

Studies of Flame Chemistry Using Synchrotron Radiation For Photoionization Mass Spectrometry

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Progress in minimizing environmental pollution associated with hydrocarbon combustion requires the development of kinetic models for the combustion of ethane, propene, propane, propyne, and higher hydrocarbons including 1,3-butadiene and benzene. Kinetic models are also needed for oxygenated hydrocarbon fuels (e.g., ethanol, propanol) with clean-burning characteristics (low NO_x, low soot). Similarly, improved descriptions of the gas phase combustion mechanisms of nitrocellulose-based propellants require knowledge of the combustion chemistry of glyoxal and formic acid in the presence of nitrogen compounds (NO, NO₂, N₂O).

Kinetic model development in all of these reaction systems is currently hampered by the lack of direct measurements of the concentrations of combustion intermediates in laboratory flames under carefully controlled and documented flame conditions. During the past two years we have constructed and successfully operated a flame-sampling photoionization mass spectrometry (PIMS) facility on the 9.0.2.3 beamline. These were the first studies to demonstrate the use of synchrotron radiation for the detection of flame species by PIMS. We now routinely measure both spatial concentration profiles and photoionization efficiency (PIE) curves for well-characterized low-pressure laminar flames. The photon flux available at end station 3 typically provides a 100-fold increase in ion signal-to-noise over that of laser sources used at Cornell and Sandia for previous PIMS flame studies. Moreover, the synchrotron provides rapid tunability over the entire range of photon energies (8 to 15 eV) of interest for the detection of combustion intermediates, a feature that cannot be matched with tunable laser sources.

Both stable and radical intermediates are detectable at mole fractions as low as 10⁻⁶. Individual isomeric species are selectively detected and identified; this is one of the most important advantages of VUV PIMS. This capability was used to establish the relative concentrations of allene and propyne isomers of C₃H₄ (mass 40) in a fuel-rich ethylene/oxygen flame. We find that the separate contributions of ethenol and

acetaldehyde isomers of C_2H_4O are also distinguishable in the PIE curve for mass 44. The determination of the allene/propyne and ethenol/acetaldehyde isomeric compositions is an exciting new development, beyond the capabilities of conventional electron-impact mass spectrometry.

COMPLETED STUDIES

1. Species concentration profiles were measured for reaction intermediates in ethylene/oxygen, 1,3-butadiene/oxygen, formic acid/hydrogen/oxygen, and glyoxal/hydrogen/oxygen flames.
2. PIE curves have been recorded for numerous flame species including CH_3 , C_2H_2 , H_2CO , C_3H_3 , C_3H_4 (allene), C_3H_4 (propyne), C_3H_6 (propene), CH_2CO (ketene), CH_3CHO (acetaldehyde), C_2H_6O (dimethyl ether), $HCOOH$ (formic acid), C_4H_2 (diacetylene), C_4H_4 (vinyl acetylene), C_4H_6 (1,3-butadiene), $(CHO)_2$ (glyoxal), $C_4H_{10}O$ (diethyl ether), and C_6H_6 (benzene).
3. Absolute photoionization cross sections for photon energies ranging from the ionization threshold to typically 1.5 to 2 eV above threshold have been determined for numerous stable flame species including acetylene, diacetylene, vinyl acetylene, ethylene, dimethyl ether, diethyl ether, acetaldehyde, 1,3-butadiene, allene, propyne, formic acid, and benzene. We record ion signals from a given "target" molecule of interest and a second "standard" molecule of known photoionization cross section using a binary mixture of the two in an argon diluent. Propene, propyne, ethylene, and acetylene are useful "standard" molecules because reliable measurements of their absolute photoionization cross sections are available in the literature.

WORK IN PROGRESS

During the past year we have refined and optimized our measurement capabilities to provide the confidence needed to routinely pursue studies of the chemistry of new flame systems. Moreover, studies of the 1,3-butadiene/oxygen flame, in particular, provide a dramatic example of the advantages that synchrotron radiation (on End Station 3) offers compared with tunable laser sources for PIMS studies of laboratory flames. These advantages include superior signal-to-noise, readily tunable photon energy over the 8 to 15 eV range of required energies, soft ionization, and the ability to acquire comprehensive species concentration measurements in a few days rather than the many weeks or months that laser PIMS measurements would require.

1. The studies of 1,3-butadiene flames are directed toward an improved understanding of the roles of C_4 and C_2 species in benzene formation. We will now study both lean and rich benzene flames. Benzene is the prototypical aromatic fuel, but little flame structure data exist for it and no low-pressure lean flame data are currently available.
2. The addition of nitrogen compounds (NO_2 , NO , N_2O) to the glyoxal/hydrogen/oxygen and formic acid/hydrogen/oxygen reaction systems is

essential for our continued studies of the gas phase chemistry of the decomposition products of nitrocellulose-based propellants.

3. New collaborative studies of flames of oxygenated hydrocarbon fuels (ethanol, propanol) will be performed to provide data needed for the kinetic modeling of reaction mechanisms.
4. Flames of higher hydrocarbons including ethane, propene, and propane will complement completed work on ethylene flames to better understand the reaction chemistry of both saturated and unsaturated hydrocarbon fuels.

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