Photochemistry of the T₂ State of Anthracene

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The chemistry of the anthracene T_2 state in room-temperature acetonitrile solution in the presence of a variety of quenchers has been investigated by two-laser flash photolysis. The decay of T_2 in the presence of ethyl bromoacetate, which is capable of undergoing reductive dehalogenation, is via electron transfer as evidenced by the detection of the anthracene radical cation, λ_{max} 720 nm. Indirect evidence shows that in benzonitrile, T_2 decay is primarily by electron transfer with a minor contribution due to energy transfer ($T_2 \rightarrow$ benzonitrile T_1). The failure to detect the cation radical indicates that back electron transfer, either following ISC or within the geminate triplet radical ion pair, is faster than cage escape. T_2 also reacts with acrylonitrile and fumaronitrile partially via 4 + 2 cycloaddition at the anthracene 9 and 10 positions. Again, indirect evidence suggests that triplet-triplet energy transfer and electron transfer also contribute to T_2 decay.

Introduction

The ability of upper excited triplet states to decay by photophysical pathways other than $T_2 \rightarrow T_1$ internal conversion has been recognized for some time.¹⁻¹¹ Early product studies showed^{1,2} that CW irradiation of anthracene in the presence of *trans*-stilbene resulted in trans—cis isomerization. Spectroscopic studies at low temperatures involving the excitation of anthracene in the presence of naphthalene resulted in naphthalene phosphorescence emission.³ In both cases, the observed behavior was attributed to intermolecular energy transfer from anthracene T_2 to the substrate.

More recently, time-resolved two-color (two-laser) studies have shown that a variety of aromatic hydrocarbons and ketones have T_2 reactivity and that in addition to energy transfer,^{6,7} Norrish type I cleavage,^{8,9} debromination,^{10,11} and reverse intersystem crossing¹¹ are all possible T_2 deactivation pathways.

As it turns out, anthracene and anthracene derivatives are especially well suited for the study of upper triplet decay processes. The T_1 and T_2 energies are $\sim 40^{12}$ and $\sim 74^{13}$ kcal/mol, respectively, and this large energy gap contributes to a relatively long T_2 lifetime ($\tau \sim 200$ ps).¹¹ It is this long lifetime that allows efficient (diffusion-controlled) intermolecular processes to compete effectively with internal conversion.

To date, with the exception of energy transfer, there have been few reports of intermolecular reactions involving T_2 states. Given the fact that the T_2 state of anthracene is long-lived and nearly isoenergetic with the S_1 state¹⁴ and that S_1 participates in a wide variety of chemical processes¹⁵ including electron transfer, 4 + 2 cycloaddition, and dimerization, it was believed that the T_2 state could also participate in these reactions.

We report here the two-laser flash photolysis study of anthracene in the presence of ethyl bromoacetate, benzonitrile, acrylonitrile, and fumaronitrile, all of which are capable, thermodynamically, of oxidizing anthracene T_2 . In addition to electron transfer, we have found that T_2 participates in energy transfer and cycloaddition.

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich unless specified otherwise. Acetonitrile, benzene, and benzonitrile were spectrophotometric grade and were used as received. Acrylonitrile (99+%) was also used as received. Ethyl bromoacetate (98%), 1,2-dimethoxybenzene (99%), and fumaronitrile (98%) were distilled prior to use. Anthracene was recrystallized from ethanol. The structures of the compounds used are given below. $CH_2 = CHCN \qquad CNCH = CHCN$ Acrylonitrile (AN) Fumaronitrile (FN)

OCH₂CH₃



Ethyl bromoacetate (EBA)

Benzonitrile (BN)



1,2-Dimethoxybenzene (DMB)

Absorption and Fluorescence Spectroscopy. Absorption spectra were obtained with a Shimadzu 2200 UV-vis dual-beam spectrophotometer using $7 \times 7 \text{ mm}^2$ quartz cells with pure solvent as reference. Fluorescence emission spectra were obtained with a Perkin-Elmer LS50 spectrofluorimeter. Samples were dilute in order to minimize the effects of self-absorption.

