

The Reactions of NH Radicals with Ethylene and Propene in the Liquid Phase

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The photolysis of hydrogen azide was studied in liquid ethylene, propene, and the mixture with ethane at the temperature of Dry Ice–methanol. The products observed were aziridine (0.18), ammonia (0.16), and nitrogen (1.0) from the ethylene solution and 2-methylaziridine (0.33), allylamine (0.12), ammonia (0.17), and nitrogen (1.0) from the propene solution. The values in parentheses show the yields relative to that of nitrogen. The relative yields were independent of the concentration of hydrogen azide in the range of $0.8\text{--}8 \times 10^{-3}$ mol dm^{-3} . The reaction of $\text{NH}(^1\Delta)$ radicals with olefin consists of three processes: the addition to double bond, the insertion into the C–H bond, and the deactivation to the $^3\Sigma^-$ state. The branching ratios and the relative rate constants of the reactions of $\text{NH}(^1\Delta)$ radicals with ethylene, propene, and ethane were estimated.

Since NH is isoelectronic with O and CH_2 , it is expected that the reactions of NH will be similar to those of O and CH_2 . In spite of many investigations, the reactions of NH are not understood well. The main reason is that most studies failed to detect the NH-containing products. Recently, we found the amine formation in the photolysis of hydrogen azide in liquid ethane, propane, and isobutane at the temperature of Dry Ice–methanol by treating the products with NaOH.^{1,2)} The amine formation was explained by the insertion reaction of the singlet $\text{NH}(^1\Delta)$ into the C–H bond of paraffin. If the singlet NH reacts with the olefin like the singlet O or CH_2 reacts with, then the formation of aziridine, the product of NH added to the double bond of ethylene, can be expected.

Many investigations in the gas phase failed to detect the aziridine formation.^{3–6)} Jacox and Milligan photolyzed a mixture of hydrogen azide and ethylene in the Ar matrix at 4 K and detected aziridine by infrared absorption spectroscopy. No kinetic study, however, was given.⁷⁾

The photolysis of hydrogen azide was studied in liquid ethylene and propene at the temperature of Dry Ice–methanol in order to investigate the reactivity of NH radicals to olefin.

Experimental

The experimental methods were essentially the same as those described in the previous papers.^{1,2)} Hydrogen azide was prepared *in vacuo* by heating a mixture containing sodium azide and an excess amount of stearic acid; it was used after having been dried with phosphorus pentoxide and degassed at -120°C . Pure grade ethylene (Yokohama Chemicals Co.), ethane, and propene (Takachiho Shoji Co.) were used after the low temperature distillation. The mixture of hydrogen azide ($8\text{--}80\ \mu\text{mol}$) and hydrocarbon ($\approx 10\ \text{mmol}$) was prepared in a quartz tube of 8 mm o.d. and liquefied at the temperature of Dry Ice–methanol. The amount of the solution was about 1 cm^3 . The solution was irradiated with a medium pressure mercury lamp (Toshiba H-400P) through a filter (Toshiba UV 27) which cut off the light shorter than 250 nm.

After the irradiation, non-condensable products at the temperature of liquid nitrogen were analyzed with a combination of a Toepler pump, a gas burette, and a CuO furnace at 300°C . The solvent hydrocarbon was evacuated at a temperature lower than -80°C . Less volatile products, including unreacted hydrogen azide, were passed through

a trap packed with NaOH coated glass wool. The products thus obtained were analyzed with GLC, using a column packed with Amine 220 on NaOH coated Celite 545 (Gasukuro Kogyo Co., 5 m in length) at 40°C . For the identification of the products, a mass spectrometer was used.

Results

The products observed in the ethylene solution of hydrogen azide were nitrogen, ammonia, and aziridine. Beside these products, small peaks of unidentified products were observed on the gas chromatogram. These peaks were too small to be analyzed. Neither methane nor hydrogen formation was observed. The products observed in the propene solution were nitrogen, ammonia, 2-methylaziridine, and allylamine.

