occur via the intermediacy of an exciplex,[10] these explanations are, at this point, tentative.

It is possible that the higher reactivity of *p*-methylbenzophenone, compared with benzophenone triplets, is also the result of a decrease in the π,π^*–n,π^* energy gap even if, in this case, the n,π^* state is expected to remain the low-lying one.

Finally, our studies with polymer systems show that the same type of behavior is observed as with small molecules. In general, the rate constants are somewhat smaller for the macromolecules, as could be expected from the change in diffusion coefficients. Solvent effects (see Table IV) seem to parallel those in small molecules; however, one should be aware that the addition of alcohols to polymer solutions in nonpolar solvents will also result in conformational changes in the macromolecule and that these must also contribute to the reactivity changes observed.

The quenching of macroketones by hydroperoxides has been suggested to be an inportant additional route for the photoinitiation of the oxidative degradation of polymers,[3,4] and the possibility of reactive quenching has been recognized.[5] This reaction may add to direct hydroperoxide photolysis as a source of radicals in photooxidizing solid polymers where ketones and hydroperoxides are produced during processing and UV exposure.[28] The solid-state analogue of reaction 1 can be expected to occur in solid polymers, but the efficiency of initiation of propagating oxidation chains will be reduced by the high probability of cage reactions of the macroradicals.[29] Polynuclear aromatics such as naphthalene, phenanthrene, and anthracene, have frequently been detected as impurities in polyolefins[30] and have been shown to sensitize photooxidative degradation;[31] hydroperoxide quenching of the excited aromatic triplets may contribute to the photoinitiation in these systems.

Experimental Section

Materials. Aqueous *tert*-butyl hydroperoxide (Aldrich; 70% hydroperoxide, 30% water) was purified by azeotropic distillation using a Dean-Stark trap to remove the water-rich distillate, dried over $MgSO_4$, and fractionally distilled. Iodometry showed ≥98% purity, and GC analysis showed the following impurity limits: acetone ≤0.01 M, Bu^tOH ≤0.02M, and Bu^tOOBu^t ≤0.05 M. Repeated distillation and further purification steps such as fractional crystallization had no effect on the quenching data.

All sensitizers were commercially available and were recrystalized or sublimed. Benzene (Aldrich, Gold Label) was purified by treatment with sulfuric acid, washed with water, then refluxed over CaH_2 under nitrogen, and distilled. All other solvents were of the highest purity commercially available and were used as received.

The polymer samples were prepared by free radical polymerization of the corresponding monomer or monomer mixtures in benzene. Conversions were kept below 20%. Further details on the purification are the same as in earlier work.[27b,32] The abundances of each monomer in the copolymers were determined by UV spectroscopy. Co(sty–VBP) contained 23% of 4-vinylbenzophenone units; co(Sty–PMA) had 39% *p*-methoxyacrylophenone units; co(MMA–PMA) contained 22% *p*-methoxyacrylophenone, and co(MMA–PVK) had 21.3% phenyl vinyl ketone moieties.

Spectra. UV spectra were recorded on a Hewlett-Packard 8450A spectrophotometer with 0.1 cm path cells. IR spectra were recorded on a Nicolet 7199 FTIR spectrophotometer, equipped with a mercury cadmium telluride detector. Solutions for IR were prepared in carbon tetrachloride, and a spectral subtraction routine used to study difference spectra.

Laser Flash Photolysis. The samples, usually 1 mL, where contained in Suprasil cells (3-mm path length, 7-mm width). They were deaerated by bubbling with oxygen-free nitrogen.

Our laser facility uses a Molectron UV-24 nitrogen laser for excitation. The data, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP-11/23 computer, which also provided suitable control for the experiment, as well as processing, storage, and hard-copy facilities. Further details have been given elsewhere.[33]

Acknowledgment. Thanks are due to Professor E. A. Lissi for the communication of unpublished results, to Professor G. Geuskens for a simulating discussion, and to S. E. Sugamori for his technical assistance.

Registry No. *tert*-Butyl hydroperoxide, 75-91-2; benzophenone, 119-61-9; *p*-methylbenzophenone, 134-84-9; acetophenone, 98-86-2; *p*-methoxyacetophenone, 100-06-1; phenanthrene, 85-01-8; anthracene, 120-12-7; 1,5-diphenyl-1,5-pentanedione, 6263-83-8; poly(phenyl vinyl ketone), 26742-84-7; hydrogen, 1333-74-0.

