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Photochemistry of Acetanilide. IV. The Photochemical Reactions in the Vapor Phase and Rigid Matrixes

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The photolysis of acetanilide in the vapor phase at 2537 Å and 120°C has been studied by means of mass spectrometry, gas chromatography, and spectrophotometry. In the vapor phase, no such rearrangements of acetanilide as in the liquid phase occurred, only the decomposition of acetanilide. Carbon monoxide and ethane were formed as the main products, and the ratio of carbon monoxide to ethane was about 2. The quantum yield of the predissociation for the N–C bond of acetanilide in the vapor phase was estimated to be 0.28 from the data of the quantum yields for the formations of carbon monoxide and ethane. A small amount of methane and traces of hydrogen and benzene were also detected. The reaction scheme of acetanilide in the vapor phase at 2537 Å and 120°C has been proposed. On the other hand, the photochemical reactions of acetanilide in the rigid matrixes (MP, ME, and EPA) at -196°C and in the PVA sheet at room temperature have also been carried out by the use of a spectrophotometer and an ESR spectrometer. In the rigid matrixes at -196°C, the photochemical rearrangements did not occur, only the back reaction resulting in the distortional structure of acetanilide; this mechanism can be explained by the stiffness of the solvent cage. The cage effect on the photochemical reaction of acetanilide is also discussed.

In previous papers[2-4] on the photochemistry of acetanilide in the liquid phase, it has been shown that the photochemical rearrangement occurs due to the predissociation through the intersystem crossing $^3\sigma_0(\text{N–C})\leftarrow S_1(\pi\pi^*)$, resulting in the fission of the N–C bond and the liberation of anilino and acetyl radicals and, subsequently, the recombination reactions between the pair radicals in a solvent cage.

In the liquid phase, in cyclohexane, for example, the cage effect on the recombination reactions which consist of the back reaction, *o*- and *p*-rearrangements is sufficiently large (the recombination ratio ≈ 0.9).[4] On the other hand, in the vapor phase where the solvent effect may be neglected,[5] it is expected that the recombination reactions do not occur, only the decomposition of acetanilide. However, the vapor pressure of acetanilide at room temperature is very low. In order to obtain a sufficient pressure for the vapor-phase photolysis, acetanilide should be heated at 120°C. Acetanilide does not decompose at 120°C without the radiation of UV light.

On the other hand, it is also interesting to investigate the photochemical reactions of acetanilide in rigid matrixes (MP, ME, and EPA) at -196°C and in a PVA sheet at room temperature, since the solvent cage consisting of these rigid matrixes may be expected to be very stiff.

This paper will report the photolysis of acetanilide in the vapor phase at 2537 Å and 120°C and the photochemical reaction of acetanilide in the rigid matrixes (MP, ME, and EPA) at 2537 Å and -196°C, and in PVA sheet at 2537 Å and room temperature; it will also include a discussion of the reaction schemes in these photochemical reactions.

Experimental

Materials. The acetanilide, ethanol, and ether were the same reagents as have been described in the previous papers.[2-4] The methanol was a Kantokagaku Co. G. R. product. The isopentane was a Tokyo Kasei G. R. product and was purified by passing it through silica gel and by distillation. The polyvinyl alcohol (PVA) was a Koso Chemical Co. G. R. product ($\overline{p}$ ~1500).

Light Source and Actinometry. A low-pressure mercury lamp with a Vycor glass filter was used as the 2537 Å radiation source. Actinometry was carried out by in the same way as has been described in a previous paper.[2] The light intensity at 2537 Å was 7.85×10^{13} photons sec^{-1} in the vapor-phase photolysis.

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

[3] H. Shizuka, *ibid.*, **42**, 52 (1969).

[4] H. Shizuka, *ibid.*, **42**, 57 (1969).

