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Photolysis of *N*-phenylglycines sensitized by polycyclic aromatic hydrocarbons
Effects of sensitizers and substituent groups and application to photopolymerization

Shingo Ikeda, Shigeru Murata*

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,
Meguro-ku, Tokyo 153-8902, Japan

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Abstract

The effects of sensitizers and substituent groups on the rate of sensitized photodecomposition of *N*-phenylglycine (NPG) were investigated under irradiation using light of 366 nm. It was found that pyrene was the most effective polycyclic aromatic hydrocarbon as a sensitizer for the NPG photodecomposition. Introduction of an electron-donating group into the aromatic ring of NPG resulted in the enhancement of the pyrene-sensitized photodecomposition rate. Especially, the photodecomposition rate of *N*-(2,4-dimethylphenyl)glycine was larger than that of parent NPG by a factor of 4.6. The results were discussed on the basis of the free-energy change for the electron transfer from NPG or its derivatives to the excited sensitizer. Furthermore, the pyrene-sensitized photodecomposition of NPGs could be utilized for a photoinitiator for free radical polymerization of acrylate monomers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *N*-Phenylglycine; Sensitized photolysis; Photoinduced electron transfer; Substitution effect; Photopolymerization

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1. Introduction

It is known that the photodecomposition of *N*-phenylglycine, $PhNHCH_2CO_2H$, and its derivatives (NPGs) can be sensitized by aromatic nitro compounds [1], quinones [2], polycyclic aromatic hydrocarbons [3] and dyes [4]. Since the photodecomposition of NPGs gives free radicals, they have been extensively studied from the standpoint of practical applications as initiators in photopolymerization for microlithography, reprography, dental restorative materials, etc. In these studies, it has been suggested that a single electron transfer from NPGs to the excited sensitizer is involved in their photodecomposition processes. Paczkowski et al. [4g–4j] reported the dependence of the rate of polymerization of an acrylate monomer on the free-energy change for the electron transfer from NPGs to the excited sensitizer in various photoinitiating systems composed of dyes and NPGs. They demonstrated that the polymerization rate was controlled not only by the rate of photoinduced electron transfer, but also by the reactivity of free radicals formed as a result of the electron transfer.

In contrast to these researches from a practical standpoint, there are few studies on the detailed mechanism of the sensitized photodecomposition of NPGs. Recently, we reported on our mechanistic studies of the pyrene-sensitized photodecomposition of NPG, in which the reaction scheme involving a single electron transfer from NPG to singlet excited pyrene through an exciplex formation and the intervention of anilinomethyl radical, $PhNHCH_2^{\bullet}$, as a reactive intermediate was established [5]. An enhancement of the efficiency of the NPG photodecomposition is important for a design of a new photoinitiating system based on polycyclic aromatic hydrocarbons and NPGs, which is expected to initiate photopolymerization by a weak UV light. In order to search the more efficient NPG photodecomposition system, we have decided to optimize a sensitizer and a free radical precursor in the polycyclic aromatic hydrocarbon-sensitized NPG photodecomposition systems. In this paper, we report the effects of sensitizers and substituent groups on the photodecomposition rate of NPGs, and discuss the results based on the free-energy change for the electron transfer from NPGs to the excited sensitizer. Furthermore, we also report that our NPGs photodecomposition systems can be practically applied to photoinitiators for free radical polymerization of acrylate monomers.

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* Corresponding author. Tel.: +81-3-5454-6596; fax: +81-3-5454-6998.
E-mail address: cmura@mail.ecc.u-tokyo.ac.jp (S. Murata).

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2. Experimental

2.1. 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.

2.2. Materials

N-Phenylglycine was purchased from Tokyo Kasei Kogyo, and was recrystallized twice from water before use. Pyrene, 9-phenylanthracene (9-PA), 9,10-diphenylanthracene (9,10-DPA), 9-cyanoanthracene (9-CA), 9,10-dicyanoanthracene (9,10-DCA) and xanthone (XTN) were purified by recrystallization from ethanol prior to use. Perylene was recrystallized from toluene. Benzophenone was recrystallized from ethanol–water (3:1). Acetonitrile was refluxed with, and distilled from CaH_2 prior to use. The acrylate monomers, isooctyl acrylate (IOA) and 2-(2-phenoxyethoxy)ethylacrylate (2,2-PEEA), were received from Nippon Kayaku and Toagosei, respectively. The NPGs having substituent groups at the *p*-position and *N*-methyl-*N*-phenylglycine were synthesized according to the procedure reported in the literature [6,7]. Almost all NPGs having methyl groups were prepared in the standard procedure from the corresponding anilines and ethyl bromoacetate. In a typical run, to a solution of the aniline (60 mmol) and ethyl bromoacetate (60 mmol) in ethanol (6 cm^3) was added sodium acetate trihydrate (90 mmol). The mixture was refluxed for 24 h with stirring. Water (20 cm^3) was added, and the organic material was extracted with ether. The solvent was evaporated under reduced pressure. To the residue was added 20% of hydrochloric acid (180 cm^3), and the reaction mixture was heated at 100 °C for 4 h. After evaporation of the solvent, water (40 cm^3) was added, and the mixture was extracted with chloroform. After the pH of the aqueous phase was adjusted to pH 4–5 with sodium carbonate, the deposited organic material was extracted with chloroform. The solvent was evaporated to give the NPGs in ca. 10% yield. The identity and purity of the material were established by ^{1}H and ^{13}C NMR spectrum. *N*-(2-Methylphenyl)glycine: light purple granules; m.p. 148–150 °C; ^{1}H NMR ($CDCl_3$) δ 2.22 (3H, s), 4.03 (2H, s), 6.52 (1H, d, $J = 8.0$ Hz), 6.76 (1H, t, $J = 7.5$ Hz), 7.10 (1H, d, $J = 7.0$ Hz), 7.16 (1H, d, $J = 7.5$ Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 17.3, 45.7, 110.1, 118.4, 122.7, 127.2, 130.4, 144.6, 175.2 ppm. *N*-(3-Methylphenyl)glycine: viscous oil; ^{1}H NMR ($CDCl_3$) δ 2.28 (3H, s), 3.94 (2H, s), 6.46 (2H, d, $J = 8.5$ Hz), 6.63 (1H, d, $J = 7.0$ Hz), 7.06 (1H, t, $J = 7.5$ Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 21.6, 46.0, 114.1, 119.8, 129.3, 139.3, 146.6, 175.5 ppm. *N*-(3,4-Dimethylphenyl)glycine: viscous oil; ^{1}H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.20 (3H, s), 3.94 (2H, s), 6.41 (1H, d, $J = 8.0$ Hz), 6.47 (1H, s), 6.97 (1H, d, $J = 8.0$ Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 18.7, 20.0, 46.6, 110.9, 115.3, 127.1, 130.4, 137.5, 144.6, 175.0 ppm. *N*-(3,5-Dimethylphenyl)glycine: light violet granules; m.p. 91–93 °C; ^{1}H NMR ($CDCl_3$) δ 2.25 (6H, s), 3.96 (2H, s), 6.28 (2H, s), 6.47 (1H, s) ppm; ^{13}C NMR ($CDCl_3$) δ 21.4, 46.2, 111.5, 121.2, 139.1, 146.3, 175.8 ppm. *N*-(2,4,6-Trimethylphenyl)glycine: viscous oil; ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s), 2.32 (6H, s), 3.81 (2H, s), 6.84 (2H, s) ppm. *N*-(2,4-Dimethylphenyl)glycine (NDMPG) was synthesized as follows: to a solution of 2,4-dimethylaniline (60 mmol) and bromoacetic acid (50 mmol) in water (ca. 30 cm^3) was added sodium acetate trihydrate (80 mmol). The mixture was heated at 100 °C for 24 h with stirring. After cooling, water (ca. 30 cm^3) was added to the reaction mixture. The pH of the mixture was adjusted to pH 8 with sodium carbonate. After extraction with chloroform, the pH of the aqueous layer was adjusted to pH 5 with hydrochloric acid. The deposited organic material was collected by filtration and dried under reduced pressure to give the NPG derivative in 14% yield as ivory granules: m.p. 144–147 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (3H, s), 2.24 (3H, s), 3.98 (2H, s), 6.44 (1H, d, $J = 7.5$ Hz), 6.92–6.96 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 17.3, 20.3, 46.2, 122.9, 127.8, 131.3, 142.3, 175.7 ppm. *N*-Phenylalanine was synthesized as follows: a solution of aniline (100 mmol) and ethyl 2-bromopropionate (50 mmol) in acetonitrile (100 cm^3) was refluxed for 8 h with stirring. Water (100 cm^3) was added to the reaction mixture, and the organic material was extracted with dichloromethane. The extract was dried over sodium sulfate, and the solvent was evaporated. To the residue was added 10% of hydrochloric acid (170 cm^3), and the reaction mixture was refluxed for 3 h. The mixture was concentrated under reduced pressure, and azeotropic distillation with benzene was performed. The precipitate was filtered and added to water (140 cm^3). The mixture was extracted with chloroform, and the extract was dried over sodium sulfate. The solvent was evaporated to give the crude product (18%), which was purified by recrystallization from water–ethanol (5:1): yellow granules; m.p. 163–165 °C; 1H NMR ($CDCl_3$) δ 1.55 (3H, d, $J = 7.0$ Hz), 4.11 (1H, q, $J = 7.0$ Hz), 6.65 (2H, d, $J = 9.0$ Hz), 6.81 (1H, t, $J = 7.0$ Hz), 7.21 (2H, t, $J = 7.5$ Hz) ppm.

