

Photochemical Behavior of Ammonia in Aqueous Suspension of TiO₂

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Ammonia is produced in huge quantities worldwide not only by commercial chemical factories but by decaying vegetation, garbage, even decomposition of the other protein materials. Ammonia with foul odor causes a serious environmental pollution in the atmosphere. Therefore, the decomposition of ammonia has attracted considerable attention in respect to environmental pollution of the atmosphere.

Earlier investigation on the decomposition of ammonia using a light was performed by means of radiolysis^{1,2} and photolysis³⁻⁸ in the gaseous state. Ammonia molecules are incorporated into water droplets and form liquid aerosols which can range in diameter with nanoscale particle.⁹ Recently, we have reported on the photochemical decomposition of aqueous ammonia in the absence and presence of oxygen using 184.9 nm UV light.¹⁰ It was found that hydrazine was mainly produced by the dimerization of NH₂ radicals and oxygen affected the formation of hydrazine. In order for a photochemical reaction to occur, reactant chemical species must absorb the light illuminated. NH_{3(aq)}, NH_{4⁺(aq)}, OH_{aq} and H₂O species exist in the aqueous ammonia solution. Since such chemical species have relatively strong intramolecular chemical force, a high enough energy is necessary to begin the photochemical reaction. It corresponds to vacuum UV light to break the chemical bond of such chemical species. The photochemical reaction of aqueous ammonia can not be carried out by a natural ultraviolet solar radiation on the earth's surface, because the solar energy reached on the earth's surface is the wavelength above $\lambda = 314$ nm UV light. It is necessary to use a photocatalyst to begin the photochemical decomposition of aqueous ammonia. Metal oxide such as titanium oxide and zinc oxide may be used for the purpose as a photocatalyst. It is well known that titanium oxide absorbs photons with energy higher than its bandgap (~3.2 eV) and electron-hole pairs, so called geminated form, are produced.¹¹ To our knowledge, there has been no report to date on the quantitative results for photochemical reaction of aqueous ammonia in the presence of TiO₂ particles. Since the photochemical reactions are very fast, products analysis is generally used to determine the photochemical behavior in a system. The aim of this study is to present the quantitative results for the photochemical reaction of the aqueous ammonia containing TiO₂ particles using 253.7 nm UV light, and to elucidate the behavior of

TiO₂ during the photochemical reaction of aqueous ammonia based on the product analysis.

Experimental Section

Lightsource and Actinometry. Irradiations were carried out at 25 °C using low pressure Hg lamp (Osram HNS 10W/ U OFR). Low pressure Hg lamp is classified into two types depending on the method of its emitting wavelength; ozone generating lamp and ozonefree lamp.¹² The ozonefree lamp used in this study emits only 253.7 nm UV light, but on the other hand ozone generating lamp emits two monochromatic lights of 184.9 and 253.7 nm. The lamp was mounted in a quartz tube which was surrounded by the solution to be irradiated. The reaction vessel was made of Pyrex and was isolated from the lamp by means of a quartz tube. The intensity of the 253.7 nm light was determined by monochloroacetic acid actinometer.^{13,14} The yield of chloride ion (Cl⁻) formed during the irradiation of aqueous monochloroacetic acid was measured by spectrophotometric method. The lamp intensity was found to be 5.37×10^{18} quanta. mL⁻¹.min⁻¹ at 25 °C from the known quantum yield, $Q(\text{Cl}^-) = 0.32$.^{13,14} No change in the intensity of the lamp was observed over the period of the experiment. The number of quanta, indicating the whole of emitted intensity from the lamp during the irradiation, was obtained by the multiplication of the lamp intensity by the irradiation time.

Reagents and General. Ammonium hydroxide (28% NH₃ in water, 99.99+ % NH₄OH) was purchased from Aldrich Chemical Co. and used as received. The TiO₂ particles (rutile, grain size ≤ 0.06 mm) were prepared according to the previous work; TiO₂ (anatase, Aldrich) was first heated for 60 min at 1150 °C in the presence of oxygen and then treated in H₂ atmosphere at 700 °C for 90 min.^{11,15} All other chemicals employed in this work were reagent grade and used without further purification. Ammonium hydroxide was diluted using quadruply distilled water, which was obtained by passing distilled water through Barnstead (U.S.A.) Nonopure II deionization system, to prepare NH₄OH solutions. For airfree aqueous ammonia, each of the distilled water and aqua ammonia were first deaerated by bubbling about 60 min with high purity argon (airliquid-korea co, 99.999% pure) and then used to prepare the

