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  10. PdAr (Me) (tmeda) (Ar=1-naphthyl) was prepared similarly to the procedure for PdAr (Me) (tmeda) (Ar=Ph, C<sub>6</sub>H<sub>4</sub>-p-Me) in reference 9. Pd(1-naphthyl) (Me) (tmeda), 54%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.08 (s, 3H, Pd-CH<sub>3</sub>), 2.01, 2.41, 2.60, 2.66 (s, 12H, N-Me<sub>2</sub>), 2.40-2.74 (m, 4H, N-CH<sub>2</sub>), 7.27, 7.43, 7.76, 8.94 (m, 7H, aromatic). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): -9.95 (Pd-CH<sub>3</sub>), 47.50, 48.00, 48.69, 49.60 (N-Me<sub>2</sub>), 59.24, 60.12 (N-CH<sub>2</sub>), 120.6, 122.4, 123.6, 124.6, 127.6, 133.4, 133.8, 136.4, 140.8, 168.1 (ipso).
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## Photochemical Reaction of Carbon Monoxide in Aqueous Methanol Containing Ammonia

Hyoung-Ryun Park\*, A-Young Sung, Chu-Ha Oh, and Chan-Jung Kim†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

†Kwangju Health and Environmental Research Institute, Kwangju 500-757, Korea

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As industrial society has been developed, fossil fuels such as coal, oil, and natural gas have been increasingly used as energy source. During the combustion of fossil fuels, obnoxious gases such as nitrogen oxides, sulfur oxides and carbon oxides are produced. These gases are the main source of air pollution. Especially, carbon monoxide is very toxic compound and oxidized in the atmosphere to give carbon dioxide which causes green house effect or ozone depletion. On the other hand, it is industrially important compound because it could be used as a raw material for chemical syntheses. Earlier investigation showed that carbon monoxide reacts with hydrogen atom to give  $\dot{\text{C}}\text{HO}$  radical<sup>1</sup> and Marz *et al.* proved the presence of this radical by ESR spectroscopy.<sup>2</sup> Arai *et al.*<sup>3,4</sup> and Getoff *et al.*<sup>5-10</sup> have studied the radiation induced reduction of CO in gas phase and in liquid phase, respectively. A problem for the reaction is, however, to use the special  $\gamma$ -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.<sup>11</sup> We also reported that the reactivity of  $\dot{\text{C}}\text{HO}$  radical formed in the reduction is higher in aqueous state than in hydrated state,<sup>12</sup> and that the carbonylation can be also occurred in the presence of other substances.<sup>13,14</sup> Ammonia generated from decomposition of a large amount of garbage, causes also a serious environmental pollution. Very recently, we have described the photochemical decomposition of aqueous ammonia.<sup>15</sup> It was found from the study that hydrazine was produced by the dimerization of  $\dot{\text{N}}\text{H}_2$  radicals. In particular, the presence of ammonia during the irradiation of aqueous organic solution could lead to the formation of amine compounds.

In the present study, methanol was selected as a model substance for an organic solvent and we have investigated the possibility of carbonylation and amination, and proposed the reaction mechanisms for the photochemical transformation of carbon monoxide in aqueous methanol.

## Experimental

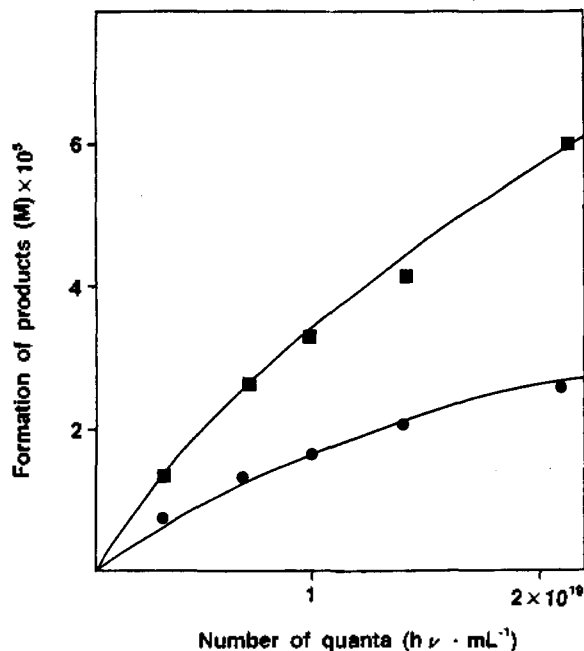
**Reagents and General.** Methanol (Aldrich Chemical Co., 99.9% A.C.S. HPLC grade) was used as received. All other chemicals were reagent grade and used without further purification. Carbon monoxide (state to be 99% pure) was purified by passing through an alkaline pyrogallol solution, followed by an alkaline sodium hydrosulphite solution sensitized by the addition of sodium anthraquinone  $\beta$ -sulphonate.<sup>16</sup> Aqueous methanol 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 methanol-ammonia mixture solution saturated with carbon monoxide, each of the compounds was first saturated by bubbling for about 60 minutes with carbon monoxide. 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.