2.3. Irradiations for analytical experiments

A solution of NPG or its derivative (1.5×10^{-2} mol dm^{-3}, 2 cm^3) in acetonitrile containing a sensitizer (5.0×10^{-4} 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 the NPG was 20–50%.

After evaporation of the solvent, the consumption of the NPG was determined by the integration of the characteristic peak of the ^{1}H NMR spectrum in the crude reaction mixture. The relative rates of the photodecomposition of the NPG, $\upsilon_{\mathrm{dec}}^{\mathrm{rel}}$, were evaluated by the consumption of the NPG.

2.4. Fluorescence quenching studies

Solutions of sensitizer (1.0×10^{-5} mol dm^{-3}) in acetonitrile 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. The rate constants for pyrene fluorescence quenching by NPGs, γk_{e}, shown in Tables 2 and 3 were calculated from the observed Stern–Volmer constants, $K_{\mathrm{SV}} = \gamma k_{\mathrm{e}} \tau_0$, and the life time of singlet excited pyrene under our conditions, τ_0. The life time was estimated to be 11.4 ns by employing the observed K_{SV} for quenching by terephthalonitrile and its quenching rate constant reported in the literature [8].

2.5. Cyclic voltammetric measurements

Cyclic voltammetric measurements were made in acetonitrile solution (10^{-3} mol dm^{-3}) with a platinum electrode, tetrabutylammonium perchlorate as a supporting electrolyte and a silver/silver chloride reference electrode. The scan rate was 0.2 V s^{-1}. All NPGs examined in this study gave an irreversible voltammogram so that the potential of the first oxidation peak was employed as an oxidation potential (E_{ox}).

2.6. Polymerization experiments

To an acetonitrile or a methanol solution (3 ml) of pyrene (1.0×10^{-4} mol dm^{-3}) and NPG or its derivatives (3.0×10^{-3} mol dm^{-3}) was added a monomer (1.4 mol dm^{-3} for IOA, 1.2 mol dm^{-3} for 2,2-PEEA). The solution was placed in a Pyrex tube, purged with argon for 20 min and sealed with a septum rubber cap. The solution was irradiated for 10 min with a 400 W high-pressure mercury lamp through a band pass filter (350 ± 25 nm) in a merry-go-round apparatus at room temperature. After the irradiation, methanol (4 ml) was added to the reaction mixture. The mixture was irradiated with ultrasonic waves for 3 min, and washed three times with methanol by decantation to remove the unreacted monomer. After dried by air, the precipitated polymer was heated at 100 °C for 1 h, and further at 120 °C for 1 h. The conversion of the monomer into the corresponding polymer was determined by the weight of the polymer. The monomer conversion obtained by this procedure was in agreement with that determined by the consumption of the monomer, which was directly determined by the integration of ^{1}H NMR spectrum in the reaction mixture obtained after the removal of the precipitated polymer. Thus, it is confirmed that the monomer was converted quantitatively into the polymer under the conditions of our polymerization experiments.

2.7. Calculations

The semiempirical molecular orbital calculations were carried out by the WinMOPAC (ver. 3.0) program package provided by Fujitsu. The geometry optimizations, as well as calculations of the heat of formation, were performed at the PM3 level of theory.

3. Results and discussion

3.1. Photodecomposition of NPG sensitized by polycyclic aromatic hydrocarbons

As reported previously, 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 (Py, 5.0×10^{-4} mol dm^{-3}) resulted in a rapid consumption of NPG [5b]. The concentration of NPG was decreased linearly with irradiation time until at least 50% of the starting material was consumed. Under our typical irradiation conditions, the initial rate of pyrene-sensitized photodecomposition of NPG was evaluated to be $\upsilon_{\mathrm{dec}}(\mathrm{Py}) = 2.1 \times 10^{-4}$ mol dm^{-3} min^{-1}. However, when we compared the rate of NPG photodecomposition sensitized by a sensitizer other than Py, $\upsilon_{\mathrm{dec}}(\mathrm{S})$, with $\upsilon_{\mathrm{dec}}(\mathrm{Py})$, a relative rate defined as $\upsilon_{\mathrm{dec}}^{\mathrm{rel}} = \upsilon_{\mathrm{dec}}(\mathrm{S})/\upsilon_{\mathrm{dec}}(\mathrm{Py})$, which could be directly obtained as a reproducible value by using a merry-go-round apparatus, sufficed for the discussion. Thus, we determined the rates of NPG photodecomposition sensitized by various sensitizers relative to that by pyrene under the identical irradiation conditions.

