Kinetics of C_6H_5 Radical Reactions with 2-Methylpropane, 2,3-Dimethylbutane and 2,3,4-Trimethylpentane

J. PARK, S. I. GHEYAS, M. C. LIN

Department of Chemistry, Emory University, Atlanta, GA 30322

Received 12 February 1999; accepted 14 May 1999

ABSTRACT: The absolute bimolecular rate constants for the reactions of C_6H_5 with 2-methylpropane, 2,3-dimethylbutane and 2,3,4-trimethylpentane have been measured by cavity ringdown spectrometry at temperatures between 290 and 500 K. For 2-methylpropane, additional measurements were performed with the pulsed laser photolysis/mass spectrometry, extending the temperature range to 972 K. The reactions were found to be dominated by the abstraction of a tertiary C–H bond from the molecular reactant, resulting in the production of a tertiary alkyl radical:

$$C_6H_5 + CH(CH_3)_3 \longrightarrow C_6H_6 + t\text{-}C_4H_9 \tag{1}$$

$$C_6H_5 + (CH_3)_2CHCH(CH_3)_2 \longrightarrow C_6H_6 + t\text{-}C_6H_{13} \tag{2}$$

$$C_6H_5 + (CH_3)_2CHCH(CH_3)CH(CH_3)_2 \longrightarrow C_6H_6 + t\text{-}C_8H_{17} \tag{3}$$

with the following rate constants given in units of $cm^3\ mol^{-1}\ s^{-1}$:

$$k_1 = 10^{(11.45 \pm 0.18)}\ e^{-(1512 \pm 44)/T}$$

$$k_2 = 10^{(11.72 \pm 0.15)}\ e^{-(1007 \pm 124)/T}$$

$$k_3 = 10^{(11.83 \pm 0.13)}\ e^{-(428 \pm 108)/T}$$

Int J Chem Kinet 31: 645–653, 1999

INTRODUCTION

Phenyl radicals play a pivotal role in the combustion of fossil fuels, particularly in the formation of polycyclic aromatic hydrocarbons (PAHs) and soots [1–3]. In a series of our kinetic studies on the reactions of C_6H_5, we have applied a newly developed ultralong path laser resonance absorption technique, that is, cavity ringdown spectroscopy (CRDS) [4–6] to acquire reliable rate constants with sensitivities down to 10^8–10^9 $cm^3\ mol^{-1}\ s^{-1}$ for the temperature range 300–523 K [6–12]. The processes investigated include O_2, NO, C_2H_2, C_2H_4, HBr, CCl_4, cycloalkanes,

---

Correspondence to: M. C. Lin (chemmcl@emory.edu)

Contract grant sponsor: Division of Chemical Sciences, Office of Energy Sciences, DOE

Contract grant number: DE-FGO2-97ER14784

among others. The kinetics and mechanisms of these reactions and the details of the CRDS technique developed for kinetic applications have recently been reviewed by the authors [13].

In the present series of studies, we center on the reactivity of C_6H_5 toward saturated hydrocarbons, with an ultimate goal of establishing specific rate constants for the abstraction of an H-atom from primary, secondary and tertiary C–H bonds. This effort requires a comprehensive kinetic measurement for a number of representative hydrocarbon molecules so as to arrive at reproducible rate constants with meaningful statistics. In this work, we measure the rate constants for C_6H_5 reactions with 2-methylpropane (isobutane, hereafter denoted as C_4H_{10}), 2,3-dimethylbutane (di-isopropyl, C_6H_{14}) and 2,3,4-trimethylpentane (C_8H_{18}). Among these gas-phase reactions, only the rate constant for the isobutane reaction has been reported [14]. This result was obtained by the conventional relative rate method and will be compared with our directly determined value later.

EXPERIMENTAL

The experimental apparatus and kinetic data acquisition by CRDS have been discussed in detail in our previous studies of C_6H_5 [6–13] and C_6H_5O [15] radical reactions. The key aspects of CRDS and the complementary pulsed laser photolysis /mass spectrometry (PLP/MS) technique, which was employed to extend the temperature range of the 2-methylpropane reaction to 972 K, are briefly summarized below.

A. CRDS

The technique measures the decay time of a pulse of probing photons with $\tau \leq 10$ ns pulse width injected inside a highly reflective optical cavity (99.99% reflectivity), half a meter in length, with and without the presence of an absorbing species. In the absence of resonance absorption by the species of interest (C_6H_5 in the present case), the nanosecond probing pulse can be lengthened to as long as 30 μs due to multiple reflections within the cavity, providing an effective path length of about 10 km. The presence of absorption will shorten the photon decay time from $t_c^o = 30$ μs to 10 ns with a broad dynamic range of 10 ns $\leq t_c \leq 30$ μs, depending on the extinction coefficient and concentration of the absorbing species. A strong absorbing species such as NO_2 can effectively diminish multiple reflections in the visible region of the spectrum at a ppm-level concentration to give rise to a 10-nanosecond CRD pulse. For C_6H_5 at 504.8 nm, $t_c \approx 0.8\, t_c^o$ under routine experimental conditions.