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

Reaction Procedure and Analysis in the Vapor Phase. The cylindrical quartz reaction cell was 10 cm long and 4.3 cm in diameter and had a ground joint and a breakable seal. About 20 mg of acetanilide was put into the reaction cell. After degassing, the reaction cell was sealed off from the vacuum system, which was free from mercury in order to avoid mercury photosensitization. The reaction cell was then heated to 120°C by an electric heater (the vapor pressure of the acetanilide at 120°C was 1.4 Torr), and then the sample was irradiated at 2537 Å.

Acetanilide (mp 115°C, bp 305°C) did not decompose at 120°C without the radiation of UV light. After irradiation, the products were introduced from the reaction cell into the system for analysis. The mixture of noncondensable products at −196°C (carbon monoxide, methane, and hydrogen) was collected into the gas burette of the Toepler gauge and analysed by a mass spectrometer after its quantity had been measured.

The volatile compounds which are condensable in liquid nitrogen (−196°C) were trapped into a LeRoy still. C_2 compounds, such as ethane, ethylene, and acetylene, were then separated from the products with higher boiling points by vacuum distillation, and were collected into the Topeler gauge. After the measurement of their quantities, the mixture was transferred into a small tube with a rubber septum at one end. The C_2 compounds were analyzed by gas chromatography with a silica gel +5% squalane column (2 m long, at 70°C) and with an active-charcoal column (3 m long, at 160°C). The C_n compounds ($n \geq 3$), such as biacetyl and benzene, which had been trapped in the LeRoy still at −150°C, were also transferred into a small tube with a rubber septum at one end. The C_n compounds were analyzed by gas chromatography by means of a dinonyl phthalate column (1 m long, at 70°C) and with a dioctyl phthalate column (1 m long, at 86°C).

The residues of nonvolatile products at room temperature were resolved in ethanol and were measured with a spectrophotometer.

Reaction Procedure and Analysis in Rigid Matrixes. The photochemical reactions of acetanilide were carried out in degassed rigid solvents (MP, EPA, and ME)*1 at 77°K and in polyvinyl alcohol (PVA) sheet*2 at room temperature. The ultraviolet and visible absorption spectra were taken with a Shimadzu SV 50A spectrophotometer. In the photochemical reaction at −196°C, a quartz Dewar flask designed for the spectrophotometry was used as the reaction cell. ESR measurements were also made in degassed rigid solvents (methylcyclohexane and ethanol) at −196°C after irradiation with 2537 Å for 30 min by the use of a JES 3110 X.

In order to disperse acetanilide homogeneously into a PVA sheet (0.17 mm thick), it was immersed in an aqueous solution of acetanilide and then dried at 70°C. The spectral change of the acetanilide in the PVA sheet upon the irradiation at 2537 Å was measured.

Results and Discussion

Photolysis of Acetanilide in the Vapor Phase. The data on the photolysis of acetanilide in the vapor phase at 2537 Å and 120°C are presented in Table 1 and in Figs. 1 and 2. Table 1 shows the reaction products in the photolysis at a very low conversion (less than 1%).

TABLE 1. REACTION PRODUCTS IN THE PHOTOLYSIS OF ACETANILIDE

Product	Relative yield
CO	100
CH_4	1.4
H_2	Trace
C_2H_6	48
	Trace

Carbon monoxide and ethane were obtained as the main products, the ratio of carbon monoxide to ethane was about 2. The amount of methane was about 1.4% that of carbon monoxide. Traces of hydrogen and benzene were also detected, but ethylene, acetylene, biacetyl, and the rearrangement products (*o*- and *p*-amino acetophenones) were not observed.

Figure 1 shows the time dependence of the product formations for carbon monoxide and ethane as a function of the irradiation time. The quantum yields for the formations of carbon monoxide and ethane were 0.28 and 0.14 respectively.

