

Mechanistic Study of Thermal Decomposition of Isoprene (2-Methyl-1,3-Butadiene) Using Flash Pyrolysis Supersonic Jet VUV Photoionization Mass Spectrometry

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The thermal decomposition of isoprene up to 1400 K was performed by flash pyrolysis with an $\sim 100 \mu\text{s}$ time scale. This pyrolysis was followed by supersonic expansion to isolate the reactive intermediates and initial products, and detection was accomplished by vacuum ultraviolet single photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) at $\lambda = 118.2 \text{ nm}$. Products CH_3 , C_2H_4 , C_3H_3 , C_3H_4 , C_4H_4 , C_4H_5 , C_5H_6 , C_5H_7 , and C_6H_6 were directly observed and provide mechanistic insights to the isoprene pyrolysis. At temperatures $\geq \sim 1200 \text{ K}$, the molecular elimination of ethene to form C_3H_4 and σ bond homolysis producing C_4H_5 and CH_3 radicals are competitive reaction pathways. The molecular elimination of acetylene to form C_3H_6 was minimal and direct C2–C3 σ bond homolysis was not observed. The C_3H_3 radicals are also observed, as a result of hydrogen loss of C_3H_4 by pyrolysis or hydrogen abstraction by the CH_3 radical from C_3H_4 . Above $\sim 1250 \text{ K}$, production of C_6H_6 was observed and identified as the combination product of the C_3H_3 radicals.

Introduction

Isoprene (2-methyl-1,3-butadiene) is the major product obtained from thermal degradation of isoprenoids¹ and is an important precursor for the formation of polyaromatic hydrocarbons (PAH) in combustion processes.^{2–4} Despite this, the pyrolysis of isoprene has been relatively little studied.^{5,6} Badger et al. found the pyrolysis of isoprene to produce large amounts of benzene, toluene, and xylenes in addition to a wide variety of PAH.⁵ The major product recovered, toluene (22%), was believed to be formed by reaction of a two-carbon unit (vinyl radical or ethylene) with an isoprene radical or isoprene itself. Benzene (15%) was thought to be formed in a similar manner, the reaction of four-carbon and two-carbon units, and the meta and para xylenes (15%) formed through dimerization of isoprene units, presumably followed by subsequent loss of C_2H_2 . The C2–C5 σ bond, being the weakest bond, was proposed to undergo homolytic cleavage to form CH_3 and C_4H_5 radicals that then abstract hydrogen from isoprene creating C_5H_7 radicals. It was demonstrated how all products observed could be formed, ultimately, from the reactions of isoprene, the four possible C_5H_7 radicals (I, II, III, IV), the $-\text{Me}$ C_4H_5 radical (V), and radicals resulting from homolysis of the C2–C3 bond, C_3H_5 and C_2H_3 . The free radicals and energetics of isoprene dissociation calculated in this work are presented in Figure 1. Perhaps consistent with that mechanism methane, propylene, ethene, and acetylene were all detected as products, however, without quantification. The work indicated the importance of isoprene and fragment units in the formation of aromatic rings. However, many possibilities were not considered and mechanistic details were not elaborated on. The work of Oro et al. followed the variation in PAH populations as a function of pyrolytic conditions, yet mechanisms were not specifically discussed.⁶

Energy economy and health concerns have prompted considerable work on thermal decompositions of hydrocarbons to

gain insight into mechanisms for PAH, and ultimately soot, formation.⁷ Of particular interest are compounds believed to be involved in formation of an aromatic ring, that process widely being considered the crucial rate-limiting step in PAH formation. In this regard, the 1,3-butadiene (1,3-BD) system has been particularly well studied^{8–17} and is expected to have relevance to the isoprene system. The primary initiation step for 1,3-BD pyrolysis was originally proposed to be cleavage of the C–C single bond, forming two vinyl radicals.^{9–11} This mechanism, however, did not accurately account for ethylene production, and unimolecular decomposition to form ethylene and acetylene^{12,13} was suggested. Disagreement with experiment was still encountered until the isomerizations to 1,2-butadiene and 2-butyne was considered. These isomerizations have now been shown to be much faster than decomposition at high temperatures,⁸ and previous work from this lab directly observed the isomerization pathway by detection of methyl and propargyl radicals under pyrolytic conditions.¹⁷ In light of the recent advancements made on the 1,3-BD system, the pyrolysis of isoprene, the 2-methyl derivative of 1,3-BD, appeared to be ripe for further investigation. In this work, we examine the ability of isoprene to isomerize and elucidate the alterations in mechanistic pathways resulting from the additional methyl group. Due to the larger photoionization cross sections of the molecular fragments of isoprene, the molecular elimination channel(s) can be assessed, along with the contribution of direct homolysis channels(s).

