3406 *J. Phys. Chem. A* **2004,** *108,* 3406−3415

Shock Tube Study of Thermal Rearrangement of 1,5-Hexadiyne over Wide Temperature and Pressure Regime

Robert S. Tranter,[§,||] Weiyong Tang,[§] Ken B. Anderson,[†,‡] and Kenneth Brezinsky*,[§]

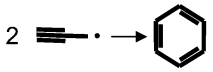
Departments of Mechanical Engineering and Chemical Engineering, University of Illinois at Chicago, 842 West Taylor Street, M/C 251, Chicago, Illinois 60607, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Received: October 31, 2003; In Final Form: January 30, 2004

The pyrolysis of 1,5-hexadiyne has been studied in a high-pressure single pulse shock tube to investigate the mechanisms involved in the production of benzene from propargyl radicals. Analysis of the reaction products by gas chromatography and matrix isolation Fourier transform infrared spectroscopy has positively identified six linear C_6H_6 species and two cyclic C_6H_6 species. Of these species *cis*-1,3-hexadien-5-yne and *trans*-1,3-hexadiene-5-yne have been unambiguously identified for the first time and provide vital information concerning a low-temperature route to benzene that does not involve the formation of fulvene; however, the data also provide support for two high-temperature paths from propargyl radicals to benzene via fulvene. Thus experimental evidence has been gained that supports two different routes to benzene formation. The mechanisms and rate coefficients that have been obtained in this work are discussed.

Introduction

Understanding the key routes to benzene formation in sooting flames[1−6] is important because it is via growth from small aromatic species that the production of soot is thought to occur. The recombination of propargyl radicals, reaction 1, is purported to be a primary route to benzene formation.



(1)

The experimental[7−11] and theoretical[12−19] studies that have been made on propargyl recombination show that reaction 1 is a gross simplification of a complex series of simultaneous and consecutive reactions that are predominantly isomerizations of C_6H_6 species. Initially, two propargyl radicals can recombine to form three stable linear C_6H_6 species, as shown below.

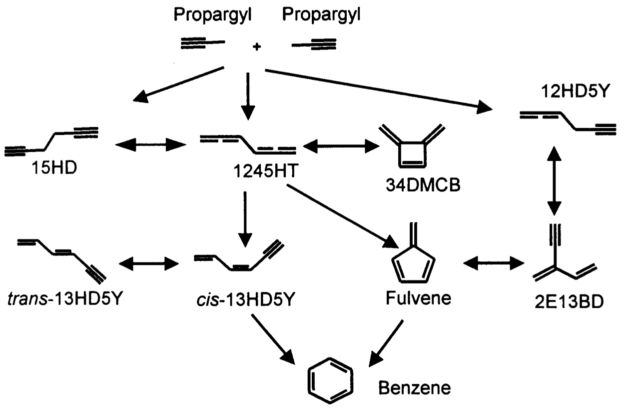
$$2HC{\equiv}CCH_2 \rightarrow HC{\equiv}CCH_2CH_2C{\equiv}CH \text{ (1,5-hexadiyne, 15HD)} \quad (2)$$

$$2HC{\equiv}CCH_2 \rightarrow H_2C{=}C{=}CHCH{=}C{=}CH_2 \text{ (1,2,4,5-hexatetraene, 1245HT)} \quad (3)$$

$$2HC{\equiv}CCH_2 \rightarrow H_2C{=}C{=}CHCH_2C{\equiv}CH \text{ (1,2-hexadiene-5-yne, 12HD5Y)} \quad (4)$$

These species then isomerize to ultimately form benzene, which at high enough temperatures and long enough reaction times can decompose to a phenyl radical and an H-atom. Additionally, theoretical studies suggest that at very high temperatures one of the metastable intermediates involved in benzene formation can decompose to phenyl + H without first forming benzene.[19] The major stable species involved in the various reaction paths from propargyl radicals to benzene are summarized in Scheme 1, which is based on the extant theoretical and experimental studies of propargyl recombination and the related pyrolysis of 1,5-hexadiyne.

SCHEME 1: Chemical Reaction Pathways Involving Stable Species for the Thermal Isomerizations of 1,5-Hexadiyne[a]



[a] The length of the arrow does not indicate the significance of the path. Abbreviations: 15HD, 1,5-hexadiyne; 1245HT, 1,2,4,5-hexatetraene; 12HD5Y, 1,2-hexadiene-5-yne; 34DMCB, 3,4-dimethylenecyclobutene; 13HD5Y, 1,3-hexadiene-5-yne; 2E13BD, 2-ethynyl-1,3-butadiene.

The experimental investigations of propargyl recombination have employed a variety of techniques and sources for producing propargyl radicals. There is general agreement that the products of reactions 2−4 are the primary recombination products and that these species can interconvert and isomerize to secondary products that ultimately lead to benzene. Alkemade and Homann[7] found 12HD5Y, reaction 4, to be the major recom-

---

* Corresponding author. E-mail: Kenbrez@UIC.edu.

[†] Present address: Department of Geology, Southern Illinois University, Carbondale, IL, 62901.

[‡] Argonne National Laboratory.

[§] University of Illinois at Chicago.

[||] Present address: Argonne National Laboratory.

10.1021/jp037310z CCC: $27.50

bination product and only a few percent of 15HD, reaction 1, at 623−673 K and 2−4 Torr, and are the only group to have directly observed and identified 1245HT, reaction 3, as a recombination product of propargyl radicals. In addition to the primary products, Alkemade and Homann observed 1,3-hexadiene-5-yne (13HD5Y) and benzene as secondary products. Benzene appeared to be formed consecutively from a linear C_6H_6 species, and Alkemade and Homann did not observe fulvene, which is often postulated as a stable intermediate between linear C_6H_6's and benzene, Scheme 1. Fahr and Nayak[8] found 15HD to account for 60% of their initial products at room temperature and 50 Torr with 25% 12HD5Y and 15% of an unidentified linear C_6H_6 species, which by comparison with Alkemade and Homann may be 1245HT. It is clear that Fahr and Nayak observed a primary product distribution different from that of Alkemade and Homann. This may be explained by Alkemade and Homann's suggestion that under their experimental conditions the 15HD is chemically activated when formed and isomerizes to 1245HT and 12HD5Y. Shock tube ARAS studies by Scherer et al.[10] on propargyl recombination were supplemented by GC−MS analysis of post shock gas samples that indicated the presence of five C_6H_6 isomers of which they were only able to positively identify benzene. Scherer et al. noted that as the benzene concentration increased with increasing reaction temperature the other species concentrations diminished. Recently, Shafir et al.[9] used a flow system at temperatures from 500 to 1000 K to study propargyl recombination and observed 15HD as the sole linear recombination product. They also observed two other C_6H_6 species, which were not identified, and benzene, which became the only product at 900 K. In addition, small quantities of fulvene were seen.

The potential energy surface for reaction 1 is complex and has been described in a series of papers,[12−19] with two of the most recent treatments being by Dean and Carstensen[18] and Miller and Klippenstein.[19] The main reaction paths from these publications are summarized in Scheme 1, and the reader is referred to ref 19 for a detailed energy level diagram. Note that in the majority of these studies the route to benzene from any of the three propargyl recombination products involves the sequential formation of fulvene and then benzene. In a very recent paper, Miller and Klippenstein[19] have suggested an additional route to benzene that does not involve fulvene but occurs via cyclization of *cis*-1,3-hexadiene-5-yne, which is formed from 1245HT. Alkemade and Homann found 1,3-hexadiene-5-yne in their experimental work on propargyl recombination. However, they did not specify if they had observed the cis or trans form and it is likely that they had not separated 1,3-hexadiene-5-yne into the cis and trans isomers chromatographically.

The theoretical studies all indicate that a variety of stable species, shown in Scheme 1, should be observed during propargyl recombination, with benzene being the ultimate product except at high temperatures where benzene also decomposes. The earlier experimental work indicates that 1,5-hexadiyne should be the dominant primary product from propargyl recombination and this species provides a convenient entry point for experimentally examining the isomerization chemistry of the propargyl recombination products, particularly if a technique is used that employs sensitive analytical techniques that can discriminate C_6H_6 isomers.

