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Mechanistic Studies of the Pyrene-Sensitized Photodecomposition of *N*-Phenylglycine: Acceleration of the Photodecomposition by the Addition of an Electron Acceptor

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The processes of the pyrene-sensitized photodecomposition of *N*-phenylglycine (NPG) have been investigated by fluorescence quenching experiments, laser flash photolysis studies, and characterization of the reaction products. A mechanism involving electron transfer from NPG to singlet excited pyrene through emissive exciplex formation, as well as the intervention of $PhNHCH_2\cdot$ as a reactive intermediate, has been established. The efficiency of NPG photodecomposition is enhanced by the addition of an electron acceptor, such as terephthalonitrile or diethyl isophthalate. The laser flash photolysis studies have revealed that the mechanism for the rate enhancement of NPG photodecomposition depends on the acceptor employed as an additive.

There have been a number of studies concerning the photodecomposition of amines sensitized by carbonyl compounds[1,2] and polycyclic aromatic hydrocarbons.[3] It is proposed that the decomposition proceeds by a mechanism involving amine radical cations as reactive intermediates, which are generated by a single electron transfer from amines to the excited sensitizers. Since these intermediates undergo α-CH deprotonation to give α-amino radicals, the sensitized photodecomposition of amines can be used to initiate chain reactions, such as the free radical-mediated polymerization of vinyl monomers.[4]

An α-carboxyl substitution of amines is highly effective in generating α-amino radicals, because facile α-decarboxylation can be a surrogate for α-CH deprotonation. Thus, *N*-phenylglycine (NPG), $PhNHCH_2CO_2H$, has been widely used as an initiator in photopolymerization.[5] It has been demonstrated that the decomposition of NPG and its derivatives can be sensitized by aromatic nitro compounds,[6] quinones,[5d,7] polycyclic aromatic hydrocarbons,[8] and dyes.[5a—c,9] In these studies, it was suggested that a single electron transfer from NPG and their derivatives to the excited sensitizers was involved in their photodecomposition processes. However, in spite of the practical values of NPG and its derivatives, few studies on the detailed mechanism of their sensitized photodecomposition have been reported.

In this paper, we report on our mechanistic studies of the photodecomposition of NPG sensitized by pyrene, where the reaction scheme involving a single electron transfer from NPG to singlet excited pyrene through an exciplex formation was confirmed. Furthermore, we demonstrate that the efficiency of the pyrene-sensitized decomposition of NPG is enhanced by the addition of an electron acceptor, such as terephthalonitrile and diethyl isophthalate. The mechanism for the rate enhancement of NPG photodecomposition is discussed based on the results obtained by using a nanosecond laser flash photolysis technique.[10]

Results

Pyrene-Sensitized Photodecomposition of NPG in the Absence of an Electron Acceptor. The irradiation (366 nm) of a degassed solution of NPG (1.5×10^{-2} mol dm^{-3}) in acetonitrile containing 1% of water in the presence of pyrene (5.0×10^{-4} mol dm^{-3}) caused a rapid consumption of NPG. Having a small, but significant, absorption at 366 nm (ε = 7.8 in acetonitrile), NPG could be photolyzed even in the absence of pyrene. As shown in Fig. 1, however, the decomposition of NPG was enhanced by a factor of about four by the addition of pyrene, the molar absorptivity of which is 220 at 366 nm. The change in the concentration of pyrene with the irradiation time shown in Fig. 1 illustrates that the sensitizer was considerably consumed as the photodecomposition of NPG progressed.

(1) Effect of Solvent on the Rate of NPG Photodecomposition. We at first examined the dependence of the rate of pyrene-sensitized photodecomposition of NPG on the solvent used in the photolysis. The rate of NPG photodecomposition in several solvents relative to that in acetonitrile, $v_{\mathrm{dec}}^{\mathrm{rel}}$, is shown in Table 1. The results showed that the use of nonpolar solvents resulted in a considerable decrease in the rate of NPG photodecomposition.

Table 1. Relative Rates of Pyrene-Sensitized Photodecomposition of NPG and Its Derivatives and Quenching of Pyrene Fluorescence in Various Solvents

Substrate	Solvent	$v_{\mathrm{dec}}^{\mathrm{rel}}$ a)	K_{SV} b) / $\mathrm{mol^{-1}\,dm^{3}}$	λ_{ex}/nm c)	$(I_{\mathrm{ex}}/I_{\mathrm{m}})^{\mathrm{rel}}$ d)
$\mathrm{PhNHCH_2CO_2H}$	Acetonitrile	1.0	60.0	454	1.0
	Acetonitrile : Benzene (3 : 2)	0.80	60.4	458	0.79
	Acetonitrile : Benzene (1 : 4)	0.75	20.9	458	0.49
	Ethyl acetate	0.50	23.7	433	2.9
	Methanol	1.6	64.9	460	0.71
$\mathrm{PhNHCH_2CO_2Et}$	Acetonitrile	0.26	100	515	0.07
$\mathrm{PhNHCH_2CO_2NBu_4}$	Acetonitrile	0.87	117	454	1.7

a) Relative rate of pyrene-sensitized decomposition of the substrate; [pyrene] = 5.0×10^{-4} mol dm^{-3}, [substrate] = 1.5×10^{-2} mol dm^{-3}. b) $K_{\mathrm{sv}} = \gamma k_{\mathrm{e}}\tau_0$; Stern–Volmer constant for quenching of pyrene fluorescence in aerated solution ([pyrene] = 1.0×10^{-5} mol dm^{-3}). c) Fluorescence maximum of exciplex. d) Relative ratio of intensity of exciplex fluorescence at λ_{ex} ([substrate] = 8.0×10^{-3} mol dm^{-3}) to intensity of pyrene fluorescnece at 393 nm observed in the absence of the substrate.

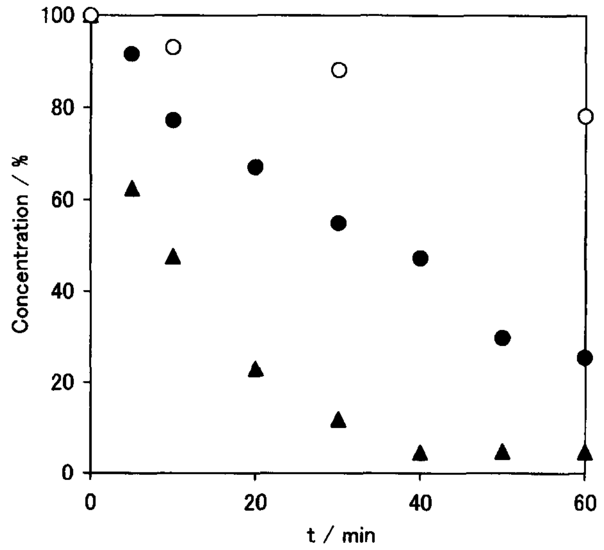


Fig. 1. Change in the concentration of NPG (●) and pyrene (▲) with irradiation time, *t*, in the pyrene-sensitized photolysis (366 nm) of NPG in acetonitirile containing 1% of water. Initial concentrations of NPG and pyrene are 1.5×10^{-2} mol dm^{-3} and 5.0×10^{-4} mol dm^{-3}, respectively. Open circles (○) show the change in the concentration of NPG under the identical conditions, except for the absence of pyrene.

