Infrared Absorption Probing of the Cl + C_3H_6 Reaction: Rate Coefficients for HCl Production between 290 and 800 K

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The reaction of Cl with propylene, C_3H_6, has been investigated as a function of temperature (293−800 K) and pressure (3−10 Torr) using the laser photolysis/infrared long-path absorption (LP/IRLPA) technique. The measured rate coefficient for HCl production is well-described by a simple Arrhenius expression $(4.9 \pm 0.5) \times 10^{-11} \exp[-(90 \pm 50)/T]$ cm^3 $molecule^{-1}$ s^{-1} (all error estimates $\pm 2\sigma$). At $T \leq 400$ K biexponential time behavior of the HCl production is observed, arising from excited C_3H_6Cl adduct dissociation, but at higher temperature single-exponential behavior is seen. Comparison of measurements in CO_2 buffer, where HCl vibrational relaxation is rapid, and in Ar buffer allows extraction of the $HCl(v=1) + C_3H_6$ vibrational relaxation rate and the fraction of vibrationally excited HCl produced in the reaction. The measured rate coefficient for $HCl(v=1)$ vibrational relaxation by C_3H_6 is $(3.7 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and the fraction of vibrationally excited HCl produced in the reaction is 0.48 ± 0.06 at 293 K. The observations are consistent with a dominant direct abstraction mechanism and a smaller contribution from addition−elimination.

Introduction

The reactions of Cl with hydrocarbons have long been a subject of study. The role of the Cl atom in stratospheric ozone depletion has increased interest in its chemistry with all atmospheric species. Removal of Cl by small hydrocarbons has therefore been extensively studied. Reactions of Cl atoms at elevated temperatures are important in incineration of current CFC and chemical weapons stockpiles and in the combustion of chlorinated plastics. Chlorine-containing contaminants in more common combustion systems, such as biomass, coal, black liquor, and waste incineration, produce toxic chlorinated organic by-products. Kinetic information for Cl reactions at elevated temperatures is useful in modeling such combustion processes. Hydrogen abstraction in the reactions of Cl with hydrocarbons is the initiation step in the chain reaction chlorination,[1,2] and the relatively facile abstraction reactions with alkanes have been extensively investigated.[3,4]

The reactions of Cl with unsaturated species have been less well-studied. Abstraction of a hydrogen atom from an alkene produces an unsaturated hydrocarbon radical, and the thermochemistry of many of these radicals remains somewhat uncertain.[5] In addition, experimental investigation of the kinetics of the HCl-producing channel (1) is complicated by the presence of an addition reaction (2) to form a chloroalkyl radical, which tends to dominate the room-temperature reactions except at low total pressures:[6]

$$Cl + C_3H_6 \xrightarrow{k_1} C_3H_5 + HCl \quad (1)$$

$$Cl + C_3H_6\ (+M) \xrightarrow{k_2} C_3H_6Cl\ (+M) \quad (2)$$

In an exothermic reaction the production of HCl may include a contribution from addition−elimination as well as direct abstraction. This work is part of a series of investigations of Cl atom reactions with saturated[7] and unsaturated hydrocarbons[8] using infrared detection of the HCl product to probe the course of the reaction. The ability to measure the HCl yield in the reaction allows reliable separation of the two reaction channels, and the time resolution inherent in CW probing allows any complicating effects of secondary reactions to be discerned.[8]

The reaction of Cl with propylene has previously been investigated as a function of pressure by Wallington and coworkers.[6] The reaction proceeds principally by addition except at low pressures (<100 Torr), where the abstraction channel is evident. Abstraction produces the highly stable allyl (C_3H_5) radical and is significantly (14.3 kcal mol^{-1}) exothermic. Kaiser and Wallington measured the abstraction reaction rate coefficient to be $(2.3 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. They also noted an increase in the allyl radical production rate as the pressure decreased below ~100 Torr. They attributed this increase to an addition−elimination contribution and measured a low-pressure HCl production rate coefficient of 3.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Abstraction reactions of Cl with alkanes have been explained in terms of a direct abstraction mechanism with a linear transition state, where the alkyl radical behaves as a spectator to the H atom transfer. It is unclear whether the reaction proceeds by a similar mechanism in systems where stable adduct formation is possible. It is possible that the production of HCl occurs almost exclusively by an addition−elimination mechanism. Direct abstraction and elimination reactions are known to exhibit markedly different vibrational energy disposal.[9−11]

Recently, the dynamics of abstraction reactions involving chlorine atoms has had renewed interest. Differential scattering and product energy disposal for the reactions of Cl with alkanes,[12−16] ethyl radicals,[17] and c-C_6D_{12}[18] have been investigated in the last few years. The abstraction reactions of Cl with alkanes have been calculated to proceed via a linear transition state,[19−21] which can also be inferred from a transition-state-theory analysis of kinetics data.[22] This is consistent with the observed low rotational energy in the HCl product from such reactions in dynamical investigations. The vibrational

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energy produced in these reactions appears to be small; dynamical studies of reactions with sufficient energy to produce HCl or DCl (v=1) show negligible v=1 production except at elevated collision energy.[16,18] However, similar, but much more exothermic, abstraction reactions of F atoms with hydrocarbons produce high vibrational excitation.[23] Direct abstractions with a significant barrier, e.g. O(^{1}D) with hydrocarbons, are known to produce vibrational inversions.[24] On the other hand, elimination reactions produce a higher degree of randomization in the product energy, and HX distributions from addition−elimination reactions can often be described using modified statistical theories.[10,11,17,25]

