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Laser-Induced Fluorescence and Mass Spectrometric Studies of the Cu + HCl Reaction over a Wide Temperature Range. Formation of HCuCl

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The kinetics and products of the Cu + HCl reaction have been studied using high-temperature fast-flow reactors (HTFFR). The rate coefficient measurements were made using laser-induced fluorescence (LIF) of Cu atoms and yielded $k(680\text{--}1500\text{ K}) = 1.2 \times 10^{-10} \exp(-7719\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Product analysis was achieved by coupling a specially designed HTFFR to a chopped molecular beam quadrupole mass spectrometer. Those observations, which covered the approximately 1150–1500 K temperature range, showed formation of CuCl and the previously unknown species HCuCl. Confirmation of the latter assignment was made using DCI. Increasing pressure and decreasing temperature favor the HCuCl formation. These findings and this molecular structure are supported by *ab initio* calculations. These also indicate passage through a $\text{CuClH} \rightarrow \text{HCuCl}$ transition state as the rate-controlling step for formation of both products, in agreement with the observed pressure independence of the overall, Cu disappearance, rate coefficients.

Introduction

Emissions of hazardous polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) from waste incinerators have contributed to strong public opposition to waste incineration. It is of critical importance to assess the conditions that lead to formation of these compounds. Initially, it was suspected that Cl₂ can act as a chlorinating agent. However, since the thermal treatment of polycyclic aromatic compounds in the presence of chlorine does not lead to formation of PCDD/PCDFs, the catalytic role of metal ions in chlorine transfer was suspected. It was then shown in the laboratory that the presence of copper(II) chloride in oxygen-rich atmospheres leads to *de novo* synthesis of PCDD/PCDFs.^{1,2} Similar processes are considered responsible for their formation in the course of waste incineration, as was confirmed when high levels of PCDD/PCDFs were found in emissions of copper-contaminated bench-scale incinerators.³ On the other hand, under oxygen-deficient conditions, thermal treatment of PCDD/PCDF samples with copper powder results in dechlorination of polycyclic aromatic structures.⁴ It is thus important to obtain kinetic information on formation of copper chlorides at incinerator temperatures.

As the first in a series of such studies we report here on the gas-phase reaction



Rate coefficients for this reaction have been measured in a high-temperature fast-flow reactor using laser-induced fluorescence to monitor the relative concentration of the copper atoms (HTFFR-LIF apparatus). In addition, a recently completed high-temperature fast-flow reactor quadrupole mass spectrometer

(HTFFR-MS) facility has been used for the first time in this work. Apart from the expected product CuCl, a previously unknown species, HCuCl, was observed. The kinetic behavior of both product species has been studied. In addition to these experimental studies at Rensselaer, an *ab initio* study has been made at North Texas, which further elucidated the mechanistic studies and provided the likely structure for HCuCl.

Technique

HTFFR-LIF. The HTFFR-LIF technique and the data analysis procedures have been discussed previously.^{5–7} In the form of the apparatus used here, a vertical quartz reaction tube (60 cm long, 2.2 cm i.d.) was radiatively heated by two horizontal columns of resistively heated SiC rods inside an insulated, water-cooled vacuum housing. Cu atoms were vaporized from Cu powder contained in a resistively heated alumina crucible and entrained by Ar bath gas. Downstream from the Cu source, oxidant, (HCl)/Ar mixtures at 4%–9% of the main Ar volume flow rate were introduced through a movable quartz ring inlet. The relative concentrations of Cu atoms were measured 10 or 20 cm downstream from this inlet through windows in the vacuum housing facing openings in the reaction tube. The laser system employed was a pulsed Lambda Physik EMG 101 excimer/FL 2002 dye laser in combination with a KDP doubling crystal. Fluorescence was generated using the $\text{Cu}(^2\text{S}_{1/2} \text{ to } ^2\text{P}_{3/2})$ transition at 324.76 nm and observed through a 324.7 nm (2.5 nm full width at half-maximum) interference filter. The fluorescence intensity was measured by an EMI 9813QA photomultiplier tube, connected to a Data Precision Analogic 6000/620 100 MHz transient digitizer.

