Pressure and Temperature Effects on Product Channels of the Propargyl (HC≡CCH$_2$) Combination Reaction and the Formation of the "First Ring"

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The propargyl (HC≡C−CH$_2$) radical is among the critical intermediates in hydrocarbon reaction systems pertinent to both the high temperatures of combustion systems and the low temperatures of planetary atmospheres. This work reports experimental results on the nature and the relative yields of the final products of the propargyl combination reaction, $C_3H_3 + C_3H_3 \rightarrow C_6H_6$ (1). Propargyl radicals, for most experiments, were generated by the 248 nm excimer laser photolysis of propargyl bromide. The 193 nm photolysis of propargyl chloride and of allene were also used in a number of experiments, particularly at higher temperatures. Product studies were performed at a pressure range of 27 mbar (20 Torr) to 933 mbar (700 Torr) and at a temperature range of 295−623 K. Final reaction products were separated, identified, and quantified using an on-line gas chromatograph/mass spectrometer system. Five isomeric C_6H_6 final products were detected including 1,5-hexadiyne, fulvene, dimethylenecyclobutene, and benzene. The relative yields of the major reaction products showed significant pressure and temperature dependencies. Under high-pressure conditions 1,5-hexadiyne is a major product with a relative yield of 51 % at $P = 933$ mbar and $T = 295$ K. However, its yield decreases to 27 % at $P = 933$ mbar and $T = 623$ K and to 1 % at $P = 27$ mbar, $T = 623$ K. Dimethylenecyclobutene, has a relative yield of 6% at 295 K and 933 mbar. It becomes the most abundant product with a relative yield of nearly 90% at 623 K and 133 mbar. Fulvene appears to be a minor product at all conditions of this study and its relative yield (∼1.5% or less) is significantly lower than the reported computational predictions. Interestingly, an appreciable amount of benzene is also formed, particularly at lower pressures with relative yields considerably higher (43% at 27 mbar and 623 K) than those predicted computationally (∼3% at $P = 27$ mbar $T = 650$ K). The results of this work suggest that the formation of dimethylenecyclobutene and benzene from the propargyl combination reaction is significantly more efficient than previously predicted. Implications of these results on modeling of combustion processes as well as planetary atmospheric processes are discussed.

Introduction

The mechanism for formation of aromatic and polyaromatic hydrocarbons (PAH) and soot in combustion processes is still far from being well understood. The formation of the "*first aromatic ring*", particularly benzene, is thought to be a critical step in soot formation mechanisms and has been the subject of continuing interest. However, the proposed soot formation mechanisms have not yet been established quantitatively.[1−5] This is due, partly, to the lack of adequate laboratory measurements to be used for calibration and refining the detailed computational predictions.

The combination reaction of propargyl (HC≡C−CH$_2$) radicals, $C_3H_3 + C_3H_3 \rightarrow C_6H_6$ (1) is believed to be a key cyclization step in hydrocarbon combustion reactions that can initiate subsequent formation of larger polyaromatic hydrocarbons and soot.[1−6] Interestingly, even at the low temperatures of planetary environments, such as the atmospheres of Saturn and Jupiter, relatively large abundances of aromatic molecules, particularly benzene, have been detected.[7,8] The current photochemical models, however, do not quantitatively reproduce the abundances and altitude variations of benzene as well as several other hydrocarbon molecules. The disagreement between the observational data and the modeling predictions is again primarily due to the lack of experimental data needed as inputs for modeling calculations. The isomerization of initially formed linear C_6H_6 isomeric products of reaction 1 and the potential for formation of benzene can be particularly significant.

Despite the importance of reaction 1, only limited experimental product[9,10] and kinetics studies have been reported. A number of recent direct and relative rate measurements agree on a room-temperature rate constant value of $k_1 = (4.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[9−13] Product studies of the propargyl radical reactions are scarce and limited to very narrow ranges of temperature and pressure conditions. The available results on the combination products indicate the possibility of formation of a variety of C_6H_6 isomeric products. By employing excimer laser photolysis and GC/MS product analysis methods,

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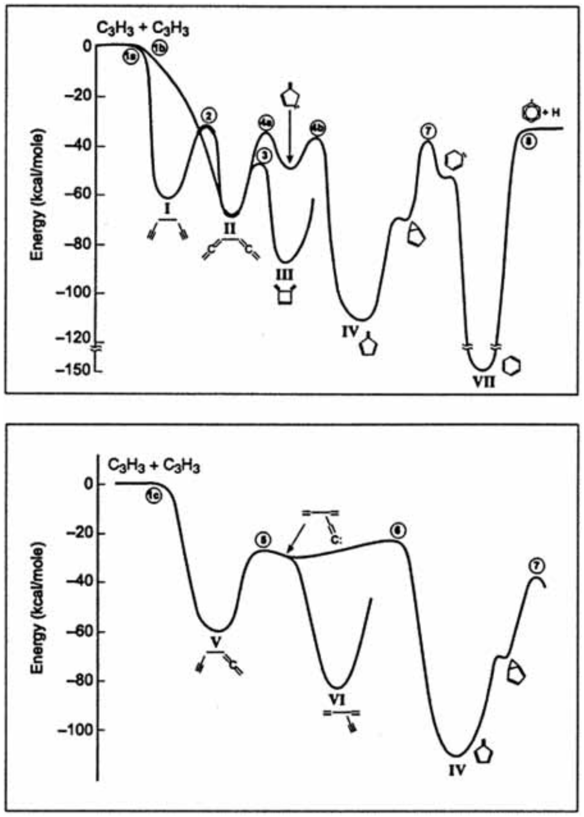


Figure 1. Potential energy diagram for the recombination of two propargyl radicals: (a) head-to-head and tail-to-tail recombination; (b) head-to-tail recombination. Reproduced with permission from *J. Phys Chem. A* **2001**, *105*, 7254.