The chemical decay time (t') of the C_6H_5 radical under the conditions convenient for kinetic measurements ranges from 200 to 5000 μs, depending on the concentration of the molecular reactants employed. The long chemical decay time comparing with that of the probing photons allows us to separate the two decay processes and derive the following relationship [5,6] for rate constant determination:

$$1/t_c = 1/\, t_c^o + B\, [A]_0\, e^{-k't'} \qquad \text{(I)}$$

$$\text{or} \quad \ln(1/t_c - 1/t_c^o) = C - k't' \qquad \text{(II)}$$

where $C = \ln(B[A]_0)$ and $[A]_0$ is the initial concentration of the C_6H_5 radical; B is a constant related to the length of the absorbing medium, index of refraction of the medium, cavity length, extinction coefficient, etc., and k' is the pseudo-first-order decay constant of C_6H_5 in the presence of a known, excess amount of a molecular reactant, RH. Repeating the measurements over a wide range of reactant concentrations, [RH], allows us to reliably determine the second-order rate constant, k'', with the commonly used formula:

$$k' = k^0 + k''\,[\mathrm{RH}] \qquad \text{(III)}$$

where k^0 is the decay constant of C_6H_5 at $[\mathrm{RH}] = 0$ due to recombination reactions ($C_6H_5 + C_6H_5$ and $C_6H_5 + NO$) as well as diffusion out of the probing zone.

In the present study, two pulsed lasers were employed for the pump and probe processes. A Lambda Physik LPX 105E excimer laser operating at 248 nm was used to photodissociate C_6H_5NO (nitrosobenzene), a convenient phenyl radical source. The decay of C_6H_5 was probed at 504.8 nm where a strong absorption peak was demonstrated to exist [5–13]. Nitrosobenzene was placed on a sealed, fritted glass disk and carried into the reactor via a mixing tube with Ar carrier gas. On the basis of the estimated concentration of C_6H_5NO ($\sim 10^{-10}$ mol/cm^3) and our measured extinction coefficient at 248 nm, the concentration of C_6H_5 is approximately 10^{-11} mol/cm^3 in the reaction zone. A tunable excimer laser (Lambda Physik EMG 201) pumped dye laser (Lambda Physik FL3002) was employed for probing. The decay signal was measured with a photomultiplier operating at 300–700 V without amplification. The signal was averaged and stored in a LeCroy model 9310M digital oscilloscope and processed with a personal computer.

B. PLP/MS

The detail of PLP/MS has been described in a recent review on the technique [16]. The C_6H_5 radical was generated by the pulsed photolysis of $C_6H_5COCH_3$ at 193 nm. The conversion of acetophenone was in the range of 29–36%. To determine the amount of the C_6H_5 formed under the present conditions, NO was used as the C_6H_5 radical scavenger. NO titration revealed that on average about 62–69% of the dissociated acetophenone produced the C_6H_5 radical. $C_6H_5COCH_3$ carried by an excess amount of He was premixed in corrugated stainless steel tubing with C_4H_{10} before being introduced into the Saalfeld-type quartz reactor [17,18] and the products of the photoinitiated reaction were supersonically sampled and ionized by electron-impact ionization. The mole fractions of $C_6H_5COCH_3$ and 2-methylpropane were typically $< 0.1\%$ and $\sim 33\%$, respectively. Kinetic modeling of the absolute concentrations of C_6H_6 and $C_6H_5CH_3$ provides reliable determination for the rate constants of the following two reactions:

$$C_6H_5 + C_4H_{10} \longrightarrow C_6H_6 + C_4H_9$$

$$C_6H_5 + CH_3 \longrightarrow C_6H_5CH_3,$$

as has been demonstrated for the C_6H_5 reactions with H_2 [19] and CH_4 [20].

C. Chemicals

The radical sources and molecular reactants were purchased from Aldrich. Nitrosobenzene was recrystallized using ethanol as solvent and vacuum-dried before use. C_4H_{10}, C_6H_{14}, C_8H_{18}, and $C_6H_5COCH_3$ were purified by trap-to-trap distillation using appropriate slush baths. The Ar and He carrier gases (Specialty Gases, 99.999% purity) were used without further purification.

RESULTS AND DISCUSSION

A. Rate Constant Determination by CRDS

A typical set of pseudo-first-order plots, $\ln(1/t_c - 1/t_c^o)$ vs. time, for C_4H_{10}, C_6H_{14}, and C_8H_{18} is presented in Figure 1. The slopes of these plots give the apparent decay constants (k') for the specific concentrations of the molecular reactants present in the system. Figure 2 illustrates the dependence of k' on reactant concentration as depicted by equation (III). From the slope of the second-order plot for each temperature, we obtain the bimolecular rate constant for the abstraction reaction

$$C_6H_5 + RH \longrightarrow C_6H_6 + R$$

where $R = C_4H_9$, C_6H_{13} and C_8H_{17}.

Table I summarizes the bimolecular rate constants for the three reactions obtained by CRDS. These results are graphically presented in Figures 3 and 4. Weighted least-squares analyses [21] of these individual data gave rise to

$$k_1 = 10^{(11.48 \pm 0.18)}\, e^{-(1532 \pm 150)/T} \qquad (IV)$$

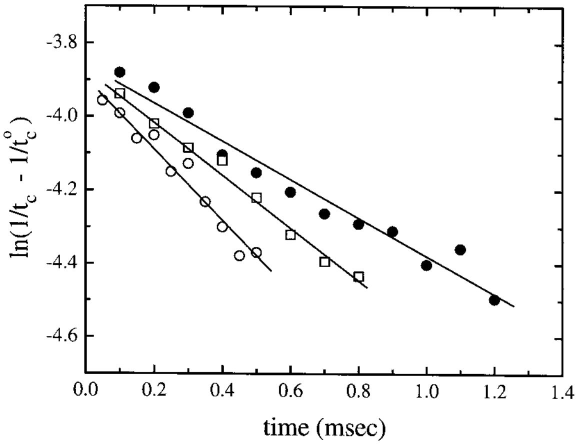


Figure 1 Typical pseudo-first-order decay plots for the reactions with C_4H_{10} (●), C_6H_{14} (□) and C_8H_{18} (○) under different, excess reactant concentrations in units of mol/cm^3. $[C_4H_{10}] = 3.87 \times 10^{-8}$ at 329 K; $[C_6H_{14}] = 2.40 \times 10^{-8}$ at 351 K; $[C_8H_{18}] = 3.02 \times 10^{-9}$ at 328 K.

