coverages; i.e., some metal ions protrude above adsorbed anions. The well-known fact that sulfides of many metals are active catalysts for a variety of reactions is generally ascribed to these protruding ions. In recent work with supported rhenium catalysts we found³¹ that sulfur "poisoning" induces a remarkable activity for hydrogenation and double-bond shift, illustrating the catalytic action of surface sulfides.

The present results do not permit to discriminate between this geometric principle (corner atoms, protruding ions) and the "electronic" principle; i.e., the positively charged Rh atoms (or ions) might have a higher intrinsic activity for hydroformylation than zerovalent Rh atoms.

V. Conclusions

1. Exposing a freshly reduced Rh/SiO_2 catalyst to a stream of highly diluted hydrogen sulfide in hydrogen, followed by reduction in hydrogen at 400 °C, results in a macroscopically uniform distribution of the sulfur atoms over the rhodium particles in the catalyst bed. The ability of the catalyst to strongly chemisorb carbon monoxide decreases linearly with the amount of sulfur dosed, up to a critical coverage with sulfur. Further dosing of sulfur does not affect CO chemisorption.

2. Adsorbed sulfur selectively blocks the Rh surface for the bridging mode of chemisorbed CO.

3. Adsorbed sulfur appears to leave adjacent Rh with a net positive charge; CO adsorbed on these atoms displays a highfrequency band in the IR region.

4. Low sulfur coverages, which reduce the capacity of chemisorbing CO by only a few percent, have a much stronger effect in reducing its ability to catalyze the hydrogenation of ethylene. This could indicate that the sites on the rhodium surface with highest hydrogenation activity also have the highest heat of adsorption for sulfur.

5. The turnover frequency for hydroformylation is increased by sulfur at low coverages. This is tentatively rationalized by assuming that Rh atoms in corner positions are most active in hydroformylation, while the adsorption of sulfur is strongest on Freundlich sites, consisting of metal atom ensembles. It is also possible that surface reconstruction of rhodium covered with sulfur leads to additional protruding Rh ions.

6. The promoting action of adsorbed sulfur is smaller than that of e.g. Zn ions reported previously. It is possible that in the latter case some chemical interaction between the metal ion and the oxygen end of coadsorbed CO enhances CO insertion into a metal-alkyl bond.

Acknowledgment. A donation toward equipment by the Shell Co. Foundation and a research grant by the Monsanto Co. are gratefully acknowledged.

Registry No. Rh, 7440-16-6; S, 7704-34-9; CO, 630-08-0; ethylene, 74-85-1.

Shock-Tube Study of Allene Pyrolysis

C. H. Wu and R. D. Kern*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148 (Received: March 30, 1987; In Final Form: June 4, 1987)

The high-temperature pyrolysis of allene was studied by analyzing reflected shock zone gas with time-of-flight (TOF) mass spectrometry. A 4.3% C₃H₄-Ne mixture yielded a carbon atom density of about 2.0×10^{17} atoms cm⁻³ over the temperature and pressure range of 1300-2000 K and 0.2-0.5 atm. Product and reactant profiles were obtained during observation times of 750 μ s. The mass balance with respect to observed carbon-containing compounds accounted for 84–100% of the total carbon atom input. The major products detected were C_2H_2 , C_4H_2 , CH_4 , and C_6H_6 , along with minor amounts of C_2H_4 , C_2H_6 , C_4H_4 , and C_6H_2 . Reasonable agreement is obtained between the experimental results and a mechanism consisting of 80 reactions which features the allene-propyne isomerization, initial decomposition via $C_3H_4 + M = C_3H_3 + H + M$, the thermochemical properties of the C_3H_3 isomers, and the role of C_3H_3 radicals in the formation of benzene. Experiments on 1,2-butadiene were performed to further elucidate the role of C₃H₃ and to understand how cyclic compounds may be formed from linear unsaturated hydrocarbons at high temperatures. Benzene yield is approximately the same from equivalent amounts of allene and 1,2-butadiene. The production of benzene observed correlates with reported soot yields in the order allene > 1,3-butadiene > acetylene.

