J. Phys. Chem. A **2002,** *106,* 5613−5617

Kinetics of the Reaction between Propargyl Radical and Acetylene

Vadim D. Knyazev* and Irene R. Slagle

Research Center for Chemical Kinetics, Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

Received: December 10, 2001; In Final Form: March 19, 2002

The reaction $C_3H_3 + C_2H_2 \rightarrow C_5H_5$ (1) has been studied using the Laser Photolysis/Photoionization Mass Spectrometry technique. Rate constants were determined in time-resolved experiments as a function of temperature (800−1100 K). Rate constants of reaction 1 are independent of the bath gas density within the experimental range, $[M] = [He] + [C_2H_2] = (1.2-2.4) \times 10^{17}$ molecule cm^{-3}. C_5H_5 was detected as a primary product of reaction 1. Formation of C_7H_7 was observed with kinetics corresponding to that of a secondary reaction and formation of C_9H_8 was also observed at even longer reaction times. The kinetics of product formation suggests the following sequence of reactions occurring under the conditions of excess acetylene used in the current work: $C_3H_3 + C_2H_2 \rightarrow C_5H_5$ (1), $C_5H_5 + C_2H_2 \rightarrow C_7H_7$ (8), and $C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$ (9). Within the above experimental range of temperatures and bath gas densities, the rate constants of reaction 1 can be described by the Arrhenius expression $k_1 = (3.9 \pm 1.8) \times 10^{-13} \exp(-(5030 \pm 449)\ K/T)$ cm^3 molecule^{-1} s^{-1}. The experimental results of the current study are compared with the computational predictions based on the model of Moskaleva and Lin (*J. Comput. Chem.* **2000**, *21*, 415).

I. Introduction

Understanding of the mechanism of formation of polycyclic aromatic hydrocarbons (PAH) and soot in the combustion of hydrocarbon fuels is of prime importance in the development of environmentally clean combustion devices. Numerous efforts have been concentrated on the elucidation of chemical pathways leading to the formation of the first aromatic ring. A review of many of these studies can be found in ref 1. Cyclopentadienyl (c-C_5H_5) radical has been identified as an important species in the processes leading to the formation of soot in combustion environments (see, for example, refs 2 and 3). Potential chemical routes leading to the formation of the cyclopentadienyl radical include the reaction between propargyl radical and acetylene.[4,5] Both C_3H_3 and C_2H_2 are known to be abundant under near sooting conditions in certain types of hydrocarbon flames (e.g., refs 6 and 7). Two groups (Kern et al.[8] and Roy et al.[9]) have experimentally studied the thermal decomposition of the cyclopentadienyl radical in shock tubes. The mechanism of c-C_5H_5 decomposition discussed by these groups involves isomerization of C_5H_5 and subsequent formation of C_3H_3 and C_2H_2 as final products, suggesting that the same sequence of elementary processes in the reverse direction may lead to the formation of c-C_5H_5 in the reaction of C_3H_3 with C_2H_2. Moskaleva and Lin[4] applied quantum chemical calculations in combination with RRKM and a modified strong collision model to study the mechanism and rate constants of the decomposition of c-C_5H_5 to C_3H_3 and C_2H_2 and those of the reverse reaction, formation of the cyclopentadienyl radical in the reaction between the propargyl radical and acetylene. These authors reported the calculated rate constants for the decomposition, association, and C_5H_5 isomerization processes over the temperature range 1000−3000 K at pressures of 100 Torr, 1 atm, and 10 atm. Recently, Moriarty et al.[5] used different quantum chemical methods (including quantum Monte Carlo and density-functional-theory approaches) and a time-dependent stochastic solution of master equations (for energy transfer) to explore the mechanism of the $C_3H_3 + C_2H_2$ reaction.

In the current work, we present the first direct experimental investigation of the reaction

$$C_3H_3 + C_2H_2 \rightarrow C_5H_5 \tag{1}$$

between the propargyl radical and acetylene. Reaction 1 was studied by the laser photolysis/photoionization mass spectrometry technique in the temperature range 800−1100 K and bath gas densities $[He] + [C_2H_2] = (1.2-2.4) \times 10^{17}$ molecule cm^{-3}.

