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Fuel Consumption and Initial Steps of Aromatic Ring Formation in a Laminar Premixed Fuel-Rich Cyclopentene Flame

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The initial steps in fuel consumption and formation of single-ring aromatic species in a fuel-rich, non-sooting premixed laminar cyclopentene flame ($\phi = 2.0$) at 37.6 Torr (50 mbar) are studied by flame-sampling photoionization molecular-beam mass spectrometry utilizing vacuum-ultraviolet synchrotron radiation. Experimental mole fraction profiles of important combustion intermediates are determined. The isomeric compositions are resolved for most intermediates. A new model for cyclopentene flames is under development based in part on our new data. Experimental and modeled mole fraction profiles compare favorably. Preliminary modeling results for fuel-consumption and benzene formation pathways are discussed. In addition, $C_5H_5CCH/C_5H_4CCH_2$ and cycloheptatriene are identified by comparison of photoionization efficiency measurements with simulations based on calculated ionization energies and Franck-Condon factors. This insight suggests a potential new route in the molecular-weight growth mechanism that is characterized by C_5-C_7 ring enlargement reactions.

1. Introduction

The formation of polycyclic aromatic hydrocarbons (PAHs) and soot is one of the most challenging chemical issues in combustion science today. The interest in this subject stems mostly from the fact that serious environmental concerns and health risks are associated with pollutant emissions from combustion devices. [1-3] A current focus in combustion chemistry research is the production of the "first aromatic ring" species as this may be the rate-limiting step in the formation of larger PAHs and soot. [4, 5] It is believed that resonantly stabilized radicals often accumulate to high concentrations and play a crucial role in aromatics formation.

In view of the potential importance of C_5 species in early soot formation processes, the present study is concerned with cyclopentene combustion chemistry under fuel-rich conditions. The fuel cyclopentene is attractive for studies because the abstraction of hydrogen atoms forms several key flame intermediates in high concentrations, including the cyclopentadienyl and cyclopentenyl radicals. The resonantly stabilized *cyclo*-C_5H_5 (cyclopentadienyl) radical is believed to be an important intermediate supporting the growth of higher hydrocarbons, PAH, and soot in rich flames. [6-11]

Nevertheless, investigations of the combustion chemistry of cyclopentene are scarce. McEnally and Pfefferle used non-premixed methane/air flames doped with cyclopentene to study hydrocarbon growth processes. [12] Lamprecht *et al.* [13] employed electron ionization mass spectrometry to study cyclopentene flames with different stoichiometries. Modeling efforts were undertaken later by Lindstedt and Rizos [6] and recently by Kamphus *et al.* [14]

This study is concerned with the initial steps of fuel consumption and aromatic-ring formation in a laminar premixed cyclopentene flame:

(a) The presence of $C_5H_5CCH/C_5H_4CCH_2$ and cycloheptatriene is confirmed by comparison of photoionization efficiency measurements with simulations based on calculated ionization energies and Franck-Condon factors. The existence of $C_5H_5CCH/C_5H_4CCH_2$ and cycloheptatriene points toward C_5-C_7 ring enlargement reactions [15] as potential new pathways in molecular-weight growth mechanisms.

(b) The thorough analysis of the flame data provides profiles of single-ring aromatic species and their precursors. Mole fraction profiles are compared with predictions based on kinetic models. The results are discussed in regard to C_5 oxidation processes and the role of C_5 intermediates in PAH and soot formation.

2. Experiment

The experiment is carried out in a low-pressure premixed flame apparatus at the Chemical Dynamics Beamline at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. The technique of flame-sampling molecular-beam photoionization time-of-flight mass spectrometry is fully described elsewhere. [16]

The investigated flame is a cyclopentene/oxygen/25% argon flame with a fuel/oxygen equivalence ratio $\phi = 2.0$ at a pressure of 37.6 Torr (50 mbar) and a cold-flow reagent velocity of 54.7 cm/s. The flame is shielded by an Ar shroud gas, and cyclopentene from Sigma-Aldrich (96%) is used without further purification.

