

Photochemical Formation of Methylamine and Ethylenediamine  
from Gas Mixtures of Methane, Ammonia, and Water

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The photolysis of mixtures of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  with a low-pressure mercury lamp led to the formation of considerable amounts of methylamine and ethylenediamine with oxygen-containing compounds, ethane, and hydrogen.  $\text{CH}_2\text{NH}_2$  radicals formed during photolysis were detected by ESR applying a spin trap technique, and it was suggested that the coupling of the radicals leads to the formation of ethylenediamine.

Methylamine and ethylenediamine are produced by heterogeneous catalytic reactions of methyl halide and ethylene chloride, respectively, with ammonia at elevated temperature and in high pressure, and both products inevitably accompany secondary and tertiary amines.<sup>1)</sup> The photolysis of methane-ammonia mixtures at 123.6 nm results in the formation of methylamine,<sup>2)</sup> but in the similar experiments conducted at 147 nm Raulin et al.<sup>3)</sup> have observed no methylamine. The photochemical formation of ethylenediamine has not been found. We report here a new synthetic process of methylamine and ethylenediamine from the gaseous mixtures of methane, ammonia, and water taking place under the illumination of light.

The photolysis of  $\text{CH}_4\text{-NH}_3\text{-H}_2\text{O}$  mixtures was performed in a reaction chamber. The light source was a 50 W quartzware low-pressure mercury lamp which mainly emits 185 and 254 nm and was situated in the reaction chamber. Flasks containing given amounts of aqueous  $\text{NH}_3$  and water, respectively, were connected to the reaction chamber and were then heated with heating mantles. Methane gas was flowed onto the water surface, and the gas mixture of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  was brought into the reaction chamber. The products and unreacted gases were cooled in a condenser attached to the chamber, and the effluent gases were again circulated with a pump. The reaction products were determined by means of a gas chromatograph, a steam chromatograph, a high performance liquid chromatograph, and an amino acid analyzer. Amino acids were also confirmed by paper chromatography using butanol-acetic acid-water as eluent. Free radicals produced during the photolysis were detected by ESR applying a spin trapping technique. The sample for ESR measurements was prepared by bubbling the reaction gas into an  $\alpha$ -phenyl N-t-butyl nitron (PBN) solution in benzene which was placed in an ESR sample tube connected to the photolytic chamber. ESR spectra were recorded on a JES-ME-IX spectrometer with 100 kHz field modulation and 1 mW X-band microwave power.

Table 1. Products obtained in the photolysis of the gas mixtures of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}^{\text{a)}$ 

		Reaction gases (mmol)		
$\text{CH}_4$	275.2	275.2	275.2	275.2
$\text{NH}_3$	28.8	144	432	1080
		Products ( $\mu\text{mol}$ )		
$\text{CH}_3\text{NH}_2$	1809 (18.8) <sup>b)</sup>	2449 (32.1) <sup>b)</sup>	2322 (46.2) <sup>b)</sup>	1704 (54.7) <sup>b)</sup>
$\text{CH}_3\text{NO}_2$	4 (-)	9 (0.1)	-	2 (0.1)
$\text{CH}_3\text{CN}$	62 (0.6)	47 (0.6)	8 (0.2)	3 (0.1)
$\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$	730 (7.6)	1248 (16.3)	1453 (28.9)	879 (28.2)
$\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$	3 (-)	-	-	4 (0.1)
$\text{NH}(\text{CH}_3\text{COOH})_2$	2 (-)	7 (0.1)	6 (0.1)	-
$\text{NH}_2\text{CH}_2\text{CN}$	120 (1.2)	9 (0.1)	-	-
Glycylglycine	4 (-)	2 (-)	-	-
Histidine	7 (-)	2 (-)	-	-
$\text{CH}_3\text{OH}$	2067 (21.5)	1202 (15.7)	643 (12.8)	278 (8.9)
$\text{C}_2\text{H}_5\text{OH}$	115 (1.2)	34 (0.4)	8 (0.2)	3 (0.1)
$\text{HCHO}$	86 (0.9)	128 (1.7)	85 (1.7)	44 (1.4)
$\text{C}_2\text{H}_6$	4600 (47.9)	2500 (32.7)	500 (10.0)	200 (6.4)
$\text{H}_2$	18900	20800	20700	22200

a) Reaction time, 5 h; rate of gas circulation,  $1 \text{ dm}^3/\text{min}$ ; reaction temperature,  $100^\circ\text{C}$ ; mercury lamp, 50 W; the number of moles of consumed water, 4.6. b) Selectivity (the percentage of the product derived from methane).

