

Photochemistry of reaction intermediates

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Abstract - The mechanisms and kinetics of the photochemistry of organic reaction intermediates have been examined using two-laser excitation techniques, and are illustrated using examples involving naphthalene chromophores. For example, excited 1-naphthylmethyl radicals are excellent electron donors, but not very good acceptors. They abstract halogens efficiently and interact with oxygen 5.5 times faster than their ground state. Other examples include the triplet states of 1,3-dinaphthylpropanone, 1,2-dinaphthylethane and acenaphthene.

INTRODUCTION

Our understanding of the chemical transformations that occur following UV-visible excitation of organic materials is almost exclusively derived from knowledge accumulated over several decades in studies using conventional lamps or solar radiation. The applications of high power lasers in a wide range of fields have grown dramatically during the last decade; in many cases the chemical consequences of laser irradiation can be quite different from those that could be anticipated on the basis of knowledge acquired using conventional light sources. While the causes of these differences are not unexpected, detailed chemical studies have not been frequent.

One of the mechanisms which can cause "laser chemistry" to be different from "lamp chemistry" is the photolysis of short lived reaction intermediates. Two closely related factors make these processes — which are quite rare with conventional light sources — relatively common in the case of high power lasers: first, the concentration of transients is usually much higher in the case of laser initiated processes, as compared with lamp excitation. This allows transients to compete with ground state precursors for light absorption. Second, the high photon flux favors light absorption by these short lived intermediates.

While two-photon processes resulting from transient photochemistry can be easily triggered in single pulse experiments, their study under these conditions is difficult as a result of many problems related to the control of the experimental conditions. We have modified our laser flash photolysis system, so as to make it ideally suited for two-laser experiments (ref. 1). In this approach the transient precursor is photolyzed with a "synthesis laser" pulse, leading to the transient of interest in primary or secondary photoprocesses. A second pulse ("photolysis laser") of a carefully selected wavelength and after a suitable delay is then used to irradiate the intermediate of interest. Depending on the lasers used in each experiment, pulse durations are in the 0.6-250 ns range.

Recent studies from our laboratory have included diarylmethyl radicals (ref. 1), naphthylmethyl radicals (ref. 2), benzophenone ketyls (ref. 3), biradicals (ref. 4), ylides (ref. 5) and carbenes (ref. 6). The overall scope of these studies is beyond the coverage of the present article. The problem of the photochemistry of reaction intermediates is presented here using selected examples involving naphthalene moieties; each of these systems has been, or will be, the subject of a full report. Specific examples include 1- and 2-naphthylmethyl radicals and the transient phenomena that occur on photoexcitation of the triplet states of 1,3-di(1-naphthyl)-2-propanone, 1,2-di(1-naphthyl)ethane and acenaphthene.

DETECTION OF EXCITED RADICALS

Our first example will also be used to describe the type of experiments performed in this work.

Several sources of 1-naphthylmethyl radicals are readily available (ref. 2). Among these, the photodecomposition of 1-halomethylnaphthalenes is quite convenient at the laser wavelengths available in our laboratory.

Figure 1 illustrates the generation process; the spectrum at the bottom-left corresponds to a solution of 1-chloromethylnaphthalene in cyclohexane. Laser excitation at 308 nm leads to the detection of a mixture of 1-naphthylmethyl radicals ($\lambda_{\max} = 365$ nm) and triplet 1-chloromethylnaphthalene ($\lambda_{\max} = 420$ nm); the latter decays more rapidly than the radical and after ca. 2.5 μ s (Fig. 1, top-left) the transient spectrum is that characteristic of the 1-naphthylmethyl radical. If the unwanted species does not decay sufficiently fast, it is always possible to selectively induce its decay (e.g. by adding a triplet quencher). The insert at the top-right in Fig. 1 shows a comparison of the decay traces monitored at 365 and 420 nm.