As polycyclic aromatic hydrocarbon sensitizers having a molar extinction coefficient at 366 nm larger than that of Py, we examined perylene (Pe), 9-PA and 9,10-DPA. Since a high reduction potential could be expected to enhance a photoinduced electron transfer process, 9-CA and 9,10-DCA were also examined as sensitizers. Furthermore, in order to compare the efficiency of polycyclic aromatic hydrocarbons in the sensitized photodecomposition of NPG with that of triplet sensitizers, we employed benzophenone (BP) and XTN as sensitizers. The relative rates of NPG photodecomposition determined by using these sensitizers, $\upsilon_{\mathrm{dec}}^{\mathrm{rel}}$, are collected in Table 1, along with their molar extinction coefficients at 366 nm ($\varepsilon_{366\,\mathrm{nm}}$). In contrast to our expectation, all sensitizers employed reduced the NPG photodecomposition rate, compared with that determined by using Py as a sensitizer.

In the previous paper, we proposed the mechanism of pyrene-sensitized photodecomposition of NPG involving an electron transfer from NPG to singlet excited Py (Py*) through an emissive exciplex formation, followed by the cleavage of NPG radical cation (NPG$^{\bullet+}$) to give PhNHCH$_2^{\bullet}$ [5b]. One of the strong pieces of evidence in support of the

Table 1
Relative rates of photodecomposition of NPG sensitized by various sensitizer and quenching of their fluorescence by NPG in Acetonitrile

Sensitizer	$v_{\mathrm{dec}}^{\mathrm{rel}}$ [a]	$\varepsilon_{366\,\mathrm{nm}}$ ($\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$)	E_{red} [b] (V vs SCE)	E^* [c] ($\mathrm{kcal\,mol^{-1}}$)	K_{SV} [d] ($\mathrm{mol^{-1}\,dm^3}$)	λ_{ex} [e] (nm)	$IF_{\mathrm{SV}}^{\mathrm{rel}}$ [f]	PQ^{rel} [g]
Py	1.0	210	−2.09	76.7	60.0	454	1.0	1.0
Pe	0.52	4300	−1.67	65.2	45.8	526	4.0	0.13
9-CA	0.46	7200	−1.58	68.6	129	–	6.5	0.070
9,10-DCA	0.48	5100	−0.98	66.9	290	–	8.0	0.059
9-PA	0.73	9800	−1.86	72.6	64.6	494	4.8	0.15
9,10-DPA	0.35	9500	−1.94	72.9	55.7	511	4.5	0.077
BP	0.58	53	−1.83	69.1	–	–	–	–
XTN	0.75	10	−1.77	74.1	–	–	–	–

[a] Relative rate of sensitized photodecomposition of NPG; [NPG] = $1.5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$; [sensitizer] = $5.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$.
[b] Reduction potential of sensitizer [8].
[c] Excited-state energy of sensitizer [8].
[d] $K_{\mathrm{SV}} = \gamma k_e \tau_0$; Stern–Volmer constant for quenching of sensitizer fluorescence by NPG in aerated solution ([sensitizer] = $1.0 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$).
[e] Fluorescence maximum of exciplex.
[f] Calculated from $\varepsilon_{366\,\mathrm{nm}}$ and K_{SV}; see text.
[g] Calculated from $v_{\mathrm{dec}}^{\mathrm{rel}}$ and $IF_{\mathrm{SV}}^{\mathrm{rel}}$; see text.

mechanism is the fact that the electron transfer from NPG to Py* is an energetically favorable process. The free-energy change for the electron transfer from NPG to the excited sensitizer employed in this study can be calculated by the Rehm–Weller equation (Eq. (1)) [9]:

$$\Delta G_{\mathrm{et}}(\mathrm{kcal\,mol^{-1}}) = 23.06(E_{\mathrm{ox}}(\mathrm{NPG}) - E_{\mathrm{red}}(\mathrm{S})) - E^*(\mathrm{S}) - w \qquad (1)$$

In this equation, E_{red}(S) and E^*(S) stand for the reduction potential and the excited-state energy of the sensitizer, respectively, both of which are collected in Table 1. Moreover, E_{ox}(NPG) and w indicate the oxidation potential of NPG (+0.99 V vs SCE) and the Coulomb term, which is assumed to be $1\,\mathrm{kcal\,mol^{-1}}$, respectively. According to the calculation, the electron transfer from NPG to the excited sensitizer is found to be exothermic with $-\Delta G_{\mathrm{et}} > 5\,\mathrm{kcal\,mol^{-1}}$ for all sensitizers employed in this study. On the basis of this calculation, it can be assumed that the NPG photodecomposition caused by the sensitizers other than Py is also initiated by the electron transfer from NPG to the excited sensitizer. However, as illustrated in Fig. 1, no simple relationship is found between logarithm of $v_{\mathrm{dec}}^{\mathrm{rel}}$ and the exothermicity of the photoinduced electron transfer process ($-\Delta G_{\mathrm{et}}$). This observation implies that the exothermicity of the initial electron transfer process is not the sole factor controlling the NPG photodecomposition rate.

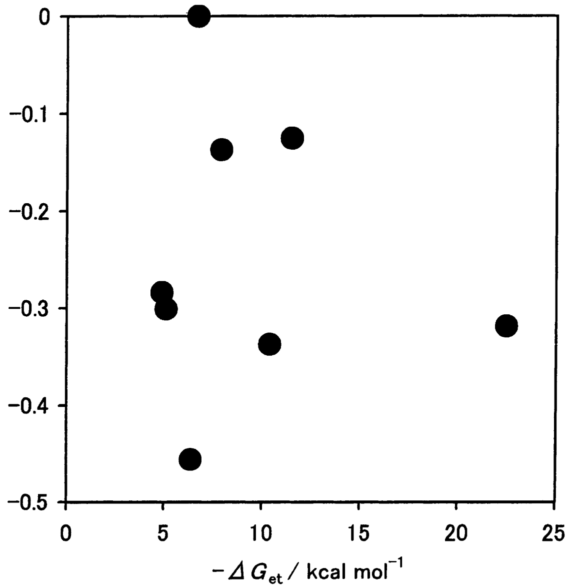
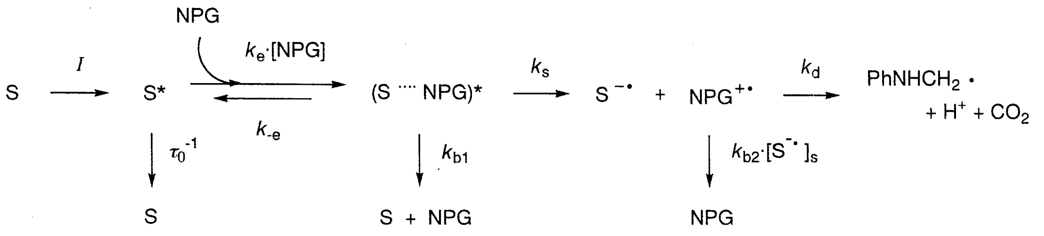


Fig. 1. Dependence of logarithm of the relative rate of NPG photodecomposition sensitized by various sensitizers, $\log v_{\mathrm{del}}^{\mathrm{rel}}$, on the exothermicity of the electron transfer from NPG to the excited sensitizer, $-\Delta G_{\mathrm{et}}$.

