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PROBING FLAME CHEMISTRY WITH MBMS, THEORY, AND MODELING

Annual Progress Report
for Period July 15, 1993, to July 14, 1994

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PROBING FLAME CHEMISTRY WITH MBMS, THEORY, AND MODELING

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Abstract

Propene/oxygen/argon flames have been mapped and modeled at fuel-lean ($\phi = 0.229$; 30 Torr) conditions and fuel-rich conditions ($\phi = 1.64$; 35 Torr). 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.

In the past year, we made extensive re-measurements of temperature because previous modeling suggested that the temperature profiles were wrong. The new measurements changed only slightly from the previous measurements. Instead, continued modeling of the lean propene flame and of ethene flames revealed that the problem was inadequacies in the earlier reaction set. Corrections from the literature and from theoretical kinetics resolved nearly all the problems except for allyl, which was overpredicted by $\times 20$ to $\times 30$. This error is corrected by identifying a new reaction of allyl+O₂ with a rate constant of $(3\pm 1)\times 10^{12}$ at 1000-1700 K, probably forming propenal+OH.

Program Scope

The scope of the program is to establish kinetics of oxidation and molecular-weight growth in C_3 hydrocarbon flames. The approach combines 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. Specific reactions to be studied are (1) oxidation reactions of O and OH with C_3 's and (2) growth reactions of C_3H_5 and C_3H_3 with themselves and with unsaturated hydrocarbons.

Significant Results

Support for this research, initiated in 1991, has led to results from flame mapping, theory applied to predicting elementary reactions, and flame modeling.

Mapping propene flames. A major portion of the work has been mapping axial profiles of mole fractions in $C_3H_6/O_2/Ar$ flat flames. We are using the MBMS apparatus built originally by Biordi and co-workers,¹ which we have adapted and modified.

Fuel-lean ($\phi = 0.229$, 30 Torr, $v_o = 57.5$ cm/s at 298 K) and fuel-rich ($\phi = 1.64$, 35 Torr, $v_o = 27.4$ cm/s at 298 K) flat flames have been mapped using MBMS, noncatalytic thermocouples, hot-wire

¹Biordi, J. C., Lazzara, C. P., Papp, J. F. *Combust. Flame*, 23:73 (1974); Biordi, J. C. *Prog. Energy Comb. Sci.*, 3:151 (1977).

anemometry, and microprobe sampling for GC/MS analysis. Profiles for 22 species and point measurements of eight species have been mapped in the fuel-lean flame. In the fuel-rich flame, 32 full profiles plus point measurements for sixteen species have been made. The species are listed in Table 1.

These data are the first complete mappings of flat flames for C₃ hydrocarbons, *i.e.*, with profiles of radical and stable species, temperatures, and area expansion ratio. The only previous MBMS measurements in a C₃ flame were for propane in the pioneering paper of Homann *et al.* in 1963,² which first demonstrated flame MBMS. There, only stable species were reported, and no area-expansion ratio or temperatures were measured. Other useful data on C₃ hydrocarbons comes from flow reactors and jet-stirred reactors. What makes the present data so valuable is measurement of radicals as well as stable species. Also, the temperatures in this burner-stabilized flame encompass low and high-temperature flame chemistry.

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. Data for different species and masses include complete profiles by MBMS, point measurements and upper bounds by MBMS, and point measurements by microprobe sampling and GC analyses.

