rinsed with ethanol, and blown dry with a stream of argon, and the ellipsometric constants were measured. The thickness of the adsorbed organic layer was calculated by using the optical constants for clean gold. Corrected thicknesses were calculated by subtracting from the ellipsometric thickness the mean of several readings obtained at long times, when desorption was essentially complete. The rate constants were determined from the logarithmic plot by least-mean-square fits to data with corrected thicknesses greater than 3 Å: the error in data representing smaller thicknesses becomes very large.

Acknowledgment. XPS spectra were obtained by using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Materials Research Laboratory. NMR spectra were obtained in the Bruker NMR Facility at Harvard. We are very grateful to Dr. D. Allara, Dr. L. Strong, Dr. M. Chaudhury, and Dr. S. Wasserman for valuable discussions and to Dr. N. Rao (E. I. Du Pont de Nemours) for the gift of fluorinated thiols.

Registry No. Au, 7440-57-5; $HS(CH_2)_2(CF_2)_5CF_3$, 34451-26-8; $HS(CH_2)_{21}CH_3$, 7773-83-3; $HS(CH_2)_{17}CH{=}CH_2$, 117559-59-8; $HS(CH_2)_{11}OSi(CH_3)_2(C(CH_3)_3)$, 117559-60-1; $HS(CH_2)_{11}Br$, 116129-34-1; $HS(CH_2)_{11}Cl$, 117559-61-2; $HS(CH_2)_{11}OCH_3$, 117559-62-3; $HS(CH_2)_{12}SCOCH_3$, 117581-30-3; $HS(CH_2)_{10}CO_2CH_3$, 73391-27-2; $HS(CH_2)_8CN$, 117559-63-4; $HS(CH_2)_{11}OH$, 73768-94-2; $HS(CH_2)_{15}CO_2H$, 69839-68-5; $HS(CH_2)_{17}CH_3$, 2885-00-9; 6-bromohexanoic acid, 4224-70-8; 16-hydroxyhexadecanoic acid, 506-13-8; 1-bromoundecane, 693-67-4; 11-bromo-1-undecene, 7766-50-9; 1-heptadecanol, 1454-85-9; 1,8-dibromooctane, 4549-32-0; *tert*-butyldimethylsilyl chloride, 18162-48-6; diisopropyl azodicarboxylate, 2446-83-5; 11-bromo-1-undecanol, 1611-56-9; 11-bromoundecanoic acid, 2834-05-1; 1,12-dibromododecane, 3344-70-5; 1-bromoeicosane, 4276-49-7; 1-bromodocosane, 6938-66-5; hexadecane, 544-76-3.

Supplementary Material Available: Details of the preparation of organic thiols (15 pages). Ordering information is given on any current masthead page.

Photochemistry and Photophysics from Upper Triplet Levels of 9,10-Dibromoanthracene[1]

W. Grant McGimpsey and J. C. Scaiano*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received May 4, 1988*

Abstract: The photochemistry of 9,10-dibromoanthracene (DBA) has been examined by using two-laser two-color techniques in benzene and in cyclohexane. Dye-laser (467 nm) excitation of the triplet in benzene leads to triplet bleaching with a quantum yield of 0.041. Upper triplets decay by a combination of processes including reverse intersystem crossing (Φ_{TS} = 0.09) resulting in dye laser induced fluorescence from S_1. In addition, approximately 4% of the triplets reexcited undergo debromination. The lifetimes of DBA upper triplets are estimated as 200 ps for T_2 and ~20 ps for T_n ($n > 2$). The quantum yield for reverse intersystem crossing is larger in cyclohexane (0.17) than in benzene (0.09); it is suggested that the difference may reflect upper triplet (T_n; $n > 2$) quenching by the solvent in the case of benzene.

Recent studies carried out in this laboratory, as well as other laboratories, have shown that for a variety of chemical systems, laser and conventional (e.g., UV lamp) irradiation can lead to different chemical consequences even when the wavelength and total energy absorbed are the same for both light sources. For the most part these studies have involved either a comparison of products obtained with the different light sources or a study of the transient phenomena associated with laser excitation.[2-23]

The origin of the observed differences lies in the occurrence of multiphoton (frequently two-photon) processes which can take place under the high photon flux supplied by pulsed lasers. That is, transients produced by the laser pulses may attain sufficiently high local concentrations during the laser pulse to compete with the ground-state precursor molecules for incident laser photons. These high transient concentrations are not obtained during lamp irradiation.