As in the pyrolysis of 1,3-BD, the experimental approach of flash pyrolysis coupled to supersonic expansion and vacuum ultraviolet (VUV) photoionization mass spectrometry offers several advantages: short reaction times to examine the initial steps of the thermal decomposition; supersonic cooling to quench the reaction and minimize recombination of the initial products and intermediates; and minimized ion fragmentation due to the “soft” VUV photoionization.^{17–19} Quantum chemistry calculations of the transition state barriers for isomerization

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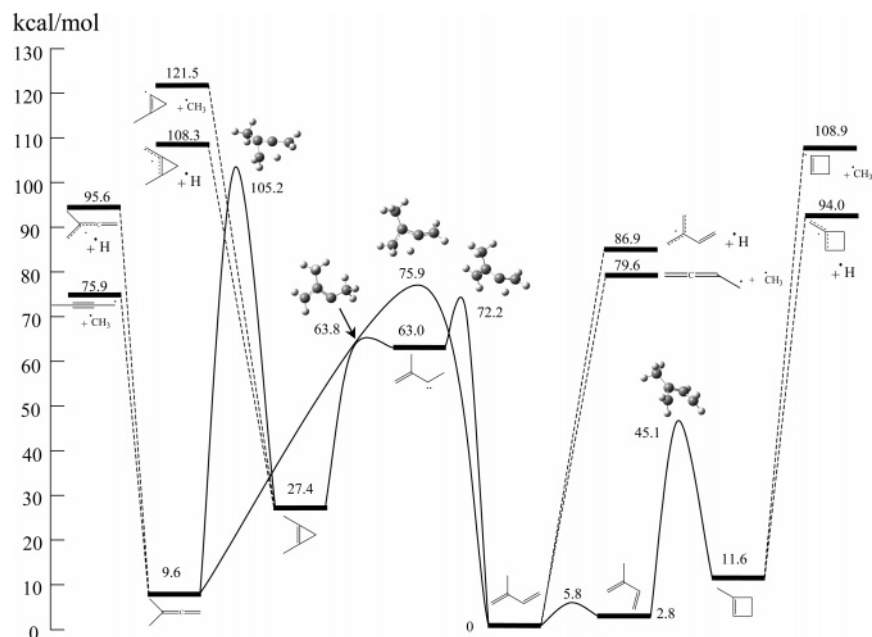


Figure 2. Energetics of the isomerization and dissociation pathways of isoprene. Enthalpies of formation and transition state energies are calculated at 0 K using the B3LYP/6-31+G(2df,p) level of theory. Vibrational frequencies were calculated at the same level of theory for computing zero-point energy corrections and verification of transition state structures.

presented in Figure 3a. A large molecular ion peak at m/e 68 is observed at 295 K; the very small peaks observed at m/e 67, 53, 42, and 40 at 295 K have respective appearance energies (AE) of 10.54–10.93,^{24–26} 11.44–11.93,^{26,27} 12.39,²⁶ and 12.76 eV,²⁶ indicating a minimal amount of multiphoton or electron impact ionization. The multiphoton ionization could be caused by a VUV (focused 118.2 nm) photon + a UV (divergent 355 nm) photon, with a total energy of 13.98 eV. The occurrence of photoelectron generation by scattered light and subsequent electron impact ionization in the photoionization region in this apparatus and the efforts made to eliminate the effect have been described previously.¹⁷ With a nozzle temperature of 700 K, a decrease in the parent m/e 68 signal is observed due to a drop in the number density, and two small new peaks at m/e 41 (AE = 14.04 eV²⁶) and m/e 39 (AE = 14.55 eV²⁶) are discernible. As the nozzle temperature is increased to 865, 1015, and then 1140 K, the peaks at m/e 53 and 67, as well as the peaks at m/e 39–42, are found to grow in relative intensities.

