

(86%) of *trans*-stilbene, mp 123.5-124 °C (lit.¹⁹ 124 °C). *cis*-Stilbene (liquid) was not detected by GC. The yields are based on quantities obtained after this step. Some physical properties of the products are as follows.

trans-1,2-Bis(4-methoxyphenyl)ethylene: mp 209-211 °C. ¹H NMR (CDCl₃) δ 7.4 (d, *J*=8.8 Hz, 4H), 6.9 (d, *J*=8.8 Hz, 4H), 6.9 (s, 2H), 3.61 (s, 6H). GC/Mass; 240 (M⁺, 100), 225 (64), 182 (13), 165 (32), 153 (26), 120(11), 89(7). 1,6-Diphenyl-1,3,5-hexatriene: mp 192-195 °C (lit.⁴²: 199-203 °C); ¹H NMR (CDCl₃) 7.41-7.24 (m, 10H), 6.80-6.56 (m, 6H). GC/Mass; 232 (M⁺, 100), 215 (17), 191 (7), 141 (43), 128 (36), 115 (32), 91 (55). *cis*-2,3-Diphenyl-2-butene GC/Mass; 208 (M⁺, 100), 193 (94), 178 (57), 165 (19), 115 (47), 91 (19), 77 (13). *t*-2,3-Diphenyl-2-butene: GC/Mass; 208 (M⁺, 100), 193 (95), 178 (58), 165 (15), 115 (49), 91 (23), 77 (19). 2,3-Diphenylbutane: GC/Mass; 210 (M⁺, 49), 119 (15), 105 (100), 91 (58), 77 (13). Bicyclohexylidene: GC/Mass; 164 (M⁺, 42), 149 (5), 135 (11), 121 (15), 107 (16), 93 (27), 124 (27), 82 (100), 67 (82), 55 (45), 41 (45).

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Photochemical Formation of Hydrazine in Aqueous Ammonia

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Although ammonia is one of the most important precursors producing nitrogen containing compounds, ammonia with foul odor, generated from decomposition of a large amount of garbage, causes a serious environmental pollution. Therefore, decomposition of ammonia has attracted considerable attention in respect to environmental pollution of the atmosphere. Large number of investigations on the decomposition of gaseous ammonia have been thus reported by means of radiolysis¹ and photolysis.²⁻⁹ Very recently, we

have described the photochemical decomposition of aqueous ammonia in the absence and presence of oxygen.¹⁰ It was found from the study that hydrazine was produced by the dimerization of $\dot{\text{N}}\text{H}_2$ radicals. Hydrazine can be used as a reducing agent and as a raw material for chemical syntheses. Consequently, it is interesting to study quantitatively on the photochemical formation of hydrazine under various experimental conditions. In aqueous ammonia solution, $\text{NH}_3(\text{aq})$, $\text{NH}_4^+(\text{aq})$, $\text{OH}^-(\text{aq})$ and H_2O species exist and

the concentrations of these species depend both on the initial concentration and the pH value of the aqueous ammonia. Since all of these species absorb vacuum UV light, their concentrations play important role on the formation of hydrazine by irradiation of vacuum UV light. Many examples of showing pH effect on various photochemical reactions are found in the literature.¹¹⁻¹⁴ Generally, pH can greatly affect the yield of product formation, helping to understand photochemical reaction mechanisms. Here we report the effects of initial concentration of ammonia as well as of the pH value on the photochemical formation of hydrazine in the irradiation of aqueous ammonia using 184.9 nm vacuum UV light.

Experimental

Aqua ammonia (Aldrich, 30% NH_3 in water) and all other chemicals (reagent grade) have been used without further purification. Water was quadruply distilled, which was obtained by passing distilled water through Barnstead (U.S.A.) Nonopure II deionization system. 80 mL of the fresh prepared NH_4OH solution was transferred into the reaction vessel and then irradiated by the low pressure Hg lamp (Osram HNS 12/oz). The intensity (I_0) of the 184.9 nm light was found to be 7.77×10^{17} quanta $\cdot \text{mL}^{-1} \cdot \text{min}^{-1}$ at 25 °C. Detailed description of the actinometry is given in the previous work.¹⁰ No change in the intensity of the lamp was observed over the period of the experiments. During the irradiation, the temperature was kept at 25.0 ± 0.1 °C using a waterbath circulator. The pH of the solution was adjusted by adding HClO_4 or NaOH .