To check the validity of the present analytical method, known amounts of ammonia and aziridine were added to the ethylene solution of hydrogen azide. After having been passed through the NaOH trap, less volatile parts were analyzed with GLC. Figure 1 shows the amounts of aziridine and ammonia recovered as functions of those introduced in the solution. The recovery was almost 100%.

Figures 2 and 3 show the relative yields of the products obtained in the ethylene and propene solutions, respectively, as functions of the concentration of hydrogen azide. The relative yields of the products

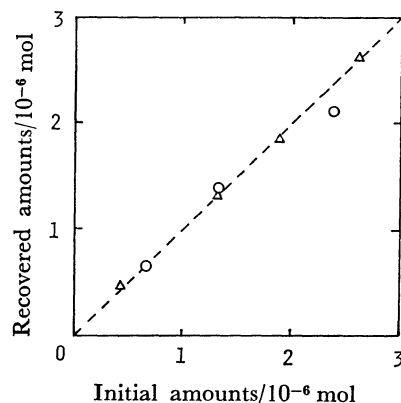


Fig. 1. The amounts of aziridine and ammonia recovered from the ethylene solution of hydrogen azide against the amounts introduced in the solution. ○: Aziridine, △: ammonia.

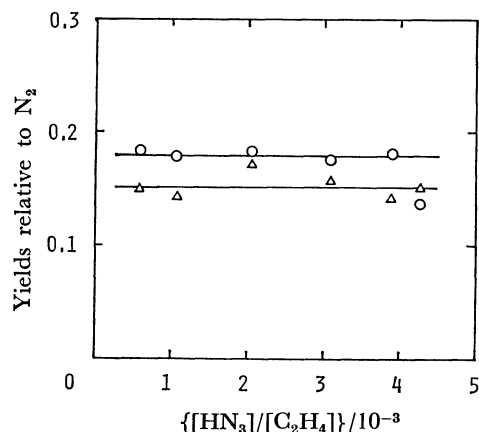


Fig. 2. Relative yields of the products as functions of the $[\text{HN}_3]/[\text{C}_2\text{H}_4]$ ratio obtained in the photolysis of the ethylene solution of hydrogen azide.
○: Aziridine, △: ammonia.

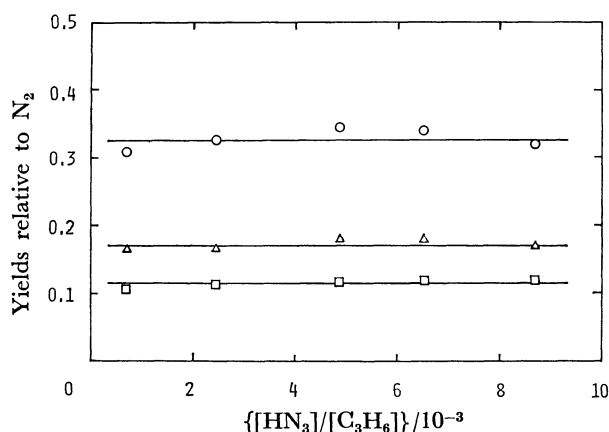


Fig. 3. Relative yields of the products as functions of the $[\text{HN}_3]/[\text{C}_3\text{H}_6]$ ratio obtained in the photolysis of the propene solution of hydrogen azide.
○: 2-Methylaziridine, □: allylamine, △: ammonia.

were independent of the concentration of hydrogen azide. The yields of aziridine and ammonia were 0.18 ± 0.02 and 0.16 ± 0.02 times that of nitrogen in the case of ethylene. In the case of propene, the yields of 2-methylaziridine, allylamine, and ammonia were 0.33 ± 0.02 , 0.12 ± 0.01 , and 0.17 ± 0.01 times that of nitrogen.

When the mixture of ethylene and ethane were used as the solvent, the ethylamine formation competed with the aziridine formation. Figure 4 shows the relative yields of the products obtained in the mixture of ethane, ethylene, and hydrogen azide, as functions of the mole fraction of ethylene. In this case, the $[\text{HN}_3]/([\text{C}_2\text{H}_4] + [\text{C}_2\text{H}_6])$ ratio was kept constant at 2.0×10^{-3} .

