

fine-structure splittings. Since the reagents approach one another with a finite velocity, the wavefunction corresponding to a single incident spin-orbit level nonadiabatically builds up amplitude on more than one electrostatic surface at smaller separations. In nonreactive systems this mixing causes collisional transitions between the fine-structure levels.^{65,66} In a semiclassical description of this process,^{42,65,66} the range of separations at which this mixing occurs is around that for which the electrostatic splittings equal the spin-orbit splittings. Since the latter is larger for Sr(³P⁰) than for Ca(³P⁰), the nonadiabatic mixing arises at smaller separations for Sr. In the extreme case of Hg(³P⁰) the spin-orbit splitting is so large that the collisions are almost entirely adiabatic.¹⁵⁻¹⁷ We would thus expect the spin-orbit effect in Sr(³P⁰) reactions to be larger than those involving Ca(³P⁰).

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Unfortunately, the experimental errors are large, but at least for the ground-state reaction pathway it appears that there is a somewhat greater spin-orbit selectivity in Sr(³P⁰) reactions, if the present results are compared with the previous results³⁸ for Ca(³P⁰) + Cl₂. For the chemiluminescence pathway, the dependence on spin-orbit state appears quite similar to within experimental error for all the Ca(³P⁰)^{37,39,40} and Sr(³P⁰) reactions studied, with the one exception of Ca(³P⁰) + SF₆, for which all the spin-orbit levels had about the same chemiluminescence cross section.⁴⁰ Perhaps more precise measurements of the spin-orbit dependent cross sections would reveal some differences between the Ca(³P⁰) and Sr(³P⁰) reactions.

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Temperature Dependence of the Lifetime of Excited Benzyl and Other Arylmethyl Radicals[‡]

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Abstract: The temperature dependence of the fluorescence lifetime of benzyl, benzyl-*d*₇, α -methylbenzyl, and triphenylmethyl radicals has been studied in 2-methyltetrahydrofuran from 77 to 300 K. Temperature independent and unusual temperature dependent relaxation pathways are observed for the excited states of all four radicals. Activation energies for the temperature-dependent relaxation process are ~ 1400 cm⁻¹ for all these radicals, and frequency factors are in the range of (2-20) $\times 10^{11}$ s⁻¹. For Ph₃C radicals, the temperature-dependent process leads to observable photochemistry. However, no photochemistry is observed to result from the thermally activated relaxation of benzyl radicals. Possible pathways of these nonradiative decay processes are discussed and contrasted with the weak temperature dependence for the relaxation of diphenylmethyl radicals. It is proposed that the temperature-dependent route for the radiationless decay of benzyl radicals results from differential vibronic mixing of the two excited states, the ¹2A₂ and ²2B₂ states. Most efficient in that mixing seems to be C-C stretching vibrational modes.

Photophysics and photochemistry of short-lived radicals in liquid solutions have recently become a focus of renewed interest.¹⁻⁷ In a typical experiment, radicals for such studies are produced by a preliminary pulse (using either pulse radiolysis^{1,2} or laser flash photolysis³⁻⁶) and are excited shortly thereafter by another laser pulse. With use of such a double-pulse technique, the photophysics and photochemistry of a series of arylmethyl radicals have been recently studied in a variety of liquids at room temperature.^{1,2,5} These studies revealed that the lowest excited doublet state of diphenylmethyl, Ph₂CH*, is remarkably long lived and is highly emissive ($\tau = 280$ ns, $\Phi_{\text{fl}} = 0.3$). While no intramolecular photochemistry was observed for Ph₂CH*, high yields of intramolecular photochemistry ($\phi_{\text{ph}} \sim 1$) were observed for the substituted Ph₂CR* (R = Ph, Me, or *c*-Pr) radicals. An electrocyclic ring closure, resulting from an increased twist angle of the phenyl rings out of the central molecular plane, has been proposed⁸ to ra-

tionalize these striking differences between Ph₂CH* and Ph₂CR*.^{1,2,9} Further studies have shown that neither the radiative nor the nonradiative decay rates of Ph₂CH* change appreciably upon decreasing the temperature down to 77 K (in 2-methylpentane/cyclohexane glass).⁹ On the other hand, for Ph₂CR* fluorescence quantum yields in the glassy matrix at 77 K are significantly higher than those for Ph₂CH* primarily due to higher radiative decay rates. However, at room temperature and in the

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liquid phase the photochemical routes for $\text{Ph}_2\dot{\text{C}}\text{R}^*$ dominate any other relaxation process.

