

Atmospheric reactions of OH with unsaturated hydrocarbons

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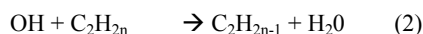
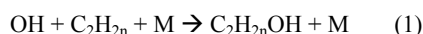
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Introduction

The reactions of OH + C₂H₄ and OH + C₂H₂ are important in both combustion and atmospheric chemistry. Both species react with OH similarly by addition of OH to the π-bond structure. The reactions also have long-range attractive forces that induce a small van der Waals well before addition. C₂H₄ is a short-lived species in the atmosphere (τ ~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 + C₂H₄ from 200-300K, but no experiments have been conducted from 200 to 290 K. Similarly, C₂H₂ + OH has been studied extensively at room temperature, but little at lower temperatures. C₂H₂ + OH has a small barrier to reaction, thus slower reaction rate than C₂H₄. A full representation of the temperature and pressure dependence for these reactions are required to assess 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+C₂H_{2n} can either transpire via the electrophilic addition of OH to the π-bond structure with a 3rd body stabilization of the hot adduct (1) or via H abstraction (2):



Reaction 2 has a relatively high barrier (~30, ~75 kJ mol⁻¹ C₂H₄, C₂H₂, respectively) and can only be accessed at higher temperatures (T>600K).

In this study, we investigate the pressure dependence of the reaction of OH + C₂H₄ 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: k₀, k_∞, and F_c. We then investigate the temperature and pressure dependence of OH + C₂H₂.

Experimental

The laser flash photolysis laser-induced fluorescence system employed for these experiments are similar to those used in previous studies¹. Briefly, the OH radicals were generated by photolysing a precursor (HNO₃ and H₂O₂ at 300K and below, (CH₃)₃COOH 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) system doubled to 281.9 nm and monitoring the subsequent fluorescence from the (A²Σ⁺ → X²Π_i) transition at 307.9 nm. The fluorescence passed through an interference filter 308 (± 1) nm and was imaged onto a photomultiplier tube (PMT). The PMT signal passed through a boxcar averager and was logged via a computer. The time decay of the OH under pseudo first-order conditions ([C₂H₄] >> [OH]) was controlled by delaying the pump and probe laser pulses using a computer-controlled delay generator (Stanford Research). Each kinetic trace consisted of approximately 150 points averaged over 5-10 samples.

The gases (C₂H₄, HNO₃/He, (CH₃)₃COOH/He and the bath gas, He, N₂, Ar, or O₂) 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.

C₂H₄ (Sigma Aldrich) was purified by freezing to 77K, degassed and diluted in He (BOC CP grade, 99.999%). C₂H₂ was purified by freezing to 77K, degassed, and evaporated slowly at 200K to minimize acetone contamination, then diluted in He. HNO₃ was prepared by the addition of H₂SO₄ to fuming nitric acid to remove NO₂, then degassed and diluted with He. The peroxide precursors (H₂O₂ and (CH₃)₃COOH) were degassed and diluted with He. Bath gases: He and N₂ (BOC CP grade 99.999%), were used straight from the cylinder.

Reaction of OH + C₂H₄

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 C₂H₄ were conducted from 4 to 500 Torr at 200, 260, 298 and 400K in He and at 298K in N₂ (Figure 1).

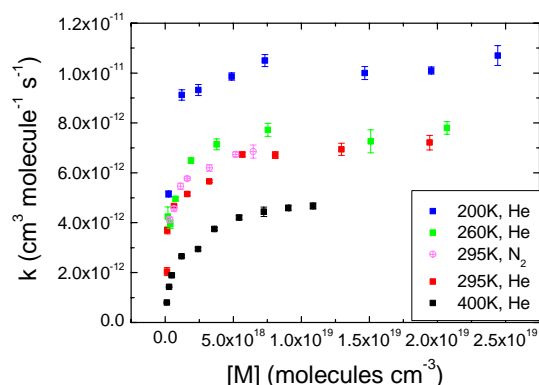


Figure 1. Bimolecular rate constants of OH+C₂H₄ at 200, 260, 295 and 400K in He and at 295K in N₂.