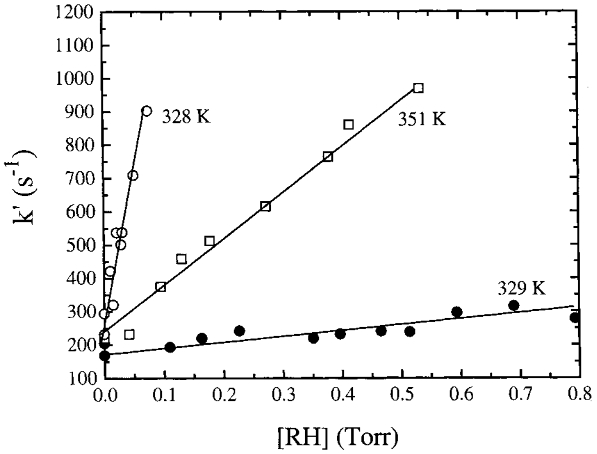


Figure 2 k' vs. [RH] for the reactions with C_4H_{10} (●), C_6H_{14} (□) and C_8H_{18} (○).

Table I Measured Bimolecular Rate Constants of C_6H_5 Reactions with 2-Methylpropane (C_4H_{10}), 2,3-Dimethylbutane (C_6H_{14}), and 2,3,4-Trimethylpentane (C_8H^{18})[a]

Reactant	T (K)	[RH] (mol/cm^3)	k (cm^3 mol^{-1} s^{-1})[b]
C_4H_{10}	295	$0–1.40 \times 10^{-7}$	$(1.23 \pm 0.61) \times 10^9$
	295	$0–3.14 \times 10^{-8}$	$(2.16 \pm 0.24) \times 10^9$
	329	$0–3.87 \times 10^{-8}$	$(2.89 \pm 0.82) \times 10^9$
	394	$0–3.85 \times 10^{-8}$	$(6.75 \pm 0.14) \times 10^9$
	416	$0–4.70 \times 10^{-8}$	$(8.91 \pm 0.16) \times 10^9$
	469	$0–2.94 \times 10^{-8}$	$(9.82 \pm 0.12) \times 10^9$
	501	$0–2.14 \times 10^{-8}$	$(2.32 \pm 0.17) \times 10^{10}$
C_6H_{14}	295	$0–2.57 \times 10^{-8}$	$(2.96 \pm 0.30) \times 10^{10}$
	298	$0–2.72 \times 10^{-8}$	$(4.80 \pm 0.68) \times 10^{10}$
	351	$0–2.40 \times 10^{-8}$	$(6.76 \pm 0.68) \times 10^{10}$
	401	$0–1.79 \times 10^{-8}$	$(8.91 \pm 1.04) \times 10^{10}$
	415	$0–1.06 \times 10^{-8}$	$(1.27 \pm 0.16) \times 10^{10}$
	435	$0–8.85 \times 10^{-9}$	$(9.92 \pm 1.06) \times 10^{10}$
	486	$0–1.48 \times 10^{-8}$	$(1.36 \pm 0.17) \times 10^{10}$
C_8H_{18}	291	$0–4.13 \times 10^{-9}$	$(2.55 \pm 0.23) \times 10^{11}$
	328	$0–3.02 \times 10^{-9}$	$(3.31 \pm 0.34) \times 10^{11}$
	387	$0–3.22 \times 10^{-9}$	$(3.10 \pm 0.20) \times 10^{11}$
	426	$0–3.17 \times 10^{-9}$	$(4.40 \pm 0.15) \times 10^{11}$
	496	$0–1.37 \times 10^{-9}$	$(4.79 \pm 0.42) \times 10^{11}$

[a] All experiments were carried out with a total pressure of 40 Torr using Ar as the carrier gas.

[b] The uncertainties represent 1σ, evaluated by weighted least-squares analysis, convoluting the errors from the determination of k' and k''.

$$k_2 = 10^{(11.72 \pm 0.15)} e^{-(1007 \pm 124)/T} \qquad (V)$$

$$k_3 = 10^{(11.83 \pm 0.13)} e^{-(428 \pm 108)/T} \qquad (VI)$$

in units of cm^3 mol^{-1} s^{-1} for the reactions with C_4H_{10}, C_6H_{14} and C_8H_{18}, respectively, in the temperature range 290–500 K.