When ethylene was added to the propene solution of hydrogen azide, the aziridine formation competed with the formations of 2-methylaziridine and allylamine, as is shown in Fig. 5. In this case, the $[\text{HN}_3]/([\text{C}_2\text{H}_4] + [\text{C}_3\text{H}_6])$ ratio was 2.5×10^{-3} .

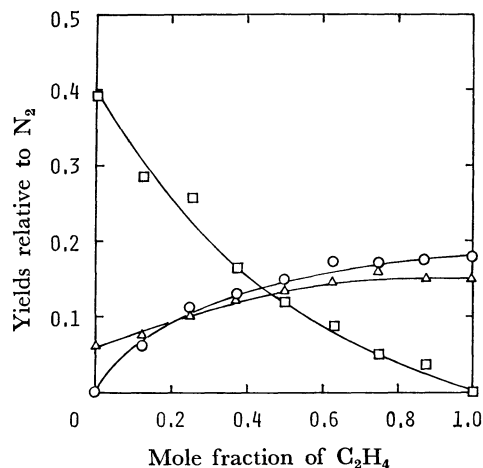


Fig. 4. Effect of ethylene on the photolysis of the ethane solution of hydrogen azide as functions of the mole fraction of ethylene.
○: Aziridine, △: ammonia, □: ethylamine.

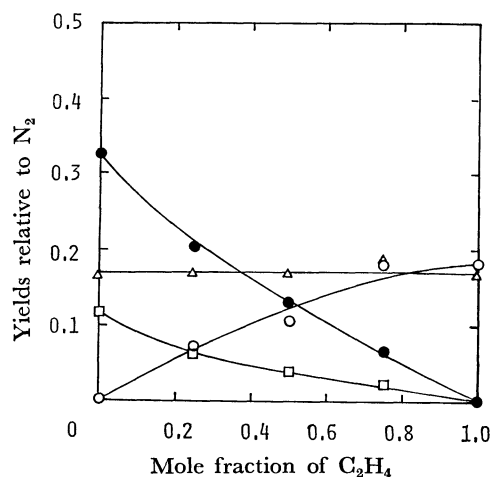
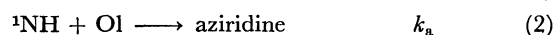
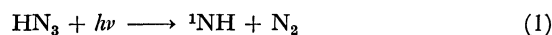
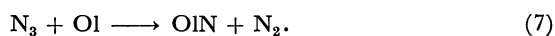
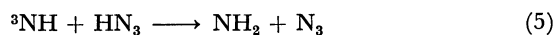


Fig. 5. Effect of ethylene on the photolysis of the propene solution of hydrogen azide as functions of the mole fraction of ethylene. The $[\text{HN}_3]/([\text{C}_2\text{H}_4] + [\text{C}_3\text{H}_6])$ ratio is 2.5×10^{-3} .
○: Aziridine, ●: 2-methylaziridine, □: allylamine, △: ammonia.

Discussion

Reaction Mechanism. In previous papers,^{1,2)} the amine formation in the photolysis of hydrogen azide in liquid paraffin was explained by the insertion of $\text{NH}(^1\Delta)$ into the C-H bond of paraffin. As was shown in Fig. 4, when ethylene was added to the ethane solution of hydrogen azide, the ethylamine formation decreased and the aziridine formation increased. In the case of propene, the allylamine/2-methylaziridine ratio was independent of the concentration of hydrogen azide, as is shown in Fig. 3. These results suggest that aziridine is formed by the addition of the singlet NH to the double bond of olefin. To explain the results obtained, the following reaction mechanism was considered:





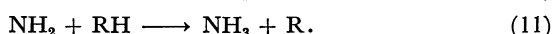
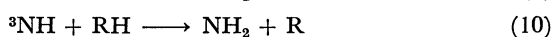
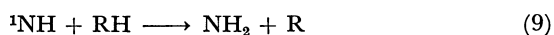
Here, ${}^1\text{NH}$ and ${}^3\text{NH}$ represent the NH radicals in the $a^1\Delta$ and $X^3\Sigma^-$ states respectively. Ol means olefin used. In the case of propene, allylamine is a possible insertion product. The insertion into the vinylic C-H bond will give vinylamine, which is known to be an unstable compound at room temperature; therefore, the vinylamine, even if formed, will not be detected.

