Absolute Rate Constant for the Reaction of Phenyl Radical with Acetylene

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Abstract

The absolute rate constant for the reaction of phenyl radical with acetylene has been measured at 20 torr total pressure in the temperature range of 297 to 523 K using the cavity-ring-down technique. These new kinetic data could be quantitatively correlated with the data obtained earlier with a relative rate method under low-pressure ($10^{-3}-10^{-2}$ torr) and high-temperature (1000–1330 K) conditions. These kinetic data were analyzed in terms of the RRKM theory employing the thermochemical and molecular structure data computed with the BAC-MP4 technique.

The calculated results reveal that the total rate constant for the $C_6H_5 + C_2H_2$ reaction (k_t) is pressure-independent, whereas those for the formation of $C_6H_5C_2H$ (k_b) and the $C_6H_5C_2H_2$ adduct (k_c) are strongly pressure-dependent. A least-squares analysis of the calculated values for 300–2000 K at the atmospheric pressure of N_2 or Ar can be given by

$$k_b = 9.5 \times 10^{-42} T^{9.33} \exp(-1{,}713/T)$$

$$k_c = 1.8 \times 10^{-7} T^{-1.63} \exp(-2{,}711/T)$$

and

$$k_t = 4.1 \times 10^{-18} T^{1.77} \exp(-1{,}152/T),$$

all in units of cm^3/s. The latter equation effectively represents the two sets of experimental data. © 1994 John Wiley & Sons, Inc.

Introduction

Phenyl radical (C_6H_5) is an important reactive intermediate in the combustion of hydrocarbon fuels. Its reaction with acetylene has been suggested as a key step leading to the production of polyaromatic hydrocarbons (PAHs), precursors to soot formation [1]:

$$C_6H_5 \xrightarrow{+C_2H_2} C_6H_5CH{=}CH \xrightarrow{+C_2H_2} C_6H_5CH{=}CHCH{=}CH$$

$$\xrightarrow{\text{cycl.}} C_{10}H_8(\text{naphthalene}) + H$$

Prior to the present series of studies, there has been no direct kinetic measurement for this and many other pivotal combustion processes due to the absence of a sensitive and reliable diagnostic technique for the detection of C_6H_5 and related aromatic

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radicals. Most kinetic data published to date have been based on the relative rate method with an assumed rate constant for the recombination of the C_6H_5 radicals which was commonly used as a reference reaction [2–5].

For the reaction of C_6H_5 with C_2H_2, Stein and co-workers [3,4] have measured its relative rate constants above 1000 K using a Knudsen cell flow reactor (P = 1–10 mtorr) in conjunction with a quadrupole mass spectrometer. From their two sets of product yields measured between 1000 and 1330 K from the reactions [3,4]:

$$C_6H_5 + C_2H_2 \xrightarrow{1} [C_6H_5C_2H_2] \longrightarrow C_6H_5C_2H + H$$

$$C_6H_5 + C_6H_5 \xrightarrow{2} C_{12}H_{10}$$

we obtained $k_1 = 10^{-10.58}e^{-4,730/T}$ cm^3/s, assuming $k_2 = 5 \times 10^{-12}$ cm^3/s. These high temperature kinetic data will be compared later with our 297–523 K results obtained by a new type of multipass laser absorption (or "cavity-ring-down") technique [6,7], recently developed by us for kinetic applications [8,9]. The validity of this new technique for kinetic studies has been tested extensively with the NH_2 + NO and C_6H_5 + NO reactions [10,11].

Experimental

The experiment was carried out with the apparatus recently constructed for the kinetics of phenyl radical reactions using the cavity-ring-down method. The details of the technique and the experimental setup have been described elsewhere [8–11] and only a brief summary is given here.

The flow tube reactor consists of a heatable Pyrex glass tube attached with two pairs of laser windows opposite of each other, allowing two split photolysis laser (248 nm) beams to cross at the center of the reactor at an angle of 15° with the reactor axis. The flow reactor was vacuum-sealed at both ends with a pair of highly reflective mirrors (R = 0.9999 at 500 nm, radius of curvature = 6 m), which form a 50-cm long, high quality optical resonator. The quality of the resonator is such that a pulse of the probing dye laser with FWHM = 5 ns can be effectively lengthened to 25 ± 5 μs, depending on the condition of the cavity.

