Table III. Magnetic Susceptibility Data[a] and Calculated μ_{eff} Values[b] for Cu_2Zn_2SOD, E_2Co_2SOD, and Cu_2Co_2SOD

sample	T, K	χ_M[a]	μ_{eff}[b]
Cu_2Zn_2SOD	280	18.5 (±1.5)	1.81
	306	15.9 (±1.2)	1.80
E_2Co_2SOD	280	106 (±3)	4.34
	306	98 (±3)	4.38
Cu_2Co_2SOD	280	124 (±5)	
	306	114 (±4)	

[a] From the Evans method.[31] χ_M values are in $m^3\ mol^{-1} \times 10^9$ and inclusive of diamagnetic correction. [b] In μ_B units. $\mu_B = 9.724 \times 10^{-24}$ J T^{-1}.

The shifts of protons of histidines bound only to cobalt(II) are in the same range as those observed in E_2Co_2SOD. This is expected if the electronic levels arising from magnetic coupling are separated by an energy smaller than kT. Indeed, magnetic susceptibility measurements between 0 and 38 °C on Cu_2Co_2SOD provided values which are, within the experimental uncertainty, equal to the sum of the magnetic susceptibilities of E_2Co_2SOD and native SOD (see Table III). These data, which are consistent with measurements previously made between 1.4 and 200 K,[41,42] indicate that the high temperature limit is a pertinent description of the Cu_2Co_2SOD.

The temperature dependence of the isotropic shifts has also been measured between 0 and 38 °C (Figure 7). The slope for the various signals is different, indicating a complex temperature dependence of the shifts. The narrow temperature range, however, prevented us from obtaining more detailed information. It may be noted that signals L, K, and O are almost temperature independent.

Conclusions

Substitution of zinc(II) with cobalt(II) in bovine erythrocyte SOD provides a derivative which allows isotropically shifted proton signals to be detected. From the ^1H NMR spectra, it can be guessed that the correlation time τ_c experienced by protons relaxed by the copper electron is about the same experienced by protons relaxed by the cobalt electrons, since comparable line widths are observed for protons interacting with either metal ion. In macromolecules, the correlation time is likely to be determined by the electronic relaxation time. Therefore, the electronic relaxation times of the two ions are about the same, although they are $\sim 10^{-9}$ s for isolated copper(II) and $\sim 10^{-11}$ s for isolated cobalt(II) ions. The comparison between the ^1H NMR spectra of E_2Co_2SOD and Cu_2Co_2SOD indicates that the overall electronic relaxation time of the latter system is of the same order of magnitude of the former system, i.e., of the order of 10^{-11} s. This is expected to occur when the magnetic-exchange coupling constant J between the two ions is larger than $\hbar$ multiplied by the higher electronic relaxation rate. This sets $J > 0.5$ cm^{-1}. On the other hand, the magnetic susceptibility measurements give $J < kT$.

Observation of the ^1H NMR signals provides a tool for monitoring the interaction of the enzyme with inhibitors. Anions like N_3^-, NCO^-, and NCS^- interact with copper(II), causing removal of a histidine from the coordination sphere of the metal. This is presumably what happens also with the native enzyme since all the spectroscopic (optical absorption and CD) data underline the essentially identical behavior of the two derivatives with anions. A tentative assignment of the NMR signals seems to indicate His 44 as the one which is removed upon anion binding; anions would therefore push away such histidine, providing a more planar CuN_3–anion moiety.

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Registry No. SOD, 9054-89-1; N_3^-, 14343-69-2; NCO^-, 661-20-1; NCS^-, 302-04-5; L-histidine, 71-00-1.

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Exploratory Study of the Intermolecular Reactivity of Excited Diphenylmethyl Radicals[1]

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Abstract: A series of intermolecular reactions of excited diphenylmethyl radicals has been examined with laser flash photolysis techniques. The radicals, $Ph_2\dot{C}H$, were generated by 308-nm photodecomposition of 1,1,3,3-tetraphenylacetone or diphenyldiazomethane. In the latter system the radicals result from reaction of diphenylcarbene with hydrogen-donor solvents. The radicals were then excited with the 337-nm pulses from a nitrogen laser, leading to the formation of the readily detectable excited state of the radical, $Ph_2\dot{C}H^*$ (λ_{max} 355 nm). The excited radical is an excellent electron donor, reacting with methyl viologen with $k_q^* = 1.3 \times 10^{10}$ M^{-1} s^{-1} in wet acetonitrile and leading to the formation of methyl viologen radical cation. $Ph_2\dot{C}H^*$ is readily quenched by amines, but no evidence for full electron transfer could be obtained, e.g., for triethylamine $k_q^* = 5.2 \times 10^8$ M^{-1} s^{-1} in cyclohexane. The excited radical is 14 times more reactive toward oxygen than its ground state, but the process seems to involve a different mechanism, probably leading to singlet oxygen generation. Halogenated substrates react readily with $Ph_2\dot{C}H^*$; for example, for CCl_4 $k_q^* = 1.6 \times 10^8$ M^{-1} s^{-1} and leads to Ph_2CHCl in a process that is presumed to involve charge transfer. Excited diphenylmethyl is not a good hydrogen abstractor in spite of the fact that its hydrogen abstraction reactions would be more exothermic than those of phenyl radicals.

The photophysics and photochemistry of organic reaction intermediates is a subject of current interest. Experiments of this type at ambient temperatures usually require two pulsed sources: one is used for "synthesis" (a laser or radiolytic pulse), while the second source (usually a laser) is used to excite the transient at a wavelength where all other reagents are transparent. Accurate and reliable timing sequences are critical, since the delay between pulses must be adjusted as a function of the intermediate's lifetime and its rate of formation. Recent studies by Meisel et al.,[4,5]

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(1) Issued as NRCC-24481.

(2) NRCC summer student, 1984.

(3) NRCC Research Associate.

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Fessenden et al.,[6,7] and Rentzepis et al.[8,9] provide excellent examples of these techniques. Occasionally these conditions can be fulfilled with a single laser pulse.[10,11]

While from a physicochemical point of view these experiments are quite interesting, continuing interest is only justified if the chemical processes in which these excited transients participate can be established in some detail. Studies already available in the literature show similar concerns with the question of reaction products. A recent study from our laboratory[11] has characterized the products of the photochemistry of a 1,5-biradical.

Intermolecular reactions of excited reaction intermediates, in particular free radicals, have received very little attention. In a recent report Turro et al.[10] examined the quenching of the fluorescence from excited $Ph_2\dot{C}OH$ by a variety of substrates. Naturally, fluorescence quenching does not yield any information concerning the chemical reactions taking place, although an educated guess is of course possible when the properties of the quencher are well established.

We have undertaken the study of the photodecomposition of several organic reaction intermediates in a variety of systems involving biradicals, carbenes, ylides, and free radicals. In this paper we report an exploratory study of intermolecular reactions of excited diphenylmethyl, a species recently characterized by Meisel et al.[4,5] Excited radicals of the benzylic type have been the subject of many studies in matrices at low temperature, where their emission and excitation spectra are well documented.[12-20] The reasons for the intense fluorescence and long lifetimes are related to the small oscillator strength of the first transition and the relatively large energy gap between ground and excited states,[5] the latter being responsible for the inefficiency of radiationless processes. In any event, we find it rather surprising that in many cases these species do not readily find fast and efficient chemical deactivation pathways. The processes studied here include quenching by electron donors and acceptors, oxygen, halogenated substrates, halides, and potential hydrogen donors. Whenever new transients were observed we have made an attempt to characterize these species, and in some systems products of the excited radical reactions were characterized.