The earlier experimental studies[20−27] on 1,5-hexadiyne thermolysis and theoretical work on propargyl recombination raise an interesting problem concerning the formation of fulvene and benzene. The experimental work tends to indicate that fulvene and benzene are formed simultaneously, i.e., fulvene is not an intermediate to benzene, or more than one route to benzene exists. The only experimental study of fulvene to benzene isomerization[28] indicates that, under the conditions of the prior 15HD experiments, fulvene to benzene conversion is too slow to be significant. This idea is also supported by a theoretical study of fulvene isomerization.[29] Conversely, most theoretical studies of propargyl recombination suggest that benzene is formed sequentially from fulvene. A very recent theoretical paper[19] may have solved this problem and includes routes to benzene that treat fulvene as an intermediate to benzene and a route to benzene that bypasses fulvene entirely.

Hence there would appear to be some disagreement between experimental and theoretical studies over the paths from propargyl to benzene and it is the intent of this work to address the disagreement by using the very clean, well characterized reaction environment of the high-pressure shock tube coupled with sensitive analytical techniques capable of unambiguously identifying C_6H_6 isomers to investigate 1,5-hexadiyne pyrolysis.

Experimental Section

The high-pressure shock tube is operated as a single pulse shock tube with tailored driven and driver section lengths to produce optimal quenching of the reactive gases at the end of the reaction period. The shock tube and the sampling techniques used in these studies have been described in detail in recent publications[30−32] and only a brief description will be given here.

Shock waves are generated by spontaneously bursting prescored diaphragms between the driver and driven sections of the shock tube, and the experiments are performed in the stable, isothermal zone behind the reflected shock wave where the temperature and pressure are T_5 and P_5, respectively. In this work experiments were performed at nominal P_5 values of 25, 50, 300, and 500 bar. The 300 and 500 bar experiments utilized prescored diaphragms made of soft brass that were 0.032 in./0.010 in. (thickness/score depth) and 0.050 in./0.016 in., respectively. For the lower pressure experiments aluminum diaphragms were used, 0.025 in./0.010 in. for 25 bar and 0.025 in./0.005 in. for 50 bar. The appropriate diaphragms were determined on the basis of prior experience and experiment.

Pressures behind the reflected shock wave and reaction times were obtained from the pressure profiles measured by a piezoelectric pressure transducer mounted axially in the end wall of the driven section. The reaction time was calculated on the basis of the method of Hidaka et al.,[33] i.e., the time between the arrival of the incident shock and P_5 falling to 80% of the reaction pressure. In this work the reaction times were 1.2−1.5 ms for 300 and 500 bar and 1.6−1.9 ms for 25 and 50 bar.

Reaction temperatures ranged from 780 to 1400 K. For the 300 and 500 bar experiments real gas effects are significant[31,34] and the temperatures were determined by using chemical thermometers,[31] with the lower temperatures being determined by extrapolation of the temperature calibration curves. The reaction temperatures in the 25 and 50 bar experiments were calculated from the incident shock velocity, and for these experiments errors in the temperature due to deviations from ideal gas behavior are expected to be small.[34] Shock velocities, required for determining temperatures both from chemical thermometers and by calculation, for all experiments were obtained by the time taken for the incident shock wave to travel between piezoelectric pressure transducers mounted along the side wall of the driven section near the end of the shock tube.

For each experiment a sample of the reagent gas was taken prior to firing the shock tube, preshock sample, and a sample of the gas near the end wall of the driven section of the shock tube was collected shortly after the arrival of the expansion wave generated from bursting the diaphragm, postshock sample. The timing for collecting the postshock sample was determined empirically.[30] Both the preshock and postshock samples are collected in electropolished stainless steel vessels stored in an oven at 50 °C prior to and after sampling. Samples could be stored for a couple of days with no discernible change in composition. Over the course of a couple of weeks a slow isomerization of fulvene to 3,4,-dimethylenecyclobutene was observed in a sample stored at 50 °C.

Reagents. The reagent mixtures were prepared manometrically in 50 L high-pressure vessels that were maintained at 45 °C and allowed to stand overnight before use. The mixtures contained 40−55 ppm 1,5-hexadiyne (>99.9%, see below), 200 ppm xenon (AGA, 99.99%) with the balance argon (BOC, 99.999%). The argon was passed over Oxisorb (Messer-Griesheim) to remove traces of O_2 prior to admission to the mixing vessel, and xenon was used as supplied. Xenon is used as an internal standard for the analytical work and to account for any dilution of the postshock sample by the driver gas, He.

1,5-Hexadiyne was obtained from GFS Chemicals in 50% solution with pentane. Prior to use the 1,5-hexadiyne was purified by a two-step distillation process. In the first step a crude separation was effected by an atmospheric pressure distillation and the fraction that distilled over up to 70 °C was collected. The distillate was almost pure pentane (bp 36 °C, mp −130 °C), and the residue in the distillation flask was about 98−99% 1,5-hexadiyne (bp 86 °C, mp −6 °C) with the remainder pentane, confirmed by GC−MS. Next a low-temperature (approximately −30 °C) vacuum distillation was performed with the 98−99% 1,5-hexadiyne to remove the remaining pentane. After this step a purity of better than 99.9% was obtained for the 1,5-hexadiyne (confirmed by GC−FID and GC−MS). The purified 1,5-hexadiyne could be stored refrigerated for extended periods without noticeable degradation.

Analytical Techniques. A variety of analytical techniques have been used in the course of this work. The bulk of the analyses were performed using our standard two-column, GC−TCD and GC−FID method with GC−MS being used to confirm molecular formulas and where possible species identities. In this technique gas samples are introduced via a sample/pressure reduction rig to two Valco gas sampling valves (GSVs) mounted on the same GC (HP 6890). The sample loops on the valves are filled simultaneously, and injections are made onto two columns maintained in the same oven. An HP−Molseive 5A column (30 m, 0.32 mm, 12 μm) is connected to a TCD and used to detect xenon, which acts as an internal standard. The second column, HP-1MS (30 m, 0.032 mm, 3 μm), is connected to an FID and was used to detect stable hydrocarbon species. In this work all species were baseline resolved and in samples from experiments where the reaction temperature was above 920 K, up to eight species were observed. Of these, 1,5-hexadiyne and benzene were positively identified by the injection of authentic standards. GC−MS analyses, using the HP1-MS column, indicated that all the observed species had the formula C_6H_6 and due to a lack of authentic standards for the analytes it was not possible to make unambiguous identifications based solely on the mass spectra. Consequently, a novel technique, GC−matrix isolation-FTIR−MS (GC−mi-FTIR−MS),[35] which was available at Argonne National Laboratories was used to obtain simultaneous mass and FTIR spectra for species eluting from the GC column. The FTIR spectra allow unambiguous assignment of species identities. In the GC−mi-FTIR−MS work a 60 m ZB-5 capillary column was used, which under the analytical conditions performs very similarly to the HP-1MS column, i.e., baseline separation achieved, same number of peaks observed and elution order is the same. The GC−mi-FTIR−MS portion of this work, including details of the technique, has been reported in a separate publication where the FTIR and MS spectra are available along with the results of density functional theory calculations that were used as aids in assigning structural identities.[35] A significant aspect of the FTIR work was that both the cis and trans isomers of 1,3-hexadiene-5-yne, 1,2-hexadiene-5-yne, and 2-ethynyl-1,3,-butadiene were positively identified. Previously, Alkemade and Homann[7] had observed what was probably a mixture of *cis*- and *trans*-1,3-hexadiene-5-yne but had not separated it into the distinct isomers. A sample total ion chromatogram is shown in Figure 1.

