Magnetic Field Effects on and Mechanism of Photoredox Reaction of Aromatic Nitro Group[1]

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Photoredox reaction mechanism of a homologous series p-$O_2NC_6H_4O(CH_2)_nNHPh$ (1) in acetonitrile and benzene is studied. The major products are p-$ONC_6H_4O(CH_2)_{n-1}CHO$ (3) and aniline derived from *intramolecular* reaction, but the presence of minor amounts of *intermolecular* reaction products, p-$O_2NC_6H_4O$-$(CH_2)_{n-1}CHO$ (4) and p-$ONC_6H_4O(CH_2)_nNHPh$ (5) is confirmed in the reaction mixture. In the presence of an external magnetic field, the yield of 3 is suppressed and those of 4 and 5 are correspondingly increased, while the rates of the disappearance of 1 and of the formation of aniline remain unchanged, suggesting the presencer of biradical recombination process accompanied by intersystem crossing in a rate-determining step. On the basis of these observations, two reaction schemes are proposed. The magnetic field effects provide strong evidence for the presence of a transient species with (nitro)N(OH)–O–CHN< group generally supposed for nitro oxygen transfer process in this type photoreaction.

In the various types of the photoreactions of aromatic nitro groups, oxidation of active methyl or methylene groups is one of the most well documented reactions.[2] In the course of the study of the photochemical and photophysical behavior of a homologous series of compounds, p-$O_2NC_6H_4O(CH_2)_nNHPh$ **1**(n), we found that the lower homologues ($n=2$—6) exhibit intramolecular photorearrangement to give **2**, while the higher homologues ($n≥8$) yield a mixture of nitrosoaldehyde **3** and aniline as a result of intramolecular photoredox reaction (Eq. 1).[3,4]

(1)

The fact that the products of the *intermolecular* photoreaction of p-nitroanisole with N-alkylanilines (alkyl =methyl, ethyl or propyl) are p-nitrosoanisole and de-alkylated aniline,[3] i.e. the products of the redox reaction, has revealed that the photorearrangement is a phenomenon limited only to the homologues in which the nitro group of an excited p-nitrophenoxyl moiety cannot be intramolecularly oriented to the suitable position of hydrogen abstraction, and, otherwise, the "normal" photoreaction of redox type predominates. The photoreaction of **1** ($n≥8$) is thus exclusively the redox type and accompanies no detectable amount of rearranged product **2**.

Generally there have been proposed two types of mechanisms for the photoredox reaction of excited aromatic nitro compounds. First mechanism starts with n,π^* triplet state of nitro group that abstracts hydrogen atom from CH group to generate radical pair, followed by oxygen transfer process from the nitro to the carbon atom. The second mechanism involves electron transfer from the substrate to the nitro compound, yielding a radical ion pair that follows the similar pathway to that of the radical pair.[2] Obviously the most significant factor differentiating these mechanisms is an electron-donating property of the reducing reagent; when the reaction is conducted in the presence of a reducing reagent such as an aromatic amine with low ionization potential, the electron transfer mechanism is proposed.[2,5] On the other hand, in the cases where good electron-donors are not provided, for instance in the presence of aliphatic amines, the radical pair mechanism prevails. Another important factor is a reaction medium. Since ion pairs are less stabilized in non-polar solvents than in polar ones, the radical pair mechanism becomes favorable as the polarity of the solvent decreases.

In all the homologues of **1**, generation of the corresponding radical ion pair **6** was observed in acetonitrile by laser-flash photolysis (Eq. 2).

(2)

Apparently this finding supports the electron transfer mechanism for the formation of **3**, but the relatively low quantum yield of **6** as well as the existence of more efficient through-bond process of the charge separation than through-space mechanism[4] may paradoxically consist of evidence against ion pair mechanism, because the through-bond process requires no proximity of the donor-acceptor pair at the time of the elec-

tron transfer and thus the high efficiency of through-bond generation of **6** does not necessarily lead to the high quantum yield of the photoreaction. Moreover, the photoredox reaction is observed in nonpolar solvent such as benzene. Thus the observation of the presence of **6** as a transient species upon irradiation of the solution of **1** does not lead unequivocally to the electron transfer mechanism.

