PROBING FLAME CHEMISTRY WITH MBMS, THEORY, AND MODELING

Annual Progress Report
for Period July 15, 1991, to July 14, 1992

Phillip R. Westmoreland

Department of Chemical Engineering; University of Massachusetts at Amherst
159 Goessmann Laboratory; Amherst, Massachusetts 01003

Phone (413) 545-1750; FAX (413) 545-1647

BITnet address: "westm@umaecs"; Internet address: "westm@ecs.umass.edu"

March 1992

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or applied, 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.

Prepared for

THE U. S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-91ER14192

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Table of Contents

Abstract.....	1
Program Scope.....	1
Recent Progress.....	1
Flame measurements.....	1
Data from the fuel-lean propene flame.....	2
Data from the fuel-rich propene flame.....	2
Mechanistic modeling.....	3
Theoretical kinetics.....	3
Adjustments to Proposal and Budgeted Spending.....	4
Future Plans.....	5
Usage of PI's time.....	5
References.....	5

List of Tables

Table 1. Species measured in low-pressure flat flames of propene/oxygen/argon at fuel-lean ($\phi = 0.229$) and fuel-rich ($\phi = 1.64$) conditions.....	7
---	---

List of Figures

Figure 1. Profiles of temperature (top) and major stable species (bottom) in the fuel-lean propene flame.....	8
Figure 2. Mole fraction profiles in the fuel-lean propene flame for (top) H and H ₂ and (bottom) CH ₃	9
Figure 3. Mole fraction profiles in the fuel-lean propene flame for (top) O-atom and (bottom) OH.....	10
Figure 4. Mole fraction profiles in the fuel-lean propene flame for (top) C ₂ H ₂ , (middle) C ₂ H ₄ , and (bottom) H ₂ CO.....	11
Figure 5. Mole fraction profiles in the fuel-lean propene flame for (top) C ₃ H ₄ and (bottom) allyl.....	12
Figure 6. Mole fraction profiles in the fuel-lean propene flame for (top) C ₃ H ₂ O and (bottom) C ₃ H ₄ O.....	13
Figure 7. Profile of C ₃ H ₆ O mole fraction in the fuel-lean propene flame.....	14
Figure 8. Mole fraction profiles in the fuel-rich propene flame for (top) H-atom and (bottom) H ₂	15
Figure 9. Mole fraction profiles in the fuel-rich propene flame for (top) CH ₂ and (bottom) CH ₃ ..	16
Figure 10. Mole fraction profiles in the fuel-rich propene flame for (top) CH ₄ and (bottom) OH.....	17
Figure 11. Mole fraction profiles in the fuel-rich propene flame for (top) H ₂ O and (bottom) C ₂ H.....	18
Figure 12. Mole fraction profiles in the fuel-rich propene flame for (top) C ₂ H ₂ and (bottom) C ₂ H ₃	19
Figure 13. Mole fraction profiles in the fuel-rich propene flame for (top) C ₂ H ₄ and (bottom) CO.....	20
Figure 14. Mole fraction profiles in the fuel-rich propene flame for (top) H ₂ CO and (bottom) O ₂	21
Figure 15. Mole fraction profiles in the fuel-rich propene flame for (top) C ₃ H ₂ and (bottom) C ₃ H ₃	22
Figure 16. Mole fraction profiles in the fuel-rich propene flame for (top) C ₃ H ₄ and (bottom) allyl.....	23

