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The Insertion Reaction of NH Singlet Radicals into the C–H Bonds of Cyclopropane and Isobutane in the Liquid Phase

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Hydrogen azide was photolyzed in liquid cyclopropane at the temperature of Dry Ice–methanol. The main products observed were nitrogen, cyclopropylamine, and ammonia. The relative yields of the products depended slightly on the concentration of hydrogen azide. The results were then compared with those obtained with paraffin and olefin. The isobutane solution of hydrogen azide was photolyzed at 0 °C. The products observed were the same as those obtained at the temperature of Dry Ice–methanol. The relative yields of the products and the concentration dependence, however, were different.

In spite of many investigations of the reactions of $O(^1D)$ and $CH_2(^1A_1)$, only a few investigations have been reported of the reactions of the NH singlet ($a^1\Delta$), which is isoelectronic with O and CH_2.[1] Recently, we have photolyzed hydrogen azide in liquid ethane, propane, isobutane, ethylene, and propene at the temperature of Dry Ice–methanol.[2–4] In the case of paraffin, the main basic products were ammonia and amines, *i.e.*, ethylamine from ethane, propyl- and isopropylamine from propane, and isobutyl- and *t*-butylamine from isobutane. The amine formations were explained by the insertion reaction of the NH singlet into the C–H bonds of paraffin. In the case of olefin, aziridines were found to be formed; they were explained by the addition reaction of the NH singlet to the double bond of olefin. When hydrogen azide was photolyzed in liquid carboxylic acid, the formation of amino acids was observed.[5,6] Recently, Kajimoto and Fueno studied the photolysis of a mixture of hydrogen azide and ethane in the gas phase at room temperature.[7] They showed that the reactions of the NH singlet with ethane give insertion, abstraction, and deactivation products with branching ratios of 60%, 10%, and 30% respectively. These studies have shown that the main reaction of the NH singlet is the insertion reaction into the C–H bond.

In the case of the paraffin solution at the temperature of Dry Ice–methanol, the relative yield of amine decreased, and that of ammonia increased, with an increase in the concentration of hydrogen azide.[2,3] In the case of olefin, however, no concentration dependence was observed.[4] The difference was tentatively explained by a "solvent effect" on Reaction 1:

$$NH(a^1\Delta) + HN_3 \rightarrow NH_2 + N_3. \qquad (1)$$

In order to get further information about the reactions of the NH singlet, hydrogen azide was photolyzed in the liquid cyclopropane at the temperature of Dry Ice–methanol, since cyclopropane is known as a hydrocarbon which shows a property intermediate between paraffin and olefin. The isobutane solution of hydrogen azide was also photolyzed at 0 °C in order to study the effects of the temperature on the reactions.

Experimental

The experimental methods were essentially the same as those described in the previous papers.[2–4] Hydrogen azide was prepared *in vacuo* by heating a mixture containing sodium azide and an excess amount of stearic acid, and was used after having been dried with phosphorus pentaoxide and degassed at −120 °C. Research-grade ethane, cyclopropane, and isobutane (Takachiho Shoji Co.) were purified by repeated trap-to-trap distillation. The mixture of hydrogen azide and hydrocarbon was prepared in a quartz tube with an o.d. of 8 mm and irradiated with a medium-pressure mercury lamp (Wako Denki Co.) through a filter (Toshiba UV 27) at the temperature of Dry Ice–methanol or 0 °C. The amount of the solution was about 1 cm^3.

After the irradiation, non-condensable products at −196 °C were analyzed with a combination of a Toepler pump, a gas burette, and a CuO furnace at 300 °C. The solvent was evacuated at about −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 columns packed with Amipack 124 (Gasukuro Kogyo Co.) and with Porapak Q. For the identification of the products, a mass spectrometer and an NMR spectrometer were used. D_2O was used as a solvent for the NMR analysis.

Results

Cyclopropane–Hydrogen Azide Solution. When hydrogen azide was photolyzed in liquid cyclopropane at the temperature of Dry Ice–methanol, the formation of a white precipitant was observed, much as in the cases of paraffin and olefin.[2–4] The non-condensable products at −196 °C were nitrogen and hydrogen. No methane formation was observed. The H_2/N_2 ratio was 0.015 ± 0.004, independent of the changes in the concentration of hydrogen azide. Among the less volatile products, ammonia and cyclopropylamine were found. Allylamine, which is expected to be formed by the isomerization of the vibrationally excited cyclopropylamine, was not found. The yields of ammonia and cyclopropylamine relative to nitrogen are plotted in Fig. 1 as a function of the concentration of hydrogen azide. For comparison, previous results obtained with propane and propene are also included in Fig. 1.[3,4] The concentration dependence obtained with cyclopropane shows behavior intermediate between that obtained with propane and with propene. The sum of the relative yields of the products, $(c\text{-}C_3H_5NH_2 + 3H_2 + 4NH_3)/N_2$, was 0.95 ± 0.06 for the concentration range examined.