Assuming that the mechanism proposed for the pyrene-sensitized photodecomposition of NPG [5b] can be applied in the case of the other sensitizers, the NPG photodecomposition mechanism can be depicted by Scheme 1. In the



Scheme 1.

scheme, k_e shows the rate of quenching of excited sensitizer by NPG to form an exciplex, which could be regarded as a contact radical ion pair, and k_{-e} exhibits the rate of return of the exciplex to the excited sensitizer and NPG. Moreover, k_s and k_d indicate the rate of dissociation of the exciplex into free radical ions and the decomposition rate of NPG$^{\bullet+}$, respectively. The rates of charge recombination in the exciplex and the free radical ions are depicted by k_{b1} and k_{b2}, respectively. Moreover, the NPG photodecomposition rate (v_{dec}) is given by Eq. (2) by using a steady-state approximation

$$v_{dec} = k_d[\text{NPG}^{\bullet+}]_s = IF_{SV}PQ \tag{2}$$

In this equation, I is the number of photons absorbed by the sensitizer, which can be represented by $I_0(1 - 10^{-\varepsilon[S]l})$, where I_0 and ε exhibit the number of photons radiated by the lamp and a molar absorption coefficient at 366 nm of the sensitizer, respectively. Under our irradiation conditions, the concentration of the sensitizer ([S]) and the cell length (l) are defined as 5.0×10^{-4} mol dm^{-3} and 1 cm, respectively. Furthermore, F_{SV}, which is depicted by $K_{SV}[\text{NPG}]/(1 + K_{SV}[\text{NPG}])$, represents the efficiency of the quenching of the sensitizer excited state by NPG. The value K_{SV}, which is equal to $\gamma k_e \tau_0$, is a Stern–Volmer constant for the quenching process, in which γ stands for $(k_{b1}+k_s)/(k_{b1}+k_s+k_{-e})$. The factor P, which is equal to $k_s/(k_s+k_{b1})$, shows the efficiency for the exciplex to dissociate into the free radical ions, while the factor Q, which is equal to $k_d/(k_d + k_{b2}[\text{S}^{\bullet-}]_s)$, shows the efficiency for NPG$^{\bullet+}$ to decompose in competition with a charge recombination with a sensitizer radical anion (S$^{\bullet-}$).

In order to gain information about the quenching factor F_{SV} of the sensitizers employed in this study, quenching of the sensitizer fluorescence by NPG was examined. The Stern–Volmer constants (K_{SV}) obtained are summarized in Table 1. Analogously to the case of Py [5b], the formation of an emissive exciplex was observed by the addition of NPG to the solution of Pe, 9-PA and 9,10-DPA. The fluorescence maximum of the exciplex (λ_{ex}) is also collected in Table 1. The quenching factor F_{SV} of the sensitizer can be calculated by using K_{SV} under our irradiation conditions ([NPG] $= 1.5 \times 10^{-2}$ mol dm^{-3}). Fig. 2 displays the relationship between the logarithm of F_{SV} and the exothermicity of the photoinduced electron transfer process ($-\Delta G_{et}$). The good correlation between them supports the assumption that the quenching of the sensitizer excited state by NPG proceeds by the electron transfer mechanism.

As mentioned above, the absorption factor (I) in Eq. (2) can be estimated by using $\varepsilon_{366\,\text{nm}}$ of the sensitizer. Thus, the IF_{SV} value for each sensitizer relative to that for Py can be calculated, which is also given in Table 1. The IF_{SV} values for the sensitizers other than Py are larger than that for Py by a factor of 4–8, indicating that Py has a great disadvantage in the processes of light absorption and quenching of the excited state by NPG. Therefore, it can be concluded that the ineffectiveness of the sensitizers other than Py for the NPG photodecomposition is attributed to the extremely small PQ factor in Eq. (2). The relative PQ values, which are evaluated by $v_{dec}^{rel}/IF_{SV}^{rel}$, are collected in the last row of Table 1.

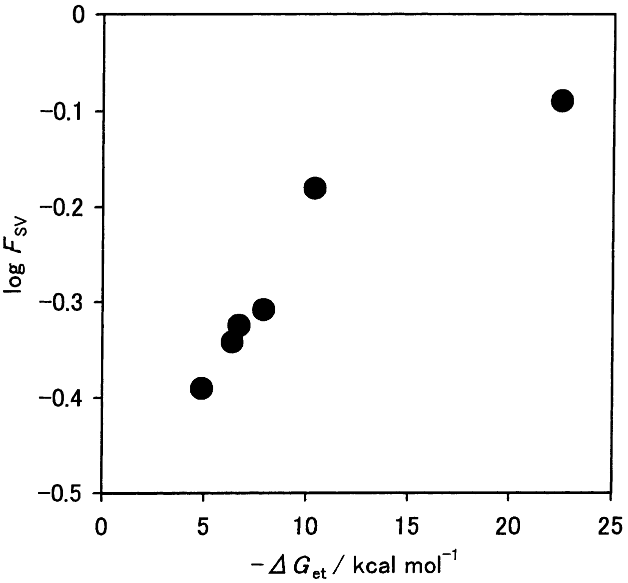


Fig. 2. Dependence of logarithm of the quenching factor for the NPG photodecomposition sensitized by various sensitizers, log F_{SV}, on the exothermicity of the electron transfer from NPG to the excited sensitizer, $-\Delta G_{et}$.

Since few experimental data on the absolute rate constants involved in the factors P and Q are available, it is difficult to give a strict explanation for the ineffectiveness of the sensitizers having a large IF_{SV} value such as 9,10-DCA. However, we should point out the following two factors controlling the PQ values of various sensitizers. The first is a charge recombination rate constant in the contact radical ion pair (k_{b1}). A rapid charge recombination in the contact radical ion pair leads to a decrease in the P value, which causes a decrease in the NPG photodecomposition rate. It has been reported that the dependence of the charge recombination rate in the contact radical ion pair on the exothermicity of the process shows the "Marcus inverted region"-like kinetic behavior, i.e., the charge recombination rate increases with decreasing the exothermicity [10]. The free-energy change for the charge recombination between NPG$^{\bullet+}$ and S$^{\bullet-}$ (ΔG_{bet}) is estimated by the following equation:

$$\Delta G_{bet}(\text{kcal mol}^{-1}) = 23.06(E_{red}(\text{S}) - E_{ox}(\text{NPG})) + w \tag{3}$$