Results

Description of the Experiment. The samples were irradiated with two laser pulses, at 308 and 337.1 nm. The delay between pulses could be adjusted in 10-ns steps for total times between 10 ns and 1 ms. A third beam, from a xenon lamp, provides the analyzing light used to monitor the changes in optical density.

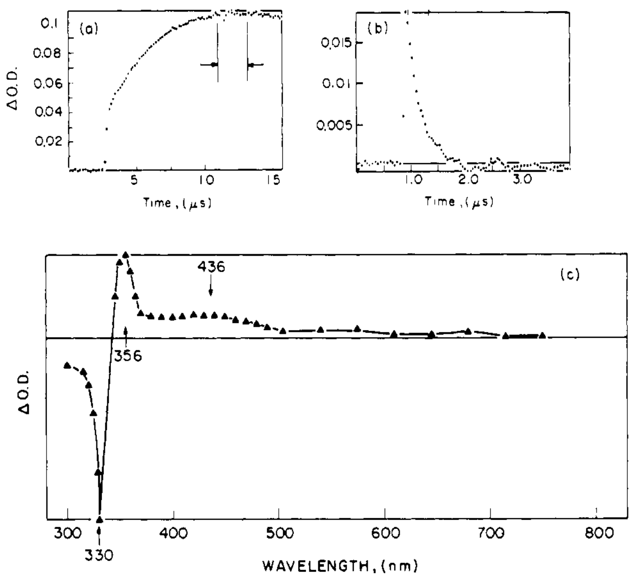

Figure 1. Transient spectrum of the excited diphenylmethyl radical. The radical was produced from a 2 × 10^{-5} M solution of Ph_2CN_2 in cyclohexane. The excitation laser was fired ~8 μs after the synthesis laser. The two traces at the top show the growth of the ground-state radical (λ = 330 nm, left) and the decay of the excited radical (λ = 430 nm, right), monitored in the time domain between the arrows (top, left).

In these particular experiments the 308-nm laser was used as a synthesis source to generate diphenylmethyl by two different routes (vide infra), while the 337.1-nm nitrogen laser was used to excite the radicals. Diphenylmethyl has an absorption maximum at 332–334 nm,[21,22] which makes the nitrogen laser ideally suited for these experiments. The 308-nm beam was used at 90° with respect to the analyzing beam. Special care was taken in aligning the system so that the three beams excite or probe the same volume of sample. A third digital delay, also in 10-ns steps, allowed the triggering of the detection system at any point of the photolysis sequence. The rest of the equipment is the same used in other laser photolysis experiments and has been described elsewhere.[23]

Generation of Diphenylmethyl and Its Excited State. Diphenylmethyl was generated by two independent routes, involving photodecomposition of diphenyldiazomethane (carbene route) and photolysis of *sym*-tetraphenylacetone (ketone route). An interesting difference between these processes is that while the latter is complete in the duration of the 308 nm laser pulse, the former, involving the intermediacy of diphenylcarbene, takes several microseconds to complete.

Carbene Route. When diphenyldiazomethane is photodecomposed in a hydrogen donor solvent, such as cyclohexane, it leads to the efficient formation of diphenylmethyl radicals according to reactions 1 and 2.[21,24] Reaction 1 involves the intermediacy

$$Ph_2CN_2 \xrightarrow{h\nu} \rightarrow Ph_2C{:} + N_2 \tag{1}$$

$$Ph_2C{:} + c\text{-}C_6H_{12} \rightarrow Ph_2\dot{C}H + c\text{-}C_6H_{11}\cdot \tag{2}$$

of the singlet carbene, but this does not play an important role in this particular solvent. Reaction 2 is a relatively slow process, and in neat cyclohexane the lifetime of the carbene is ~2 μs at room temperature.[21] Thus, it is important that in this particular case the 308 nm laser pulse (~5 ns) is sufficiently short that radicals cannot be reexcited by the synthesis pulse.

Figure 1 shows the transient spectrum obtained by 337.1-nm excitation of the radicals about 8 μs following the 308-nm pulse. Note that transient spectra of this type usually report ΔOD, not OD. In this particular case, because of the way in which the

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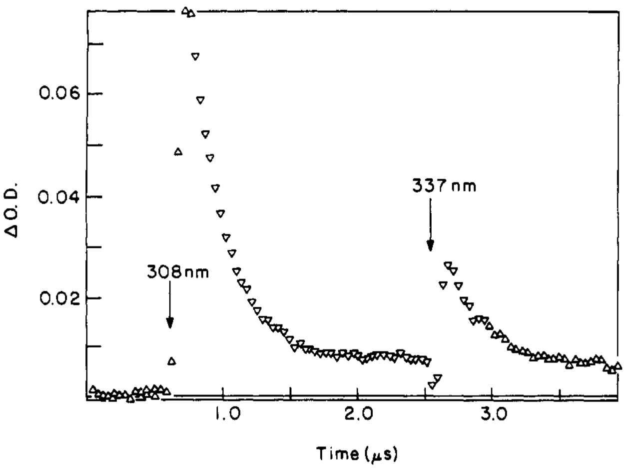


Figure 2. Transient decay of the excited diphenylmethyl radical monitored at 360 nm. The first trace is from a biphotonic process from the synthesis excimer (λ = 308 nm) laser. The second decay is from the excitation of the ground-state radical by the N_2 (λ = 337 nm) laser fired ~2 μs after the synthesis laser. The solvent is 4:1 acetonitrile:water.

experiment is performed, the vertical values correspond to absorbance differences between the excited radical and its ground state. Thus, the bleaching peak (inverted) at ~330 nm[25] agrees well with the absorption maximum for diphenylmethyl in its ground state. At 343 nm we observe an isobestic point between the ground and excited states of the radical, while the absorption maximum at 355 nm corresponds to a $D_1 \rightarrow D_n$ transition. The spectrum is in good agreement with that reported by Meisel et al.[4,5] The lifetime of the excited radical, τ_*, was (260 ± 10) ns and was monitored in four different ways: at the two absorption bands (360 and 440 nm), at the fluorescence band at ~530 nm, and by the recovery of the bleaching signals in the 330–320 nm region. The value of τ_* is in agreement with that reported by Meisel et al. in wet acetonitrile.

All "carbene route" experiments were carried out with a flow system because of the very low concentrations of diazo compound (typically 2 × 10^{-5} M) used.