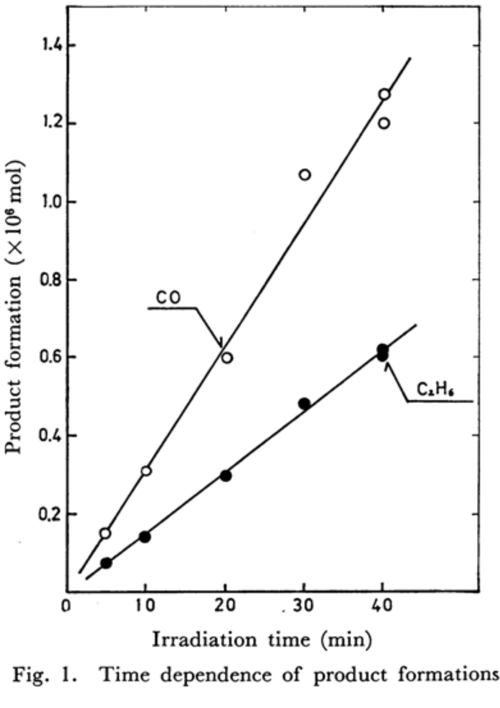

Fig. 1. Time dependence of product formations.

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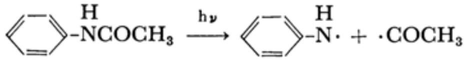
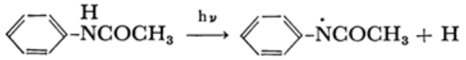
*1 MP, methylcyclohexane : isopentane=2 : 1; EPA, ether : isopentane : ethanol=1 : 1 : 1; ME, methanol : ethanol=1 : 1.

*2 PVA sheet was preheated at 80°C. See Y. Tanizaki and S. Kubodera, *J. Mol. Spectry.*, **24**, 1 (1967).

Figure 2 shows the spectral change in acetanilide in this photolysis; no rearrangement of acetanilide occurs in the vapor phase at 2537 Å, judging from the absence of any characteristic absorption bands of *o*- and *p*-amino acetophenones.[2)]

Several reactions may be considered as the primary dissociation step in the photolysis of acetanilide:


(1)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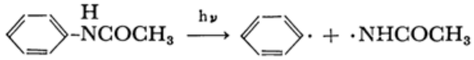
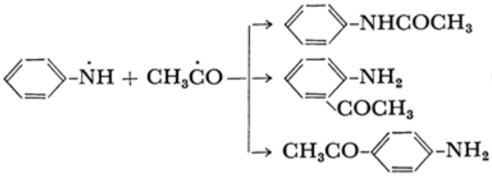

(3)

The experimental results on the formations of ethane and carbon monoxide as the main products give very strong evidence for the acetyl radical formation (Eq. (1)). The acetyl radical is known to decompose rapidly and exclusively to the methyl radical and to carbon monoxide above 100°C.[6)] All the acetyl radicals formed here by Eq. (1) may, therefore, be assumed to decompose to methyl radicals and carbon monoxide molecules.

The formation of ethane can be explained by the recombination reaction between methyl radicals, and that of a small amount of methane, by the hydrogen-atom abstraction of the methyl radical. When a trace of NO (~0.1 Torr) was added to acetanilide, the formation of ethane was efficiently reduced. This result indicates that the methyl radical is formed in the photolysis of acetanilide and is scavenged by NO.

As has been described above, the rearrangement products of acetanilide were not observed in the vapor-phase photolysis. This means that no recombination reactions between anilino and acetyl radicals, such as the back reaction, *o*- and *p*-rearrangements (Eq. (4)), occurred because of the absence of a solvent cage in the vapor phase.


(4)

In view of the quantum yields for the formation of carbon monoxide and ethane, the dissociation quantum yield of acetanilide in the vapor-phase photolysis at 2537 Å and 120°C was estimated to be ~0.28, which is almost the same value as that obtained in the liquid phase (0.25).[4)] It may be assumed that the predissociation by the intersystem crossing ${}^3\sigma_0(\text{N–C})\leftarrow S_1(\pi\pi^*)$ occurs in the vapor phase as well as in the liquid phase.

