Temperature Dependence of the Reactions of Phenyl Radicals with 1,1-Diphenylethylene, Carbon Tetrachloride, and Cyclohexene†

Dean Weldon, Stacey Holland, and J. C. Scaiano*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5

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The reaction of phenyl radicals with 1,1-diphenylethylene (DPE), carbon tetrachloride, and cyclohexene has been examined over a range of temperatures using laser flash photolysis techniques. The activation energies are 0.71 ± 0.04, 3.53 ± 0.11 and 2.32 ± 0.33 kcal/mol, and the preexponential factors, expressed as log (A/$M^{-1}s^{-1}$), are 9.19 ± 0.03, 8.96 ± 0.09, and 9.02 ± 0.26, for DPE, CCl_4, and c-C_6H_{10}, respectively. In particular the CCl_4 data provide a much needed reference for competitive studies.

Several absolute rate constants for the reactions of phenyl radicals in solution have been reported during the last 15 years.[1−4] Most of those involving unsubstituted phenyl radicals in solution derive from our 1983 article.[1] In addition, a few values have been reported in the gas phase,[5−7] and in aqueous solution for *p*-carboxyphenyl radicals.[3,8−10] In fact, an early article by Madhavan, Schuler, and Fessenden[8] reported the first absolute values in solution. The same radical has also been examined in recent work.[10] To the best of our knowledge, the temperature dependence of phenyl radical reactions has not been examined in solution, and only a very few systems have been examined in the gas phase.[5−7]

Our choice of substrates deserves some comment. Carbon tetrachloride has been a frequent choice as reference substrate by those carrying out competitive studies.[11−14] Absolute values of the rate constants and the corresponding activation parameters facilitate the conversion of data from competitive studies into absolute values. The reasons are somewhat different in the case of cyclohexene. In our earlier work,[1] our sources of phenyl radicals were the photodecompositions of iodobenzene and of benzoyl peroxide. The latter decomposes to benzoyloxyl radicals, that at the time were believed to decarboxylate very rapidly to yield phenyl radicals. In the late 1980s, work by Ingold's and Tokumaru's groups, using laser and ESR techniques, showed that decarboxylation of benzoyloxyl radicals is not as fast as assumed in our earlier report.[15−19] We were fortunate in our earlier phenyl radical study that most rate constants were verified with iodobenzene (which obviously cannot incorporate benzoyloxyl-related errors) as a radical precursor. A worrisome exception was the case of cyclohexene, a system where the rate constant was not verified with iodobenzene as a phenyl radical precursor;[1] further, the presence of allylic hydrogens makes it a good candidate for high reactivity toward oxygen-centered radicals.[20] Our choice of cyclohexene as a second substrate was a reflection of the concerns mentioned above. Our use of 1,1,2-trichloro-trifluoroethane (Freon-113) as solvent follows on our earlier observation that it is a relatively unreactive solvent toward phenyl radicals.

The kinetic studies reported herein were carried out with laser flash photolysis techniques (see Experimental Section). Phenyl radicals are not readily detectable in the spectral region (near UV and visible) where typical phenyl radical precursors (such as iodobenzene or benzoyl peroxide) are transparent. We thus resorted to the "probe technique", a method that we developed about 20 years ago and that has proven useful in the study of numerous free radicals and other reaction intermediates.[21] In the probe technique, one needs to identify a substrate that upon reaction with the intermediate of interest yields a product with a convenient absorption in the spectral region accessible. The "product" may be a transient that is long-lived in the time scale of interest. In our earlier work on phenyl radicals,[1] we used diphenylmethanol (yielding diphenyl ketyl radicals) or β-methylstyrene (yielding readily detectable benzylic

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† Dedicated to Professor A. L. J. Beckwith, a friend who knows how to enjoy a good rate constant, on the occasion of his retirement from the Australian National University.

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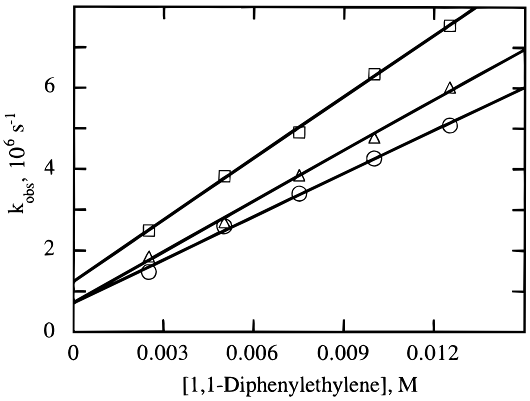

Figure 1. Concentration dependence of the growth rate constant, k_{growth}, for the reaction of phenyl radical with 1,1-diphenylethylene in freon-113 at three different temperatures, 41 °C (□), −1 °C (△), and −33 °C (○). Monitored at 330 nm.

radicals) as probes for the phenyl radical. In the present study, we have used 1,1-diphenylethylene as probe. Thus, reactions 1 and 2 yield a strongly absorbing free radical (**I**) with λ_{max} ~330 nm.