In order to obtain a further insight into the reaction mechanism of this photoreaction, we studied magnetic field effect (MFE) on the reaction rate and product distribution; an external magnetic field is known to affect the rate process of intersystem crossing (ISC) between the singlet and triplet states of biradicals involved in the rate-determining step, so far as their energy levels are almost the same.[6]

An interesting feature closely connected with the through-bond electron transfer is that the exchange interaction integral, customarily written as $|J|$, between the unpaired electrons in the radical ion pair **6** is expected to be negligibly small in these higher homologues or, in other words, the singlet and triplet states of the radical pair is energetically almost degenerate. If this condition is satisfied, we can expect for the radical pair to undergo the effects of an external magnetic field.

Experimental

Materials.   The preparation of the starting material for the photoreaction has been reported.[4] The authentic sample of nitroaldehyde **4(12)** was prepared by the oxidation of the corresponding alcohol, as follows:

12-(p-Nitrophenoxy)-1-dodecanol.   A mixture of 0.70 g (5 mmol) of p-nitrophenol, 1.33 g (5 mmol) of 12-bromo-1-dodecanol, 0.40 g of potassium carbonate, and 0.20 g of tetrabutylammonium bromide in 15 ml of water was heated at 100°C with stirring for 4 h. The reaction mixture was poured in 50 ml water, extracted with chloroform, and the combined extracts were dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was recrystallized from ethanol, giving 1.44 g (89%) of colorless crystals: Mp 95—96°C; ^1H NMR ($CDCl_3$) $\delta=1.2$—1.9 (21H, broad s+m, $(CH_2)_{10}$ and OH), 3.60 (2H, t, $J=7$ Hz, CH_2-OH); 4.01 (2H, t, $J=7$ Hz, $ArOCH_2$), 6.84 (2H, d, $J=10$ Hz, o-H), and 8.10 (2H, d, $J=10$ Hz, m-H). Found: C, 66.73; H, 9.14; N, 4.21%. Calcd for $C_{18}H_{29}NO_4$: C, 66.84; H, 9.04; N, 4.33%.

12-(p-Nitrophenoxy)dodecanal 4(12).   A solution of 0.32 g (1mmol) of 12-(p-nitrophenoxy)-1-dodecanol in 3 ml of dichloromethane was added to a stirred solution of 0.32 g (1.5 mmol) of pyridinium chlorochromate in 2 ml dichloromethane in one portion. After 2 h of stirring, 25 ml of ether was added, and the reaction mixture was filtered through Florisil on a sintered-glass filter. The filtrate was washed with two 10-ml portions of 4% aqueous NaOH solution. After removing the solvents under reduced pressure, the residue was recrystallized from hexane–benzene (4:1) mixture, giving 0.27 g (84%) of colorless crystals: Mp 59—60°C; ^1H NMR ($CDCl_3$) $\delta=1.2$—1.8 (18H, broad s+m, $(CH_2)_9$), 2.41 (2H, dt, $J=3$ and 6 Hz, CH_2–CHO), 4.07 (2H,

t, $J=6$ Hz, $ArOCH_2$), 6.89 (2H, d, $J=10$ Hz, o-H), 8.13 (2H, d, $J=10$ Hz, m-H), and 9.73 (1H, t, $J=3$ Hz, CHO). Found: C, 67.08; H, 8.52; N, 4.53%. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36%.

Photoreaction.   Spectroscopic grade solvents were used. All sample solutions were deaerated by several freeze-pump-thaw cycles before irradiation. The sample solution in a quartz cell of 1 cm path length was irradiated with UV light from an Ushio 500 W Xe arc filtered by a combination of Toshiba glass filters (UV-D33S, UV-25, and UV-33), which corresponds to the excitation within the acceptor moiety. The light intensity from the Xe arc was monitored by a photosensor with a beam splitter (UV-25) and the output signal from the sensor was accumulated. The intensity fluctuation was less than 0.6%.