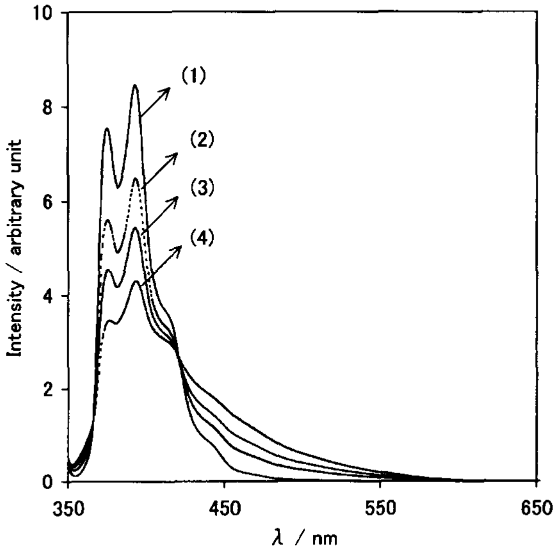
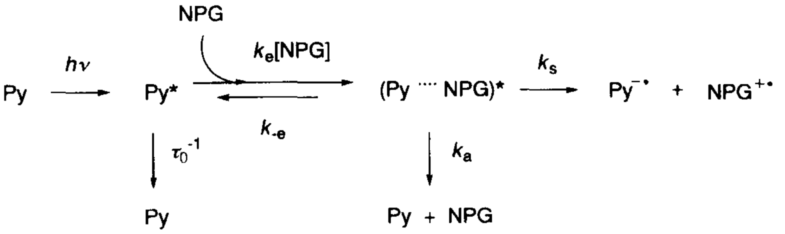


Fig. 2. Fluorescence spectra of pyrene recorded in the presence of NPG in the concentration of (1) 0, (2) 4, (3) 8, and (4) 16×10^{-3} mol dm^{-3} in acetonitrile on excitation at 340 nm ([pyrene] = 1.0×10^{-5} mol dm^{-3}).

(2) Quenching of Pyrene Fluorescence by NPG. In order to identify the excited state of pyrene which is involved in NPG photodecomposition, and to obtain a clue to our understanding the effect of the solvent described above, quenching of the fluorescence of pyrene by NPG was examined next. The fluorescence spectrum of pyrene in the presence of various concentration of NPG in acetonitrile is illustrated in Fig. 2. The figure displays that the addition of NPG causes a quenching of pyrene fluorescence, as well as the formation of an emissive exciplex, the fluorescence maximum of which is estimated to be 454 nm by an analysis of the spectrum. Assuming that the dynamic processes of excited pyrene involving exciplex formation are shown in Scheme 1,[11] a Stern–Volmer treatment of the quenching data gives the value $K_{\mathrm{sv}} = \gamma k_{\mathrm{e}}\tau_0 = 60.0\ \mathrm{mol^{-1}\,dm^{3}}$, where γ stands for $(k_{\mathrm{a}}+k_{\mathrm{s}})/(k_{\mathrm{a}}+k_{\mathrm{s}}+k_{-\mathrm{e}})$. In all solvents employed for the NPG decomposition, exciplex emission was observed, though the intensity of the emission recorded under the same NPG concentration, as well as Stern-Volmer constant, K_{sv}, was dependent on the solvent. The results are summarized in Table 1.

(3) Photodecomposition of Ethyl Ester and Tetrabutylammonium Salt of NPG. As mentioned in the introductory part, it is known that α-carboxyl substitution enhances the electron transfer-induced decomposition of amines. We examined the pyrene-sensitized photodecomposition of ethyl ester and tetrabutylammonium salt of NPG, and compared their reactivity with that of NPG. The results are also given in Table 1, together with the data of quenching of pyrene fluorescence by these NPG derivatives. Thus, it has been



Scheme 1. (Py = pyrene)

found that the photodecomposition rate of the ethyl ester, the radical cation of which cannot undergo α-decarboxylation, is considerably slow, though it is a good quencher of singlet excited pyrene. This observation indicates the effectiveness of an α-carboxyl group in an electron transfer-induced decomposition of amines. The photodecomposition rate of tetrabutylammonium salt of NPG is comparable to that of NPG, suggesting that the degree of acid dissociation of NPG is not practically responsible for the photodecomposition rate under our reaction conditions.

Pyrene-Sensitized Photodecomposition of NPG in the Presence of an Electron Acceptor. In the course of our mechanistic studies of the pyrene-sensitized decomposition of NPG, we found that the efficiency of NPG decomposition was enhanced by the addition of an electron acceptor, such as terephthalonitrile (TPN). Thus, the initial rate of photodecomposition of NPG (1.5×10^{-2} mol dm^{-3}) in the irradiation (366 nm) of a degassed solution in acetonitrile containing 1% of water in the presence of pyrene (5.0×10^{-4} mol dm^{-3}) and TPN (1.5×10^{-2} mol dm^{-3}) was increased by a factor of 1.9, compared with that in the absence of TPN. Furthermore, in the NPG photodecomposition in the presence of TPN, pyrene was recovered nearly quantitatively. We examined the effect of a variety of electron acceptors on the pyrene-sensitized decomposition of NPG.

(1) Relative Rates of NPG Photodecomposition in the Presence of an Electron Acceptor. The initial rate of the pyrene-sensitized decomposition of NPG in the presence of various electron acceptors relative to that in the absence of electron acceptors, $v_{\mathrm{dec}}^{\mathrm{rel}}$, was obtained under the defined conditions ([pyrene] = 5×10^{-4} mol dm^{-3}, [NPG] = [acceptor] = 1.5×10^{-2} mol dm^{-3}, in acetonitrile containing 1% water, 366 nm). The results are given in Table 2, along with the reduction potentials, E_{red}, of the electron acceptors employed as additives. As shown in the table, the addition of not only TPN, but also diethyl terephthalate (DETP), isophthalonitrile (IPN), and diethyl isophthalate (DEIP), enhanced the efficiency of NPG decomposition. A similar magnitude of the enhancement of NPG decomposition was also observed in methanol. On the other hand, the suppression of NPG decomposition was found upon the addition of pyromellitonitrile (PMN) and benzonitrile (BN). Unfortunately, anhydrides, such as pyromellitic dianhydride (PDA) and phthalic anhydride (PA), could not be employed as additives in a photoinitiating system using NPG, because NPG was rapidly consumed, even in the dark, owing to a thermal reaction of NPG with anhydrides.[14] Though attempts to isolate the product obtained from NPG and PA were not successful, it was tentatively identified as *N*-carboxymethyl-*N*-phenylphthalamic acid on the basis of its NMR spectrum, which would be formed by a nucleophilic attack of the NPG nitrogen on the carbonyl carbon of PA.

