

Rate Constant Measurements for Reactions of OH with Organic Compounds

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Overview

Design and analysis of combustion system require predictive models, and the chemical kinetics component of modeling is extremely important. Detailed kinetic modeling of high-temperature fuel oxidation can consist of hundreds to thousands of reaction rate constants which can come from experimental measurements, theoretical calculations, and estimation methods. The reaction of the highly reactive hydroxyl radical (OH) with fuel is a major fuel consumption pathway, and accurate knowledge of the rate constant for this reaction is essential to develop an accurate kinetic mechanism describing high-temperature fuel oxidation.

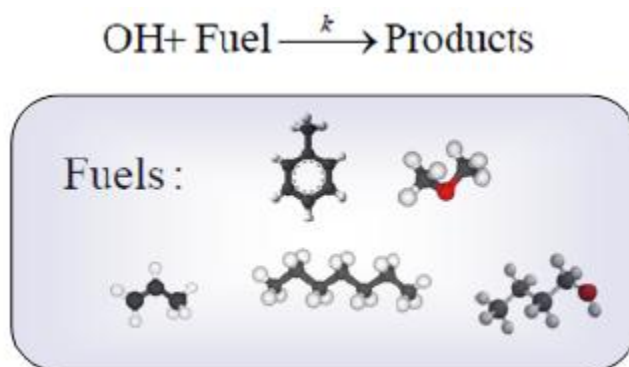


Figure 1: Reaction of the hydroxyl radical with an organic compound

In our research, we design and conduct shock tube experiments to directly measure the rate constants for reactions of OH with organic fuels. In particular, we are interested in aromatics, ketones, ethers, alkanes, alkenes, and alcohols. We use tert-butyl hydroperoxide as an OH precursor, which has advantages of being stable on metal surfaces, easy to handle, and dissociating rapidly upon shock heating at temperatures as low as 900 K. tert-Butyl hydroperoxide dissociates into OH and methyl radicals and an acetone molecule via a two-step dissociation mechanism (Figure 2).

1. Upon shock heating, the peroxi bond cleaves forming an OH radical and a *tert*-butoxy radical
2. The *tert*-butoxy radical falls apart into a methyl radical and acetone

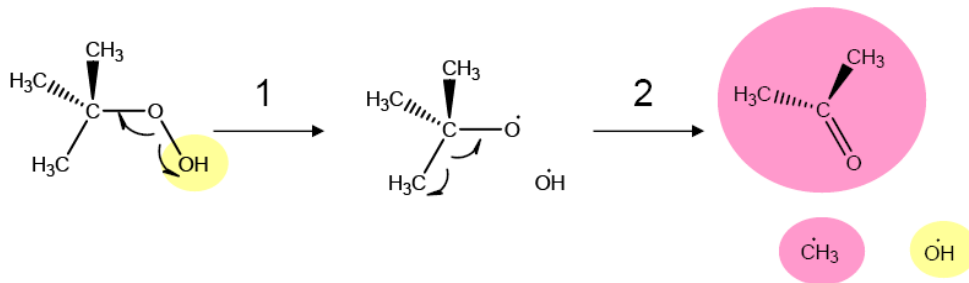
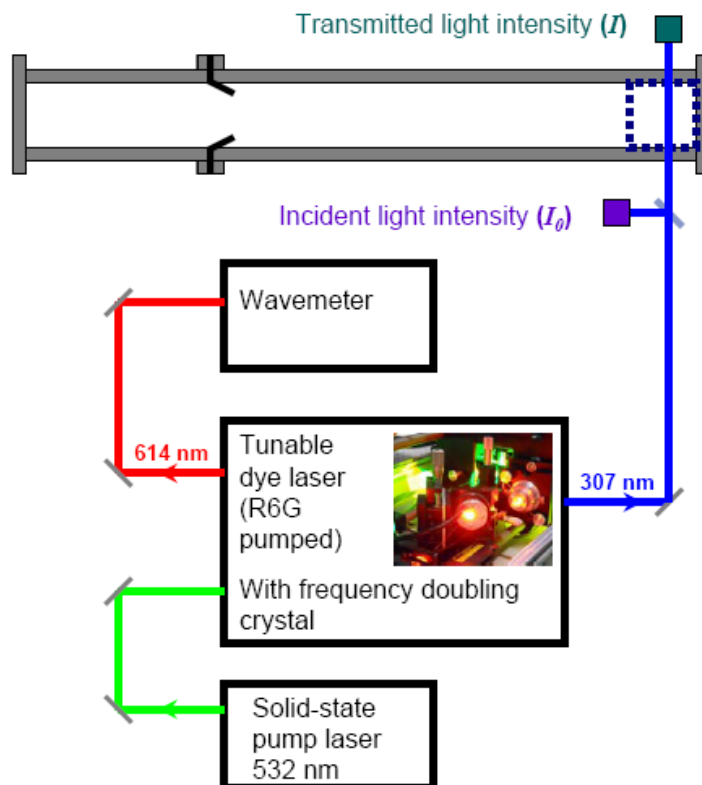


Figure 2: The two-step decomposition mechanism of *tert*-butyl hydroperoxide.

Narrow-linewidth laser absorption by OH at 307 nm allows us to quantitatively measure the OH concentration time-history from previously measured absorption coefficients for the A—X electronic transition band of OH. The diagnostic is capable of a minimum detectivity of ~ 0.5 ppm OH at 1200 K and 1 atm. By designing experiments with the organic compound in excess of the *tert*-butyl hydroperoxide, the measured OH concentration time-history will decay exponentially in time, and we can use a pseudo-first order kinetic analysis to determine the rate constant. More commonly, however, we use a detailed kinetic model to account for any secondary reactions for a more accurate the rate constant determination.



Beer-Lambert Law: $I / I_0 = \exp(-k * P * x_{OH} * L)$

Figure 3: Schematic of the quantitative OH detection diagnostic used in shock tube experiments

- ❖ Bimolecular reaction kinetics
 - ❖ $\text{OH} + \text{Fuel} \xrightarrow{k} \text{Products}$
 - ❖ $\text{Rate} = -d[\text{OH}]/dt = k [\text{Fuel}][\text{OH}]$

- ❖ Pseudo first-order kinetics
 - ❖ $\text{Rate} ([\text{Fuel}] \gg [\text{OH}]) = k'[\text{OH}] = -d[\text{OH}]/dt$
 - ❖ $k' = k [\text{Fuel}] \sim \text{constant}$
 - ❖ $\ln [\text{OH}] = \ln [\text{OH}]_{t=0} - k' t$

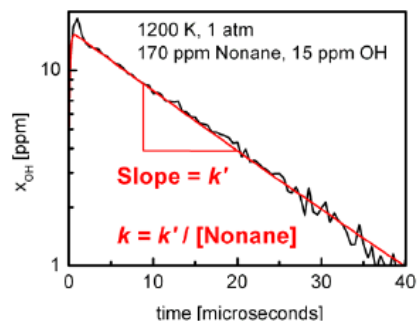


Figure 4: Sample measured OH concentration trace and pseudo-first order kinetic analysis

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