Laser Flash Photolysis. Apparatus. Three pulsed lasers were used as excitation sources. UV excitation was provided either by a Lumonics EM510 XeCl excimer laser (308 nm, 30 mJ/pulse, 8-ns pulse duration) or by the frequency-tripled output of a Continuum "Surelite" Nd/YAG laser (355 nm, <50 mJ, 6 ns). Visible excitation was provided by a Candela SLL 250 flashlamppumped dye laser (420-700 nm, <250 mJ, 350 ns). The monitoring system consisted of a pulsed 150-W xenon lamp as the light source, an Acton Research Corp. 27.5-cm focal length microprocessor-controlled monochromator equipped with two gratings-a wavelength-neutral holographic grating and a conventional grating blazed at 750 nm for enhanced red sensitivityand a six stage Burle 4840 photomultiplier attached to the exit slit. Signal capture was by a Tektronix 7912 HB transient digitizer. I_0 values were obtained by a home-built sample and hold unit, which also provided a DC offset to the signal, and were transferred to the computer through a Sciemetric Labmate Intelligent Lab Interface. The Labmate was also used to control the photomultipler voltage as well as electronic shutters in the path of the laser and monitoring beams. The monitoring lamp pulser, digitizer, lasers, and sample and hold unit were all triggered

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with a Stanford Research Systems digital delay pulse generator which provided variable amplitude, independently delayed TTL pulses which allowed synchronization and gating of each instrument. The pulse generator, monochromator, Labmate, and digitizer were interfaced (RS-232, GPIB parallel bus) to an AT&T 80286 PC responsible for both execution of the data acquisition programs and data analysis.

Sample Preparation. Samples in a typical experiment either were static ($7 \times 7 \text{ mm}^2$ quartz cells, 3-mL volume) or were flowed through a specially constructed quartz flow cell which ensures that a fresh volume of sample is irradiated by each laser pulse. The optical density of samples at the laser wavelength was <0.5. All samples unless otherwise noted were outgassed with dry nitrogen.

Product Studies. Product studies were carried out using GC and GC-MS analysis of static samples which had been subjected to two-laser irradiation. A continuously degassed sample was irradiated by approximately 500 pairs of laser pulses (UV pulse followed by dye laser pulse after a $0.75-1-\mu$ s delay). A control experiment was also performed in which the sequence of the lasers was reversed, thus allowing the effects of the UV pulse alone to be measured.

Synthesis of Dibenzobicyclo[2.2.2]octa-5,7-diene-2-carbonitrile (4+2 Cycloaddition Product). A solution of 10 g of anthracene and 4 mL of acrylonitrile in 20 mL of xylene was heated in a sealed bomb at 170 °C for 8 h, yielding the cycloaddition product, I, in ca. 75% yield.¹⁶ It was subsequently recrystallized from ethanol and identified by GC-MS.



Results and Discussion

Two-Laser Photochemistry of Anthracene Alone. Irradiation of a degassed solution of anthracene (1 mM) in acetonitrile (MeCN) by either a 308-nm excimer laser or a 355-nm frequencytripled YAG laser resulted in the production of the anthracene triplet state, T₁, detected by its T-T absorption spectrum (λ_{max}) 425 nm).¹⁷ The formation of the T_1 state of anthracene is known to proceed via $S_1 \rightarrow T_2$ ISC¹⁸ followed by T_2-T_1 relaxation. In addition to the T-T absorption, a second, minor absorption band was detected with λ_{max} 720 nm. This weak transient absorption, which decays by mixed first- and second-order kinetics, is assigned to the anthracene radical cation based on literature values obtained by photochemical and electrochemical techniques.^{19,20} Support for this assignment is also given by the fact that the absorption band at λ 720 nm is absent in nonpolar solvents such as cyclohexane, i.e., the radical cation is stabilized in acetonitrile. In addition, the absorption was quenched at nearly a diffusioncontrolled rate ($k_q = 9.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) by the addition of tetra*n*-butylammonium bromide (bromide acts as a cation scavenger). A laser dose study showed that the cation radical was produced monophotonically and that there was no significant difference in production observed by changing the excitation wavelength from 308 to 355 nm.

Suppan and co-workers¹⁹ have attributed radical cation formation, which they also found to be inefficient, to monophotonic ionization of the thermally equilibrated anthracene S_1 state followed by solvation of the ejected electron by MeCN. Since the ionization is from the thermally equilibrated state and is therefore endergonic by ca. 8 kcal/mol, it is not surprising that radical cation formation is inefficient. In fact, it is possible that



Figure 1. Transient absorption spectra for anthracene in acetonitrile in the presence of 1 M ethyl bromoacetate (EBA) obtained following onelaser (355-nm) and two-laser (355- \pm 445-nm) flash photolysis. Spectra were measured 1.5 μ s after the 355-nm pulse. In the two-laser experiment, the 445-nm pulse followed the 355-nm pulse by 1 μ s.

trace concentrations of water, which is present in even the most rigorously purified MeCN, may account for the majority of radical cation formation observed in their experiments as well as our own. This would appear to be confirmed by our observation of an increased yield of radical cation when 9:1 MeCN:H₂O was used as solvent.

