Radiation Synthesis of Ethylamine from Ethane–Ammonia Systems. Effect of Nitric Oxide Addition

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Formation of ethylamine was observed in the γ-radiolysis of the ethane–ammonia system: the maximum G value was 0.5. Using oxygen as a radical scavenger, it was found that the ethylamine was formed *via* radical and ion intermediates. Addition of excess nitric oxide suppressed the ethylamine yield, but $G(C_2H_5NH_2)$ increased to 1.2 on addition of an optimum amount. This was attributed to the reduction of acetaldoxime by hydrogen atoms or alkyl radicals, after acetaldoxime had been formed by the reaction between ethyl radicals and the nitric oxide added as a scavenger.

Radiolysis of mixtures of hydrocarbons and ammonia has been studied by many workers. Ethylamine was produced in the irradiated ethylene–ammonia system[1] and propylamine was reported to be formed in the n-butane–ammonia system.[2]

In this study, the radiolysis of the ethane–ammonia system and especially the mechanism of ethylamine formation was examined. When an optimum amount of nitric oxide was added to the ethane–ammonia system, the ethylamine yield was enhanced, but when added in excess, the usual radical scavenging action of nitric oxide was observed. A mechanism was proposed for the formation of the amine in the presence of the additive.

Experimental

Ethane (99.7%, Takachiho Chemical) was used after purification by trap to trap distillation in a vacuum line. Ammonia (99.99%, Matheson) was dried with sodium metal and purified likewise. Nitric oxide (99.8%, Takachiho Chemical) was used after removal of non-condensible gases at -196 °C. Oxygen (99.7%) was used without further purification.

Gases were irradiated at room temperature by ^{60}Co gamma rays at 5.4×10^5 R/hr, in 40 ml Pyrex glass ampoules. The dose of gamma rays was measured with a Fricke dosimeter. The G value was calculated assuming that the mass absorption coefficient was proportional to the total number of electrons in the system.

Radiolysis products, amines and hydrocarbons were analyzed by a gas chromatograph equipped with a flame ionization detector at 70 °C. To obtain reproducible results with ethylamine, grease, metal and rubber were eliminated as much as possible, and nitrogen gas mixed with 10% ammonia was used as carrier gas. The column consisted of a 2 m (10% KOH+10% TEPA on Porapak Q) and a 1 m (10% KOH+10% Quadrol on Porapak Q) column. Nitric oxide, hydrogen and methane were analyzed by volumetry and mass spectrometry.

Results and Discussion

Ethylamine Formation from Ethane–Ammonia System. When ethane–ammonia mixtures were irradiated, hydrogen, nitrogen methane, propane, n-butane and methylamine were formed besides ethylamine. Yield of ethylamine, n-butane and others are shown in Fig. 1 as a function of the mixing ratio. The yield of n-butane
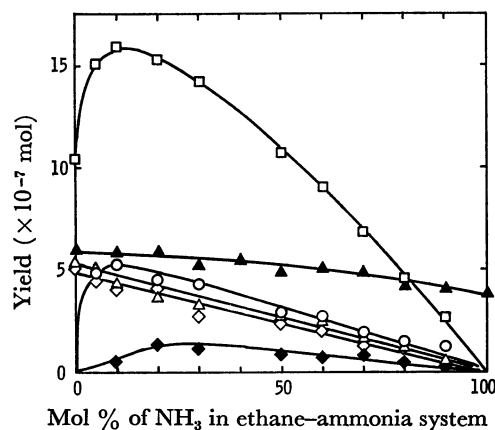

Fig. 1.   Composition dependence of product yields.
$\bigcirc$; ethylamine, $\square$; n-butane, $\blacklozenge$; methylamine, $\triangle$; methane, $\diamondsuit$; propane, $\blacktriangle$; hydrogen ($\times 0.1$)
Gamma rays; total dose 10 Mrad. Irradiated gas; total amount $C_2H_6+NH_3=3.43 \times 10^{-3}$ mol, pressure 2 kg/cm^2, in 40 ml glass ampoules.

increased with increasing ammonia concentration until $C_2H_6/NH_3=90/10$, then decreased almost linearly on further addition of ammonia. The yield of ethylamine showed similar characteristics with a maximum G value of 0.5 at the same ammonia content.

