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Laser flash photolysis study of triphenylimidazole

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Abstract

Laser flash photolysis of the photocyclization of triphenylimidazole (TPI) in ethyl alcohol at 308 nm. indicates that the dihydrophenanthroimidazole (DHPI) intermediate is produced rapidly, has a lifetime of 0.25 ms, and returns predominantly back to triphenylimidazole. Analysis of the decay channels for this intermediate indicates two rate constants: (1) $k_1 = 3.3 \times 10^3\ s^{-1}$, associated with reversion back to triphenylimidazole and (2) $k_2 = 0.67 \times 10^2\ s^{-1}$, which is associated with the conversion of the dihydrophenanthroimidazole to the photoproduct, 2-phenyl-9,10-phenanthroimidazole. The photoproduct is readily observed as an increasing component in the biexponential fluorescence decay data. Fluorescence lifetimes for triphenylimidazole and 2-phenyl-9,10-phenanthroimidazole (PPI) in ethyl alcohol were determined to be 1.76 and 8.21 ns, respectively, with no additional components in the fluorescence decay as the photochemistry proceeds. An additional transient absorption observed in the 450 nm. region, with a lifetime of 0.7 μs, decaying faster than the dihydrophenanthroimidazole intermediate, is assigned to the triplet state of triphenylimidazole.

Keywords: Laser flash photolysis; Photocyclization; Triphenylimidazole; Fluorescence; Transient absorption

1. Introduction

We have previously characterized the photocyclization of triphenylimidazole (TPI) as a unimolecular singlet state reaction with a low quantum yield. In vacuum degassed ethyl alcohol its fluorescence yield is 0.19 and photochemical quantum yield is 2.2×10^{-3} [1,2]. The behavior of this system is related to the photocyclization of stilbene derivatives [3]. Using conventional μs flash photolysis we observed that the dihydrophenanthroimidazole intermediate (DHPI) is formed, absorbing at 350 and 550 nm, and has a relatively slow decay channel with a lifetime of 1.5 ms [2]. Among some of the unresolved issues regarding the photochemistry of this molecule are: (i) the geometrical changes of the ortho-phenyls at the 4 and 5 positions from their initial 40° torsion angle, relative to the imidazole plane, to the dihydrophenanthroimidazole intermediate, ending with a planar phenanthrene group as 2-phenyl-9,10-phenanthroimidazole (PPI); (ii) additional decay channels of this intermediate; (iii) the role of the triplet state in the relaxation of TPI, and (iv) the singlet lifetimes of TPI, DHPI, and PPI,

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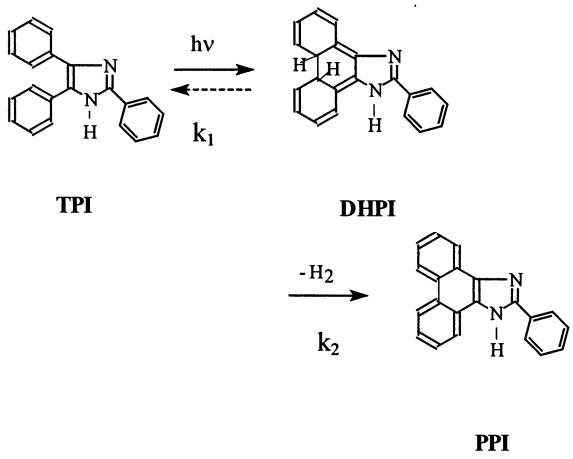
since their is a changing fluorescence spectrum as the photocyclization proceeeds. This singlet state photochemical process is summarized as follows:



In an earlier study we suggested that the inefficiency of this process is due to reversion of DHPI intermediate back to starting TPI. Since we were only able to see the DHPI relaxation channel of 1.5 ms in μs flash photolysis, we have initiated a laser flash photolysis study of TPI, complemented with fluorescence lifetime measurements, to address some of the above issues. An attempt to characterize the geometrical changes of this photocyclization by time resolved resonance Raman was made difficult by the large fluorescence contribution from the DHPI produced in this system during laser excitation.

2. Experimental

2.1. Materials

TPI was obtained from Aldrich Chemical and recrystallized from ethyl alcohol to yield a colorless powder. Spectrograde solvents were used as received.

2.2. Apparatus

Laser flash photolysis at 308 nm (XeCl) employed a 20 ns pulsewidth operating at 10 Hz, with a 200 ml solution of 5.8×10^{-5} M TPI in ethyl alcohol pumped through a closed circulating system. A tungsten–halogen lamp was used as the analyzing source, with an optical path of 4 cm, and the detection system comprised a cooled gated intensified diode array. The transient spectra were measured in two segments, covering the wavelength range 320–440 nm and 400–600 nm.