Ketone Route. Laser photodecomposition of *sym*-tetraphenylacetone (TPA) yields diphenylmethyl radicals according to reactions 3 and 4.

$$Ph_2CHCOCHPh_2 \xrightarrow{h\nu} \rightarrow Ph_2CH\dot{C}O + Ph_2CH\cdot \quad (3)$$

$$Ph_2CH\dot{C}O \rightarrow Ph_2\dot{C}H + CO \quad (4)$$

All the steps in this mechanism, including the ones that have been left implicit (intersystem crossing and triplet cleavage), are extremely fast, and the reaction leads to a pair of diphenylmethyl radicals in the duration of the laser pulse.[26] As a result, some excitation of diphenylmethyl radicals (which have some absorption at 308 nm) is unavoidable during the synthesis pulse. The concentration of TPA, usually 1 mM, was chosen so as to have good absorption at 308 nm (OD_{308} = 0.23 for a 7 mm optical path), while minimizing synthesis by the 337.1-nm laser (OD_{337} = 0.01).[30] A flow system was employed for all spectral studies, while flow or fresh static samples were found to be adequate for single-lifetime measurements in the absence or presence of quenchers.

Table I. Lifetime of Excited Diphenylmethyl Radicals in Various Solvents at 300 K

solvent	τ^*,[a] ns
cyclohexane	255
benzene	251
tetrahydrofuran	256
1,4-cyclohexadiene	60
Bu_3SnH	170
acetonitrile (dry)	232
acetonitrile:water (4:1)	265
methanol	236
ethanol (95%)	256
2-propanol	254
tert-butyl alcohol	259
Freon-113	229
$CHCl_3$	223
$CDCl_3$	223
CCl_4	<5
1,1,2-trichloroethane	236
dibromomethane	104
tetrachloroethylene	16

[a] Typical error ±10 ns.

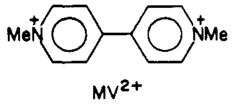
Figure 2 illustrates the formation of excited diphenylmethyl radicals by the synthesis (308 nm) as well as the nitrogen (337.1 nm) lasers for a sample where the former is quite large. Kinetic analysis of either trace yields τ_* = (265 ± 10) ns in 1:4 water:acetonitrile for both sources. Similar agreement was observed at other wavelengths (e.g., the fluorescence at 530 nm), clearly showing that the same species is formed in both cases. Note that the "early" (308 nm) formation of the excited radicals was not observed when using the "carbene route", in agreement with predictions based on the radical formation kinetics for both processes.

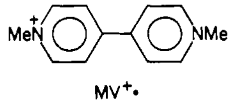
The transient spectrum obtained from TPA was identical with that of Figure 1. This is a rather interesting point that deserves comment: transient spectra are usually precursor dependent in the regions where the precursors absorb. This is due to the fact that ΔOD, not OD, is usually plotted. This is not the case for the excited species, since the actual precursor is in both cases the same, i.e., the ground state of the radical.

The lifetime determined in methanol was slightly shorter than that in other solvents, i.e., τ_* = 236 ± 10 ns. Several lifetimes have been summarized in Table I, including values in 1,4-cyclohexadiene and halogenated solvents which are discussed in some detail in separate subsections.

Intermolecular Reactions of Excited Diphenylmethyl Radicals. Different types of reactions of excited radicals have been examined: quenching by electron donors and acceptors, oxygen scavenging, interaction with potential hydrogen donors, reaction with halide ions, quenching by halogenated substrates (in particular CCl_4), and the effect of water on the lifetimes.

Electron Transfer to Methyl Viologen. The bipyridinium salt methyl viologen (MV^{2+}, also called paraquat) is a well-known electron acceptor, well suited for laser flash studies as a result of the strong absorption bands at 398 and 603 nm characteristic of its reduced form, $MV^{+\cdot}$.[31]


MV^{2+}


$MV^{+\cdot}$

Excited states are generally expected to be better electron donors and acceptors in comparison with the corresponding ground states. Thus, while ground-state $Ph_2\dot{C}H$ does not react with MV^{2+}, its excited state can be expected to be quite reactive.

Addition of MV^{2+} to methanol solutions of TPA in which excited $Ph_2\dot{C}H^*$ is generated leads to a shortening of its lifetime (monitored at 360 nm). The experimental rate constant for

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[25] It is not possible to monitor at λ_{max} because this is too close to the wavelength of the nitrogen laser (337.1 nm).

[26] The lifetime of triplet TPA and that of the $Ph_2CH\dot{C}O$ radical have not been reported in the literature. However, judging from the values for dibenzyl ketone and other more substituted derivatives.[27-29] the overall generation process must take less than 5 ns.

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[30] The energy of the 337-nm pulse is also lower than that of the 308-nm pulse. For instance, when the data in Figure 2 were recorded the energies per pulse were 28 and 5 mJ at 308 and 337 nm, respectively.

[31] E.g.: Small, R. D.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828. Patterson, L. R.; Small, R. D., Jr.; Scaiano, J. C. *Radiat. Res.* **1977**, *72*, 218.

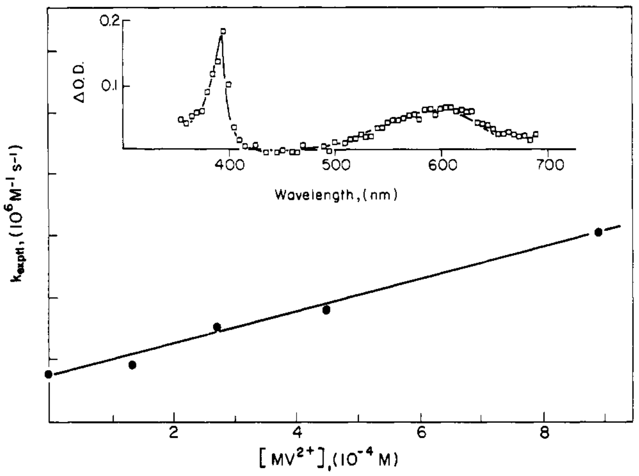


Figure 3. Quenching of the excited diphenylmethyl radicals by methyl viologen. The insert shows the transient spectrum for $[MV^{2+}] = 1 \times 10^{-3}$ M, [TPA] = 1×10^{-3} M. The time window for the spectrum was 0.22 to 1.04 μs after the 337-nm laser. The 337-nm laser is fired 2.8 μs after the 308-nm laser.

transient decay, k_{exptl} follows clean first-order (i.e., single exponential) kinetics, is given by eq 5, where $k_q{}^*$ is the bimolecular

$$k_{exptl} = \tau_*{}^{-1} + k_q{}^*[MV^{2+}] \quad (5)$$

rate constant for quenching of excited diphenylmethyl radicals. Figure 3 shows a plot of k_{exptl} as a function of electron acceptor concentration, from which we obtain $k_q{}^* = (1.3 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} (errors reported as $\pm 2\sigma$ throughout). We propose that $k_q{}^*$ corresponds to the electron transfer of reaction 6.

$$Ph_2\dot{C}H^* + MV^{2+} \rightarrow Ph_2CH^+ + MV^{+}\cdot \quad (6)$$

However, it should be noted that quenching does not necessarily imply that full electron transfer has taken place. In order to establish this point, we recorded the difference spectrum (ΔOD, as usual) of the residual absorption generated during the decay of $Ph_2\dot{C}H^*$ in the presence of 10^{-3} M MV^{2+}. This is included as an insert in Figure 3 and is identical with the known spectrum of $MV^{+}\cdot$; while we have not carried out detailed quantum yield studies, judging from the signal intensity, the electron transfer reaction to MV^{2+} must be the dominant mode of decay for $Ph_2\dot{C}H^*$ under our experimental conditions.[32]

We note that while MV^{2+} is essentially transparent at 337.1 nm, it does have some absorption at 308 nm; excitation at this wavelength leads to the formation of some of the reduced form, $MV^{+}\cdot$, via direct excitation. This does not interfere with the experiment, since we selectively monitor a differential effect caused by 337.1-nm excitation which does not lead to direct photodecomposition in the concentration range examined.