The relationship between logarithm of PQ^{rel} and the exothermicity of the charge recombination process ($-\Delta G_{bet}$) is displayed in Fig. 3. It should be pointed out that there is a tendency for the PQ values to decrease with a decrease in $-\Delta G_{bet}$. This finding indicates the possibility that the rate of the charge recombination in the contact radical ion pair plays an important role in controlling the rate of sensitized photodecomposition of NPG. Thus, one possible reason for the remarkable effectiveness of Py as a sensitizer for the NPG photodecomposition is a retardation in the charge

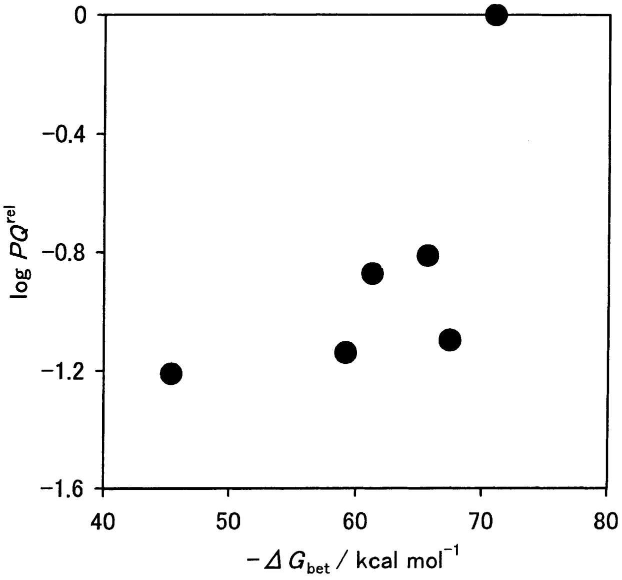


Fig. 3. Dependence of logarithm of the relative *PQ* factor for the NPG photodecomposition sensitized by various sensitizers, $\log PQ^{\text{rel}}$, on the exothermicity of the charge recombination between $\text{NPG}^{\bullet+}$ and the sensitizer radical anion, $-\Delta G_{\text{bet}}$.

recombination in the contact radical ion pair, which is due to the large exothermicity of the process.

The second factor controlling the *PQ* values is a reactivity of the sensitizer radical anion ($\text{S}^{\bullet-}$) which depends on the electronic and steric structure of $\text{S}^{\bullet-}$. An increase in the rate of disappearance of $\text{S}^{\bullet-}$ by reactions, such as protonation, fragmentation, etc., leads to an decrease in the steady-state concentration of $\text{S}^{\bullet-}$ ($[\text{S}^{\bullet-}]_\text{s}$), which causes an increase in the *Q* value. However, this factor is unlikely to be the predominant factor controlling the rate of sensitized photodecomposition of NPG, because the *Q* value seems to be close to unity regardless of the sensitizers. This assumption is based on the following evaluation: Mariano and coworkers [6] determined the rates of unimolecular decarboxylation of the radical cation of *N*-methyl-*N*-phenylglycinate to be in the range 10^6–$10^7\,\text{s}^{-1}$. Assuming that this value can be applied to the rate of the decomposition of $\text{NPG}^{\bullet+}$ (k_d), it is reasonable to think that $k_\text{d} \gg k_{\text{b2}}[\text{S}^{\bullet-}]_\text{s}$ is valid in all sensitizers even if the charge recombination between the free radical ions proceeds at the diffusion-controlled rate constant ($k_{\text{b2}} =\sim 10^{10}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$), because $[\text{S}^{\bullet-}]_\text{s}$ should be much less than $10^{-4}\,\text{mol}\,\text{dm}^{-3}$ under our irradiation conditions ($[\text{S}] = 5 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$, high-pressure mercury lamp).

Taking very small extinction coefficients at 366 nm into account, triplet sensitizers BP and XTN are effective in initiating the NPG photodecomposition. As mentioned before, it is probable that the electron transfer from NPG to the excited triplet sensitizer is involved in the NPG photodecomposition process. However, the mechanism of the NPG photodecomposition sensitized by polycyclic aromatic hydrocarbons cannot be applied directly to the BP- and XTN-sensitized photodecomposition, because it is reasonable to think that the mechanism involving a proton transfer from $\text{NPG}^{\bullet+}$ to the ketyl radicals $\text{BP}^{\bullet-}$ and $\text{XTN}^{\bullet-}$ having a large proton affinity participates largely in the NPG photodecomposition. The NPG photodecomposition, as well as the NPG-initiated photopolymerization, sensitized by quinones [2] and dyes [4] has been discussed on the basis of this mechanism.

In conclusion, it is found that Py is the most effective of the sensitizers examined in this study for the NPG photodecomposition, although the processes of light absorption and quenching of its excited state by NPG are much less effective compared with the other sensitizers. We propose that the effectiveness of Py is mainly attributed to a retardation in the charge recombination in the contact radical ion pair owing to the large exothermicity of the process.

3.2. Photodecomposition of NPG derivatives sensitized by pyrene

Next, we examined the effect of substituent groups of NPG on the rate of sensitized photodecomposition. In order to search the efficient NPG photodecomposition system, Py was employed as a sensitizer by reference to the results described above. In order to compare the rate of photodecomposition of the NPGs having a substituent group X with that of parent NPG, we determined a relative photodecomposition rate defined as $v_{\text{dec}}^{\text{rel}} = v_{\text{dec}}(\text{X})/v_{\text{dec}}(\text{H})$, which could be obtained as described in the above section.

3.2.1. Effect of the substituent group at the p-position

In contrast to extensive investigation of the substituent effect of NPG on the rate of free radical polymerization of a monomer initiated by a dye-NPG photoinitiating system [4g–4j], few studies of the substituent effect on the rate of NPG photodecomposition, which is one of the most important factors controlling the rate of free radical polymerization, have been reported. The relative rates of the photodecomposition of NPGs having various substituents at the *p*-position ($v_{\text{dec}}^{\text{rel}}$) were determined, which are collected in Table 2, along with their rate constants for quenching of Py fluorescence (γk_e) and their oxidation potentials (E_ox). Unfortunately, the Py-sensitized photodecomposition rate of *N*-(4-methoxyphenyl)glycine (E_ox; 0.80 V vs SCE) could not be determined, because this derivative was decomposed in the presence of Py even in the dark. Moreover, $v_{\text{dec}}^{\text{rel}}$ of *N*-(4-nitrophenyl)glycine (E_ox; 1.57 V vs SCE) could not obtained owing to its large absorption at 366 nm. Since the NPGs having *p*-CN and *p*-CF_3 groups showed an emission at 450 and 351 nm, respectively, their γk_e's could not be determined.

