

Substituent Effects on the Photochemistry of Diphenylketyl Radicals: Elucidation of the Rate Constants and Quantum Yields of Relaxation Processes from the Excited Radicals¹

Robert W. Redmond,² J. C. Scaiano,^{*,3} and Linda J. Johnston^{*}

Contribution from the Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received January 27, 1992

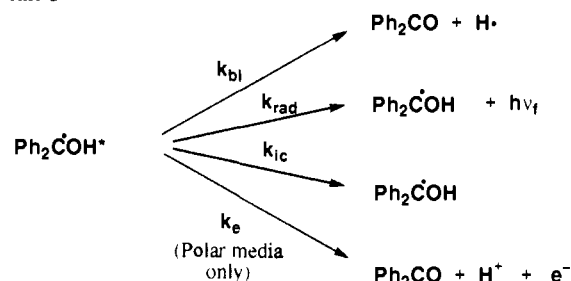
Abstract: Two-color, two-laser flash photolysis has been employed to carry out a structure-reactivity investigation on excited diphenylketyl radicals. The effects of varying substitution at the 4 and 4' positions on the probabilities of radiative, nonradiative, and photobleaching processes have been elucidated in a quantitative manner. Rate constants and quantum yields have been measured for all of the above processes, allowing the complete relaxation schemes for these radicals to be obtained. Substituent effects have a large effect on observed fluorescence parameters such as lifetime and quantum yield. The relative invariability of radiative rate constant (k_{rad}) demonstrates that this is due to the much larger substituent effects on both the photobleaching (k_{bl}) and internal conversion (k_{ic}) rate constants. The strong correlation observed between the latter rate constants suggests that the O-H bond of the ketyl radical is important for both k_{bl} and k_{ic} ; as a result, bleaching quantum yields show only modest dependence on substitution. The photophysical and photochemical properties of the excited radicals show a dependence on the electron-withdrawing character of the substituent, with disubstitution enhancing the monosubstitution effect.

Introduction

The phenomenon of sequential two-photon absorption is not uncommon in laser-induced processes due to the relatively high concentration of transient intermediates generated within the duration of the laser pulse. In cases where the transient has significant absorption at the laser excitation wavelength, it may compete with the ground-state precursor for the absorption of incident photons, particularly in the later part of the laser pulse. This can often, but not always, result in a different overall photochemistry from the situation of simple one-photon absorption by the precursor. The occurrence of two-photon processes may be inferred from laser dose dependences of photogenerated products. However, a quantitative analysis of photochemical events resulting from sequential two-photon processes within a single laser pulse is inherently complex due to the fact that the concentrations of the ground-state and, more importantly, the transient intermediates will vary both temporally and spatially in a manner which is determined by the profile of the laser pulse and the relative geometry of the detection system.

Complex modeling of the ground-state and transient concentrations during the laser pulse may be attempted and can certainly differentiate between one- and two-photon processes. However, considering the uncertainty in the parameters involved, this method cannot be expected to achieve a degree of accuracy appropriate for quantitative measurements.⁴ The situation may be simplified to a large extent by the application of a two-photon, two-color approach, whereby selective excitation of precursor and intermediate at appropriate wavelengths and time delay such that no spectral overlap exists allows the photoprocesses originating from the excited intermediate to be followed. This approach has been extensively used in this and other laboratories to investigate the behavior of excited reaction intermediates for which little was previously known.⁵⁻¹¹ We note that while this approach centers on the use of pulsed lasers, an alternate approach (the laser-jet

Scheme I



technique) based on cw lasers has also been employed and has proven particularly useful from a synthetic point of view.¹²⁻¹⁵

We have more recently used a combination of two-photon, two-color laser techniques with various detection systems to develop quantitative methods for the analysis of radiative, nonradiative, and chemical processes occurring from excited intermediates.¹⁶⁻¹⁸ These techniques have the potential for the complete analysis of all the decay pathways for excited transient intermediates, thus allowing detailed studies of structure-reactivity relationships. Although such studies are commonplace in low-intensity photochemistry, there are very few examples in the small volume of reported work on excited intermediates. We have previously demonstrated significant substituent effects on the fluorescence properties of substituted diphenylketyl^{19,20} and diphenylmethyl²¹ radicals and on the photochemistry of 10-substituted anthrone ketyl radicals.^{22,23} In this paper, we describe a more extensive

(1) Issued as NRCC-33298.

(2) Present address: Wellman Laboratories of Photomedicine, Massachusetts General Hospital, Boston, MA 02114.

(3) Present address: Department of Chemistry, University of Ottawa, Ottawa, ON, Canada K1N 6N5.

(4) Arnold, B. R.; Scaiano, J. C. *Macromolecules* **1992**, *25*, 1582.

(5) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22.

(6) Scaiano, J. C.; Johnston, L. J. *Org. Photochem.* **1989**, *10*, 309.

(7) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056.

(8) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.

(9) Tokumura, K.; Itoh, M. *Nippon Kagaku Kaishi* **1989**, 1311.

(10) Schade, C.; Mayr, H.; Arnett, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 567.

(11) Weir, D. *J. Phys. Chem.* **1990**, *94*, 5870.

(12) Wilson, R. M.; Hannemann, K.; Schnapp, K. A.; Memarian, H. R.; Azadnia, A. In *SPSE Proceedings: Summer Symposium on Photochemistry for Imaging*; SPSE—The Society for Imaging Science and Technology: White Bear Lake, MN, 1988; p 167.

(13) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *The Spectrum* **1991**, *4*, 8.

(14) Wilson, R. M.; Hannemann, K.; Heineman, W. R.; Kirchoff, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 4743.

(15) Adam, W.; Finzel, R.; Kita, F. *Tetrahedron Lett.* **1991**, *32*, 2211.