Fluorescence lifetime measurements utilized 1 cm cells in a right angle configuration, and a photon counting detection system. A frequency doubled Rhodamine pumped Nd:YAG laser having a pulse width of 5 ps served as the excitation source. These solutions were purged with argon before measuring the fluorescence lifetimes. UV absorption spectra were recorded with a Perkin-Elmer Lambda 2 spectrophotometer and steady state fluorescence spectra were recorded with a Perkin-Elmer Model LS-50 spectrofluorophotometer.

3. Results

Laser flash photolysis of a 5.8×10^{-5} M solution of TPI in ethyl alcohol, employing a circulator pump to refresh the solution under investigation, gives rise to transient absorption spectra which are shown in Fig. 1 for the region 320–440 and in Fig. 2 for the region 400–600 nm. The excited singlet state is not observed due to its short lifetime. The spectra clearly indicate absorption bands at 350 and 550 nm, which are intense and cover the temporal range from 1 μs to 5 ms and whose bands agree with the DHPI intermediate that we previously observed in conventional flash photolysis [2]. Noteworthy is that the optical density of the transient at 350 nm did not show any signs of decay during the temporal range 200 ns to 1.0 μs. In fact the transient absorption spectra are superimposable for the region 320–410 nm at delay times of 0.2, 0.5 and 1.0 μs i.e. an equilibrium population of DHPI is established, which decays by two dominant routes. Since the decay of DHPI does not occur until after 1 μs, its population is the same as it was at 200 ns, i.e. the quantum yield of DHPI formation is small. This behavior, together with our earlier report of the slow 1.5 ms relaxation channel for DHPI [2] is

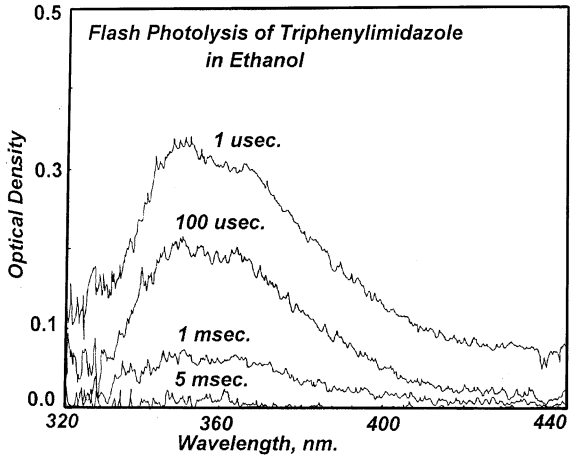


Fig. 1. Time resolved transient absorption spectra for the laser flash photolysis of 5.8×10^{-5} M triphenylimidazole in ethyl alcohol covering the range 320–440 nm (308 nm exc.). Although the spectra shown cover the submicrosecond regime, it is noteworthy that the transient absorption spectra in the region 320–410 nm. are superimposable at the smaller delay times of 0.2, 0.5 and 1.0 μs.

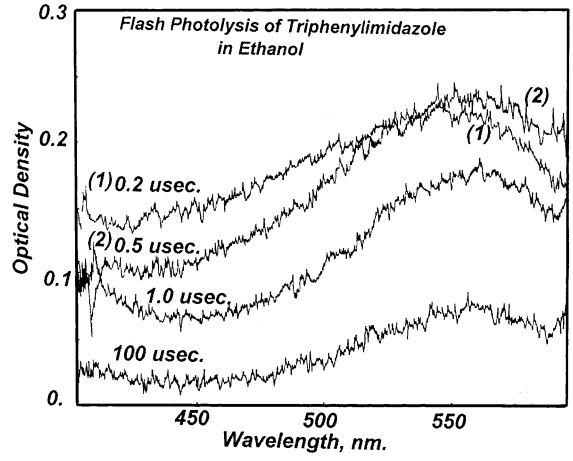


Fig. 2. Time resolved transient absorption spectra for the laser flash photolysis of 5.8×10^{-5} M triphenylimidazole in ethyl alcohol covering the range 400–600 nm (308 nm exc.).

consistent with the following two decay channels for DHPI: (i) a faster decay corresponding to DHPI → TPI, and (ii) a slower decay of DHPI → PPI. Analysis of the shorter lived component in the transient spectra at 350 nm region indicates a relaxation time of 0.3 ms, which is significantly faster than the 1.5 ms decay channel observed in conventional μs flash photolysis for the conversion of DHPI → TPI. These two kinetic processes lead to a 0.25 ms lifetime for the DHPI intermediate. We have previously shown that the photocyclization proceeds via the excited singlet, and addition of cis-piperylene does not influence the quantum yield.