We have investigated several chemical systems which exhibit two-photon behavior that is very different from the corresponding one-photon behavior. In particular, we have identified a variety of systems which are essentially photostable under one-photon

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lamp irradiation, but which readily undergo two-photon reactions; e.g., Norrish type I cleavage.[21,22] This two-photon behavior can be understood in terms of the energy requirements for bond cleavage. For example, the energy of the lowest triplet state of benzil is ~54 kcal/mol, while the C(O)–C(O) bond strength is ~66 kcal/mol. Thus, one-photon cleavage from the lowest triplet state is endothermic by ~12 kcal/mol. However, reexcitation of the benzil triplet state by absorption of a second photon results in the production of an upper triplet state which possesses more than sufficient energy to facilitate cleavage.[21]

Bond cleavage is not always the necessary outcome of triplet state reexcitation. For example, reexcitation of the benzophenone triplet state in benzene leads to the repopulation of ground-state benzophenone without the generation of any new products. Recent work from our group suggests that the deactivation process responsible for these observations involves electronic energy transfer to the solvent.[23]

In this paper we report a detailed, quantitative study of another type of upper triplet state photochemistry, i.e. reverse intersystem crossing in 9,10-dibromoanthracene. Fluorescence following $T_2 \rightarrow S_1$ intersystem crossing is a well-established process in this system and is frequently the basis of techniques used to study triplet-state properties. For example, the temperature dependence of 9,10-dibromoanthracene fluorescence produced as a result of $T_2 \rightarrow S_1$ intersystem crossing following sensitization by a series of triplet ketones has been used to establish a value of 74.6 kcal/mol for the T_2 state.[24a] In addition, several groups have investigated the efficiency of the $T_2 \rightarrow S_1$ process.[24b-27] To date, however, no study has given a detailed account of $T_2 \rightarrow S_1$ efficiency measurements (Φ_{TS}), nor have triplet bleaching quantum yields (Φ_{BL}) been correlated with Φ_{TS} determinations.

Experimental Section

9,10-Dibromoanthracene (DBA) (Aldrich) was purified by recrystallization from benzene. Benzophenone (Aldrich) was doubly recrystallized from ethanol. Aberchrome-540 (Aberchromics, Ltd., Cardiff) was used as received. The solvents cyclohexane and benzene (Aldrich, Gold Label) and toluene (BDH, Omnisolv) were used as received.

Transient extinction coefficients were estimated by comparison with benzophenone by using energy transfer techniques. The extinction coefficient for triplet benzophenone was, in turn, determined under our exact experimental conditions by using the Aberchrome-540 method which we have recently reported.[28] In the case of DBA, our values deserve some comment. For the purposes of our study, it is not important to determine precise maximum extinction coefficients, but rather, to be able to measure triplet concentrations accurately. Thus, our measurements were not necessarily carried out at the exact position for the maximum, but rather at a convenient wavelength near the maximum which is selected in order to minimize scattered light from the dye laser during two-laser experiments. Further, the monochromator slit used in our experiments (usually 1 mm) may be somewhat wide for the narrow-band features of the DBA triplet spectrum, although it facilitates other aspects of our measurements. As already pointed out, this does provide an accurate calibration for the determination of triplet concentrations. The values of ζ (to distinguish them from true extinction coefficients, ϵ) obtained are 25 000 (430 nm, benzene), 19 100 (430 nm, cyclohexane), and 4200 M^{-1} cm^{-1} (445 nm, cyclohexane). These values are lower limits for the true extinction coefficients. Quantum yields for triplet bleaching were also determined by using the Aberchrome-540 method.

While our laser system and our method of performing two-laser experiments has been described in some detail elsewhere,[5,29] the measurements carried out in this work are such that they warrant a brief description of the experimental arrangement. All experiments were carried out in deaerated solutions and employed a flow system which ensured that a fresh (unirradiated) volume of solution would be irradiated by each laser pulse. Further, the flow system allowed us to obtain DBA measurements and the Aberchrome-540 measurements in the same reaction cell. (The cell was identically positioned in both cases, thus ensuring that the volume of sample irradiated by both lasers was identical.)

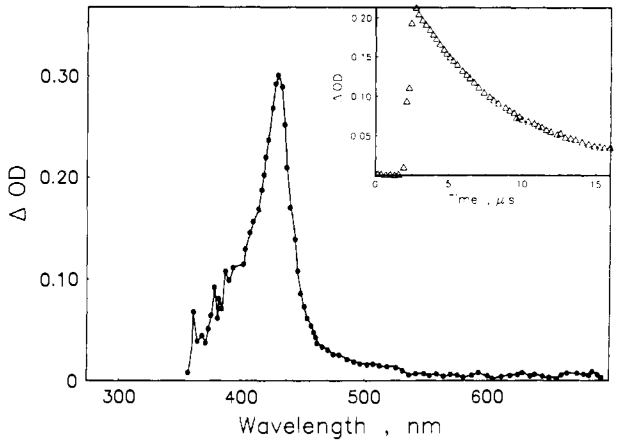

Figure 1. T-T absorption spectrum for DBA in benzene induced by 308-nm laser excitation. Insert: triplet decay trace monitored at 420 nm.

Triplet generation was carried out with the 308-nm pulses from a Lumonics TE860-2 excimer laser (~5 ns, ≤20 mJ/pulse). The triplets were, in turn, reexcited with the pulses from a Candela UV-500M dye laser, normally tuned at 467 nm (~250 ns, ≤100 mJ/pulse). For measurement of transient absorptions, the signals from a RCA-4840 photomultiplier were initially captured by a Tektronix R7912 transient digitizer and were then processed by a PDP11/23 computer, which also controlled a variety of experimental parameters (e.g., monitoring wavelength and pulsing of lasers). Fluorescence spectra, on which the fluorescence intensities are based, were recorded by using EG & G gated intensified optical multichannel analyzer (OMA), which was controlled by a PDP11/73 computer via an EG & G model 1461 interface.

