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Photodissociation of Hexaarylbiimidazole. 1. Triplet-State Formation†

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The mechanism of photodissociation of 2-chlorohexaarylbiimidazole is studied by laser flash photolysis in organic liquids and by EPR methods in polymer and low-molecular-weight organic matrices. It is found that at low temperatures (~10 K) the ultraviolet irradiation produces a triplet hexaarylbiimidazole rather than the radicals. No triplet-state decomposition into radicals is observed, supporting the results of indirect measurements reported by other researchers. At higher temperatures, the radicals formed from the dissociation of the singlet state dominate. This is the first direct observation of the hexaarylbiimidazole triplet reported to date. The results are explained by considering the molecular structure and hexaarylbiimidazole mobility.

Introduction

Hexaarylbiimidazole (HABI, 1) was first synthesized by Hayashi and Maeda.[1] These authors reported a remarkable phototropy of this compound and conducted the first EPR experiments that proved that phototropy is stipulated by the reversible photodissociation of HABI into two triarylimidazolyl (lophyl, 2)

1   2

$$HABI \xrightarrow{h\nu} 2 \text{ lophyl}^\bullet \qquad (1)$$

$$2 \text{ lophyl}^\bullet \rightarrow HABI \qquad (2)$$
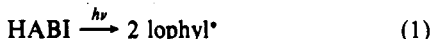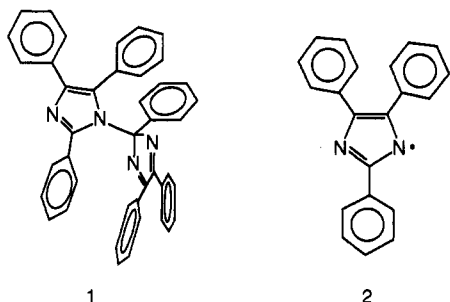
radicals according to reactions 1 and 2.[1,2]

The absorption bands of HABI lie in the UV region with λ_{max} = 278 nm in benzene, while the absorptin bands of the lophyl radical in benzene are in the visible region with λ_{max} = 351 and 574 nm. Reversible photochromism prompted investigations of the HABI photodissociation. Wilks and Willis deduced thermodynamic parameters of reactions 1 and 2 and using kinetic analysis suggested a possibility of radical trimer formation.[3,4] The solvent and temperature effects on the reaction path of (1) and (2) investigated by spectroscopic and EPR methods were reported by Prokhoda et al.[5] They observed the formation of different HABI isomers at different temperatures and thermal rearrangement of HABI isomers. Krongauz and co-workers presented an analysis of the mechanism of reactions 1 and 2 and reported the formation of a lophine trimer as well.[6–8]

The high yield of lophyl radicals in solid matrices and their low sensitivity to the presence of oxygen[4] stimulated industrial interest in the use of HABI as a photoinitiator and photosensitizer for a wide variety of imaging materials and resulted in extensive spectroscopic and electrochemical investigations of substituted HABIs.[9–15] HABI found applications in many imaging materials, most recently in photopolymers used for holographic recording where HABI is present at concentrations up to 4% dissolved in

a plasticized polymer matrix together with photosensitizing dye, monomer, and chain-transfer and terminating agent.[16] In spite of the wide use of HABI as an initiator and sensitizer, the mechanism of HABI photodissociation and the factors determining its effectiveness as a photoinitiator remain unclear. Studies of HABI photodissociation by Krongauz and co-workers in polar and nonpolar solvents at room temperature and in matrices at liquid nitrogen temperature[5–7] indicated that, in benzene solutions, reaction 1 photosensitized by singlet excited benzene at 253.7 nm occurs with a probability close to 0.5. By contrast, the decomposition of the triplet excited HABI, formed by photosensitization with triplet excited benzophenone at 365 nm, has a low probability of only 0.075. In their studies, the existence of the triplet state of HABI was deduced on the basis of spin conservation in triplet sensitization. So far, the triplet state of HABI has eluded direct detection.

Since there is a substantial industrial interest in developing new photopolymerizable composites, we report here investigation of HABI photodecomposition by optical and EPR methods over a wide temperature range. We directly observe the HABI triplet state in several low-molecular-weight organic matrices as well as in solid polymers at low temperatures. We also report our studies of transient species involved in reactions 1 and 2 by flash photolysis in a nanosecond time range, which could not be reached by the methods employed in earlier investigations.[9–13] A mechanism of

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radical formation from the excited HABI is proposed.