Irradiation of the triplet state by a pulsed, flashlamp-pumped dye laser tuned to the T-T absorption band (λ_{dye} 445 nm) ca. 1 μ s after the initial UV pulse caused no observable change in the triplet decay kinetics or the transient absorption spectrum. It is surprising that although excitation of T_1 with 445-nm photons initially produces an upper excited triplet state, T_n , with energy in excess of 100 kcal mol⁻¹, no further ionization was detected. Given the observation made by Suppan et al.¹⁹ that ionization occurs from a thermally equilibrated excited S_1 state, we assume that a similar fast relaxation mechanism (in this case $T_n \rightarrow$ thermally equilibrated T_2) is responsible for the lack of efficient cation production following triplet excitation (S1 and T2 are nearly isoenergetic). When this inefficient ionization is coupled with the very small concentration of T_1 , the species absorbing the dye laser pulse, it is understandable that no further cation absorption was detected.

Two-Laser Photochemistry of Anthracene with Electron Acceptors. (a) Ethyl Bromoacetate. In order to confirm that electron transfer takes place from anthracene T₂ by observation of the radical cation spectrum, ethyl bromoacetate (EBA) was chosen as an electron acceptor. EBA is known to undergo rapid dissociation following electron capture to give bromide ion and ethoxycarbonylmethyl radical.²¹ Furthermore, substitution of the literature values for the oxidation and reduction potentials of anthracene (+1.16 V)²² and EBA (-1.60 V)²³ into the Rehm-Weller equation²⁴ indicates that electron transfer from either the S_1 state or the T_2 state of anthracene is exergonic. Figure 1 (square symbols) shows the transient absorption spectrum from 600 to 780 nm obtained following one-laser (UV) photolysis of a solution of anthracene in MeCN with added 1 MEBA (spectrum was obtained 1.5 μ s after the excimer laser pulse). In addition to the T-T absorption band (not shown, λ_{max} 425 nm), the anthracene radical cation absorption was observed at λ 720 nm. The absorption due to the radical cation was significantly enhanced when compared to the absorption in the absence of EBA, thus confirming the participation of EBA in the oxidation of anthracene. Fluorescence quenching with EBA ($k_q = 5.0 \times 10^7$



Figure 2. Decay of transient absorption following two-laser (355: + 445-nm) flash photolysis of anthracene in acetonitrile in the presence of 1 M ethyl bromoacetate (EBA). Top, a, monitored at 720 nm; bottom, b, monitored at 430 nm.

 $M^{-1}s^{-1})^{25}$ and the lack of triplet T_1 quenching indicate that onephoton cation radical production takes place at least partially through the singlet manifold.

The role of T_2 in the oxidation of anthracene was investigated by performing a two-laser experiment on a solution of anthracene in MeCN with added 1 M EBA. Figure 1 (round symbols) also shows the transient absorption spectrum obtained 1.5 μ s after the excimer laser pulse and 500 ns after the dye laser pulse, i.e., at the same time as in the one-laser spectrum. No new absorption bands are produced by the dye laser. However, the absorbance at 720 nm due to the anthracene radical cation is approximately twice the value obtained in the one-laser experiment.

Figure 2 gives the kinetic behavior of this system under twolaser photolysis. Figure 2b shows the dye-laser-induced bleaching of the T-T absorption at 430 nm. This bleaching indicates that the upper triplet state produced by absorption of the dye laser pulse decays by a process or processes that do not regenerate the T₁ state. Figure 2a shows the concomitant jump in the radical cation absorption. Thus, it appears that triplet T₂ decay leads to radical cation production. Since the yield of back intersystem crossing (T₂ \rightarrow S₁) in unsubstituted anthracene is very small,²⁶⁻²⁹ dye-laser-enhanced production of radical cation must take place via interaction of EBA with T₂. This observation also indicates that at least a minor amount of the radical cation produced in the UV (one) laser experiment is via quenching of T₂.

