

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231401764>

Photodissociation of Hexaarylbiimidazole. Part 2. Direct and Sensitized Dissociation

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · JUNE 1992

Impact Factor: 2.78 · DOI: 10.1021/j100180a040

CITATIONS

45

READS

14

3 AUTHORS, INCLUDING:



Vadim Krongauz

Baxter International Inc.

76 PUBLICATIONS 529 CITATIONS

SEE PROFILE

Photodissociation of hexaarylbiimidazole. 2. Direct and sensitized dissociation

An Dong Liu, Alexander D. Trifunac, and Vadim V. Krongauz

J. Phys. Chem., **1992**, 96 (1), 207-211 • DOI: 10.1021/j100180a040 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on April 10, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/j100180a040> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

The Journal of Physical Chemistry is published by the American Chemical Society,
1155 Sixteenth Street N.W., Washington, DC 20036

Photodissociation of Hexaarylbiimidazole. 2. Direct and Sensitized Dissociation[†]

An-Dong Liu, Alexander D. Trifunac,*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

and Vadim V. Krongauz*

Imaging Research and Development, Experimental Station Laboratory, E. I. du Pont de Nemours and Company, P.O. Box 80352, Wilmington, Delaware 19880-0352 (Received: May 13, 1991; In Final Form: July 26, 1991)

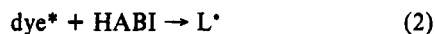
Photodissociation of a widely used photopolymerization initiator, 2-chlorohexaarylbiimidazole (*o*-Cl-HABI), is studied in dichloromethane solution in the absence and presence of the visible light photosensitizing dye, 2,5-bis[(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-1-yl) methylene]cyclopentanone (JAW). Laser flash photolysis at 480 nm is employed. In the absence of JAW, the *o*-Cl-HABI dissociates into triarylimidazolyl radicals (L[•]). In the presence of JAW, an increase in L[•] formation is observed. The mechanism of this photosensitization of dissociation is explored. It is concluded that this increase occurs by the dissociation of the *o*-Cl-HABI radical anion formed by electron transfer from the excited singlet state of JAW to *o*-Cl-HABI. The observed formation of L[•] radicals exhibits a linear dependence on *o*-Cl-HABI concentration. The rate constant of electron transfer obtained from this dependence is equal to $(2.2 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. No reaction between the excited triplet state of JAW and *o*-Cl-HABI is found.

Introduction

Hexaarylbiimidazole (HABI or Lophine dimer, L₂) and its derivatives, especially, 2-chlorohexaarylbiimidazole (*o*-Cl-HABI or 2-Cl-HABI) have been used as free radical initiators in photopolymer imaging for more than two decades.^{1–3} A variety of the HABI-based systems are commercially available. Most recently the holographic photopolymers were added to the list of materials utilizing *o*-Cl-HABI.³ The application of HABI is based on well-established properties of thermal or UV-photolytic dissociation. The homolysis of HABI produces long-lived 2,4,5-triarylimidazolyl radicals (lophyl radicals, L[•]).^{1–4}

With the recent development of laser technology and electronic imaging, the use of inexpensive long-wavelength-emitting lasers is increasing. Therefore, the development of the imaging materials sensitive to visible and infrared light has become important. The properties of already available materials are being reevaluated as well. Photopolymers based on *o*-Cl-HABI provide reliable, oxygen insensitive, thin coatings for imaging purposes. Substantial economic advantages can be realized, if these materials could be imaged in the longer wavelength region. *o*-Cl-HABI has a strong absorption band in the UV region with $\lambda_{\text{max}} = 265 \text{ nm}$ and $\epsilon_{265 \text{ nm}} = 2.79 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.⁴ In addition, it has a broad weak absorption band in the visible region.² This weak and broad visible absorption band has been neglected in previous studies, and the function of the visible light on the direct dissociation of HABI was not examined.

Aromatic aminoketones have been employed as visible sensitizers of *o*-Cl-HABI.^{3,5–7} This photosensitization was found empirically, and the mechanism of the process was not specified. The following sensitization scheme of L[•] formation was suggested by Smothers et al.:³



In this kinetic scheme, the dye sensitizer absorbs visible light and forms an excited state. The reaction between this excited state and the ground-state HABI produces the L[•] radical. Reaction 2 can occur by energy transfer or an electron- or proton-transfer process or can be a chemical reaction between dye excited state and HABI. The only work where the photosensitization of HABI by energy transfer was experimentally demonstrated was con-

ducted with the UV-light excitation, using a different class of sensitizers.⁸ The practical importance of the development of photopolymers sensitive to visible and infrared light and lack of conclusive experimental data on the existing JAW-HABI visible light sensitive material prompted us to undertake the studies presented below. We attempted to determine whether the functional excited state of the dye is a singlet or a triplet and whether HABI sensitization from this excited state or from some type of a ground-state redox reaction occurs. Finally, we wanted to determine whether this sensitization is based on energy, electron, or proton transfer. The study of the direct and dye- (JAW) sensitized dissociation of *o*-Cl-HABI by the 480-nm laser flash photolysis is presented below.