Flame gases are sampled through the ~0.2 mm orifice of a quartz sampling cone on the flow axis of a flat-flame burner. Translation of the burner toward or away from the quartz sampling cone allows mass spectra to be taken at any desired position within the flame. A skimmer placed downstream on the axis of the expanded jet forms a molecular beam that passes into the differentially pumped ionization region, where it is crossed by tunable vacuum ultraviolet light. The resulting photoions are separated by pulsed-extraction time-of-flight mass spectrometry and detected with a multi-channel plate. A multiscaler records the TOF mass spectra.

3. Species Identification

We identify various C_7H_6 and C_7H_8 isomers by comparing the experimental photoionization efficiency (PIE) spectra with theoretical simulations based on calculated ionization energies and Franck-Condon factors (FCF). The FCF calculations are carried out using a program developed by Winter and Zwier. [17] Input parameters are rovibrational properties which are obtained from

B3LYP/6-311++G** [18, 19] density functional calculations using the Gaussian 98 software [20] and unrestricted spin wavefunctions.

3.1. Identification of C_7H_6 and C_7H_8 Isomers

The photoionization efficiency curves for C_7H_6 and C_7H_8 are shown together with the results of the FCF analysis in Fig. 1. For both profiles, a threshold near 8.2 eV can be clearly seen. Calculated ionization energies of several isomers of C_7H_6 and C_7H_8 are also indicated. The theoretical ionization energies are obtained from an approximation to QCISD(T)/6-311++G(3df,2pd) energies given by E[QCISD(T)/6-311G**] + E[MP2/6-311++G(3df,2pd)] - E[MP2/6-311G**], with these energies obtained with the MOLPRO quantum chemistry package [21] and employing spin-restricted wavefunctions.

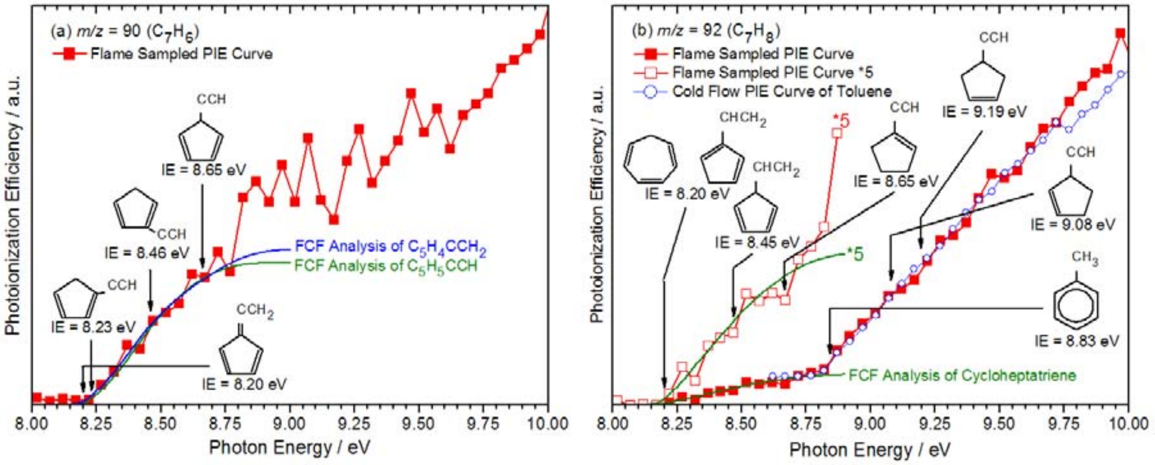

Figure 1: Comparison between flame-sampled PIE curve for (a) *m/z* = 90 (C_7H_6) and (b) *m/z* = 92 (C_7H_8) with the PIE spectra simulated based on a Franck-Condon factor analysis and the cold-flow PIE spectrum of toluene. Calculated ionization energies of some isomers are indicated.

For C_7H_6, the theoretical ionization energies of -CHCHCHCHC(C=CH_2)- (8.20 eV) and -CH_2CHCHCHC(C≡CH)- (8.23 eV) are well within the experimental and computational error limits of the observed threshold near 8.2 eV. For C_7H_8, the observed threshold near 8.2 eV can be explained by either the -C(CH=CH_2)CHCH_2CHCH- or the cycloheptatriene isomers, as the observed and calculated ionization thresholds are in very good agreement.