A stack plot of mass spectra for isoprene (15%) in argon carrier gas with nozzle temperatures of 1215, 1255, 1300, 1340, and 1400 K is presented in Figure 3b. At 1215 K, the parent ion continues to decrease in intensity with concomitant increases in all of the previous observed peaks. The growth of the peak at m/e 40 is significantly greater than the others in the m/e 39–42 region. Two new peaks are observed at m/e 52 and 54, along with the slightly growing m/e 53 peak. In the 1255 K trace, the peaks at m/e 40, 52, and 54 continue to increase in relative intensity. Peaks at m/e 15, 28, 66, and 78 are now clearly detected. At 1300 K, the trend continues with m/e 40 and 52 displaying the greatest augmentation of intensity, and at 1340 K the peak at m/e 52 is nearly equal to the parent peak at m/e 68, whereas the m/e 53 peak starts to decrease. At this temperature, new peaks at m/e 50 and 65 are observed. At a nozzle temperature of 1400 K, the highest temperature presented, the parent peak continues to diminish as the relative intensities of other peaks increase.

A stack plot of mass spectra for isoprene (1.5%) in argon carrier gas with nozzle temperatures of 1200, 1230, 1310, 1330, and 1390 K is presented in Figure 3c. The concentration was

reduced by an order of magnitude to evaluate the extent of secondary reactions in gas phase and surface reactions. The pyrolysis mass spectra are essentially the same in both experiments, except with the diluted sample the amount of m/e 15 and 39 observed increases, whereas the m/e 78 peak is attenuated. This indicates that the surface reactions and secondary gas-phase reactions are not significant in the $\sim 100 \mu\text{s}$ short time scale of the flash pyrolysis.

Discussion

Equilibrium Structures and Isomerization. Energies of C_5H_8 isomers and their transition states of formation were calculated to characterize the reaction profile and elucidate the lowest energy pathways in the pyrolysis of isoprene. The results are presented graphically in Figure 2. The molecular parameters of isoprene calculated here in this work were found to be consistent with prior calculations.^{28–30} The trans isomer is found to lie 2.8 kcal/mol below the gauche conformation with a 5.8 kcal/mol barrier to rotation. As can be seen from the figure, several isomers are readily accessed. The gauche conformation of isoprene can undergo electrocyclic ring closure by surmounting a 42.3 kcal/mol barrier to produce 1-methyl cyclobutene, 11.6 kcal/mol higher in energy than the reference trans isoprene. The conrotatory ring opening of methylcyclobutene has activation energy calculated in this work of 33.5 kcal/mol, in reasonable agreement with the experimental value of 35.1 kcal/mol.³¹

Similar to 1,3-BD,¹⁷ both conformers of isoprene are expected to be capable of undergoing 1,2 hydrogen shift across the C3–C4 bond of isoprene to produce a singlet carbene intermediate. The transition state for that process was calculated to be 72.2 kcal/mol above trans isoprene. Carbene moieties are not stable and are known to readily form corresponding cyclopropenes. 1,2-dimethylcyclopropene was found to lie 27.4 kcal/mol above isoprene, and the barrier to its formation, in reference to the carbene compound, is only 0.8 kcal/mol. In 1,3-BD, the carbene/cyclopropene intermediate can isomerize further via a sequential 1,2 hydrogen shift to 1,2-BD or to 2-butyne.¹⁷ In the case of isoprene, however, the absence of a vinylic hydrogen by CH_3 substitution significantly retards the rates of similar processes