Product yields in the absence and presence of an external magnetic field were determined with a Hitachi U-3200 spectrophotometer or with a Waters 590 high-performance liquid chromatograph (HPLC) equipped with a model 481 LC spectrophotometer. Absorption spectra of species in the photolyzed solution were separately obtained by the LC-UV method, i.e. each component in the reaction mixture was analyzed by means of HPLC and was recorded on spectrophotometer fitted with a diode array detector (Union Giken MCPD-350). The quartz cuvette containing the sample solution was placed between the pole pieces of an electromagnet (Tokin SEE-9G). The field strength was monitored by a gaussmeter, the residual magnetic field being less than 0.08 mT.

Results and Discussion

Photoproducts.   In the previous papers,[3,4] our attention was focused mostly on the major photoproduct **3**. However for further study of the reaction mechanism, close examination of the reaction mixture by HPLC was newly carried out with a special attention on minor products. For this purpose, we adopted benzene as a solvent instead of acetonitrile used in the previous papers, because in this medium the formation of the by-products was suppressed both in number and amount and a secondary photoreaction of the products was much slower.

In the reaction mixtures irradiated in benzene, the presence of two components, one with p-nitrophenoxyl and other with p-nitrosophenoxyl chromophore were confirmed (see Fig. 2).   The p-nitrophenoxyl chromophore of one component was identified by comparing its absorption spectrum obtained by LC-UV method (see Experimental) with reference spectrum of a model compound, p-nitrophenethole, and the structure was identified for the case of the $n=12$ homologue as 12-(p-nitrophenoxy)dodecanal **4(12)** by comparison of the retention time of HPLC and the UV spectrum with the authentic sample. The other product with nitroso-phenoxyl chromophore was identified as N-[12-(p-nitrosophenoxy)dodecyl]aniline **5(12)** on the basis of the close resemblance of the LC-UV spectrum with the superposed spectrum of p-nitrosoanisole and N-methylaniline.[7] The production of **4** and **5** was also noted

in the reaction in acetonitrile, but they readily underwent secondary photodegradation. An attempt to isolate these photoproducts from the reaction mixture by removing the solvent was unsuccessful, probably because the products readily react with each other in the concentrated solution. The production of 4 and 5 suggests the occurrence of *intermolecular* photoredox process, yielding 4 as an oxidized and 5 as a reduced product, even in a highly diluted solution (10^{-4} M or less, $M = mol\,dm^{-3}$).

MFE   (i) Product Distribution.   Deaerated benzene solutions of 1(12) were irradiated in the absence and presence of an external magnetic field. In a routine work, a field strength of 0.64 T was arbitrarily adopted. As a typical example representing the photochemical behavior of the higher homologues of 1, the $n = 12$ homologue was used on account of the high quantum yield.[4]

Spectral change of the solutions during irradiation in the absence and presence of the magnetic field is illustrated in Figs. 1A and 1B, respectively. Comparison of the spectral curves irradiated for the same pe-

riod clearly shows retardation of the increase of the absorbance at ca. 340 nm in the presence of the magnetic field. This absorbance corresponds to the production of the major photoproduct 3, i.e. *p*-nitrosophenoxyl chromophore. Close examination of the spectral curves shows that on short-period irradiation (0—4 min) an isosbestic point is observed at 326 nm, while on prolonged photolysis the deviation from the point becomes appreciable.
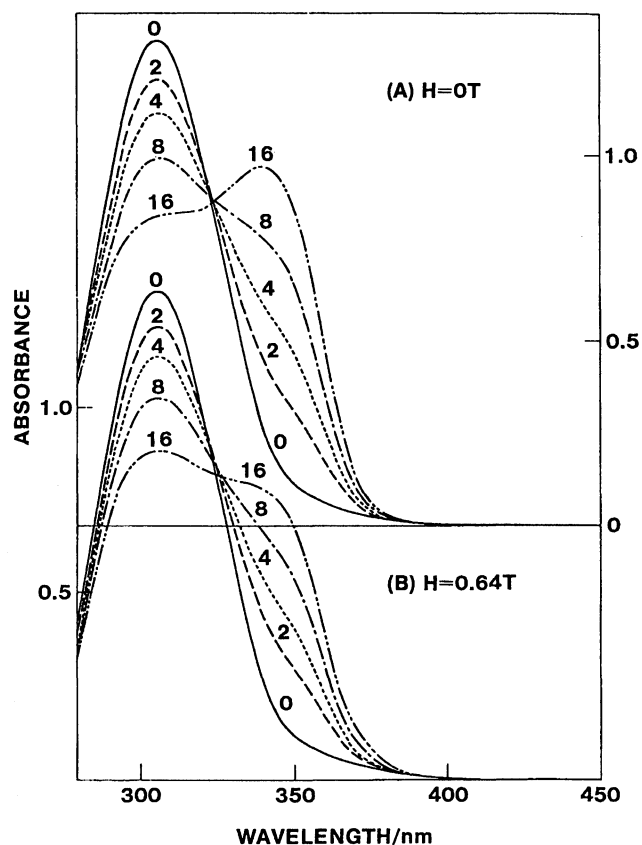
A typical example of the MFE on the constituent of the products is noted in the high performance liquid chromatograms illustrated in Fig. 2.

