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Photochemistry of Acetanilide. II. The Primary Processes in the Photochemical Reaction

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The photochemical primary processes of acetanilide have been discussed on the basis of the quantum yields in various solvents, the dependences of the quantum yields on the excitation wavelength, and the emission spectra. The quantum yields of the products (*o*-aminoacetophenone and *p*-aminoacetophenone) at 2537 Å decreased greatly in polar solvents. A non-linear relationship between the quantum yield and the fraction of hydrogen-bonded acetanilide in the cyclohexane-ethanol solution was obtained. No variation in the quantum yield was observed upon the change of the excitation from 2537 to 2740 Å. These results indicate the occurrence of a radiationless internal conversion, $S_1(\pi\pi^*)\leftarrow S_2(\pi\pi^*)$. The relative fluorescence intensity in a polar solvent was larger than that in a nonpolar solvent. On the basis of these studies, it can reasonably be considered that the primary process in the photochemical reaction of acetanilide involves predissociation.

In a previous paper[2] on the photochemical reaction of acetanilide, it has been shown that the quantum yields under various conditions and the kinetic data of benzene photosensitization indicate a mechanism *via* the lowest excited singlet state, $S_1(\pi\pi^*)$, not the triplet state, $T_1(\pi\pi^*)$.

The excitation of acetanilide at 2537 Å occurs from the ground state, S_0, to the secondary excited singlet state, $S_2(\pi\pi^*)$. The occurrence of a nonradiative internal conversion, $S_1(\pi\pi^*)\leftarrow S_2(\pi\pi^*)$, is to be expected. Since acetanilide has a carbonyl group involving non-bonding electrons, it is also interesting to consider the role of $S_1(n\pi^*)$ or $T_1(n\pi^*)$ in the photochemical primary processes. Measurements of fluorescence and phosphorescence spectra are useful for obtaining knowledge of electronic excited states in acetanilide. The purpose of the present work is to clarify the mechanism of photochemical primary processes in acetanilide.

This paper will report on the measurements of quantum yields in various solvents, the relationship between the quantum yield and the fraction of hydrogen-bonded acetanilide, the effect of the excitation wavelength of the quantum yield, measurements of emission spectra, and a theoretical estimation of the n-π^* energy level relative to the π-π^* energy levels by means of the intramolecular charge transfer theory.[3] It will also include a discussion of the primary processes in this photochemical reaction.

Experimental

The experimental procedure and reagents were similar to those previously described.[2] A low-pressure mercury lamp was used as the 2537 Å radiation source with a Vycor glass filter, while a high-pressure mercury lamp was used in the 2740 Å range with an interference filter UV-D-25. The fluorescence and phosphorescence spectra were observed by means of a Hitachi MPF-2 Spectrophotofluorometer and an Aminco Bowman Spectrophotofluorometer respectively. In these measurements, the concentrations of the solutions were adjusted so that the values of optical density were 0.600 at 2537 Å. The methylcyclohexane, ether, and ethanol were Tokyo Kasei Co. G. R.-grade products, while the methylcyclohexane was purified by passing it through silica-gel and by distillation.

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[2] H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968).

[3] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura and S. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954); S. Nagakura, *J. Chem. Phys.*, **23**, 1441 (1955).

