for a specific E_{rel} and T_{rot} . As the impact parameter increases the Ar-CH₄ intermolecular interaction becomes weaker.

Interesting trends are observed when the average changes in rotational and vibrational energy are compared as a function of either $T_{\rm rot}$ or impact parameter. The average vibrational energy change $\langle \Delta E_{\rm vib} \rangle$ is evaluated from $\langle \Delta E_{\rm rel} \rangle$ and $\langle \Delta E_{\rm rot} \rangle$ via the relationship $\langle \Delta E_{\rm rel} \rangle + \langle \Delta E_{\rm rot} \rangle + \langle \Delta E_{\rm vib} \rangle = 0$. For a fixed impact parameter and relative translational energy $\langle \Delta E_{\rm rot} \rangle$ decreases with increase in $T_{\rm rot}$. In contrast $\langle \Delta E_{\rm rot} \rangle$ increases. The combined effect of these two quantities is for $\langle \Delta E_{\rm rel} \rangle$ to increase as $T_{\rm rot}$ is increased. This is because $\langle \Delta E_{\rm rot} \rangle$ decreases more rapidly than $\langle \Delta E_{\rm vib} \rangle$ increases with increase in rotational temperature.

For a series of calculations with the impact parameter and $T_{\rm rot}$ held constant and the relative translational energy varied, one finds that the $\langle E_{\rm rel} \rangle$ and $\langle \Delta E_{\rm rot} \rangle$ values exhibit significantly different trends. The increase in $\langle \Delta E_{\rm rot} \rangle$ as the relative translational energy is increased in nearly balanced by the decrease in $\langle \Delta E_{\rm vib} \rangle$. As a result only small changes in $\langle \Delta E_{\rm rel} \rangle$ are observed. This condition is illustrated in Figure 6 where $\langle \Delta E_{\rm rel} \rangle$ and $\langle \Delta E_{\rm rot} \rangle$ are plotted vs. $E_{\rm rel}$ for b = 1 and 2 Å.

V. Summary

The microscopic dynamics of intermolecular energy transfer

between water or methane containing 100.0 kcal/mol of vibrational energy and an argon atom has been studied vs. impact parameter, initial relative translational energy, and initial molecular rotational energy. Some of the important findings of this study are the following.

1. Increasing the initial rotational energy has the effect of broadening the distribution of energy transfer from the excited molecule, as well as broadening the distribution for collision-induced vibrational to rotational intramolecular energy transfer. The average value of $\Delta E_{\rm rel}$ increases with increase in initial molecular rotational energy, while the average $\Delta E_{\rm rot}$ decreases.

2. For a fixed impact parameter and initial molecular rotational temperature the average value of $\Delta E_{\rm rot}$ increases approximately linearly with initial $E_{\rm rel}$. In contrast the tendency for average $\Delta E_{\rm rel}$ is to remain constant or decrease with $E_{\rm rel}$.

3. Collision-induced vibrational to rotational intramolecular energy transfer is more extensive than intermolecular energy transfer between argon and the excited molecule.

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Photophysics of Arylmethyl Radicals at 77 K. Structure–Photoreactivity Correlation

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Five arylmethyl radicals, $Ph_2\dot{C}H$, DBHP, $Ph_2\dot{C}CH_3$, $Ph_3\dot{C}$, and $Ph_2\dot{C}-c$ -Pr were generated in glassy matrices at 77 K and their absorption, excitation, and emission spectra were studied in detail. Under similar conditions, fluorescence quantum yields and lifetimes have been determined and the various processes contributing to the radiative and nonradiative relaxation to the ground state have been analyzed. It is concluded that the larger twist angle of the phenyl groups of the last three radicals in the above list is the main reason for the increased rate constant of radiative relaxation and for the increased quantum yield of fluorescence. The smaller twist angle of $Ph_2\dot{C}H$ and DBHP· red shifts their absorption spectra and the resulting increased symmetry causes a decrease in the oscillator strength for their excitation to the lowest excited state. The same structural effects are invoked to rationalize the differences in photoreactivity between the first excited states of these two groups of radicals previously observed at room temperature.

Introduction

The spectroscopy and photophysics of benzyl radicals have been the subject of intensive studies during the past three decades. Absorption and fluorescence spectra of benzyl radicals were measured in the gas phase and in frozen matrices at low temperatures and a large number of molecular orbital calculations have been performed on benzyl and similar structures.¹⁻⁴ Recently we accomplished a study on the photophysics and photochemistry of arylmethyl radicals in the liquid phase at room temperature.⁵ A major finding in this study was the observation that slight structural changes (e.g., $Ph_2\dot{C}H$ vs. $Ph_2\dot{C}CH_3$) in the radicals produced pronounced differences in their photoreactivity. It was then suggested that these changes cause significant differences in the twist angles of the phenyl groups around their bond to the central carbon. In an effort to substratiate this hypothesis, we undertook the present complementary study of the photophysics and spectroscopy of the same radicals in frozen matrices at 77 K.

In general, the lowest excited state of a radical is always of a doublet spin multiplicity. Thus, intersystem crossing from the lowest doublet excited state to the quartet manifold is very unlikely. Since the energy level of the lowest quartet state will be situated above the lowest excited doublet state, the only two relaxation pathways for the latter (barring photochemistry) will be radiative or nonradiative relaxations. This peculiar ordering of the excited states of radicals make them rather attractive targets for studying radiative and nonradiative relaxation processes. In closed-shell systems, intersystem crossing to the triplet manifold and back to the ground state singlet quite often complicates such studies. However, the reactivity of the radicals often leads one to resort

 ⁽a) Porter, G.; Wright, F. J. Trans. Faraday Soc. 1955, 51, 1469.
 (b) Grajcar, L.; Leach, S. J. Chim. Phys. 1964, 61, 1523.
 (c) Cossart-Magos, C.; Leach, S. J. Chem. Phys. 1972, 56, 1534; 1976, 64, 4006.
 (d) Schuler, H.; Kusjakow, Spectrochim. Acta 1961, 17, 356.
 (e) Watts, A. T.; Walker, S. J. Chem. Soc. 1962, 4323.