Fahr and Nayak[9] studied the propargyl self-reaction at $T = 298$ K at a total pressure of about 67 mbar. Three C_6H_6 isomeric products were detected in that study with 1,5-hexadiyne ($HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$) being the major product with a yield of ∼60%. This product is formed from the "head-to-head" addition of two propargyl radicals. In addition, formation of 1,2-hexadien-5-yne ($H_2C{=}C{=}CH{-}CH_2{-}C{\equiv}CH$, ∼25%) the product of "head-to-tail" addition and also an unidentified isomer of C_6H_6 were reported in that work. Alkemade and Homann,[10] using a low-pressure flow reactor, generated propargyl radicals from the reaction $Na + C_3H_3X \rightarrow C_3H_3 + NaX$ (X = Cl or Br) and analyzed the products by nozzle beam mass spectrometry and by GC/MS. They studied the propargyl reactions at pressures of 2.6 and 5.3 mbar and temperatures of 623 and 673 K and identified five C_6H_6 isomeric products. 1,5-Hexadiyne, 1,2-hexadien-5-yne, and 1,2,4,5-hexatetraene were the primary products and benzene and 1,3-hexadiene-5-yne were the secondary products. Stein et al.,[6] from pyrolysis studies of 1,5-hexadiyne in flow reactors, deduced an isomerization route for the formation of benzene. Miller and Melius,[1] from modeling and computational studies of acetylene flames, concluded that the first aromatic ring is likely to be formed by the self-combination of propargyl radicals. More recently, Miller and Klippenstein[2] reported comprehensive computational studies of the reaction $C_3H_3 + C_3H_3$ over broad ranges of pressure and temperature conditions. Applying the known experimental results on the propargyl reactions as a basis, they deduced thermal rate coefficients, potential energy surfaces for various isomerization paths, and product distributions versus temperature and pressure. Figure 1, reproduced from ref 2a, illustrates the potential energy diagram for the propargyl recombination reaction and subsequent isomerization pathways. There are no detailed experimental pressure and temperature product studies of the propargyl combination reaction to confirm or calibrate the computation predictions of this complex system.

Detailed knowledge of the isomeric distribution of C_6H_6 products and effects of temperature and pressure on the yield and nature of the products are of significance. In continuation of our efforts to understand properties of propargyl radicals, the present study examines, more systematically than earlier experimental studies, the effect of pressure and temperature on product distributions of the propargyl combination reaction. The results are compared with other available experimental results and with theoretical predictions.

Experimental Procedures

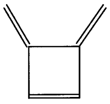
This study employs excimer laser photolysis for generating the radicals and gas chromatography/mass spectroscopy (GC/MS) methods for separation, identification, and quantification of final reaction products. A brief description of our methods is presented here. The output of an excimer laser is passed through a temperature controlled quartz reaction cell. Sample temperatures from 295 to 623 K are achieved with a typical gradient of less than 4% across the cell. For studies above ambient temperature, the gas mixture is preheated to the desired temperature in a heat exchanger prior to entering the heated reaction cell. The sample temperature is monitored at the entrance and exit ports as well as the center of the reaction cell. A self-enclosed gas-circulating pump is used to flow the gas mixture through the reaction cell and in a closed-loop volume. The active photolysis cell volume is about 3% of the total system volume. The cell contents were replaced several times each second, faster than the 0.5 Hz photolysis laser repetition rate. Therefore, the photolysis of products is always kept at a negligible level.

For most experiments, propargyl radicals were generated from the 248 nm photolysis of dilute mixtures of C_3H_3Br (5×10^{14} to 3×10^{16} molecules cm^{-3}) in He (27−933 mbar). In addition, the 193 nm photolysis of C_3H_3Cl/He and C_3H_4 (allene)/He were also used as propargyl radical sources. Propargyl radical concentrations range from 7×10^{12} to 8×10^{14} molecules per cm^{-3}. At these radical concentrations, 99.8% of the radicals have reacted in 0.01−0.9 s, which is less than the 1−2 s time period between laser shots. Hence, the reaction is complete between laser shots. The final reaction products were analyzed using an on-line GC interfaced with a flame ionization (FID) detector and a quadrupole mass spectrometer (MS). Following the photolysis, the reaction mixture was admitted into an evacuated injection loop and directly injected into two separate capillary columns (Al_2O_3 coated) by admitting the carrier gas into the collection/injection loops. Temperature programming of the oven was required to separate the products. The retention times of the gas chromatograph and responses of FID and MS were calibrated by the injection of a number of available C_6H_6 isomeric standard samples.

The experiments were conducted at four different temperatures: 295, 398, 523, and 623 K. Up to 523 K, C_3H_3Br showed no measurable thermal decomposition. However, at 623 K C_3H_3Br showed significant thermal decomposition. Thus this precursor was not used for product studies at 623 K. On the other hand, C_3H_3Cl is thermally stable under all temperature conditions of this study. Thus, for product studies at 623 K, C_3H_3Cl was used as the radical precursor.

Radical precursors with highest available purity were purchased commercially (C_3H_3Br, Fluka,[14] 97%; C_3H_3Cl, Aldrich, 98%; Allene, Matheson, 95%). C_3H_3Br and C_3H_3Cl, which are liquids at room temperature, were used after successive freeze−pump−thaw cycles. The precursor was mixed with ultrahigh purity He (Spectra Gases, 99.999%), and experiments were conducted at various total pressures from 27−933 mbar. The 1,5-hexadiyne (GFS Chemicals) sample, used in this work both for calibration and for synthesis of other C_6H_6 isomers, had a 97% stated isomeric purity and was diluted/stabilized in pentane (50%).

