

Measuring Rate Constants and Product Branching for Reactions Relevant to Combustion and Atmospheric Chemistry

by

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Abstract

Over the last century there have been countless experimental measurements of the overall reaction kinetics of gas-phase radicals, often with the aid of lasers. In more recent decades, *ab initio* predictions of product branching using quantum chemical calculations combined with modern rate theories have become common. However, there are few experimental measurements against which to validate predicted product branching, even for an important reaction system such as hydroxyl radical addition to acetylene that is critical to oxidation chemistry both in the atmosphere and in combustion. As a result, many of the kinetic parameters that appear in commonly used combustion mechanisms are based purely on predictions. The few experiments that do attempt to quantify product branching generally fall into two categories, each with unique advantages/disadvantages: crossed molecular beams (CMB) that simulate single collision conditions, or end-product analysis of a complex, thermalized process, such as pyrolysis. Laser flash photolysis (LFP) with molecular beam mass spectrometry (MBMS) offers a compromise between CMB and end-product experiments: the reaction conditions are thermalized but still simple enough that primary products can be quantified with confidence.

This thesis describes a unique apparatus, and the improvements made to it, that combines LFP and MBMS for primary product branching quantification, as well as multiple-pass laser absorbance spectrometry (LAS) for accurate measurements of overall kinetics. The full capability of this LFP/MBMS/LAS apparatus is demonstrated for the chemically interesting phenyl radical + propene reaction system, which has been implicated as a potential source of second aromatic ring formation under combustion conditions. Overall kinetic measurements are also reported in this work either for systems that involve a newly discovered reactive species (various cycloaddition reactions of the simplest Criegee Intermediate formed in atmospheric ozonolysis) or that was disputed in the literature (vinyl radical + 1,3-butadiene, which has been implicated as a potential source of benzene in combustion). Finally, this thesis shows how detailed chemical insights made either experimentally or theoretically can be translated into applications *via* the Reaction Mechanism Generator (RMG). The application discussed is natural gas high temperature pyrolysis for the production of C2 commodity chemicals.

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