All experiments were carried out under slow flow conditions using Ar as the carrier gas. Reaction mixture containing a trace amount of C_6H_5NO, the phenyl radical precursor, and a known amount of acetylene was premixed outside the reactor by means of corrugated stainless steel tubing. The partial pressures of acetylene and the Ar carrier gas were accurately measured with calibrated mass flowmeters (Hastings and MKS).

Argon (Spectral Gasses, 99.999%) and C_2H_2 (Matheson, 99.6%) were withdrawn directly from their cylinders without further purification. Nitrosobenzene (Aldrich, 96%, solid at room temperature) was placed on a sealed, fritted glass disc and carried into the reactor via the mixing tube with the Ar carrier gas.

Kinetic Data Acquisition

The cavity-ring-down technique measures the decay time of a pulse of probing photons injected into a well-aligned optical cavity consisting of a pair of highly reflective mirrors [8–11]. We have shown that the photon decay time, t_c, measured at t' after the generation of the radical of interest with a pulsed UV laser in the presence of a known concentration of a molecular reactant, can be related to the first-order decay constant of the radical by the equation:

$$\ln(1/t_c - 1/t_c^\circ) = B - k't' \tag{1}$$

where t_c° is the photon decay time measured in the absence of the radical and $B = \ln(cl\varepsilon[R]_0/nL)$. The quantities related to the experimental constant (B) are the velocity of light (c), the length of absorbing medium (l), the extinction coefficient of the radical at the probing wavelength (ε), the initial concentration of the radical ($[R]_0$ at $t' = 0$), the refractive index of the reaction medium (n) and the cavity length ($L = 50$ cm). The validity of eq. (1) is illustrated by Figure 1 for the decay of C_6H_5 measured at 504.8 nm, in the presence of the indicated amounts of C_2H_2. The slopes of the straight lines give the values of the pseudo-first-order rate constant, k', for the disappearance of C_6H_5 in the presence of a specific amount of C_2H_2. The values of k' vary with the concentration of C_2H_2 according to the eq. [8,11]:

$$k' = k^\circ + k''[C_2H_2] \tag{2}$$

where k° is the decay constant of the radical measured in the absence of C_2H_2 and k'' is the bimolecular rate constant for the $C_6H_5 + C_2H_2$ reaction. k'' can be obtained directly from the slope of a k' vs. $[C_2H_2]$ plot as presented in Figure 2.

The biomolecular rate constant thus obtained for six temperatures between 297 and 523 K at a constant pressure of 20 torr (mainly Ar) are summarized in Figure 3(A), in comparison with those measured by Stein and co-workers [3,4] for the temperature range 1000–1300 K under 1–10 mtorr low-pressure conditions. Our data determined under the lower-temperature, higher-pressure conditions can be effectively represented by the Arrhenius equation: $k_1 = 10^{-12.43\pm0.12}e^{-(1{,}560\pm240)/T}$ cm^3/s, which differs noticeably from that of Stein and co-workers: $k_1 = 10^{-10.6}e^{-4{,}730/T}$ cm^3/s. The difference, however, is fully consistent with that predicted by our model based on the RRKM theory of unimolecular reactions [12] to be discussed below. Our low-temperature rate constant compares reasonably with those of alkyl radical reactions with acetylene, obtained under similar experimental conditions, as summarized in

