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Photochemistry of Acetanilide. III. The Secondary Processes in the Photochemical Reaction

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The photochemical secondary processes of acetanilide have been studied. The photochemical reaction of *p*-methylacetanilide at 2537 Å did not produce the *p*-rearrangement product, but the *o*-rearrangement one. The quantum yields of the *o*-rearrangement and of the disappearance of *p*-methylacetanilide were 0.09_2 and 0.12 respectively. Comparing the quantum yields of acetanilide with those of *p*-methylacetanilide, the values of the quantum yields for the predissociation of the N-C bond, the back reaction, and the recombination ratio were estimated to be 0.25, 0.10, and 0.9 respectively. These results indicate that the recombination reaction between the pair radicals formed by the predissociation of the N–C bond occur efficiently in a solvent cage. The rate constants of the back reaction, the *o*-rearrangement, and the *p*-rearrangement were proportional to the odd π electron densities of the anilino radical. No intermediate was observed by the flash photolysis. The small dependence of the quantum yields of acetanilide on the temperature supports the predissociation mechanism previously described.[2] On the basis of these studies, the mechanism of the photochemical reaction of acetanilide in the liquid phase has been proposed.

In the second paper of this series,[2] it has been shown that the photochemical primary process of acetanilide involves the predissociation caused by intersystem crossing, ${}^3\sigma_0(\text{N–C}) \leftarrow s_1(\pi\pi^*)$. It is expected that, in the liquid phase, the recombination between the pair radicals formed by the predisso-

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[2] H. Shizuka, This Bulletin, **42**, 52 (1969).

ciation will occur with a high probability; this is the so-called "cage effect".[3] Many investigations of the cage effect have been reported by Noyes and by others.[4–10]

In order to determine the photochemical secondary processes of acetanilide, it is necessary to obtain the values of the quantum yields for the predissociation of the N–C bond, Φ_{dis}, the back reaction, Φ_B, and the recombination ratio, β. Considering their UV absorption spectra, the electronically-excited states in acetanilide and p-methylacetanilide are the same in a first approximation. Therefore, the photochemical primary process of p-methylacetanilide would be the same as that of acetanilide. However, the photochemical reaction of p-methylacetanilide at 2537 Å did not produce the p-rearrangement product but, rather, the o-rearrangement product, because its p-position is blocked by the methyl group.

The values of Φ_{dis} and Φ_B may be estimated by comparing the quantum yields of acetanilide with those of p-methylacetanilide.

On the other hand, flash photolysis is useful in detecting some intermediates, and the effect of the temperature on the quantum yield is also useful in discussing the mechanism of the photochemical reaction of acetanilide. This paper will report on the photochemical reactions of p-substituted acetanilide at 2537 Å, the dependence of the quantum yield on the temperature, the data of flash photolysis, and the estimations of Φ_{dis}, Φ_B, and β, it will also include a discussion of the photochemical secondary processes of acetanilide.

Experimental

The experimental technique was similar to that previously described.[2,11] The flash apparatus was an ordinary one. The excitation flash lamp with 150 mmHg of xenon gas, was made of quartz. The condenser for the excitation flash lamp with a capacity of 25μF was charged to 4 kV; the energy corresponded to 200 J. The pulse had a half-value width of about 50μsec. The flash lamp for spectroscopy, with 150 mmHg of xenon, was made of quartz. The condenser for the spectral flash lamp with a capacity of 8μF was charged to 4 kV; the energy corresponded to 64 J. The pulse had a half-value width of about 20μsec.

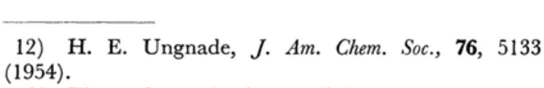
p-Methyl-, p-chloro-, p-bromo-, p-iodo-, and p-nitroacetanilides were prepared by treating reagent-grade products of p-substituted anilines with glacial anhydride and were purified by repeated recrystallizations from water. p-Amino- and p-hydroxyacetanilides were Tokyo Kasei Co. reagent-grade products and were purified by recrystallization from water.

Results and Discussion

1) Irradiation of *p*-Substituted Acetanilides at 2537 Å.

The absorption spectra of the solutions of p-substituted acetanilides were similar to that of acetanilide, except in the case of p-nitroacetanilide.[12] The spectra of all the solutions of p-substituted acetanilides except p-nitroacetanilide changed markedly by upon irradiation with a 2537 Å light. The photochemical reactions of p-substituted acetanilides may be classified into the following four types.

