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Kinetics of Phenyl Radical Reactions Studied by the "Cavity-Ring-Down" Method

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Phenyl radical (C_6H_5) is believed to be a most important reactive intermediate, responsible for the production of polyaromatic hydrocarbons (PAHs), precursors to soot formation in hydrocarbon combustion reactions.[1] Despite its relevancy to one of the most important problems in combustion chemistry today, there have been very limited gas-phase studies on the kinetics of C_6H_5 reactions. In fact, there has been only one absolute rate measurement which appeared recently in the literature.[2] The results of this study, however, may be questionable, as will be discussed later. The majority of approximately a dozen rate constants for C_6H_5 reactions in the gas phase reported to date have been measured with the relative rate method, based on a wide range of assumed values for the rate constant of the reference reaction, $C_6H_5 + C_6H_5 \rightarrow C_{12}H_{10}$.[3–5]

In this communication, we report the absolute values of rate constants for several C_6H_5 reactions at room temperature obtained with a new multipass laser absorption technique. This technique was first employed for spectroscopic measurements of weak transitions by O'Keefe et al.,[6,7] who referred to it as the "cavity-ring-down" method. In the present study, we have extended the use of this potentially very powerful and sensitive technique for kinetic measurement for the first time.

In our kinetic study, two lasers were employed sequentially. The first (KrF) laser operating at 248 nm was used to photolyze nitrosobenzene for the production of the C_6H_5 radical. The photolysis laser was introduced into the reaction system through three quartz ports perpendicular to the axis of the flow-tube reactor. The second tunable pulsed laser (Laser Photonics N_2-laser pumped dye laser) was introduced into the system to probe the radical along the axis of the flow reactor, which was vacuum-sealed with a pair of custom-made, highly reflective mirrors ($R = 0.9999$ at 500 nm). The two mirrors were carefully aligned with a He–Ne laser to form a low-loss optical resonator.

Similar to O'Keefe's spectroscopic studies,[6,7] our kinetic measurement was carried out by determining the photon lifetime of the probing laser pulse injected into the optical cavity through one of the cavity mirrors. The photon decay time measured with a photomultiplier behind the second cavity mirror can be described by the equation[8]

$$-\mathrm{d}\phi/\mathrm{d}t = \phi(\alpha cl/nL + 1/t_c^\circ) \qquad (1)$$

where ϕ is the number of photons injected into the cavity, t_c° is the photon decay time in the absence of absorbing species (whose presence shortens the decay time), l is the length of the absorbing medium, L is the cavity length formed by the two mirrors, n is the index of refraction of the absorbing medium, c is the velocity of light, and α is the absorption coefficient. Integration of eq 1 gives rise to

$$\phi = \phi_0 \exp(-t/t_c) \qquad (2)$$

where

$$1/t_c = \alpha cl/nL + 1/t_c^\circ \quad \text{or} \quad 1/t_c - 1/t_c^\circ = \alpha cl/nL \qquad (3)$$

In eq 3, the absorption coefficient α is the product of the extinction coefficient ϵ and the concentration of the absorbing species of interest, $[A]_{t'}$, at t' after the firing of the photodissociation laser. The photolysis laser generates an initial concentration of the absorbing species ($[A]_0$) which decays exponentially in the presence of an excess amount of a molecular reactant. Thus, eq 3 can be written as

$$1/t_c - 1/t_c^\circ = (cl\epsilon/nL)A_0 \exp(-k't')$$
$$\text{or } \ln(1/t_c - 1/t_c^\circ) = B - k't' \qquad (4)$$

where $B = \ln(cl\epsilon[A]_0/nL)$ and k' is the pseudo-first-order decay constant of the reactive species (C_6H_5).