Figure 17. Mole fraction profiles in the fuel-rich propene flame for (top) C_3H_6 and (bottom) CO_2	24
Figure 18. Mole fraction profiles in the fuel-rich propene flame for (top) C_4H_2 and (bottom) C_4H_4	25
Figure 19. Mole fraction profiles in the fuel-rich propene flame for (top) C_4H_6 and (bottom) C_4H_8	26
Figure 20. Mole fraction profiles in the fuel-rich propene flame for (top) C_4H_{10} and (bottom) C_5H_4	27
Figure 21. Mole fraction profiles in the fuel-rich propene flame for (top) mass 65, C_5H_5 or C_4HO , (middle) mass 66, C_5H_6 or C_4H_2O , and (bottom) mass 67, C_5H_7 or C_4H_3O	28
Figure 22. Mole fraction profiles in the fuel-rich propene flame for (top) C_6H_2 and (bottom) C_6H_6	29
Figure 23. Arrhenius plot of predicted bimolecular rate constant for $C_3H_3 + C_3H_3 \rightarrow$ phenyl + H ($cm^3 mol^{-1} s^{-1}$) via hexadiyne at very low pressure,.....	30

PROBING FLAME CHEMISTRY WITH MBMS, THEORY, AND MODELING

Annual Progress Report for Period July 15, 1991, to July 14, 1992

(Submitted March 1992)

Abstract

The program objective is to establish kinetics of combustion and molecular-weight growth in C_3 hydrocarbon flames as part of an ongoing study of flame chemistry. Specific reactions to be studied are (1) the oxidation reactions of O and OH with C_3 's and (2) the growth reactions of C_3H_5 and C_3H_3 with themselves and with unsaturated hydrocarbons. Our approach combines molecular-beam mass spectrometry (MBMS) experiments which give concentrations of stable species and free radicals in low-pressure flat flames; theoretical predictions of rate constants by thermochemical kinetics, Bimolecular Quantum-RRK, RRKM, and master-equation theory; and whole-flame modeling using full mechanisms of elementary reactions.

Detailed MBMS flame data are the principal results of the first nine months of the grant. Spatial profiles of temperature, area expansion ratio, and mole fraction have been mapped in two low-pressure flat flames, one fuel-lean ($\phi = 0.229$) and the other fuel-rich ($\phi = 1.64$) in propene/oxygen/argon. Species identities and trends suggest certain chemical pathways, but reaction theory and flame modeling are beginning to provide specific, quantitative insights into oxidation and growth chemistry.

Program Scope

The scope of the program is to establish kinetics of combustion and molecular-weight growth in C_3 hydrocarbon flames using molecular-beam mass spectrometry (MBMS) experiments on low-pressure flat flames; theoretical predictions of rate constants by thermochemical kinetics, Bimolecular Quantum-RRK, RRKM, and master-equation theory; and whole-flame modeling using full mechanisms of elementary reactions.

Recent Progress

Work so far in the first year has emphasized measurements in fuel-lean and fuel-rich propene flat flames at low pressures. In parallel to the experimental work, theoretical and modeling research has examined chemically activated reactions important in the propene flame.

Flame measurements. Axial profiles of mole fractions have been measured in the MBMS apparatus built originally by Biordi¹ and modernized by us. The flames were supported on a 10-cm-diameter sintered-bronze burner, positioned relative to a fixed quartz MBMS probe aligned with the

flame axis. Formed by supersonic expansion through the 0.125-mm probe orifice and a 10-mm skimmer orifice, the beam was chopped at 555 Hz and introduced into a quadrupole mass spectrometer with electron-impact ionizer. Both analog and pulse-counting signal detection were used. Major species (except H_2O) were calibrated directly, minor species were calibrated by the method of relative ionization cross-sections, and the H_2O calibration was inferred from an O-atom balance in the post-flame gas.

Profiles of area expansion ratio and temperature permit fluxes and net reaction rates to be calculated from the mole-fraction data. Area expansion ratio $A(z)$ was measured by hot-wire anemometry in a cold flow of gas. Using the resistive-heating method of Kent² to correct for radiative and convective heat losses, temperatures were measured with 76- μm -diameter Pt/Pt-13%Rh thermocouples, butt-welded and coated with a noncatalytic $\text{Y}_2\text{O}_3\text{-BeO}$ film. Temperatures were too high for Kent's method in the hottest part of the flame, so unheated thermocouple data were corrected computationally for radiative heat loss using the heated/unheated thermocouple data from the cooler regions (Fig. 1, top). These $A(z)$ and $T(z)$ data are also used in the flame modeling, allowing the reaction mechanism to be tested.