^{(2) (}a) Norman, I.; Porter, G. Proc. Roy. Soc. London, Ser. A 1955, 230, 399. (b) Johnson, P. M.; Albrecht, A. C. J. Chem. Phys. 1968, 48, 851. (c) Friedrich, D. M.; Albrecht, A. C. J. Chem. Phys. 1973, 58, 4766. (d) Okamura, T.; Obi, K.; Tanaka, I. Chem. Phys. Lett. 1973, 20, 90; 1974, 24, 218. (e) Okamura, T.; Tanka, I. J. Phys. Chem. 1975, 79, 2728. (f) Laposa, J. D.; Morrison, V. Chem. Phys. Lett. 1974, 28, 270. (g) Bromberg, A.; Friedrich, D. M.; Albrecht, A. C. Chem. Phys. 1974, 6, 353. (h) DiMauro, L.; Wood, D. E.; Lloyd, R. V. J. Chem. Phys. 1983, 78, 5920.

 ^{(3) (}a) Porter, G.; Strachan, E. Spectrochim. Acta 1958, 12, 299. (b)
 Watmann-Grajcar, L. J. Chim. Phys. 1969, 66, 1023. (c) Friedrich, D. M.;
 Albrecht, A. C. Chem. Phys. 1974, 6, 366. (d) Ono, Y.; Ikeshoji, T.; Mizuno,
 T. Chem. Phys. Lett. 1975, 34, 451. (e) Hiratsuka, H.; Okamura, T.; Tanaka,
 I.; Tanizaki, Y. J. Phys. Chem. 1980, 84, 285. (f) Izmida, T.; Ichikawa, T.;
 Yoshida, H. J. Phys. Chem. 1980, 84, 60. (g) Andrews, L.; Miller, J. H.;
 Keelan, B. W. Chem. Phys. Lett. 1980, 71, 207.

^{(4) (}a) Longuet-Higgins, H. C.; Pople, J. A. Proc. Phys. Soc. London, Ser. A 1955, 68, 591. (b) Kruglyak, Y. A.; Mozdor, E. V. Theor. Chim. Acta 1969, 15, 365. J. Chim. Phys. 1969, 15, 374. (c) Watmann-Grajcar, L. J. Chim. Phys. 1969, 66, 1018. (d) Baudet, J.; Berthier, G. J. Chim. Phys. 1963, 60, 1161. (e) Branciard-Larcher, C.; Migirdicyan, E.; Baudet, J. Chem. Phys. 1973, 2, 95. (f) Chang, H. M.; Jaffe, H. H.; Masamanidis, L. A. J. Phys. Chem. 1975, 79, 1118.
(5) Bromberg, A. Schmidt, K. H.; Mairel, D. J. Am. Chem. 2010. (c) 1201.

⁽⁵⁾ Bromberg, A.; Schmidt, K. H.; Meisel, D. J. Am. Chem. Soc. 1984, 106, 3056. J. Am. Chem. Soc. 1985, 107, 83.



Figure 1. Absorption and fluorescence spectra of $Ph_2\dot{C}H$ produced by γ -radiolysis of $Ph_2C(H)Cl$ in MCH/2MP glass at 77 K.

to cryogenic techniques in the study of the radicals, and this may introduce other nagging difficulties. In the present study, anions which are produced along with the radicals by dissociative electron attachment represent such a complication. Nevertheless, we do believe that the present study sheds some light on the relaxation processes of the lowest excited state of the arylmethyl radicals. Most gratifying, we also believe that the present study does substantiate in a paradoxical way our contention that the twist angle in these radicals is the origin of the difference in their photoreactivities.

Experimental Section

Chemicals. Unless otherwise indicated, all chemicals were purchased from Aldrich and purified by the following standard laboratory methods: diphenylmethyl chloride, Ph₂CHCl, vacuum distilled; diphenylmethanol, Ph₂CHOH, 1,1-diphenylethanol, Ph₂C(CH₃)OH, and cyclopropyldiphenylmethanol, Ph₂C(c-Pr)-OH, recrystallized from *n*-heptane; triphenylmethyl chloride, Ph₃CCl, and triphenylmethanol, Ph₃COH, recrystallized from isooctane and benzene, respectively; 10,11-dihydro-5*H*-dibenzo-[*a,d*]cycloheptanol (DBHP-OH, dibenzosuberol) and its chloride



DBHP-OH

analogue DBHP-Cl, both recrystallized from 10% ether in *n*-heptane mixtures. Methylcyclohexane (MCH) and 2-methylpentane (2MP) (both from Phillips 66) were passed through an alumina column. The following materials were used without further purification: 9,10-diphenylanthracene (DPA), triphenylmethane, diphenylmethane, 10,11-dihydro-5*H*-dibenzo-[a,d]cycloheptane (DBHP-H) and 1,1-diphenylethane (Wiley Organics).

Instrumentation. Absorption spectra were recorded on a Varian 2300 spectrophotometer. Emission spectra, excitation spectra, and quantum yields were determined on a Perkin-Elmer Model MPF-44B spectrofluorimeter, equipped with a DSCU-2 corrected spectra unit. Emission lifetimes were measured following excitation of the sample at 337 nm with 10-ns half-width pulses from a Molectron UV24 N₂ laser. The emitted light was passed through a Bausch and Lomb monochromator and monitored by an IP28 photomultiplier. The output signal was digitized on a Biomation 8100 transient recorder and then averaged and stored on a LSI 11/23 minicomputer. The collected data were then transferred to a VAX 11/780 computer for kinetic evaluation.

