AROMATICS OXIDATION AND SOOT FORMATION IN FLAMES

Progress Report for Period 15 August 1993 - 30 June 1994

Submitted to:

Fundamental Interactions Branch
Division of Chemicals
Office of Basic Energy Sciences
Department of Energy
Washington, DC 20545

Submitted by:

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Principal Investigator: J. B. Howard
(617) 253-4574

DOE Contract No. DE-FG02-84ER13282

DOE Report No. DOE/ER/13282-10

Anticipated amount of unexpended funds at end of
current budget period: less than 10% of funds available.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ja

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

AROMATICS OXIDATION AND SOOT FORMATION IN FLAMES

SCOPE

This project is concerned with the kinetics and mechanisms of aromatics oxidation and soot and fullerenes formation in flames. The objective of the aromatics oxidation work is to identify and measure the concentration of important intermediates and products in benzene oxidation, and to determine reaction mechanisms and kinetics properties consistent with the behavior seen in flames. The research on soot formation is concerned primarily with the particle inception stages, but the work includes study of soot structure at all stages of growth in order to obtain mechanistic information from evidence of growth steps recorded in the structure of particles. The ultimate objective is to understand how nascent soot particles are formed from high molecular weight compounds, including the roles of planar and curved PAH and the relationship between soot and fullerenes. The objective of the proposed research on fullerenes is to develop a more comprehensive understanding of the range of fullerenes formed in flames, the nature of the precursor species, and the mechanisms and kinetics of the formation reactions.

PROGRESS THIS PERIOD

Benzene Oxidation

Temperature and concentration profiles of stable species were measured using molecular beam mass spectrometry in a low-pressure premixed rich $H_2 - O_2 - Ar$ flame with a small amount of C_6H_6 added. Under the conditions studied benzene destruction was dominant over formation and growth reactions. Data consistency was verified by elemental flux balances, accounting for both ordinary and thermal diffusion. The reactions $CO + OH = CO_2 + H$, $CO + H_2O = CO_2 + H_2$, and $H_2 + OH = H + H_2O$ were found to be in equilibrium in the post-flame zone, within the limits of error of the relative ionization cross-section (RICS) method of calibrating for radical species. If the mass 16 signal in the post-flame zone is indeed O-atom as it appears to be, the reaction $O + H_2 = OH + H$ is also in partial equilibrium there. Radical concentrations for these equilibria were determined using cross-sections at 20-25 eV, instead of 70-75 eV. Also, where possible the cross-sections were for the simple ionization process instead of total ionization. With 70-75 eV total cross-sections, the reactions are measured to be just outside of equilibrium, implying that Bittner's suggestion that the error in the RICS method is 30% does not seem warranted for H and OH. Re-evaluation of Bittner's data with the new cross-sections results in no change of conclusion regarding partial equilibria in that flame.

Models used to date for H_2-O_2 combustion chemistry predict the O_2 profile poorly. The models predict the above partial equilibrium but significantly overpredict the mole fractions of O, H and OH. The discrepancy is a factor of 10 for H and OH, and 2 for O-atom. C_2 hydrocarbon combustion models predict well the CO/OH concentration ratio and the water-gas partial equilibria. Although the correct interpretation of ionization efficiency curves for several species, in particular C_6H_6 is still under study, it seems possible that a reduction pathway is competitive with oxidation in this flame.

Fullerenes Formation

Corannulene, $C_{20}H_{10}$, a bowl-shaped polycyclic aromatic hydrocarbon whose curvature and carbon framework are similar to those of fullerenes, has been hypothesized to be a fullerene precursor but had never been identified in flames. We have identified corannulene in fullerene-producing flames and also in conventional flames that do not produce fullerenes. The identification was achieved using a combination of analytical methods including high performance liquid chromatography with UV-vis spectrometric detection, and gas chromatography coupled with infrared and mass spectrometric detection. The presence of corannulene in fullerene-forming flames is consistent with the hypothesis that corannulene is a fullerene precursor. The presence of corannulene in fullerene-deficient flames may suggest that at least some stages of fullerene formation chemistry are more generally operative in flames than had previously been known.