The photophysics of the most interesting radical in this family of radicals, the prototype benzyl radical, have never been studied in the liquid phase. Extensive studies, however, have established that PhCH_2^* is rather long lived ($\tau = 1\text{--}1.5 \mu\text{s}$) in glassy matrices at 77 K.¹⁰ In view of the very weak dependence of the decay rate of $\text{Ph}_2\dot{\text{C}}\text{H}^*$ on temperature and since the electrocyclic reaction mentioned above is unavailable to PhCH_2^* , one may naively expect the latter excited state to be long lived in the liquid phase at ambient temperature as well. This, however, is not the case as is established in the present report.

Experimental Section

Laser flash photolysis experiments were conducted with the computer-controlled apparatus previously described in detail.^{4,11} Radicals were produced with use of the 248-nm pulses of a KrF excimer laser (Lambda Physik EMG101 MSC) and subsequently excited by 320-nm pulses from a Quanta Ray DCR-1 YAG laser with PDL dye laser (using a DCM dye and a frequency doubling crystal). Both laser beams coincide at the sample cell wall facing the monochromator. The 248-nm light was not focused while a cylindrical lens was used in conjunction with the 320-nm light. Total energy of the 320-nm light was ca. 3 mJ per pulse. For transient absorption studies, an ISA DH-10 double-grating monochromator was used in order to reduce scattered light effects for the studies of the benzyl radical since the observation wavelength was very close to the excitation wavelength. Photomultiplier signals were recorded and digitized by a Tektronix R-7912 digitizer.

Temperature was varied by blowing heated or cooled nitrogen through a dewar tube surrounding the cell and equipped with optical suprasil windows. For measurement of the temperature, a thermocouple was inserted into the metallic cell holder in contact with the cell itself (3 × 7 mm silica). For transient absorption studies at room temperature, a flow cell was used.

Benzyl chloride and diphenylmethyl chloride (both Aldrich) were distilled under reduced pressure. Benzyl-*d*₇ chloride (Aldrich) and (1-chloroethyl)benzene (Pfaltz and Bauer) were used as received. Triphenylmethyl chloride (Aldrich) was recrystallized from isooctane. 2-Methyltetrahydrofuran and acetonitrile (both Aldrich) were distilled over LiAlH_4 and P_2O_5 , respectively. All other solvents were of highest purity commercially available and were used without further purification. Solutions were prepared and deaerated by bubbling nitrogen for at least 15 min, immediately before irradiation.

Results and Discussion

Arylmethyl radicals were produced from the parent arylmethyl chloride by flash photolysis ($\lambda_{\text{ph}} = 248 \text{ nm}$) of their deaerated solutions. Production of the benzylic radicals has been verified in each case by following their absorption in the near-UV region of the spectrum (see inset to Figure 1). These radicals were then excited (1–5 μs after their production in the fluid solutions; at low enough temperatures the radicals are stable for many minutes) by the second harmonic of a Nd:Yag pumped dye laser ($\lambda_{\text{exc}} = 320 \text{ nm}$). The sequence of events leading to the formation and excitation of benzyl radicals is shown in Figure 1. It was also verified that the fluorescence at low temperatures described below results from excitation of the benzyl radicals by comparing the vibrationally structured emission spectra with those previously reported.¹²

No emission could be observed from $\text{Ph}\dot{\text{C}}\text{H}_2^*$ in a variety of solvents at room temperature. These include methanol, cyclohexane, methylcyclohexane, 2-methyltetrahydrofuran (2-MTHF), perfluoromethylcyclohexane, perfluoro ether, 20% H_2O in glycerol, or neat glycerol (viscosity 1500 cP). The lack of any measurable emission from excited benzyl radicals has also been observed by Scaiano¹³ in a variety of solvents. Furthermore, when the absorption of $\text{Ph}\dot{\text{C}}\text{H}_2$ was monitored at $\lambda_{\text{max}} = 318 \text{ nm}$, no bleaching of this absorption could be observed at the end of the excitation pulse (Figure 1). We therefore conclude that excitation of $\text{Ph}\dot{\text{C}}\text{H}_2$