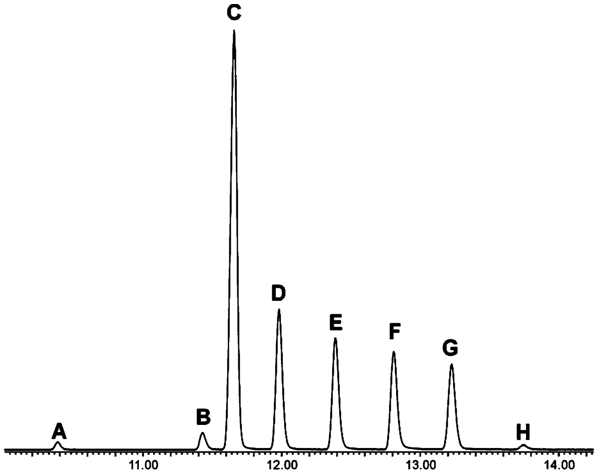


Figure 1. Total ion chromatogram from GC−mi-FTIR−MS analysis of a post shock sample from 1,5-hexadiyne pyrolysis: (A) 2-ethynyl-1,3-butadiene; (B) 1,5-hexadiyne; (C) 3,4-dimethylenecyclobutene; (D) fulvene; (E) *cis*-1,3-hexadiene-5-yne; (F) *trans*-1,3-hexadiene-5-yne; (G) benzene; (H) 1,2-hexadene-5-yne.

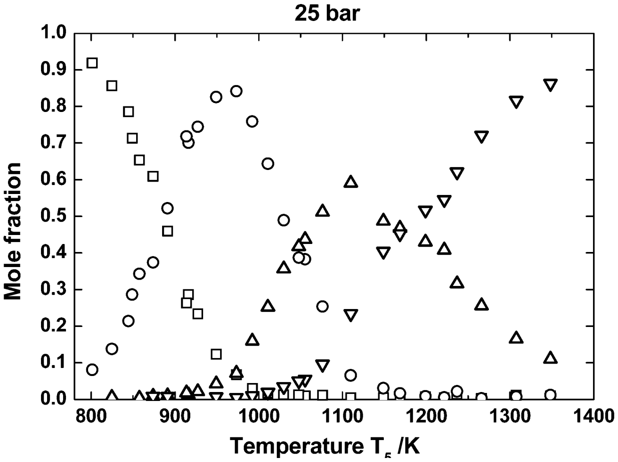


Figure 2. Major species observed from 1,5-hexadiyne pyrolysis at 25 bar ([1,5-hexadiyne]$_0$ = 42 ppm): (□) 1,5-hexadiyne; (○) 3,4-dimethylenecyclobutene; (△), fulvene; (▽) benzene.

Results

The species concentration profiles with respect to temperature are shown for the 25, 50, 300, and 500 bar experiments in Figures 2−9, note concentrations are shown as mole fractions relative to initial 15HD concentration. Figure 10 shows that over the variation in pressure of a factor of 20 in these experiments

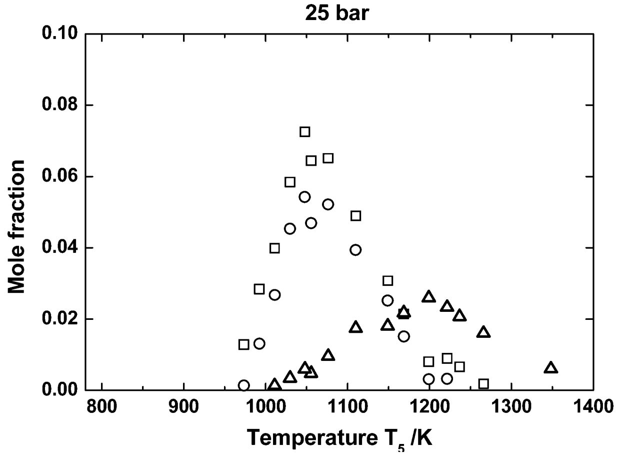


Figure 3. Minor species observed from 1,5-hexadiyne pyrolysis at 25 bar ([1,5-hexadiyne]$_0$ = 42 ppm): (□) *cis*-1,3-hexadiene-5-yne; (○) *trans*-1,3-hexadiene-5-yne; (△) 2-ethynyl-1,3-butadiene.

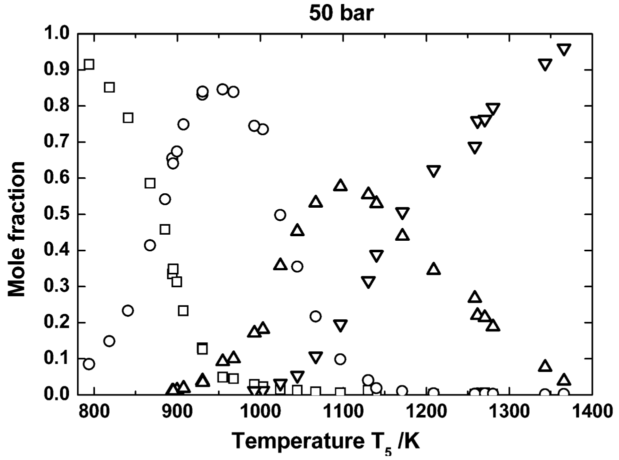


Figure 4. Major species observed from 1,5-hexadiyne pyrolysis at 50 bar ([1,5-hexadiyne]$_0$ = 42 ppm): (□) 1,5-hexadiyne; (○) 3,4-dimethylenecyclobutene; (△) fulvene; (▽) benzene.

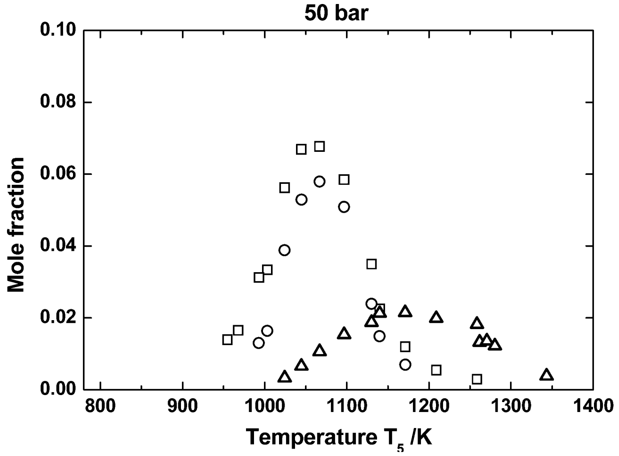


Figure 5. Minor species observed from 1,5-hexadiyne pyrolysis at 50 bar ([1,5-hexadiyne]$_0$ = 42 ppm): (□) *cis*-1,3-hexadiene-5-yne; (○) *trans*-1,3-hexadiene-5-yne; (△) 2-ethynyl-1,3-butadiene.

there are no significant differences for each experimental range in the 15HD profiles and similar results are obtained for all the other species observed.

At temperatures below about 900 K, 1,5-hexadiyne is quantitatively converted to 3,4,-dimethylenecyclobutene (34DMCB) and no other species are observed. Around 950 K the concentration of 34DMCB reaches a maximum and small amounts of fulvene are formed. When the reaction temperature reaches 1000 K, approximately 50% of the 34DMCB has been consumed, significant concentrations of fulvene are present and traces of benzene, *cis*-1,3-hexadiene-5-yne (*cis*-13HD5Y) and *trans*-1,3-hexadiene-5-yne (*trans*-13HD5Y) are formed. About

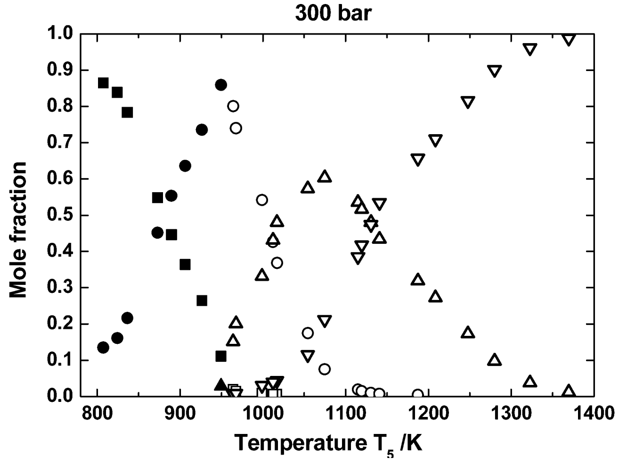


Figure 6. Major species observed from 1,5-hexadiyne pyrolysis at 300 bar. Closed symbols: [1,5-hexadiyne]$_0$ = 40 ppm. Open symbols: [1,5-hexadiyne]$_0$ = 46 ppm. Key: (■, □) 1,5-hexadiyne; (●, ○) 3,4-dimethylenecyclobutene; (▲, △) fulvene; (▼, ▽) benzene.

