SENSITIZED PHOTOLYSIS AND TRIPLET ENERGY OF ETHYL P-AZIDOBENZOATE

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Polymers with azido group are widely used as negative-working photoresists. Azido polymers photocrosslink efficiently through active nitrene as an intermediate [1], and can be sensitized effectively by triplet sensitizers to match the requirements in industry [2,3]. To thoroughly understand the sensitization mechanism of the azido polymer, elucidation of energy transfer process is essential. Although great effort has been devoted to solve this problem [4], energy transfer rate from sensitizers to the azide and the triplet energy level of the azide itself are still controversial [5]. In the present paper, energy transfer rate from such sensitizers as benzophenone, acetophenone, thioxanthone (TX), 2,4-diisopentylthioxanthone (DITX), and phenanthrene to one of the aromatic azides, i.e., ethyl p-azidobenzoate (EAZB) has been investigated by measuring the quantum yield of nitrogen evolved from EAZB under light irradiation, and by measuring the decay of T-T absorption of the sensitizer with the aid of laser flash photolysis technique.

Energy diagram and

![Scheme 1. Schematic energy diagram and photochemical processes for the azide/sensitizer systems.](image)

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photochemical processes for the azide/sensitizer systems are schematically shown in Scheme 1. Under the light irradiation, concentration of the triplet sensitizer, \([3S^*]\), is assumed to be stationary, i.e., \(d[3S^*]/dt=0\). Based on this assumption, the overall quantum yield of azide decomposition, \(\phi\), is expressed as follows [5];

\[
\frac{1}{\phi} = \frac{1}{\phi_{ST}}(1 + \frac{k_d}{k_{et}[A]} \frac{k_{p}+k_{D}}{k_{p}})
\]  

(1)

where \(\phi_{ST}\) is the quantum yield for intersystem crossing of the sensitizer, and [A], the concentration of the azide. Because azides in the triplet state exclusively decompose into nitrene and nitrogen as an initial step of chemical reactions [1,4], the overall quantum yield of azide decomposition, \(\phi\), can be measured by volume of the evolved nitrogen under a fixed experimental condition. Actually, volume of the evolved nitrogen has been measured with the ethanol solution of DITX/EAZB (3.9 x 10^{-4} M for DITX) by capacitance manometer (MKS Baratron 223 AH) within 20% decomposition of the azide; the result is shown in Fig. 1. A good linear relationship holds between \(\phi^{-1}\) and \([\text{EAZB}]^{-1}\). From the slope and intercept, \(k_d/k_{et}\) value is determined to be 1.2 x 10^{-2}.

The \(k_d\) value has

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Sensitizer} & E_T / \text{kcal mol}^{-1} & k_d / \text{s}^{-1} & k_{et} / \text{M}^{-1}\text{s}^{-1} \\
\hline
\text{Acetophenone} & 74.1 & 2.4 \times 10^6 & 5.6 \times 10^7 \\
\text{Benzophenone} & 69.2 & 1.4 \times 10^6 & 3.4 \times 10^7 \\
\text{Thioxanthone} & 65.5 & 1.7 \times 10^5 & 1.5 \times 10^7 \\
\text{DITX} & 64.0 & 1.0 \times 10^5 & 8.5 \times 10^6 \\
\text{Phenantrone} & 62.0 & 1.0 \times 10^3 & 1.4 \times 10^4 \\
\hline
\end{array}
\]
been determined in the present study from the decay of the triplet state of DITX to be \(1.0 \times 10^5\) s\(^{-1}\). From the observed \(k_d\) value, \(k_{et}\) is evaluated to be \(8.5 \times 10^6\) M\(^{-1}\)s\(^{-1}\). Entirely the same experiment has been extended to the ethanol solutions of the other sensitizer/EAZB systems; the results are tabulated in Table 1. \(k_{et}\) values range over \(10^4\)-\(10^7\). In Fig. 2, \(k_{et}\) value is plotted against the triplet energy (\(E_T\)) of the sensitizer. \(k_{et}\) tends to saturate at \(E_T = 65\) kcal/mol. Although the \(k_{et}\) values are two orders of magnitude smaller than the diffusion-controlled rate constant, this result suggests that the triplet energy of EAZB is \(=65\) kcal/mol.

Energy transfer rate can be determined directly by measuring the decay of T-T absorption of the sensitizer/EAZB system. Fig. 3 shows transient absorption spectra of the ethanol and 2-methyltetrahydrofuran (MTHF) solutions of TX excited with a Nd:YAG laser (Quanta-Ray DCR-1). A 605 nm band of the ethanol solution is assigned to T-T absorption band. Decay rate of the 605 nm band has been measured as a function of EAZB concentration. Stern-Volmer plot of \(k_d\) for

**Fig. 2.** Dependence of \(k_{et}\) on the triplet energy of the sensitizer (\(E_T\)) for some sensitizer/EAZB systems.

**Fig. 3.** Transient absorption spectra of the (a) ethanol and (b) MTHF solutions of TX excited at 355 nm with a Nd:YAG laser.
TX/EAZB is shown in Fig. 4, together with the result of DITX/EAZB. $k_{et}$ is evaluated to be $8.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for TX and $3.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for DITX. Energy transfer rates from TX and DITX to EAZB are nearly diffusion-controlled. Combined with the result in Fig. 2, this result strongly suggests that the triplet energy of EAZB is $\approx 65$ kcal/mol.

Energy transfer rate evaluated from Eq. 1 is fifty times smaller than the value determined by laser flash photolysis technique. This is due to the photoinitiated autocatalytic chain decomposition of the azide proposed by Waddell and Go [6].

References