Data from the fuel-lean propene flame. Temperatures and concentration profiles of 20 species (Table 1, Figs. 1-7) have been mapped in a fuel-lean $\text{C}_3\text{H}_6/\text{O}_2/\text{Ar}$ flame at a fuel-equivalence ratio of $\phi = 0.229$, pressure of 30.00 ± 0.01 Torr, and burner velocity of 57 cm/s (298 K). Point measurements of five other species were also made. An important reference point is the position of the maximum temperature of 1935 K, occurring at 12.4 mm axial distance from the burner (Fig. 9).

Fuel propene was quickly converted to H_2 and CO , which were in turn converted to H_2O and CO_2 (Figs. 1,2). H-atom (Fig. 2) was rapidly formed and destroyed, reaching a maximum mole fraction of 0.001 or 0.1%. In contrast, O and OH (Fig. 3) reached slightly above the 1% level.

Most of the hydrocarbon chemistry occurred in a narrow region from 3 to 6 mm from the burner where the temperature was about 1500-1900 K. Concentrations of alkenes and oxygenated hydrocarbons (H_2CO , $\text{C}_3\text{H}_2\text{O}$, $\text{C}_3\text{H}_4\text{O}$, $\text{C}_3\text{H}_6\text{O}$) peaked near 4 mm, while radicals and alkynes peaked at higher temperatures slightly further away from the burner. Detection of the C_3 oxygenates (Figs. 6-7) is especially useful because we speculate that they are direct products of the chemically activated reactions between C_3H_x radicals and O or OH. Data for these species, although sparse, allow direct inference of rate constants from rates of formation, temperatures, and reactant concentrations.

Data from the fuel-rich propene flame. In a fuel-rich $\text{C}_3\text{H}_6/\text{O}_2/\text{Ar}$ flame, full profiles of 32 species have been mapped, and point measurements were made for seven species (Table 1, Figs. 9-22). Flame conditions were $\phi = 1.64$, 35.00 ± 0.01 Torr, and 27.3 cm/s velocity. In this flame, the maximum temperature reached 2265 K at 8.0 mm.

The primary flame zone in this flame is much wider than in the lean flame, with rapid hydrocarbon chemistry occurring in the region from 3 to 12 mm. The balance among H (Fig. 8), OH (Fig.

9), and O shifted as well, with H and OH reaching mole fractions of 0.0016 and 0.0018 but O so low as to be obscured by CH₄. The H₂O profile (Fig. 11) shows an overshoot which can be attributed to excess H₂O formation by OH, followed by H attack on the H₂O. On the other hand, CO₂ shows a monotonic increase in mole fraction (Fig. 17), indicating that CH₂ oxidation was not forming significant amounts of the prompt CO₂ that had been observed in a fuel-rich C₂H₂ flame.

Notable features of the hydrocarbon data set are a complete set of C₃ profiles from C₃H₂ to C₃H₆ (Figs. 15-17) and measurements of CH₂ (Fig. 9), C₂H (Fig. 11), and C₂H₃ (Fig. 12), which have been achieved in few other flames. Sets of data for C₄'s (Figs. 18-20), C₅'s (Figs. 20-21), and C₆'s (Fig. 22) were also collected. The C₄H₈ (Fig. 19) and C₄H₁₀ (Fig. 20) data apparently have contributions due to feed impurities, a potentially useful complication.

Mechanistic modeling. An initial mechanism has been constructed and is being tested against the C₃ flame data. The flame-modeling codes are modifications of those developed by Smooke and Sandia National Laboratories, and sensitivity to reaction and parameter choices are being analyzed both by Sandia sensitivity codes and by our Reaction-Path Analysis method.