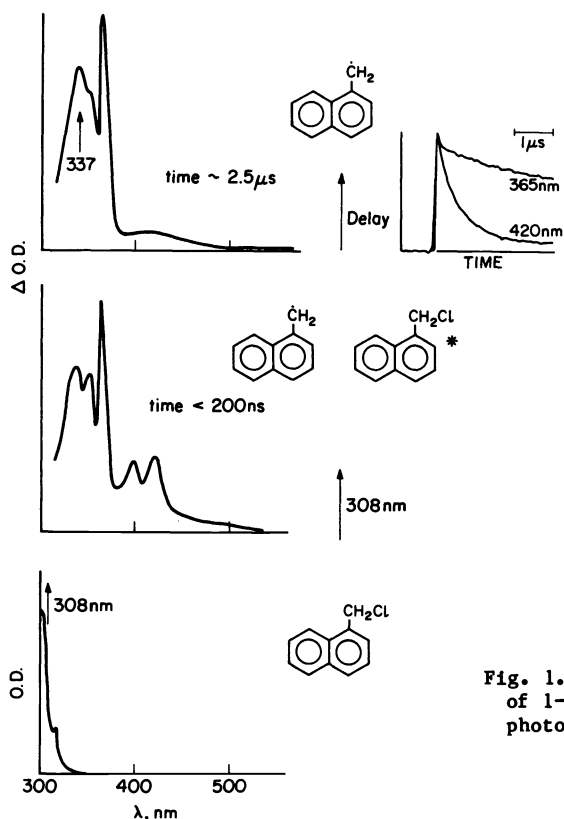


Fig. 1. Diagram illustrating the generation of 1-naphthylmethyl radicals by 308 nm photolysis of 1-chloromethylnaphthalene.

Thus, several microseconds after 308 nm excitation we are ready to carry out a laser flash experiment on the 1-naphthylmethyl radicals. By use of a nitrogen laser at 337 nm it is possible to excite the radical under conditions where the precursor (1-chloromethylnaphthalene) is transparent. Selective excitation of the radical under these conditions leads to transient absorptions (Fig. 2, top-left) that can be characterized as those due to excited 1-naphthylmethyl radicals. The decay lifetime of these signals is ~ 35 ns (see Table 1) at room temperature and matches well the value that can be obtained monitoring the doublet-doublet emission (Fig. 2, right) from the radical (ref. 2). The energy levels in Fig. 2 provide a rough idea of the energies of the various states involved. Table 1 compares the lifetime of excited 1-naphthylmethyl radicals with those of various other radicals examined in our laboratory. Fluorescence spectra for representative naphthalene-related radicals, recorded using an optical multichannel analyzer (OMA) with a 20 ns gate are illustrated in Fig. 3.

TABLE 1. Lifetimes of excited radicals in solution at room temperature

Radical	Solvent	τ^* , ns	Reference
1-Naphthylmethyl	cyclohexane	35.0	2
2-Naphthylmethyl	cyclohexane	27.4	a
1-Bromo-2-naphthylmethyl	cyclohexane	24.5	a
Diphenylmethyl	cyclohexane	255	1
Duryl	toluene	5.0	a
Diphenylketyl	toluene	3.9	3
Diphenylketyl- $0-d$	toluene- d_8	8.7	3

^aUnpublished work.