$$\mathrm{PhI} \xrightarrow{h\nu} \mathrm{Ph}^\bullet + \mathrm{I}^\bullet \tag{1}$$

$$\mathrm{Ph}^\bullet + \mathrm{CH_2{=}CPh_2} \rightarrow \underset{\mathbf{I}}{\mathrm{PhCH_2{-}\dot{C}Ph_2}} \tag{2}$$

The growth of **I** following laser excitation follows pseudo first order kinetics (k_{growth}) according to eq 3[22]

$$k_{growth} = k_0 + k_2[\mathrm{Ph_2C{=}CH_2}] \tag{3}$$

where k_0 is the rate constant for radical decay in the absence of scavenger, and in this case, may be dominated by reaction with the solvent. Figure 1 shows plots from 1,1-diphenylethylene according to eq 3 at three different temperatures. From the slopes one obtains k_2's of (3.54 ± 0.13) × 10^8 M^{-1} s^{-1}, (4.16 ± 0.15) × 10^8 M^{-1} s^{-1}, (5.05 ± 0.11) × 10^8 M^{-1} s^{-1} at −33 °C, −1 °C, and 41 °C, respectively.

Addition to the system of a substrate that does not yield a signal upon reaction with phenyl radicals (e.g. CCl_4, see reaction 4) leads to growth kinetics for **I** that can be expressed by eq 5.

$$\mathrm{Ph}^\bullet + \mathrm{CCl_4} \rightarrow \mathrm{PhCl} + \mathrm{Cl_3C}^\bullet \tag{4}$$

$$k_{growth} = k_0 + k_2[\mathrm{Ph_2C{=}CH_2}] + k_4[\mathrm{CCl_4}] \tag{5}$$

Thus, if the concentration of 1,1-diphenylethylene is kept constant, and that of the substrate (carbon tetrachloride in the example above) is changed, eq 5 allows the determination of the rate constant for reaction 4, even if this reaction involves reactants and products, all of which are invisible to the technique employed. A similar analysis allows the determination of rate constants for cyclohexene where the dominant reaction is presumed to be abstraction of allylic hydrogens. Typical quenching plots are shown in Figure 2. The experiments can be repeated at various temperatures, thus leading to the Arrhenius plots of Figure 3. Full details of each determination are available as supporting information. Analysis of the slopes and intercepts in Figure 3 give the data of Table 1.

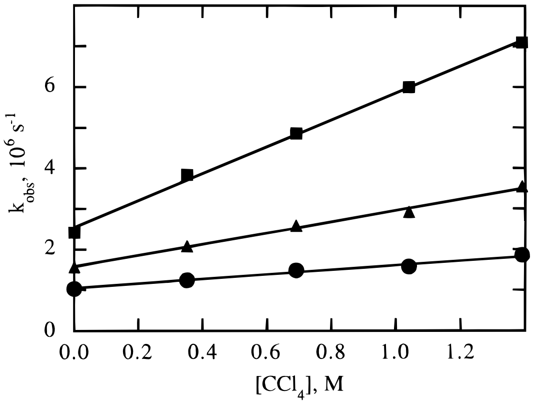

Figure 2. Concentration dependence of the growth rate constant, k_{growth}, for the reaction of phenyl radical with CCl_4 in freon-113 at three different temperatures, 40 °C (■), 0 °C (▲), and −33 °C (●). Probed with 2 mM 1,1-diphenylethylene and monitored at 330 nm.

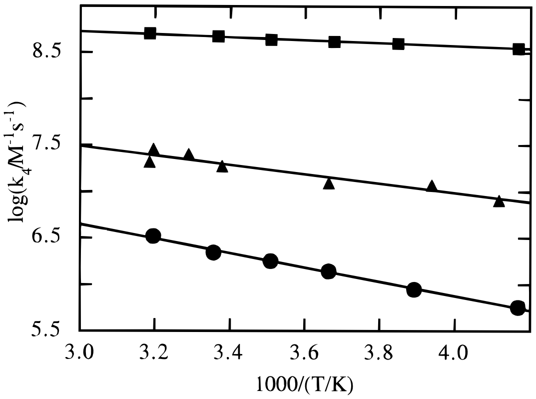

Figure 3. Arrhenius plots for the temperature dependence of the reactions of 1,1-diphenylethylene (■), cyclohexene (▲), and carbon tetrachloride (●) with phenyl radicals in freon-113. The phenyl radicals were produced from 308 nm laser flash photolysis of iodobenzene. In the cases of cyclohexene and carbon tetrachloride the reactions were probed with 2 mM 1,1-diphenylethylene.