In the case of paraffin, Reaction 8 was assumed for the reaction of N_3 .^{1,2)}



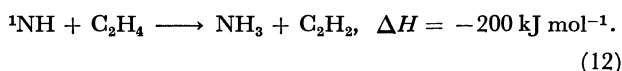
Since olefin is known as a radical scavenger, Reaction 7 is assumed instead of Reaction 8. The product OlN will give a polymer.⁸⁾

As shown in Figs. 2 and 3 and in the previous papers,^{1,2)} the relative yield of ammonia in the olefin solution was larger than that in the paraffin solution and was independent of the concentration of hydrogen azide. The following reactions might be considered for the ammonia formation:

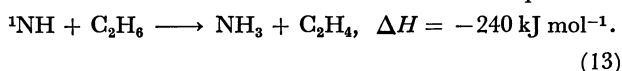


Here, RH denotes an hydrocarbon molecule. If these reactions are taken into the mechanism, it is necessary to assume that the rate of the abstraction by ${}^1\text{NH}$ or ${}^3\text{NH}$ from ethylene is almost the same as that from propene and faster than that from paraffin including isobutane. This assumption is not acceptable, since olefin is known as a radical scavenger and the rate is faster than that of the hydrogen atom abstraction. The rate of the abstraction is known to depend on the strength of the C-H bond included.

Another possible mechanism for the ammonia formation is a molecular hydrogen abstraction from hydrocarbon:



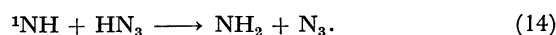
Reaction 12 can successfully explain the concentration dependence of the ammonia formation. If Reaction 12 occurred in the case of ethylene, we should also consider the similar reaction in the case of paraffin:



By the inclusion of Reaction 13 in the mechanism, the concentration dependence of the ammonia formation should have an intercept. This was not the case, as was shown in the previous paper.²⁾ There is no reason to assume that Reaction 12 is important in the case of olefin while the similar reaction is not important in the case of paraffin. Thus it may be concluded that a reaction such as Reaction 12 is not important.

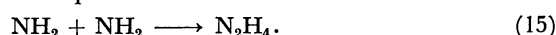
The remaining sources of ammonia are Reactions

5, 6, and 14:



In fact, Reaction 14 has been considered to be important in the case of paraffin to explain the result that the relative yield of amine decreased with an increase in the concentration of hydrogen azide.²⁾ In the case of olefin, Reaction 14 should not be important, since the relative yield of aziridine or amine is constant for the change in the concentration of hydrogen azide. Thus, the remaining sources of ammonia are Reactions 5 and 6.

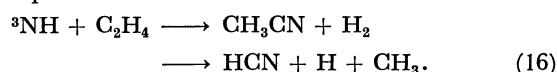
In the case of paraffin, Reaction 15 has been considered to explain the material balance and the concentration dependence of the ammonia formation:



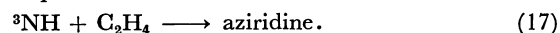
If Reaction 15 is included in the mechanism, the relative yield of ammonia should linearly increase with an increase in the concentration of hydrogen azide. In the case of olefins, however, this is not the case, as is shown in Figs. 2 and 3. That is, the rate of Reaction 15 is negligibly small in the olefin solution.

As was discussed above, it was necessary to ignore Reactions 14 and 15 to explain the results obtained with the olefin solution. In the case of paraffin, the rate of Reaction 14 has been considered to depend on the solvent.²⁾ Although the detailed interaction is unknown, the solvent effect seems to be the only way to explain the difference in the hydrogen azide concentration dependence of ammonia formation in paraffin and in olefin solutions.