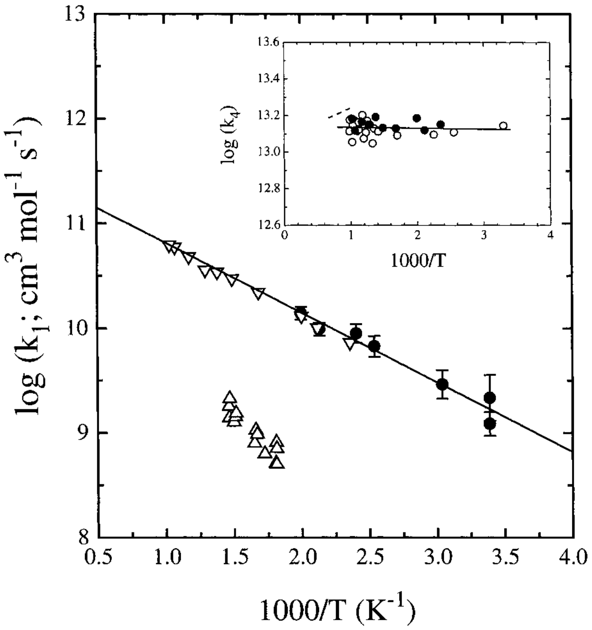


Figure 3 Arrhenius plots for the C_6H_5 reactions with C_4H_{10}. ●, this work by CRDS; ▽, this work by PLP/MS; Δ, ref. [14]. The result of ref. [14] was reevaluated using the result of Ref. 25 for the recombination reaction of phenyl radicals. Inset: Arrhenius plot of the modeled rate constant for the $C_6H_5 + CH_3$ reaction. ○, ref. [20]; ●, this work; dotted line, the recommended result of Tsang and Kiefer [26].

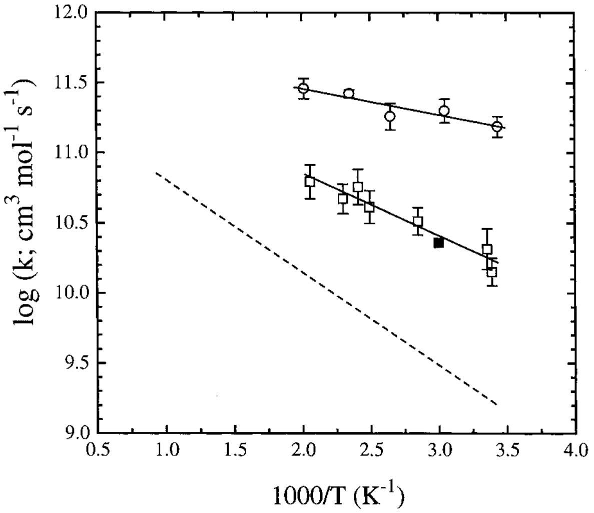


Figure 4 Arrhenius plots for the C_6H_5 reactions with C_6H_{14} (□) and C_8H_{18} (○). ■, ref. [23] for the reaction $C_6H_5 + C_6H_{14}$; dashed line, this work for the $C_6H_5 + C_4H_{10}$ reaction.

Table II Experimental Conditions,[a] Product Yields,[b] and Modeled Rate Constants[c] in the PLP/MS Experiment at the Temperatures Studied

Temp (K)	P_{tot} (mTorr)	$[C_6H_5COCH_3]_0$	$[C_6H_5]_0$	$[C_4H_{10}]_0$	$[C_6H_6]$ exp.	$[C_6H_6]$ model	$k_1 \times 10^{-10}$	$[C_6H_5CH_3]$ exp.	$[C_6H_5CH_3]$ model	$k_4 \times 10^{-13}$
424	3075	1.73	0.77	1014	0.303	0.304	0.73	0.186	0.177	1.41
472	3055	1.66	0.81	1008	0.348	0.360	1.02	0.171	0.173	1.31
500	3072	1.59	0.76	1013	0.373	0.372	1.31	0.169	0.169	1.53
594	3079	1.51	0.78	1016	0.439	0.440	2.20	0.158	0.158	1.35
672	3081	1.45	0.64	1016	0.430	0.431	2.96	0.124	0.094	1.35
725	3097	1.32	0.70	1022	0.471	0.471	3.43	0.118	0.114	1.55
774	3074	1.07	0.57	987	0.411	0.412	3.59	0.077	0.077	1.41
852	3090	1.31	0.61	992	0.466	0.464	4.81	0.078	0.075	1.46
936	3100	1.28	0.63	995	0.501	0.499	5.94	0.062	0.062	1.31
972	3071	1.34	0.66	986	0.515	0.513	6.21	0.077	0.074	1.51

[a] All concentrations are given in mTorr.

[b] Product yields were measured at t = 15 msec. Typically 3–4 runs were carried out for each temperature.

[c] In units of $cm^3\ mol^{-1}\ s^{-1}$.

B. Rate Constant Determination for C_6H_5 + C_4H_{10} by PLP/MS

For the 2-methylpropane reaction, we have also applied the PLP/MS technique and extended our temperature range up to 972 K to corroborate the two complementary techniques developed by us for C_6H_5 reaction rate measurements. The PLP/MS technique with acetophenone as the C_6H_5 source has been employed recently in our studies of the reactions with H_2, CH_4 and small alkanes containing solely primary C–H bonds (i.e., C_2H_6 and *neo*-C_5H_{12}) covering the temperature range 500–1000 K. For the H_2 [19] and CH_4 [20] reactions, excellent agreement exists between the PLP/MS and FTIR spectrometric data, using nitrosobenzene as the thermal source of C_6H_5 in the latter experiments. For the present C_6H_5 + C_4H_{10} reaction, we are particularly interested in the kinetic data above 500 K for comparison with those of C_2H_6 and *neo*-C_5H_{12} reactions which involve solely the primary C–H bonds.