Calibration samples of dimethylenecyclobutene (dmcb) (I) and fulvene (II) were synthesized for this work through thermolysis of 1,5-hexadiyne at specific flow and temperature conditions. The methods for synthesis of these C_6H_6 isomers were similar to those used in the Huntsman and Wrister[15] and Kent and Jones[16] studies. The reactor consisted of a 60 cm by 1.0 cm (i.d.) helixed quartz tube that was partially filled with quartz beads and heated by clamshell heating elements. A temperature uniformity within about 2 K was obtained along the heated zone. A steady and controlled flow of dry nitrogen as the carrier gas was used to sweep the 1,5-hexadiyne vapor (at atmospheric pressure and at room temperature) through the heated reactor. Reaction products were collected in cold traps, immersed in dry ice/acetone slush (∼220 K). Dimethylenecyclobutene was produced with isomeric yields of about 98% at a reactor temperature of 665 K and 76% at a reactor temperature of 680 K, both at a nitrogen flow of 30 cm^3/min. The isomeric impurity in the collected samples, as determined by the GC/MS analysis, was mainly benzene. Fulvene was produced with an isomeric purity of about 70% at a reactor temperature of 795 K. The impurities were primarily dimethylenecyclobutene and benzene. At a reactor temperature of about 825 K the collected C_6H_6 isomeric product mix contained 14% fulvene, 80% benzene, and 2% dimethylenecyclobutene.



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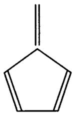

II

Results

In the present study, propargyl radicals were generated using C_3H_3Br, C_3H_3Cl, and allene as precursors. For temperatures of 295, 398, and 523 K, the majority of the experiments were conducted using C_3H_3Br as the precursor. Additional experiments were conducted using C_3H_3Cl as the precursor. There are two reasons for using C_3H_3Cl. First, thermal decomposition of C_3H_3Br at temperatures higher than about 530 K precludes its use as a precursor at high temperatures. On the other hand, the thermal stabilities of C_3H_3Cl and allene allow for the temperature range to be extended beyond 523 K. Second, there is concern regarding the fate of the Br atoms that are produced in the photolysis of C_3H_3Br. Br atoms could potentially interfere with the propargyl combination reaction and possibly change the C_6H_6 isomeric product distributions. Because the reactivities of Cl and Br atoms are distinctly different, any substantial contributions from reactions of these halogen atoms, affecting the final C_6H_6 isomeric products, should be identifiable through the final product analysis. To go one step further, experiments were conducted using allene as the propargyl radical precursor, thus eliminating the halogen altogether. The results for each precursor are presented separately and then compared.

a. 248 nm Photolysis of C_3H_3Br. The photodissociation dynamics of C_3H_3Br at 248 nm has previously been studied in detail using molecular beam/TOF mass selective detection methods.[17−19]

TABLE 1: Relative Yields (%) of C_6H_6 Isomeric Products Determined Subsequent to the 248 nm Photolysis of Dilute Mixtures of C_3H_3Br/He (1/750)[a]

		relative yields (%) of C_6H_6 products				
T/K	P/mbar	1,5-hexadiyne	1,2-hexadien-5-yne	dmcb	fulvene	benzene
295	27	40	33.5	13	1.5	12
	67	42	36.5	11.5	1	9
	133	40.4	40	15	0.6	4
	332	44	41.5	12.5	0.5	1.5
	600	47.6	40	11.5	0.4	0.5
	933	50.7	38	10	0.3	1
398	27	34.5	32.5	15	0.5	17.5
	67	39	37	11.5	0.5	12
	133	43	41	10.4	0.1	5.5
	332	43	43	11.4	0.1	2.5
	600	46.5	42.5	8	-	3
	933	47	43	7	-	3
523	27	26.5	21	27	0.5	25
	67	31	30	28	0.2	10.8
	133	36.8	35	23	0.2	5
	332	38	37.5	21.5	-	3
	600	43	38	17	0.1	1.9
	933	45.5	36.4	14	0.1	4

[a] Photolysis time: 10 min at 0.5 Hz. Laser energy = 155 mJ per pulse.

$$HCCCH_2Br \xrightarrow{248\ nm} HCCCH_2 + Br$$

It has been shown that the 248 nm excitation results in exclusive C−Br bond fission, generating solely propargyl radicals and Br atoms. In contrast, the 193 nm photolysis of propargyl bromide, used in a number of previous reported studies, often also generates significant quantities of hydrocarbon radicals other than propargyl, such as C_3H_2 (∼30%) and CH_3CC (∼26%), which may introduce additional uncertainties on kinetic and product studies.[17−19]

GC/MS analysis of the photolyzed C_3H_3Br/He samples indicated formation of five C_6H_6 isomeric final products. The retention times (RT) of the C_6H_6 isomeric products, under conditions of our method, vary from 11 to 26 min (with a RT resolution of 5 s). The retention times and cracking patterns of four of the product peaks agreed with those of calibration samples of benzene (RT = 11.7 min), fulvene (RT = 13.3 min), dimethylenecyclobutene (dmcb, RT = 12.7 min) and 1,5-hexadiyne (RT = 25.6 min). The isomeric structure of one of the C_6H_6 products (RT = 22.5 min) could not be identified with certainty due to unavailability of the required calibration samples. However, it is likely that this product is 1,2-hexadien-5-yne, which is expected to be formed from the "head-to-tail" addition of propargyl radicals. The formation of this isomer had been reported in two previous experimental product studies[9,10] (one from this laboratory) and also had been predicted by computational study of the propargyl combination reaction.[2]

Table 1 lists the experimental conditions and the relative yields of the C_6H_6 isomeric products determined at various pressure and temperature conditions. It is assumed that the five C_6H_6 isomers were the only C_6H_6 products and the sum of the yields of all five products was equated to 100%. The relative yield of each product was then calculated as a percentage of the total C_6H_6 product yield. Figure 2 shows the relative yield of 1,5-hexadiyne versus pressure at various temperatures. Identical symbols are used for each radical precursor used in the present study. Also, symbols are color coded to reflect the

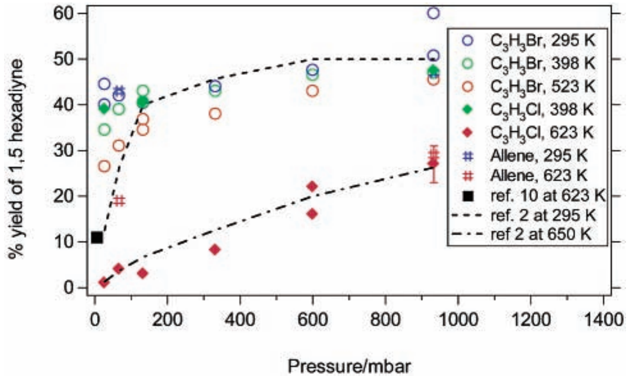

Figure 2. Relative yield of 1,5-hexadiyne as a function of pressure at $T = 295$, 398, 523, and 623 K, using different C_3H_3 precursors as listed.