(16) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

(17) Redmond, R. W.; Wayner, D. D. M.; Kanabus-Kaminska, J. M.; Scaiano, J. C. *J. Phys. Chem.* **1989**, *93*, 6367.

(18) Redmond, R. W.; Scaiano, J. C. *Chem. Phys. Lett.* **1990**, *166*, 20.

(19) Johnston, L. J.; Loughnot, D. J.; Scaiano, J. C. *Chem. Phys. Lett.* **1986**, *129*, 205.

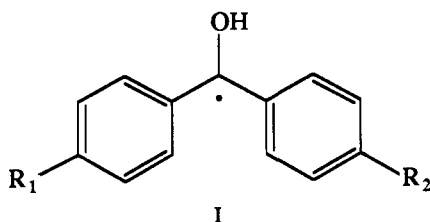
(20) Johnston, L. J.; Loughnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518.

(21) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1986**, *128*, 156.

(22) Netto-Ferreira, J. C.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* **1989**, 435.

(23) Netto-Ferreira, J. C.; Murphy, W. F.; Redmond, R. W.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4472.

study on the effect of substituents on the relaxation of a number of excited diphenylketyl radicals (I). This system was chosen



since the parent radical has already been subjected to detailed study and has been shown to exhibit a variety of relaxation modes.²⁴⁻²⁹ These include fluorescence, nonradiative deactivation, photobleaching with loss of a hydrogen atom, and photoionization in polar solvents (Scheme I).^{19,20,30} Therefore, it is of interest to investigate whether substitution on the parent diphenylketyl radical will perturb the efficiencies of the relaxation processes of Scheme I. Two-color flash photolysis has allowed us to obtain a quantitative picture of the relaxation and reaction processes which occur from these excited reaction intermediates.

Experimental Section

General. Benzophenone and 4-methyl-, 4,4'-dimethyl-, 4-methoxy-, 4,4'-dichloro-, 4,4'-dibromo-, and 4-(trifluoromethyl)benzophenones were obtained from Aldrich. 4-Cyanobenzophenone was purchased from Lancaster. All ketones were recrystallized before use. Benzhydrol and 4,4'-dimethoxybenzhydrol were obtained from Aldrich and recrystallized twice from aqueous ethanol. The other non-commercially available substituted benzhydrols were prepared by reduction of the corresponding ketone with sodium borohydride in ethanol. The crude product was then extracted and purified by recrystallization or chromatography. The purity was checked using GC or HPLC analysis. 1,4-Cyclohexadiene was obtained from Aldrich and purified by vacuum distillation immediately prior to use. Di-*tert*-butyl peroxide (MC&B) was passed through an activated alumina column prior to use to remove impurities (particularly hydroperoxides). Benzene (Aldrich) and toluene (BDH, Omnisolv) were spectrophotometric grade and were used as received.

Ground-state absorption spectra were measured using a Hewlett-Packard HP8451-A UV-visible diode array spectrophotometer. GC analyses were carried out on a Perkin-Elmer Model 8320 capillary gas chromatograph employing a 12-m J&W bonded-phase vitreous silica BP1 column.

Laser Flash Photolysis. The two-color laser flash photolysis facility has been described.³¹⁻³³ In two-color experiments, the radical precursors were irradiated with 308-nm pulses from a Lumonics TE860-2 excimer laser (5 ns, <20 mJ/pulse) with the radicals thus formed being irradiated in turn, following a suitable delay, by the 337-nm output from a Moletron UV-24 nitrogen laser (8 ns, <10 mJ/pulse) or by the frequency-doubled 532-nm line from an attenuated Lumonics Hyperlyag 750 Nd:YAG laser (8 ns, <10 mJ/pulse). Both beams were aligned for maximal overlap within the 7 × 7 mm² Suprasil flow-through sample cuvettes used. In all cases, laser energies were significantly attenuated by the use of calibrated neutral density filters. Solutions were purged with nitrogen and were continuously flowing during the experiment to avoid accumulation of products from the irreversible photodegradation of the samples. Two-laser actinometry for transient photobleaching and integrated fluorescence emission measurements was carried out as previously described,¹⁶⁻¹⁸ using an EG&G Series III gated intensified optical multichannel analyzer (OMA). The laser flash photolysis system is used

Table I. Fluorescence Maxima, Lifetimes, and Quantum Yields for Substituted Diphenylketyl Radicals in Deaerated Benzene (Spectra and Quantum Yields) or Toluene (Lifetimes) at Room Temperature

R ₁	R ₂	λ _{f,max} (nm)	τ _f (ns) ^a	Φ _f ^a	τ _{rad} (ns) ^b
H	H	575	3.9 ^c	0.11	36
H	CH ₃	585	3.5	0.09	39
CH ₃	CH ₃	595	3.1 ^d	0.06	52
H	OCH ₃	610	<1 (0.84) ^e	0.02	
OCH ₃	OCH ₃	630	<1 (0.13) ^e	0.003	
Cl	Cl	600	5.3	0.12	44
Br	Br	605	<1 (0.84) ^e	0.02	
H	CF ₃	590	6.0	0.15	40
H	CN	613	7.8 ^d		

^a Estimated errors of ±10%. ^b τ_{rad} = τ_f/Φ_f. ^c Reference 19. ^d Reference 20. ^e Calculated from τ_f = τ_{rad}(mean) × Φ_f.