The amount of hydrazine identified by a Varian Saturn GC-MS system [DB-5 capillary column 50 m $\times$ 0.25 μm , EI method, product; m/z (rel. intensity): 17(10), 31(16), 32(100)] was determined by spectrophotometric method.¹⁵ An aliquot (1 mL) of the irradiated solution was treated with *p*-dimethylaminobenzaldehyde as a complexing reagent. The molar extinction coefficient (ϵ) of the colored complex was $69600 \text{ M}^{-1}\text{cm}^{-1}$ at 458 nm in these experiments. This method was interfered neither by the presence of other nitrogen-containing compounds such as hydroxylamine nor by the pH value of the solution.

Results and Discussion

The yield of hydrazine produced by the irradiation of aqueous ammonia solution is shown in Figure 1 as a function of the number of quanta. At higher ammonia concentrations there is an observable increase in the yield of hydrazine formation. At a given ammonia concentration its yield was not linear with the number of quanta; therefore, the first order rate law is inadequate. In particular, the formation of hydrazine from the irradiation of 0.01 M aqueous ammonia stops increasing when the number of quanta was larger than 5×10^{19} quanta $\cdot \text{mL}^{-1}$. It means that a back reaction leads to decomposition of hydrazine by attack of radicals formed during the photochemical reaction. The initial quantum yield (Q_i), calculated from the slope of the curve as it passes through the origin, was determined and presented in Figure 2 as a function of the initial concentration of aqueous ammonia. As shown in Figure 2, the formation of

hydrazine increased with increasing the initial concentration of ammonia in aqueous solution. It suggests that the photochemical formation of hydrazine is effected by the concentration of ammonia or ammonium ion in the solution.

Ammonia is dissolved in water into $\text{NH}_4^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. There are $\text{NH}_3(\text{aq})$, $\text{NH}_4^+(\text{aq})$, $\text{OH}^-(\text{aq})$ and H_2O species in the solution. In the irradiation of the solutions using 184.9 nm, all of these species absorb the 184.9 nm light. The molar extinction coefficients (ϵ) of $\text{NH}_3(\text{aq})$, H_2O and $\text{OH}^-(\text{aq})$ were reported to be $500 \text{ M}^{-1}\text{cm}^{-1}$, $0.032 \text{ M}^{-1}\text{cm}^{-1}$ and $3600 \text{ M}^{-1}\text{cm}^{-1}$, respectively.^{10,16,17} From the calculation using these values, it was found that most of the 184.9 nm light was absorbed by aqueous ammonia at high concentration (about 1 M NH_4OH). In this case, photolysis of ammonia is occurs mainly. As a result, H and NH_2 radicals are produced from the electronically excited ammonia. Hydrazine is then produced by the dimerization of NH_2 radicals as shown in reaction (1).

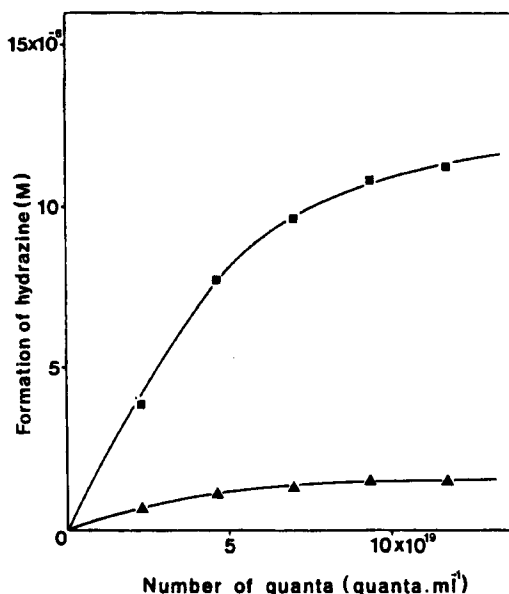


Figure 1. Formation of hydrazine after irradiation of aqueous ammonia as a function of the number of quanta: (■) in the 0.1 M aqueous ammonia, (▲) in the 0.01 M aqueous ammonia.

