

Gas-Phase Chemistry of Cu^+ with Alkyl Chlorides

Roger W. Jones and Ralph H. Staley*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received September 4, 1979

Abstract: Volatilization/ionization of copper metal by a pulsed laser is utilized as a source of Cu^+ for studies of its ion chemistry by ion cyclotron resonance spectroscopy. The gas-phase ion-molecule reactions of Cu^+ with methyl, ethyl, propyl, and butyl chlorides, chlorobenzene, and various chloro-substituted methanes and ethylenes are reported. Chloride transfer to Cu^+ is observed with a number of species for which this process is exothermic. Cu^+ reacts with alkyl halides by dehydrochlorination with retention of HCl or alkene by Cu^+ . Another dehydrochlorination and displacements follow to give a Cu^+ with two alkyl chloride and/or alkene ligands. Ligand exchange reactions of Cu^+ complexes with two ligands are readily observed, and equilibrium constants can be obtained. Relative ligand binding energies for the ethyl chloride system are $\text{MeCN} > \text{C}_2\text{H}_4 > \text{EtCl} > \text{HCl}$.

Investigations of the gas-phase ion chemistry of atomic metal cations with organic molecules provide insights into reaction pathways and can reveal novel structures of organometallics. Also, ligand binding energies and other thermochemical data for metal species can be obtained without the complication of solvent interactions. Thermal sources convenient for the production of alkali ions have facilitated their study by ion cyclotron resonance (ICR) spectroscopy¹ as well as with high-pressure mass spectrometry² and beam techniques.³ Studies of other metal cations have been limited for lack of suitable sources. A number of atomic metal cations produced as fragments in the electron impact ionization of volatile organometallics have been studied in ICR drift experiments by Ridge and co-workers.⁴ However, these studies are complicated by reactions with the parent organometallic, and studies with mixtures of two or more reactant organic neutrals or using pulsed ICR techniques are difficult at best. A pulsed laser volatilization/ionization source of atomic metal cations which is convenient for study of their gas-phase ion chemistry by ICR has recently been described by Freiser and co-workers.⁵ We report here studies using such a source to examine the gas-phase ion chemistry of Cu^+ with organic chlorides.

Experimental Section

General features of the instrumentation and techniques of ICR have been described elsewhere.^{6,7} Our instrument has a 12-in. pole piece electromagnet which can be operated to about 11.5 kG. The cell is similar to one described by McIver⁷ and has stainless steel plates spaced 2.5 cm apart. It is 7.8 cm long with one end open.

A capacitance bridge circuit with the cell as one of the capacitors is used to detect the ions.⁸ The signal from the balance point goes to a lock-in amplifier through an LM310 opamp. The lock-in reference output is gated to a pulse transformer which drives the bridge through LM310 opamps. The level on the balance capacitor side is adjusted to balance the bridge when there are no ions. Dc potentials for the cell plates are supplied through the transformer center tap and through a 1-M Ω resistor to the balance point. Output from the lock-in is processed by a boxcar amplifier. Magnetic field is scanned to obtain a mass spectrum.

Copper ions are produced by focusing the beam of a doubled Nd:YAG laser (λ 532 nm) through a sapphire window and the open end of the cell onto a 0.5-cm long, 16-gauge Cu wire target mounted on the far end of the cell. The laser is typically operated with 10-ns pulses of 30–50 mJ at 4–8 pps. The beam is focused to a 0.8-mm diameter spot at the target giving a power density of 600–1000 MW/cm². Volatilization/ionization of solids by pulsed laser sources has been previously utilized analytically with quadrupole mass spectrometers; the thermal plasma formed by the laser pulse produces kinetically hot monatomic ions.⁹ This is consistent with our observation that signal increases with trapping potential up to at least +5 V. Signal is independent of target potential below the drift plate potential but decreases with increasing target potential above the drift plate potential and is

cut off above the trapping potential. With a +5-V trapping potential the Cu^+ signal is about 100 times larger than typical signals obtained with electron-beam ionization. Stability improves to about $\pm 20\%$ from pulse to pulse and signal level approaches a more normal range as trapping potential is reduced to +1 V. Signal level and stability also vary with laser pulse energy. Above a threshold, signal level increases slowly with laser pulse energy but stability improves noticeably. We typically operate at 20% above threshold in laser energy and pulse the trapping plates to a lower value for 2 ms around the laser pulse to improve stability. The target potential is maintained below the drift plate potential.

A mass spectrum with the copper source and no added gases shows ⁶³Cu (69%) and ⁶⁵Cu (31%) in their natural ratio. No Cu^{2+} or Cu_2^+ is detected. Typically, studies of Cu^+ reactions are carried out by obtaining mass spectra at 50, 100, and 200 ms with about 4×10^{-6} Torr of added gas. Calibrant gases are sometimes added to check mass assignments. Reaction pathways are elucidated by obtaining double-resonance spectra for each species observed. Plots of variation of ion abundance with time are recorded for major species.

