II}L$ was added to the solutions.

$$(CuL^2)^+ + Cl_3CCOO^- \rightarrow {}^{\cdot}CCl_2CO_2^- + Cu(L^2)Cl^+ \quad k_{18} = 7.0 \pm 2.0\ M^{-1}s^{-1} \qquad (18)$$

Volume of Activation

The volume of activation of reaction (2) for Cu^+_{aq} was derived by measuring the pressure effect on the rate of this reaction in the presence of fumarate as the rate constant for the reaction of Cu^{I}(fumarate) with Cl_3CCOO^- is too slow to be measured.[6] The volume of activation was derived analogously to the method used for the reaction of Cu^+_{aq} with O_2.[9] The observed volume of activation $\Delta V_2^{\neq}(Cu^+_{aq})_{obs} = -9.9 \pm 1.0$ mL/mol. However, as $\Delta V_1^0 = -4.5 \pm 1.0$ mL/mol one calculates $\Delta V_2^{\neq}(Cu^+_{aq}) = -14.4 \pm 2.0$ mL/mol. This result clearly demonstrates that reaction (2) proceeds via an associative transition state in agreement with expectations.

Ligand Effects on the Reactivity of $Cu^{I}L$

Before analyzing the ligand effect on the reaction mechanism and kinetics, the thermodynamics of the chlorine abstraction, the rate-determining step in most of the systems studied, should be considered.

The ΔH of the reactions between Cu^I and Cl_3CCOO^- in aqueous solution can be roughly estimated using the equation $\Delta H = \Delta H(Cl-CCl_2) - \Delta H^0_f(Cl_g) - \Delta H^0_f(Cl^-_{aq}) + [\Delta H^0_f(Cu^{2+}_{aq}) - \Delta H^0_f(Cu^+_{aq})]$. Thus $\Delta H = 3.5$ kcal mol^{-1} and $\Delta H = -2.7$ kcal mol^{-1} is obtained for Cu^+_{aq} and $[Cu^IL^2]^+$, respectively. [The calculation is based on data from ref.[16] assuming that the solvation energy of the radical $^{\cdot}CCl_2CO_2^-$ does not differ considerably from that of Cl_3CCOO^-. The ΔH calculation for $(Cu^IL^2)^+$ is based on the redox potential of the complex assuming a small ΔS value for this redox process.]

The small free energy gain, if any, in these reactions in combination with the low rates for the self exchange rate of Cu^I [$k(Cu^+_{aq}/Cu^{2+}_{aq}) = 5 \cdot 10^{-7}$ M^{-1}s^{-1}][17] and the probably low self exchange rate for the couple $Cl_3CCOO^-/{}^-Cl_3CCOO^-$ suggests that reaction (2) proceeds by the inner sphere mechanism and not by the outer sphere mechanism. The large negative volume of activation measured for reaction (2) verified this expectation.

Since the Cu^I complexes act as reducing agents in these reactions with Cl_3CCOO^- it seemed reasonable to expect that the rate constants of these reactions will be correlated to the redox potential of the $Cu^{II/I}L$ couples. The measured rate constants of these reactions for the different complexes and their redox potentials are summed up in Table 2. The results point out that there is no simple correlation between the redox potentials of the Cu^I complexes and the observed rate constants. The results thus demonstrate that the rate of this reaction also depends on other factors; in the following paragraphs these effects are discussed.

Table 2. A comparison between the rate constants of the reaction of the Cu^I complexes with that of $Cl_3CCO_2^-$ along with their redox potentials

Complex	k [M^{-1}s^{-1}][a]	$E^0_{Cu(II)L/Cu(I)L}$ [V]
Cu^+_{aq}	6.0	0.15
$(Cu^IL^2)^+$	7.0	−0.12[b]
$Cu^I(NH_3)_2^+$	1.2	0.032[c]
$Cu^I(CH_3CN)^+$	0.62	0.34[c]
$(Cu^IL^1)^+$	0.14	−0.035[d]
$Cu^I(CH_3CN)_2^+$	0.075	0.41[c]
Cu^I(fumarate)$^+$ [e]	< 0.015	0.38[c]

[a] The error limits for the rate constants are ± 15%. [b] Data taken from ref.[8] [c] The redox potentials were calculated using the stability constants of the complexes (error limits ± 10%). [d] Data taken from ref.[7] [e] Data taken from ref.[4]

$Cu^I(CH_3CN)^+$ and $Cu^I(CH_3CN)_2^+$ are weaker reducing agents than Cu^+_{aq} and indeed their rates of reaction with Cl_3CCOO^- are considerably smaller than that of Cu^+_{aq}, as expected. (However, other factors might contribute to the low reactivity of $Cu^I(CH_3CN)_2^+$, see below.)

Though $(Cu^IL^1)^+$ is a better reducing agent than $Cu^I(NH_3)_2^+$ its reactivity is lower. This observation is probably due to the steric hindrance imposed by the ligand. The reaction of $(Cu^IL^2)^+$ with Cl_3CCOO^- probably first requires a ligand exchange step, most likely a release of the alkene bonding. Still the rate of this reaction is similar to that of Cu^+_{aq} and 45 times faster than that of $(Cu^IL^1)^+$ despite the steric hindrance that the L^2 ligand imposes on the central copper cation. This is attributed to the redox potential of $(Cu^IL^2)^+$.