A ⁶⁰Co γ -source (2.5 krad/min) was used for γ -irradiation and the light from a 450-W Osram xenon lamp, filtered through a CoSO₄/NiSO₄ solution,⁶ was used for UV photolysis.





Figure 2. Absorption and fluorescence spectra of DBHP- produced from DBHP-Cl by γ -radiolysis.

Sample Preparation and Procedure. Samples for irradiation were prepared at room temperature in Suprasil cells (5×10 mm), degassed by the freeze-thaw technique, and sealed under vacuum.

Radicals, prepared by γ -irradiation in the glassy matrix at 77 K, were transferred quickly either to a quartz dewar with flat suprasil windows filled with liquid N₂ for absorption and lifetime measurements or to a round quartz dewar for fluorescence quantum yield measurements. All studies at 77 K were performed in a 3:1 mixture of MCH and 2MP, respectively.

Results

Benzyl-type radicals trapped in the glassy matrices may be obtained by γ -irradiation of the arylmethyl halide or the hydroxy analogue. Dissociative electron attachment (reaction 1) produces

$$R_{1} - C - X \xrightarrow{e^{-}} R_{1}C + X^{-}$$
(1)

$$R_{3} - R_{3}R_{3} - R_{3}$$

$$R_{1}, R_{2}, R_{3} = Ar, H, etc.$$

$$X = CI, OH$$

the radical under such conditions.⁷ Identical or similar radicals may be generated photochemically by UV irradiation of the analogue arylmethane derivative at 77 K.

The structures of the five radicals investigated in the present study are as follows:



The emission and absorption spectra of these radicals are given in Figures 1–5. A typical excitation spectrum is shown in Figure 6.

In general, the electronic absorption and the emission spectra of arylmethyl radicals I–V resemble the spectra of the prototype benzyl radical. Three distinct absorption bands, in the visible, near-UV, and UV regions, can be detected. The visible band is

^{(7) (}a) McCarthy, R. L.; McLachlan, A. Trans Faraday Soc. 1960, 56, 1187.
(b) Gallivan, J. B.; Hamill, W. H. Trans. Faraday Soc. 1965, 61, 1960.
(c) Mittal, J. P.; Hayon, E. Nature (London) 1972, 240, 20. (d) Hagemann, R. J.; Schwarz, H. A. J. Phys. Chem. 1967, 71, 2694.

TABLE I: Fluorescence Lifetimes and Fluorescence Quantum Yields of Arylmethyl Radicals in MCH/2MP Glass at 77 K

radical	parent molecule	irrad	$ au_0$, ns	Φ_{f}	
PhĊH ₂ ^a	PhCH ₂ Cl	γ	770		
PhCH ₂ ^b	PhCH ₃	ŬV	1280	0.39	
Ph ₂ ĊH	Ph ₂ CH–Cl	γ	285 ± 15	0.29 ± 0.05	
Ph ₂ ĊH	Ph ₂ CH–OH	Ŷ	320 ± 15		
₽h₅ĊH	Ph ₂ CH-H	ÚV	$430 \pm 20 (410^{\circ})$		
DBHP.	DBHP-Cl	γ	270 ± 15	0.22 ± 0.06	
DBHP-	DBHP-OH	Ŷ	295 ± 15	0.08 ± 0.03	
DBHP-	DBHP-H	ÚV	340 ± 20		
Ph₁Ċ	Ph ₃ C-Cl	γ	175 ± 10	0.73 ± 0.13	
Ph₂Ċ	Ph ₁ C–OH	$\dot{\gamma}$	140 ± 5	0.59 ± 0.08	
Ph₁Ċ	Ph ₃ C-H	ΰv	$235 \pm 15 (330^{\circ})$		
Ph ₂ CCH ₃	Ph ₂ C(OH)CH ₃	γ	130 ± 5	0.72 ± 0.10	
Ph ₂ CCH ₃	Ph ₂ CHCH ₃	ΰv	220 ± 15		
Ph ₂ Ċ-c-Pr	Ph ₂ C(OH)-c-Pr	γ	150 ± 5	0.56 ± 0.05	

^a Reference 15a, in 3-methylhexane glass. ^bReference 2e, in EPA glass. ^cReference 2d, in isopentane glass.



Figure 3. Absorption and fluorescence spectra of Ph_2CCH_3 produced from $Ph_2C(CH_3)OH$ by γ -radiolysis.



Figure 4. Absorption and fluorescence spectra of $Ph_3\dot{C}$ produced from Ph_3CCl by γ -radiolysis.



Figure 5. Absorption and fluorescence spectra of Ph_2C -c-Pr produced from the corresponding carbinol by γ -radiolysis.



Figure 6. Emission (dashed) and excitation (solid) spectra of Ph₃C radicals produced by γ -radiolysis of triphenylmethanol in MCH/2MP glass at 77 K. For emission spectrum $\lambda_{exc} = 320$ nm; for excitation spectrum $\lambda_{em} = 550$ nm was chosen to show the mirror image of the two spectra.

much weaker than the other two bands. In all cases, strong, easily detectable fluorescence was observed. As can be seen in Figures 1–6, there is a clear mirror image relation between the fluorescence and the visible part of the excitation spectra. In all radicals studied at 77 K, the intensity of the 0–0 transition was the strongest among the emission and absorption bands.

Lifetime Measurements. Fluorescence lifetimes were evaluated at least at two different emission wavelengths and are given in Table I. For the Ph₂CH, Ph₃C and DBHP radicals, lifetimes were measured on samples prepared by three different methods. Two of these preparations were by γ -irradiation of either the chloro or the hydroxy derivative of the arylmethyl moiety. In the third method radicals were prepared by UV irradiation of the arylmethane analogue. Cyclopropyldiphenylmethyl radicals were generated only by γ -irradiation of the hydroxy derivative.