Thus, the reaction scheme of the photolysis of acetanilide in the vapor phase at 2537 Å and 120°C may be represented as follows:

$$S_0 + h\nu \longrightarrow S_2(\pi\pi^*) \tag{5}$$

$$S_2(\pi\pi^*) \xrightarrow{k_{IC}} S_1(\pi\pi^*) \tag{6}$$

$$S_1(\pi\pi^*) \xrightarrow{k_S} S_0 \tag{7}$$

$$S_1(\pi\pi^*) \xrightarrow{k_F} S_0 + h\nu' \tag{8}$$

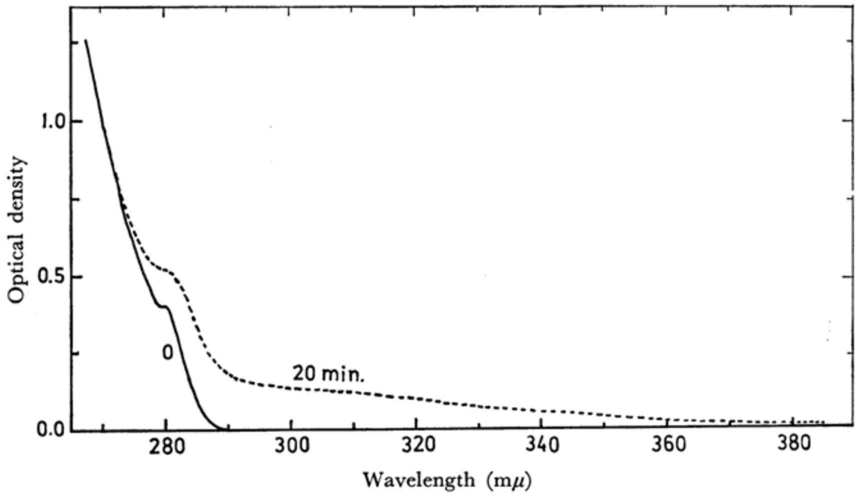
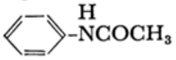


Fig. 2. Spectral change of acetanilide dissolved in ethanol solution after irradiation in the gas phase. —— before, ---- after


In gas phase (120°C). Irrad. 2537 Å

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6) W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 46 (1956).

$$S_1(\pi\pi^*) \xrightarrow{k_C} T_1(\pi\pi^*) \tag{9}$$

$$S_1(\pi\pi^*) \xrightarrow{k_{dis}} \phi\text{-}\dot{N}H + \dot{C}OCH_3 \tag{10}$$

$$\dot{C}OCH_3 \xrightarrow{k_1} \dot{C}O + \dot{C}H_3 \tag{11}$$

$$2\dot{C}H_3 \xrightarrow{k_2} C_2H_6 \tag{12}$$

$$\dot{C}H_3 + RH \xrightarrow{k_3} CH_4 + R\cdot \tag{13}$$

Photochemical Reaction of Acetanilide in the Rigid Matrix. Figures 3(a) and 3(b) show the changes in the UV spectra of acetanilide in MP and ME degassed rigid matrixes at 2537 Å and −196°C respectively. In both cases, absorption band II decreased with the lapse of the irradiation time. The spectral change in acetanilide in the EPA rigid matrix is similar to that in ME. The absorption bands of the anilino radical (3088 Å) and the cation radical (4288 Å) which were observed in the photolysis of aniline[7] did not appear in the case of acetanilide. However, if the reaction cell was warmed up to room temperature after irradiation for 40 min in a MP rigid matrix, the spectral change of acetanilide was scarcely observed in a MP solution. Similar results were also obtained with a ME rigid matrix.

In order to detect the anilino and acetyl radicals, or the cation radical of acetanilide, ESR measurements of acetanilide in the rigid matrixes (degassed methyl cyclohexane and ethanol) at 2537 Å and −196°C were carried out, but no significant ESR signals were observed. The absence of the anilino radical and of the cation radical of acetanilide may be explained as follows:

1) The intersystem crossing $^3\sigma_0$(N–C)←S_1 ($\pi\pi^*$), which produces anilino and acetyl radicals becomes less feasible at low temperatures due to the temperature dependence of the crossing probability. The acetyl radical can not escape from a solvent cage nor rearrange to the *o*- or *p*-position of the anilino radical. The only possible reaction is the back reaction, because the solvent cage in a glass at a low temperature is quite stiff.