Introduction

In studying soot formation during combustion processes, it is essential to understand the mechanisms of hydrocarbon pyrolyses. Among organic fuels, allene is an interesting compound that has attracted increased attention in recent years.^{1,2} Dissocation of allene was studied by Collin and Lossing³ in 1957 who derived bond dissociation energies for allene, propyne (methylacetylene), and 1,2-butadiene and the heat of formation of C_3H_3 radical. These values have been the subject of more recent work.^{4,5} Detailed investigations of allene pyrolysis have been conducted by several groups.⁶⁻⁹ Levush et al.⁶ determined the product profiles from allene and propyne by using a flow system over the temperature range of 1173-1430 K. They also obtained first-order rate constants for the allene-propyne isomerization. The isomerization was faster than any decomposition process under the conditions of their study. Recent single-pulse shock-tube (SPST) studies of the isomerization support this contention.⁹⁻¹² Walsh has proposed that isomerization occurs via the intermediate cyclopropene.¹³⁻¹⁵ Theoretical ab initio calculations made by Honjou

⁽¹⁾ Colket, M. B. Proceedings of the 15th Shock Tube Symposium; Stanford University Press: Stanford, CA, 1986; 311.

⁽²⁾ Frenklach, M. Shock Tube Study of the Fuel Structure Effects on the Chemical Kinetic Mechanisms Responsible for Soot Formation; 1983; NASA CR-174661. Also Frenklach, M.; Clary, D. W.; Ramachandra, M. K. ibid.; Part II; 1985; NASA CR-174880.

 ⁽³⁾ Collin, J.; Lossing, F. P. J. Am. Chem. Soc. 1957, 79, 5848.
 (4) King, K. D. Int. J. Chem. Kinet. 1978, 10, 545.

⁽⁵⁾ Tsang, W. Int. J. Chem. Kinet. 1978, 10, 687.

⁽⁶⁾ Levush, S. S.; Abadzhev, S. S.; Shvechuk, V. U. Neftekhimiya 1969, 9, 215.

⁽⁷⁾ Sakakibara, Y. Bull. Chem. Soc. Jpn. 1964, 37, 1262.

⁽⁸⁾ Sakakibara, Y. Bull. Chem. Soc. Jpn. 1964, 37, 1268.

⁽⁹⁾ Lifshitz, A.; Frenklach, M.; Burcat, A. J. Phys. Chem. 1976, 80, 2437.

⁽¹⁰⁾ Lifshitz, A.; Frenklach, M.; Burcat, A. J. Phys. Chem. 1975, 79, 1148.

⁽¹¹⁾ Bradley, J. N.; West, K. O. J. Chem. Soc., Faraday Trans. 1 1975,

^{71, 967.} (12) Simmie, J. M.; Melvin, D. J. Chem. Soc., Faraday Trans. 1 1978,

^{74, 1337.}



Figure 1. C_3H_4 decay profile at 1607 K. The dotted lines represent the computed profiles for allene, A, and propyne, P. The solid line, m/e 40, represents an addition of the dotted lines.

 TABLE I: Experimental Conditions for 4.3% Allene Mixture

| Т, К | $\rho_5 \times 10^6$, mol cm ⁻³ | $[C] \times 10^{-17}$, atoms cm ⁻³ | | |
|------|---------------------------------------------|------------------------------------------------|--|--|
| 1340 | 2.093 | 1.626 | | |
| 1466 | 2.235 | 1.737 | | |
| 1559 | 2.332 | 1.812 | | |
| 1607 | 2.380 | 1.849 | | |
| 1654 | 2.425 | 1.884 | | |
| 1704 | 2.471 | 1.920 | | |
| 1711 | 2.477 | 1.925 | | |
| 1758 | 2.250 | 1.958 | | |
| 1851 | 2.599 | 2.019 | | |
| 1915 | 2.651 | 2.060 | | |
| | | | | |

et al.¹⁶ have shown that direct 1,3 H shift in allene to propyne isomerization involves a potential energy barrier of 94.9 kcal mol⁻¹. They proposed the following sequence of reaction paths: allene \rightarrow vinylmethylene \rightarrow cyclopropene \rightarrow propenylidene \rightarrow propyne.