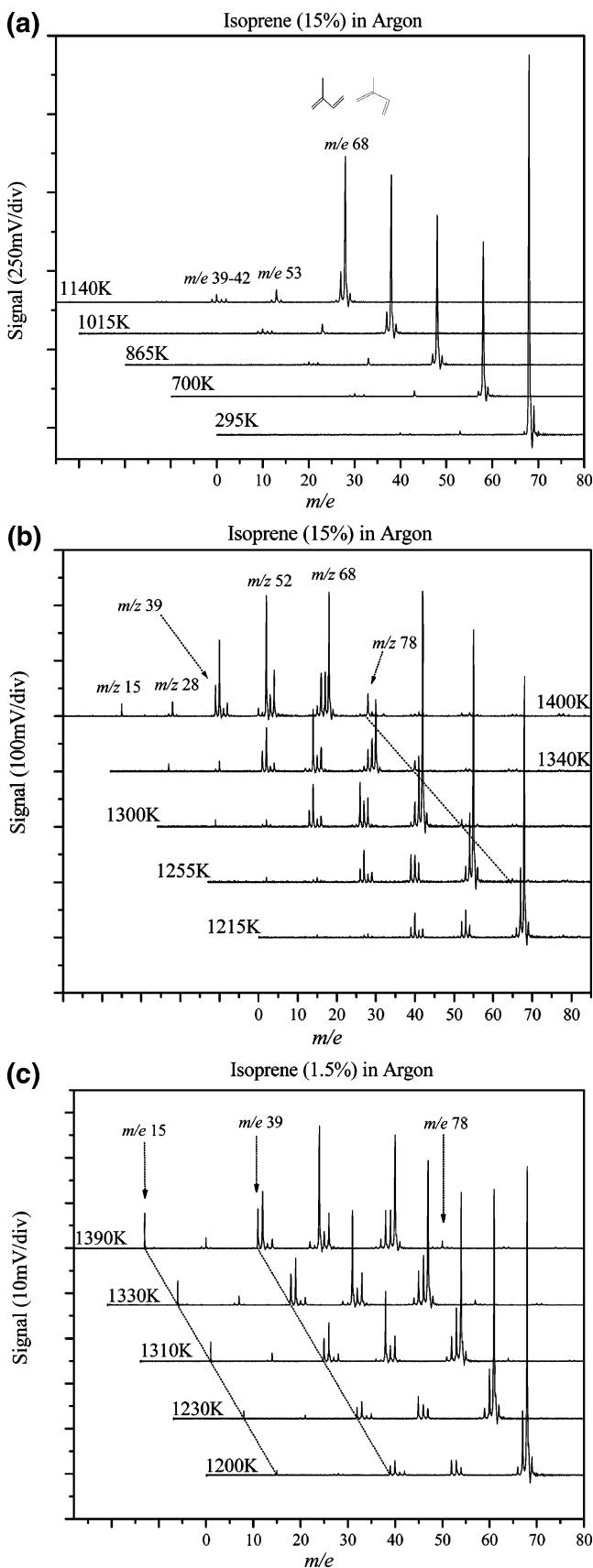


Figure 3. (a) Stack plot of mass spectra for pyrolysis of isoprene (15% in Ar) with internal nozzle temperatures from room temperature (295 K) to 1140 K. (b) Stack plot of mass spectra for pyrolysis of isoprene (15% in Ar) with internal nozzle temperatures from 1215 to 1400 K. (c) Stack plot of mass spectra for pyrolysis of isoprene (1.5% in Ar) with internal nozzle temperatures from 1200 to 1390 K. Mass spectra are shifted for clarity.

and therefore tend to undergo ring opening rather than further isomerization.³²

The 1,3 hydrogen shift is also known to be relatively facile and the barrier to directly forming dimethylallene in this manner was calculated to be 75.9 kcal/mol. Alternatively, dimethylallene can be formed from the carbene or cyclopropene intermediates. In this work, the transition from dimethylcyclopropene to dimethylallene was calculated to be 105.2 kcal/mol indicating that pathway is unlikely. Dimethylallene has a heat of formation of 9.6 kcal/mol relative to trans isoprene.

C₄H₄, C₄H₅, and C₄H₆ Production. The *m/e* 53 peak appears and increases at relatively low temperatures, and above 1200 K, the growth of the *m/e* 15 peak also becomes visible, suggesting production of the C₄H₅ and CH₃ species via homolytic dissociation of isoprene. The heats of reaction for the radicals produced by the homolytic cleavage of a methyl group from the isoprene isomers were calculated and are presented in Figures 1 and 2. For the simple homolytic cleavage of methyl from isoprene, the *i*-C₄H₅ radical + CH₃ radical product channel is found to be 79.6 kcal/mol higher in energy relative to trans isoprene, with the C₄H₅ radical V significantly stabilized by a resonance energy of at least 9.7 kcal/mol. For the homolysis of dimethylallene minus methyl radical, the heat of reaction is only 75.9 kcal/mol above isoprene due to a propargyl-type resonance in the methylallenyl radical product. This work predicts that the methylallenyl radical is 3.7 kcal/mol more stable than the *i*-C₄H₅ radical, which is larger than the 2.4 kcal/mol predicted by Hansen et al.³³ Heat of reaction for homolysis of the methylcyclobutene isomer to produce the methyl and cyclobutene radicals is 108.9 kcal/mol relative to trans isoprene. The heat of reaction of the methylcyclopropene and methyl radicals from homolysis of dimethylcyclopropene is calculated to be 121.5 kcal/mol. Therefore, the likely mechanism for methyl loss in isoprene is isomerization via C3–C1 1,3 hydrogen shift to dimethylallene and subsequent dissociation to the CH₃ and methylallenyl radicals as well as direct homolytic dissociation of isoprene to the CH₃ and *i*-C₄H₅ radicals. Compared to 1,3-BD, the CH₃ substitution in isoprene provides a possible direct CH₃ loss pathway. However, the CH₃ substitution removes one vinylic hydrogen and raises the energetics for subsequent 1,2 CH₃ shift to isomerize to dimethylallene (analog to 1,2-BD in 1,3-BD isomerization) or the alkyne (analog to 2-butyne in 1,3-BD isomerization). Consequently, the 1,3 hydrogen shift isomerization to dimethylallene becomes the more favorable isomerization pathway and leads to CH₃ loss.