Photolysis of DBHP-H in the glassy matrix yields two distinctly different radicals. One radical is of the diphenylmethyl type, II, and the other of the *o*-xylenyl type, VI. The emission spectrum



of the mixture of these two radicals extends from 500 to 620 nm. The shorter wavelengths portion of this spectrum is most probably due to VI while the longer wavelength portion is due to II. Lifetime measurements at $\lambda = 500-530$ nm yield a single expo-



Figure 7. Internal method for fluorescence quantum yield measurement. γ -irradiated sample of 3×10^{-5} M DPA and 2×10^{-3} M DBHP-Cl in MCH/2MP at 77 K: (--) fluorescence of DBHP and residual fluorescence of DPA; $\lambda_{exc} = 320$ nm; (---) same sample, $\lambda_{exc} = 357$ nm, only DPA fluorescence is observed; (---) excitation spectrum of same sample, $\lambda_{em} = 374$ nm; only DPA is detectable; (+++) excitation spectrum of same sample, $\lambda_{em} = 532$ nm; only DBHP is detectable (spectrum distorted due to high absorbance). The visible band of DBHPis too weak to observe under these conditions.

nential decay ($\tau_0 = (1.25 \pm 0.1) \times 10^{-6}$ s). At $\lambda \ge 540$ nm the fluorescence decay could be evaluated as a double exponential decay. Fixing the slower exponential decay at the lifetime value mentioned above yields for the faster decay (3.4 ± 0.4) $\times 10^{-7}$ s. In the present study we are interested only in the latter radical, i.e., II. This complication of course does not arise in the radiolytically prepared radicals.

Quantum Yield Measurements. Fluorescence quantum yields were determined by the relative method of comparing the integrated intensity of the corrected emission spectra of the radicals to that obtained for 9,10-diphenylanthracene, whose quantum yield was assumed to be unity.⁸ The clear spectral separation of the absorption and emission bands of the radicals from those of DPA, enables measurements of absorption and emission spectra of both the radicals and the reference in the same sample cell. Typical spectra are given in Figure 7. Quantum yield measurements are very sensitive to geometry and positioning of the samples in the fluorescence spectrometer. Having the two solutes in the same matrix decreases substantially the errors resulting from such difficulties. Initially, we compared results obtained with DPA as external reference to those obtained with DPA as an internal reference. The comparison was performed on diphenylmethyl, triphenylmethyl, and DBHP radicals, obtained by γ -irradiation of the chloro derivatives. Similar results within experimental error have been obtained with both methods. No change could be observed in the absorption spectra of DPA following the radiolysis. The low concentration of DPA relative to the parent arylmethyl compounds ensures scavenging of the electrons exclusively by the latter. It should be noted that the emission spectra recorded in this work are corrected spectra (for wavelength dependence of both photomultiplier sensitivity and lamp intensity). This permits direct comparison of integrated intensities at different regions of the spectra. Once the similarity between the results of both methods had been established, repeated runs and further samples were studied only by the internal method. No correction for index of refraction was necessary in the external method (same solvent for reference and sample) and certainly not for the internal one.8

The quantum yield, ϕ_x , of the tested radical was calculated according to eq 2, where Φ_r is the absolute quantum yield of the

$$\phi_{\rm x} = \Phi_{\rm r} \frac{S_{\rm x} f_{\rm r}}{S_{\rm r} f_{\rm x}} \tag{2}$$

reference, f_r and f_x are the fractions of light absorbed by the reference and the studied radical, respectively, and S_r and S_x are the integrated areas under the corrected emission spectra of the reference and the investigated radical, respectively.

The results of the quantum yield measurements are summarized in Table I.

Absorption Spectra. As mentioned above, the arylmethyl radicals have three absorption bands in the UV, near-UV, and visible regions. Due to its small extinction coefficient, the band in the visible range is difficult to observe in the absorption mode. However, since this is the emissive state, a detailed recording of this band is essential in understanding the radiative and nonradiative processes within the excited radicals. A relatively high concentration ($\sim 10^{-4}$ M) of radicals has been obtained after 2 h of γ -irradiating 2×10^{-3} M of the chloride or after 3 h of irradiating 5×10^{-3} M of the carbinol. The absorption spectra of the radicals are given in Figures 1–5.

The molar extinction coefficients at the wavelength of maximum absorption of the visible and the near-UV bands for the radicals studied here were determined relative to that of the visible band of the triphenylmethyl radical, previously determined at room temperature to be 656 M⁻¹ cm⁻¹ at $\lambda_{max} = 516$ nm.⁹ The temperature effect on extinction coefficients of the radicals was checked by comparing the ratio of the heights of the near-UV absorption bands to their areas. Results for room temperature were taken from our previous pulse radiolysis study.⁵ Results for 77 K were obtained at the present study using γ -irradiation. For the visible region of the triphenylmethyl radical, the comparison was also done at room temperature on a sample prepared by Gomberg's method.¹⁰ An average increase of 15% in the height-to-area ratio was observed for the UV bands of all radicals studied here at 77 K as compared to room temperature. If we assume that the oscillator strength is independent of temperature, then the reason for this increase is due to an increase in the extinction coefficients at λ_{max} . We therefore estimate $\epsilon_{max} = 750$ M^{-1} cm⁻¹ for the visible band of triphenylmethyl radical at 77 K. From this value and the absorption spectrum recorded at 77 K, ϵ_{max} in the near-UV of the latter radical is calculated to be 2.5 \times 10⁴ M⁻¹ cm⁻¹. We further assume that the ratio between ϵ_{max} of Ph₃C to ϵ_{max} of all other radicals studied in the near-UV range is the same at 77 K as at room temperature. We thus convert the ϵ_{max} (UV) values we obtained previously for these radicals⁵ to the present conditions. From the absorption spectra of these radicals at 77 K, we obtained the ratio between ϵ_{max} of the near-UV band to ϵ_{max} of the visible band and thus finally calculate the value of the latter. We had to resort to this indirect method to estimate the extinction coefficients in the absence of a reliable method for direct measurement of radical concentrations in the glassy matrix.

