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The Reactions of NH($a^1\Delta$) with Ethane, Propane, and Isobutane in the Liquid Phase

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The photolysis of HN_3 was studied in liquid ethane, propane, and isobutane at the temperature of Dry Ice–methanol. In the reaction mixtures, quaternary ammonium salts were formed between the basic products and HN_3. The products were analyzed after having been passed through a trap containing NaOH, in which the salts were decomposed. The main products observed were nitrogen and amines: ethylamine from ethane, propyl- and isopropylamine from propane, and *i*-butyl, and *t*-butylamine from an isobutane solution. Ammonia and hydrogen were also formed as minor products. Possible reaction mechanisms are discussed. It is suggested that about 80% of the singlet NH is inserted into the C–H bond of paraffin to form amine and that 20% of it is deactivated to the ground triplet state by the reactions with paraffin. The relative efficiencies of the insertion into primary, secondary, and tertiary C–H bonds were estimated to be 1.0, 1.9, and 2.3 respectively.

The reactions of O and CH_2 with hydrocarbons have been extensively investigated. There are many similarities between O and CH_2 in the reactions. Triplet O(^{3}P) and $CH_2(^3B_1)$ are added to the double bond of olefin and abstract a hydrogen atom from paraffin. Singlet O(^{1}D) and $CH_2(^1A_1)$ are inserted into the C–H bond of paraffin and are added to the double bond of olefin.[1–6]

Since NH is isoelectronic with O and CH_2, the reactions of NH can be expected to be similar to those of O and CH_2.[7] Although there have been many studies of NH using the spectroscopic method,[8] the reactions of NH with hydrocarbons have not yet been established.[9–12] The main reason for this is that, except in a few studies, no NH-containing products could be detected.[13,14] This may be due to the following facts: (1) the insertion or addition products initially formed have so large an energy that only decomposition products can be observed and (2) a basic NH-containing product, if formed, may react with NH_3 or HNCO, which is often used as a source of NH, to form a quaternary ammonium salt. Because of its low vapor pressure, the salt is hard to analyze with GLC.

With these factors in mind, HN_3 was photolyzed in liquid ethane at the temperature of Dry Ice–methanol, as was briefly shown in a previous letter.[15] When less volatile products were treated with NaOH, the formation of ethylamine and ammonia could be detected. Propyl- and isopropylamine could also be detected from the propane solution. These amine formations were attributed to the insertion of the singlet NH ($a^1\Delta$) into the C–H bond of paraffin. In this paper, a kinetic study will be described and new results obtained with isobutane will be presented.

Experimental

The experimental method was the same as was briefly shown in the previous letter.[15] The details will now be given here.

HN_3 was prepared *in vacuo* by heating a mixture containing sodium azide (Koso Chemical Co.) and an excess amount of stearic acid (Tokyo Kasei Kogyo Co.) to approximately 100 °C. The HN_3 was dried with a trap containing P_2O_5, and the fraction condensable at −120 °C was stored in a Pyrex bulb covered with Al foil. The purified HN_3 was kept at a pressure of less than 50 Torr and/or was condensed at the temperature of liquid nitrogen. Pure-grade ethane, propane, and isobutane (Takachiho Shoji Co.) were used after distillation at −130, −120, and −110 °C respectively.

The mixture of HN_3 and hydrocarbon was prepared in a quartz tube 8 mm in o.d. using a mercury-free vacuum line equipped with calibrated volumes and a Wallace-Tiernan dial manometer (Nagano Keiki Co.). The quartz tube has a stopcock and a ground joint attached to it so that it was detachable from the vacuum line. The mixture was liquefied in a transparent quartz Dewar flask at the temperature of Dry Ice–methanol. The amount of the solution was about 1 ml. The solution of HN_3 thus prepared was irradiated with a medium-pressure mercury lamp (Wako Denki Co.) through a filter which cuts off the light shorter than 250 nm (Toshiba UV 27). Thus, the effective light was limited to between 320 and 250 nm.