Species	Fuel-lean	Fuel-rich	Species	Fuel-lean	Fuel-rich
H	Profile	Profile	C ₄ H ₃	-	Profile
H ₂	Profile	Profile	C ₄ H ₄	-	Profile
CH ₂	MBMS point	Profile	C ₄ H ₅	-	Profile
CH ₃	Profile	Profile	Mass 54	Profile (C ₃ H ₂ O)	Profile (C ₄ H ₆)
Mass 16	Profile (O)	Profile (CH ₄)	C ₃ H ₅ O	Profile	-
OH	Profile	Profile	Mass 56	Profile (C ₃ H ₄ O)	Profile (C ₄ H ₈)
H ₂ O	Profile	Profile	C ₃ H ₅ O	Profile	-
C ₂ H	-	Profile	Mass 58	Profile (C ₃ H ₆ O)	Profile (C ₄ H ₁₀)
C ₂ H ₂	Profile	Profile	C ₅ H ₄	-	Profile
C ₂ H ₃	MBMS bound	Profile	C ₅ H ₅	-	Profile
C ₂ H ₄	Profile	Profile	C ₅ H ₆	-	Profile
CO	Profile	Profile	C ₅ H ₇	-	Profile
Mass 29	Profile (HCO)	MBMS point	C ₆ H ₂	-	Profile
Mass 30	Profile (H ₂ CO)	Profile	Mass 75	-	MBMS point
O ₂	Profile	Profile	Mass 76	-	MBMS point
HO ₂	MBMS bound	-	Mass 77	-	MBMS point
H ₂ O ₂	MBMS bound	-	C ₆ H ₆	-	Profile
C ₃ H ₂	-	Profile	Benzene	-	GC point
C ₃ H ₃	MBMS bound	Profile	Mass 79	-	MBMS point
C ₃ H ₄	Profile	Profile	Mass 80	-	MBMS point
Propyne	MBMS point	-	Mass 92 (Toluene)	-	MBMS, GC point
Propadiene	MBMS point	-	Phenylacetylene	-	GC point
Ar	Profile	Profile	Styrene	-	GC point
C ₃ H ₅	Profile	Profile	Ethylbenzene	-	GC point
C ₃ H ₆	Profile	Profile	Allylbenzene	-	GC point
CH ₃ CHO	MBMS point	-	o-Methylstyrene	-	GC point
CO ₂	Profile	Profile	Indene	-	GC point
C ₄ H ₂	-	Profile	Naphthalene	-	GC point

²Homann, K. H., Mochizuki, M., Wagner, H. Gg. *Z. Phys. Chem., N. F.*, 37:299 (1963).

Another very interesting feature was the presence of C₃ oxygenates in the lean flame. The highest mole fraction was reached by C₃H₄O, identified by its ionization potential as propenal (acrolein). Brezinsky *et al.*³ had proposed that acrolein could be formed during combustion of butadiene by allyl reactions with O and HO₂. From similar mechanistic considerations, C₃H₂O is expected to be propynal (HC≡C-CH=O). C₃H₆O appears to be propanal, possibly mixed with methyloxirane (propylene oxide).

In the fuel-rich flame, notable features of the data include a complete set of C₃ profiles from C₃H₂ to C₃H₆ and measurements of CH₂, C₂H, and C₂H₃, achieved in few other flames.

In the past year, temperatures have been re-mapped and alternative noncatalytic coatings have been investigated. Temperatures were previously measured with Y₂O₃-BeO-coated, 76-μm-diameter, Pt/Pt-13%Rh thermocouples, experimentally corrected for convective and radiative cooling. Heat had made the thermocouples sag during the measurements, creating uncertainty about the positions being measured, and species modeling suggested that the measurements near the burner might be too high. An alternative coating, Cerambond, proved unsatisfactory because of its thickness, roughness, and porosity, but re-measurement with the Y₂O₃-BeO-coated thermocouple was successful.

The true temperature profiles were only slightly further from the burner. In the lean flame, temperature reached 1000 K at 1.46 mm from the burner, and the maximum temperature was 1959 K at 12 mm. These improved temperature data allowed us to identify features of the flame mechanism that caused the predictions of too-early consumption.

Theory: BAC-MP4 calculations. BAC-MP4 calculations are being used to predict key thermochemistry of chemical species and transition states. Benson's methods of group additivity and thermochemical kinetics work well when the right groups and transition-state models can be identified. However, Melius's BAC-MP4 method⁴ is a powerful way of going beyond this limitation, combining *ab initio* electronic-structure calculations with a small number of general corrections.

As shown in Table 2, calculations in the past year have focused on species and transition states for C₂H₃+O₂ and allyl + O, OH, and O₂, important for reaction and flame modeling described below.

Theory: Prediction of rate constants. A hierarchy of Quantum-RRK, RRKM, and Master Equation theories is being used to predict needed rate constants.

At typical flame temperatures and pressures, we predict⁵ that direct propargyl (C₃H₃) combination forms the open-chain C₆H₆ species 1,5-hexadiyne, 1,2,4,5-hexatetraene, and

³Brezinsky, K., Burke, E. J., Glassman, I. *20th Symp. (Intl.) on Combustion*, The Combustion Institute, Pittsburgh, 613 (1985).

⁴Melius, C. F., in Bulusu, S. U. (Ed.), *Chemistry and Physics of Energetic Materials*, Kluwer Academic Publishers: Dordrecht, 21 (1990); Ho, P., and Melius, C. F., *J. Phys. Chem.*, 94:5120 (1990).