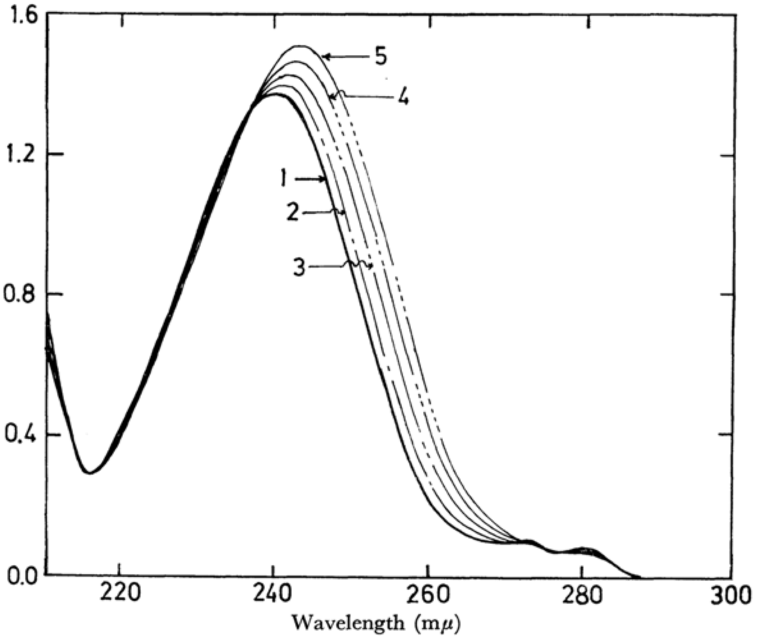

Fig. 1. Spectra of acetanilide in ethanol-cyclohexane mixture at room temperature. Ethanol concentrations are: 1, 0; 2, 0.041; 3, 0.082; 4, 0.205; and 5, 0.410 mol/*l*.

Experimental Results

1) Effect of Solvent. The quantum yields in various solvents were measured in a manner similar to that described in a preceding paper.[2] The results are shown in Table 1.

TABLE 1. QUANTUM YIELDS OF THE PRODUCTS IN VARIOUS SOLVENTS AT 2537 Å

Solvent	Quantum yield (Φ)	
	Φ_o	Φ_p
Cyclohexane[2]	7×10^{-2}	6×10^{-2}
Ether	4.3×10^{-2}	3.7×10^{-2}
Ethanol	1.7×10^{-2}	1.4×10^{-2}
H_2O	4.8×10^{-3}	1.8×10^{-3}

Φ_o: Φ of *o*-aminoacetophenone
Φ_p: Φ of *p*-aminoacetophenone

Polar solvents decreased the quantum yields. The dependence of quantum yields on the solvents was examined by means of the method reported by Shinzawa and Tanaka.[4] The ultraviolet spectra of acetanilide in an ethanol - cyclohexane solution varied with the composition of the solvents, as is shown in Fig. 1. The concentrations of ethanol were about 100 times greater than those of acetanilide.

Acetanilide has been revealed, by means of a study of its ultraviolet spectra, to form hydrogen bonds with dioxane and cyclohexanone as proton acceptors.[5] Assuming a hydrogen bond between

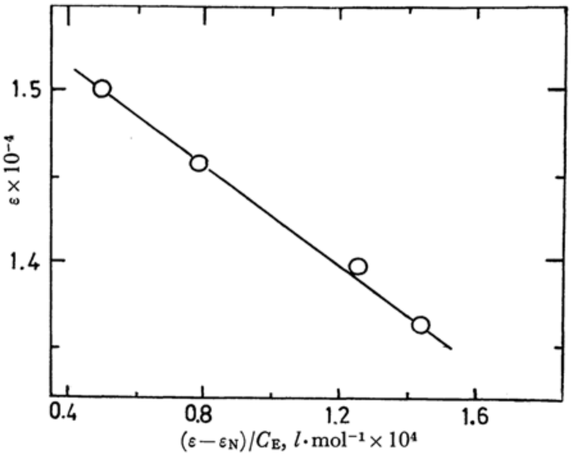

Fig. 2. Plot of ε against $(\varepsilon-\varepsilon_N)/C_E$ to obtain the equilibrium constant K of the bond formation using the relation.
$\varepsilon=-(\varepsilon-\varepsilon_N)/C_E K+\varepsilon_H$; slope of the curve indicates reciprocal value of K observed for 243 mμ at room temperature; ε, molar extinction of acetanilide in ethanol-cyclohexane solution; ε_N, molar extinction of acetanilide in cyclohexane; ε_H, molar extinction of hydrogen-bonded acetanilide; and C_E, concentration of ethanol.
$K=6.5\ l\cdot\text{mol}^{-1}$ for 243 mμ

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4) K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964).

5) S. Suzuki and H. Baba, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 366 (1960).

