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PHOTOCHEMICAL TRANSFORMATION OF CARBON MONOXIDE IN AQUEOUS AMMONIA

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Abstract – The photochemical transformation of carbon monoxide in aqueous ammonia solution has been investigated at 25±0.1°C using 184.9 nm UV light. Amination and carbonylation processes were carried out by irradiating the aqueous ammonia solution saturated with carbon monoxide, and the formation of formamide, urea, hexamethylenetetramine, formaldehyde, glyoxal and hydrazine was observed. The formation of hydrazine was affected by the presence of ammonia, and the formation of carbonyl compounds such as formaldehyde and glyoxal was influenced by the presence of carbon monoxide. The formation of formamide, urea and hexamethylenetetramine was affected by both ammonia and carbon monoxide. The initial quantum yields of the products were determined and probable mechanisms for the photochemical reaction were presented on the basis of product analysis.

INTRODUCTION

Photochemical reactions of carbon monoxide have recently attracted considerable attentions, since the carbon monoxide, a highly toxic compound, is released from the combustion of fossil fuels and oxidized in the atmosphere to carbon dioxide which causes green house effect or ozone depletion. On the other hand, it is an industrially important compound because it could be used as a raw material for various chemical syntheses. Arai *et. al.*[1], Charles *et. al.*[2] and Getoff *et. al.*[3-6] have reported that the radiation can induce reduction of CO in both gas and liquid phase. A problem of the reaction is, however, to use the special γ-ray device requiring various safety equipments. To circumvent this difficulty, we have employed photochemical method using UV light at 184.9 nm and reported the result along with the reaction mechanism for the chemical reaction of aqueous carbon monoxide.[7] We postulated that carbon monoxide reacted with a hydrogen atom to give a $\cdot$CHO radical and also reported that the reactivity of the $\cdot$CHO radical formed in the reduction was higher in aqueous state than in hydrated state,[8] and that the carbonylation could be also occurred in the presence of other substances.[9,10]

Ammonia generated from decomposition of a large amount of garbage causes also a serious environmental pollution. Most of the investigations on the photochemical reaction of ammonia were carried out in gas phase. Very recently, we have described the photochemical decomposition of aqueous ammonia.[11] It was found in the study that hydrazine was produced by the dimerization of $\cdot NH_2$ radicals.

In this study, aqueous ammonia solution saturated with carbon monoxide was irradiated with vacuum UV light of 184.9 nm. The presence of carbon monoxide during the irradiation of aqueous ammonia could lead to the formation of carbonyl compounds. The purpose of this study is to present quantitative results for photochemical reaction of aqueous ammonia saturated with carbon monoxide using vacuum UV light of 184.9 nm, and to propose the primary photochemical reaction mechanisms on the product analysis.

MATERIALS AND METHODS

Light source and actinometry. Irradiations were carried out at 25±0.1°C using low pressure Hg lamp (Osram HNS 10W/oz). Low pressure Hg lamp is classified into two types depending on the method of its emitting wavelength; ozone generating lamp and ozone-free lamp.[12] The ozone generating lamp used in this study emits two monochromatic lights of 184.9 and 253.7 nm, whereas the ozone-free lamp emits only 253.7 nm UV light. 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 using a quartz tube. The intensity of the 184.9 nm light was determined by ethanol actinometer.[13] In order to perform the chemical actinometry, 5 M air-free aqueous ethanol was prepared and irradiated. The yield of hydrogen produced after irradiation of the solution was plotted against the irradiation time. The lamp intensity was obtained by the slope using the known quantum yield, $Q(H_2) = 0.40$,[13] which was found to be 2.33×10^{17} hv $\cdot$ $mL^{-1} \cdot min^{-1}$ at 25 ± 0.1°C. It corresponds to about 22% of the intensity at 253.7 nm. No change in intensity of the lamp was observed over the period of the experiments. The yield of hydrogen produced after irradiation of air-free aqueous ethanol was measured by a thermal conductivity gas chromatography [Yanaco (Japan) Model G180-T; Molesieve 5 Å packed column; carrier gas: He]. The output of the gas chromatograph was integrated using a integrator (Varian 4290).

