Hydrazine Formation in the γ-Radiolysis of an Aqueous Solution of Ammonia

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The effect of additives on the γ-radiolysis of liquid ammonia has been studied by only a few investigators.[1,2] In the present work, the hydrazine formation in the γ-radiolysis of a mixture of liquid ammonia and water at a high-dose irradiation was studied. Hydrazine was determined by the Watt and Chrisp method.[3] Figure 1 shows the relationships between the yield of hydrazine and the concentration of ammonia at room temperature and at $-50°C$. At the irradiation temperature of $-50°C$, the yield of hydrazine increases gradually to a maximum value at about 85 mol. %, and then decreases with an increase in the concentration of ammonia. On the other hand, the maximum yield of hydrazine is obtained at about 50 mol. % of ammonia when irradiation is performed at room temperature. The yield of hydrazine at $-50°C$ is larger than that at room temperature at 100 mol. % of ammonia. The dashed lines represent the yield of hydrazine which may be expected if the formation of hydrazine is unaffected by the presence of water.

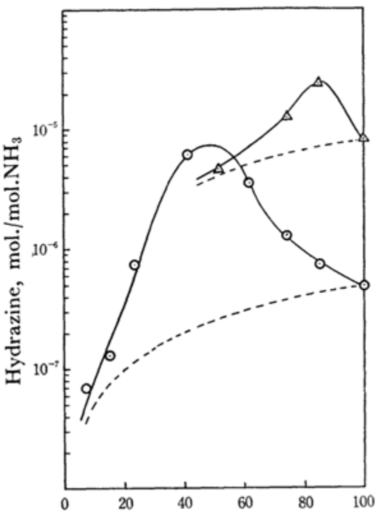

Fig. 1. Yield of hydrazine as a function of ammonia concentration at room temperature and at $-50\pm2°C$ when irradiated to a total dose of 9.15×10^6 r. at a dose rate of 4.5×10^4 r./hr.
○ Room temperature
△ $-50\pm2°C$

As is shown in Fig. 1, the observed yields of hydrazine are larger than those to be expected from the molar fraction of ammonia and water. This indicates that the formation of hydrazine is influenced in some way by the interaction of ammonia with water. From the ionization potential[4] and the proton affinity[5] for ammonia, the proton transfer to ammonia may be expected to occur:

$$NH_3 + H_2O^+ \rightarrow NH_4^+ + OH \qquad (1)$$

though another possibility cannot be excluded:

$$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$$

The enhancement in the yield of hydrazine can be explained if the neutralization of NH_4^+ were to produce amino radicals as follows:

$$NH_4^+ + e^-_{amm} (\text{or } e^-_{aq}) \rightarrow \cdot NH_2 + H_2 \qquad (2)$$

$$\cdot NH_2 + \cdot NH_2 \rightarrow N_2H_4 \qquad (3)$$

On the basis of the above mechanism, we may say that the addition of ammonium ion would also contribute to the increment in the formation of hydrazine.

The details of this will be described elsewhere.

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