Fig. 1(a) shows that the -CHCHCHCHC(C=CH_2)- and the -CH_2CHCHCHC(C≡CH)- isomers are hard to distinguish by Franck-Condon factor analysis. The calculated near-threshold PIE curves for both species look similar and fit the observed data between 8.2 and 8.75 eV quite well. However, the calculations suggest that we can rule out the presence of the -CHCHCH_2CHC(C≡CH)- and -CHCHCHCHCH(C≡CH)- isomers.

For C_7H_8, the Franck-Condon factor analysis reveals that the cycloheptatriene and the -C(CH=CH_2)CHCH_2CHCH- isomers are difficult to distinguish. The calculated near-threshold photoionization efficiency curves for both species look similar and fit the observed data between 8.2 and 8.8 eV satisfactorily. The simulated PIE curve is shown for cycloheptatriene in Fig. 1(b). A similar fit can be achieved by considering the five-membered -C(CH=CH_2)CHCH_2CHCH- ring species. However, from the chemical point of view, it is puzzling why the

-C(CH=CH_2)$CHCH_2$CHCH- isomer should be the only detectable five-membered C_7H_8 species. The high H-atom concentration in the flame may favor H-atom migration around the five-membered ring and at least the thermodynamically most stable -C(CH=CH_2)CH_2CHCHCH- (calc. IE = 7.92 eV) should also be detectable. [22] However, no signal is observed below 8.2 eV and we therefore conclude that signal above the observed threshold is due to the presence of cycloheptatriene.

3.2. Flame Chemistry of C_7H_6 and C_7H_8

We propose that the C_7H_6 isomers in the environment of the fuel-rich cyclopentene flame are likely formed by the C_5H_5 (cyclopentadienyl) + C_2H_2 (acetylene) $\rightleftarrows$ C_7H_6 + H reaction. This reaction has been studied theoretically by Fascella *et al.* [15] Possible pathways forming the -CH_2CHCHCHC(C≡CH)- isomer are less obvious. However, in the H-atom-rich environment of a fuel-rich flame it is conceivable that hydrogen atom migration around the cyclopentadiene ring takes place and converts the initial -CHCHCHCHCH(C≡CH)- isomer into the most stable -CH_2CHCHCHC(C≡CH)- tautomeric species.

Information about the combustion chemistry of cycloheptatriene is scarce. The reaction between benzene and methylene is a potential direct route leading to cycloheptatriene. It can also be formed by isomerization of C_7H_8 isomers, including toluene or five-membered ring species. [15]

The C_7H_6 isomers are important intermediates in the formation of aromatic species in the fuel-rich cyclopentene flame. C_7H_6 might react with acetylene to ultimately form indene, or H-atom addition might open a new route to a five-membered ring C_7H_7 radical species which undergoes isomerization to form the resonantly stabilized cycloheptatrienyl or benzyl radicals. [15] Both radical species are quite stable, and thus they are good precursor candidates for forming multiring structures including indene and naphthalene. [7, 8, 15]

4. Flame Analysis and Combustion Chemistry Model

Besides the species identification, the goals of the experimental part of this study are to determine mole fraction profiles of many key intermediates to assist in kinetic modeling and to help identify the main decomposition pathways of cyclopentene and the main routes toward formation of small aromatic hydrocarbons. Mole fraction profiles are derived according to the method described by Cool *et al.* [23] The mole fractions for species with well known photoionization cross sections have a probable uncertainty of ±40%. When estimated photoionization cross sections are used, for example for *cyclo*-C_5H_5 and fulvene, the mole fractions should be correct within a factor of two to four. This level of accuracy is sufficient for many kinetic modeling purposes.