a) Photochemical Reactions of p-Methyl- and p-Chloroacetanilides. Figure 1(a) shows the spectral change in a cyclohexane solution of p-methylacetanilide at 2537 Å. The absorption Band II (243 mμ) decreased and new bands appeared with maxima of 228 and 363 mμ as the irradiation time increased; there were three isosbestic points at 213, 235, and 260 mμ. The product which had absorption peaks at 228. and 363 mμ was assigned to 2-amino-5-methylacetophenone (o-rearrangement product) by gas chromatography. A similar spectral change was observed in the case of p-chloroacetanilide, as is shown in Fig. 1(b).
The quantum yields were obtained spectrophotometrically in cyclohexane.[*1] The disappearance quantum yields of p-methyl- and p-chloroacetanilides were 0.12 and 0.13 respectively at 20°C. The quantum yields of 2-amino-5-methyl- and 2-amino-5-chloroacetophenones were 0.09_2 and 0.09_7 respectively. These photochemical reactions are analogous to those reported by Kobsa for p-t-butylphenylacetate derivatives,[13] as is shown in Eqs. (1) and (2):



(1)

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[3] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[4] F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

[5] R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

[6] R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); *ibid.*, **78**, 5486 (1956).

[7] R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961).

[8] J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3274 (1954).

[9] L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

[10] H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964); G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964).

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

[12] H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 5133 (1954).

[*1] The molar extinction coefficients, ε:

p-methylacetanilide Band II 243 mμ	13800
2-amino-5-methylacetophenone 363 mμ	3600
p-chloroacetanilide Band II 246 mμ	14300
2-amino-5-chloroacetophenone 365 mμ	3000

[13] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

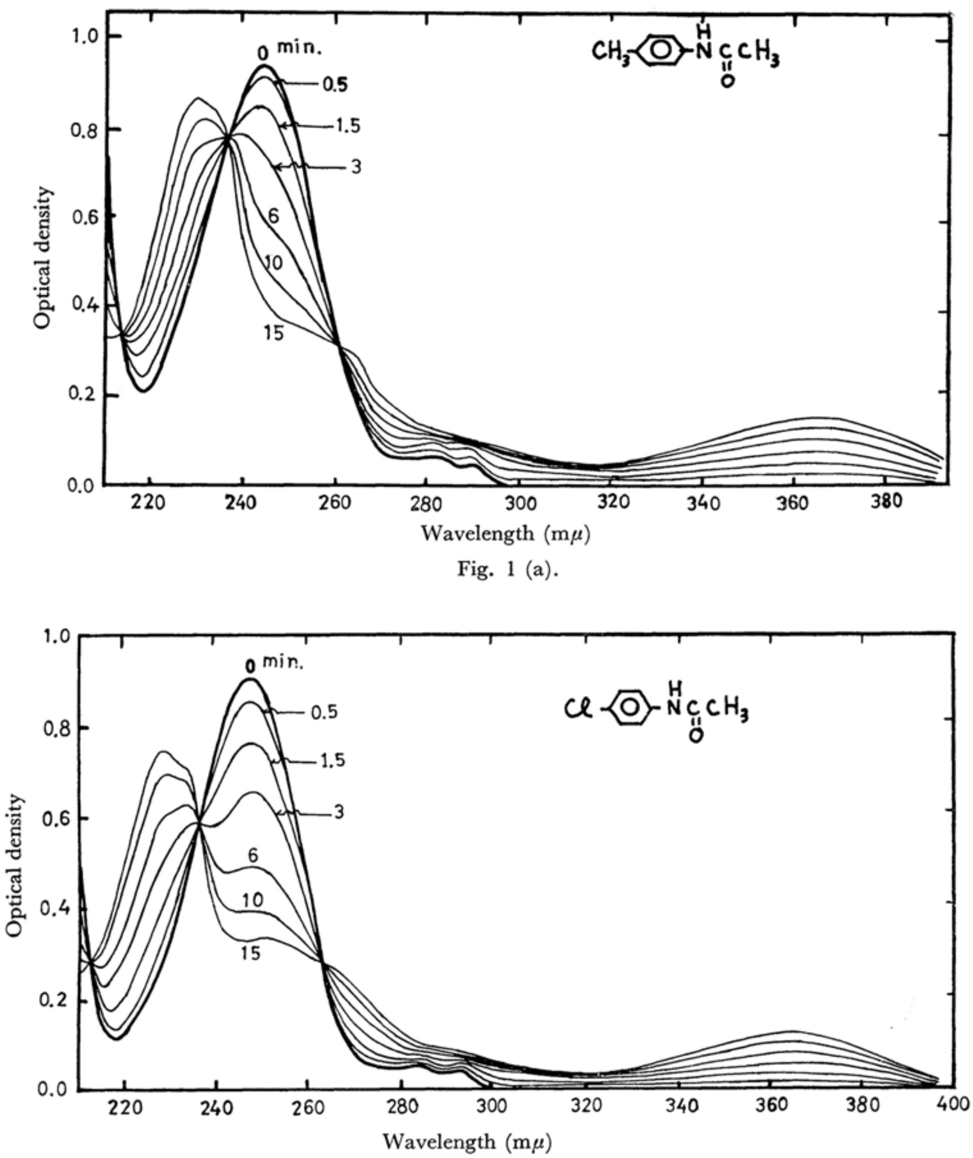
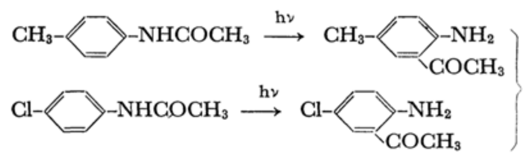


Fig. 1 (a).