Kinetic data for the C_4H_{10} reaction obtained by PLP/MS are summarized in Table II. The measured absolute yields of C_6H_6 and $C_6H_5CH_3$, as have been demonstrated in our earlier studies of the $C_6H_5 + H_2$ and CH_4 reactions, can be readily modeled using the mechanism established for these systems (see Appendix A) to give the rate constants for the two reactions:

$$C_6H_5 + RH \longrightarrow C_6H_6 + R \qquad (1)$$

$$C_6H_5 + CH_3 \longrightarrow C_6H_5CH_3 \qquad (4)$$

where R = H, CH_3 or C_4H_9 (in the present case). It is particularly gratifying to note that the values k_4 determined in this series of studies with and without the molecular reactants (H_2, CH_4 and C_4H_{10}) added, agree quantitatively as illustrated in the inset of Figure 3 with a high degree of reproducibility. A least-squares analysis of k_4 obtained from these different sets of experiments mentioned earlier gave

$$k_4 = (1.39 \pm 0.07) \times 10^{13} \exp[-(15 \pm 35)/T]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}},$$

which is nearly identical with the result derived from the data excluding those of C_4H_{10}, $k_4 = (1.38 \pm 0.08) \times 10^{13} \exp[-(23 \pm 36)/T]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ [20]. As the yields of $C_6H_5CH_3$ depend strongly on the initial concentrations of CH_3 and C_6H_5 (which were assumed to be the same as the amount of C_6H_5NO determined in our titration experiment for each experimental run), the close agreement in the values of k_4 from the different studies suggests that the simultaneous modeling of the yields of C_6H_6 and $C_6H_5CH_3$ measured can provide a reliable determination of the abstraction reaction (1). The result of our sensitivity analysis (see Appendix B) using the SENKIN program [22] indicates that the concentration of benzene varied positively and strongly with k_1, but negatively and strongly with k_4 and k_5 as we had observed in our previous studies of C_6H_5 reactions with H_2 and CH_4.

The kinetically modeled values of k_1 summarized in Table II are also presented in Figure 3 for comparison with those measured by CRDS. As is evident from the figure, the results obtained by absolute yield measurements with PLP/MS agree fully with those determined by the decay of C_6H_5 by CRDS. A least-squares analysis of both sets of data covering the 295–972 K temperature range gave rise to the following expression

$$k_1 = 10^{11.45 \pm 0.10} e^{-(1512 \pm 44)/T} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

C. Reaction Mechanism

The activation energies for the abstraction of an H-atom by C_6H_5 from C_4H_{10}, C_6H_{14}, and C_8H_{18} are 3.0 ± 0.3, 2.0 ± 0.25, and 0.85 ± 0.21 kcal/mol, respectively. The values are lower than those for the H-atom abstraction by C_6H_5 from the secondary C–H bonds in c-C_5H_{10} and c-C_6H_{12}, 4.1 and 3.8 kcal/mol, respectively [8]. These results suggest that in the present systems the reactions involve primarily the tertiary C–H bonds, resulting in the formation of t-alkyl radicals:

$$C_6H_5 + HC(CH_3)_3 \longrightarrow C_6H_6 + C(CH_3)_3 \quad (1)$$

$$C_6H_5 + (CH_3)_2(CH)_2(CH_3)_2 \longrightarrow C_6H_6 + (CH_3)_2CCH(CH_3)_2 \quad (2)$$

$$C_6H_5 + (CH_3)_2CHCH(CH_3)CH(CH_3)_2 \longrightarrow C_6H_6 + (CH_3)_2CCH(CH_3)CH(CH_3)_2 \quad (3)$$

The conclusion is consistent with the result obtained by Bridger and Russell [23] from a series of relative rate measurements at 333 K in solution using the $C_6H_5 + CCl_4 \rightarrow C_6H_5Cl + CCl_3$ reaction as a reference standard. The averaged relative reactivities of C_6H_5 toward the p-, s-, and t-CH bonds of alkanes at 333 K were determined to be 1–1.2 : 9.3 : 44. At the higher end of the temperature range studied in the present work (1000 K), however, the contribution from the primary C–H bonds of the CH_3-groups in these molecules may become significant because of their great numbers and higher activation energies.

The preceding conclusion has been substantiated by our preliminary results obtained for the C_6H_5 reactions with C_2H_6 and neo-C_5H_{12} by PLP/MS at temperatures between 667–980 K. On the per-bond basis, the ethane rate constant is nearly the same as that of the neopentane reaction at 1000 K, but smaller by a factor of 2.7 at 600 K. Accordingly, for our comparison purposes, the averaged single primary C–H bond rate constant

$$k_{p\text{-}CH} \approx 5 \times 10^{10} \exp(-2950/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \text{(VII)}$$

was employed.

In Figure 5, we compare the total rate constants measured for the three reactions with the estimated total primary C–H abstraction rate constants, $N \times k_{p\text{-}CH}$, where N = 9, 12, and 15 for 2-methylpropane, 2,3-dimethylbutane and 2,3,4-trimethylpentane, respectively. As is evident from the figure, the total rate constants for these reactions are significantly greater than the estimated total primary rate constants in the temperature range covered by CRDS (290–500 K). The result clearly suggests that the rate constants measured for these three reactions are the dominated by t-CH bond attacks. For the C_4H_{10} reaction, to which the primary C–H abstraction contribution is greatest (see Fig. 5), the estimated contribution amounts to about 7% at 500 K and about 40% at 1000 K.