2) The ionization potential of acetanilide (9.07 eV)[3] is larger than that of aniline (7.70 eV).[8]

From these results and considerations, it may be concluded that the spectral change in acetanilide in the rigid matrix at 2537 Å and −196°C was not caused by the *o*- and *p*-rearrangements, but by the back reaction between the pair radicals, resulting in the distorted structure of acetanilide (S_0'), which had only a little π-electron-conjugated system between anilino and acetyl groups. Equations (14) and (15) show the reaction scheme of the photochemical reaction of acetanilide in the rigid matrix at 2537 Å and −196°C.

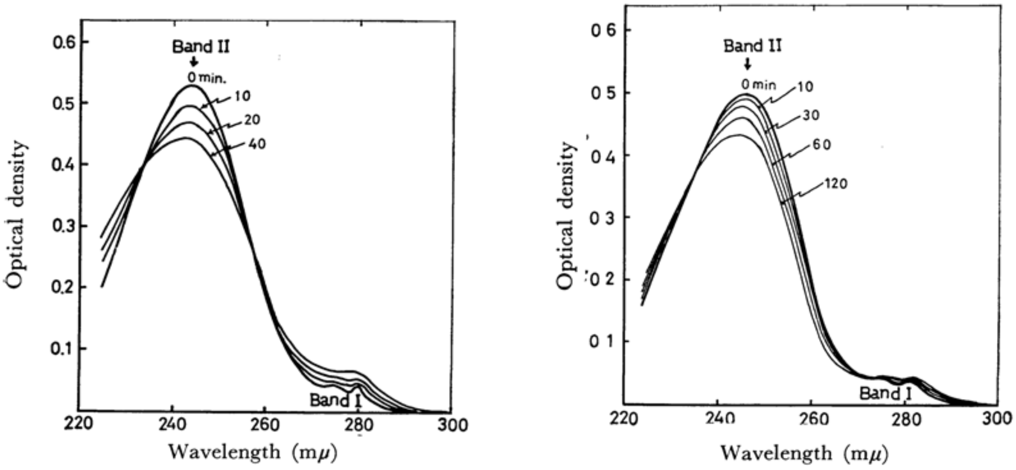
$$S_1(\pi\pi^*) \xrightarrow{k_{dis}} (\phi\text{-}\dot{N}H + \dot{C}OCH_3)^\dagger \tag{14}$$

$$(\phi\text{-}\dot{N}H + \dot{C}OCH_3)^\dagger \longrightarrow S_0' \tag{15}$$

†: a stiff solvent cage.

When the reaction cell was warmed to room temperature, S_0' turned back to the ground state of acetanilide, S_0.

The photochemical reaction of acetanilide in



(a) (b)

Fig. 3. Spectral change of acetanilide in the rigid matrixes at 2537 Å and −196°C. Numbers refer to time in minutes.
(a) in MP glass (b) in ME glass

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[7] I. Norman and G. Porter, *Proc. Roy. Soc.* (*London*), **A230**, 399 (1955); E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

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

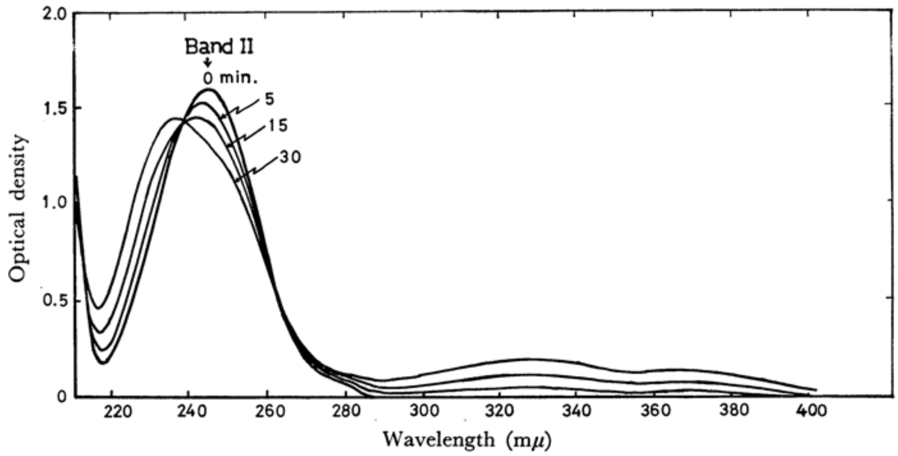

Fig. 4. Spectral change of acetanilide in PVA sheet at 2537 Å and room temperature.