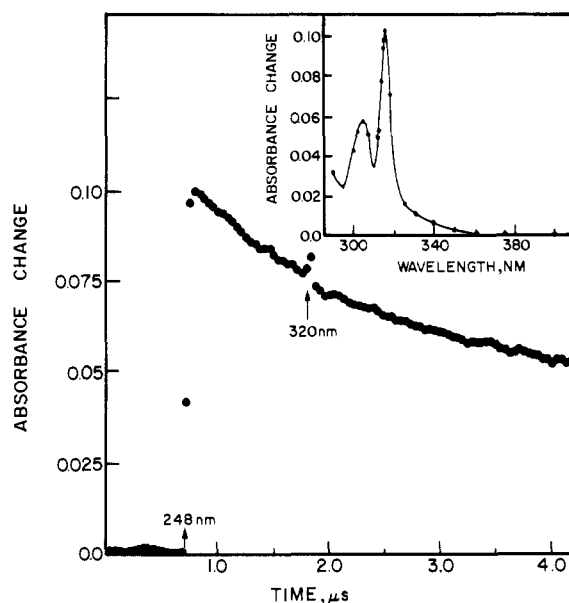
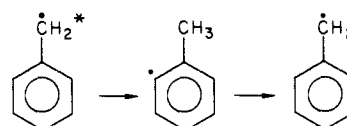


Figure 1. Formation and excitation of benzyl radicals produced in deaerated solution of $1.0 \times 10^{-2} \text{ M PhCH}_2\text{Cl}$ in cyclohexane at 22 °C. The first pulse is from the excimer laser, $\lambda_{\text{ph}} = 248 \text{ nm}$, and the second pulse is from the dye laser, $\lambda_{\text{exc}} = 320 \text{ nm}$. Absorption followed at $\lambda_{\text{max}} = 318 \text{ nm}$. Note no persistent bleaching or increased absorption following the second pulse. Inset shows the transient absorption spectrum of PhCH_2 0.8 μs following the first laser pulse in the same system.

does not lead to any persistent photochemistry.¹⁴ While the possibility of some photochemical process which rapidly ($\leq 20 \text{ ns}$) reverts to the original radical in its ground state cannot be completely excluded, no such route is straightforwardly obvious. The possibility of a photochemical hydrogen abstraction from the solvent (e.g., alcohols) is rejected since this reaction would yield toluene and an α -hydroxy alkyl radical, none of which could produce back benzyl radicals at the time scale involved. Furthermore, note that no fluorescence could be observed at room temperature in perfluorinated solvents. The possibility of an intramolecular 1,3-hydrogen atom migration to yield *o*-tolyl radical



is considered unlikely. While the second step in such a scheme has been shown to be very fast,¹⁵ one would expect a pronounced deuterium isotope effect on such a reaction. None is observed (vide infra).

Since PhCH_2^* is very long lived in the solid matrix at 77 K, we decided to study the temperature dependence of its fluorescence lifetime in 2-MTHF. Results of these studies are collected in Figure 2. From 77 to $\sim 115 \text{ K}$ the lifetime seems to be temperature independent. Above the latter temperature a thermally activated pathway decreases the lifetime of the fluorescence. An obvious and often adopted¹⁶ way to rationalize this behavior is to assume that the observed relaxation is a sum of temperature-independent, k^0 , and a temperature-dependent, $k(T)$, relaxation constants:

$$k_{\text{obsd}} = k^0 + k(T) = k^0 + A \exp(-\Delta E/RT) \quad (1)$$

k^0 then includes the radiative (k_r^0) and nonradiative (k_{nr}^0) decay

(14) In cyclohexane, slight bleaching ($\leq 10\%$) of the radical absorption was observed at $\lambda = 300\text{--}310$ and $330\text{--}340 \text{ nm}$. This is probably due to photolysis of products other than benzyl radicals. However, in the region of λ_{max} of benzyl radical, no bleaching could be observed.

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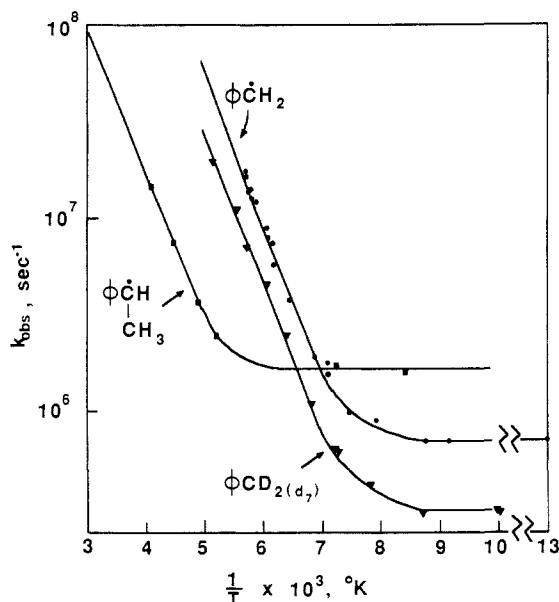