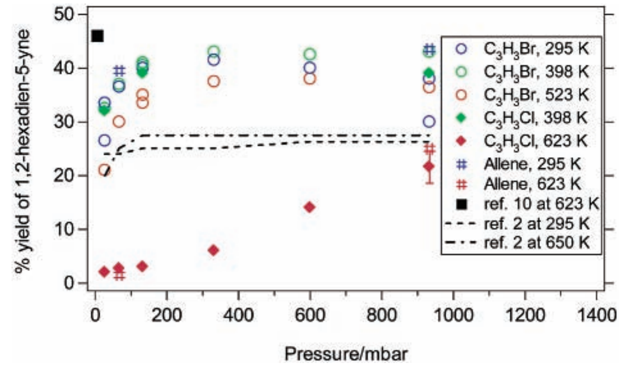

Figure 3. Relative yield of 1,2-hexadien-5-yne versus pressure at $T = 295$, 398, 523, and 623 K, using different C_3H_3 precursors as listed.

temperature of the data sets. Results from other experimental or theoretical studies are represented in black.

1,5-Hexadiyne, formed from the "head-to-head" addition of two propargyl radicals, is one of the major products at high pressure and low temperature ($P = 933$ mbar, $T = 295$ K) with a relative yield of about 50%. Its relative yield is reduced significantly to about 26% at high temperature and low pressure ($P = 27$ mbar, $T = 523$ K). The yield of 1,5-hexadiyne appears to increase with pressure and decrease with increasing temperature.

Figure 3 shows the relative yield of the isomeric product that is believed to be 1,2-hexadien-5-yne versus pressure at various temperatures. 1,2-Hexadien-5-yne is another major product with relative yields comparable to 1,5-hexadiyne. For temperatures between 295 and 523 K, the relative yield appears to be fairly independent of pressure between 133 mbar and 933 mbar. Below 133 mbar, the relative yield decreases with decreasing pressure. The relative yield appears to increase with pressure and decrease with increasing temperature.

Figure 4 displays the relative yield of dimethylenecyclobutene versus pressure at various temperatures. Dimethylenecyclobutene is another major product of the propargyl combination with substantial yields, particularly at elevated temperatures. For temperatures between 295 and 523 K, the relative yield of this product increases with temperature and increases with decreasing pressure. The pressure dependence appears to be more pronounced at higher temperatures.

The relative yield of fulvene versus pressure at various temperatures is shown in Figure 5. Fulvene is a minor product under all conditions of this study with a relative yield of 1.5% or less.

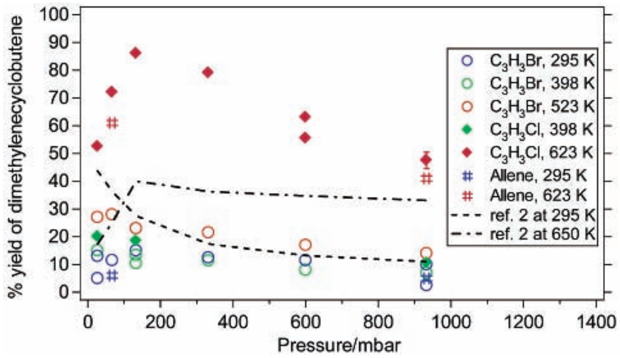

Figure 4. Relative yield of dimethylenecyclobutene versus pressure at $T = 295$, 398, 523, and 623 K, using different C_3H_3 precursors as listed.

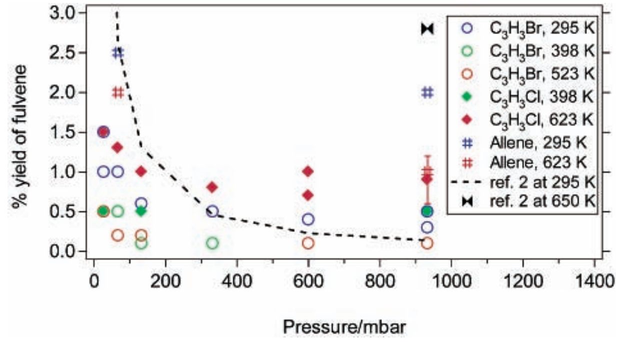

Figure 5. Relative yield of fulvene versus pressure at $T = 295$, 398, 523, and 623 K, using different C_3H_3 precursors as listed.

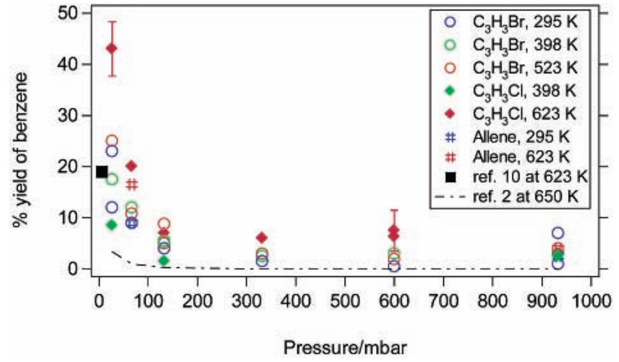

Figure 6. Relative yield of benzene versus pressure at $T = 295$, 398, 523, and 623 K, using different C_3H_3 precursors as listed.

Figure 6 shows the relative yield of benzene versus pressure at various temperatures. Appreciable amounts of benzene are formed, particularly at lower pressures with a relative yield as high as ~25% at $T = 523$ K and $P = 27$ mbar. The relative yield of benzene increases rapidly with decreasing pressure. The relative yield appears to increase slightly with temperature.