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_∞ 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.

$$k = \frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}} F \quad \text{where} \quad \log F = \frac{\log F_{cent}}{1 + (\log(\frac{k_0[M]}{k_\infty}))^2} \quad (3)$$

Three constants can be derived from fitting to the Troe formalism, k_o , k_∞ , and F_{cent} . However, each of these may also have a temperature dependence, given by:

$$k_\infty = A_{k_\infty} \left(\frac{T}{300} \right)^n \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

$$k_o = A_{k_o} \left(\frac{T}{300} \right)^m \quad (5)$$

$$F_c = (1-a) \exp\left(\frac{-T}{T^{***}}\right) + a \exp\left(\frac{-T}{T^*}\right) + \exp\left(\frac{T^{**}}{T}\right) \quad (6)$$

As the lowest pressure in our experiments is 4 Torr, the low pressure rate coefficients (k_o) 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 $k_\infty(T)$ (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 $-115.1 \text{ kJ mol}^{-1}$ and tight transition state of 13.6 kJ mol^{-1} above the zero point energy beyond the well. A_{k_∞} and n were varied to determine the minimum X^2 fit to He data from 423K-200K of several laboratories⁴⁻⁸. The $\langle \Delta E \rangle$ used for He was 130 cm^{-1} . The temperature of k_o was found by fitting (Marquardt 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.

Troe parameter	A_{k_∞}, A_{k_o} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} /$ $(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^2$	n,m	E_A (J mol^{-1})
k_∞	$5.06 (\pm 0.40) \times 10^{-12}$	0	-1234
k_o	$2.05 (\pm 0.40) \times 10^{-29} [\text{He}]$	-4.79 (± 0.19)	
F_c	$0.88 (\pm 0.05)$		

Table 1. Troe parameters that were deduced from master equation calculations. K_{inf} from a X^2 fit to several data sets in He, k_o from a Troe fit to the master equation calculations.

Results $\text{C}_2\text{H}_2 + \text{OH}$

The reaction of $\text{C}_2\text{H}_2 + \text{OH}$ was studied from 5 to 450 Torr for 5 different temperatures of 210, 233, 253, 298 and 373K in He and at 298K in N_2 . Individual experiments were conducted similarly to C_2H_4 under pseudo first-order conditions. Care was taken to minimize O_2 in the reaction cell, as O_2 adds to the reaction complex to regenerate OH. The results are given in Figure 2:

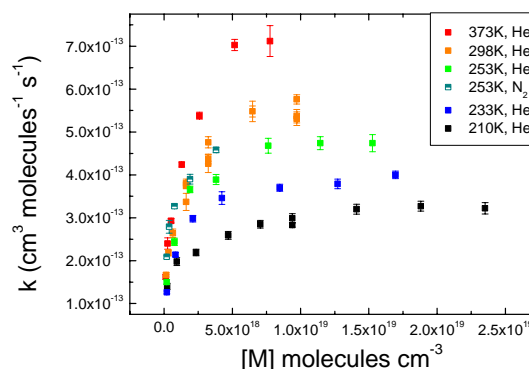


Figure 2. Pressure dependence of $\text{C}_2\text{H}_2 + \text{OH}$ over different T.

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 $3.4 (\pm 0.2) \text{ kJ mol}^{-1}$ which agrees with theoretical calculations of $6.5 (\pm 4.0) \text{ kJ mol}^{-1}$ within error. Previous experiments⁹ have determined a barrier of $5.4 (\pm 0.4) \text{ kJ mol}^{-1}$.

Conclusions

The reaction of $\text{OH} + \text{C}_2\text{H}_4$ has been studied and modeled to behave as a barrier-less addition over the temperature range of 200-400K.

The reaction of $\text{OH} + \text{C}_2\text{H}_2$ 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 C_2H_2 and C_2H_4 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

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