(2) Quenching of Pyrene Fluorescence by an Electron Acceptor. The dynamic processes of quenching of singlet excited pyrene by electron acceptors, such as TPN, have been extensively studied.[15—17] It is reasonable to assume that the enhancement of the NPG decomposition by the addition of an electron acceptor is responsible for the efficient quenching of singlet excited pyrene by the additive. Thus, we obtained Stern-Volmer constants, K_{sv}, for the quenching of pyrene fluorescence by electron acceptors employed as additives in the NPG photodecomposition in acetonitrile, which are given in

Table 2. Relative Rates of Pyrene-Sensitized Photodecomposition of NPG and Quenching of Pyrene Fluorescence by Various Electron Acceptors in Acetonitrile

Electron acceptor	E_{red} (V vs SCE)	$v_{\mathrm{dec}}^{\mathrm{rel}\ \mathrm{a)}}$	$K_{\mathrm{sv}}$$^{\mathrm{b)}}$ / mol^{-1} dm^3
None	—	1.0	60.0$^{\mathrm{c)}}$
Pyromellitonitrile (PMN)	$-0.73^{\mathrm{d)}}$	0.52	363
Terephthalonitrile (TPN)	$-1.63,^{\mathrm{e)}}$ $-1.68^{\mathrm{d)}}$	1.9	240
Diethyl terephthalate (DETP)	$-1.74^{\mathrm{e)}}$ $(-1.68)^{\mathrm{f)}}$	1.9	184
Isophthalonitrile (IPN)	$-1.88^{\mathrm{d)}}$	2.3	93.3
Diethyl isophthalate (DEIP)	$< -1.9^{\mathrm{e)}}$ $(-2.01)^{\mathrm{f)}}$	2.0	<5
Benzonitrile (BN)	$-2.45^{\mathrm{d)}}$	0.76	<5

a) Relative rate of pyrene-sensitized decomposition of NPG; [pyrene] = 5.0×10^{-4} mol dm^{-3}, [NPG] = [Acceptor] = 1.5×10^{-2} mol dm^{-3}. b) $K_{\mathrm{sv}} = k_{\mathrm{q}}\tau_0$; Stern–Volmer constant for quenching of pyrene fluorescence in aerated solution ([pyrene] = 1.0×10^{-5} mol dm^{-3}). c) Quenching by NPG. d) Ref. 12. e) This work. f) Reduction potential of the corresponding dimethyl derivative reported in Ref. 13.

Table 2. No exciplex emission was observed in the quenching of pyrene fluorescence by these electron acceptors. The table indicates that no simple relationship is observed for the NPG decomposition rate with K_{SV} for pyrene fluorescence quenching by the electron acceptor used as an additive, which tends to increase with its reduction potential. In particular, the addition of DEIP causes an effective enhancement of the NPG decomposition, though the observed K_{SV} values imply that singlet excited pyrene is quenched preferentially by NPG, even in the presence of DEIP. These observations suggest that the rate of quenching of singlet excited pyrene by the electron acceptor employed as an additive is not the sole factor controlling the rate of NPG photodecomposition.

Laser Flash Photolysis Studies. In order to gain information about the mechanism of the pyrene-sensitized decomposition of NPG in the absence and presence of an electron acceptor, a direct observation of transient species involved in the photoreaction was carried out by using a nanosecond laser flash photolysis technique (355 nm, 13 ns, 0.7 mJ/pulse).

(1) In the Absence of an Electron Acceptor. The transient absorption spectra recorded by the laser excitation of a deoxygenated solution of NPG (1.5×10^{-2} mol dm^{-3}) in acetonitrile in the presence of pyrene (5×10^{-4} mol dm^{-3}) are shown in Fig. 3. A transient species having an intense absorption band with a maximum at 493 nm was detected immediately after a laser pulse, which can be characterized as pyrene radical anion ($\mathrm{Py}^{-\bullet}$).[4b,18] This transient decayed according to first-order kinetics; the first-order rate constant for decay of $\mathrm{Py}^{-\bullet}$ was estimated to be 1.7×10^{6} s^{-1}. A similar transient spectrum and the decay profile of $\mathrm{Py}^{-\bullet}$ were obtained in methanol. Thus, the detection of $\mathrm{Py}^{-\bullet}$ in the pyrene-sensitized photodecomposition of NPG strongly suggests that the decomposition of NPG is initiated by a single electron transfer from NPG to photoexcited pyrene.

As the intensity of the absorption due to $\mathrm{Py}^{-\bullet}$ decreased, a new absorption appeared at 401 nm (Fig. 3). This new band can be assigned to the absorption of 1-hydro-1-pyrenyl radical (PyH•),[4b,18b] the formation of which is reasonably interpreted in terms of a protonation of $\mathrm{Py}^{-\bullet}$. There have been a number of reports concerning the detection of $\mathrm{Py}^{-\bullet}$ and PyH• in pyrene–trialkylamine systems in polar solvents using the laser flash photolysis technique.[4b,18b]

(2) In the Presence of TPN. The transient absorption spectrum recorded in the presence of TPN (2.0×10^{-3} mol dm^{-3}), which is shown in Fig. 4, was completely different from that recorded in the absence of TPN. No absorption due to $\mathrm{Py}^{-\bullet}$ was observed, but intense absorption bands with maxima at 445 and 343 nm were detected immediately after laser excitation. These bands can be characterized as a pyrene radical cation ($\mathrm{Py}^{+\bullet}$)[18a,18c] and a radical anion of terephthalonitrile ($\mathrm{TPN}^{-\bullet}$),[19] respectively. The rate constant for the decay of $\mathrm{Py}^{+\bullet}$, k(445 nm), which was dependent on NPG concentration, [NPG], was obtained by an analysis of the decay profile by using a pseudo-first-order treatment. The rate constant for hole transfer from $\mathrm{Py}^{+\bullet}$ to NPG, k_{ht}, was obtained from a plot of the observed $\mathrm{Py}^{+\bullet}$ decay rate constant, k(445 nm), against [NPG]. Figure 5 displays a plot of k(445 nm) versus [NPG], which gives a straight line. Based on the relationship depicted by

$$k(445\ \mathrm{nm}) = k_0 + k_{\mathrm{ht}}\cdot[\mathrm{NPG}] \qquad (1)$$

a least-squares analysis of the plot gives $k_{\mathrm{ht}} = 1.1\times10^{10}$ mol^{-1} dm^{3} s^{-1}.

These observations have revealed that in the pyrene-sensitized decomposition of NPG in the presence of TPN, the processes of the formation of an NPG radical cation ($\mathrm{NPG}^{+\bullet}$), which leads to the decomposition of NPG, are completely different from those in the absence of TPN; the quenching of singlet excited pyrene by TPN to give $\mathrm{Py}^{+\bullet}$, followed by

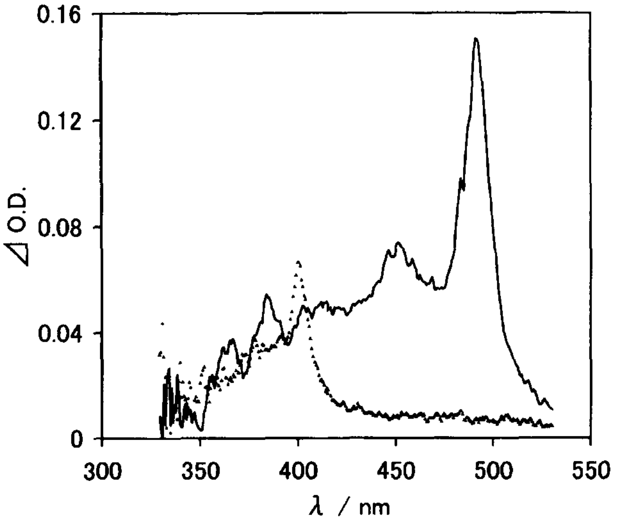


Fig. 3. Transient absorption spectra of a solution of pyrene (5.0×10^{-4} mol dm^{-3}) and NPG (1.5×10^{-2} mol dm^{-3}) in acetonitrile recorded at the delay time of 50 ns (solid line) and 5 μs (dotted line) after a laser pulse (355 nm, 13 ns).