Experimental Section

Materials and Sample Preparation. *o*-Cl-HABI and the dye sensitizer JAW were synthesized according to known procedures.⁴ Dichloromethane (HPLC or spectrophotometric grade, Aldrich and Baxter) was used without further purification. The concentration of *o*-Cl-HABI in dichloromethane varied from 10^{–3} to 0.1 M, while the concentration of JAW was always 10^{–5} M. Argon and oxygen (UHP grade) were obtained from Matheson and Scott Specialty Gases. All experiments were carried out at room temperature.

Laser Flash Photolysis. The excitation source used in this experiment was a Lambda Physik FL 3002 dye laser, pumped by a Questek 2440 excimer laser. The duration of the dye laser pulse was ~20 ns, and the maximum output energy was 20 mJ/pulse. To avoid two photon processes, 0.3–1.0 mJ/pulse was used in most experiments. A kinetic spectrophotometer (Figure 1) was used to monitor the transient absorption and emission. This spectrophotometer consisted of a pulsed 70-W Xe-arc lamp, a SPEX

(1) Cohen, A. B.; Walker, P. In *Imaging Processes and Materials*; Sturge, J., Walworth, V., Shepp, A., Eds.; Van Nostrand Reinhold: New York, 1989; Chapter 7.

(2) Delzenne, G. A. *Adv. Photochem.* **1979**, *11*, 1.

(3) Smothers, W. K.; Monre, R. M.; Weber, A. M.; Keys, D. E. *Practical Holography IV. Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1212*, 20.

(4) Cescon, L. A.; Coraor, G. R.; Dessauer, R.; Silversmith, E. F.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2262.

(5) Dueber, T. E. U.S. Patent 4,162,162, 1979.

(6) Dueber, T. E.; et al. U.S. Patent 4,454,218, 1984.

(7) Dueber, T. E.; et al. U.S. Patent 4,535,052, 1985.

(8) Prokhada, A. L.; Krongauz, V. A. *Khim. Vys. Energ.* **1969**, *3*(6), 495–501; **1970**, *4*(2), 176.

[†] Work at Argonne performed under Contract No. 85264 with Du Pont and under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract No. W-31-109-ENG-38.

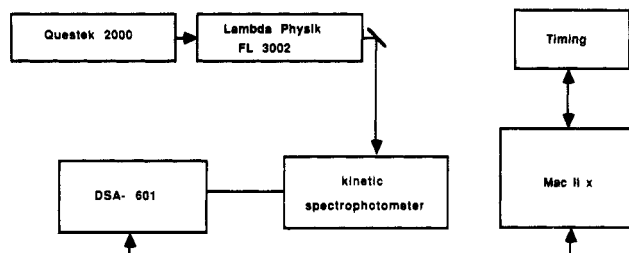


Figure 1. Block diagram of the flash photolysis apparatus.

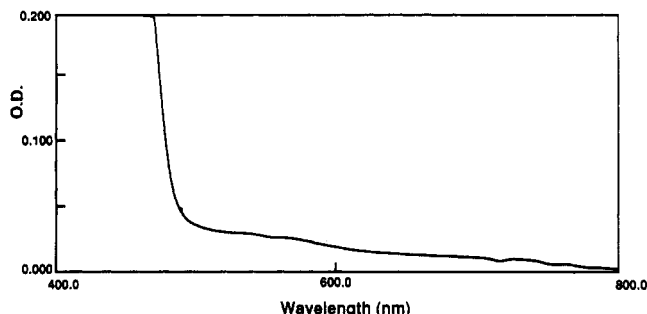


Figure 2. Absorption spectrum of *o*-Cl-HABI (0.1 M) in dichloromethane. Note a weak and broad absorption of *o*-Cl-HABI in the visible region.

minimate monochromator, and an Hamamatsu R1913 photomultiplier tube. A Tektronix digitizing signal analyzer, DSA 601, with the sampling rate of up to 10^9 sample/s, was used to record transient signals. The bandwidth of the input amplifier of the DSA was set at 100 MHz for this experiment. The data acquisition was controlled by a National Instruments's lab VIEW program installed on a Macintosh IIX computer. Between 4 and 20 laser pulses were used for signal averaging.

Steady-State Measurements. The steady-state studies were carried out on a Perkin-Elmer Lambda 4B UV/vis spectrophotometer and a SPEX Fluorolog 2 spectrofluorometer.