Fig. 1(b).

Fig. 1. Spectral changes of cyclohexane solutions of *p*-methylacetanilide (a) and of *p*-chloroacetanilide (b) with lapse of irradiation time at 2537 Å.



(2)

where Ar represents a phenyl substituent.

b) Photochemical Reactions of p-Bromo- and p-Iodo-Acetanilides. Figure 2(a) shows the spectral change in the solution of *p*-bromoacetanilide. The Absorption Band II (250 mμ) decreased and new bands with the maxima of 225, 290, and 365 mμ appeared, but with no clear isosbestic point such as those in the cases of *p*-methyl- and *p*-chloroacetanilides. The appearance of the 290 mμ peak probably indicates that *p*-aminoacetophenone was also produced by the irradiation with 2537 Å.[11] A similar spectral change was observed in the case of *p*-iodoacetanilide, as is shown in Fig. 2(b). In the photochemical reactions of *p*-bromo- and *p*-iodoacetanilides, it is reasonable to assume that the predissociation at the C–Br or at the C–I bond was caused by irradiation, resulting in acetanilide. Therefore, the *p*-rearrangement at 2537 Å might occur as well as the *o*-rearrangement.

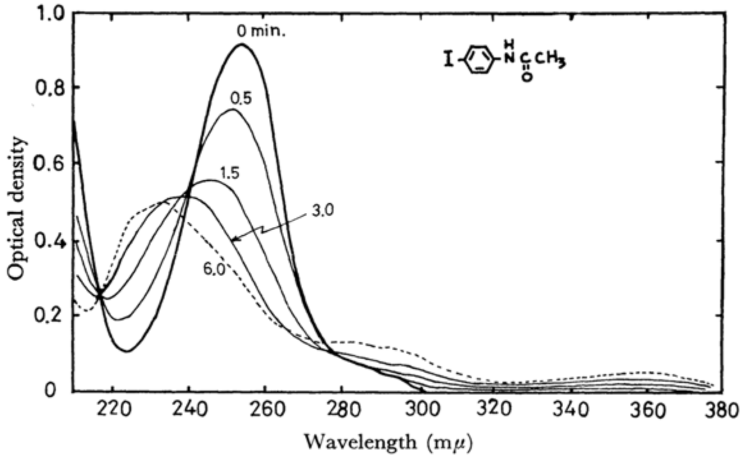


Fig. 2(a).

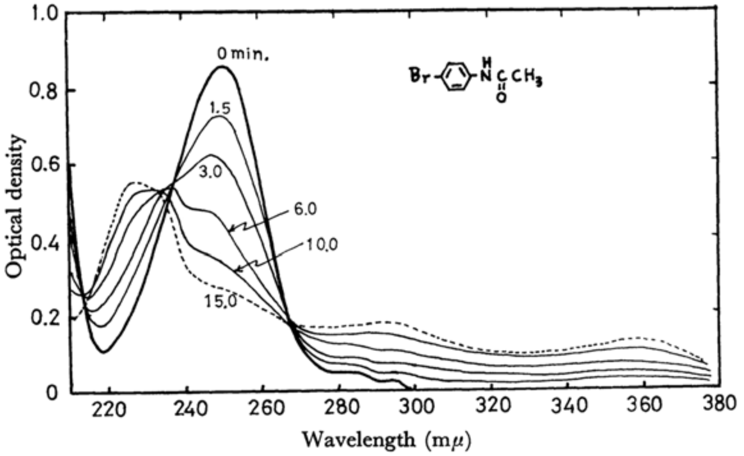


Fig. 2(b).

Fig. 2. Spectral changes of cyclohexane solutions of *p*-bromoacetanilide (a) and of *p*-iodoacetanilide (b) at 2537 Å.

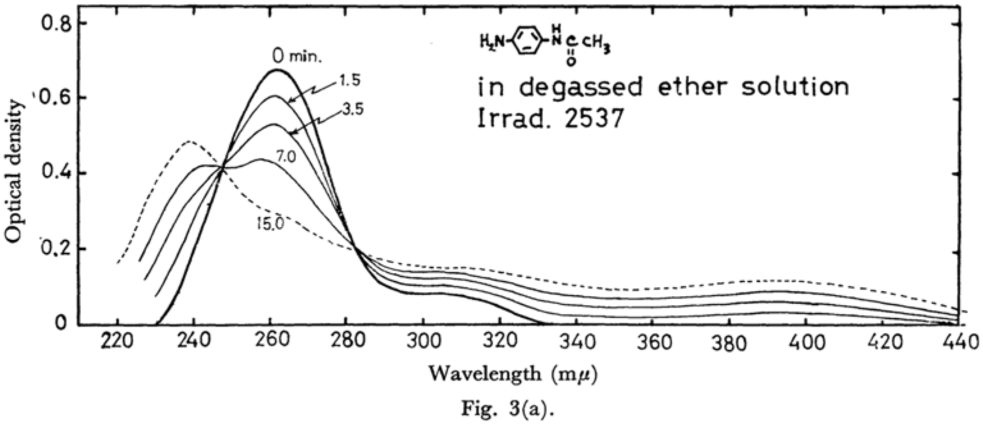


Fig. 3(a).