Quenching by Amines. Amines, which are known to be excellent electron donors, do not appear to react significantly with the ground state of $Ph_2\dot{C}H$, at least not in the range of concentrations and time scales required (vide infra) for studies of excited-state reactivity. As with other quenchers, it was convenient to monitor excited-state decay at 360 or 355 nm. Triethylamine was an excellent quencher in both polar and nonpolar solvents. Figure 4 shows the corresponding plots in cyclohexane and in methanol. In the former we obtain $k_q{}^* = (5.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1}. Table II summarizes the kinetic data for this and other quenchers.

In an attempt to establish if the process involved full electron transfer, we examined diamine I for which recent work from our laboratory has shown that the corresponding radical cation shows a strong absorption band with maximum at ~600 nm.[34]

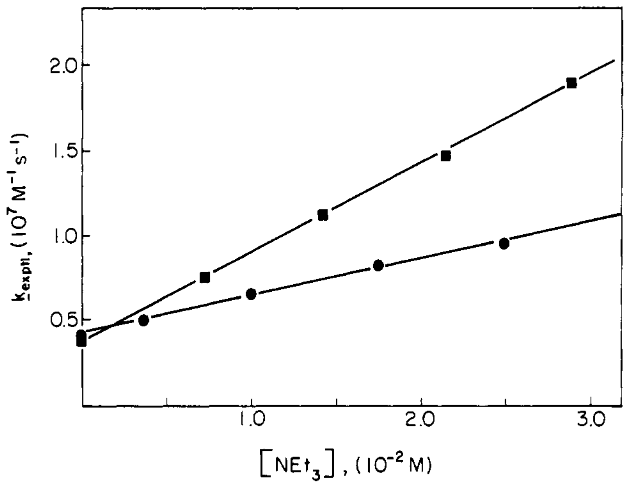
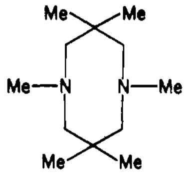


Figure 4. Quenching of excited diphenylmethyl radicals by triethylamine in methanol (●) and cyclohexane (■).

Table II. Rate Constants for Intermolecular Reactions of Excited Diphenylmethyl Radicals at 300 K

quencher	solvent	$k_q{}^*$,[a] M^{-1} s^{-1}
methyl viologen	acetonitrile:water[b]	$(1.3 \pm 0.2) \times 10^{10}$
carbon tetrachloride	methanol	$(1.6 \pm 0.1) \times 10^8$
triethylamine	cyclohexane	$(5.2 \pm 0.2) \times 10^8$
triethylamine	methanol	$(2.1 \pm 0.1) \times 10^8$
diamine I	cyclohexane	$(4.5 \pm 0.4) \times 10^9$
methylmethacrylate	cyclohexane	$(4.0 \pm 0.6) \times 10^6$
1,4-cyclohexadiene	cyclohexane	$(1.1 \pm 0.2) \times 10^6$
oxygen	cyclohexane	$(8.7 \pm 0.8) \times 10^9$

[a] Errors as $\pm 2\sigma$. [b] 4:1 acetonitrile water.



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The diamine quenched the excited state of $Ph_2\dot{C}H$ at close to the diffusion-controlled rate (Table II), which argues strongly in favor of charge-transfer interactions; however, we could not detect the corresponding radical ion in spite of several efforts under varying experimental conditions.

Quenching by Oxygen. The quenching of excited diphenylmethyl radicals by oxygen was monitored at 360 nm with the same approach as with other quenchers and controlling the oxygen concentration by bubbling mixtures of N_2/O_2 of known composition through the samples. For comparison, we also recorded the rate of reaction for the ground state, which had not been examined in an earlier study of free radical reactivities toward oxygen.[35] In this case the signals were monitored at 332 nm. The corresponding plots are shown in Figure 5 which lead to quenching rate constants of $(6.3 \pm 0.5) \times 10^8$ and $(8.7 \pm 0.8) \times 10^9$ M^{-1} s^{-1} for the ground and excited states, respectively. Why is the excited state 14 times more reactive than the ground state? In principle, one can suggest three simple mechanisms for the interaction between the excited radical and oxygen, i.e.:

$$Ph_2\dot{C}H^* + O_2 \rightarrow Ph_2C(H)OO\cdot \quad (7)$$

$$Ph_2\dot{C}H^* + O_2 \rightarrow Ph_2C{:} + HO_2\cdot \quad (8)$$

$$Ph_2\dot{C}H^* + O_2 \rightarrow Ph_2\dot{C}H + {}^1O_2 \quad (9)$$

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[32] Meisel[5] reports $\epsilon_{355} = 3.3 \times 10^4$ M^{-1} cm^{-1} for $Ph_2\dot{C}H$, while for $MV^{+}\cdot$ $\epsilon_{605} = 1.3 \times 10^4$ M^{-1} cm^{-1}.[33] On this basis it is possible to obtain a rough estimate of the fraction of quenching events which lead to full electron transfer as 70–80%.

[33] Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372. Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524.

[34] Scaiano, J. C.; Stewart, L. C.; Livant, P.; Majors, A. W. *Can. J. Chem.* **1984**, *62*, 1339.

[35] Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

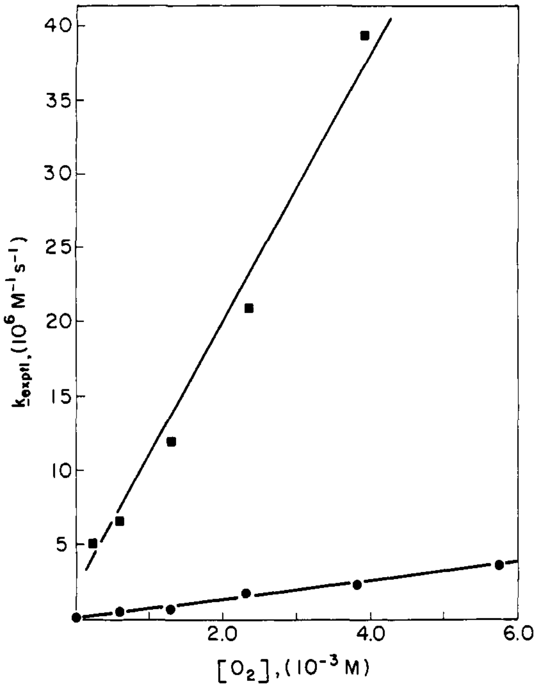


Figure 5. Quenching of the transient absorption of the ground-state (●) and excited-state (■) diphenylmethyl radical by O_2.