Irradiations were made at  $25.0 \pm 0.1$  °C using low pressure Hg lamp (Osram HNS 12/oz), which emitted two monochromatic lights of 184.9 nm and 253.7 nm. Actinometry of the lamp was described in detail in the previous work.<sup>15</sup> The lamp intensity of 184.9 nm was found to be  $2.33 \times 10^{17}$  quanta  $\cdot$  mL<sup>-1</sup>  $\cdot$  min<sup>-1</sup> at 25.0 °C. Methanol, ammonia, and carbon monoxide did not absorb the simultaneously emitted light at 253.7 nm. No change in the intensity of the lamp was observed over the period of the experiment. Absorbance and UV-spectrum were measured by Uvikon model 943 spectrophotometer.

**Products analysis.** In order to obtain the mass spectra of the products, the irradiated aqueous solution was concentrated using rotary vacuum evaporator. The sample was then analyzed using Varian saturn GC-MS system (DB-5 capillary column 50 m  $\times$  0.25  $\mu$ m EI method) [product; m/e (rel. intensity), hexamine: 42(25), 58(10), 85(12), 111(20), 140(100); formaldehyde: 28(10), 29(100), 30(35); ethyleneglycol: 29(20), 31(100), 33(30), 43(10); glyoxal: 28(13), 29(100), 30(28), 31(70), 58(12); 1,1-dimethylhydrazine: 28(30), 30(30), 42(100), 45(80), 60(75); dimethylamine: 15(20), 18(35), 28(30), 44(100), 45(80); formamide: 27(12), 29(30), 45(100); ethylenediamine: 18(20), 30(100), 43(13), 60(8)]. The identifications were made by comparison of fragmentation patterns with those of known amounts of the pure substances. The identified products from the MS spectra were reconfirmed by comparison with retention times of the separated GC peaks of the standard chemicals using a Varian Model 3700 gas chromatography. Qualitative analysis was performed by estimating the area ratio of the products and 1-pentanol as an internal standard. The amount of the formaldehyde, glyoxal, and hydrazine was determined by spectrophotometric method.<sup>17-19</sup>

## Results and Discussion

The photolysis of the aqueous methanol-ammonia mixture solution ( $X_{\text{MeOH}}=0.10$ ,  $X_{\text{ammonia}}=5 \times 10^{-4}$ ) saturated with carbon monoxide at 184.9 nm yields carbonyl compounds such as formaldehyde and glyoxal, and amine compounds such as hydrazine, methoxyamine, hexamine, 1,1-dimethylhydrazine, dimethylamine, ethylenediamine and formamide.



**Figure 1.** Formation of products after irradiation of methanol-ammonia mixture solution saturated with carbon monoxide at 25 °C ( $X_{\text{MeOH}}=0.10$  and  $X_{\text{ammonia}}=5 \times 10^{-4}$ ) as a function of the number of quanta: (■) is 1,1-dimethylhydrazine, (●) is dimethylamine.

No product was observed during the irradiation at 253.7 nm. The formation of two of the products obtained from the irradiation of the mixture solution is representatively presented in Figure 1 as a function of the number of quanta.

As shown in Figure 1, the product yields were not increased in proportion to the number of quanta. Therefore, we determined the initial quantum yields ( $Q_i$ ), obtained from the slope of tangent line of the curve shown in Figure 1 and they are summarized in Table 1.

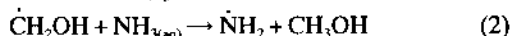
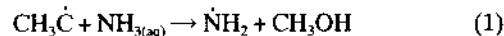
In aqueous methanol-ammonia mixture solution, most of the reactants absorb the 184.9 nm. The molar extinction coefficient ( $\epsilon$ ) of  $\text{NH}_3(\text{aq})$  was determined to be  $15.0 \text{ M}^{-1} \text{ cm}^{-1}$  at 184.9 nm and these of methanol and  $\text{H}_2\text{O}$  were reported to be  $7.0 \text{ M}^{-1} \text{ cm}^{-1}$  and  $3.2 \times 10^{-2} \text{ M}^{-1} \text{ cm}^{-1}$ , respectively.<sup>20,21</sup> However, carbon monoxide does not absorb at