After the irradiation, non-condensable gases 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 solvents (ethane, propane, and isobutane) were evacuated at −130, −120, and −110 °C respectively, Less volatile products, including unreacted HN_3, were passed through a trap packed with NaOH-coated glass wool at 80 °C. The products thus obtained were analyzed by GLC using a column packed with amine 220 on Celite 545 (Gasukuro Kogyo Co., 5 m in length) at 40 °C. For the separation of ammonia and propane, a column packed with NaOH-coated Porapak Q (30 cm in length) was used at 80 °C. A mass spectrometer was also used for the identification of the product.

Results

When HN_3 was photolyzed in liquid ethane, propane, or isobutane at the temperature of Dry Ice–methanol, a white precipitant was observed to be formed. The non-condensable products at the temperature of liquid nitrogen were nitrogen and hydrogen. The amounts of hydrogen formed from the ethane, propane, and isobutane solutions were independent of the changes in the concentration of HN_3 and were, respectively, 5.6±1.0, 4.3±2.0, and 5.3±1.4% of that of the nitrogen formed. No methane formation was found in any case examined.

The condensable products observed were ammonia and amines: ethylamine from ethane, propyl- and isopropylamine from propane, and *i*-butyl- and *t*-

butylamine from isobutane solutions. Without having been passed through the NaOH trap, the peak of neither ammonia nor amine was observed on the gas chromatogram. Probably, a quaternary ammonium salt was formed in the reaction mixtures between the basic products and the reactant HN_3. The complete recovery of the products was checked by using authentic samples of amine and HN_3 dissolved in liquid hydrocarbon at the temperature of Dry Ice–methanol.

Because of the formation of a white precipitant in the solution and dew on the wall of the Dewar flask, the amount of the product was not reproducible; however, the product ratio was found to be reproducible. Figure 1 shows the plots of the product ratios, NH_3/N_2 and RNH_2/N_2, as functions of $[HN_3]/[RH]$. Here, R represents C_2H_5, C_3H_7, or C_4H_9. As is shown in Fig. 1, the ratio of RNH_2/N_2 decreased with an increase in the concentration ratio of $[HN_3]/[RH]$, while the ratio of NH_3/N_2 increased.

In the cases of propane and isobutane solutions, we obtained no evidence of the formation of C_6 or C_8 hydrocarbons, which are possible products of the C_3H_7 or C_4H_9 radicals, if formed. For both cases, two kinds of amines were formed, corresponding to the two types of C–H bonds present. Figure 2 shows plots of the product ratios, propylamine/isopropylamine and *i*-butylamine/*t*-butylamine, as functions of $[HN_3]/[RH]$. The product ratios were independent of the changes in the concentration ratio; they were 1.6 ± 0.2 and 4.0 ± 0.4 in propane and isobutane solutions respectively.

Figure 3 shows plots of $(RNH_2+3H_2+4NH_3)/N_2$ as functions of the concentration ratio of $[HN_3]/[RH]$. The ratios were less than unity in every case examined.

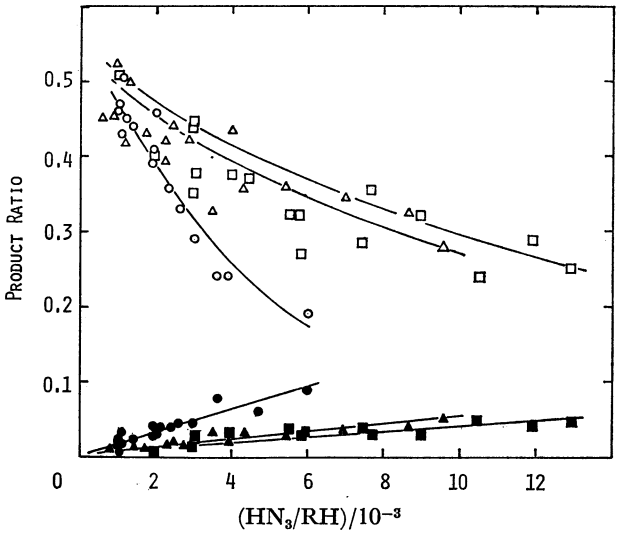

Fig. 1. Effect of concentration ratio of $[HN_3]/[RH]$ on the product ratios of RNH_2/N_2 (open symbols) and NH_3/N_2 (closed symbols).
○: R=C_2H_5, △: R=C_3H_7, □: R=C_4H_9.