The highest energy barrier for this reaction pathway was calculated to be $68.4 \text{ kcal mol}^{-1}$. Recent shock-tube work by Kakumoto et al.¹⁷ is consistent with this finding.

The purpose of this study is to present experimental results for the high-temperature decomposition of allene. The major product profiles are constructed and modeled with a mechanism that includes the isomerization reaction and the formation of cyclic compounds from linear unsaturated hydrocarbons. Experiments on 1,2-butadiene pyrolysis were performed to assess the role of C_3H_3 radical in the formation of benzene.

Experimental Section

The procedure and apparatus have been described in detail elsewhere.¹⁸ Allene (Matheson research grade; 93%) and 1,2butadiene (CTC Organics) were vacuum distilled. The cracking pattern of allene at room temperature and that of 1300 K, a no-reaction shock temperature, were similar. The mass spectral sensitivities of allene, methane, and benzene were derived at no-reaction conditions with an ionizing potential of 35 eV. The mixtures were diluted in Matheson research grade neon. The initial concentrations of allene and 1,2-butadiene were chosen in order to yield $\sim 2.0 \times 10^{17}$ carbon atoms cm⁻³ in the reflected



Wu and Kern



Figure 2. C_3H_4 decay profile at 1758 K. The notations are the same as in Figure 1.



Figure 3. C_3H_4 decay profile at 1915 K. The notations are the same as in Figure 1.

shock zone. The experimental conditions of reflected zone temperature, total density (ρ_5), and carbon atom concentration are listed in Table I. Modeling calculations were performed with the constant reflected wave velocity option of CHEMKIN.¹⁹

Results and Discussion

1 5

The TOF data for m/e 40 (C₃H₄) are shown in Figures 1-3 at three selected temperatures: 1607, 1758, and 1915 K. The dotted lines represent the computed profiles for allene and propyne which are determined mostly by the allene \rightarrow propyne isomerization and were calculated with the rate constants listed in Table II. The solid line, the m/e 40 profile, represents an addition of the dotted lines and fits the TOF data satisfactorily. Isomerization rate constants reported previously and those employed herein are displayed in Figure 4.

The TOF results for the 4.3% C_3H_4 -Ne mixture are shown in Figures 5-9. The major products are CH₄, C₂H₂, C₄H₂, and C₆H₆. The minor species include C₂H₄, C₂H₆, C₄H₄, C₄H₆, and C₆H₂. After isomerization is substantially complete, allene and propyne subsequently decompose to C₃H₃ and H. C₃H₃ has the same thermochemical properties when derived either from allene or propyne since the allenyl and propargyl radicals are identical. The heat of formation of C₃H₃ radical at 300 K is taken as 81.5 kcal mol⁻¹ as determined by King.⁴ This is in close agreement with a value of 82.7 kcal mol⁻¹ as suggested by Tsang.⁵ The heats of formation for allene and propyne were taken to be 45.9 and 44.3 kcal mol⁻¹, respectively.²⁰ The initial step of C-H scission

⁽¹³⁾ Walsh, R. J. Chem. Soc., Faraday Trans. 1 1976, 72, 2137.

 ⁽¹⁴⁾ Hopf, H.; Priebe, H.; Walsh, R. J. Am. Chem. Soc. 1980, 102, 1210.
 (15) Bailey, I. M.; Walsh, R. J. Chem. Soc., Faraday Trans. 1 1978, 74,

^{1146.} (16) Honjou, N.; Pacansky, J.; Yoshimine, M. J. Am. Chem. Soc. 1984,

⁽¹⁷⁾ Kakumoto, T.; Ushirogouchi, T.; Saito, K.; Isamaura, A. J. Phys.