This article is organized as follows. Section I is an introduction. The experimental method, procedures, and results are reported in section II. A discussion is presented in section III.

II. Experimental Section

In this section, the experimental apparatus used is described and the photolysis routes of the free radical precursor are characterized. The method and procedures used to determine the rate constants are explained next. Finally, the experimental results on the rate constants and products of reaction 1 are presented.

Apparatus. Details of the experimental apparatus[10] have been described previously. Pulsed 248-nm unfocused collimated radiation from a Lambda Physik 201 MSC KrF excimer laser was directed along the axis of a 50-cm-long 1.05-cm i.d. heatable tubular quartz reactor coated with boron oxide.[11] The laser was operated at 4 Hz and at a fluence of ∼ 350 mJ/pulse. The energy flux of the laser radiation inside the reactor was in the range of 0.1−5.3 mJ/cm^2 per pulse depending on the degree of laser beam attenuation. Gas flowing through the tube at ∼4 m s^{-1} (in order to replace the photolyzed gas with a fresh reactant gas mixture between the laser pulses) contained the free radical precursor, 1,3-butadiene, in low concentrations, acetylene in varying concentrations, and the carrier gas, helium. The gas was continuously sampled through a 0.04-cm-diameter tapered hole in the wall of the reactor (gas-sampling orifice) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion

---

* Corresponding author. E-mail: knyazev@cua.edu.

10.1021/jp0144909 CCC: $22.00

was photoionized using an atomic resonance lamp, mass selected in an EXTREL quadrupole mass filter, and detected by a Daly detector.[12] Temporal ion signal profiles were recorded from 30 ms before each laser pulse to 15−45 ms following the pulse by using an EG&G ORTEC multichannel scaler interfaced with a PC computer. Typically, data from 1000 to 9000 repetitions of the experiment were accumulated before the data were analyzed. The sources of ionizing radiation were chlorine (8.9−9.1 eV, CaF_2 window, used to detect C_3H_3, C_3H_5, C_5H_5, C_9H_8, C_9H_9, and C_7H_7) and hydrogen (10.2 eV, MgF_2 window, used to detect C_3H_5, C_5H_4, C_7H_6, C_9H_7, C_9H_9, 1,3-C_4H_6, $C_{11}H_{10}$, and $C_{11}H_{11}$) resonance lamps.

Photolysis of Radical Precursors. Propargyl radicals were produced by the 248-nm photolysis of 1,3-butadiene, which has been shown[13,14] to occur primarily via three routes:

$$1,3\text{-}C_4H_6 \xrightarrow{248\text{ nm}} CH_3 + C_3H_3 \qquad (2a)$$

$$\rightarrow C_2H_2 + C_2H_4 \qquad (2b)$$

$$\rightarrow C_4H_4 + H_2 \qquad (2c)$$

Reaction 2 was studied by Haller and Srinivasan[13] and Gollin et al.[14] at room temperature where the dominance of channels 2a and 2b has been demonstrated. The experiments performed in the current work involve the photolysis of 1,3-C_4H_6 at temperatures significantly higher than room temperature, 800−1100 K. The photolysis routes of butadiene and their relative importance can, therefore, differ from those observed by the authors of refs 13 and 14. In the current work, the products of channel 2a were observed directly by photoionization mass spectrometry. In addition, a signal was observed at the mass of C_2H_3 ($m/e = 27$), thus providing evidence of vinyl radical formation in the photolysis of 1,3-butadiene. Furthermore, in the presence of acetylene, formation of the products of the reactions of CH_3, C_2H_3, and C_3H_3 with C_2H_2 was detected (vide infra). The radical product detected at $m/e = 39$ can be easily identified as the propargyl radical due to its thermal stability at temperatures as high as 1100 K. All other isomers of C_3H_3 are expected to thermally decompose at lower temperatures under the conditions (pressure and time scales) of the experiments used in the current study.