It was critical to carry out fluorescence and transient absorption measurements under identical experimental conditions. The simplest way to achieve this was to use a beam splitter (a 4% reflecting quartz plate) so that the same sample and experimental geometry could be used for both measurements. With this beam splitter, transmitted monitoring light could be directed into the monochromator-photomultiplier detection system for the transient absorption measurements, or fluorescence could be reflected into the OMA, without moving the sample cell or changing the overlap of the lasers.

Results

Laser excitation (308 nm) of a solution of DBA results in the efficient production of the DBA triplet state ($\Phi_{isc} \sim 0.8$–0.9,[30,31] $\lambda_{max}^{abs} = 430$ nm[32]). Figure 1 shows the T-T absorption spectrum obtained in benzene following laser excitation at 308 nm and an insert showing the decay of the triplet state monitored at 420 nm. When the 308-nm pulse was followed after 1 μs by 467-nm dye-laser excitation, the latter led to efficient bleaching of the T-T absorption. Figure 2 shows the decay of the triplet absorption under conditions of one- and two-laser excitation. Figure 2 also shows the intense fluorescence emission (negative deflection in Figure 2B) which takes place concurrent with the dye-laser pulse. The spectrum of this emission is identical with the prompt DBA fluorescence induced by the 308-nm excitation and was absent when the dye-laser pulse was not preceded by the 308-nm pulse. This clearly illustrates that triplet formation is a prerequisite for intense dye laser induced fluorescence. Figure 3 shows a timing diagram illustrating the sequence of the various events involved in the two-laser experiments. The delay between the two laser pulses is typically around 1 μs, and the OMA gate timing also was 1 μs. The timing of the OMA gates (see Figure 3) was selected in order to record all the fluorescence from either the 308-nm or the dye-laser pulse. For the short 308-nm pulse a much shorter gate would have been adequate, but for consistency we

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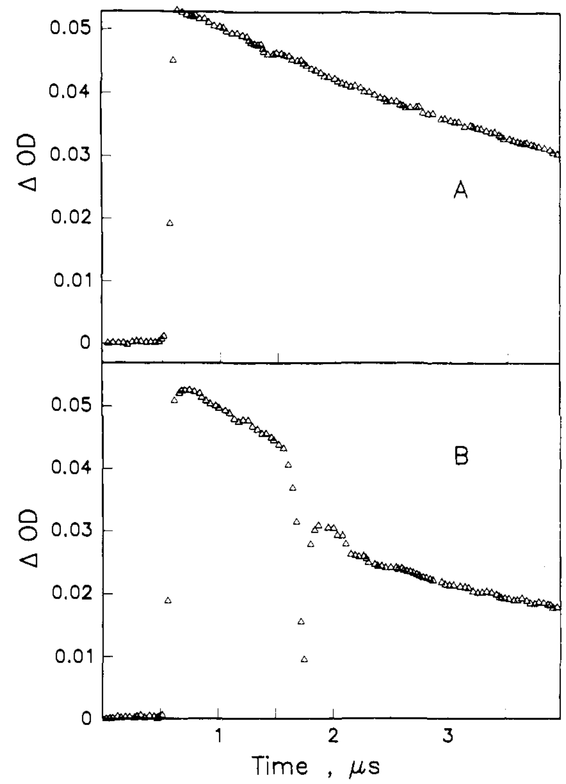

Figure 2. Decay of triplet DBA in benzene monitored at 430 nm under conditions of one-laser (A) and two-laser (B) excitation. Note the negative deflection due to dye laser (467 nm) induced fluorescence in trace B.

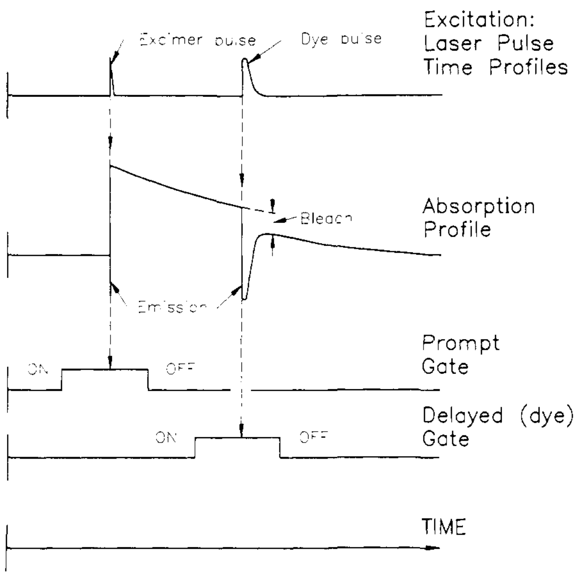

Figure 3. Timing diagram illustrating the sequence of events in a typical two-laser experiment.

