Remarkable Effect of Electron Acceptors on Pyrene-Sensitized Decomposition of *N*-Phenylglycine

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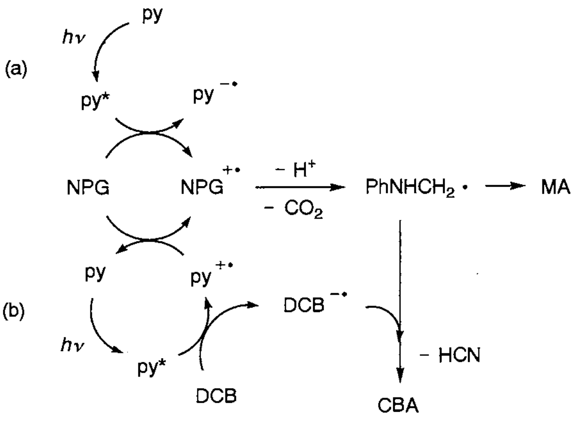
The efficiency of the pyrene-sensitized decomposition of *N*-phenylglycine (NPG) was enhanced by the addition of an electron acceptor, such as *p*-dicyanobenzene. The reaction mechanism is discussed on the basis of observed Stern-Volmer constants for quenching of singlet excited state of pyrene (py*) and transient absorption spectra. Examination of various electron acceptors shows that the efficient quenching of py* by electron acceptors does not necessarily result in an increase in the NPG decomposition rate.

N-Phenylglycine (NPG), $PhNHCH_2CO_2H$, has been widely used as a photoinitiator in photopolymerization[1] and a sacrificial electron donor in photocatalytic systems.[2] Though it was reported that aromatic nitro compounds,[3] quinones,[1d,4] polycyclic aromatic hydrocarbons,[5] and dyes[1a-c,6] could sensitize the decarboxylation of NPG and its derivatives, the detailed processes of their photochemical decomposition have not yet been elucidated. In the course of our mechanistic studies of pyrene-sensitized decomposition of NPG, we found that the efficiency of the decomposition was enhanced by the addition of an electron acceptor, such as *p*-dicyanobenzene (DCB). In this paper, we report the remarkable effect of electron acceptors on the pyrene-sensitized decomposition of NPG, where the reaction scheme involving the pyrene-mediated electron transfer from NPG to an electron acceptor is proposed on the basis of photophysical measurement.

Irradiation (366 nm) of a degassed solution of NPG (15 mM) in acetonitrile containing 1% of water in the presence of pyrene (0.5 mM) for 30 min caused a consumption of 45% of the starting material.[7] Spectroscopic and chromatographic analyses of the photoreaction mixture revealed a considerable consumption of pyrene (88%), and the formation of *N*-methylaniline (MA), aniline, and formanilide. These compounds were already reported as the photoproducts obtained in the sensitized-photolyses of NPG.[5,6] On the other hand, under conditions identical to those described above, except for the presence of DCB (15 mM),[8] the initial rate of photodecomposition of NPG was increased by a factor of 1.9, compared with that in the absence of DCB. Though the distribution of the photoproducts was similar to that obtained in the absence of DCB, the additional product identified as *N*-(*p*-cyanobenzyl)aniline (CBA)[9] was isolated (5%), and pyrene was recovered nearly quantitatively from the reaction mixture. Thus, it was found that the addition of DCB enhanced the efficiency of the pyrene-sensitized decomposition of NPG. This observation would give a suggestion on an increase in initiating efficiency in a photoinitiating system using NPG as an initiator.

In order to gain information about the mechanism of the pyrene-sensitized decomposition of NPG in the presence of DCB, Stern-Volmer constants for quenching of pyrene fluorescence by NPG and DCB were measured in acetonitrile. The least-square analysis of the quenching data revealed that the Stern-Volmer constant for quenching of singlet excited state of pyrene (py*) by DCB was 4.0 times that by NPG ($k_q\tau_0$ = 60.0 and 240 for NPG and DCB, respectively). It was already reported that the electron transfer from NPG to the excited singlet state of the sensitizer was involved in the decomposition of NPG sensitized by polycyclic aromatic hydrocarbons.[5] Thus, it seems reasonable to assume that in the absence of DCB, py* is quenched by NPG to give a pair of pyrene radical anion ($py^{-\bullet}$) and $NPG^{+\bullet}$.[10] The latter would be readily deprotonated and decompose to anilinomethyl radical, $PhNHCH_2\cdot$, and CO_2 (Scheme 1a). On the other hand, taking into account the quenching data, the one-electron oxidation of NPG with pyrene radical cation ($py^{+\bullet}$) produced initially through the electron transfer from py* to DCB would be involved in the pyrene-senstized decomposition of NPG in the presence of DCB (Scheme 1b). This mechanism can explain satisfactorily the recovery of pyrene, as well as the additional formation of CBA.



Scheme 1.

A strong piece of evidence in support of the mechanism proposed in the scheme was obtained by the direct observation of the transients involved in the pyrene-sensitized decomposition of NPG using nanosecond laser flash photolysis technique (355 nm, 13 ns, 0.7 mJ/pulse). The transient absorption spectrum recorded of a degassed solution of pyrene and NPG in acetonitrile is shown in spectrum A in Figure 1. The spectrum exhibits an intense absorption band with a maximum at 493 nm, which corresponds to $py^{-\bullet}$.[13,14] On the other hand, the transient absorption spectrum recorded in the presence of DCB (spectrum B in Figure 1) was completely different from spectrum A. The absorption bands with λ_{max} = 445 and 343 nm shown in spectrum B can be assigned to $py^{+\bullet}$[13a,d] and $DCB^{-\bullet}$,[15] respectively.