Theoretical kinetics. At typical flame temperatures and pressures, we have predicted³ that direct propargyl (C₃H₃) combination forms the open-chain C₆H₆ species 1,5-hexadiyne, 1,2,4,5-hexatetraene, and 4,5-hexadienyne in preference to cyclic C₆H₆ species 3,4-dimethylenecyclobutene, fulvene, and benzene (, , and vs. , , and). These chemically activated reactions, analyzed by a new Q-formalism of Bimolecular Quantum-RRK, have rate constants and rates that are consistent with C₆H₆ data from a C₂H₂/O₂/Ar flat flame, but the mass 78 signal would be due to linear C₆H₆'s rather than to benzene, at least initially. Cyclic C₆H₆'s may be generated by thermal isomerizations, as shown in studies of hexadiyne pyrolysis.⁴

Entropy effects interfere with direct chemically activated formation of benzene or of phenyl + H. The energy of propargyl combination is higher than any barriers to rearrangement, which might seem to suggest rapid, barrierless conversion to the most stable C₆H₆ isomer, benzene. However, each rearrangement proceeds via a tight, concerted transition state with consequently low A_∞-factors. At the same time, decompositions of the chemically activated hexadiyne and hexatetraene have high A_∞-factors.

Rate constants at low pressure give the limiting possibility of direct formation of phenyl + H. Collisional energy transfer is necessary to stabilize C₆H₆ isomers at any significant rate, but the collision rate can be made vanishingly small by calculations at very low pressures. As shown in Figure 23, if phenyl + H and C₆H₆ to C₃H₃'s are the only decomposition channels left, direct phenyl formation from C₃H₃ + C₃H₃ has a low rate constant relative to k_∞. Again, the reason is that reaching a chemically activated benzene state is difficult due to the entropic effects.

Adjustments to Proposal and Budgeted Spending

Plans for the first year of the grant which had been proposed and summaries of the work that has been carried out include:

- (a) Map the stoichiometric propene/O₂/Ar flat flame: mole fractions with MBMS, temperatures (construct thermocouples and resistive heating circuit), area-expansion ratios (construct hot-wire anemometer), stable species and stable isomer resolution by GC/MS (develop sampling and analysis protocol).

Action: Studying the stoichiometric propene flame was postponed in order to begin mapping the fuel-lean flame (scheduled for year 2) and the fuel-rich flame (scheduled for years 1-2). The stoichiometric flame may be studied later, but flame predictions will be examined to decide whether the experiment is likely to give insights different from the other two conditions.

The thermocouple system and hot-wire anemometer were constructed and operated, and the microprobe/GC procedure is being tested.

- (b) Select conditions and begin mapping the fuel-rich propene/O₂/Ar flat flame.

Action: The fuel-rich flame (scheduled to extend over years 1 and 2) was mapped during year 1.

- (c) Develop Quantum-RRK multiple isomerization and master equation codes.

Action: A Quantum-RRK multiple isomerization code was developed in the period before the grant was awarded, and it has been refined as a part of this grant. A simple master-equation code was developed (chemically activated association, but no isomerization). A master equation for these association reactions will be developed.

- (d) Predict kinetics for possible C₃H₃+C₃H₃ and C₃H₃+C₃H₄ paths to aromatics.

Action: C₃H₃+C₃H₃ kinetics were developed further. C₃H₃+C₃H₄ kinetics were studied briefly, but no feasible route to aromatics was yet found. Molecular modeling and the master-equation code described above are needed for major progress.

- (e) Construct initial mechanism and test against reference CH_4 , C_2H_2 , and C_2H_4 flames.

Action: A mechanism is being tested against the 1-atm C_2H_4 flame data of Taylor⁵ as an initial case. Literature data will be used to test other flames later this year.