The plot of the logarithm of $v_{\text{dec}}^{\text{rel}}$, as well as γk_e, against $\sigma_\text{p}{}^+$ is illustrated in Fig. 4. The linear relationship between $\log v_{\text{dec}}^{\text{rel}}$ and $\sigma_\text{p}{}^+$ indicates that the Py-sensitized photodecomposition of NPGs proceeds via an ionic transition state, which can be stabilized by the substitution of

Table 2
Relative rates of pyrene-sensitized photodecomposition of *p*-substituted NPG and quenching of pyrene fluorescence in acetonitrile

Substituent	$v_{\mathrm{dec}}^{\mathrm{rel}}$ [a]	γk_{e} [b] ($10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$)	E_{ox} [c] (V vs SCE)
CN	0.33	– [d]	1.42
CF_3	0.31 [e]	– [d]	1.31
Cl	0.80	9.5	1.10
H	1.0	5.2	0.99
Et	2.0	10.1	0.92
Me	2.0	11.6	0.89

[a] Relative rate of pyrene-sensitized decomposition of *p*-substituted NPG; [pyrene] $= 5.0 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$; [NPG] $= 1.5 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$.

[b] Rate constant for quenching of pyrene fluorescence by *p*-substituted NPG.

[c] Oxidation potential of *p*-substituted NPG measured in this work.

[d] Not determined owing to the emission of the *p*-substituted NPG.

[e] In methanol.

an electron-donating group. On the other hand, the plot of $\log \gamma k_{\mathrm{e}}$ vs $\sigma_{\mathrm{p}}{}^{+}$ gives a V-shape line, suggesting that the mechanism of quenching of Py fluorescence by NPGs is dependent on the electronic property of the *p*-substituent group. This assumption is supported by the V-shape relationship between $\log \gamma k_{\mathrm{e}}$ and a free-energy change for the electron transfer from NPGs to singlet excited Py calculated by the equation similar to Eq. (1) (ΔG_{et}), which is displayed in Fig. 5. We propose that an energy transfer mechanism participates in quenching of Py fluorescence by the NPGs having an electron-withdrawing group such as Cl. The excellent correlation between $\log v_{\mathrm{dec}}^{\mathrm{rel}}$ and ΔG_{et} illustrated in Fig. 5 suggests that the Py-sensitized photodecomposition rate of NPGs is controlled by an electron-donating ability of the substituent group.

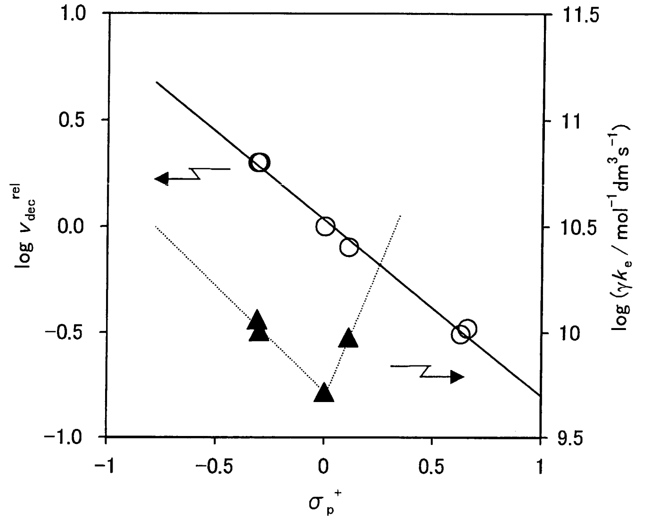


Fig. 4. Hammett plot of logarithm of the relative rate of pyrene-sensitized photodecomposition of *p*-substituted NPGs, $\log v_{\mathrm{dec}}^{\mathrm{rel}}$ (○), and logarithm of the rate constant for quenching of pyrene fluorescence by NPGs, $\log \gamma k_{\mathrm{e}}$ (▲), against $\sigma_{\mathrm{p}}{}^{+}$.

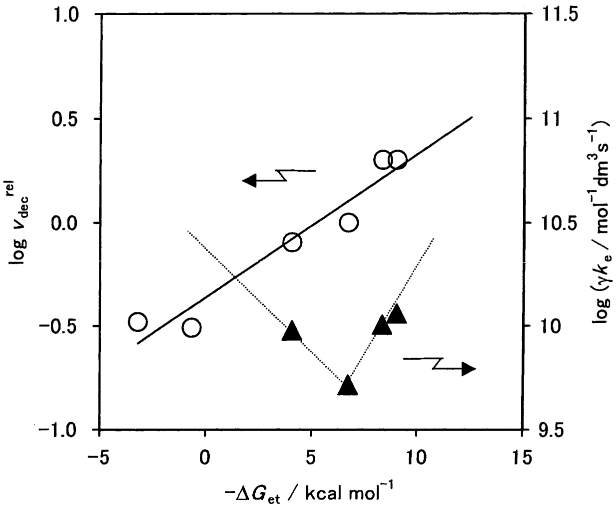


Fig. 5. Dependence of logarithm of the relative rate of pyrene-sensitized photodecomposition of *p*-substituted NPGs, $\log v_{\mathrm{dec}}^{\mathrm{rel}}$ (○), and logarithm of the rate constant for quenching of pyrene fluorescence by NPGs, $\log \gamma k_{\mathrm{e}}$ (▲), on the exothermicity of the electron transfer from NPGs to singlet excited pyrene, $-\Delta G_{\mathrm{et}}$.

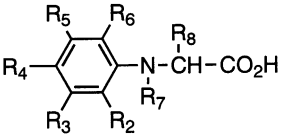
3.2.2. Effect of the position and the number of methyl groups

As shown in the preceding section, the introduction of methyl group at the *p*-position of NPG enhanced the efficiency of the Py-sensitized photodecomposition. In order to search the NPGs having larger photoreactivity, the effect of the position and the number of methyl groups on the photodecomposition rate were examined next. Nine NPGs having various numbers of methyl groups at various positions were synthesized, and their Py-sensitized photodecomposition rate was measured and compared with that of parent NPG.

The relative photodecomposition rates of various methyl-substituted NPGs, as well as their rate constants for quenching of Py fluorescence (γk_{e}) are shown in Table 3, along with their oxidation potentials (E_{ox}). It should be pointed out that the efficiency of the photodecomposition is enhanced most largely when methyl groups are introduced into the 2- and 4-positions of the aromatic ring of NPG (entry 5). The plots of the logarithm of $v_{\mathrm{dec}}^{\mathrm{rel}}$ and γk_{e} against a free-energy change for the electron transfer from NPGs to singlet excited Py (ΔG_{et}) are illustrated in Figs. 6 and 7, respectively. Fig. 6 displays a good correlation between $\log v_{\mathrm{dec}}^{\mathrm{rel}}$ and ΔG_{et}, suggesting that the photodecomposition rate of NPGs having methyl groups at the various positions is controlled by their electron-donating ability, analogously to the case of the above-mentioned *p*-substituted NPGs. On the other hand, as shown in Fig. 7, the quenching rate constants larger than those expected from the exothermicity for the electron transfer process were observed in the cases of *N*-(2-methylphenyl)glycine (entry 2) and *N*-phenylalanine (entry 10). In analogy with the case of the *p*-Cl derivative, this observation also appears to imply the participation of an