From the evaluated extinction coefficients, and from the recorded absorption spectra of Figures 1-5, we calculate the oscillator strengths of the near-UV and visible bands for the five radicals investigated here using⁶

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) \, \mathrm{d}\bar{\nu} \tag{3}$$

where f is the oscillator strength and $\epsilon(\bar{\nu})$ is the extinction coefficient at wavenumber $\bar{\nu}$. The spectroscopic parameters maximum wavelength of the absorption bands, extinction coefficients, and oscillator strengths are summarized in Table II.

Radiative Lifetimes. The radiative lifetime, $\tau_{r_{r_{i}}}$ is inversely proportional to the oscillator strength of the first electronic absorption band. Various modification of the fundamental Einstein equation have been employed in calculating the radiative lifetimes of organic compounds. In the present study, we calculated the

 ^{(9) (}a) Ziegler, K.; Ewald, L. Annales 1929, 473, 163.
 (b) Taub, I. A.;
 Harter, D. A.; Sauer, M. C.; Dorfman, L. M. J. Chem. Phys. 1964, 41, 979.
 (10) Gomberg, M. J. Am. Chem. Soc. 1900, 23, 757.

TABLE II: Spectroscopic Parameters of the Radicals Produced by $\gamma\text{-}Irradiation$ at 77 K

			oscillator strength		
radical	λ _{max} ,ª nm	${\rm M}^{\epsilon_{\rm max}}, {\rm M}^{-1} {\rm ~cm}^{-1}$	direct	from lifetime ^b	
PhĊH ₂	465°	70 ^d		9.8×10^{-4e}	
Ph₂ĊH	523	370	1.1×10^{-3}	2.1×10^{-3}	
	336	3.1×10^{4}	0.31		
DBHP	534	250	6.7 × 10 ⁻⁴	1.7×10^{-3}	
	351	1.5×10^{4}	0.26		
Ph₃Ċ	516	750	2.2×10^{-3}	9.2×10^{-3}	
	340	2.5×10^{4}	0.38		
Ph₂ĊCH₃	519	340	2.0×10^{-3}	1.1×10^{-2}	
	336	1.4×10^{4}	0.14		
Ph₂Ċ-c-Pr	516	250	1.6×10^{-3}	6.1×10^{-3}	
-	338	1.4×10^{4}	0.13		

^a Wavelength of strongest absorption line in the band. ^bCalculated by using $f \simeq 1.5/n^2 \nu_0^2 \tau_r$. ^cReference 15a. ^dReference 2g. ^eReference 2e.

TABLE III: Calculated and Experimentally Determined Rate Constants for Radiative and Nonradiative Decay of the Lowest Excited Doublet State of the Radicals

radical	$k_r^{a}(expt), s^{-1} \times 10^{-6}$	k_r^{b} (calcd), s ⁻¹ × 10 ⁻⁶	$k_{\rm nr}^{\ a}({\rm expt}),$ s ⁻¹ × 10 ⁻⁶	$\frac{k_{\rm nr}^{\ c}({\rm calcd})}{{\rm s}^{-1}\times10^{-6}}$	$\Phi_{\rm f}^{d}$ -(calcd)
PhĊH ₂	0.30 ^e	0.24	0.48 ^e	0.45	0.35
Ph ₂ ĊH	1.0	0.6	2.5	0.76	0.44
DPHP.	0.81	0.37	2.9	0.65	0.36
Ph ₃ Ċ	4.2	1.2	1.5	0.27	0.82
Ph ₂ ĊCH ₃	5.5	1.1	2.1	0.40	0.73
Ph ₂ Ċ-c-Pr	3.7	0.84	2.9	0.40	0.68

^a Experimentally determined from fluorescence lifetimes and fluorescence yields of Table I for the radical formed from the chloride derivative by γ -radiolysis when available. ^b Calculated by using eq 4. ^c Calculated according to ref 2g. ^d Calculated as $k_r(\text{calcd})/(k_r(\text{calcd}) + k_{nr}(\text{calcd}))$. ^eReference 2g.

radiative rate constant, k_r , according to the equation derived by Strickler and Berg:¹¹

$$k_{\rm r} = 1/\tau_{\rm r} = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}^{-3} \rangle_{\rm av}^{-1} \int \frac{\epsilon(\bar{\nu})}{\bar{\nu}} \, \mathrm{d}\bar{\nu} \qquad (4)$$

where $\langle \bar{\nu}^{-3} \rangle_{av} = \bar{\nu}^{-3} \epsilon(\bar{\nu}) \, d\bar{\nu} / \int \epsilon(\bar{\nu}) \, d\bar{\nu}$ and *n* is the index of refraction. For comparison, we calculated k_r according to the simpler version⁶

$$k_{\rm r} = 2.88 \times 10^{-9} \bar{\nu}_0^2 n^2 \int \epsilon(\bar{\nu}) \, \mathrm{d}\bar{\nu}$$
 (5)

where $\bar{\nu}_0$ is the frequency of the 0–0 transition. Both methods yield practically the same results (~10%). Experimental values of k_r were evaluated from the experimentally determined fluorescence quantum yields and from the observed lifetimes of the fluorescence.