⁵Thomas, S. D., Communal, F., Westmoreland, P. R. "C₃H₃ Reaction Kinetics in Fuel-Rich Flames," Preprints of Div. of Fuel Chemistry, American Chemical Society, 36:1448-1455 (1991).

Table 2. Summary of BAC-MP4 calculations.

Species names	$\Delta H_{f,298}$, kcal/mol			S_{298} , cal/mol K		
	BAC	Lit.	Diff	HF31G*	Lit.	Diff
$\text{CH}_4 \rightarrow \text{CH}_2(\text{singlet}) + \text{H}_2$	102.76			51.95		
$\text{C}_2\text{H}_3\text{CO}$	28.28			68.96		
$\rightarrow \text{C}_2\text{H}_3\text{O} + \text{O}$	43.16			69.41		
c- $\text{CH}_2\text{CH}_2\text{OO}$, dioxetane	27.61			65.76		
c- CH_2CHOO , dioxetanyl	49.78			65.36		
$\text{CHO-CH}_2\text{OH}$	-72.40	-75.1	2.7	69.86	73.8	-3.9
		(est'd)			(est'd)	
$\text{CHO-CH}_2\text{O}$, formylmethoxy	-12.95			69.43		
$\rightarrow \text{CHO} + \text{CH}_2\text{O}$	-12.43			66.38		
$\text{C}_2\text{H}_3\text{CH}_2\text{OH}$, allyl alcohol	-30.35	-30.0	-0.4	69.80	73.5	-3.7
$\text{C}_2\text{H}_3\text{CH}_2\text{O}$, allyloxy	25.89			69.92		
$\rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{H}$	46.36			70.11		
$\rightarrow \text{C}_2\text{H}_3 + \text{CH}_2\text{O}$	47.09			75.35		
$\text{C}_2\text{H}_3\text{CHO}$, propenal	-14.19	-18.0	3.8	66.81	71.0	-4.2
					(est'd)	
$\text{C}_2\text{H}_3\text{CH}_2\text{CH}_2 \rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_4$	-30.35			69.80		

4,5-hexadienyne in preference to cyclic C_6H_6 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 C_6H_6 data from a $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ flat flame, but the mass 78 signal would be due to linear C_6H_6 's rather than to benzene, at least initially. Rate constants at low pressure give the limiting possibility of direct formation of phenyl + H. If phenyl + H and C_6H_6 to C_3H_3 's are the only decomposition channels left, direct phenyl formation from $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ has a low rate constant relative to k_∞ . In both cases, the reason is that reaching a chemically activated benzene state is difficult due to the entropic effects.

Allyl reactions have been emphasized because of their importance in modeling the propene flames and the poor state of understanding them. We have predicted rate constants for reactions of allyl with H, CH_3 , O, OH, O_2 , HO_2 , and itself with the results summarized briefly as:

O + allyl is absent from both sets. Chemically activated allyloxy may decompose to form H + propenal and/or $C_2H_3 + H_2CO$. Low-temperature, low-pressure measurements give $k = 1.8 \cdot 10^{14}$ with H + propenal as the only products detected,⁶ and simple estimates favor H + propenal slightly. Using the BAC-MP4 method, our transition-state calculations instead indicate that the $C_2H_3 + H_2CO$ channel is favored in $C_2H_3CH_2O\cdot$ decomposition. We plan G2-level calculations to resolve this contradiction.

OH + allyl forms chemically activated allyl alcohol, which may undergo isomerizations and decompositions. By proposing that allyl alcohol may decompose concertedly by a sigmatropic process to $C_2H_2 + H_2CO + H_2$, we predict that this is the dominant OH + allyl product channel ($k = 1.5 \cdot 10^{13}$) at low pressures and high temperatures.

O_2 + allyl proves most interesting, as will be discussed in the section on flame modeling. Chemically activated reactions of allyl with O_2 are limited by the energetics and looseness of breaking the new allyl- O_2 bond. At low temperature, the adduct is favored, but falloff slows its formation. At high temperatures, Bozzelli and Dean⁷ predict 14 possible product channels other than C_3H_5OO with rate constants only as high as 10^9 , and we calculate similar numbers. The high concentration of O_2 compensates only to a modest extent for the low rate constants.