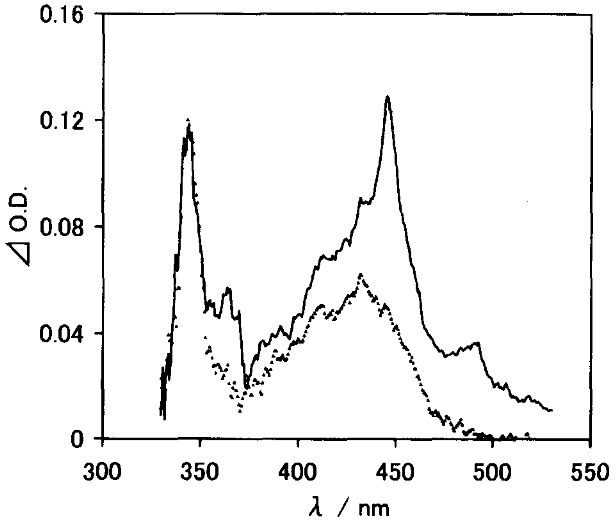


Fig. 4. Transient absorption spectra of a solution of pyrene (5.0×10^{-4} mol dm^{-3}), NPG (2.0×10^{-3} mol dm^{-3}), and TPN (2.0×10^{-3} mol dm^{-3}) in acetonitrile recorded at the delay time of 60 ns (solid line) and 200 ns (dotted line) after a laser pulse (355 nm, 13 ns).

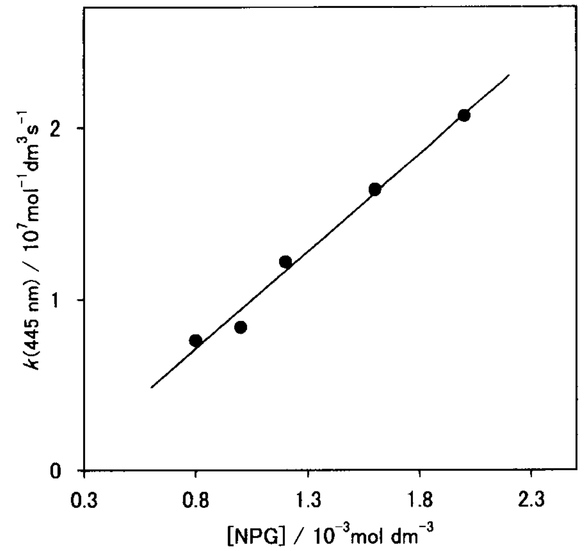


Fig. 5. Dependence of the rate constant for the decay of $Py^{+\bullet}$, k(445 nm), on the concentration of NPG in the pyrene-sensitized photolysis of NPG in the presence of TPN in acetonitrile ([pyrene] = 5.0×10^{-4} mol dm^{-3}, [TPN] = 2.0×10^{-3} mol dm^{-3}).

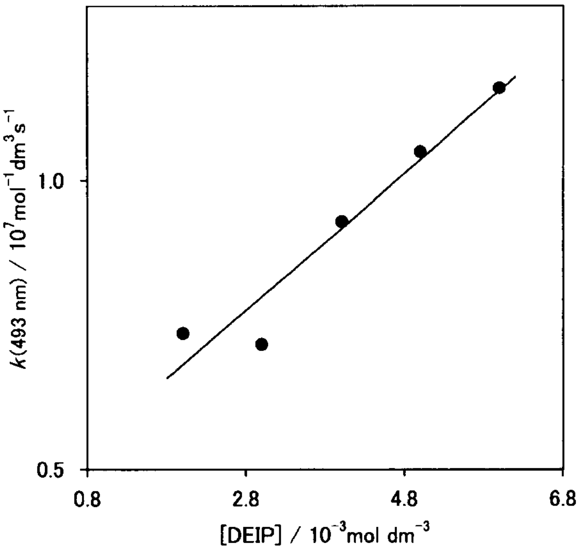


Fig. 6. Dependence of the rate constant for the decay of $Py^{-\bullet}$, k(493 nm), on the concentration of DEIP in the pyrene-sensitized photolysis of NPG in the presence of DEIP in acetonitrile ([pyrene] = 5.0×10^{-4} mol dm^{-3}, [NPG] = 5.0×10^{-3} mol dm^{-3}).

efficient hole transfer from $Py^{+\bullet}$ to NPG, which occurs with a rate constant close to the diffusion-controlled limit (1.9×10^{10} mol^{-1} dm^3 s^{-1} in acetonitrile).[12]

(3) In the Presence of DEIP. As shown in Table 2, DEIP showed a remarkable effect on the enhancement of the NPG photodecomposition rate, which was comparable to that of TPN. Taking into account the much smaller K_{SV} for the quenching of pyrene fluorescence by DEIP than NPG, the mechanism of NPG photodecomposition in the presence of DEIP should be different from that in the presence of TPN described above. Upon laser excitation of a solution of NPG (5.0×10^{-3} mol dm^{-3}) in acetonitrile in the presence of pyrene (5.0×10^{-4} mol dm^{-3}) and DEIP (5.0×10^{-3} mol dm^{-3}), a transient absorption assigned to $Py^{-\bullet}$ (λ_{max} = 493 nm) was observed, while no absorption characterized as $Py^{+\bullet}$ was detected. The $Py^{-\bullet}$ decay rate constant, k(493 nm), which could be estimated by an analysis of the decay profile by using a pseudo-first-order treatment, was dependent on the DEIP concentration, [DEIP]. Figure 6 shows a plot of the observed k(493 nm) versus [DEIP], which gives a straight line. From the slope of the plot, the rate constant for the electron transfer from $Py^{-\bullet}$ to DEIP, k_{et}, is obtained on the basis of

$$k(493\ \mathrm{nm}) = k_0' + k_{et}\cdot[\mathrm{DEIP}]. \tag{2}$$

A least-squares analysis of the plot shown in Fig. 6 gives $k_{et} = 1.2\times10^9$ mol^{-1} dm^3 s^{-1}.