Thus, it could be concluded that the mechanism of the generation of $NPG^{+\bullet}$, which leads to the decomposition of NPG, is changed by the addition of DCB. Furthermore, an effective

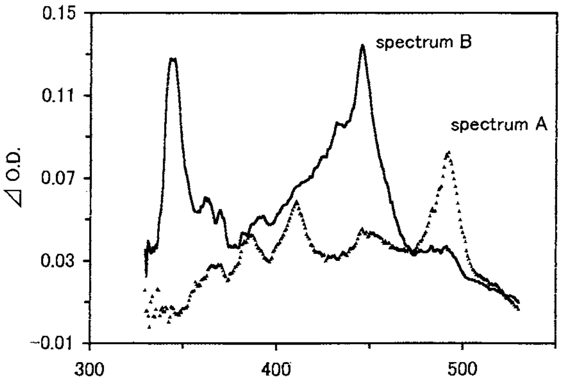


Figure 1. Transient absorption spectrum of a solution of pyrene (0.5 mM) and NPG (2 mM) in acetonitrile recorded in the absence (spectrum A) and in the presence of DCB (2 mM, spectrum B). The delay time after the laser pulse was 130 ns for A and 60 ns for B.

quenching of py* by DCB, as well as the retardation of charge recombination process due to the effective charge separation in the pyrene-mediated electron transfer from NPG to DCB, seems to be the reason for the enhancement of efficiency of the NPG decomposition in the presence of DCB.

Table 1. Relative rates of pyrene-sensitized photodecomposition of NPG[a] and quenching of pyrene fluorescence by various acceptors in acetonitrile

Acceptor	k_{dec}^{rel}	$k_q\tau_0$[b] (M^{-1})	k_q^{rel}	E_{red} (V vs. SCE)
none	1.0	60.0[c]	1.0[c]	-
TCB	0.5	363	6.1	- 0.73[d]
DCB	1.9	240	4.0	- 1.68[d]
IPN	2.3	93.3	1.6	- 1.88[d]
BN	0.8	< 5	< 0.1	- 2.45[d]
PDA	> 5[e]	358	5.9	- 0.55[f]
PA	> 5[e]	306	5.1	- 1.31[f]
DETP	1.9	184	3.0	- 1.16[g]
DEIT	2.0	< 5	< 0.1	- 1.47[g]

TCB = 1,2,4,5-Tetracyanobenzene, DCB = *p*-Dicyanobenzene, IPN = *m*-Dicyanobenzene, BN = Benzonitrile, PDA = Pyromellitic dianhydride, PA = Phthalic anhydride, DETP = Diethyl terephthalate, DEIP = Diethyl isophthalate. [a][Pyrene] = 0.5 mM, [NPG] = [Acceptor] = 15 mM. [b]Measured under air. [c]Quenching by NPG. [d]Reference 11. [e]NPG is consumed by a thermal reaction with acceptor; See text. [f]Reference 18. [g]Reference 16.

Next we examined the effect of a variety of electron acceptors on the pyrene-sensitized decomposition of NPG. The relative rate constants for the NPG decomposition (k_{dec}^{rel}) obtained in the presence of various electron acceptors are summarized in Table 1, together with their reduction potential (E_{red}) and relative rate constants for quenching of py* (k_q^{rel}). From the table, it is revealed that the efficient quenching of py* does not necessarily result in an increase in the NPG decomposition rate. In particular, the addition of TCB, which is one of the most effective quenchers of py*, caused a significant retardation of the NPG decomposition. However, this observation can be explained in terms of an acceleration of the charge recombination rate in the radical ion pairs with the high charge transfer degree, which was already reported in pyrene-nitrile systems.[16] Though anhydrides, such as PDA and PA, are excellent quenchers of py*, they cannot be used in a photoinitiating system using NPG because a nucleophilic reaction of NPG with anhydrides occurs readily.[17]

Moreover, the remarkable effect of IPN and DETP on the NPG decomposition is explained by the mechanism analogous to that proposed in the case of DCB, while the acceleration of the NPG decomposition in the presence of DEIT appears to be curious because the rate constant for quenching of py* by DEIT is considerably slower than that by NPG. This observation would be interpreted in terms of a retardation of the charge recombination between the initially-formed radical ion pair, $NPG^{+\cdot}$ and $py^{-\cdot}$, since the energetically-favored electron transfer from $py^{-\cdot}$ to DEIT causes the effective separation of the positive and negative charges. Work is in progress to elucidate the detailed mechanism of the pyrene-sensitized decomposition of NPG and to apply this system to a practical photoinitiator.

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7 Under identical conditions except for the absence of pyrene, a consumption of NPG was no more than 12%.

8 Molar absorptivities of pyrene, NPG, and DCB at 366 nm in acetonitrile are 220, 7.8, and < 0.5, respectively.

9 Spectroscopic data for CBA: ^{1}H NMR ($CDCl_3$) δ 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); MS m/z (rel intensity) 208 (M^+, 100), 116 (M^+ - C_6H_5NH, 31), 106 (M^+ - C_6H_4CN, 40).

10 The free energy for electron transfer from NPG (E_{ox} 0.72 V vs. SCE)[1d] to pyrene (E_{red} -2.09 V vs. SCE)[11] in its singlet state (E_S 77 kcal mol^{-1}) is calculated by the Rehm-Weller equation[12] to be -13 kcal mol^{-1}.

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14 A transient absorption band with a maximum at 411 nm shown in spectrum A is tentatively assigned to triplet excited state of pyrene.[13]

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17 Though attempts to isolate the product obtained from NPG and PA were not successful, it was tentatively identified as *N*-phenyl-*N*-(carboxymethyl)phthalamic acid on the basis of its NMR spectrum: ^{1}H NMR ($CDCl_3$) δ 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).

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