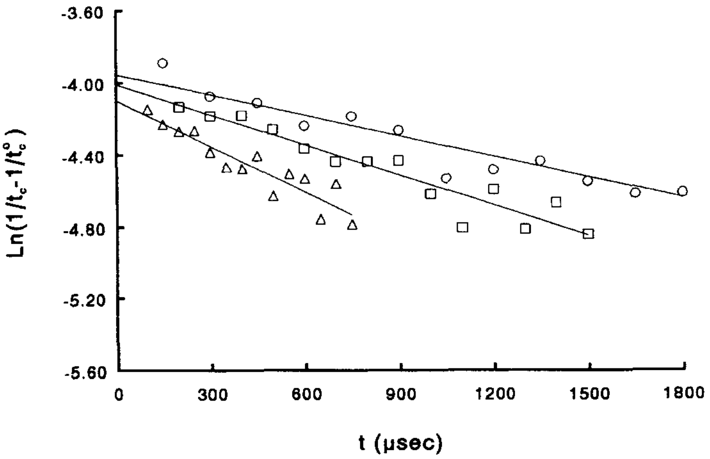

Figure 1. Typical pseudo-first-order decay plots under different, excess C_2H_2 concentration conditions: (○) $[C_2H_2] = 0$; (□) $[C_2H_2] = 4.42 \times 10^{16}$; and (△) $[C_2H_2] = 5.78 \times 10^{16}$, all in molecules/cm^3. The slopes of these plots give the first-order decay constants, k'.

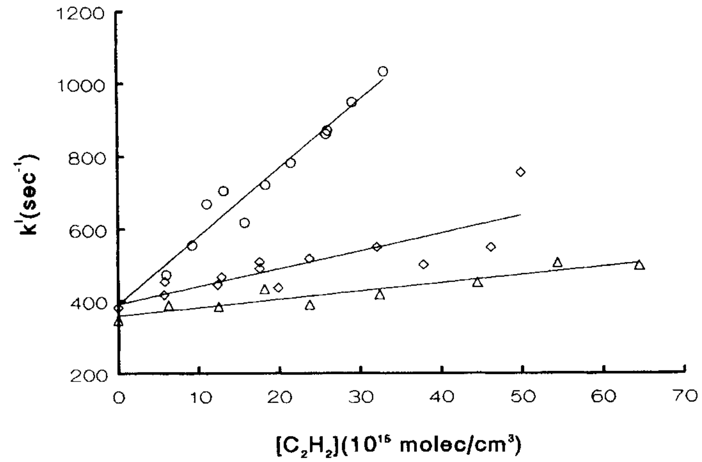

Figure 2. k' vs. $[C_2H_2]$ at different temperatures: (△) $T = 297$ K; (◇) $T = 373$ K; and (○) $T = 473$ K. Linear least-squares fit yields the second-order rate constants, k''.

Table I. It should be mentioned that Preidel and Zellner [13] have recently attempted to measure the rate constant for the $C_6H_5 + C_2H_2$ reaction with the conventional multipass absorption method to no avail. Their stated upper limits are given in Figure 3(A).

Theoretical Interpretation of Kinetics and Mechanism

The reaction of C_6H_5 with C_2H_2, as indicated earlier, occurs exclusively by the addition/H-atom elimination mechanism via a vibrationally excited $C_6H_5CH{=}CH$ (phenylvinyl radial) adduct. The mechanism is schematically depicted in Figure 4, which was constructed on the basis of the heats formation of C_6H_5, C_2H_2, $C_6H_5C_2H_2$,

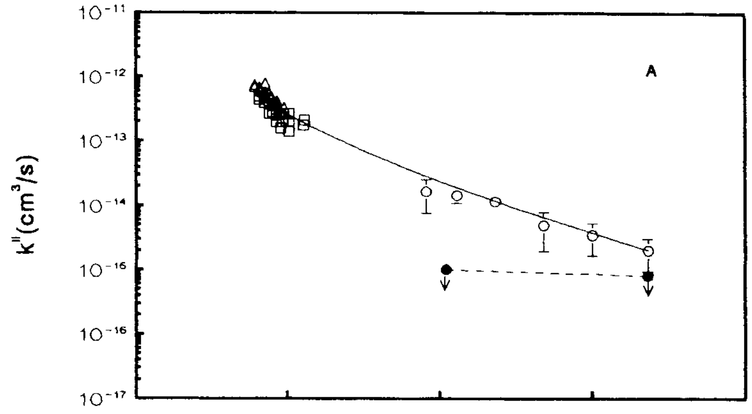

Figure 3 (A) The Arrhenius plot for $C_6H_5 + C_2H_2$ reaction: (○) This work; (□) ref. [3]; (△) ref. [4]; and (●) ref. [13]. Solid curve is the RRKM result. (B) Results of the $C_6H_5 + C_2H_2$ reaction from refs. [3] (□) and [4] (△). Dashed line is the linear least-squares fit to these two sets of data, giving $k_0 = 2.65 \times 10^{-11} \exp(-4{,}730/T)$ cm³/s. The solid curve is the calculated RRKM value.