Figure 2. The dependence of fluorescence lifetime on temperature for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ (\bullet), PhCD_2^* (d_7) (\blacktriangledown), and $\text{PhC}(\text{CH}_3)\text{H}^*$ (\blacksquare) in 2-MTHF. Results for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ include $[\text{Ph}\dot{\text{C}}\text{H}_2\text{Cl}]$ in the range $8.6\text{--}86\text{ mM}$. Solid lines are best fits obtained with the parameters given in Table I. $\lambda_{\text{exc}} = 320\text{ nm}$; fluorescence followed at 480 nm .

Table I. Kinetic Parameters for Relaxation of Benzyl and Other Arylmethyl Radicals

radical	k^0, s^{-1}	A, s^{-1}	$\Delta E, \text{cal/mol}$
$\text{Ph}\dot{\text{C}}\text{H}_2$	$(7.0 \pm 0.4) \times 10^5$	$(8.7 \pm 0.5) \times 10^{11}$	3830 ± 190
$\text{PhCD}_2(d_7)$	$(3.0 \pm 0.2) \times 10^5$	$(1.6 \pm 0.2) \times 10^{12}$	4260 ± 210
$\text{Ph}\dot{\text{C}}\text{H}(\text{CH}_3)$	$(1.6 \pm 0.2) \times 10^6$	$(2.6 \pm 0.2) \times 10^{11}$	4740 ± 240
$\text{NpCH}_2^{a,b}$		5.0×10^7	300
$\text{Ph}_2\dot{\text{C}}\text{H}^a$	$(2.9 \pm 0.2) \times 10^6$	$(2.0 \pm 0.5) \times 10^7$	825 ± 300
$\text{Ph}_3\dot{\text{C}}$	$(4.2 \pm 0.3) \times 10^6$	$(2.7 \pm 0.3) \times 10^{11}$	4600 ± 230

^aDue to the weak temperature dependence for these radicals, A and ΔE are subject to large errors. ^bReference 6, Np = naphthyl; only approximate values treated as $k = Ae^{-\Delta E/RT}$ are reported.

rate constants which were previously analyzed in detail for the benzyl radical and several of its derivatives excited at 77 K .^{9,17} The corresponding solid line in Figure 2 has been calculated with use of $k_{\text{obsd}} = (7.0 \times 10^5) + (8.7 \times 10^{11}) \exp(-1915/T) \text{ s}^{-1}$ (i.e., $\Delta E = 3.83\text{ kcal/mol}$).

The same temperature dependence within experimental error is obtained for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ in methylcyclohexane. Similarly, in perfluoro ether, fluorescence from $\text{Ph}\dot{\text{C}}\text{H}_2^*$ could be observed only at $T \leq 180\text{ K}$. The effect of concentration of the parent benzyl chloride molecule on the rate of decay of the fluorescence of benzyl radicals was studied at $-100\text{ }^\circ\text{C}$ in the concentration range 8.6×10^{-3} to $8.6 \times 10^{-2}\text{ M}$, could be observed, thus excluding the possibility of quenching of the excited state by the parent molecule. Repetitive pulsing with the excimer laser (10 Hz for 40 s) prior to the excitation pulse has no effect on the fluorescence lifetime. The temperature-dependent component does not, therefore, result from the buildup of photolysis products.

The temperature dependence of the fluorescence lifetime of the perdeuterated benzyl- d_7 radical and of the phenylethyl radicals ($\text{Ph}\dot{\text{C}}\text{H}(\text{CH}_3)$) has also been measured. Results are similar to the benzyl radicals as can be seen in Figure 2. While for $\text{PhCD}_2(d_7)$ the temperature independent pathway is ~ 2.5 times slower than that for $\text{Ph}\dot{\text{C}}\text{H}_2$, the temperature-dependent process has similar activation energies and preexponential factors for both. Somewhat higher activation energy is obtained for $\text{Ph}\dot{\text{C}}\text{H}(\text{CH}_3)$. Table I summarizes the kinetic parameters obtained for the excited states of the four radicals presently studied. We may note here