Based on published extinction coefficients for anthracene triplet $(\epsilon = 30\ 000\ M^{-1}\ cm^{-1})^{30}$ and cation radical $(\epsilon = 11\ 600\ M^{-1}\ cm^{-1})^{,31}$ it is possible to roughly estimate the fraction of bleached triplets which lead to cation radical to be 85%.

(b) Benzonitrile. In order to investigate anthracene upper triplet state processes with a nondissociative electron acceptor, benzonitrile (BN) was used as a quencher in place of EBA. While the reduction potential of BN^{32} is more negative than that of EBA, electron transfer from anthracene T₂ is still approximately thermoneutral. When a solution of anthracene in MeCN with

added 1 M BN was irradiated with a UV laser, a transient absorption spectrum showed the formation of the anthracene triplet state. In contrast to the EBA experiment, no anthracene radical cation absorption was detected. Similarly, when a twolaser experiment was performed, bleaching of the triplet-triplet absorption band was observed, but again, no radical cation absorption was detected.

Triplet-triplet energy transfer is also a possible T₂ deactivation process (E_{T_1} for BN is 77 kcal/mol³³), which would lead to triplet bleaching but not to radical cation formation. Although energy transfer from anthracene T₂ would be slightly endergonic under these conditions, the high concentration of BN could still lead to a large rate. In order to test for the possibility of energy transfer, a two-laser experiment was carried out using 1 M 1.2-dimethoxybenzene (DMB) in place of BN. DMB is a much poorer electron acceptor than BN, while its T_1 energy is 70 kcal/mol,³⁴ making energy transfer from anthracene T_2 to DMB exergonic by 5 kcal/ mol. Thus, triplet bleaching should be primarily due to energy transfer. Indeed, the magnitude of bleaching in DMB could be regarded as an upper limit for BN if only energy transfer occurs. In fact, we found the magnitude of bleaching with DMB much smaller than with BN. This result suggests that at least a portion of the bleaching in the presence of BN is due to electron transfer. To test this hypothesis, the amount of bleaching was compared for cyclohexane and MeCN solutions each containing 3 M BN. We would expect the rate of electron transfer to be quite sensitive to solvent polarity, while the rate of energy transfer should be polarity independent. In fact, the extent of bleaching observed in cyclohexane was approximately half that observed in MeCN, thus lending support to the hypothesis that T₂ quenching occurs via electron transfer.

Since no chemical products were formed in the BN experiments and since anthracene radical cation was not detected, we conclude that back electron transfer within the initially produced geminate triplet radical ion pair (RIP) must be rapid, presumably at least an order of magnitude faster than the rate of cage escape, ca. 10^8 M^{-1} s^{-1,35} One pathway for deactivation would require rapid $T \rightarrow S$ ISC within the RIP and simultaneous or subsequent back electron transfer, yielding both molecules in their ground states.

In order to test this hypothesis, we have carried out a two-laser experiment in which the sample was placed in a magnetic field (H = 300 G). Under these conditions, ISC should be less efficient, possibly leading to enhanced cage escape and observation of radical cation. Unfortunately, no radical cation absorption was observed. It is possible that a larger magnetic field is required in order to slow the ISC rate sufficiently to allow cage escape to compete. Further experiments are planned with a larger magnet.

Another possibility is back electron transfer without ISC, such that the T_1 state of either BN or anthracene is populated. In an extensive analysis, Roth and Schilling showed that such a process is not only feasible but may indeed be more favorable than processes involving ISC.³⁶ Unfortunately, this highly plausible pathway cannot be confirmed under our experimental conditions, since the T–T absorption of BN is not observable and production of triplet anthracene would merely result in a decrease in the observed bleaching.

When this transient evidence is considered along with the fact that no stable photoproducts were detected by GC-MS, it is probable that the major process responsible for triplet bleaching in the presence of BN is electron transfer and furthermore that the lack of new transient or stable products is due to rapid in-cage BET.