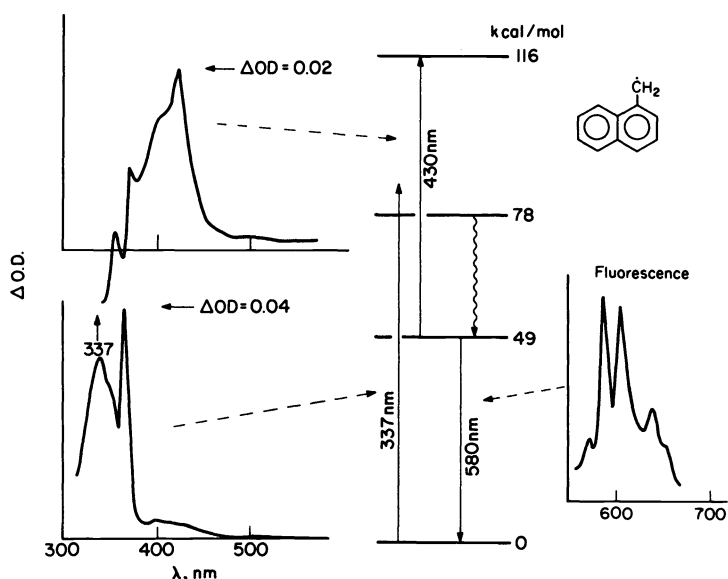


Fig. 2 Generation of excited radicals by excitation of 1-naphthylmethyl radicals at 337 nm, and approximate energy levels involved.

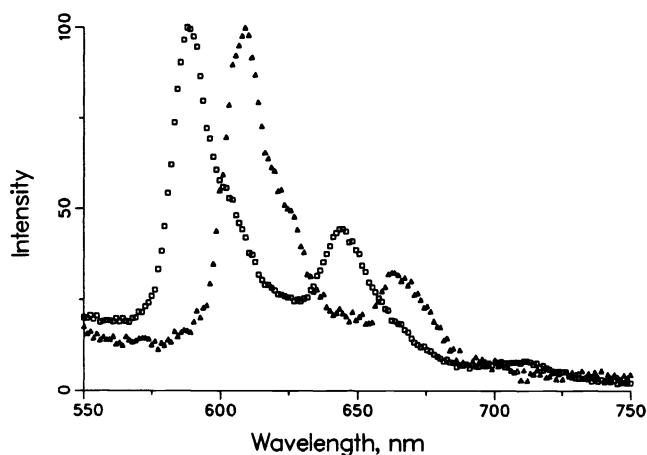


Fig. 3. Fluorescence spectra of 2-naphthylmethyl (□) and 1-bromo-2-naphthylmethyl (Δ) radicals at 20°C.

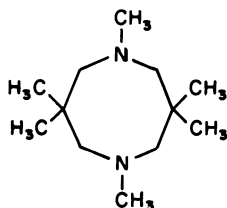
Interestingly the absorption spectrum of the excited radical (Fig. 2) shows some resemblance to those of typical naphthalene triplets. This raises the question as to whether the excited radical should be regarded as a typical excited naphthalene which contains a rather unconventional substituent; i.e. carrying a radical center.

Reactivity of excited radicals

The detection of excited radicals opens the door to studies of their reactions, from both a mechanistic and a kinetic point of view. The basic question is to what extent the additional energy available will make the radical more reactive than its ground state. From a strictly enthalpic viewpoint, typical free radical reactions would be expected to be fast, since reactions such as hydrogen abstraction will be substantially more exothermic than those of highly reactive species such as phenyl or methyl radicals.

Excited 1-naphthylmethyl radicals are excellent electron donors, reacting with the electron acceptor methyl viologen (MV^{+2}) to yield its reduced form (MV^+) with rate constants in excess of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Quenching by electron donors is not nearly as efficient. For example, reaction with diamine **I** occurs with $k_q = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in cyclohexane, but does not lead to full electron transfer; i.e. the readily detectable radical-cation from **I** was not observed. Even more surprisingly, the excited states of 1- or 2-naphthylmethyl radicals were not quenched by

triethylamine, to the extent that even using the amine as solvent did not lead to any detectable change in their lifetimes or fluorescence spectra.



II

The reaction of free radicals with oxygen to yield peroxy radicals is one of their more common reactions. Fig. 4 shows plots of experimental rate constants for radical decay as a function of oxygen concentration for the ground and excited state 1-naphthylmethyl radicals, showing that the latter interacts with oxygen 5.5 times faster than the ground state radical. Surprisingly, quenching of the excited state does not lead to peroxy radicals, but rather to the recovery of ground state radical. It is possible that quenching generates singlet oxygen; further experiments will be needed to establish if this is the case.