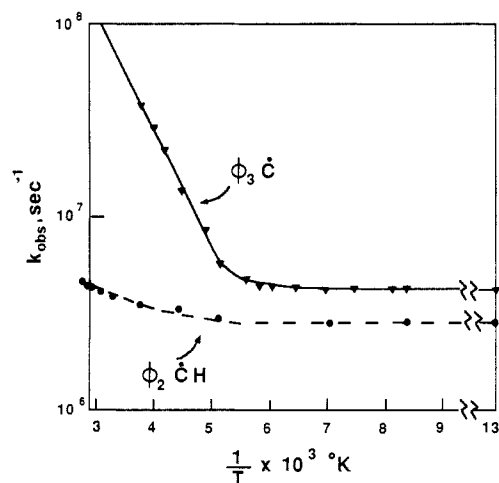


Figure 3. Temperature dependence of the fluorescence lifetime of $\text{Ph}_3\dot{\text{C}}$ (\blacktriangledown) and $\text{Ph}_2\dot{\text{C}}\text{H}$ (\bullet). $\lambda_{\text{exc}} = 320\text{ nm}$, fluorescence followed at 530 nm .

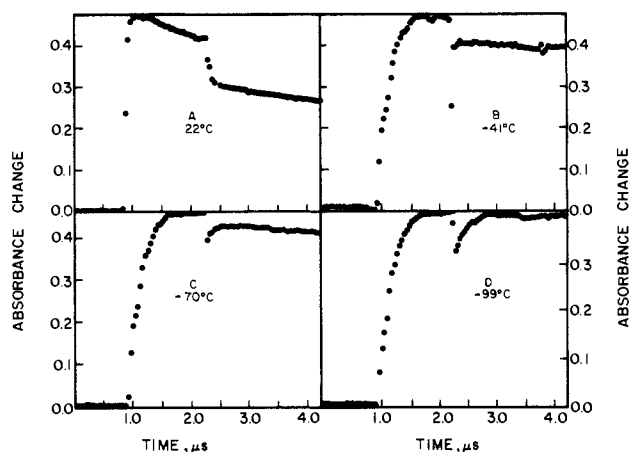


Figure 4. Photochemistry of $\text{Ph}_3\dot{\text{C}}$ in 2-MTHF as a function of temperature. Absorption followed at $\lambda = 335\text{ nm}$; note persistent bleaching following excitation pulse at temperatures $\geq -70\text{ }^\circ\text{C}$ increasing with increasing temperature (parts A-C). The seemingly slow formation following the 248-nm pulse is an artifact resulting from scattered light from the dewar.

that the decrease in lifetime of $\text{Ph}\dot{\text{C}}\text{H}_2^*$ is due primarily to an increase in the rate of a nonradiative decay mode rather than a radiative rate. The fluorescence quantum yields for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ and $\text{PhCD}_2^*(d_7)$ have been determined to be 0.39 and 0.47 , respectively, at 77 K .^{10c} A substantial increase in radiative decay rate would then be incompatible with the more than an order of magnitude decrease in the excited state lifetime observed in the present study.

The temperature dependence of the lifetime of $\text{Ph}_3\dot{\text{C}}^*$ is quite similar to that of $\text{Ph}\dot{\text{C}}\text{H}_2^*$ (Figure 3). Yet there is a major difference between the relaxation processes of these two radicals. While no photochemistry seems to result from excitation of $\text{Ph}\dot{\text{C}}\text{H}_2^*$, relaxation of $\text{Ph}_3\dot{\text{C}}^*$ does produce persistent bleaching of its ground-state absorption at $\lambda = 335\text{ nm}$. The production of this photochemical product is observed only in the temperature region where the decay rate is accelerated (Figure 4). Apparently increasing the temperature opens up an activation-controlled photochemical channel for relaxation of $\text{Ph}_3\dot{\text{C}}^*$. Analysis according to eq 1 yields the corresponding solid line in Figure 3 calculated with use of the parameters given in Table I. In view of these results, in particular those for benzyl radicals, we decided to systematically study the temperature dependence of the lifetime of $\text{Ph}_2\dot{\text{C}}\text{H}^*$ as well. This required warming the solution nearly to the boiling point of the solvent, thus rendering the accuracy of these measurements inferior to those of the other radicals. As can be seen in Figure 4, these measurements verify the previous observations^{2,9} of a rather weak temperature dependence for the

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lifetime of $\text{Ph}_2\dot{\text{C}}\text{H}^*$. The present results provide the kinetic parameters given in Table I.

In an effort to proceed beyond the phenomenological description, we are now faced with the following observations for the three successive substitutions of phenyl rings on the central carbon atom of arylmethyl radicals: (a) for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ a prominent thermally activated physical (no observable photochemical) relaxation pathway is available; (b) for $\text{Ph}_2\dot{\text{C}}\text{H}^*$ no photochemical pathway is thermally activated while the physical relaxation is only weakly temperature dependent; (c) for $\text{Ph}_3\dot{\text{C}}^*$ a photochemical process is activated upon increasing temperature.

