

**THE LASER VERSUS THE LAMP:
REACTIVITY OF THE DIPHENYL KETYL RADICAL IN THE GROUND AND EXCITED STATES**

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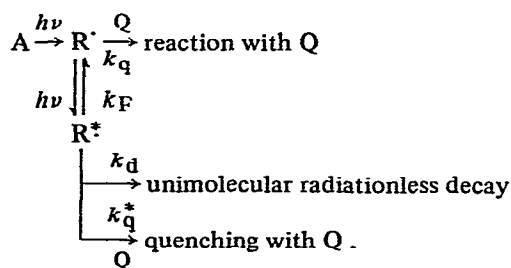
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The diphenyl ketyl radical which is formed upon photolysis of α -phenyl benzoin is produced in its excited state upon intense pulsed laser irradiation. Using the techniques of time-resolved absorption and emission spectroscopy, reaction rate constants for the ground and excited states of this radical were obtained. For the radical quenchers employed, the excited state reactivity is found to be typically several orders of magnitude greater than that of the ground state. It is concluded that the excited state of diphenyl ketyl radical reacts predominantly by electron transfer processes.

1. Introduction

Carbon-centered free radicals are among the best known and most important intermediates in organic chemistry [1]. In fluid solution, nearly all of the known reactions of radicals occur from the ground states of these species. Scheme I displays the conventional paradigm employed to interpret free radical



chemistry which occurs after a radical, $R\cdot$, is produced by photoexcitation in the presence of sufficient quantity of substrate Q to make the rate of decay of $R\cdot$ pseudo first order. When conventional lamps are employed to produce $R\cdot$, production and reaction of $R\cdot$ contribute little to the overall chemistry, i.e. the equation

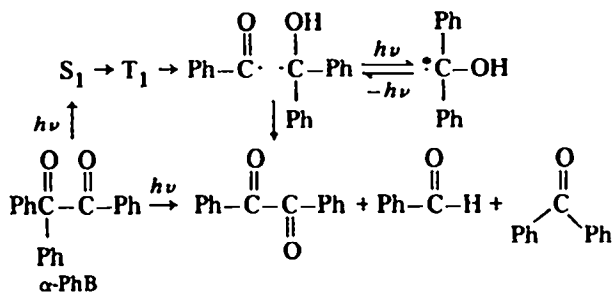
$$k_q [R\cdot] [Q] \gg I_a k_q^* [Q] / (k_d + k_f + k_q^* [Q]) \quad (1)$$

holds [1,2]. In eq. (1), I_a is the light intensity absorbed by $R\cdot$ in einsteins per second, k_f the rate constant of fluorescence of R^* , k_d the rate constant of radiationless unimolecular decay, k_q the rate constant for reaction of $R\cdot$ with Q and k_q^* the rate constant for quenching of R^* with Q. Because of the typically short lifetime of $R\cdot$ in fluid solutions, I_a is typically very small so that eq. (1) is valid even if quenching of R^* is efficient.

Favorable conditions for producing R^* in sufficient concentration for experimental study require (1) use

of a high-intensity excitation source such as a laser and (2) a radical, R^{\cdot} , which possess an extinction coefficient sufficiently high that R^{\cdot} , when produced from precursor A, will compete with residual A for the laser photons. These conditions are required whether steady state or pulsed laser excitation is employed. However, the reactivities of R^{\cdot} and R° may be distinguished by monitoring the time-resolved absorption of R^{\cdot} and the time-resolved emission of R° . Such a procedure has been skillfully employed recently by Eissenthal and co-workers [3] to investigate the bimolecular reactivity of diphenyl carbene in its ground and excited states. It was found that for common substrates the bimolecular reactivity of excited diphenyl carbene was generally one or more orders of magnitude greater than that of ground state diphenyl carbene.

In a previous report we have demonstrated that pulsed laser photolysis of α -phenyl benzoin (α -PhB) results in homolytic cleavage of the ketone to generate a diphenyl ketyl radical which can be excited within the laser pulse (scheme II) [4]. The diphenyl ketyl



Scheme II.

radical fluorescence is experimentally identical to that observed upon photoreduction of benzophenone [5-7]. The goal of this investigation was to compare the reactivities of the ground and excited states of the ketyl radical toward a series of substrates. In order to facilitate comparisons, onium salts and simple olefins used in previous work [9] were employed as radical quenchers. The same substrates are of interest because of their role as initiators of polymerization [9,10].