In the present work, the rate coefficient for HCl production in the Cl + C_3H_6 reaction is measured as a function of temperature between 293 and 800 K. Additionally, the fraction of vibrationally excited HCl is measured at 293 K. Biexponential time traces are observed for HCl production at temperatures ≤ 400 K, implying a contribution from some excited adduct dissociation channel, either elimination or C−Cl fission. A sizable fraction, 48 ± 6%, of the HCl produced in the reaction is formed vibrationally excited at 293 K, which is consistent with predominance of direct abstraction. The temperature dependence of the rate coefficient is slightly positive over the observed temperature region.

Experiment

Apparatus. The present experimental apparatus is similar to that used in our previous studies of Cl + hydrocarbon kinetics.[7,8] The measurements are performed in a stainless-steel slow-flow reactor equipped with resistive heaters. Chlorine atoms are formed by pulsed 193 nm laser photolysis of CCl_4, and the progress of the reaction is monitored by time-resolved absorption on the R(2) line of the $H^{35}Cl$ fundamental vibrational transition. The infrared laser light is produced by difference frequency mixing of the output of a single-frequency Ar^+ laser and a ring dye laser in $LiNbO_3$.[26] The reactor is placed within a multipass cell of a modified Herriott design which allows long absorption paths in combination with precise temperature control. The Herriott cell uses off-axis paths in a spherical resonator; by propagating the pump beam along the resonator axis, the region of pump−probe overlap is confined to the center of the cell, where the temperature is well-controlled (±3 K at 800 K). The multipass cell is described more fully elsewhere.[27] The probe laser is split into separate reference and signal beams, which are imaged on matched InSb detectors. The reference beam is sent through an IR polarizer, which allows the incident intensities on the two detectors to be matched. The difference (signal − reference) is digitized, averaged for 100−500 photolysis pulses, and transferred to a microcomputer for analysis and storage.

The buffer gas (either CO_2 99.99% or Ar 99.9999%), the CCl_4 photolytic precursor, and the propylene reactant (99%) enter the reactor through separate calibrated mass flow controllers. The flow of reactants in these experiments is sufficient to refresh the reaction mixture every one or two photolysis laser shots, at an excimer repetition rate of 1.9 Hz. The reactant is present in great excess (~100×) over the Cl atoms, ensuring pseudo-first-order kinetic conditions. Since Ar is extremely inefficient in relaxing vibrationally excited HCl ($k \sim 10^{-16}$ cm^3 molecule^{-1} s^{-1}),[28] CO_2 buffer is used to ensure rapid thermal equilibration of HCl produced in the reaction.[29] Under the conditions of these experiments the vibrational relaxation rate is 10−300 times the HCl production rate. The absorption signal in CO_2 is therefore a reliable indicator of the total HCl concentration. Measurements in Ar are used in determinations of vibrational relaxation rate coefficients.

Determination of rate coefficients for HCl production in the presence of a competing addition reaction requires measurement of the yield of HCl produced, i.e., $\phi_{HCl} = [HCl]_\infty/[Cl]_0$. In the present experiments C_3H_6 and C_3H_8 are flowed alternately through the cell while holding the photolysis conditions constant. The HCl yield is then determined by comparison of the transient absorption strengths for HCl arising from Cl + C_3H_6 and Cl + C_3H_8, assuming $\phi_{HCl} = 1$ for Cl + propane.

Kinetics. Analysis of the kinetics behavior in the present study requires two distinct treatments, depending on whether the reaction is measured in CO_2, where the absorption signal is proportional to the total HCl concentration, or in Ar, where the absorption signal is influenced by nonequilibrium vibrational populations. The two cases are discussed separately below.

The production of HCl in the Cl + propylene system can occur by two pathways, either direct abstraction or addition followed by HCl elimination. To model the data taken with CO_2 as the buffer gas, a modified Lindemann mechanism can be used, taking into account both stabilization and addition−elimination:

$$\mathrm{Cl} + \mathrm{C_3H_6} \xrightarrow{k_a} \mathrm{HCl} + \mathrm{C_3H_5} \qquad (3)$$

$$\xrightarrow{k_E} \mathrm{HCl} + \mathrm{C_3H_5}$$

$$\mathrm{Cl} + \mathrm{C_3H_6} \xrightarrow{k_b} \mathrm{C_3H_6Cl^{\#}} \qquad (4)$$

$$\xrightarrow{k_M} \mathrm{C_3H_6Cl}$$

This mechanism assumes that the stabilized chloropropyl radical does not redissociate. The rate coefficient designated k_b is an effective rate coefficient for production of a partially stabilized adduct. This composite rate coefficient can be rationalized as a reversible initial association followed by partial stabilization to where dissociation back to reactants becomes negligible (but elimination is still possible):

$$\mathrm{Cl} + \mathrm{C_3H_6} \underset{k_{-\alpha}}{\overset{k_\alpha}{\rightleftharpoons}} \mathrm{C_3H_6Cl^{\#\#}} \xrightarrow{k_\beta} \mathrm{C_3H_6Cl^{\#}} \qquad (5)$$