Equation 4 describes the existence of a linear relationship between the measured photon decay times with and without the absorbing species (t_c and t_c°, respectively) and the chemical decay time of the species. This relationship is illustrated in Figure 1A for the reaction of C_6H_5 with NO, HBr, O_2, and C_2H_2. The slopes of these plots give the pseudo-first-order decay constants for C_6H_5 in the presence of different concentrations of individual reactants. The absolute values of second-order rate constants, k'', for individual reactions can then be obtained from the slopes of the linear plots of k' vs concentration as depicted in Figure 1B. In Table I we summarize the second-order rate constants measured at room temperature for several selected C_6H_5 reactions.

At this juncture, it should be pointed out that the magnitudes of various decay times referred to above limit the dynamic range of this new kinetic technique. The probing dye laser has a pulse width (FWHM) of about 10 ns, which effectively limits the shortest chemical and photon decay times one can measure for a strong absorbing species. In the present case, the chemical decay time (which depends on the reactivity and concentration of the radical of interest) in the absence of a molecular reactant lasted as long as 5–10 ms, depending on the pumping speed used (see Figure 1A for the [R] = 0 case). The photon decay time, t_c, may have a dynamic range of $10 \text{ ns} \le t_c \le t_c^\circ$, where the value of t_c° in vacuum depends on the quality of the optical cavity (i.e., reflectivity of the two mirrors and mirror alignment). In the present study near 500 nm, t_c° was found to vary typically within 25 ± 5 μs. The exact values of t_c and t_c° were measured with a multichannel analyzer for every data point shown in Figure 1A with the photolysis laser on and off, respectively, for each flowing reaction mixture studied. No absorption by any of the reactants (listed in Table I) and their reaction products was noted within the spectral range probed, 480–510 nm. The absorption spectrum of the C_6H_5 radical produced by the photodissociation of C_6H_5-NO at 248 nm measured in the present study agrees closely with that reported by Porter and Ward[9] in the same spectral region. On the basis of these facts, the chemical decay time of C_6H_5 under the present experimental conditions had a dynamic range of $\sim 10^2$ with $t_c^\circ < t' < 5$ ms.

Some of the reactions studied here have been investigated recently by Preidel and Zellner[2] at low temperatures using the conventional multipass absorption technique and by Stein and co-workers[4,5] using the relative rate method for temperatures above 1000 K. For those reactions commonly studied by the three groups, $C_6H_5 + C_2H_2$ and C_2H_4, the agreement among the three has been rather poor. Of the four reactions (O_2, C_2H_2, C_2H_4, and NO) studied by us and also by Preidel and Zellner,

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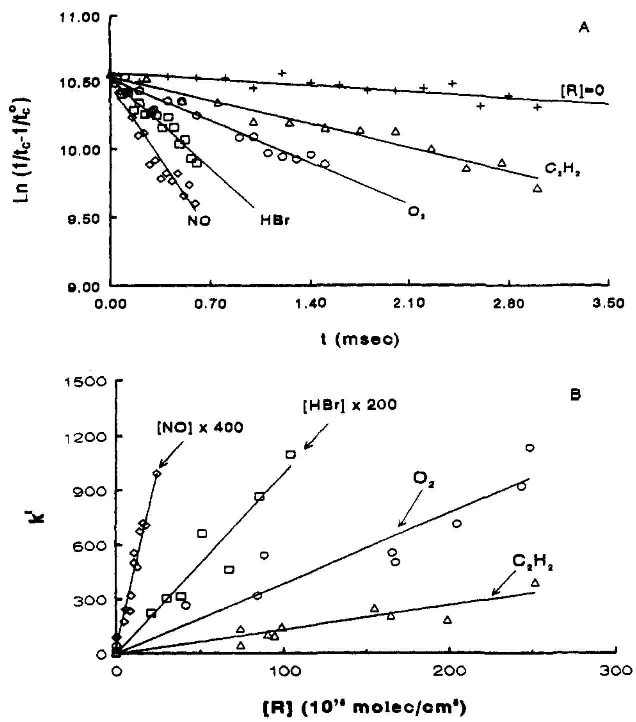

Figure 1. (A) Typical pseudo-first-order plots for C_6H_5 reactions with NO, HBr, O_2, and C_2H_2. (B) Typical k^1 vs reactant concentration plots for C_6H_5 reactions with indicated reactants. The concentrations of NO and HBr have been multiplied by the factors indicated so as to scale with other slower reactions.