The chromatograms were monitored at 308 nm, the wavelength corresponding to the absorption maximum of *p*-nitrophenoxyl group, and the peak area due to 4 is accordingly much exaggerated. Comparison of the corresponding peaks in Figs. 2A and 2B shows that the peak area of 3 decreases in the presence of the magnetic field and those of 4 and 5 increase, while the area of aniline is kept almost unchanged. These findings suggests competitiveness of the intramolecular and intermolecular reactions forming 3 and 4+5 pair, respectively. Since the structure of these two products suggests that they are formed by a similar reaction process, i.e. the oxidation of the methylene group adjacent to the amino nitrogen with an oxygen atom of the nitro group to release aniline, it is not unreasonable to conclude that the products are derived from the same intermediate. In other words, 3 and 4+5 correspond to the in-solvent-cage and out-of-cage products of a biradical precursor,

Fig. 1.   Photoreaction of 1(12) in benzene as detected by UV-absorption spectroscopy (A) in the absence and (B) in the presence of an external magnetic field (0.64 T). The numerals attached to the curves refer to the irradiation time in minute. Excitation source; 500-W Xe arc with combined color glass filters (Toshiba UV-D33S, UV-25, and UV-33).
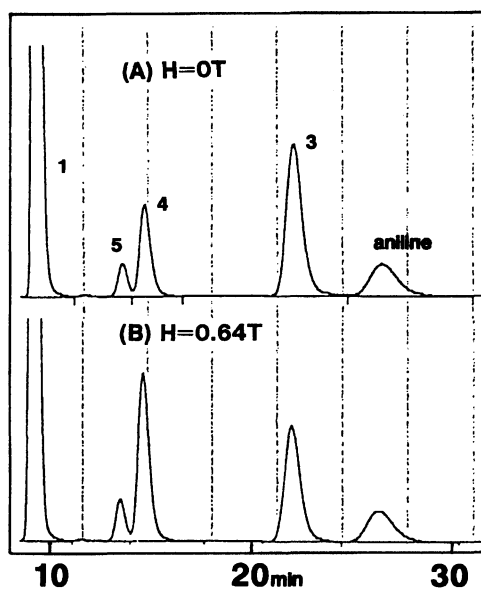
Fig. 2.   Chromatograms of the irradiated (8 min) benzene solutions of 1(12)(normal-phase column, Merck Lichrosorb Si 60, monitored at 308 nm; solvent, benzene : THF = 100 : 1); (A) in the absence and (B) in the presence of an external magnetic field (0.64 T). The numerals attached to the peaks refer to the compound number (Eq. 1).

Table 1. Magnetic Field Effects on the Formation and Disappearance Yields for 1(12)

| Irradiation Condition | | Formation $(I^H/I^0)^{a)}$ of | | | | Disappearance of 1 |
Solvent	Time/min	3	4	5	Aniline	$(I^H/I^0)^{a)}$
CH_3CN	2	$0.96\pm0.02^{b)}$			$0.99\pm0.02^{b)}$	$1.02\pm0.04^{b)}$
	4	0.93 ± 0.02			0.99 ± 0.02	1.02 ± 0.03
	8					1.00 ± 0.03
	12	0.93 ± 0.03				0.99 ± 0.04
	16	0.89 ± 0.02				0.99 ± 0.02
C_6H_6	8	$0.82\pm0.02^{c)}$	1.43 ± 0.05	1.39 ± 0.05	1.00 ± 0.03	1.04 ± 0.06

a) I^H and I^0 refer to the peak areas in the chromatogram recorded after the phtolysis in the presence
and absence of an external magnetic field (0.64 T), respectively. b) Each value is an average of two or
three independent experiments. c) Not inserted to $t=0$ min.

respectively.