**Table 1.** Initial quantum yield ( $Q_i$ ) of the products after irradiation ( $\lambda=184.9$  nm) of aqueous methanol-ammonia mixture solution ( $X_{\text{MeOH}}=0.10$  and  $X_{\text{ammonia}}=5 \times 10^{-4}$ ) in the absence and presence of CO at 25 °C

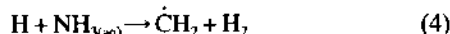
Products	$Q_i$ When saturated with	
	Ar	CO
Formaldehyde	$1.91 \times 10^{-1}$	$6.77 \times 10^{-1}$
Ethyleneglycol	$1.08 \times 10^{-2}$	$2.15 \times 10^{-3}$
Glyoxal	$5.19 \times 10^{-4}$	$5.52 \times 10^{-3}$
Hydrazine	$6.32 \times 10^{-6}$	$2.10 \times 10^{-6}$
Methoxyamine	$6.02 \times 10^{-2}$	$3.44 \times 10^{-2}$
Hexamine	$1.42 \times 10^{-3}$	$9.03 \times 10^{-3}$
1,1-dimethylhydrazine	$1.20 \times 10^{-3}$	$1.05 \times 10^{-3}$
Dimethylamine	$7.53 \times 10^{-3}$	$1.20 \times 10^{-3}$
Formamide	$3.91 \times 10^{-6}$	$1.72 \times 10^{-4}$
Ethylenediamine	$<10^{-6}$	$<10^{-6}$

184.9 nm.<sup>22</sup> From the calculation using these values, it was found that most (about 96.5%) of the 184.9 nm was absorbed by methanol in aqueous methanol-ammonia mixture solution ( $X_{\text{MeOH}}=0.10$ ,  $X_{\text{ammonia}}=5 \times 10^{-4}$ ). It means that methanol plays an important role in the irradiation of the given concentration of the mixture solution.

Somntag reported that the liquid phase of methanol electronically excited is mainly splitted into either H and  $\dot{\text{C}}\text{H}_2\text{OH}$  radicals ( $\geq 75\%$ ) or H and  $\dot{\text{C}}\text{H}_3\text{O}$  ( $\geq 13\%$ ) radicals, and  $\dot{\text{C}}\text{H}_3\text{O}$  radical is converted rapidly to  $\dot{\text{C}}\text{H}_2\text{OH}$  radical.<sup>20</sup> The formation of formaldehyde and ethyleneglycol can be explained by the disproportionation process and by the dimerization process of  $\dot{\text{C}}\text{H}_2\text{OH}$  radical, respectively. However,  $\dot{\text{C}}\text{H}_3\text{O}$  and  $\dot{\text{C}}\text{H}_2\text{OH}$  radicals can also react with ammonia in aqueous methanol-ammonia solution as in reaction (1) and (2).



The hydrogen radical produced can attack both methanol and ammonia competitively as in reactions (3) and (4), leading to the formation of  $\dot{\text{C}}\text{H}_2\text{OH}$  radical and  $\dot{\text{N}}\text{H}_2$  radical.



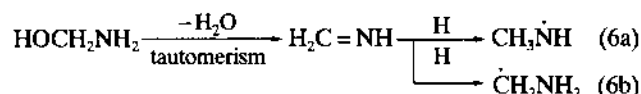
In the irradiation of the aqueous methanol-ammonia mixture solution in the absence of carbon monoxide, the initial quantum yield of formaldehyde is about 10 times greater than that of ethyleneglycol as shown in Table 1, implying that  $\dot{\text{C}}\text{H}_2\text{OH}$  radicals reacted *via* disproportionation process rather than *via* dimerization process. However, when the methanol-ammonia mixture solution is saturated with carbon monoxide, the formation of formaldehyde and glyoxal increased whereas that of ethyleneglycol decreased as shown in Table 1. The result indicates that the hydrogen radical reacted as well by the reactions (3) and (4) as by the reaction (5). Although the solubility of carbon monoxide in the given concentration of methanol-ammonia mixture solution could not find, it might be deduced that carbon monoxide is more soluble in aqueous methanol-ammonia mixture solution than in water (solubility is about  $1 \times 10^{-3}$  M),<sup>23</sup> since the solubility of carbon monoxide in methanol and ammonia is larger than that in water.<sup>23</sup>