Each one of these mechanisms would be expected to lead to different transient phenomena. Thus, reaction 7 is analogous to the ground-state reaction and would not be expected to lead to ground-state recovery when monitored in the region of strong absorption (e.g., around 330 nm). Reaction 8 would be anticipated to lead to minimal recovery due to abstraction from cyclohexane by the carbene; however, the cyclohexane reaction is relatively slow and the main path for the carbene would probably be reaction 10 leading to the corresponding carbonyl oxide which absorbs strongly at 410 nm.[36,37]

$$Ph_2C: + O_2 \rightarrow Ph_2COO \qquad (10)$$

On the other hand, reaction 9 would be expected to lead to a full recovery of the ground-state absorption. Obviously, mixed reaction paths are a possibility that would be difficult to rule out conclusively. Figure 6 shows a decay trace for ground-state $Ph_2\dot{C}H$, where 337-nm excitation is shown to produce only a short transient perturbation, leading to quantitative recovery of the ground-state absorption.[38] The expanded scale shows a detail of the recovery, which under the conditions of the figure occurs with a lifetime of 195 ns. No new absorptions were observed at 410 nm, thus indicating that reaction 8 followed by reaction 10 did not make any significant contribution. Judging from the signals at 330 nm, it is clear that reaction 9 represents the predominant reaction path. As is usual with $^1O_2$ sources, reaction 9 will be expected to incorporate some inefficiency leading to some excited-state deactivation without singlet oxygen generation. The details of this partition between efficient and inefficient quenching cannot be established at this point.[39]

Reaction with Potential Hydrogen Donors. The lifetime of excited diphenylmethyl radicals was determined in 1,4-cyclohexadiene[40] as solvent with TPA as the radical source and led to τ_* = 60 ns (see Figure 7), as compared with ca. 260 ns in an inert solvent (Table I). A quenching plot with cyclohexane as solvent led to k_q^* = (1.1 ± 0.2) × 10^6 M^{-1} s^{-1}. Figure 7 shows that the signal at 327 nm (due to ground-state $Ph_2\dot{C}H$ and recorded in 1,4-cyclohexadiene as solvent) does not recover efficiently following the decay of the excited radical, indicating some permanent chemical change. This may be due to the occurrence of hydrogen abstraction,

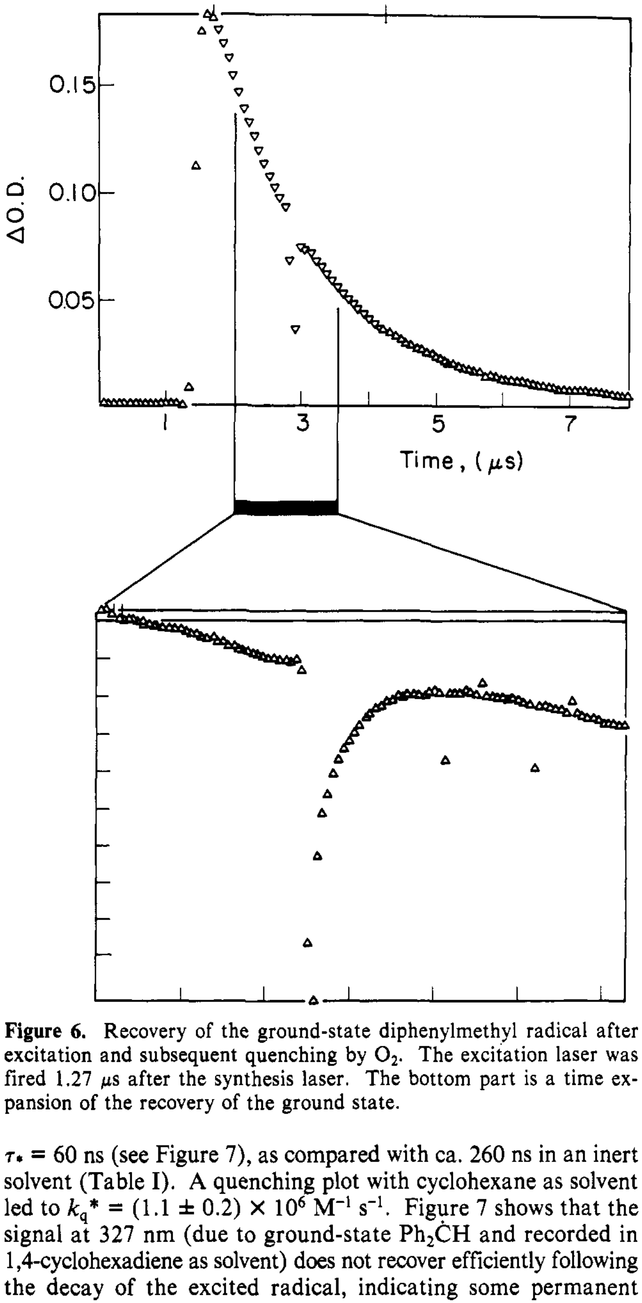
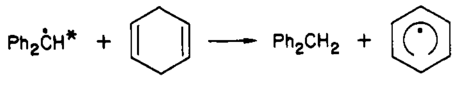


Figure 6. Recovery of the ground-state diphenylmethyl radical after excitation and subsequent quenching by O_2. The excitation laser was fired 1.27 μs after the synthesis laser. The bottom part is a time expansion of the recovery of the ground state.



II

(11)

Unfortunately our attempts to detect the weak (ϵ < 100 M^{-1} cm^{-1}) signals from II in the 500–600 nm region were unsuccessful; however, given the very weak nature of this band and the experimental difficulties in a measurement of this nature this cannot be taken to rule out H abstraction as the quenching mechanism.

Another well-established[41,42] hydrogen donor used was tri-*n*-butyltin hydride. When this was used as solvent the lifetime of $Ph_2\dot{C}H^*$ was 170 ns. If this reduction of the lifetime is due solely to hydrogen abstraction, it would lead to $k \sim 4 \times 10^5$ M^{-1} s^{-1},

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(36) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

(37) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623.

(38) In fact there is a slight increase in optical density compared to expectations if the decay was to proceed with the same rate constant. This may be due to the fact that excited radicals recover, rather than decay during this period, thus effectively inhibiting the irreversible decay of the ground state.

(39) Even in the well-studied case of benzophenone triplet the yield of $^1O_2$ is a matter of current interest and controversy. See, for example: Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679.

(40) 1,4-Cyclohexadiene is an excellent hydrogen atom donor, see: Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

(41) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1055, 7047.