2. Experimental

Materials. α -Phenylbenzoin ($C_6H_5COC(C_6H_5)_2OH$),

p-chlorobenzenediazonium tetrafluoroborate ($p\text{-ClC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$), methylmethacrylate (MMA), and acetonitrile were prepared and purified as previously described [4]. Diphenyliodonium tetrafluoroborate [$(C_6H_5)_2I^+\text{BF}_4^-$] was recrystallized from H_2O/CH_3CN (2 : 1) [11], dimethylphenylsulfonium tetrafluoroborate [$(CH_3)_2C_6H_5S^+\text{BF}_4^-$] from CH_3CN [12], trimethylsulfonium iodide [$(CH_3)_3S^+I^-$] from ethanol [13], triphenylbenzylphosphonium chloride [$(C_6H_5)_3C_6H_5CH_2P^+Cl^-$] (Aldrich) from H_2O . Triphenylsulfonium tetrafluoroborate [$(C_6H_5)_3S^+\text{BF}_4^-$] [14] was precipitated from acetonitrile by addition of diethyl ether and acrylonitrile (VEB Laborchemie Apolda) was vacuum distilled.

Laser photolysis. Absorption spectra were recorded using the previously described apparatus [15], using the second harmonic of a ruby laser (347 nm, 70 mJ, 16 ns), or a Lambda Physik excimer laser (351 nm, 100 mJ, 15 ns). Time-resolved emission experiments were performed as described previously [4], using a pulsed nitrogen laser LIF 200 (ZWG AdW Berlin, 337 nm, 25 μJ , 0.5 ns).

3. Results

3.1. Reactions of the diphenyl ketyl radical in the ground state

The ground state reactivity of the ketyl radical was examined by laser flash photolysis of α -PhB. The transient absorption spectrum, 15 ns after the laser pulse is shown in fig. 1a. The species with the maxi-

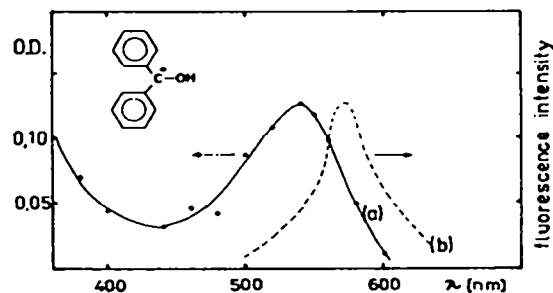


Fig. 1. (a) Transient absorption spectrum of the diphenyl ketyl radical, and (b) fluorescence spectrum of the diphenyl ketyl radical (in CH_3CN/CH_3CN from α -PhB = 5×10^{-3} mol l^{-1} and 1×10^{-2} mol l^{-1}) in oxygen free solution.

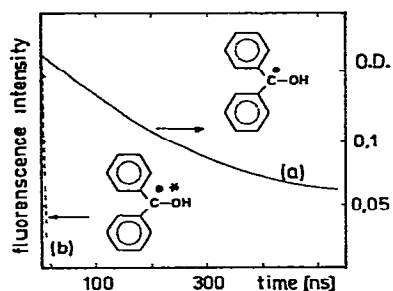


Fig. 2. Decay curves of (a) the absorption of the ground state of the diphenyl ketyl radical and (b) the fluorescence of the excited state.

imum absorption at 540 nm is assigned to the diphenyl ketyl radical [16]. Photolysis of α -PhB also leads to the formation of a benzoyl radical [17] (scheme II). This species has absorption maxima at 370 and 460 nm. However, the extinction coefficient of the forbidden σ, π^* transitions of this radical are very small compared to those of the π, π^* transitions of the ketyl radical ($\epsilon_{355} = 2.7 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{545} = 5.5 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Thus, absorptions due to the ketyl radical only are observed. The decay of the transient absorption, shown in fig. 2a, follows second-order kinetics in the absence of dissolved oxygen. From the slope of a plot of $1/[R^*]$ versus time (fig. 3), a bimolecular rate constant ($k = 3.4 \times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$) can be determined \ddagger .

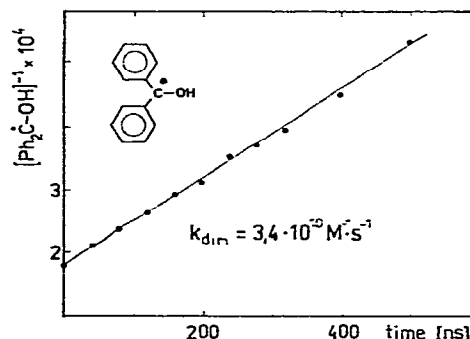


Fig. 3. Second-order kinetic treatment of the decay of the diphenyl ketyl radical absorption.

In the presence of a sufficiently high concentration of a quencher, the radical decay becomes a pseudo-first order, $k = k_q [Q]$. The bimolecular rate constants for the reaction of the radical with the quencher can thus be determined from the slope of a plot of the pseudo-first-order rate constant versus quencher concentration. The results for several substrates, together with some literature values are summarized in table 1.