Experimental Section

Materials. HABI, 2-Cl–HABI, and 2,3-$(CH_3O)_2$–HABI were synthesized according to known procedures (method B, ref 9). Dichloromethane (spec), poly(vinyl acetate) (PVA), and toluene (spec pure) were purchased from Aldrich and used without further purification.

Sample Preparation. 10^{-5} M HABI solutions were used in flash photolysis experiments. All solutions were degassed by argon gas bubbling. The concentration of HABI in organic matrices used in EPR measurements varied from 10^{-3} to 10^{-5} M. All samples used in EPR experiments were degassed by the freeze–pump–thaw cycle method. The HABI concentration in poly(vinyl acetate) matrices was 3% by weight, and these samples were used without degassing.

EPR Measurements. The EPR studies were carried out on an X-band Varian E-109 spectrometer interfaced with a Macintosh II computer for data collection. The HABI samples were irradiated directly in the EPR cavity by continuous UV light of the 300-W xenon arc lamp or by the pulsed output (λ = 308 nm) of an excimer laser (Lumonics). During the experiments the samples were placed in an Air Products Heli-Tran cryostat and maintained at the desired temperature in the range from 4 to 180 K.

Optical Spectroscopic Measurements. Steady-state absorption spectra were recorded by using a Perkin-Elmer Lambda 4b spectrophotometer. The fluorescence emission spectra were collected by using a Spex Fluorolog spectrofluorimeter. All measurements were conducted at room temperature.

Flash Photolysis. Transient absorption experiments were carried out at room temperature. The 308-nm light (100 mJ/pulse) from a Lumonics excimer laser was used for excitation. The time resolution of the system was 20 ns. A pulsed xenon arc lamp was used as a probe light source. The transient absorption was recorded on a Tektronix (DSA 601) digital scope with a maximum sampling rate of 1 GHz. Data acquisition and storage was done with a Macintosh IIx minicomputer.

Results and Discussion

Optical Spectroscopy. The absorption and emission spectra of HABI have been studied.[5,9,10] Our measurements of the absorption and fluorescence emission spectra (excited at 308 nm) recorded in dichloromethane solution of 2-Cl–HABI are in agreeement with those reported in the literature. 2-Cl–HABI strongly absorbs in the UV region with the major absorption maximum at 270 nm, and exhibits maximum fluorescence emission at 375 nm. These data indicate that the energy difference between the ground and first singlet excited states of 2-Cl–HABI is close to 3 eV.

When HABI dissociates into lophyl radicals, the originally colorless solution becomes red. Correspondingly, the transient absorption spectrum recorded in time from 0 to 1.0 ms after pulsed irradiation of a dichloromethane solution of 2-Cl–HABI by 308-nm light shows strong absorption in the visible region corresponding to lophyl radicals. The recorded transient absorption maxima are at 365 and 550 nm (Figure 1), in agreement with previously reported data.[5–13] The data show a relatively high stability of lophyl radicals even in solutions at room temperature: after 1 ms, more than $^2/_3$ of the generated radicals are still present. The rate constants for the reaction of lophyl recombination reported in the literature[9] are also relatively low, ranging (depending on the solvent) from ~300 to ~800 (L mol^{-1} sec^{-1}). The reason for such slow recombination of lophyl radicals is interesting and is currently being investigated.

Structure. Previous optical spectroscopy studies suggest that the lophyl radical is nearly planar with a delocalized excess electron. However, the 2-Cl–HABI molecule must be nonplanar, and it cannot have a π-electron system delocalized over the whole molecule. Indeed, if 2-Cl–HABI were planar, the electrons would be delocalized in a larger π system than in lophyl, and it would absorb light of a longer wavelength than the lophyl radical. We conducted calculations of the most stable HABI structure by the Alchemy minimizer in a Macintosh II computer. These
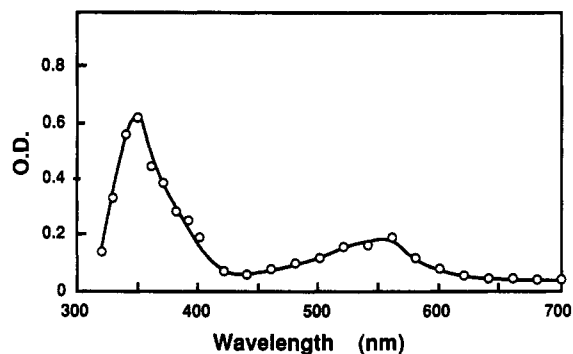

Figure 1. Transient absorption of the lophyl radical formed from the dissociation of 2-Cl–HABI (10^{-5} M) in CH_2Cl_2 at room temperature by 308-nm light.

straightforward computations yield a nonplanar, stable HABI structure 1, consistent with the conclusions based on the optical studies.