Analysis of the MFE on the relative amounts of the products and starting material was carried out in more detail by HPLC. The results are summarized in Table 1. The data of **4** and **5** obtained in either solvent were not adopted for the analysis described below, since the peak areas of these compounds were too small, especially at the initial stage of the reaction, to give reliable results. We can see from this Table that the formation (I^H/I^0) of **3** is sensitive to the external magnetic field and that the effect is also dependent on the irradiation time, whereas neither the yield of aniline nor the disappearance rate of the starting material is dependent on the irradiation time. The time dependence of I^H/I^0 value indicates the participation of a consecutive photoreaction of nitrosophenoxyl derivative as is also suggested by the deviation of the spectral curves from the isosbestic point (Fig. 1).

(ii) Field Strength and Chain Length. Since the I^H/I^0 value drifts with irradiation time, especially remarkable in acetonitrile, it is necessary to determine an experimental parameter describing the MFE in this solvent free from the influence of the secondary photodegradation, which was obtained by the following procedure. When the secondary photodegradation of the primary product disappearance is taken into account (Eq. 3),

$$1 \xrightarrow{k_1} 3 \xrightarrow{k_2} \qquad (3)$$
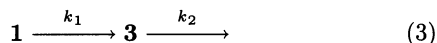
the concentration of the primary photoproduct, C_p, is expressed by

$$C_p = \frac{C_i k_1}{k_2 - k_1} \left[\exp(-k_1 t) - \exp(-k_2 t) \right], \qquad (4)$$

where C_i is the initial concentration of the starting material, and k_1 and k_2 are the formation and disappearance rate constants of the photoproduct, respectively.

The extrapolation of C_p^H/C_p^0 to $t=0$ gives k_1^H/k_1^0, where superscripts H and 0 refer to the presence and the absence of an external magnetic field, respectively. At the initial stage of the reaction, the absorbance change $A(=A(t)-A(0))$ can be regarded as practically proportional to the concentration of the product **3**, since the absorption of the products **4** and **5** or other unidentified

products little contributes to the absorption maximum of the starting material. The relative rate parameter k_1^H/k_1^0 is determined by extrapolating the absorbance change ratio to $t=0$ (Eq. 5).

$$\lim_{t\to 0}(A^H/A^0) = \lim_{t\to 0}(C_p^H/C_p^0) = k_1^H/k_1^0 \qquad (5)$$

The absorbance data at 345 nm from 0 to 4 min irradiation were used for the evaluation of k_1^H/k_1^0. This procedure assumes that the secondary process is independent of the magnetic field, i.e. $k_2^H/k_2^0=1$.

The plot of the MFE parameter k_1^H/k_1^0 against the field strength for 1(12) shows the saturation of the effects in the region 0.01—0.1 T (Fig. 3), suggesting that the hyperfine interaction mechanism is more important than the Zeeman mechanism. Additionally, the relation of the chain length n with MFE was determined as depicted in Fig. 4. For the lower homologues ($n=2$—6) that undergo the photorearrangement, the MFE was not observed, whereas the photoredox reaction of the higher homologues ($n\geq8$) revealed the effect; that is, the switching of the reaction type corresponds to the effectiveness of the magnetic field.

Mechanism of the Photoredox Reaction. Though the main objective of the present paper is the elucidation of the photoredox reaction mechanism, it
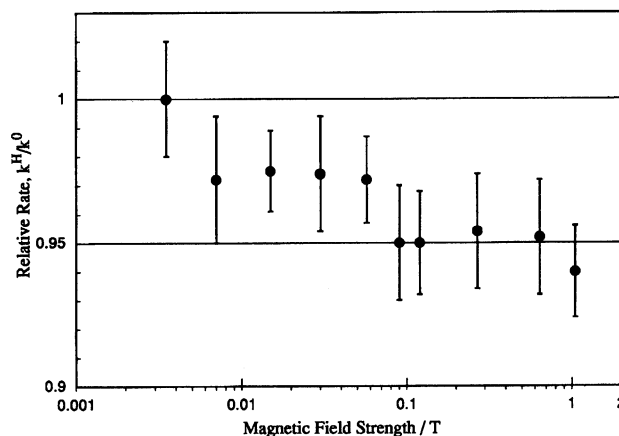