Table I. Rate Constants (in cm³/s) for C_6H_5 Reactions with Selected Molecules at Room Temperature (297 K)

reactant	this study	Preidel and Zellner[a]	Fahr and Stein[b]
HBr	$(1.99 \pm 0.24) \times 10^{-12}$		
CH_2O	$(2.90 \pm 0.56) \times 10^{-14}$		
O_2	$(3.87 \pm 0.43) \times 10^{-15}$	$\leq 10^{-17}$	
C_2H_2	$(1.51 \pm 0.26) \times 10^{-15}$	$\leq 8 \times 10^{-16}$	(2.4×10^{-16})
C_2H_4	$(8.38 \pm 0.60) \times 10^{-16}$	$\leq 8 \times 10^{-17}$	(1.1×10^{-16})
C_6H_6		$\leq 1.1 \times 10^{-15}$	(2.9×10^{-18})
NO	$(1.97 \pm 0.13) \times 10^{-11}$	1.1×10^{-11}	
NO_2		8.2×10^{-12}	
C_4H_4	$(7.99 \pm 2.99) \times 10^{-15}$		

[a] Reference 2. [b] Reference 5. The values given in parentheses were extrapolated from data obtained above 1000 K. The high-temperature rate constants were evaluated by assuming a value of 5×10^{-12} cm³/s for the C_6H_5 recombination reaction.

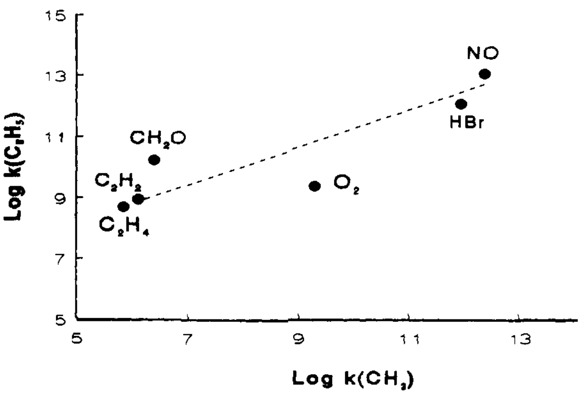

Figure 2. Correlation between selected rate constants for phenyl and methyl radical reactions at room temperature. (For convenience of scaling, the rate constants are given in units of cm³/mol s). k_{CH_3} for HBr and NO are from refs 10 and 11, respectively, and the rest of the reactions from ref 12.

only one reaction, C_6H_5 + NO, appears to be in reasonable agreement. This agreement may actually be fortuitous, because Preidel and Zellner,[2] who employed a CW Ar^+ laser operating at 488 nm probing the shoulder of a known absorption band reported by Porter and Ward,[9] failed to measure all but two of the nine reactions studied. In our experiments, we monitored two of the strongest absorption bands near 505 nm,[9] resulting in much faster C_6H_5 decay times than those reported by Preidel and Zellner.[2] It is quite likely that these authors actually measured the reactions of other reactive species which might also be generated by the photodissociation of their precursor molecules at 248 nm. Our results given in Table I correlate reasonably with the corresponding CH_3 radical reactions[10-12] as illustrated in Figure 2.

To summarize, for the first time we have applied a new multipass laser absorption (or "cavity-ring-down") method to a kinetic study. The results of C_6H_5 radical reactions obtained in this preliminary study reveal that the technique is potentially quite powerful for not only spectroscopic but also quantitative kinetic measurements. For C_6H_5, an important "benchmark" aromatic radical, the ability of measuring its absolute reaction rates finally appears to be technically feasible.

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Supplementary Material Available: Experimental details, including a schematic diagram of the experimental setup; wavelength scans of C_6H_5; absorption band positions of C_6H_5 (6 pages). Ordering information is given on any current masthead page.

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