No evidence of phenyl radicals was observed under the present experimental conditions. Products of phenyl radical reactions such as biphenyl (from phenyl combination) or 3-phenyl-1-propyne (from phenyl + propargyl) were not found in the postreaction mixtures.

Various temperature programming of the GC oven and using different flow rates of the carrier gas, neither changed the number of the separated C_6H_6 peaks nor changed their relative intensities which suggest overlap of more than one C_6H_6 isomeric peaks appears to be unlikely.

The error bars shown in all the figures are estimates of the range of experimental measurements, obtained on different days, and their magnitudes are determined by taking the difference between two repeated sets of measurements taken at selected conditions of pressure and temperature. The uncertainty associ-

TABLE 2: Relative Yields (%) of C_6H_6 Isomeric Products Formed Subsequent to the 193 nm Photolysis of Dilute Mixtures of C_3H_3Cl/He (1/750)[a]

		relative yields (%) of C_6H_6 products				
T/K	P/mbar	1,5-hexadiyne	1,2-hexadien-5-yne	dmcb	fulvene	benzene
295	27	47	34.5	10	1	7.5
	133	48.5	40	9.5	0.5	1.5
	332	46	41	11	0.5	1.5
	933	54.5	38	6	0.5	1
398	27	39	32	20	0.5	8.5
	133	40.5	39	18.5	0.5	1.5
	933	47.5	39	10.5	0.5	2.5
523	27	27	21.5	31	1.5	19
	133	37.5	32.5	27	1	2
	933	45	36	16.5	1	1.5
623	27	1	2	52.5	1.5	43
	67	4	2.7	72	1.3	20
	133	3	3	86	1	7
	332	8.2	6	79	0.8	6
	600	22	14	55.5	1	7.5
	933	27	21.6	47.5	0.9	3

[a] Photolysis time: 10 min at 0.5 Hz. Laser energy = 65 mJ per pulse.

ated with repeated FID measurements of the same sample is ∼5%. A more comprehensive and precise assessment of the experimental error requires collecting a large number of data points for each experimental condition, which is not feasible with the analysis method used in this study. Product yields determined from repetitive measurements at a number of pressure and temperature conditions are also shown in Figures 2−6. The uncertainty shown typically reflects the upper limit of the range of repeated measurements. Measurements taken at different experimental conditions denoted by the same color and symbol were taken on the same day, and the uncertainties for the same-day measurements are typically less than 50% of the uncertainties for different-day measurements.

b. 193 nm Photolysis of C_3H_3Cl. Previous studies of the 193 nm photodissociation dynamics of propargyl chloride has been shown to generate primarily propargyl radicals and Cl atoms and also minor quantities of C_3H_2.[16−18]

$$C_3H_3Cl \xrightarrow{193\ \text{nm}} C_3H_3 + Cl \qquad 93\%$$

$$C_3H_3Cl \xrightarrow{193\ \text{nm}} C_3H_2 + HCl \qquad 7\%$$

No information is available on the reactivity and chemical properties of the C_3H_2 diradical. However, due to relatively low concentrations of this radical, contributions of its reactions are expected to be insignificant on the final product yields.

Product studies were performed at T = 295, 398, 523, and 623 K for pressures between 27 mbar and 933 mbar. No thermal dissociation of C_3H_3Cl under the conditions of this study was noted. As in the case of the product studies of C_3H_3Br photolysis, five C_6H_6 isomeric products, 1,5-hexadiyne, benzene, fulvene, dimethylenecyclobutene, and possibly 1,2-hexadien-5-yne, were detected. Table 2 lists the relative yields of the C_6H_6 isomeric products at various temperatures and pressures.

For comparison, the C_6H_6 isomeric product yields determined from photolysis C_3H_3Cl are displayed in Figures 2−6 together with the corresponding data determined from photolysis of C_3H_3Br. As shown in Figure 2, the relative yield of 1,5-hexadiyne at 398 K is in good agreement with the yields obtained for C_3H_3Br at the same temperature. At 623 K, the relative yield of this product decreases dramatically, especially at low pressure.

Similarly, Figure 3 shows that the relative yield of 1,2-hexadiene-5-yne at 398 K agrees well with the corresponding result obtained for C_3H_3Br. The relative yield decreases dramatically at 623 K.

The relative yield of dimethylenecyclobutene (dmcb), displayed in Figure 4, at 398 K is consistent with the corresponding data for C_3H_3Br. The relative yield of dmcb at 623 K rises rapidly with pressure to a broad peak around 133 mbar and then falls off gradually as pressure is further increased.

Figure 5 shows that, within experimental uncertainty, the relative yield of fulvene is consistent with the values obtained from photolysis of C_3H_3Br. At 623 K, the relative yield appears to increase slightly with decreasing pressure.

Figure 6 shows that, within the experimental uncertainty, the relative yield of benzene at 398 K is consistent with the corresponding results determined from C_3H_3Br photolysis. At 623 K, the relative yield of benzene increases sharply at low pressure.

The magnitude of the relative yields of the C_6H_6 isomeric products and their pressure and temperature dependencies are in relatively good agreement with the results obtained from the C_3H_3Br precursor. The overall qualitative and quantitative results derived from product studies of the above two propargyl halides precursors of the propargyl radicals are in good agreement. This indicates that there are no significant contributions from reactions of Br or Cl atoms on the branching ratios of final C_6H_6 isomeric products.

No halogenated reaction products were detected with our methods. This suggests that the GC columns used for these studies may not be best suited for separating and identifying the halogenated species and/or possibly a significant fraction of the halogens are reacted on the walls of the reactor and the gas handling lines.