Cyclopropane–Ethane–Hydrogen Azide Solution. When ethane was added to a cyclopropane solution of hydrogen

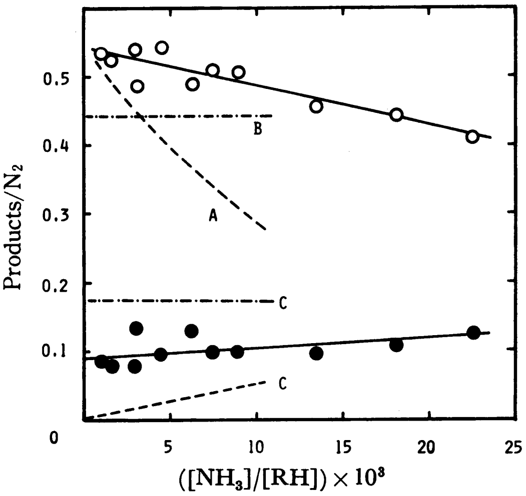

Fig. 1. Yields of cyclopropylamine (○) and ammonia (●) relative to nitrogen as a function of the concentration of hydrogen azide. (------) and (-·-·-) show the results obtained in the propane and propene solutions (from Refs. 3 and 4). A: (propyl- and isopropylamine)/N_2, B: (methylaziridine+allylamine)/N_2, C: NH_3/N_2.

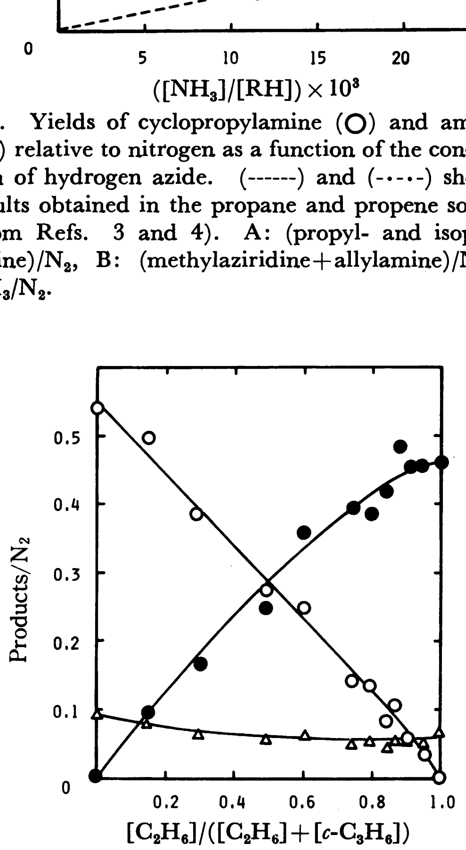

Fig. 2. Effects of ethane on the photolysis of cyclopropane solution of hydrogen azide as a function of the mole fraction of ethane. The $[HN_3]/([C_2H_6]+[c\text{-}C_3H_6])$ ratio is 2.07×10^{-3}. ○: $c\text{-}C_3H_5NH_2/N_2$, ●: $C_2H_5NH_2$, △: NH_3/N_2.

azide, the relative yield of cyclopropylamine decreased, while the yield of ethylamine increased. The results obtained at the constant concentration of hydrogen azide, $[HN_3]/([C_2H_6]+[c\text{-}C_3H_6])=2.07\times10^{-3}$, are plotted in Fig. 2 as a function of the mole fraction of ethane, *X*.

Isobutane–Hydrogen Azide Solution at 0 °C. In order to investigate the effects of the reaction temperature, hydrogen azide was photolyzed in liquid isobutane at 0 °C. The products obtained at 0 °C were essentially the same as those obtained at the temperature of Dry Ice–methanol. Figure 3 shows the concentration dependence of the relative yields of ammonia and amines (the sum of isobutyl- and *t*-butylamine). The results