Rate coefficient measurements were made under pseudo-first-order conditions, $[\text{Cu}] \ll [\text{Ox}] \ll [\text{Ar}]$, in the stationary inlet mode.⁷ Rate coefficients, k_i , for each temperature, pressure, and average velocity were obtained by using five different oxidant concentrations providing a variation by a factor of 5. k_i

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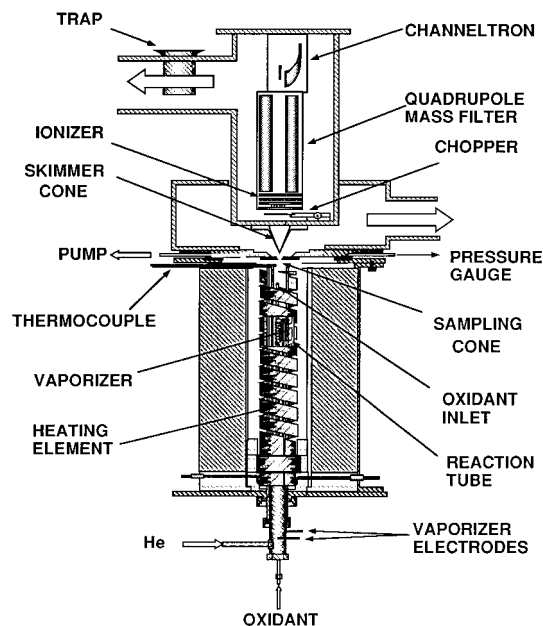


Figure 1. Schematics of the HTFFR-MS apparatus.

and σ_{ki} were calculated by applying a weighted linear regression⁸ to plots of $\ln [\text{Cu}]_{\text{relative}}$ vs $[\text{HCl}]$. These calculations yielded straight lines with slopes equal to $-k_i t$, where t is reaction time.

The gases used were Ar (99.998%) from the liquid (Praxair), HCl (99.995%) from Spectra, and 10.8% HCl (99.99%) in Ar (99.995%) from Matheson. The latter were passed through drierite (CaSO_4) drying towers.

HTFFR-MS. The reactor part of the HTFFR-MS apparatus (Figure 1) consists of a quartz reaction tube (2.2 cm i.d.) surrounded by a helical SiC resistance heating element, thermal insulation, and a steel vacuum housing. The movable crucible for Cu evaporation and the movable oxidant (HCl or DCl) inlet were fed from the bottom, upstream, end of the reactor. This inlet was an open 2 mm i.d. alumina tube. A fixed flexible Pt/Pt(13% Rh) thermocouple was fed in just below the reactor top plate, with its tip 8 cm from the mass spectrometer entrance orifice. The HTFFR was evacuated through seven 6 mm i.d. holes in this plate, which was welded to the base of the stainless steel mass spectrometer housing. The base plate accommodated a replaceable entrance cone, with a 0.7 mm entrance orifice. The two-stage vacuum system was evacuated by two 25 cm diffusion pumps, filled with Dow Corning DC-705 fluid, and connected to mechanical pumps through valves and foreline traps. The quadrupole assembly included an Extrel Model 041-1 axial ionizer, an Extrel Model 7-324-9 (9 mm rod diameter) quadrupole mass analyzer, and a conversion dynode channel electron multiplier Galileo Electro Optics Model 4870. The control electronics, power supplies, and photon counter were plugged into an Extrel C50 MM mainframe. The skimmer cone for molecular beam formation has a 0.3 mm orifice. The chopper is a 200 Hz oscillator tuning fork. Many details of this facility are described by Santana.⁹

The ionizing electron energies used in this work were 17–19 eV. As a check on the operation of the system, the $^{63}\text{Cu}/^{65}\text{Cu}$ and $\text{H}^{35}\text{Cl}/\text{H}^{37}\text{Cl}$ ratios were measured and found to be 2.1 and 3.1, respectively, as compared to the natural ratios¹⁰ of 2.2 and 3.1, respectively.

In the HTFFR-LIF apparatus the heating elements extend well downstream from the observation windows, and only small temperature gradients (± 5 to ± 15 K)⁵ were present in the reaction zone. The presence of the mass spectrometer precludes such a reactor arrangement here. To obtain an idea of the

temperature profile, readings with a movable thermocouple were made in separate experiments. A hole was drilled in the bottom of an empty alumina crucible, heated as for the actual experiments, and a thermocouple was inserted through it. As in the kinetic measurements, the crucible inlet was located 15 cm, and the HCl inlet 13 cm, upstream from the mass spectrometer entrance. Under these conditions the temperature dropped by about 15 K cm^{-1} . A somewhat stronger drop occurred closer to the cone (40 K cm^{-1}) with a drop of about 140 K over the last centimeter. The temperatures reported for the Cu + HCl experiments must therefore be considered as nominal.