Experimental Method and Procedures. Experiments were conducted under pseudo-first-order conditions with the concentrations of C_2H_2 (in the range $(4.1-52.3) \times 10^{15}$ molecule cm^{-3})) in large excess over propargyl ($[C_3H_3]_0 \leq (0.8-18) \times 10^{10}$ molecule cm^{-3}). The observed exponential decay of the C_3H_3 radical was attributed to reaction 1 and heterogeneous loss:

$$C_3H_3 \rightarrow \text{heterogeneous loss} \qquad (3)$$

The propargyl ion signal profiles were fitted to an exponential function ($[C_3H_3]_t = [C_3H_3]_0\exp(-k't)$) by using a nonlinear least squares procedure. In a typical experiment to determine k_1, the kinetics of the decay of C_3H_3 radicals was recorded as a function of concentration of acetylene. In such series of measurements of k' with different concentrations of acetylene, the concentration of helium was adjusted to keep the total bath gas concentration ($[M] = [He] + [C_2H_2]$) constant. Values of k_3 were determined in the absence of C_2H_2. Values of k_1 were then obtained from the slopes of the linear k' vs $[C_2H_2]$ dependences. Experiments were performed to establish that the decay constants did not depend on the initial C_3H_3 concentration (provided that the concentration was kept low enough to ensure that radical−radical reactions had negligible rates in comparison to the reaction with C_2H_2), the concentration of the radical precursor or the laser intensity. Rate constants of reaction 1 were determined at $T = 800-1100$ K and bath gas concentrations $[M] = (1.2-2.4) \times 10^{17}$ molecule cm^{-3}. A typical k' vs $[C_2H_2]$ plot is presented in Figure 1. The intercept at $[C_2H_2] = 0$ corresponds to the rate of heterogeneous decay of C_3H_3 radicals, k_3. The experimental conditions and the values of the bimolecular rate constants k_1 determined in this study are presented in Table 1.

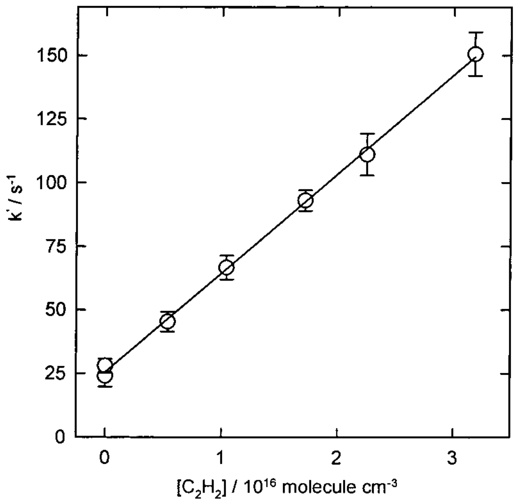


Figure 1. First-order C_3H_3 decay rate k' vs $[C_2H_2]$. The intercept at $[C_2H_2] = 0$ corresponds to the rate of heterogeneous decay of C_3H_3. $T = 1100$ K, $[He] + [C_2H_2] = 1.2 \times 10^{17}$ molecule cm^{-3}, $[C_3H_3]_0 \leq 5.2 \times 10^{10}$ molecule cm^{-3}, $[1,3\text{-}C_4H_6] = 1.92 \times 10^{14}$ molecule cm^{-3}.

TABLE 1: Conditions and Results of Experiments to Determine the Rate Constants k_1 of the Reaction between Propargyl Radical and Acetylene

T/K	[M] [a]	[1,3-C_4H_6] [b]	$[C_2H_2]$ [c]	$[C_3H_3]_0$ [d]	I [e]	k_3/s^{-1}	k_1 [f]
800	12.0	3.08	1.27−4.85	3.1	2.11	2	0.69 ± 0.08
800	24.0	3.69	0.644−3.17	2.6	0.96	5.4	0.68 ± 0.11
900	12.0	4.85	1.17−4.03	0.8	0.24	8.2	1.47 ± 0.28
900	12.0	4.85	1.17−4.52	4.9	1.42	6	1.56 ± 0.20
900	12.0	4.85	1.21−5.23	18	5.33	5.8	1.74 ± 0.23
1000	12.0	6.42	0.89−4.53	7.1	1.18	9	2.41 ± 0.28
1000	24.0	30.9	0.731−3.10	10	0.25	20.7	2.64 ± 0.61
1100	12.0	19.2	0.535−3.18	5.2	0.22	25.6	3.90 ± 0.43
1100	12.0	19.2	0.408−1.62	2.6	0.11	24.4	3.99 ± 0.63