Actinometry. Relative intensity of the incident laser beam was monitored by a photodiode (FND 100, made by EG & G) connected to a pulse integrator circuit. The photodiode was calibrated by a $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ chemical actinometer.⁹ The actinometer was an aqueous solution containing 5×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$ and 2×10^{-2} M methyl viologen (MV^{2+}). Quantum yields for production of MV^{2+} , $\Phi = 0.25$, and $\epsilon_{600\text{nm}} = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, were assumed.⁹ These measurements showed that the incident photon concentration used in these experiments was in the range $(0.3\text{--}1.5) \times 10^{-4}$ einsteins/pulse.

Results and Discussion

Direct *o*-Cl-HABI Dissociation at 480 nm. Like many aromatic molecules, *o*-Cl-HABI absorbs strongly in the UV region. However, it also has a weak absorption "tail" extending into the visible region of the spectrum.² The absorption spectrum of a 0.1 M solution of *o*-Cl-HABI in dichloromethane is presented in Figure 2. The extinction coefficient of *o*-Cl-HABI at 480 nm determined from this spectrum is $0.86 \text{ M}^{-1} \text{ cm}^{-1}$. Although this value is small, the direct photodissociation of *o*-Cl-HABI by 480-nm laser irradiation was observed. The transient absorption spectrum recorded $1 \mu\text{s}$ after 480-nm laser irradiation of a 0.1 M *o*-Cl-HABI solution is shown in Figure 3. The absorption around 550 nm can be attributed to the L^{\bullet} radical formed by the dissociation of *o*-Cl-HABI.^{4,8,10} The time evolution of the absorbance at 550 nm is presented in the insert in Figure 3. The fast formation and slow decay of this absorption are also characteristic of the L^{\bullet} radical.¹⁰ The experiments conducted at varying laser intensities demonstrate that the concentration of the

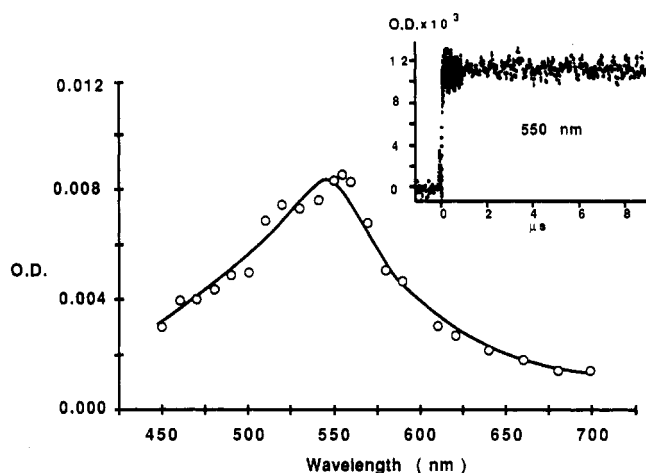


Figure 3. Transient absorption spectrum observed $1 \mu\text{s}$ after the 480-nm laser irradiation of a 0.1 M *o*-Cl-HABI solution in dichloromethane. The insert is the time profile of the absorption at 550 nm due to the lophyl radical.

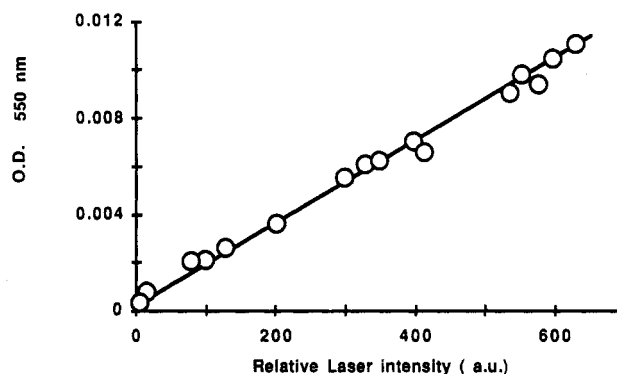
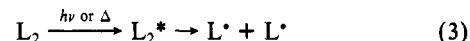


Figure 4. Plot showing the linear increase of OD at 550 nm as the relative intensity of the 480-nm laser pulse increases. The ODs were recorded $1 \mu\text{s}$ after the 480-nm laser irradiation of a 0.1 M *o*-Cl-HABI solution in dichloromethane.

lophyl radicals increases linearly with the laser intensity (Figure 4). This linear dependence indicates that under our experimental conditions (480-nm laser excitation and laser intensity $< 5 \times 10^{17}$ photons/ cm^2) the dissociation of *o*-Cl-HABI is a one-photon process. This finding is consistent with a simple homolysis of *o*-Cl-HABI (L_2).^{4,8}