Table I. Two-Laser Induced Photochemistry and Photophysics of DBA at Room Temperature

	cyclohexane	benzene
(I) Determination of Triplet Bleaching Quantum Yields[a]		
(a) monitoring λ	445 nm	430 nm
(b) ϵ_{TT}^{λ}	4200 M^{-1} cm^{-1}	25 000 M^{-1} cm^{-1}
(c) λ_{dye}	467 mn	467 nm
(d) Φ_{BL}^{467} (Aberchrome)	0.065 (toluene)	
(e) ϵ^{494} (Aberchrome)	8200 M^{-1} cm^{-1} (toluene)	
(f) ΔOD^{e} (at λ)[b]	0.040	0.251
(g) $\Delta\Delta OD^{d}$ (at λ)[c]	0.0084	0.0621
(h) $\Delta\Delta OD^{494}$ (Aberchrome)	0.0043	0.0066
(i) match ratio at 467 nm[d]	0.94	0.86
(j) Aberchrome dye attenuation[e]	18%	24%
(k) Φ_{BL}^{DBA}	0.042 ± 0.01	0.041 ± 0.01
(II) Determination of Φ_{TS}		
(l) delay between lasers	1 μs	1 μs
(m) gate	1 μs	1 μs
(n) $E_{dye}{}^{d}/E_{308}{}^{e,f}$	0.756	0.540
(o) Φ_{TS}	0.17 ± 0.04	0.09 ± 0.02

[a] Φ_{BL}^{DBA} is calculated according to $\Phi_{BL}^{DBA} = (\Delta\Delta OD^{d}/\Delta\Delta OD^{494})(\epsilon^{494}/\epsilon_{TT}^{\lambda})\Phi_{BL}^{467}$ (match ratio) (attenuation), where the values originate from the following entries: $\Phi_{BL}^{DBA} = [(g)/(h)][(e)/(b)](d)(i)[(j)/100]$. [b] See eq 7. [c] See eq 8. The ratio of entries (g) and (f) is the fraction of triplets bleached by the dye laser. [d] The technique requires that the optical densities induced by 308-nm excitation be matched at the dye-laser wavelength (467 nm). Small deviations from 1.0 in this ratio are readily corrected for. The ratio given corresponds to Aberchrome/DBA. [e] Best results are achieved when comparable bleaching signals are obtained for sample and actinometer. Some attenuation was required for the actinometer runs. [f] See eq 6.

employed identical gates for both lasers. As expected, minor changes (i.e., ±200 ns) in the positioning or duration of the gates did not have any significant effect on the integrated fluorescence intensities (fluorescence intensities were measured by integrating the spectra between 400 and 435 nm). Since benzene has been proposed to quench at least some upper triplet states by an energy-transfer mechanism,[23] we carried out a series of comparative studies using cyclohexane, a solvent in which similar energy-transfer mechanisms are not possible. The combined results of these measurements are given in Table I; full details of the nomenclature used are provided in the Discussion section (vide infra). Experiments in benzene and in cyclohexane were matched, i.e., absorbances of DBA triplets at the dye-laser wavelength (467 nm) were the same in both solvents. This was achieved by adjusting the 308-nm laser dose with neutral-density filters. In the DBA triplet-bleaching quantum-yield experiments (which utilize the Aberchrome-540 two-photon actinometry)[28] it was necessary to attenuate the dye-laser pulse when measuring the extent of the bleaching of Aberchrome-540. This attenuation was required to obtain bleaching of a magnitude similar to that obtained for DBA. When similar bleaching magnitudes are measured, errors associated with this method can be minimized. Typically, an 18 or 24% transmittance filter was employed.

In addition to fluorescence, another possible consequence of DBA triplet-state reexcitation is carbon–bromine bond cleavage. In order to investigate the importance of this reaction, a two-laser experiment (308 nm pulse followed by a 467-nm pulse) with DBA in benzene was performed.

The major transient product of carbon–bromine bond cleavage in benzene is the bromine atom–benzene π-complex which is known to have a broad absorption with λ_{max} 550 nm.[33] Figure 2 shows the bleaching of the DBA triplet absorption at 430 nm resulting from the dye-laser pulse. At 550 nm (where the triplet absorption is weak but measurable), however, little or no bleaching was observed. This lack of bleaching may be indicative of production of the π complex which absorbs at 550 nm and compensates for the triplet bleaching. However, a transient absorption spectrum obtained following the dye-laser pulse failed to reveal any major spectral changes. Clearly, any two-laser π-complex formation must have a low quantum efficiency. In order to improve our ability to monitor these changes, we tuned the dye laser at 433 nm, where the DBA triplet extinction coefficient is 1 order of magnitude greater. Figure 4 shows the DBA triplet decay following two-laser (308 nm followed by 433 nm) excitation. The monitoring wavelengths are 420 and 550 nm (420 nm was chosen to minimize the scattered light from the 433-nm dye laser). Figure 4 clearly shows production of a new transient species which is consistent with π-complex formation. The 550 nm trace has been corrected for any changes associated with the dye-laser pulse only (direct excitation of DBA by the dye laser is minor).