[a] Concentration of the bath gas ($[M] = [He] + [C_2H_2]$) in units of 10^{16} molecule cm^{-3}. [b] In units of 10^{13} molecule cm^{-3}. [c] In units of 10^{16} molecule cm^{-3}. [d] In units of 10^{10} molecule cm^{-3}. The C_3H_3 concentrations were obtained by measuring the photolytic depletion of 1,3-C_4H_6 at high fluency of the photolyzing laser and scaling the results in proportion to the laser intensity. The values of $[C_3H_3]_0$ in the table represent an upper limit since they were obtained assuming a 100% yield of C_3H_3 in the photolysis of 1,3-C_4H_6. [e] Laser intensity in mJ $pulse^{-1}$ cm^{-2}. [f] In units of 10^{-15} cm^3 $molecule^{-1}$ s^{-1}.

Low initial concentrations of propargyl radicals ensured that radical−radical reactions had negligible rates compared with that of the reaction of propargyl radical with C_2H_2. The upper limit of the potential influence of the radical−radical reactions on the experimental values of the rate constants can be estimated by comparing the values of the product $k_R[R]$ with the pseudo-first-order rate constant, $k_1[C_2H_2]$, of reaction 1 obtained with the largest concentration of C_2H_2 used in each particular experiment. Here, k_R is the rate constant of a radical−radical reaction in question and [R] is the concentration of the radicals. Taking $k_R = 3.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (the value of the rate constant of the $C_3H_3 + CH_3$ reaction at 800 K obtained under similar conditions[26]) and using the upper-limit estimate of the C_3H_3 concentration for [R], one obtains values of the $k_R[R]/(k_1[C_2H_2])$ ratio in the 0.5−7% range, well below the experimental uncertainties of the k_1 values. It should be emphasized that the real contribution from radical−radical reactions can be expected to be even less because (1) the concentrations of C_3H_3 given in Table 1 were obtained under the assumption of 100% yield of channel 1a in the photolysis of C_4H_6 and (2) rate constants of radical−radical reactions are expected to decrease with temperature (see, for example, ref 26); thus, the value of k_R used above is an overestimation. Finally, variation of $[C_3H_3]_0$ by a factor of 22 (see Table 1) has no effect on the experimental value of k_1 within the experimental uncertainties.

The sources of error in the measured experimental parameters were subdivided into statistical and systematic and propagated to the final values of the rate constants using different mathematical procedures for propagating systematic and statistical uncertainties.[15] The error limits of the experimentally obtained rate constant values reported in this work represent a sum of 2σ statistical uncertainty and estimated systematic uncertainty.

One potential complication that could affect the values of k_1 obtained in this study is due to the possibility of formation of reactive species (the presence of which can influence the kinetics of propargyl radicals) by the photolysis of acetylene. The high-temperature 248-nm photolysis of acetylene was investigated by us earlier in the experimental study of the reaction of vinyl radical with C_2H_2.[16] In that work, products of acetylene photolysis were investigated at $T = 630-980$ K, acetylene concentrations of $(1-2) \times 10^{15}$ molecule cm^{-3}, and relatively high photolyzing laser radiation intensity (50−180 mJ cm^{-2} pulse^{-1}). C_2H_3, C_4H_2, and C_4H_4 were observed as products of acetylene photolysis and their formation was attributed to a mechanism consisting of reactions 4−7:

$$C_2H_2 \xrightarrow{248\text{ nm}} C_2H + H \tag{4}$$

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{5}$$

$$H + C_2H_2 \rightarrow C_2H_3 \tag{6}$$

$$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H \tag{7}$$

On the basis of this experimental investigation[16] it was established that the products of C_2H_2 photolysis, while observable at high laser fluences, have only negligible concentrations when low laser intensities (3−18 mJ cm^{-2} pulse^{-1}) were used with acetylene concentrations of up to 2×10^{15} molecule cm^{-3}.