There is clear evidence of a second, shorter lived transient absorption at 400–450 nm with a half-life of 0.7 μs, which is most evident in spectrum (1) of Fig. 2. The short fluorescence lifetime of the starting TPI and the photoproduct, PPI (see below) preclude this transient being a singlet state, and we have assigned this transient to the triplet state of TPI. In view of the small photochemical yield, and $\varphi_F + \varphi_T \approx 1$, i.e. the dominant relaxation mode appears to be intersystem crossing. Within 1 μs essentially all the triplets have decayed, while DHPI is longer lived, as is seen in Figs. 1 and 2. The decreasing triplet population of TPI at 450 nm is evident in the temporal range 0.2–1.0 μs, whereas the population of DHPI at 350 nm is constant during the same period.

Experiments employing two pulsed lasers, i.e. 308 nm, to excite the singlet state of TPI and 370 nm to probe transients showed increased fluorescence, which is due to absorption and fluorescence of DHPI, and PPI, since TPI does not absorb the latter wavelength. Transient DHPI fluorescence is seen at delay times of 175 ns and 1 ms, confirming that its formation occurs in the nanosecond time scale; however, it does not compete favorably with the formation of the triplet state of TPI.

Additional information regarding the mechanism of this photocyclization was obtained by fluorescence lifetime measurements. Irradiation of an argon purged solution of 2.4×10^{-6} M TPI in ethyl alcohol at 308 nm indicates a dual fluorescence, whose contribution changes as the starting TPI is converted cleanly to PPI. A summary of the fluorescence lifetime data is presented in Table 1, where it is seen that the lifetimes for TPI and PPI are constant at 1.76 and 8.21 ns, as the photolysis proceeds. The major change occurring is reflected in columns 5 and 6, which show that a decreasing TPI concentration is replaced with an increase in PPI. These data are indicative of a clean photochemical event from TPI to PPI, in

Table 1
Fluorescence lifetime data for triphenylimidazole in ethyl alcohol[a]

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	f_1[b]	f_2[b]
1.	14 453	1.77	220	8.03	0.936	0.064
2.	14 114[c]	1.74	506	8.21	0.855	0.145
3.	13 955	1.75	604	7.96	0.835	0.165
4.	13 916[d]	1.76	615	8.18	0.829	0.171
5.	13 930	1.75	660	8.33	0.816	0.184
6.	13 643	1.76	700	8.54	0.801	0.199

[a] Conc. $= 2.4 \times 10^{-6}$ M; 308 nm excitation; 380 nm fluorescence. $I_F(t) = A_1 e_1^{-t/\tau} + A_2 e_2^{-t/\tau}$.
[b] $f_1 = A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$ and $f_2 = A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$ [4].
[c] Measured at 360 nm.
[d] Measured at 410 nm.

which both molecules fluoresce. A similar behavior was observed in acetonitrile, where the corresponding lifetimes are 1.80 and 9.17 ns The fluorescence of the DHPI is not seen in these experiments, since it does not absorb the 308 nm excitation, i.e. only TPI and PPI contribute to the fluorescence. In contrast, the dual laser experiment using 308 nm to produce singlets and 370 nm to probe transients led to a significant increase in fluorescence, due to the conversion of TPI to DHPI, followed by absorption and emission of the latter.

4. Discussion

The results presented are consistent with a unimolecular photochemical process in which the DHPI intermediate is present at 100 ns, has two decay channels, with only one fifth of their population proceeding to the photoproduct, PPI. From the two relaxation modes of DHPI we have determined its lifetime to 0.25 ms. In contrast, the triplet state, absorbing in the 450 nm region, is the dominant relaxation mode of the TPI excited singlets. The triplet is evident in the first 100 ns, and its lifetime of 0.7 μs is much shorter than either of the two decay channels of DHPI. The fluorescence lifetime data support this interpretation since the values of 1.76 and 8.21 ns, assigned to TPI and PPI, respectively, remain constant, and vary only in their contributions, as the photocyclization proceeds.

In view of the TPI fluorescence lifetime of 1.76 ns and its fluorescence quantum yield of 0.19 in ethyl alcohol, it is apparent that the rate constant for the initial photocyclization step from the TPI singlet state to DHPI is $\leq 4 \times 10^8\ s^{-1}$. This result may not be surprising since AM1 calculations with MOPAC [5] for the optimized geometry of the ground state of TPI predicts the phenyl groups at positions 4 and 5 to have a torsional angle of 38° relative to the imidazole plane. The dominant radiationless decay of the excited singlet state is intersystem crossing to the triplet state in the nanosecond regime, which together with the fluorescence yield of TPI, leads to the small photochemical yield.

In summary, the flash photoexcitation of TPI shows that the DHPI intermediate is present at 100 ns, has a lifetime of 0.25 ms, and only begins to decay after 1 μs. The disappearance of the triplet state is much faster than that of DHPI. There are two major relaxation routes for DHPI: (1) a major decay channel of DHPI back to TPI with a $k_1 = 3.3 \times 10^3\ s^{-1}$ and (2) a slower decay process with $k_2 = 0.7 \times 10^2\ s^{-1}$, which we reported earlier, that accounts for the low quantum yield conversion of DHPI to the photoproduct, PPI.

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