Table 3

Relatives rates of pyrene-sensitized photodecomposition of methyl-substituted NPG and quenching of pyrene fluorescence in acetonitrile



Entry	R_2	R_3	R_4	R_5	R_6	R_7	R_8	$v_{\mathrm{dec}}^{\mathrm{rel}}$ [a]	γk_e [b] (10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$)	E_{ox} [c] (V vs SCE)
1	H	H	H	H	H	H	H	1.0	5.2	0.99
2	Me	H	H	H	H	H	H	0.40	10.0	1.04
3	H	Me	H	H	H	H	H	0.52	–[d]	1.03
4	H	H	Me	H	H	H	H	2.0	11.7	0.89
5	Me	H	Me	H	H	H	H	4.6	14.3	0.71
6	H	Me	Me	H	H	H	H	2.2	–[d]	0.86
7	H	Me	H	Me	H	H	H	0.74	–[d]	0.99
8	Me	H	Me	H	Me	H	H	3.4	9.6	0.90
9	H	H	H	H	H	Me	H	1.7	6.6	0.96
10	H	H	H	H	H	H	Me	0.54	6.4	1.04

[a] Relative rate of pyrene-sensitized decomposition of methyl-substituted NPG; [pyrene] = 5.0×10^{-4} mol dm^{-3}, [NPGs] = 1.5×10^{-2} mol dm^{-3}.

[b] Rate constant for quenching of pyrene fluorescence by methyl-substituted NPG.

[c] Oxidation potential of methyl-substituted NPG measured in this work.

[d] Not determined owing to the emission of the methyl-substituted NPG.

energy transfer mechanism in quenching of Py fluorescence by the NPGs having a relatively high E_{ox}.

3.2.3. Discussion on the effect of substituent groups

Thus, we have found that the exothermicity for the electron transfer from NPGs to singlet excited Py ($-\Delta G_{\mathrm{et}}$) can be used for predicting the Py-sensitized photodecomposition rate of NPGs having various substituent groups (Figs. 5 and 6), while the rate constants for quenching of Py fluorescence by NPGs are not simply correlated with $-\Delta G_{\mathrm{et}}$ (Figs. 5 and 7).

It should be noted that the Py-sensitized photodecomposition rates of *N*-(4-methylphenyl)glycine (NMPG) and NDMPG are enhanced by a factor of 2.0 and 4.6, respectively, compared with that of parent NPG, which is attributable to their larger $-\Delta G_{\mathrm{et}}$, in other words, their lower E_{ox}. The large $-\Delta G_{\mathrm{et}}$ results in an increase in the rate constant for quenching of the excited sensitizer (γk_e) as shown in Fig. 7. Assuming that the scheme proposed for the Py-sensitized photodecomposition of NPG (Scheme 1) can be applied to the photodecomposition of these NPGs, it is reasonable to think that an increase in γk_e causes an

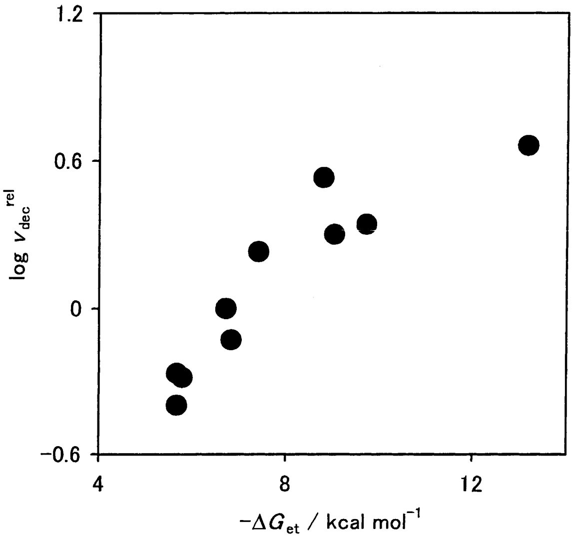


Fig. 6. Dependence of logarithm of the relative rate of pyrene-sensitized photodecomposition of methyl-substituted NPGs, log $v_{\mathrm{dec}}^{\mathrm{rel}}$, on the exothermicity of the electron transfer from NPGs to singlet excited pyrene, $-\Delta G_{\mathrm{et}}$.

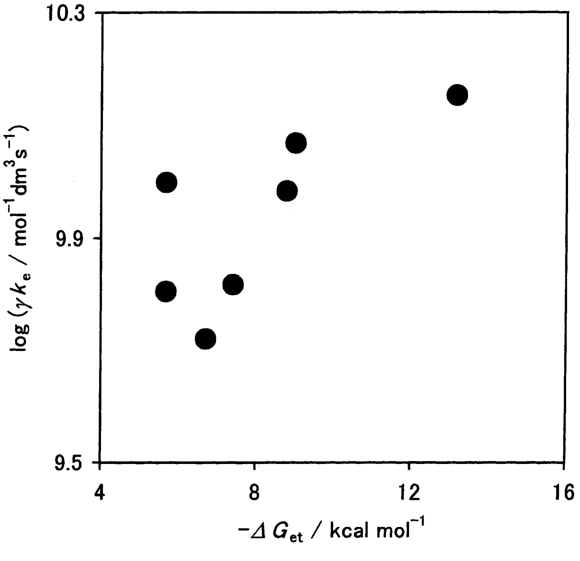


Fig. 7. Dependence of logarithm of the rate constant for quenching of pyrene fluorescence by methyl-substituted NPGs, log γk_e, on the exothermicity of the electron transfer from NPGs to singlet excited pyrene, $-\Delta G_{\mathrm{et}}$.

increase in the quenching factor F_{SV}, which leads to the enhancement of the photodecomposition rate (v_{dec}). However, because the F_{SV}'s for NMPG and NDMPG calculated from the observed γk_e's under our irradiation conditions are 1.4 and 1.5 relative to that for NPG, respectively, the large photodecomposition rates of these NPGs cannot be explained solely by the increase in the quenching rate constants.

Moreover, these NPGs seem to have disadvantages concerning the factors P and Q. Because of their lower E_{ox}, the exothermicity of the charge recombination between NPGs$^{\bullet+}$ and Py$^{\bullet-}$ ($-\Delta G_{bet}$) for these NPGs is smaller than that for parent NPG, which would result in an increase in the charge recombination rate constant in the contact ion pair (k_{b1}). Furthermore, it is possible that the decomposition rate constant of NPGs$^{\bullet+}$ (k_d) is influenced by the substituent group introduced into the aromatic ring of NPG. The substituent effect on the driving force for the decomposition of NPGs$^{\bullet+}$ can be evaluated by an enthalpy change for the following isodesmic reaction (ΔH_f(X)).

$$p\text{-XC}_6\text{H}_4\text{NHCH}_2\text{CO}_2\text{H}^{\bullet+} + \text{PhNHCH}_2^{\bullet} \rightarrow p\text{-XC}_6\text{H}_4\text{NHCH}_2^{\bullet} + \text{PhNHCH}_2\text{CO}_2\text{H}^{\bullet+}$$

The plot of ΔH_f(X), which is calculated for X = CH_3O, CH_3, Cl, CF_3, and NO_2 using the PM3 method, against σ_p^+ is illustrated in Fig. 8. The figure shows that the substituent group having an electron-donating ability gives a positive value of ΔH_f(X), indicating that the driving force for the decomposition of NPGs$^{\bullet+}$ is reduced by the introduction of an electron-donating group into the aromatic ring of NPG. Taking this into account, it cannot be expected that the decomposition rate constant of the radical cation of NPGs having methyl groups is larger than that of parent NPG.