Applying a steady state approximation for $C_3H_6Cl^{\#\#}$ gives $k_b = k_\alpha k_\beta/(k_{-\alpha} + k_\beta)$. The kinetic equations implied by this mechanism can be straightforwardly solved, yielding a biexponential expression for the HCl concentration as a function of time:

$$\mathrm{HCl}(t) = [\mathrm{Cl}]_0(A - B\mathrm{e}^{-(k_a+k_b)[\mathrm{C_3H_6}]t/2} - C\mathrm{e}^{-(k_E+k_M)t/2}) \qquad (6)$$

where A, B, and C are functions of the individual rate coefficients. In this kinetics scheme the relationship of the individual rate coefficients to the effective rate coefficients k_1 and k_2 may not be transparent. The HCl yield under all conditions is the ratio of the effective rate coefficients for the channels producing HCl to the rate coefficient for removal of Cl atoms:

$$\phi_{\mathrm{HCl}} \equiv \frac{[\mathrm{HCl}]_\infty}{[\mathrm{Cl}]_0} = A = \frac{k_a + k_b(k_E/(k_E + k_M))}{(k_a + k_b)} \equiv \frac{k_1}{k_1 + k_2} \qquad (7)$$

This provides a link between the observed time constants and the effective rate coefficients k_1 and k_2. The quantity $k_a + k_b$ is readily identified as the total rate coefficient ($k_1 + k_2$), and the rate coefficient for HCl production, k_1, is then given by $\phi_{HCl}(k_a + k_b)$. The rate coefficient k_1 can be deduced by fitting a biexponential to the observed data and plotting the sum of the two fitted time constants as a function of propylene concentration. The slope of such a plot is then the total rate coefficient ($k_1 + k_2$), which yields k_1 when multiplied by the HCl yield.

As the temperature increases, the dissociation of the adduct is sufficiently fast that a steady state approximation can be made for $C_3H_6Cl^{\#}$. The HCl concentration then exhibits simple exponential behavior, with a rise time constant equal to the pseudo-first-order rate coefficient for Cl atom removal, i.e.,

$$[\mathrm{HCl}](t) \propto 1 - \mathrm{e}^{-(k_1+k_2)[\mathrm{C_3H_6}]t} \tag{8}$$

Under these conditions, the rate coefficient for HCl production can be directly extracted as the HCl yield times the slope of an HCl rise-time-vs-$[C_3H_6]$ plot.

For measurements in Ar buffer, the vibrational relaxation is slow, and the kinetics equations that describe the system must take into account the production of HCl(v=1). Reaction 1 is therefore rewritten as

$$\mathrm{Cl} + \mathrm{C_3H_6} \xrightarrow{k_1[\mathrm{C_3H_6}]} f\,\mathrm{HCl}(v{=}1) + (1-f)\mathrm{HCl}(v{=}0) + \mathrm{C_3H_5} \tag{9}$$

where f is the fractional HCl population formed in v=1. The full kinetics system includes collisional vibrational relaxation. In Ar buffer, the relaxation by the buffer and photolyte are negligible, and the vibrational relaxation proceeds essentially exclusively by collisions with C_3H_6.

$$\mathrm{HCl}(v{=}1) \xrightarrow{k_{\mathrm{VET}}[\mathrm{C_3H_6}]} \mathrm{HCl}(v{=}0) \tag{10}$$

Because the HCl formation is much faster than vibrational relaxation under the conditions of these experiments, an insignificant error is introduced in treating the initial Cl + C_3H_6 reaction as a simple step instead of the more detailed treatment outlined above. The full kinetics system is therefore described as eqs 2, 9, and 10. These equations form a simple A → B → C type reaction scheme, which is easily solved by standard methods to give

$$\frac{[\mathrm{HCl}(v{=}0)]_t}{\phi_{\mathrm{HCl}}[\mathrm{Cl}]_0} = 1 + \frac{(k_{\mathrm{VET}} - (1-f)(k_1+k_2))\mathrm{e}^{-(k_1+k_2)[\mathrm{C_3H_6}]t}}{((k_1+k_2) - k_{\mathrm{VET}})} - \frac{f(k_1+k_2)\mathrm{e}^{-k_{\mathrm{VET}}[\mathrm{C_3H_6}]t}}{((k_1+k_2) - k_{\mathrm{VET}})}$$

$$\frac{[\mathrm{HCl}(v{=}1)]_t}{\phi_{\mathrm{HCl}}[\mathrm{Cl}]_0} = \frac{f(k_1+k_2)(\mathrm{e}^{-k_{\mathrm{VET}}[\mathrm{C_3H_6}]t} - \mathrm{e}^{-(k_1+k_2)[\mathrm{C_3H_6}]t})}{((k_1+k_2) - k_{\mathrm{VET}})} \tag{11}$$