NH₄OH solutions. The same treatment is also employed to prepare the NH₄OH solution saturated with O₂. An aliquot of TiO₂ was added in 80 mL of the fresh prepared aqueous ammonia solution and then irradiated using low pressure Hg lamp. During the irradiation, the solutions were stirred to keep the homogenous suspension and the temperature of the solutions was kept at 25 °C using a waterbath circulator. The pH of the solutions was adjusted by adding HClO₄ or NaOH. Absorbance and UV spectrum were recorded on Uvikon (model 943) spectrophotometer.

Analysis. To remove the titanium oxide, the irradiated solution was first centrifuged and taken the liquid phase. It was then extracted using diethyl ether (5 mL). In order to obtain the MS spectra of the products in their irradiated aqueous ammonia, the extracted solution was analyzed using a Varian Saturn GCMS system (DB5 capillary column 50 m × 0.25 μm, EI method) [product; m/z (rel. intensity)] hydrazine: 17(10), 31(16), 32(100). Identifications and determinations were made by comparison with the fragmentation patterns of known amounts of the pure substance. The identified products from the MS spectra were reconfirmed by comparison with the retention time of the separated GC peaks of the standard chemical, which was performed by a Varian Model 3700 gas chromatography. Since the gas chromatographic method for the determination of hydrazine is less stable, the amount of hydrazine produced was determined by spectrophotometric method.¹⁶ Aliquot (1 mL) of the irradiated solutions were treated with *p*-dimethylaminobenzaldehyde as a complexing reagent. The molar extinction coefficient (ϵ) of colored complex was determined to be 74100 L mol⁻¹cm⁻¹ at 458 nm in these experiments. From the statistical analysis, the relationship of the calibration curve is a strong linear relation between of the concentration of hydrazine and absorbance. The linear regression equation is $Y(\text{absorbance}) = 0.736 \times (\text{conc. of hydrazine}) + 0.0079$. The correlation coefficient between two components is approximately equal to 0.9991, implying a very positive linear relationship. This method was interfered neither by the presence of the other nitrogencontaining compounds such as hydroxylamine nor by the pH values in the solution.

Results and Discussion

In order to investigate the photocatalytic behavior of TiO₂ particles, NH₄OH solution containing suspension of TiO₂ was irradiated with 253.7 nm UV light. Hydrazine was the main product during the irradiation and any other products were not observed in this experimental condition. The formation of hydrazine as a function of the number of quanta is presented in Figure 1. The product yield depended both on the amount of TiO₂ contained in aqueous ammonia and on the number of quanta. As the amount of TiO₂ increases in the solution, the yield of hydrazine increases. The hydrazine formation as a function of the number of quanta was not linearly proportional to an equation of the first degree. This behavior indicates that a back reaction occurred in the

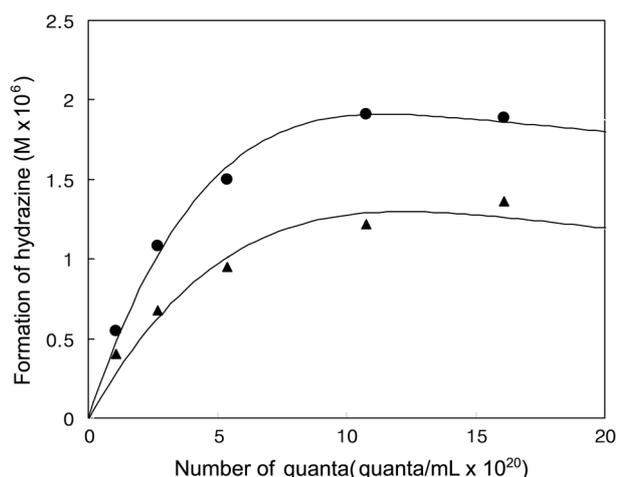


Figure 1. Formation of hydrazine after irradiation of aerated 0.5 M aqueous ammonia containing TiO₂ as a function of the number of quanta: (●) is 0.4 mg/mL; (▲) is 0.2 mg/mL.