For the propene flame as well as for many other, vinyl's reaction with O_2 is also an important puzzle, in particular whether an O + C_2H_3O channel opens at high temperatures. Earlier experimental⁸ and theoretical⁹ studies paint a consistent picture that $HCO + H_2CO$ forms at low temperatures and pressures with a negative activation energy. Most current reaction sets use the experimental products and rate constant for all temperatures and pressures. However, theory⁷ clarifies that the rate constant is downward curving on the Arrhenius plot, dropping much lower than extrapolation from the low-temperature fit. Chemically activated decomposition of the hot adduct to O + C_2H_3O may contribute,^{5,7} depending on the high-pressure-limit rate constant for the reverse reaction, $\cdot CH_2CHO + O$ association. This transition state was examined with local density-functional theory (double-numerical-plus-polarization basis sets) and BAC-MP4 calculations. Density-functional calculations indicated that this association has a barrier sufficient to prevent the O-atom channel from contributing, but BAC-MP4 calculations give a barrierless reaction with a modest A-factor. The channel would contribute but would not be major.

⁶Slagle, I. R., Bernhardt, J. R., Gutman, D., Hanning-Lee, M. A., Pilling, M. J. *J. Phys. Chem.*, 94:3652 (1990).

⁷Bozzelli, J. W., Dean, A. M. *J. Phys. Chem.*, 97:4427 (1993).

⁸Slagle, I. R., Park, J.-Y., Heaven, M. C., Gutman, D. *J. Am. Chem. Soc.*, 106:4356 (1984).

⁹Westmoreland, P. R. *Combust. Sci. and Tech.*, 82:151 (1992).

Theory: Quantum reaction theories and codes. New theoretical approaches and codes are under development. Of special interest is state-to-state energy transfer in chemically activated reactions. Multiple-isomerization cases like $C_3H_3+C_3H_3$, $C_3H_5+O_2$, and $C_2H_3+O_2$ may be especially affected.

A new Fortran code was developed for calculations using our Q-formalism of Bimolecular Quantum-RRK. Multiple chemically activated isomerizations, including branches, are treated by maintaining the beta-type modified strong-collision model for stabilization. Calculations of rate constants may be made on any computer that has a Fortran compiler, but special PC graphics are added.

For simple thermal decompositions, we are using our Quantum-RRK codes and RRKM/Master-Equation codes written by Gilbert and co-workers.¹⁰ The Gilbert RRKM codes use an ASCII input file of numbers and species names. We have written a Fortran program for interactive input of the needed information. It writes both a user-readable file of the input parameters and a parameters-only file in the form needed by the Gilbert code.

We are collaborating with Wing Tsang of NIST-Gaithersburg to write a Fortran code for chemically activated reactions that accounts for collisional energy transfer with a staircase model. The initial version considers only association/stabilization and association/decomposition reactions (e.g., $CH_3+CH_3 \rightarrow C_2H_6$ or C_2H_5+H , respectively). This work is in progress.

Flame modeling. Modeling the propene data tested, showed needs, and helped development of kinetics for propene destruction, allyl destruction, and formation of C_3 oxygenates. Tests against the propene and literature C_2H_4 flame data also showed the importance of uncertainties about C_2H_4 and C_2H_3 oxidation/growth kinetics. The sequence of reaction pathways in propene combustion and the balance among them was clearly established.

We have focused on tests using four reaction sets:

- Our development set for C_1 - C_3 reactions presently includes 323 reversible reactions and 59 species. Major sources were (1) the C_1 and C_2 reaction mechanism of Miller and Bowman,¹¹ (2) C_3 and C_4 reactions in the mechanism of Dagaut *et al.*,¹² (3) modifications in the C_2H_2 mechanism of Miller *et al.*,¹³ (4) improvements to the Miller and Bowman mechanism by Michaud *et al.*,¹⁴ and (5) our modifications for allyl chemistry, described above, and for propenal chemistry.
- A set developed by Dagaut *et al.*¹⁵ (DCBG) for predicting effluent concentrations from propene combustion in jet-stirred reactors. Tested conditions were equivalence ratios ϕ from 0.15 to 4.0, pressures from 101 to 808 kPa, and temperatures from 900 to 1200 K. Only forward rate constants were specified, so thermochemistry had to be added.

¹⁰Gilbert, R.G., Smith, S.C., and Jordan, M.J.T., Programs RRKM.FOR (1/8/93), BRW.FOR (6/29/91), GEOM.FOR, MAS55.FOR (11/19/92), and MAS77.FOR (10/23/91), University of Sydney, Australia.