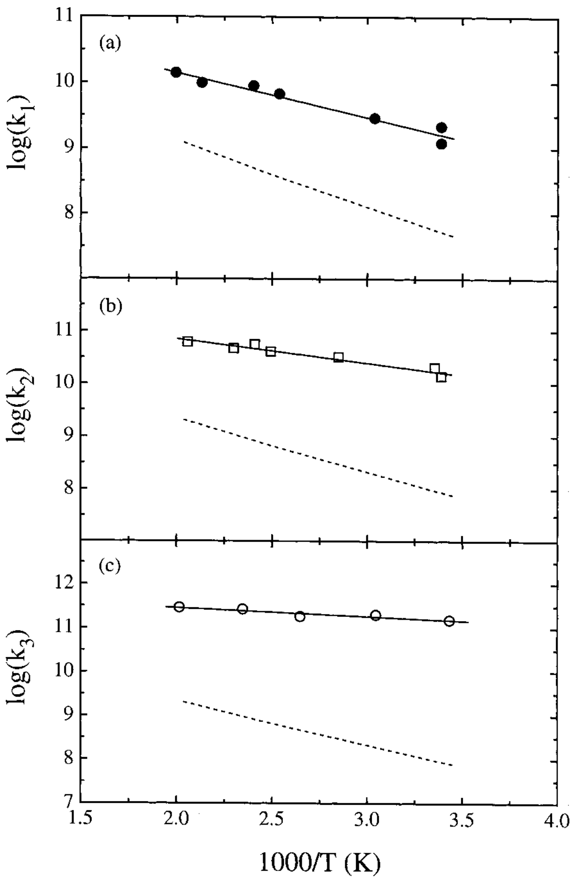


Figure 5 The comparison of the total rate constants measured for the three reactions (●, C_4H_{10}; □, C_6H_{14}; ○, C_8H_{18}) with the estimated total primary C–H abstraction rate constants (dashed lines).

The number of t-CH bonds increases from 1 to 3 for reactions (1)–(3). The increase is approximately reflected by the ratio of the A-factors, A_1:A_2:A_3 = 1:1.9:2.4, although the absolute values of k_1, k_2, and k_3 deviate widely from the 1:2:3 t-CH bond ratio. At

300 K, the averaged absolute rate constant increases from 1.8×10^9 cm^3 mol^{-1} s^{-1} for C_4H_{10} to 1.8×10^{10} cm^3 mol^{-1} s^{-1} for C_6H_{14} and 1.6×10^{11} cm^3 mol^{-1} s^{-1} for C_8H_{18}, approximately 10 times greater for each *t*-CH bond increment. At 500 K, the averaged absolute rate constants vary from 1.4×10^{10} to 7.2×10^{10} to 2.9×10^{11} cm^3 mol^{-1} s^{-1} for reactions (1)–(3), with a factor of about 4–5 increase for each C–H bond increment. These data suggest that the key factor controlling the rates of the three reactions is probably the interaction dynamics between C_6H_5 and the hydrocarbon reactants, influenced strongly by the accessibility of C_6H_5 to the small H-atom in the presence of the large number of the less reactive CH_3-bonds (i.e., steric hindrance). Clarification of the rate-controlling factor may be greatly aided by ab initio quantum calculations for the three different types of C–H bonds in varying molecular sizes. For both $C_6H_5 + H_2$ and CH_4 reactions, the results of our recent calculations using a modified Gaussian-2 method indicates a promising prospect for the mechanistic interpretation of these reaction systems [19,20,24] at a relatively high theoretical level.

D. Comparison with Other Studies

For reaction (1), Duncan and Trotman-Dickenson [14] had previously reported the following expression for the temperature range 550–680 K: $k_1 = 6 \times 10^{11}$ e$^{-3370/T}$ cm^3 mol^{-1} s^{-1} based on the assumed, large rate constant for the reference reaction: $C_6H_5 + C_6H_5 \rightarrow C_{12}H_{10}$, $k_5 = 1.0 \times 10^{14}$ cm^3 mol^{-1} s^{-1}. The absolute rate constant for the C_6H_5 recombination reaction has been measured recently in our laboratory in the temperature range 300–500 K, $k_5 = 1.39 \times 10^{13}$ e$^{-56/T}$ cm^3 mol^{-1} s^{-1} [25]. We have used this new result to rescale Duncan and Trotman-Dickenson's data. The rescaled results which are about 2.7 times smaller have been included in Figure 3 for comparison with our values. As is evident from the figure, Duncan and Trotman-Dickenson's results are a factor of 20–30 lower than our values across their temperature range studied. The validity of these authors' work for C_6H_5 reactions with this and other molecules reported in the same paper (CH_4, *c*-C_3H_6, and $C_6H_5COCH_3$), obtained by steady-state photolysis of acetophenone at unspecified wavelengths, should be further examined in the near future using different kinetic methods. For $C_6H_5 + CH_4$ our recent results obtained by PLP/MS and FTIR spectrometry [20] were also found to be significantly higher than that reported by the same authors.

As mentioned previously, Bridger and Russell [23] studied the reaction of C_6H_5 with a large number of hydrocarbons in solution using $C_6H_5 + CCl_4$ as the reference standard. For C_6H_{14} and C_8H_{18}, they reported the relative rate constants at 333 K, $k_H/k_{Cl} = 1.19$ for C_6H_{14} and 0.97 for C_8H_{18}. Using the absolute rate constant obtained by CRDS for $C_6H_5 + CCl_4 \rightarrow C_6H_5Cl + CCl_3$ in the temperature range 297–523 K [8], $k_{Cl} = 1.2 \times 10^{12}$ e $^{-1379/T}$ cm^3 mol^{-1} s^{-1}, we arrived at the values $k_2 = 2.3 \times 10^{10}$ and $k_3 = 1.9 \times 10^{10}$ cm^3 mol^{-1} s^{-1}. The former agrees closely with our result, $k_2 = 2.5 \times 10^{10}$ cm^3 mol^{-1} s^{-1}, whereas the latter is lower than ours by as much as factor of 10 at the same temperature. We have previously compared our absolute rate constant for *c*-C_5H_{10} and *c*-C_6H_{12} with Bridger and Russell's solution data using the CCl_4 reaction as the reference standard; the agreement was found to be reasonable for *c*-C_6H_{12} and less satisfactory for *c*-C_5H_{10} [8].

