Atmospheric reactions of OH with unsaturated hydrocarbons

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Introduction
The reactions of OH + C\(_2\)H\(_4\) and OH + C\(_2\)H\(_2\) are important in both combustion and atmospheric chemistry. Both species react with OH similarly by addition of OH to the \(\pi\)-bond structure. The reactions also have long-range attractive forces that induce a small van der Waals well before addition. C\(_2\)H\(_4\) is a short-lived species in the atmosphere (\(\tau \approx 1-2\) hours) and is an important sink of OH. Current kinetic evaluations for atmospheric chemistry in the stratosphere and troposphere recommend no temperature dependence on the high pressure rate constant for OH + C\(_2\)H\(_4\) from 200-300K, but no experiments have been conducted from 200 to 290 K. Similarly, C\(_2\)H\(_2\) + OH has been studied extensively at room temperature, but little at lower temperatures. C\(_2\)H\(_2\) + OH has a small barrier to reaction, thus slower reaction rate than C\(_2\)H\(_4\). A full representation of the temperature and pressure dependence for these reactions are required to test their importance in OH loss in the upper troposphere as well as to increase precision in models using both species as tracers for anthropogenic influences on air masses.

The reaction of OH + C\(_2\)H\(_{2n}\) can either transpire via the electrophilic addition of OH to the \(\pi\)-bond structure with a 3\(^{rd}\) body stabilization of the hot adduct (1) or via H abstraction (2):

\[
\text{OH} + \text{C}_2\text{H}_{2n} + \text{M} \rightarrow \text{C}_2\text{H}_{2n}\text{OH} + \text{M} \quad (1)
\]

\[
\text{OH} + \text{C}_2\text{H}_{2n} \rightarrow \text{C}_2\text{H}_{2n-1} + \text{H}_2\text{O} \quad (2)
\]

Reaction 2 has a relatively high barrier (~30, ~75 kJ mol\(^{-1}\) C\(_2\)H\(_n\), C\(_2\)H\(_2\), respectively) and can only be accessed at higher temperatures (T>600K).

In this study, we investigate the pressure dependence of the reaction of OH + C\(_2\)H\(_2\) in the range 200-400K in a laser flash photolysis, laser-induced fluorescence (FP-LIF) system. The experimentally determined pressure dependences are then used to constrain a 1-dimensional Master Equation model to determine both the effects of the pre-reaction complex and the Troe parameters describing the pressure dependence of a 3-body reaction: \(k_o, k_\infty, F_c\). We then investigate the temperature and pressure dependence of OH + C\(_2\)H\(_2\).

Experimental
The laser flash photolysis laser-induced fluorescence system employed for these experiments are similar to those used in previous studies\(^1\). Briefly, the OH radicals were generated by photolyzing a precursor (HNO\(_3\) and H\(_2\)O\(_2\) at 300K and below, (CH\(_3\))\(_3\)COOH at 400K) at 248nm using a KrF Excimer laser (50-150 mJ, 5Hz). The OH was observed by excitation using a Nd:YAG (Spectra Physics) pumped dye-laser (Rhodamine 6G) (50-150 mJ, 5Hz). The PMT signal passed through a boxcar averager and then is imaged onto a photomultiplier tube (PMT). The time decay of the OH under pseudo first-order conditions (C\(_2\)H\(_4\) >\(>[\text{OH}]\)) was controlled by delaying the pump and probe laser pulses using a computer-controlled delay generator (Stanford Resarch). Each kinetic trace consisted of approximately 150 points averaged over 5-10 samples.

The gases (C\(_2\)H\(_4\), HNO\(_3\)/He, (CH\(_3\))\(_3\)COOH/He and the bath gas, He, N\(_2\), Ar, or O\(_2\)) were introduced into the cell through a mixing manifold using mass flow controllers to regulate flow. The gases entered a temperature-controlled reaction cell. The pressure in the cell was regulated by throttling the exit valve of the cell. The total flow was > 10 s.c.c.m. per Torr total pressure, ensuring that the gases were swept through the cell between laser pulses. The temperature was measured inside the cell by type K (high T) and N (low T) thermocouples probing near the reaction zone ensuring temperatures were known to ±3K.

C\(_2\)H\(_4\) (Sigma Aldrich) was purified by freezing to 77K, degassed and diluted in He (BOC CP grade, 99.999%), C\(_2\)H\(_2\) was purified by freezing to 77K, degassed, and evaporated slowly at 200K to minimize acetone contamination, then diluted in He. HNO\(_3\) was prepared by the addition of H\(_2\)SO\(_4\) to fuming nitric acid to remove NO\(_2\), then degassed and diluted with He. The peroxo precursors (H\(_2\)O\(_2\) and (CH\(_3\))\(_3\)COOH) were degassed and diluted with He. Bath gases: He and N\(_2\) (BOC CP grade 99.999%), were used straight from the cylinder.

Reaction of OH + C\(_2\)H\(_4\)
Experiments were conducted under variable T and P conditions using different reaction cells for temperatures above or below room temperature. The reactions were run under pseudo first-order conditions such that the decay of OH followed a single exponential. Bimolecular plots were then constructed to determine the overall rate constant from individual pseudo first-order rate constants.