In the current study, the concentrations of acetylene were larger than those used in our earlier work[16] by approximately an order of magnitude. Correspondingly, the photolyzing laser radiation was an order of magnitude less, so that the concentrations of the products of acetylene photolysis are expected to be similar to that of the earlier work, i.e., negligible. An upper limit of concentrations of the products of the C_2H_2 photolysis of 3×10^{10} molecule cm^{-3} was calculated by comparing the signals of C_2H_3 and C_4H_4 obtained in the C_2H_2 photolysis at high laser intensities with those obtained when known concentrations of C_2H_3 were created under the same conditions using the photolysis of vinyl bromide[17] and by scaling the calculated concentrations linearly with the photolyzing laser intensity. To even further eliminate the possibility that k_1 values could be affected by interference from the products of the acetylene photolysis, experiments were conducted to ensure that a significant variation of the photolyzing laser intensity (up to a factor of 22) had no influence on the measured values of k_1.

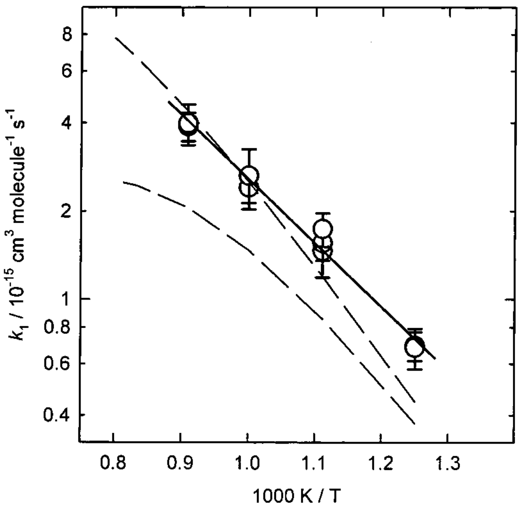


Figure 2. Temperature dependence of the rate constant of reaction 1. Symbols: experimental results of the current study. Solid line: Arrhenius fit (expression I). Dashed lines: calculations performed[18] on the basis of the model of reactions 1 and 14 by Moskaleva and Lin.[4] Upper dashed curve represents the results of calculations performed for helium bath gas at the pressure of 100 Torr; lower dashed line, calculations performed for helium bath gas pressure of 1 Torr.

The chemicals 1,3-butadiene (>99.5%) and acetylene (>99.6%, with the main impurity being air, which was removed by vacuum distillation) were obtained from Matheson and MG Industries, respectively, and were purified by vacuum distillation prior to use. Helium (>99.999%, <1.5 ppm of O_2, MG Industries) was used without further purification.

Results of the Rate Constant Measurements. The rate constants of reaction 1 obtained in the experimental study are presented in Table 1 and in Figure 2. The temperature dependence of k_1 (Figure 2) can be represented by the following Arrhenius expression:

$$k_1 = (3.9 \pm 1.8) \times 10^{-13} \exp(-(5030 \pm 449)K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{I}$$

Error limits given here for the preexponential factor and the activation energy represent the uncertainty of the fit only and are reported as 2σ. Uncertainties of individual k_1(T) values are given in Table 1 and include both systematic and statistical components. No pressure dependence of the k_1 values was observed in the experimental range of bath gas densities ($[M] = [He] + [C_2H_2] = (1.2-2.4) \times 10^{17}$ molecule cm^{-3}).

Products. C_5H_5 was identified as a primary product of reaction 1 with the characteristic growth time of the C_5H_5 signal matching that of the C_3H_3 decay. Formation of C_7H_7 was observed with kinetics corresponding to that of a secondary reaction and formation of C_9H_8 was also observed at even longer reaction times. The kinetics of product formation suggests the following sequence of reactions occurring under the conditions of excess acetylene used in the current work:

$$C_3H_3 + C_2H_2 \rightarrow C_5H_5 \tag{1}$$

$$C_5H_5 + C_2H_2 \rightarrow C_7H_7 \tag{8}$$

$$C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H \tag{9}$$

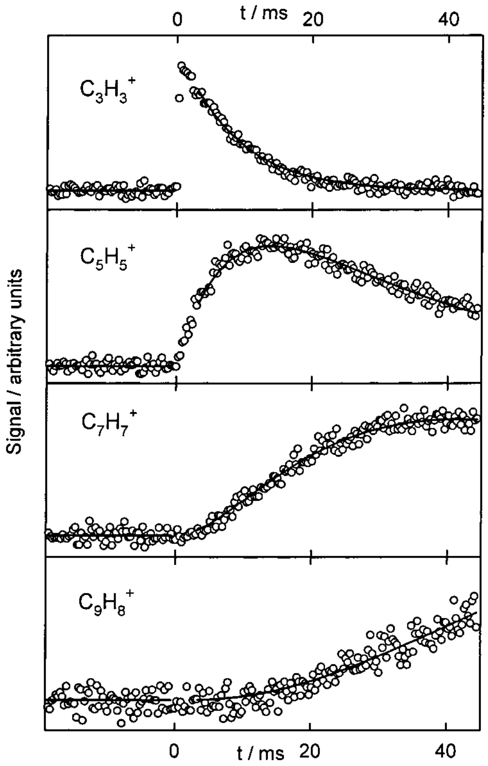


Figure 3. An example of the temporal profiles of the ion signals of the propargyl radicals (upper plot, decay due to reaction 1), primary C_5H_5 product of reaction 1, and secondary products: C_7H_7 and C_9H_8. T = 1000 K, [He] + $[C_2H_2]$ = 1.2 × 10^{17}, $[C_3H_3]_0 \leq 7.1 \times 10^{10}$, $[1,3\text{-}C_4H_6] = 6.42 \times 10^{13}$, $[C_2H_2] = 4.53 \times 10^{16}$ molecule cm^{-3}, laser intensity is 1.18 mJ pulse^{-1} cm^{-2}. Lines through the data are from a fit with the kinetic mechanism of reactions 1, 8, and 9. The parameters of the fit are $k' = 118.4$ s^{-1} and pseudo-first-order rates of reactions 8 and 9 are 39.3 and 25.8 s^{-1}, respectively.

Figure 3 presents the temporal ion signal profiles obtained for the decay of C_3H_3 in the presence of excess acetylene and for the formation of the C_5H_5, C_7H_7, and C_9H_8 products. Lines through the data are from a fit with the kinetic mechanism of reactions 1, 8, and 9.

Other species observed as products of reactions that follow the photolysis of 1,3-butadiene in the presence of excess C_2H_2 are C_3H_4 and C_4H_4. Formation of these species was attributed to the reactions of other products of the 1,3-C_4H_6 photolysis with acetylene:[16,19]

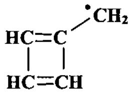
$$CH_3 + C_2H_2 \rightarrow C_3H_4 + H \tag{10}$$

$$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H \tag{11}$$

A number of potential primary and secondary products of the reaction of C_3H_3 with acetylene was searched for but not observed: C_3H_5, C_5H_4, C_7H_6, C_9H_7, C_9H_9, $C_{11}H_{10}$, and $C_{11}H_{11}$. Signals of all chemical species were monitored at their corresponding parent ion masses.

III. Discussion

The current study provides the first direct determination of the rate constants of the reaction of propargyl radical with acetylene producing C_5H_5. The isomeric structure of the C_5H_5 product cannot be determined on the basis of experimental information alone. It can be asserted, however, that the C_5H_5 product of reaction 1 is thermally stable at temperatures up to 1100 K and bath gas densities of (1.2−2.4) × 10^{17} molecule cm^{-3} and, therefore, is most likely a delocalized radical. Although the highly stable cyclopentadienyl radical appears to be the most plausible product of reaction 1 (This is also supported by the results of quantum chemical calculations, vide infra.), there exist other delocalized isomeric configurations of C_5H_5, for example,



(II)

or

$$\bullet CH_2{-}CH{=}CH{-}C{\equiv}CH \tag{III}$$

Thus, caution is advised in interpreting the results of the reaction product analysis of the current study.