Chem. 1987, 91, 183. (18) Kern R D. Singh H J. Ecclinger M A. Winkeler D W Course

⁽¹⁸⁾ Kern, R. D.; Singh, H. J.; Esslinger, M. A.; Winkeler, P. W. Symp.
(Int.) Combust. [Proc.] 1982, 19th, 1351.
(19) Mitchell, R. E.; Kee, R. J. "A General Purpose Computer Code for

⁽¹⁹⁾ Mitchell, K. E.; Kee, R. J. "A General Purpose Computer Code for Predicting Chemical Kinetics Behavior Behind Incident and Reflected Shocks"; Sandia National Laboratories: Albuquerque, NM, 1982.

⁽²⁰⁾ Weast, R. C. Handbook of Chemistry and Physics, 60th ed.; CRC Press: Boca Raton, FL, 1979-1980; D-82.

Shock-Tube Study of Allene Pyrolysis



Figure 4. Log k_{uni} vs 1/T for conversion of allene to propyne: A, ref 6; B, ref 10; C, ref 11; D, results herein; E, ref 17.



Figure 5. 4.3% allene decay profiles. The symbols denote \blacktriangle , 1915 K; O, 1758 K; and \blacklozenge , 1607 K. The lines represent model calculations.

from either allene (87.7) or propyne (89.3) occurs with a similar energy; Lifshitz et al.⁹ employed a value between 80 and 90 kcal mol⁻¹. We used the same rate constant for the dissociation of allene and propyne, reactions 2 and 3; our value is somewhat lower than that used by Kiefer.²¹

Reactions 4 and 5 are overall reactions that take place via C_3H_5 intermediates. Wagner and Zellner^{22,23} studied H atom addition reactions to allene and propyne (reactions 4 and 5 of Table II) in an isothermal flow reactor over a temperature and pressure



Figure 6. C_2H_2 growth profiles in the pyrolysis of 4.3% allene. The symbols and lines are the same as in Figure 5.



Figure 7. C_6H_6 growth profiles, same symbols as in Figure 5.



Figure 8. C_4H_2 growth profiles, same symbols as in Figure 5.

range of 273-473 K and 1-20 Torr. They suggested four different reactions which result from H atom attachment to either the terminal or nonterminal carbon atoms in allene and propyne. These reactions are listed in Table III along with their rate parameters.²²⁻²⁴ These four reactions lead to three different isomers of C_3H_5 since reactions I and III lead to the same isomer. The different isomers are designated as $C_3H_5(A)$, $C_3H_5(B)$, and $C_3H_5(C)$. Before going into the details of the reactions involving C_3H_5 radical, we discuss the thermochemistry of C_3H_5 .

⁽²¹⁾ Kiefer, J. H.; Al-Alami, M. Z.; Budach, K. A. J. Phys. Chem. 1982,

⁽²²⁾ Wagner, H. Gg.; Zellner, R. Ber. Bunsen-Ges. Phys. Chem. 1972, 76, 518.

⁽²³⁾ Wagner, H. Gg.; Zellner, R. Ber. Bunsen-Ges. Phys. Chem. 1972, 76, 667.

⁽²⁴⁾ Kerr, J. A.; Moss, S. J. Handbook of Bimolecular and Termolecular Gas Reactions; CRC Press: Boca Raton, FL, 1981; Vol. II.

TABLE II: Allene Reaction Mechanism and Rate Constants: $k = AT^{\theta} \exp(-E/RT)$ (mol, cm, s, and cal)