Table 1. Kinetic Data from the Variable Temperature Studies

substrate	E_a, kcal/mol	log (A/M^{-1} s^{-1})	k(M^{-1} s^{-1}) at 25 °C
1,1-diphenylethylene	0.71 ± 0.07	9.19 ± 0.03	(4.66 ± 0.04) × 10^8
CCl_4	3.53 ± 0.11	8.96 ± 0.09	(2.33 ± 0.06) × 10^6
cyclohexene	2.32 ± 0.33	9.02 ± 0.26	(2.07 ± 0.14) × 10^7

For CCl_4, the values compare well with gas phase data which gives log (A/M^{-1} s^{-1}) of 9.10 ± 0.08 and an activation energy of 2.8 ± 0.2 kcal/mol.[5,7] The room temperature rate constants are in line with those reported earlier by Lorand[23] and by our group.[1] For cyclohexene, the rate constants at room temperature are about 1 order of magnitude lower than reported earlier, suggesting that benzoyloxyl radicals must have introduced errors in our earlier determination of this value, where the relatively modest reactivity of phenyl and high reactivity of benzoyloxyl must have compounded to lead to the high rate constant reported earlier.[1]

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[22] The fate of the iodine atoms has been discussed in an earlier publication (see ref 1). They do not interfere with the determination of k_{growth}.

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In particular, the CCl_4 data should provide a much needed reference for competitive studies in solution. While data for other substrates has recently become available in aqueous solution, it should be noted that reactivities by phenyl and *p*-carboxyphenyl appear to be somewhat different, at least in the case of oxygen.[2-4] Similarly with other substrates there are significant differences (occasionally exceeding a factor of 2) reported between phenyl and substituted derivatives;[3] in any event, it is clear that the fact that phenyl is a σ-radical still makes these differences smaller than they would be otherwise. Further, studies with CCl_4, the "standard" reference substrate, are limited to organic media, where CCl_4 is soluble.

We believe that for other substrates in our earlier report,[1] there is no need to revise the values for phenyl radical reactivity. Among the few substrates that were not examined with iodobenzene as a phenyl precursor, carbon tetrachloride is unreactive toward benzoyloxyl, and our current results agree well with the earlier report.[1] Further, under the conditions of our earlier work benzoyloxyl can decarboxylate photochemically in a two-photon process[16] (thus adding an instantaneous source of phenyl), and unsubstituted benzoyloxyl has a lifetime of ca. 500 ns at infinite dilution and shorter under most experimental conditions.[15,16]

Given the essentially identical values of the three preexponential factors determined here, as well as the gas phase value for CCl_4, we suggest that when the temperature dependence is not available, it may be a reasonable approximation to assume a value of $\log (A/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = 9.1$. While not perfect, such an approximation will allow the estimation of rate constants at other temperatures.

Experimental Section

1,1,2-Trichlorotriflouroethane (freon-113) (99+%, spectrophotometric grade) and cyclohexene (99+%) were purchased from Aldrich and used as received. Carbon tetrachloride (99.9%, HPLC grade) was purchased from Sigma-Aldrich and was also used as received. 1,1-Diphenylethylene (97%, Aldrich) and iodobenzene (98%, Acros) were first passed through a small plug of silica gel prior to usage.

1,1-Diphenylethylene Quenching. A solution of iodobenzene (PhI) in freon-113 was prepared such that its absorbtion was ~0.3 at the excitation wavelength (308 nm). A 0.556 M stock solution of 1,1-diphenylethylene (DPE) in freon-113 was also prepared (1:10 dilution). For each sample, a specific volume of the DPE solution was injected via syringe into a 7 mm × 7 mm square quartz cuvette. Typical volumes injected were 20, 40, 60, 80, or 100 μL. The sample was then diluted to 4.0 mL with the PhI solution. The solution, capped with a white rubber septum, was then purged of oxygen by bubbling nitrogen into the solution through a syringe needle for 10 min. The septum was fitted with a second needle to allow the gases to escape. To minimize solvent evaporation, the cuvette was immersed in an ice bath for the duration of the deoxygenating. After 10 min, the cuvette was removed from the nitrogen line, and the septum was wrapped with parafilm. Once in the laser flash photolysis system, the samples were each allowed 10 min to thermally equilibrate with the particular temperature of the system. The kinetic traces are an average of each sample being exposed 10 times by the system. Ten exposures gives excellent averaged signals, while minimizing product build-up. A fresh sample was prepared for each measurement.

Cyclohexene Quenching. Because the products of the reaction of $Ph^\bullet$ and cyclohexene are invisible, DPE was added to the solutions as a probe. A 2 mM solution of DPE was added to a 36 mM solution of PhI in freon-113. The samples were then treated identically as above except that the aliquots of pure cyclohexene were injected only after the 10 min oxygen purge. Once injected with cyclohexene, the samples were then purged for an additional 2 min.

Carbon Tetrachloride Quenching. As for cyclohexene, DPE was used as a probe for the reaction of CCl_4 with $Ph^\bullet$. Unlike cyclohexene, the CCl_4 was added before the 10 min purge. Because the reaction of CCl_4 with $Ph^\bullet$ is much slower, larger volumes of CCl_4 were required. This required the addition of both PhI and DPE to the CCl_4 in order to match the 36 mM and 2 mM concentrations in freon-113.

Kinetic Measurements. The laser system employed in these experiments uses a Lumonics EX-530 for 308 nm excitation. Pulse duration is ca. 6 ns, and typical pulse energies are between 5 and 50 mJ. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitizer and transferred to a Power-Macintosh computer that controlled the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier.[24,25]

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Supporting Information Available: Tables S1−S19 of rate constants and quenching plots (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, see any current masthead page for ordering information.

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