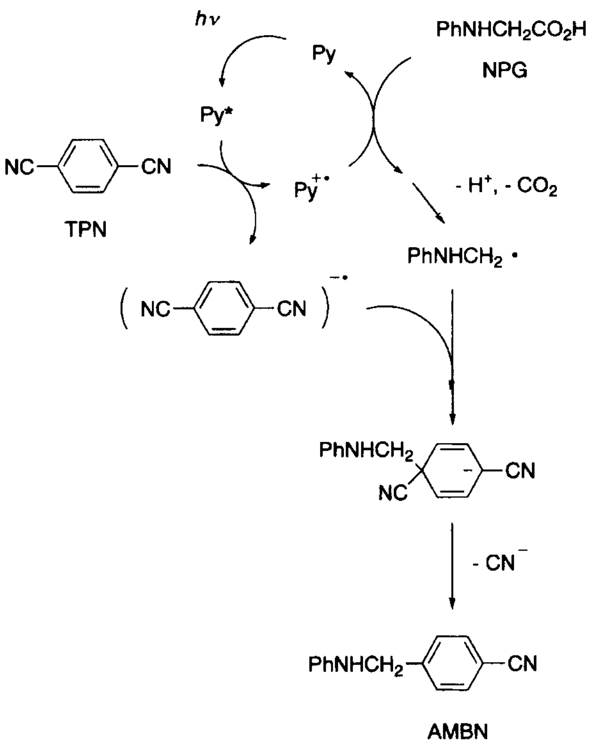
Thus, laser flash photolysis studies suggest that the rate enhancement of the NPG decomposition by the addition of DEIP is attributed to an efficient electron transfer from $Py^{-\bullet}$ to DEIP, which would suppress the back electron transfer between an ion pair of $Py^{-\bullet}$ and $NPG^{+\bullet}$ formed initially by the quenching of photoexcited pyrene by NPG.

Product Studies in the Pyrene-Sensitized Photodecomposition of NPG. It was reported that the photolysis of NPG sensitized by polycyclic aromatic hydrocarbon gave a complex mixture including aniline and formanilide, which would be formed through the reaction of anilinomethyl radical, $PhNHCH_2\cdot$, generated by the decarboxylation of $NPG^{+\bullet}$, with oxygen.[8] In order to establish the intervention of $PhNHCH_2\cdot$, the photoproducts were examined in the pyrene-sensitized photodecomposition of NPG.

(1) Photoproducts Obtained in the Absence of an Electron Acceptor. A degassed solution of NPG (1.5×10^{-2} mol dm^{-3}) in acetonitrile containing 1% of water in the presence of pyrene (5.0×10^{-4} mol dm^{-3}) was irradiated for 30 min with a high-pressure mercury lamp (366 nm). Spectroscopic and chromatographic analyses of the obtained photoreaction mixture revealed the formation of *N*-methylaniline (NMA), aniline and formanilide in 16, 15, and 5% yield, respectively, based on the consumed NPG (45%). These compounds have already been reported as the photoproducts obtained in the sensitized photolysis of NPG.[8,9] As mentioned in a previous section, pyrene was considerably consumed (88%), but no identifiable photoproducts derived from pyrene were obtained.

The formation of NMA was completely quenched in the irradiation of an oxygenated solution, while irradiation in the presence of Bu_3SnH (3.0×10^{-2} mol dm^{-3}) resulted in an increase in the yield of NMA at the expense of that of aniline. Moreover, when the pyrene-sensitized photolysis of NPG was carried out in the presence of both Bu_3SnH and methyl methacrylate, the adduct **1** could be obtained in 49% yield. The formation of **1** is reasonably explained in terms of trapping of $PhNHCH_2\cdot$ with methyl methacrylate, followed by hydrogen-atom abstraction by the resulting radical from Bu_3SnH. The results of product studies in the pyrene-sensitized photolysis of NPG in the absence of an electron acceptor are summarized in Scheme 2, which clearly shows the intervention of $PhNHCH_2\cdot$ in the pyrene-sensitized photodecomposition of NPG.

(2) Photoproducts Obtained in the Presence of TPN. The distribution of the photoproducts obtained in the irradiation of a degassed solution of NPG in the presence of pyrene and TPN (1.5×10^{-2} mol dm^{-3}) was similar to that obtained in the absence of TPN. However, the additional product was isolated in 5% yield from the reaction mixture, which was identified as *p*-anilinomethylbenzonitrile (AMBN) by a comparison of the spectroscopic data with those of the authentic material. The formation of AMBN also presents a piece of evidence in support of the intervention of $PhNHCH_2\cdot$, since AMBN would be formed by the attack of $PhNHCH_2\cdot$ on *ipso*-position of $TPN^{-\bullet}$, followed by the elimination of CN^- (Scheme 3). The formation of *p*-anilinomethylbenzonitrile derivatives was reported in the direct photolysis of tetrabutylammonium *N*-methyl-*N*-phenylglycinate in the presence of TPN.[19] Note again that the sensitizer was recovered nearly quantitatively from the reaction mixture obtained by the pyrene-sensitized photolysis of NPG in the presence of TPN. The recovery of the sensitizer can be also explained satisfactorily by the mechanism illustrated in Scheme 3.



Scheme 3. (Py = pyrene)

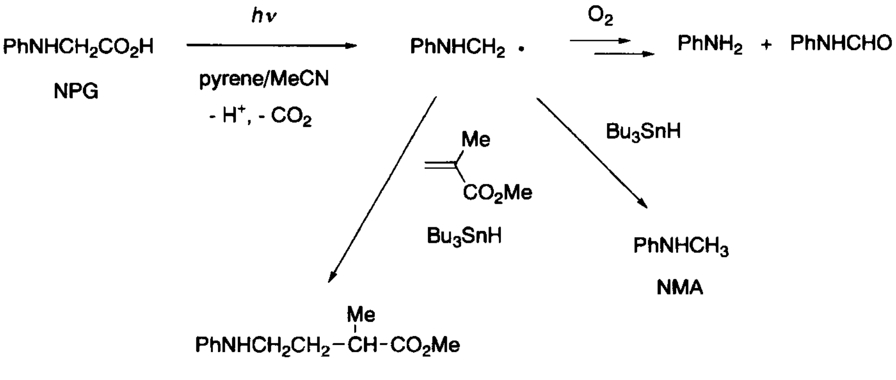
Discussion

It was proposed that the sensitized photodecomposition of NPG proceeds by a mechanism involving the generation of $NPG^{+\bullet}$ through electron transfer from NPG to the excited sensitizer, followed by its decarboxylation to give $PhNHCH_2\cdot$.[5a,6—9] Our observations concerning the pyrene-sensitized photodecomposition of NPG have provided unambiguous evidence supporting the intervention of the electron-transfer processes and the generation of $PhNHCH_2\cdot$ during the course of NPG photodecomposition. The free-energy change for the electron transfer from NPG to singlet excited pyrene is calculated by the Rehm-Weller equation[20] to be -13 kcal mol^{-1}, which implies that the electron transfer is an energetically favorable process.[21]

Moreover, we have found that the addition of an electron acceptor is effective to increase the efficiency of NPG photodecomposition. It should be emphasized, however, that the mechanism of NPG decomposition, that is, the processes of the formation of $NPG^{+\bullet}$, in the presence of an electron acceptor, such as TPN, is found to be completely different from that in the absence of an electron acceptor. The role of an electron acceptor in the pyrene-sensitized photodecomposition of NPG is now discussed by considering the factors responsible for the NPG decomposition.

Mechanism of the NPG Decomposition in the Absence of an Electron Acceptor. On the basis of the data of pyrene fluorescence quenching by NPG and laser flash photolysis studies, it is concluded that $NPG^{+\bullet}$, which leads to the decomposition of NPG, is produced by electron transfer from NPG to singlet excited pyrene through an emissive exciplex formation. The mechanism which we propose for the pyrene-sensitized photodecomposition of NPG is illustrated in Scheme 4.