(42) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

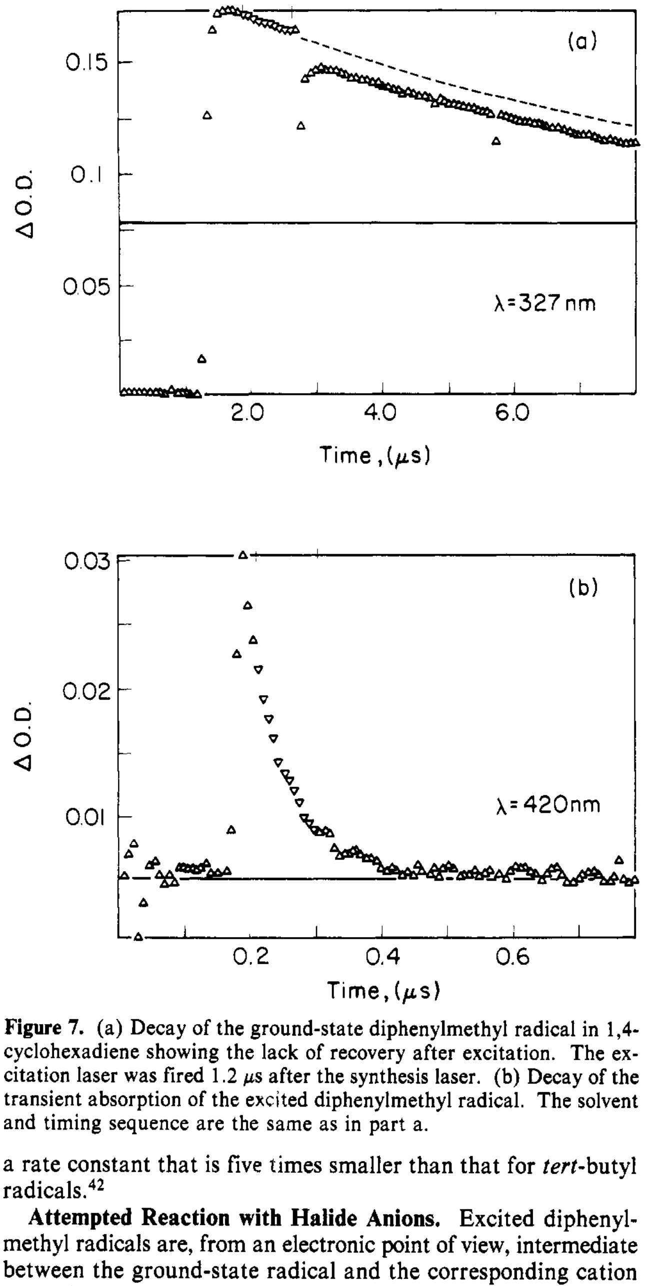


Figure 7. (a) Decay of the ground-state diphenylmethyl radical in 1,4-cyclohexadiene showing the lack of recovery after excitation. The excitation laser was fired 1.2 μs after the synthesis laser. (b) Decay of the transient absorption of the excited diphenylmethyl radical. The solvent and timing sequence are the same as in part a.

a rate constant that is five times smaller than that for *tert*-butyl radicals.[42]

Attempted Reaction with Halide Anions. Excited diphenylmethyl radicals are, from an electronic point of view, intermediate between the ground-state radical and the corresponding cation (one of the electrons being "half-way" out). These experiments were carried out in 1:4 water:methanol with TPA as a radical source. The excited-state lifetime in this solvent was 280 ns, and addition of 0.2 M KBR had no effect on the lifetime, while 0.2 M NaCl *increased* the excited lifetime to 310 ns, presumably an ionic strength effect. The transient studies did not provide any indication of new chemical processes. If we estimate that a 10% shortening of the lifetimes would be readily detectable, then for both Cl^- and Br^- $k_q^* \ll 1.5 \times 10^6$ M^{-1} s^{-1}.

Quenching by Halogenated Solvents. When chloroform was used as a solvent the lifetime of $Ph_2\dot{C}H^*$ was 223 ns, somewhat shorter than that in non-chlorinated solvents (see Table I). The same value was obtained in chloroform-*d*, which seems to rule out hydrogen abstraction as the mechanism for lifetime shortening. Another chlorinated solvent, Freon-113, gave $\tau_* = 229$ ns.

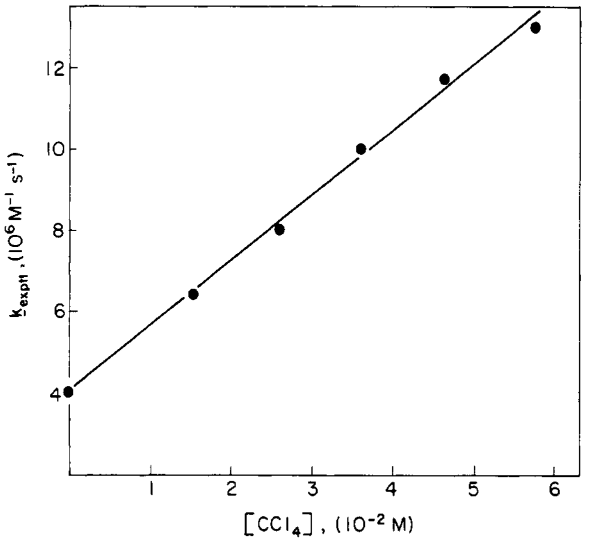
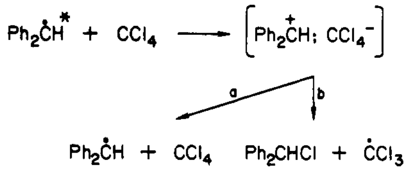


Figure 8. Quenching of the excited diphenylmethyl radical by CCl_4.

When CCl_4 was used as solvent no excited species were detected. However, experiments where the ground-state absorption was monitored at 330 nm revealed that excitation of the radical occurred with concomitant bleaching (depletion) of the ground state. A quenching plot in which CCl_4 was added to a methanol solution (Figure 8) led to $k_q^* = (1.6 \pm 0.1) \times 10^8$ M^{-1} s^{-1}. Other halogenated solvents, such as 1,1,2-trichloroethylene, dibromomethane, and tetrachloroethylene, also led to reduced excited-state lifetimes (Table I). The last one may involve some attack at the double bond. A charge-transfer mechanism leading to halogen abstraction seems likely; for example, in the case of CCl_4 we propose



We could not find any evidence for free Ph_2CH^+, suggesting that the ions do not leave the geminate cage.[43] The product Ph_2CHCl was characterized by gas chromatography and suggests that the reactive path b plays an important role. The trichloromethyl radical presumably leads to typical recombination or abstraction products.

To show the excited state is the reactive species a product analysis by GC was undertaken on two samples of 1 mM tetraphenylacetone in CCl_4. Sample A was photolyzed by the 308-nm laser then 0.4 μs later by the 337-nm laser. Sample B had the timing sequence reversed. Both samples were photolyzed by 1200 laser pulses with a 15% transmission filter on the 308-nm laser to minimize biphotonic processes with just one laser.

The main product of sample B was the recombination product tetraphenylethane although some Ph_2CHCl was observed. In sample A the yield of Ph_2CHCl was much greater. The yield of Ph_2CHCl relative to tetraphenylethane was 0.80 and 0.21 for samples A and B, respectively. Since the excited-state radical should only be produced by 337-nm excitation in sample A during reaction, the product yields are entirely consistent with the reaction mechanism of eq 12.

Effect of Water on the Lifetimes. The lifetime of $Ph_2\dot{C}H^*$ in dry, freshly distilled acetonitrile was 232 ns. Addition of 0.08 M water led to an increase to 252 ns, while further increases quickly stabilized the lifetime at 265 ns, the value for $[H_2O] \geqslant 10$ M. This may suggest that hydrogen bonding plays a role in determining the excited radical lifetime and at the same time that the excited state is a relatively polar species. Table I illustrates this effect in several solvents.