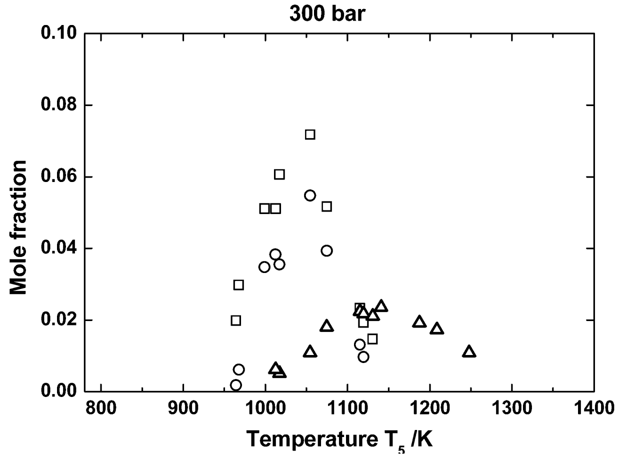


Figure 7. Minor species observed from 1,5-hexadiyne pyrolysis at 300 bar ([1,5-hexadiyne]$_i$ = 46 ppm): (□) *cis*-1,3-hexadiene-5-yne; (○) *trans*-1,3-hexadiene-5-yne; (△) 2-ethynyl-1,3-butadiene.

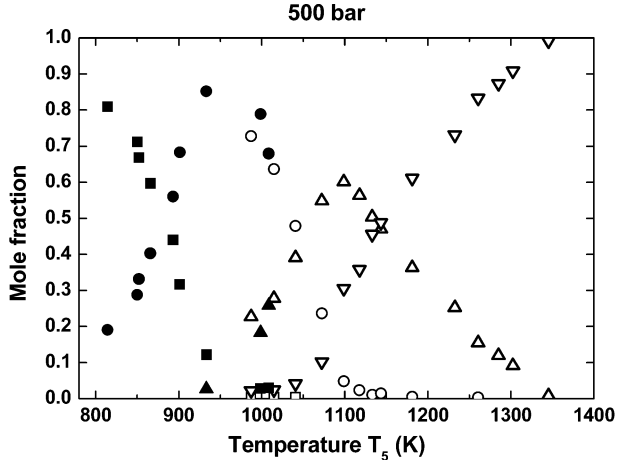


Figure 8. Major species observed from 1,5-hexadiyne pyrolysis at 500 bar. Closed symbols: [1,5-hexadiyne]$_0$ = 55 ppm. Open symbols: [1,5-hexadiyne]$_0$ = 48 ppm. Key: (■, □) 1,5-hexadiyne; (●, ○) 3,4-dimethylenecyclobutene; (▲, △) fulvene; (▼, ▽) benzene.

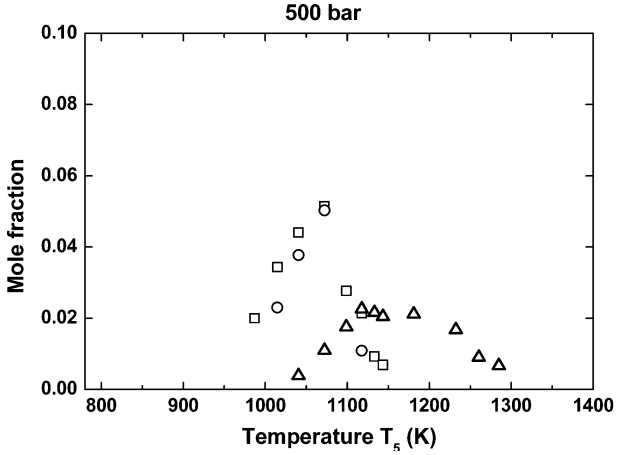


Figure 9. Minor species observed from 1,5-hexadiyne pyrolysis at 500 bar ([1,5-hexadiyne]$_0$ = 48 ppm): (□) *cis*-1,3-hexadiene-5-yne; (○) *trans*-1,3-hexadiene-5-yne; (△) 2-ethynyl-1,3-butadiene.

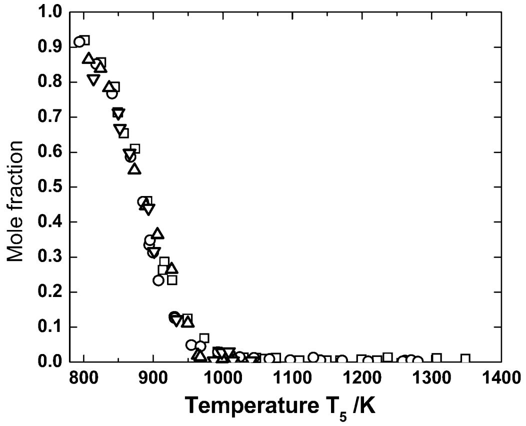


Figure 10. Effect of reaction pressure on 1,5-hexadiyne consumption: (□) 25 bar; (○) 50 bar; (△) 300 bar; (▽) 500 bar.

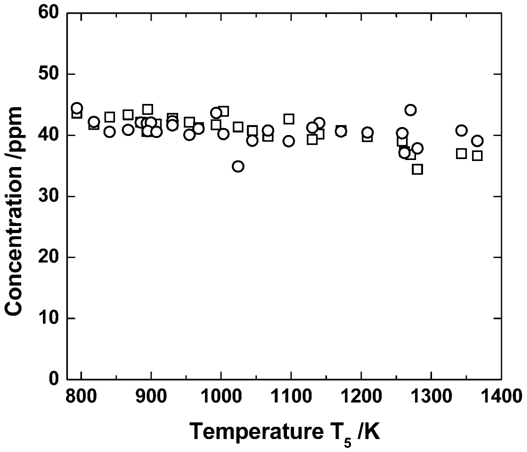


Figure 11. Carbon balance at 50 bar ([1,5-hexadiyne]$_0$ = 42 ppm): (□) postshock; (○) preshock.

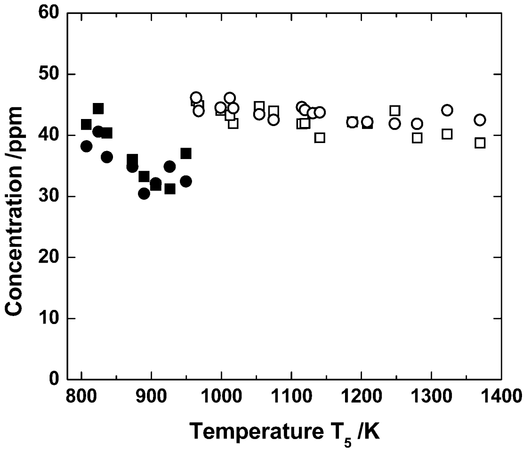


Figure 12. Carbon balance at 300 bar. Closed symbols: [1,5-hexadiyne]$_0$ = 40 ppm. Open symbols: [1,5-hexadiyne]$_0$ = 46 ppm. (■, □) postshock; (●, ○) preshock.

50 K after *cis*- and *trans*-13HD5Y appear, 2-ethynyl-1,3-butadiene (2E13BD) is formed. The two rotamers of 13HD5Y are formed in almost equal proportions with about 10−20% more of the cis form than the trans form and the maximum mole fraction of the cis form is around 0.07 at 1100 K. Both the cis and trans rotamers are completely consumed by 1200 K. The mole fraction of 2E13BD builds slowly from 1000 K to a maximum of 0.02 at 1200 K and is completely consumed by 1350 K. The benzene concentration increases steadily from its appearance at 1000 K to a maximum at 1400 K where it is the only stable species present.

A very small peak in the chromatographic analysis that corresponded to 1,2-hexadiene-5-yne was observed and in the samples analyzed by GC−mi-FTIR−MS gave good quality FTIR spectra; see ref 35 for details. However, due to the low concentration, ng/L level, it was not possible to accurately quantify this peak. 1,2,4,5-Hexatetraene was not observed at all in the kinetic or FTIR analyses.

