Infrared Absorption Measurements of the Kinetics of Cl atom Reactions with $\text{C}_3\text{H}_n$ (n=4,6) Unsaturated Hydrocarbons between 300-850 K.

John T. Farrell, Jeffrey S. Pilgrim, and Craig A. Taatjes
Combustion Research Facility
Mail Stop 9055
Sandia National Laboratory
Livermore, CA 94551-0969 USA
E-mail: jtfarre@ca.sandia.gov
cataatj@ca.sandia.gov

The reactions of Cl atoms with the unsaturated $\text{C}_3\text{H}_n$ (n=4,6) hydrocarbons propylene, allene, and methyl acetylene have been investigated as a function of temperature (292-850 K) and pressure (3-10 Torr) using the Laser Photolysis/Infrared Long-Path Absorption technique. The reaction of Cl atoms with these hydrocarbons proceeds via abstraction to form HCl and addition to form either a chloropropyl or chloroallyl radical. The contribution of these channels to the total rate can be separated by careful measurement of the temporal evolution and yield of the HCl product. For example, at $T = 293$ K, the Cl + propylene rate coefficient is pressure dependent (between 3 to 10 Torr) and the HCl time evolution is biexponential. The data indicate that abstraction and addition contribute equally to the total rate coefficient at about 5 Torr. The abstraction channel becomes increasingly important at higher temperature, and at $T \geq 500$K is the only channel that contributes significantly the the total rate, as evidenced by unity HCl yield, pressure independent rate coefficients, and simple exponential temporal evolution of the HCl. The rate coefficient for HCl production is well described over the temperature range of 292<T<800 K by the simple Arrhenius expression:

$$k_{\text{propylene}} = (5.2 \pm 0.5) \times 10^{-11} \exp[-(138 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The temperature dependence of the Cl + propylene rate coefficient and the Arrhenius fit are shown in Figure 1.

The Cl + allene reaction exhibits slightly different behavior. At 292 K, almost no HCl is generated ($\phi_{\text{HCl}} = 0.03$), indicating that addition (without subsequent HCl loss) is the dominant reaction channel. The HCl yield increases at higher temperature more slowly.
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than with propylene, and doesn’t reach unity until $T \geq 800$ K. Between 400-800 K, the rate coefficient for the HCl producing channels is given by the simple Arrhenius expression:

$$k_{\text{allene}} = (4.1 \pm 1.2) \times 10^{-10} \exp[-(1745 \pm 224)/T] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

This expression reproduces the data well except at low temperature, where slight curvature is apparent. A modified Arrhenius expression, $k = A'(T/298)^2 e^{E_a/kT}$ is invoked, which gives:

$$k_{\text{allene}} = (1.14 \pm 0.14) \times 10^{-11} (T/298)^2 \exp[(386 \pm 104)/T] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

The rate coefficients (total and abstraction) vs temperature and the Arrhenius fits are shown in Figure 2.

![Figure 1: Arrhenius plot for Cl + C$_3$H$_6$ → HCl + C$_3$H$_5$](image_url)
The reactions of Cl with propylene and allene are both sufficiently energetic to produce vibrationally excited HCl, and indeed a significant fraction of the HCl produced in both reactions is vibrationally excited. Measurement of the HCl production in Ar buffer, which is extremely inefficient at quenching HCl vibrational excitation, permits the branching fraction into v=1 and the rate coefficient for vibrational relaxation of HCl by the hydrocarbon to be estimated. With both propylene and allene, about half the HCl is generated in v=1. The fraction of vibrationally excited HCl produced in each reaction, along with the rate coefficient for HCl relaxation, are given in Table 1.

Results will also be presented for the Cl + methyl acetylene reaction, which has recently been studied in our laboratory.
TABLE 1. Branching fractions into $v_{\text{HCl}}=1$ and vibrational relaxation rate coefficients.

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<th>$f_{v=1}^a$</th>
<th>$k_{\text{VET}}^b$</th>
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<tr>
<td>Cl + Propylene</td>
<td>0.48 ± 0.6</td>
<td>3.7 ± 0.7</td>
</tr>
<tr>
<td>Cl + Allene</td>
<td>0.55 ± 0.8</td>
<td>2.8 ± 0.5</td>
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$^a$ The fraction of vibrationally excited HCl produced in the Cl + propylene and Cl + allene reactions.

$^b$ Units of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The numbers in the parentheses indicate experimental uncertainties ($\pm 2\sigma$ precision only) in the last digit.

Presentation mode: We prefer to present this paper in a poster session.

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