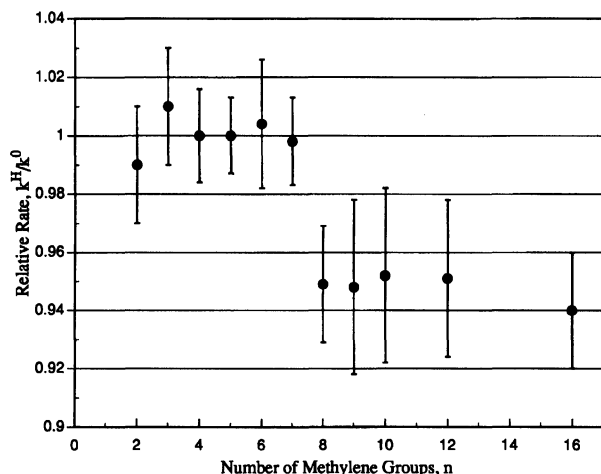Fig. 3. MFE on the relative rate k^H/k^0 as a function of the field strength for 1(12).

Fig. 4. MFE on the relative rate k^H/k^0 as a function of the chain length.

is necessary to give comments on the behavior of the lower ($n \leq 6$) homologues. The absence of MFE in the photorearrangement of 1(2) and 1(3) is consistent with the already confirmed base-catalysis mechanism[4,8,9] in which a major rate-determining step is proton transfer from the N–H group to the base to yield an anilide type anion (Eq. 6),


(6)
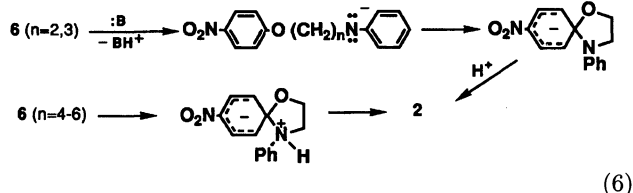
hence this ionic reaction has no mechanistic basis for undergoing MFE. The behavior of the next higher homologous group ($n=4$—6) for which the supposed mechanism in such a polar solvent as acetonitrile is a charge separation-recombination type, is difficult to understand, since the initially formed triplet radical ion pair ^{t}6 has to undergo intersystem crossing to yield the singlet ^{s}6 as a precursor for a spiro-Meisenheimer type complex. The possible reasons for the apparent ineffectiveness of the magnetic field are (1) the effect is so small as to be submerged under the experimental errors, (2) the exchange integral $|J|$ is not negligible in these lower homologues, because the two aromatic nuclei should be in close proximity in the product forming step, or (3) the ISC process is not rate-determining, but the next recombination step of ^{s}6 (i.e. encouter process of the two radicals) is slower. For this last interpretation, the fact that the electron transfer is mainly through bond mechanism[4,10] may be cited as supporting evidence, because, in that case, ^{t}6 can be formed in either extended or coiled conformation and only the latter less populated conformation with the reaction centers closely arranged is favorable for the subsequent step.

The MFE's observed for the photoredox reaction of the $n \geq 8$ homologues should be discussed in connection with the ISC process, possibly involved in the pathway from the excited nitrophenoxyl group of 1 through the generation of nitrosophenoxyl group (Scheme 1).

The first ISC step of the reaction is from the singlet to the triplet state of the excited p-nitrophenoxyl group. The lifetime of both the singlet and triplet states of nitrobenzenes are generally difficult to estimate, because most derivatives rarely provide spectroscopically detectable information of the excited states such as fluorescence or phosphorescence. From a variety of evidence,[2a,2c,11] however, it may not be unreasonable to estimate the rate constant of the ISC to be in the order of 10^{11}—10^{12} s^{-1}. This fast step cannot be responsible for the observed MFE's, because the singlet as well as the triplet nitrobenzene can equally abstract a hydrogen atom and no large difference is expected between the reactivities of these two states (hence, no MFE on the reaction rate is expected), and because the observed reaction is as slow as in competition with the out-of-cage intermolecular reaction, the maximum rate constant of which is in the order of 10^{10} (diffusion rate constant estimated from the viscosity of the two solvents).