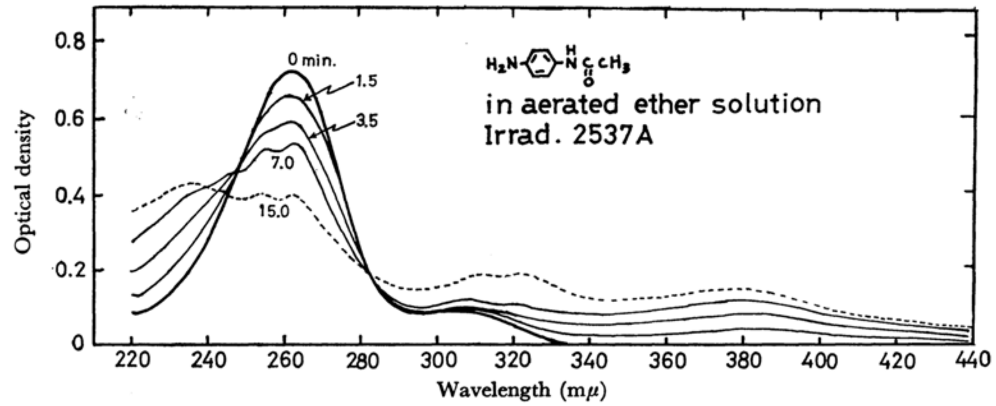


Fig. 3(b).

Fig. 3. Spectral changes of ether solutions of *p*-aminoacetanilide at 2537 Å.
(a) degassed (b) aerated

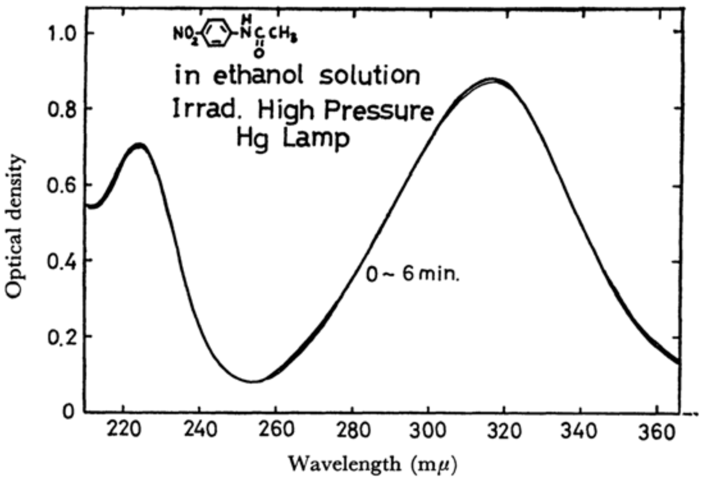


Fig. 4. The spectral change of ethanol solution of *p*-nitroacetanilide by irradiation with a high pressure mercury lamp.

c) *Photochemical Reactions of p-Amino- and p-Hydroxyacetanilides.* *p*-Amino- and *p*-hydroxyacetanilides had very poor solubilities in cyclohexane at room temperature. Therefore, ether was used as the solvent. Figure 3(a) shows the spectral change in a degassed ether solution of *p*-aminoacetanilide at 2537 Å. The Absorption Band II (262 mμ) decreased and new bands with the maxima of 237 and 395 mμ appeared, as well as those of *p*-methyl- and *p*-chloroacetanilides. However, in an aerated ether solution, the spectral change was different from that in a degassed solution, as is shown in Fig. 3(b).

In the case of an aerated ether solution, the Absorption Band II (262 mμ) decreased and new peaks appeared at 237, 243, 254, 263, 322, and 378 mμ. The increase in the 237 mμ peak corresponds to the *o*-rearrangement. The appearance of peaks at 243, 254, and 263 mμ in an aerated solution of *p*-aminoacetanilide was similar to that in an aerated solution of *p*-phenylenediamine at 2537 Å found by Hinohara.[14] Similar results were observed in the cases of degassed and aerated ether solutions of *p*-hydroxyacetanilide at 2537 Å.

It may be considered that, in the presence of dissolved oxygen, 2,5-diaminoacetophenone (the *o*-rearrangement product) was oxidised to the corresponding imine.

d) *Phntochemical Reaction of p-Nitroacetanilide.* Scarcely no spectral change was observed in an aerated ethanol solution of *p*-nitroacetanilide upon irradiation with a high-pressure mercury lamp, as is shown in Fig. 4.

