Photochemistry of Radicals and Biradicals[1]

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Contents

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I. Introduction

The photochemistry of reactive intermediates has been an area of increasing interest over the last 10 years.[2–7] Much of this interest has been prompted by the fact that laser-initiated photochemical reactions often yield different products from conventional lamp irradiations. In some cases the differences arise simply from an increased concentration of reactive intermediates. For example, in a radical reaction such effects may be noted as an increased yield of radical coupling products as compared to hydrogen abstraction reactions. However, in many cases the different chemistry results from two-photon processes. In principle, a two-photon process may involve one of two possible pathways. First, simultaneous absorption of two photons can generate an upper excited state which undergoes chemical decay pathways that are unavailable to the lowest excited state of the molecule. Such processes are rare for the laser fluences normally encountered in the UV–visible lasers used for studies of organic photochemistry and are not the subject of this review. In the second and more common case, the intensity dependence arises from sequential two-photon absorption, whereby the first photon is absorbed by a precursor which rapidly produces an intermediate that absorbs a second photon within the same laser pulse. Examples of such behavior are now well-documented for a variety of reactive intermediates, including free radicals, biradicals, carbenes, and singlet and triplet excited states.[2–7] The primary requirements for such two-photon behavior are the rapid formation of the intermediate relative to the duration of the laser pulse and sufficient absorption by the intermediate at the laser wavelength so that it can compete favorably with the ground state for absorption of the incident laser pulse. The lifetimes of most reactive intermediates are such that such two-photon chemistry is not expected under conditions of lamp irradiation.

This review will cover the photochemistry of radicals and biradicals in solution at room temperature and will emphasize those examples where time-resolved experiments (often in combination with product studies) have been used to obtain a reasonably complete description of the photochemistry and photophysics for a given species. Particular emphasis will be placed on two-laser flash photolysis and related techniques, as these are potentially more useful than single-laser techniques in which it is not always straightforward to selectively excite the intermediate of interest. A detailed understanding of the photochemistry of any species obviously requires some information on the nature of the initial excited states. Since much of this comes from either absorption or fluorescence measurements, several sections of the review are devoted to the spectroscopy of radicals and biradicals in solution. Low-temperature work on the emission of radicals and biradicals is included only where the work is directly relevant to studies in solution at room temperature. Matrix isolation work is also excluded. In such studies the lifetimes of reactive intermediates are lengthened to the point that conventional methods can be used to study them. Although this approach can provide much useful information, the reactivity of the intermediate is frequently quite different from that in solution, and it is often difficult to distinguish between matrix effects and photochemical reactions of an intermediate.[8] The next section will briefly describe the various techniques that have been used to study the photochemistry of

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radicals and biradicals and the commonly used methods for generating these species. The luminescence and transient absorption properties of radicals and biradicals will then be presented, followed by a discussion of the intramolecular and intermolecular photochemistry of these intermediates.

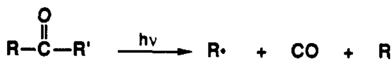
II. Methods

The occurrence of photochemical reactions of excited intermediates is freqently inferred from observations of the intensity dependence of either transient phenomena or product distributions using pulsed laser excitation. Such experiments can provide valuable preliminary information. However, they must frequently be supplemented by studies in which the intermediate of interest can be generated and then selectively excited for studies of its photophysics and photochemistry. This generally requires the use of two-laser techniques as described in some detail in several recent reviews.[3,4,7,9] In this approach a synthesis laser generates the reactive intermediate and is then followed, after a suitable delay, by a second laser pulse at a wavelength such that only the intermediate (and not its precursor) is excited. The excited state of the transient can then be monitored directly by its luminescence or transient absorption using laser flash photolysis techniques. Alternatively, in cases where absorption or luminescence experiments are not feasible, the occurrence of irreversible depletion of the ground state can at least provide evidence that the excited intermediate does undergo chemical decay pathways. Transient absorption measurements can also frequently provide evidence for intermediates produced from the initial excited radical or biradical. Such two-laser techniques have also been applied to product studies, although these are generally somewhat more difficult than the time-resolved studies. The laser-jet technique recently developed by Wilson and co-workers shows considerable potential in terms of overcoming the problems associated with two-laser product studies.[10,11] This method uses a CW laser focused on a fine jet of sample and allows the production of substantial yields of products resulting from multiphoton chemistry. The laser-jet approach is reviewed elsewhere in this issue and will only be mentioned here in cases where it is directly relevant to the discussion of a particular system that has also been studied by time-resolved techniques.

Although most two-laser techniques have used nanosecond lasers, the same method has also been applied on a picosecond time scale.[12] A related technique that has been used in several cases involves the use of pulse radiolysis to synthesize the initial intermediate, followed by laser excitation to generate its excited state.[13,14] The two-laser method for studying the photochemistry of reactive intermediates has also recently been extended to the quantitative determination of quantum yields by Scaiano and co-workers.[15-17] For example, the bleaching of the in situ generated colored form of the fulgide dye Aberchrome-540 has been calibrated as an actinometer for UV-visible two-laser photobleaching experiments.[15] Techniques and standards for carrying out two-laser fluorescence quantum yield measurements for excited radicals have also recently been developed.[16,17]

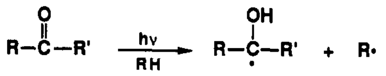
A variety of photochemical methods for generating both radicals and biradicals are well established in the literature. Those which have found the most frequent use in studies of the photochemistry of radicals are listed in reactions 1–4. Of these, photochemical homolysis of a carbon–halogen bond has been used extensively for the generation of various arylmethyl radicals, largely since a variety of substituted arylmethyl halides are readily available. The generation of radicals via photolysis of a ketone (or ester or sulfone) precursor as shown in reaction 2 has the advantage of generating two radicals (R = R′) at the same time, although the route has not been too widely used. Ketyl radicals are readily accessible by hydrogen abstraction from the parent alcohol (reaction 3) or by hydrogen abstraction from a suitable donor by the triplet excited state of the corresponding ketone (reaction 4). Pulse radiolysis methods have also been used to generate radicals from the corresponding halide, according to reaction 5. Most

$$R{-}X \xrightarrow{h\nu} R\cdot + X\cdot \qquad (1)$$



$$R{-}C(=O){-}R' \xrightarrow{h\nu} R\cdot + CO + R'\cdot \qquad (2)$$

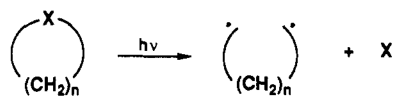
$${}^tBuO\cdot + R{-}H \xrightarrow{h\nu} R\cdot + {}^tBuOH \qquad (3)$$



$$R{-}C(=O){-}R' \xrightarrow[RH]{h\nu} R{-}\dot{C}(OH){-}R' + R\cdot \qquad (4)$$

$$R{-}X \xrightarrow{e^-} R\cdot + X^- \qquad (5)$$

studies of the photochemistry of biradicals rely on cleavage reactions of cyclic ketones or azo compounds to generate the species of interest. In most cases the initial bond-breaking step is followed by subsequent rapid loss of either nitrogen or carbon monoxide (reaction 6, X = N_2 or CO). Intramolecular hydrogen abstraction reactions (reaction 7) have also been used in some cases.



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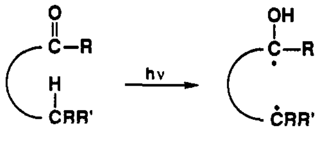

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III. Luminescence

A. Radicals

A number of radicals show readily detectable and relatively long-lived fluorescence emission in solution at room temperature and as a result luminescence techniques have been widely used to study the excited states of these species. Substituted benzyl radicals have been among the most widely studied, largely as a result of their convenient absorption and emission properties

Table I. Fluorescence Spectra and Lifetimes for Substituted Benzyl Radicals in Solution at Room Temperature

substituent	solvent	λ_{max}, nm	τ, ns	ref(s)
H	hexane	475[a]	<1	18
4-CH_3	hexane	485[a]	14	18
4-Cl	hexane	470[a]	81	18
4-CN	hexane		58	19, 20
4-F	hexane		200	20
4-OCH_3	hexane	490	120	20, 21
4-Br	hexane		2	22
4-NO_2	hexane		35	22
4-Ph	hexane		12	22
	benzene	576	14	23
3-$ClCH_2$	isopentane	471		8
4-(4-CH_3Ph)	benzene	582	10	23
4-$PhCH_2O$	hexane		58	22
2,4,5-$(CH_3)_3$	toluene	508	5	4
2,3,4,5,6-$(CH_3)_5$	toluene	503	5.5	4
α-CN	hexane	477	<4	24

[a] Read from figure in original reference.

Table II. Fluorescence Spectra[a] and Lifetimes for Substituted Arylmethyl Radicals in Solution at Room Temperature

radical	solvent	$\lambda_{max}(\lambda_{0,0})$, nm	τ, ns	ref(s)
1-naphthylmethyl	hexane	616 (595)	13	25
	cyclohexane	586 (586)	35	26
	methanol	590 (590)	35	26
	benzene		32	26
	hexane	612 (589)	34	27
(2-methyl-1-naphthyl)-methyl	hexane	594 (594)		25, 28
2-naphthylmethyl	hexane	610 (610)	13	25, 29
	methanol	607 (607)	27	23
	triethylamine[b]	605 (605)	27	23
(1-bromo-2-naphthyl)-methyl	cyclohexane	624 (624)	24	23
	benzene	630 (630)	20	23
	methanol	626 (626)	22	23
cyano-1-naphthylmethyl	hexane	(618)	29	24
	methanol[b]		18	24
9-anthrylmethyl	hexane	545 (545)	21	28, 30
2-phenanthrylmethyl	toluene	593 (693)	79	23

[a] Both λ_{max} and $\lambda_{0,0}$ values are given for radicals which show vibrational structure. [b] Lifetimes in a variety of other solvents are available in the original reference.

and their ease of generation from halide precursors. The available luminescence data for substituted benzyl radicals and other monoarylmethyl radicals are listed in Tables I and II, respectively. Data for other diaryl and triarylmethyl radicals are collected in Table III. In general these radicals show fluorescence spectra in the 500–700-nm region; in most cases some vibrational structure is observed. The absorption spectra of most arylmethyl radicals are dominated by a strong D_0–D_n transition in the UV region and the weak D_0–D_1 transition is not readily detectable for comparison with the emission data. For benzyl and diphenylmethyl radicals fairly detailed studies of substituent effects have been reported.[18,20,22,32] In each case substitution of either electron-donating or -withdrawing substituents leads to red-shifts in the fluorescence maxima.