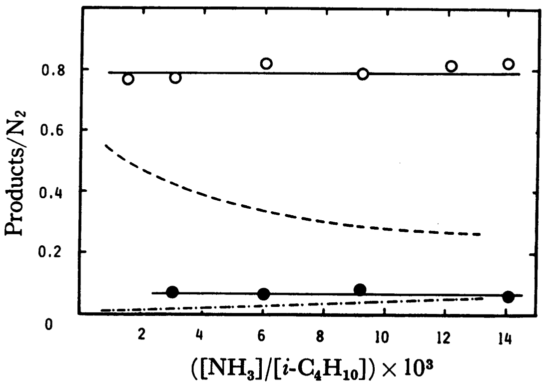

Fig. 3. Yields of isobutyl- and *t*-butylamines (○) and ammonia (●) relative to nitrogen as a function of the concentration of hydrogen azide at 0 °C. The results obtained at the temperature of Dry Ice–methanol are also shown for the amines (------) and ammonia (-·-·-) (from Ref. 3).

obtained at the temperature of Dry Ice–methanol are also included for comparison.[3] The relative yields of the products were independent of the changes in the concentration of hydrogen azide at 0 °C: $(i\text{-}C_4H_9NH_2+t\text{-}C_4H_9NH_2)/N_2=0.79\pm0.03$, $NH_3/N_2=0.06\pm0.01$, $H_2/N_2=0.03\pm0.01$, and $i\text{-}C_4H_9NH_2/t\text{-}C_4H_9NH_2=4.3\pm0.03$. The $i\text{-}C_4H_9NH_2/t\text{-}C_4H_9NH_2$ ratio obtained at 0 °C is almost equal to that obtained at the temperature of Dry Ice–methanol. The sum of the relative yields, $(i\text{-}C_4H_9NH_2+t\text{-}C_4H_9NH_2+3H_2+4NH_3)/N_2$, was close to unity, and thus different from that obtained at a lower temperature.

Discussion

Cyclopropane–Hydrogen Azide Solution. As has been discussed in previous papers,[2–4] the following general reaction mechanism can also be considered in the case of cyclopropane:

$$HN_3 + h\nu \rightarrow {}^1NH + N_2, \tag{2}$$

$$\rightarrow H + N_3, \tag{3}$$

$${}^1NH + HN_3 \rightarrow NH_2 + N_3 \quad k_a, \tag{4}$$

$${}^1NH + RH \rightarrow RNH_2 \quad k_i, \tag{5}$$

$$\rightarrow {}^3NH + RH \quad k_d, \tag{6}$$

$${}^3NH + HN_3 \rightarrow NH_2 + N_3, \tag{7}$$

$$NH_2 + HN_3 \rightarrow NH_3 + N_3, \tag{8}$$

$$H + HN_3 \rightarrow H_2 + N_3, \tag{9}$$

$$2NH_2 \rightarrow N_2H_4, \tag{10}$$

$$2N_3 \rightarrow 3N_2, \tag{11}$$

where ${}^1NH$ and ${}^3NH$ represent the NH radicals in the first excited singlet state ($a^1\Delta$) and the ground triplet state ($X^3\Sigma^-$) respectively. RH and RNH_2 are cyclopropane and cyclopropylamine respectively.

Since the $(RNH_2+3H_2+4NH_3)/N_2$ ratio was close to unity, Reaction 10 can be neglected in the case of cyclopropane, much as in the case of propene. In the case of propane, however, Reaction 10 was important to explain the facts that (1) the $(RNH_2+3H_2+4NH_3)/$

N_2 ratio was less than unity and (2) the NH_3/N_2 ratio approached zero when the concentration of hydrogen azide approached zero (*cf.* Fig. 1).

In the above reaction mechanism, the hydrogen-atom abstraction by the NH triplet is neglected;

$$^3NH + RH \rightarrow NH_2 + R, \qquad (12)$$

because the reaction is about 36 kJ mol^{-1} endothermic. Reaction 13 may also be unimportant at a low temperature because of its large activation energy.[8] If Reactions

$$NH_2 + RH \rightarrow NH_3 + R \qquad (13)$$

12 and 13 were important in the present system, the cyclopropyl radical, R, would abstract a hydrogen atom from hydrogen azide:

$$R + HN_3 \rightarrow RH + N_3. \qquad (14)$$

As it is, it is difficult to distinguish these reactions from Reactions 7 and 8.