Because the absorption probes the v=1 ← 0 transition, the observed signal is proportional to the degeneracy-weighted difference between the populations in the upper (v=1, J=3) and lower (v=0, J=2) levels. Rotational relaxation is sufficiently fast to maintain a Boltzmann distribution in rotations. The absorption is therefore proportional to $F_{\mathrm{B,lower}}[\mathrm{HCl}(v{=}0)]_t/g_{\mathrm{lower}} - F_{\mathrm{B,upper}}[\mathrm{HCl}(v{=}1)]_t/g_{\mathrm{upper}}$, where F_{B} is the rotational Boltzmann fraction and g is the rotational degeneracy ($2J + 1$) for the upper or lower state of the transition. Using eq 11, the time behavior of the observed absorption signal is thus given by

$$\text{absorption} \propto 1 - \frac{(1+\epsilon)f(k_1+k_2)}{((k_1+k_2) - k_{\mathrm{VET}})}\mathrm{e}^{-k_{\mathrm{VET}}[\mathrm{C_3H_6}]t} + \left[\frac{(1+\epsilon)f(k_1+k_2)}{((k_1+k_2) - k_{\mathrm{VET}})} - 1\right]\mathrm{e}^{-(k_1+k_2)[\mathrm{C_3H_6}]t} \tag{12}$$

where ϵ is a correction for the different rotational Boltzmann fractions in the upper and lower levels,

$$\epsilon = \frac{Q_{\mathrm{rot}}^{v=1}\mathrm{e}^{-J_{\mathrm{lower}}(J_{\mathrm{lower}}+1)B_{v=0}/kT}}{Q_{\mathrm{rot}}^{v=0}\mathrm{e}^{-J_{\mathrm{upper}}(J_{\mathrm{upper}}+1)B_{v=1}/kT}} \approx \mathrm{e}^{85.4/T} \qquad \text{for HCl R(2)} \tag{13}$$

Here Q is a rotational partition function and B is a rotational constant. If population is formed in v=2, a similar expression can be derived where f represents the total fraction in $v > 0$, under the approximation that Δv=−2 collisional relaxation is insignificant. However, the time behavior of the v=1 ← 0 signal then exhibits an additional component proportional to $t \exp(-k'_{\mathrm{VET}}t)$, where k'_{VET} depends on the rate coefficients for v=2 → 1 and v=1 → 0 vibrational relaxation.

Results

The reaction of Cl with propylene is pressure dependent because of the contribution of the addition channel to the reaction rate. As seen in our investigation of the Cl + C_2H_4 reaction, the details of the time behavior of the HCl production are important to unraveling the competing channels.[8] In the Cl + propylene reaction, the HCl traces are biexponential at temperatures of 293 and 400 K and at 3, 5, and 10 Torr. A typical trace is shown in Figure 1a along with a fit to a biexponential form. The best single-exponential fit is shown for comparison. At higher temperatures simple exponential behavior is observed, as shown in Figure 1b. These experiments are performed in CO_2 buffer to ensure that the observed signal is proportional to the total HCl concentration.

Equation 6 is used to model the observed HCl production in these experiments. The sum of the decay constants extracted from a biexponential HCl trace is plotted vs $[C_3H_6]$, as shown in Figure 2, and the total rate coefficients for Cl removal are determined from the slope of such a plot. The experimental intercept includes contributions from Cl diffusion out of the probe region and possible reactions of Cl with impurities in the CO_2 buffer. In addition, the long-time behavior of the HCl signal must include a correction for diffusion of the HCl. As a result, the absolute value of the intercept is not sufficiently accurate to provide a reliable estimate of the adduct removal rate ($k_M + k_E$). However, the slope is well-determined, which provides a good measure of the reaction rate coefficient.

The rate coefficients for HCl production, k_1, as a function of temperature are given in Table 1 and shown in Figure 3. The temperature dependence is slightly positive and the effective rate coefficient (taken from a weighted average of 3, 5, and 10 Torr determinations) can be described over the range 293−800 K by a simple Arrhenius expression, $(4.9 \pm 0.5) \times 10^{-11} \exp[-(90 \pm 50)/T]$ cm^3 molecule^{-1} s^{-1}, where the error bars are $\pm 2\sigma$ and represent the precision of the fit. The rate coefficients for HCl production do not depend on pressure to within experimental error in the narrow pressure range investigated in these experiments, 3−10 Torr. However at room temperature the HCl yield of the reaction changes by a factor of 1.5 over this range, from 0.57 at 3 Torr to 0.39 at 10 Torr. The 293 K rate coefficients k_1 and k_2 are measured to be equal at 5 Torr total pressure (i.e., $\phi_{\mathrm{HCl}} = 0.5$), in good agreement with the determination of Kaiser and Wallington.[6] The total