Reagents and General procedure. Aqua ammonia (28% NH_3 in water, 99.99+% NH_4OH) was purchased from Aldrich Chemical Co. and used as received. All other chemicals employed in this work were guaranteed grade and used without further purification. Carbon monoxide (99% pure) was purified by passing through an alkaline pyrogallol solution, followed by an alkaline sodium hydrosulphite solution sensitized by the addition of sodium anthraquinone β-sulphonate.[14] Aqueous ammonia solution was prepared using quadruply distilled water, which was obtained by passing the distilled water through Barnstead (U.S.A.) Nonopure II deionization system. In order to prepare the aqueous ammonia solution saturated with carbon monoxide, each of the compounds, distilled water and aqua ammonia was first saturated by bubbling for about 60 minutes with carbon monoxide. The concentration of ammonia changed after bubbling of carbon monoxide was determined by spectrophotometric method mentioned in previous work.[11] 100 mL of the freshly prepared solution was transferred into the irradiation vessel and bubbled again with CO for about 3 minutes before the irradiation. UV-spectrum was measured by Uvikon model 943 UV-spectrophotometer. The molar extinction coefficient (ϵ) of aqueous ammonia at 184.9 nm was found to be 15.0 $M^{-1}cm^{-1}$. Ammonia did not absorb the simultaneously emitted light at 253.7 nm.

Product analysis. In order to obtain the well-defined MS spectra of the products, the irradiated aqueous ammonia solution saturated with carbon monoxide was concentrated using a rotary vacuum evaporator. The sample was then analyzed using Varian saturn GC-MS system (DB-5 capillary column 60 m $\times$ 0.25 μm EI method) [product; m/e (rel. intensity), hexamethylenetetramine: 42(25), 58(10), 85(12), 111(20), 140(100); urea: 19(10), 30(15), 42(22), 43(40), 44(37), 59(45), 60(100); formaldehyde: 28(10), 29(100), 30(35); hydrazine; 17(10), 31(16), 32(100); formamide: 27(12), 29(30), 45(100); glyoxal: 28(20), 29(100), 57(80), 58(25)]. Identification of the photoproducts was made by comparison of fragmentation patterns with those of the known pure substances. The identified products from the MS spectra were reconfirmed by comparison with retention times of the separated GC peaks of standard chemicals using a Varian Model 3700 gas chromatography. Quantitative analysis of hexamethylenetetramine and formamide was performed by estimating the area ratio of the products and by using 1-pentanol as an internal standard in gas chromatography. The yield of hydrazine, formaldehyde and glyoxal was analyzed by spectrophotometric method. In order to determine the amount of hydrazine, an aliquot (1 mL) of the irradiated solutions was treated with p-dimethylaminobenzaldehyde as a complexing reagent.[15] The molar extinction coefficient (ϵ) of the colored complex was 66700 $M^{-1}cm^{-1}$ at 458 nm in these experiments, which was not interfered by the presence of the other nitrogen-containing compounds such as hydroxylamine and formamide. Quantitative determination of formaldehyde was performed by Hanz method.[16] The developed color was characterized by the absorbance maximum at 412 nm. The presence of the other compounds such as glyoxal, ammonia, and formamide did not interfere the measurement. The amount of glyoxal was also determined by treatment with p-dinitrophenylhydrazine.[17]

RESULTS AND DISCUSSION

Photolysis of the 1.0 M aqueous ammonia solution saturated with carbon monoxide at 184.9 nm yielded carbonyl compounds such as formaldehyde and glyoxal, and amine compounds such as hexamethylenetetramine, hydrazine, urea and formamide. No product observed during the irradiation only at 253.7 nm. As shown in the Figures, the product yields did not increase in proportion to the number of quanta. This behavior indicates that some secondary reactions, which contributes to the formation of the other products, occurred in the system. Therefore, we determined the initial quantum yields (Q_i) of the products from the tangent line of the curve shown in the figures, which were summarized in Table 1.