Material deposited from fullerene forming flames onto the water-cooled surface of the combustion chamber was found to contain several thermally metastable adducts of fullerenes C_{60} and C_{70} with cyclopentadiene. These adducts appear to be Diels-Alder cycloaddition products which readily undergo cycloreversion to their component molecules upon heating. The kinetics of cycloreversion of $C_{60}C_5H_6$ was studied by time-resolved measurement of concentration of the adduct using 1H NMR integration at different temperatures in the range 80-95°C. The forward Diels-Alder reaction C_{60} plus C_5H_6 was inhibited through addition of maleic anhydride as a scavenger. Arrhenius parameters were found to be $\log A = 12.59 \pm 0.4$, consistent with normal first-order retro-Diels-Alder reactions, and $E = 26.7 \pm 2.2$ kcal/mol, which is 16 kcal/mol lower than the prototypical reaction of ethylene with cyclopentadiene and 5-15 kcal/mol lower than most retro-Diels-Alder reactions. This relatively low E is most likely due to destabilization of the adduct from loss of aromaticity, as well as to resonance stabilization of the transition state.

A kinetic mechanism was constructed for the formation of fullerenes C_{60} and C_{70} in flames, based on types of reactions used in describing growth of polycyclic aromatic hydrocarbons (PAH), and including additional chemical processes needed to describe evolution of the unique structural features of fullerenes. The mechanism consists of types of reactions, each characterized with an approximate rate coefficient, including processes for ring formation (via H-atom abstraction, C_2H_2 addition, and cyclization leading to ring closing), reactive coagulation of aromatic molecules, and cage closing via H_2 elimination and ring closing, but also allowing for additional processes such as intramolecular rearrangements. Although alternatives to corannulene as an intermediate are mentioned, the proposed mechanism is based on corannulene and other related PAH of C_{5v} symmetry.

Preliminary kinetic testing of the mechanism, using approximate rate coefficients based on analogous flat PAH reactions, shows the mechanism to be plausible within the uncertainties of the rate coefficients and the experimental data on fullerenes formation rate. The predicted fullerene formation times extend over a range that includes the experimentally observed times, and the predicted C_{70}/C_{60} ratio agrees well with flame data. Predicted fullerene formation rates are increased strongly by increased C_2H_2 and decreased H_2 concentrations, and moderately by increased H-atom concentrations.

PUBLICATIONS DURING 1993 AND 1994

- Rotello, V.M., Howard, J.B., Yadav, T., Conn, M.M., Viani, E., Giovane, L.M., and Lafleur, A.L.: "Isolation of Fullerene Products from Flames: Structure and Synthesis of the C₆₀-Cyclopentadiene Adduct", *Tetrahedron Letters*, **34**, 1561-1562 (1993).
- Anacleto, J.F., Quilliam, M.A., Boyd, R.K., Howard, J.B., Lafleur, A.L., and Yadav, T.: "Charge-Transfer Ionspray LC-MS Analyses of Fullerenes and Related Compounds from Flame-Generated Materials", *Rapid Communications in Mass Spectrometry*, **7**, 229-234 (1993).
- Giovane, L.M., Barco, J.W., Yadav, T., Lafleur, A.L., Marr, J.A., Howard, J.B., Rotello, V.M.: "Kinetic Stability of the C₆₀-Cyclopentadiene Diels-Alder Adduct, *J. Phys. Chem.*, **97**, 8560-8561 (1993).
- Pope, C.J., Marr, J.A., and Howard, J.B.: "Chemistry of Fullerenes C₆₀ and C₇₀ Formation in Flames", *J. Phys. Chem.*, **97**, 11001-11013 (1993).
- Lafleur, A.L., Howard, J.B., Marr, J.A., and Yadav, T.: "Proposed Fullerene Precursor Corannulene Identified in Flames Both in the Presence and Absence of Fullerenes Production", *J. Phys. Chem.*, **97**, 13539-13543 (1993).
- Pope, C.J., and Howard, J.B.: "Further Testing of the Fullerene Formation Mechanism with Predictions of Temperature and Pressure Effects", *Twenty-Fifth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh (1994).