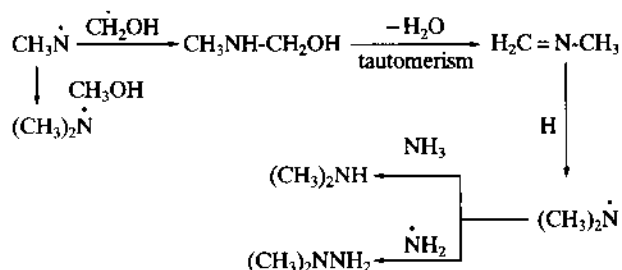
Because of these competition reactions, the yield of  $\dot{\text{C}}\text{H}_2\text{OH}$  radicals diminished and less ethyleneglycol produced in the irradiation of the aqueous methanol-ammonia mixture solution, saturated with carbon monoxide. The  $\dot{\text{C}}\text{HO}$  radicals produced by the reaction (5) can react with each other *via* both disproportionation process and dimerization process to form formaldehyde and ethyleneglycol. This is the reason why the yield of formaldehyde and ethyleneglycol increased in the presence of carbon monoxide.

The formation of hydrazine and methoxyamine can be explained by the dimerization of  $\dot{\text{N}}\text{H}_2$  radical and by the combination of  $\dot{\text{C}}\text{H}_3\text{O}$  radical and  $\dot{\text{N}}\text{H}_2$  radical, respectively. Less formation of hydrazine and methoxyamine in the presence of carbon monoxide indicates that less  $\dot{\text{N}}\text{H}_2$  radical produced because hydrogen radical reacted with carbon monox-

ide. As the reaction probability of the reaction (5) increases, that of reaction (4) decreases. In addition to  $\dot{\text{C}}\text{H}_3\text{O}$  radical,  $\dot{\text{C}}\text{H}_2\text{OH}$  radical can also react with  $\dot{\text{N}}\text{H}_2$  radical, leading to the formation of methanolamine. However, methanolamine is very unstable and is converted into an imine by amine-imine tautomerism. The imine was then attacked by hydrogen radical as in reaction (6), producing  $\dot{\text{C}}\text{H}_3\dot{\text{N}}\text{H}$  and  $\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_2$  radicals.



The  $\dot{\text{C}}\text{H}_3\dot{\text{N}}\text{H}$  and  $\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_2$  radicals produced by reaction (6) can react with chemical species contained in the mixture solution. The  $\dot{\text{C}}\text{H}_3\dot{\text{N}}\text{H}$  radical reacts both with methanol and with  $\dot{\text{C}}\text{H}_2\text{OH}$  radical. The substance formed by the combination with  $\dot{\text{C}}\text{H}_3\dot{\text{N}}\text{H}$  radical and  $\dot{\text{N}}\text{H}_2\text{OH}$  radical is converted into  $(\text{CH}_3)_2\dot{\text{N}}$  radical by amine-imine tautomerism and by attack of hydrogen radical as shown in Scheme 1.  $(\text{CH}_3)_2\dot{\text{N}}$  radical can be also produced by the reaction of  $\dot{\text{C}}\text{H}_3\text{NH}$  radical with methanol. The formation of 1,1-dimethylhydrazine and dimethylamine can be interpreted by the reaction between  $(\text{CH}_3)_2\dot{\text{N}}$  radical and ammonia or  $(\text{CH}_3)_2\dot{\text{N}}$  radical and  $\dot{\text{N}}\text{H}_2$  radical.



Scheme 1.

In the presence of carbon monoxide, reaction probability of the reaction (3) decreases because of competition reaction with reaction (5) and less  $\dot{\text{C}}\text{H}_2\text{OH}$  radical produced. As a result, the yields of 1,1-dimethylhydrazine and dimethylamine are diminished.

$\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_2$  radical formed by the reaction (6) can also react with chemical species such as methanol,  $\dot{\text{C}}\text{H}_2\text{OH}$  radical,  $\dot{\text{C}}\text{H}_3\text{O}$  radical and ammonia. However, methanolamine, ethanolamine, and aminemethoxymethane were not detected under the given experimental condition. It implies that the  $\dot{\text{C}}\text{H}_2\text{NH}_2$  radical reacts with chemical species such as methanol,  $\dot{\text{C}}\text{H}_2\text{OH}$  radical and  $\dot{\text{C}}\text{H}_3\text{O}$  radical very slowly and these reactions can be negligible. However, hexamine was produced with relatively large initial quantum yield. From the result, it might be deduced that  $\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_2$  radical attacks ammonia and then formed diaminomethane as in Scheme 2, since hexamine was produced by the reaction of diaminomethane and formaldehyde.<sup>24</sup> However, diaminomethane was not detected by the analytical method used in this study. It may conclude that diaminomethane reacted with formaldehyde very quickly. In addition to hexamine, ethylenediamine is also detected. It means that  $\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_2$  radicals underwent their dimerization process. However, hexamine was much more produced than ethylenediamine. This result in-