The effect of addition of oxygen to this system was studied. The yield of n-butane was effectively reduced on addition of the radical scavenger, oxygen, as shown in Table 1. Therefore, n-butane should be formed predominantly by the following radical reaction:
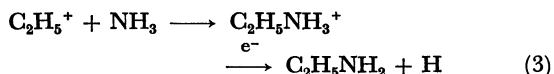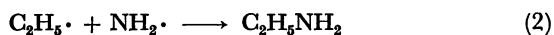
TABLE 1.   EFFECT OF ADDED OXYGEN IN THE RADIOLYSIS OF THE ETHANE–AMMONIA SYSTEM

% added oxygen	Yields	
	ethylamine ($\times 10^{-7}$ mol)	n-butane ($\times 10^{-7}$ mol)
0	4.90	13.65
0.48	4.45	4.10
1.20	3.63	1.10
3.12	3.02	0.75
6.72	3.37	0.73
12.72	3.30	0.75

Gamma rays; total dose$=8.64$ Mrad; Irradiated gas; composition $C_2H_6/NH_3=90/10$, pressure$=2$ kg/cm, in 40 ml glass ampoules.

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow n\text{-}C_4H_{10} \qquad (1)$$
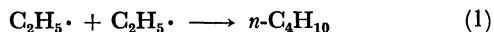
On the other hand, the ethylamine formation was considerably suppressed by addition of 3.12% oxygen, but not further affected by further addition of oxygen. This suggests the following two reactions for ethylamine formation: the radical reaction 2, which is inhibited by the presence of oxygen, and the ionic reaction 3, which is not.

$$C_2H_5\cdot + NH_2\cdot \longrightarrow C_2H_5NH_2 \qquad (2)$$

$$C_2H_5^+ + NH_3 \longrightarrow C_2H_5NH_3^+$$
$$\xrightarrow{e^-} C_2H_5NH_2 + H \qquad (3)$$

In the radiolysis[1] and the photolysis[3] of the ethylene–ammonia system, ethylamine formation has been attributed to the radical reaction. An ionic reaction similar to Reaction 3 has been suggested for propylamine formation in the radiolysis of the n-butane–ammonia system.[2]

Ethylamine Formation in the Presence of Nitric Oxide.
The effect of added nitric oxide on the radiolysis of the ethane–ammonia system was studied for the mixture containing 10% ammonia (the composition at which the maximum yield of ethylamine was observed (Fig. 2)).
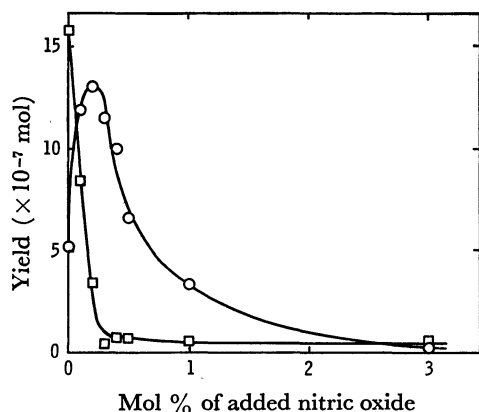

Fig. 3. Effect of absorbed dose on n-butane formation and nitric oxide consumption.
n-butane yield for added nitric oxide concentration, □; 0.1%, ◨; 0.2%, ■: 0.4%, residual amount of nitric oxide ($\times 0.1$) for initial concentration, ⊖; 0.1%, ⊙; 0.2%, ◎; 0.4%.
Gamma rays; dose rate 5.4×10^5 R/hr. Irradiated gas; composition $C_2H_6/NH_3 = 90/10$, pressure 2 kg/cm², in 40 ml glass ampoules.