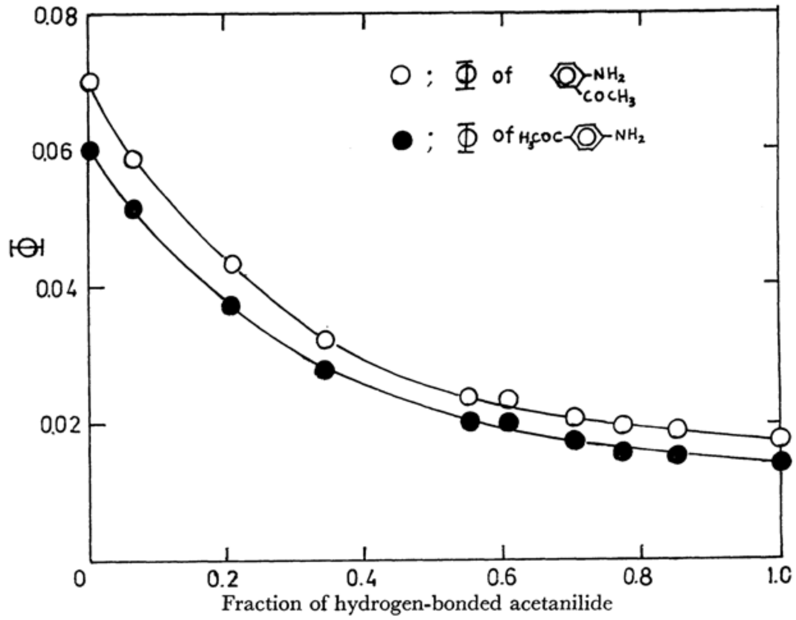

Fig. 3. Plot of quantum yield against fraction of hydrogen-bonded acetanilide molecules.

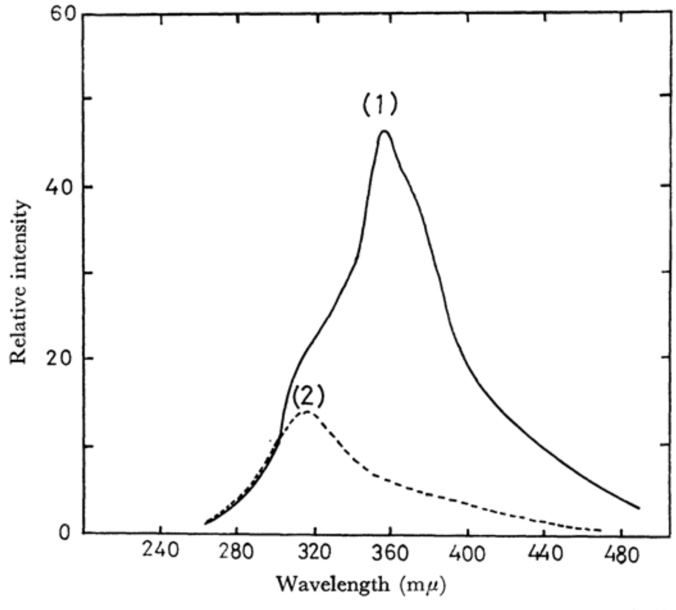

Fig. 4. Fluorescence spectra of acetanilide by the excitation at 2537 Å at room temperature.
(1): In ethanol (2): In cyclohexane

acetanilide and ethanol in the present study, the equilibrium constant, K, of the bond formation was calculated by the method obtained by Baba and Nagakura.[6] The value of K obtained from Fig. 2 was ~6.5 l/mol.

In order to ascertain the relation between the quantum yield and hydrogen-bond formation, the quantum yields are plotted in Fig. 3 against the fractions of the hydrogen-bonded molecules calculated from the K value.

A non-linear relationship was obtained, as is shown in Fig. 3.

2) Effect of Excitation Wavelength. A high-pressure mercury lamp was used for the 2740 Å

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6) H. Baba and S. Nagakura, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*) **72**, 3 (1951); S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

range, which corresponds to the lowest excited singlet state, $S_1(\pi\pi^*)$,[7] with an interference filter, UV-D-25. The quantum yields of *o*-aminoacetophenone and *p*-aminoacetophenone by irradiation with a 2740 Å range light were 0.07 and 0.06 respectively in a cyclohexane solution. No effect of excitation wavelength on the quantum yields was observed from 2537 to 2740 Å.

3) Emission Spectra. In order to study the behavior of acetanilide in electronically-excited states, the emission spectra were measured. Figure 4 shows the fluorescence spectra of acetanilide in ethanol and cyclohexane solutions.

These data are summarized in Table 2.

TABLE 2. FLUORESCENCE AND PHOSPHORESCENCE SPECTRA OF ACETANILIDE AT 2537 Å.