Formation of the C_7H_7 and C_9H_8 products observed in the experimental system used in the current study suggests the sequence of reactions 1, 8, and 9. Similarly to the C_5H_5 primary product of reaction 1, the exact chemical identity of the C_7H_7 and C_9H_8 secondary products cannot be established on the basis of the experimental data alone. However, the thermal stability of C_7H_7 suggests that this radical is also stabilized through electron delocalization. Benzyl radical appears to be a likely isomer, which is supported by the experimental and computational evidence of the formation of cyclopentadienyl in the thermal decomposition of the benzyl radical.[20−24]

In 1988 Frenklach et al.[25] suggested a pathway in the pyrolysis of allene-acetylene mixture leading from the propargyl radical to the benzyl radical. These authors proposed that the first-ring cyclization is not the formation of phenyl or benzene but rather the formation of benzyl via a sequential addition of two C_2H_2 molecules to C_3H_3. One particular sequence of reactions suggested by Frenklach et al. is[25]

$$C_3H_3 + C_2H_2 \rightarrow CH_2{=}C{=}CH{-}CH{=}CH\bullet \tag{12}$$

$$\begin{aligned} &CH_2{=}C{=}CH{-}CH{=}CH\bullet + C_2H_2 \rightarrow \\ &\quad CH_2{=}C{=}CH{-}CH{=}CH{-}CH{=}CH\bullet \rightarrow C_7H_7\ (\text{benzyl}) \end{aligned} \tag{13}$$

The results of the current study, although confirming the $C_3H_3 \rightarrow C_5H_5 \rightarrow C_7H_7$ progression via consecutive reactions with acetylene, do not agree with the particular mechanism of reactions 12 and 13 because these reactions involve linear nondelocalized C_5H_5 and C_7H_7 isomers. At the pressures used in the current experimental study, these isomers can be expected to decompose thermally at temperatures below 800 K, which contradicts the observed thermal stability of the C_5H_5 and the C_7H_7 primary and secondary products of reaction 1.

If cyclopentadienyl radical (c-C_5H_5) is the product of reaction 1, then the reverse reaction is that of decomposition of c-C_5H_5 to propargyl and acetylene:

$$c\text{-}C_5H_5 \rightarrow C_3H_3 + C_2H_2 \tag{14}$$

Reaction 14 was studied experimentally by Kern et al.[8] and Roy et al.[9] in shock tubes. Both groups observed formation of C_2H_2 in the pyrolysis of cyclopentadiene, which was attributed to reaction 14. The authors of refs 8 and 9 used quantum chemical calculations to explore the mechanism of reaction 14 and presented identical mechanisms consisting of initial isomerization (1,2-H atom shift) producing a nondelocalized cyclic C_5H_5 radical with subsequent ring opening via two possible pathways and final decomposition of the produced linear C_5H_5 species into C_3H_3 and C_2H_2. Moskaleva and Lin[4] applied high-level quantum chemical calculations to study the mechanism of reactions 1 and 14. The sequence of elementary steps in the reaction mechanism presented by these authors is similar to those of refs 8 and 9. Moskaleva and Lin[4] applied the RRKM method and the modified strong collision model to calculate the rate constants of reactions 1 and 14 and reported the rate constant temperature dependences over the range of 1000−3000 K at the pressures of 100 Torr, 1 atm, and 10 atm. More recently, Moriarty et al.[5] used quantum chemical methods (including quantum Monte Carlo and density-functional-theory) and a master equation approach (time-dependent stochastic solution of master equations) to explore the mechanism of the $C_3H_3 + C_2H_2$ reaction. The potential energy surface produced by these authors includes the pathways of refs 4, 8, and 9, as well as other potential reaction routes, including those leading to the formation of the delocalized C_5H_5 radical species given by formulas II and III. The final values of rate constants and the relative importance of potential reaction pathways have not yet been reported by these authors as this work is currently in progress.[5]

The low preexponential factor obtained in the current study for the rate constant temperature dependence of reaction 1 (formula I) is consistent with the mechanism of chemical activation characterized by a "loose" entrance and "tight" exit transition states. This conclusion is in qualitative agreement with the mechanism of reactions 1 and 14 proposed by Kern et al.,[8] Roy et al.,[9] Moskaleva and Lin,[4] and Moriarty et al.[5]

Figure 2 presents the experimental values of the reaction 1 rate constants obtained in the current study (symbols and solid line) in comparison with the values calculated by Moskaleva and Lin[18] (two dashed lines) on the basis of their model of reactions 1 and 14.[4] The upper dashed line represents the data calculated for helium as bath gas at a pressure of 100 Torr; the lower dashed line is for the helium pressure of 1 Torr. The conditions used for the calculations do not coincide exactly with those used in the current study where the experimental pressure was in the 9.9−24.9 Torr range with acetylene being a substantial fraction of the bath gas (up to 44%). Nevertheless, the calculated k_1 values of Moskaleva and Lin are in agreement with the experimental results of the current work within a factor of 2. The sources of relatively minor differences between the calculated and the experimental k_1 values cannot be unequivocally identified; such factors as the differences in the bath gas pressures and composition, uncertainties of the model parameters, imperfections of the modified strong collision model, or intrinsic shortcomings of the RRKM method could be among potential reasons.