Hydrogen abstraction is a relatively slow process, the rate constant being only $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for reaction of excited 1-naphthylmethyl with Bu_3SnH compared to $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for ground state phenyl radicals (ref. 7).

Excited benzylic radicals have been generally found to be excellent halogen abstractors. For example, excited 1-naphthylmethyl reacts with carbon tetrachloride with $k = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, a value comparable with that for phenyl radicals ($7.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (ref. 8). The reactions of excited radicals with carbon tetrachloride and other halogen donors are likely to involve charge transfer interactions.

THE 'RELUCTANT' NORRISH TYPE I REACTION OF 1,3-DI(1-NAPHTHYL)-2-PROPANONE (II)

Bichromophoric substrate II provides an interesting example. Laser excitation at 308 nm or lamp excitation at $\lambda > 300 \text{ nm}$ leads to inefficient but readily detectable Norrish Type I cleavage. The reasons for this inefficiency [II has actually been reported to be photostable (ref. 9)] are related to the fact that the Norrish Type I reaction is predominantly a triplet process (ref. 10); however, for this substrate, the lowest lying triplet state is located in the naphthalene moiety, rather than the carbonyl group. Laser photolysis of II leads to the detection of a typical, though relatively broad naphthalene-like triplet state, Fig. 5. Typical lifetimes for this triplet are in excess of 10 μs and under conditions of pulsed laser excitation incorporate some second order decay arising from T-T annihilation. Excitation of this triplet state at wavelengths in the 430-460 nm range using the pulses from a flash pumped dye laser ($\sim 250 \text{ ns}$ wide, typically 40-200 mJ/pulse) leads to bleaching of the triplet state, Fig. 6 (left). However, when the analyzing wavelength is changed to 370 nm where the triplet has only weak absorptions, but the 1-naphthylmethyl radical has a strong maximum, the trace reveals the formation of an absorption (Fig. 6, right) that spectroscopic studies (Fig. 5) reveal as due to 1-naphthylmethyl radicals. No luminescence was detected in the 550-700 nm region; the result is consistent with the idea that two-photon cleavage of II leads to ground state radicals.

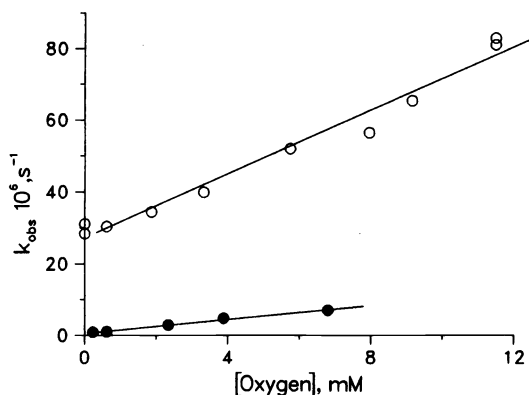


Fig. 4. Quenching of the transient absorption of ground state (●) and excited state (○) 1-naphthylmethyl radicals by oxygen in cyclohexane at 300 K.

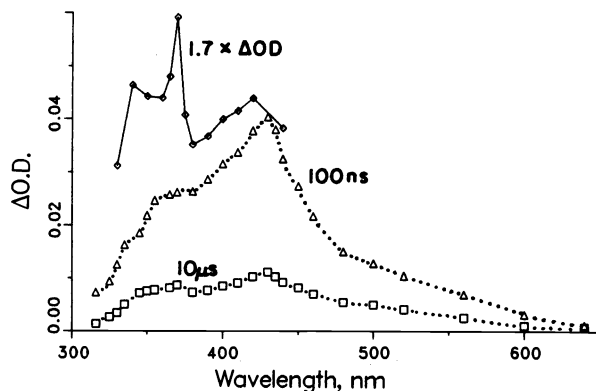


Fig. 5 Transient spectrum obtained by 308 nm excitation of II and (top) band from 1-naphthylmethyl radicals produced upon dye laser excitation.