\ddagger This rate constant corresponds to the reaction of $\text{Ph}_2\dot{\text{C}}\text{-OH}$ with PhCO to give α -PhB. Since the dimerization reaction of the $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals is also very fast, a portion of the $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals remain (fig. 2b). We have studied the dimerization reaction of the remaining radicals on a microsecond time-scale [18], and have determined a rate constant of $7.2 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$.

Table 1

Reaction rate constants of the diphenyl ketyl radical in the ground state (k_q) and the excited state (k_q^*) and the half-wave reduction potentials of the radical quenchers; rate constants measured in CH_3CN using $[\alpha\text{-PhB}] = 5 \times 10^{-3} \text{ mol l}^{-1}$

Q	k_q ($\text{mol}^{-1} \text{ s}^{-1}$)	k_q^* ($\text{mol}^{-1} \text{ s}^{-1}$)	E_{red} (V) a)
$p\text{-ClC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$	8×10^9	2.1×10^{10}	0.35 [20]
$(\text{C}_6\text{H}_5)_2\text{I}^+\text{BF}_4^-$	3×10^7	1.2×10^{10}	-0.16 [21]
$(\text{C}_6\text{H}_5)_3\text{S}^+\text{BF}_4^-$	4×10^7	1.5×10^{10}	-1.06 [22]
$(\text{CH}_3)_2\text{C}_6\text{H}_5\text{S}^+\text{BF}_4^-$		9.7×10^9	-1.55 [22] b)
$(\text{CH}_3)_3\text{S}^+\text{I}^-$		1.2×10^9	-1.85 [22]
$(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_5\text{CH}_2\text{P}^+\text{Cl}^-$	10^6	10^8	-1.59 [23]
CBr_4		3.8×10^{10}	-0.30 [24]
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	9×10^3	1.7×10^{10}	-1.80 [25]
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	3.8×10^3 c)	2.6×10^9	-1.88 [26]
O_2	2.5×10^9		

a) Versus SCE.

b) Assumed to be equal to the value for $(\text{CH}_3)_2(p\text{-CH}_3\text{C}_6\text{H}_5)\text{S}^+\text{BF}_4^-$.

c) $\text{Ph}_2\dot{\text{C}}\text{-OH}$ was produced by Ph_2CO photoreduction [19].

3.2. Reactions of the diphenyl ketyl radical in the excited state

As previously described, irradiation of α -PhB using a pulsed nitrogen laser leads to a fluorescence which is due to the doublet-doublet transition of the diphenyl ketyl radical product. The fluorescence spectrum is a mirror image of the absorption spectrum (fig. 1). The 0-0 energy of the π, π^* transition can be estimated to be $49.7 \text{ kcal/mol}^{-1}$ from the intersection of the absorption and emission spectra. As shown in fig. 2, the lifetime of the excited ketyl radical is much shorter than that of the corresponding ground state. The fluorescence decay exhibits a normal exponential decay. The lifetime of the emission which is determined after deconvolution of the system response [27] (τ_0) is 2.35 ns^{**} . In fig. 4 one can see that there is good agreement between the calculated and experimental data for the deconvolution.

The fluorescence lifetime does not depend upon the concentration of dissolved oxygen. The rate constants for reaction were determined by analysis of the fluorescence lifetime as a function of quencher concentration,

$$\tau_0/\tau = 1 + k_q^* \tau_0 [Q] \quad (2)$$

For all of the substrates examined, the Stern-Volmer plots were strictly linear. The rate constants which were determined in this manner are summarized in table 1.

** This lifetime is considered to be a better value than that reported previously by us (ref. [4], vide supra).

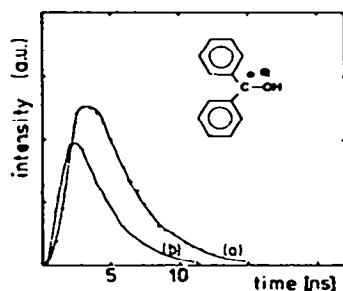


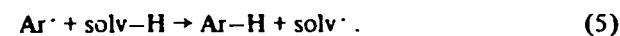
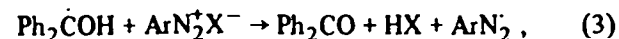
Fig. 4. (a) Measured fluorescence decay of the excited state of the diphenyl ketyl radical and calculated data (circles) and (b) the system response.

4. Discussion

Based on the conventional paradigms for radical reactivity, it is reasonable to expect that the ketyl radical will react via an electron or hydrogen transfer or a double bond addition mechanism. In the former two cases, benzophenone could be formed as a final product (scheme II). The reactivity of the diphenyl ketyl radical can be anticipated in terms of a simple molecular orbital scheme (fig. 5).

The radical quenchers can be classified in terms of their half-wave reduction potentials, $E_{red}^{1/2}$, as those whose LUMO energies are equal to, or less than the SOMO of the ground state radical (quenchers Q_1), and those whose LUMO energies are greater than the SOMO energy of the radical (quenchers Q_2).