Structure 1 illustrates that the two imidazolyl rings are twisted almost 90 degrees relative to each other. Due to the repulsion between the crowded aromatic protons no two aromatic rings lie in the same plane. The C–N bond in HABI must be rather weak. We are not aware of any quantitative measurements of its bond dissociation energy. The enthalpy of lophyl radical formation in a variety of solutions is, indeed, rather low and is close to 19 kcal/mol.[4]

Triplet State of 2-Cl–HABI. According to the literature,[5–9] the dissociation of the HABI into lophyl radicals occurs from the singlet excited state while the dissociation of the triplet excited states has a very low probability. These conclusions were derived by an indirect method of measuring the lophyl radical quantum yield. However, the low quantum yield of lophyl radicals observed in the photosensitization of HABI by triplet excited benzophenone at 365 nm might also be attributed to the low efficiency of the triplet energy transfer. To substantiate these conclusions, it is necessary to observe directly the formation and decay of the HABI triplet state and to study its relationship with the lophyl radical formation kinetics. This task cannot be accomplished by optical methods alone, since the triplet state of a dimer and the radicals formed by the dissociation of the same dimer often have very similar absorption bands. Indeed, our attempts to observe separate or distinct transient absorption of triplet HABI were not successful. Thus, we combine optical and EPR methods to study the problem, since the EPR spectra of triplet states can be easily characterized.[17]

Since our studies were carried out in a poly(vinyl acetate) (PVA) matrix, we characterized some of the PVA properties. The pure PVA matrix irradiated by UV light gave at low temperatures a quartet EPR spectrum with a hyperfine splitting, $a(3H)$ = 2.3 mT (23.0 G) and a g factor of 2.0023, which can be confidently assigned to the methyl radical. The methyl radical is apparently produced as a result of photodegradation of the PVA matrix under the influence of UV irradiation. Although the UV photodegradation of PVA has been studied previously,[18] methyl radical formation has not been previously reported. The mechanism of reported methane gas formation was not analyzed in detail. Moreover, the possible matrix decomposition was ignored in the earlier work on the mechanism of image formation in polymers.[15,19–21] In our studies we had to ensure that photodegradation of the matrix does not interfere with the photodissociation of HABI.

When the PVA matrix containing 2-Cl–HABI (3% by weight) was irradiated by the UV light at 8 K, the observed EPR spectrum

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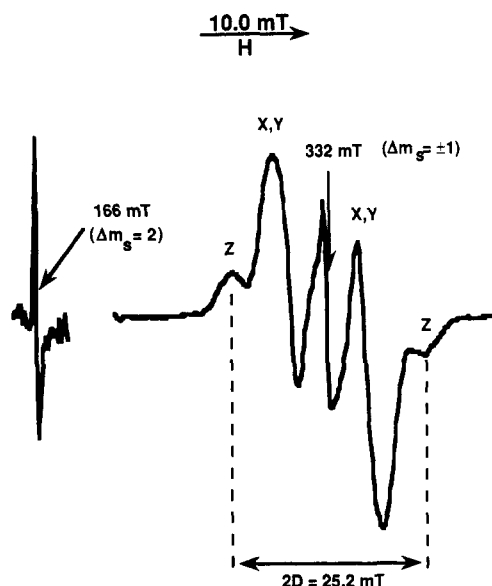
Figure 2. EPR spectrum observed after UV irradiation of a 2-Cl–HABI (3% by weight)/poly(vinyl acetate) system at 8 K showing features assigned to the triplet state of the 2-Cl–HABI molecule.