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Phenyl Radical Kinetics[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6. *Received October 4, 1982*

Abstract: The reactions of phenyl radicals with 17 substrates have been examined by using laser flash photolysis techniques. Absolute rate constants were determined for all the reactions in Freon 113 at 298 K by using iodobenzene or benzoyl peroxide as radical precursors. The following are some representative rate constants, which include all possible modes (or sites) of attack on each substrate: benzene, $(4.5 \pm 0.3) \times 10^5$ M^{-1} s^{-1}; chlorobenzene, $(1.18 \pm 0.13) \times 10^6$ M^{-1} s^{-1}; methyl methacrylate, $(1.8 \pm 0.3) \times 10^8$ M^{-1} s^{-1}; carbon tetrachloride, $(7.8 \pm 0.7) \times 10^6$ M^{-1} s^{-1}; tetrahydrofuran, $(4.8 \pm 0.6) \times 10^6$ M^{-1} s^{-1}; toluene $(1.7 \pm 0.7) \times 10^6$ M^{-1} s^{-1}.

The reactions of phenyl radicals in solution have been the subject of many studies that have led to numerous measurements of relative rate constants.[3-7] However, virtually no absolute rates have been reported. In fact, the only direct, time resolved measurement of their reactions deals with *p*-carboxyphenyl radicals

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in aqueous solvents.[8] This study, by Fessenden, Schuler, and Madhavan,[8] involved very precise measurements; however, the experimental conditions, ring substitution, and restrictions on the nature of the substrates (i.e., solubility in water) make it desirable to carry out a detailed kinetic study under conditions closer to those of immediate interest for the organic chemist.

Among the competitive studies, one of particular interest is a report by Lorand et al.[9] on the decomposition of phenylazotriphenylmethane, where the kinetic assumptions involved seem, with hindsight, very reliable and lead to several estimated rate constants. These rate constants are generally in agreement with our direct measurements (vide infra) and with the values reported by Schuler et al.[8]

In this study we have used laser flash photolysis techniques to examine the reactivity of photogenerated phenyl radicals in solution. The sources of phenyl radicals were iodobenzene and benzoyl peroxide. Both the substrates have an interesting photochemistry of their own; however, these aspects are not the subject of this study and have not been examined in any detail. In this sense, we have only been concerned with establishing that the processes under study reflected solely the behavior of phenyl radicals.

Results and Discussion

All experiments were carried out on deaerated samples at 298 K by using the pulses (308 nm, ~4 ns, up to 80 mJ) from an excimer laser for excitation. Static or flow systems were used depending on the experiment.

In the case of iodobenzene, it is clear that the only important primary photoprocess is the cleavage of the C–I bond, although, judging from the signals observed, even this process may be somewhat inefficient, perhaps reflecting extensive cage recombination. These experiments were always carried out by using a flow system in order to prevent the accumulation of molecular iodine in the reaction cell.

When benzoyl peroxide was used as a phenyl precursor, one could envision more complex photoprocesses than in the case of iodobenzene;[10-14] however, we do not find evidence for any processes involving benzoyloxy radicals interfering with the measurements described herein.[15] This aspect of the problem will be discussed in further detail in a separate section, but the main observation is that in the photochemistry of benzoyl peroxide in solution at 298 K, the only transient species of importance, 10 or more nanoseconds after laser excitation is the phenyl radical. Both flow and static systems were used in these experiments.

The search for an inert solvent proved to be a difficult one. Phenyl radicals readily add to aromatic substrates and olefins, and they undergo abstraction reactions with most hydrocarbons and halogenated compounds. Perfluorinated hydrocarbons, which could be expected to be unreactive, were very poor solvents for most substrates of interest. Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) proved to be the most convenient choice, even if some chlorine abstraction is likely to take place and benzoyl peroxide has only a very limited solubility (around 0.03 M).

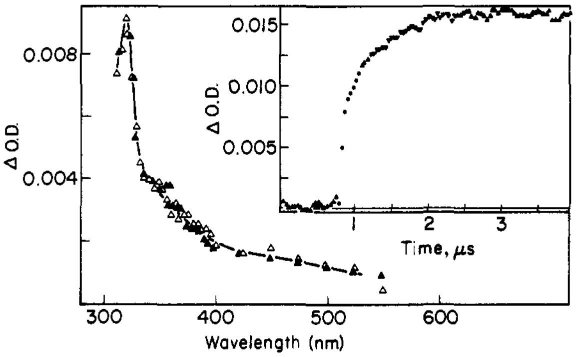
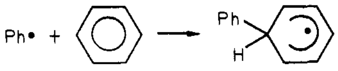


Figure 1. Spectrum obtained by addition of phenyl to styrene with iodobenzene (Δ) and benzoyl peroxide (▲) as radical precursors. Insert: Buildup trace obtained at 317 nm with benzoyl peroxide as the precursor.