To obtain adequate signal intensities, the Cu vaporizer had to be heated to about 1500 K, which led to minimum temperatures in the reaction zone of nominal 1150 K. As the heating elements of the reactor cannot be used above 1500 K, the experiments were limited to the 1150–1500 K range.

The HCl used was from the Spectra cylinder above, 99% DCl was obtained from Cambridge Isotope Labs, and 99.99% He was supplied by Matheson. These gases were dried as for the LIF experiments.

Results and Discussion

Rate Coefficients Determination. Table 1 summarizes the individual rate coefficients, k_i , measured and the conditions under which they were obtained. The conditions varied include the following: $[\text{Ar}]$ ranging from 0.8×10^{17} to 7.1×10^{17} molecules cm^{-3} , corresponding to pressures from 13 to 96 mbar, average gas velocities, \bar{v} from 9 to 100 m s^{-1} , and reaction zone lengths selected at 10 or 20 cm. The k_i measurements were determined to be independent of these parameters by examining plots of $[k(T) - k_i]/k(T)$, where $k(T)$ is obtained from eq 2, vs the particular parameter. The data were randomly distributed above and below the zero line of the ordinate. The data shown in Figure 2 exhibit a positive temperature dependence with no observable curvature. They are well-fitted by a linear regression^{11,12} to $k_1(T) = A \exp(-E \text{ K}/T)$ which yields

$$k_1(680\text{--}1500 \text{ K}) = 1.22 \times 10^{-10} \exp(-7719 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (2)$$

Variances and covariance are $\sigma_A^2 = 3.86 \times 10^{-2} \text{ A}^2$, $\sigma_{AE} = 3.71 \times 10^1 \text{ A}$, and $\sigma_E^2 = 3.72 \times 10^4$, with corresponding $2\sigma_k$ precision limits varying from $\pm 8\%$ to $\pm 20\%$ depending on temperature. Using a $\pm 10\%$ uncertainty in the reactor flow profile,^{5–7} along with a conservative $\pm 20\%$ for possible systematic errors, yields confidence intervals of $\pm 24\%$ to $\pm 30\%$.

Reaction Mechanism. To identify the reaction products, mass spectrometric measurements were made. The reproducibility of the peak heights was found to be $\pm 20\%$. First background spectra with only the Cu/He mixture flowing were taken, and then HCl was added. Within the 97–103 amu region a number of peaks increased above the background. These, and their probable identification, are as follows: 97, $^{63}\text{Cu}(\text{OH})_2$; 98, $^{63}\text{Cu}^{35}\text{Cl}$; 99, $\text{H}^{63}\text{Cu}^{35}\text{Cl}$, $^{65}\text{Cu}(\text{OH})_2$; 100, $^{65}\text{Cu}^{35}\text{Cl}$; 101, $\text{H}^{65}\text{Cu}^{35}\text{Cl}$, $\text{H}^{63}\text{Cu}^{37}\text{Cl}$; 102, $^{65}\text{Cu}^{37}\text{Cl}$; 103, $\text{H}^{65}\text{Cu}^{37}\text{Cl}$. The mass 97 peak suggests the presence of residual water vapor in the mass spectrometer, which hinders the direct identification of mass 99. However, masses 101 and 103 indicate the presence of H^{63}CuCl .

To check this identification, experiments with DCl instead of HCl were made. These showed the appearance of mass 104. The other DCuCl peaks overlap CuCl peaks, but a strong upward shift in the intensity of mass 102 relative to mass 100 was observed. Simultaneously, the three HCuCl peaks became quite small, and this remaining presence may be attributed to