All chemicals were obtained from commercial sources and were used without further purification other than degassing by repeated freeze-pump-thaw cycles. Values for rate constants and product distributions for the reactions observed are included where possible as a guide to the practicing ion chemist. Absolute accuracies are limited to a factor of 2 by pressure measurements. Pressure was measured using a flange-mounted Bayard-Alpert ion gauge located 50 cm from the cell on the pump side. Relative accuracy of rate constants and product ratios is $\pm 15\%$ or better. All experiments were carried out at ambient temperature, which is typically 25 °C in our laboratory.

Results

Ethyl Chloride. Variation of ion abundance with time for the copper source in the presence of 4×10^{-6} Torr of ethyl chloride (EtCl) is shown in Figure 1. The initial reaction is dehydrochlorination, reactions 1 and 2. Both of the possible product channels are observed: elimination of C_2H_4 with retention of HCl by Cu^+ and elimination of HCl with retention of C_2H_4 by Cu^+ . In a second reaction step the HCl bound to Cu^+ in the product of reaction 1 is displaced by ethyl chloride, reaction 3. This reaction could also be dehydrochlorination with retention of C_2H_4 . However, some retention of HCl to give $\text{Cu}(\text{HCl})_2^+$ would also be expected. Since no $\text{Cu}(\text{HCl})_2^+$ is observed, we infer that reaction 3 is predominantly displacement. The product of reaction 2, $\text{Cu}(\text{C}_2\text{H}_4)^+$, also reacts with a second ethyl chloride, reactions 4, 5, and 6. Displacement, reaction 4, and dehydrochlorination with retention of HCl, reaction 5, cannot be distinguished since both the reactants and products are structural isomers having the same mass. The other dehydrochlorination product, $\text{Cu}(\text{C}_2\text{H}_4)_2^+$, obtained by retention of C_2H_4 , reaction 6, is observed in this case and amounts to about 5% of the total $\text{CuC}_2\text{H}_5\text{Cl}^+$ signal from the $\text{Cu}(\text{EtCl})^+$ and $\text{Cu}(\text{C}_2\text{H}_4)(\text{HCl})^+$ products of reactions 3, 4,

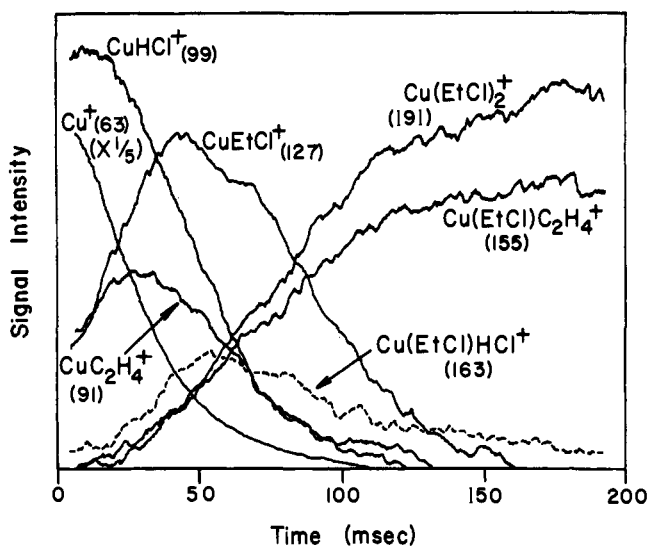


Figure 1. Variation of ion abundance with time following a 50-mJ, 10-ns laser pulse focused onto a copper wire target in the presence of 4×10^{-6} Torr of ethyl chloride (EtCl). The *m/e* value for the isotopic peak which was followed for each ion species is given in parentheses.