It is possible to determine a rough estimate for the quantum yield of π-complex formation by comparing the dye laser induced

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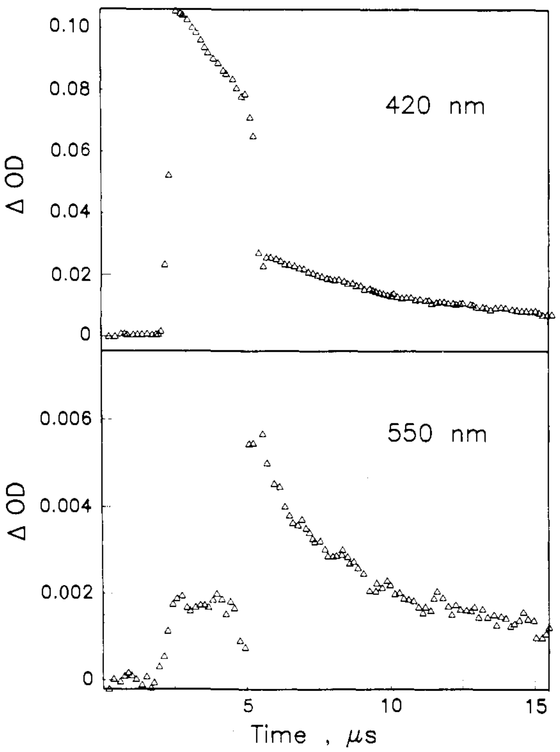

Figure 4. Matched absorption traces for a two-laser experiment (dye laser at 433 nm) monitored at 420 nm (top) and 550 nm (bottom). The increased absorption at 550 nm upon dye-laser excitation (i.e. time ~ 5 μs) is attributed to the π-complex of bromine atoms with benzene.

bleaching at 420 nm and the signal growth at 550 nm. In order to make this comparison, it is necessary to correct for the underlying triplet bleaching at the latter wavelength. Thus the actual π-complex absorption is the sum of the 550-nm absorption and the expected triplet bleaching.

Figure 4 shows an enhanced absorption at 550 nm following dye-laser excitation corresponding to $\Delta OD^{550} = 0.0022$. This value needs to be corrected for the underlying triplet bleaching which can be readily estimated from the bleaching observed at 420 nm and the known ratio of extinction coefficients at the two wavelengths; this leads to a corrected ΔOD^{550} of 0.0030. From this, and taking into account the triplet and π-complex[34] extinction coefficients, we estimate that 4% of the triplets bleached lead to π-complex formation in benzene. This corresponds to the quantum yield of 0.0016 for photodebromination of the triplet.

Alternatively, triplet-state reexcitation may result in $T_2 \rightarrow T_1$ luminescence, although this could escape detection in our bleaching studies. Such luminescence has been previously observed by Gillispie and Lim using photon-counting techniques.[35] In our experiments, when the triplet state of DBA is excited with the pulses from a dye laser tuned to 700 nm, $S_1 \rightarrow S_0$ emission was observed (by OMA detection), but no $T_2 \rightarrow T_1$ emission (expected at ~840 nm) was observed. The failure to detect $T_2 \rightarrow T_1$ emission may not be surprising considering the low quantum yield expected for this process ($\sim 10^{-6}$) and may partially reflect our own instrumental detection limits in this spectral region.

In order to explore the possible direct contribution of T_n ($n > 2$) to the TS intersystem crossing, we have carried out comparative two-laser experiments using 700-nm and 467-nm dye-laser wavelengths for triplet-state excitation. When 700-nm excitation is used, there is insufficient energy to access any T_n levels higher than T_2, while with 467-nm excitation it is possible to populate higher levels of the triplet manifold. In each case the integrated dye laser induced fluorescence intensity was determined as a function of added 1,3-octadiene ($E_T \sim 58$ kcal/mol), which acts as a T_n ($n > 2$) quencher; i.e. it cannot quench S_1 or T_1 efficiently.[36] In a mechanism where 1,3-octadiene (Q) quenches both T_2 and T_n, the fluorescence intensity (or quantum yield) is given by eq 1. Where I^0 and I_Q are the integrated fluorescence intensities

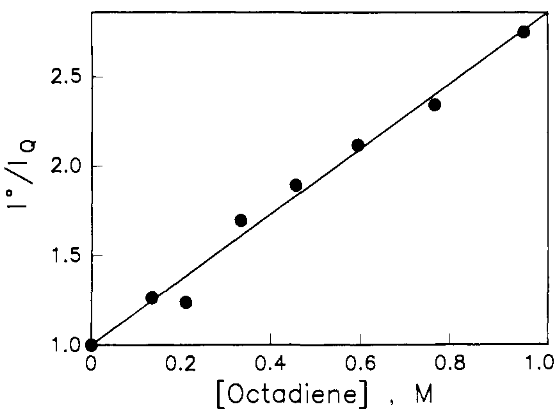

Figure 5. Stern–Volmer plot for the quenching of the dye laser (467 nm) induced fluorescence by 1,3-octadiene in cyclohexane.