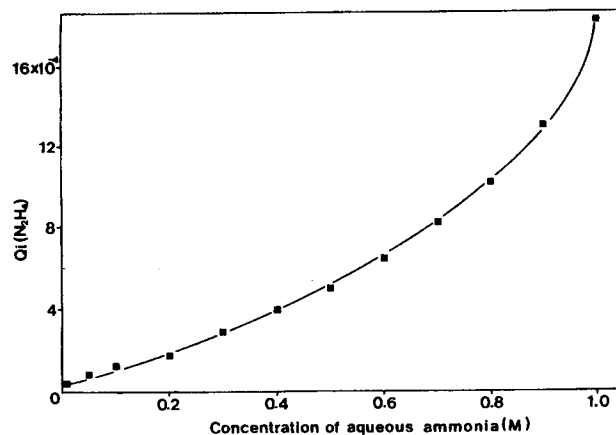
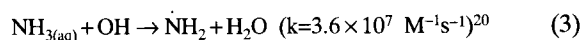
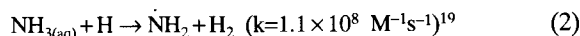


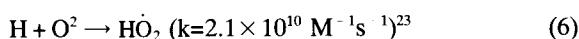
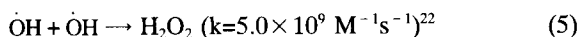
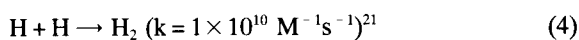
Figure 2. Initial quantum yield of hydrazine produced as a function of the initial concentration of ammonia.



However, as the initial concentration of aqueous ammonia is decreased, the fraction of absorption by water is increased. Then, photolysis of water is no longer negligible. Getoff *et al.* reported¹⁸ that electronically excited water formed by absorbing 184.9 nm light could be splitted into H atom ($Q_i=0.30$), OH radical ($Q_i=0.30$) and so called "solvated electron", e^-_{aq} ($Q_i=0.03$). Consequently, more primary radicals produced in the photolysis of water. In addition to direct photolysis of ammonia, these radicals can attack ammonia as in reactions (2) and (3) to produce $\dot{\text{N}}\text{H}_2$ radicals. Although the amount of solvated electron produced is small, it may combine with ammonium ion in the solution and convert into ammonia and hydrogen atom.



Since the absorption of light by ammonia competes with the absorption of light by water, the more $\dot{\text{N}}\text{H}_2$ radicals are produced by the direct photolysis of ammonia, the less $\dot{\text{N}}\text{H}_2$ radicals are produced by attack of H and OH radicals as in reactions (2) and (3). In the low concentration of aqueous ammonia, the $\dot{\text{N}}\text{H}_2$ radicals produced by attack of H and OH radicals play an important role on the formation of hydrazine. In addition to the reactions (2) and (3), H and OH radicals can react with each other in order to produce hydrogen molecule as in reaction (4) or hydrogen peroxide as in reaction (5). Furthermore, hydrogen molecules can combine with oxygen in the solution, leading to the formation of hydrogen peroxide radicals as in reaction (6). It means that the reactions (2), (4) and (6) as well as the reactions (3) and (5) are competitive, respectively.



When the initial concentration of ammonia is decreased, the reaction probability of the reaction (2) is decreased and those of reactions (4) and (6) are increased. For the same reason, reaction probability of reaction (3) is also decreased. Since less $\dot{\text{N}}\text{H}_2$ radicals produced with decreasing the initial concentration of aqueous ammonia, the formation of hydrazine decreases. This result indicates that the formation of hydrazine depends only on the amount of $\dot{\text{N}}\text{H}_2$ radicals. This is the reason why the initial quantum yield of hydrazine is decreased with decreasing the initial concentration of aqueous ammonia as shown in Figure 2. To test this hypothesis, we attempted to detect hydrogen molecule and hydrogen peroxide produced by irradiating aqueous ammonia. But their yields were too small to be detected and is considered to be negligible.

Since $\dot{\text{N}}\text{H}_2$ radicals may be produced from the ammonium ion and solvated electron (e^-_{aq}) formed by the photolysis of water reacts with hydronium ion very rapidly in acidic solution as shown as in reaction (7), the yield of hydrazine is effected by pH value of the aqueous ammonia solution. Therefore, we have studied on the effect of pH value in the photochemical reaction of aqueous ammonia.

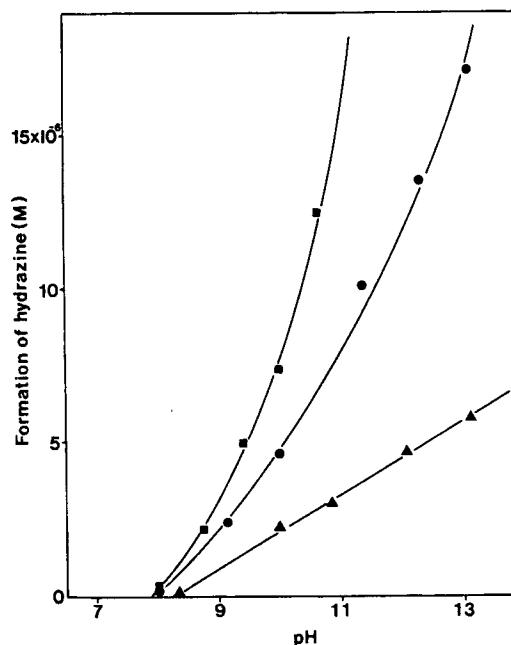
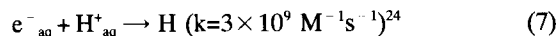
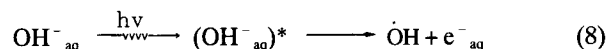