and 5. If the same product ratio applies for reactions 5 and 6 as does for reactions 1 and 2, and if no $\text{Cu}(\text{C}_2\text{H}_4)^+$ reacts by displacement, reaction 4, then $\text{Cu}(\text{C}_2\text{H}_4)_2^+$ should amount to 7% of $\text{CuC}_2\text{H}_5\text{Cl}^+$. This is about equal to the amount observed. $\text{Cu}(\text{C}_2\text{H}_4)^+$ thus appears to be reacting mainly by dehydrochlorination, but some displacement cannot be excluded. The $\text{Cu}(\text{C}_2\text{H}_4)_2^+$ product of reaction 6 does not react further. Reaction of the $\text{Cu}(\text{EtCl})^+$ and $\text{Cu}(\text{C}_2\text{H}_4)(\text{HCl})^+$ products of reactions 3, 4, and 5 again presents some ambiguities. It appears that the $\text{Cu}(\text{EtCl})^+$ from reactions 3 and 4 reacts by another dehydrochlorination, reactions 7 and 8, and that the $\text{Cu}(\text{C}_2\text{H}_4)(\text{HCl})^+$ from reaction 5 reacts by displacement of HCl, reaction 9. The observed product ratio of 64% for reaction 7 and 36% for reactions 8 and 9 together (they cannot be distinguished) is in reasonable agreement with the product ratio of 59 and 41% predicted by this interpretation. EtCl displaces HCl in $\text{Cu}(\text{EtCl})(\text{HCl})^+$ to give $\text{Cu}(\text{EtCl})_2^+$, reaction 10, which does not react further. $\text{Cu}(\text{EtCl})(\text{C}_2\text{H}_4)^+$ does not react further. In summary, Cu^+ and Cu^+ with an EtCl or C_2H_4 ligand react with EtCl by dehydrochlorination with HCl and C_2H_4 retained in a ratio of about 3:1. Cu^+ with an HCl ligand reacts with EtCl by displacement of the HCl ligand. When two EtCl and/or C_2H_4 ligands are bound to Cu^+ , there is no further reaction. The total reaction rate constant for reactions 1 and 2 is $3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The subsequent reactions proceed at comparable rates.

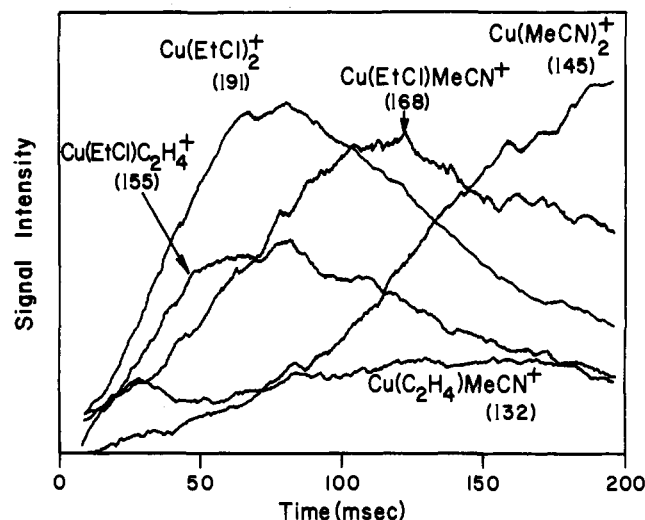
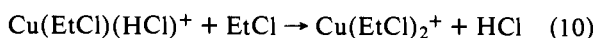
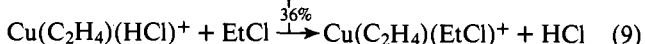
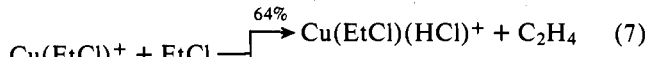
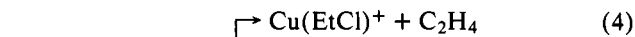
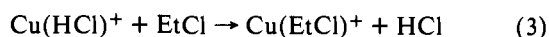
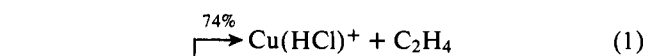
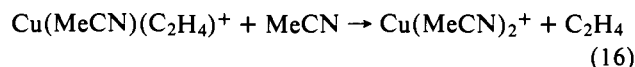
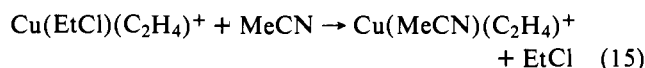
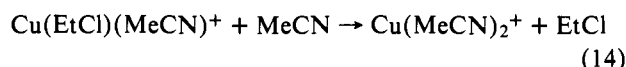
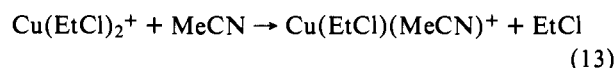
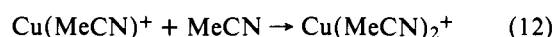
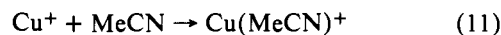
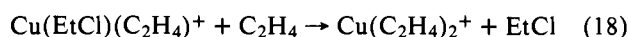
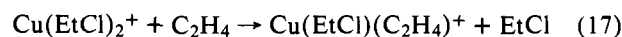


Figure 2. Variation of ion abundance with time for the Cu^+ source with a 28:1 mixture of ethyl chloride and acetonitrile at a total pressure of 5.7×10^{-6} Torr. Following the initial reactions which produce $\text{Cu}(\text{C}_2\text{H}_4)(\text{EtCl})^+$ and $\text{Cu}(\text{EtCl})_2^+$, MeCN is seen to readily displace both C_2H_4 and EtCl intact. In $\text{Cu}(\text{C}_2\text{H}_4)(\text{EtCl})^+$, EtCl is preferentially displaced. The *m/e* value for the isotopic peak which was followed for each species is given in parentheses.