The prominent peak at *m/e* 52 in the pyrolysis of isoprene presumably comes from overall loss of CH₄. This could occur by bond homolysis of isoprene to produce CH₃ and C₄H₅ radicals with subsequent loss of a hydrogen atom forming C₄H₄, or by direct molecular elimination of methane. The subsequent loss of hydrogen atom from methylallenyl and *i*-C₄H₅ radicals was calculated to be endothermic by 57.1 and 53.4 kcal/mol for butatriene and for vinylacetylene 58.4 and 51.1 kcal/mol respectively, indicating these as facile processes. The direct molecular elimination of methane from isoprene to form butatriene was calculated to have a heat of reaction of 30.7 kcal/mol, while the same process to form vinylacetylene is 28.6 kcal/mol (Figure 1); however, the direct molecular elimination of methane is known to have activation energies above the simple bond enthalpies. In this work, the activation energies for formation of vinylacetylene or butatriene by molecular elimination of methane are 107.1 and 103.1 kcal/mol, respectively, consistent with previous calculation.³⁴ These results indicate that σ bond homolysis of isoprene is favored over molecular

elimination of methane, and the C_4H_4 product at m/e 52 is produced by subsequent H loss of the methylallenyl radicals.

The peak at m/e 54 observed in the pyrolysis cannot be the result of molecular elimination of CH_2 . The heats of formation are calculated to be prohibitive, 114.8 kcal/mol from isoprene, and additionally the CH_2 created would be detectable with an ionization energy of 10.35 eV.³⁵ C_4H_6 can be formed by H-abstraction by C_4H_5 radicals, however, the relative intensity observed at m/e 54 displays no concentration dependence, and therefore, it may be that m/e 54 is largely a photoionization fragment. The ionization energies for cyclopropene and cyclobutene are 9.67 and 9.1 eV, respectively,³⁶ and photofragments of that type have apparently been observed from photooxidized surfaces of methylcyclobutene and dimethylcyclopropene derivatives.³⁶

C_3H_4 and C_2H_4 Production. Direct molecular eliminations resulting in the cleavage of the C2–C3 bond were considered and relative energies are presented in Figure 1. Two such molecular elimination pathways possible for isoprene are molecular elimination of acetylene to produce propene or elimination of ethylene to produce allene (shown in Figure 1) and/or propyne. The heat of reaction for the C_2H_2 + propene product channel is found to be 39.2 kcal/mol above *trans*-isoprene, whereas the C_2H_4 + allene channel is more favorable by 4.6 kcal/mol at an energy of 34.6 kcal/mol. The elimination pathway for acetylene is believed to proceed through a vinylidene species,¹⁰ and when the vinylidene intermediate is considered, the energy level is increased to 79.8 kcal/mol (Figure 1). In a similar manner, one could envision the molecular elimination of ethene to proceed through a methyl carbene intermediate; this consideration leads to a product energy level of 105.2 kcal/mol. As can be seen in Figure 3, the amount of m/e 42, corresponding to propene from molecular elimination of acetylene, is less in comparison to the m/e 40 peak, for the C_3H_4 species; the molecular product channel producing ethene and C_3H_4 (allene and/or propyne) is more important. The transition state energy barrier for the ethene molecular elimination process to form allene was calculated in this work to be 74.0 kcal/mol, which is slightly smaller than those of CH_3 bond homolysis. The molecular elimination of ethene should be a favorable channel, and the growth of m/e 40 at elevated temperatures can then be attributed to this process.

The C2–C3 bond homolysis channel of isoprene to produce C_2H_3 and C_3H_5 radicals is 103.0 kcal/mol above *trans* isoprene (Figure 1). The absence or very minor peak growth at m/e 27 and 41 indicates that these radicals are not formed in appreciable amounts, as a prior work on nitroethylene pyrolysis has demonstrated that the vinyl radical produced in pyrolysis under these conditions should be readily detected. Therefore, isoprene does not undergo C2–C3 homolysis to an appreciable extent, consistent with the higher energy requirement.

