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

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

\[ k_q[R'][Q] \geq I_\lambda k_q^*[Q]/(k_d + k_F + k_q^*[Q]) \]  

holds [1,2]. In eq. (1), \( I_\lambda \) is the light intensity absorbed by R' 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' with Q and \( k_q^* \) the rate constant for quenching of R' with Q. Because of the typically short lifetime of R' in fluid solutions, \( I_\lambda \) 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, \( R' \), which possess an extinction coeffi-
cient sufficiently high that \( R' \), 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 \( R \) and \( R' \) may be distinguished by
monitoring the time-resolved absorption of \( R \) and the
time-resolved emission of \( R' \). Such a procedure has
been skillfully employed recently by Eisenthal 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 bimolec-
ular reactivity of excited diphenyl carbene was gener-
ally 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 \( \alpha \)-phenyl benzoin (\( \alpha \)-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
\[
\text{Ph} - \text{C} - \text{C} - \text{Ph} \quad \rightarrow \quad \text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{Ph} - \text{C} - \text{H} + \text{Ph}
\]
\( \alpha \)-PhB
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. \( \alpha \)-Phenylbenzoin \( (C_6H_5COC(C_6H_5)_2OH) \),
\( p \)-chlorobenzenediazonium tetrafluoroborate
\( (p\text{-CIC}_6\text{H}_4\text{N}_2\text{BF}_4) \), methylmethacrylate (MMA), and
acetonitrile were prepared and purified as previously
described [4]. Diphenyliodonium tetrafluoroborate
\( ((C_6H_5)_2I\text{BF}_4) \) was recrystallized from
\( \text{H}_2\text{O}/\text{CH}_3\text{CN} (2:1) [11] \), dimethylphenylsulfonium
tetrafluoroborate \( ((\text{CH}_3)_2\text{C}_6\text{H}_5\text{S}^+\text{BF}_4^-) \) from
\( \text{CH}_3\text{CN} [12] \), trimethylsulfonium iodide
\( (\text{CH}_3)_2\text{S}^+\text{I}^- \) from ethanol [13], triphenylbenz-
phosphonium chloride \( ((C_6H_5)_3\text{C}_6\text{H}_5\text{CH}_2\text{P}^+\text{Cl}^-) \)
(Aldrich) from \( \text{H}_2\text{O} \). Triphenylsulfonium tetra-
fluoroborate \( ((C_6H_5)_3\text{S}^+\text{BF}_4^-) \) [14] was precipi-
tated from acetonitrile by addition of diethyl
er and acrylonitrile (VEB Laborchemie Apolda) was
vacuum distilled.

Laser photolysis. Absorption spectra were re-
corded 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 ex-
periments were performed as described previously
[4], using a pulsed nitrogen laser LIF 200 (ZWG
AdW Berlin, 337 nm, 25 \( \mu \text{J} \), 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 \( \alpha \)-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 \( \text{CH}_3\text{CN} \) from \( \alpha \)-PhB = 5 \( \times \) 10\(^{-3} \) mol \text{lt} \(^{\text{-1}} \)
and 1 \( \times \) 10\(^{-2} \) mol \text{lt} \(^{\text{-1}} \) in oxygen free solution.](image)
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.

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.

Table 1

<table>
<thead>
<tr>
<th>Q</th>
<th>$k_q$ (mol$^{-1}$ s$^{-1}$)</th>
<th>$k_q^*$ (mol$^{-1}$ s$^{-1}$)</th>
<th>$E_{1/2}$ (V) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-C$_6$H$_4$N$_2$+BF$_4^-$</td>
<td>$8 \times 10^9$</td>
<td>$2.1 \times 10^{10}$</td>
<td>0.35 [20]</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$I$^+$BF$_4^-$</td>
<td>$3 \times 10^7$</td>
<td>$1.2 \times 10^{10}$</td>
<td>-0.16 [21]</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$S$^+$BF$_4^-$</td>
<td>$4 \times 10^7$</td>
<td>$1.5 \times 10^{10}$</td>
<td>-1.06 [22]</td>
</tr>
<tr>
<td>(CH$_2$)$_2$C$_6$H$_5$S$^+$BF$_4^-$</td>
<td>$9.7 \times 10^9$</td>
<td>$1.5 \times 10^{10}$</td>
<td>-1.55 [22] $^b$</td>
</tr>
<tr>
<td>(CH$_3$)$_2$S$^+$</td>
<td>$1.2 \times 10^8$</td>
<td>$1.85 \times 10^{10}$</td>
<td>-1.59 [23]</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$C$_6$H$_5$CH$_2$P$^+$Cl$^-$</td>
<td>$10^6$</td>
<td>$10^8$</td>
<td>-1.85 [24]</td>
</tr>
<tr>
<td>CBr$_4$</td>
<td>$3.8 \times 10^9$</td>
<td>$10^9$</td>
<td>-0.30 [24]</td>
</tr>
<tr>
<td>CH$_3$=C(CH$_3$)COOCH$_3$</td>
<td>$9 \times 10^3$</td>
<td>$1.7 \times 10^9$</td>
<td>-1.80 [25]</td>
</tr>
<tr>
<td>CH$_2$=C(CH$_3$)COOCH$_3$</td>
<td>$3.8 \times 10^3$ $^c$</td>
<td>$2.6 \times 10^9$</td>
<td>-1.88 [26]</td>
</tr>
<tr>
<td>O$_2$</td>
<td>$2.5 \times 10^9$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Versus SCE.

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

$^c$ Ph$_2$C=OH was produced by Ph$_2$CO 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 kcal/mol 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] (τo) 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,

\[ \tau_0/\tau = 1 + k_0^*\tau_0[Q] \]  

(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).

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, \( E_{1/2} \), 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:

\( \text{Ph}_2\text{COH} + \text{ArN}^+_2X^- \rightarrow \text{Ph}_2\text{CO} + \text{HX} + \text{ArN}_2^- \).  

(3)

\( \text{ArN}_2^- \rightarrow \text{Ar}^- + \text{N}_2 \).  

(4)

\( \text{Ar}^- + \text{solv}^- \rightarrow \text{Ar}^- + \text{solv}^- \).  

(5)

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

The free energy \( \Delta G \) 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.](image-url)
\[ \Delta G = E_{1/2, \text{Ph}_2 CO}^{\text{ox}} - E_{1/2, Q_1}^{\text{red}} \]  

The value of \( E_{\text{ox,Ph}_2 COH} \) can be estimated to be \( \approx 0.7 \) V.\( ^{\dagger} \) Hence, using the literature values of \( E_{\text{red}} \) for the radical quenchers, the values of \( \Delta G \) 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 \( p\)-Cl\( \text{C}_6\text{H}_4\text{N}_2\text{BF}_4 \) (\( \Delta G = -1.0 \) 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 (\( E_D \)),

\[ \Delta G = (E_{1/2, \text{Ph}_2 CO}^{\text{ox}} - E_D) - E_{1/2, Q_1}^{\text{red}} \]  

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.

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