Mixtures of ethyl chloride with acetonitrile (CH_3CN) were also studied. Cu^+ reacts with acetonitrile alone by direct condensation; this occurs twice, reactions 11 and 12, and the final product $\text{Cu}(\text{MeCN})_2^+$ does not react further. The apparent rate constant at 6.5×10^{-6} Torr is $1 \times 10^{-10} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ for both reactions. Variation of ion abundance with time for a mixture with 5.5×10^{-6} Torr of ethyl chloride and 0.2×10^{-6} Torr of acetonitrile is shown in Figure 2. Reactions 1–10 proceed as in ethyl chloride alone to give $\text{Cu}(\text{EtCl})_2^+$ and $\text{Cu}(\text{EtCl})(\text{C}_2\text{H}_4)^+$. MeCN readily displaces both EtCl and C_2H_4 in these products to give $\text{Cu}(\text{MeCN})_2^+$ as the final product in the mixture, reactions 13–16. Attack of MeCN on $\text{Cu}(\text{EtCl})(\text{C}_2\text{H}_4)^+$ exclusively displaces EtCl to give $\text{Cu}(\text{MeCN})(\text{C}_2\text{H}_4)^+$, reaction 15. The double-resonance spectrum for $\text{Cu}(\text{EtCl})(\text{MeCN})^+$ shows no contribution from $\text{Cu}(\text{EtCl})(\text{C}_2\text{H}_4)^+$.



In a mixture with ethyl chloride, ethylene readily displaces EtCl in $\text{Cu}(\text{EtCl})_2^+$ and $\text{Cu}(\text{EtCl})(\text{C}_2\text{H}_4)^+$ to give $\text{Cu}(\text{C}_2\text{H}_4)_2^+$ as the final product, reactions 17 and 18. Cu^+ does not react with ethylene alone. Other reactions of ethylene with the intermediates in reactions 1–10 may also occur in processes which were not directly observed giving products which are also produced by other pathways.



Propyl and Butyl Chlorides. Chloride transfer is the major initial reaction for *n*-propyl chloride, isopropyl chloride, and

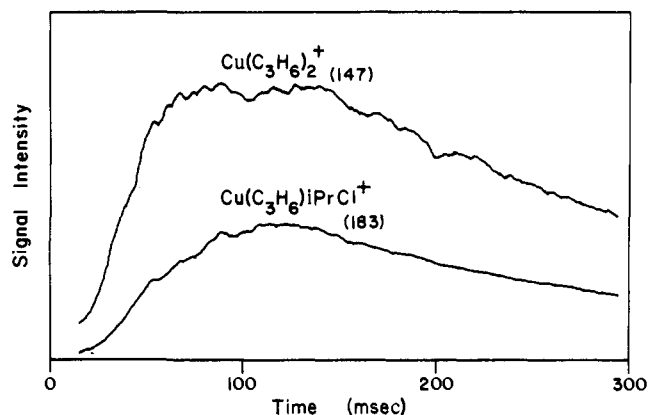
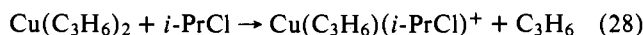
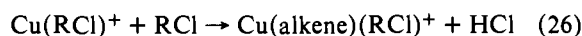
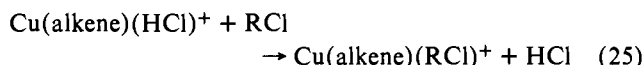
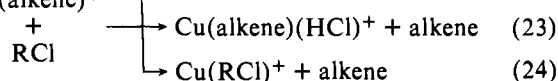
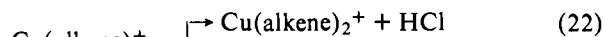
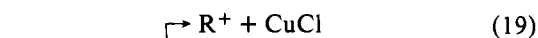
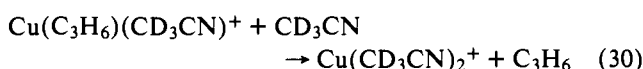
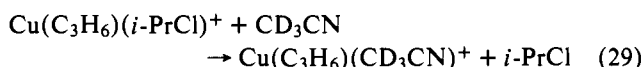


Figure 3. Variation of ion abundance with time for the Cu^+ source with a 4:1 mixture of isopropyl chloride (*i*-PrCl) and propylene (C_3H_6) at a total pressure of 7×10^{-6} Torr. Following initial reactions, the ligand exchange reaction $\text{Cu}(\text{C}_3\text{H}_6)(i\text{-PrCl})^+ + \text{C}_3\text{H}_6 \rightleftharpoons \text{Cu}(\text{C}_3\text{H}_6)_2^+ + i\text{-PrCl}$ reaches equilibrium; the equilibrium constant for an average of five determinations is $K = 7.2 \pm 1.2$. Only the final product species are shown. As in pure isopropyl chloride, $\text{Cu}(i\text{-PrCl})_2^+$ was not observed. The *m/e* value for the isotopic peak which was followed for each ion species is given in parentheses.