(Figure 2) differed greatly from that of methyl radical. This spectrum contains two main features. One feature is a 20 mT (200 G) wide quartet, centered at 332 mT (3320 G). The other feature is a sharp, singlet peak centered at 166 mT (1660 G). The spectrum of Figure 2 is assigned to the triplet state[17] of 2-Cl–HABI. Methyl radical signals were too weak to be detected in the PVA matrix containing 2-Cl–HABI. The optical density of 3% 2-Cl–HABI solution in PVA is nearly ten times higher than that of the neat PVA matrix. Therefore, the incident light is mostly absorbed by 2-Cl–HABI, forming strong EPR signals of the 2-Cl–HABI triplet state.

The signals observed on the EPR spectrum of 2-Cl–HABI in the PVA matrix around 332 mT (3320 G) (Figure 2) can be attributed to the $\Delta m_s = \pm 1$ transition, (m_s is the spin quantum number) while the singlet signal observed at half-field is clearly due to the $\Delta m_s = 2$ transition. The triplet-state species gives rise to zero-field splitting resulting from the dipole–dipole interaction of the two interacting unpaired electrons. The parameters characterizing the zero-field splitting in triplet-state EPR studies are D and E.[22] The values of these parameters are related to the distance between unpaired electrons and to the symmetry of the molecule and can be deduced from the spectrum.[23,24] The spectrum for a randomly oriented triplet species usually consists of three pairs of peaks arising from the transitions corresponding to various orientations of the molecule in the external magnetic field. The $\Delta m_s = \pm 1$ transition observed for 2-Cl–HABI in the PVA matrix consists of two pairs of signals. The third pair of peaks is not observed apparently because of the broad x and y features and a very small E value; thus, the x and y features coincide. In the CH_2Cl_2 matrix, the triplet spectrum of 2-Cl–HABI is better resolved showing three pairs of signals at 6 K. The spacing of the z features provides the value of the zero-field splitting $2D$.

By use of this value, the estimate of the mean distance r between the two unpaired electrons is computed by eq 1[22,23] where r is in

$$r = (2.78 \times 10^9/D)^{1/3} \qquad (1)$$

picometers (pm) and D is in milliteslas. For 2-Cl–HABI, r is calculated to be 604 pm (6.04 Å). This value is comparable to the distance, r_c, between the centers of the two phenyl π systems
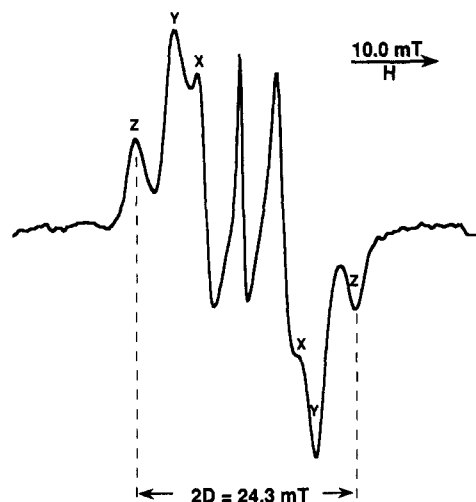

Figure 3. EPR spectrum observed after 308-nm laser irradiation of a HABI/toluene system at 6 K, showing features assigned to the triplet state of the parent HABI.

TABLE I: Zero Field Splittings, D, and Mean Separation, r, of the Two Unpaired Electrons in Triplet HABIs

triplet HABIs	solvent	T, K	D, mT	r, pm	method of generation
2-Cl–HABI	PVA	8	12.6	604	xenon UV lamp
2-Cl–HABI	CH_2Cl_2	6	12.3	609	xenon UV lamp
2,3-dimethoxy–HABI	CH_2Cl_2	5	13.2	594	xenon UV lamp
HABI	toluene	5	12.2	611	308-nm laser

on one side of the molecule. This is reasonable, since it was shown earlier that the two phenyl rings are not in the same plane so that the unpaired electrons are not delocalized.

The triplet state of the unsubstituted HABI can also be generated in the toluene matrix by irradiation of the frozen solution by 308-nm laser light (Figure 3). In unsubstituted HABI the mean distance between the two unpaired electrons was also around 600 pm (6.00 Å). The $2D$ and r values for the triplet state of 2-Cl–HABI and 2,3-dimethoxy–HABI in CH_2Cl_2 as well as those for parent HABI are listed in Table I. These data indicate that $2D$ and r do not depend on the solvent and the substituent groups on HABI.