The fluorescence lifetimes in Tables I–III cover over 2 orders of magnitude in time scale from a value of <1 ns for the parent benzyl radical to 390 ns for the diphenylmethyl-d_{10} radical. Although fluorescence lifetimes in the range of 1–1.5 μs had been observed for benzyl radical in glasses at 77 K some years ago,[37,38] it is only recently that its emission has been studied at or near room temperature.[18,39] These studies demonstrate that the benzyl radical exhibits a thermally activated decay pathway above ~115 K (E_a ~ 4 kcal/mol), in addition to the usual temperature-independent relaxation at lower temperature. The data for the temperature dependence of radical fluorescence in this and related systems are listed in Table IV. Theoretical studies have established that the $2B_2$ excited state is at only slightly higher energy than the emissive lowest excited $1A_2$ state in the parent benzyl radical.[43] Differential vibronic mixing of these two close-lying excited states has been proposed to provide a temperature-dependent route for radiationless decay of the excited radical.[39]

Consideration of the data in Table I shows that the lifetimes of benzyl radicals vary substantially with the substituent in the aromatic ring. For example, the 4-chlorobenzyl radical has a fluorescence lifetime of 81 ns in hexane at room temperature, despite the fact that its lifetime of 0.96 μs at 77 K is only slightly different from that of benzyl.[18] The pronounced effects of substitution at the 4-position of the aromatic ring have been attributed to subtle changes in the energy levels and vibrational modes for the two close-lying $1A_2$ and $2B_2$ excited states.[18] The observation of substantial temperature dependence for the fluorescence lifetimes of the 4-methyl- and 4-chloro-substituted radicals also supports this theory. The 4-methoxy radical exhibits a red-shifted emission with much less vibrational structure than other benzyl radicals and has little temperature dependence (E_a of 1.1 kcal, Table IV). These results indicate that the D_1 and D_2 states are sufficiently separated that nonradiative relaxation via the D_2 state does not contribute significantly to the 120-ns excited-state lifetime for this radical at room temperature.[21]

Anomalous behavior has been observed for the 4-cyanobenzyl radical, both in terms of its absorption spectrum and chemical reactivity, as discussed below; these effects have been attributed to the fact that the $2B_2$ state is the lowest excited state in this radical.[19] Support for this hypothesis comes from fluorescence polarization studies at 77 K which confirm that the lowest excited state is $1A_2$ for benzyl and 4-fluorobenzyl but $2B_2$ for 4-cyanobenzyl radicals.[44] Little information is currently available on the effects of multiple substitution on benzyl radical fluorescence lifetimes. The lifetimes obtained upon substitution of three or five methyl groups are intermediate between those of benzyl and 4-methylbenzyl radicals (Table I), although these have not all been measured in the same solvent.

The excited state of the parent diphenylmethyl radical differs from benzyl in two respects: first, it has a much longer lifetime at room temperature (Table III), and second, it shows little temperature dependence (E_a of 0.83 kcal/mol, Table IV).[13,31,39] Again theoretical calculations are useful in explaining these results. In this case the second excited state is calculated to be substantially higher in energy (0.36 eV) than D_1, and temperature-dependent internal conversion cannot be expected to have much effect on the fluorescence lifetime at room temperature. 1-Naphthylmethyl radicals are similar to diphenylmethyl in that their room

Table III. Fluorescence Spectra[a] and Lifetimes for Substituted Di- and Triarylmethyl Radicals in Solution at Room Temperature

radical	solvent	λ_{max} ($\lambda_{0,0}$), nm	τ, ns	ref(s)
diphenylmethyl[b]	acetonitrile	526 (526)	280	13
	cyclohexane	(528)	255	31, 32
	methanol		236	31
	chloroform[c]		223	31
	0.2 M SDS		259 (120)[d]	9
	0.05 M CTAC		254 (140)[d]	9
	0.05 M CTAB		194 (127)[d]	9
diphenylmethyl-d_1	cyclohexane		250	4
diphenylmethyl-d_{10}	cyclohexane	(527)	390	32
(4-methylphenyl)phenylmethyl	cyclohexane	(535)	218	32
(3,4-dimethylphenyl)phenylmethyl	cyclohexane	(535)	212	32
(4-chlorophenyl)phenylmethyl	cyclohexane	(537)	197	32
bis(4-chlorophenyl)methyl	cyclohexane	(546)	178	32
(4-bromophenyl)phenylmethyl	cyclohexane	(538)	142	32
(4-carbomethoxyphenyl)phenylmethyl	cyclohexane	(552)	130	32
(4-cyanophenyl)phenylmethyl	cyclohexane	(560)	80	32
	hexane	(555)	72	24
(4-methylphenyl)(4-cyanophenyl)methyl	cyclohexane	(566)	83	32
cyanodiphenylmethyl	hexane	(522)	110	24
	methanol[c]		41	24
chlorodiphenylmethyl	various	560–600	2–4	33
triphenylmethyl	cyclohexane	520 (520)		12
perchlorotriphenylmethyl[e]	carbon tetrachloride	605	7	34
(4-benzoylphenyl)diphenylmethyl[f]	benzene	616	15	35
10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl	acetonitrile[g]	540 (540)	265	14
9-phenylxanthenyl	*n*-heptane	590	≤5	36

[a] Both λ_{max} and $\lambda_{0,0}$ values are given for radicals which show vibrational structure. [b] Fluorescence quantum yields of 0.3 (acetonitrile[13]) and 0.31 (cyclohexane[16]) have been reported. [c] Lifetimes in a variety of other solvents are available in the original reference. [d] Different lifetimes are obtained using 1,1-diphenylacetone or 1,1,3,3-tetraphenylacetone (in parentheses) as the radical precursor. [e] $\Phi_F = 0.3$ (ref 34). [f] $\Phi_F = 0.14$ (ref 35). [g] $\Phi_F = 0.26$ (ref 14).

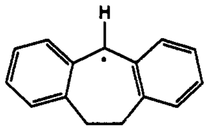
Table IV. Activation Parameters for the Fluorescence Decay of Excited Radicals

radical	solvent	E_a, kcal/mol	log *A*	ref
benzyl[a]	2-methyltetrahydrofuran	3.83	11.94	39
benzyl	3-methylpentane	4.0		18
4-methylbenzyl	3-methylpentane	6.2, 2.0[b]		18
4-chlorobenzyl	3-methylpentane	5.3, 0.83[b]		18
4-methoxybenzyl	3-methylpentane	1.1		21
benzyl-d_7[a]	2-methyltetrahydrofuran	4.26	12.20	39
4-phenylbenzyl	toluene	−0.07	7.79	23
phenylethyl	2-methyltetrahydrofuran	4.74	11.41	39
1-naphthylmethyl	methanol	0.3	7.7	26
2-phenanthrylmethyl	toluene	0.6	7.56	23
diphenylmethyl[a]	2-methyltetrahydrofuran	0.83	7.30	39
triphenylmethyl[a]	2-methyltetrahydrofuran	4.6	11.43	39
diphenylketyl	toluene	1.11	9.22	40
diphenylketyl-*O*-*d*	toluene-d_8	1.75	9.4	40
bis(4-methylphenyl)ketyl	toluene	1.20	9.39	41
bis(4-chlorophenyl)ketyl	toluene	1.55	9.19	41
(4-cyanophenyl)phenylketyl	toluene	1.5	9.23	41
methoxydiphenylmethyl	toluene	1.55	9.5	41
10,10-dimethylanthrone ketyl	toluene	1.25	8.43	5
10,10-dimethylanthrone ketyl-*O*-*d*	toluene	0	7.43	5
3,5-diphenyl-2-furanoxyl	2-methyltetrahydrofuran	0.35		42

[a] Temperature-independent lifetime at low temperature. [b] Two activation energies extracted from curved Arrhenius plots.

temperature lifetimes (Table II, ~30 ns) are much longer than benzyl and theoretical calculations indicate a large gap between D_1 and D_2.[45]

The data in Table II indicate similar lifetimes for the few substituted naphthylmethyl radicals that have been examined. A much wider range of substituents has been investigated for diphenylmethyl radicals (Table III). In general, ring substitution is observed to decrease the lifetime of the excited radical and a correlation between the energy gap between D_1 and D_0 (as measured by the position of the 0,0 band for the emission) and the excited state lifetime has been observed.[32] Substitution of either chloro or cyano at the α-position leads to a pronounced shortening of the fluorescence lifetime;[24,33] for the α-cyano radicals larger solvent-induced changes in lifetime and spectra are observed than for ring-substituted radicals.[24] It has been suggested that coupling to higher energy vibrational modes may enhance the decay of the first excited doublet in these cases. In neither case is the enhanced excited state decay for the α-substituted radical attributed to chemical reaction. Radical 1 in which the two diphenylmethyl rings have been attached via a two methylene unit chain also provides an interesting example. The higher degree of planarity of the two phenyl rings results in a red-shift of the emission maximum, but its fluorescence lifetime is within experimental error of that of the parent diphenylmethyl radical.[14]



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The long lifetime of the excited diphenylmethyl radical makes it a useful probe in a variety of systems. For example, the excited-state lifetime has been examined in micellar media (Table III) and been shown to depend on both the nature of the micelle (size, ionic charge) and the diphenylmethyl precursor.[9] When 1,1-diphenylacetone is used to generate the radicals, the diphenylmethyl radical is produced in the presence of a small mobile acetyl radical which rapidly exits the micelle. Under these conditions the excited-state lifetime is similar to that in homogeneous solution and is unaffected by a magnetic field. For micelles with bromide counterions there is some decrease in the excited-state lifetime since bromide acts as an excited radical quencher. However, when two diphenylmethyl radicals are generated within a single micelle from 1,1,3,3-tetraphenylacetone, the excited-state lifetime is approximately half that in homogeneous solution (Table III). The excited radical pair is thought to retain its triplet character and the observed decay is the sum of the rate constants for fluorescence and for spin evolution to a singlet pair which decays either by chemical means or by deactivation to a ground-state radical pair. The lengthening of the excited radical lifetime in the presence of a magnetic field using tetraphenylacetone as the precursor is consistent with this hypothesis.