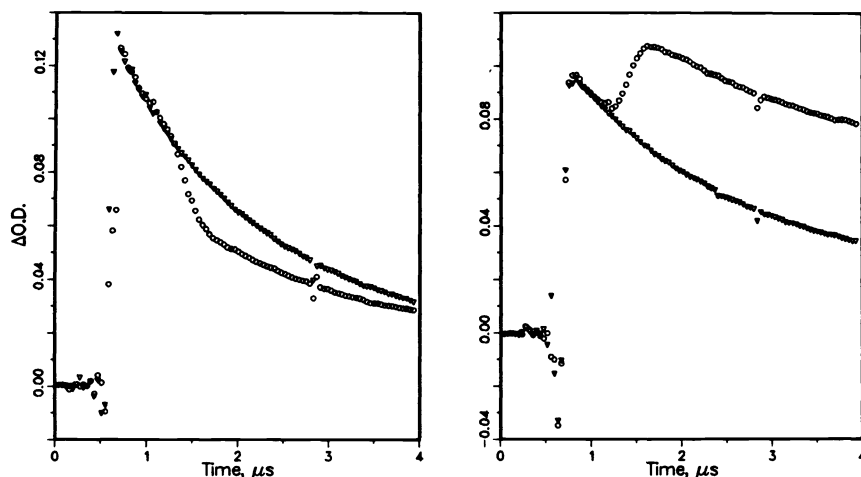


Fig. 6. One and two laser excitation of **II**, monitored at 410 nm (left) and 370 nm (right).

Preliminary product studies show a considerable increase in the yield of 1,2-dinaphthylethane (**III**) under conditions of two-photon irradiation, confirming the cleavage of the triplet following dye laser excitation. We use the term "reluctant" Norrish Type I reaction to describe these systems, where the reaction is very inefficient under conditions of one-photon excitation, but where the efficiency can be significantly enhanced when the triplet state absorbs a second photon. Various examples of this type are now being examined in our laboratory.

TWO-PHOTON CLEAVAGE OF 1,2-DI(1-NAPHTHYL)ETHANE (**III**)

This example is closely related to that discussed above, although it does not involve a carbonyl chromophore. Excitation of **III** at 308 nm leads to its triplet state; the corresponding spectrum is very similar to the monochromophoric model, 1-methylnaphthalene. The triplet spectrum of **III** is shown in Fig. 7. Dye laser excitation of triplet **III** leads to bleaching at the wavelengths where triplet absorption is intense. The changes observed are qualitatively similar to, but smaller in magnitude than, those observed in the case of **II**. At this point it is not clear if the reduction in signal is due to decreased quantum efficiency or to a lower spectral overlap between the dye laser pulse and the triplet state of **III**. In any event, it is clear that the upper excited states of naphthalenes can funnel their energy to the β -bond to lead to molecular cleavage, a process that will also be favored by the entropic gains associated with fragmentation.

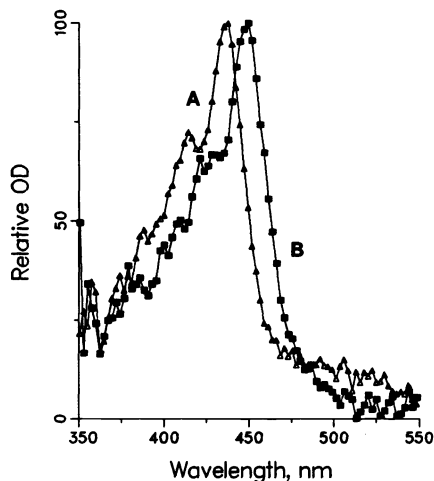


Fig. 7. Triplet spectra for **III** (A) and for acenaphthene (B) in benzene.

