

Temperature Dependent Rate Constant for the OH + O₃ Chain Reaction via High
Resolution Infrared Laser Absorption Methods

by

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Temperature Dependent Rate Constant for the OH + O₃ Chain Reaction via High Resolution Infrared Laser Absorption Methods

This directed by Professor David J. Nesbitt

The goal of this work is to determine the rate constant of the catalytic chain reaction of hydroxyl radical (OH) with ozone (O₃). This chain reaction proceeds in two steps: (1) OH + O₃ → HO₂ + O₂, with rate constant k_1 , and (2) HO₂ + O₃ → OH + 2 O₂, with rate constant k_2 . These rate constants are determined by observing the temporal profile of OH radical via direct infrared absorption, and fitting the data to a model consistent with the exact solution for the entire chain reaction process. The technique of direct infrared absorption allows us to probe the kinetics over an order of magnitude greater dynamic range of ozone concentration than previous studies, which provides clearer separation between the chain induction ($k_{\text{ind}} = k_1 + k_2$), propagation, and termination steps. By utilizing a temperature-controlled flow tube, we are able to extract the temperature dependence of the kinetics as well. The Arrhenius form for $k_{\text{ind}} = k_1 + k_2$ between 334 and 240K is determined to be

$$k_{\text{ind}}(T) \left[\frac{\text{cm}^3}{\text{sec}} \right] = (2.93^{+0.42}_{-0.38}) \times 10^{-12} \exp\left(\frac{-(1030 \pm 50)\text{K}}{T(\text{K})}\right). \text{ This value is}$$

significantly higher than the values currently recommended for use in atmospheric models. Kinetic analysis of k_{ind} below 240K and the ratio of k_2/k_{ind} have also been investigated.

To All My Teachers in Life

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