To further examine potential effects of halogen atoms on the C_6H_6 final product distributions, in a number of experiments, excess amounts of heptane (up to 13 mbar) were added to the C_3H_3Cl/He mixtures. Reactions of halogen atoms with saturated hydrocarbon molecules, through hydrogen abstractions, are generally fast with rate constants of the order of 5×10^{-11} cm^3 molecule^{-1} s^{-1}.[20] The presence of excess heptane is expected to effectively remove or substantially reduce the Cl atoms generated from the photolysis. The C_6H_6 isomeric product distributions determined from the C_3H_3Cl/heptane/He mixtures, within the uncertainties of these measurements, were in good agreement with those determined without added heptane, reaffirming the insignificant effect of halogen atom reactions on the C_6H_6 isomeric final products. Reactions of halogen atoms, particularly Cl atoms, with propargyl halides are generally fast.[13,21] Although these reactions may affect the kinetics of the propargyl decay, they appear to have no appreciable effect of the C_6H_6 product distribution, as is evident from the present results.

c. 193 nm Photolysis of Allene. The photodissociation of allene at 193 nm wavelength produces primarily propargyl radicals and also minor quantities of C_3H_2.[22,23]

$$C_3H_4\ \text{(allene)} \xrightarrow{193\ \text{nm}} C_3H_3 + H \qquad 89\%$$

$$\rightarrow C_3H_2 + H_2 \qquad 11\%$$

This method for generating propargyl radicals has an advantage of not having halogen as a primary photolysis product. However, it has the disadvantage of simultaneously producing, in addition to propargyl radicals, a significant quantity of H atoms. A photodissociation channel producing propargylene radicals

TABLE 3: Relative Yields (%) of C_6H_6 Isomeric Products, Determined Subsequent to the 193 nm Photolysis of Dilute Mixtures of Allene/He (2/750)[a]

		relative yields (%) of C_6H_6 products				
T/K	P/mbar	1,5-hexadiyne	1,2-hexadien-5yne	dmcb	fulvene	benzene
295	67	43	39.5	6	2.5	9
	933	47	43.5	5	2	2.5
523	67	41	30.5	15	2	11.5
	933	43	44	9	1	3
623	67	19	1.5	61	2	16.5
	933	29	25	41	1	4

[a] Photolysis time: 20 min at 1 Hz. Laser energy = 65 mJ per pulse.

(C_3H_2) with a yield of about 11% has also been reported.[22,23] The major reactions following photolysis of allene are expected to be

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6$$

$$C_3H_2 + H \rightarrow C_3H_3$$

$$C_3H_3 + H \rightarrow C_3H_4$$

$$C_3H_4 + H \rightarrow C_3H_5 \text{ (allyl)}$$

$$C_3H_5 + C_3H_5 \rightarrow C_6H_{10}$$

$$C_3H_5 + C_3H_5 \rightarrow C_3H_4 + C_3H_6$$

$$C_3H_5 + H \rightarrow C_3H_6$$

$$C_3H_3 + C_3H_5 \rightarrow C_6H_8$$

Except for the propargyl combination reaction, no other major reaction produces C_6H_6 products. Therefore, the C_6H_6 products of the propargyl combination reaction can be studied using this radical precursor.

Dilute mixtures of allene/He were photolyzed at 193 nm at pressures of 67 mbar and 933 mbar, and temperatures of 295, 523, and 623 K. No significant thermal dissociation of allene occurs under the conditions of this study. The product studies focused only on the nature and relative yields of C_6H_6 isomeric products. As in the cases of the propargyl halide results, five C_6H_6 isomeric products, 1,5-hexadiyne, benzene, fulvene, dimethylenecyclobutene (dmcb), and possibly 1,2-hexadien-5-yne, were separated and detected. Table 3 lists the relative yields of the C_6H_6 isomeric products at various temperatures and pressures.

For comparison with the results for the propargyl halides, some of the data for allene are displayed in Figures 2−6. As shown in Figure 2, the relative yield of 1,5-hexadiyne at 295 K and 933 mbar is in good agreement with the corresponding yields determined from C_3H_3Br and C_3H_3Cl photolysis at the same temperature. At 623 K, the relative yield at 933 mbar agrees well with the corresponding data for C_3H_3Cl.

At 623 K, 67 mbar, the relative yield is somewhat greater than the corresponding yield for C_3H_3Cl. However, it is lower than the relative yields (obtained for C_3H_3Br and C_3H_3Cl) at the same pressure but lower temperatures. Hence it still falls within the range of consistency with the propargyl halide results.

Figure 3 shows that at both 295 and 623 K, the relative yields of 1,2-hexadien-5-yne are in good agreement with the corresponding data for C_3H_3Br and C_3H_3Cl.

As Figure 4 shows, the relative yields of dimethylenecyclobutene at both 295 and 623 K are in good agreement with the corresponding yields obtained from C_3H_3Br and C_3H_3Cl precursors.

The relative yield of fulvene appears to be somewhat higher for allene than for the propargyl halide precursors, but still it is a minor product. Also there are generally larger deviations between the three sets of results for products that have low relative yields. This is expected because even small deviations of the determined yields of the major products will have a significant effect on the percent deviation of the relative yields for minor products.

The relative yields of benzene produced from photolysis of allene at 295 and 623 K is shown in Figure 6 and are in good agreement with the corresponding data obtained for C_3H_3Br and C_3H_3Cl.

The C_6H_6 isomeric product distributions obtained using allene as the propargyl precursor are generally in good agreement, both qualitatively and quantitatively, with the product distributions obtained using halogenated precursors, C_3H_3Br and C_3H_3Cl. This strongly supports the conclusion that the halogen atoms generated in the photolysis of C_3H_3Br and C_3H_3Cl have no significant effect on the C_6H_6 isomeric product distribution.

Discussion

The collective results for C_3H_3Br, C_3H_3Cl, and allene indicate 1,5-hexadiyne is a major product particularly at high-pressure and low-temperature conditions, with yields as high as ~55%. Its relative yield, as shown in Figure 2, decreases with decreasing pressure and/or increasing temperature, and at low pressures of about 27 mbar and at 623 K, 1,5-hexadiyne becomes a minor product with a relative yield of ~1%. The relative yield obtained by Alkemade and Homann[10] at 623 K, denoted by the solid square in Figure 1, is consistent with the results of the current study. The broken lines indicate the theoretical yields computed by Miller and Klippenstein[2] at 295 and 650 K. The present results for the relative yield of 1,5-hexadiyne are in good agreement with the computational results, especially at high-pressure and high-temperature conditions.