We found that $2D$ and r values for 2-Cl–HABI triplets do not depend on temperature. Temperature independence of D and r values suggests that we are not observing the triplet of the radical pair structure formed from two lophyl radicals, since the mean distance between the unpaired electrons could be temperature dependent in the absence of chemical bonding.

The results presented thus far suggest that we are observing the triplet excited state of the HABI molecule. A discussion of all the alternative explanations is presented below.

Triplet-State Decay. UV irradiation of 2-Cl–HABI in a PVA matrix at low temperature (≈ 6 K) gives rise to the triplet state exclusively. The EPR signal due to the lophyl radical, which has a peak width of 0.9 mT (9 G) and $g = 2.0023$,[25] is very weak. When the sample containing the triplet HABI molecules is warmed to 40 K, the triplet EPR signals start to decay. The rate of signal decay increases at higher temperatures. At 130 K only the residual triplet signal can be observed. We do not observe any appearance of the lophyl radical signal in the center of the spectrum with the decay of the HABI triplet. The EPR signal of the lophyl radical is stable below 200 K.[3–8] If triplet HABI would dissociate into two lophyl radicals, some of the radicals would diffuse out of polymer cages at higher temperatures, and the growth of the lophyl EPR signal would be detected. Thus, the absence of the lophyl radical signal indicates that the decay pathways of the triplet state do not include dissociation into lophyl radicals. This result supports

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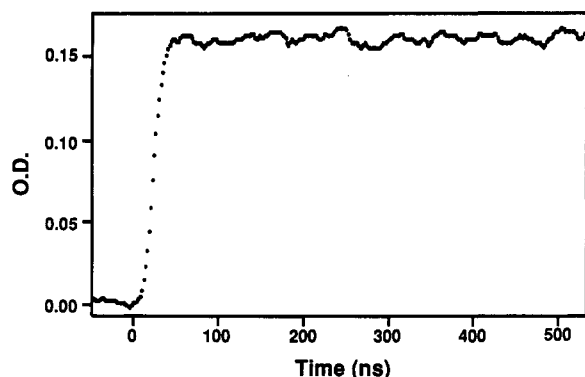
Figure 4. Transient absorption curve recorded at 550 nm corresponding to the absorption maximum of lophyl radicals after irradiation of a CH_2Cl_2 solution containing 10^{-5} M 2-Cl-HABI at room temperature by 308-nm light.

the previous finding[5] that HABI in its triplet state has low probability of dissociation into lophyl radicals. In other words, the lophyl radicals are formed exclusively from the dissociation of HABI from the excited singlet state.

Lophyl Radical Formation. Complementary information is obtained by studying lophyl radical formation in dichloromethane solution at room temperature of 2-Cl-HABI irradiated by 308-nm laser light. The accumulation of lophyl radicals is monitored in the flash photolysis experiment as a function of time by recording the change in the optical density of the solution at the wavelength of 550 nm corresponding to the absorption maximum of lophyl radicals (Figure 4). The concentration of lophyl radicals increases sharply in the first 20 to 40 ns after the exposure pulse. Then, the signal remains constant until about 800 ns. After 800 ns the optical density at 550 nm decreases. The observed behavior indicates that the 2-Cl-HABI dissociation from the singlet excited state is completely relatively fast when radical diffusion out of the cage is possible. At the same time, the slow rate of radical recombination, even in solution at room temperature, confirms our assumptions based on the simple model computations that substantial structural changes have to take place for planar lophyl radicals to recombine into a highly asymmetric HABI molecule. This observation again supports our conclusion that in a solid matrix (as least at higher temperature) the triplet state of HABI is not formed by radical recombination. This conclusion is supported by our EPR data.