Kajimoto and Fueno have proposed that a part of the reaction of the NH singlet with ethane in the gas phase at room temperature is a hydrogen-atom abstraction.[7] A similar reaction is expected to occur in the present system because the reaction is about 115 kJ mol^{-1} exothermic:

$$^1NH + RH \rightarrow NH_2 + R. \qquad (15)$$

If NH_2 and R abstracted a hydrogen atom from hydrogen azide, Reaction 15 would be indistinguishable from Reaction 6. In the liquid phase, however, NH_2 and R recombine because of the cage effect:

$$NH_2 + R \rightarrow RNH_2. \qquad (16)$$

In this case, Reaction 15 is indistinguishable from Reaction 5. If Reaction 16 competed with Reactions 8 and 14, the NH_3/N_2 ratio would increase and the RNH_2/N_2 ratio would decrease with an increase in the concentration of hydrogen azide. This is consistent with the results obtained in the paraffin and cyclopropane solutions at the temperature of Dry Ice–methanol. This assumption, however, cannot explain the concentration dependence of the products obtained in the cases of the olefin solutions at the temperature of Dry Ice–methanol and isobutane solution at 0 °C.

Since Reaction 5 is about 460 kJ mol^{-1} exothermic, a vibrationally excited cyclopropylamine is formed; this will be isomerized to allylamine unless stabilized by a collision. In the cases of CH_2 reactions with cyclopropane, the isomerization of the initially formed vibrationally excited methylcyclopropane has been observed in the gas phase at room temperature.[9] Since no allylamine formation could be observed, the stabilization of the vibrationally excited cyclopropylamine must be efficient under the present experimental conditions.

Assuming the above reaction mechanism, Reactions 2—11, the rate constant ratios, k_a/k_i and $k_i/(k_i+k_d)$, can be estimated to be 6.4 ± 1.1 and 0.83 ± 0.01 respectively by the method described in the previous papers.[3,4] Here, the a, i, and d subscripts denote the abstraction reaction of hydrogen atom from hydrogen azide, the insertion reaction, and the deactivation of the singlet NH respectively. McDonald *et al.* have estimated the values of k_a and k_i+k_d in the gas phase at room temperature.[10] Their $k_a/(k_i+k_d)$ ratio was 2.6, about a half of the present results.

The k_a/k_i ratio was 49 in the case of propane.[3] In the case of propene, no concentration dependence was observed;[4] this means that the k_a/k_i ratio was less than unity. Thus, the difference in the concentration dependence of the yields of amine and ammonia may be explained by the difference in the k_a/k_i ratio.

Relative Rate of the Insertion. Using the results shown in Fig. 2, the relative rate can be estimated for the insertion of the NH singlet into ethane (k_{ei}) and cyclopropane (k_{ci}):

$$^1NH + C_2H_6 \rightarrow C_2H_5NH_2 \quad k_{ei}, \qquad (17)$$

$$^1NH + c\text{-}C_3H_6 \rightarrow c\text{-}C_3H_5NH_2 \quad k_{ci}. \qquad (18)$$

Assuming Reactions 17 and 18, the following relation can be obtained:

$$C_2H_5NH_2/(C_2H_5NH_2 + c\text{-}C_3H_5NH_2) = X/(f(1-X) + X), \qquad (19)$$

where X is the mole fraction of ethane and where f is the k_{ci}/k_{ei} ratio. The left-hand-side of Eq. 19 is plotted against the weighted mole fraction, assuming various values for f. When f is assumed to be $1.0_5\pm0.1$, a good linearity is obtained, as is shown in Fig. 4; the insertion rate of the NH singlet into the C–H bond of cyclopropane is almost equal to that of ethane. Incidentally, Cvetanović and his co-workers estimated the relative rate of the reactions of $O(^1D)$ with cyclopropane and ethane to be 1.0_5 in the gas phase.[11]

As Fig. 2 shows, the relative yields of ethylamine were almost constant for the mole fractions of ethane larger than 0.85. This behavior may be explained by Reactions 2—11 under the assumption that the value of k_a depends on the mole fraction of ethane. The following relation is obtained for the yields of ethylamine:

$$\begin{aligned} &C_2H_5NH_2/(C_2H_5NH_2 + c\text{-}C_3H_5NH_2 \\ &\quad + H_2 + NH_3 + 2N_2H_4) \\ &\quad = C_eX/(C_eA\,k_a/k_i + X + (1-X)fC_e/C_c, \qquad (20) \end{aligned}$$

where C_e and C_c are the fractions of the insertion of the NH singlet into ethane and cyclopropane respectively. A is the mole fraction of hydrogen azide; $2.0_7\times10^{-3}$. The left-hand-side of Eq. 20 is plotted in Fig. 5 as a function of the mole fraction of ethane. The amount of

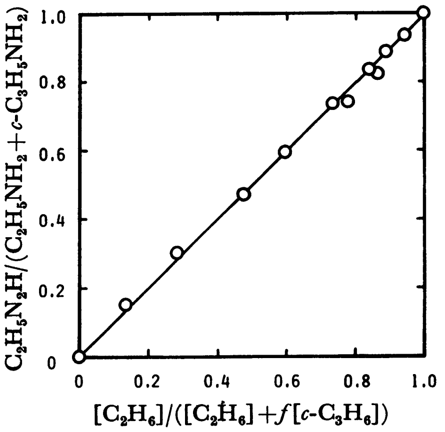

Fig. 4. Plots of $C_2H_5NH_2/(C_2H_5NH_2+c\text{-}C_3H_5NH_2)$ as a function of the weighted mole fraction of ethane, $f=1.05$. See the text for detail.