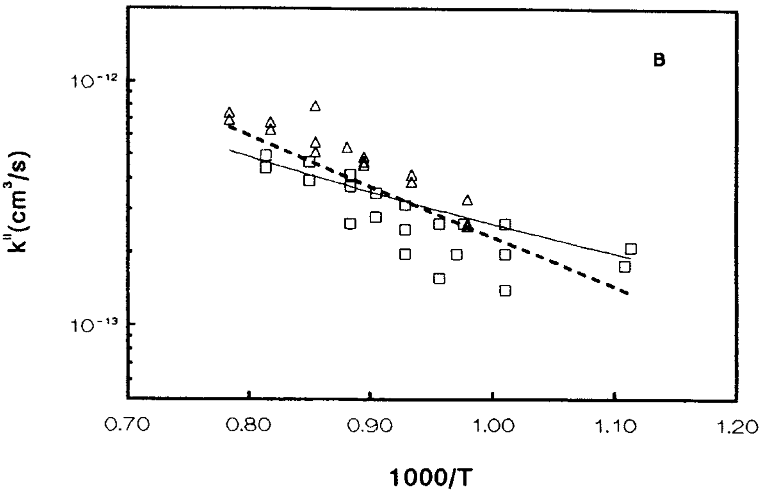

Figure 3. (continued)

and others calculated by the BAC-MP4 method (bond-additivity corrected Møller-Plesset 4th order perturbation) [14–16]. According to the energetic scheme we may write the reaction mechanism as follows:

$$\begin{array}{l} C_6H_5 + C_2H_2 \underset{-a}{\overset{a}{\longleftrightarrow}} C_6H_5C_2H_2^{\dagger} \xrightarrow{b} C_6H_5C_2H + H \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \xrightarrow{c} C_6H_5C_2H_2(+M) \end{array}$$

As depicted, the vibrationally excited adduct, $C_6H_5C_2H_2^{\dagger}$, may undergo decomposition to yield $C_6H_5C_2H$ + H via step (b) and, to a lesser extent, to return to the reactants, C_6H_5 + C_2H_2 via step (−a), or undergo collisional stabilization to produce the thermalized $C_6H_5C_2H_2$ radical via step (c). The stabilized $C_6H_5C_2H_2$ radical is essential for the polymerization process, ultimately giving rise to PAHs.

TABLE I. Comparison of Arrhenius parameters for the reaction of acetylene with various hydrocarbon radicals.

Radical	$A/10^{-13}$ cm^3/s	E (kcal/mol)	Ref.
CH_3	4.2	7.7	[a]
C_2H_5	0.83	7.0	[a]
n-C_3H_7	18.2	9.0	[b]
i-C_3H_7	1.7	7.6	[a]
t-C_4H_9	1.7	7.7	[d]
C_2H_3	33.2	5.0	4,[c]
C_6H_5	265	9.4	3,4,[c]
	3.7	3.1	This work

[a] J. A. Kerr and S. J. Moss, *CRC Handbook of Biomolecular and Termolecular Gas Reactions,* CRC Press, Boca Raton, Florida, 1981, p. 131–141, Vol. II.

[b] K. W. Watkins and D. K. Olsen, *J. Phys. Chem.,* **76,** 1089 (1972).

[c] High-temperature, low-pressure results.

[d] J. A. Kerr and M. J. Parsonage, Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds, Butterworths, London, 1972.