TABLE 1: Summary of Rate Coefficient Measurements of Cu + HCl^a

reaction zone length, cm	P, mbar	[M], 10 ¹⁷ cm ⁻³	[HCl] _{max} , 10 ¹⁴ cm ⁻³	F, arbitrary units	\bar{v} , m/s	T, K	$k + \sigma_k$, cm ³ molecule ⁻¹ s ⁻¹
20	12.9	0.8	44.2	41	70	1135	9.24 ± 2.28 (−14) ^b
20	28.5	1.9	70.3	52	44	1111	9.36 ± 1.60 (−14)
10	28.8	1.9	71.4	95	43	1098	7.36 ± 1.22 (−14)
10	28.4	2.0	79.0	81	61	1046	4.37 ± 0.72 (−14)
20	28.4	2.0	79.2	37	61	1043	5.10 ± 0.85 (−14)
10	21.9	1.7	58.9	83	45	918	5.68 ± 1.04 (−14)
10	33.6	2.7	90.8	153	29	915	3.76 ± 0.59 (−14)
20	34.2	2.7	91.9	176	29	921	4.77 ± 0.78 (−14)
20	20.2	1.6	54.0	209	49	926	6.60 ± 1.26 (−14)
20	24.2	1.7	45.1	40	59	1064	1.28 ± 0.23 (−13)
10	24.2	1.6	44.9	93	59	1068	1.42 ± 0.25 (−13)
20	39.6	3.7	166.9	112	16	773	6.06 ± 0.92 (−15)
20	63.5	6.2	169.3	205	16	742	2.77 ± 0.40 (−15)
20	28.3	2.5	123.2	72	16	808	7.64 ± 1.26 (−15)
20	27.7	2.3	111.0	48	18	878	1.79 ± 0.31 (−14)
10	27.7	2.3	112.9	52	18	863	1.40 ± 0.23 (−14)
10	47.6	4.0	183.5	76	11	867	1.46 ± 0.22 (−14)
20	18.1	1.2	47.3	47	51	1090	8.64 ± 1.73 (−14)
20	36.5	2.0	8.8 ^c	169	30	1323	3.36 ± 0.53 (−13)
10	36.5	2.0	11.0 ^c	141	30	1317	5.17 ± 0.82 (−13)
10	36.4	2.0	33.6	204	30	1344	4.26 ± 0.72 (−13)
20	24.0	1.8	104.0	65	45	958	3.26 ± 0.58 (−14)
20	34.2	2.6	92.6	85	31	946	3.75 ± 0.60 (−14)
10	34.4	2.7	185.0	54	30	917	2.65 ± 0.42 (−14)
20	48.7	5.2	327.6	55	16	678	1.78 ± 0.27 (−15)
20	69.4	6.8	435.5	77	12	734	4.49 ± 0.66 (−15)
10	69.4	6.8	468.9	119	12	740	4.42 ± 0.63 (−15)
10	74.8	7.1	621.4	198	9	762	3.65 ± 0.56 (−15)
20	74.1	6.9	263.4	251	9	779	6.94 ± 1.05 (−15)
20	12.7	0.8	23.8	110	100	1191	3.56 ± 0.89 (−13)
10	13.1	0.8	50.8	50	100	1180	1.91 ± 0.47 (−13)
20	96.0	5.7	9.6 ^c	51	14	1229	2.06 ± 0.29 (−13)
20	54.9	2.9	11.9 ^c	92	27	1393	4.47 ± 0.68 (−13)
20	28.5	1.4	7.1 ^c	118	55	1446	7.54 ± 1.27 (−13)
20	62.1	3.0	5.0 ^c	29	26	1503	1.21 ± 0.20 (−12)

^a The measurements are reported in the sequence in which they were obtained. ^b Should be read as $(9.24 \pm 2.28) \times 10^{-14}$. ^c Used 10.8% HCl in Ar; otherwise used (99.995%) HCl.

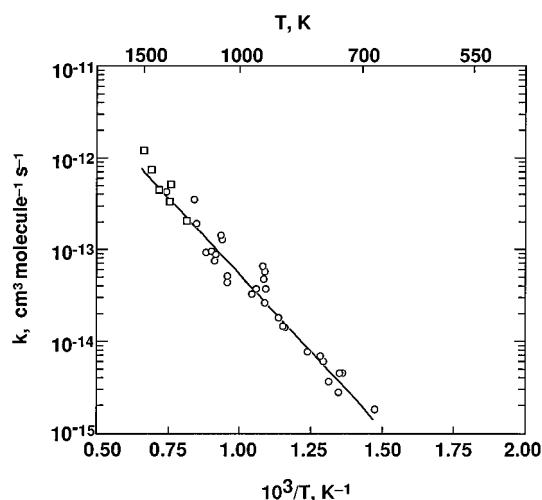
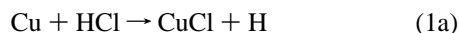


Figure 2. Summary of the Cu + HCl rate coefficients: (○) measurements taken using HCl (99.995%) from Spectra; (□) measurements taken using 10.8% HCl (99.99%) in Ar from Matheson; (—) fit of the measurements, eq 2.