Table 1. Initial quantum yield (Q_i) of hydrazine after irradiation ($\lambda = 253.7$ nm) of the aqueous ammonia containing TiO₂ (0.4 mg/mL) at 25 °C

| Initial conc. of ammonia (M) | Q _i (× 10 ⁵) when saturated with | | |
|------------------------------|---|------|----------------|
| | Ar | Air | O ₂ |
| 1.0 | 0.42 | 0.42 | 0.41 |
| 0.5 | 0.31 | 0.30 | 0.32 |
| 0.1 | 0.23 | 0.24 | 0.24 |

system lead to the decomposition of hydrazine by an attack of the radicals formed during the photochemical reaction. It is therefore calculated the initial quantum yield (Q_i), obtained from the slope of the tangent line of the curve in Figure 1, were determined and summarized in Table 1.

There are NH_{3(aq)}, NH_{4⁺(aq)}, OH_{aq} and H₂O chemical species in the aqueous ammonia solution. All of these chemical species did not absorb the 253.7 nm UV light.¹¹ However, TiO₂ particles absorb photons with energy higher than its bandgap (3.2 eV) which corresponds to a light with about 400 nm.^{12,17} In the irradiation of aqueous ammonia solution containing TiO₂ particles by 253.7 nm UV light, only TiO₂ absorbed all of the light at the initial process of the reaction. It means that the photochemical formation of hydrazine begins by the absorption of TiO₂ particles. It is well known that the electronically excited TiO₂ by the absorption of UV light is created as the geminated form on the surface of the TiO₂ as presented in equation (1).^{12,17} The fact that yield of hydrazine depended on the amount of TiO₂ in the aqueous ammonia supports that TiO₂ played an important role in the formation of hydrazine.

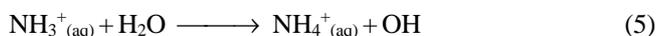
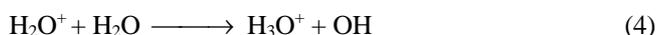


The electronhole pairs, so called geminated form (TiO₂⁺·e⁻) is identical with (h⁺·e⁻). Positive hole (h⁺) is acting as an oxidizing agent. The electron on the surface of the TiO₂ particles can diffuse away and becomes solvated electron

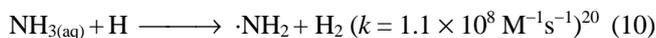
(e_{aq}^-) in the solvent. The positive hole (h^+) can be also converted into H_2O^+ and $NH_3^+_{(aq)}$ by the reaction with H_2O and $NH_3_{(aq)}$ as in reaction (2) and (3).



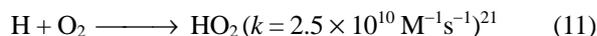
The H_2O^+ and $NH_3^+_{(aq)}$ species can react with H_2O , and OH radicals can be formed by the reaction (4) and (5). The OH radicals produced can attack ammonia in the solution and the NH_2 radicals were formed as in reaction (6). In addition to the reaction, the OH radicals can also react with each other leading to hydrogen peroxide as in reaction (7). The formation of hydrazine could be, therefore, explained by the dimerization process of NH_2 radicals in reaction (8).



In addition to positive hole (h^+), the solvated electron (e_{aq}^-) on the surface of the electronically excited TiO_2 particles is also able to react with hydronium ion (H^+_{aq}) as in reaction (9). The hydrogen atom produced by the reaction (9) can attack ammonia and more NH_2 radicals thereby produced as in reaction (10).



If there is oxygen in the aqueous ammonia solution, the hydrogen atom produced by the reaction (9) can also react with oxygen molecule very fast and yield hydrogen peroxide radicals as in reaction (11). Because the reactions (9) and (10) are in competition, the photochemical formation of hydrazine diminishes in the presence of oxygen.



However, the formation of hydrazine is independent of the presence of oxygen in the irradiation of aqueous ammonia as shown in Table 1. From the result, we conclude that hydrogen atom was not formed in the irradiation of aqueous ammonia containing titanium oxide. The hydronium ion produced by reaction (4) does not react with solvated electron but combined with ammonia molecule very rapidly as in reaction (12) in this experimental condition.