Experiments of C\(_2\)H\(_4\) were conducted from 4 to 500 Torr at 200, 260, 298 and 400K in He and at 298K in N\(_2\) (Figure 1).

![Figure 1. Bimolecular rate constants of OH+C\(_2\)H\(_4\) at 200, 260, 295 and 400K in He and at 295K in N\(_2\).](image)

Thermal equilibrium was established easily in He and no condensation effects were observed at lower temperatures. In disagreement with atmospheric chemistry kinetic evaluations, there is a large change in \(k_o\) from 200-300K, where the 200K data is ~80% higher than at 295K. The high pressure limit also appears to have been reached at a lower pressure for the 200K data than for the 400K data. In order to characterize the dependence of the rate constants on pressure, a Troe formalism (Equation 3) can be used to fit the data at each temperature.

\[
k = \frac{k_o [M]}{1 + \frac{k_o [M]}{k_\infty}}
\]

\[
\log F = \frac{\log F_{\text{cent}}}{1 + \left(\frac{\tau - \tau_{\text{cent}}}{\tau_{\text{cent}}/\tau}\right)^2}
\]
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Three constants can be derived from fitting to the Troe formalism, $k_o$, $k_e$, and $F_c$. However, each of these may also have a temperature dependence, given by:

$$k_e = A_k \left( \frac{T}{300} \right)^\gamma \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (4)

$$k_o = A_k \left( \frac{T}{300} \right)^\gamma$$  \hspace{1cm} (5)

$$F_c = (1 - \alpha)\exp \left( -\frac{T}{\bar{E_c}} \right) + a\exp \left( -\frac{T}{\bar{E_o}} \right) + \exp \left( \frac{T}{\bar{E_c}} \right)$$  \hspace{1cm} (6)

As the lowest pressure in our experiments is 4 Torr, the low pressure rate coefficients ($k_e$) at each temperature are not well defined. Thus, the global temperature dependence of all three Troe parameters cannot be determined by fitting Equations 4-6 alone, so a more explicit method, master equation calculations, are employed. The calculations follow a methodology that has been described previously.² ³

The master equation was used to fit the pressure dependence of observations first by initializing the microcanonical rate coefficients ($k(E)$) of the reactants using an inverse Laplace transform of $k_o(T)$ (Equation 4). There is no indication from the calculations that long-range forces affect the pressure dependence of this reaction under the pressures studied. Thus, the calculations were executed for a 1-well system, of depth -115.1 kJ mol⁻¹ and tight transition state of 13.6 kJ mol⁻¹ above the zero point energy beyond the well. $A_{k_o}$ and $n$ were varied to determine the minimum $\chi^2$ fit to He data from 423K-200K of several laboratories. The $<\Delta E>$ used for He was 130 cm⁻¹. The temperature of $k_o$ was found by fitting (Marpardt prescription) the master equation calculations from varying temperature and pressure conditions to Equation 5, as no significant temperature dependence of $F_c$ was found. The final Troe parameters are given in Table 1.

![Figure 2. Pressure dependence of C₂H₂ + OH over different T.](image)

The temperature dependence indicates a reaction barrier to the addition complex. No irregular fall off was observed at low temperatures to indicate the presence of a van der Waals complex. An Arrhenius expression, given by Equation 3, has been used to deduce an activation energy for this reaction of 3.4 (±0.2) kJ mol⁻¹ which agrees with theoretical calculations of 6.5 (±4.0) kJ mol⁻¹ within error. Previous experiments have determined a barrier of 5.4 (±0.4) kJ mol⁻¹.

### Conclusions

The reaction of OH + C₂H₄ has been studied and modeled to behave as a barrier-less addition over the temperature range of 200-400K.

The reaction of OH + C₂H₄ has been studied and exhibits temperature-dependent behaviour indicative of a small activation energy barrier of 3.4 kJ mol⁻¹.

While calculations on the potential energy surface of both reactions of C₂H₂ and C₂H₄ with OH show a shallow (7.7 kJ mol⁻¹) van der Waals complex, the existence does not appear to affect the pressure fall-off of the reaction rate over the conditions of 5-450 Torr and 200-400K for both reactions.

### References

7. D Fulle et al., PCCP, 101 1433 (1997)

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<th>Troe parameter</th>
<th>$A_{k_o}$, $A_{k_e}$</th>
<th>cm³ molecule⁻¹ s⁻¹ / (cm³ molecule⁻¹ s⁻¹)²</th>
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<td>$F_c$</td>
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Table 1. Troe parameters that were deduced from master equation calculations. $k_{inf}$ from a $\chi^2$ fit to several data sets in He, $k_e$ from a Troe fit to the master equation calculations.

### Results C₂H₂ + OH

The reaction of C₂H₂ + OH was studied from 5 to 450 Torr for 5 different temperatures of 210, 233, 253, 298 and 373K in He and at 298K in N₂. Individual experiments were conducted similarly to C₂H₄ under pseudo first-order conditions. Care was taken to minimize O₂ in the reaction cell, as O₂ adds to the reaction complex to regenerate OH. The results are given in Figure 2.