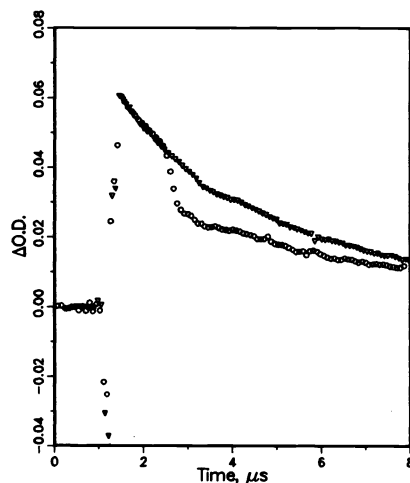
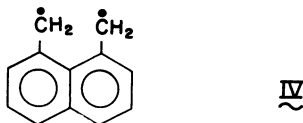


Fig. 8. Comparison of one and two laser signals in the photochemistry of acenaphthene.

PHOTBLEACHING OF TRIPLET ACENAPHTHENE

The triplet state of acenaphthene (Fig. 7) shows typical T-T absorption characteristics ($\lambda_{\text{max}} = 440 \text{ nm}$) for a substituted naphthalene. The absorption spectrum is sharper than those observed for **II** and is red shifted (with respect to naphthalene and **III**). Under our experimental conditions the decay of the absorptions follows a mixture of first and second order kinetics, the latter reflecting T-T annihilation. When we monitor at $\sim 330 \text{ nm}$ we observe long lived luminescence; a spectroscopic study of the characteristics of this luminescence using an OMA as detector shows that this long lived emission occurs in the same region as the fluorescence from acenaphthene, suggesting that it should be assigned to delayed fluorescence resulting from T-T annihilation. The delayed fluorescence did not show the vibrational resolution which was clear in the case of the prompt fluorescence. It remains to be established if this difference is instrumental in origin (very different experimental conditions are used in both measurements) or if it reflects an intrinsic property of the system. The traces in Fig. 8 show a comparison of one and two-laser experiments. The bleaching of Fig. 8 was accompanied by a sudden reduction of the delayed luminescence at 330 nm, as would be expected from a reduction of the triplet concentration.

At this point our two-laser experiments on this system should be regarded as very preliminary in nature. Dye laser irradiations were carried out at 460 nm using broadband pulses. In spite of the fact that the spectral overlap between the laser and the triplet was not ideal (Fig. 8) the bleaching observed was remarkably efficient. A cleavage similar to that suggested for **II** would account for this bleaching and would lead to biradical **IV**, which has so far escaped detection. Unfortunately, if one assumes that its spectral characteristics would be similar to those of other 1,8-naphthoquinodimethanes (ref. 11) one would expect absorptions around 330 nm, a region where measurements are quite difficult as a result of the delayed luminescence mentioned before. Additional experiments are currently underway.



CONCLUSION

The photochemistry of organic reaction intermediates offers a wide variety of new chemical and mechanistic possibilities. While all the two-photon experiments described herein have been carried out using two-laser excitation, it should be emphasized that quite frequently this is not a requirement, but should be viewed as a technique which facilitates the study of biphotonic processes. There are numerous systems where single pulse excitation will initiate two-photon processes (wanted or unwanted), but their characterization under these poorly controlled conditions would be extremely difficult.

In spite of the uncertainties which still remain in some of these mechanisms, it is quite clear that naphthalenes have a rather rich two-photon photochemistry, which in some cases parallels the one-photon processes, although with increased efficiency, while in other cases it presents new reaction paths, distinct from those that can be initiated in one-photon processes. Excited free radicals show mostly typical excited state behavior, rather than dramatically enhanced free radical character, while naphthalene triplets capable of producing resonance stabilized radicals seem to generally do so upon excitation into the higher levels of the triplet manifold.

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