In aqueous ammonia solution saturated with carbon monoxide, NH_3 and H_2O species absorb the light of 184.9 nm. However, carbon monoxide does not absorb the light of 184.9 nm.[18] The molar extinction coefficient(ϵ) of NH_3 was determined to be 15.0 $M^{-1}cm^{-1}$ at 184.9 nm and that of H_2O was reported[19] to be 3.2 X 10^{-2} $M^{-1}cm^{-1}$. From the calculation using these values, it was found that most(ca. 89.4%) of the 184.9 nm was absorbed by ammonia in the 1.0 M aqueous ammo-

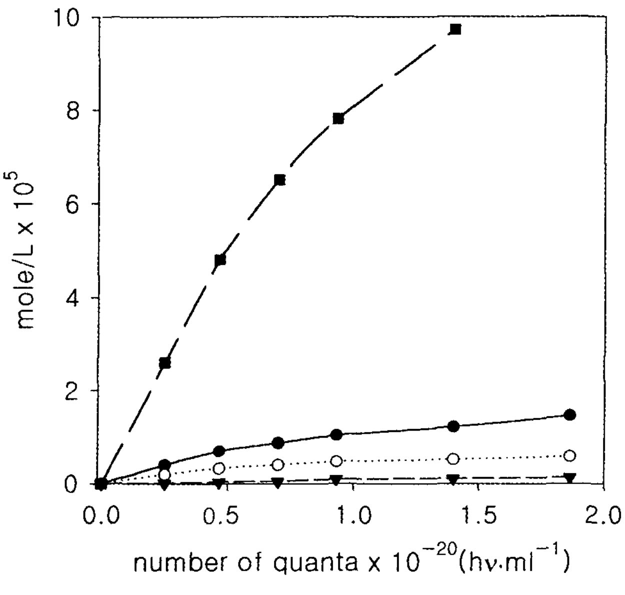

Figure 1. Formation of the products after irradiation of 1.0 M aqueous ammonia saturated with CO as a function of the number of quanta.; (●) N_2H_4, (○) HCHO, (▼) $(CHO)_2$, (■) hexamethylenetetramine.

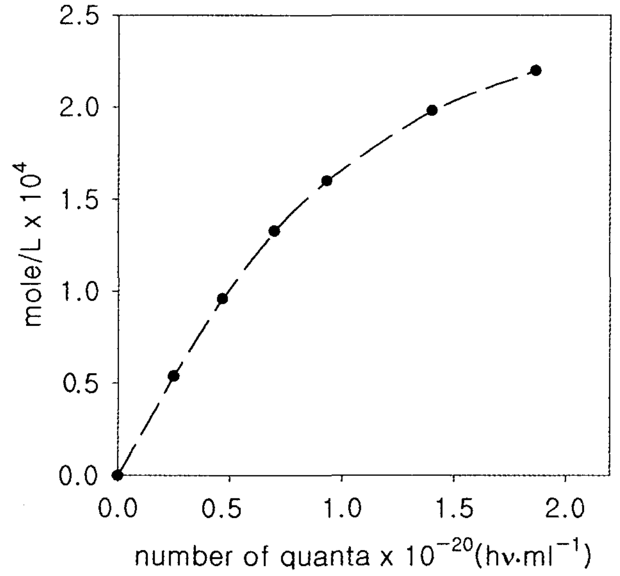

Figure 2. Formation of NH_2CHO (●) after irradiation of 1.0 M aqueous ammonia saturated with CO as a function of the number of quanta.

nia solution saturated with carbon monoxide. It means that ammonia plays an important role in the irradiation at given concentration of this solution.