When samples of iodobenzene or benzoyl peroxide in Freon 113 were irradiated in the laser flash system, extremely weak signals were observed which could not be analyzed in sufficient detail. When benzene was added to samples containing benzoyl peroxide as a precursor, we observed the formation of a transient species with $\lambda_{max} \sim 330$ nm, which we assign to the phenylcyclohexadienyl radical generated in reaction 1.[16]



(1)

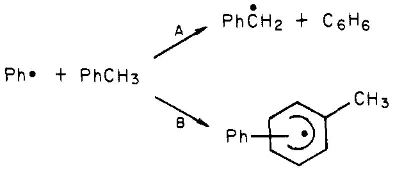
The formation of this transient was not instantaneous, but rather, it followed pseudo-first-order kinetics. The buildup traces obtained by using iodobenzene as a precursor followed the same kinetics (vide infra) as those obtained with benzoyl peroxide; however, the transient spectra showed an additional band at ca. 465 nm. This band was formed much faster than the cyclohexadienyl radical and is in full agreement with the known absorption of the iodine atom–benzene complex[17,18] and is thus assigned to this species.

The case of benzene is typical of a wide range of substrates which, upon reaction with phenyl radicals, yield free radicals that are suitable for direct detection; i.e., they show strong optical absorptions in the visible or near-UV region. Substrates such as styrene and β-methylstyrene react via addition at the double bond, as illustrated in reaction 2 for styrene, and yield intense signals

$$\mathrm{Ph\cdot + Ph\text{-}CH{=}CH_2 \rightarrow Ph\text{-}\dot{C}H\text{-}CH_2\text{-}Ph} \qquad (2)$$

at around 320 nm, due to the substituted benzyl radicals (Figure 1).

Good signals were also obtained in the case of substrates such as toluene, cumene, and p-xylene, although in these systems they are likely to result from a combination of two parallel reaction paths, as illustrated in reaction 3.



(3)

In this particular case it seems likely that hydrogen abstraction (process A) is the main reaction path; however, it should be noted that studies of the type described here cannot accurately evaluate

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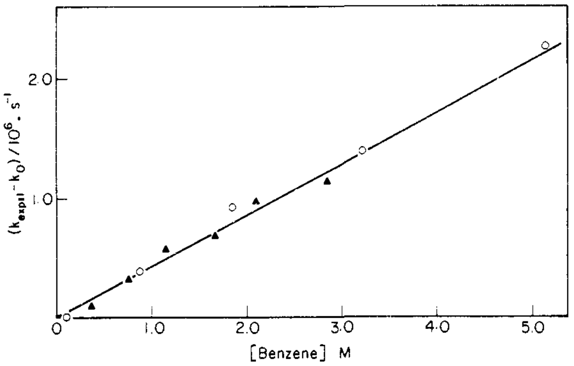

Figure 2. Reaction of phenyl radicals derived from 0.0176 M IC_6H_5 (○) or 0.0269 M benzoyl peroxide (▲) with benzene. Extrapolated value for [benzene] = 0 substracted from each data point.

the relative importance of each reaction path. The rate constants measured when more than one path is available correspond to the sum for *all* possible reaction paths, regardless of which one is responsible, or mostly responsible, for the signals observed.[19-23] It is not the object of this study, nor would it be easy with this technique, to establish the relative importance of the various reaction paths; these parameters can be determined more easily and accurately by using analytical techniques.

Another example where intense signals were observed is the case of diphenylmethanol,[24] which yields the easily detectable (λ_{max} = 540 nm) diphenylhydroxymethyl radical, reaction 4.

$$\mathrm{Ph\cdot + Ph_2CHOH \rightarrow Ph_2\dot{C}OH + C_6H_6} \qquad (4)$$

In all these systems the kinetic analysis is identical. The detectable radical product is formed with pseudo-first-order kinetics, which can be analyzed according to eq 5

$$\log \frac{A_\infty}{A_\infty - A_t} = k_{exptl}t \qquad (5)$$

where k_{exptl} is a first-order experimental rate constant, t is the time, A_∞ is the transient optical density in the plateau region (see insert in Figure 1), and A_t is the optical density at time t.

The values of k_{exptl} are related to the rate constants of interest according to eq 6

$$k_{exptl} = k_0 + k_X[X] \qquad (6)$$

where k_X is the bimolecular rate constant for reaction of phenyl with a substrate X, which is able to generate a detectable optical signal upon reaction. The parameter k_0 is a rate constant that includes all first- and pseudo-first-order processes that the phenyl radicals undergo in the absence of substrate X and which are not affected by X. In our particular system k_0 will be mainly determined by abstraction from the solvent and some addition to the aromatic ring in the phenyl radical precursor.

The rate constants, k_X, can be determined by measuring k_{exptl} for different concentrations of X and plotting according to eq 6. When values for more than one type of experiments are combined (e.g., using different radical sources), it is better to plot ($k_{exptl} - k_0$) vs. [X], since the values of k_0 are dependent upon experimental conditions, such as radical source and its concentration. Figure 2 shows the corresponding plot for benzene and also illustrates the excellent agreement obtained by using iodobenzene or benzoyl peroxide. The value obtained from the slope was $k_X = (4.5 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. It should be noted that the value of k_0 substrated was the extrapolated one, since when [X] = 0, the signals, while detectable (vide infra), are quite weak. Thus, the corresponding k_0 values were obtained from plots of k_{exptl} vs. [X] for each series of measurements. The same approach described here for benzene was employed with most of the substrates, which led to signals suitable for direct detection. However, other substrates of interest do not lead to any easily detectable signals; for these, it is possible to use a "probe" technique that we have described earlier for *tert*-butoxy radicals[19-23] and used quite extensively for *tert*-butoxy as well as silyl radicals.[25,26] Thus, laser generation of phenyl radicals in the presence of two substrates, X and Y, of which at least X yields a detectable signal, leads to a pseudo-first order buildup of the signal such that k_{exptl} will follow eq 7.