Product variations are listed in Table 1. This result says that methylamine and ethylenediamine are major components in the nitrogen-containing products, and the total selectivities of these amines reach up to 83% at the highest concentration of ammonia. Since the yield of the secondary and tertiary amines is very low, this may constitute a unique method of preparing methylamine and ethylenediamine. The only amino acid listed is histidine, but small quantities of glutamic acid ( $0.1 \mu\text{mol}$ ), glycine ( $2.0 \mu\text{mol}$ ), and alanine ( $0.2 \mu\text{mol}$ ) were also detected. The products other than the amines involve methanol, ethanol, formaldehyde, ethane, and hydrogen. The yields of the oxygen-containing compounds and ethane decrease with an increase of the ammonia concentration. but the yield of hydrogen tends to increase slightly.

The ESR spectrum of PBN adduct of the radicals formed in the photolysis, under the experimental condition of  $[\text{CH}_4] = 275.2 \text{ mmol}$  and  $[\text{NH}_3] = 144 \text{ mmol}$ , is shown in Fig. 1A. The spectra obtained in the control experiments are also given for  $\text{H}_2\text{O}-\text{CH}_3\text{NH}_2$  and  $\text{H}_2\text{O}-\text{NH}_3$  systems in Figs. 1B and 1C. The hyperfine coupling constants of the corresponding PBN adducts are listed in Table 2 along with the radical assigned. The spectrum B was assigned to  $\cdot\text{CH}_2\text{NH}_2$  on the basis of the following reasons: (i) the major products are  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$  (48.4%).  $\text{C}_2\text{H}_6$  (32.7%), and  $\text{CH}_3\text{OH}$  (15.7%) as shown in Table 1 and the ESR signals of PBN- $\text{OCH}_3$  can

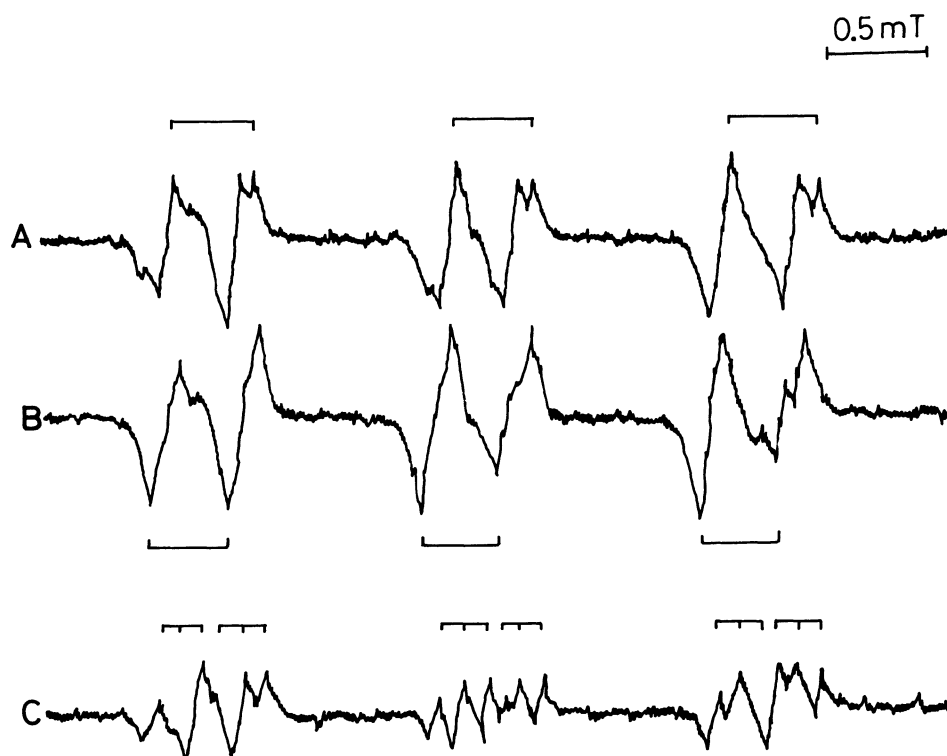


Fig. 1. ESR spectra obtained from the systems of  $\text{H}_2\text{O}-\text{CH}_4-\text{NH}_3$  (A),  $\text{H}_2\text{O}-\text{CH}_3\text{NH}_2$  (B), and  $\text{H}_2\text{O}-\text{NH}_3$  (C).