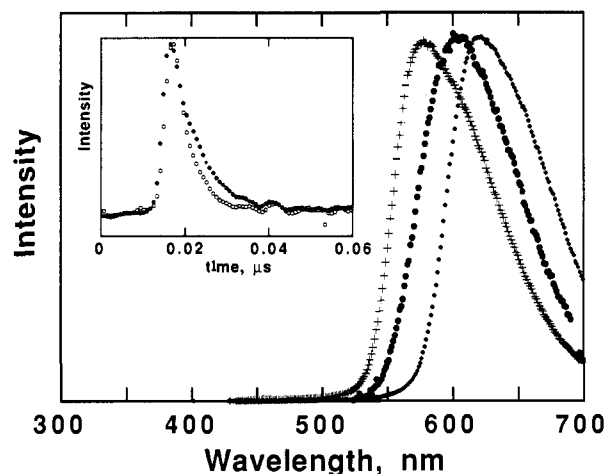


Figure 1. Fluorescence emission spectra for the unsubstituted (+), 4-(trifluoromethyl)-substituted (●), and 4-methoxy-substituted (◆) diphenylketyl radicals in benzene. Insert shows fluorescence decay profiles for the 4-(trifluoromethyl)-substituted (●) and the unsubstituted radical (○).

to determine the absorbance (ΔOD_i) of the transient at the exact time and wavelength of the second laser pulse, and the magnitude of the phenomenon being observed (e.g., bleached absorption or integrated fluorescence emission) is then measured as a function of ΔOD_i (varied by changing the 308-nm laser power) with irradiation at constant energy of the second laser. The slopes of the resulting plots of amplitude vs absorbed energy are then taken as being proportional to the yield of the process and the quantum yields for fluorescence and photobleaching are evaluated from eqs 1 and 2, respectively. The superscripts R and S refer

$$\Phi_f^S = \Phi_f^R \times (\text{Slope}_f^S / \text{Slope}_f^R) \quad (1)$$

$$\Phi_{bl}^S = \Phi_{bl}^R \times (\text{Slope}_{bl}^S / \text{Slope}_{bl}^R) \times (\epsilon_{bl}^R / \epsilon_{bl}^S) \quad (2)$$

to reference and sample, Φ_f and Φ_{bl} are quantum yields of fluorescence and photobleaching, Slope_f and Slope_{bl} are slopes of absorbed energy dependence plots of fluorescence emission and photobleached absorption, and ε_{bl} is the extinction coefficient of the radical at the wavelength where bleaching is monitored.

All actinometry was carried out relative to the unsubstituted benzophenone ketyl radical (Φ_f = 0.11 and Φ_{bl} = 0.27), which was previously calibrated against Aberchrome-540 (photobleaching at 515 nm)¹⁶ and the diphenylmethyl radical (fluorescence).¹⁸ Only relative Φ_{bl} values can be obtained with 337-nm excitation. Fluorescence lifetimes were measured using the 600-ps pulse from a PRA LN-100 nitrogen laser (337 nm, <1 mJ/pulse) as the excitation source with fast photomultiplier-based detection.

Results

Fluorescence. Substitution of the parent diphenylketyl radical at the 4 and/or 4' position has a dramatic effect on the fluorescence emission properties of the excited radicals, as shown in Table I. In all cases, substitution leads to a red shift in the fluorescence emission (Figure 1), in line with similar results observed for the fluorescence spectra of substituted diphenylmethyl radicals.²¹ Fluorescence lifetimes for the ketyl radicals were measured by

(24) Naqvi, K. R.; Wild, U. P. *Chem. Phys. Lett.* **1976**, *41*, 570.

(25) Topp, M. R. *Chem. Phys. Lett.* **1976**, *39*, 423.

(26) Baumann, H.; Schumacher, K. P.; Timpe, H. J.; Rehák, V. *Chem. Phys. Lett.* **1982**, *89*, 315.

(27) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207.

(28) Baumann, H.; Merkel, C.; Timpe, H. J.; Graness, A.; Kleinschmidt, J.; Gould, I. R.; Turro, N. J. *Chem. Phys. Lett.* **1984**, *103*, 497.

(29) Hiratsuka, H.; Yamazaki, T.; Maekawa, T.; Hikida, T.; Mori, Y. J. *Phys. Chem.* **1986**, *90*, 774.

(30) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 398.

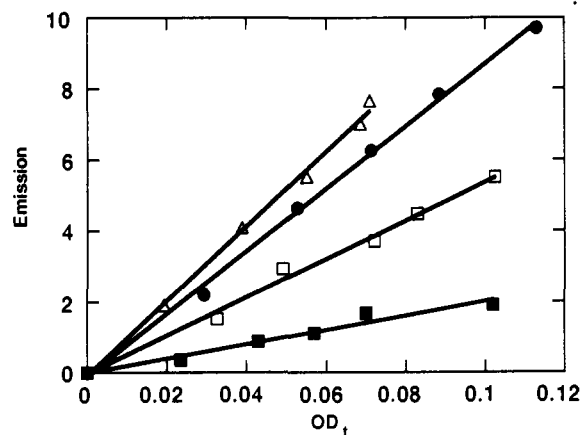
(31) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(32) Scaiano, J. C.; Tanner, M.; Weir, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(33) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.