The principal alteration in budget plans was emergency spending of capital funds for replacement components in the vacuum system. System modifications were required during this period due to failures of the mass-spectrometer's diffusion pump. When the 4-inch diffusion pump failed, it proved to be beyond repair and had to be replaced. Its cryogenic backstreaming trap also had to be replaced by a new trap and an elbow because of the custom nature of the original pump's connections. The diffusion-pump system for the skimmer chamber also had to be replaced. On the bright side, 4-inch pumps were replaced with 6-inch pumps which have higher pumping speeds and reduce natural interferences from background gases.

The other major equipment replacement was done with no capital cost. Electronic controls (digital mass programmer) for the quadrupole mass spectrometer failed, but the manufacturer (Extrel) no longer manufactures or repairs that component. We developed software to mimic its function using an existing IBM-compatible PC with digital-to-analog converter.

Future Plans

Work in the next year will extend and analyze the data set described here. Fluxes and net reaction rates are being calculated from the data for each species, and predictions of flame modeling are being compared to the data. To identify and measure the C_6H_6 isomers, microprobe samples are being drawn from the molecular-weight-growth zone; analyses are by GC and GC/MS. An RRKM code for chemically activated reactions is being developed using the Q-formalism for multiple internal rearrangements, which had been developed using Bimolecular Quantum-RRK theory.³

Usage of PI's time

Approximately 10% of the PI's time was spent on the project in the initial portion of the grant, primarily on training and supervision of the graduate students on the project, development of procedures and theory, and communication of results. This fraction of time should remain constant on average.

References

1. Biordi, J. C., Lazzara, C. P., Papp, J. F. *Combustion and Flame* 1974, 23, 73; Biordi, J. C. *Prog. Energy Comb. Sci.* 1977, 3, 151.
2. Kent, J. H. *Combustion and Flame* 1970, 14, 279.

3. Thomas, S. D., Communal, F., Westmoreland, P. R. " C_3H_3 Reaction Kinetics in Fuel-Rich Flames," Preprints of Div. of Fuel Chemistry, American Chemical Society, 36, No. 4, 1448-1455 (1991); presented at the Symposium on Combustion Chemistry, 202nd National Meeting of ACS, New York NY, August 25-30, 1991.
4. Stein, S. E., Walker, J. A., Suryan, M. M., Fahr, A. *23rd Symp. (Intl.) on Combustion*, The Combustion Institute, Pittsburgh, 85 (1990).
5. Taylor, B. R. Ph.D. dissertation, Dept. of Chem. Eng., M.I.T., 1983.

Table 1. Species measured in low-pressure flat flames of propene/oxygen/argon at fuel-lean ($\phi = 0.229$) and fuel-rich ($\phi = 1.64$) conditions. In addition, point measurements were made for masses 75, 76, 77, 79, 80, and 92 in the fuel-rich flame.

Species	Fuel-lean	Fuel-rich	Species	Fuel-lean	Fuel-rich
H	Profile	Profile	C ₃ H ₃	Point	Profile
H ₂	Profile	Profile	C ₃ H ₄	Profile	Profile
CH ₂	Point	Profile	Ar	Profile	Profile
CH ₃	Profile	Profile	C ₃ H ₅	Profile	Profile
Mass 16	Profile (O)	Profile (CH ₄)	C ₃ H ₆	Profile	Profile
OH	Profile	Profile	CH ₃ CHO	Point	-
H ₂ O	Profile	Profile	CO ₂	Profile	Profile
C ₂ H	-	Profile	C ₄ H ₂	-	Profile
C ₂ H ₂	Profile	Profile	C ₄ H ₄	-	Profile
C ₂ H ₃	Point	Profile	Mass 54	Profile (C ₃ H ₂ O)	Profile (C ₄ H ₆)
C ₂ H ₄	Profile	Profile	Mass 56	Profile (C ₃ H ₄ O)	Profile (C ₄ H ₈)
CO	Profile	Profile	Mass 58	Profile (C ₃ H ₆ O)	Profile (C ₄ H ₁₀)
Mass 29	Profile (HCO)	Point	C ₅ H ₄	-	Profile
Mass 30	Profile (H ₂ CO)	Profile	C ₅ H ₅	-	Profile
O ₂	Profile	Profile	C ₅ H ₆	-	Profile
HO ₂	Point	-	C ₅ H ₇	-	Profile
H ₂ O ₂	Point	-	C ₆ H ₂	-	Profile
C ₃ H ₂	-	Profile	C ₆ H ₆	-	Profile