Solvent	Fluorescence at room temperature		Phosphorescence at 77°K	
	$\lambda_{\max}$ (mμ)	$I^{\mathrm{F}}_{\mathrm{rel}}$	$\lambda_{\max}$ (mμ)	$I^{\mathrm{P}}_{\mathrm{rel}}$
Cyclohexane	317	13		
Methylcyclohexane			373	1
Ethanol	356	47	388	30

The concentrations were adjusted so that the optical densities at 2537 Å were 0.600.

$I^{\mathrm{F}}_{\mathrm{rel}}$ and $I^{\mathrm{P}}_{\mathrm{rel}}$ are the relative intensities of the fluorescence and phosphorescence maxima respectively.

In view of its red shift in a polar solvent, it is reasonable to assume that the fluorescence was the emission from $S_1(\pi\pi^*)$ to S_0. The phosphorescence can be assigned to the emission from the triplet state, $T_1(\pi\pi^*)$, to S_0, since the lifetime of the phosphorescence was a few seconds at 77°K. The natural radiative lifetime, τ_0, was calculated from Eq. (1):

$$\tau_0 = \frac{3.47\times10^8}{(\bar{\nu}_{\max})^2\int\varepsilon(\bar{\nu})\mathrm{d}\bar{\nu}} = 1.12\times10^{-7}\mathrm{sec} \tag{1}$$

where $\bar{\nu}_{\max}$ is the wave number of Absorption Band I,[7] which corresponds to $S_1(\pi\pi^*)$, $3.65\times10^4\mathrm{cm}^{-1}$, and where $\int\varepsilon(\bar{\nu})\mathrm{d}\bar{\nu}$ is the experimental extinction coefficient integrated over the width of Band I, 2.32×10^6 cm/mmol. The fluorescence lifetime is given by:

$$\tau_{\mathrm{F}} = \tau_0\cdot Q_{\mathrm{F}} = \sim10^{-10}\mathrm{sec} \tag{2}$$

where Q_{F} is the fluorescence quantum yield of acetanilide in a cyclohexane solution, and where the order of magnitude is $\sim10^{-3}$, a value which was obtained by comparison with the relative fluorescence intensity of carbazole, whose fluorescence quantum yield is 0.35.[8]

Discussion

It has been reported that, in the nitrone→oxazirane photoisomerization, the lifetime of the excited nitrone molecule should be shorter than the relaxation time ($\sim10^{-11}$ sec)[9] of the arrangement between solute and solvent, since the linear relationship between the decrease in the quantum yield of the nitrone in anet hanol-cyclohexane solution and the fraction of hydrogen-bonded nitron molecules indicates that no rearrangement of solvent surrounding the excited nitrone molecule occurs before the photochemical reaction of the nitrone takes place.[4] In constrat to this, a non-linear relationship between the decrease in the quantum yield of acetanilide in an ethanol-cyclohexane solution and the fraction of hydrogen-bonded acetanilide was obtained, as is shown in Fig. 3. It is a possible explanation that the lifetime of an excited acetanilide molecule is longer than the relaxation time ($\sim10^{-11}$ sec)[9] of the arrangement of solute and solvent, and that therefore the radiationless internal conversion, $S_1(\pi\pi^*)\leftarrow S_2(\pi\pi^*)$, may occur.

In addition to this, no variation in the quantum yield was observed upon the change of excitation wavelength from 2537 to 2740 Å. This finding supports the occurrence of an internal conversion, $S_1(\pi\pi^*)\leftarrow S_2(\pi\pi^*)$, and of a Boltzmann distribution in $S_1(\pi\pi^*)$.

The n-π^* absorption band in acetanilide could not be observed, even at high concentrations ($\sim3\times10^{-3}$ mol/l). It is known that n-π^* transition in the molecules with a carbonyl group adjacent to the electron-donating group result in a large blue shift.[10] These phenomena have been theoretically explained by Nagakura *et al.*[3] and by Baba.[10] A theoretical estimation of the n-π^* energy level relative to π-π^* levels was carried out by means of the intramolecular charge transfer theory.[3]

The highest occupied (H_{B}, H_{S}) and the lowest vacant levels (V_{B}, V_{S}) were determined by means

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[7] H. Baba and S. Suzuki, *J. Chem. Phys.*, **32**, 1706 (1960).

[8] D. W. Ellis and B. S. Solomon, *ibid.*, **46**, 3497 (1967).

[9] E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); *Z. Elektrochem.*, **61**, 962 (1957).