Carbon balances have been calculated for every experiment and are presented for the 50 and 300 bar experiments in Figures 11 and 12. It is quite clear that the carbon balances at 50 and 300 bar are good although there may be a small deficit at the very highest temperatures of this work and similar carbon balances are observed for the 25 and 500 bar experiments. The good carbon balances indicate that all species are being recovered. The lack of species with formulas other than C_6H_6 clearly indicates that no fragmentation and hence no chain processes are occurring under the conditions of these experiments. Consequently, there should be no low activation barrier process such as radical recombination reactions that can occur during the quenching of the reactive gases by the rarefaction waves in the shock tube and the reaction times can be obtained with confidence by the normal method mentioned above.

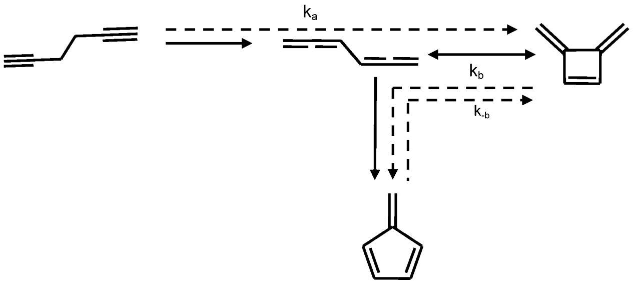
The experimental datasets are available in the Supporting Information.

Discussion

Thermal Rearrangement Rate Coefficients. *1,5-Hexadiyne to 3,4-Dimethylenecyclobutene.* Because 3,4-dimethylenecyclobutene is the only significant product from the thermal rearrangement of 1,5-hexadiyne at relatively low temperatures from 780 to 950 K, it is possible to determine the rate coefficients of reaction 5 at different reaction pressures if it is assumed that the hexatetraene intermediate rapidly cyclizes to the cyclobutene, represented by k_a in Scheme 2. The mechanism of this process is discussed below.

From the experimental data, k_a's at different reaction pressures were calculated by least-squares fit, as shown in Figure 13. The individual rate expressions for each pressure range and the literature expressions for k_a are presented in Table 1. Also shown in Figure 13 is the computational result of Melius et al. for k_a,[14] which predicts rate coefficients that are about 3 orders of magnitude larger than the experimental values. Miller and

SCHEME 2: 1,5-Hexadiyne Conversion to 3,4-Dimethylenecyclobutene and Fulvene[a]



[a] Dashed lines represent overall processes for which rate coefficients have been extracted. See text for details.

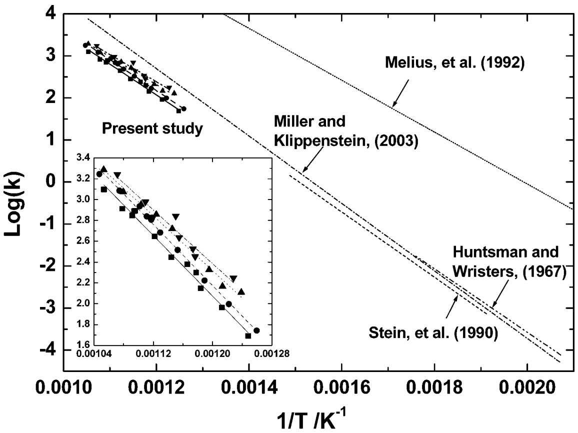


Figure 13. Arrhenius plots for reaction 1,5-hexadiyne → 3,4-dimethylenecyclobutene. In the inset symbols represent experimental data and lines represent linear fits to the data. Key: solid line and ■, 25 bar; dashed line and ●, 50 bar; dotted line and ▲, 300 bar; dashed−dotted line and ▼, 500 bar. Data from Miller and Klippenstein,[19] Melius et al.,[14] Stein et al.,[25] and Huntsman and Wristers.[20] See Table 1 for detailed rate parameter values.

TABLE 1: Rate Coefficients for Conversion of 1,5-Hexadiyne to 3,4-Dimethylenecyclobutene[a]

pressure/bar	temperature/K	log(*A*)	*E*/kcal	source
25	780−950	10.82	33.36	p.w.
50	780−950	10.98	33.57	p.w.
300	780−950	10.22	30.11	p.w.
500	780−950	10.12	29.50	p.w.
1.013	523−723	11.7	35.50	25
1.013	473−563	11.4	34.40	21
b		12.28	28.22	14
c		12.28	36.61	19

[a] See text for discussion of reaction path. [b] Theoretical computation. [c] Theoretical computation. *A* and *E* were obtained by extrapolation from Figure 6 in ref 19.

Klippenstein[19] modified the barrier heights for 1,5-hexadiyne going to 1,2,4,5-hexatetraene and 1,2,4,5-hexatetraene to 3,4-dimethylenecyclobutene by 1.0 kcal/mol and 0.71 kcal/mol, respectively, and obtain good fits to the Stein et al.[25] and Huntsman and Wristers[20] data. An Arrhenius expression for reaction 5 has been estimated from Figure 6 in ref 19, and the rate coefficients have been extrapolated to the high temperatures of the current work. The extrapolated expression overpredicts the current data by about a factor of 3 to 4 but maintains good agreement with the Stein et al. data at low temperatures. Figure 13 also shows a small, essentially negligible, increase in the rate coefficients from the current work as the pressure increases from 25 to 500 bar. For a 20-fold increase in pressure, *k* increases by about a factor of 1.5.

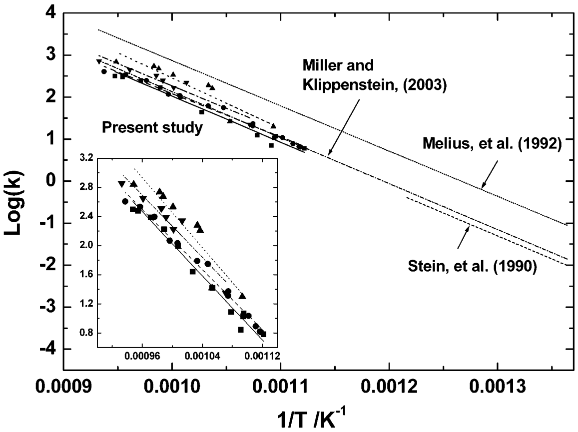


Figure 14. Arrhenius plots for reaction 3,4-dimethylenecyclobutene → fulvene. In the figure symbols represent experimental data, and lines represent linear fits to the data. Key: solid line and ■, 25 bar; dashed line and ●, 50 bar; dotted line and ▲, 300 bar; dashed−dotted line and ▼, 500 bar. Data from Miller and Klippenstein,[19] Melius et al.,[14] and Stein et al.[25] See Table 2 for detailed rate parameter values.

TABLE 2: Rate Coefficients for Conversion of 3,4-Dimethylenecyclobutene to Fulvene[a]

pressure/bar	temperature/K	log(*A*)	*E*/kcal	source
25	780−950	13.03	50.22	p.w.
50	780−950	12.38	47.12	p.w.
300	780−950	14.43	54.83	p.w.
500	780−950	12.92	48.74	p.w.
1.013	523−723	12.9	50.00	25
b		13.63	49.26	14
c		13.07	50.08	19

[a] See text for discussion of reaction path. [b] Theoretical computation. [c] Theoretical computation. *A* and *E* were obtained by extrapolation from Figure 8 in ref 19.