Figure 1. Profiles of temperature (top) and major stable species (bottom) in the fuel-lean propene flame.

Figure 2. Mole fraction profiles in the fuel-lean propene flame for (top) H and H₂ and (bottom) CH₃.

Figure 3. Mole fraction profiles in the fuel-lean propene flame for (top) O-atom and (bottom) OH.

Figure 4. Mole fraction profiles in the fuel-lean propene flame for (top) C₂H₂, (middle) C₂H₄, and (bottom) H₂CO.

Figure 5. Mole fraction profiles in the fuel-lean propene flame for (top) C_3H_4 and (bottom) allyl.

Figure 6. Mole fraction profiles in the fuel-lean propene flame for (top) C_3H_2O and (bottom) C_3H_4O .

Figure 7. Profile of C_3H_6O mole fraction in the fuel-lean propene flame.

Figure 8. Mole fraction profiles in the fuel-rich propene flame for (top) H-atom and (bottom) H_2 .

Figure 9. Mole fraction profiles in the fuel-rich propene flame for (top) CH_2 and (bottom) CH_3 .

Figure 10. Mole fraction profiles in the fuel-rich propene flame for (top) CH_4 and (bottom) OH .

Figure 11. Mole fraction profiles in the fuel-rich propene flame for (top) H₂O and (bottom) C₂H.

Figure 12. Mole fraction profiles in the fuel-rich propene flame for (top) C_2H_2 and (bottom) C_2H_3 .

Figure 13. Mole fraction profiles in the fuel-rich propene flame for (top) C_2H_4 and (bottom) CO.

Figure 14. Mole fraction profiles in the fuel-rich propene flame for (top) H₂CO and (bottom) O₂.

Figure 15. Mole fraction profiles in the fuel-rich propene flame for (top) C₃H₂ and (bottom) C₃H₃.

Figure 16. Mole fraction profiles in the fuel-rich propene flame for (top) C_3H_4 and (bottom) allyl.

Figure 17. Mole fraction profiles in the fuel-rich propene flame for (top) C_3H_6 and (bottom) CO_2 .

Figure 18. Mole fraction profiles in the fuel-rich propene flame for (top) C_4H_2 and (bottom) C_4H_4 .

Figure 19. Mole fraction profiles in the fuel-rich propene flame for (top) C_4H_6 and (bottom) C_4H_8 .

Figure 20. Mole fraction profiles in the fuel-rich propene flame for (top) C₄H₁₀ and (bottom) C₅H₄.

Figure 21. Mole fraction profiles in the fuel-rich propene flame for (top) mass 65, C_5H_5 or C_4HO , (middle) mass 66, C_5H_6 or C_4H_2O , and (bottom) mass 67, C_5H_7 or C_4H_3O .

Figure 22. Mole fraction profiles in the fuel-rich propene flame for (top) C_6H_2 and (bottom) C_6H_6 .

Figure 23. Arrhenius plot of predicted bimolecular rate constant for $C_3H_3 + C_3H_3 \rightarrow \text{phenyl} + H$ ($\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$) via hexadiyne at very low pressure, shown as square symbols. Short dashed line is an Arrhenius fit; long-dashed line is a fit to $A \cdot T^b \cdot \exp(-C/T)$.

END

**DATE
FILMED**

6 / 12 / 92