| | reaction | A | В | Ε | ref |
|----|--------------------------------------------------|----------------------|-----|----------------------|---------|
| 1 | $C_3H_4A^a = C_3H_4P^b$ | 2.0×10^{13} | 0.0 | 62.0×10^{3} | pw |
| 2 | $C_{3}H_{4}A + M = C_{3}H_{3} + H + M$ | 1.0×10^{17} | 0.0 | 70.0×10^{3} | pw |
| 3 | $C_{3}H_{4}P + M = C_{3}H_{3} + H + M$ | 1.0×10^{17} | 0.0 | 70.0×10^{3} | pw |
| 4 | $C_{3}H_{4}A + H = C_{2}H_{2} + CH_{3}$ | 2.0×10^{13} | 0.0 | 2.4×10^{3} | 38 |
| 5 | $C_{3}H_{4}P + H = C_{2}H_{2} + CH_{3}$ | 2.0×10^{13} | 0.0 | 2.4×10^{3} | 38 |
| 6 | $C_3H_4P = C_2H + CH_3$ | 4.2×10^{16} | 0.0 | 1.0×10^{5} | 28 |
| 7 | $C_{3}H_{4}A + H = C_{3}H_{3} + H_{2}$ | 1.0×10^{12} | 0.0 | 1.5×10^{3} | 21 |
| 8 | $C_{3}H_{4}P + H = C_{3}H_{3} + H_{2}$ | 1.0×10^{12} | 0.0 | 1.5×10^{3} | 21 |
| 9 | $C_{1}H_{4}A + C_{2}H = C_{1}H_{1} + C_{2}H_{2}$ | 1.0×10^{13} | 0.0 | 0.0 | est |
| 10 | $C_{3}H_{4}P + C_{2}H = C_{3}H_{3} + C_{2}H_{2}$ | 1.0×10^{13} | 0.0 | 0.0 | est |
| 11 | $C_{1}H_{4}A + CH_{3} = C_{1}H_{3} + CH_{4}$ | 2.0×10^{12} | 0.0 | 7.7×10^{3} | 21 |
| 12 | $C_{3}H_{4}P + CH_{3} = C_{3}H_{3} + CH_{4}$ | 2.0×10^{12} | 0.0 | 7.7×10^{3} | 21 |
| 13 | $C_{1}H_{1} + CH_{1} = C_{2}H_{3} + C_{2}H_{3}$ | 1.0×10^{13} | 0.0 | 37.5×10^{3} | 28 |
| 14 | $2CH_3 = C_2H_6$ | 2.0×10^{13} | 0.0 | 0.0×10^{3} | 33 |
| 15 | $C_1H_1 + CH_1 = C_4H_6$ | 5.0×10^{12} | 0.0 | 0.0 | est |
| 16 | $C_{3}H_{4}A + C_{3}H_{3} = C_{6}H_{6} + H$ | 2.2×10^{11} | 0.0 | 2.0×10^{3} | est |
| 17 | $2C_1H_1 = C_6H_6(L)$ | 6.0×10^{13} | 0.0 | 0.0 | est |
| 18 | $2C_{1}H_{1} = C_{6}H_{6}$ | 3.0×10^{11} | 0.0 | 0.0 | est, 28 |
| 19 | $2C_{1}H_{1} = 3C_{2}H_{2}$ | 5.0×10^{11} | 0.0 | 0.0 | est, 28 |
| | 1.3-butadiene mechanism | | | | 29 |
| | benzene mechanism | | | | 34 |
| | acetylene mechanism | | | | 35 |
| | | | | | |

 ${}^{a}C_{3}H_{4}A$, allene. ${}^{b}C_{3}H_{4}P$, propyne.

TABLE III: Rate Parameters and C₃H₅ Isomers



The heats of formation of the C_3H_5 isomers may be determined as

| >c=c-c< 104 | >с=с́—сн₃ | + | н |
|-------------|-----------------------------------|---|--------|
| (4.88) | C ₃ H ₅ (A) | | (52.1) |
| propene | | | |

Values in parentheses are the heats of formation of the corresponding species at 300 K. Taking the C-H bond dissociation energy in propene to be the same as that in ethylene, 104 kcal/mol, leads to 56.78 kcal mol⁻¹ for the heat of formation of $C_3H_5(A)$. Dean²⁵ has used the following heats of reaction for C-H bond rupture in hydrocarbon radicals.

The value for $\Delta H_{f,300}$ C₃H₅(B) is determined to be 39.11 kcal, which compares favorably to that for allyl radical, 40.6 kcal mol⁻¹,



Figure 9. CH₄ growth profiles, same symbols as in Figure 5.

listed by Benson.²⁶ Similarly, the value for $C_3H_5(C)$ is 62.8 kcal mol⁻¹. Using any of the three values of ΔH_f for C_3H_5 isomers

⁽²⁵⁾ Dean, A. M. J. Phys. Chem. 1985, 89, 4600.