Table II. Absorption Maxima and Extinction Coefficients for Substituted Diphenylketyl Radicals in Benzene

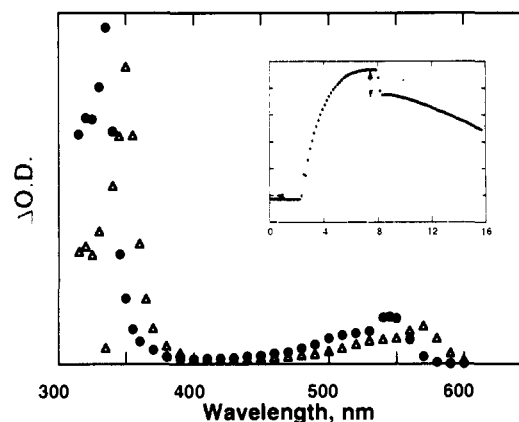
R ₁	R ₂	$\lambda_{\max}(\text{UV})$ (nm)	$\lambda_{\max}(\text{vis})$ (nm)	$\epsilon_{\max}(\text{UV})^a$ (M ⁻¹ cm ⁻¹)	$\epsilon_{\max}(\text{vis})^a$ (M ⁻¹ cm ⁻¹)	ϵ_{330}^a (M ⁻¹ cm ⁻¹)
H	H	335	545	22 800	3300	19 000
H	CH ₃	340	550	27 700	3900	20 000
CH ₃	CH ₃	340	560	25 800	3000	17 000
H	OCH ₃	345	550	18 400	3200	12 200
OCH ₃	OCH ₃	350	560	18 400	1700	9800
Cl	Cl	345	565	23 500	3400	13 600
Br	Br	350	570	24 000	3100	10 700
H	CF ₃	335	550	15 300	3250	12 150
H	CN	350	565	18 100	3200	9100

^a Estimated errors of $\pm 20\%$.**Figure 2.** Plots showing dependence of integrated fluorescence emission as a function of transient optical density at 337 nm (OD_t) for (Δ) unsubstituted radical, (\bullet) 4-methyl-substituted, (\square) 4,4'-dimethyl-substituted, and (\blacksquare) 4-methoxy-substituted diphenylketyl radicals.

337-nm excitation of radicals generated by 308-nm excitation of the parent ketone in toluene. The lifetimes (Table I) range from 7.8 ns for the 4-cyano derivative to less than the resolution of the apparatus (around 1 ns, as determined by the laser pulse duration and detection rise time) for the 4-methoxy, 4,4'-dimethoxy and 4,4'-dibromo derivatives at room temperature in toluene (cf. 3.9 ns for the unsubstituted radical). Representative emission decays are shown as an insert in Figure 1. The lifetimes of excited ketyl radicals increase substantially when the temperature is lowered;¹⁹ however, even on cooling to -50°C , the lifetimes of the emission for some of the shorter lived derivatives were not resolvable from the detection response time.

For fluorescence yield determinations, the radical was formed from hydrogen abstraction by *tert*-butoxyl radical (generated by 308-nm photolysis of di-*tert* butylperoxide) from the appropriately substituted benzhydrol (0.02–0.03 M), followed by excitation of the radical at 337 nm. Ring substitution led to large changes in the fluorescence quantum yield, which was obtained by integrating the fluorescence spectrum (Figure 2). Knowledge of the lifetime and fluorescence quantum yield allows the radiative lifetime (τ_{rad}) of the radicals to be calculated as $\tau_{\text{rad}} = \tau_f / \Phi_f$. Table I also includes the calculated radiative lifetimes and shows that for those excited radicals where both τ_f and Φ_f were measurable, very little difference in τ_{rad} is observed (see Scheme I). This is consistent with the measurement (see Table II) of similar extinction coefficients for all of the substituted ketyl radicals, suggesting that they have similar radiative lifetimes. Assuming that the substituent has a negligible effect on the radiative lifetime of the radical, it is possible to estimate the fluorescence lifetimes of those excited radicals where the emission was too short lived for our instrument. Using the measured fluorescence quantum yields and taking a radiative lifetime of 42 ns (mean of those calculated in Table I) gives the values in parentheses in column 4 of Table I.

Radical Absorption Spectra. In order to evaluate quantum yields of photobleaching, the absorption spectra and extinction coefficients of all the substituted ketyl radicals were measured by generating the radicals by 308-nm photolysis of the corresponding

**Figure 3.** Absorption spectra of unsubstituted (\bullet) and 4,4'-dibromo- (Δ) diphenylketyl radicals in benzene. Insert shows a typical photobleached transient (monitored at 330 nm) arising from (308 + 337)-nm irradiation of the unsubstituted radical.

ketone in benzene containing 0.05 M of the hydrogen donor 1,4-cyclohexadiene. The triplet state of benzophenone has been shown to react with this donor with a rate constant of $2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and a radical yield of 0.94 in benzene.³⁴ The rate constants for hydrogen abstraction by substituted benzophenones have been examined and show only modest substituent effects, and this concentration of diene should be sufficient to quench $>98\%$ of the triplets in all cases.^{35,36} The extinction coefficients for the substituted radicals were determined by comparing the slopes of the energy dependence of radical absorption following the laser pulse (vide supra) to that of the unsubstituted radical and assuming a quantum yield of 0.94 for all radicals studied.³⁷ The extinction coefficients for the unsubstituted radical shown in Table II are based on Aberchrome-540 actinometry.¹⁶ In all cases, a visible band was observed in addition to a more intense (>5 times) UV band (see Figure 3 for examples), and the extinction coefficients and wavelengths for both peaks are listed in Table II. Photobleaching yields were measured at 330 nm, and extinction coefficients used in the calculations (at 330 nm, not the maximum) are given in Table II. Consideration of the λ_{\max} values in Table II shows that, similar to fluorescence emission spectra, all substituents result in a red shift of the absorption spectrum, i.e., a

(34) Encinas, W. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.(35) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093.(36) In cyclopentane, the rate constants for triplet decay are 1.9×10^6 and $10.3 \times 10^6 \text{ s}^{-1}$ for 4,4'-dimethoxy- and 4-(trifluoromethyl)benzophenone, respectively, as compared to $5.3 \times 10^6 \text{ s}^{-1}$ for benzophenone.³⁵ Since the rate constant for reaction of triplet benzophenone with 1,4-cyclohexadiene is substantially faster than that for cyclopentane, it is reasonable to assume that the substituent effects on this reaction will be smaller than those for cyclopentane.(37) The yield of ketyl radical would be expected to decrease if there is substantial charge-transfer quenching of the triplet for electron-withdrawing substituents. However, a yield of 0.65 for ketyl radical has been measured for the reaction of triplet decafluorobenzophenone with 1,4-cyclohexadiene.⁴⁰ Therefore, it is reasonable to assume that the effects for the substituents examined in the present work will be much smaller than that observed for the perfluoroketone.