Actually, most of ammonia existed as ammonium ion in acidic aqueous solution. To test that ammonium ion takes also part in the formation of hydrazine, the photochemical reaction of 0.5 M NH_4OH containing suspension of TiO_2 (0.4 mg/mL) has been carried out as a function of pH values in the solution. The formation of hydrazine was not detected in acidic solution, but in basic solution as in Figure 2. It

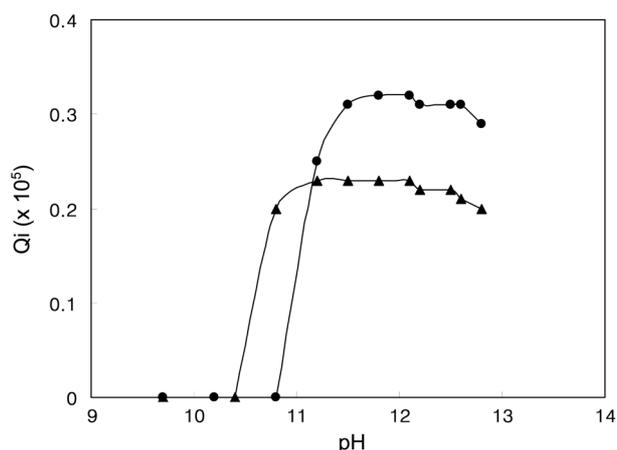
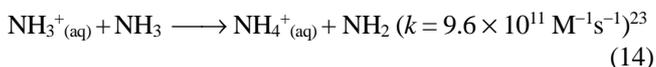


Figure 2. Initial quantum yield (Q_i) of hydrazine after irradiation of the aerated aqueous ammonia containing TiO_2 (0.4 mg/mL) as a function of the pH values in the solution: (●) is 0.5 M NH_4OH ; (▲) is 0.1 M NH_4OH .

suggests that hydrazine was not produced from ammonium ion but from neutral ammonia molecule. This result is quite similar to our previous result.²²

The photochemical formation of hydrazine is also dependent of the amount of ammonia in the solution. As shown in Table 1, the initial quantum yield of hydrazine increased as the contents of ammonia increased in the reactant solution. Since hydrazine is only produced by the dimerization process of NH_2 radicals in the experimental system, their amount is important to produce hydrazine. If NH_2 radicals were formed only by the attack of OH radicals as in reaction (6), the initial quantum yields of hydrazine have nearly same value regardless of the initial concentration of ammonia. However, the fact that the yield of hydrazine depended on the initial concentration of ammonia supports that ammonia is also contributed to the formation of hydrazine. Because the reactions (6) and (7) are in competition, the OH radicals less attack the NH_3 molecules in the irradiation of dilute aqueous ammonia than in that of concentrated ammonia, leading to lower yield of hydrazine. However, H_2O^+ and $NH_3^+_{(aq)}$ formed by the reaction with H_2O and $NH_3_{(aq)}$ as in reaction (2) and (3) can not only react with H_2O but with $NH_3_{(aq)}$ as in reactions (13) and (14). It was reported that the rate constant for the reaction (14) was very fast in the gas phase.²³ This result supports that the reaction (13) and (14) could be happen on the surface of TiO_2 particles in the irradiation of aqueous ammonia solution. The reaction probability for the reactions (13) and (14) increases in higher concentration of aqueous ammonia solution and more NH_2 radicals thereby produced. This is a reason why hydrazine gives the higher yield with increasing the concentration of ammonia.



In conclusion, TiO₂ particle was a good photocatalyst and hydrazine was produced mainly during the irradiation of the NH₄OH solution containing suspension of TiO₂ using 253.7 nm UV light. The photochemical reaction was only begun by the light energy absorption of TiO₂ particles in the experimental conditions. Hydrazine was produced by the dimerization process of the NH₂ radicals. The yield of hydrazine depended both on the amount of TiO₂ contained in aqueous ammonia and on the number of quanta. The OH radicals formed by the reaction of H₂O with positive hole (h⁺) on the surface of the electronically excited TiO₂ particles take part mainly in the decomposition process of ammonia leading to the formation of NH₂ radicals. In addition to this, NH₃ molecule is also reacted with positive hole (h⁺) on the surface of the TiO₂ particles and converted into NH₂ radicals. Thus, more hydrazine is produced with increasing the concentration of ammonia. The formation of hydrazine is independent on the presence of oxygen in the irradiation of aqueous ammonia. The formation of hydrazine was not detected in acidic solution and its formation was detected only in basic solution (at pH > 10). It indicates that hydrazine was formed from neutral ammonia molecule rather than from ammonium ion.

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