(c) Acrylonitrile and Fumaronitrile. One- and two-laser studies, similar to those using BN, were performed with 1 M acrylonitrile (AN) as quencher in MeCN. In both the one-laser (UV) and two-laser experiments, T-T absorption was observed, but there was no evidence for the production of radical cation, even in the presence of the 300-G magnetic field. Under two-laser irradiation, dye-laser-induced bleaching was detected. Product studies indicated that in both the one- and two-laser experiments, a stable photoproduct, dibenzobicyclo[2.2.2]octa-5,7-diene-2-carbonitrile, was formed. However, ca. 4 times as much product was detected in the two-laser experiment as in the one-laser experiment. Substitution of an equimolar quantity of fumaronitrile for AN led to qualitatively the same results. Acrylonitrile has been reported to quench the S₁ state of naphthalene and anthracene by cycloaddition reactions. While the authors identified the product of naphthalene quenching to be the 2 + 2 cycloadduct, they did not identify the product of anthracene quenching.³⁷

Since BN and AN have similar reduction potentials,³⁸ we assume that electron transfer from T_2 is a major decay pathway. The triplet RIP formed by electron transfer could then collapse to the 4 + 2 cycloadduct. A concerted cycloaddition, the usual pathway for thermal Diels–Alder reactions, would not be possible for the triplet RIP. However, if rapid ISC takes place as we have suggested for the anthracene/BN system, there would presumably be no restriction on concerted cycloaddition from the singlet RIP; reactions of diene radical cations with neutral dienophiles appear to follow such a path.³⁹

Alternatively, the triplet RIP could undergo sequential bond formation via the triplet 1,6-biradical II which could subsequently ring close after ISC.



Given that the anthracene S_1 and T_2 states are nearly isoenergetic and that the lifetimes are 6 ns⁴⁰ and ~200 ps, respectively, it may appear unusual that the bimolecular interaction of AN with the two-photon transient, anthracene T_2 , leads to a greater amount of cycloaddition product than its interaction with S_1 . However, if one considers that the dye laser has a much longer pulse duration and considerably larger pulse energy than either of the UV sources used, it is not surprising that more cycloaddition product is observed under two-laser irradiation.

Triplet-triplet energy transfer ($T_2(anthracene) \rightarrow AN$) is also a feasible T_2 deactivation pathway. This process is exothermic by ca. 18 kcal/mol ($E_{T_1}(AN) = 58$ kcal/mol).⁴¹ Similar energytransfer processes have been reported for a variety of systems including 9,10-dibromoanthracene ($E_{T_2} = 74.6$ kcal/mol)¹¹ in the presence of 1,3-octadiene ($E_{T_1} \sim 58$ kcal/mol).¹¹ Since T-T absorption for ³AN* is not observable under our experimental conditions, we would not expect dye laser excitation of the anthracene triplet followed by energy transfer to provide new transient species. We have also carried out two-laser experiments with anthracene in MeCN in the presence of 1,3-cyclohexadiene ($E_{T_1} \sim 53$ kcal/mol)¹² and observed bleaching similar to that observed for AN. Thus, energy transfer could be competitive with electron transfer.

Summary and Conclusions

When EBA was used as a T_2 quencher, UV laser irradiation alone resulted in the production of anthracene radical cation, presumably as a result of both S_1 quenching and T_2 quenching following $S_1 \rightarrow T_2$ ISC. The radical cation was identified based on literature values, on its greater stability in polar vs nonpolar solvents, and on its reactivity with Br⁻, a known cation scavenger. Dye-laser-induced bleaching of the T-T absorption was accompanied by enhanced production of the radical cation via reaction of T_2 .

The anthracene T-T absorption was bleached in two-laser experiments with both BN and DMB in MeCN and with BN in cyclohexane and MeCN. These results indicate that both energy transfer and electron transfer are responsible for T_2 deactivation. The failure to detect anthracene radical cation is likely due to the inability of cage escape to compete with back electron transfer either following ISC or in the geminate triplet RIP itself.

In the presence of acrylonitrile and fumaronitrile, T_2 decays by a 4 + 2 cycloaddition reaction as is evidenced by the dyelaser-induced bleaching of the T-T absorption and the observation by GC-MS of the cycloaddition products. Two-laser experiments with 1,3-cyclohexadiene and 1,3-cyclooctadiene, which have T₁ energies similar to acrylonitrile and fumaronitrile, indicate that triplet-triplet energy transfer is also a possible T_2 decay pathway. While electron transfer is also thermodynamically feasible based on the known redox data for anthracene, acrylonitrile, and fumaronitrile, transient evidence for the production of radical ions was not obtained. While a large rate for BET may be responsible for this absence, it is also possible that following electron transfer efficient bond formation and/or ISC prevent the production of free radical ions. Quantum yield experiments are currently being carried out in order to quantify these T₂ decay pathways.

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