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Spectroscopic and Kinetic Study of an Intramolecular Aromatic Nucleophilic Photosubstitution. Reaction Mechanism of a Photo-Smiles Rearrangement

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Photo-Smiles rearrangement reaction of *N*-[ω-(*p*-nitrophenoxy)alkyl]aniline was studied by measuring the absorption spectra of transient species. Two intermediates **A** and **B** were observed and were assigned to a solvated ion pair and the Meisenheimer complex, respectively. The reaction scheme, starting material→intramolecular charge transfer on excitation→**A**→**B**→final product, was derived from the relative yields and lifetimes of **A** and **B** as well as from the effects of solvent polarity, of triethylamine and oxygen, and of the alkyl chain length on each step of reaction.

A great number of studies on aromatic nucleophilic photosubstitution have been carried out, main interest being focused on the orientation rule.[1] However, works in which the reaction mechanism has been elucidated through direct observation of intermediates are only a few. Cornelisse *et al.*[2] and also Duddel and Richards[3] studied the reactions of 3,5-dinitroanisole and *o*-, *m*-, and *p*-nitroanisoles, respectively, with the hydroxide ion by flash and laser photolysis. They concluded that the reaction proceeded *via* the triplet state except for *m*-nitroanisole.

A photo-Smiles rearrangement is known as an intramolecular nucleophilic photosubstitution reaction in which a nucleophile and a reaction center coexist within a molecule. Mutai *et al.*[4] studied the reaction in which *N*-[ω-(*p*-nitrophenoxy)alkyl]aniline (abbreviated hereafter to $(I)_n$, *n* being the number of methylene in the alkyl chain) converted into an alcohol $(II)_n$ in polar solvents by irradiation with light of about 300 nm (see Fig. 1). They reported that the reaction proceeded unimolecularly and proposed a tentative reaction scheme. In the present study, we have intended to elucidate the reaction mechanism by observing directly the intermediates with the aid of laser photolysis.

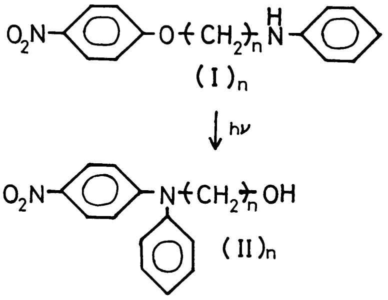

Fig. 1. Photo-Smiles rearrangement of *N*-[ω-(*p*-nitrophenoxy)alkyl]aniline, $(I)_n$.

Experimental

The starting material $(I)_n$ with $n=2$, 3, and 4 were prepared as mentioned previously[5] and purified by chromatography. Acetonitrile, benzene, cyclohexane (Wako, Spectrograde), ethanol (Nakarai, Spectrograde), and tetrahydrofuran (Wako, Special Grade) were used as solvents without further purification. Sample solution for the transient absorption measurements (about 1×10^{-3} mol·dm^{-3}) were degassed by repeating freeze-pump-thaw cycles. *N*-Methylaniline (NMA) (Wako, Special Grade) and *p*-nitroanisole (PNA) (Tokyo Kasei, Special Grade) which were regarded as two components of $(I)_n$ were used as references after distillation *in vacuo* and recrystallization, respectively.

An N_2 laser (Molectron UV-24 with peak height of 900 kw and pulse duration of 10 ns) was used as a pulse excitation source of reaction. A monitor light source was designed and constructed using a Xe flash lamp (EG & G 3CP-2). This system was able to emit rectangular shaped radiation pulses with 50 μs duration by the discharge through an LC delaying circuit.[6] By the use of this system, the transient absorption in μs region was measured with enough accuracy. A current regulated I_2-W lamp, chopped with a mechanical shutter, was used for the measurement of longer lived species (≈1 ms).

Time profile and spectra of transient species were measured by using a Jarrell-Ash JE-25 monochromator equipped with an HTV R-666S photomultiplier. A Hitachi 200-20 spectrophotometer was used for ordinary absorption measurements. All the experiments were made at room temperature.

Results and Discussion

Spectral change caused by 365 nm light irradiation of $(I)_2$ in acetonitrile is shown in Fig. 2. $(II)_2$ was produced by the irradiation of the sample in acetonitrile with the 313 or 365 nm light of Hg lamp or the defocused N_2 laser beam. Several isosbestic points were observed. This indicates that the reaction is clean and straightforward, being suited for the kinetic study of the reaction. The spectra of $(I)_2$ are safely reproduced by the superposition of those of PNA and NMA, whereas Mutai found a weak CT absorption band at 360 nm for the compounds of $n=2$ and 3.[7] This implies the existence of weak interaction in the ground state molecule. Thus it is suggested that considerable amounts of the molecules take sandwich configuration in their ground state.