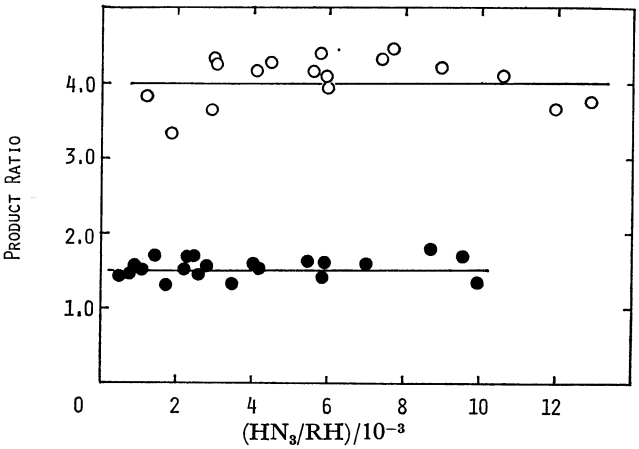

Fig. 2. Effect of concentration ratio of $[HN_3]/[RH]$ on the product ratios of propylamine/isopropylamine (●) and *i*-butylamine/*t*-butylamine (○).

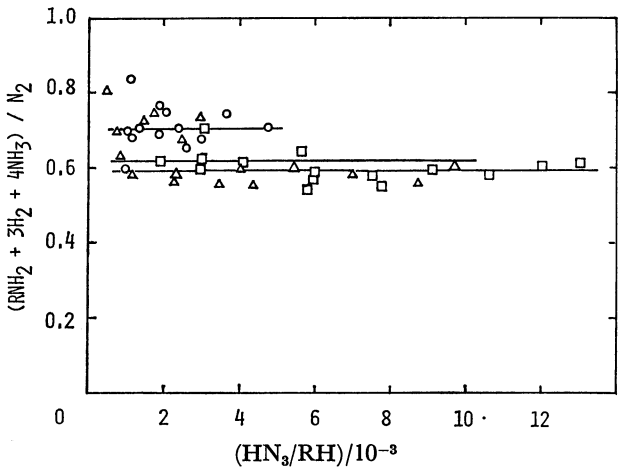

Fig. 3. Plots of $(RNH_2+3H_2+4NH_3)/N_2$ as functions of concentration ratio of $[HN_3]/[RH]$.
○: R=C_2H_5, △: R=C_3H_7, □: R=C_4H_9.

Discussion

As was discussed in the previous letter, the following reaction mechanism can explain the results obtained in the ethane and propane solutions of HN_3 at the temperature of Dry Ice–methanol:[15]

$$HN_3 + h\nu \longrightarrow {}^1NH + N_2 \qquad \alpha \qquad (1)$$

$$\longrightarrow H + N_3 \qquad (1-\alpha) \qquad (2)$$

$$^1NH + HN_3 \longrightarrow NH_2 + N_3 \qquad k_a \qquad (3)$$

$$^1NH + RH \longrightarrow RNH_2 \qquad k_h \qquad (4)$$

$$NH_2 + HN_3 \longrightarrow NH_3 + N_3 \qquad (5)$$

$$H + HN_3 \longrightarrow H_2 + N_3 \qquad (6)$$

$$2NH_2 \longrightarrow N_2H_4 \qquad (7)$$

$$2N_3 \longrightarrow 3N_2, \qquad (8)$$

where ^1NH represents an NH radical in the first excited singlet state ($a^1\Delta$).

Baronavski *et al.* showed that the 266 nm-laser photolysis of HN_3 gives rise to NH fragments exclusively in the $a^1\Delta$ state without being vibrationally excited.[14] They also showed that a similar thing could be said when HN_3 was photolyzed with the light of wavelengths

between 290 and 310 nm. Their conclusions agree well with the results obtained in the study of the flash photolysis of HN_3 using light longer than 200 nm.[16]