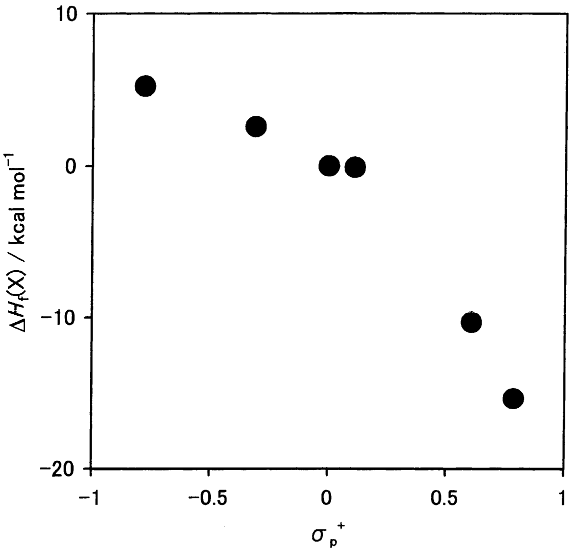


Fig. 8. Hammett plot of the enthalpy change for the isodesmic reaction concerning the decomposition of the radical cation of p-substituted NPGs, ΔH_f(X), against σ_p^+.

Thus, the reason for the large enhancement of the photodecomposition rate observed in 4-methyl, and further in 2,4-dimethyl-substituted NPG is not completely elucidated at the present stage, although it can be ascribed in part to an acceleration of quenching of the sensitizer excited state. We propose that a hydrogen abstraction of the free radical from the substituent methyl group, as well as the decarboxylation through a direct excitation of the NPGs, might be involved in the photodecomposition process of these NPGs.

3.3. Application to the photopolymerization

Finally, we examined the usefulness of the Py-sensitized NPGs photodecomposition system as an initiator for free radical polymerization of an acrylate monomer. We employed IOA, $CH_2{=}CHCO_2(CH_2)_5CH(CH_3)_2$, and 2,2-PEEA, $CH_2{=}CHCO_2(CH_2)_2O(CH_2)_2OPh$, as a monomer in our polymerization experiments, because the polymerization was readily monitored by the precipitation of the polymer owing to the low solubility of the polymers of these acrylate monomers in methanol. The efficiency of the polymerization initiated by the Py-sensitized photodecomposition of NPGs was evaluated by the conversion of the monomer into the corresponding polymer determined after the irradiation under the definite conditions. The results are summarized in Table 4.

The table shows that the polymerization of the acrylate monomers initiated by the photodecomposition of NPG is largely accelerated by the addition of Py. Moreover, the efficiency of the polymerization is dependent on the substituent group of the NPGs employed as an initiator. N-(4-Trifluoromethylphenyl)glycine (NTFPG), which had a smaller rate of photodecomposition (Table 2), was much less effective as a photoinitiator for polymerization than parent NPG. It is well known that the photopolymerization rate is controlled not only by the rate of photodecomposition of an initiator, but also by the reactivity of free radicals formed as

Table 4
Conversion of the monomer in the polymerization initiated by the pyrene-sensitized NPGs photodecomposition system[a]

Initiator	Monomer conversion (%)	
	IOA[b]	2,2-PEEA[c]
NPG[d]	–[e]	8.2
NPG	11.1	20.5
NMPG	7.6	10.3
NDMPG	29.8	26.8
NTFPG	–[e]	<3

[a] A monomer solution containing pyrene (1.0×10^{-4} mol dm^{-3}) and an initiator (3.0×10^{-3} mol dm^{-3}) was irradiated with light of 366 nm for 10 min.

[b] IOA was used as a monomer (1.4 mol dm^{-3} in acetonitrile).

[c] 2-(2-Phenoxyethoxy)ethylacrylate was used as a monomer (1.2 mol dm^{-3} in methanol).

[d] In the absence of pyrene.

[e] Not determined.

a result of the photodecomposition with a monomer [4g–4j]. As mentioned in the previous section, the introduction of an electron-donating group into the aromatic ring of NPG results in the enhancement of the Py-sensitized photodecomposition rate. However, it is reasonable to think that the reactivity of the resulting anilinomethyl radical with an acrylate monomer is reduced, because the electron-donating group raises the SOMO level of the anilinomethyl radical, which causes an increase in the energy gap between SOMO of the anilinomethyl radical and HOMO of the acrylate monomer [11]. As shown in Table 4, NMPG was less effective as a photoinitiator for free radical polymerization than parent NPG, which is probably due to a decrease in the reactivity of the resulting anilinomethyl radical. However, it should be noted that a remarkable enhancement of the efficiency of the photopolymerization was observed by the use of NDMPG as an initiator. This observation indicates that, in the case of NDMPG, a large acceleration of the photodecomposition rate overcomes the decrease in the rate of the reaction between the resulting dimethyl-substituted anilinomethyl radical and an acrylate monomer.

Thus, it is found that the Py-sensitized photodecomposition of NPGs can be employed as an efficient photoinitiation system for polymerization of an acrylate monomer. In particular, it is expected that NDMPG can be utilized for an excellent photoinitiator for free radical polymerization.

4. Conclusions

In order to search the efficient NPG photodecomposition system, the rate of NPG photodecomposition sensitized by various sensitizers, as well as the Py-sensitized photodecomposition rate of NPGs having a variety of substituent groups, has been investigated. It is found that Py is the most effective of the sensitizers examined in this study for the NPG photodecomposition, which would be mainly attributed to a retardation in the charge recombination in the contact radical ion pair owing to the large exothermicity of the process. Moreover, we have found that the Py-sensitized photodecomposition rate of NPGs having various substituent groups can be evaluated by the exothermicity for the electron transfer from the NPGs to singlet excited Py ($-\Delta G_{\mathrm{et}}$). In other words, the oxidation potential of the NPGs (E_{ox}) can be used for predicting their Py-sensitized photodecomposition rate. In the course of these studies, it is found that *N*-(2,4-dimethylphenyl)glycine (NDMPG) is highly reactive in the Py-sensitized photodecomposition. Furthermore, the Py-sensitized photodecomposition of NPGs can be employed as an efficient photoinitiation system for free radical polymerization of an acrylate monomer. It should be noted that NDMPG is more effective as a photoinitiator for polymerization than parent NPG.

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