We could not directly determine the absolute rate constant of the in-cage reaction, but we can roughly estimate its value in benzene as follows: The rate of in-cage reaction, i.e. formation of 3 is expressed by $k_{in}[1]$, where k_{in} is the rate constant in question. The rate of the formation of 5 (or 4), on the other hand, is expressed by $k_{out}[1]^2$, where k_{out} is the rate constant of the out-of-cage reaction and equal to a diffusion coefficient if we assume that the redox reaction occurs on every collision of escaped molecules from the solvent cage. At the initial stage of the reaction, the concentration [1] is 10^{-4} mol dm^{-3} and if we assume $k_{out} = 10^{10}$ dm^3 mol^{-1} s^{-1}, the ratio of the rate, rate($intermolecular$)/rate($intramolecular$) = $k_{in}/(k_{out} \times 10^{-4}) = k_{in} \times 10^{-6}$ s^{-1}. From the HPLC we obtain [3]/[5]=ca. 10, that can be regarded to be nearly equal to the rate ratio. Thus using this value, we obtain $k_{in} = 10^7$ s^{-1}. The obtained value is one or two orders less than the hydrogen abstraction rate constants observed for o-nitrobenzyl type compounds.[12] The difference is probably due to whether the hydrogen atom to be abstracted is almost always within the reaction range of the nitro group in o-nitrobenzyl compound or the availability of the hydrogen is strongly dependent on the thermal motion of the polymethylene chain in 1.

In order to construct a possible reaction mechanism subsequent to the generation of the triplet nitrophenoxyl group, we have to take into account the oxygen-transfer process from the nitro group to the CH$_2$ carbon atom adjacent to the anilino nitrogen as well as ISC process. Accordingly, the conceivable pathways are roughly divided into two types; (1) through charge sep-
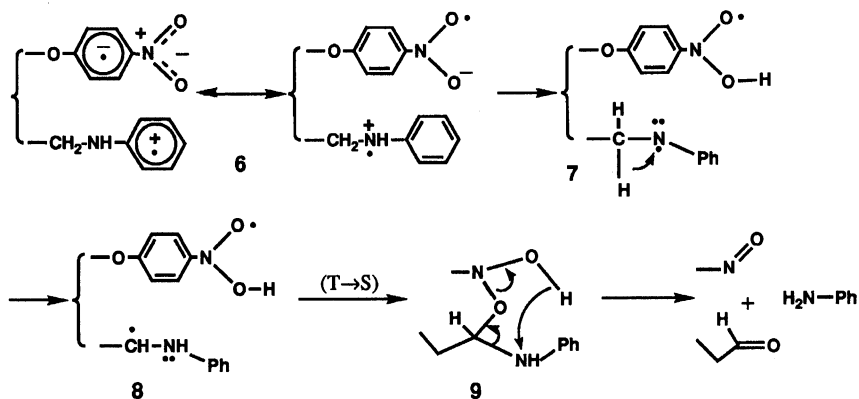
Scheme 1.
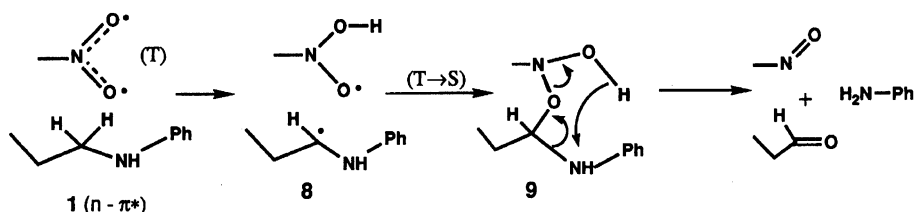
Scheme 2.