the PVA sheet was observed by spectrophotometry at 2537 Å and at room temperature, as is shown in Fig. 4. Absorption band II decreased and new peaks at 325 and 365 mμ, which correspond to the *o*- and *p*-amino acetophenones respectively, appeared with an increase in the irradiation time. It is assumed that a pair of radicals can rearrange because the PVA matrix at room temperature contains an amorphous structure.

Table 2 shows the quantum yields for the formations of *o*- and *p*-amino acetophenones at 2537 Å in PVA, ethanol, and ME.

TABLE 2. THE QUANTUM YIELDS AT 2537 Å IN PVA, ETHANOL, and ME

Solvent	Temp. °C	Quantum yield (Φ)		
		Φ_o	Φ_p	Φ_o/Φ_p
PVA	Room temp.	0.003_8	0.001_6	2.4
Ethanol[a]	20	0.01_7	0.01_4	1.2
Ethanol	− 70	0.005_1	0.002_1	2.4
ME	−196	0	0	—

a) See Footnote 3.

Φ_o and Φ_p are the quantum yields for the formations of *o*- and *p*-amino acetophenones respectively at 2537 Å.

The quantum yields in the PVA sheet at room temperature decreased considerably in comparison with that in ethanol at 20°C. It seems that the back reaction in the PVA matrix is more predominant than the *o*- and *p*-rearrangements because the solvent cage in the PVA matrix is stiffer than that in ethanol at 20°C. The quantum yields in ethanol at −70°C were smaller than those in ethanol at 20°C. The dependence of the quantum yield in ethanol on the temperature from 20 up to 50°C has previously been described.[3,4] The viscosity of ethanol in this range of temperature does not change very much, but it increases significantly at lower temperatures (*e.g.*, −70°C).[9] Therefore, in addition to the effect of the activation energy (E_{dis} ∼1.5 kcal/mol in ethanol)[4] of the photochemical reaction of acetanilide, the cage effect becomes more important at lower temperatures because of the increasing stiffness of the solvent cage.

The ratios of Φ_o/Φ_p in PVA at room temperature and in ethanol at −70°C were about twice that of ethanol at 20°C. This indicates that the dependence of the *p*-rearrangement on the stiffness of the solvent cage is larger than that of the *o*-rearrangement because in a stiff solvent cage the *p*-positions of the anilino radical and the acetyl radical are separated by a longer path.

Conclusion

In the vapor phase at 2537 Å and 120°C, the decomposition of acetanilide took place, forming carbon monoxide and ethane (CO/C_2H_6 ≈2) as the main products, instead of rearrangement. In the rigid matrix at −196°C, the rearrangements do not occur either, only the back reaction. These differences in the photochemical reaction of acetanilide are mainly caused by the cage effect on the recombination reactions between anilino and acetyl radicals formed by the intersystem crossing $^3\sigma_0$ (N–C)$\leftarrow S_1(\pi\pi^*)$.

The authors are greatly indebted to Associate Professor Yuji Mori of the Tokyo Institute of Technology for his generous and very helpful discussions concerning this paper.

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[9] See "Kagaku-benran, Kisohen" (Chemical Index of The Chem. Soc. Japan), Maruzen, Tokyo (1966), p. 505. The effect of temperature on the viscosity of ethanol.

Temp., °C	−40	−20	0	10	20	30	40	50
Viscosity, (centi poise)	4.79	2.38	1.78	1.46	1.19	1.00	0.825	0.701