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 10. PdAr (Me) (tmeda) (Ar=1-naphthyl) was prepared similarly to the procedure for PdAr (Me) (tmeda) (Ar=Ph, C₆H₄-p-Me) in reference 9. Pd(1-naphthyl) (Me) (tmeda), 54%. ¹H NMR (CDCl₃, δ): 0.08 (s, 3H, Pd-CH₃), 2.01, 2.41, 2.60, 2.66 (s, 12H, N-Me₂), 2.40-2.74 (m, 4H, N-CH₂), 7.27, 7.43, 7.76, 8.94 (m, 7H, aromatic). ¹³C{¹H} NMR (CDCl₃, δ): -9.95 (Pd-CH₃), 47.50, 48.00, 48.69, 49.60 (N-Me₂), 59.24, 60.12 (N-CH₂), 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

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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 CHO radical¹ and Marz *et al.* proved the presence of this radical by ESR spectroscopy.² Arai *et al.*^{3,4} and Getoff *et al.*⁵⁻¹⁰ 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 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.¹¹ We also reported that the reactivity of CHO radical formed in the reduction is higher in aqueous state than in hydrated state,¹² and that the carbonylation can be also occurred in the presence of other substances.^{13,14} 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.¹⁵ It was found from the study that hydrazine was produced by the dimerization of $\dot{N}H_2$ 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 β -sulphonate.¹⁶ 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 ± 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.¹⁵ The lamp intensity of 184.9 nm was found to be 2.33×10^{17} quanta \cdot mL⁻¹ \cdot min⁻¹ 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 $50 \text{ m} \times 0.25 \mu\text{m}$ 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.¹⁷⁻¹⁹

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.

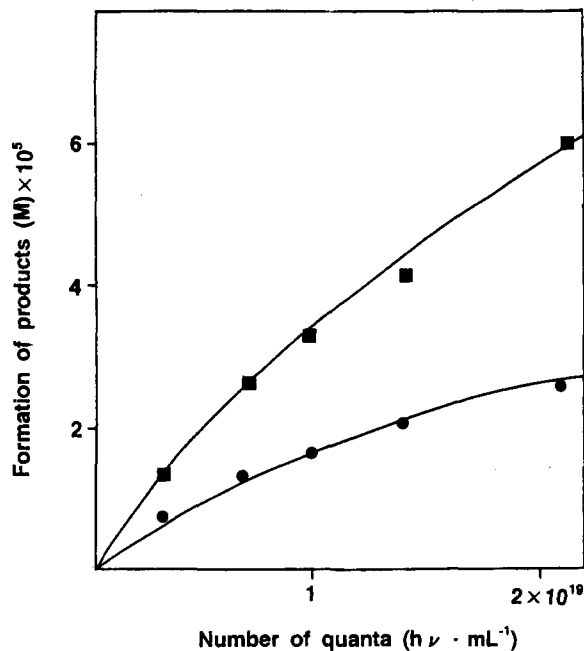


Figure 1. Formation of products after irradiation of methanol-ammonia mixture solution saturated with carbon monoxide at 25 °C ($X_{\text{MeOH}}=0.10$ and $X_{\text{ammonia}}=5 \times 10^{-4}$) as a function of the number of quanta: (■) is 1,1-dimethylhydrazine, (●) is dimethylamine.

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.

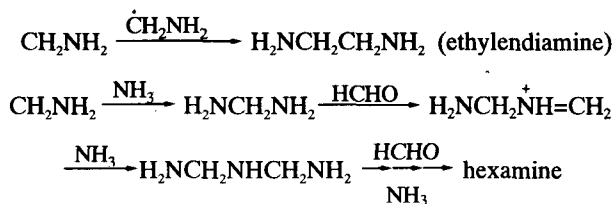
As shown in Figure 1, the product yields were not increased in proportion to the number of quanta. Therefore, we determined the initial quantum yields (Q_i), obtained from the slope of tangent line of the curve shown in Figure 1 and they are summarized in Table 1.

In aqueous methanol-ammonia mixture solution, most of the reactants absorb the 184.9 nm. The molar extinction coefficient (ϵ) 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 H_2O 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.^{20,21} 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	1.91×10^{-1}	6.77×10^{-1}
Ethyleneglycol	1.08×10^{-2}	2.15×10^{-3}
Glyoxal	5.19×10^{-4}	5.52×10^{-3}
Hydrazine	6.32×10^{-6}	2.10×10^{-6}
Methoxyamine	6.02×10^{-2}	3.44×10^{-2}
Hexamine	1.42×10^{-3}	9.03×10^{-3}
1,1-dimethylhydrazine	1.20×10^{-3}	1.05×10^{-3}
Dimethylamine	7.53×10^{-3}	1.20×10^{-3}
Formamide	3.91×10^{-6}	1.72×10^{-4}
Ethylenediamine	$<10^{-6}$	$<10^{-6}$

dicates that the reaction of $\dot{\text{C}}\text{H}_2\text{NH}_2$ radical with ammonia is superior than its dimerization process under the given condition.



Scheme 2.

In the presence of carbon monoxide, more hexamine was formed as shown in Table 1. The presence of carbon monoxide enhanced the production of formaldehyde. As a result, the formation of hexamine is also facilitated.

In summary, in the irradiation 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 UV light, carbonylation and amination were performed. The photochemical reaction was mainly initiated by attack of the H, $\text{CH}_3\dot{\text{O}}$ and $\dot{\text{C}}\text{H}_2\text{OH}$ radicals formed during the photolysis of methanol, and formaldehyde, ethyleneglycol, glyoxal, hydrazine, 1,1-dimethylhydrazine, dimethylamine, hydrazine, and formamide were produced as major products. In the presence of carbon monoxide, it reacts with H radical competitively, leading to the formation of $\dot{\text{C}}\text{HO}$ radical. The $\dot{\text{C}}\text{HO}$ radical enhanced the production of formaldehyde and glyoxal. With increasing the yield of formaldehyde, more hexamine was produced. However, the formation of ethyleneglycol and the other amination compounds except hexamine decreased in the presence of carbon monoxide.

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