The results of the calculated and experimentally determined k_r are summarized in Table III. We note that k_r thus calculated are significantly smaller than the experimentally determined rate constant. Stated otherwise, we note in Table II that oscillator strengths calculated from experimentally measured radiative lifetimes are clearly larger than those measured directly from absorption spectra. This discrepancy is attributed to the charge-transfer state which results from the neighboring anion (Cl⁻ or OH⁻) produced by reaction 1 in close proximity to the radical.¹⁵ This state appears as an underlying broad band in the absorption spectrum in the region of the lowest excited doublet state and is not accounted for in the direct calculation of the oscillator strength. It seems from this comparison that the charge-transfer state contributes significantly to the radiative relaxation process.

Lifetimes of Radiationless Process. The theory of radiationless process from a discrete level to a quasicontinuum in organic molecules has been studied extensively.¹² Most successful in

predicting rates of radiationless processes is Siebrand's method which was utilized to calculate rates of intersystem crossing in a variety of aromatic molecules.¹³ The same method proved useful in predicting rates of radiationless processes in benzyl radical and its methylated derivatives and provided a rationale for the significant isotope effect on their lifetimes.^{2g} Using the same parameters previously used for benzyl radicals (albeit with the correct energy gap and number of active hydrogen and carbon atoms of the corresponding radical), we calculated the rates of the radiationless processes, k_{nr} (calcd), given in Table III. Clearly, the radicals presently studied are of different geometry from that of benzyl radicals and use of the same parameters for both groups of radicals could not be expected to reliably predict the radiationless rates. In particular, in view of the dominant role that the ortho hydrogens contribute to the radiationless decay rate in benzyl and in view of the strong interaction between the same hydrogen atoms of two neighboring rings in the other radicals, such a calculation is a gross oversimplification. However, addition of a site-specific rate constant of $k_{22} \simeq 1.2 \times 10^6 \, {
m s}^{-1}$ to account for this interaction would bring the calculated $k_{\rm nr}$ close to the experimentally observed values. In addition, the problem of the nearby counterion, invoked above to account for the low k_r (calcd), is expected to contribute to k_{nr} as well through its effect on the Franck-Condon factors. At any rate, regardless of problems associated with the calculated rates, it can be seen in Table III that the experimental values for k_{nr} of all five radicals are quite similar, $k_{\rm nr}({\rm expt}) = (2.2 \pm 0.7) \times 10^6 \, {\rm s}^{-1}$. On the other hand, $k_{\rm r}({\rm expt})$ increase by a factor of ~4 on going from the group of Ph_2CH and DBHP. to the group of Ph_3C , Ph_2CCH_3 , and Ph_2C c-Pr.

Discussion

The general resemblance between the spectra of the radicals presently studied and benzyl radicals has already been mentioned above. Closer examination, however, reveals significant differences. As can be seen in Table II, both the visible band and the near-UV band are red-shifted as compared to that of benzyl radicals and their extinction coefficients are larger than that of benzyl. This increase in the extinction coefficient also increases the rate constant for the radiative decay of the lowest excited state of these radicals which is in turn reflected in the higher quantum yield of fluorescence for some of them (Table I). These observations might be rationalized on the basis of the reduced symmetry of the five radicals presently studied as compared to the higher symmetry of the benzyl radical. Due to the crowding of the closely spaced ortho hydrogen atoms, the phenyl rings have to rotate out of the plane defined by the three bonds around the central carbon atom.¹⁴ Thus while the benzyl radical is of the C_{2v} symmetry group, all the radicals studied here, except Ph_3C , are of the C_2 symmetry group. The latter, i.e., the $Ph_3\dot{C}$ radical, is of the C_3 rather than the D_{3h} symmetry group.

The extent of the twist of the phenyl groups out of the central molecular plane will determine the degree of conjugation of the π -system with the unpaired electron at the central carbon. Increased plnarity will increase the degree of conjugation and therefore will lower the energy level of the first excited state. On the other hand, due to the decrease in symmetry, a larger twist angle can be expected to increase the oscillator strength of this transition. These expectations do materialize when comparing the spectroscopic features of benzyl radicals with the five radicals presently studied. Furthermore, within the group of these five radicals, the lowest transition of Ph2CH or DBHP is red-shifted as compared to the other three radicals (Ph_3C , Ph_2CCH_3 , and Ph₂C-c-Pr, see Table II). A striking example of the effect of increased twist angle is the blue shift observed in the absorption spectrum of $Ph_3\dot{C}$ when compared to $Ph_2\dot{C}H$. Apparently addition of the third phenyl group reduces the conjugation of the π -system

⁽¹¹⁾ Strickler, S. J.; Berg, R. A. J. Chem. Phys. 1962, 37, 814. (12) Freed, K. F. Acc. Chem. Res. 1978, 11, 74.

⁽¹³⁾ Siebrand, W. J. Chem. Phys. 1966, 44, 4055; 1967, 46, 440; 1967, 47, 2411.

^{(14) (}a) Lewis, G. N.; Lipkin, D.; Magel, T. T. J. Am. Chem. Soc. 1944, 66, 1579. (b) Hoffman, R.; Bissell, R.; Franum, G. J. Phys. Chem. 1969, 73, 1789.