The behavior of triphenylmethyl radical is similar to that of benzyl in that it has a short fluorescence lifetime (<1 ns) at room temperature and shows a strong temperature dependence (E_a = 4.6 kcal/mol, Table IV).[39] However, in this case the temperature dependence is related to a chemical decay pathway for the excited state, as discussed in section V. Similar results have been observed for the phenethyl radical.[14,39]

Fluorescence emission is also readily detected from a variety of diarylketyl radicals and the data are summarized in Table V. For most of these radicals the fluorescence emission shows the expected mirror-image relationship with the absorption spectrum. In agreement with the results for diphenylmethyl radicals, substitution at the 4-position of the diphenylketyl radical also leads to red-shifted emission spectra. The room temperature lifetimes for most diphenylketyl radicals are relatively short (<10 ns) and are not substantially different from the values of ~20 ns reported for various ketyl radicals at 77 K.[56] Deuterium substitution at the hydroxyl position has a particularly marked effect, lengthening the lifetime from 3.9 to 8.7 ns. This substantial deuterium isotope effect on the excited-state lifetime reflects the importance of the O–H bond in chemical and nonradiative decay routes of the excited radical, as discussed in more detail in section V.[41,52] Modest temperature dependences have been measured for several diphenylketyl radicals (E_a = 1–2 kcal, Table IV) and have been shown to reflect activation energies for both chemical reaction and internal conversion.[40,41] In contrast to the effects of deuterium substitution at the hydroxyl group, ring substitution leads to dramatically shorter excited-state lifetimes for some diphenylketyl radicals.[41,51] A detailed analysis of radiative, nonradiative, and chemical decay pathways for substituted diphenylketyl radicals has led to the conclusion that the rates for both chemical and nonradiative decay pathways are substantially increased for the shorter-lived radicals, although changes in the latter largely determine the excited-state lifetimes.[51]

Several related anthrone ketyl radicals have been studied. These have relatively long excited-state lifetimes, in spite of the fact that they still undergo efficient chemical reaction. The deuterium isotope effects for these radicals are more modest than those observed for diphenylketyl radicals.[52,53] Another bridged system, the dibenzosuberone ketyl radical has an excited-state lifetime (5.5 ns, Table V) which is intermediate between those for the parent diphenylketyl radical and the anthrone ketyls.[3]

The excited states of only a few heteroatom-centered radicals have been detected by fluorescence spectroscopy at room temperature. Table V lists the available data for furanoxy radicals which have lifetimes in the 6–13-ns range, show very little temperature dependence (Table IV) and do not undergo any irreversible chemistry.[42,54] Fluorescence has also been reported for the stable 2,4,6-tri-*tert*-butylphenoxyl radical.[57] However, the observed 430-nm emission is actually at much shorter wavelength than the lowest energy absorption of this radical (625 nm) so more work is obviously required to establish the nature of the emitting state.[58] Long-lived fluorescence from other heteroatom-centered radicals (e.g. phenyldimethylsilyl and thiophenoxy)[59,60,61] has been observed at 77 K and room temperature fluorescence has been recorded for the *p*-aminophenylthiyl radical.[62]

B. Biradicals

There are relatively few biradicals for which emission has been detected and a number of these have been examined only in glasses at low temperature. This is primarily a reflection of the short lifetime for the ground states of these species.[63] Almost all of the biradicals which have been examined are ground-state triplets and the observed emission thus corresponds to triplet–triplet fluorescence. The available data for both room-temperature and low-temperature glasses is collected in Table VI for biradicals 2–10 (Scheme I). Comparison of the fluorescence maxima for the xylylene biradicals (3 and 4)[8] with those reported for benzyl radicals indicates that the biradicals fluoresce at shorter wavelengths. Similar effects are observed for the various naphthoquinodimethane biradicals (6–10),[67–69] as compared to the 1- or 2-naphthylmethyl radicals. All of these biradicals have a mechanism for delocalization of the radical sites throughout the connecting framework. However, the unconjugated biradical, 5, has a fluorescence spectrum which is very similar to that of the parent diphenylmethyl radical.[66]

As the data in Table VI indicate, there are few lifetime determinations for biradicals at room temperature. Excited biradical 5 has a lifetime of 2.5 ns which is

Table V. Fluorescence Spectra and Lifetimes for Ketyl and Furanoxyl Radicals in Solution at Room Temperature

radical	solvent	λ_{max}, nm	τ, ns	ref(s)
$(C_6H_5)_2C^{\bullet}OH$[a–c]	methyltetrahydrofuran	577		46
	cyclohexane		2.5	47
	acetonitrile		5.1	47
	acetonitrile	564	2.35	48, 49
	toluene	574	3.9	40, 41
	cyclohexane		2.7	41
$(C_6H_5)_2C^{\bullet}OD$	toluene-d_8	570	8.7	40, 41
$(C_6D_5)_2C^{\bullet}OH$	toluene-d_8		4.4	40
$(C_6D_5)_2C^{\bullet}OD$	toluene-d_8	570	10.5	40, 41
$(C_6H_5)_2{}^{13}C^{\bullet}OH$	toluene		3.9	40
$(C_6H_5)_2C^{\bullet}OCH_3$	toluene	587	3.5	40, 41
$(C_6H_5)_2C^{\bullet}OCl$[d]	Freon 113	~530		50
$(4\text{-}CH_3\text{-}C_6H_4)(C_6H_5)C^{\bullet}OH$	toluene	585	3.5	51
$(4\text{-}CH_3C_6H_4)_2C^{\bullet}OH$	toluene	588	3.1	41
$(4\text{-}CH_3OC_6H_4)(C_6H_5)C^{\bullet}OH$	toluene	610	<1	51
$(4\text{-}CH_3OC_6H_4)_2C^{\bullet}OH$	toluene	623	<1	41, 51
$(4\text{-}ClC_6H_4)_2C^{\bullet}OH$	toluene	596	5.9	41
$(4\text{-}BrC_6H_4)_2C^{\bullet}OH$	toluene	605	<1	51
$(4\text{-}CNC_6H_4)(C_6H_5)C^{\bullet}OH$	toluene	613	7.8	41
$(4\text{-}CF_3C_6H_4)(C_6H_5)C^{\bullet}OH$	toluene	590	6.0	51
$(2\text{-}C_5H_4N)(C_6H_5)C^{\bullet}OH$	toluene	567	5.9	4
$(3\text{-}C_5H_4N)(C_6H_5)C^{\bullet}OH$	toluene	580	4.2	4
$(4\text{-}C_5H_4N)(C_6H_5)C^{\bullet}OH$	toluene	559	7.4	4
$(4\text{-}BrC_6H_4)(CH_3)C^{\bullet}OH$	benzene	593	6.1	4
$(4\text{-}C_6H_5C_6H_4)(CH_3)C^{\bullet}OH$	benzene	587	5.6	4
anthrone ketyl	benzene	580	18	52
10,10-dimethylanthrone ketyl	toluene	560	33	53
10,10-dimethylanthrone ketyl-*O-d*	toluene-d_8	560	44	52, 53
10,10-dibenzylanthrone ketyl	toluene	564	7.9	52
10,10-dibenzylanthrone ketyl-*O-d*	toluene-d_8	564	9.7	52
dibenzosuberone ketyl	toluene	575	5.5	3
3,5-diphenyl-2-furanoxyl	1:2 benzene/di-*tert*-butyl peroxide	617	10.7	42, 54
	pyridine	624	6.6	42
3-(4-methylphenyl)-5-phenyl-2-furanoxyl	1:2 benzene/di-*tert*-butyl peroxide	627	12.5	42, 54
	pyridine	651	9.3	42
3-(4-methoxyphenyl)-5-phenyl-2-furanoxyl	1:2 benzene/di-*tert*-butyl peroxide	640	11.6	42, 54
	pyridine	660	10.7	42

[a] $\Phi_F = 0.11$ in benzene (ref 17); previous values of (1–10) × 10^{-6} in various solvents are unlikely to be correct (ref 55). [b] Data in other solvents available in original reference. [c] Data (fluorescence maxima only) for several other substituted diphenyl ketyl radical are also available in ref 6. [d] Tentative assignment.

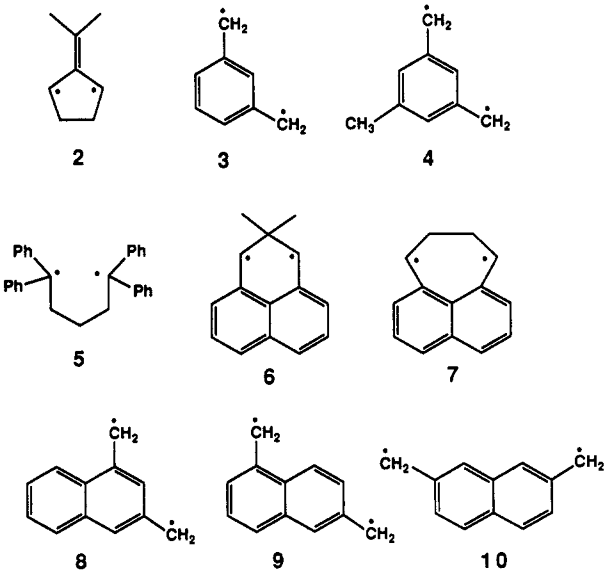
Table VI. Fluorescence Spectra and Lifetimes for Excited Triplet Biradicals (See Scheme 1 for Structures)

biradical	solvent	*T*, K	$\lambda_{0,0}$ (λ_{max}), nm	τ, ns	ref(s)
2[a]	hexane	rt	(430)	0.28 (0.9)[b]	64, 65
3[c]	ethanol glass	77	438 (438)		8
4	3-methylpentane glass	77	452 (452)		8
5	benzene	rt	520 (520)	2.5	66
6	EPA glass	77	498	560	67
7	EPA glass	77	512 (512)	190	68
8[d]	2-methyltetrahydrofuran	77	525 (525)		69
9[d]	ethanol glass	77	545 (545)		69
10[d]	2-methyltetrahydrofuran	77	562 (562)	*e*	69

[a] Singlet biradical. [b] Lifetime at 77 K in parentheses. [c] Similar spectra were observed at room temperature in isopentane. [d] Similar spectra were observed at room temperature in 2-methylbutane. [e] At 6 K a nonexponential decay with 50- and 150-ns components was observed.

approximately 2 orders of magnitude shorter than that for the corresponding excited diphenylmethyl radical.[66] The excited singlet biradical **2** has a lifetime of 280 ps, although in this case data for related radicals are not available.[64] Lifetimes in the range of several hundred nanoseconds have been observed for several other biradicals at 77 K.