Here L_2^* represents the electronically excited or thermally excited states of L_2 . The quantum yield of the L^{\bullet} radical ($\Phi_{(\text{L}^{\bullet})}$) by direct dissociation is determined as 1.2 ± 0.24 (i.e. the quantum yield of homolysis of HABI molecule is 0.6 ± 0.12), measured at concentrations of *o*-Cl-HABI from 0.01 to 0.1 M in dichloromethane. To obtain the quantum yield, the extinction coefficient of the L^{\bullet} radical ($\epsilon_{(\text{L}^{\bullet})}$) at 550 nm is taken as $2800 \text{ M}^{-1} \text{ cm}^{-1}$.⁴ The error limit of $\Phi_{(\text{L}^{\bullet})}$ was obtained by assuming the sum of the errors of the actinometry ($\pm 10\%$) and that of the transient absorption measurements ($\pm 10\%$ at low optical density). It is not clear at this stage whether the L_2^* formed by 480-nm laser irradiation is in a thermally excited state or an electronically excited state. This is related to the lack of knowledge about the absorption tail of *o*-Cl-HABI in the visible region. One possible explanation is that the observed homolysis of HABI may proceed through the thermal dissociation activated by the visible laser irradiation. Clearly, more work is needed to reveal the details of this direct dissociation of HABI by visible excitation.

Photosensitizer (JAW) Flash Photolysis. In order to understand the sensitized dissociation of *o*-Cl-HABI by the visible dye sensitizer JAW, the properties of the dye were studied by steady-state and flash photolysis experiments. The absorption spectrum of JAW in dichloromethane (dielectric constant $\epsilon = 8.93 \text{ M}^{-1} \text{ cm}^{-1}$)

(9) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.

(10) Qin, X.-Z.; Liu, A.-D.; Trifunac, A. D.; Krongauz, V. V. *J. Phys. Chem.* **1991**, *95*, 5822.

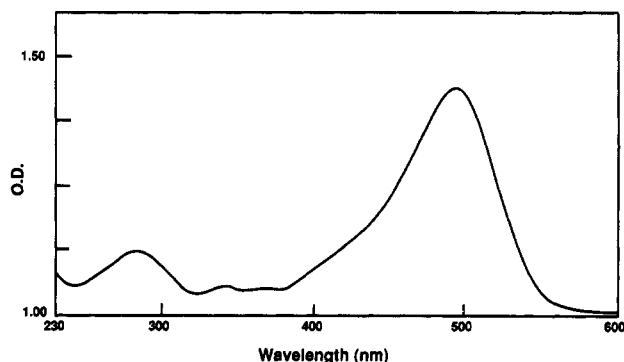


Figure 5. Absorption spectrum of JAW in dichloromethane.

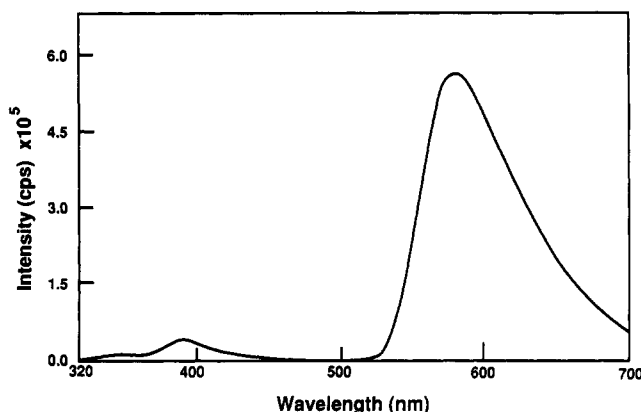


Figure 6. Fluorescence spectrum of JAW in dichloromethane.

displays a strong broad band with a peak at 497 nm (Figure 5). Another absorption band appears around 280 nm. The 497-nm peak exhibits a red shift with an increase in solvent polarity (from a very weak absorption at 450 nm in cyclohexane ($\epsilon = 2.02 \text{ M}^{-1} \text{ cm}^{-1}$) to a strong absorption at 520 nm in methanol ($\epsilon = 32.63 \text{ M}^{-1} \text{ cm}^{-1}$)). The 280-nm absorption band shows a small red shift. The absorption band around 497 nm in the dichloromethane solution is assigned to the charge-transfer (CT) transition. The band at 280 nm is assigned to the $\pi-\pi^*$ transition as observed in many aromatic compounds. The fluorescence spectrum of JAW in dichloromethane is presented in Figure 6. The strong emission (peak at 578 nm in dichloromethane) also has a red shift (from 500 nm in cyclohexane to 680 nm in methanol) and is clearly due to the CT state. The quantum yield of the fluorescence is 0.21 obtained by comparison to the standard of 9,10-diphenyl anthracene.¹¹