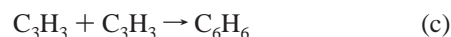
All of these features indicate that cleavage of the C2–C3 bond in isoprene is not homolytic and that the molecular elimination of C_2H_4 to produce C_3H_4 is the dominant molecular elimination pathway.

C_3H_6 and C_5H_7 Production. The energy values of the possible $-H$ radicals from equilibrium *trans*-isoprene structure are presented in Figure 1. The $-H$ radicals of isomers are presented in Figure 2. Radicals I, II, and IV are vinylic radicals with fairly similar energetics, lying 108.0, 104.3, and 109.9 kcal/mol above the *trans*-isomer of isoprene (H atom energy considered). The allyl radical III has a weaker C–H bond with an energy of 99.6 kcal/mol, and when allowed to delocalize to the most stable conformation, a value of 86.9 kcal/mol is

obtained. The minus hydrogen radical of methylcyclobutene has a heat of reaction of 94.0 kcal/mol (delocalized), whereas dimethylcyclopropene minus hydrogen atom was found to be 108.3 kcal/mol relative to *trans*-isoprene (Figure 2). The allylic radical of dimethylallene is slightly higher energy than for methylcyclobutene, 95.6 kcal/mol. The peak observed at m/e 67 corresponds to C_5H_7 . Since it is found to be unaffected by changes in concentration, it is likely the result of H elimination by thermolysis, presumably via the lowest energy pathway, H + allyl radical III. Alternatively, H abstraction from isoprene by radicals such as CH_3 and C_4H_5 could also produce C_5H_7 .

The peak at m/e 66 could be the result of molecular elimination of H_2 from isoprene. The heat of formation of 2-methyl-but-1-ene-3-yne is calculated to be 39.8 kcal/mol. As mentioned previously, this process has been observed in the pyrolysis of 1,3-BD with an estimated transition state of 94.7 kcal/mol.⁸ The peak at m/e 66 may also be the decomposition of the isoprenyl radical (allyl radical III), m/e 67.

C_3H_3 and C_6H_6 Production. The formation of m/e 78 is an indication that combinations are indeed occurring in this experimental regime. Two general pathways are accepted as playing a role in the production of C_6H_6 , (1) four carbon plus two carbon reactions and (2) three carbon self-combination. In this experiment, the following possible routes to C_6H_6 are conceivable.



The amounts of C_4H_2 and C_2H_2 in this pyrolysis are not sufficient for pathways a and b to be plausible. The self-reaction of C_3H_3 , pathway c has been well studied³⁹ and is believed to be most facile in production of an aromatic ring. A noticeable delineation of the data collected at lower concentrations is the increased levels of CH_3 and C_3H_3 radicals, which implicates the involvement of these species in secondary reactions.

The heat of reaction to form C_3H_3 radical and hydrogen from C_3H_4 (allene) is calculated to be 88.6 kcal/mol, the weakest C–H bond predicted in this system. The C_3H_3 radical can be produced from the pyrolysis of allene at elevated temperatures. In addition, allene can readily isomerize to propyne,³² which could also decompose to H + C_3H_3 radical. Alternatively, hydrogen abstraction by the CH_3 radicals from allene/propyne can also generate C_3H_3 . As the isoprene precursor concentration increases, the amount of CH_3 detected diminishes as it abstracts hydrogen from allene/propyne to form methane, not detectable by this apparatus. The created C_3H_3 radicals then combine to produce an increase in m/e 78 intensity and overall diminishment of m/e 39. Experiments with propargyl bromide confirm the propensity for C_3H_3 radicals to self-combine producing m/e 78 in this experimental regime.

Conclusions

Isoprene undergoes fast isomerizations to several different species at elevated temperatures. At ≈ 1200 K in this pyrolytic system, thermal bond decomposition is observed producing C_4H_5 and CH_3 , in addition to the unimolecular elimination of C_2H_4 to produce C_3H_4 . Quantum chemistry calculations indicate that σ bond homolysis to form methylallenyl and *i*- C_4H_5 radicals may be competing processes. Molecular elimination of acetylene to form C_3H_6 was found to be a very minor pathway, and direct homolysis of C2–C3 bond was not observed at any tempera-

tures. The C_3H_3 radicals observed could be produced from the pyrolysis of C_3H_4 or via the hydrogen abstraction from C_3H_4 by the CH_3 radicals created in the σ bond homolysis. At temperatures ≥ 1250 K production of C_6H_6 is observed due to the C_3H_3 self-combination reaction. Combinations of C_4H_5 radicals are not prominent and therefore must be much slower than the corresponding process for C_3H_3 radicals.

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