Assuming that the rate of NPG decomposition, v_{dec}, is



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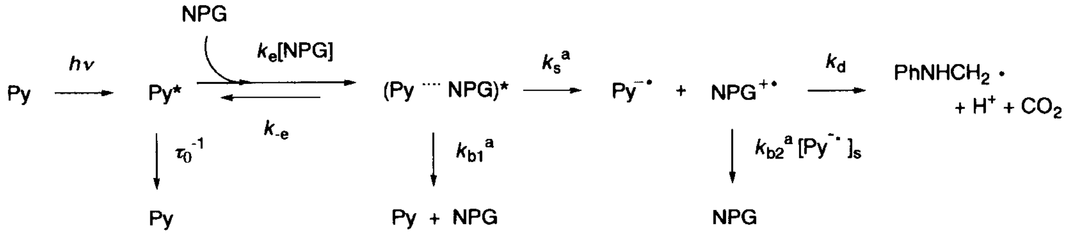
Scheme 2.



Scheme 4. (Py = pyrene)

proportional to the product of the rate constant for the decomposition of $NPG^{+\bullet}$, k_d, and its steady-state concentration, $[NPG^{+\bullet}]_s$, v_{dec} is given by Eq. 3 by using a steady-state approximation,

$$v_{dec} = k_d \cdot [NPG^{+\bullet}]_s = I \cdot F^a_{sv} \cdot P_a \cdot Q_a. \qquad (3)$$

In this equation, I is the number of photons absorbed by the sensitizer, and F^a_{sv}, which is depicted by $K_{sv} \cdot [NPG]/(1+K_{sv} \cdot [NPG])$, shows the efficiency of the quenching of pyrene fluorescence by NPG. Furthermore, P_a and Q_a, which are equal to $k^a_s/(k^a_s+k^a_{b1})$ and $k_d/(k_d+k^a_{b2} \cdot [Py^{-\bullet}]_s)$, respectively, represent the efficiency for the exciplex to dissociate into free radical ions and the efficiency for $NPG^{+\bullet}$ to decompose in competition with a back electron transfer, respectively. The rate constants, k's, are defined as shown in Scheme 4.

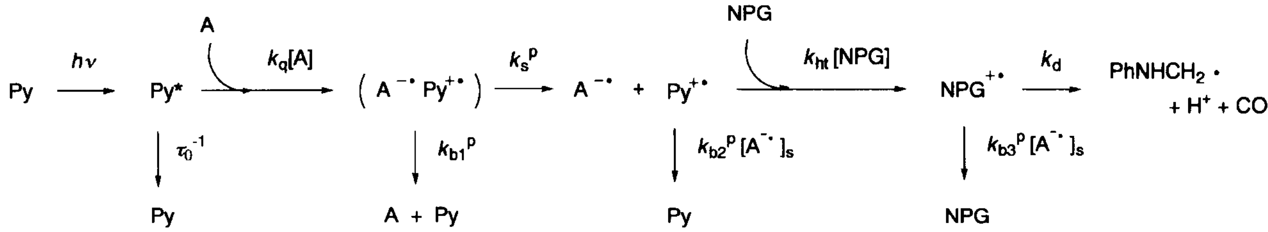
As shown in Table 1, the rate of NPG photodecomposition, as well as K_{sv} for pyrene fluorescence quenching, is dependent on the solvent employed in the photolysis. An estimation of the F^a_{sv} value at $[NPG] = 1.5 \times 10^{-2}$ mol dm^{-3} using the observed K_{sv} gives 0.55 and 1.0 for ethyl acetate and methanol, respectively, relative to acetonitrile. Since the observed rates of NPG decomposition in ethyl acetate and methanol are 0.50 and 1.6 relative to that in acetonitrile, respectively, it is found that $P_a \cdot Q_a$ in Eq. 3 is also an important factor controlling the rate of NPG photodecomposition. It is reasonable to think that the use of polar solvents causes in an increase in not only the quenching factor, F^a_{sv}, but also the P_a value, owing to an accelerated dissociation of the exciplex into free radical ions, both of which contribute to an enhancement of NPG photodecomposition.

Mechanism of the NPG Decomposition in the Presence of an Electron Acceptor. As shown in Table 2, the rate of pyrene-sensitized photodecomposition of NPG is affected by the addition of an electron acceptor, and no simple relationship is observed for the NPG decomposition rate with K_{sv} for pyrene fluorescence quenching by the electron acceptor used as an additive. It should be pointed out that the mechanism of the NPG decomposition in the presence of an electron acceptor is dependent on whether K_{sv} of the electron acceptor employed is greater than that of NPG or not. Taking into account the concentration of NPG and the acceptor under the conditions employed in our experiments, in the case of the acceptors with K_{sv} greater than that of NPG, such as PMN, TPN, DETP, and IPN, singlet excited pyrene is expected to be quenched by the acceptor in preference to NPG. On the other hand, in the case of DEIP and BN, K_{sv} of which is much smaller than that of NPG, it is reasonable to assume that NPG quenched the singlet excited state of pyrene preferentially. The results of laser flash photolysis studies are consistent with these expectations; a transient absorption due to $Py^{+\bullet}$ was observed by the laser excitation of a solution of NPG in the presence of pyrene and TPN, while $Py^{-\bullet}$ was detected in the presence of DEIP.

Scheme 5 shows the mechanism which we propose for the pyrene-sensitized photodecomposition of NPG in the presence of an electron acceptor having K_{sv} greater than that of NPG. The same steady-state treatment as that employed in a previous section leads to Eq. 4 for the rate of pyrene-sensitized photodecompositon of NPG, v_{dec}, in the presence of an acceptor, A,

$$v_{dec} = k_d \cdot [NPG^{+\bullet}]_s = I \cdot F^p_{sv} \cdot P_p \cdot Q_p \cdot R_p \qquad (4)$$

where F^p_{sv}, which is depicted by $K_{sv} \cdot [A]/(1+K_{sv} \cdot [A])$, shows the efficiency of quenching of pyrene fluorescence by the acceptor. P_p and Q_p are depicted by $k^p_s/(k^p_s+k^p_{b1})$ and $k_{ht} \cdot [NPG]/(k_{ht} \cdot [NPG]+k^p_{b2} \cdot [A^{-\bullet}]_s)$, respectively, using the rate constants, k's, defined as shown in Scheme 5. P_p represents the efficiency for the contact radical ion pair to dissociate into free radical ions, while Q_p represents the efficiency for $Py^{+\bullet}$ to transfer a hole to NPG in competition with a back electron transfer. The laser flash photolysis studies have revealed that the hole transfer from $Py^{+\bullet}$ to NPG proceeds with an extremely large rate constant, k_{ht}, which is not inconsistent with the large exothermicity of this process (-10 kcal mol^{-1}).[22] On the basis of this observation, Q_p



Scheme 5. (Py = pyrene)

can be estimated to be unity. The final term, R_p, which is equal to $k_\mathrm{d}/(k_\mathrm{d}+k^\mathrm{p}_\mathrm{b3}\cdot[\mathrm{A}^{-\bullet}]_\mathrm{s})$, shows the efficiency for $\mathrm{NPG}^{+\bullet}$ to decompose in competition with a back electron transfer.