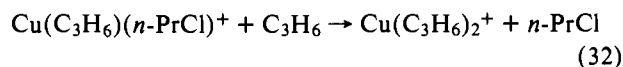
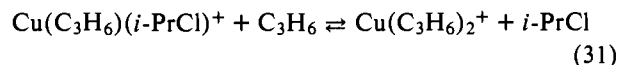
all four butyl chloride isomers. This amounts to 55% of total reaction in *n*-PrCl, 65% in *i*-PrCl, 66% in *n*-BuCl, 94% in *i*-BuCl, 81% in *sec*-BuCl, and 100% in *t*-BuCl. Further reactions of the product carbocations with the neutral alkyl chlorides occur in some cases but were not pursued in detail in this study. Dehydrochlorination of the propyl and butyl chlorides by Cu^+ , reactions 20 and 21, competes with chloride transfer in all of these systems except *t*-BuCl. Retention of the alkene, reaction 20, predominates in all cases. Retention of HCl, reaction 21, is observed only with *i*-PrCl, where it is 4% of the product distribution compared to 31% for $\text{Cu}(\text{C}_3\text{H}_6)^+$. Following the initial dehydrochlorination another dehydrochlorination and displacements lead to the final products $\text{Cu}(\text{alkene})_2^+$ and $\text{Cu}(\text{alkene})(\text{RCl})^+$, reactions 22–27. Again, retention of alkene, reaction 22, predominates, amounting to 50% for *n*-PrCl, 90% for *i*-PrCl, 75% for *n*-BuCl, and 75% for *sec*-BuCl. The relative product distribution for *i*-BuCl could not be determined for this sequence because of the low initial yield of dehydrochlorination, 6%. The $\text{Cu}(\text{HCl})^+$ produced in the *i*-PrCl system reacts to give $\text{Cu}(i\text{-PrCl})^+$, reaction 27, which reacts further in reaction 26. No $\text{Cu}(\text{HCl})_2^+$, $\text{Cu}(\text{RCl})(\text{HCl})^+$, or $\text{Cu}(\text{RCl})_2^+$ were observed in any of these systems. There is some ambiguity in these systems, as with EtCl, in determining whether some of the intermediate steps are dehydrochlorinations or displacements. For example, reactions 23 and 24 and 25 and 26 cannot be distinguished since both the products and reactants have the same mass. The overall rate constants for the initial reactions 19–21 together were measured to be about $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in all cases. Subsequent steps proceed at comparable rates. In *i*-PrCl there was a slow, $k = 0.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, displacement of C_3H_6 by *i*-PrCl in $\text{Cu}(\text{C}_3\text{H}_6)_2^+$, reaction 28. In the other systems the $\text{Cu}(\text{alkene})_2^+$ and $\text{Cu}(\text{alkene})(\text{RCl})^+$ products were stable.



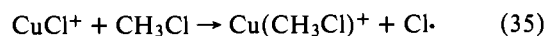
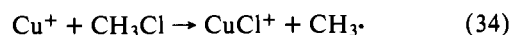
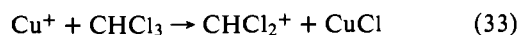
A mixture of isopropyl chloride with acetonitrile- d_3 (CD_3CN) was examined to establish whether the ligands in $\text{Cu}(\text{C}_3\text{H}_6)_2^+$ and $\text{Cu}(\text{C}_3\text{H}_6)(i\text{-PrCl})^+$ could be displaced intact. CD_3CN (*m/e* 44) was used instead of CH_3CN (*m/e* 41) to give a better mass separation from C_3H_6 (*m/e* 42). Both C_3H_6 and *i*-PrCl are readily displaced by CD_3CN , reactions 29 and 30. Other reactions of CD_3CN with intermediates in reactions 19–28 may occur but were not specifically identified because of overlapping isotope patterns and small mass separations in the species involved.



In a mixture with isopropyl chloride, propylene is seen to displace isopropyl chloride in $\text{Cu}(\text{C}_3\text{H}_6)(i\text{-PrCl})^+$, reaction 31. Double-resonance spectra show that this reaction proceeds in both directions. Equilibrium is approached after about 200 ms, Figure 3. Five mixtures having different isopropyl chloride: propylene presence ratios give an average equilibrium constant of $K = 7.2 \pm 1.2$. In a mixture with *n*-propyl chloride, propylene displaces *n*-PrCl in $\text{Cu}(\text{C}_3\text{H}_6)(n\text{-PrCl})^+$, reaction 32. This reaction proceeds only in the forward direction.