Cornell *et al.* assumed the reactions of triplet NH with ethylene to explain the formation of HCN, CH_3CN , H_2 , and CH_4 in the photolysis of a mixture of hydrogen azide and ethylene in the gas phase at room temperature:⁴⁾



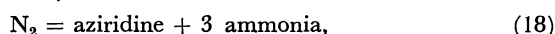
If Reaction 16 is included in the mechanism, the H_2 and CH_3CN formations should be observed. However, these were not found, as shown in the Results section. An intermediate of Reaction 16 may be a vibrationally excited aziridine in the triplet state, which may be efficiently deactivated to the ground state under the present experimental conditions:



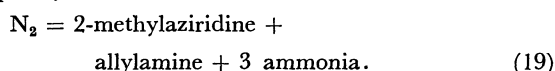
A similar addition reaction to the double bond of olefin has been considered in the cases of triplet O and CH_2 .⁹⁻¹²⁾ If Reaction 17 is included in the mechanism, the relative yield of ammonia should increase while that of aziridine should decrease with an increase in the concentration of hydrogen azide, because of the competition between Reactions 5 and 17. This is not the case, as shown in Figs. 2 and 3. That is, the addition reaction, if it occurred, should be negligible compared with Reaction 5. In the case of O atoms, the addition rate of the triplet oxygen has been measured to be about two orders of magnitude slower than that of the singlet O atoms at room temperature.¹⁰⁾ In the case of NH radicals, Cornell

et al. estimated the rate of Reaction 16 to be about $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature.⁴⁾ Recently, McDonald *et al.* have determined the rate constant for the reactions of the singlet NH with ethylene to be $2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature.¹³⁾ That is, the rate of triplet NH is about three orders of magnitude smaller than that of the singlet NH. If Reaction 17 has some activation energy, the rate will become smaller under the present experimental conditions.

Material Balance. From the above reaction mechanism, the following relations are expected to hold between the amounts of the products: for ethylene;

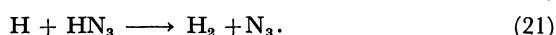
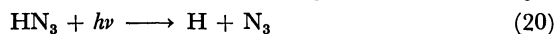


for propene;

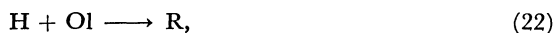


Using the values shown in Figs. 2 and 3, the (aziridine+3 ammonia)/N₂ and the (2-methylaziridine+allylamine+3 ammonia)/N₂ ratios can be estimated to be 0.67 ± 0.08 and 0.96 ± 0.04 respectively. In the case of propene, the ratio is close to unity, while the ratio in the case of ethylene is considerably smaller than unity. That is, about 30% of NH-containing products are missing in the case of ethylene. Similar results have been obtained in the case of paraffin, and hydrazine was assumed to be the missing product (Reaction 15). In the case of ethylene, however, the hydrazine formation was ignored, as was discussed in the previous section. It is necessary to consider another mechanism for the missing products. This point will be discussed later.

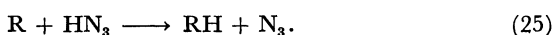
In the case of paraffin, hydrogen formation has been observed. This was explained by assuming that about 9% of the photodissociation of hydrogen azide leads to the formation of hydrogen atom and N₃:²⁾



In the presence of an excess amount of olefin, the scavenging of hydrogen atoms by olefin may be more important than Reaction 21. This explains the absence of hydrogen formation in the olefin solution:



where R denotes a C₂H₅ or C₃H₇ radical. There is a possibility that the reaction of R affects the total yield of nitrogen. The following reactions can be considered for the reactions of alkyl radicals:



If Reaction 23 is important, the nitrogen formation is not affected and Eqs. 18 and 19 still hold. If Reaction 24 is important, Reaction 20 has to be taken into account for the formation of nitrogen. The correction is about 9%. If Reaction 25 is important, the correction of 18% is necessary for the yield of nitrogen. Although it is difficult to decide which reaction is important under the present experimental

conditions, the correction of 18% is too large for the case of propene.