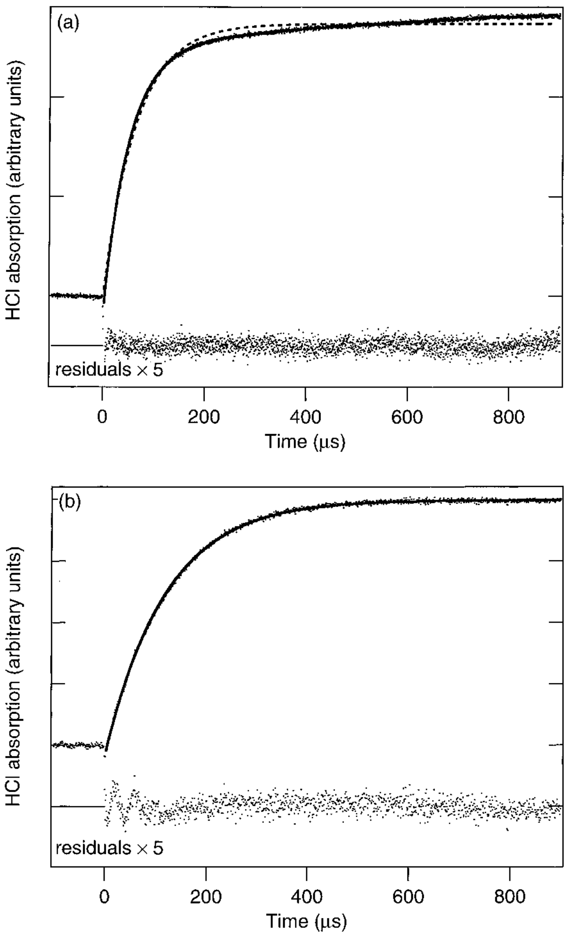

Figure 1. Time-resolved absorption traces of HCl produced in the reaction Cl + C_3H_6. (a) Biexponential behavior observed at 293 K, 3 Torr total pressure (CO_2 buffer). The propylene concentration is 3.06×10^{14} cm^{-3}. The solid line is a fit to a biexponential form, and the residuals to the fit are shown below. The best single-exponential fit is shown as the dashed line for comparison. (b) Simple exponential behavior observed at higher (>400 K) temperatures. The trace shown was taken at 600 K, 5 Torr total pressure (CO_2 buffer), with a propylene concentration of 7.62×10^{13} cm^{-3}. The solid line is a fit to an exponential form, and the residuals to the fit are shown below.

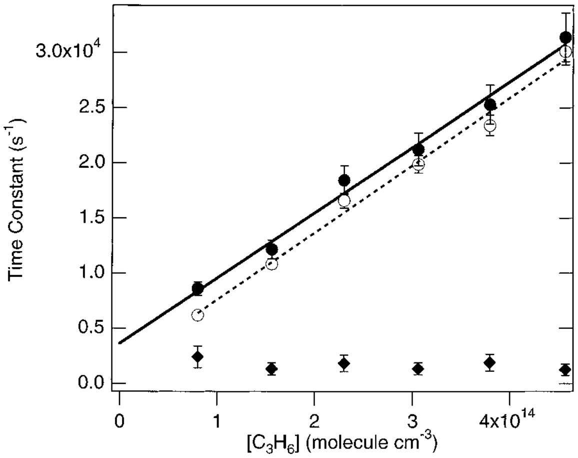

Figure 2. Sample plot of the sum of the two biexponential time constants (solid circles) vs [C_3H_6], at 3 Torr total pressure and 293 K. The slope yields the effective total rate coefficient, and the intercept reflects the removal rate of excited C_3H_6Cl adduct as well as diffusion and background reactions of Cl atoms. The individual time constants τ_1 (open circles) and τ_2 (solid diamonds) are also shown for comparison. The slower time constant τ_2 is independent of [C_3H_6], indicating that $(k_a + k_b)$ [C_3H_6] ($\approx \tau_1$) > $(k_M + k_E)$ for these concentrations.

TABLE 1: Measured Cl + C_3H_6 Rate Coefficients

T (K)	pressure	$k_1 + k_2$[a]	ϕ_{HCl}[b]	k_1[a]
293				**3.7 ± 0.6**[c]
	3 Torr	6.4 ± 0.2	0.57 ± 0.04	3.6 ± 0.3
	5 Torr	7.8 ± 0.8	0.50 ± 0.06	3.9 ± 0.5
	10 Torr	9.1 ± 0.8	0.39 ± 0.04	3.5 ± 0.5
400				**3.7 ± 0.5**[c]
	3 Torr	4.7 ± 0.2	0.77 ± 0.07	3.6 ± 0.3
	5 Torr	5.3 ± 0.3	0.69 ± 0.09	3.7 ± 0.4
	10 Torr	6.4 ± 0.7	0.62 ± 0.02	3.9 ± 0.6
500				**4.3 ± 0.6**[c]
	3 Torr	4.2 ± 0.3		4.2 ± 0.3
	5 Torr	4.2 ± 0.3	0.99 ± 0.04	4.2 ± 0.3
	10 Torr	4.7 ± 0.7	0.95 ± 0.05	4.7 ± 0.7
600				**4.3 ± 0.4**[c]
	3 Torr	4.1 ± 0.3		4.1 ± 0.3
	5 Torr	4.4 ± 0.2	0.98 ± 0.06	4.4 ± 0.2
	10 Torr	4.7 ± 1.0	0.90 ± 0.14	4.7 ± 1.0
700				**4.4 ± 0.7**[c]
	3 Torr	4.2 ± 0.3		4.2 ± 0.3
	5 Torr	4.6 ± 0.3		4.6 ± 0.3
	10 Torr	4.6 ± 1.0		4.6 ± 1.0
800	3 Torr	4.2 ± 0.4	1.1 ± 0.2	**4.2 ± 0.4**[c]

[a] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Error bars are $\pm 2\sigma$ (precision only). [b] For calculations of k_1 the HCl yield is taken to be unity above 500 K. [c] Weighted average of determinations at all pressures. Error bars ($\pm 2\sigma$) represent statistical and estimated systematic errors.

rate coefficients as a function of pressure at 293 K also agree very closely with the measurements of Kaiser and Wallington.