Figure 3. pH dependence on the formation of hydrazine by the irradiation of aqueous ammonia: (■) in the 0.5 M aqueous ammonia, (●) in the 0.1 M aqueous ammonia, (▲) in the 0.01 M aqueous ammonia. Applied number of quanta at 184.9 nm: $I = 9.32 \times 10^{19} \text{ quanta} \cdot \text{mL}^{-1}$.

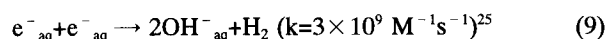
tochemical reaction of aqueous ammonia.



As shown in Figure 3, the formation of hydrazine was not detected in acidic solution. The results suggest that hydrazine was not produced from ammonium ion but from neutral ammonia molecule. To verify these experimental results, 0.1 M aqueous ammonium chloride and ammonium bromide solutions as an ammonium ion source were irradiated under the same experimental conditions. Hydrazine was not produced in any cases. The formation of hydrazine was increased rapidly in basic solutions. This behavior can explain the presence of OH^-_{aq} ion. Electronically excited hydroxide ion can be splitted into OH radical and solvated electron, e^-_{aq} as in reaction (8).¹⁷ As the fraction of light absorption by OH^-_{aq} is increased in basic solution, the formation of OH radicals increases by reaction (8).



The OH radical formed by reaction (8) takes part also in the decomposition process of ammonia as shown in reaction (3) and thereby $\dot{\text{N}}\text{H}_2$ radicals are also produced. In addition to OH radical, the produced solvated electron, e^-_{aq} is combined with each other very rapidly rather than reacts with ammonium ion in basic solution as shown in reaction (9).



The hydroxide ion formed by reaction (9) participates in the reaction (8) and convert into OH radicals again. The radicals take part in the decomposition of ammonia as in reac-

tion (3) and thereby more hydrazine is produced. This chain reaction can explain the reason why the formation of hydrazine was increased rapidly in basic solutions.

In conclusion, the photochemical formation of hydrazine was observed only in basic solution (at pH higher than 8). It implies that hydrazine is formed from neutral ammonia molecule rather than ammonium ion. The formation of hydrazine rapidly increases in basic solution because the fraction of absorption by OH^-_{aq} increases and the OH radicals and e^-_{aq} are produced much more. The produced solvated electron, e^-_{aq} combines with each other to form hydroxide ion. As a result, OH radical is produced again and it contributes also to the formation of hydrazine. Besides, the formation of hydrazine increases as the initial concentration of ammonia is increased.

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Substituent Effect for Epoxide Opening of Halo-Tricyclic Models Related to Dynemicin A

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A new type of antibiotic, dynemicin A (**1**) is characterized as a unique molecular structure and interesting biological profile.¹ Its potent antibiotic and antitumor activities have been attributed to ability to generate, upon *in vivo* activation benzenoid diradicals that damage DNA.² It has been known that activation of **1** resulting in cycloaromatization of enediyne moiety is triggered by epoxide opening induced by development of electron density at C9.³ Accordingly, the epoxide opening should be considered as a critical step for activation of dynemicin A and its biological activity. In the previous study, it was observed that methyl group at para position to the epoxide could exert as an ac-

tivating substituent in acid-catalyzed epoxide opening of dynemicin A model.⁴ On the other hand, halides with inductive effect will serve as deactivating substituents in the epoxide opening. This study notes the electronic sensitivity of halides toward acid-induced epoxide opening for dynemicin A mimic model compounds (**2a-2e**).

Compound **2a** was easily synthesized as follows (Scheme 1). Reduction of C6 by tributyltin hydride (Bu_3SnH) and N5 protection with phenyl chloroformate ($\text{ClCO}_2\text{C}_6\text{H}_5$) transformed 7,8,9,10-tetrahydrophenanthridine (**3**) to compound **4**.⁵ Continuously, treatment of **4** with *m*CPBA yielded the epoxide **2a**. The halide substituted compounds **2b-2e**