Figure 3 shows the time dependence of the transient absorption of $(I)_2$ observed at 450 nm in acetonitrile.

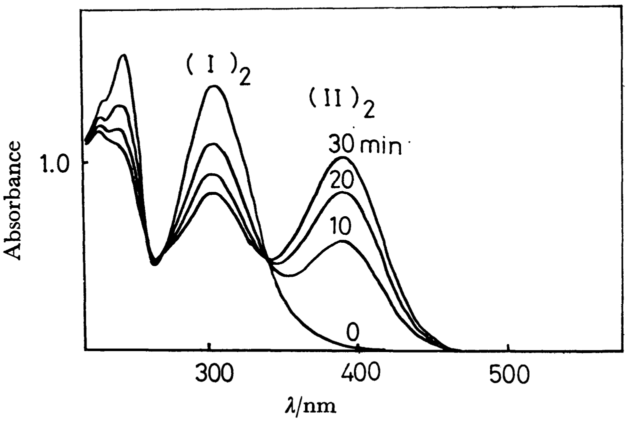

Fig. 2. Spectral change of $(I)_2$ in acetonitrile irradiated at 365 nm for 0, 10, 20, and 30 min, respectively.

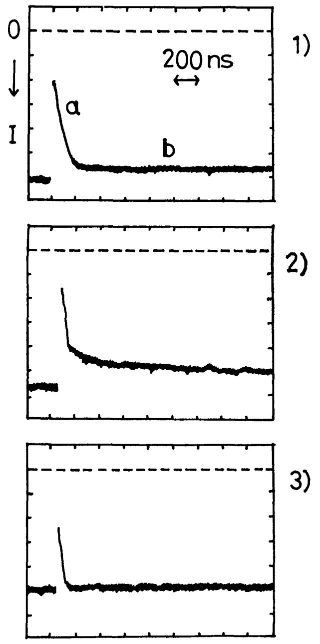

Fig. 3. Decay curve of transient absorption of $(I)_2$ in acetonitrile at 450 nm.

1) $(I)_2$ only, 2) with $N(C_2H_5)_3$ ($\approx 1\times 10^{-1}$ mol·dm^{-3}), 3) with O_2.

The decay curve of the absorption can be analyzed as composed of two components, **a** and **b**. Component **a** absorbs strongly but decays very fast, whereas component **b** is weak but long lived. The observation of these two components indicates the existence of two kinds of intermediates. Hereafter the intermediates which show the **a** and **b** components are referred to as **A** and **B**, respectively.

Figure 4 shows the absorption spectrum of **A**, which has a maximum at 450 nm, a shoulder in the shorter wavelength region, and a long tail in the longer wavelength region. The spectrum was not observed when either PNA or NMA was irradiated separately by the N_2 laser under the present experimental condition. The masking of nitrogen of the NMA component by addition of 0.1 mol·dm^{-3} hydrochloric acid also resulted in the nonoccurrence of **A**. The absorption spectrum of **A** is independent of *n*, the number of the methylene group in the alkyl chain. Thus, it is concluded that decay component **a** is caused by the coexistence of PNA and NMA moieties.

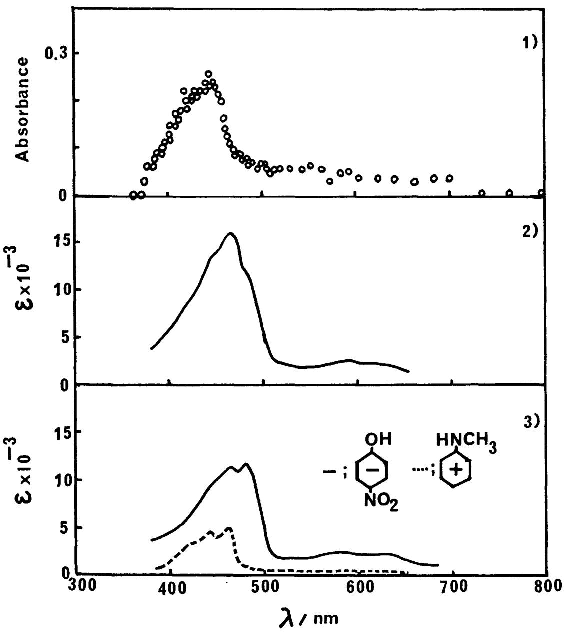

Fig. 4. Absoprtion spectra of **A** and the authentic species.

1) Absorption spectrum of **A** of $(I)_2$ in acetonitrile solution 10 ns after the excitation, 2) the 1:1 superposition of the absorption spectra of the NMA cation radical and the *p*-nitrophenol anion radical, 3) absorption spectra of the *p*-nitrophenol anion radical (Ref. 8b) and the NMA cation radical (Ref. 8a).