Electronically excited ammonia by the absorption of 184.9 nm UV light leads mainly to the formation of H· and $\cdot NH_2$ radicals.[11] These highly reactive species can react with each other or attack the other compounds in the solution like ammonia. The formation of hydrazine can be explained by their dimerization process of $\cdot NH_2$ radicals as presented in reaction (1).

$$2 \cdot NH_2 \longrightarrow N_2H_4 \qquad (1)$$

The hydrogen atom produced by the electronically excited ammonia can also attack ammonia as shown in reaction (2). This reaction facilitates the decomposition of ammonia and thereby much more $\cdot NH_2$ radicals are produced. Since a small part of the applied UV light (*ca.* 10.6%) was absorbed by H_2O in given experimental conditions, the H· and ·OH radicals formed from the photolysis of water take part also in the decomposition process of ammonia as shown in reactions (2) and (3). Although the hydrogen atom can react with each other to produce hydrogen molecules, the formation of $\cdot NH_2$ radicals in reaction (2) is more probable because the reaction probability of the reaction defined by multiplication of the concentration and the rate constant is greater than that of the reaction (4). To test this hypothesis, we tried to detect of hydrogen molecules produced by the irradiation. But the yield for the hydrogen molecules formation was so small that it could be negligible. This result supports that the hypothesis described above is reasonable.

$$NH_3(aq) + H\cdot \longrightarrow \cdot NH_2 + H_2 \qquad (2)$$

$$NH_3(aq) + \cdot OH \longrightarrow \cdot NH_2 + H_2O \qquad (3)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (4)$$

However, when the aqueous ammonia solution was saturated with carbon monoxide, the formation of the hydrazine decreased compared with the case of air-free aqueous ammonia. The initial quantum yield of the hydrazine was found to be 1.32×10^{-4} in the irradiation of the 1.0 M aqueous ammonia saturated with carbon monoxide, whereas it was reported to be 4.81×10^{-3} in the irradiation of the 1.0 M air-free aqueous ammonia solution under the same experimental condition. This result indicates that carbon monoxide, affects the decomposition process of aqueous ammonia. Although the solubility of carbon monoxide in aqueous ammonia solution could not be found, it might be deduced that carbon monoxide in 1.0 M aqueous ammonia solution is as soluble as in water (solubility is about 1×10^{-3} M at 25℃),[20] Since the mole fraction of water is very large, one can assume that solubility of carbon monoxide in aqueous ammonia solution is 1×10^{-3} M at 25℃. In the presence of carbon monoxide, the produced hydrogen atoms participate not only in the reaction (2) but also in the combination with carbon monoxide as shown in reaction (5).

$$H\cdot + CO \longrightarrow \cdot CHO \qquad (5)$$

Because the reactions (2) and (5) are a competing with each other, the formation of hydrazine decreased in the irradiation of 1.0 M aqueous ammonia saturated with carbon monoxide. The ·CHO radicals produced by the reaction (5) can react with each other *via* both disproportionation and dimerization processes to form formaldehyde and glyoxal as shown in reaction (6).

$$2 \cdot CHO \longrightarrow HCHO + CO \qquad (6a)$$

$$ \longrightarrow (CHO)_2 \qquad (6b)$$

In addition to hydrogen atom, $\cdot NH_2$ radicals produced could react with carbon monoxide and thereby $NH_2CO\cdot$ radicals could be produced as shown in reaction (7). The formation of formamide and urea could be explained by the attack

Table 1. Initial quantum yield (Q_i) of the products after irradiation (λ = 184.9 nm) of 1.0 M aqueous ammonia at 25℃.