Fig. 2. Effect of added nitric oxide on product yields.
○; ethylamine, □; n-butane
Gamma rays; total dose 10 Mrad. Irradiated gas; composition $C_2H_6/NH_3 = 90/10$, pressure 2 kg/cm², in 40 ml glass ampoules.

Fig. 4. Effect of absorbed dose on ethylamine yield. initial concentration of nitric oxide, ○; 0%, ◑; 0.1%, ◐; 0.2%, ●; 0.4%.
Experimental conditions; same as in Fig. 3.

The yield of ethylamine increased significantly on adding small amounts of nitric oxide, then decreased on further addition, while the yield of n-butane decreased monotonically. The maximum $G(C_2H_5NH_2)$ value, 1.2, obtained with 0.2% added NO was 2.4 times larger than that obtained without the additive.

It is difficult to interpret the increase of the ethylamine yield with a slight addition of nitric oxide according to the mechanisms (2) and (3). Nitric oxide addition should suppress ethylamine formation by either the radical or ionic reaction 2 or 3, because nitric oxide is able to scavenge ethyl and amino radicals, or because it interacts with ethyl cations due to its very low ionization potential ($IP = 9.24$ eV). Therefore, a third mechanism must be considered for the enhanced formation of amine (See following section).

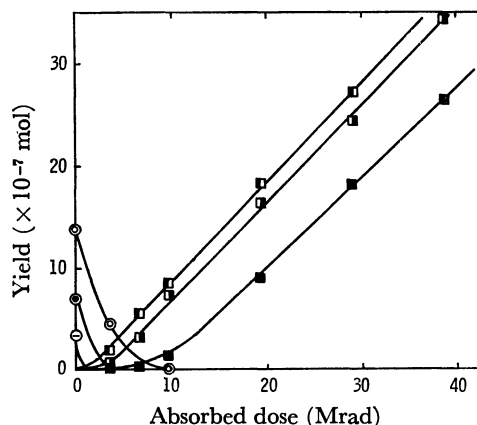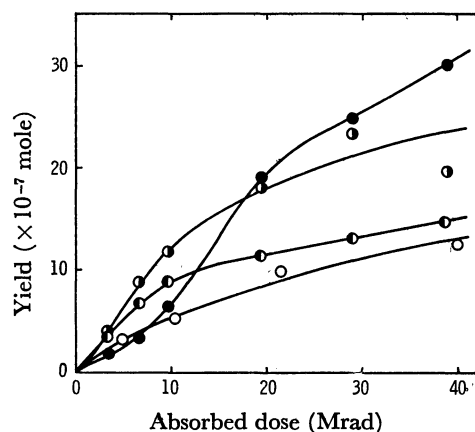*Effect of Dose in the Presence of Nitric Oxide.* At

nitric oxide concentrations of 0.1, 0.2, and 0.4%, the effect of absorbed dose on the radiolysis of the ethane–ammonia–nitric oxide system was studied. The yield of n-butane and the amount of nitric oxide which remained are shown in Fig. 3, and the yield of ethylamine in Fig. 4. In each system, the nitric oxide concentration decreased rapidly. An initial $G(-NO)$ value of 22.5 was obtained for the system containing 0.4% nitric oxide.

In the formation of n-butane, induction periods appeared. Their length was closely related to the initial concentration of nitric oxide. The longest period was observed with 0.4% nitric oxide. Reaction 1 is suppressed during the induction period when nitric oxide is present. After all the nitric oxide is consumed, the amount of n-butane formed increases linearly with the absorbed dose.

The ethylamine yield in the absence of nitric oxide

increased linearly with the absorbed dose at relatively low doses and was close to saturation at about 30 Mrad. On addition of 0.1 and 0.2% nitric oxide, the yield over the whole range of absorbed dose was about 1.2 and 2 times larger, respectively, than in the system without the additive. On addition of 0.4% nitric oxide, the yield of ethylamine was smaller than that of the system without nitric oxide up to an absorbed dose of 10 Mrad. The region where the yield of ethylamine was smaller may be regarded as the induction period for ethylamine formation. After the induction period, i.e. after the nitric oxide had disappeared, the yield of ethylamine increased significantly. It must be noted that this phenomenon is similar to that in the n-butane formation.