TABLE IV:	Analysis of the	e Various Decay	Processes of	the Excited S	tate of Arylmeth	yl Radicals by	y Comparison betw	een Radiolytically	Produced
Radicals and	Photolytically	Produced Radic	als						

radical	parent molecule	irrad	$k_0 \times 10^{-6},$ s ⁻¹	$k_{\rm r}^{a} \times 10^{-6},$ s ⁻¹	$k_{\rm Q}^b \underset{\rm s^{-1}}{\times 10^{-6}},$	$k_{\rm nr}^{c} \underset{\rm s^{-1}}{\times} 10^{6},$
Ph ₂ ĊH	Ph ₂ CH-Cl	γ	3.51	1.02	1.19	1.30
Ph ₂ ĊH	Ph ₂ CH–OH	γ	3.12		0.79	
Ph ₂ ĊH	Ph ₂ CH-H	ÛV	2.32			
DPHP.	DBHP-CI	γ	3.70	0.81	1.2	1.69
DPHP.	DBHPOH	Ŷ	3.39	0.27	0.89	2.23
DPHP	DBHP-H	ŪV	2.50			
Ph ₃ Ċ	Ph ₃ C-Cl	γ	5.71	4.20	1.46	<0.5
Ph ₃ Ċ	Ph ₃ C–OH	Ŷ	7.14	4.21	2.89	<0.5
Ph ₃ Ċ	Ph ₃ C-H	ÚV	4.25			
Ph ₂ ĊCH ₃	Ph ₂ C(OH)CH ₃	γ	7.69	4.54	3.15	<0.5
Ph ₂ CCH ₃	Ph ₂ CH(OH)CH ₃	ÚV	4.54			

^aCalculated as $k_0\Phi_f$ in the radiolytic experiments. ^bCalculated according to eq 7. ^cCalculated as $k_0 - (k_Q + k_f)$.

with the unpaired electron. Similarly the oscillator strength of the more planar radicals ($Ph_2\dot{C}H$ and DBHP·) is smaller than that of the more twisted radicals. This increase of the oscillator strength of the latter three radicals is the main reason for the shorter lifetimes of their excited states and the higher quantum yields for fluorescence on their relaxation to the ground state. This difference in the geometry of $Ph_2\dot{C}H$ and DBHP· as compared to $Ph_3\dot{C}$, $Ph_2\dot{C}CH_3$, and $Ph_2\dot{C}$ -c-Pr could also be deduced from molecular models and has been previously invoked in order to explain the difference in photochemical reactivity between these two groups of radicals.

In comparing the spectroscopic features of the benzyl radical with those of the presently studied ones, we get further evidence for the reduced symmetry of the latter radicals. While in the benzyl radical spectrum the 0–0 transition is not the most intense line, it is the strongest line in the spectra of the other radicals. The higher intensities of lines other than the 0–0 transition in the benzyl radical were attributed to "borrowed" intensities from higher levels which significantly contribute to the weak but symmetry allowed transition.^{3c} Due to the higher oscillator strength of this transition in the other arylmethyl radicals, the contribution from "borrowed" intensities is less pronounced.

Differences between the more planar radicals (Ph₂CH and DBHP.) and the more twisted ones (Ph₂CCH₃, Ph₂C-c-Pr, and Ph_3C) can also be observed in the vibrational structure of the fluorescence and absorption spectra of these two groups of radicals. Thus, for Ph₂CH and DBHP the first observable vibrational line in the fluorescence spectra is at 700 and 710 cm⁻¹, respectively. This corresponds probably to a C-C bending mode. On the other hand, for Ph₃C, Ph₂CCH₃, and Ph₂C-c-Pr the first observable line is at 1060, 1049, and 1020 cm⁻¹, respectively. These probably correspond to C-C stretch modes. However, it should be noted that both groups of radicals exhibit a clear mirror image relation between the absorption (or excitation) and the emission spectra. We can, therefore, conclude that the geometry of the ground state is well preserved in the first excited state. This preservation is necessary in our previously reported hypothesis for the reasons leading to the different photochemical behavior of these two groups.

Due to difficulties in obtaining homogeneous distribution of the radicals when produced from the arylmethane parent molecule by UV photolysis, we focus our attention on fluorescence quantum yields from the radicals when produced by γ -radiolysis. While quantum yields measured from the latter technique are more reliable, there are difficulties associated with this method of radical production. It has already been previously shown that the anion produced by the radiolysis (Cl⁻ or OH⁻ in the present study) may have an effect on the photophysics and spectroscopic features of the radical due to its spacial close proximity to the radical.¹⁵ Thus, for all the radicals presently studied, a broad band centered in the range of 450 nm may be observed in the absorption and excitation spectra when using the γ -radiolysis technique. These broad bands are attributed to charge-transfer transitions from the "counterion" to the radical. When produced photolytically, the absorption spectra of the radicals do not contain these bands. Since these broad bands appear in the excitation spectra (as well as in the absorption spectra), the charge-transfer state clearly contributes to the fluorescence intensity. However, its effects on quantum yields of fluorescence are difficult to assess. Furthermore, the effect on fluorescence quantum yields would depend on the counterion and its distance from the radical. Thus, in the presently studied systems, the presence of OH⁻ ions in close proximity to the radicals reduce somewhat the fluorescence quantum yields as compared to those obtained when Cl⁻ is produced in the vicinity of the radicals (Table I). A clear effect of the counterion is also seen in the fluorescence lifetime measurements. Whenever the lifetime of fluorescence was measured for radicals produced photochemically and radiolytically, the latter gave shorter lifetimes (Table I).