outgassing in the mass spectrometer. CuCl can be attributed to the abstraction reaction



which is 49 ± 5 kJ mol⁻¹ endothermic.^{13,14} To investigate whether the HCuCl could possibly have formed heterogeneously, a number of experiments were performed in which HCl was alternately introduced up- and downstream of the Cu

crucible and with a clean and copper-coated reaction tube. HCuCl was present under all conditions in about the same ratio to CuCl. This makes surface reactions unlikely as a major source for HCuCl, and its formation may be attributed to



In order to establish the reaction path, and a likely structure for HCuCl, the Cu/HCl potential energy surface (PES) was investigated computationally. Geometries and harmonic vibrational frequencies ν_e were calculated at the Hartree–Fock (HF) level of theory using the minimal STO-3G basis set augmented with polarization functions on Cl and Cu.¹⁵ Calculations were carried out with the Gaussian-90 program,¹⁶ and the spin expectation values, $\langle S^2 \rangle$, are close to the ideal value of 0.75 for the doublet species, which indicates that the results are not significantly affected by spin contamination. The stability of the HF wave function, with respect to relaxation of internal constraints, was verified at each stationary point.¹⁷ The HF/STO-3G* data are summarized in Table 2 and Figure 3. The known molecules HCl, CuCl, and CuH provide comparisons to check the reliability of the *ab initio* calculations, and the computed bond lengths of 1.287, 2.019, and 1.476 Å agree well with the experimental values of 1.275, 2.051, and 1.463 Å,¹⁸ respectively. HF frequencies are typically too high compared to experimental values:¹⁵ here we find excellent accord if the *ab initio* values are scaled by a factor of 0.86, and for HCl, CuCl, and CuH the computed (measured¹⁸) values of ν_e are 2982 (2991), 422 (415), and 1925 (1941) cm⁻¹, respectively. We would not normally expect HF calculations with a small basis

TABLE 2: *Ab Initio* Data for the Cu + HCl PES

species	HF/STO-3G* energy, au ^a	$\langle S^2 \rangle$	state	ν_e , ^b cm ⁻¹
H	-0.46658	0.750	² S	
Cl	-454.54626	0.757	² P	
Cu	-1621.77366	0.751	² S	
HCl	-455.15788	0	¹ Σ	2982
CuCl	-2076.44314	0	¹ Σ	422
CuH	-1622.32841	0	¹ Σ	1925
CuClH	-2076.94599	0.755	² A'	146, 349, 2928
transition state	-2076.90583	0.785	² A'	1435i, 298, 1502
HCuCl	-2077.02168	0.761	² Σ	425 (2), 440, 1963

^a 1 au \approx 2625 kJ mol⁻¹. ^b Scaled by 0.86.

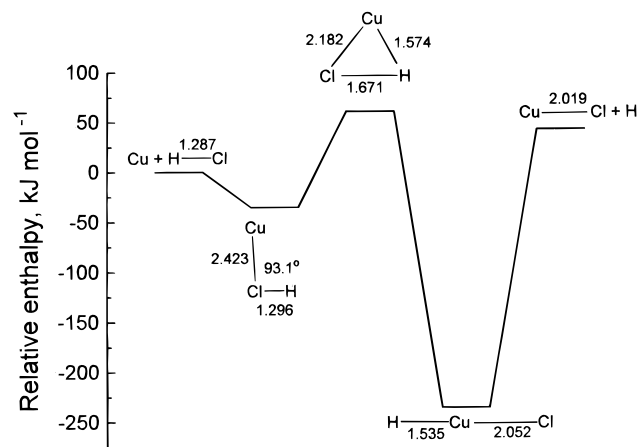


Figure 3. *Ab initio* potential energy surface for Cu + HCl, showing HF/STO-3G* enthalpies at 0 K relative to Cu + HCl, and geometries of stationary points with distances in 10⁻¹⁰ m.

set to yield accurate energies, but in this case there is fair agreement between the computed and measured ΔH_0 for the processes Cu + HCl \rightarrow CuCl + H and Cu + HCl \rightarrow CuH + Cl for which the HF/STO-3G* energies, combined with the zero-point vibrational energies approximated as $1/2 h\nu_e$, yield ΔH_0 of 42 and 143 kJ mol⁻¹, respectively. The corresponding experimental values are 49 and 164 kJ mol⁻¹.¹⁸