Table III. Relative Fluorescence Quantum Yields and Quantum Yields for Bleaching of Substituted Diphenylketyl Radicals at 337 and 532 nm

R ₁	R ₂	Φ_{bl} (337 nm) ^a (rel)	Φ_{bl} (532 nm) ^a (rel)	Φ_f (Φ_f rel) ^b
H	H	1.0 ^c	1.0 ^c	0.11 (1.0)
H	CH ₃	0.66	0.95	0.09 (0.82)
CH ₃	CH ₃	0.82	0.97	0.06 (0.55)
H	OCH ₃	0.60	1.03	0.02 (0.18)
OCH ₃	OCH ₃	0.61	0.61	0.003 (0.03)
Cl	Cl	0.84	0.12 (1.09)	
Br	Br	0.29	0.31	0.02 (0.18)
H	CF ₃	0.78	0.93	0.155 (1.41)

^a Estimated errors of $\pm 25\%$. ^b Estimated errors of $\pm 10\%$.
^c Reference substrate.

lowering of the D₁-D₀ energy gap with respect to the unsubstituted radical.

Photobleaching. Initial photobleaching experiments were carried out using the 337-nm nitrogen laser to excite into the UV absorption band of the ketyl radicals. The ketyl radicals were generated from *tert*-butoxyl radicals plus benzhydrol, as outlined for the fluorescence yield measurements. Photobleaching of the radicals was observed in each case; a bleaching trace is shown as an insert in Figure 3. The bleaching of the absorption at 330 nm (ΔOD_{bl}) follows a linear dependence on ground-state radical concentration, as measured by its absorption at the laser wavelength. The Φ_{bl} values measured for all radicals relative to the unsubstituted radical at each excitation wavelength (and not in absolute terms) are given in Table III. While some variation in the relative Φ_{bl} values is observed, the range is not nearly as broad as that for fluorescence. Fluorescence yields vary by almost 2 orders of magnitude, whereas the photobleaching yields differ by, at most, a factor of 3. Thus, there does not seem to be a direct correlation between Φ_f and Φ_{bl} .

A possible explanation for this observation arises when one considers the energy level scheme for the ketyl radical shown in Figure 4. In the above experiments, the ketyl radicals are excited in their UV bands corresponding to a D₀ → D_n transition, whereas the emission observed results from D₁ → D₀ relaxation. It is possible that photobleaching may arise from either D₁ or D_n states or from both. If the photobleaching is predominantly derived from an upper state, no correlation between fluorescence and photobleaching would be expected, as the two processes would originate from different electronic states. It was possible to test this hypothesis by exciting the visible absorption band of the ketyl radicals using the frequency-doubled 532-nm line from the Nd/YAG laser. If the above explanation were correct, one might expect a considerable difference in photobleaching yields on 337- and 532-nm excitation, as in the latter case only the D₁ state responsible for the radical fluorescence will be accessible. Experiments were therefore carried out using the 308-nm pulse followed by 532-nm excitation, again monitoring the bleaching at 330 nm. The relative yields of photobleaching measured from these experiments are compared to those obtained from 308-/337-nm excitation in Table III.

While there are minor differences between *relative* quantum yields at 337 and 532 nm (see Table III), it is clear that the changes in 532 nm values of Φ_{bl} do not parallel the much larger changes in Φ_f . If there is any real difference between the two sets of data, it is more likely to arise from nonreactive deactivation pathways (e.g., solvent quenching) from the upper states initially populated by UV excitation. Such deactivation could conceivably involve energy transfer to the solvent in a manner similar to that reported for upper triplet states of benzophenone.³⁸ Another possible deactivation mechanism could involve the quartet states of the radical. These have been reported to have lifetimes of several microseconds.³⁹ Our data do not suggest the intermediacy

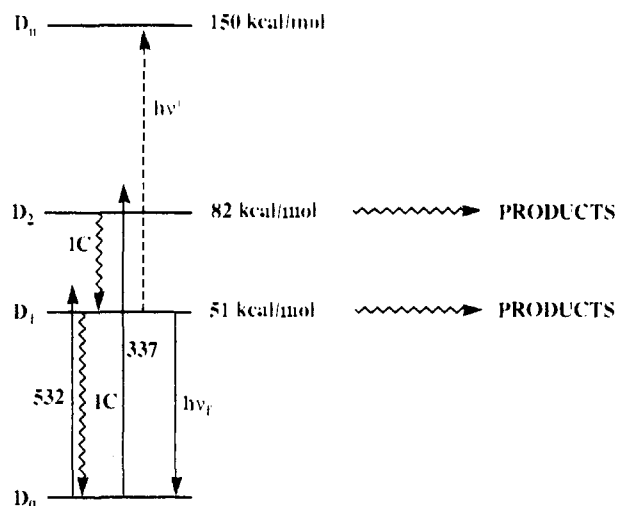


Figure 4. Energy level diagram for diphenylketyl radical showing the possibility for product formation from the first or second excited doublet state. The D₁ energy level is based on the absorption/fluorescence spectra, D₂ on the UV absorption band in the radical, and D_n simply on an upper state that could be populated by UV excitation of D₁.

of any long lived intermediates of this type. It is important to emphasize that the errors in Φ_{bl} are around 25%; thus, for example, for the 4-methyl derivative we estimated earlier a quantum yield Φ_{bl} of 0.39 ± 0.12 ,²⁰ which should be compared with the value of 0.25 ± 0.06 , which can be derived from the present data.