⁽²⁶⁾ Benson, S. W. Thermochemical Kinetics, 2nd ed.; Wiley: New York, 1976; p 299.

in the modeling calculation does not change the computed profiles for the major species. The only difference is a change in the C_3H_5 concentration. In the present study, the observed C_3H_5 concentration has been estimated to be not more than 5×10^{-10} mol cm⁻³, which suggests that the heat of formation of C_3H_5 is not a crucial factor in allene pyrolysis.

We can approximate the energy requirement for 1,3 H shift in $C_3H_5(C)$ and $C_3H_5(B)$ as



which shows that overall 1,3 H shift in $C \rightarrow B$ equals the two steps of 1,2 H shift in which each step involves 6.0 and 17.7 kcal/mol⁻¹, respectively. $C_3H_5(B)$ is the allyl radical which is more stable than A and C. A and C readily decompose to CH_3 and C_2H_2 as suggested by Simmie et al.²⁷ which make the overall reactions 4 and 5 of Table II exothermic by 7.2 and 8.8 kcal mol⁻¹, respectively. Acetylene formed via reactions 4 and 5 is a stable species that increases in amount until its concentration is sufficient to carry out the sequence $C_2H_2 \rightarrow C_4H_2 \rightarrow C_6H_2 \rightarrow$ polyacetylenes.

Reaction 6 occurs via rupture of C-C bond in propyne9 involving a dissociation energy of 117 kcal mol⁻¹ and may constitute a minor channel at high temperatures.²⁸ Reactions 7 and 8 are H atom abstraction reactions for which the energies of activation are the same as those used by Kiefer.²¹ However, it was necessary to lower the A factors by a factor of 5 in order to achieve a better fit of the experimental data. The rate parameters for reactions 11 and 12 have been taken from ref 21.

The consumption of C3H3 involves several possibilities. Reaction 13 of Table II can be expressed as

$$-C \equiv C - C^{\bullet} + CH_{3} \rightarrow -C \equiv C - C^{\bullet} - C^{\bullet} - C^{\bullet} - C^{\bullet} - C^{\bullet} - C^{\bullet} + C_{2}H_{5}$$

After forming C_4H_6 (1-butyne), the C-C bond adjacent to the triple bond is broken to form C_2H and C_2H_5 radicals. The rate constant is estimated in ref 28.

Terminating steps for C₃H₃ and CH₃ radicals appear in reactions 14 and 15. Reaction 15 is a composite of two reactions leading to different C_4H_6 isomers:

$$-C \equiv C - C^{\bullet} + CH_{3} \rightarrow -C \equiv C - C - C - C - (15a)$$

$$>C = C = \dot{c} + CH_3 \rightarrow >C = C = C - \dot{c} - (15b)$$

Hydrogen atom reactions with the resulting C_4H_6 lead to two additional isomers of C_4H_6 .

 C_4H_6 (1,2-butadiene) + H \rightarrow C_4H_6 (1,3-butadiene) + H (15c)

$$C_4H_6$$
 (1-butyne) + H \rightarrow C_4H_6 (2-butyne) + H (15d)

The total concentration of C_4H_6 (including four isomers) is not

(27) Simmie, J. M.; Eubank, C. S.; Gardiner, W. C. J. Phys. Chem. 1982, 86, 800.