Scheme I



IV. Transient Absorption

Absorption spectra for the first excited doublet states of radicals have been recorded in relatively few cases, in contrast to the large amount of fluorescence data available for these species. This reflects primarily the

Table VII. Absorption Spectra and Lifetimes for Excited Radicals in Solution at Room Temperature

radical	solvent	λ_{max}, nm	τ, ns	ref
4-cyanobenzyl	hexane	295	58	19
4-methoxybenzyl	hexane	340	112	21
4-phenylbenzyl	benzene	385	14	23
1-naphthylmethyl	cyclohexane	430	35[a]	26
cyano-1-naphthylmethyl	hexane	415	29	24
2-phenanthrylmethyl	toluene	400	75	23
diphenylmethyl	acetonitrile	355	280	13
	cyclohexane	355	260	31
(4-cyanophenyl)phenylmethyl	hexane	370	72	24
cyanodiphenylmethyl	hexane	358	110	24
10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl	cyclohexane	360	260	14
triphenylmethyl	cyclohexane	440		12
perchlorotriphenylmethyl	carbon tetrachloride	440	8	34
diphenylketyl	cyclohexane	350		47
bis(4-chlorophenyl)ketyl	cyclohexane	370		47

[a] Lifetime data in other solvents are available in the original reference.

increased difficulty of carrying out absorption measurements for short-lived species. The available data are summarized in Table VII. The observed spectra for a variety of arylmethyl radicals show λ_{max} values in the 300–400-nm region, with shifts to longer wavelength with increasing substitution. In the case of the 4-cyanobenzyl radical the 45-nm shift in the absorption spectrum has been attributed to a change in the nature of the lowest excited doublet from $1A_2$ to $2B_2$, as discussed above.[19] Monitoring the decays of either the transient absorption spectrum or the fluorescence gives results which are identical within experimental error for all radicals which have been examined using both techniques.

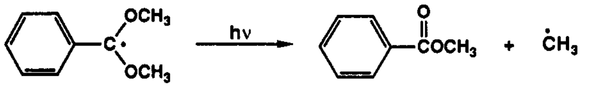
There are to date no reports of absorption spectra for the first excited state of biradicals.

V. Intramolecular Reactivity

A. Radicals

In some cases the short lifetimes of excited-state radicals result from rapid intramolecular chemical decay pathways. In general the involvement of chemical decay processes can be deduced from the observation of irreversible bleaching upon excitation of the radicals in a two-laser flash photolysis experiment. In cases where the observed photobleaching leads to absorptions due to transient or stable products, these transient absorption measurements can also provide important mechanistic information. However, it is essential to complement this data with product studies under both lamp and laser irradiation in order to provide a detailed understanding of the overall chemistry of the excited radical.

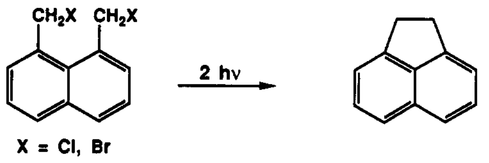
Most of the monoarylmethyl radicals for which fluorescence data are provided in Tables I and II do not undergo any irreversible chemistry from their first excited doublet states in nonreactive solvents. An exception to the general photostability of benzyl radicals is provided by α,α-dimethoxybenzyl. In this case a combination of ESR experiments and product studies at various light intensities has demonstrated that the excited radical undergoes efficient cleavage to yield methyl benzoate and methyl radicals (reaction 8).[70,71] The thermal chemistry of the radical also involves the same cleavage reaction, in addition to the usual radical coupling and hydrogen abstraction reactions.



(8)

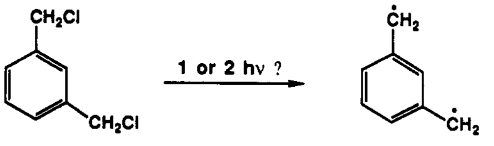
Although neither 1- or 2-naphthylmethyl radicals undergo any net chemistry from their first excited doublet states, excitation of 1-bromo-2-naphthylmethyl radical in benzene leads to irreversible bleaching. In benzene the photobleaching is accompanied by the formation of an additional transient at 540 nm which can be readily assigned to the previously characterized bromine atom/benzene complex.[23] Thus, transient absorption experiments provide convincing evidence for loss of bromine atom from the excited radical, although product studies were inconclusive as to the ultimate fate of the 1,3-biradical expected as a product of this reaction. Comparison of the lifetimes for the 2-naphthylmethyl and 1-bromo-2-naphthylmethyl radicals yields an estimate of 1.2×10^7 s^{-1} for the loss of bromine atom, assuming that bromine has no effect on the photophysics of the latter radical.

The loss of halogen atom to generate a biradical following excitation of an intermediate radical has also been raised as a possibility in two other examples. Firstly, acenaphthene has been observed as one of the products in the laser irradiation of both 1,8-bis(bromomethyl)naphthalene and 1,8-bis(chloromethyl)naphthalene (reaction 9).[72] The absence of acenaphthene in lamp-irradiated samples and its increased yield at high laser fluences led to the suggestion that it was formed via biphotonic generation of a biradical intermediate, presumably via an intermediate 8-(halomethyl)-1-naphthylmethyl radical. The photochemistry of the dibromo compound has recently been examined using laser-jet techniques.[73] The results of both direct and benzophenone-sensitized irradiations also indicate that acenaphthene is formed via excitation of the intermediate naphthylmethyl radical.



(9)

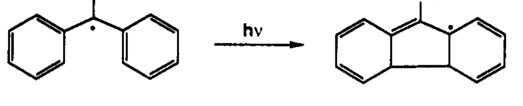
Secondly, the production of the *m*-xylylene biradical by 248-nm excitation of 3-(chloromethyl)benzyl chloride has recently been studied extensively in matrices and, to a lesser extent, in solution (reaction 10).[8,74] In this work an absorption assignable to an intermediate benzyl radical (either 3-methyl- or 3-(chloromethyl)benzyl) as well as emission from the biradical were both observed at room temperature. However, it was not possible to



(10)

establish whether the biradical was formed via a one-photon process involving simultaneous cleavage of two C–Cl bonds or via a sequential two-photon process involving either an initial 3-(chloromethyl)benzyl radical or an upper triplet state of the precursor dichloride.[8] It is obvious that even detailed transient and product studies are not always sufficient to establish conclusively the mechanisms for chemical transformations involving species with similar absorption and emission properties. Therefore, conclusions based solely on intensity-dependent product studies must certainly be regarded as preliminary.

The intramolecular photochemistry of the triphenylmethyl radical has been examined using time-resolved techniques by a number of groups. For example, Meisel and co-workers observed permanent bleaching of the radical and the concomitant formation of a product which absorbed at 490 nm, had a lifetime in excess of 100 μs, and was assigned to the cyclized phenylfluorenyl radical (reaction 11).[14] This observation is consistent with the results of much earlier steady-state photolyses of the same radical which had demonstrated 9-phenylfluorene-derived photoproducts.[75] A later study using three-pulse picosecond transient absorption studies demonstrated that excitation of the triphenylmethyl radical produced a short-lived first excited doublet state that was readily detectable by both absorption and fluorescence.[12] The excited state decayed within $\sim$10 ns to yield the same 490 transient that was assigned to the cyclized radical in the previous study. The formation of 9-phenylfluorene upon laser-jet irradiation of α,α,α-triphenylacetophenone as a triphenylmethyl radical precursor has also been reported.[10]

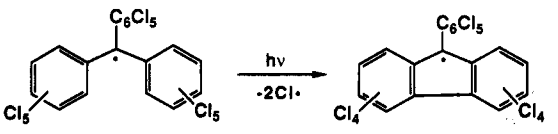


(11)

Recent results obtained by 248- or 308-nm excitation of triphenylmethyl radical in aqueous solution have demonstrated that photoionization to yield triphenylmethyl cation provides another decay route for the excited radical (reaction 12).[76] In this case the observation of radical depletion with the concomitant formation of both the trityl cation at 420 nm and the solvated electron at 650–700 nm provides unequivocal proof for the proposed mechanism. It is also interesting to note that the same cation can be generated from the triphenylmethyl radical precursor (triphenylmethane or triphenylacetate) with a single 248-nm laser pulse in what is presumed to be a three-photon process.[76]

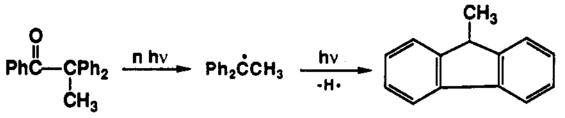
$$Ph_3C\cdot \xrightarrow{h\nu} Ph_3C^+ + e^-_{(solv)} \qquad (12)$$

The chemistry of the stable perchlortriphenylmethyl radical has also been examined by flash photolysis and product studies.[34] In this case, the stable perchloro-9-phenylfluorenyl radical is formed with a quantum yield of 0.3 (reaction 13) via the intermediacy of two transient intermediates. These were tentatively assigned to an intermediate with an internal charge transfer structure (Ar$_2$C$^+$Ar$^{\bullet -}$) and a ring-closed structure with disrupted aromaticity that ultimately loses two chlorine atoms to generate the final product. The related (p-benzoylphenyl)diphenylmethyl radical has also been shown to undergo reversible photobleaching with the formation of hydrogen abstraction products, in addition to minor amounts of other materials which include 4-(9-fluorenyl)benzophenone.[35]



(13)

Diphenylethyl and cyclopropylmethyl radicals have been reported to undergo efficient photobleaching in acetonitrile and to yield a transient at 480 nm similar to that obtained from triphenylmethyl radical.[14] On this basis it was suggested that the chemistry involved a similar cyclization to that shown in reaction 11. Laser-jet techniques have recently confirmed this hypothesis for the diphenylethyl radical produced by irradiation of α,α-diphenylpropiophenone.[10] The major product under these conditions was 9-methylfluorene, formed by cyclization of the 1,1-diphenylethyl radical (reaction 14). Interestingly, in this case the initial Norrish type I cleavage of the precursor ketone must also occur via a multiphoton process, since low-intensity irradiation gives primarily products of phenyl migration rather than α-cleavage.