The alternative explanation for the apparent lack of correlation between fluorescence and photobleaching yields is that the rate of internal conversion is not constant for all the ketyl derivatives. Knowledge of the quantum yields of fluorescence and photobleaching allows the extraction of quantum yields (Φ_{ic}) of internal conversion (D₁ → D₀), the only other process occurring in nonpolar media.^{20,30} Equation 3 neglects any wavelength dependence of Φ_f .

$$\Phi_{ic} = 1 - (\Phi_f + \Phi_{bl}) \quad (3)$$

Knowledge of all three quantum yields in addition to the fluorescence lifetime τ_f , where

$$\tau_f = 1/k_f = 1/(k_{rad} + k_{bl} + k_{ic}) \quad (4)$$

allows the rate constants (k) for the individual processes to be calculated as

$$k = \Phi \times k_f \quad (5)$$

Values of quantum yields and rate constants for fluorescence, internal conversion, and photobleaching are given in Table IV for all the substituted radicals studied. To the best of our knowledge, Table IV is unique in that this detail and quality of information is not available for any other group of excited radicals. Values in parentheses for Φ_{bl} and Φ_{ic} are based exclusively on data from 532-nm excitation, rather than on the average of 337- and 532-nm data.

The unsubstituted radical is known to undergo photobleaching by O-H cleavage to give benzophenone and a hydrogen atom.²⁰ Our experiments for the substituted radicals are consistent with the same mechanism, since no additional transients were observed as a result of ketyl radical bleaching. For the dibromo-substituted radical, bleaching traces (308 nm followed by 532 nm) were recorded at a variety of wavelengths to check for the possibility of loss of bromine atom, which, under our conditions, should be detectable as the bromine atom-benzene π -complex with λ_{max} at 550 nm.³⁸ However, there was no evidence for differences in the amounts of bleaching of the visible and UV bands or for the formation of any new transients as a result of excitation of the

(38) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.

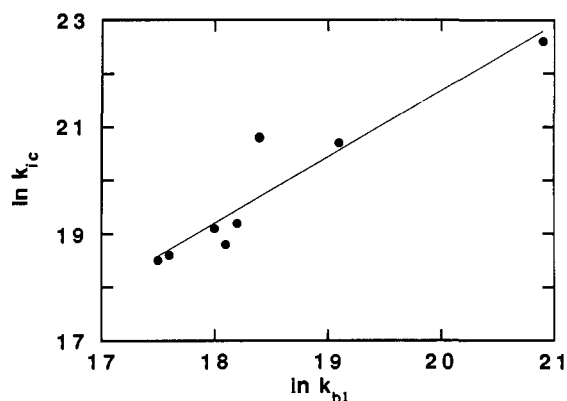
(39) Thurnauer, M. C.; Meisel, D. *Chem. Phys. Lett.* **1982**, *92*, 343.

(40) Boate, D. R.; Johnston, L. J.; Scaiano, J. C. *Can J. Chem.* **1989**, *67*, 927.

Table IV. Quantum Yields for Fluorescence, Bleaching, and Internal Conversion for Substituted Diphenylketyl Radicals and Calculated Rate Constants for Radiative, Bleaching, and Nonradiative Decays

R ₁	R ₂	k _f ^{a,b} (10 ⁸ s ⁻¹)	Φ _f ^c	k _{rad} ^b (10 ⁷ s ⁻¹)	Φ _{bl} ^{d,f}	k _{bl} ^b (10 ⁷ s ⁻¹)	Φ _{ic} ^f	k _{ic} ^b (10 ⁸ s ⁻¹)
H	H	2.6	0.11	2.8	0.27 (0.27)	7.0	0.62 (0.62)	1.6
H	CH ₃	2.9	0.09	2.6	0.22 (0.25)	6.4	0.67 (0.64)	1.9
CH ₃	CH ₃	3.2	0.06	1.9	0.24 (0.26)	7.7	0.70 (0.68)	2.2
H	OCH ₃	(12)	0.02	(2.4)	0.16 (0.28)	19	0.82 (0.70)	9.8
OCH ₃	OCH ₃	(77)	0.003	(2.4)	0.16 (0.16)	123	0.84 (0.84)	64.7
Cl	Cl	1.9	0.12	2.3	0.23 (0.23)	4.4	0.65 (0.65)	1.2
Br	Br	(12)	0.02	(2.4)	0.08 (0.08)	9.5	0.90 (0.90)	10.7
H	CF ₃	1.7	0.15	2.5	0.23 (0.25)	3.9	0.62 (0.60)	1.1
H	CN	1.3						

^aNumbers in parentheses were calculated assuming a radiative lifetime of 42 ns. ^bEstimated errors of ±20%. ^cEstimated errors of ±10%. ^dEstimated errors of ±25%. ^eValues are average of 337- and 532-nm measurements, assuming a quantum yield of 0.27 for photobleaching at both wavelengths.²⁰ ^fValues in parentheses are based on 532-nm data only.

**Figure 5.** Correlation of rate constants for internal conversion (k_{ic}) and photobleaching (k_{bl}) displayed as a double-log plot.

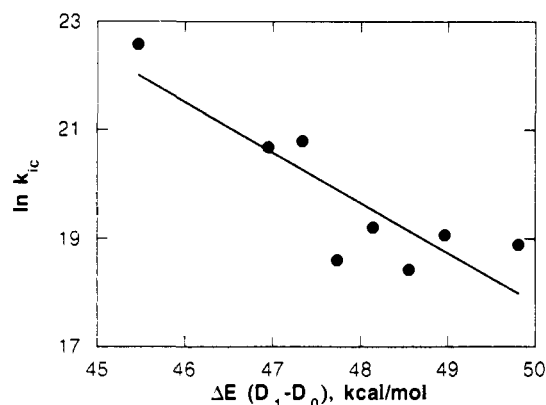
radical. These results suggest that the loss of bromine does not contribute to the observed photobleaching for the dibromo-substituted radical.