Discussion

The spectroscopy of benzylic radicals, including diphenylmethyl, is well understood, largely through luminescence studies in matrices at low temperature.[12-20] Recently, Meisel et al. in a pioneering contribution have shown that these excited radicals can be readily detected using nanosecond spectroscopy techniques if the appropriate pulsed sources and timing sequences are available.[4] More

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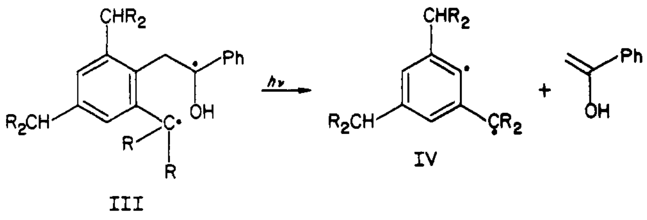
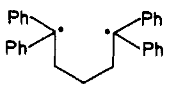
(43) Ph_2CH^+ shows an absorption band at 456 nm, see: Volz, H.; Mayer, W. D. *Liebigs. Ann. Chem.* **1975**, 835.

recent work from the same laboratory[5] has examined the question of structural effects on the spectroscopy and lifetimes of a series of related radicals. Fessenden et al.[7] and independently Turro et al.[10] have examined the behavior of excited diphenylhydroxymethyl radicals; in particular Turro's group[10] has measured several rate constants based on fluorescence quenching studies. These studies have generally concentrated on kinetic and spectroscopic questions, but have not dealt with the actual chemical reactions involved. In another study from our laboratory we have shown that III undergoes photocleavage to yield IV, which is ultimately responsible for the formation of products resulting from transient photodecomposition.[11,44]



Recently, we have shown that V can be photodecomposed readily.[46] Our experiments also indicate that the main product of this biphotonic process can be readily prepared in at least 15–20% yield.[47] These high yields suggest that with adequate optimization these reactions could be of synthetic value, providing new pathways not available through ground-state or monophotonic chemistry.



V

We are now in the process of examining several biphotonic reactions, placing our emphasis in systems where we feel the chemistry can be established in some detail; our experiments in this report have been chosen trying to meet this criterium.

It is rather interesting that the lifetime of $Ph_2\dot{C}H^*$ is rather insensitive to the solvent, changing by less than 10% in methanol, cyclohexane, and wet acetonitrile. This suggests a very low reactivity toward hydrogen abstraction, which is further supported by the data for 1,4-cyclohexadiene and tri-*n*-butyltin hydride, as well as other substrates, such as 2-propanol. In this sense, it should be noted that abstraction by excited diphenylmethyl would be substantially more exothermic than abstraction by phenyl or methyl radicals. Thus, the low reactivity of $Ph_2\dot{C}H^*$ should be attributed to the lack of radical-like properties, not to an unfavorable enthalpy change. For example, phenyl radicals react with 2-propanol with $k = 1.4 \times 10^6\ M^{-1}\ s^{-1}$.[48] By contrast, $Ph_2\dot{C}H^*$ is at least 50 times less reactive.

As in the case of stable molecules, electron donor/acceptor properties are drastically enhanced upon excitation; the rate constant obtained for reaction with MV^{2+} is for all practical purposes diffusion controlled.[49]

The reaction with carbon tetrachloride is another example where charge transfer must play an important role; however, here the reaction ultimately leads to atom rather than full electron transfer. Similar charge transfer mechanisms have been established for ground-state radicals centered on Si, Ge, and Sn.[52]

In the case of amines we also suspect charge transfer as the factor determining the rates; however, we do not see a clear indication of ultimate chemical change revealing charge transfer; in fact even an inverse solvent effect (see Table II) is apparent. One can only speculate that perhaps an exciplex-like mechanism, ultimately leading to excited-state quenching, may be operative.

$Ph_2\dot{C}H^*$ does not seem to react with chloride or bromide, a reaction that is very fast in the case of the corresponding cation. It could be argued that if the radical anion Ph_2CHX^- was formed its favored reaction path would be loss of X^-.[17,53] However, this could provide a pathway for excited-state deactivation. Clearly it does not.

Reaction with molecular oxygen is interesting in that $Ph_2\dot{C}H^*$ follows the reaction path which is typical of excited states, not free radicals. Thus, it would seem that at least for this particular system the following general ideas apply:

(i) Typical excited-state characteristics, such as an enhancement of electron donor/acceptor properties and energy transfer ability are observed for $Ph_2\dot{C}H^*$. This probably reflects the π,π^* character of the lowest excited state of $Ph_2\dot{C}H$.[12]

(ii) Free-radical characteristics are far below what could be expected from other systems with comparable exothermicity. Thus, $Ph_2\dot{C}H^*$ reactivity in hydrogen abstraction is well below those of reactive radicals such as Ph•, CH_3• or *t*-BuO•, even when enthalpy changes would favor a higher reactivity for $Ph_2\dot{C}H^*$.

(iii) $Ph_2\dot{C}H^*$ does not seem to have any "carbocation-like" properties, even if it is formally an intermediate state between the radical and the carbocation. This is evidenced by the lack of reactivity toward Cl^-, Br^-, and hydroxylic substrates.

(iv) $Ph_2\dot{C}H^*$ appears to participate readily in halogen abstraction reactions, in particular in the case of carbon tetrachloride. This reactivity is probably a reflection of the electron-donor ability of the excited radical.

(v) The increase in lifetime upon addition of water, while small, is a very reproducible effect and may indicate a higher polarity in the excited-state as compared with the ground-state radical. A similar lifetime enhancement appears to occur upon addition of salts such as NaCl.

A difference with results reported by Meisel et al.[5] is worth noting. We have not observed extensive irreversible photochemistry of $Ph_2\dot{C}H$, as reported;[5] however, we do observe some product formation at 480 nm. This is a minor process and has not been pursued in any detail. The differences in behavior can be readily understood in the framework of the mechanism proposed by Meisel et al.[5] These authors report that $Ph_2\dot{C}H^*$ is photodecomposed by excitation near its absorption maximum ($\lambda_{max} = 355$ nm).[54] In their case the radical excitation source is a frequency doubled ruby laser, delivering pulses at 347 nm,[5] as compared with our use of a nitrogen laser at 337.1 nm for this purpose. The 10-nm difference between the two lasers is far from trivial; $Ph_2\dot{C}H$ shows a remarkably sharp absorption band at 332–334 nm,[21] while $Ph_2\dot{C}H^*$ absorbs at 355 nm (see Figure 1 and ref 4 and 5). Thus, the 347-nm laser is well suited for reexcitation of $Ph_2\dot{C}H^*$ because it is too far from the sharp band of the ground state at 332–334 nm. By contrast, the nitrogen laser is ideally suited for ground-state excitation, and the probability of absorption by $Ph_2\dot{C}H^*$ is negligible. Most likely, the energy per pulse is higher in the ruby laser used by Meisel et al.[5] as compared with our nitrogen laser which is usually in the 4–10 mJ/pulse range. In summary, the difference in irreversible photochemistry of $Ph_2\dot{C}H$ between our results and those reported earlier[5] can be readily explained on the basis of the small difference in excitation wavelength, and it provides strong support for the explanation offered by Meisel et al.[5]

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(44) The details of the monophotonic chemistry of arylacetophenones have been discussed by Meador and Wagner.[45]

(45) Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 4484.