It should be noted that the efficiency of quenching, F^p_sv, is an important factor, but not the only one controlling the rate of NPG photodecomposition. Interestingly, the addition of PMN, which has the largest F^p_sv value of the electron acceptors employed in our experiments, caused a significant retardation in the NPG photodecomposition. We believe that this retardation is attributed to a rapid charge recombination in the contact ion pair, $\mathrm{Py}^{+\bullet}\mathrm{PMN}^{-\bullet}$, which largely reduces the P_p value in Eq. 4. Mataga and his co-workers reported that the quantum yield of ionic photodissociation of a pyrene-PMN system was much smaller, compared with that of a pyrene-TPN system.[15] Our observation is not inconsistent with their results.

We found that the addition of DEIP, though it is a poor quencher of singlet excited pyrene than NPG, enhanced NPG decomposition. In this case, it is reasonable to think that Scheme 4 can be employed as a reaction scheme for NPG decomposition, and that the rate of NPG decomposition is depicted by Eq. 3. The laser flash photolysis studies have revealed that an efficient electron transfer from $\mathrm{Py}^{-\bullet}$ to DEIP ($k_\mathrm{et} = 1.2\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$) occurs in the presence of DEIP. The free-energy change for this electron-transfer process is calculated to be $-2\ \mathrm{kcal\,mol^{-1}}$, employing the reduction potential reported for dimethyl isophthalate (E_red -2.01 V vs. SCE)[13] as that of DEIP. This additional process leads to a suppression of the back electron transfer process, $k^\mathrm{a}_\mathrm{b2}\cdot[\mathrm{Py}^{-\bullet}]_\mathrm{s}$, which would contribute to an enhancement of the NPG photodecomposition owing to an increase of the Q_a value in Eq. 3.[23] No rate enhancement of the NPG decomposition was observed in the addition of BN. This observation is reasonably interpreted by the fact that the electron transfer from $\mathrm{Py}^{-\bullet}$ to BN is an unfavorable process with a free-energy change of $+8\ \mathrm{kcal\,mol^{-1}}$.

Conclusions

The processes of the pyrene-sensitized photodecomposition of NPG have been investigated by fluorescence quenching experiments, laser flash photolysis studies, and characterization of the reaction products. The mechanism involving electron transfer from NPG to singlet excited pyrene through exciplex formation, as well as the intervention of $\mathrm{PhNHCH_2}\bullet$ as a reactive intermediate, has been established.

We have found that the efficiency of the NPG photodecomposition is enhanced by the addition of an electron acceptor, and that the mechanism for the rate enhancement of NPG photodecomposition depends on the acceptor employed as an additive. In the case of an acceptor having a higher reduction potential, such as TPN, pyrene-sensitized photodecomposition proceeds by a mechanism different from that in the absence of an acceptor. Therefore, it is difficult to identify the reason for the rate enhancement, but the efficient quenching of the singlet excited state of pyrene by TPN seems to be a predominate factor responsible for the observed rate enhancement ($v^\mathrm{rel}_\mathrm{dec} = 1.9$), because the F^p_sv value for TPN ($[\mathrm{A}] = 1.5\times10^{-2}\ \mathrm{mol\,dm^{-3}}$) in Eq. 4 is larger than by a factor of 1.7, compared with the F^a_sv value for NPG ($[\mathrm{NPG}] = 1.5\times10^{-2}\ \mathrm{mol\,dm^{-3}}$ in acetonitrile) in Eq. 3. On the other hand, in the case of DEIP, it is reasonable to think that the efficient electron transfer from $\mathrm{Py}^{-\bullet}$ to DEIP, which would suppress the charge recombination between an ion pair, $\mathrm{Py}^{-\bullet}$ $\mathrm{NPG}^{+\bullet}$, is responsible for the rate enhancement.[24]

Our observations provide a new strategy for an efficient photoinitiating system containing NPG, the design and preparation of which are ongoing in our laboratory.

Experimental

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 and 125 MHz, respectively. UV-vis spectra were obtained with a JASCO V-560 spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-777 spectrofluorometer. EI-MS spectra were recorded on a JEOL JMS-600H mass spectrometer. Gel permeation liquid chromatography was carried out on a JAI LC-08 equipped with a JAIGEL-H column. The HPLC analyses were carried out on a JASCO 880 high-pressure liquid-chromatograph system equipped with a SIL C18T-5 column. Cyclic-voltammetric measurements were made in acetonitrile solution ($10^{-3}\ \mathrm{mol\,dm^{-3}}$) with a platinum electrode, tetrabutylammonium perchlorate as a supporting electrolyte, and a silver/silver chloride reference electrode.

Materials. *N*-Phenylglycine (NPG) was purchased from Tokyo Kasei Kogyo Co., Ltd., and was recrystallized twice from water before use. Ethyl *N*-phenylglycinate was prepared according to the procedure described in the literature.[25] Pyrene, pyromellitonitrile (PMN), terephthalonitrile (TPN), isophthalonitrile (IPN), diethyl terephthalate (DETP), and phthalic anhydride (PA) were purified by recrystallization from ethanol prior to use. Pyromellitic dianhydride (PDA) was recrystallized from ethyl acetate. Benzonitrile (BN) was distilled under reduced pressure prior to use. Diethyl isophthalate (DEIP) was obtained by refluxing a solution of isophthalic acid in ethanol in the presence of sulfuric acid, and purified by distillation under reduced pressure. $\mathrm{Bu_3SnH}$ was used without further purification, and methyl methacrylate was used after removal of hydroquinone by passage through a column of silica gel. Acetonitrile, benzene and ethyl acetate were refluxed with, and distilled from $\mathrm{CaH_2}$ prior to use. Methanol was purified by distillation.

Preparation of Tetrabutylammonium *N*-Phenylglycinate. An aqueous solution (170 cm^3) of NPG (0.50 g, 3.3 mmol) containing 2.2 cm^3 of tetrabutylammonium hydroxide (40% in water) was stirred for 2 h at 60 °C. The organic material was extracted with dichloromethane, and the extract was dried over sodium sulfate. The solvent was evaporated and the residue was dried under vacuum to give 0.54 g (41%) of tetrabutylammonium *N*-phenylglycinate. The identity and purity of the material were established by ^{1}H NMR spectrum: viscous oil; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 1.00$ (12H, t, $J = 7.5$ Hz), 1.40—1.47 (8H, m), 1.61—1.68 (8H, m), 3.33 (8H, t, $J = 8.5$ Hz), 3.61 (2H, s), 6.56—6.59 (3H, m), 7.12 (2H, t, $J = 8.0$ Hz).

Preparation of *p*-Anilinomethylbenzonitrile (AMBN). To a solution of aniline (61 mg, 0.65 mmol) and *p*-bromomethylbenzonitrile (Aldrich, 0.10 g, 0.52 mmol) in acetonitrile (10 cm^3) was added potassium carbonate (85 mg, 0.62 mmol), and the mixture was refluxed for 18 h with stirring. After filtration, water was added to the reaction mixture and the organic material was extracted with chloroform. The extract was dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was separated by preparative TLC with hexane–dichloromethane (1 : 1) to give 24 mg (22%) of AMBN as yellow viscous oil; ^{1}H NMR ($CDCl_3$) $\delta = 4.20$ (brs, 1H), 4.43 (s, 2H), 6.57 (2H, d, $J = 8.5$ Hz), 6.74 (1H, t, $J = 8.5$ Hz), 7.17 (2H, t, $J = 8.5$ Hz), 7.48 (2H, d, $J = 8.5$ Hz), 7.63 (2H, d, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 47.8$, 110.9, 112.8, 118.1, 118.8, 127.7, 129.3, 132.4, 145.4, 147.4; MS m/z (rel intensity) 208 (M^+, 100), 116 ($M^+-C_6H_5NH$, 31), 106 ($M^+-C_6H_4CN$, 40).