Dimethylenecyclobutene to Fulvene. At temperatures above about 950 K in the current work all the 1,5-hexadiyne has been consumed, 3,4-dimethylenecyclobutene reaches a maximum, and fulvene begins to appear. By assuming at temperatures above 950 K that the reaction system can be modeled by the formation of 3,4-dimethylenecyclobutene being reversible to 1,2,4,5 hexatetraene and the 1245HT isomerizing to fulvene, Scheme 2, one can obtain k_b in Scheme 2. Obviously such a process is a simplification of the sequence of elementary reactions involved[12,17] in converting 3,4-dimethylenecyclobutene to fulvene; it assumes that all intermediate species are highly reactive and that additional channels are negligible. Using such a scheme, rate coefficients, k_b, have been obtained and are shown in Figure 14 where they are compared with values from Stein et al.[25] and theoretical calculations by Miller and Klippenstein,[19] and Melius et al.[14] The current work has yielded rate coefficients, Table 2, that are in good agreement with the low-temperature values from Stein et al. and the extrapolated values from Miller and Klippenstein that have been estimated from Figure 8 of ref 19. Once again Melius et al. overpredict the measured rate coefficients over the whole temperature range, this time by a factor of 3−4. It should be noted that in the present work the temperature range where 3,4-dimethylenecyclobutene and fulvene are the only products is limited; however, the other species, *cis*- and *trans*-1,3 hexadien-5-yne, that could be formed from thermolysis of 3,4-dimethylenecyclobutene are only ever present in very low concentrations and the formation of these species instead of fulvene should lead to only minor errors in the deduced rate coefficients.

Mechanism of Formation of 3,4-Dimethylenecyclobutene. The thermal rearrangement of 1,5-hexadiyne has been studied by Huntsman and Wristers[20] in a static system (210−232 °C) and a flow system (250−550 °C). In both sets of experiments they observed 3,4-dimethylenecyclobutene as the sole product. Huntsman and Wristers have suggested that 3,4-dimethylenecyclobutene is formed from 1,5-hexadiyne by a two-step process (see Scheme 2) involving a Cope rearrangement to 1,2,4,5-hexatetraene followed by rapid cyclization of 1245HT to 3,4-dimethylenecyclobutene. A direct route from 15HD to 34DMCB has also been suggested by Huntsman and Wristers.[20] However, on the basis of the large negative entropy of activation observed (−9.4 e.u. at 300 °C) and consideration of the Woodward−Hoffmann rules, Jones et al.,[23] Huntsman and Wristers, and others[20−22] concur that 3,4-dimethylenecyclobutene is formed via a Cope rearrangement of 1,5-hexadiyne followed by a rapid cyclization of 1,2,4,5-hexatetraene.

Henry and Bergman[24] also report that at 250 °C they observed only 3,4-dimethylenecyclobutene in the thermolysis of 1,5-hexadiyne; however, at 620 °C in a vacuum flow tube they observed a mixture of 3,4-dimethylenecyclobutene, fulvene, and benzene. In atmospheric flow reactor studies of 1,5-hexadiyne pyrolysis Stein et al.[25] observed 3,4-dimethylenecyclobutene as the only product for temperatures less than 460 °C and residence times of approximately 30 s. However, in very low-pressure pyrolysis (VLPP) studies on the same system, Stein et al. [25] found that benzene and fulvene were formed along with 3,4-dimethylenecyclobutene at temperatures from 250 °C to around 700 °C. In the current work 34DMCB is the only product formed from 15HD and at 950 K about 90% of the initial 15HD has been converted to 34DMCB, with 10% 15HD remaining in the post shock gases, Figures 2, 4, 6, and 8. It may be expected that 1,2,4,5-hexatetraene should be observed in the product analysis; however, in the current and previous studies of 1,5-hexadiyne pyrolysis 1245HT has not been found. Hopf [26] has studied the thermal isomerization of 1245HT to 34DMCB and subsequent analysis by Huntsman showed the isomerization to be considerably faster than the formation of 1245HT from 15HD.[21] Thus the lack of 1,2,4,5-hexatetraene in the present studies is not a surprise as 1245HT is most likely converted effectively instantaneously into 34DMCB. The only experimental observation of 1245HT in propargyl recombination studies was made by Alkemade and Homann[7] where it is formed as a primary recombination product of two propargyl radicals and accounts for 7−19% of the total products.

The theoretical papers by Miller and Klippenstein and others[12−19] permit 15HD to isomerize to 1245HT and then to 34DMCB, which is consistent with the experimental work described above. In the latest publication on propargyl recombination by Miller and Klippenstein[19] they have simulated the experimental data from Stein et al.,[25] and the results of their calculations give good agreement with the observed 3,4-dimethylenecyclobutene concentrations. Thus, the present work is consistent with previous observations; it can be concluded that the mechanism for the formation of 3,4-dimethylenecyclobutene from 1,5-hexadiyne involves the formation of 1,2,4,5-hexatetraene, which isomerizes quickly on the time scale of all extant experiments to 3,4-dimethlylenecyclobutene.

Mechanism of Formation of Fulvene and Benzene. The formation of fulvene and benzene in propargyl recombination and 1,5-hexadiyne experiments are complex processes and there has been some debate as to whether fulvene is formed before benzene and then isomerizes to benzene or if fulvene and benzene are formed simultaneously. Prior experimental evidence favors simultaneous formation and theoretical studies favor the consecutive route. Our experimental work combined with the results of other investigators, suggests, as discussed in the following paragraphs, that in fact both processes are occurring and the dominant route is dependent on temperature.

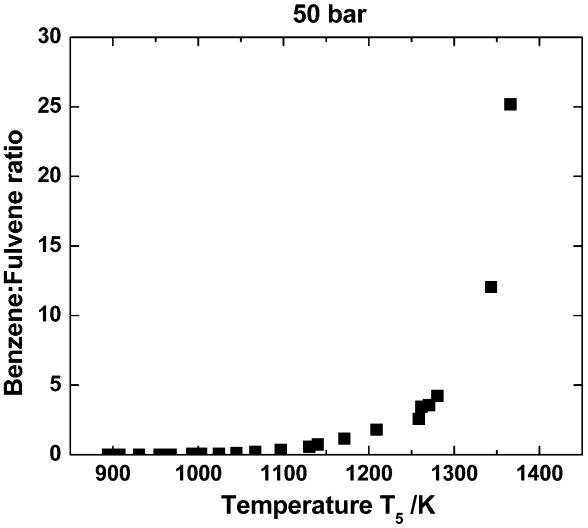


Figure 15. Benzene:fulvene ratios observed in 1,5-hexadiyne pyrolysis at 50 bar postshock pressure. Similar trends were found for the 25, 300, and 500 bar experiments.

In Figures 2, 4, 6, and 8 it is quite clear, from our work, that fulvene begins to be formed at around 920−950 K which is about the same temperature that 34DMCB reaches its maximum concentration. Benzene first appears at 1000−1050 K. The benzene:fulvene ratios for the 50 bar experiments are shown in Figure 15 and it is obvious that there is a dramatic steady increase in this ratio from the onset of benzene formation up to 1400 K where benzene is the sole product; similar trends were observed for the 25, 300, and 500 bar experiments.

This large change in the benzene:fulvene ratio appears to indicate that benzene is formed from fulvene and seems to be in direct contrast to the lower temperature studies of Stein et al. who observed only relatively small changes in the benzene: fulvene ratio for large extents of consumption of the initial 15HD. However, Stein et al.'s data extend only to temperatures that are slightly higher than the maximum in their fulvene concentration whereas in the current work the reaction was followed to a temperature where benzene was the only product. Over the extended temperature range of the current work the fulvene maximum is found to occur between 1090 and 1110 K and at the fulvene maximum the benzene:fulvene ratio is about 2:1 to 2.6:1, which is very similar to the values observed by Stein et al. At their highest reaction temperatures, beyond the temperature of the fulvene maximum, Stein et al. noticed a slight decrease in the fulvene concentration with a corresponding increase in the benzene concentration that corresponds to the trend in the current work and again appears to support the contention that benzene is formed form fulvene. However, in Stein et al.'s work, due to the small changes involved, they could not conclusively state that fulvene was being converted to benzene.