Since the excited state of the photochemically produced radicals are longer-lived than those produced radiolytically, we may assign a "quenching" rate constant, k_Q , to the "counterion" effect for the latter case. The observed rate constant for fluorescence decay of the radiolytically produced radicals will then include the three terms:

$$k_0 = k_r + k_{nr} + k_Q \tag{6}$$

In the photochemically produced radicals, $k_Q = 0$, since we assume that the hydrogen atoms thus produced have no effect on the fluorescence lifetime of the radicals. Thus, k_Q may be estimated from the difference between the observed rate constants in the radiolytical and photochemical experiments (eq 7). The results

$$k_{\rm Q} = (k_0)_{\rm rad} - (k_0)_{\rm ph} \tag{7}$$

of such an analysis are compiled in Table IV. As could be expected, the introduction of another decay mode, the "quenching" mode, will decrease the experimentally derived k_{nr} . These experimentally derived values (last column, Table IV) may now be compared with the calculated values of k_{nr} (Table III). Considering the large approximations and the experimental limits of errors, the correspondence between the calculated and experimental values may be considered satisfactory. As already mentioned, the counterion probably increases both the radiative and the nonradiative rate constants of the free radical. In this regard, we may note that the quantum yields for fluorescence calculated from k_r (calcd) and k_{nr} (calcd) (last column, Table III) are quite similar to the experimentally determined quantum yields, although each of the calculated rate constants is much smaller than the experimental values. Furthermore, we also note that the fluorescence quantum yield presently determined is practically the same as the one determined at room temperature for Ph₂CH and DBHP.5

Conclusions

A major incentive for the present study is an effort to correlate the structure of the radicals of the arylmethyl series with their

^{(15) (}a) Irie, M.; Shimizu, M.; Yoshida, H. J. Phys. Chem. 1976, 80, 2008.
(b) Izumida, T.; Tanabe, Y.; Ichikawa, T.; Yoshida, H. Bull. Chem. Soc. Jpn. 1979, 52, 235.



Figure 8. Schematic diagram for the photophysics and photochemistry of arylmethyl radicals at 77 K and at room temperature.

photophysical and photochemical properties. We may recall here that in our previous study on the photophysics and photochemistry of the same radicals in various liquids and at room temperature we observed that $Ph_2\dot{C}H$ and DBHP undergo practically no photochemical reaction from the lowest excited doublet state. We now note that the quantum yield for their fluorescence is practically the same at 77 K as at room temperature. On the other hand, $Ph_3\dot{C}$, $Ph_2\dot{C}CH_3$, and $Ph_2\dot{C}$ -c-Pr undergo a photochemical process with quantum yield close to unity when excited to the lowest doublet state at room temperature. Paradoxically, these same three radicals strongly fluoresce, and with fluorescence quantum yields higher than those of the other two radicals, at 77 K. As is revealed in Table III, the main reason for the increase in the fluorescence quantum yields of the group of three radicals is the increase in the rate constant for their radiative decay. The nonradiative decay rate is similar for the two groups of radicals. A common structural difference between the two groups is thus sought to rationalize two seemingly opposing observations.

It was originally proposed that the higher photochemical reactivity at room temperature results from an increased twist angle of the phenyl groups around their bond to the central carbon atom. As shown in Table II and discussed above, the increased twist angle should also cause an increase in the oscillator strength. The latter should lead to an increased fluorescence quantum yield, provided photochemical pathways are frozen out as apparently is the situation in the frozen matrix at 77 K. The same structural effect is thus responsible for the blue shift in the absorption spectra, the increased fluorescence quantum yield at 77 K, as well as the increased photochemical quantum yield at room temperature. In Figure 8 we summarize schematically our current conclusions on the photochemical and photophysical processes in the five arylmethyl radicals studied above in the two temperature regimes.

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Registry No. DBHP-, 96165-78-5; DBHP-Cl, 1210-33-9; DBHP-OH, 1210-34-0; DBHP-H, 833-48-7; Ph₂C-c-Pr, 17787-94-9; Ph₂CH·, 4471-17-4; Ph₃C·, 2216-49-1; Ph₂CCH₃, 51314-23-9; Ph₂CHCl, 90-99-3; Ph₂CHOH, 91-01-0; Ph₂CH₂, 101-81-5; Ph₃CCl, 76-83-5; Ph₃COH, 76-84-6; Ph₃CH, 519-73-3; Ph₂C(OH)CH₃, 599-67-7; Ph₂CHCH₃, 612-00-0; Ph₂C(OH)-c-Pr, 5785-66-0.

Laser Studies of Energy Relaxation in Gas-Phase Ion Photodissociation

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Two-photon dissociation of gas-phase ions provides a means of characterizing collisional and radiative relaxation processes in vibrationally excited ions. The dependence of photodissociation on the repetition rate of a chopped-laser source gives a way of measuring relaxation rates which is particularly free of complicating experimental artifacts, with pulse-rate effects becoming noticeable for chopping rates slower than half the relaxation rate. Radiative (collisionless) relaxation rates were determined for parent ions of o-dichlorobenzene (16 s⁻¹), p-dichlorobenzene (15 s⁻¹), pentafluorobromobenzene (75 s⁻¹), and bromobenzene (2 s⁻¹), following excitation by 515-nm light.

Introduction

The dissipation of internal energy from excited gas-phase ions can be followed by exploiting the sequential two-photon dissociation process first described by Freiser and Beauchamp¹ which is understood in terms of a simple model:

$$A^{+} \frac{h\nu}{I\sigma_{1}} A^{+} + \frac{fost}{fos} A^{+} + \frac{h\nu}{I\sigma_{2}} \text{ fragments}$$

$$\frac{h_{c}\rho}{k_{r}}$$

(1) Freiser, B. S.; Beauchamp, J. L. Phys. Chem. Lett. 1977, 35, 35.

Absorption of the first photon by ion A^+ is followed by rapid internal conversion to give the vibrationally excited ion A^{+*} . This species may dissociate following absorption of a second photon, or it may revert to the pool of thermal A^+ ions by energy relaxation through either collisional or radiative energy loss mechanisms. Appropriate analysis of the kinetics of the overall photodissociation process has the potential ability to characterize both the collisional (k_c) and radiative (k_r) relaxation processes.

In gathering information about the two-photon kinetics of such a process, variables under convenient control are pressure, light intensity, and light pulse characteristics. The variation of light intensity in steady-irradiation experiments has not yet been a very fruitful approach. Pressure-variation studies have been useful in

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