Discussion

The diphenylketyl radical proves to be an interesting system for substituent structure-reactivity studies. The complex interrelationship of radiative, nonradiative, and photochemical processes which occur from the excited radical allows substituent effects to be studied in detail if quantitative information (i.e., quantum yields and rate constants) is available. We have demonstrated that the combination of two-color flash photolysis with various detection techniques opens up enormous possibilities in the study of *excited* reaction intermediates. This approach leads to the elucidation of the overall reaction scheme for the excited radicals studied, and analysis of the data thus obtained allows the substituent effects on the diphenylketyl radical to be understood.

The fluorescence yield data suggest a dramatic substituent effect on the excited-state properties of the radical. The fluorescence yield increases with increasing electron-withdrawing character of the substituent, with the exception of the dibromo derivative (vide infra). However, when the fluorescence lifetime data are taken into account, it is evident that there is a negligible substituent effect on the *radiative* lifetime of the radicals, indicating that the dramatic differences in the fluorescence yields result from substituent effects on the rate constants for nonradiative and photobleaching processes. The data in Table IV illustrate this point. For example, for the dimethoxy-substituted radical, the photobleaching and internal conversion rate constants are enhanced by factors of 18 and 40, respectively, over values observed for the unsubstituted radical. Previous results have indicated that, for the unsubstituted radical, loss of a hydrogen atom is responsible for the photobleaching in solvents such as toluene.²⁰ A similar mechanism has also been demonstrated for the efficient photobleaching of the anthrone and 10,10-dimethylantrone ketyl radicals in toluene.²³ The present results are consistent with the same interpretation.

It is interesting to note that there is a strong correlation between the increases in the rates of internal conversion and photobleaching,

**Figure 6.** Semilogarithmic plot of natural log of the rate constant for internal conversion as a function of the $D_1 \rightarrow D_0$ energy gap.

as shown in Figure 5. Previous results for isotope effects on the sum of radiative and nonradiative decay for the diphenyl ketyl radical (O-H versus O-D) had indicated that the radiationless decay pathway involved the O-H stretching mode.¹⁹⁻²⁰ The present correlation for the substituted radicals supports this hypothesis. Hammett plots (not shown) based on σ^+ show that both k_{bl} and k_{ic} correlate reasonably well, although the former shows a much larger sensitivity to ring substitution. ρ values are -0.79 ($R = 0.94$) and -0.08 ($R = 0.90$) for k_{bl} and k_{ic} , respectively. This suggests some charge development in the transition state for bleaching and, to a lesser extent, for internal conversion.

The rate constant for $D_1 \rightarrow D_0$ internal conversion also exhibits a correlation with the energy gap between ground and first excited doublet states. Figure 6 shows the dependence of $\ln k_{ic}$ on the energy gap (taken as the energy corresponding to the wavelength maximum in the emission spectrum). Such behavior is in agreement with the expectation of increased probability of internal conversion as the energy gap between states decreases. A similar correlation has been established for substituted diphenylmethyl radicals.²¹ Evidently, even if bleaching and internal conversion are coupled processes, the dependence of the latter on factors such as isotope (H/D) substitution and charge development may be somewhat moderated by its strong dependence on the $D_1 \rightarrow D_0$ energy gap.

As pointed out above, the dibromo derivative seems anomalous in its behavior in that much lower fluorescence and photobleaching yields are observed than may be expected according to the overall trend observed. Close inspection of the rate constants for this derivative shows that radiative and photobleaching rate constants are not substantially different from the other non-electron-donating groups, but an order of magnitude increase is seen in the non-radiative rate constant. This increase in efficiency in the non-radiative relaxation of the dibromo derivative may be due to several factors: (a) Cleavage of a carbon-bromine bond to yield bromine atoms. This was considered, but the absorption of the anticipated benzene-bromine atom π -complex could not be detected. (b) Excited-state cleavage may be followed by geminate back-reaction to yield the radical in the ground state. (c) The presence of the

two heavy bromine atom substituents may induce rapid relaxation within the doublet manifold, thus providing a further nonradiative pathway for relaxation of the excited radical. The heavy atom effects of point c are the most likely cause of the efficient excited-state relaxation.

Acknowledgment. We thank Arezou Azarani for preparing several of the substituted benzhydrols and S. E. Sugamori and G. M. Charette for technical assistance. Fluorescence spectra for a variety of the diphenylketyl radicals were initially recorded by Dr. D. J. Lougnot.

Use of an Aryldiamine Pincer Ligand in the Study of Tantalum Alkylidene-Centered Reactivity: Tantalum-Mediated Alkene Synthesis via Reductive Rearrangements and Wittig-Type Reactions

Hendrikus C. L. Abbenhuis,[†] Nantko Feiken,[†] David M. Grove,[†] Johann T. B. H. Jastrzebski,[†] Huub Kooijman,[†] Paul van der Sluis,[†] Wilberth J. J. Smeets,[†] Anthony L. Spek,[‡] and Gerard van Koten*[†]

Contribution from the Debye Research Institute, Department of Metal-Mediated Synthesis, Bijvoet Research Institute, Department of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands. Received April 6, 1992