As shown in Figure 3, there is no barrier to the formation of a loose adduct between Cu and HCl, predicted to be bound by around 35 kJ mol⁻¹. This is too weakly bound to be a significant sink for Cu in the experiments, but the complex can rearrange, over a significant barrier, to form more stable HCuCl, which is predicted to be about 235 kJ mol⁻¹ exothermic with respect to Cu + HCl. This is a plausible sink for atomic Cu in the presence of HCl, as well as CuCl + H. The *ab initio* PES suggests that the rate-limiting step for the observed consumption of Cu is passage through a transition state for CuClH \rightarrow HCuCl. Based on this assumption, the rate constant for consumption of Cu is derived by application of transition state theory¹⁹

$$k = \frac{k_B T}{h} \frac{Q_{TS}}{Q_{Cu} Q_{HCl}} \exp\left(-\frac{E_0}{RT}\right) \quad (3)$$

The partition functions Q are calculated from the *ab initio* moments of inertia and vibrational frequencies, and E_0 is the HF/STO-3G* energy of the transition state relative to Cu + HCl, including zero-point corrections. A fit of k as a function of T yields the *ab initio* Arrhenius parameters $A = 2.5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $E_a = 69$ kJ mol⁻¹ at 1000 K. These are reasonably close to the experimental quantities, eq 2, which supports the computed mechanism for the reaction.

The PES of Figure 3 predicts that pressure increases would allow more reaction complexes to be trapped in the HCuCl well

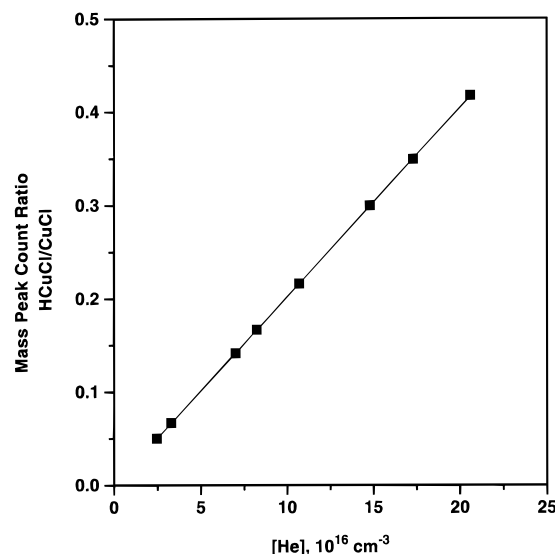


Figure 4. Pressure dependence of the mass peak count ratio HCuCl/CuCl (mass 103/mass 102) at $T \approx 1200$ K, $[HCl] = 5.6 \times 10^{14}$ molecules cm⁻³, and $\bar{v} = 25$ m/s: (■) individual measurements and (—) fit of the measurements.

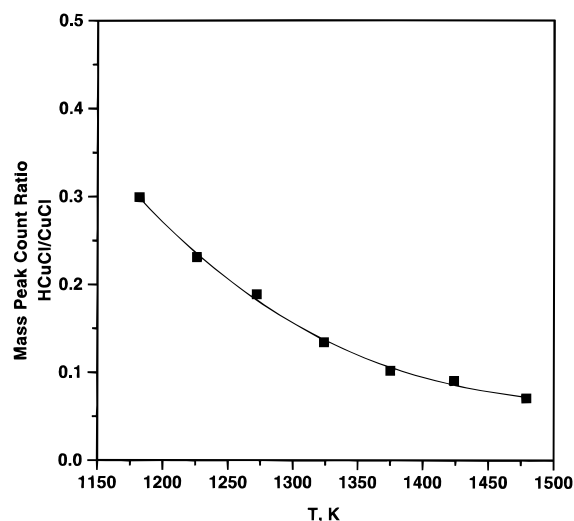


Figure 5. Temperature dependence of the mass peak count ratio HCuCl/CuCl (mass 103/mass 102) at $[He] = 1.07 \times 10^{17}$ molecules cm⁻³, $[HCl] = 2.7 \times 10^{14}$ molecules cm⁻³, and $\bar{v} = 34$ m/s: (■) individual measurements and (—) fit of the measurements.