The quenching mechanism by the substitution of

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[14] T. Hinohara, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

the nitro group has been explained by Tanaka *et al.*[15]; internal quenching is caused by the atomic rearrangement of the nitro group (especially the oxygen atom) in the excited Franck-Condon state. Kokubun and Kobayashi supported this quenching mechanism on the basis of their investigation of the fluorescence quantum yield and the lifetime of *m*-nitrodimethylaniline.[16]

2) Estimation of Dissociation and Back-reaction Quantum Yields. The quantum yields for *p*-X substituted acetanilides at 2537 Å are summarized in Table 1. By *p*-methyl or *p*-chloro substitution, the disappearance quantum yields decreased, the quantum yields of the *o*-rearrangement increased, and the *p*-rearrangement did not occur.

TABLE 1. QUANTUM YIELDS FOR *p*-X SUBSTITUTED ACETANILIDE AT 2537 Å

X	Quantum yield (Φ)					
	Observed			Calculated		
	Φ_o	Φ_p	Φ_{dec}	Φ_N	Φ_B	Φ_{dis}
H[a]	0.07	0.06	0.15	0.02	0.10	0.25
CH_3	0.09_2	0	0.12	0.02_8	0.13	0.25
Cl	0.09_7	0	0.13	0.03_3	0.14	0.27

a) See Footnote 11.

Φ_o and Φ_p are the quantum yields of *o*- and *p*-rearrangements respectively; Φ_{dec}, the decrease quantum yield of acetanilide; Φ_N, the quantum yield of *p*-X substituted aniline; Φ_B, the quantum yield of the back reaction, and Φ_{dis}, the dissociation quantum yield for the N–C bond.

In the present work, aniline could not be observed by the spectrophotometric method.[11] Elad reported the formation of aniline as well as of *o*- and *p*-aminoacetophenones in the photochemical reaction of acetanilide.[17] Therefore, the quantum yields of *p*-X aniline (Φ_N) may be evaluated approximately by Eq. (3):

$$\Phi_N \approx \Phi_{dec} - (\Phi_o + \Phi_p) \tag{3}$$

The electronically excited states in acetanilide and *p*-methylacetanilide are the same in a first approximation, since the shapes of their UV absorption spectra are about the same. Therefore, it is reasonable to assume that these photochemical reactions can occur through the same primary processes; the dissociation quantum yields for the N–C bond have the same value, as is shown in Eq. (4):

$$\Phi^{H}_{dis} \approx \Phi^{CH_3}_{dis} \tag{4}$$

On the other hand, the observed quantum yields, Φ_o, Φ_p, and Φ_{dec}, of *p*-methylacetanilide differ from those of acetanilide, as is shown in Table 1. These differences can be explained as follows. In the photochemical primary process, anilino and acetyl radicals are produced by the intersystem crossing, ${}^3\sigma_0(\text{N–C}) \leftarrow S_1(\pi\pi^*)$.[2] The *p*-position being blocked in the anilino radical by the methyl group, the acetyl radical can not move to the *p*-position. Therefore, the acetyl radical which is expected to rearrange at the *p*-position follows this course:

1) recombination with the anilino radical at the *o*-position, which causes an increase in the Φ_o.

2) recombination with the anilino radical at the nitrogen dot; this is the back reaction, which decreases the Φ_{dec} and increases the Φ_B.

3) abstraction reaction, resulting in *p*-X-aniline formation, which in turn increases the Φ_N.

In order to estimate the dissociation and back-reaction quantum yields, the ratio of Φ_B to 1/2 Φ_o was obtained as follows:

$$\Delta\Phi_o = \Phi^{CH_3}_o - \Phi^{H}_o = 0.022 \tag{5}$$

$$\Delta\Phi_B = \Phi^{CH_3}_B - \Phi^{H}_B = \Phi^{H}_{dec} - \Phi^{CH_3}_{dec} = 0.03 \tag{6}$$

where:

$$\Phi^{H}_{dis} = \Phi^{H}_B + \Phi^{H}_{dec}, \quad \Phi^{CH_3}_{dis} = \Phi^{CH_3}_B + \Phi^{CH_3}_{dec}$$

and $\Phi^{H}_{dis} = \Phi^{CH_3}_{dis}$

$$\frac{\Delta\Phi_B}{\frac{1}{2}\,\Delta\Phi_o} = 2.9 \tag{7}$$

$$\frac{\Phi_B}{\frac{1}{2}\;\Phi_o} \approx \frac{\Delta\Phi_B}{\frac{1}{2}\,\Delta\Phi_o} = 2.9 \tag{7'}$$