A large number of theoretical calculations predict the two lowest electronic excited states of $\text{Ph}\dot{\text{C}}\text{H}_2$ to lie very close to one another (<0.1 eV).¹⁸ The debate regarding the assignment of the first excited state seems to have settled on the 1^2A_2 state.^{19,20} However, the possibility that the nearby 2^2B_2 state may provide the channeling mode for the thermally activated relaxation process observed for $\text{Ph}\dot{\text{C}}\text{H}_2^*$ should be considered. Vibronic mixing of several vibrational modes of the 1^2A_2 state with the ground vibronic level of the 2^2B_2 state has been shown to account for the unusual fluorescence intensity pattern from excited benzyl radicals.¹⁹ At 77 K the $1^2\text{A}_2 \rightarrow 1^2\text{B}_2$ radiationless decay of a series of deuterated and methylated benzyl radicals has been explained largely on the basis of the Franck-Condon factors of the accepting modes, the C-H stretches.¹⁷ The ortho hydrogens were seen to be particularly effective in these radiationless transitions.¹⁷ The deuterium isotope effect, previously observed at 77 K,¹⁰ and seen in the temperature-independent region of Figure 2, is thus explicable as arising from these same Franck-Condon factors.

The strong temperature-dependent relaxation mode is quite unusual and more difficult to understand. The mechanisms used to rationalize the form of eq 1 traditionally fall into two types.¹⁶ The first mechanism is based on the thermal population of vibrational levels of the initial electronic state, whereas the second invokes thermal population of a second electronic excited state. Let us first examine the viability of the first mechanism in the case of benzyl radicals. For this mechanism to be effective, the intrinsic relaxation rates for the relaxation from the thermally populated higher vibrational levels have to change with the changes in vibrational quanta. This difference in rates can be calculated by using the theories of radiationless transitions from single vibronic levels.²¹ Such calculations show that there is usually an increase in the radiationless rate upon excitation to higher vibrational levels in a particular electronic manifold.²¹ For instance, in benzene, Freed and co-workers^{16a,21} find this general rule to hold except in a few cases where the excited normal mode is of a higher frequency in the initial electronic state than the same vibration in the final electronic state. On the basis of these calculations, Heller, Freed, and Gelbart^{16a} also show that a small deuterium isotope effect is expected for this mechanism. Since the relative rates of the radiationless transitions are greater for the deuterated than for the hydrogenated compound, the normal deuterium effect is

$$(A/k^0)_D > (A/k^0)_H \quad (2)$$

where A and k^0 are the empirical parameters defined by eq 1.

From Table I it can be seen that for benzyl radicals inequality 2 is satisfied. This, however, is a rather subtle effect, at the limit of our experimental accuracy. However, more convincingly, the preexponential factor in the theory of Freed and co-workers^{16a} is approximately equal to the number of thermally populated

vibrational modes at ΔE multiplied by an average of the radiationless rate from these levels. Actual computations on benzene^{16a} show that the radiationless rates increase by less than an order of magnitude on going from the vibrationless level to the third vibrational state. Thus, A/k^0 would be expected to be of the order of 100 or less. For the case of naphthalene, where the temperature dependence was assigned to the vibrational mechanism,^{16a} A/k^0 is ca. 4.²² In the case of benzyl radicals, this ratio is $>10^6$ (Table I), and therefore, we conclude that a pure vibrational mechanism is unlikely. Furthermore, if such a vibrational mechanism was operating for benzyl radicals, its absence in $\text{Ph}_2\dot{\text{C}}\text{H}$ and naphthylmethyl radicals would be difficult to explain (vide infra).