on the path to CuCl + H, while temperature should have the opposite effect. This is borne out by the results presented in Figures 4 and 5 for the mass count ratios 103 (HCuCl)/102 (CuCl). The influence of temperature on the individual peaks is shown in Figures 6 and 7. It may be seen that CuCl formation has a strong positive temperature dependence, whereas HCuCl displays a weak negative dependence. This is in keeping with the positive activation energy for the overall reaction (eq 2 and Figure 2). Similar behavior as for masses 102 and 103 was observed for the pairs 100 and 101 and also for 98 and 99, when the latter was corrected for the Cu(OH)₂ contribution. Assuming approximate proportionality between count ratios and concentration, there figures suggest that, under the conditions of this work, the majority of reactions events lead to CuCl + H. As there is no information on the fragmentation behavior of HCuCl, this is a tentative conclusion.

Conclusions

In the present work, a high-temperature flow reactor, suitable for studies of metallic species, has been coupled to a quadrupole

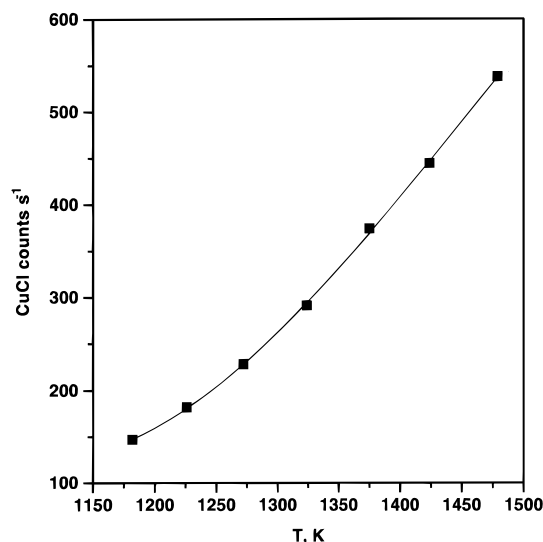


Figure 6. Temperature dependence of CuCl (mass 102) at $[\text{He}] = 1.07 \times 10^{17} \text{ molecules cm}^{-3}$, $[\text{HCl}] = 2.7 \times 10^{14} \text{ molecules cm}^{-3}$, and $\bar{v} = 34 \text{ m/s}$: (■) individual measurements and (—) fit of the measurements.

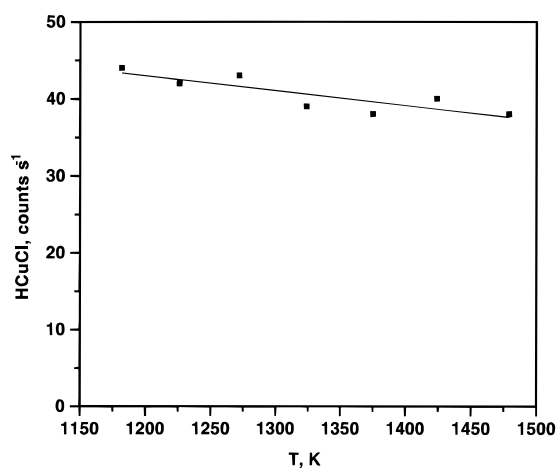


Figure 7. Temperature dependence of HCuCl (mass 103) at $[\text{He}] = 1.07 \times 10^{17} \text{ molecules cm}^{-3}$, $[\text{HCl}] = 2.7 \times 10^{14} \text{ molecules cm}^{-3}$, and $\bar{v} = 34 \text{ m/s}$: (■) individual measurements and (—) fit of the measurements.

mass spectrometer. We believe that this is the first time such an experimental facility has been constructed and used. The resulting product analysis has shown the presence of a second product, in addition to CuCl. On the basis of *ab initio* calculations, it is identified as having the HCuCl structure. Both products result from passage through a common transition state. There appears to have been no previous observations of HCuCl. However, there have been numerous experimental,^{20–23} and theoretical^{24–31} examples of metal atoms inserting into covalent bonds.

The preexponential factor of eq 2 is close to the gas kinetic rate coefficient, as has also been observed for other metal atom reactions with HCl, specifically Al,³² Cr,³³ Li,³⁴ Na,^{35,36} and K.³⁷ These reactions are normally assumed to proceed as abstraction reactions, but some could conceivably also have an insertion channel.

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spectrometer was constructed over a number of years, with financial support mainly from AFOSR. We thank W. F. Flaherty, who was the principal builder of the HTFFR-MS apparatus, for his assistance with this work.

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