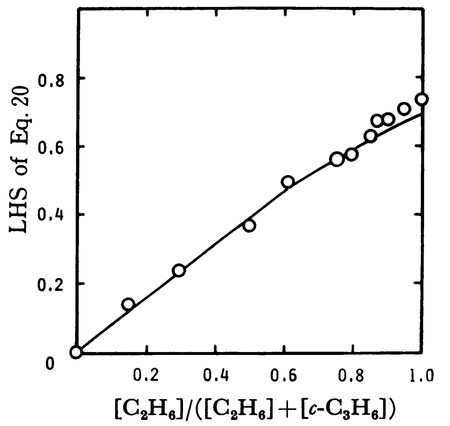

Fig. 5. Plots of the left-hand-side of Eq. 20 (○) as a function of the mole fraction of ethane. The solid curve shows the calculated ones. See the text for detail.

$$N_2H_4 = (1/5)(N_2 - C_2H_5NH_2 - c\text{-}C_3H_5NH_2 - 3H_2 - 4NH_3). \tag{21}$$

N_2H_4 was estimated using Eq. 21, as was done in a previous paper.3) The right-hand-side of Eq. 20 is estimated by assuming Eq. 22 for the values of k_a/k_i at various mole fractions of ethane:

$$k_a/k_i = (k_a/k_i)_c{}^x(k_a/k_i)_c{}^{(1-x)}, \tag{22}$$

where the e and c subscripts mean the values obtained in a pure ethane solution and in a pure cyclopropane solution respectively. The results are shown in Fig. 5 as a solid curve. As Fig. 5 shows, the agreement is satisfactory.

Effects of Reaction Temperature. As Fig. 3 shows, the relative yields of the products were independent of the changes in the concentration of hydrogen azide in the case of isobutane at 0 °C. These observations may be explained by assuming a small value of k_a/k_i (less than unity) under the assumed reaction mechanism. As was shown in a previous paper,3) the k_a/k_i ratio was 40 in liquid isobutane at the temperature of Dry Ice–methanol. If the decrease in the k_a/k_i ratio can be explained by the temperature dependence on k_i, the insertion reaction should have an activation energy larger than 21 kJ mol^{-1}. The effect of the reaction temperature was also observed in the k_d/k_i ratio, which is equal to $NH_3/(i\text{-}C_4H_9NH_2+t\text{-}C_4H_9NH_2)$ at 0 °C under the assumed reaction mechanism; *i.e.*, $k_d/k_i=$ 0.08 at 0 °C and 0.33 at the temperature of Dry Ice–methanol.3) From these values, the activation energy of k_i can be estimated to be about 8 kJ mol^{-1} larger than that of k_d.

In the case of O(^{1}D), no temperature effect has been observed for the insertion reaction.12) For the reactions of the NH singlet, the temperature effect on the rate has not been studied. If the rate is independent of the changes in the reaction temperature, much as in the case of O(^{1}D), it is necessary to assume that k_a will decrease with an increase in the reaction temperature. As has been discussed above, we had to assume various values of k_a for different solutions and different temperatures. This might be due to the status of hydrogen azide in the hydrocarbon solutions. If hydrogen azide molecules were determined in isobutane to be in the form of a "cluster" at low temperatures, a large k_a value can be expected; hydrogen azide molecules are always present near the NH singlet formed by photolysis in a solution. At higher temperatures, this "cluster" may be decomposed by the motion of the solvent molecule, and a small k_a value can be expected. The size of the "cluster" may also depend on the solvent. If such a "cluster" was formed, the photolysis would take place inhomogeneously in the solution, and the recombination of NH_2 would become important. Such a "cluster," if formed, will play a significant role in the ethane, propane, and isobutane solutions at the temperature of Dry Ice–methanol.

As has been discussed above, the reactions of the NH singlet in liquid hydrocarbons are complicated. Further studies are necessary to elucidate the complete reaction mechanism.

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