(14)

The parent diphenylmethyl radical does not undergo irreversible photochemistry upon 337-nm excitation in various solvents,[31] in contrast to its efficient bleaching upon 347-nm excitation in ethanol or water.[14] These results may be readily understood on the basis of two-photon excitation of the diphenylmethyl radical at 347 nm where the excited radical (λ_{max} = 355 nm, Table VI) absorbs strongly but at which point the ground-state radical absorption ($\lambda_{max} \sim$ 335 nm) has decreased substantially. Cleavage of the C–H bond to generate a carbene was originally suggested as a possible mechanism for the biphotonic bleaching of the diphenylmethyl radical.[14] However, a different conclusion has been reported recently, based on the laser-jet irradiation of α,α-diphenylacetophenone in methanol and carbon tetrachloride.[77] In carbon tetrachloride the ketone undergoes two-photon chemistry to give diphenylmethyl chloride via trapping of an excited diphenylmethyl radical by solvent (see section VI). However, in methanol a three-photon reaction yields the methyl ether product derived from trapping of diphenylmethyl cation by solvent (reaction 15). The latter reaction is postulated to occur via sequential two-photon absorption of the diphenylmethyl radical (i.e., a three-photon process from the ketone precursor). The laser-jet results also demonstrate that, at least under these conditions, the two-photon chemistry of the diphenylmethyl radical does not involve carbene formation.[77]

$$Ph_2\dot{C}H \xrightarrow[-e^-]{2\,h\nu} Ph_2\overset{+}{C}H \xrightarrow[-H^+]{CH_3OH} Ph_2CHOCH_3 \qquad (15)$$

The laser-initiated photochemistry of diphenylmethyl radical precursors in poly(methyl methacrylate) films at energies above and below the ablation threshold has also been examined.[78] A model including absorption of a second photon by the excited diphenylmethyl radical with the subsequent formation of a relatively long-lived intermediate satisfactorily explains the variation in ground- and excited-state radical intensities under conditions of high intensity laser irradiation. Thus, it appears that biphotonic chemistry is a relatively common occurrence for this particular radical.

A related bridged diphenylmethyl radical (1) undergoes efficient photobleaching in polar solvents but is stable in cyclohexane. In acetonitrile the bleaching is accompanied by the formation of a transient absorbing at 410 nm, which has a lifetime of 2.5 μs. Consecutive two-photon absorption by the first excited doublet state is again proposed to account for the results.[14] The authors suggest a mechanism involving bond cleavage to generate a carbene plus hydrogen atom to account for the bleaching. In cyclohexane the carbene either recombines with the hydrogen atom or abstracts hydrogen to regenerate ground-state radical, whereas in alcohol it gives insertion products, thus accounting for the permanent bleaching. The authors suggest that the 410-nm transient in acetonitrile is due to formation of *o*-xylylene from the carbene. Product studies would be required to confirm the proposed mechanisms, particularly in light of the observation of photoionization pathways for similar excited radicals.

Although there is currently no definite proof for carbene formation via excited-radical chemistry in solution at room temperature, there is some precedent for this reaction from low-temperature matrix work. For example, photolysis of diphenylmethyl dichloride in a 2-methyltetrahydrofuran glass at 77 K produces the α-chlorodiphenylmethyl radical which can be further irradiated to generate diphenylcarbene (reaction 16).[79] Both the radical and carbene have been identified on the basis of their fluorescence spectra.

$$\mathrm{Ph_2CCl_2} \xrightarrow[\cdot\mathrm{Cl}\cdot]{h\nu} \mathrm{Ph_2\dot{C}Cl} \xrightarrow[77\ \mathrm{K}]{h\nu} \mathrm{Ph_2C}\!: \qquad (16)$$

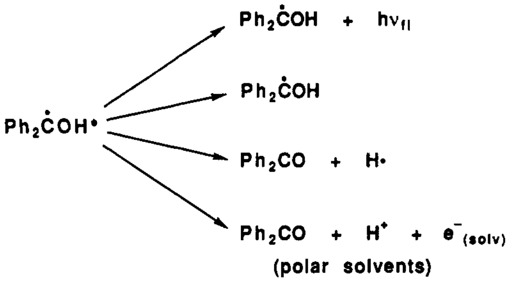
The photochemistry of several diarylketyl radicals has been examined in considerable detail. Efficient and irreversible bleaching of the parent diphenylketyl radical is observed upon excitation of either the UV or visible bands of this radical in both polar and nonpolar solvents.[41,47,80] In cyclohexane, two-laser transient techniques have been used to measure a quantum yield of 0.27 ± 0.06 (Table VIII) for photobleaching of the ketyl radical upon 515-nm dye-laser excitation.[41] Product studies have demonstrated that the bleaching leads to a decreased yield of ketyl radical derived products and an increased yield of benzophenone when the radical is generated either by hydrogen abstraction from benzhydrol by *tert*-butoxyl radical or by photoreduction of benzophenone. These results indicate that the photobleaching results from loss of hydrogen atom from the excited radical to yield benzophenone, Scheme II. In cyclohexane the hydrogen atom reacts with solvent to generate a cyclohexyl radical plus molecular hydrogen which has been detected directly by Raman spectroscopy. The observation of increased solvent-derived products as a result of the photobleaching in cyclohexane provides further confirmation for the O–H bond cleavage. The combination of fluorescence (0.11 in benzene)[17] and bleaching quantum yields[41] for this system indicates that, despite the efficient chemical decay pathways, approximately two-thirds of the radicals decay via nonreactive radiationless decay.[81] The substantial effects of deuterium substitution at the hydroxyl position are also consistent with chemical decay via O–H bond cleavage. An isotope effect of 2.7 has been measured for the quantum yields of O–H/O–D bleaching in toluene. This value, in combination with the isotope effects of the fluorescence decay of the two radicals, leads to estimates of $k_H/k_D = 5.8$ for chemical decay and $k_H/k_D = 1.9$ for the sum of radiative and nonradiative decay. This indicates that the O–H bond is also important in the nonradiative decay of the ketyl radical.

Table VIII. Quantum Yields for Photobleaching[a] of Diarylketyl Radicals

radical	solvent	Φ_{bl}	ref
$(C_6H_5)_2C^{\bullet}OH$	cyclohexane	0.27	41
$(C_6H_5)_2C^{\bullet}OH$	toluene	0.22	52
$(C_6H_5)_2C^{\bullet}OH$	acetonitrile	0.10	80
$(C_6H_5)_2C^{\bullet}OD$	cyclohexane	0.1[b]	41
$(4\text{-}CH_3C_6H_4)(C_6H_5)C^{\bullet}OH$	benzene	0.26	51
$(4\text{-}CH_3C_6H_4)_2C^{\bullet}OH$	benzene	0.26	51
$(4\text{-}CH_3OC_6H_4)(C_6H_5)C^{\bullet}OH$	benzene	0.28	51
$(4\text{-}CH_3OC_6H_4)_2C^{\bullet}OH$	benzene	0.16	51
$(4\text{-}ClC_6H_4)_2C^{\bullet}OH$	benzene	0.23	51
$(4\text{-}BrC_6H_4)_2C^{\bullet}OH$	benzene	0.08	51
$(4\text{-}CF_3C_6H_4)(C_6H_5)C^{\bullet}OH$	benzene	0.25	51
anthrone ketyl	toluene	0.20	52
10,10-dimethylanthrone ketyl	toluene	0.46	52
10,10-dibenzylanthrone ketyl	toluene	0.75	52

[a] See text for discussion of mechanisms for photobleaching. [b] Based on the assumption that the extinction coefficients for the deuterated and undeuterated ketyl radicals are the same.

Scheme II

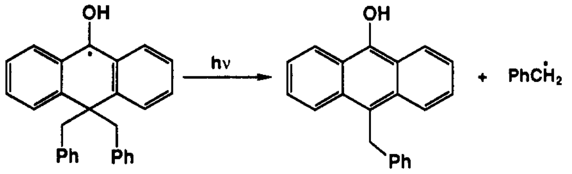


The photolysis (515 nm) of diphenylketyl radicals in acetonitrile also leads to photobleaching, although with a lower quantum yield (0.10, Table VIII).[80] In this case, two-laser flash photolysis experiments show that the bleaching is accompanied by the formation of benzophenone radical anion with λ_{max} at 710 nm. The results indicate that an additional decay pathway involving photoejection of an electron which is then captured by benzophenone to give the observed radical anion accounts for some of the decay of the ketyl radical in polar solvents (Scheme II). Further, the formation of radical anion accounts for only 20% of the observed bleaching, leading to the conclusion that O–H bond cleavage to give benzophenone remains the dominant route for chemical decay. The overall photobleaching yield is lower in acetonitrile than in cyclohexane despite the presence of an additional reaction pathway. Since previous results indicate that the O–H bond is also involved in nonradiative decay[41] it is likely that polar solvents modify the partitioning between reactive and nonreactive decay for this species.

A detailed investigation of substituent effects on fluorescence lifetimes and quantum yields and photobleaching quantum yields in nonpolar solvents has recently been reported for substituted diphenylketyl radicals.[51] Fluorescence quantum yields and lifetimes decrease by over 1 order of magnitude for substituents such as methoxy and bromo (Table V). In contrast the quantum yields for photobleaching (Table VIII) vary by at most a factor of 3, leading to the conclusion that the effects on the excited-state lifetime are largely determined by changes in the rates of nonradiative decay. Both the rates for chemical decay and nonradiative decay correlate with the energy gap between the lowest and first excited doublet states.

Restricting the conformational mobility of the ring system in ketyl radicals leads to substantial increases in the lifetime of the excited state. However, despite the relatively long excited-state lifetime of the 10,10-dimethylanthrone ketyl radical (33 ns, Table V), excitation at 515 nm in toluene leads to photobleaching with a quantum yield of 0.46 (Table VIII).[52] The photobleaching results in cleavage of the O–H bond, as demonstrated by the detection of hydrogen gas by Raman spectroscopy and by the deuterium isotope effect on the fluorescence lifetime. The parent anthrone ketyl radical is photobleached with a quantum yield of 0.20. The calculated photocleavage rate constants are similar for both the unsubstituted and the dimethylanthrone ketyls, indicating that the methyl substituents affect primarily the radiationless deactivation of the excited radical.