We observed that the triplet HABI molecules have a short lifetime at temperatures above 40 K even in the matrix, so that the experiments conducted at 77 K[5-8] could not detect it. At room temperature, the irradiation of 2-Cl-HABI in a PVA matrix (3% by wt) yields only lophyl radicals. The observed EPR spectrum has a peak-to-peak width of 0.9 mT (9 G) and a g factor of 2.0023, which are in good agreement with the published data.[25] At room temperature, the lophyl radical is not stable, even in the PVA matrix. However, it has sufficiently long lifetime so that it can be cooled down to 4 K. Upon cooling to the temperature at which the triplet HABI should be observed, the triplet of HABI is not formed. If this sample containing lophyl radicals is again warmed from 4 K, the EPR signal has no appreciable decay until the temperature exceeds 200 K. The high stability of the lophyl radical in a matrix is not surprising considering the severity of steric restrictions towards recombination. The slow diffusion in polymer matrices[20,21] and low radical concentration also contribute to the low recombination rate. Even smaller radicals in polymer matrices have substantial lifetimes in the absence of oxygen.[26] It is not surprising that lophyl radicals, which do not recombine in the matrix at low temperatures, are unable to form a triplet excited state of HABI.

Mechanism of HABI Triplet-State and Radical Formation. We mentioned above that UV irradiation of 2-Cl-HABI in PVA and
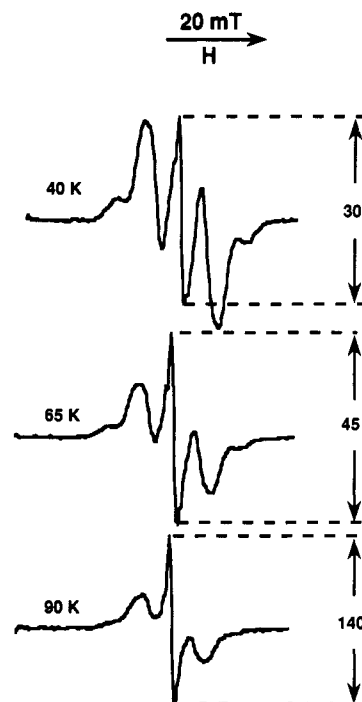

Figure 5. EPR spectra observed after UV irradiation of a 2-Cl-HABI (3% by weight)/poly(vinyl acetate) system at (a) 40, (b) 65, and (c) 90 K. The numbers at the right indicate relative intensities of the lophyl radical.

other matrices generates exclusively the triplet state at low temperatures (<6 K) while producing only lophyl radicals at room temperature. At intermediate temperatures, UV irradiation of the 2-Cl-HABI/PVA system produces triplet-state species and lophyl radicals as is clear from the EPR spectra of the irradiated system recorded at three different temperatures (Figure 5), where the spectra show coexistence of the triplet state and the lophyl radical. Noticeably, the ratio of the concentration of the formed radicals to that of the triplet state species increases as temperature increases. We discuss the conceivable pathways for triplet and radical formation, and we address the question of whether encounters of two lophyl radicals can produce a triplet state of HABI.

We have mentioned the literature data, and our finding that lophyl radicals do not recombine upon their rewarming to 200 K indicates that the long-range translational diffusion of these species is very slow. The lophyl radical is simply too large. Indeed, the long-range migration of molecular species equal in size to lophyl radicals occurs in polymer matrices with diffusion coefficients of the order of only 10^{-10} to 10^{-13} cm^2/sec.[27,28]　(In comparison, that for water is close to 10^{-5} cm^2/sec.) The finding that recombination of the lophyl radicals is relatively slow, even in liquid, indicates steric factors in addition to diffusional restriction to recombination. This is supported by the modeling of spatial structures of HABI and lophyl radicals presented above: during dissociation newly formed radicals have to become planar to have stable π-electron structure, while the recombination of these radicals requires rotation of phenyl substituents to form a "porcupine-like" HABI molecule. It appears that the rates of rotational motion or wagging vibrations are determining factors in the kinetics of reactions 1 and 2.

Such considerations show that gross mass transport should not play an important part in determining the kinetics of reactions 1 and 2. However, we believe that the observed effects can be correlated with the other modes of lophyl motion. At high temperatures, the excited HABI molecule can rotationally and vibrationally reorganize to split into two planar lophyl radicals. The planar radicals can shift relative to each other, further reducing

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SCHEME I
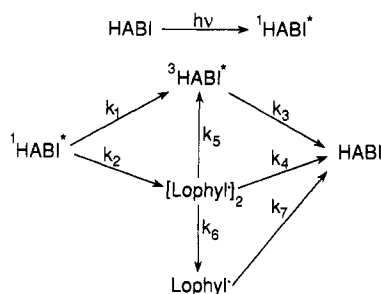
the possibility of the recombination. Thus, the equilibrium is shifted toward radical formation. At lower temperatures, especially below 90 K, rotational diffusion of the lophyl radical or reorientation of its phenyl groups within the cage becomes more difficult. Thus, the HABI molecule, excited by absorbed light, has more difficulty in dissipating the absorbed energy by dissociation with concurrent reorientation, and intersystem crossing into the triplet excited state provides an alternative stabilization path.