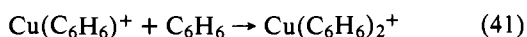
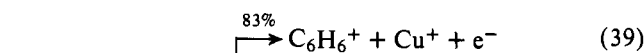
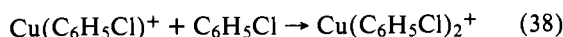
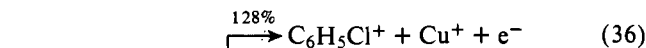


Other Chlorides. Cu^+ reacts rapidly with chloroform (CHCl_3) by chloride transfer, reaction 33; the rate constant is $5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. With methyl chloride there is a slow reaction to give CuCH_3Cl^+ ; the rate constant is $0.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Double resonance shows that this proceeds through CuCl^+ . A small peak is found for this species in the mass spectrum; the mass assignment of CuCl^+ (*m/e* 98) was checked by calibration against $\text{Cu}(\text{MeCN})^+$ (*m/e* 104) generated by addition of MeCN. These results suggest that the reaction sequence, reactions 34 and 35, is taking place. Other one-carbon chlorides that were studied were basically unreactive, although small amounts of the chloride transfer products could be detected after 200 ms. These amounted to 10% CF_2Cl^+ in CF_2Cl_2 at 5.4×10^{-6} Torr, 15% CHFC_2^+ in CHFC_2Cl at 2.3×10^{-6} Torr, and 3% CHCl_2^+ in CH_2Cl_2 at 3.3×10^{-6} Torr. Some (<5% conversion) $\text{Cu}(\text{CH}_2\text{Cl}_2)^+$ was also observed in the CH_2Cl_2 system.

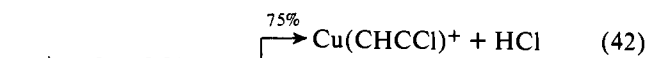


In phenyl chloride, significant production of the phenyl chloride parent cation is observed. Double resonance confirms that this is due to reaction by Cu^+ . We believe that this process is collisional ionization, reaction 36, as explained below in the Discussion section. Condensation of Cu^+ with phenyl chloride is also observed, reaction 37. Mass scans and double-resonance spectra showed no evidence for intermediates in this condensation. The rate constant for disappearance of Cu^+ in this

system, reaction 37, is $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $5 \times 10^{-6} \text{ Torr}$. A second condensation is observed to proceed at six times slower rate, reaction 38. The same chemistry is seen for Cu⁺ with benzene, reactions 39–41. The rate for reaction 40 is $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $4 \times 10^{-6} \text{ Torr}$, and reaction 41 is six times slower. The indicated product yields for reactions 36–40 are relative to the initial Cu⁺ abundance and are derived from the observed ratio of products at long times at $4 \times 10^{-6} \text{ Torr}$.



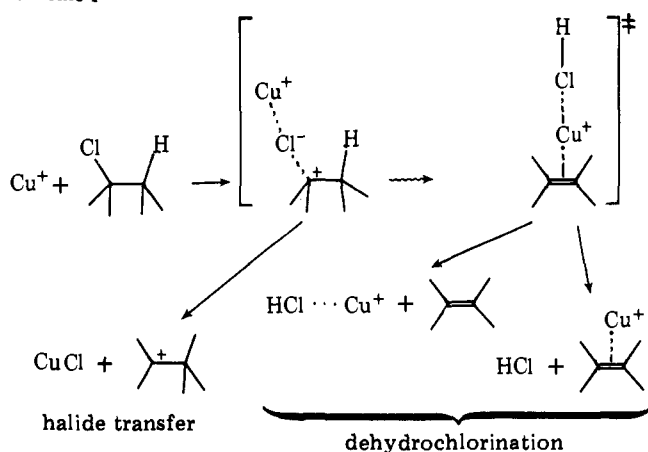
1,1-Dichloroethylene (CH_2CCl_2) reacts rapidly ($k = 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with Cu⁺ by dehydrochlorination and direct condensation, reactions 42 and 43. The double-resonance spectrum of $\text{Cu}(\text{CH}_2\text{CCl}_2)^+$ shows no contribution from $\text{Cu}(\text{CHCCl})^+$. A small amount (2%) of $\text{C}_2\text{H}_2\text{Cl}^+$ is also observed. The other chloro-substituted ethylenes are basically unreactive, although a small amount of conversion to products is observed after 200 ms: 10% $\text{Cu}(\text{C}_2\text{H}_3\text{Cl})^+$, $\text{Cu}(\text{C}_2\text{H}_2)^+$, and $(\text{C}_2\text{H}_3)_2\text{Cl}^+$ in $\text{C}_2\text{H}_3\text{Cl}$ at $4.5 \times 10^{-6} \text{ Torr}$ and 11% C_2Cl_4^+ and 5% C_2Cl_3^+ in C_2Cl_4 at $3.3 \times 10^{-6} \text{ Torr}$. No products were detected in *trans*-1,2-dichloroethylene or trichloroethylene.