Recent experiments on the photoelectron spectroscopy of $C_3H_5^-$ and the gas-phase acidity of C_3H_6 have provided a relatively precise determination of $\Delta H^\circ_{f,298}(C_3H_5) = 41.5 \pm 0.4$ kcal mol^{-1}.[30,31] The Cl + $C_3H_6 \rightarrow$ HCl + C_3H_5 reaction is 14.3 ± 0.6 kcal mol^{-1} exothermic, energetic enough to populate v=1 ($\Delta H = -5.8$ kcal mol^{-1}) but not v=2 ($\Delta H = +2.5$ kcal mol^{-1}). The present experiments take advantage of the relatively slow vibrational relaxation of HCl by Ar and by the CCl_4 photolyte to probe the production of vibrationally excited HCl in the reaction. A typical absorption signal in Ar buffer is shown in Figure 4. The rise of the absorption is fit extremely well by a single exponential, and preliminary measurements on the $v=2 \leftarrow 1$ transition (Figure 5) exhibit decay constants matching the rise of the $v=1 \leftarrow 0$ absorption.

Since the formation of HCl is much more rapid than vibrational equilibration, and since the absorption probes the difference between the two populated vibrational levels, the extraction of the branching fraction f is qualitatively similar to the absorption-vs-gain method pioneered by the Leone group.[32] In that method, used to determine spin−orbit branching fractions in halogen atom (I, Br) photofragments, an extrapolation of the exponential relaxation back to $t = 0$ is compared to the $t \rightarrow \infty$ signal to establish the initial population fraction. In contrast, the production of HCl is fast, but not instantaneous, on the time scale of the vibrational equilibration. The time profiles are therefore explicitly fitted to the functional form given by the kinetics scheme. The total rate coefficient for Cl removal ($k_1 + k_2$), is fixed at the value determined independently in CO_2 buffer, and the Ar buffer signals are fitted using eq 12 to extract k_{VET} and f.

The channel to v=2 is endothermic and is hence expected to contribute only at elevated temperature. No evidence is seen for significant v=2 population at room temperature. However, at the highest temperatures of this study, 800 K, nearly 25% of the Cl + C_3H_6 collisions have sufficient kinetic energy to populate v=2. Interpretation of vibrational fractions extracted by this method at higher temperatures is somewhat problematic. Therefore results are reported only at 293 K, where the v=2 population is small. The branching fraction to HCl(v=1) is 0.48

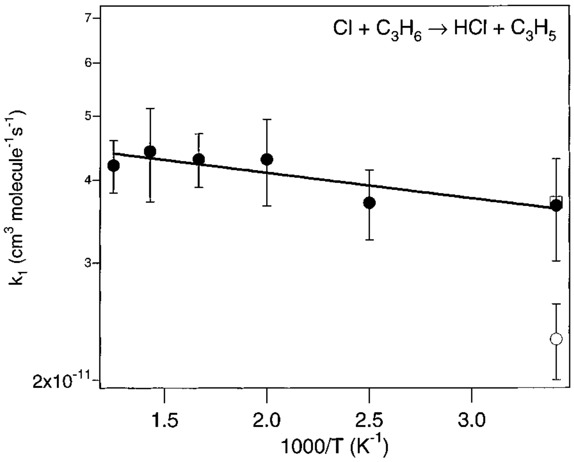

Figure 3. Arrhenius plot of k_1, the effective rate coefficient for HCl production in the Cl + C_3H_6 reaction, taken from a weighted average of determinations at 3, 5, and 10 Torr total pressure (CO_2 buffer). This rate coefficient is the sum of direct abstraction and addition−elimination pathways. Also shown are previous determinations of k_1 (open square) and the direct abstraction rate coefficient (open circle) from ref 6.

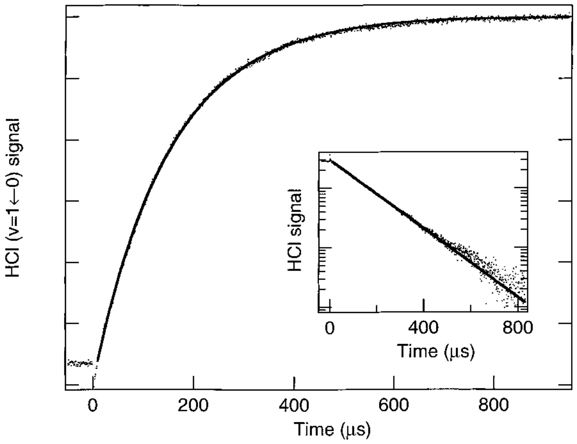

Figure 4. Absorption trace (v=1 ← 0) of HCl produced in the Cl + C_3H_6 reaction, taken in Ar buffer. Significant amounts of HCl(v=1) are produced in this reaction. The trace is well-fit by a single exponential, as shown in the inset. Because vibrational relaxation of HCl by Ar is negligible, the time constant represents the vibrational relaxation rate for HCl(v=1) + C_3H_6. Absorption traces in Ar buffer allow the fraction of vibrationally excited HCl produced in the reaction to be estimated (see text).