¹¹Miller, J. A., Bowman, C. T. *Prog. Energy Combust. Sci.*, 15:287 (1989).

¹²Dagaut, P., Cathonnet, M., Boettner, J. C. *Combust. Sci. and Tech.*, 71:111 (1990).

¹³Miller, J. A.; *et al.* 23rd Symp. (Intl.) on Combustion, 187 (1990).

¹⁴Michaud, M.G., Westmoreland, P.R., Feitelberg, A.S. 24th Symp. (Intl.) on Combustion, 879 (1992).

¹⁵Dagaut, P., Cathonnet, M., Boettner, J. C., Gaillard, F. *Combust. Flame* 71:295 (1988).

- A set developed by Wilk *et al.*¹⁶ (WCPW) for propene oxidation in a static reactor at 530 to 740 K and pressures near 1 atm; forward and reverse rate constants were specified, so no thermochemistry had to be added. WCPW described oxidation emphasizing peroxy and peroxide chemistry. This emphasis is more appropriate to the lower temperatures of that system, and should not be assumed to be valid at the higher temperatures in the present propene flames. While the WCPW reaction set includes $C_3H_xO_x$ chemistry, it does not include chemistry for C_4 and higher hydrocarbons, so it is not suited to fuel-rich flames.
- Our modifications of the WCPW set that account more fully for allyl chemistry.

Mole fraction profiles were calculated using the PREMIX/Chemkin codes of Sandia¹⁷ on a DECstation 5000 Model 240 workstation. Experimental temperatures and area expansion ratios were input to the programs. Reaction paths are analyzed with the aid of a post-processor for interactive display and manipulation of Chemkin results¹⁸ which I had helped develop at NIST.

Flame modeling: Lean propene flame. Destruction of propene in the fuel-lean flame was a combination of (1) direct oxidation by O atom and (2) oxidation of abstraction-produced allyl by O_2 , O, and HO_2 via chemically activated $C_3H_xO_y^*$ routes. Modeling revealed a previously unrecognized reaction of allyl+ O_2 with $k = 3 \cdot 10^{12} \text{ cm}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}$ at 1000-1750 K.

Propene destruction is largely by O-atom attack for all four sets. Agreement with the present measurements (Fig. 1 and 2) supports not only the latter three sets' treatment of $O+C_3H_6$ but also the general predictions for the radical pool. The first set predicts too-rapid destruction of C_3H_6 , solely because of the treatment of $HOCO$; on the other hand, it is the only set to make a reasonable prediction of H_2 . The overall destruction by O is by a well-established rate constant. Then one-third of the overall rate constant was assigned to each of the channels CH_3+CH_3+CO (from immediate decomposition of CH_3CO), C_2H_5+HCO , $C_2H_4+H_2CO$. Such branching among channels has not been confirmed over the full range of temperature and pressures. Klemm *et al.*¹⁹ recently measured a slightly lower CH_3 yield from $O+C_3H_6$, 0.5 ± 0.15 at room temperature and 300-600 Pa, and they suggested CH_3+CH_2CHO as another product channel. This branching is being tested.

Propene is also destroyed by OH. Using the WCPW set, 20% of propene destruction is predicted to occur by OH to make allyl. The $OH+C_3H_6$ reactions of DCBG are very different, though. They cause slightly more of the propene destruction than does O-atom, forming $C_2H_5+H_2CO$, allyl+ H_2O , and $H_2O + CH_3-CH=CH^*$ in order of decreasing importance.

¹⁶Wilk, W. J., Cernansky, N. P., Pitz, W. J., and Westbrook, C. K. *Combust. Flame* 77:145 (1989).

¹⁷Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A., *A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames*, Sandia National Laboratories Report No. SAND85-8240, 1985; PREMIX Version 2.5, CHEMKIN II version 3.2, and TRANFIT version 1.6.

¹⁸Burgess, D. R. F., Jr., Program senk3plot, National Institute of Standards and Technology, Gaithersburg MD, 1993.

¹⁹Klemm, R. B., Kuo, S.-C., Tao, W., Wichmaarachchi, M. A., Gleason, J. F., Brookhaven National Laboratory report 49103, 1993.

A central uncertainty is the chemistry for allyl oxidation. The prediction for allyl (Fig. 3) was the poorest for any of the species profiles, rising 20 to 30 times higher than the measurements. Because allyl formation rates are reasonable, insufficient rates of allyl destruction apparently cause the

Figure 1. Profiles of temperature ($\blacktriangledup$) and of mole fractions for C_3H_6 (∇) and CO (Δ). Prediction using DCBG is ----; using WCPW is - · - ·; modification of WCPW is

Figure 2. Profiles of mole fractions for major species O_2 ($\circ$), H_2O ($\diamond$), and CO_2 ($\square$).