The rate of the back reaction was 2.9 times that of the *o*-rearrangement. Thus, the values of $\Phi^{CH_3}_B$, Φ^{H}_B, $\Phi^{CH_3}_{dis}$, and Φ^{H}_{dis} are given by:

$$\Phi^{CH_3}_B = \frac{1}{2}\Phi^{CH_3}_o \times 2.9 = 0.13 \tag{8}$$

$$\Phi^{CH_3}_{dis} = \Phi^{CH_3}_B + \Phi^{CH_3}_{dec} = 0.25 \tag{9}$$

$$\Phi^{H}_B = \frac{1}{2}\Phi^{H}_o \times 2.9 = 0.10 \tag{10}$$

$$\Phi^{H}_{dis} = \Phi^{H}_B + \Phi^{H}_{dec} = 0.25 \tag{11}$$

The values of Φ^{Cl}_B and Φ^{Cl}_{dis} were also estimated:

$$\Phi^{Cl}_B = \frac{1}{2}\Phi^{Cl}_o \times 2.9 = 0.14 \tag{12}$$

$$\Phi^{Cl}_{dis} = \Phi^{Cl}_B + \Phi^{Cl}_{dec} = 0.27 \tag{13}$$

As has previously been described,[2] the fluorescence lifetime, τ_F, is of the order of magnitude of $\sim 10^{-10}$ sec. The dissociation rate constant, k_{dis}, can be evaluated as follows:

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[15] I. Tanaka, Y. Mori *et al.*, Presented at the Symposium on Electronic state, Osaka, Oct., 1966.

[16] H. Kokubun and M. Kobayashi, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

[17] D. Elad, *Tetrahedron Letters*, **1963**, 873. D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

$$\left.\begin{array}{lll} S_1(\pi\pi^*) & \xrightarrow{k_s} & S_0 \\ S_1(\pi\pi^*) & \xrightarrow{k_F} & S_0 + h\nu' \\ S_1(\pi\pi^*) & \xrightarrow{k_c} & T_1(\pi\pi^*) \\ S_1(\pi\pi^*) & \xrightarrow{k_{dis}} & \phi\text{-NH} + \underset{\underset{\text{O}}{\|}}{\text{C}}\text{CH}_3 \end{array}\right\} \quad (14)^{\text{b)}}$$

b) See Footnote 2.

$$\varPhi_{dis}^{\text{H}} = \frac{k_{dis}}{k_s + k_F + k_c + k_{dis}} = 0.25 \qquad (15)$$

$$k_{dis} = \frac{0.25}{\tau_F} = \sim 10^9\,\text{sec}^{-1} \qquad (16)$$

3) Secondary Processes. The photochemical rearrangement of acetanilide was an intramolecular reaction, since no effect of the quantum yield on the concentration has been observed.[11] It is interesting to note that the value of the high recombination ratio (β) between anilino and acetyl radicals in the liquid phase is quite high, as is shown in Eq. (17):

$$\left.\begin{array}{l} \beta_{\text{H}} = \dfrac{\varPhi_o^{\text{H}} + \varPhi_p^{\text{H}} + \varPhi_B^{\text{H}}}{\varPhi_{dis}^{\text{H}}} = 0.92 \\ \beta_{\text{CH}_3} = \dfrac{\varPhi_o^{\text{CH}_3} + \varPhi_B^{\text{CH}_3}}{\varPhi_{dis}^{\text{CH}_3}} = 0.89 \\ \beta_{\text{Cl}} = \dfrac{\varPhi_o^{\text{Cl}} + \varPhi_B^{\text{Cl}}}{\varPhi_{dis}^{\text{Cl}}} = 0.88 \end{array}\right\} \qquad (17)$$

These results indicate that the recombination reaction between pair radicals occurs efficiently in a solvent cage. The little hydrogen-atom abstraction from the solvent may be caused by the anilino or the acetyl radical. Figure 5 shows the reaction model in a solvent cage.

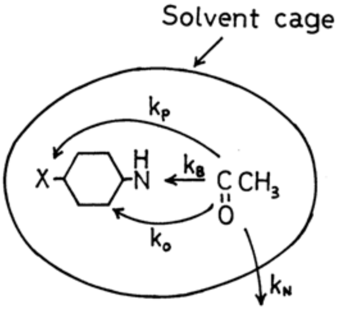
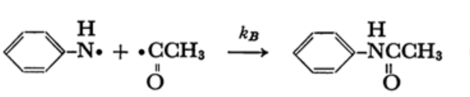


Fig. 5. Reaction model in a solvent cage.

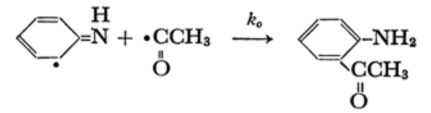
The photochemical secondary processes of acetanilide can be represented as in the following equations:

Recombination Reactions.

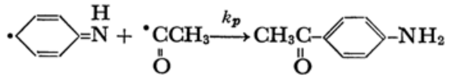
a) Back reaction:


(18)

b) *o*-Rearrangement:


(19)

c) *p*-Rearrangement:


(20)

where k_B, k_o, and k_p are the rate constants of the back reaction, the *o*-rearrangement, and the *p*-rearrangement respectively. In the recombination reaction between the pair radicals, the correlation between the rate constants (k_B, k_o, and k_p) and the odd π electron densities (ρ_7, ρ_2, and ρ_4) was obtained as follows. To the first approximation,the odd π electron densities of the anilino radical were obtained from a semiempirical ASMO-CI calculation on aniline,[18] as is shown in Fig. 6.