The related 10,10-dibenzylanthrone ketyl radical undergoes even more efficient photobleaching (Table VIII, $\Phi_{\rm bl} = 0.75$), but in this case chemical decay involves predominantly loss of a benzyl radical from the 10 position (reaction 17).[52] The fact that there is still a significant isotope effect on the fluorescence lifetime indicates that the O–H bond does have a significant effect on the excited-radical deactivation, although it has not been established whether it affects the nonradiative or chemical processes. Interestingly, a related radical (11) does not undergo significant photobleaching under similar conditions to those used for the anthrone ketyl radicals.[52]



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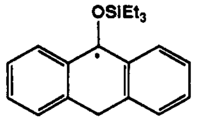

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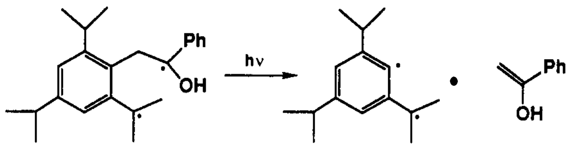
The photochemistry of 4-methoxybenzoyloxyl radical has also been briefly examined. Two-laser flash photolysis experiments show that the radical is photobleached upon 700-nm excitation into its lowest energy absorption band.[82] The observed bleaching presumably results from photodecarboxylation to generate the 4-methoxyphenyl radical, in agreement with earlier matrix results for benzoyloxyl radicals.[83]

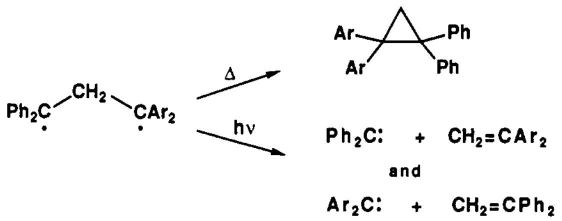
B. Biradicals

Despite the short lifetimes of most excited biradicals, a few biradical photorearrangements have been observed in fluid solution. Several of these involve cleavage reactions of biradicals. One of the earlier examples involves the photochemistry of the 1,4-biradical generated by intramolecular hydrogen abstraction in 2,4,6-triisopropylacetophenone.[84] Under laser irradiation the product distribution is substantially different from that at lower light intensity and indicates that excitation of the biradical results in β-cleavage to generate acetophenone enol plus a 1,3-biradical (reaction 18). The final products result from hydrogen abstraction by the 1,3-biradical to give a benzylic radical which gives the usual radical coupling products.



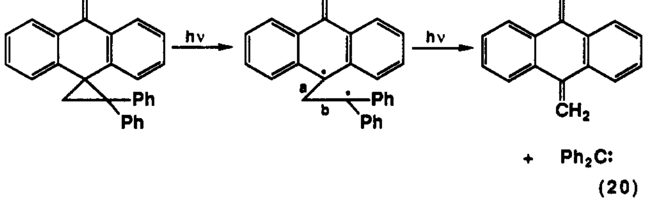
(18)

A similar cleavage has also been suggested for 1,1,3,3-tetraarylpropane-1,3-diyl biradicals generated by addition of diaryl carbenes to diaryl olefins.[11] In this case the products of laser-jet irradiation indicate that excitation of the biradical leads to a cleavage reaction that regenerates carbene plus olefin (reaction 19), in contrast to the usual thermal ring closure reaction for the ground-state biradical.



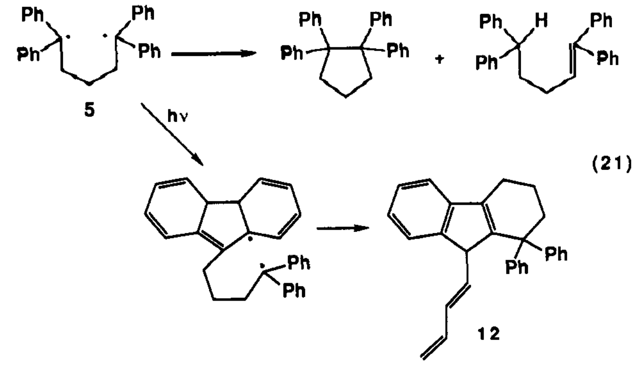
(19)

Recent laser-jet results for another 1,3-biradical derived from a cyclopropyl-substituted anthrone (reaction 20) suggest that cleavage of excited 1,3-biradicals may be a relatively general phenomenon.[10] In this case only cleavage of bond b (reaction 20) to generate diphenylcarbene plus 10-methylene anthrone is observed. The authors rationalize the selective cleavage on the basis of their expectations that the bond β to the excited chromophore will cleave preferentially and that for this system the anthrone chromophore will have the lower energy.



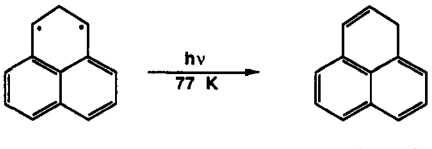
(20)

In contrast to the above results, the photochemistry of 1,5-biradical 5 has been shown to involve initial cyclization of one of the diphenylmethyl radical centers (reaction 21).[66] Two laser transient absorption experiments provide evidence for the irreversible depletion of the ground-state biradical and for the formation of a new transient at 480 nm which has been tentatively assigned to the cyclized biradical with one of the radical centers in a fluorenyl ring. This biradical ultimately rearranges to the final product (12) isolated in low yields from two-laser product studies. More recently, the identity of the final product has been confirmed by its isolation in 40% yield from the laser-jet irradiation of 1,1,6,6-tetraphenylcyclohexanone.[10] Thus, in this case the photochemistry of the biradical involves a cyclization reaction which is now well-documented for a number of alkyl- and aryl-substituted diphenylmethyl radicals.



(21)

Low-temperature rearrangements of several biradicals have also been reported. For example, a photoinduced 1,3-hydrogen shift has been observed upon irradiation of a naphthoquinodimethane biradical in a rigid glass at 77 K (reaction 22).[85] More recently, the related biradical (7) has been shown to photorearrange quantitatively to divinylnaphthalene at 77 K (reaction 23).[86] Although the thermal decay of 7 produces some divinylnaphthalene, the major decay route for the biradical at room temperature is cyclization to naphthocyclobutane. A final example of low-temperature biradical photochemistry is provided by the photorearrangement of singlet biradical 2 (reaction 24) which competes with the usual thermal decay of the biradical by dimerization.[87]



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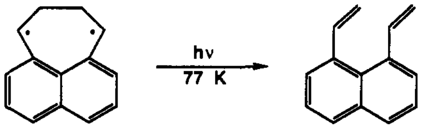

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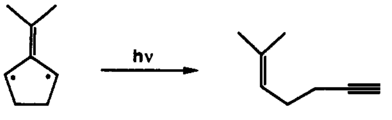

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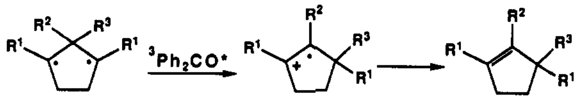
(24)

The sensitized photochemistry of 1,3-cyclopentanediyl biradicals has also been observed using laser-jet techniques.[73,88] In this case benzophenone-sensitized photolysis of an azoalkane precursor generates the biradical of interest. The biradical then reacts with a second triplet benzophenone to give a polar radical cation intermediate which leads to alkyl or hydrogen migration products (reaction 25). These products are similar to those observed upon 185-nm photolysis of the same biradical precursors and are in marked contrast to the usual dimers and bicyclic products formed in the thermal decay of these biradicals. This particular example provides a novel example of the use of sensitization techniques to study the photochemistry of reactive intermediates.



(25)

The intramolecular photochemistry of ylides has also been briefly examined. For example, the photobleaching of the carbonyl ylide formed by reaction of acetone with fluorenylidene leads to oxirane-derived products that are the same as those formed by the thermal decay of this species.[89] Carbonyl oxides formed from oxygen addition to diphenylcarbene are also efficiently photobleached.[90]

VI. Intermolecular Reactivity

The intermolecular reactivity of a variety of excited doublet states of free radicals has been examined in some detail. In general these experiments have been carried out for systems in which the excited radicals are relatively long-lived, as this facilitates measurement of quenching rate constants by directly monitoring the fluorescence lifetime of the radical as a function of the quencher concentration. As a result there is considerable data for benzyl, diphenylmethyl, and naphthylmethyl radicals which do not undergo any net chemistry from their first excited doublet states. Nevertheless, even for these radicals one is usually restricted to measurements of rate constants that are in excess of 10^6 M^{-1} s^{-1}. Although the fluorescence quenching experiments provide a convenient method for measuring rate constants, they yield little in the way of mechanistic information. However, in some cases the fluorescence measurements have been supplemented by product studies, investigations of substituent effects, or transient absorption measurements, all of which can potentially yield important mechanistic data.

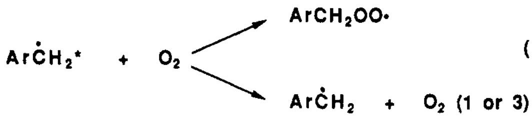
A considerable amount of data is now available for various intermolecular reactions of excited radicals. For example, there have been a number of studies of their reactivity toward species that typically react with ground-state radicals (e.g., oxygen, hydrogen donors, other radicals). A number of investigations have also indicated that excited free radicals show enhanced donor or acceptor character relative to the corresponding ground-state radicals, although in many cases detailed mechanisms have not been established. Specific examples are discussed below, with particular emphasis on those systems for which sufficient data is available to determine the chemical pathways responsible for the observed reactivity.

The reactivity of several substituted benzyl radicals toward oxygen has been examined in some detail (Table

Table IX. Intermolecular Reactivity of Excited Radicals with Oxygen

radical	solvent	k, $M^{-1}\,s^{-1}$	ref
4-fluorobenzyl	hexane	1.9×10^{10}	22
4-chlorobenzyl	hexane	1.8×10^{10}	22
4-(benzyloxy)benzyl	hexane	2.3×10^{10}	22
4-methoxybenzyl	hexane	2.2×10^{10}	22
4-cyanobenzyl	hexane	6.7×10^{9}	22
1-naphthylmethyl	cyclohexane	4.7×10^{9}	26
2-phenanthrylmethyl	benzene	5.7×10^{9}	23
diphenylmethyl	cyclohexane	8.7×10^{9}	31

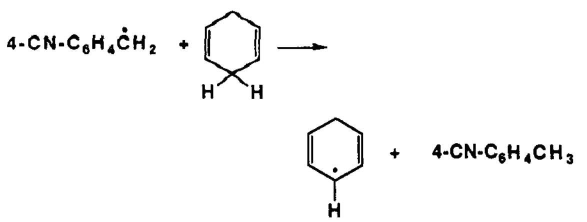
IX).[22] With the exception of 4-cyanobenzyl, the rate constants are in excess of 10^{10} M^{-1} s^{-1}, and are all approximately 1 order of magnitude higher than the quenching rate constants ($<3 \times 10^9$ M^{-1} s^{-1}) for the corresponding ground-state radicals. The results have been interpreted in terms of a diffusion-controlled physical quenching mechanism for the excited radicals, in contrast to irreversible addition of oxygen to ground-state benzyl to yield peroxy radicals (reaction 26). The anomalously low reactivity of excited 4-cyanobenzyl toward oxygen has been rationalized on the basis of a change in mechanism to reactive quenching via peroxy radical formation for this species. This conclusion is supported by the observation of a small depletion of the ground-state radical when it is excited in a two-laser transient experiment. It has been suggested that this change in mechanism for oxygen quenching is characteristic of the $2B_2$ lowest excited state for the 4-cyanobenzyl radical, in contrast to the physical quenching mechanism postulated for other substituted benzyl radicals with lowest $1A_2$ excited states.[22]



(26)

Excited-state diphenylmethyl and 1-naphthylmethyl radicals also react rapidly with oxygen with rate constants (Table IX) that are considerably in excess of those measured for the ground-state radicals.[26,31] For example, ground- and excited-state diphenylmethyl radicals react with oxygen with rate constants of 6.3×10^8 and 8.7×10^9 M^{-1} s^{-1}, respectively.[31] For both diphenylmethyl and 1-naphthylmethyl radicals the complete recovery of the ground-state radical absorption suggests a physical quenching mechanism, presumably with some formation of singlet oxygen (reaction 26).