CONCLUSION

The cavity ringdown spectrometric method, first developed in this laboratory for kinetic applications in 1991, has been employed to determine the absolute rate constants for C_6H_5 reactions with 2-methylpropane, 2,3-dimethylbutane and 2,3,4-trimethylpentane in the temperature range 290–500 K. For 2-methylpropane, we have extended the temperature range to 972 K by means of the PLP/MS technique; the results obtained by the two different methods agree closely. The A-factors of these reactions were found to increase from $10^{11.45}$ for C_4H_{10} to $10^{11.72}$ for C_6H_{14} and $10^{11.83}$ for C_8H_{18} in units of cm^3 mol^{-1} s^{-1}, reflecting approximately the ratio of the number of the tertiary C–H bonds in these molecules, 1:2:3. However, the activation energies for these reactions, 3.0 ± 0.1, 2.0 ± 0.25, and 0.85 ± 0.21 kcal/mol, respectively, decrease rapidly with increasing molecular size. This finding suggests that the key rate-controlling factors in these reactions aside from the radical-molecule attractive potential (which increases with molecular size), may lie in the accessibility of the *t*-CH bonds in these molecules which becomes more exposed and accessible as their molecular size increases.

The rate constants of these reactions in the temperature range covered by CRDS (290–500 K) result primarily from a tertiary C–H bond abstraction. For the C_4H_{10} reaction, the contribution from the primary C–H attack, based on our preliminary data of C_6H_5 reactions with ethane and neopentane, amounts to about 7% at 500 K and about 40% at 1000 K. Both experimental and theoretical studies are underway to acquire a wide body of information on the relative reactivities of phenyl toward different types of C–H bonds in a variety of hydrocarbons.

The authors gratefully acknowledge the support of this work by the Division of Chemical Sciences, Office of Energy Sciences, DOE, under contract no. DE-FGO2-97ER14784.

Appendix A Reactions and Rate Constants[a] Used in the Modeling of the $C_6H_5 + C_4H_{10}$ Reaction in the PLP/MS Experiment

Reactions	A	n	E_a	Ref.[c]
1. $C_6H_5 + C_4H_{10} => C_6H_6 + C_4H_9$	2.82E + 11[b]	0.0	3004	This work
4. $CH_3 + C_6H_5 = C_7H_8$	1.39E + 13	0.0	30	This work
5. $C_6H_5 + C_6H_5 = C_{12}H_{10}$	1.39E + 13	0.0	111	
6. $C_4H_9 + C_4H_9 => C_8H_{18}$	1.24E + 16	−1.5	0	27
7. $C_4H_9 + C_4H_9 => C_4H_{10} + C_4H_8$	3.46E + 12	0.0	0	27
8. $C_6H_5 + C_4H_9 => C_{10}H_{14}$	4.15E + 14	−0.75	56	d
9. $C_6H_5 + C_4H_9 => C_6H_6 + C_4H_8$	1.26E + 13	0.0	−600	e
10. $CH_3 + C_4H_9 => CH_4 + C_4H_8$	1.26E + 13	0.0	−600	27
11. $CH_3 + C_4H_9 => C_5H_{12}$	1.63E + 13	0.0	−600	27
12. $C_6H_5 + CH_4 = C_6H_6 + CH_3$	1.42E + 06	2.0	10100	
13. $2CH_3(+M) = C_2H_6\ (+M)$ LOW / 1770E + 50 −9.670 6220.00/ TROE/ .5325 151.00 1038.00 4970.00/ $CO/1.50/C_4H_{10}/3.00/C_6H_5COCH_3/5/HE/.70/$	2.12E + 16	−1.0	620	
14. $C_6H_5 + C_7H_8 => C_6H_6 + C_7H_7$	4.15E − 03	4.5	−1590	
15. $C_6H_5 + C_6H_5COCH_3 => C_6H_6 + C_6H_5COCH_2$	4.15E − 03	4.5	−1590	
16. $C_6H_5 + C_6H_5COCH_3 => C_{12}H_{10}COCH_3$	1.00E + 12	0.0	4000	
17. $CH_3 + C_7H_8 = CH_4 + C_7H_7$	5.50E + 11	0.0	12000	
18. $C_7H_7 + C_7H_7 => C_{14}H_{14}$	2.51E + 11	0.4	0	
19. $CH_3 + C_6H_5COCH_3 => CH_4 + H_5COCH_2$	5.01E + 10	0.0	7400	
20. $C_6H_5COCH_2 + CH_3 => C_6H_5COC_2H_5$	5.00E + 12	0.0	0	
21. $C_6H_5COCH_2 + C_6H_5 => C_{12}H_{10}COCH_2$	1.19E + 13	0.0	220	
22. $C_6H_5COCH_2 + C_6H_5COCH_2 => (C_6H_5COCH_2)_2$	2.51E + 11	0.4	0	
23. $C_6H_5COCH_2 => C_6H_5 + CH_2CO$	4.00E + 14	0.0	29400	
24. $C_{12}H_{10}COCH_3 => C_{12}H_{10} + CH_3CO$	1.00E + 08	0.0	0	
25. $CH_3 + CH_3CO = CH_3COCH_3$	4.04E + 15	−0.8	0	
26. $CH_3CO + M = CH_3 + CO + M$	8.74E + 42	−8.6	22420	

[a] Rate constants are defined by $k = A\,T^n \exp(-E_a/RT)$ and in units cm^3, mol, and s; E_a is in the units of cal/mol.