Figure 10. Concentration profiles of C_6H_6 and $C_6H_6(L)$ obtained from model calculations at three different temperatures: $C_6H_6(L)$, (--) 1607 K, (---) 1758 K, (---) 1915 K; C₆H₆, (---) 1607 K, (---) 1758 K, (---) 1915 K.

more than 5×10^{-10} mol cm⁻³. For simplicity in modeling, we regard the structure of C_4H_6 as 1,3-butadiene and employ the published rate constants for its decomposition.²⁹

There are several pathways for C_3H_3 to form C_6H_6 . One overall reaction that leads to benzene is

$$C_{3}H_{3} + C_{3}H_{4}(A) \rightarrow C_{6}H_{6} + H$$
 (16)

which consists of several steps:

$$C_3H_3 + C_3H_4(A) \rightarrow C_6H_7 \rightarrow c-C_6H_7 \rightarrow C_6H_6 + H$$

The recombination of C_3H_3 can result in either linear C_6H_6 or benzene.

$$C_1H_1 + C_1H_1 \rightarrow C_cH_c(L) \tag{17}$$

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6 \tag{18}$$

Benzene may be formed by reactions of two C_3H_3 radicals. Hurd et al.^{30,31} suggested that C₃H₃ radical first forms :CH-CH=CH via 1,2 H shift; two C_3H_3 cyclize to form benzene. In this study, we suggest reactions 16 and 18 as the main routes to form benzene. The mass spectra for C_6H_6 species, m/e 78, represents not only benzene but also linear structures such as hexa-1,5-diyne and hexa-1,2-diene-5-yne which have been observed in the photolysis of ketene in the presence of C_2H_2 and C_2H_4 .³² Canosa-mas et al. showed that the ratio of the above two linear C_6H_6 isomers $C \equiv C - C - C = C = C - C - C \equiv C$ is 1.34 ± 0.06 . They did not detect benzene.³²

In order to determine whether the peak at m/e 78 was due to benzene and/or linear structures of C_6H_6 , two model calculations were performed: one with (17) forming $C_6H_6(L)$ only, omitting (16) and (18); and the other with (16) and (18) forming benzene and (17) forming $C_6H_6(L)$. The computed profiles of benzene and $C_6H_6(L)$ under the conditions of the present investigation are plotted in Figure 10, which shows that benzene concentrations are higher by 3-4 of orders of magnitude. If we assume C_6H_6 to be linear only, then the concentrations for m/e 78 predicted by the model $(10^{-13}-10^{-14} \text{ mol cm}^{-3})$ are far below the TOF detectability limits (~10^{-10} mol cm^{-3}). The concentration of m/e78 was determined to be around 5×10^{-9} mol cm⁻³, which cor-

⁽²⁸⁾ Colket, M. B.; Seery, D. J. Presented at the 20th Symposium (International) on Combustion, Ann Arbor, MI, 1984; poster paper PS 55.

⁽²⁹⁾ Kiefer, J.; Wei, H. C.; Kern, R. D.; Wu, C. H. Int. J. Chem. Kinet.

<sup>1985, 17, 225.
(30)</sup> Hurd, C. D.; Macon, A. R.; Simon, J. I.; Levetan, R. V. J. Am. Chem. Soc. 1962, 84, 4509.

⁽³¹⁾ Hurd, C. D.; Macon, A. R. J. Am. Chem. Soc. 1962, 84, 4524. (32) Canosa-mas, C. E.; Ellis, M.; Frey, H. M.; Walsh, R. Int. J. Chem. Kinet. 1984, 16, 1103.



Figure 11. C_6H_6 growth profiles of 4.3% 1,2-butadiene pyrolysis. The symbols denote \Box , 1918 K; \blacktriangle , 1738 K; and O, 1625 K. The lines are smooth curves through the data points.

TABLE IV: Carbon Atom Mass Balance for Allene Pyrolysis; Percentage Conversion at 750-µs Observation Time

| T ₅ , K | C ₃ H ₄ | C ₂ H ₂ | C ₄ H ₂ | C ₆ H ₆ | total |
|--------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------|
| 1607 | 67 | 21 | | 6 | 94 |
| 1758 | 26 | 47 | 8 | 6 | 87 |
| 1915 | 13 | 57 | 12 | 2 | 84 |

responds to the magnitude of benzene predicted by reactions 16 and 18. The remaining reactions are taken from previously published mechanisms for methane, ethane, ethylene, acetylene, 1,3-butadiene, and benzene pyrolyses.^{27,29,33-35} The rate parameters are referenced in Table II. The term pw (present work) refers to rate constants determined by experimental data obtained herein. The term est (estimated) refers to those rate constants which affect the modeling process but which lack sufficient experimental data to strongly support their values.