The 480-nm laser flash excitation of JAW in dichloromethane leads to the formation of transient species evident in the transient absorption spectrum (Figure 7). The spectrum shows a strong absorption with a peak at 830 nm along with broad weak bands in the spectral region of 300–800 nm. In the argon-saturated solution, the decay kinetics of the 830-nm absorption is predominantly first order. The half-life of this decaying absorption is 3.6 μs . The time profile at 830 nm is shown in the right insert in Figure 7. The least-squares fit to the first-order kinetics gives $k = 2.76 \times 10^5 \text{ s}^{-1}$. Figure 7 also shows a bleaching of the ground state in the 500-nm band. In the left insert, the recovery kinetics is presented. The least-squares fit gives an almost identical first-order rate constant, $k = 2.85 \times 10^5 \text{ s}^{-1}$, indicating that the decay of the 830-nm band and the recovery of the 500-nm band of the ground state are closely related. Furthermore, it was found that oxygen can strongly quench the absorption at 830 nm (in oxygen-saturated solutions, transient decay was first order with $k = 2.07 \times 10^7 \text{ s}^{-1}$). This allows assignment of the 830-nm band to the triplet-triplet absorption of JAW. Additional support for this assignment came from Shvedova and co-worker's observa-

tions.¹² In laser flash photolysis studies of several ketocyanine dyes which have similar structures with JAW, they observed similar transient absorption species in the visible region. Quenching of this transient species by oxygen and the energy transfer from this species to the triplet energy acceptor allowed this absorption to be assigned the dye triplet.¹² The extinction coefficient of the triplet-triplet absorption of JAW in dichloromethane at 830 nm was obtained as $2.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ by using the singlet depletion method,¹³ and the quantum yield of the intersystem crossing was calculated to be 0.33.

The 480-nm Sensitized Dissociation of *o*-Cl-HABI. Having examined *o*-Cl-HABI and JAW separately, we studied the 480-nm laser photolysis of dichloromethane solutions containing both JAW (10^{-5} M) and *o*-Cl-HABI (10^{-3} – 10^{-1} M). In order to avoid complications due to the dark redox reaction of HABI with JAW in concentrated solutions, all solutions were made fresh and mixed in a darkroom just before the laser exposure. Absorption spectra of freshly mixed solutions were found to be exactly the same as combinations of the absorption spectra of JAW and *o*-Cl-HABI taken separately. No shift of the JAW absorption maximum was observed. This indicated that there was no formation of the JAW-HABI complex in the ground state in the concentration range used. Upon 480-nm laser exposure, several transient species were observed. Figure 8 shows the transient absorption spectra recorded in such a mixed solution. The absorption spectra recorded 100 ns after the laser pulse shows the overlapping of the absorption of the JAW ground state (around 500 nm) which was depleted by the laser pulse, the absorption of the triplet-triplet of JAW in the region of >600 nm, and the absorption of the L^* radical around 550 nm. After 5 μs , most features assigned to JAW disappeared and the spectra were dominated by the L^* radical absorption at 550 nm. The long life time of lophyl radicals allows quantitative comparison of the sensitized dissociation of HABI in JAW-HABI mixtures and the direct dissociation of HABI in "HABI only" solutions. In "HABI only" solutions, the concentration of lophyl radicals increases linearly with the HABI concentrations, as is demonstrated in Figure 9A. In "HABI + JAW" solutions, an increase of $\text{OD}_{550 \text{ nm}}$ was found at all concentrations of HABI and the data are shown in Figure 9A as the scattered points. The concentration of JAW was maintained at $1 \times 10^{-5} \text{ M}$. The flash photolysis of JAW gives a small long-lived transient absorption (on the millisecond scale) in the visible region. The contribution of this unknown absorption to $\text{OD}_{550 \text{ nm}}$ in Figure 9A is about 0.005 and is assumed not to change with the variation of the HABI concentrations. The sensitized dissociation of HABI ($\Delta[L^*]$) then could be obtained from the following equations:

$$\Delta(\text{OD}_{550 \text{ nm}}) = \text{OD}_{550 \text{ nm}}(\text{JAW}+\text{HABI}) - \text{OD}'_{550 \text{ nm}}(\text{HABI}) - \text{OD}'_{550 \text{ nm}}(\text{JAW}) \quad (4)$$

$$\Delta[L^*] = \Delta(\text{OD}_{550 \text{ nm}}) / (\epsilon_{(L^*)} l) \quad (5)$$

where l is the optical length of the reaction cell and $\epsilon_{(L^*)}$ is the extinction coefficient of the lophyl radicals at 550 nm taken as $2800 \text{ M}^{-1} \text{ cm}^{-1}$. $\text{OD}'_{550 \text{ nm}}(\text{HABI})$ and $\text{OD}'_{550 \text{ nm}}(\text{JAW})$ are the corrected value of absorbances at 550 nm contributed from HABI and JAW alone. Both of them are less than the corresponding value in the single-component solutions if the incident photon numbers are the same. The values of $\Delta[L^*]$ are plotted in Figure 9B. A straight line is obtained by plotting this concentration dependence of sensitized dissociation of HABI as the reciprocal of quantum yield of formation of lophyl radicals as a function of HABI's concentration. This is presented in Figure 10.