Transient intermediate **A** was observed clearly in polar solvents such as acetonitrile, ethanol and tetrahydrofuran, but not in nonpolar solvents such as benzene and cyclohexane. This solvent effect on the occurrence of **A** suggests the highly polar character of **A**.

Shida *et al.* reported the spectra of the *p*-nitrophenol anion radical and the NMA cation radical obtained by γ-ray irradiation at low temperature.[8] The 1:1 superposition of the spectra of both ions which are reproduced in Fig. 4, 3 is similar to the spectrum of **A** (compare Fig. 4, 1) with Fig. 4, 2)). Since the spectrum of the PNA anion radical is expected to be similar to that of the *p*-nitrophenol anion radical, the spectrum of **A** may be regarded as a superposition of those of the PNA and NMA ions. From this fact and the above-mentioned necessity of the coexistence of PNA and NMA moieties for the occurrence of **A**, we can conclude that **A** is a solvated ion pair in which both ions are bridged with the methylene chain.

Transient intermediate **A** is formed within the excitation pulse time (10 ns). Its lifetime is about 60—100 ns in the degassed acetonitrile solutions and reduces to about 20 ns after bubbling of the solution with O_2 gas for 3 min (see Table 1). In spite of the oxygen effect, **A** cannot be assigned to the lowest triplet state of $(I)_2$ in view of the fact that the spectrum of **A** is different from the T-T absorption spectra of nitro-

Table 1. Effects of $N(C_2H_5)_3$ and O_2 on the intermediates

	Lifetime of **A**	The relative yield of **B** to **A**
$(I)_2+N(C_2H_5)_3$	25 ns	0.15
$(I)_2$ only	65	0.07
$(I)_2+O_2$	≈20	<0.04
$(I)_3+N(C_2H_5)_3$	27	0.14
$(I)_3$ only	73	0.06
$(I)_3+O_2$	≈20	<0.03
$(I)_4+N(C_2H_5)_3$	25	0.19
$(I)_4$ only	98	0.12
$(I)_4+O_2$	≈20	<0.04

anisoles,[3] aniline and *N*,*N*-dimethylaniline.[9] The oxygen effect on the decay of **A** may be interpreted as the quenching of the aromatic anion by O_2.

Mutai *et al.* observed that the reaction $(I)_2 \rightarrow (II)_2$ was accelerated by addition of $N(C_2H_5)_3$.[4] We studied the effect of O_2 besides $N(C_2H_5)_3$ on the rate of the reaction by monitoring the absorbance at the peak of $(II)_2$ (at 395 nm) and the results are shown in Fig. 5. The addition of O_2 was found to decrease the rate.

Furthermore, we studied the effects of $N(C_2H_5)_3$ and O_2 on the decay of transient absorption and the results are shown in Fig. 3. The observed values of lifetime are listed in Table 1, together with the relative yield of **B** to **A** which is the ratio of absorbance of **B** observed 1 μs after the excitation to that of **A** observed 10 ns after irradiation. The addition of O_2 decreases the lifetime of **A** as well as the relative yield of **B**. The addition of $N(C_2H_5)_3$ decreases the lifetime of **A** but increases the relative yield of **B**. These results mean that O_2 quenches the ion pair and intercepts formation of **B** from **A** whereas $N(C_2H_5)_3$ accelerates the formation. The retarding effect of O_2 and the accelerating effect of $N(C_2H_5)_3$ were observed for formation of the final product, too. This is one of the evidences that intermediates **A** and **B** observed spectroscopically really participate in the reaction.

Figure 6 shows the absorption spectrum of **B** produced from $(I)_2$ in the presence of $N(C_2H_5)_3$ (1 μs after excitation). A similar spectrum of **B** was also observed in the absence of $N(C_2H_5)_3$ although S/N ratio became worse. As a stable intermediate of aromatic substitutions, the Meisenheimer complex (see Fig. 6) is well known. Ohsawa observed the absorption spectrum of the complex of PNA with amine with the results shown in Fig. 6.[10] We can see from the figure that the spectrum of **B** is similar to that of the complex. Therefore **B** is assigned to the Meisenheimer complex. The lifetime of **B** in the presence of $N(C_2H_5)_3$ is about 1—several ms for $n=2$, 3, and 4. Furthermore the spectral feature was found to be almost independent of n.