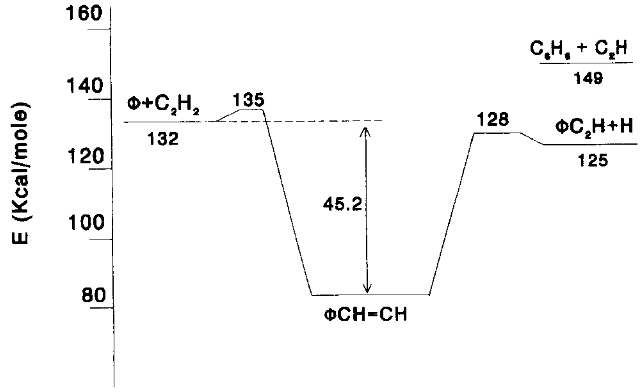

Figure 4. Energy diagram for $C_6H_5 + C_2H_2$.

The effects of temperature and pressure on the total rate of the $C_6H_5 + C_2H_2$ reaction and the product branching ratio, $C_6H_5C_2H$ vs. $C_6H_5C_2H_2$, can be calculated theoretically with the following equations, which were previously derived on the basis of the RRKM theory for a biomolecular reaction occurring by a long-lived intermediate [17,18]:

$$k_b = \frac{1}{h}\frac{Q_{tr}^{\ddagger}}{Q_{C_6H_5}Q_{C_2H_2}}e^{-E_a^{\circ}/RT}\int_0^{\infty}\frac{k_b(E)f(E^{\ddagger})}{\omega + k_{-a}(E) + k_b(E)}\,dE^{\ddagger} \tag{3}$$

$$k_c = \frac{1}{h}\frac{Q_{tr}^{\ddagger}}{Q_{C_6H_5}Q_{C_2H_2}}e^{-E_a^{\circ}/RT}\int_0^{\infty}\frac{\omega f(E^{\ddagger})}{\omega + k_{-a}(E) + k_b(E)}\,dE^{\ddagger} \tag{4}$$

where

$$k_i(E) = C_i\Sigma P_i(E_i^{\ddagger})/hN(E), \quad i = -a \text{ or } b \tag{5}$$

$$f(E^{\ddagger}) = \Sigma P_a(E_a^{\ddagger})\exp(-E_a^{\ddagger}/RT). \tag{6}$$

In the above equations, "‡" represents transition state quantities. k_b and k_c are the thermally-averaged rate constants for the formation of $C_6H_5C_2H$ and $C_6H_5C_2H_2$ via channels (b) and (c), respectively. Q's are the total partition function of the reactants and $Q_{tr}^{\ddagger}$ is the product of the translational and rotational partition functions of the transition state associated with the addition step (a), which has an energy barrier $E_a^{\circ} = 3.1$ kcal/mol at 0 K. The effective collision frequency, $\omega = \beta Z[\mathrm{M}]$, was calculated with Troe's weak collision approximation [19], using an averaged collision step-size of 1.0 kcal/mol. $E_a^{\ddagger}$ is the excess energy above the transition state for the reaction step (a).

The molecular and transition state parameters used in the present calculation are summarized in Table II. Otherwise stated, all the quantities including heats of formation, moments of inertia and vibrational frequencies of stable molecules, were obtained by BAC-MP4 calculations for self-consistency. The transition state parameters for the addition process were adjusted to match the room temperature rate constant measured in the present study which represents the sum:

$$k_t = k_b + k_c \tag{7}$$

The branching ratios for the production of phenyl acetylene and phenylvinyl radical are by definition given by $\alpha_b = k_b/k_t$ and $\alpha_c = k_c/k_t = 1 - \alpha_b$, respectively.

TABLE II. Molecular and transition state parameters computed by the BAC-MP4 method for the C_6H_5 + C_2H_2 reaction.