Consider the mechanisms for observed dye-sensitized dissociation of HABI. The electronic energy transfer from the singlet excited state of JAW to *o*-Cl-HABI is not energetically feasible (in the dichloromethane solution, *o*-Cl-HABI emits at 375 nm and JAW emits at 578 nm). The energy of the lowest JAW triplet

(11) Berlan, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1965; p 14.

(12) Shvedova, L. A.; Borisevich, Y. E.; Tatikolov, A. S.; Kuz'min, V. A.; Krasnaya, Z. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1983, 1290.

(13) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* 1986, 15, 1.

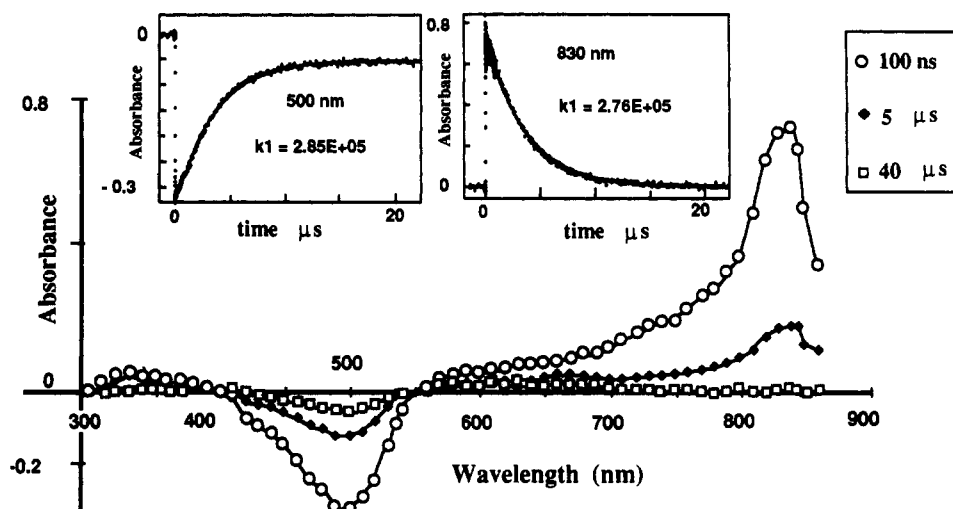


Figure 7. Transient absorption spectra observed after irradiation of a 10^{-5} M JAW solution in dichloromethane by a 480-nm laser pulse.

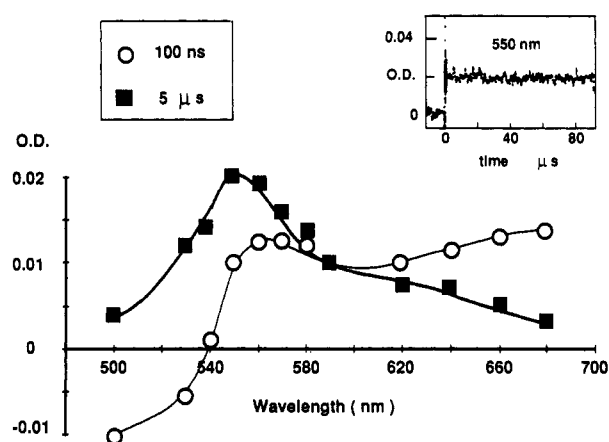


Figure 8. Transient absorption spectra observed at 100 ns and 5 μ s after 480-nm laser irradiation of a dichloromethane solution containing both *o*-Cl-HABI and JAW. The insert shows the time profile of the OD at 550 nm.

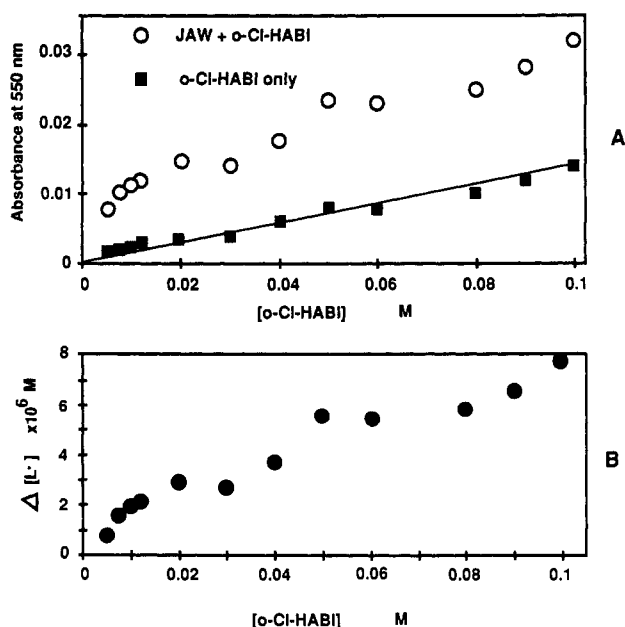


Figure 9. Concentration dependence of OD at 550 nm observed after 480-nm laser irradiation of dichloromethane solutions containing both JAW and *o*-Cl-HABI and of those containing only *o*-Cl-HABI (A); and the net increases of the lophyl radical concentration at different *o*-Cl-HABI concentrations observed for the solutions containing 10^{-5} M JAW (B).