A direct experimental investigation of the fulvene to benzene isomerization by Gaynor et al.[28] has generated an Arrhenius rate expression that permits simulations of the present data using a simple model, Table 3, to determine if fulvene to benzene isomerization is possible, Figures 16 and 17. The simulations indicate that fulvene to benzene isomerization does take place at our conditions but should not be significant until approximately 1200 K. Because our experiments indicate that significant amounts of benzene are observed at temperatures

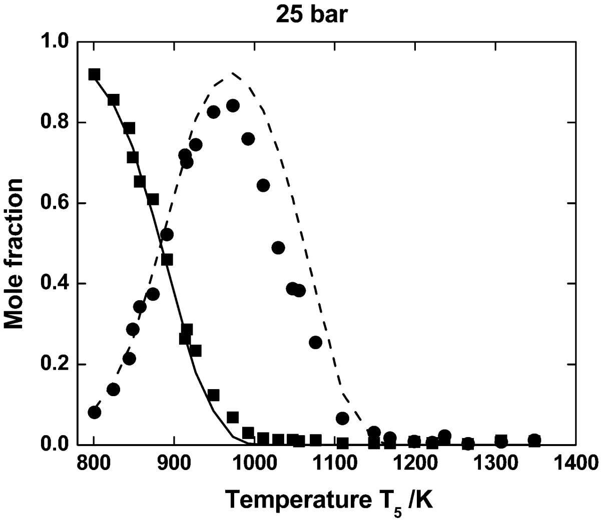


Figure 16. Simulation of 25 bar experimental data using the three-step model. Detailed rate parameter values are shown in Table 3. Symbols represent experimental data, and lines represent simulation results. Key: solid line and ■, 1,5-hexadiyne; dashed line and ●, 3,4-dimethylenecyclobutene.

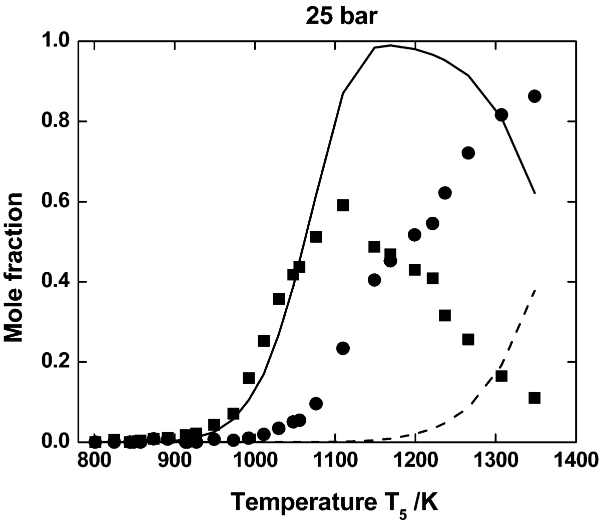


Figure 17. Simulation of 25 bar experimental data using the three-step model. Detailed rate parameter values are shown in Table 3. Symbols represent experimental data, and lines represent simulation results. Key: solid line and ■, fulvene; dashed line and ●, benzene.

TABLE 3: Simple Model Used to Simulate 25 Bar Experimental Data. 15HD = 1,5-hexadiyne, 34DMCB = 3,4-dimethylenecyclobutene

reaction	log(*A*)	*E*/kcal	source
15HD => 34DMCB	10.82	33.36	p.w.
34DMCB => Fulvene	13.03	50.22	p.w.
Fulvene => Benzene	13.49	68.2	28

as low as 1050 K either there is another route to benzene or the rate coefficients generated by Gaynor may be suspect. This latter point was addressed by Madden et al. [29] who have used ab initio calculations to investigate fulvene to benzene isomerization. They concluded that the activation energy obtained by Gaynor et al. may be too low and if this is the case the onset of fulvene to benzene conversion should not occur until even higher temperatures than the ones observed in our experiment. Consequently, both Gaynor et al.'s rate coefficient and an even more refined one from Madden et al. suggest that the lower temperature formation of benzene observed in our work may result from a path not involving fulvene. Further support for the simultaneous, parallel formation of fulvene and benzene in 15HD pyrolysis can be gained from the experimental work by Henry and Bergmann on 3,4-dimethylenecyclobutene pyrolysis at 890 K,[24] in which they observe a higher benzene:fulvene ratio than found by Coller et al.[22] in the direct pyrolysis of 15HD at the same temperature. Alkemade and Homann[7] interpret the relatively large difference in benzene:fulvene ratios from pyrolysis of 34DMCB and 15HD to indicate an additional path to benzene not involving fulvene that is accessible in the 15HD experiments. Thus it would appear that fulvene can be converted to benzene at high temperatures but that there is also the possibility of the existence of a lower temperature path directly to benzene.

The possibility of a low-temperature benzene route that does not involve fulvene was addressed in part by a recent reexamination of the propargyl recombination potential energy surface, PES, by Miller and Klippenstein,[19] who have simulated the experimental data of Stein et al.[25] They have shown that their model, which includes a nonfulvene route to benzene via *cis*-1,3-hexadiene-5-yne and some small modifications to barrier heights, fits the experimental work of Stein et al. well. Miller and Klippenstein also show that not including this route as in the original Miller and Melius model[13,14] overpredicts fulvene and underpredicts benzene and 3,4-dimethylenecyclobutene. The new model of Miller and Klippenstein based on their calculated PES predicts that the nonfulvene path to benzene should include the formation of *cis*-1,3-hexadiene-5-yne and *trans*-1,3-hexadiene-5-yne; see Scheme 1. In our current work we were able to quantitatively measure the formation of *cis*-1,3-hexadiene-5-yne and *trans*-1,3-hexadiene-5-yne, confirming the theoretical predictions of Miller and Klippenstein. It is clear from our experimental measurements shown in Figures 3, 5, 7, and 9 that these species are observed, albeit at low concentrations (maximum mole fractions are 0.07 cis and 0.06 trans), in a relatively narrow temperature range between about 950 and 1180 K and that there is a slight excess of the cis to trans isomer. The low concentrations of cis and trans 13HD5Y at temperatures below 1180 K, where benzene formation is significant, indicate that *cis*-13HD5Y, as postulated by Miller and Klippenstein, is efficiently converted to benzene. By 1180 K benzene accounts for 40% of the species in the current work even though fulvene to benzene isomerization should be insignificant at these temperatures. Supplemental confirmation of the postulated path involving *cis*-13HDY in Scheme 1 is found in the results of Hopf and Muso[36] who have studied the thermolysis of both *cis*- and *trans*-13HD5Y and found that both isomers and benzene are generated regardless of which isomer is used as the starting material.

Thus it appears from the current work that benzene and fulvene are formed simultaneously at temperatures below around 1180 K with benzene being predominantly formed by the isomerization of *cis*-1,3-hexadiyne-5-yne, which is in accord with the recent theoretical prediction by Miller and Klippenstein.[19] At higher temperatures the isomerization of fulvene to benzene, indicated by the growth of benzene as the fulvene concentration decreases, should be important, and if it is assumed that this becomes so at the fulvene maximum, i.e., 1100 K, then some adjustment to the fulvene to benzene rate expression of Gaynor et al. may be warranted.

Finally, fulvene can also be formed from 2-ethynyl-1,3-butadiene, Scheme 1, which has been observed in these experiments in small quantities. The exact importance of this route to the total fulvene concentration will have to be determined from detailed modeling.

Mechanism of Formation of 2-Ethynyl-1,3-butadiene. 2-ethynyl-1,3-butadiene appears between 1150 and 1300 K with a maximum mole fraction of 0.02 in these experiments. This species can only be formed from 1,2-hexadiene-5-yne, a species that is inaccessible on the Miller and Klippenstein PES when starting with 1,5-hexadiyne without first dissociating 15HD to propargyl radicals. In the low-concentration kinetic work, 1,2-hexadiene-5-yne was observed but the concentrations were too low to measure quantitatively. In the higher concentration samples prepared for GC−mi-FTIR−MS analysis a small but well formed peak was observed whose spectrum confirmed that the species was 1,2-hexadiene-5-yne, and comparison between the FTIR analyses and the GC−MS, GC−FID analyses indicates that trace amounts of 1,2-hexadiene-5-yne are present in the kinetic samples. A second potential route to 2-ethynyl-1,3-butadiene not involving dissociation of 15HD is from the isomerization of benzene through fulvene, and this has been observed by Nakashima et al.[37] in very vibrationally hot benzene. However, in the present thermally excited work it is very unlikely that the temperatures are high enough to drive benzene back to 2-ethynyl-1,3-butadiene. The presence of trace amounts of 1,2-hexadiene-5-yne tend to suggest that some of the original 1,5-hexadiyne has either decomposed to propargyl radicals that have then recombined with a fraction forming 12HD5Y or that there is a direct isomerization path from 15HD to 12HD5Y that is not included on the Miller and Klippenstein PES.