Products	Q_i when saturated with	
	Ar[11]	CO
Hydrazine	4.81×10^{-3}	1.32×10^{-4}
Formaldehyde	----	4.65×10^{-5}
Glyoxal	----	8.08×10^{-6}
Formamide	----	1.74×10^{-3}
Hexamethylenetetramine	----	2.78×10^{-4}
Urea	----	detected

of the radical to ammonia as shown in reaction (8).

$$\cdot NH_2 + CO \longrightarrow NH_2CO \cdot \quad (7)$$

$$NH_2CO \cdot + NH_3 \longrightarrow NH_2CHO + \cdot NH_2 \quad (8a)$$

$$\qquad\qquad \longrightarrow NH_2CONH_2 + H \cdot \quad (8b)$$

However, the initial quantum yield of the formamide was the greatest among the products as shown in Table 1. This result might be interpreted that the $\cdot NH_2$ radical, produced by the reaction (8a), reacted with carbon monoxide again as in reaction (7) to give much more $NH_2CO \cdot$ radicals. Because of this chain reaction, the yield of formamide increased in the irradiation of 1.0 M aqueous ammonia saturated with carbon monoxide. In order to test this hypothesis, we performed the quantitative analysis of urea being produced by the irradiation. Although the formation of urea was identified using a GC-MS, its yield could not be determined, because the urea formed by the irradiation was very unstable in aqueous solution.

The formation of hexamethylenetetramine could be explained by the secondary photochemical reaction, since it was produced by the reaction of diaminomethane and formaldehyde.[21] As shown in reaction (9), the $\cdot NH_2$ radical could attack formaldehyde being produced by the irradiation of the aqueous ammonia saturated with carbon monoxide to form $H_2NCH_2O \cdot$ radical. This radical attacked ammonia, leading to the formation of methanolamine. The $\cdot NH_2$ radical produced by the reaction (10) reacted with formaldehyde again as in reaction (9) regenerating much more $NH_2CHO \cdot$ radicals and $\cdot NH_2$ radicals.

$$\cdot NH_2 + HCHO \longrightarrow H_2NCH_2O \cdot \quad (9)$$

$$H_2NCH_2O \cdot + NH_3 \longrightarrow H_2NCH_2OH + \cdot NH_2 \quad (10)$$

Since the methanolamine is very unstable, it is converted in to an imine by dehydration. The imine was then attacked by hydrogen radical as in reaction (11) to form $CH_3NH \cdot$ and $\cdot CH_2NH_2$ radicals.

$$H_2NCH_2OH \xrightarrow{-H_2O} H_2C{=}NH \xrightarrow{H \cdot} CH_3NH \cdot \quad (11a)$$

$$\qquad\qquad\qquad \longrightarrow \cdot CH_2NH_2 \quad (11b)$$

The $\cdot CH_2NH_2$ radicals produced by reaction (11b) attacks ammonia, leading to diaminomethane and then further reactrons with formaldehyde and ammonia formed hexamethylenetetramine as shown in Scheme 1. Although $\cdot CH_2NH_2$ radicals can react with each other *via* dimerization process to form ethylenediamine, it was not detected by the analytical method used in this study. It implies that the reaction probability of dimerization process to form ethylenediamine is very unplausibele.

$$\cdot CH_2NH_2 \xrightarrow{NH_3} H_2NCH_2NH_2 \xrightarrow[-H_2O]{HCHO} H_2NCH_2\text{-}N{=}$$

$$\xrightarrow{NH_3} H_2NCH_2NHCH_2NH_2 \xrightarrow[NH_3]{HCHO} \text{hexamethylenetetramine}$$

Scheme 1.

In conclusion, formaldehyde, glyoxal, formamide, urea, hydrazine, and hexamethylenetetramine were observed after the irradiation of 1.0 M aqueous ammonia solution saturated with carbon monoxide at 25℃ using 184.9 nm UV light. Hydrazine was produced by dimerization process of $\cdot NH_2$ radicals formed by the photochemical reaction of aqueous ammonia. The hydrogen atom, formed from the electronically excited ammonia reacted with carbon monoxide to produce $\cdot CHO$ radical. Formaldehyde and glyoxal were formed by the disproportionation process and the dimerization process, respectively. The $\cdot NH_2$ radical combined also with carbon monoxide, leading to $NH_2CO \cdot$ radical, which was converted into formamide. The formation of hexamethylenetetramine could be explained by the combined photochemical and chemical reactions, initiated by the reaction of formaldehyde and $\cdot NH_2$ radical as a key step.

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