aration, i.e. via the triplet $^t6$, followed by intramolecular hydrogen transfer (Scheme 1), and (2) through direct hydrogen abstraction from CH_2NH moiety by the nitro group in p-nitrophenoxyl group (Scheme 2). For Scheme 2, there might arise an issue whether the triplet state is π,π^* or n,π^*, since the π,π^* triplet has been reported to be less effective or almost ineffective for hydrogen abstraction.[2c,2d,13] Furthermore, introduction of an electron-donating group in the ring of nitrobenzene generally stabilizes π,π^* triplet by lowering the energy level and the tendency is further promoted in polar solvents.[14] p-Nitrophenoxyl group thus stands on a subtle point with regard to the photochemical behavior, but the hydrogen abstraction reaction of p-nitroanisole observed in isopropyl alcohol (polar than acetonitrile)[15] strongly supports the possibility of the reaction from n,π^* state or the state with strong n,π^* character.

The mechanism shown in Scheme 1 is based on the fact that the radical ion pair 6 generated by through-bond electron transfer has been noted in all the homologues, though the quantum yields are not high.[4] The hydrogen transfer process in 6, from the one-electron deficient cation radical $^{+\bullet}NHPh$ group to the nitro oxygen, is probably a transfer of a proton rather than a neutral hydrogen atom, since the positively charged anilino group has a much stronger proton donating ability (pK_a is estimated to be 14.5 ± 1)[9] than the CH_2 group adjacent to this charged moiety, and moreover the proton accepting moiety has an excessively negative charge. If the resulting biradical 7 directly recombines to form a covalent bond, i.e. between N and O atoms, the transient intermediate would give products different from those actually obtained. In order to include in the

Scheme the oxygen-transfer precess, this proton transfer further requires intramolecular migration of a hydrogen atom to the neighboring anilino nitrogen, thus generating a triplet radical pair 8 which combines via ISC to form an $-N-O-CH-$ cyclic intermediate 9. On the other hand, if the direct abstraction of a hydrogen atom from the $-CH_2-$ group occurs in 6, the product is an ion pair and no MFE, characteristic for the radical-pair process, cannot be expected in the subsequent reaction.

Scheme 2 starts from the n,π^* state of the nitro group, which through abstraction of a hydrogen atom from the CH_2 group directly generates the triplet radical pair 8, and 8 in turn yields the cyclic intermediate 9. In this Scheme no ionic species is involved.

The essential difference between these two Schemes is whether the process involves an ionic species such as 6. Since ionic species can be generated only in polar solvents, the ionic process (Scheme 1) is possible only in acetonitrile among the solvents used for the present study. Scheme 2, on the other hand, is possible in both polar and nonpolar solvents. Thus, the reaction in benzene belongs to Scheme 2. In acetonitrile, it is difficult to determine whether either of the two or both processes are working, but Scheme 1 seems to make a minor (if any) contribution because the decay rate of $6(n=10$ and 11) estimated from the transient absorption is in the order of 10^8 s^{-1}, one order faster than k_{in} (vide supra).

It is noteworthy that in both Schemes the radical pair recombination process accompanying intersystem crossing of 8 is involved. The intermediate 9 is often suggested as a possible intermediate for the photoredox reactions of aromatic nitro groups, but has not been

proved by any physical or chemical evidence such as spectroscopy or isolation. Isotope effects[5,7] on the reaction rates suggest the hydrogen abstraction process as one of the rate-determining processes, and the isolation of N-[(2-nitrosophenyl)hydroxymethyl]-1-naphthalenecarboxamide (11) from the irradiated solution of N-(2-nitrobenzyl)derivative (10) at $-78°C$ (Eq. 7)
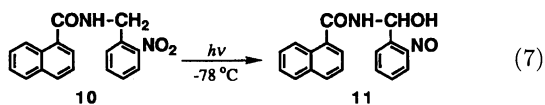
as an intermediate for the production of o-nitrosobenzaldehyde and naphthamide[16] is consistent with the intermediacy of 9, because 11 can be formed from 9 by intramolecular hydrogen transfer from OH to N–O–C oxygen and subsequent cleavage of the heterocyclic ring, but not directly from a biradical like 8.[17] Although present report does not provide a direct evidence either, together with these facts, the MFE observed provides strong supporting evidence for the presence of 9.

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17) In the Schemes, the final stage subsequent to the formation of 9 is depicted as one-step formation of the products (3 and aniline), but this does not necessarily deny a multistep pathway through an precursor similar to 11.