Species or Transition State	$\Delta H^\circ_{f,0}$ (kcal/mol)	i	I_i (amu)	ν_j (cm)
C_6H_5	83	A	135.3	361, 389, 569, 572,
		B	150.8	613, 675, 759, 822,
		C	286.7	884, 894, 920, 947,
				972, 999, 1101, 1110,
				1244, 1251, 1392, 1413,
				1464, 1487, 2994, 3002,
				3012, 3018, 3023
C_2H_2	54	A	0.0	729, 729, 612, 612
		B	25.0	1974, 3287, 3374
		C	25.0	
$C_6H_5C_2H_2^\ddagger$ (a)	140[a]	A	240	191(3), 502(5),
		B	731	720(5), 906(6),
		C	992	1156(6), 1190,
		Ir[b]	20.0	1446(5), 3002(7)
$C_6H_5C_2H_2$	91	A	161.4	209, 215, 372, 421,
		B	530.9	423, 535, 569, 587
		C	692.4	631, 701, 723, 771,
		Ir[b]	20.0	785, 844, 880, 899,
				918, 931, 971, 1027
				1114, 1123, 1150, 1190,
				1247, 1293, 1371, 1426,
				1451, 1486, 1501, 2919,
				2990, 2997, 3006, 3016,
				3023, 3067
$C_6H_5C_2H_2^\ddagger$ (b)	128[c]	A	161.4	123(3), 502(5),
		B	530.9	720(5), 906(6), 1161(7),
		C	692.4	1446(5), 2919, 3016(6)
		Ir[b]	20.0	

[a] Based on our experimental activation energy, $E_a{}^\circ = 3.1$ kcal/mol.

[b] Internal rotation corresponding to the $C_6H_5 \cdots C_2H_2$ torsional vibration.

[c] Based on the assumption that the activation energy for H + $C_6H_5C_2H \rightarrow C_6H_5C_2H_2$ is the same as that for H + $C_3H_4 \rightarrow CH_3C_2H_2$, 4.3 kcal/mol calculated by the BAC-MP4 method (ref. [20]).

For the production of $C_6H_5C_2H$ from the decomposition of the chemically activated $C_6H_5C_2H_2{}^\dagger$, the transition state is assumed to be semi-rigid with a thermal frequency factor $A_b = 1 \times 10^{14}$ s^{-1}, analogous to that calculated for the decomposition of CH_3CHCH into CH_3C_2H + H [20]. Thus, the geometrically averaged vibrational frequencies of $C_6H_5C_2H_2$ were slightly adjusted to match the above A-factor without varying its moments of inertia. These transition state parameters for step (b) are also included in Table II.

The calculated temperature and pressure effects on the total rate constant and the branching ratio for phenyl acetylene production, α_b are summarized in Table III and graphically presented in part in Figure 5. As indicated by the results, the total rate constant for the reaction is independent of the system pressure, whereas the branching ratio is strongly pressure-dependent. Under the conditions employed by Stein and coworkers [3,4], P= 1–10 mtorr, T = 1000–1300 K, and $k_c = 0$, $k_b = k_t$. On the other hand, under the conditions used in the present study, P = 20 torr, T = 297–523 K, we measured the total rate constant $k_t = k_b + k_c$ which is theoretically found to be

TABLE III. Effects of temperature and pressure on the total rate constant for the C_6H_5 + C_2H_2 reaction and the branching ratio for $C_6H_5C_2H$ formation.[a]

	T									
	297		500		1000		1250		1500	
P	α_b	k_t	α_b	k_t	α_b	k_t	α_b	k_t	α_b	k_t
0.001	0.48	0.20	0.92	2.41	1.0	25.7	1.0	48.2	1.0	75.8
0.01	0.12	0.20	0.68	2.41	1.0	25.7	1.0	48.2	1.0	75.8
1.0	1.85×10^{-3}	0.20	7.90×10^{-2}	2.42	0.94	25.7	0.99	48.2	1.0	75.8
20	9.33×10^{-5}	0.20	5.96×10^{-3}	2.42	0.66	25.8	0.94	48.2	0.99	75.9
100	1.87×10^{-5}	0.20	1.24×10^{-3}	2.42	0.41	25.9	0.82	48.3	0.97	75.9
760	2.46×10^{-6}	0.20	1.65×10^{-4}	2.42	0.14	26.0	0.54	48.6	0.87	76.1

[a] Total rate constants ($k_t = k_b + k_c$) are given in units of 10^{-14} cm^3/s and the branching ratio for $C_6H_5C_2H$ formation is defined as $\alpha_b = k_b/k_t$. Temperature and pressure given in units of K and torr, respectively.

pressure-independent (see Table III). Accordingly, the calculated total rate constant for the entire temperature range $297 \leq T \leq 1330$ K correlates quite well with these two independent sets of experimental data obtained under totally different conditions. It should be noted, however, that under the atmospheric combustion conditions: T = 1500 K and P = 760 torr, both $C_6H_5C_2H$ and $C_6H_5C_2H_2$ are produced by the C_6H_5 + C_2H_2 reaction (see Table III and Fig. 5).