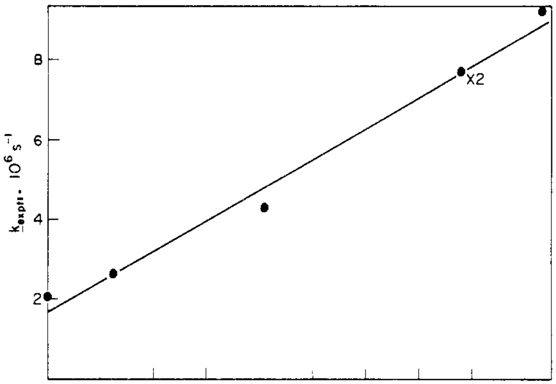

Figure 3. Representative plot for the reaction of phenyl radicals with carbon tetrachloride, based on the data from Table XXXVI of the supplementary material with benzoyl peroxide as the radical precursor and β-methylstyrene as the probe.

$$k_{exptl} = k_0 + k_X[X] + k_Y[Y] \qquad (7)$$

Thus, at constant [X]

$$k_{exptl} = k_0' + k_Y[Y] \qquad (8)$$

This approach can be used for systems where Y does not yield a useful signal, such as the case of carbon tetrachloride illustrated in Figure 3, as well as for systems where the signals from Y are, while detectable, not convenient for direct measurement or where an additional verification of the result is desired.

It should be pointed out that the kinetic analysis presented above assumes that second-order processes (particularly phenyl–phenyl recombination) are unimportant under our experimental conditions. This was verified in experiments similar to those discussed in an earlier report on *tert*-butoxy radicals;[19] in general, radical–radical processes were not of importance in any of these experiments.[27] Experiments involving phenyl were considerably more difficult than earlier measurements involving alkoxy,[19-23] silyl,[25,26] or stannyl[28,29] radicals; this is mostly due to the need to monitor at shorter wavelengths, the frequent requirement for flow systems, triggering of chain processes that tend to deplete the sample, and, in some cases, the need to monitor the signals at a wavelength quite close to that used for excitation; e.g., for benzyl radicals $\lambda_{max} \sim 317$ nm,[30] which should be compared with the

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Table I. Rate Constants for the Reactions of Phenyl Radicals in Freon 113 at 298 K