Electron transfer from the ground state of the radical is exothermic only to Q_1 , e.g. the onium salts (fig. 5a). The onium radicals which are the products of this reaction have previously been detected both spectroscopically and by means of their fragmentation products [4,9,10,28]. As a typical example, the reactions of the diphenyl ketyl radical with a diazonium salt are given below:



Similar reactions with iodonium and sulfonium salts lead to aryl radicals and iodobenzene or diphenylsulfide as products.

The free energy ΔG for the electron transfer reactions is given by

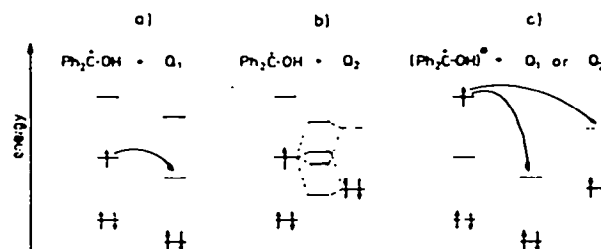


Fig. 5. Simple molecular orbital diagram for the reactions of the diphenyl ketyl radical in the ground (a) and (b) and excited (c) states, respectively with substrates of differing HOMO energies.

$$\Delta G = E_{1/2, \text{Ph}_2\dot{\text{C}}-\text{OH}}^{\text{ox}} - E_{1/2, \text{Q}_1}^{\text{red}} \quad (6)$$

The value of $E_{\text{ox}, \text{Ph}_2\dot{\text{C}}\text{OH}}$ can be estimated to be ≈ 0.7 V[‡]. Hence, using the literature values of E_{red} for the radical quenchers, the values of ΔG for the reactions can be estimated: For $\Delta G > 0.3$ eV, the rate constant for an electron transfer reaction will be $k \approx 10^6$ mol⁻¹ s⁻¹, and for $\Delta G \leq 0.5$ eV, the rate constant will reach the value for diffusion control [29,30]. The k_{q} values for $p\text{-ClC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ ($\Delta G = -1.0$ eV) and $(\text{C}_6\text{H}_5)_3\text{S}^+\text{BF}_4^-$ ($\Delta G = 0.3$ eV) agree well with this prediction.

The molecular orbital scheme for the olefins acrylonitrile and methylmethacrylate is shown in fig. 5b. In this case the SOMO lies between the HOMO and LUMO of the quenchers, and thus electron transfer is expected to be less efficient to these quenchers, as is observed experimentally. For reaction of the diphenyl ketyl radical with other olefins, radical addition or hydrogen atom transfer processes have been suggested [4].

The excited state of the ketyl radical has a higher energy than the doublet ground state (49.7 kcal/mol⁻¹) as a result of the promotion of one electron into the next highest orbital as shown in fig. 5c. Assuming that electronic energy transfer processes do not occur, since both the singlet and triplet energies of the quenchers are greater than 50 kcal/mol⁻¹, then we expect that electron transfer processes may account for the fluorescence quenching for all of the substrates. For the excited radical, the free-reaction energy is increased by the doublet excitation energy (E_{D}),

$$\Delta G = (E_{1/2, \text{Ph}_2\dot{\text{C}}-\text{OH}}^{\text{ox}} - E_{\text{D}}) - E_{1/2, \text{Q}}^{\text{red}} \quad (7)$$

Therefore, the higher rates of electron transfer from the excited radical, for which the reaction is exothermic, can be explained in terms of the excess energy available to the excited state. The kinetic data do not, however, indicate whether the transferred electron is rapidly re-transferred to give the ground state ketyl radical, and, hence, to result in no net chemical reaction.

[‡] $E_{1/2, \text{Ph}_2\dot{\text{C}}\text{OH}}^{\text{ox}}$ is not known. Assuming a linear correlation of the E_{ox} values for $\text{R}_2\dot{\text{C}}\text{OH}$ for $\text{R} = \text{H}, \text{CH}_3$ (ref. [29], vide infra) using the E_{red} values for the corresponding ketones R_2CO , the value $E_{1/2, \text{Ph}_2\dot{\text{C}}\text{OH}}^{\text{ox}} = -0.7$ eV can be estimated for $E_{\text{red}, \text{Ph}_2\text{CO}} = -1.3$ V (ref. [24], vide supra).

5. Conclusion

The result of a comparison of the reactivity of diphenyl ketyl radical in its ground and excited states show that the reactions of the excited state of the diphenyl ketyl radical can be many orders of magnitude larger than the corresponding reactions of the ground state radical. This situation is similar to that observed for the reactions of the excited state of diphenyl carbene [3]. From our results we conclude that both the reactivity and the selectivity of excited states of radicals will be different from those of their corresponding ground states.

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