Thus, we are left with the electronic mechanism as a likely explanation for the temperature-dependent relaxation of benzyl radicals. Such a mechanism may show an inverse deuterium effect.^{16a,c} If the electronic mechanism involves the actual thermal population of the second excited state (2^2B_2), then the activation energy would represent its energy relative to the first excited state (1^2A_2). The activation energy measured in the present study (ca. 0.170 eV) is, however, significantly larger than the calculated energy gap (albeit, calculated for an isolated molecule) between the 2^2B_2 and 1^2A_2 states.¹⁸ Furthermore, as mentioned above, Leach and co-workers have already shown¹⁹ that the ground vibronic level of the 2^2B_2 is mixed to a considerable extent with some low-frequency (<700 cm^{-1}) vibronic levels of the 1^2A_2 state. For the electronic mechanism to operate in the relaxation of excited benzyl radicals, we therefore need to invoke differential mixing of the two electronic states for each vibronic level of the 1^2A_2 manifold. Physically, the activation energy would then correspond to a set of vibrational energies of the 1^2A_2 vibronic levels that are most strongly mixed with the 2^2B_2 vibronic levels. This is quite reasonable since the activation energies, ~ 1400 cm^{-1} , are in the range of C-C stretching vibrations. It is, however, realized here that the assignment of the electronic mechanism is tentative since the above discussion is based on the assumption that the medium is inert. This, as will be shown below, is not strictly correct.

A comparison with fluorescence lifetime of benzyl and benzyl- d_7 radicals in the gas phase and in the condensed media is also of interest. Recent measurements of fluorescence lifetime indicate that the lifetime of $\text{Ph}\dot{\text{C}}\text{H}_2^*$ in the gas phase at low pressures (≤ 1.0 Torr) is somewhat shorter than in the solid matrix at 77 K.²³ Furthermore, it is pressure independent in this range and has the same value for several vibronically specific excitations. Only for the longer lived benzyl- d_7 is some pressure dependence observed.²³ The fluorescence lifetimes in these gas-phase experiments are substantially longer than those presently observed in the condensed phase at room temperature. To reconcile these two observations, we have to conclude that either the excited radicals have not attained thermal equilibrium during the lifetime of their excited state in the gas-phase experiments or that solvent-induced perturbations provide some mixing of states in the present experiments. While the low pressures used in the gas-phase experiments indicate toward the former explanation, the latter cannot presently be dismissed. The difference between the gas phase and liquid phase in benzene is generally attributed to solvent-induced perturbations.²⁴ In fact, it can be shown that mixing of states by solvent perturbations can have large effects on the radiationless decay rate.²⁵ It may well be that the behavior of benzyl radicals is analogous to that of benzene.

The weak temperature dependence in the relaxation of $\text{Ph}_2\dot{\text{C}}\text{H}^*$, previously reported^{2,9} and presently verified, is in sharp contrast to the prominent temperature dependence of $\text{Ph}\dot{\text{C}}\text{H}_2^*$. Close examination shows a mild but systematic increase of the decay rate at the higher temperatures (Figure 3). The activation energy and frequency factor for the temperature dependence of the decay

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were obtained from a fit to eq 1 and are given in Table I. These values, however, are subject to a large experimental error since the weak temperature dependence imposes extension of the measurements nearly to the boiling point of the solvent (2-MTHF). Nevertheless, the activation energy and even more clearly the frequency factor are much smaller for $\text{Ph}_2\dot{\text{C}}\text{H}$ than for $\text{Ph}\dot{\text{C}}\text{H}_2$. In fact, the magnitude of the ratio A/k^0 for $\text{Ph}_2\dot{\text{C}}\text{H}$ is just what would be expected for the vibrational mechanism to be operative. However, a definitive assignment of the mechanism for the radiationless decay in this system will require a study of the deuterium isotope effect and a careful study of the temperature dependence of the fluorescence quantum yield of $\text{Ph}_2\dot{\text{C}}\text{H}$.

Regardless of the exact mechanism, the weak ("normal") temperature dependence in the decay of $\text{Ph}_2\dot{\text{C}}\text{H}^*$ may be invoked in support of the electronic mechanism in benzyl radicals. Using an open-shell semiempirical SCF-MO method in combination with configuration interactions, Kanamaru and Nagakura calculate the second electronic excited state of $\text{Ph}_2\dot{\text{C}}\text{H}$ to be 0.356 eV above the first one.²⁶ If coupling to the second excited state is required for the efficient temperature dependent internal conversion, then, even with a frequency factor as large as the one measured for benzyl radicals, only a marginal decrease in the lifetime of $\text{Ph}_2\dot{\text{C}}\text{H}^*$ could be expected at room temperature. Again, the assumption is made here that the gas-phase-calculated value (0.356 eV) is only slightly affected by the solvent. It is also interesting to note here that naphthylmethyl radicals ($\text{Np}\dot{\text{C}}\text{H}_2$) resemble $\text{Ph}_2\dot{\text{C}}\text{H}$ radicals rather than benzyl radicals, both phenomenologically and in the calculated energy levels of their excited states. The measured lifetime of $\text{Np}\dot{\text{C}}\text{H}_2^*$ at room temperature is more than an order of magnitude longer^{6,27} than the lifetime of $\text{Ph}\dot{\text{C}}\text{H}_2^*$ extrapolated from the present results to room temperature. Furthermore, a rough estimate of the activation energy and frequency factor for $\text{Np}\dot{\text{C}}\text{H}_2^*$ (ca. 300 cal/mol and $4 \times 10^7 \text{ s}^{-1}$, respectively)⁶ are quite similar to those measured here for $\text{Ph}_2\dot{\text{C}}\text{H}$. On the other hand, the SCF-LCI calculations of Carsky and Zahradnik^{18c} place the second electronic excited state of $\text{Np}\dot{\text{C}}\text{H}_2$ far above (~ 0.8 eV) its lowest excited state.