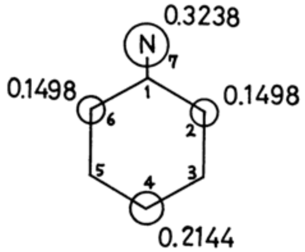


Fig. 6. Odd π electron densities of anilino radical.[18]

$$k_B : k_o : k_p = \varPhi_B : \frac{1}{2}\varPhi_o : \varPhi_p = 1 : 0.35 : 0.6 \qquad (21)$$

$$\rho_7 : \rho_2 : \rho_4 = 1 : 0.46 : 0.66 \qquad (22)$$

$$k_B : k_o : k_p \approx \rho_7 : \rho_2 : \rho_4 \qquad (23)$$

The rate constants, k_B, k_o, and k_p, were proportional to the odd π electron desities, ρ_7, ρ_2, and ρ_4 respectively. These results lend some support to the radical mechanism for the photochemical secondary processes in acetanilide. The recombination between the pair radicals in a solvent cage may occur within several collisions, since k_B, k_o, and k_p are all larger than k_N. It is assumed that these recombination rate constants are of the order of magnitude of 10^{11}—$10^{12}\,\text{sec}^{-1}$, considering the number of collisions between solute and solvent to be about $10^{13}\,\text{sec}^{-1}$.[19]

No intermediate could be observed by the flash

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[18] H. Baba, This Bulletin, **34**, 76 (1961); N. Mataga, *ibid.*, **36**, 1607 (1963). The highest occupied molecular orbital of aniline ψ_4:

$$\psi_4 = 0.356\chi_1 + 0.387(\chi_2 + \chi_6) - 0.133(\chi_3 + \chi_5) - 0.463\chi_4 - 0.569\chi_7$$

Odd electron densities were obtained from the square of the coefficient of atomic orbital χ_i in ψ_4

[19] *E. g.*, M. Tamura, "Kokagaku," Shibundo, Tokyo (1947), p. 160; M. Koizumi, "Kokagaku-gairon," Asakurashoten, Tokyo (1963), p. 78.

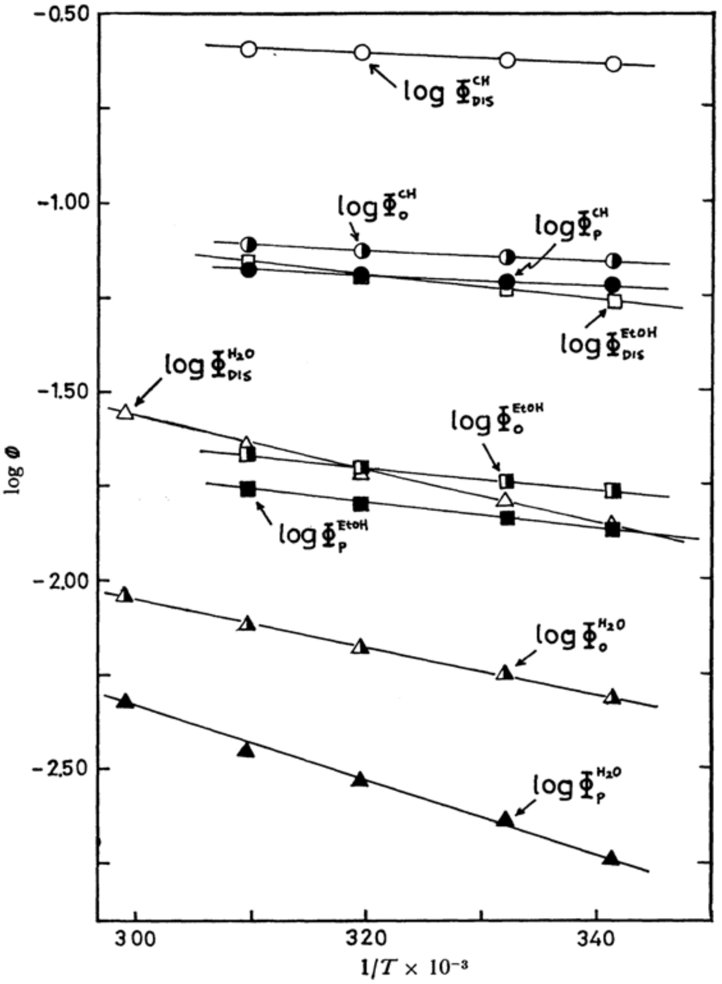

Fig. 7. Plots of logarithm of quantum yields against reciprocal of temperature.

technique. The absorption of the products appeared within the shortest delay time (20 μsec) observed.

4) Dependence of the Quantum Yield on the Temperature. The quantum yields (Φ) in various solvents were measured while varying the temperature in the range from 20 to 70°C. The quantum yields depended on the temperature; plots of log Φ against $1/T$ fell on a straight line, as is shown in Fig. 7. Moreover, a linear relationship was obtained between log Φ_{dis}*2 and $1/T$. The activation energies in the photochemical rearrangement of acetanilide were calculated to be as shown in Table 2.