± 0.06, and the vibrational relaxation rate coefficient for HCl(v=1) + C_3H_6 is $(3.7 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 293 K. Comparison of measurements in CO_2 and Ar buffer shows that a high degree of vibrational excitation persists up to the highest temperatures of this study; however, reliable extraction of vibrational populations where v=2 is significantly populated would require careful monitoring of v=3 ← 2, v=2 ← 1, and v=1 ← 0 transitions.

Discussion

In previous studies of the Cl + propylene reaction, an increase in the effective rate for HCl production as the pressure decreased from 100 to 10 Torr was ascribed to an addition−elimination mechanism. The present results yield a 293 K rate coefficient for the HCl product channel of 3.7 ± 0.6 cm^3 molecule^{-1} s^{-1}, which is in close agreement with the low-pressure rate coefficient reported by Kaiser and Wallington (open square in Figure 3).[6] The observation in the present work of biexponential time traces at temperatures ≤ 400 K tends to support the conclusion that addition−elimination contributes to the HCl production channel at low pressures.

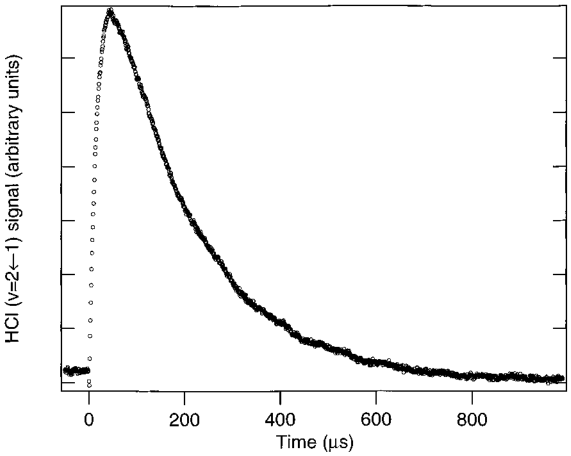

Figure 5. Absorption trace (v=2 ← 1) of HCl produced in the Cl + C_3H_6 reaction, taken in Ar buffer. The decay of the (v=2 ← 1) absorption matches the rise of the (v=1 ← 0) signal.

Biexponential traces are observed only when the excited adduct dissociation rate is significantly slower than the Cl removal rate. As a result, the present data cannot distinguish HCl arising from elimination from that arising from dissociation to Cl + C_3H_6 followed by rapid abstraction. Kaiser and Wallington have estimated that the dissociation of the initially formed adduct back to reactants is 18 times the elimination rate.[6] A rapid redissociation of the initial adduct is of course assumed in the derivation of the phenomenological rate coefficient k_b. However, the present data could also be fit by a mechanism that assumes that the excited adduct dissociates exclusively back to reactants, i.e., simply making the adduct formation step reversible and ignoring the possibility of elimination. The effective rate coefficients for HCl production extracted using such a mechanism are in good agreement with those extracted assuming elimination.

The heats of formation of many halogenated hydrocarbon radicals have not been measured experimentally, although there is considerable interest in the thermochemistry of these species. In the present work the dissociation of the initially formed complex is treated as arising from a nonthermal distribution in the chloropropyl radical. It seems unlikely that the behavior is characteristic of dissociation of thermalized radicals for several reasons. First, the observation by Kaiser and Wallington that the allyl radical yield decreases with increasing pressure implies that the allyl arises from incompletely stabilized adduct species. Second, the measured HCl yield would certainly be unity if the completely thermalized radicals were the source of the long-time HCl production. In fact the HCl yield is only 0.39 at 10 Torr and 293 K. Finally, effective equilibrium constants obtained by extracting forward and reverse rates for C_3H_6Cl formation (assuming adduct dissociation exclusively to reactants) are markedly pressure dependent. The present low-pressure measurements therefore appear unsuited for extracting thermochemical information on the chloropropyl radical. However, higher pressure measurements which account for both elimination and C−Cl bond fission may prove useful in this regard.

One of the central questions in this and in other exothermic Cl + hydrocarbon reactions is the relative importance of direct abstraction vs addition−elimination mechanisms in the reaction. In the present experiments the temperature dependence of the rate coefficient k_1 is measured to be nearly flat (E_a/R = 90 ± 50 K) between 292 and 800 K. The exothermic direct abstraction channel can be expected to have little temperature dependence. The abstraction reactions of Cl with ethane and propane, which are also exothermic, display activation energies of $E_a/R = 135 \pm 26$ and 0 ± 10 K, respectively, over a similar temperature range.[7] In the limit that collisional stabilization of the adduct is negligible (i.e., the low-pressure limit), the addition−elimination rate will be proportional to the initial adduct formation. The temperature dependence of the addition−elimination channel will therefore be that of the high-pressure limiting association rate coefficient, which is also expected to be small. The rate coefficients measured in the present work are consistent with a combination of direct abstraction and addition−elimination channels in the $Cl + C_3H_6 \rightarrow HCl + C_3H_5$ reaction.