In the absence of added hydrocarbon, the main reaction of the singlet NH is the abstraction of a hydrogen atom from HN_3 to form an excited NH_2 which can fluoresce.[14,17] In the presence of hydrocarbon, the insertion reaction of the singlet NH into the C–H bond of paraffin is assumed for the formation of amine. The insertion reaction is similar to that observed in the case of the singlet O and CH_2.[1-6] An alternative mechanism for the amine formation is the so-called "radical-abstraction recombination" mechanism:

$$^1NH + RH \longrightarrow NH_2 + R \quad (9)$$

$$NH_2 + R \longrightarrow RNH_2. \quad (10)$$

If these reactions are predominant, more isopropylamine should be formed than propylamine and more *t*-butylamine should also be formed than *i*-butylamine, since the bond-dissociation energy of the secondary or tertiary C–H bond is smaller than that of the primary C–H bond.[18] If we found C_6 or C_8 hydrocarbons as products, Reaction 9 would be important. This was not the case in the present study, as was shown in the Results section. That is, the amine is formed mainly by Reaction 4.

Konar *et al.* proposed a reaction mechanism in which a part of the primary photodissociation of HN_3 is to N_3 and H, followed by a hydrogen-atom abstraction from HN_3. This mechanism can explain the hydrogen formation in the 213.9 nm photolysis of HN_3 at room temperature.[11] By measuring the decay of the concentration of hydrogen atoms, Bras and Combourieu have estimated the rate constant of the reaction of hydrogen atoms with HN_3 to be $1.5\times 10^{13}\exp(-2300/T)$ cm^3 mol^{-1} s^{-1}.[19] As the exit channel of the reaction of hydrogen atoms, they proposed the formation of NH_2 and N_2, which is different from Reaction 6:

$$H + HN_3 \longrightarrow NH_2 + N_2. \quad (11)$$

When Reaction 11 is included in the mechanism instead of Reaction 6, it is necessary to consider a reaction mechanism which can explain the hydrogen formation. It was difficult to construct such a mechanism. We, therefore, conclude that the rate constant estimated by Bras and Combourieu is that for Reaction 6, but not for Reaction 11.

The abstraction of a hydrogen atom from paraffin by H or NH_2 is a possible reaction:

$$H + RH \longrightarrow H_2 + R \quad (12)$$

$$NH_2 + RH \longrightarrow NH_3 + R. \quad (13)$$

These reactions, however, can be neglected under the present experimental conditions, because of the following reasoning: (1) the bond dissociation energy of H–N_3 is smaller than that of R–H,[18] (2) since the activation energies of the reactions are about 20 to 40 kJ mol^{-1},[20,21] the rates of these reactions should be very slow at the temperature of Dry Ice–methanol, and (3) no possible products formed from the recombination of R could be detected in the present study, as was shown in the Results section.

In Reaction 7, a hydrazine formation was assumed, although we failed to detect the hydrazine formation. Without including Reaction 7, the following equation can be expected to hold between the amounts of the products:

$$RNH_2 + 3H_2 + 4NH_3 = N_2. \quad (14)$$

As was shown in Fig. 3, the ratios of $(RNH_2+3H_2+4NH_3)/N_2$ were less than unity for any solvent examined. That is, about 30 to 40% of the NH-containing products are missing in this study. When Reaction 7 is included in the mechanism, the following relation can be expected to hold:

$$RNH_2 + 3H_2 + 4NH_3 + 5N_2H_4 = N_2. \quad (15)$$

A steady-state treatment of the above mechanism gives the following relations:

$$\alpha = X/(X+H_2) \quad (16)$$

$$X/RNH_2 = 1 + k_a[HN_3]/k_h[RH]. \quad (17)$$

Here, X is defined as follows:

$$X = N_2 - 3(H_2+NH_3+N_2H_4). \quad (18)$$

The amount of N_2H_4 formed can be estimated using Eq. 15. The relations of Eqs. 16 and 17 are plotted in Figs. 4 and 5 respectively as functions of the concentration ratios, $[HN_3]/[RH]$.

As is shown in Fig. 4, the ratio of $X/(X+H_2)$ is independent of the changes in the $[HN_3]/[RH]$ ratio and also the changes in the solvent examined. The values of α is estimated to be 0.91 ± 0.03 from the ratio in Fig. 4. That is, about 91% of the primary photodissociation of HN_3 gives rise to the first excited singlet state, while the remaining part corresponds to the dissociation into H and N_3. This part is slightly larger than that estimated in the gas-phase photolysis of HN_3 at 213.9 nm.[11] Bradley *et al.* pointed out that the fraction of the primary photodissociation of HNCO into H and NCO decreases with the decrease in the excitation wavelength in the gas-phase photolysis of HNCO.[22] A similar effect of the wavelength might explain the difference between the results obtained by Konar *et al.* and those of the present study.