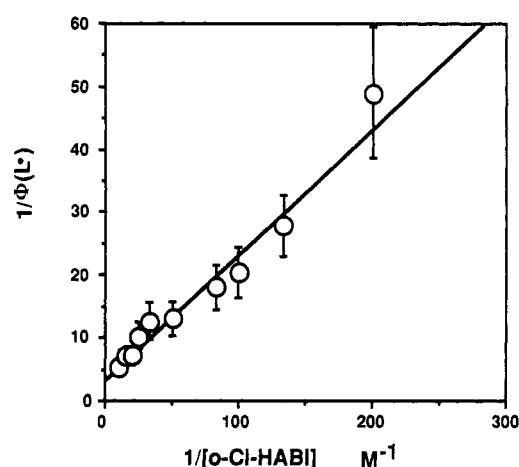


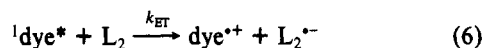
Figure 10. Concentration dependence of the quantum yield of sensitized dissociation of *o*-Cl-HABI in 480-nm laser flash photolysis. The concentration of the sensitizer JAW was maintained at 1×10^{-5} M.

is estimated to be 40.8 kcal mol⁻¹ (assuming in the charge-transfer transition the energy difference between singlet and triplet is 8.7 kcal mol⁻¹¹⁴). The energy of the lowest triplet state of *o*-Cl-HABI is estimated to be 53.4 kcal mol⁻¹ (assuming in π - π^* transition the energy difference between singlet and triplet is 22.9 kcal mol⁻¹¹⁴). Therefore, the energy transfer from the JAW triplet to HABI is also not energetically feasible. From the flash photolysis experiment, the decay of the JAW triplet at 830 nm was found to be the same in the "JAW only" and "JAW + HABI" solutions. This evidence supports the absence of interactions between the JAW triplet and HABI. Even if triplet energy transfer were feasible, one would not expect the increase of lophyl radicals to result from triplet HABI since the earlier experiments on benzophenone triplet-state photosensitization⁸ and our recent work¹⁰ have concluded that the *o*-Cl-HABI triplet has a very low probability to form and dissociate into lophyl radicals.

Another possible mechanism of sensitized dissociation of HABI is charge-transfer sensitization. In the recent time-resolved fluorescence quenching measurements using the single photon counting technique,¹⁵ an electron-transfer quenching process of ¹JAW* by *o*-Cl-HABI was observed and it was indicated that the electron transfer took place within picoseconds. Unpublished data from Serino and co-workers indicated the reduction potential of *o*-Cl-HABI is -1.35 V and an electron transfer sensitization mechanism was proposed:¹⁶

(14) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976.

(15) Lin, Y.; Liu, A.-D.; Trifunac, A. D.; Krongauz, V. V. *J. Phys. Chem.*, submitted for publication.



According to this electron-transfer mechanism, the JAW-sensitized dissociation of *o*-Cl-HABI observed in this experiment could be attributed to the dissociation of the *o*-Cl-HABI anion radicals formed by the electron transfer from $^1\text{JAW}^*$ to HABI. Considering that the charge separation between amino and ketone groups in JAW would increase upon excitation, a complete loss of an electron from the amino group in an excited JAW to HABI is possible. Eaton¹⁷ has reviewed many cases of dye-sensitized photopolymerizations and indicated that, for nearly all photopolymerizations initiated by absorption of visible light, electron transfer is the only viable mechanism. The photoinduced oxidation of electron-rich substances by lophyl radicals was observed by Cescon and co-workers,¹⁸ Riem and co-workers,¹⁹ and MacLachlan and Riem.²⁰ Moreover, ortho substitution on the phenyl ring with electron-withdrawing groups will increase reactivity toward an electron donor.²¹ It is possible that the dimer *o*-Cl-HABI has a tendency similar to the monomer radicals to abstract an electron from excited JAW. More information is needed to confirm this electron-transfer mechanism in the sensitized dissociation of HABI.

To obtain the rate constant of the electron transfer from $^1\text{JAW}^*$ to *o*-Cl-HABI (k_{ET}), we assume that the concentration of $^1\text{JAW}^*$ is in the steady state during the laser pulse and for each quenching of $^1\text{JAW}^*$ by reaction 6 one lophyl radical will be produced by reaction 7. Considering other quenching processes for $^1\text{JAW}^*$, such as fluorescence (k_{f}), internal conversion (k_{ic}) and intersystem crossing (k_{isc}), we use a Stern-Volmer-type equation:

$$1/\Phi(\Delta\text{L}^\cdot) = (k_{\text{ET}} + k_{\text{q}})/k_{\text{ET}} + (k_{\text{f}} + k_{\text{ic}} + k_{\text{isc}})/(k_{\text{ET}}[\text{L}_2]) \quad (8)$$

where $\Phi(\Delta\text{L}^\cdot)$ is the quantum yield of net increases of the lophyl radicals produced from the sensitization, and k_{q} is the quenching rate constant of $^1\text{JAW}^*$ by HABI molecular as described by the reaction below



Reaction 9 is not an electronic energy-transfer reaction which should produce $^1\text{L}_2^*$ and subsequent lophyl radicals. It represents the process of quenching of $^1\text{JAW}^*$ by L_2 without producing lophyl radicals.