The temperature-dependent relaxation of $\text{Ph}_3\dot{\text{C}}^*$ has been shown above to lead to a photochemical process the nature of which has been previously discussed in detail.^{2,9} The similar parameters obtained for this radical as for benzyl radicals (Table I) indicate that the population of similar vibrational modes is involved in the nonradiative process, which leads to the photochemical process. While rotation of the phenyl groups away from the central plane of the radical is required, C-C motions lead to the electrocyclic photochemical reaction.

Finally, we return to the possibility of a photochemical reaction in the temperature-dependent decay route of benzyl radicals. It has already been shown above that any bimolecular reaction, including a reaction with the solvent, can be rejected as a possible

pathway for this decay. Hydrogen atom migration seems unlikely due to the lack of deuterium kinetic isotope effect, and any homolytic bond cleavage is rejected on energetic grounds. In the case of benzene, however, excitation to the first excited singlet state leads to valence photoisomerization, both in the gas phase and the liquid phase with measurable quantum yield.²⁸ Such a crossing to an isomeric potential surface in the benzyl radical cannot be excluded, provided this isomer converts back to the benzyl radical very efficiently and very rapidly. If this mechanism holds, then the difference between $\text{Ph}\dot{\text{C}}\text{H}_2^*$ and $\text{Ph}_2\dot{\text{C}}\text{H}^*$ may result from an increased energy gap between the lowest excited state and the isomeric potential energy surface in the latter. Contrary to the case of benzene and alkylbenzenes where the benzvalene isomers could be isolated, in the case of benzyl radicals, if a similar isomeric form is the cause for the reduced lifetime at elevated temperatures, its lifetime has to be shorter than a few nanoseconds. In the absence of positive observation of such photochemistry, we excluded this possibility from our discussion.

Conclusions

A major interest in investigating the photophysics and photochemistry of radicals is the opportunity to study radiationless decay in the absence of intersystem crossing processes. Since the spin-forbidden doublet-quartet transitions could not significantly contribute to the decay of the first excited doublet state, it is hoped that in favorable cases detailed information regarding the radiationless processes could be obtained. The benzyl radical provides a situation where the close proximity of a second electronic state leads to a very unusual strong temperature dependence of the excited state lifetime. For further light to be shed on the radiationless transitions in such radicals, experimental information is now needed on the lifetime of single vibrational levels under collisionless conditions ($\Delta\lambda \leq 1 \text{ \AA}$, $P \leq 0.1$ Torr). On the other hand, in order to sort out the role of the medium in these transitions, information on the lifetime of the excited benzyl radical at the high-pressure limit is also necessary. Both types of studies are within the reach of modern laser techniques. Among the arylmethyl radicals studied so far, the $\text{Ph}_2\dot{\text{C}}\text{H}$ radical seems the least complex system. The "normal" mild temperature dependence of its decay rate is attributed to the vibrational mechanism and in that sense is quite similar to $S_1 \rightarrow T_1$ transitions in many aromatic hydrocarbons. However, excitation of radicals also provides new routes to interesting intramolecular² and intermolecular⁵ photochemistry, as the cases $\text{Ph}_3\dot{\text{C}}$ and $\text{Ph}_2\dot{\text{C}}\text{H}$ have shown.

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Registry No. $\text{Ph}\dot{\text{C}}\text{H}_2$, 2154-56-5; $\text{Ph}\dot{\text{C}}\text{H}_2(d_7)$, 2154-55-4; $\text{Ph}\dot{\text{C}}\text{H}(CH_3)$, 2348-51-8; $\text{Ph}_2\dot{\text{C}}\text{H}$, 4471-17-4; $\text{Ph}_3\dot{\text{C}}$, 2216-49-1.

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