Several studies of the reactivity of excited radicals toward dienes have been reported, and the data are summarized in Table X. In one example, a large substituent effect has been measured for the fluorescence quenching of excited benzyl radicals with 1,4-cyclohexadiene in hexane.[19] The rate constants varied from 3.2×10^9 for 4-cyano to 9.4×10^5 M^{-1} s^{-1} for 4-methoxy, with intermediate values for 4-chloro and 4-fluoro. For the 4-cyano radical transient absorption measurements showed the formation of 1,4-cyclohexadienyl radical, demonstrating that at least some of the fluorescence quenching leads to hydrogen atom abstraction (reaction 27) for this particular radical. As in the oxygen quenching results for excited benzyl radicals, the authors attribute the anomalous behavior of the 4-cyano radical to the change from a $1A_2$ to a $2B_2$ lowest excited state. The enhanced reactivity of the $2B_2$ state toward hydrogen abstraction is thought to reflect a higher unpaired electron density at the benzyl position.[19] It is further postulated that the intermediate behavior of 4-chloro- and 4-fluorobenzyl radicals may result from mixing of the two close-lying excited states, although the occurrence of hydrogen abstraction has not been demonstrated for either of these species.



(27)

Relatively slow rate constants have been measured for quenching of the excited states of 1-naphthylmethyl (5×10^6 M^{-1} s^{-1}) and diphenylmethyl (1.1×10^6 M^{-1} s^{-1}) radicals by 1,4-cyclohexadiene (Table X).[26,31] For the diphenylmethyl radical depletion of the ground-state radical again provides support for a mechanism involving hydrogen abstraction. In contrast to these results, α-cyano or 4-cyano substitution leads to an enhanced reactivity of excited-state diphenylmethyl and 1-naphthylmethyl radicals toward dienes.[24] For example, the rate constants for reaction with 1,3-cyclooctadiene and 2,5-dimethyl-2,4-hexadiene vary from 3×10^8 to 1×10^{10} M^{-1} s^{-1} in hexane (Table X). The observed correlation between the free energies predicted by the Rehm–Weller equation for single electron transfer and the quenching rate constants for 2,5-dimethyl-2,4-hexadiene (as well as other quenchers examined in the same study) suggests a mechanism involving electron transfer quenching. The reduction potentials of α-cyanoarylmethyl radicals are all very similar; thus, the variation in relative oxidizing ability (as measured by quenching rate constants) is determined solely by the available D_1–D_0 energy of the radical, resulting in higher quenching rate constants for the diphenylmethyl examples.[24] However, it should be noted that no evidence for separated ions has been observed, even in polar solvents.

It is interesting to note that quite different conclusions have been reached as to the reason for the unusually high reactivity of the excited states of cyano-substituted benzyl and diphenylmethyl radicals toward dienes.[19,24] It is obvious that detailed product studies are required to establish the importance of the various possible competing pathways in these reactions. There is some evidence for irreversible chemistry involving hydrogen abstraction in several cases; however, the results certainly do not suggest efficient hydrogen abstraction reactions as a general rule for excited state radicals.

Charge (or electron) transfer quenching (with the excited radical as the acceptor, reaction 28) has also been suggested in the reaction of excited doublet states with a variety of amines (Table XI).[24,31] For example, the rate constants for triethylamine quenching of excited diphenylmethyl radical increase approximately

$$Ar_2\dot{C}H^* + \text{donor} \longrightarrow Ar_2CH^- + \text{donor}^{+\bullet} \qquad (28)$$

Table X. Rate Constants for Reaction of Excited Radicals with Olefins and Dienes in Solution at Room Temperature

quencher	radical	solvent	k, M^{-1} s^{-1}	ref
1,4-cyclohexadiene	4-cyanobenzyl	hexane	3.2×10^9	19
	4-chlorobenzyl	hexane	2.0×10^8	19
	4-fluorobenzyl	hexane	6.3×10^6	19
	4-methoxybenzyl	hexane	9.4×10^5	19
	1-naphthylmethyl	neat	$\sim 5 \times 10^5$	26
	diphenylmethyl	cyclohexane	1.1×10^6	31
	10,10-dimethylanthrone ketyl	toluene	8.4×10^5	53
1,3-cyclooctadiene	1-naphthylmethyl	hexane	5×10^4	24
	cyano-1-naphthylmethyl	hexane	3.8×10^8	24
	diphenylmethyl	hexane	3.4×10^8	24
	(4-cyanophenyl)phenylmethyl	hexane	2.9×10^8	24
	cyanodiphenylmethyl	hexane	1.2×10^9	24
2,5-dimethyl-2,4-hexadiene	cyano-1-naphthylmethyl	hexane	1.6×10^{10}	24
	diphenylmethyl	hexane	3.2×10^8	24
	(4-cyanophenyl)phenylmethyl	hexane	1.4×10^{10}	24
	cyanodiphenylmethyl	hexane	1.6×10^{10}	24
methyl methacrylate	diphenylmethyl	cyclohexane	4.0×10^6	31
	diphenylketyl-*O*-*d*	toluene-d_8	3.9×10^9	40
	10,10-dimethylanthrone ketyl	toluene	3.9×10^8	53

Table XI. Rate Constants for Reaction of Excited Radicals with Amine and Aromatic Donors in Solution at Room Temperature

quencher	radical	solvent	k, M^{-1} s^{-1}	ref
triethylamine	1-naphthylmethyl	neat	$<2 \times 10^6$	2
	cyano-1-naphthylmethyl	hexane	1.4×10^9	24
	diphenylmethyl	methanol	2.1×10^8	31
	diphenylmethyl	hexane	4.2×10^8	24
	(4-cyanophenyl)phenylmethyl	hexane	1.5×10^{10}	24
	cyanodiphenylmethyl	hexane	2.3×10^{10}	24
	10,10-dimethylanthrone ketyl	toluene	1.4×10^9	53
n-butylamine	diphenylmethyl	hexane	1.3×10^7	24
	(4-cyanophenyl)phenylmethyl	hexane	6.7×10^7	24
	cyanodiphenylmethyl	hexane	9.7×10^9	24
1,3,3,5,7,7-hexamethyl-1,5-diazacyclooctane	diphenylmethyl	cyclohexane	4.5×10^9	31
	1-naphthylmethyl	cyclohexane	2.6×10^9	26
N,*N*-diethylaniline	perchlorotriphenylmethyl	carbon tetrachloride	1.55×10^{10}	34
triphenylamine	perchlorotriphenylmethyl	carbon tetrachloride	1.03×10^{10}	34
1-methylnaphthalene	diphenylmethyl	hexane	2.9×10^7	24
	(4-cyanophenyl)phenylmethyl	hexane	6.4×10^7	24
	cyanodiphenylmethyl	hexane	1.7×10^{10}	24
thianthrene	perchlorotriphenylmethyl	carbon tetrachloride	1.45×10^{10}	34

2-orders of magnitude upon 4-cyano or α-cyano substitution (Table XI).[24] An even larger rate enhancement is observed for α-cyano substitution of the 1-naphthylmethyl radical. Despite the observed correlation between the rates of amine quenching and the free-energy change for electron transfer, the ionic products of such an electron-transfer reaction have not been detected,[24] even for a cyclic diamine which has a readily visible radical cation.[26,31] These results indicate either that quenching involves charge-transfer interactions but does not lead to full electron transfer or that rapid back-electron transfer within the geminate pair prevents the observation of free ions in solution.

The reaction of 1-methylnaphthalene with several excited diphenylmethyl radicals is also faster for cyano-substituted radicals (Table XI).[24] Electron-transfer reactions are thought to be important here as well, since the failure to detect triplet naphthalene rules out the possibility of energy transfer in this system. However, there is currently only a single example where electron transfer to an excited radical has been conclusively demonstrated by direct transient detection of the product ions. Thus, the excited state of the stable (trichlorophenyl)methyl radical reacts with electron donors (triphenylamine and *N*,*N*-diethylaniline) at a diffusion-controlled rate.[34] Transient absorption measurements demonstrate that the fluorescence quenching is accompanied by formation of the donor radical cations.