Acknowledgment. This research was supported by Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, under Grant No. DE/FG02-98ER14463.

References and Notes

(1) Richter, H.; Howard, J. B. *Prog. Energy Combust. Sci.* **2000**, *26*, 565.

(2) Melius, C. F.; Colvin, W. E.; Marinov, N. M.; Pitz, W. J.; Senkan, S. M. *Symp. Int. Combust. Proc.* **1996**, *26*, 685.

(3) Moskaleva, L. V.; Mebel, A. M.; Lin, M. C. *Symp. Int. Combust. Proc.* **1996**, *26*, 521.

(4) Moskaleva, L. V.; Lin, M. C. *J. Comput. Chem.* **2000**, *21*, 415.

(5) Moriarty, N. W.; Krokidis, X.; Lester, W. A., Jr.; Frenklach, M. Work in Progress. Preliminary Report "The Addition Reaction of Propargyl and Acetylene: Pathways to Cyclic Hydrocarbons". Presented at 2nd Joint Meeting of the U.S. Sections of the Combustion Institute, Oakland, California, March 2001. Abstract 102.

(6) Westmoreland, P. R.; Dean, A. M.; Howard, J. B.; Longwell, J. P. *J. Phys. Chem.* **1989**, *93*, 8171.

(7) Miller, J. A.; Melius, C. F. *Combust. Flame* **1992**, *91*, 21.

(8) Kern, R. D.; Zhang, Q.; Yao, J.; Jursic, B. S.; Tranter, R. S.; Greybill, M. A.; Kiefer, J. H. *Symp. Int. Combust. Proc.* **1998**, *27*, 143.

(9) Roy, K.; Horn, C.; Frank, P.; Slutsky, V. G.; Just, T. *Symp. Int. Combust. Proc.* **1998**, *27*, 329.

(10) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342.

(11) Krasnoperov, L. N.; Niiranen, J. T.; Gutman, D.; Melius, C. F.; Allendorf, M. D. *J. Phys. Chem.* **1995**, *99*, 14347.

(12) Daly, N. R. *Rev. Sci. Instrum.* **1960**, *31*, 264.

(13) Haller, I.; Srinivasan, R. *J. Chem. Phys.* **1964**, *40*, 1992.

(14) Gollin, G. J.; Deslauriers, H.; De Mare, G. R.; Poirier, R. A. *J. Phys. Chem.* **1990**, *94*, 134.

(15) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(16) Knyazev, V. D.; Stoliarov, S. I.; Slagle, I. R. *Symp. Int. Combust. Proc.* **1996**, *26*, 513.

(17) Slagle, I. R.; Park, J.-Y.; Heaven, M. C.; Gutman, D. *J. Am. Chem. Soc.* **1984**, *106*, 4356.

(18) Moskaleva, L. V.; Lin. M. C. Private communications.

(19) Diau, E. W.; Lin, M. C. *J. Chem. Phys.* **1994**, *101*, 3923.

(20) Jones, J.; Bacskay, G. B.; Mackie, J. C. *J. Phys. Chem. A* **1997**, *101*, 7105.

(21) Hippler, H.; Reihs, C.; Troe, J. *Z. Phys. Chem. (Neue Folge)* **1990**, *167*, 1.

(22) Braun-Unkhoff, M.; Frank, P.; Just, Th. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1417.

(23) Colket, M. B.; Seery, D. J. *Symp. Int. Combust. Proc.* **1994**, *25*, 883.

(24) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411.

(25) Frenklach, M.; Yuan, T.; Ramachandra, M. K. *Energy Fuels* **1988**, *2*, 462.

(26) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem. A* **2001**, *105*, 3196.