Relative Rate Constant. Assuming the above reaction mechanism, the following rate constant ratios can be estimated by using the yields of products shown in Figs. 2 and 3.

$$k_{ae}/k_{de} = \text{aziridine/ammonia} = 1.1 \pm 0.2 \quad (26)$$

$$k_{ap}/k_{dp} = 2\text{-methylaziridine/ammonia} = 1.9 \pm 0.1 \quad (27)$$

$$k_{ip}/k_{dp} = \text{allylamine/ammonia} = 0.67 \pm 0.04 \quad (28)$$

$$k_{ap}/k_{ip} = 2\text{-methylaziridine/allylamine} = 2.9 \pm 0.3, \quad (29)$$

where subscripts a, i, and d stand for the addition, insertion, and deactivation reactions of the singlet NH with ethylene (e) or propene (p) respectively.

From the results shown in Fig. 5, the relative rate constant of the reaction of the singlet NH with ethylene to that with propene can also be estimated. Using the steady-state treatment, Eqs. 30, 31, and 32 can be obtained for the relative yields of the products:

$$\text{aziridine}/\text{N}_2 = k_{ae}c/k_e X \quad (30)$$

$$2\text{-methylaziridine}/\text{N}_2 = k_{ap}c/k_p (1-X) \quad (31)$$

$$\text{allylamine}/\text{N}_2 = k_{ip}c/k_p (1-X), \quad (32)$$

where $X = k_e[\text{C}_2\text{H}_4]/(k_e[\text{C}_2\text{H}_4] + k_p[\text{C}_3\text{H}_6])$. The symbol c means $(\text{N}_2 - 2\text{NH}_3)/\text{N}_2$, which was almost independent of the fraction of ethylene, as is shown in Fig. 5. k_e and k_p are the sum of the rate constants for the addition, insertion, and deactivation of the singlet NH with ethylene and propene respectively.

In order to estimate the k_e/k_p ratio, a weighted mole fraction, X' , is introduced, which is defined as follows:

$$X' = f[\text{C}_2\text{H}_4]/(f[\text{C}_2\text{H}_4] + [\text{C}_3\text{H}_6]), \quad (33)$$

where f is a weighted factor. If $f = k_e/k_p$, then $X = X'$. Assuming a value for f , the values of X' can be calculated for any mole fraction of ethylene. If the f factor is equal to k_e/k_p , the plots of the left-hand-side of Eqs. 30, 31, and 32 against X' should give straight lines for each product. Such plots are made by varying the f factor until good linearities can be obtained for every product. When the f factor was assumed to be 1.6, good linearities could be obtained, as are shown in Fig. 6; that is, $k_e/k_p = 1.6$.

A similar relative rate constant for the reaction of the singlet CH₂ with ethylene and propene has been estimated to be 0.77 in the gas phase.⁹⁾ For the singlet O, $2.2/6.0 = 0.37$ has been reported.¹⁰⁾ The trend in the reactivity of the singlet NH is in the opposite direction to those of the singlet O and CH₂; the ratio for NH is larger than unity, while those for O and CH₂ are smaller than unity. No proper interpretation can be found for this anomaly at present.

From the slopes of the straight lines in Fig. 6, the k_{ae}/k_e , k_{ap}/k_p , and k_{ip}/k_p ratios can be estimated to be about 0.30, 0.48, and 0.17 respectively. Combining these values with those estimated from Eqs. 26–29, the k_{de}/k_e and k_{dp}/k_p ratios can be estimated to be 0.27 and 0.25 respectively. These values are listed in Table 1. Although the $(k_{ap} + k_{ip} + k_{dp})/k_p$ ratio is close to unity, the $(k_{ae} + k_{de})/k_e$ ratio is only 0.57. That is, some reaction path is missing in the case of ethylene. The extent of the missing reaction cor-

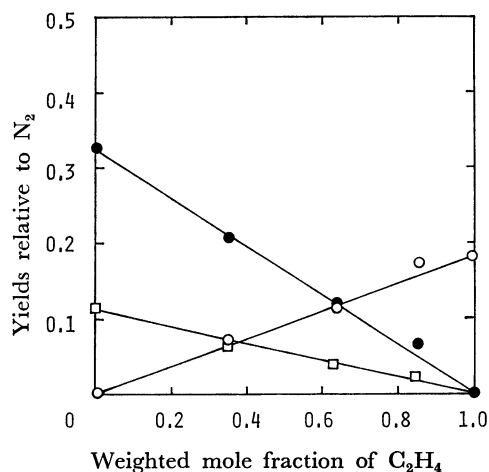


Fig. 6. Plots for Eqs. 30, 31, and 32 as functions of the weighted mole fraction of ethylene.