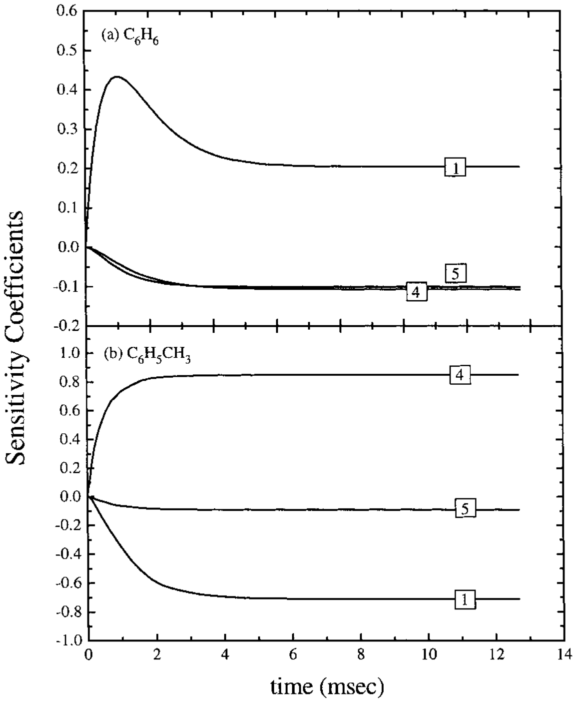
[b] Read as 2.82×10^{11}.

[c] Ref. 20 otherwise noted.

[d] Assumed; based on the reaction value of $\sqrt{k_5 \cdot k_6}$.

[e] Assumed; based on the reaction (10).

Appendix B The result of sensitivity analyses for C_6H_6 (a) and $C_6H_5CH_3$ (b) formed in the photolysis of $C_6H_5COCH_3$ in the presence of 2-methylpropane at 972 K. The condition is given in Table II. Sensitivity coefficients less than 0.01 are not included in the figure.



BIBLIOGRAPHY

1. Glassman, I. Combustion, 2nd ed.; Academic Press: New York, 1986.
2. Fahr, A.; Mallard, S. G.; Stein, S. E. Twenty-first Symposium (International) on Combustion 1986, The Combustion Institute, Pittsburgh, PA, 825.
3. Fahr, A.; Stein, S. E. Twenty-second Symposium (International) on Combustion 1988, The Combustion Institute, Pittsburgh, PA, 1023.
4. O'Keefe, A.; Deacon, D. A. G. Rev Sci Instrum 1988, 59, 2544.
5. Yu, T.; Lin, M. D. J Am Chem Soc 1993, 115, 4371.
6. Lin, M. C.; Yu, T. Int J Chem Kinet 1993, 25, 875
7. Yu, T.; Lin, M. C. Int J Chem Kinet 1994, 26, 771.
8. Yu, T.; Lin, M. C. J Phys Chem 1995, 99, 8599.
9. Yu, T.; Lin, M. C.; Melius, C. F. Int J Chem Kinet 1994, 26, 1095.
10. Yu, T.; Lin, M. C. J Am Chem Soc 1994, 116, 9571.
11. Yu, T.; Lin, M. C. Combust Flame 1995, 100, 169.
12. Yu, T.; Lin, M. C. J Phys Chem 1994, 98, 9697.
13. Park, J.; Lin, M. C. American Chemical Society Special Publication Series on Cavity Ringdown Spectroscopy, 720, Chapter 13, 196, 1999.
14. Duncan, F. J.; Trotman-Dickenson, A. F. J Chem Soc 1962, 4672.
15. Yu, T.; Mebel, A. M.; Lin, M. C. J Phys Org Chem 1995, 8, 407.
16. Park, J.; Lin, M. C. Recent Research Development in Physical Chemistry, Transworld Research Network, 2, 965, 1998.
17. Wyatt, J. R.; DeCorpo, J. J.; McDowell, W. V.; Saalfeld, F. E. Rev Sci Instrum 1974, 45, 916.
18. Wyatt, J. R.; DeCorpo, J. J.; McDowell, M. V.; Saalfeld, F. E. Int J Mass Spectrom Ion Phys 1975, 16, 33.
19. Park, J.; Dyakov, I. V.; Lin, M. C. J Phys A: 101 1997, 8839.
20. Tokmakov, I. V.; Park, J.; Gheyas, S. I.; Lin, M. C. J Phys A, 1999, 103, 3636.
21. Cvetanovic, R. J.; Singleton, D. L.; Paraskevopoulos, G. J Phys Chem 1979, 83, 50.
22. Luts, A. E.; Lee, R. K.; Miller, J. A. SENKIN: A FORTRAN Program for Predicting Homogeneous Gas-Phase Chemical Kinetics with Sensitivity Analysis; Sandia National Laboratories Report No. SANDIA 89-8009, 1989.
23. Bridger, R. F.; Russell, G. A. J Am Chem Soc 1963, 85, 3754.
24. Mebel, A. M.; Lin, M. C.; Yu, T.; Morokuma, K. J Phys A 1997, 101, 3189.
25. Park, J.; Lin, M. C. J Phys A 1997, 101, 14.
26. Tsang, W.; Kiefer, J. H. In The Chemical Dynamics and Kinetics of Small Radicals; Liu, K., Wagner, A. F., Eds.; World Scientific: Singapore, 1996; Part I, p 58.
27. NIST Chemical Kinetics Database, 2Q98 (1998).