Figure 3. Allyl mole fractions compared to predictions with DCBG ----, WCPW - · - ·, and modified WCPW

excessively high allyl predictions. Falloff was added for allyl decomposition along with H, O, OH, HO₂, and O₂ reactions described above. Allyl was still overpredicted.

The reaction of allyl+O₂ was re-considered because allyl formation by C₃H₆+OH → allyl + H₂O is at a plausible rate. Even with a fast rate constant, only O₂ is in high enough concentration to destroy allyl at a rate close to this formation rate. This reaction cannot be disproportionation to give propadiene+HO₂, based on that reaction's endothermicity (7.5 kcal/mol) and on reasonable estimates of rate constants. A chemically activated step, which would proceed at $3.6 \cdot 10^{12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ or less (k_{∞} for C₃H₅OO formation) is more likely. Based on our calculations, propenal+OH would be the most likely product if the calculations of Bozzelli and Dean⁵ had overpredicted stabilization. As another possibility, if a channel exists with a lower barrier from C₃H₅OO than they had considered, it could compete more successfully against reversion to C₃H₅+O₂ than their proposed channels.

As shown in Fig. 3, the allyl prediction is brought to excellent agreement by using a rate constant of $1.7 \cdot 10^{12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for allyl+O₂ → C₂H₂+H₂CO+OH (analogous to the proposed decomposition products of allyl alcohol). The agreement suggests that this rate constant holds from about 1000 K to ≥1750 K. Other species are little affected by this new rate constant. Exceptions include overprediction of C₂H₂ and (to a lesser extent) H₂CO, which implies that the test products are not correct. If C₂H₃CHO+OH are used as products with $k = 3.6 \cdot 10^{12}$, allyl is again in excellent agreement,

and C_2H_2 and H_2CO return to excellent agreement. However, C_2H_3CHO (C_3H_4O) becomes a factor of ten too high. This overprediction could be caused by inadequate C_2H_3CHO destruction kinetics.

Predictions close to the burner are much lower than the measured points, which are nearly constant. The low prediction implies that allyl is being destroyed too fast below 1000 K by the proposed reaction. A chemically activated decomposition becomes less important when the corresponding addition/stabilization is important, here the competing channel to form C_3H_5OO . This latter channel would likely dominate at low temperatures, but the new bond is so weak that the reaction should be at equilibrium. The addition/stabilization reaction would thus consume little or no allyl. At higher temperatures, falloff of the C_3H_5OO channel allows the new channel to proceed more effectively. Its rate constant must be less than or equal to k_{∞} for association/stabilization.

To summarize, the missing reaction appears to be $allyl + O_2$ with a rate constant of $(3 \pm 1) \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 1000 and 1700 K. Its most probable products are $OH + \text{propenal}$. At low temperatures, rate constants to addition/decomposition products become small and stabilization should be favored. Further experiments and calculations are needed to establish temperature and pressure dependence of the rate constant, to confirm its products, and to explain its steps.

Flame modeling: Rich propene flame. Last year's Annual Report presented a detailed description of modeling in the fuel-rich flame, and this work continues. Key features are summarized below. These calculations have solely used our development reaction set.

In contrast to the fuel-lean flame, larger roles were played by propyl oxidation, $H + \text{propene} \rightarrow CH_3 + C_2H_4$, $H + \text{Allyl} \rightarrow CH_3 + C_2H_3$, and C_4 formation. Little $O + C_3H_6$ occurred. Propene destruction was dominated by H and OH abstracting the allylic hydrogen to make allyl and by the chemically activated association/decomposition reaction $H + C_3H_6 \rightarrow CH_3 + C_2H_4$.

Predicted allyl is only a factor of three too high after the reaction $allyl + H \rightarrow CH_3 + C_2H_3$ is added with a theoretical rate constant. Early in the flame, allyl was consumed by combination to make C_6H_{10} and, at slightly higher temperatures, allyl was regenerated by the reverse decomposition. In the rich flame, this reversible sink resulted in a hump on the low-temperature side of the predicted allyl peak. No such behavior was observed in the data, and this effect is apparently an artifact of the reaction set. However, the amount of allyl combination indicates that C_6H_{10} destruction kinetics must be added because C_6H_{10} would be an oxidation intermediate. Beyond the allyl maximum, the dominant destruction channel was $allyl + H \rightarrow CH_3 + C_2H_3$.