○: Aziridine, ●: 2-methylaziridine, □: allylamine. $f=1.6$ (see Text).

TABLE 1. VALUES OF RELATIVE RATE CONSTANTS

	C ₂ H ₄		C ₃ H ₆	
Addition	[1.00] ^{a)} (0.30) ^{b)}		1.0	(0.48)
Insertion				
Vinyl ^{c)}	1.43	(0.43)	0.21	(0.10)
Allyl	0	0	0.35	(0.17)
Deactivation	0.90	(0.27)	0.52	(0.25)
Total	3.33	(1.00)	2.08	(1.00)

a) The rate of aziridine formation in the ethylene solution is assumed to be unity. b) The values in parentheses show the relative values for each olefin, assuming the total rate to be unity. c) Values estimated on the assumption that the missing reaction is the insertion into the vinylic C-H bond.

responds to the amount of the missing NH-containing products, which was discussed in the previous section. The missing product might be vinylamine, since this compound is known to be unstable at room temperature.

The following relations can also be obtained by using the steady-state treatment:

$$\text{2-methylaziridine/aziridine} = k_{ap}[\text{C}_3\text{H}_6]/k_{ae}[\text{C}_2\text{H}_4] \quad (34)$$

$$\text{allylamine/aziridine} = k_{ip}[\text{C}_3\text{H}_6]/k_{ae}[\text{C}_2\text{H}_4]. \quad (35)$$

The k_{ap}/k_{ae} and k_{ip}/k_{ae} ratios were estimated to be 1.0 ± 0.1 and 0.32 ± 0.05 respectively, using the results shown in Fig. 5. The rate of the addition to the double bond of ethylene is almost equal to that of propene. The relative rate constants are summarized in Table 1.

From the results shown in Fig. 4, it is possible to estimate the relative rate of the insertion into the C-H bond of ethane to the addition to the double bond of ethylene.



When competition between Reactions 36 and 2 is considered, the following relation can be obtained:

$$\text{ethylamine/aziridine} = k_{36}[\text{C}_2\text{H}_6]/k_{ae}[\text{C}_2\text{H}_4]. \quad (37)$$

The k_{36}/k_{ae} ratio is estimated to be 0.82 ± 0.05 . Since ethane has 6 C-H bonds, the addition reaction is about $6/0.82=7.3$ times faster than the insertion reaction per C-H bond. This value can be compared with $3 k_{ap}/k_{ip}=8.6$, i.e., the addition reaction is 8.6 times faster than the insertion into the allylic C-H bond of propene. In the case of the singlet O, DeMore estimated this ratio to be $0.37/0.071=5.2$ in the Ar solution at 87 K.¹¹⁾ For the singlet CH₂, this ratio was larger than 10, depending on the source of the CH₂.¹²⁾ The ratio obtained with the singlet NH is between the ratios obtained with the singlet O and CH₂.

Table 1 shows that the branching ratio for the deactivation (Reaction 4) by ethylene is almost the same as that by propene and slightly larger than that by paraffin.²⁾ In this article, Reaction 4 followed by Reactions 5 and 6 is assumed to be responsible for the ammonia formation. However, Reaction 9, the hydrogen atom abstraction from hydrocarbon by the singlet NH, is indistinguishable from Reaction 4 only from the kinetics. If Reaction 9 should be considered instead of Reactions 4 and 5, the branching ratio for the deactivation would be that of Reaction 9. In this case, it is necessary to assume that the rate of the abstraction from ethylene is faster than those from propene and from paraffin, as was discussed already.

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