Irradiations for Preparative Experiments. A solution of pyrene, NPG and additives was placed in a Pyrex tube, and purged with argon for 15 min. The tube was sealed with a septum rubber cap, and placed in a Pyrex vessel containing water. The irradiation was conducted by using a 400-W high-pressure mercury lamp through cutoff glass filter (> 350 nm). The distance between the lamp and the samples was ca. 13 cm. After irradiation, the solvent was removed under reduced pressure. The residue was separated by GPC with a chloroform eluent. The identity and purity of new products were established by the ^{1}H NMR and ^{13}C NMR spectra.

(1) In the Presence of Bu_3SnH and Methyl Methacrylate. A solution of pyrene (2 mg, 0.01 mmol), NPG (23 mg, 0.15 mmol), Bu_3SnH (88 mg, 0.30 mmol) and methyl methacrylate (150 mg, 1.50 mmol) in acetonitrile (10 cm^3) was irradiated for 2 h. Separation of the reaction mixture afforded the adduct **1**. The yield of **1** was 49%, which was determined by the integration of ^{1}H NMR in a crude reaction mixture on the basis of consumed NPG. Methyl 4-anilino-2-methylbutanoate (**1**): viscous oil; ^{1}H NMR ($CDCl_3$) $\delta = 1.21$ (3H, d, $J = 7.5$ Hz), 1.72—1.79 (1H, m), 1.95—2.03 (1H, m), 2.57—2.64 (1H, m), 3.15 (2H, t, $J = 7.3$ Hz), 3.67 (3H, s), 6.60 (2H, d, $J = 7.5$ Hz), 6.70 (1H, t, $J = 7.0$ Hz), 7.17 (2H, t, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 17.31$, 33.31, 37.39, 41.78, 51.70, 112.71, 117.34, 129.24, 148.10, 176.87.

(2) In the Presence of TPN. A solution of pyrene (1 mg, 0.005 mmol), NPG (23 mg, 0.15 mmol) and TPN (19 mg, 0.15 mmol) in acetonitrile (10 cm^3) was irradiated for 10 min. *p*-Anilinomethylbenzonitrile (AMBN) was isolated from the reaction mixture. The identification of AMBN was established by the agreement of its spectroscopic data with those of an authentic sample. The yield of AMBN was 5%, which was determined by the integration of ^{1}H NMR in the crude reaction mixture on the basis of consumed NPG.

(3) In the Presence of PA. We first analyzed the reaction mixture obtained in the irradiation of a solution of NPG in acetonitrile containing pyrene and PA to find that NPG was almost completely consumed. We found, however, that NPG reacted nearly quantitatively with PA, even in the dark. Thus, a mixture of NPG (11 mg, 0.075 mmol) and PA (11 mg, 0.074 mmol) in acetonitrile (5 cm^3) was allowed to stand for 30 min in the dark at room temperature. After removing the solvent under reduced pressure, the ^{1}H NMR of the crude reaction mixture revealed the complete consumption of NPG and the formation of a new product. Though attempts to isolate the product was not successful because of its instability during the GPC separation, it was tentatively identified as *N*-carboxymethyl-*N*-phenylphthalamic acid on the basis of its ^{1}H NMR spectrum: ^{1}H NMR ($CDCl_3$) $\delta = 4.71$ (2H, s), 7.12—7.16 (2H, m), 7.21 (2H, t, $J = 7.5$ Hz), 7.27—7.35 (2H, m), 7.36 (2H, d, $J = 7.5$ Hz), 7.88 (1H, d, $J = 7.5$ Hz).

Irradiations for Analytical Experiments. A solution of NPG (1.5×10^{-2} mol dm^{-3}, 2 cm^3) in acetonitrile or other solvents containing pyrene (5.0×10^{-4} mol dm^{-3}) and an electron acceptor (1.5×10^{-2} mol dm^{-3}) was placed in a Pyrex tube, and purged with argon for 15 min. The tube was sealed with a septum rubber cap, placed in a merry-go-round apparatus, and irradiated with a 400-W high-pressure mercury lamp through a band-pass filter (350±25 nm) at room temperature. The distance between the lamp and the sample tube was 7.5 cm. The photolysis was stopped at an early stage of the reaction, when the conversion of NPG was 20—50%. After evaporation of the solvent, the products were identified by ^{1}H NMR spectrum. *N*-Methylaniline (NMA), aniline, and formanilide were identified by comparison of the spectroscopic data with those of authentic material. The consumption of NPG and pyrene, as well as the yield of the products, was determined by the integration of each characteristic peak of the ^{1}H NMR spectrum in the crude reaction mixture. The relative rates of NPG decomposition, $v_{\rm dec}^{\rm rel}$, were evaluated by the consumption of NPG.

Fluorescence Quenching Studies. Solutions of pyrene (1.0×10^{-5} mol dm^{-3}) in acetonitrile or other solvents containing various amounts of quenchers were placed in 10 mm quartz tubes. Fluorescence spectra were measured at room temperature under air on excitation at 340 nm. Relative fluorescence intensities (I_0/I) were determined by measuring the peak of heights for the maxima.

Laser Flash Photolysis Studies. The laser flash photolysis experiments were performed by using a pulsed Q-switch Nd : YAG Laser (SOLAR LF114) as the excitation source. All of the spectra were recorded by the use of THG of the laser that provided UV pulses at 355 nm with duration of 13 ns and a pulse energy of ca. 0.7 mJ/pulse. Transient absorption signals were monitored by employing a 10-W xenon flash lamp beam which was passed through the sample perpendicular to the excitation beam. A sample solution was placed in a flask, purged with N_2 before and during measurements, and flowed into a quartz cuvette (5×10 mm) by a magnetic gear pump. The transient absorption spectra were recorded in the wavelength range of 330 to 630 nm.

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22 For the calculation of the free energy change for hole transfer, +1.16 V was employed for the oxidation potential of pyrene ($E_{\rm ox}$ vs SCE).[12]

23 It is possible that the decomposition of DEIP$^{-\bullet}$, which is formed through the electron transfer from Py$^{-\bullet}$ to DEIP, is responsible for the suppression of the back electron transfer process. To validate this assumption, however, further studies on the reactivity of DEIP$^{-\bullet}$ are required.

24 Since the electron acceptors employed in these experiments have no absorption at 366 nm in acetonitrile, the number of photons absorbed by pyrene, I in Eqs. 3 and 4, would not be affected by the addition of electron acceptors. Thus, the relative rate of pyrene-sensitized decomposition of NPG obtained in the presence of an electron acceptor, $v_{\rm dec}^{\rm rel}$, corresponds to the relative quantum yield of NPG decomposition, $\Phi_{\rm dec}^{\rm rel}$.

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