Abstract: The potentially terdentate, monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2-2,6]^-$ provides an excellent tool for the study of tantalum alkylidene-centered reactivity. Transmetalation of $[TaCl_3(CH-t-Bu)(THF)_2]$ with $1/2[Li\{C_6H_3(CH_2NMe_2)_2-2,6\}_2]$ affords the alkylidene complex $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(CH-t-Bu)]$ (**1**) in 90% yield. Complex **1** belongs to the space group *Cc* with $a = 12.983$ (2) Å, $b = 12.384$ (1) Å, $c = 11.969$ (1) Å, $\beta = 95.43$ (1)°, and $Z = 4$. The hexacoordinate tantalum center in **1** has an irregular ligand array in which the aryldiamine ligand adopts a new pseudofacial N,C,N-coordination mode. A Wittig-type reaction of the alkylidene complex **1** with acetone or benzaldehyde affords $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(\mu-O)]_2$ (**2**) in virtually quantitative yield. A similar reaction of **1** with $PhCH=NR$ affords $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(NR)]$ ($R = Me, SiMe_3$). Complex **2** belongs to the space group *Pc* with $a = 10.800$ (4) Å, $b = 11.804$ (3) Å, $c = 12.539$ (4) Å, $\beta = 108.67$ (3)°, and $Z = 2$. Complex **2** is a dimer with bridging oxo functions and has a distorted pentagonal bipyramidal ligand array around each tantalum center. Complex **1** with ethene and propene gives a rearrangement reaction that affords alkene adducts $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2C=CHR)]$ ($R = CH_2-t-Bu$ and Me , respectively). $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2C=CHCH_2-t-Bu)]$ belongs to the space group *P1* with $a = 8.320$ (1) Å, $b = 9.041$ (2) Å, $c = 14.054$ (3) Å, $\alpha = 94.53$ (2)°, $\beta = 90.75$ (2)°, $\gamma = 92.86$ (2)°, and $Z = 2$. The overall structure is distorted pentagonal bipyramidal. The chirality in the coordinated alkene determines the conformation of both five-membered Ta-C-C-C-N chelate rings. NMR experiments show the alkene complexes to be rigid in solution; the bonding of the alkene to the metal center is best described as resulting in a metallacyclopropane unit.

Introduction

Multidentate ligand systems, both cyclic¹ and acyclic,² can be designed to bind transition metals in a predictable manner. The steric constraints of such ligands and the nature of the donor atoms determine to a large extent the stability and properties of the metal complexes. In the special case of bis-ortho chelation, a terdentate monoanionic aryl ligand like $[C_6H_3(CH_2NMe_2)_2-2,6]^-$ (= NCN) partially encapsulates the complexed metal but still leaves sufficient distinctly positioned sites for the resulting complex to serve as a model compound for the study of elementary reaction processes.³ It has now been established that otherwise unstable or even transient stages in these processes are stabilized by the NCN ligand and can be isolated.⁴

A terdentate bonded NCN unit is a six-electron donor, just like the commonly employed η^5 -cyclopentadienyl ligand. These ligands, in octahedral complexes, are complementary in their coordination chemistry in the sense that an η^5 -bonded cyclopentadienyl ligand provides facial coordination, while the NCN ligand is designed to adopt a meridional bonding mode (Figure 1).⁵

In late transition metal chemistry, the three hard donor atoms of the NCN monoanion have been shown to enhance the nu-

cleophilic character of Ni(II) and Pt(II) centers, as well as to stabilize the higher formal oxidation states of Ni(III) and Pt(IV).⁶

(1) (a) Lotz, T. J.; Kaden, T. A. *Helv. Chim. Acta* 1978, 61, 1376. (b) Bencini, A.; Fabrizzi, L.; Poggi, A. *Inorg. Chem.* 1981, 20, 2544. (c) Lecomte, J. P.; Lehn, J. M.; Parker, D.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Chem. Commun.* 1983, 296. (d) Lemaire, M.; Buter, J.; Vriesema, B. K.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* 1984, 309.

(2) (a) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* 1980, 102, 4373. (b) Newkome, G. R.; Fronczek, F. R.; Deutsch, W. A.; Kawato, T.; Kohli, D. K.; Puckett, W. E.; Olivier, B. D.; Chiari, G. *J. Am. Chem. Soc.* 1981, 103, 3423. (c) Giannoccaro, P.; Vassapallo, G.; Sacco, A. *J. Chem. Soc., Chem. Commun.* 1980, 1136. (d) Briggs, J. R.; Constable, A. G.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* 1982, 1225. (e) Nemeš, S.; Jensen, C.; Binamira, E.; Kaska, W. C. *Organometallics* 1983, 2, 1442. (f) Rimmli, H.; Venanzi, L. M. *J. Organomet. Chem.* 1984, 260, C52. (g) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* 1983, 2, 682.

(3) Van Koten, G.; Terheijden, J.; Van Beek, J. A. M.; Wehman-Ooyevaar, I. C. M.; Muller, F.; Stam, C. H. *Organometallics* 1990, 9, 903 and references cited therein.

(4) (a) Terheijden, J.; Van Koten, G.; Van Beek, J. A. M.; Vriesema, B. K.; Kellogg, R. M.; Zoutberg, M. C.; Stam, C. H. *Organometallics* 1987, 6, 89. (b) Van Koten, G. *Pure Appl. Chem.* 1989, 61, 1681.

(5) (a) Terheijden, J.; Van Koten, G.; De Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* 1983, 2, 1882. (b) Grove, D. M.; Van Koten, G.; Mul, W. P.; Van der Zeijden, A. A. H.; Terheijden, J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* 1986, 5, 322. (c) Van der Zeijden, A. A. H.; Van Koten, G.; Luijk, R.; Vrieze, K.; Slob, C.; Krabbendam, H.; Spek, A. L. *Inorg. Chem.* 1988, 27, 1014.

* To whom correspondence should be addressed.

[†] Debye Research Institute.

[‡] Bijvoet Research Institute.