Predictions for C_6H_6 are promising but preliminary. The set used kinetics for $C_3H_3 + C_3H_3 \rightleftharpoons C_6H_6$ by Wu and Kern,²⁰ who had considered C_6H_6 to be benzene; no other C_6H_6 was measured in our microprobe GC/MS measurements. The maximum benzene mole fraction prediction was a factor of 10 higher and 2 mm nearer the burner than that observed for mass 78. Destruction of benzene was only by the reverse of the formation reaction, as benzene oxidation kinetics were incomplete.

²⁰Wu, C. H., Kern, R. D. *J. Phys. Chem.*, 91:6291 (1987).

Flame modeling: Ethene flames. Key problems in modeling the fuel-rich propene flame are ethene oxidation and vinyl + O₂ kinetics. We have predicted flame structures for two flame sets, which confirm that the reactions converting C₂H₄ to C₂H₃ and C₂H₃ to C₂H₂ are unsatisfactorily understood. Modeling the propene and ethene flames indicates the need for MBMS measurements in stoichiometric and rich ethene-O₂ flames.

The only complete set of ethene flame data for modeling is from the thesis of Mahnen,²¹ which was never fully published. He mapped a fuel-lean flame (6.55% C₂H₄, 93.45% O₂ for a fuel equivalence ratio of 0.21) with MBMS at a pressure of 40 Torr for H, H₂, CH₂, CH₃, O, OH, H₂O, C₂H₂, C₂H₃, C₂H₄, CO, CH₂O, O₂, CO₂, temperature, and area expansion ratio.

This set predicted many species in the Mahnen flame, but it had particularly poor predictions of the C₂H₃ and C₂H₂ profiles. The peak in the predicted C₂H₃ profile was six times higher than the peak in Mahnen's data, while the predicted C₂H₂ peak was 70% lower than the data. However, the predicted maxima for both of these profiles did occur at the same distance as the maxima in the data, roughly 0.17 to 0.18 cm above the burner.

The immediate fate of the ethene was predicted to be almost equally split between two major pathways, C₂H₄+O → CH₃+HCO and C₂H₄+OH or H → C₂H₃+H₂O or H₂. All of the methyl subsequently formed formaldehyde (CH₂O). Seventy percent of the methyl did so by reaction with O, while the remainder formed CH₃O or CH₂OH first. The vinyl followed three separate paths. Over half of the vinyl also formed formaldehyde by reaction with O₂, while the balance was evenly split between forming C₂H₂ by decomposition or CH₂CO from O. The key uncertainties are rate constants for H+C₂H₄ abstraction and for C₂H₃+O₂.

We also modeled the next most complete set, data from the thesis of Taylor²² which also was never fully published. He mapped an atmospheric-pressure, fuel-rich flame (10.78% C₂H₄ and 89.22% air for a fuel equivalence ratio of 1.729) for H, H₂, CH₄, H₂O, C₂H₂, C₂H₄, CO, C₂H₆, Ar, C₃H₆, C₃H₈ and CO₂. The first temperatures and mole fractions are in the post-flame zone at 2.5 mm from the burner. Temperatures closer to Taylor's burner were estimated in this work using predictions for a freely propagating flat flame. Modeling of this rich flame reveals different paths than in the very lean Mahnen flame. Temperatures in the flame zone, which may be in error because of their estimation, cause predicted mole fractions to become very different from the data.

Interactions with Other DOE Projects

Interactions include:

- Assistance from Carl Melius in setting up and learning how to use the BAC-MP4 codes;
- Beta-testing "mview," Carl Melius's new graphical interface to the BAC-MP4 codes;

²¹Mahnen, G., doctoral thesis, Université Catholique de Louvain, Belgium, 1973.

²²Taylor, B. R., doctoral thesis, Department of Chemical Engineering, M.I.T., 1984.

- Calculations of propene combustion for Fred Dryer at his flow-reactor conditions;
- Interactions with Bruce Klemm about our modeling with his new C_3H_6+O data;
- Interactions with David Gutman and Irene Slagle to plan new experiments for their laser photolysis/laser photoionization apparatus;
- Collaboration with Wing Tsang on rate-constant estimation and development of a chemical-activation RRKM/Master Equation code for general distribution;
- Continued use of Sandia's Chemkin and Premix codes for modeling flat flames and other combustion systems; and
- Setting up a symposium at the Fall 1994 AIChE Annual Meeting on "Computational Chemistry and Its Industrial Applications," in which I expect the participation of several DOE/BES principal investigators.