entry[a]	substrate	k/M^{-1} s^{-1} [b,c]	information[d]		
			source	detection	method
1 (II)	benzene	**$(4.5 \pm 0.3) \times 10^5$**		combined: 2, 3	
2 (III)		$(4.6 \pm 0.5) \times 10^5$	PhI	D	F
3 (IV)		$(4.2 \pm 0.7) \times 10^5$	BZP	D	F
4 (V)	chlorobenzene	**$(1.18 \pm 0.13) \times 10^6$**		combined: 5, 6	
5 (VI)		$(1.10 \pm 0.14) \times 10^6$	PhI	D	F
6 (VII)		$(1.27 \pm 0.28) \times 10^6$	BZP	D	F
7 (VIII)	styrene	**$(1.10 \pm 0.10) \times 10^8$**		combined: 8, 9	
8 (IX)		$(1.10 \pm 0.10) \times 10^8$	BZP	D	S
9 (X)		$(1.11 \pm 0.19) \times 10^8$	BZP	D	S
10 (XI)	β-methylstyrene	**$(3.0 \pm 0.3) \times 10^7$**		combined: 11–13	
11 (XII)		$(2.2 \pm 0.4) \times 10^7$	PhI	D	F
12 (XIII)		$(3.2 \pm 0.3) \times 10^7$	BZP	D	F
13 (XIV)		$(2.7 \pm 0.5) \times 10^7$	BZP	D	S
14 (XV)	methyl methacrylate	**$(1.8 \pm 0.3) \times 10^8$**		combined: 15–18	
15 (XVI)		$(1.9 \pm 0.4) \times 10^8$	PhI	P(PhCl)	F
16 (XVII)		$(1.6 \pm 0.1) \times 10^8$	BZP	P(β-MS)	F
17			BZP	P(BZH)	S
18			PhI	P(β-MS)	F
19 (XVIII)		$(1.5 \pm 0.7) \times 10^8$	BZP	P(β-MS)	F
20 (XIX)	cyclohexene	**$(2.8 \pm 0.2) \times 10^8$**	BZP	P(BZH)	S
21 (XX)	toluene	**$(1.7 \pm 0.7) \times 10^6$** [e]		combined: 22–24	
22 (XXI)		$(1.6 \pm 0.5) \times 10^6$	PhI	D	F
23			BZP	D	S
24 (XXII)	cumene	**$(1.4 \pm 0.7) \times 10^7$** [e]		combined: 25–28	
25 (XXIII)		$(1.7 \pm 0.5) \times 10^7$	BZP	P(β-MS)	S
26 (XXIV)		$(9.3 \pm 3.2) \times 10^6$	BZP	D	S
27			BZP	P(β-MS)	S
28 (XXV)		$(1.04 \pm 0.13) \times 10^7$	BZP	P(BZH)	S
29 (XXVI)	*p*-xylene	**$(2.4 \pm 0.1) \times 10^6$**		combined: 30, 31	
30			BZP	D	S
31 (XXVII)		$(2.5 \pm 0.4) \times 10^6$	PhI	D	F
32 (XXVIII)	isopropanol	**$(1.38 \pm 0.07) \times 10^6$**	PhI	P(β-MS)	F
33 (XXIX)	benzhydrol	**$(2.03 \pm 0.2) \times 10^7$**		combined: 34, 35	
34 (XXX)		$(2.05 \pm 0.5) \times 10^7$	BZP	D	S
35 (XXXI)		$(2.07 \pm 0.7) \times 10^7$	BZP	D	S
36 (XXXII)	acetonitrile	**$(1.04 \pm 0.18) \times 10^5$**	PhI	P(β-MS)	F
37 (XXXIII)	tetrahydrofuran	**$(4.8 \pm 0.6) \times 10^6$**		combined: 38–40	
38			BZP	P(β-MS)	S
39			BZP	P(BZH)	S
40 (XXXIV)		$(5.1 \pm 0.7) \times 10^6$	PhI	P(β-MS)	F
41 (XXXV)	carbon tetrachloride	**$(7.8 \pm 0.7) \times 10^6$**		combined: 42, 43	
42			BZP	P(BZH)	S
43 (XXXVI)		$(7.8 \pm 1.0) \times 10^6$	BZP	P(β-MS)	F
44 (XXXVII)	2-bromobutane	**$(2.3 \pm 0.4) \times 10^6$**	PhI	P(β-MS)	F
45 (XXXVIII)	1-bromopropane	**$(1.05 \pm 0.1) \times 10^6$**	PhI	P(β-MS)	F
46 (XXXIX)	benzoyl peroxide	**$(2.1 \pm 0.7) \times 10^7$**	BZP	D	S

[a] Roman numerals refer to the corresponding supplementary table. [b] Total rate constant for the reaction, including all possible paths and sites of attack. [c] Best value in bold type. [d] Abbreviations used: BZP = benzoyl peroxide; D = direct detection; P = probe technique, with probe indicated in parentheses; β-MS = β-methylstyrene; BZH = diphenylmethanol; F = flow cell; S = static experiment. [e] Error estimated by authors and corresponding to $\sim 4\sigma$.

excitation wavelength of 308 nm.

A summary of our results is presented in Table I, while full kinetic details are provided as supplementary material in Tables II–XXXIX (see paragraph at end of paper regarding supplementary material). Almost every measurement was repeated under different experimental conditions, frequently changing the radical source, probe substrate, or experimental method (flow or static). In general, we find satisfactory agreement under different sets of experimental conditions, with the exception of toluene and cumene, where, despite numerous efforts—only a few of which have been included in Table I—we could neither avoid a large dispersion of the data nor fully understand its origin.

For each substrate in Table I we have included the results of each independent series of experiments, as well as our choice of a "best" value. The choice of a best value and its error in each case is usually a combination of simple statistical measurements, such as the correlation coefficient, on the number of measurements and, to some extent, in the rather subjective evaluation of the experimental problems encountered during the study. In any case, since the various results are presented in Table I, the reader has all the elements to make an alternative choice, though we believe that a detailed analysis of the data in the supplementary material would usually lead to the same choice as presented herein.

In most cases, our choice of best value results simply from a simultaneous analysis of all the data for a given substrate. In this case, it is necessary to plot the "normalized" rates, as $(k_{\text{exptl}} - k_0)$ or $(k_{\text{exptl}} - k_0')$, as applicable. In the latter case, two values of k_0' are available: the experimental one as well as the extrapolated value based on the linear regression for that set of values. In order to be consistent with the approach described earlier in the case of measurements based on direct detection, we have always substrated the extrapolated value of k_0'; this also avoids overweighting that particular experimental point. Since a plot of $(k_{\text{exptl}} - k_0)$ or $(k_{\text{exptl}} - k_0')$ is expected to have an intercept equal to zero, the origin was introduced in our calculations, with a weight equal to the number of independent series of experiments carried out for that particular substrate.