The current experiments have also measured the fraction of vibrationally excited HCl produced in the reaction. These measurements allow qualitative conclusions on the nature of the reaction. The fraction of vibrationally excited HCl produced in the reaction is large, 0.48 at 293 K. The production of v=1 requires approximately 60% of the reaction exothermicity to be channeled into HCl vibration. Dynamical studies have demonstrated that direct abstractions tend to exhibit much higher f than addition−elimination reactions. The relatively high vibrational energy suggests that direct abstraction may dominate in $Cl + C_3H_6 \rightarrow HCl + C_3H_5$.

A secondary question is whether a mechanism similar to that which occurs in Cl + alkane reactions, where the transition state is linear and the alkyl radical is largely a spectator in the reaction, may be applicable to the Cl + propylene reaction. Studies of vibrational excitation in Cl + alkane reactions seem to indicate a tendency toward low vibrational excitation in the HCl product, although there have been few experiments where the reaction exothermicity has been sufficient to populate vibrationally excited levels. Recent investigations of the reactions of Cl with $(CH_3)_3CD$ and $(CH_3)_3CH$ show small vibrational excitation and suggest that reagent translational energy increases vibrational excitation in the HCl products.[14,15] However, the reactions to form HCl require excess translational energy to reach v=1, and the production of vibrationally excited DCl from $(CH_3)_3CD$, where the reaction exothermicity is great enough to populate v=1, was not investigated. The reaction of Cl with deuterated cyclohexane was investigated by Park et al., who measured the rotational, vibrational, and translational energy of the DCl product.[18] The reaction is 8 kcal mol^{-1} exothermic, which is sufficient to populate DCl(v=1) (6.1 kcal mol^{-1}). The DCl was seen to be formed rotationally cold and 95% in v=0; excess translational energy in the reactant was preferentially channeled into translational energy of the products.[18] The present reaction is more exothermic, but the large partitioning of the reaction exothermicity into the HCl vibration may indicate a qualitatively different potential energy surface for the Cl + propylene reaction.

The reaction of Cl atoms with alkyl radicals may be more analogous to the present reaction. For example, the Cl + ethyl reaction is also highly exothermic and can produce HCl by either a direct abstraction or an addition−elimination mechanism. Which mechanism occurs in Cl + ethyl is not completely clear.[2] Seakins et al. measured the vibrational branching fractions for HCl(v>0) produced in the reaction $Cl + C_2H_5$ using FTIR emission studies. They observed a monotonically decreasing vibrational distribution, but with significant vibrational excitation.[17] They could obtain reasonable agreement with the experimental values using a modified statistical theory which partitioned the reaction exothermicity at a transition state for elimination, using a reduced vibrational frequency for the HCl. This was interpreted to indicate an addition−elimination mechanism was dominant for the Cl + ethyl reaction. A similar calculation can be carried out for the Cl + propylene reaction, using an effective HCl vibrational frequency at the transition state of 1400 cm^{-1} and taking the other frequencies of the transition state from *ab initio* calculations on the allyl radical.[33,34] Such a calculation would predict a fraction of vibrationally excited HCl of only ~15%. Sum rule treatments which allow the energy required to overcome the barrier to be preferentially partitioned into HCl vibration may rationalize a larger predicted fraction of HCl(v=1). Typically, 25−35% of the barrier energy has been seen to appear as HX product vibration for three- and four-center elimination reactions.[35] Since the average fraction of the reaction energy partitioned into HCl vibrational energy in the Cl + propylene reaction is $(0.48 \pm 0.06) \times (8.5/(14.3 \pm 0.6)) = 0.28 \pm 0.03$, a sum rule description in which nearly all of the reaction exothermicity is treated as barrier energy could match the experimental observation. A more detailed calculation of the potential energy surface, especially the transition state to HCl elimination, is likely necessary to definitively predict vibrational distributions for direct abstraction and addition−elimination in this system. However, the present results appear consistent with the HCl being produced predominantly via a direct abstraction mechanism in the Cl + propylene reaction and suggest a relatively smaller role for an addition−elimination mechanism.

The reaction of Cl with C_3H_6 appears to release more energy into vibration than other Cl + hydrocarbon abstraction reactions. The large fraction of the exothermicity partitioned into product vibrational energy, characteristic of an "early release" reaction, suggests that the abstraction transition state occurs while the Cl atom is more than the equilibrium HCl bond distance from the H atom.[36] In dynamical studies of other abstraction reactions, increased product vibrational excitation has appeared to be correlated with higher energetic barriers to the reaction; however the activation energy of the $Cl + C_3H_6 \rightarrow HCl + C_3H_5$ reaction is only 0.17 ± 0.10 kcal mol^{-1}. A detailed dynamical study of the rotational and vibrational energy disposal in this system, especially as a function of initial translational energy, would be extremely helpful in resolving the questions raised by the present kinetic data.

Conclusions

The rate coefficient for HCl production in the reaction of Cl atoms with propylene has been measured between 293 and 800 K. The time profiles for HCl production at $T \leq 400$ K display biexponential behavior, which may indicate some role of an addition−elimination channel in the reaction. At higher temperatures the production of HCl shows a simple exponential behavior. The rate coefficient shows a slightly positive dependence on temperature, which is consistent with other exothermic Cl + hydrocarbon abstraction reactions. Significant (48 ± 6%) population of HCl(v=1) is seen in the reaction, supporting the conclusion that direct abstraction is the dominant mechanism for HCl production.

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