4.1. Flame Chemistry and Preliminary Modeling Results

A reaction set with kinetics, thermochemistry, and transport properties is under development for high-temperature cyclopentene oxidation. The set incorporates cyclopentene and cyclopentenyl reactions into the set of Law *et al.* [24] Table 1 presents those additional reactions that proved most significant to the model predictions, described below. Using this model, mole fraction profiles of all major species, as well as some minor and radical species, were calculated. In general, the agreement between the flame model predictions and the experimental data of the major species overall is good. The comparison for the major species H_2, H_2O, CO, O_2, Ar, CO_2, and C_5H_8 (fuel) is shown in Fig. 2. The largest discrepancies occur for molecular hydrogen and water. The H_2 profile is underpredicted by about 20% throughout the postflame zone and the modeled H_2O profile is overpredicted relative to the data by about 15%. However, the shapes of the predicted and experimental H_2O profiles agree well.

Table 1. C_5H_x reactions of importance in modeling the $\phi = 2.0$ cyclopentene flame; $k = AT^n \exp(-C/RT)$ in mol, cm, s, cal, K units.

Reaction	*A*	*n*	*C*	Source
• *Consumption of cyclopentene by decomposition:*				
cyclopentene $\rightleftharpoons$ 1,3-cyclopentadiene + H_2	1.1×10^{13}	0	58800	(a)
• *Consumption of cyclopentene by abstraction of allylic H:*				
cyclopentene + H $\rightleftharpoons$ cyclopent-2-enyl + H_2	2.3×10^{5}	2.5	2490	(b)
cyclopentene + OH $\rightleftharpoons$ cyclopent-2-enyl + H_2O	4.16×10^{6}	2.0	298	(c)
• *Consumption of cyclopentene by abstraction of nonallylic secondary H:*				
cyclopentene + H $\rightleftharpoons$ cyclopent-3-enyl + H_2	1.30×10^{6}	2.4	4470	(d)
• *Consumption of cyclopentene by chemically activated reactions:*				
allyl + C_2H_4 $\rightleftharpoons$ cyclopentene + H	6.03×10^{9}	0	11490	(e)
• *Consumption of cyclopentenyl:*				
cyclopent-2-enyl $\rightleftharpoons$ 1,3-cyclopentadiene + H	2.4×10^{13}	0	47500	(f)
cyclopent-3-enyl $\rightleftharpoons$ 1,3-cyclopentadiene + H	2.4×10^{13}	0	47500	(f)

(a) Analysis of NIST database; "Chemical Kinetics Database on the Web", Standard Reference Database 17, Version 7.0 (Web Version), Release 1.4.1, National Institute of Standards and Technology, Gaithersburg MD (2006); (b) 4/3**k*(H + propene), Ref. [24]; (c) 4/3**k*(OH + propene), Ref. [24]; (d) *k*(propane + H = isopropyl), Ref. [24]; (e) Ref. [25]; (f) est. by relations of Ref. [26]

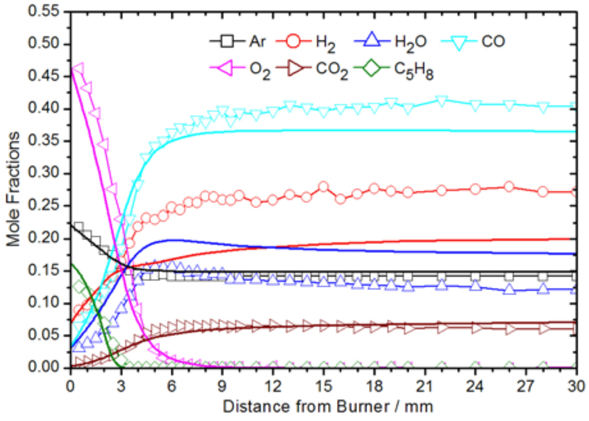

Figure 2: Experimental (lines and symbols) and modeled (lines) mole fraction profiles of major species