Some lines in Table I include experiments for which no rate constant has been included. These correspond to studies that only led to two or three measurements of k_{exptl}; enough to warrant their inclusion in a generalized analysis of the data but not sufficient to generate a separate rate constant.

In the case of benzoyl peroxide, we also carried out a study in an attempt to establish the possible importance of reactions of phenyl radicals with the peroxide. This study was based on the direct detection of the very weak signals that result in solutions of the peroxide in Freon 113 and involves the measurement of k_{exptl} for different concentrations of the peroxide. The data, which have also been included in Table I, suggest a high reactivity of phenyl toward benzoyl peroxide, although it should be noted that these measurements are extremely difficult and perhaps subject to more error than suggested by the statistical analysis of the data.

A Case against Benzoyloxy Radicals. The purpose of this section is to present the evidence and arguments that led us to conclude that the possible involvement of benzoyloxy radicals did not need to be taken into consideration in the analysis of the data obtained by using benzoyl peroxide as a precursor. No attempt is made at this point to examine, discuss, or understand in any detail the behavior of benzoyloxy radicals.[31]

Naturally, a rather straightforward argument is that since we have not detected any systematic difference between experiments using iodobenzene or benzoyl peroxide, it is reasonable to assume that the data must reflect the behavior of a common intermediate, present in both systems: only phenyl radicals meet this condition.[33]

Studies by Bevington et al.[34] have established that at 298 K the ratio of rate constants for benzoyloxy addition to styrene and cleavage is $k_9/k_{10} = 4.76$.

$$\mathrm{PhC(O)O\cdot + PhCH{=}CH_2 \rightarrow Ph\dot{C}H{-}CH_2OC(O)Ph} \qquad (9)$$

$$\mathrm{PhC(O)O\cdot \rightarrow Ph\cdot + CO_2} \qquad (10)$$

Thus, in the range of styrene concentrations used in our experiments (0.002–0.03 M) we would expect between 86 and 99% of the benzoyloxy radicals to undergo cleavage. Further, this is likely to be an underestimation since there are indications that the direct photodecomposition of benzoyl peroxide can yield phenyl radicals in the primary photochemical step.[10]

The high reactivity measured toward halogen donors (Table I) is another argument in favor of phenyl, since benzoyloxy seem highly unlikely to undergo halogen abstraction reactions.

Finally, we also carried out an experiment in carbon tetrachloride as the solvent which further supports the arguments presented above. In this case, we photodecomposed benzoyl peroxide in the presence of various concentrations of styrene and monitored the yield of substituted benzyl radicals, $\mathrm{Ph\dot{C}HR}$, which, in this case, we attribute to $\mathrm{Ph\dot{C}H{-}CH_2Ph}$.[35] If phenyl reacts solely according to eq 11 and 12, the signals due to substituted

$$\mathrm{Ph\cdot + Cl_4C \rightarrow PhCl + Cl_3C\cdot} \qquad (11)$$

$$\mathrm{Ph\cdot + PhCH{=}CH_2 \rightarrow Ph\dot{C}H{-}CH_2Ph} \qquad (12)$$

benzyl radicals are expected to follow a Stern–Volmer type of dependence, i.e.,

$$\frac{1}{\Delta\mathrm{OD}} = \alpha + \alpha\,\frac{k_{11}[\mathrm{Cl_4C}]}{k_{12}[\mathrm{styrene}]} \qquad (13)$$

Figure 4 shows a plot according to eq 13, which leads to $k_{11}/k_{12} = 0.0453$, which compares well with our own measurements but, more importantly, with measurements based on product studies in which phenyl-derived products were examined.[7]

In summary, our results show that in Freon 113 at 298 K the vast majority of the benzoyloxy radicals generated in the photodecomposition of benzoyl peroxide cleave to yield phenyl radicals. The cleavage seems to occur with a rate constant around or above $10^8\ \mathrm{s^{-1}}$.

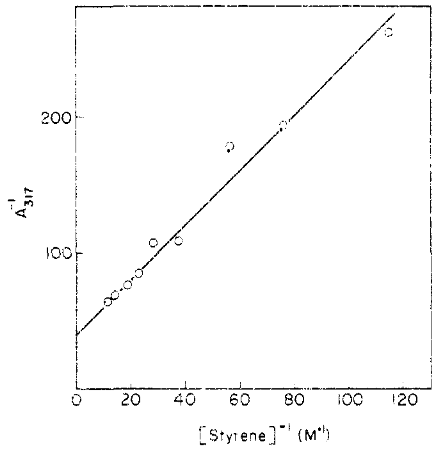

Figure 4. Stern–Volmer type of plot (see eq 13) for the reaction of phenyl radicals (from benzoyl peroxide, 0.0216 M) with styrene in carbon tetrachloride as the solvent.