Discussion

The observed chemistry of Cu⁺ with alkyl chlorides (RX) can be understood in terms of the reaction mechanism of Scheme 1, which was previously proposed to explain the reactivity of Li⁺ and NO⁺ with alkyl halides.^{1,10} Initial association of Cu⁺ with RX at the chloride site is followed by halide

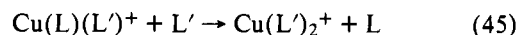
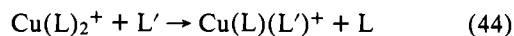
Scheme 1



transfer to give R⁺, if this is exothermic, or internal rearrangement to give a Cu(alkene)(HCl)⁺ complex which dissociates to Cu(alkene)⁺ or Cu(HCl)⁺. Retention of HCl is favored for EtCl, where it competes with retention of ethylene. For the propyl and butyl chlorides, retention of propylene or butylene is favored. These results suggest that the favored product is thermodynamically determined with a relative ligand binding energy order of HCl < RCl < alkenes, which is also consistent with the displacement results. EtCl is an exception where HCl is retained in preference to C₂H₄ in the initial reactions 1 and 2. This may be due either to a reversal of the thermodynamic preference with only one ligand on Cu⁺ or to kinetic factors.

Dehydrochlorination proceeds twice with Cu⁺. The complex formed after the first reaction step, Cu(alkene)⁺ or Cu(HCl)⁺, can react again with RX either by displacement to give Cu(RX)⁺ or by another dehydrochlorination. Some of the possible intermediate steps cannot be distinguished since the products have the same mass. However, results for ethyl, propyl, and butyl chlorides suggest that in the reaction of Cu⁺ complexes with one ligand, Cu(L)⁺, dehydrochlorination with retention of alkene predominates with L = alkene or RCl and displacement predominates with L = HCl, where it is exothermic.

Cu⁺ complexes with two ligands react only by ligand displacement, reactions 44 and 45, with more strongly bound ligands displacing more weakly bound ligands. The preferred direction of these reactions may be used to infer relative ligand binding energies. Results for EtCl imply a binding energy order MeCN > C₂H₄ > EtCl > HCl. Similarly, results for *i*-PrCl imply MeCN > C₃H₆ \approx *i*-PrCl > HCl. The *i*-PrCl-C₃H₆ ligand exchange reaction 31, between complexes containing at least one C₃H₆ ligand, Cu(C₃H₆)(*i*-PrCl)⁺ and Cu(C₃H₆)₂⁺, is observed to reach equilibrium with $K = 7.2 \pm 1.2$. This suggests that it may be possible to construct a scale of relative ligand binding energies for two-ligand Cu⁺ complexes by further studies of ligand exchange equilibria. Such scales have been obtained for H⁺,¹¹ Li⁺,¹ and cyclopentadienyl-Ni⁺¹² with one ligand. Indeed, further ligand exchange studies with Cu⁺ are being successfully pursued in our laboratory and have already related more than 40 molecules in a relative ligand binding energy ladder.¹³ A lower limit for the binding energy of HCl to Cu⁺ can be inferred from the occurrence of reaction 21 of $D(\text{Cu}^+ - \text{HCl}) \geq 16.4 \pm 1.1 \text{ kcal/mol}$.¹⁴



The observed chemistry for Cu⁺ is similar to that which has been previously reported for Li⁺, Na⁺, Fe⁺, Co⁺, and Ni⁺.¹⁴ Our results provide no evidence on the question of whether initial formation of the Cu(RX)⁺ is followed by insertion of Cu⁺ into the carbon-chlorine bond as proposed by Ridge⁴ for reaction of atomic transition metal cations with alkyl halides. Our results for reaction of Cu⁺ with *i*-PrCl agree with the preliminary results reported by Freiser et al., who obtained evidence for the occurrence of reactions 19–22, 24, and 27.⁵

Chloride transfer, reaction 19, is observed for Cu⁺ with *n*-PrCl, CHCl₃, *i*-BuCl, *n*-BuCl, *i*-PrCl, *sec*-BuCl, and *t*-BuCl. As indicated in Table I, chloride affinities of the corresponding ion for each of these species are less than the chloride affinity of Cu⁺ so that chloride transfer is exothermic. With EtCl, CHFCl₂, CF₂Cl₂, CH₂Cl₂, C₆H₅Cl, C₂H₃Cl, and CH₃Cl little or no reaction by chloride transfer is observed, as expected, since this is endothermic as shown by the relative chloride affinities in Table I. In addition, little or no reaction by chloride transfer was observed for Cu⁺ with CCl₂CH₂, *trans*-CHClCHCl, CHClCCl₂, or C₂Cl₄, indicating that chloride