$$\frac{\Phi_F^0}{\Phi_F} = \frac{I^0}{I_Q} = (1 + k_2^{ET}\tau_{T_2}[Q])(1 + k_n^{ET}\tau_{T_n}[Q]) \qquad (1)$$

in the absence and presence of quencher and $k_2^{ET}\tau_{T_2}$ and $k_n^{ET}\tau_{T_n}$ are the Stern–Volmer constants for T_2 and T_n ($n > 2$), respectively. If no quenching of T_n takes place, i.e., if

$$k_n^{ET}\tau_{T_n}[Q] \ll 1$$

then, eq 1 reduces to the familiar form of the Stern–Volmer expression, eq 2.

$$\frac{I^0}{I_Q} = 1 + k_2^{ET}\tau_{T_2}[Q] \qquad (2)$$

Thus, the plots of I^0/I_Q vs [Q] should be different for 467-nm and 700-nm excitation if upper T_n states are involved in the process under 467-nm excitation. Specifically, the apparent slope would be higher for 467-nm excitation since the last term in brackets in eq 1 would then be greater than 1.0. When these experiments were performed we did not observe any significant difference in the Stern–Volmer slopes obtained for 467-nm and 700-nm excitation. However, it should be noted that these comparative experiments are subject to relatively large errors (±30%) originating from a variety of experimental parameters including laser jitter and changes in the overlap between the two laser beams. While individual experiments appeared to suggest small differences between the two excitation wavelengths, repetition of the experiments several times indicated that these differences, real or not, are quite clearly within the reproducibility of our experiments. The value obtained in cyclohexane was $k_2^{ET}\tau_{T_2} = 1.9$ M^{-1} (see Figure 5). Virtually the same value was obtained in benzene. The value has not been corrected for a small amount of singlet quenching that occurs with a Stern–Volmer slope of 0.13 M^{-1}.

In another experiment we measured the effect of added benzene on the fluorescence intensity. For DBA, benzene should act exclusively as a T_n quencher, since its lowest triplet is higher in energy than the T_2 state of DBA. When 700-nm triplet excitation was used, addition of benzene did not change the fluorescence intensity. This result is expected since 700-nm excitation only accesses T_2, which cannot be quenched by benzene. When 467-nm excitation was used there was a slight decrease in fluorescence intensity (~10%) at benzene concentrations ≥1 M. From this we estimate $\tau_{T_n} \geq 20$ ps. This reduction in emission intensity is not surprising since in pure benzene Φ_{TS} is much lower than in cyclohexane (see Table I).

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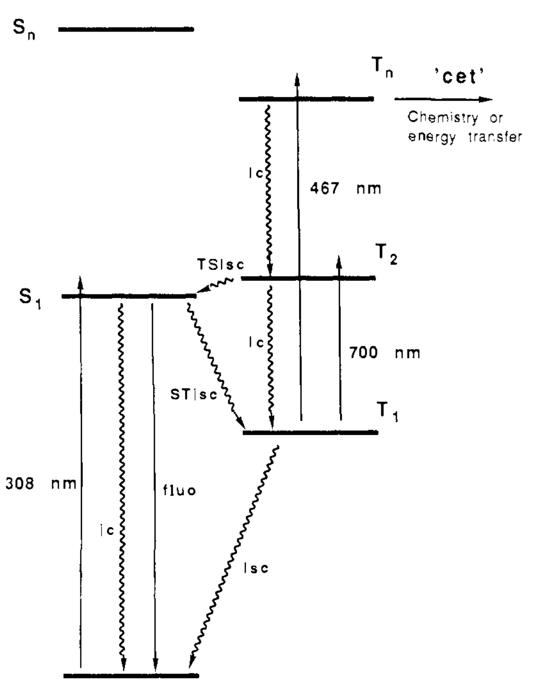

Figure 6. Energy-level diagram illustrating the processes involved in the one- and two-photon photochemistry of DBA.

Discussion

In order to discuss the results presented above, it is necessary to develop a model that will permit us to establish a correlation between the various steps involved in the photochemistry of triplet DBA. Figure 6 shows the processes involved and the nomenclature used. We note that we use T_n in our nomenclature and we will discuss in which case processes assigned to T_n may actually be attributed to T_2. Excitation of the triplet state of DBA at 467 nm promotes the molecule to T_3 or a higher T_n level. Excitation at 700 nm directly populates the T_2 level.

The emission intensity (E^e) induced by 308-nm excimer-laser excitation is given by

$$E^e = \alpha I^e \Phi_{FL}{}^e \tag{3}$$

where I^e is the absorbed laser dose from the 308-nm laser, $\Phi_{FL}{}^e$ is the quantum yield for prompt fluorescence and α is an experimental parameter which is a constant for a matched set of experiments. We use superscript e and d to indicate processes or quantum yields related to the 308 nm excimer or dye laser, respectively.