Comparison with Reported Data. We feel that our studies provide a solid kinetic base that should make it possible to put earlier competitive studies on an absolute reactivity scale.

In those cases where a direct comparison with earlier reports is possible, either in the form of actual rate constants or ratios of reactivities, one finds that the agreement is, in general, quite satisfactory. For example, Lorand et al.[9] report $k = 1.03 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$ for benzene at 319 K, in excellent agreement with our value of $4.5 \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$ at 298 K. Similarly, for $\mathrm{Cl_4C}$ Lorand et al.[9] report values in the $(2.7\text{–}5.8) \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$ range; our value for this substrate is $7.8 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$.

Our values are also comparable yet somewhat lower than those reported by Schuler et al.,[8] perhaps the result of solvent effects although the comparison is too limited (primarily for benzene and 2-propanol) to elaborate in any detail on the origin of these differences. The rate constants we report are much larger than those estimated by deTar;[36] Janzen and Evans have already pointed out that deTar's rate values are probably in error.[37]

The relative reactivities that can be calculated from our data are generally in satisfactory agreement with the values at 333 K reported in the literature.[3,6,7] Thus, the reactivity ratios for toluene, *p*-xylene, cumene, cyclohexene, acetonitrile, styrene, methyl methacrylate, and carbon tetrachloride are in good agreement with those reported,[3,6,7] with the only exception of cyclohexene,[3] where our ratio with carbon tetrachloride (the most common reference substrate) is ~35, while Russell[3] reports 4.4 for the abstraction reaction; the difference in temperature and addition reactions could explain at least some of the difference.

Finally, phenyl radicals are clearly very reactive species; the rate constants indicate that in many cases the reactivity exceeds that of other highly reactive radicals such as *tert*-butoxy. This is true even in the case of hydrogen abstraction from substrates such as toluene where the ratio of reactivities is around 7. Additions to vinyl monomers such as styrene and methyl methacrylate are extremely fast processes.

Further studies involving the temperature dependence of phenyl radical reactions, their primary role in emulsion polymerization, and the examination of substituent effects in the radical all seem viable using the techniques developed in this study and are, in most cases, planned or in a preliminary stage.

A Comment on the Fate of Iodine Atoms. The generation of iodine atoms, and consequently molecular iodine, is inevitable when iodobenzene is used as a phenyl radical precursor. Molecular iodine can be simply "washed out" with the use of a flow cell, but the iodine atoms undergo complexation reactions in the time scale

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(31) Preliminary work suggests that only at low temperatures may it be possible to examine photogenerated benzoyloxy using nanosecond techniques. It should also be noted that in view of Skell's[32] suggestion that different electronic states of acetyloxy can lead to different reactivity, one could conceive that photogenerated benzoyloxy radicals may have a different behavior than thermally generated ones. While these questions are not examined herein, their importance is recognized, and suitable studies are planned.

(32) Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967–968.

(33) Further, since in the case of the iodobenzene–benzene system one of the transients is clearly the $\mathrm{I{\cdot}C_6H_6}$ complex, it seems reasonable that the other species formed must result from the only other moiety in the radical precursor, i.e., phenyl.

(34) Bevington, J. C.; Lewis, T. D. *Trans. Faraday Soc.* **1958**, *54*, 1340–1344.

(35) Trichloromethyl radicals are unlikely to add to styrene in the nanosecond time scale for the low styrene concentrations used here.

(36) De Tar, D. F. *J. Am. Chem. Soc.* **1967**, *89*, 4058–4068.

(37) Janzen, E. G.; Evans, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 205–206.

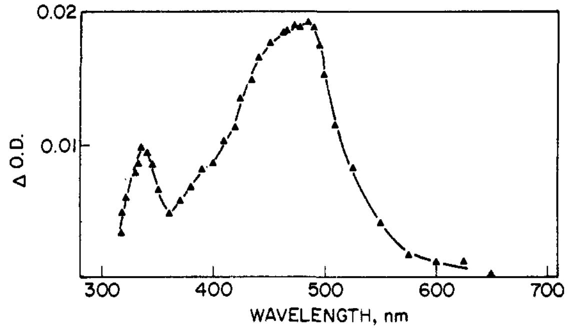

Figure 5. Transient spectrum showing the phenylcyclohexadienyl peak (330–340 nm), as well as the peak assigned to the complex between iodine atom and benzene (λ_{max} = 470 nm). Obtained by using iodobenzene (0.015 M) and benzene (1.8 M) in Freon 113.

of our study. Some exploratory experiments in the case of benzene led to a well-defined absorption band in the visible region (Figure 5), the formation of which seemed to be at least 100 times faster than the reactions of phenyl radicals; thus, while iodine atoms do generate absorptions, the time scale involved is sufficiently different from that in phenyl reactions that they do not interfere with the kinetic analysis. Further, in the UV region used for monitoring (usually 320–340 nm) the cyclohexadienyl bands are considerably stronger.