Another aliphatic isomeric product, which we believe to be 1,2-hexadien-5-yne, is also a major product at temperatures up to about 520 K and appears to have a weak pressure dependency at temperatures up to ~520 K. The relative yield of this product, as shown in Figure 3, on average is about 35% for temperatures from 295 K to about 520 K. At $T = 623$ K and $P = 933$ mbar, however, the relative yield of 1,2-hexadien-5-yne is reduced to about 20% and it is reduced further by reducing the pressure to about 2% at 27 mbar. As shown in Figure 3, the relative yield obtained by Alkemade and Homann at 623 K is somewhat higher than the current data. The theoretical results indicate an average yield of about 25%, which does not change significantly, within the conditions of this study, with either pressure or temperature. For temperatures between 295 and 623 K, the current experimental results are in qualitative agreement with the computational predictions. At 623 K, however, the relative yield of 1,2-hexadien-5-yne decreases more rapidly than theory predicts. Furthermore, at 623 K the experimental yield shows more dramatic pressure dependence than the yield predicted theoretically.

The present results also indicate that dimethylenecyclobutene is another major product of the propargyl combination with substantial yields, particularly at elevated temperatures. The relative yield of this product also depends on pressure and is generally higher at low pressures. As shown in Figure 4, the present results agree well with the theoretical results at 295 K. At 623 K, the highest temperature of this study, the experimental yield of dimethlylenecyclobutene increases from 48% at $P =$ 933 mbar to 86% at $P = 133$ mbar and then decreases to about

50% at 27 mbar. This qualitative pressure dependence mimics the theoretical yield at 650 K. However, the present results indicate that a greater yield of dimethylenecyclobutene is obtained at 623 K than theory accounts for.

Fulvene appears to be a minor product at all conditions of this study, with yields lower than those predicted by theory. Figure 5 shows that at 295 K, the current results are in agreement with theory at high pressure. At lower pressure, theory predicts significantly higher yield than the current results indicate. This discrepancy is even more pronounced at high temperature. Only one data point, at 933 mbar and 650 K, is shown from the theoretical prediction; the theoretical predictions of the fulvene yield at lower pressures are significantly larger than the experimental values and fall outside the range of scales in Figure 5.

Benzene, on the other hand, is produced with substantial yields even at the low to moderate temperatures of this study. Between pressures of 933 and about 133 mbar the relative yield of benzene is less than 10% for all temperatures of this study. However, the benzene yield increases substantially at lower pressures and reaches more than 40% at 27 mbar and 623 K. In contrast, the relative yield of benzene predicted by theory is much less at 27 mbar and, 650 K, it is less than 4%.

In general, at higher temperatures and lower pressures more aromatic and less aliphatic products are formed. There is no evidence for the formation of phenyl radicals under our experimental conditions. Detection of biphenyl and/or 3-phenyl-1-propyne, which can be produced from phenyl + phenyl and phenyl + propargyl reactions, respectively, would have been indications of phenyl radical formation. However, none of those products was detected at various pressure and temperature conditions of this study. In agreement with the theoretical predictions, the formation of phenyl radicals, even at the highest temperature and the lowest pressure of this study is insignificant.

To assess the potential thermolysis, pyrolysis and/or photolysis of the C_6H_6 products under the present experimental conditions, dilute mixtures of 1,5-hexadiyne/He, or benzene/He were circulated in the reactor at 623 K, the highest temperature used in this study, both with and without exposing them to the 193 nm laser irradiation. The time duration of sample circulation, the laser energies, and the irradiation times were similar to those used in the present propargyl reaction experiments. A significant amount of 1,5-hexadiyne was thermally converted to dimethylenecyclobutene, at an approximate rate of about 1.4×10^{-2} s^{-1}. This thermal rate translates into about 50% conversion of 1,5-hexadiyne to dimethylenecyclobutene at the highest temperature of the present propargyl reaction experiments. GC/Ms analysis of the 1,5-hexadiyne sample after irradiation at 193 nm revealed a number of products including dimethylenecyclobutene as well as some light hydrocarbons. The test experiments indicated that the thermally produced dimethylenecyclobutene at 623 K appeared to undergo substantial photoylsis at 193 nm. Future experiments are being planned to quantify the photolysis of dimethylenecyclobutene, 1,5-hexadiyne, and a number of other isomers of C_6H_6. At 623 K, benzene was photolyzed at an approximate rate of 3.2×10^{-3} s^{-1}, which translates into about 5% photolysis of benzene (at 193 nm) in the propargyl reaction experiments. No appreciable thermolysis of benzene was observed at 623 K. The potential photolysis of the products at 248 nm is expected to be less significant than at 193 nm. The absorption cross-section of 1,5-hexadiyne is significantly lower at 248 nm (0.3×10^{-19} cm^2 molecule^{-1}, at 425 K) than at 193 nm (1.4×10^{-19} cm^2 molecule^{-1}, at 425 K).[24] Also, comparison of the C_6H_6 product distributions at 248 nm (C_3H_3Br) and 193 nm (C_3H_3Cl and allene) at temperatures lower than 623 K show that, within the measurement uncertainties, the product distributions are in fairly good agreement. This suggests that the photolysis of C_6H_6 products up to 523 K is not significant at 248 or 193 nm. Also, these results suggest that, at higher temperatures of this study, in addition to the chemical activation paths, there are contributions from thermal processes. The separate contributions of these two pathways to the final product formation cannot be differentiated using our experimental method.