The reactivity of several excited radicals toward potential donors such as halides has been examined. The data summarized in Table XII indicate that quite detailed studies have been carried out for diphenylmethyl radicals. The parent diphenylmethyl radical reacts with carbon tetrachloride with a rate constant of 1.6×10^8 M^{-1} s^{-1} in methanol, with the concomitant bleaching of the ground state.[31] A mechanism involving charge transfer quenching of the excited radical with the ultimate formation of diphenylmethyl chloride was originally suggested on the basis of the observation of an increased yield of this material in a two-laser product study. Later results showing a much slower rate of quenching for cyano-substituted diphenylmethyl radicals as compared to the parent were consistent with such a charge-transfer pathway.[24] However, the recent observation of diphenylmethyl cation as a product of the quenching of excited diphenylmethyl radicals by carbon tetrachloride in acetonitrile confirms that full electron transfer does occur in this system (reaction 29).[91] Cation yields approaching 100% under some

Table XII. Rate Constants for Reaction of Excited Radicals with Halides and Aromatic Acceptors in Solution at Room Temperature

quencher	radical	solvent	k, $M^{-1}\ s^{-1}$	ref
carbon tetrachloride[a]	diphenylmethyl	methanol	1.6×10^{8}	31
	diphenylmethyl	hexane	7×10^{6}	24
	diphenylmethyl	acetonitrile	3.3×10^{8}	91
	1-naphthylmethyl	methanol[b]	$\sim 4 \times 10^{6}$	26
	1-naphthylmethyl	hexane	4×10^{6}	24
	2-phenanthrylmethyl	benzene	1×10^{6}	23
carbon tetrabromide	diphenylmethyl	hexane	2.8×10^{10}	24
	(4-cyanophenyl)phenylmethyl	hexane	4.3×10^{9}	24
	cyanodiphenylmethyl	hexane	$<1 \times 10^{6}$	24
	diphenylketyl	acetonitrile	3.8×10^{10}	49
m-dicyanobenzene	diphenylmethyl	acetonitrile	4.3×10^{9}	91
p-dicyanobenzene	diphenylmethyl	acetonitrile	1.6×10^{10}	91
methyl benzoate	diphenylmethyl	acetonitrile	1×10^{6}	91
methyl *p*-chlorobenzoate	diphenylmethyl	acetonitrile	3×10^{6}	91
methyl *m*-chlorobenzoate	diphenylmethyl	acetonitrile	1.1×10^{8}	91
methyl *p*-bromobenzoate	diphenylmethyl	acetonitrile	1.3×10^{8}	91
methyl *m*-bromobenzoate	diphenylmethyl	acetonitrile	2.3×10^{8}	91
methyl *p*-cyanobenzoate	diphenylmethyl	acetonitrile	5.2×10^{9}	91
methyl *p*-(trifluoromethyl)benzoate	diphenylmethyl	acetonitrile	4.2×10^{9}	91
methyl *p*-nitrobenzoate	diphenylmethyl	acetonitrile	1.3×10^{10}	91
dimethyl terephthalate	diphenylmethyl	acetonitrile	2.0×10^{8}	91
benzyl chloride	diphenylmethyl	acetonitrile	1.3×10^{6}	91
benzyl bromide	diphenylmethyl	acetonitrile	3.6×10^{6}	91
p-bromobenzyl bromide	diphenylmethyl	acetonitrile	8.6×10^{7}	91
p-fluorobenzyl bromide	diphenylmethyl	acetonitrile	9.0×10^{6}	91
m-fluorobenzyl bromide	diphenylmethyl	acetonitrile	1.1×10^{8}	91
p-cyanobenzyl bromide	diphenylmethyl	acetonitrile	5.2×10^{9}	91
p-nitrobenzyl bromide	diphenylmethyl	acetonitrile	1.7×10^{10}	91
methyl viologen	diphenylmethyl	4:1 acetonitrile/water	1.3×10^{10}	31
	1-naphthylmethyl	methanol	3.8×10^{10}	26
	1-naphthylmethyl	cyclohexane	2.6×10^{9}	26

[a] Reactions of 2-naphthylmethyl, cyano-1-naphthylmethyl, cyanodiphenylmethyl, and 4-cyanodiphenylmethyl were all too slow to measure in neat carbon tetrachloride.[23,24] [b] Based on only two concentrations.

conditions demonstrate that back-electron transfer does not compete with fragmentation of $CCl_4^{\bullet -}$ in this case.

$$\begin{tikzcd} \mathrm{Ph_2\dot{C}H^{*}} + \mathrm{CCl_4} \arrow[r] & \left[\mathrm{Ph_2\overset{+}{C}H}\quad \mathrm{CCl_4^{-\cdot}}\right] \arrow[d] \\ & \left[\mathrm{Ph_2\overset{+}{C}H}\quad \mathrm{\dot{C}Cl_3}\quad \mathrm{Cl^{-}}\right] \end{tikzcd} \qquad (29)$$

Diphenylmethyl chloride has also recently been observed as a two-photon product in the laser-jet photolysis of diphenylmethyl radical precursors.[77]

The reactions of excited diphenylmethyl radical with a series of substituted methyl benzoates and benzyl bromides in acetonitrile has also been examined.[91] The rate constants are on the order of $10^6\ M^{-1}\ s^{-1}$ for the parent ester and bromide and increase to $\sim 10^{10}\ M^{-1}\ s^{-1}$ for strongly electron-withdrawing substituents (Table XII). Both transient absorption and time-resolved conductivity measurements demonstrate that substantial yields of diphenylmethyl cation are formed in these reactions. It is concluded that both back-electron transfer and cage escape are unusually rapid in this system, on the basis of estimates of the rates of fragmentation of the benzyl bromide radical anions. Further, back-electron transfer competes efficiently with fragmentation, in contrast to the results for carbon tetrachloride.

A final example in which electron-transfer reactions have been clearly documented is provided by the reactions of diphenylmethyl and 1-naphthylmethyl radicals with methyl viologen (MV^{2+}, reaction 30). These reactions occur with rate constants $>10^{10}\ M^{-1}\ s^{-1}$ in polar solvents and the characteristic absorption of the reduced form of the acceptor is readily detectable using laser flash photolysis.[26,31]

$$\mathrm{Ar\dot{C}H_2^{*}} + \mathrm{MV^{2+}} \longrightarrow \mathrm{ArCH_2^{+}} + \mathrm{MV^{+\cdot}} \qquad (30)$$

The reactions of a variety of excited radicals with miscellaneous substrates have been summarized in Table XIII. Although there is insufficient data for most of these substrates to see any real trends, two sets of experiments are noteworthy. Firstly, the intermolecular reactivity of excited diphenylketyl radicals with a variety of salts has been examined.[49] The rate constants are several orders of magnitude faster than those for the corresponding ground-state radical and have been suggested to involve electron transfer, leading to reduction of the salts.[49] A few other rate constants for reaction of diarylketyl radicals with both electron donors and acceptors have also been measured (Tables XI–XIII).

Secondly, Table XIII also lists data for the reaction of excited diphenylmethyl radical with stable free radicals.[92] The rate constants are all in the range of (2–8) × $10^9\ M^{-1}\ s^{-1}$ in polar and nonpolar solvents. Irreversible beaching of the ground-state diphenylmethyl radical is observed in methanol and acetic acid, but not in benzene or acetonitrile. This leads to the conclusion that radical–radical addition is not responsible for the observed reactivity toward stable free radicals, at least in the latter two solvents. The authors favor a mechanism involving electron transfer to the excited diphenylmethyl radical, followed by either rapid

Table XIII. Rate Constants for Reaction of Excited Radicals with Miscellaneous Quenchers in Solution at Room Temperature

quencher	radical	solvent	k, M^{-1} s^{-1}	ref
cyclohexane	diphenylketyl	neat	4×10^7	47
2-propanol	diphenylketyl	acetonitrile	5×10^8	47
	10,10-dimethylanthrone ketyl	toluene	9.3×10^8	53
tri-*n*-butylstannane	1-naphthylmethyl	neat	$\sim 4 \times 10^5$	26
	1-naphthylmethyl[a]	cyclohexane	$\sim 1 \times 10^7$	26
di-*tert*-butyl peroxide	diphenylketyl	benzene[b]	1.9×10^9	41
trifluoroacetic anhydride	diphenylmethyl	acetonitrile	1.4×10^8	91
di-*tert*-butylnitroxide	diphenylmethyl[c]	benzene	3.1×10^9	92
		acetonitrile	5.3×10^9	92
2,2,6,6-tetramethyl-piperidinyl-1-oxy	diphenylmethyl[c]	benzene	4.8×10^9	92
		acetonitrile	5.0×10^9	92
4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxy	diphenylmethyl[d]	benzene	3.2×10^9	92
		acetonitrile	4.8×10^9	92
galvinoxyl	diphenylmethyl	benzene	7.8×10^7	92
$4\text{-ClC}_6H_4N_2^+BF_4^-$	diphenylketyl	acetonitrile	2.1×10^{10}	49
$(C_6H_5)_2I^+BF_4^-$	diphenylketyl	acetonitrile	1.2×10^{10}	49
$(C_6H_5)_3S^+BF_4^-$	diphenylketyl	acetonitrile	1.5×10^{10}	49
$(CH_3)_2C_6H_5S^+BF_4^-$	diphenylketyl	acetonitrile	9.7×10^9	49
$(CH_3)_3S^+I^-$	diphenylketyl	acetonitrile	1.2×10^9	49
$(C_6H_5)_3C_6H_5CH_2P^+Cl^-$	diphenylketyl	acetonitrile	10^8	49

[a] Based on two concentrations. [b] Based on Stern–Volmer quenching of the radical fluorescence. [c] Similar values have also been measured in other solvents.[92]

reverse electron transfer (benzene and acetonitrile) or protonation of the diphenylmethyl anion leading to irreversible bleaching (methanol and acetic acid).[92]

VII. Conclusions

A variety of radicals and biradicals have excited state lifetimes in the tens to hundreds of nanoseconds range in fluid solution at room temperature. Detailed studies of the luminescence properties of arylmethyl radicals which do not undergo efficient intramolecular reactions have led to a reasonably detailed picture of the factors that affect excited-state lifetimes. Although substituted arylmethyl and diarylketyl radicals have been widely studied, there is very little data available on the excited-state behavior of heteroatom-centered species.

The intramolecular chemistry of excited radicals has been shown to involve a variety of processes, such as cleavage reactions (loss of halogen, hydrogen atom), photoionization in polar solvents, and cyclization. However, in spite of several fairly detailed studies, the factors that control the competition between various possible decay pathways are still unclear. Cleavage reactions and cyclizations similar to those observed for excited radicals are also common in biradical chemistry. In this regard it is important to note that most of these processes are usually not observed for the ground-state radical or biradical, although they have considerable precedent in ground-state chemistry for other intermediates.

In terms of intermolecular reactivity, excited doublet states show enhanced reactivity toward oxygen, although the reactions are mostly due to physical quenching rather than oxygen addition to generate peroxy radicals. There is some evidence for enhanced rates of reaction with potential hydrogen atom donors such as dienes, but it remains to be established whether or not hydrogen abstraction is a general reaction for excited radicals. However, excited radicals do show enhanced electron-donor and -acceptor properties when compared to the ground-state radicals. There are now several examples that demonstrate clearly that reactions with acceptors result in electron transfer from excited radicals to generate carbocation intermediates. Reduction of excited radicals is considerably less well-documented at this stage, although there is no doubt that some of these species are efficiently quenched by potential donors.

Developing a detailed understanding of the photochemistry and photophysics of reactive intermediates is obviously essential for understanding the complex multiphoton chemistry that often occurs during laser irradiation. This will continue to be an important area given the increased use of high-power lasers in a wide variety of fields. Although there has been substantial progress over the last decade, much remains to be done before it will be possible to predict what sort of behavior is to be anticipated for any particular excited intermediate.

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