Dye laser induced fluorescence emission will be given by

$$E^d = \alpha I^d \Phi_{FL}{}^d \tag{4}$$

where $\Phi_{FL}{}^d$ is the quantum yield of fluorescence from S_1 induced by photoexcitation of T_1. It should be emphasized that while this fluorescence is the result of a two-photon process, $\Phi_{FL}{}^d$ is actually the quantum yield for a one-photon process at the dye-laser wavelength. In turn $\Phi_{FL}{}^d$ is given by

$$\Phi_{FL}{}^d = k_{TS}\tau_{T_n}\Phi_{FL}{}^e = \Phi_{TS}{}^d\Phi_{FL}{}^e \tag{5}$$

thus,

$$\frac{E^d}{E^e} = \frac{I^d\Phi_{TS}{}^d}{I^e} \tag{6}$$

The left term in eq 6 is the ratio of integrated fluorescence intensities induced by the dye and 308-nm laser pulses. The ratio I^d/I^e can be determined by using the transient absorption changes due to triplet DBA (formation or bleaching) as a calibration. The following proportionalities are expected to hold for the triplet generated by the 308-nm pulse (ΔOD^e) and that bleached by the dye laser ($\Delta\Delta OD^d$). These values are obtained under conditions identical with those used for the emission experiments:

$$\Delta OD^e \propto I^e\Phi_{ST}{}^e \tag{7}$$

$$\Delta\Delta OD^d \propto I^d\Phi_{BL}{}^d \tag{8}$$

Combining eq 6–8 leads to

$$\frac{E^d}{E^e} = \Phi_{TS}{}^d \frac{\Phi_{ST}{}^e}{\Phi_{BL}{}^d} \frac{\Delta\Delta OD^d}{\Delta OD^e} \tag{9}$$

from which $\Phi_{TS}{}^d$ can be experimentally determined, since all other terms in the equation, with the exception of $\Phi_{ST}{}^e$, are experimental values. The value of $\Phi_{ST}{}^e$ has been reported as 0.80 in benzene[30] and 0.90 in cyclohexane.[31] It is clear that minor variations in this value will not have a very significant effect on $\Phi_{TS}{}^d$ since it seems established that $0.8 < \Phi_{ST}{}^e < 0.95$.

The values of $\Phi_{TS}{}^d$ obtained are 0.17 and 0.09 in cyclohexane and benzene, respectively. Interestingly, the values in the two solvents are significantly different in spite of the fact $\Phi_{BL}{}^d$ values are very similar for both (see Table I).

The observation that $\Phi_{TS}{}^d > \Phi_{BL}{}^d$ deserves some comment, since upon initial consideration this may appear to be contradictory. It should be noted (see Figure 6) that the majority of the molecules that reach S_1 (whether by direct absorption or via TS) actually decay via intersystem crossing to T_1 and therefore do not lead to triplet bleaching. The predicted bleaching, if "chemistry or energy transfer" (cet) (Figure 6) did not take place, would be given by

$$\Phi_{BL}{}^d \text{ (no cet)} = \Phi_{TS}{}^d(1 - \Phi_{ST}{}^e) \tag{10}$$

which leads to "expected" bleaching yields of ca. 0.03 and 0.015 in cyclohexane and benzene, respectively (typical errors are ±30%). The value in cyclohexane is smaller than $\Phi_{BL}{}^d$, yet within experimental error, and the difference does not require extensive comment. It is sufficient to say that a small yield of C–Br bond cleavage may contribute to this difference.

In the case of benzene, the value of 0.015 derived from eq 10 is much smaller and is outside the experimental error of the value $\Phi_{BL}{}^d = 0.041$ obtained by using the Aberchrome-540 method (see Table I). Two factors may contribute to this difference: first, C–Br cleavage may occur, but again the quantum yield for this process has been established to be quite low. Our results do not allow us to establish if this cleavage occurs from T_2 or a higher T_n level. Second, recent studies from our laboratory have shown that upper triplet levels can readily transfer energy to aromatic molecules[37] in solution or to pure aromatic solvents.[23] The T_2 level of DBA cannot populate the T_1 level of benzene, since the process is energetically unfavorable; however, energy transfer is energetically feasible from T_n or higher triplet levels ($n > 2$). It is possible that in spite of very short triplet lifetimes these levels may contribute to the observable bleaching.

We come now to a crucial question; what is the nature of the triplet level responsible for TS ISC? From a qualitative point of view it is clear that direct excitation into T_2 (at 700 nm) leads to intense S_1 fluorescence. Unfortunately, the Aberchrome-540 method cannot be used at 700 nm. It is tempting to say that, given the relatively intense 700 nm dye laser induced fluorescence combined with the very low T-T extinction coefficient at this wavelength, one need not invoke a higher triplet level, T_n, to explain the very intense fluorescence induced by 467-nm dye-laser excitation (given the larger T-T extinction coefficient at this wavelength). However, the larger than expected bleaching quantum yield in benzene suggests that T_n must be sufficiently long lived to undergo intermolecular energy transfer. That one of the processes responsible for bleaching in benzene is energy transfer is supported by a parallel two-laser experiment performed with anthracene in benzene. Again, considerable dye laser induced bleaching is observed. In anthracene, however, the TS process is known to be inefficient (no dye laser induced fluorescence is observed) and no C–Br bond cleavage can take place, thus eliminating other upper triplet decay routes. In addition, no bleaching was observed in cyclohexane. Thus, at least part of the bleaching