Now let us consider whether the direct recombination of lophyl radicals into triplet HABI can also be a possible reaction path. The radicals in the cage should originally have singlet spin multiplicity since they are produced via the singlet excited state, and hyperfine interactions can induce the $S \rightarrow T_0$ transitions (in the magnetic field of the EPR spectrometer). However, this singlet radical pair could undergo fast recombination, requiring a high rate of intersystem crossing in the radicals to give rise to a triplet radical pair. So radical recombination is not a very likely path for forming triplet HABI at higher temperature. Considering the rate of rotational diffusion of phenyl groups in solution or in a higher temperature polymer matrix,[29] one would expect the singlet radical pair lifetime to be shorter than a few nsec. On the other hand, the formation of the triplet state as a result of recombination of *unseparated* radicals at low temperatures cannot be ruled out by the above considerations, but the direct formation of triplet by $S \rightarrow T$ intersystem crossing prior to HABI photodissociation is a more likely path because we know that phosphorescence in most cases is observable only in solid solutions.[30] Also, data on the lifetime of fluorescent probes in a polymer matrix[31] support direct singlet–triplet interconversion of excited HABI at lower temperatures. It is known that decreasing the rate of rotational and vibrational relaxation increases the singlet lifetime.[29,30] In the present case it also prevents the molecular rearrangements required for HABI dissociation. Thus, both singlet lifetime increases and fast dissociation of HABI is restricted, allowing the HABI excited singlet state to exist longer. Therefore, slower S $\rightarrow$ T interconversion has a chance to occur. That is the most likely explanation for the observed behavior. Overall the HABI dissociation scheme can be summarized as shown in Scheme I.

Summarizing the above discourse, we can conclude that the triplet state forms only due to severe restrictions of vibrational and rotational rearrangements in polymer matrices at low temperatures. The behavior is similar to that observed for low-temperature photoisomerization of the spiropyran/merocyanine system, which exhibits factor of 100–400 slower rate of spiropyran ring opening in a poly(methyl methacrylate) film than in solvent.[31] Similarly, the restriction of rotation of phenyl groups decreases the rate of *trans-/cis*-stilbene photoisomerization in polymers.[31] The formation of the HABI triplet in low-temperature matrices is another example of hindered photoinduced rearrangement in the matrix.

The HABI triplet state has not been observed and studied previously, therefore the rate constants of intersystem crossing, k_1, radical recombination to the triplet state in a cage, k_5, and triplet state decay, k_3, have not been measured. Surprisingly, even the rate of singlet state dissociation, k_2, is not known. Only the rate of lophyl radical recombination in solution, k_4, has been examined.[3–9] Even straightforward studies[3–8] show deviation of the recombination rate from second-order reaction kinetics, indicating the complexity of the observed processes.

Conclusion

We have investigated the mechanism of the primary photochemical transformations hexaarylbiimidazole undergoes upon the absorption of UV light.

The dissociation of HABI into lophyl radicals and the reverse reaction of lophyl radical recombination are accompanied by the rotation of phenyl substituents. The experiments were carried out in poly(vinyl acetate) and other organic matrices at extremely low temperatures. Under these conditions, the triplet state of HABI and some substituted HABIs were directly observed. We have observed that the dissociation of HABI occurs via the singlet excited state. These findings are in accord with the indirect evidence reported by other researchers.[5–8] The existence of the triplet state exclusively at low temperatures provides the possibility of using HABI photoexcitation as a probe for matrix rigidity and polymer free volume.

We have also observed a very slow recombination of lophyl radicals in the polymer matrix. The long lifetime of these radicals explains the efficiency of HABI as a photoinitiator in matrix polymerization.

There has been little work done in recent years on the properties of the HABI molecule and the mechanism of its reactions. Lophyl radicals react via electron- or proton-transfer reactions with various compounds,[32] and as with many other photochromic reactions, reactions 1 and 2 are affected by magnetic fields.[33] Currently, we are continuing work on the HABI photodissociation mechanism.

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