The relative yields of 1,5-hexadiyne and 1,2-hexadien-5-yne determined in the present study are 20−30% lower than the corresponding relative yields determined (at $T = 298$ K, $P = 67$ mbar) in the earlier results of Fahr and Nayak.[9] However, not all the isomeric products detected and identified in the present work were detected in that earlier product study. The use of superior GC columns in the present study has enabled better separation of various C_6H_6 isomeric products and hence also resulted in more reliable isomeric product identification and quantitative. Also, the availability of the calibration samples of fulvene and dimethylenecyclobutene, which were synthesized for the present study, facilitated the identification of these two important products.

The product studies of the propargyl combination reaction reported by Alkemade and Homann[10] are performed at pressures of 3 and 6 mbar and temperatures of 623 and 673 K. This work reported the detection of five isomers of C_6H_6; 1,5-hexadiyne, 1,2-hexadien-5-yne, and 1,2,4,5-hexatetraene, which were identified as primary products, and benzene and 1,3-hexadien-5-yne as secondary products. 1,2,4,5-Hexatetraene and 1,3-hexadiene-5-yne have not been observed in the present study. On the other hand, dimethylenecyclobutene and fulvene, which have been identified in the present study, were not reported in the Alkemade and Homann study. We are not certain about the sources of these disagreements between the nature of the products determined from the two studies. However, the possibility of heterogeneous and surface reactions with the methods used in ref 10 cannot be ruled out. As mentioned earlier, propargyl radicals, in Alkemade and Homann's study were produced using a heated low-pressure flow reactor and a multislit diffusion burner where the propargyl radicals were produced from the reaction of sodium vapor and propargyl halides. The products were analyzed after freezing-out the condensables at the end of each experiment. It is feasible that decomposition/polymerization of propargyl halides occur on the hot metallic burner surfaces or other metallic surfaces on the system, resulting in products different from those produced from the gas-phase propargyl combination reaction. The product analysis method used in that previous study did not allow for discrimination of products formed from such reactions.

The extensive computational study of the propargyl combination reaction reported by Miller and Klippenstien[2] examines the effects of temperature and pressure on the kinetics and predict the nature and relative yields of various C_6H_6 isomeric products. Figure 1, reproduced from ref 2a, illustrates the potential energy diagram for the propargyl recombination reaction and subsequent isomerization pathways. Qualitatively, the agreement between the theoretical predictions and the present experimental results is relatively good, such that most of the major predicted C_6H_6 isomeric products have been identified experimentally. Also, the experimental results agree with the predictions on the general trends of the relative yields, versus pressure and temperature, for a number of major products such as 1,5-hexadiyne, benzene, and dimethylenecyclobutene. However, quantitatively the agreement between the predicted product distributions and experimental results is not good for all the products. The best agreement between the computational predictions and the experimental results appear to be for 1,5-hexadiyne. The poorest agreement between theory and the present results appear to be for benzene. Benzene is a major product particularly at low pressures and its formation appears to be considerably more efficient than computational predictions. The disagreement between experimental results and theoretical predictions can be due to the fact that the constraints set for theoretical calculations were based on the available but inadequate experimental data. It appears that the extent of the barriers and/or the depth of the wells for various isomerizations/transition states in the path(s) from linear C_6H_6's to benzene may have to be reevaluated to allow for more efficient formation of dimethylenecyclobutene and benzene.

Substituted and larger propargyl-like radicals such as $Ph-C\equiv C-CH_2$ or substituted 1,5-hexadiynes are known to undergo reactions comparable to those of propargyl combination and 1,5-hexadiyne isomerization to benzene. It is feasible that formation of larger aromatic species from reactions of phenyl-substituted propargyl radicals also occur efficiently. Hence the cyclization efficiency of the C_6H_6 products from propargyl combination seen in this work may also apply to the formation of larger polycyclic aromatic hydrocarbons.

An interesting and important finding of this work, which is also relevant to the photochemical models of Saturn and Jupiter, is the significant benzene formation and the drastic pressure effect on the yield of benzene. As shown in Figure 6, the extrapolation of the product C_6H_6 yields to low pressures, typical of planetary atmospheric pressures ($<$15 mbar), suggests that benzene is a major product of the propargyl combination with a yield of about 40%, irrespective of the temperature. Inclusion of these results may account for some of the benzene deficiencies as predicted using the current photochemical models in comparison with the observational data.

Conclusions

The nature and the relative yields of C_6H_6 isomeric products formed from the propargyl combination reaction have been determined and the effects of pressure and temperature on the product yields have been examined. Propargyl radicals were generated by the 248 nm excimer laser photolysis of propargyl bromide and 193 nm photolysis of propargyl chloride and of allene. The final reaction products were separated, identified, and quantified using an on-line gas chromatograph/mass spectrometer system. Product studies were performed at a pressure range of 27−933 mbar and at a temperature range of 298−623 K. Five C_6H_6 isomeric final products were detected and four isomers, 1,5-hexadiyne, fulvene, dimethylenecyclobutene, and benzene, were identified using known C_6H_6 isomeric reference samples. The fifth C_6H_6 isomer is believed to be 1,2-hexadiene-5-yne. The relative yields of the final C_6H_6 isomeric products have significant pressure and temperature dependencies. At high pressures and low temperatures the aliphatic products, 1,5-hexadiyne and 1,2-hexadiene-5-yne are the major products. At low pressures and high temperatures, dimethylenecyclobutene and benzene are the major products. At higher temperatures of this study, in addition to the chemical activation paths, there are contributions from thermal processes as well. These results indicate that the initially formed linear C_6H_6 isomeric products, formed from the propargyl combination reaction, can isomerize more efficiently than previously predicted, leading to the formation of cyclic products. Surprisingly, the relative yield of fulvene appears to be less than those of dimethylenecyclobutene and benzene. The findings of this detailed experimental product study of the propargyl combination reaction can aid in refining the computational efforts and reassessment of the parameters used for modeling of PAH and soot formation mechanisms.

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(14) Certain commercial instruments, materials and computational programs are identified in this paper to adequately specify the experimental or computational procedures. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the instruments, materials, and computational programs identified are necessarily the best available for the purpose.

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