(46) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607.

(47) Johnston, L. J.; Scaiano, J. C., unpublished results.

(48) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

(49) Excited aromatic hydrocarbons and ketones readily react with MV^{2+} to yield its reduced form.[50,51]

(50) Das, P. K. *Tetrahedron Lett.* **1981**, *22*, 1307.

(51) Davidson, R. S.; Bonneau, R.; Fornier De Violet, P.; Joussott-Dubien, J. *Chem. Phys. Lett.* **1981**, *78*, 475.

(52) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343. Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 571.

(53) Hamill, W. H.; Guarino, J. P.; Ronayne, M. R.; Ward, J. A. *Discuss. Faraday Soc.* **1963**, *36*, 169. Capellos, C.; Allen, A. O. *J. Phys. Chem.* **1969**, *73*, 3264.

(54) Note that in our case this would require a triphotonic process, i.e., $TPA \xrightarrow{h\nu} Ph_2\dot{C}H \xrightarrow{h\nu} Ph_2\dot{C}H^* \xrightarrow{h\nu}$ products.

Finally, the recent literature on excited free radicals has been dominated by a controversy relating to the reactivity of the σ and π states of succinimidyl and related radicals.[55-58] Indeed, much of this stimulating work has concentrated on whether it is necessary or not to invoke an excited state of the radical.[56,57] Our results here do not allow us to address this question in any detail; we would like, however, to point out that excitation of $Ph_2\dot{C}H$ involves a π,π^* transition as opposed to the σ and π states involved in the succinimidyl controversy and that the energy gap is large in $Ph_2\dot{C}H$, a factor that would probably make radiationless relaxation faster for succinimidyl than for $Ph_2\dot{C}H^*$.

Experimental Section

Materials. 1,1,3,3-Tetraphenylacetone (TPA) was prepared by modification of the method reported by Dean et al.[59] The ethyl diphenylacetate and sodium route was used. The steam distillation was omitted and instead the ether extract was cooled in an ice bath to yield off-white crystals. Two recrystallization from ethanol yielded white crystals with an uncorrected melting point of 133–134 °C.

The 60-MHz NMR spectrum of the product in chloroform-*d* gives a singlet at 5.2 ppm for the –CH– protons and a multiplet centered at 7.2 ppm with respect to Me_4Si. The integrated ratio of the aromatic vs. methylene peaks was within 5% of the expected 10:1 value.

The solution IR of tetraphenylacetone in CCl_4 gave a strong single CO stretch at 1723 cm^{-1}.

Diphenyldiazomethane was prepared according to a literature procedure.[60]

All other reagents and solvents were commercially available and were used as received, except for the following ones that were purified as indicated: acetonitrile (Fisher) refluxed over CaH_2 for 2 h before distillation; triethylamine was shaken with NaOH before distillation; and methyl viologen (K and K) was recrystallized twice from methanol before use.

General Techniques. UV–visible spectra were recorded in a Varian-219 spectrometer. Products of the reaction with carbon tetrachloride were identified by gas chromatography. The NMR spectra were obtained on a Varian EM-360 spectrometer. GC analyses were carried out on a Perkin-Elmer 8320 capillary gas chromatograph with a J and W bonded phase vitreous silica BP1 column of 12 m length.

Laser Photolysis. Our laser flash photolysis facility has been described in some detail in an earlier publication.[23] However, a number of changes introduced in the last few years and recent modifications to carry out two-laser experiments justify some description of these changes. The basic monitoring system, including lamp, lenses, monochromator, detector, and transient digitizer remain the same as before.[23] The computer has been upgraded to a PDP-11/23 operated under an RT-11 (Version 4.0) extended memory operating system. Color filters and neutral density filters are now controlled by the software, and in the case of the former they are selected to minimize sample irradiation and to eliminate second-order components through the monochromator system. Temperatures are read via a Cole Parmer (Casper) DPT-600 controller and Pt-thermometer interfaced with the 16-bit DRV11 interface and multiplexer.

All delays required in order to achieve the proper sequence of events are now controlled by 5-decade digital units built around Evans Associates 4145-2 modules. This allows timing sequences of up to 1 ms to be reproducibly adjusted in 10-ns steps. This is essential in experiments of the type described here.

Four lasers are now available in any sequence, and up to three can be incident on the sample, in addition to the monitoring beam. (i) The first is a Molectron UV-24 nitrogen laser delivering 337.1-nm pulses of up to 10 mJ/pulse and ~8-ns duration. This beam is incident on the sample at 15° with respect to the monitoring beam. (iii) The second is a Lumonics TE-860-2 excimer laser delivering pulses at various wavelengths, depending on the gas mixture. In this case we used Xe–HCl which corresponds to 308-nm pulses of up to 80 mJ/pulse and ~5-ns duration. This beam was incident at 90° with respect to the monitoring beam. The other two lasers were not used in this work, but they are included here to have an adequate description of the system for future reference. (iii) The third is a PRA Megaplus nitrogen laser which delivers ~1.3-mJ pulses at 337.1 nm of 600-ps duration. This beam uses a similar optical train to that described in (i). (iv) The fourth is a Candela 500M dye laser upgraded to operate at 1 Hz delivering pulses which with Rhodamine 6G are of 200–250 ns duration and up to 2.5 J/pulse. Appropriate frequency doubling crystals make wavelengths in the 265–310 nm range available, and a pulse slicer (Model 51016 from Laser Metrics) allows the time duraction to be adjusted down to ca. 10–20 ns. Naturally, doubling and slicing are carried out at the expense of the energy per pulse. This beam is used at 80 °C with respect to the monitoring beam.

Finally, we would like to comment on a source of errors in lifetime measurements in the case of photoexcited transients. The very nature of the experiment is such that the decay of the excited radical is superimposed on transient processes involving the ground-state species; these are either buildup or decay in the case of the carbene route and decay in the case of TPA. Some error can result if this slope is not taken into consideration; 5–7% error in the lifetime can easily be introduced before the need for base line corrections becomes evident through visual observation of the traces. The lifetimes measured can be longer or shorter than the correct value dependong on whether they are superimposed on buildup or decay traces, respectively.

Acknowledgment. Thanks are due to Drs. R. W. Fessenden and D. Meisel for sharing their results before publication and to S. E. Sugamori and G. Charette for their technical assistance.

Registry No. I, 17288-12-9; diphenylmethyl, 4471-17-4; methyl viologen, 1910-42-5; carbon tetrachloride, 56-23-5; triethylamine, 121-44-8; methyl methacrylate, 80-62-6; 1,4-cyclohexadiene, 628-41-1; oxygen, 7782-44-7; 1,1,3,3-tetraphenylacetone, 7476-11-1; diphenyldiazomethane, 883-40-9.

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(60) Smith, L. I.; Howard, K. L. "Organic Synthesis"; Wiley: New York, 1955; Collect. Vol. III, p 351.