My 1992-93 sabbatical at the National Institute of Standards and Technology was a non-DOE interaction that was very useful for our DOE project. On a half-time basis, I worked in a team with Wing Tsang, Michael Zachariah, and Donald Burgess to develop the full thermochemistry and kinetics for modeling hydrofluorocarbon chemistry in flames. In that time, I learned how to use a variety of semi-empirical molecular-orbital codes, molecular mechanics codes, DMol (a density-functional *ab initio* code), Gaussian 92, and the BAC-MP4 code. We now use Hyperchem (PC-based molecular graphics, semi-empirical molecular-orbital codes, molecular mechanics codes) and Gaussian 92 on computers at the University of Massachusetts for our DOE research, and we will soon install the BAC-MP4 code.

Future Plans

We propose to emphasize the following areas in the next year:

- Mapping of propadiene-doped propene flames, scheduled to begin in the last quarter of the current project year;
- Improved modeling of the propene flames and of other reference flames;
- Theoretical calculations of thermochemistry and kinetics indicated as important by the modeling and experiments, in particular allyl+O₂, vinyl+O₂, and $2C_3H_3 \rightarrow \text{benzene}$; and
- Continued development of theory and codes for chemically activated reactions with state-to-state energy transfer.

Usage of PI's Time

Approximately 10% of the PI's time has been spent on the project, 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.

Publications, Presentations, and Submissions in the Past Three Years from DOE-Sponsored Research

Theses and dissertations:

1. Scott D. Thomas, "Molecular-Beam Mass Spectrometry and Mechanistic Modeling of Lean and Rich Propene Flames," Ph.D. dissertation, University of Massachusetts, September 1992.
2. Melissa G. Michaud, "Modeling and Measurement of Pollutants in Flames," M.S. thesis, University of Massachusetts, September 1992.

Submissions:

3. S. D. Thomas and P.R. Westmoreland, "Concentrations and Oxidation Chemistry Measured in a Lean Propene Flame," submitted to *Combustion and Flame*.
4. S. D. Thomas and P.R. Westmoreland, "Allyl Oxidation Chemistry in a Lean Propene Flame," submitted and accepted for a Work-in-Progress Poster (WIP-25-440) at the *Twenty-Fifth Symposium (International) on Combustion*.
5. P. R. Westmoreland, "Modeling the Lean Combustion of Propylene," submitted and accepted for the 1994 Annual Meeting of AIChE, San Francisco CA, November 13-19, 1994.

Papers in preparation for submission by the end of the project year:

6. S. D. Thomas and P.R. Westmoreland, "Concentrations and Oxidation Chemistry Measured in a Rich Propene Flame," to be submitted to *Combustion and Flame*.
7. P.R. Westmoreland, "Kinetics of Allyl Radical," to be submitted to *Journal of Physical Chemistry*.

Presented papers and invited seminars in 1993-94 (based all or in part on DOE-supported research):

8. "Fundamental Kinetics of Hydrocarbon/Chlorine Flames," Dow Chemical Company, Freeport TX, October 15, 1993.
9. P. R. Westmoreland, "Obtaining the Mechanism for Lean Propylene Combustion from a Detailed Reaction Set," Paper 20b, 1993 Annual Meeting of AIChE, St. Louis MO, November 7-12, 1993.
10. "Creating Reaction Mechanisms from *Ab Initio* Theories and Process Modeling," Yale University, Department of Chemical Engineering, New Haven CT, February 4, 1994.
11. "Understanding Flame Chemistry by Experiment, Theory, and Modeling," E. I. Du Pont, Jackson Laboratory, Deepwater NJ, February 11 and April 22, 1994.
12. "Perspectives on the Chemistry of Chlorinated Hydrocarbon Incineration," Symposium on Incineration of Chlorinated Hydrocarbons, Dow Chemical Company, Midland MI, February 22, 1994.
13. "Oxidation Chemistry Measured in a Lean Propylene Flame," ARCO Chemical Company, Newtown Square PA, February 28, 1994.
14. "Obtaining Flame Chemistry from Experiment, Theory, and Modeling," Army Research Laboratory, Aberdeen Proving Ground MD, March 22, 1994.

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