Similar signals were also observed for toluene and other alkylbenzenes. The signals were either much weaker or absent in the case of vinyl monomers.

Experimental Section

Materials. Benzoyl peroxide (Aldrich) was purified by reprecipitation by methanol from a chloroform solution. Iodobenzene (Eastman) was used as received. Freon 113 from various sources (Fluka, Aldrich, or Matheson) was purified by refluxing on calcium carbonate followed by fractional distillation. Diphenylmethanol was doubly sublimed. All other substrates were purified by distillation or recrystallization. In the case of vinyl monomers special care was taken to eliminate stabilizing additives.

Procedure. Static experiments were carried out with samples (usually 2 mL) contained in Suprasil cells made of square (7 × 7 mm^2) quartz tubing. They were deaerated by using oxygen-free nitrogen. Care was taken to use fresh samples for each measurement.

Flow experiments were carried out in a flow system where the reaction cell had been built of the same material (7 × 7 mm^2 Suprasil tubing) mentioned above. The solutions were prepared by adding the solutes to priorly deaerated solvent in a nearby container and bubbling with oxygen-free nitrogen for a few additional minutes. The container was connected to the reaction cell with Teflon tubing.

Laser Photolysis Facility. The apparatus used has been described in considerable detail in an earlier publication.[38] Since that report was published, a number of modifications have been introduced; the main one, and directly relevant to this work, is the addition of a Lumonics TE-860-2 excimer laser, which for the present study was operated with Xe–HCl–He mixtures and produced pulses at 308 nm (~4 ns, up to 80 mJ). These pulses were used for sample excitation at 90° with respect to the analyzing beam. Further details of the modifications to our instrument will be reported elsewhere.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance.

Registry No. Phenyl radical, 2396-01-2; benzene, 71-43-2; chlorobenzene, 108-90-7; styrene, 100-42-5; β-methylstyrene, 637-50-3; methyl methacrylate, 80-62-6; cyclohexene, 110-83-8; toluene, 108-88-3; cumene, 98-82-8; *p*-xylene, 106-42-3; 2-propanol, 67-63-0; benzhydrol, 91-01-0; acetonitrile, 75-05-8; tetrahydrofuran, 109-99-9; carbon tetrachloride, 56-23-5; 2-bromobutane, 78-76-2; 1-bromopropane, 106-94-5; benzoyl peroxide, 94-36-0.

Supplementary Material Available: Tables (Tables II–XXXIX) giving detailed kinetic data (28 pages). Ordering information is given on any current masthead page.

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(38) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

Reaction of Cumene with Ozone To Form Cumyl Hydrotrioxide and the Kinetics of Decomposition of Cumyl Hydrotrioxide

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Abstract: Cumene forms a charge-transfer complex with ozone in a number of solvents (e.g., with absorption at 360 nm in acetone). When this CT complex is photolyzed at −75 °C or warmed above −40 °C, reaction occurs to form both cumyl hydrotrioxide and ring-ozonated products (in a ratio of about 70/30). The decomposition of the hydrotrioxide, $PhCMe_2OOOH$, can be monitored by proton NMR in acetone-d_6 using either the CH_3 or the OOOH hydrogens; the decomposition is first order and gives activation parameters of $E = 16.0 \pm 0.1$ kcal/mol and $\log A = 10.4 \pm 0.1$. These values agree with literature data on the decomposition of aroyl hydrotrioxide (from the reaction of ozone with aromatic aldehydes) and on the decomposition of trioxides of cyclic and acyclic acetals, but they are far from the values of $E = 23$ kcal/mol and $\log A = 16$ calculated using thermokinetic methods. The low activation parameters undoubtedly result from a chain decomposition of the trioxide. Therefore, we also studied the decomposition in the presence of an inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (BHT), to eliminate the chain decomposition. In the presence of BHT, the activation parameters become $E = 23.9 \pm 0.1$ kcal/mol and $\log A = 16.4 \pm 0.1$, in agreement with theory. In addition, we can follow the disappearance of the phenolic hydrogen of BHT, and it disappears with the same rate constant as does cumyl hydrotrioxide, indicating that every decomposition of the hydrotrioxide leads to two scavengeable free radicals. In the presence of BHT, the hydrotrioxide decomposes to give cumyl alcohol as the only organic product; in the absence of BHT a small yield of acetophenone also is formed, perhaps as a result of the production of the cumyltrioxyl radical in a chain process and its exothermic loss of dioxygen and subsequent β-scission of the cumyloxyl radical. This is the first time that the hydrotrioxide of a hydrocarbon has been characterized by NMR and that Arrhenius parameters for decomposition of a hydrotrioxide have been obtained that agree with thermokinetic predictions.

The reaction of cumene with ozone is of interest from two perspectives. First, the mechanism for the reaction of hydrocarbons with ozone is under intense scrutiny,[1-3] and cumene, with its unique and reactive hydrogen, is an attractive substrate.

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