[10] H. Baba, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **72**, 74, 341 (1951).

	$n\pi^*$ absorption band (Å)
HCHO	2940
CH_3COCH_3	2790
CH_3COCl	2345
CH_3COOH	2040
CH_3CONH_2	2050

of aniline and acetone, using experimental knowledge of their ionization potentials[11] and their near-UV absorption spectra. The highest occupied orbital of aniline (H_B) interacts with the lowest vacant orbital (V_B) of the substituent group (carbonyl group). Consequently, two new levels, W_n and W_e, result, as is shown in Fig. 5.

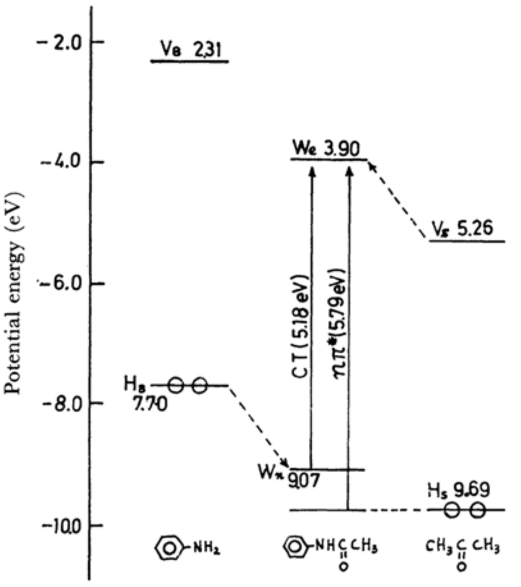

Fig. 5. Estimation of n–π^* transition in acetanilide

Their wave functions, Ψ, and energy levels, W_n and W_e can be represented as follows:

$$\Psi = a\varphi_B + b\varphi_S \tag{3}$$

$$W_n = \frac{1}{2}[H_B + V_S - \{(H_B - V_S)^2 + 4\beta^2\}^{1/2}] \tag{4}$$

$$W_e = \frac{1}{2}[H_B + V_S + \{(H_B - V_S)^2 + 4\beta^2\}^{1/2}] \tag{5}$$

where φ_B and φ_S are the wave functions for the H_B and V_S levels respectively and where β is the exchange integral.

Baba and Suzuki have reported that the lower excited singlet states in acetanilide consist of $S_1(\pi\pi^*)$ ($^1B_2$, 4.532 eV) and $S_2(\pi\pi^*)$ ($^1A_1$, 5.183 eV).[7] The $W_e \leftarrow W_n$ excitation corresponds to the $^1A_1 \leftarrow {}^1A_1$ transition and has a polarization of the transition dipole along the long axis.[7] Therefore, this transition is assigned to $S_2(\pi\pi^*) \leftarrow S_0$. The $S_1(n\pi^*)$ transition energy in acetanilide can then be estimated as 5.79 eV, as is shown in Fig. 5. The n–π^* transition energy is larger than that of $S_2(\pi\pi^*)$. Considering the energy levels as shown in Fig. 5, the photochemical reaction of acetanilide can not occur through the n–π^* state.

It has also been shown that $S_1(\pi\pi^*)$ in acetanilide is the lowest excited singlet state from the fluorescence spectra. The energy difference, ΔE, between $h\nu$ and $h\nu'$ can be calculated from the experimental data of absorption[12] and the emission spectra:

$$\left.\begin{aligned}(\Delta E)_{\text{CH}} &= 4900\ \text{cm}^{-1}\\ (\Delta E)_{\text{EtOH}} &= 8500\ \text{cm}^{-1}\end{aligned}\right\} \tag{6}$$

ΔE was larger in the polar solvent than in the nonpolar solvent. This indicates that the potential curve of the lowest excited singlet state, $S_1(\pi\pi^*)$, in the polar solvent lines below that in the nonpolar solvent. The repulsive potential curve of $^3\sigma_0$(N–C) may be approximately the same in polar and nonpolar solvents, since, in general, the triplet energy level is scarcely affected at all by a poar solvent. As has been described above, excited acetanilide molecules in $S_1(\pi\pi^*)$ are distributed according to the Boltzmann law. Therefore, the potential barrier which corresponds to the energy difference between their crossing point and the zero point energy level in $S_1(\pi\pi^*)$ may be larger in polar solvents. The effect of polar solvents on the quantum yield was very large, and the quantum yield decreased significantly in polar solvents, as is shown in Table 1. Moreover, the fluorescence intensity in a polar solvent was larger than that in a nonpolar solvent, as Table 2 shows.