In order to assess the importance of C_3H_3 radical in benzene formation, we performed experiments on a 4.3% 1,2-butadiene mixture and compared the benzene production observed with that obtained from our allene mixture. The C-C bond in 1,2-butadiene apparently has the weakest; Dean²⁵ suggested a value of 76.5 kcal/mol. 1,2-Butadiene should rupture initially to CH₂=C=CH and CH₃ radicals. The other possible route is C-H bond rupture, which requires about 86 kcal/mol.⁻¹ Detailed work on 1,2-butadiene is in progress.³⁶ The main purpose of 1,2-butadiene experiments here is to examine the amount of C_6H_6 formed. The plateau concentration of C_6H_6 has the same magnitude as that obtained from allene and is shown in Figure 11. If the two mixtures have approximately the same concentration of C_3H_3 radicals and produce like amounts of benzene, it is reasonable to assume that C_3H_3 does indeed play a key role.

Lastly, we try to correlate the order of soot yields determined by laser extinction³⁷ (LEX) and TOF studies. The total carbon balance from the TOF work is listed in Table IV, which shows that the maximum carbon atom deficiency is about 16%. The laser extinction study reveals that the soot yield for allene is about 3 times greater than that of 1,3-butadiene. The TOF studies display the amount of missing total carbon atoms in the order benzene > allene > 1.3 butadiene > acetylene, which is the same order reported in the LEX for 2 × 10¹⁷ carbon atoms cm⁻³ at temperatures and pressures of 1300–2500 K and 0.2–0.6 atm. These two studies agree with regard to the appearance of maximum soot yield (LEX) and the maximum concentration of benzene (TOF). Furthermore, the (LEX) soot yield order is the same as the benzene production in the TOF experiments: allene > 1,3-butadiene > acetylene.

This finding is consistent with the proposal that aromatic rings condense to form preparticle soot nuclei during the inception period. Fuels that easily produce benzene rings also exhibit strong sooting tendencies.

Conclusions

(1) The major products of allene pyrolysis are C_2H_2 , C_4H_2 , CH_4 , and C_6H_6 ; minor products are C_2H_4 , C_2H_6 , C_4H_4 , C_4H_6 , and C_6H_2 . (2) The amount of benzene formed from mixtures containing equal concentrations of allene and 1,2-butadiene is about the same. C_3H_3 is proposed to be the major species leading to the formation of benzene. (3) The comparison of soot yields and the concentration of benzene have the order benzene > allene > 1,3-butadiene > acetylene, which supports the notion that aromatic rings are important for soot nuclei growth.

Acknowledgment. We gratefully acknowledge the U.S. Department of Energy for supporting this research under Contract No. DE-FG05-85ER/13340. Many thanks to Professor Kiefer for helpful discussions and to Dr. Hari Singh for his valuable assistance in preparing the manuscript.

Registry No. Allene, 463-49-0.

⁽³³⁾ Baulch, D. L.; Duxburry, J. Combust. Flame 1980, 37, 313.

⁽³⁴⁾ Kiefer, J. H.; Mizerka, L. J.; Patel, M. R.; Wei, H. C. J. Phys. Chem. 1985, 89, 2013.

⁽³⁵⁾ Wu, C. H.; Singh, H. J.; Kern, R. D. Int. J. Chem. Kinet. 1987, 19, 975.

⁽³⁶⁾ Kern, R. D.; Singh, H. J. Presented at the 194th National Meeting of the American Chemical Society, New Orleans, LA, August 1987.

⁽³⁷⁾ Frenklach, M.; Taki, S.; Durgarasad, M. B.; Matula, R. A. Combust. Flame 1983, 54, 81.

⁽³⁸⁾ Warnatz, J.; Bockhorn, H.; Moser, A.; Wenz, H. W. Symp. (Int.) Combust., [Proc.] 1982, 19th, 197.