Some preliminary simulations have been performed to try to assess the relative importance of dissociation of 15HD to two propargyl radicals, reverse of reaction 2, and isomerization of 15HD to 12HD5Y. A rate coefficient for dissociation of 15HD to two propargyls, k_{-2} (reaction 2), was obtained from a QRRK calculation by Dean.[38] Rates for reactions 2 and 3 were taken from ref 18. There does not appear to be a published rate coefficient expression for reaction 4, and this was estimated to be half of that for reaction 2 on the basis of Alkemade and Homann's product distributions. For the isomerization of 15HD to 12HD5Y we have used the rate coefficient expression for a 1,3 H-atom shift in propyne to give allene.[39] The results of this preliminary and necessarily crude modeling indicate that at temperatures above 1100 K dissociation of 15HD to propargyl can be significant but that recombination to 15HD, reaction 2, is the favored fate of the propargyl radicals with small amounts forming 1245HT and 12HD5Y in approximately 1.5:2 proportions, which is roughly similar to the distribution seen by Alkemade and Homann. The model also indicates that direct isomerization of 15HD to 12HD5Y is negligible. However, these results should be treated with caution. If, as the model predicts, 1245HT and 12HD5Y are formed in 1.5:2 ratio then 1245HT should have been observed in the analysis of the postshock samples and there is absolutely no indication that this species is present even in the concentrated samples prepared for GC−mi-FTIR−MS analysis. It is therefore suggested that the isomerization of 15HD to 12HD5Y may be more significant than indicated by this preliminary modeling work and a thorough theoretical investigation of the mechanism may be warranted.

Conclusions

An extensive experimental study of the pyrolysis of 1,5-hexadiyne has been performed at four reaction pressures of 25, 50, 300, and 500 bar and temperatures from 780 to 1400 K. Eight stable C_6H_6 isomers have been positively identified in this work, including the important observation for the first time of *cis*-1,3-hexadiene-5-yne and *trans*-1,3-hexadiene-5-yne. These two species and their appearance temperatures conclusively demonstrate the existence of a low-temperature route to benzene that does not require the formation and subsequent isomerization of fulvene. Thus, for the lower temperatures in this work, fulvene and benzene are formed simultaneously by separate reaction paths. Recent theoretical analyses of the likely reaction paths appear to be completely consistent with this observation. Furthermore, 1,2-hexadiene-5-yne and its isomerization product 2-ethynyl-1,3-butadiene were observed at reaction temperatures that are probably too low for dissociation of 1,5-hexadiyne back to two propargyl radicals. On the current potential energy surfaces the only route to 12HD5Y from 15HD is via dissociation and recombination, and the most recent work indicates that the PES may need to be modified to include a direct route between 15HD and 12HD5Y. Last, a high-temperature fulvene to benzene route, predicted by the PES, is confirmed by our experimental evidence.

Acknowledgment. We thank Dr L. B. Harding of Argonne National Laboratories for performing the DFT calculations that were used in interpreting the FTIR spectra. R.S.T., W.T., and K.B. are grateful to the National Science Foundation for support under contract CTS 0109053. K.B.A. gratefully acknowledges the support of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contract number W-31-109-ENG-38.

Supporting Information Available: Tables of experimental data containing reaction conditions and species concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Miller, J. A. *Proc. Combust. Inst.* **1996**, *20*, 461.
(2) Miller, J. A. *Faraday Discuss.* **2001**, *119*, 461.
(3) Richter, H.; Howard, J. B. *Prog. Energy Combust. Sci.* **2000**, *26*, 565.
(4) D'Anna, A.; Violi, A.; D'Allessio, A. *Combust. Flame* **2000**, *121*, 418.
(5) Kern, R. D.; Chen, H.; Kiefer, J. H.; Mudipalli, P. S. *Combust. Flame* **1995**, *100*, 177.
(6) Lindstedt, P. *Proc. Combust. Inst.* **1998**, *27*, 269.
(7) Alkemade, U.; Homann, K. H. *Z. Phys. Chem.* **1989**, *161*, 19.
(8) Fahr, A.; Nayak, A. *Int. J. Chem. Kinet.* **2000**, *32*, 118.
(9) Shafir, E. V.; Slagle, I. R.; Knyazev, V. D. *J. Phys. Chem. A* **2003**, *107*, 8893.
(10) Scherer, S.; Just, T.; Frank, P. *Proc. Combust. Inst.* **2000**, *28*, 1511.
(11) DeSain, J. D.; Taatjes, C. A. *J. Phys. Chem. A* **2003**, *107*, 4843.
(12) Thomas S. D.; Communal F.; Westmoreland, P. R. *ACS, Div. Fuel Chem.*, **1991**, 1449.
(13) Miller, J. A.; Melius, C. F. *Combust. Flame* **1992**, *91*, 21.
(14) Melius, C. F.; Miller, J. A.; Evleth, E. M. *Proc. Combust. Inst.* **1992**, *24*, 621.
(15) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2001**, *105*, 7254.
(16) Klippenstein, S. J.; Miller, J. A. *J. Phys. Chem. A* **2002**, *106*, 9267.
(17) Carstensen, H.-H., Dean, A. M. *Proceedings of the Third Joint Meeting of the U.S. Sections of The Combustion Institute,* Chicago, March, 16−18, 2003.
(18) Carstensen, H.-H.; Dean, A. M. Private communication.
(19) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 7783.
(20) Huntsman, W. D.; Wristers, H. J.*J. Am. Chem. Soc.* **1967**, *18*, 342.
(21) Huntsman, W. D. *Intra-Sci. Chem. Rep.* **1972**, *6*, 151.
(22) Coller, B. A. W.; Heffernan, M. L.; Jones, A. J. *Aust. J. Chem.* **1968**, *21*, 1807.
(23) Kent, J. E., Jones, A. J. *Aust. J. Chem.* **1970**, *23*, 1059.
(24) Henry, T. J.; Bergman, H. G. *J. Am. Chem. Soc.* **1972**, *9*, 5103.

(25) Stein, S. E.; Walker, J. A.; Suryan, M.; Fahr, A. *Proc. Combust. Inst.* **1990**, *23*, 85.

(26) Hopf, H. *Chem. Ber*. **1971**, *104*, 1499.

(27) Tang, W.; Tranter, R. S.; Brezinsky, K.; Raju, A. S. K. *Proceedings of the Third Joint Meeting of the U.S. Sections of The Combustion Institute*, Chicago, March, 16−18, 2003.

(28) Gaynor, B. J.; Gilbert, R. G.; King, K. D.; Harman, P. J. *Aust. J. Chem.* **1981**, *34*, 449.

(29) Madden, L. K.; Mebel, A. M.; Lin, M. C.; Melius, C. F. *J. Phys. Org. Chem.* **1996**, *9*, 801.

(30) Tranter, R. S., Fulle, D.; Brezinsky, K. *Rev. Sci. Instrum.* **2001**, *72*, 3046.

(31) Tranter, R. S.; Sivaramakrishnan, R.; Srinivasan, R.; Brezinsky, K. *Int. J. Chem. Kinet.* **2001**, *33*, 722.

(32) Tranter, R. S.; Sivaramakrishnan, R.; Brezinsky, K.; Allendorf, M. D. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2001.

(33) Hidaka, Y.; Shiba, S.; Takuma, H.; Suga, M. *Int. J. Chem. Kinet*. **1985**, *17*, 441.

(34) Davidson, D. F.; Hanson, R. K. *Isr. J. Chem*. **1996**, *36*, 321.

(35) Anderson, K. B.; Tranter, R. S.; Tang, W.; Brezinsky, K.; Harding L. *J. Phys. Chem. A* 2004, 108, 3403.

(36) Hopf, H.; Musso, H. *Angew. Chem. Int. Ed.* **1969**, *8*, 680.

(37) Nakshima, N., Yatsuhasi, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 579−593.

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

(39) Kiefer, J. H.; Mudipalli, P. S.; Sidhu, S. S.; Kern, R. D.; Jursic, B. S.; Xie K.; Chen, H. *J. Phys. Chem. A* **1997**, *101*, 4057.