The comparison between modeled and experimental profiles for selected minor species is shown in Fig. 3. In panel (a) mole fraction profiles of the key C_3 species C_3H_3 and C_3H_5 are presented. The peak mole fraction of propargyl is slightly overpredicted and that of allyl is slightly underpredicted. However, experiment and model agree within the given error limits. The modeled results for the C_5H_5 and C_5H_6 intermediates are compared with the experimental results in Fig. 3(b). As can be seen, cyclopentadiene (C_5H_6) is slightly overpredicted; nevertheless it matches the experimental value within the error limits. However, the C_5H_5 mole fraction is predicted to be 15 times higher than the experimental results. This might be due to experimental uncertainties, unreliable rate constants for C_5H_5 oxidation pathways, and the fact that not all C_5H_5 reaction paths are included in the current model. Predicted mole fraction profiles of fulvene and benzene C_6H_6 isomers are compared with the experimental results in Fig. 3(c). Both fulvene and benzene mole fractions are predicted to be a factor of 2 higher than the experimental results, however, this agrees within the experimental error limits.

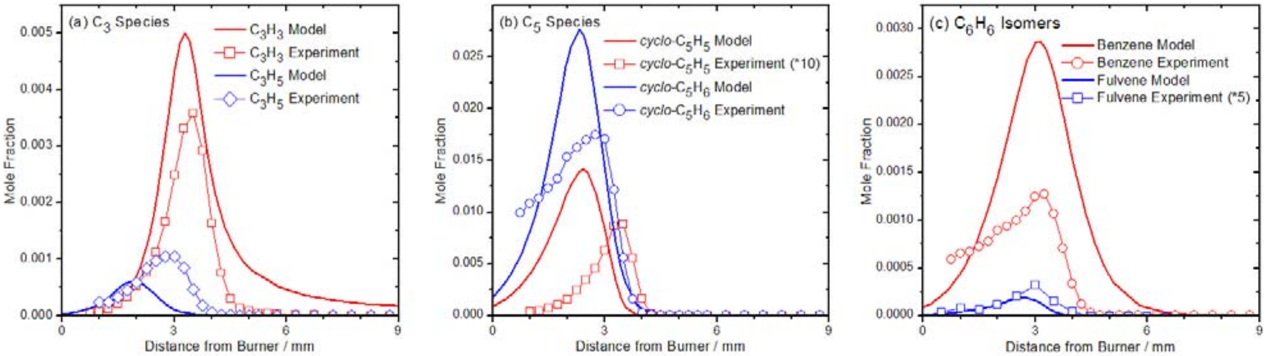

Figure 3: Comparison between experimental and modeled mole fraction profiles: (a) C_3H_3, C_3H_4 (allene and propyne) and C_3H_5, (b) C_5H_5 and C_5H_6, (c) C_6H_6 (fulvene and benzene)

4.1.1. Main Consumption Pathways of Cyclopentene

The present modeling implies that in this flame, cyclopentene consumption is dominated (60%) by elimination of H_2 to form cyclopentadiene:

$$\textit{cyclo}\text{-}C_5H_8 \rightleftarrows \textit{cyclo}\text{-}C_5H_6 + H_2 \tag{1}$$

Another significant channel for cyclopentene consumption is the reaction with H-atoms to form cyclopentenyl (*cyclo*-C_5H_7) radicals:

$$\textit{cyclo}\text{-}C_5H_8 + H \rightleftarrows \textit{cyclo}\text{-}C_5H_7 + H_2 \tag{2}$$

In the present work, H and OH abstractions to form allylic cyclopent-2-enyl and nonallylic cyclopent-3-enyl consume 32% of the fuel. The chemically activated H-atom addition/decomposition to make allyl and ethylene

$$\textit{cyclo}\text{-}C_5H_8 + H \rightleftarrows C_3H_5 + C_2H_4 \tag{3}$$

contributes with 8% to the cyclopentene consumption.

Both cyclopentenyl radicals are consumed almost solely through H-elimination leading to cyclopentadiene:

$$\textit{cyclo}\text{-}C_5H_7 \rightleftarrows \textit{cyclo}\text{-}C_5H_6 + H \tag{4}$$