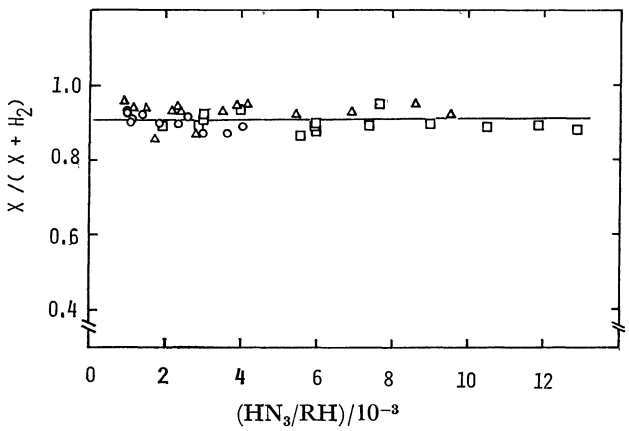

Fig. 4. Plots of $X/(X+H_2)$ as functions of concentration ratio of $[HN_3]/[RH]$.
○: R=C_2H_5, △: R=C_3H_7, □: R=C_4H_9.

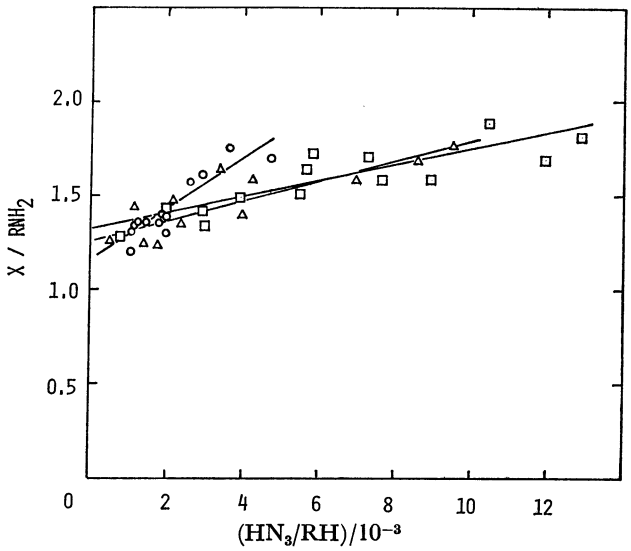

Fig. 5. Plots of X/RNH_2 as functions of concentration ratio of $[HN_3]/[RH]$.
○: R=C_2H_5, △: R=C_3H_7, □: R=C_4H_9.

As is shown in Fig. 5, the plots of X/RNH_2 give straight lines for any solvent examined, as was expected from Eq. 17. The intercepts, however, are different from unity. In order to explain the non-unity intercepts, the following reactions are considered to hold:

$$^1NH + RH \longrightarrow {}^3NH + RH \qquad k_h' \qquad (19)$$

$$^3NH + HN_3 \longrightarrow NH_2 + N_3. \qquad (20)$$

Here, ^3NH denotes NH in the ground triplet state, $(X^3\Sigma^-)$. A similar deactivation process has been considered in the reactions of the singlet O and CH_2.[1-6] The triplet NH will abstract a hydrogen atom preferentially from HN_3, as was considered to hold in the case of the singlet NH. The rate constant of Reaction 20 has been estimated, in the study of the shock-wave decomposition of HN_3, to be 3.0×10^{11} exp $(-800/T)$ cm^3 mol^{-1} s^{-1}.[23] Because of its low activation energy, Reaction 20 may be more important than Reaction 21 under the present experimental conditions:

$$^3NH + RH \longrightarrow NH_2 + R. \qquad (21)$$

By the inclusion of Reactions 19 and 20 in the mechanism, Eq. 17 changes its form as follows:

$$X/RNH_2 = (k_h+k_h')/k_h + k_a[HN_3]/k_h[RH]. \qquad (22)$$

From the slope and the intercept of the straight line in Fig. 5, the values of $k_h/(k_h+k_h')$ and k_a/k_h can be estimated. The results are summarized in Table 1. As is shown in Table 1, about 80% of the singlet NH is inserted into the C–H bond of paraffin, while the remaining part is deactivated to the ground triplet state by the reaction with paraffin. The rate constant of the reaction of the singlet NH with paraffin is about two orders of magnitude smaller than that with HN_3 at the temperature of Dry Ice–methanol.