It is reasonable to assume the intersystem crossing

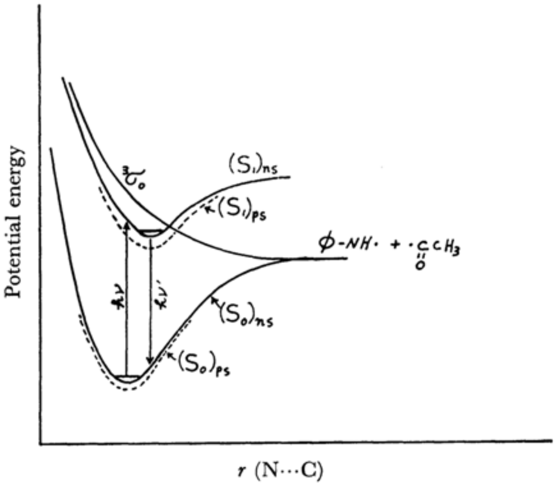

Fig. 6. A schematic potential energy diagram for $\phi\text{-}\overset{\text{N}}{\text{H}}\cdots\underset{\overset{\|}{\text{O}}}{\text{C}}\text{CH}_3$ system.

ns: nonpolar solvent ps: polar solvent

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11) Ionization potential data are obtained from following references.

Aniline: K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); R. Bralsfold, P. V. Harris and W. C. Price, *Proc. Roy. Soc.*, **A258**, 459 (1960).

Acetone: K. Watanabe, *J. Chem. Phys.*, **22**, 1895 (1954).

between $S_1(\pi\pi^*)$ and $^3\sigma_0$(N–C) repulsive state. Figure 6 shows a schematic potential energy diagram.

It has also been found that the quantum yield for the predissociation is dependent on the temperature and that this temperature dependency is affected by the polarity of a solvent.[13] Thus, the deactivation processes ($k_S+k_F+k_C$; see below) become more important than the nonpolar solvents. The primary processes in the photochemical reaction at 2537 Å can be represented by the following equations:

$$S_0 \xrightarrow{h\nu} S_2(\pi\pi^*) \tag{8}$$

$$S_2(\pi\pi^*) \xrightarrow{k_{ic}} S_1(\pi\pi^*) \tag{9}$$

$$S_1(\pi\pi^*) \xrightarrow{k_S} S_0 \tag{10}$$

$$S_1(\pi\pi^*) \xrightarrow{k_F} S_0 + h\nu' \tag{11}$$

$$S_1(\pi\pi^*) \xrightarrow{k_c} T_1(\pi\pi^*) \tag{12}$$

$$S_1(\pi\pi^*) \xrightarrow{k_{dis}} \phi\text{-NH}\cdot + \cdot\text{COCH}_3 \tag{13}$$

$$T_1(\pi\pi^*) \xrightarrow{k_T} S_0 \tag{14}$$

$$T_1(\pi\pi^*) \xrightarrow{k_p} S_0 + h\nu'' \tag{15}$$

Although this singlet-triplet transition, $^3\sigma_0$(N–C)← $S_1(\pi\pi^*)$, is spin-forbidden, it must have a high transition probability to compete with the other deactivation processes for the lowest excited singlet state, $S_1(\pi\pi^*)$, in acetanilide. The probability of the $^3\sigma_0$(N–C)←$S_1(\pi\pi^*)$ transition may result from the vibronic coupling between $S_1(\pi\pi^*)$ and $T_1(n\pi^*)$.

In conclusion, the photochemical reaction of acetanilide occurred from the lowest excited singelt state, $S_1(\pi\pi^*)$. The $S_1(\pi\pi^*)$ state might cross over to the $^3\sigma_0$(N–C) repulsive state, resulting in the fission of the N–C bond and the liberation of the ϕ-NH and $COCH_3$ radicals in their doublet ground states. It is reasonable to consider that the primary processes in this photochemical reaction involve the predissociation of the N–C bond.

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12) Absorption band I: 274 mμ in cyclohexane, 273 mμ in ethanol,

13) H. Shizuka, This Bulletin, **42**, 57 (1969).