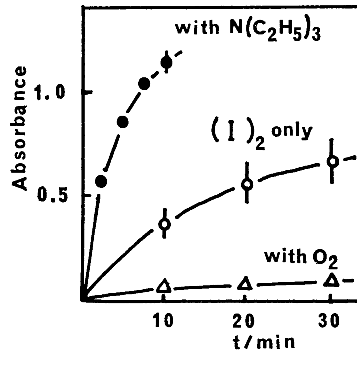

Fig. 5. Effects of O_2 and $N(C_2H_5)_3$ on the rate of reaction $(I)_2 \rightarrow (II)_2$ in acetonitrile with the irradiation of 365 nm light.

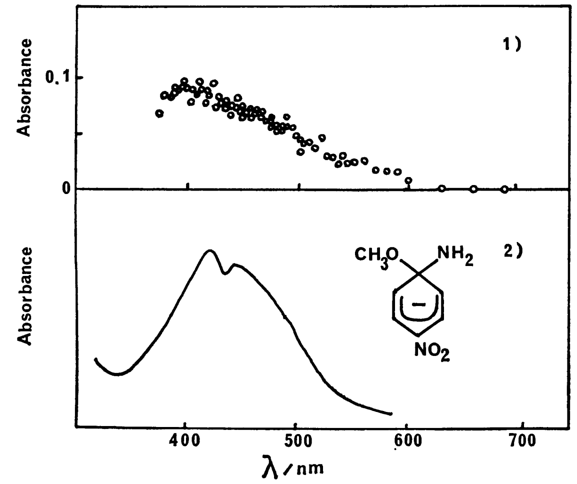

Fig. 6. Absorption spectra of **B** and the authentic species.
1) Absorption spectrum of **B**, 2) absorption spectrum of 1-methoxy-1-amino-4-nitrocyclohexadienide (Ref. 10).

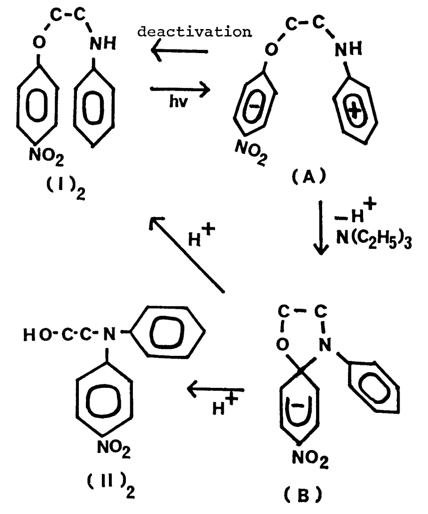

Fig. 7. A conclusive mechanism of the photo-Smiles rearrangement of $(I)_2$.

Figure 7 shows a conclusive mechanism of the reaction. A slight interaction may occur between the two ending groups in the ground state of the starting material $(I)_2$, as suggested by the appearance of a weak charge transfer band. When the sandwich type molecule is excited, a charge separation takes place efficiently through the orbital overlap and then the charge-transfer complex is solvated to form an ion pair.[11]

The process **A**→**B** corresponds to the Meisenheimer complex formation probably accompanied with abstraction of H^+ and **B** is converted into $(II)_2$ gradually by abstracting H^+ from $HN(C_2H_5)_3^+$. At the stage of **A** to **B**, the basicity of the NMA cation may be considered to be weaker than that of $N(C_2H_5)_3$. Therefore H^+ transfers from **A** to $N(C_2H_5)_3$. This may reasonably explain the enhancement of the relative yield of **B** by the addition of $N(C_2H_5)_3$. The above explanation implies that the presence of H^+ acceptor such as amine is necessary for the forward reactions. Actually, when the solvent acetonitrile was distilled repeatedly with P_2O_5, the photo-Smiles reaction rate was markedly slow. The fact that commercially available spectroscopic grade acetonitrile is positive solvent for the reaction suggests the presence of impurities which act as catalysts in thermal reaction steps, although they are not detectable by gas and liquid chromatography.

As a whole, the photosensitized Smiles rearrangement is such a reaction that a substitution takes place between the cation and anion radicals produced by irradiation of light. Nagakura and Tanaka predicted theoretically that the radicals formed by charge transfer interaction played an important role in the aromatic substitution reaction.12) The observation of the ion pair as the reaction intermediate in the present study shows that the photo-Smiles reaction is a typical example for their prediction.

Generally speaking, the orientation rule is known to be different for thermal and photo aromatic substitutions. Mutai *et al.*, however, reported that the photo-Smiles reaction is para directing with regard to the NO_2 group as is usual for the thermal nucleophilic substitution.4) This agrees with the theoretical prediction by Nagakura and Tanaka12a) that the free valency of the nitrobenzene anion is largest at the para position. In other words, photo-Smiles reaction is triggered by irradiation of light and the substitution takes place through interaction between the ground state cation and anion radicals in pair.

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