$Cu^I(NH_3)_2^+$ is a considerably stronger reducing agent than Cu^+_{aq}; however, $Cu^I(NH_3)_2^+$ is considerably less reactive towards Cl_3CCOO^- than Cu^+_{aq}. This observation is attributed to the fact that when the linear $Cu^I(NH_3)_2^+$ complex, which has an sp hybridization, reacts with Cl_3CCOO^- in an inner sphere process the hybridization has to be changed, probably to an sp^3 one, a process which costs energy and therefore slows down the reaction. A similar argument probably contributes to the low reactivity of $Cu^I(CH_3CN)_2^+$. On the other hand Cu^+_{aq} is $Cu(H_2O)_4^+$,[18] i.e. it has an sp^3 hybridization and the reaction probably proceeds by a ligand exchange step followed by the chlorine abstraction.

The complex $Cu^I(HOOCCH{=}CHCOO^-)$ is the least reactive complex towards Cl_3CCOO^- though it is a better reducing agent than $Cu^I(CH_3CN)_2^+$. The low reactivity of $Cu^I(HOOCCH{=}CHCOO^-)$ is attributed to the fact that the Cu^I forms a d-π* complex with the fumarate. This type of binding reduces the electron density in the position *trans* to the ligand and therefore decreases the complex reactivity. A similar phenomenon was found for the reaction between $Cu^I(HOOCCH{=}CHCOO^-)$ and dioxygen.[9]

Finally it should be pointed out that if $[Cu^IL^2]^+$ would be used under catalytic conditions the rate-determining step would not be the chlorine abstraction reaction but the decomposition of $L^2Cu^{II}-R$ which might complicate the reaction mechanism as reactions of $^{\cdot}R$ with $L^2Cu^{II}-R$ are plausible.[8] The stabilization of $L^2Cu^{II}-R$ is attributed to the redox potential of the $(CuL^2)^{2+/+}$ couple. Thus, the results point out that the cathodic shift of the redox potential of the $Cu^{II/I}$ couple might in some cases complicate catalytic processes. The transient $L^2Cu^{II}-CCl_2CO_2^-$ is the most stable LCu^{II}-alkyl complex in aqueous solution, observed to date.[15,19]

Conclusion

The implications of the results, presented in this study, on catalytic processes catalyzed by Cu^I complexes, in which the redox step is the rate-determining step, are:

1. Solvents such as acetonitrile, that form complexes with Cu^I and anodically shift its redox potential, decrease the reactivity. Therefore, in catalytic systems, the use of solvents that do not form Cu^I complexes will considerably improve the rate of the processes.

2. The observation that the $Cu^I(HOOCCH{=}CHCOO^-)$ complex reacts considerably slower than Cu^+_{aq} with Cl_3CCOO^- suggests that it would be advantageous to work in catalytic systems, which are all carried out in organic solvents, in the absence of a large excess of alkenes.

3. Ligands such as L^1 and L^2, which have substituents that bind to the central cation only in its uncommon oxida-

tion state, might be used to improve the properties of processes that are redox-catalyzed.

4. Even ligands that accelerate the rate of the redox step might slow down the catalytic processes if they stabilize one of the intermediates in the catalytic process.

Experimental Section

Materials: All solutions were prepared from A. R. grade chemicals and from distilled water further purified by passing through a Milli Q Millipore setup, final resistivity > 10 MΩ/cm. L^1 and L^2 were synthesized and analyzed by procedures described in refs.[7,8] Cl^- was analyzed by using a Dionex ion chromatograph. Solutions of $[Cu^IL^1]^+$ and $[Cu^IL^2]^+$ were prepared by the comproportionation process, reaction (19). Solid copper was added to deaerated solutions containing $CuSO_4$ and excess of L^1 or L^2 at $pH = 6.5$.

$$Cu^0_{(s)} + (Cu^{II}L)^{2+}_{aq} + L \rightleftarrows 2\,(Cu^IL)^+ \tag{19}$$

$(L = L^1 \text{ or } L^2)$

Solutions of $Cu^I(NH_3)_2^+$ were prepared by comproportionation of $Cu(NH_3)_4^{2+}$ in 1 M NH_3.

Kinetic Measurements: Reactions with half lives longer than 2 s were carried out using a fast mixing cell (SFA-11 Rapid Kinetics Accessory Hi-Tech Scientific Ltd.), which was connected to a Hewlett Packard 8452A diode array spectrophotometer. Stopped flow experiments were carried out using an SX.18 Applied PhotoPhysics stopped flow that enables kinetic measurements of reactions with lifetimes of 2 ms. The detector was a 05−109 Spectra Kinetics Monochromator that enabled measurements in the range of 200−700 nm. The optical path was 10 nm.

Pulse-Radiolysis Experiments: These were carried out using the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1−1.5μs with a 200-mA current of 5-MeV electrons. The dose per pulse was 3−30 Gray. Irradiations were carried out in a 4-cm spectrosil optical cell, the analyzing light passed through the cell three times. A 150-W Xenon lamp produced the analyzing light. The experimental setup was identical to that described earlier in detail.[11] For dosimetry, an N_2O-saturated solution containing $1.0\cdot10^{-3}$ M KSCN was used. The yield of $(SCN)_2^{\cdot-}$ was measured by taking $\varepsilon_{475} = 7600$ $M^{-1}cm^{-1}$ and the dose per pulse was calculated assuming $G(SCN)_2^{\cdot-} = 6.0$[20] and an optical path of 12.3 cm. High-pressure pulse-radiolysis experiments for the determination of volumes of activation were carried out using the technique recently described in detail.[21]

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