Table I. Chloride Affinities of Ions Studied in This Work^a

R ⁺	$\Delta H_f(R^+)$	$\Delta H_f(RCl)$	$D(R^+-Cl^-)^i$
CH ₃ ⁺	264 ^b	-20.0 ± 0.5 ^g	228
C ₂ H ₃ ⁺	271 ^b	5.0 ⁱ	210
C ₆ H ₅ ⁺	275 ^c	12.2 ± 0.2 ^j	207
CH ₂ Cl ⁺	228.8 ± 0.4 ^d	-22.8 ± 0.3 ^g	196
CF ₂ Cl ⁺	130 ± 2 ^e	-117.5 ± 2 ^g	192
CHFCI ⁺	179 ± 5 ^f	-67.7 ± 3 ^g	191
C ₂ H ₅ ⁺	219 ^b	-26.7 ⁱ	190
Cu ⁺	260.7 ± 0.5 ^g	21.8 ± 0.4 ^g	183
n-C ₃ H ₇ ⁺	207 ^b	-31.0 ± 0.2 ^j	182
CHCl ₂ ⁺	211.2 ± 0.4 ^{d,h}	-24.6 ± 0.2 ^k	180
i-C ₄ H ₉ ⁺	198 ^b	-38.1 ± 2.0 ^j	180
n-C ₄ H ₉ ⁺	200 ^b	-35.1 ± 2.0 ^j	179
i-C ₃ H ₇ ⁺	191 ^b	-33.6 ± 1.0 ^j	169
sec-C ₄ H ₉ ⁺	183 ^b	-38.6 ± 2.0 ^j	166
t-C ₄ H ₉ ⁺	167 ^b	-43.7 ± 0.6 ^j	155

^a All data are given in kcal/mol for 298 K. ^b H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 2*, **6** (1977). ^c R. A. W. Johnstone and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1209 (1972). ^d A. S. Werner, B. P. Tsai, and T. Baer, *J. Chem. Phys.*, **60**, 3650 (1974). ^e J. M. Ajello, W. T. Huntress, and P. Rayerman, *ibid.*, **64**, 4746 (1976). ^f S. G. Lias and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **23**, 273 (1977). ^g Reference 14b. ^h F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972). ⁱ S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, New York, 1976. ^j Reference 14a. ^k A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 117 (1974). ^l $\Delta H_f^\circ(Cl^-) = -55.9 \pm 0.5$ from ref g.

affinities for the corresponding ions for each of these species are greater than $D(Cu^+-Cl^-) = 183$ kcal/mol.

The reaction of Cu⁺ with MeCl to give CuCl⁺, reaction 48, parallels reactions observed by Ridge et al. of Cr⁺, Fe⁺, Co⁺, Ni⁺, and Hg⁺ with MeI and Fe⁺ and Co⁺ with MeBr.⁴ We have also observed this process for Ti⁺ with MeCl.¹⁵ The subsequent apparent displacement of Cl· by MeCl to give CuMeCl⁺ is not paralleled by the subsequent chemistry in any of these other systems, however.

The reactivity observed in several of the systems examined in this work suggests that some of the Cu⁺ produced by the laser volatilization/ionization process is kinetically or internally hot enough to affect its reactivity. The reaction of Cu⁺ to produce C₆H₅Cl⁺ and C₆H₆⁺ in C₆H₅Cl and C₆H₆, reactions 36 and 39, can be best accounted for as collisional ionization since the ionization potential of Cu (7.726 eV) is less than those of C₆H₅Cl (9.07 eV) and C₆H₆ (9.25 eV).¹⁶ We rule out simple charge-transfer ionization because for this mechanism, as the reaction complex dissociates, the electron should jump to the species of lower ionization potential even if the two dissociating species are kinetically hot. The collisional ionization mechanism is supported by the observation that the total yield of products in these reactions is substantially above 100% when normalized to the reactant Cu⁺ abundance. The small amounts of parent ion and parent minus chloride ion seen in several of the chloro-substituted methanes and ethylenes

studied are probably due to collisional ionization and chloride-transfer processes induced by energetic Cu⁺ ions. However, the small extent of reaction in these systems readily distinguishes them from systems where exothermic chloride transfer takes place; these show rapid and *complete* reaction. The occurrence of endothermic reaction processes due to reaction by hot Cu⁺ does suggest caution in drawing thermochemical inferences from data obtained using the laser source with other metals where thermochemical values may not be so well established as for copper. However, no result in this study is contrary to thermochemical expectations, and the true exothermic processes are readily distinguished from endothermic processes proceeding by reaction with hot Cu⁺.

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