Again, this increase in the amine yield at high dose for large initial nitric oxide concentration can not be explained by the two amine formation mechanisms (2) and (3). After the induction period, the nitric oxide may be assumed to be exhausted and alkyl radicals be formed without being scavenged. Therefore, a third mechanism was studied which explained the increased amine formation with these assumptions.

Role of Acetaldoxime in Ethylamine Formation. It has been known that a nitroso compound or its oxime tautomer is formed when an alkyl radical is scavenged by nitric oxide.[4] The formation of cyclohexylamine has been reported in the radiolysis of liquid cyclohexane with nitric oxide added.[5] The reaction pathway consisted of the scavenging of a cyclohexyl radical by nitric oxide and the reduction of the tautomer, cyclohexanonoxime, by alkyl and hydrogen radicals. Similarly, the following reactions may be expected to give ethylamine in the ethane–ammonia system;
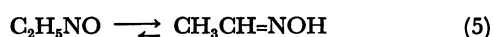
$$C_2H_5\cdot + NO \longrightarrow C_2H_5NO \qquad (4)$$

$$C_2H_5NO \rightleftarrows CH_3CH=NOH \qquad (5)$$

$$CH_3CH=NOH \xrightarrow{R\cdot,\; H\cdot} C_2H_5NH_2 \qquad (6)$$

TABLE 2.   EFFECT OF ADDITIVES ON $G(C_2H_5NH_2)$

Reaction system	$G(C_2H_5NH_2)$
$C_2H_6(90)+NH_3$ (10)	0.5
$C_2H_6(90)+NH_3(10)+NO$ (0.2%)	1.2
$C_2H_6(100)+NO$ (0.1−1%)	<0.1
$C_2H_6(90)+NH_3(10)+CH_3CH=NOH$ (2%)	1.2
$C_2H_6(100)+CH_3CH=NOH$ (2%)	≈0.1
$NH_3(100)+CH_3CH=NOH$ (2%)	0.3

Gamma rays; total dose=10 Mrad. Irradiated gas; pressure 2 kg/cm, in 40 ml glass ampoules.

Reaction 6 could occur in the gas phase, since the vapor pressure of acetaldoxime is 10.0 Torr at 25.8 °C.

Table 2 shows the $G(C_2H_5NH_2)$ values which were obtained for various combinations of the reactants, ethane and ammonia, as well as the additives, nitric oxide and acetaldoxime. For ethane–ammonia mixtures above, the maximum G value was 0.5, but was 1.2 in the presence of 0.2% nitric oxide. The value was also 1.2 for the ethane, ammonia and 2% acetaldoxime mixture.

The direct reaction between ethane and nitric oxide or acetaldoxime and that between ammonia and acetaldoxime can be excluded from the mechanism for the enhanced ethylamine formation. Acetaldoxime added to the ethane–ammonia mixture plays the role of the intermediate in ethylamine formation as effectively as nitric oxide does. Thus, the third mechanism (expressed by Reactions 4, 5, and 6) seems plausible from these qualitative results. As shown in Figs. 2 and 4, the ethylamine yield increased at an optimum amount of nitric oxide, and decreased with addition of excess. These observations are also consistent with the proposed mechanism.

Nitric oxide has been used as a radical scavenger in radiolysis. However, it has been noted that its use sometimes makes the main reaction scheme more complex.[6] This study exemplifies a case in which the scavenging reaction of nitric oxide results in yields of the product that are the same as those obtained without the additives, clearly showing the necessity of taking care in using this compound in the study of radiolysis. At the same time, it has been demonstrated that a radical scavenger could be used to enhance the formation of a reaction product, as has been shown in one other system.[7] This point is of interest for preparative radiation chemistry.

References

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