A minor pathway is a ring-opening via β-scission to form a linear C_5H_7 pentenyl isomer which can subsequently decompose to smaller fragments including allyl and acetylene:

$$\textit{linear}\text{-}C_5H_7 \rightleftarrows C_3H_5 + C_2H_2 \tag{5}$$

Under our current flame conditions, 51% of cyclopentadiene is consumed by H-atoms via abstraction to form the resonantly stabilized cyclopentadienyl, and abstractions by CH_3, OH, and O contribute another 6.7, 6.5, and 2.7% for a total of 67% *cyclo*-C_5H_6 consumption by abstraction:

$$\textit{cyclo}\text{-}C_5H_6 + R \rightleftarrows \textit{cyclo}\text{-}C_5H_5 + RH \qquad (6)$$

The other one-third of consumption is mainly by chemically activated H-atom addition/decomposition to make allyl and acetylene:

$$\textit{cyclo}\text{-}C_5H_6 + H \rightleftarrows C_3H_5 + C_2H_2 \qquad (7)$$

The key reactive C_5-ring species in this cyclopentene flame is probably the cyclopentadienyl radical. The thermal decomposition reaction of *cyclo*-C_5H_5 starts with a fast ring opening process to form the linear $CHCCHCHCH_2$ isomer, which subsequently dissociates into acetylene and propargyl radicals:

$$\textit{cyclo}\text{-}C_5H_5 \rightleftarrows \textit{linear}\text{-}C_5H_5 \rightleftarrows C_2H_2 + C_3H_3 \qquad (8)$$

Reaction (8) accounts for 84% of the model's cyclopentadienyl consumption, with most of the remaining balance proceeding by O-atom attack to make cyclopentadienone. Thus, propargyl is a major decomposition product of the fuel and can then initiate PAH growth.

4.1.2. Formation Pathways of Benzene

Modeling indicates that propargyl-propargyl self-combination dominates benzene (or phenyl + H) formation in this fuel-rich cyclopentene flame:

$$C_3H_3 + C_3H_3 \rightleftarrows C_6H_6 \text{ or } (C_6H_5 + H) \qquad (9)$$

Propargyl radicals are present in relatively large concentrations since they are primarily formed according to reaction (8) as a decomposition product of cyclopentadienyl radicals. However, modeling that assumes reaction (9) being the only formation pathway of benzene leads to an underprediction of the benzene mole fraction.

The following reaction sequence is also found to be an important path towards fulvene and benzene: [10]

$$CH_3 + C_5H_5 \rightleftarrows C_5H_4CH_3 + H \rightleftarrows C_5H_4CH_2 \text{ (fulvene)} + H + H \qquad (10)$$

Modeling results including reactions (9) and (10) as possible benzene formation pathways are shown in Fig. 3(c). A modest overprediction of fulvene and benzene is visible, which might reflect the fact that C_5H_5 mole fractions are predicted to be too large.

A minor contribution towards fulvene/benzene formation results from the reaction of allyl with propargyl radicals according to

$$C_3H_5 + C_3H_3 \rightleftarrows \ldots + \text{fulvene}, \qquad (11)$$

where the allyl (C_3H_5) can come from reactions (3) and (7).

Other pathways, including addition reactions of acetylene to *n*-C_4H_3 and *n*-C_4H_5 radicals, [27-31] are found to be of little or no importance in this fuel-rich cyclopentene flame.

5. Conclusions

This paper focuses on the combustion chemistry of cyclopentene, which is investigated in unprecedented detail employing flame-sampling molecular beam mass spectrometry and flame model predictions. The discovery of the five-membered C_7H_6 and seven-membered C_7H_8 isomers is of particular interest as both species essentially can be formed by reactions of cyclopentadienyl radicals with acetylene. This species identification indicates important pathways towards aromatic species. Subsequent reactions of acetylene with radicals generated by H addition or H loss from the C_7H_6 and C_7H_8 rings are potential pathways leading to indene. [15] These pathways deserve to be explored in future flame chemistry models.

A new model is under development and special attention is paid towards fuel consumption and initial steps in the formation of aromatic rings. In general, the theoretical results are in good agreement with experimentally derived mole fraction profiles. Cyclopentene is mainly consumed by H_2 elimination and H-atom abstraction to form cyclopentadiene and cyclopentenyl radicals, respectively. Benzene is largely formed by propargyl-propargyl self-recombination with minor contributions from the cyclopentadienyl + methyl reaction.

Acknowledgments

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