TABLE 2. ACTIVATION ENERGIES IN THE PHOTOCHEMICAL REACTION OF ACETANILIDE

Solvent	Activation energy, kcal/mol		
	E_o	E_p	E_{dis}
Cyclohexane	0.6_0	0.6_1	0.6
Ethanol	1.4_5	1.6_0	1.5
Water	2.8_2	4.1_5	3.0

E_o, E_p, and E_{dis} are the activation energies of the *o*-rearrangement, the *p*-rearrangement, and the dissociation for the N–C bond respectively.

The values of the activation energies in polar solvents were larger than those in nonpolar solvents. However, even these values were very low in comparison with those of the hydrogen-atom abstraction reaction by radicals.[20] These results also suggest that hydrogen-atom abstraction reactions are not involved in the *o*- and *p*-rearrangements:

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*2 The Φ_{dis} values were estimated as follows:

$$\Phi_{dis} \approx \Phi_B + \Phi_o + \Phi_p \approx 2.43\,\Phi_o + \Phi_p$$

[20] *E. g.*, M. H. J. Wijnen, *J. Am. Chem. Soc.*, **80**, 2394 (1958).

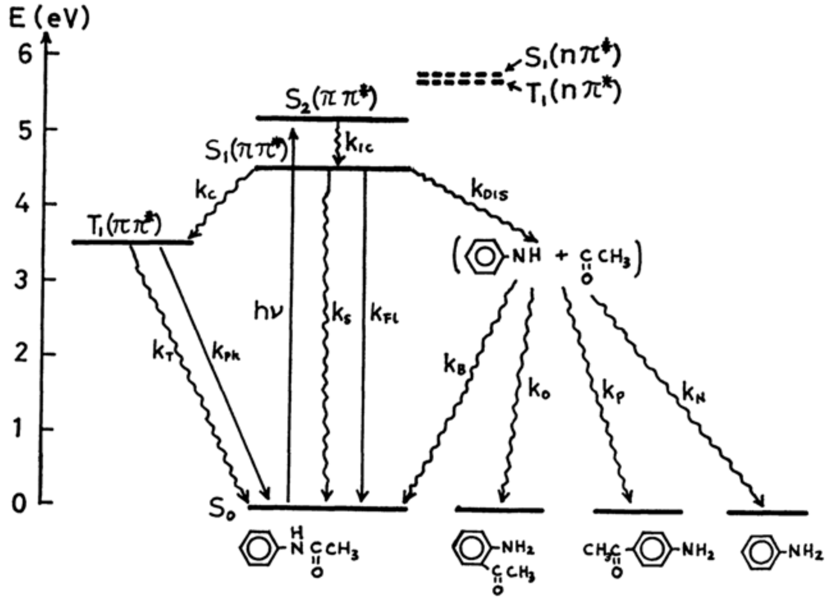
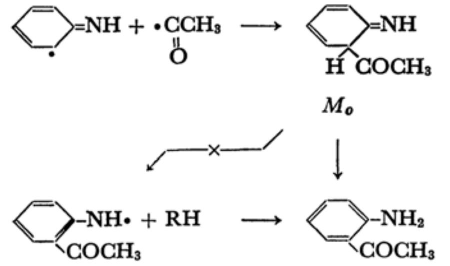
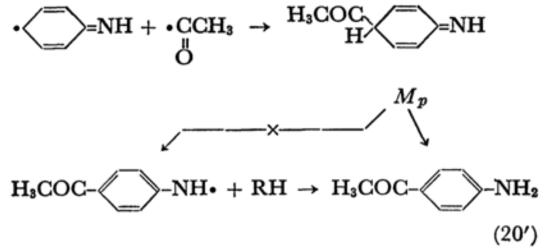


Fig. 8. Energy state diagram for acetanilide.



(19′)



(20′)

Since the M_o and M_p intermediates might have highly vibrational and rotational energies when a pair of radicals recombine, the values of their lifetimes would be very short; probably one may assume an order of magnitude of $\sim 10^{-12}$ sec. In fact, no intermediate could be observed by means of the flash technique, as has been mentioned above. It is more reasonable to consider that the rearrangements occurred immeadiately, as is shown in Eqs. (19) and (20).

The results regarding the activation energies for the dissociation quantum yields E_{dis}, lend some support to a photochemical primary process[2] which involves the predissociation of the N–C bond in acetanilide.

Conclusion

From these studies, the reaction scheme of acetanilide at 2537 Å can be written as is shown in Fig. 8.

The mechanism of the photochemical reaction of acetanilide involves the lowest excited singlet state, $S_1(\pi\pi^*)$; the predissociation by intersystem crossing, $^3\sigma_0(\text{N–C}) \leftarrow S_1(\pi\pi^*)$, and the recombination reaction between the pair radicals in a solvent cage.

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