(16) Mooney, W. F., III. Personal communication.

(17) Eaton, D. F. *Topics in Current Chemistry*; Vol. 156, Springer-Verlag: Berlin, 1990, p 199. Eaton, D. F.; Horgan, A. G.; Horgan, J. P. *J. Photochem. Photobiol., A* **1991**, *58*, 373.

(18) Cescon, L. A.; Corar, G. R.; Dessauer, R.; Deutsch, A. S.; Jackson, H. L.; MacLachlan, A.; Marcali, K.; Potrafke, E. M.; Read, R. E.; Silversmith, E. F.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2267.

(19) Riem, R. H.; MacLachlan, A.; Corar, G. R.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2272.

(20) MacLachlan, A.; Riem, R. H. *J. Org. Chem.* **1971**, *36*, 2275.

(21) Cohen, R. L. *J. Org. Chem.* **1971**, *36*, 2280.

The sum of ($k_{\text{f}} + k_{\text{ic}} + k_{\text{isc}}$) could be derived from the measurement of the fluorescence lifetime in the "JAW only" solution. The lifetime of $^1\text{JAW}^*$ was measured as 1.53 ns,¹⁵ hence the sum of ($k_{\text{f}} + k_{\text{ic}} + k_{\text{isc}}$) is $4.5 \times 10^8 \text{ s}^{-1}$. The fitting of the straight line in Figure 10 gives

$$1/\Phi(\Delta\text{L}^\cdot) = 3.2116 + 0.20911(1/[\text{L}_2]) \quad (10)$$

Then $(k_{\text{ET}} + k_{\text{q}})/k_{\text{ET}} = 3.2116$ and $(k_{\text{f}} + k_{\text{ic}} + k_{\text{isc}})/k_{\text{ET}} = 0.20911 \text{ M}$. We obtain $k_{\text{ET}} = (2.2 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{q}} = (4.8 \pm 0.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The indicated error limit represents the accuracy of the slope determination from the plot in Figure 10. k_{ET} and k_{q} are close to those of diffusion-controlled-reaction rate constants. This indicates that sensitization of HABI is a process with low activation energy and perhaps has little if any orientation restrictions. From the complementary work of Lin and co-workers in this laboratory,¹⁵ it is known that the electron transfer in the HABI-JAW system is a relatively short distance process (<12 Å). The short range of electron transfer and its restriction by the rate of the JAW and HABI diffusional encounter requires close proximity of the sensitizer and HABI in order to initiate the photopolymerization efficiently. Together with the short lifetime of the JAW excited singlet state, one can explain why in the imaging materials based on HABI and the visible dye sensitizer the HABI has to be present at a relatively high concentration (1–3% weight).³ Further improvements in the efficiency of lophyl radical production should be also possible by developing a sensitizer having a longer lived excited singlet state. More work in this area is in progress.

Conclusions

The industrial use of dyes for the visible-light sensitization of photopolymerization is expanding. In most cases, the dye excited state reacts with either the electron donor or electron acceptor initiating photopolymerization.^{17,22} We studied the behavior of one such initiator, *o*-Cl-HABI, photosensitized to visible light by JAW. The increase of lophyl radicals yielded upon *o*-Cl-HABI visible-light photolysis in the presence of JAW was quantified for the first time. As reported for other visible-light-sensitized radical formations,²² it was concluded that the activation of HABI by JAW involved electron transfer from the excited singlet state of JAW to HABI. The rate constant of this electron transfer was deduced using the data on concentration dependence of quenching of $^1\text{JAW}^*$ by *o*-Cl-HABI. The value of the electron-transfer rate constant was determined to be $(2.2 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. To the best of our knowledge, this is the first time that this rate was measured. We hope that additional confirmation of the charge transfer as a path for visible-light photosensitization will make further selection of suitable sensitizers a simpler task.

Acknowledgment. We thank Dr. K. Schmidt for building the flash photolysis apparatus and for many helpful discussions. We would also like to acknowledge discussions with Drs. Dan Meisel, Myron Sauer, Jr., David Werst, Yi Lin, and Xue-Zhi Qin.

(22) Timple, H. J.; Neuenfeld, S. *Kontakte (Darmstadt)* **1990**, *2*, 28–35.