The fact that the total rate constant is pressure-independent can be readily understood. The production of $C_6H_5C_2H$ + H is exothermic by 7 kcal/mol. Its transition state is also situated approximately 7 kcal/mol below that of the addition process (a). Thus, both the production of $C_6H_5C_2H$ measured by Stein and co-workers [3,4] at 10^{-3}–10^{-2} torr pressure and the removal of the phenyl radical measured in the

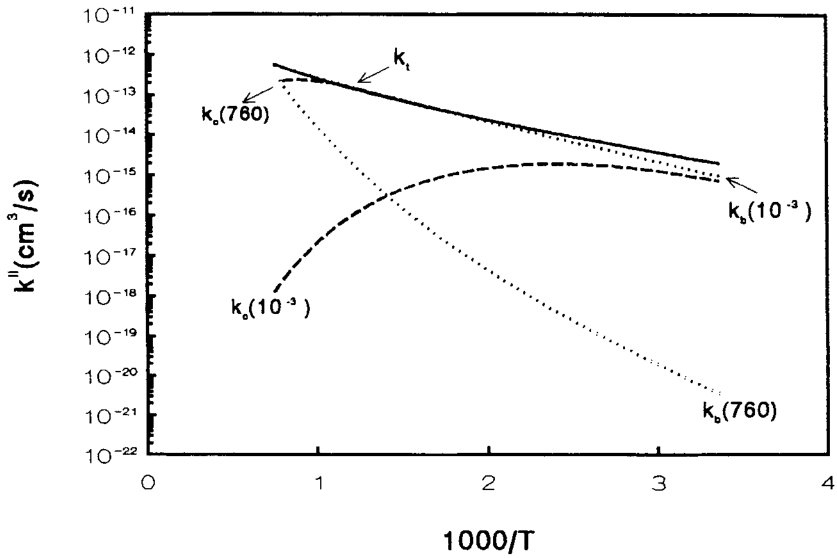

Figure 5. Results of RRKM calculations at different pressures as indicated: (—) Total rate of C_6H_5 + C_2H_2; (---) recombination rate; and (···) decomposition rate.

present work at 20 torr pressure are controlled exclusively by the addition process, which is a pressure-independent bimolecular reaction. The individual product yields under our conditions ($P = 20$ torr, $T = 297-523$ K) are, however, sensitive to both temperature and pressure as clearly indicated by the results presented in Table III.

To summarize, the rate constant reported by Stein co-workers [3,4] at high temperatures ($T = 1000-1300$ K) and low pressures ($10^{-3}-10^{-2}$ torr) for the formation of phenyl acetylene in the $C_6H_5 + C_2H_2$ reaction, assuming a phenyl recombination rate constant of 5×10^{-12} cm^3/s, can be quantitatively correlated with the total rate constant for the reaction measured at $P = 20$ torr and $T = 297-523$ K by means of the cavity-ring-down method. On the basis of the results of our TST-RRKM calculations, the formation of $C_6H_5C_2H$ and the adduct, $C_6H_5C_2H_2$ depends strongly on the pressure of the system, whereas the total rate constant for the $C_6H_5 + C_2H_2$ reaction is pressure-independent. A least-squares analysis of the calculated rate constants for 300–2000 K at the atmospheric pressure of Ar of N_2 can be given in units of cm^3/s by

$$k_b = 9.5 \times 10^{-42} T^{9.33} \exp(-1{,}713/T)$$
$$k_c = 1.8 \times 10^{-7} T^{-1.65} \exp(-2{,}711/T)$$
$$k_t = 4.1 \times 10^{-18} T^{1.77} \exp(-1{,}152/T).$$

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