Table 1. Summary of the rate constant ratios

Reactant	$k_h/(k_h+k_h')$	k_a/k_h	$k_h/k_{a\,rel}$	$k_{h\,rel}$
C_2H_6	0.86±0.04	125±21	1.0	1.0
C_3H_8	0.79±0.02	49± 9	2.6	1.6
i-C_4H_{10}	0.75±0.04	40± 9	3.1	1.9

The value of k_a has been estimated to be 5.6×10^{13} cm^3 mol^{-1} s^{-1} in the gas phase at room temperature.[14,16] Paur and Bair estimated the activation energy to be very small, if present at all.[16] In the liquid phase at the temperature of Dry Ice–methanol, the rate of Reaction 3 (k_a) may be expected to be fast and close to the diffusion-controlled rate. That is, k_a depends on the nature of the solvent, such as the viscosity. In the third column of Table 1, the relative values of k_h/k_a are listed.

Using the values of the product ratios shown in Fig. 2, it is possible to estimate the relative efficiencies of the insertion per C–H bond, k_s/k_p and k_t/k_p. Here, the subscripts p, s, and t represent the primary, secondary, and tertiary C–H bonds of paraffin respectively:

$$6k_p/2k_s = \text{propylamine/isopropylamine} = 1.6 \pm 0.2 \qquad (23)$$

$$9k_p/k_t = i\text{-butylamine}/t\text{-butylamine} = 4.0 \pm 0.4. \qquad (24)$$

Thus, $k_s/k_p=1.9\pm0.2$ and $k_t/k_p=2.3\pm0.2$. That is, the efficiencies of the insertion into the secondary and tertiary C–H bonds are about twice that into the primary C–H bond. In the case of the singlet O (^1D), a non-discriminative insertion has been observed.[24] On the other hand, the efficiency of the insertion of the singlet CH_2 ($^1A_1$) into the secondary or tertiary C–H bond is slightly larger than that into the primary C–H bond.[25] The reason for these differences is not clear at present.

The relative insertion rate of the singlet NH into ethane, propane, and isobutane can be estimated using the values of k_s/k_p, k_t/k_p and by including the numbers of the C–H bond. The results thus obtained are listed in the fourth column of Table 1. The difference between the third and fourth columns is within the factor of two and may be mainly due to the difference in k_a.

Since we included Reactions 19 and 20 in the reaction mechanism, the NH_2 radicals are formed *via* two reaction paths, Reactions 3 and 20. If Reaction 7, the formation of N_2H_4, is not included in the mechanism, the ratio of the yield, $(NH_3/RNH_2)_0$, should be equal to the k_h'/k_h ratio, where the subscript 0 denotes the value obtained by extrapolation to a zero concentration of HN_3. This is not the case, as is expected from the results shown in Fig. 1. If Reaction 7 is included, the following relations are expected to hold:

$$NH_3/(N_2H_4)^{1/2} = k_5[HN_3]/k_7^{1/2} \qquad (25)$$

$$((NH_3+2N_2H_4)/RNH_2)^{1/2} = k_h'/k_h. \qquad (26)$$

Since the yield ratios, N_2H_4/N_2, calculated were nearly independent of the change in the concentration of HN_3, the NH_3/N_2 ratio should linearly increase with an increase in the concentration of HN_3. This is the case shown in Fig. 1. Using the data of Figs. 1 and 3, the $((NH_3+2N_2H_4)/RNH_2)_0$ ratios were estimated to be 0.2, 0.3, and 0.3 respectively for the cases of ethane, propane, and isobutane. These values

are consistent with those estimated from the $k_h/(k_h+k_h')$ ratios shown in Table 1; *i.e.*, the assumption of the N_2H_4 formation well explains all of the experimental results obtained here.

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