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in anthracene (and probably DBA as well) must be due to energy transfer from T_n ($n > 2$) to the solvent. The T_2 energies of both donors lie well below the T_1 energy of benzene, i.e. 73.0[35] and 74.4[38] < 85 kcal/mol.[39] Clearly then, if T_n is long enough lived to undergo intermolecular energy transfer, it could conceivably undergo ISC back to the singlet manifold. However, our quenching experiments with 1,3-octadiene suggest that only T_2 is involved and that any contributions from other upper states (at least those generated by 467-nm excitation) are within the errors of these measurements.

Our results led to $k_2^{ET}\tau_{T_2}$ = 1.8 M^{-1} for 1,3-octadiene as quencher. From this value it is possible to estimate a value for τ_{T_2}: Since the T_2 state of DBA is close to the lowest triplet state of xanthone, we assume that energy transfer to 1,3-octadiene occurs with approximately the same rate constant in both systems. For the latter we measured[37] $k_9 \sim 1 \times 10^{10}$ M^{-1} s^{-1}. From this we estimate $\tau_{T_2} \sim$ 200 ps.

Conclusions

Our results lead to the following conclusions:

(i) Back intersystem crossing (TS) following dye-laser excitation (467 nm) of T_1 occurs with quantum yields of 0.17 and 0.09 in cyclohexane and benzene, respectively. Quite clearly T_2 participates directly in this process. T_n ($n > 2$) is sufficiently long lived to participate in intermolecular energy transfer to the solvent (benzene) in a process which we believe is responsible for the lower Φ_{TS} value measured in benzene; however, this state (T_n) does not need to be invoked as a direct participant in the TS process.

(ii) Despite the fact that triplet excitation at 467 nm results in the production of a T_n state with more than sufficient energy to induce C-Br cleavage, this process is relatively inefficient, occurring with $\Phi_{-Br} \sim 1.6 \times 10^{-3}$. This accounts for only ca. 4% of the triplets bleached in benzene.

(iii) Lifetimes can be estimated for T_2 from 1,3-octadiene quenching experiments and for T_n from benzene quenching data. These lead to $\tau_{T_2} \sim$ 200 ps and $\tau_{T_n} \sim$ 20 ps.

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General-Base Catalysis of Nucleophilic Substitution at Carbon[1]

Paul E. Dietze[2] and William P. Jencks*

Contribution No. 1665 from the Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02254. *Received June 10, 1988*

Abstract: The bimolecular reaction of [4-(trifluoromethyl)benzyl]methyl(4-nitrophenyl)sulfonium ion with trifluoroethanol is catalyzed by substituted acetate ions and other buffer bases in 50% trifluoroethanol-water (v/v) at 40 °C and ionic strength 0.5 M ($NaClO_4$). The Brønsted β value is 0.26, but there is no significant solvent deuterium isotope effect. The reactions with water and ethanol do not show catalysis and there is no catalysis of the reaction of (4-trifluoromethyl)benzyl bromide.

One of the curious problems of enzymology is the question of how enzymes catalyze simple displacement reactions. In addition to decreasing the requirement for entropy loss by induced intramolecularity, stabilization of the transition state by ionic and nonpolar interactions, and possibly compression, enzymes might catalyze displacement reactions by general-base catalysis of proton removal from hydroxylic nucleophiles in the transition state.[3-6] There is evidence for such general-base catalysis in nonenzymatic reactions for attack at sp^2 carbon (or the equivalent general acid catalysis in the reverse reaction),[7-9] for substitution on silanes,[10] and for displacement at sp^3 carbon in intramolecular reactions,[5,11-16] but it has not been reported for bimolecular displacement reactions at sp^3 carbon. We are interested in why this might be the case, and in order to characterize these reactions further, we have examined general-base catalysis of solvolysis in the presence of alcohols with different pK_a. General-base-catalyzed reactions of hydroxylic nucleophiles generally show an increased Brønsted β value with decreasing pK_a of the alcohol that is described by a positive interaction coefficient, $p_{xy'} = \partial\beta/-\partial pK_{nuc} = \partial\beta_{nuc}/-\partial pK_{BH}$, so that catalysis should be easier to detect with more acidic alcohols.[17]

We report here that buffer bases catalyze the reaction of [4-(trifluoromethyl)benzyl]methyl(4-nitrophenyl)sulfonium tetrafluoroborate, **1**, with trifluoroethanol, but not with ethanol or water, in the solvent. This substrate was choosen because there is some evidence that benzyl compounds with electron-withdrawing substituents[18] and sulfonium ions[16,19] have unusually large amounts

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(2) Present address: Department of Chemistry, University of Maryland at Baltimore County, Baltimore, MD 21228.

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