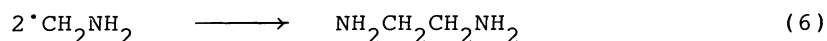
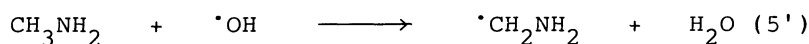
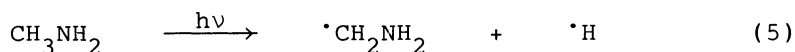
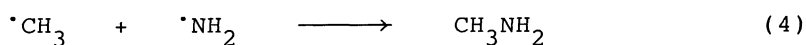
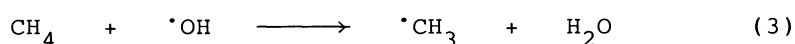
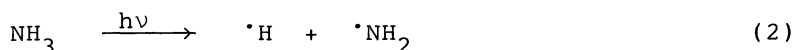
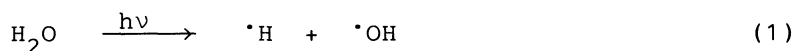
Table 2. ESR parameters of nitroxide radicals trapped by PBN

Spectrum in Fig. 1	Radical source	Hyperfine coupling constants of nitroxide / mT		Radical trapped
A	$\text{H}_2\text{O}, \text{NH}_3, \text{CH}_4$	$a^{\text{N}} = 1.48$	$a_{\beta}^{\text{H}} = 0.36$	$\cdot\text{CH}_2\text{NH}_2$
B <sup>a)</sup>	$\text{H}_2\text{O}, \text{CH}_3\text{NH}_2$	$a^{\text{N}} = 1.462$	$a_{\beta}^{\text{H}} = 0.351$	$\cdot\text{CH}_2\text{NH}_2$
C	$\text{H}_2\text{O}, \text{NH}_3$	$a^{\text{N}1} = 1.475$ $a^{\text{N}2} = 0.088$	$a_{\beta}^{\text{H}} = 0.290$	$\cdot\text{NH}_2$

a)  $\text{CH}_3\text{NH}_2$  was introduced into the photolytic chamber where  $\text{H}_2\text{O}$  had been pre-irradiated for 1 h. However, simultaneous irradiation of  $\text{H}_2\text{O}-\text{CH}_3\text{NH}_2$  yielded about 50:50 mixtures of the radicals corresponding to B and another spectrum (B'). The ESR parameters for B' were  $a^{\text{N}1} = 1.479$ ,  $a_{\beta}^{\text{H}} = 0.118$ ,  $a^{\text{N}2} = 0.220$  mT, and the trapped radical can be assigned to  $\text{CH}_3\text{NH}\cdot$ .

be seen as a minor component in Fig. 1A ( $a^{\text{N}} = 1.360$ ,  $a_{\beta}^{\text{H}} = 0.185$  mT),<sup>4)</sup> (ii) the coupling constants obtained are close to those of  $\text{PBN}-\text{CH}_3$  ( $a^{\text{N}} = 1.420$ ,  $a_{\beta}^{\text{H}} = 0.345$  mT)<sup>5)</sup> but  $\text{PBN}-\text{CH}_3$  was not detected for the system of  $\text{H}_2\text{O}-\text{CH}_4$ , and (iii) hyperfine splitting of amino nitrogen was not detected. However, the hfs of amino nitrogen should be observed in the nitrogen-centered PBN adduct ( $\text{PBN}-\text{NR}_2$ ), as in fact we obtained  $a^{\text{N}2} = 0.088$  mT for  $\text{H}_2\text{O}-\text{NH}_3$  (Table 2-C). Furthermore, the agreement of the hyperfine coupling constants for spectra A and B leads to the conclusion that the

radical trapped by PBN in the photolysis of  $\text{H}_2\text{O}-\text{NH}_3-\text{CH}_4$  mixtures is reasonably assigned to  $\cdot\text{CH}_2\text{NH}_2$ . Photolysis of water and ammonia occurs at 185 nm to form  $\cdot\text{OH}$ <sup>6)</sup> and  $\cdot\text{NH}_2$ ,<sup>7)</sup> respectively. OH radicals abstract a hydrogen atom from methane,<sup>8)</sup> and the coupling reaction of  $\cdot\text{CH}_3$  and  $\cdot\text{NH}_2$  results in the formation of methylamine. The photolysis of methylamine<sup>9)</sup> and/or the H-abstraction from methylamine by OH radical give  $\text{CH}_2\text{NH}_2$  radicals which finally lead to ethylenediamine. Thus, the photochemical formation of methylamine and ethylenediamine is considered to follow the scheme.



The reaction routes on the oxygen-containing compounds and ethane were discussed elsewhere,<sup>10)</sup> but the detailed mechanism involving the formation of amino acids is under study.

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