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The C–C Bond Rupture in the Radiolysis of Liquid *n*-Hexane

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The effects of added N_2O, NO, N_2O-NO mixture and NH_3 on the yields of fragment products of *n*-hexane in the γ-radiolysis of liquid *n*-hexane at 40°C have been investigated. All of these additives decrease to a certain extent the *G*-values of fragment products. The decreases of the *G*-values at sufficiently high N_2O concentration ($\sim$0.3 mol/*l*) are approximately the same as those in the presence of NH_3. The degrees of contribution of neutralization process and other processes to the C–C bond rupture have been separately estimated from the decreases at sufficiently high concentration of N_2O, NO and N_2O-NO mixture. It is shown that processes other than neutralization may play rather an important role than neutralization in the C–C bond rupture. The effect of added NH_3 on the yields of fragment products of *n*-hexane may be attributable to either the proton transfer from n-$C_6H_{14}^+$ to NH_3 or the charge transfer from n-$C_6H_{14}^+$ to NH_3.

A reaction scheme appears to have been adopted for radiolysis of non-polar liquid hydrocarbons such as *n*-hexane and cyclohexane that a parent ion and an electron which are produced by ionization recombine in a very short time,1) and that the resulting excited molecule decomposes as a neutral molecule.2) We reported previously3) the effect of nitrous oxide added as an electron scavenger on the hydrogen yield from the γ-radiolysis of several liquid hydrocarbons, and especially for cyclohexane we were able to elucidate the respective contribution of neutralization and other processes to the hydrogen yield.

The contributions of neutralization and other processes to C–C bond rupture in radiolysis of liquid hydrocarbons, however, appears not to have been made clear.4,5) Therefore, we have studied the C–C bond rupture in the γ-radiolysis of liquid *n*-hexane by examining the effects of added nitrous oxide known to be an electron scavenger,3,6) ammonia known to be a proton scavenger,7–9) and nitric oxide known to be a radical scavenger10) on the γ-radiolysis of liquid *n*-hexane. *n*-Hexane was selected as a suitable substance because of its higher yields2) of fragment products than those of cyclohexane.11)

Experimental

Materials. Research grade *n*-hexane obtained from Phillips Petroleum Co. was passed through a silica gel column to remove unsaturates, degassed by a few cycles of freezing-pumping-thawing on a vacuum line, and was stored up in a vessel after passage through a soda asbestos column and a magnesium perchlorate column to keep away from carbon dioxide and water. Purity of the *n*-hexane was 99.98 mol%. As the additives, were used nitrous oxide, ammonia and nitric oxide without further purification as received from Takachiho-shoji Co.

Sample Preparation and Irradiation. A nearly definite volume, about 0.1 cc, of liquid *n*-hexane was led from the storing vessel to an ampoule of hard glass kept at the liquid nitrogen temperature. The ampoule was 5 mm o.d., 3 mm i.d., and 2 cm long. In the absence of additives, the ampoule was sealed off at the upper part, and in the case of mixing an additive, its definite quantity was led as in the case of *n*-hexane. Then, the ampoule was sealed off. The samples were irradiated at 40°C in a ^{60}Co γ-source at a dose rate of 9.92×10^{19} eV/g·h to a total dose of 1.19×10^{21} eV/g. In estimating the dose, $G(Fe^{3+})=8.2$ in the Fricke dosimeter saturated with nitrogen was used with the correction of the electron density of *n*-hexane.

Product Analysis. In the absence of the additives, the non-condensable products, hydrogen and methane, were measured by a gas burette attached to a Toepler pump and a cuprous oxide furnace kept at 260°C.

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2) T. J. Hardwick, *J. Phys. Chem.*, **64**, 1623 (1960).

3) S. Sato, R. Yugeta, K. Shinsaka and T. Terao, This Bulletin, **39**, 156 (1966).

4) Recently, Iida *et al.* studied the formation of methane in the radiolysis of liquid neopentane and isooctane by using N_2O or SF_6 as an electron scavenger. S. Iida and S. Sato, unpublished.

5) Recently, K. Tanno *et al.* studied the fragmentation of excited ions in the radiolysis of neopentane and isooctane in the liquid phase. K. Tanno, T. Miyazaki, K. Shinsaka and S. Shida, to be published shortly in *J. Phys. Chem.*

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Hydrogen, one of the products in *n*-hexane - ammonia system, was measured in the same manner. In *n*-hexane - nitrous oxide system, the non-condensable products were hydrogen, nitrogen and methane. Hydrogen and the other gaseous mixture which was composed of nitrogen and methane were analyzed as in the case of pure *n*-hexane, and then each quantity of nitrogen and methane was calculated by using the quantity of the mixture and the compositions obtained from the mass spectra of the mixture. The fragment products were analyzed gas chromatographically. An irradiated sample and a measured amount of *cis*-2-butene, which was used as a quantitative marker for gas chromatographic analysis, were completely vaporized and mixed in an adequate-sized reservoir filled with nitrogen gas at a little higher pressure than the atmospheric one, and an aliquot of the gaseous mixture was injected by a syringe into a gas chromatograph with a flame ionization detector. A 3 m column of activated alumina with tailing reducer was used at 80°C.

Additive Concentration. Concentration of the additives was estimated by assuming that the additives were completely dissolved in the liquid phase of *n*-hexane at 40°C. The assumption would be justified by the fact that the volume of gas phase in an irradiated ampoule was less than one-fifth of the inner total volume, and by the inference that the solubilities of the additives in *n*-hexane would not so much differ from those in other hydrocarbons.[3)]

Results

All of the additives, used in this work, decreased to a certain extent the *G*-values of the fragment products as shown in Figs. 1—7. The *G*-values decreased rapidly in low concentration of the additives and became approximately constant values respectively in higher concentration. These constant values are represented by G_A in the case of addition of nitrous oxide (Figs. 1, 2 and 3), G_B in that of nitric oxide (Figs. 4 and 5), G_C in that

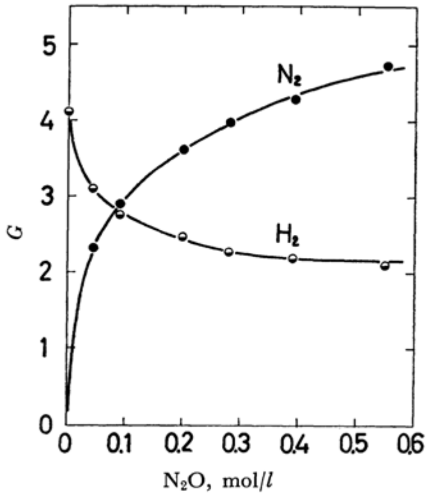

Fig. 1. Yields of nitrogen and hydrogen from N_2O - *n*-hexane solution.

—●— N_2, —◒— H_2

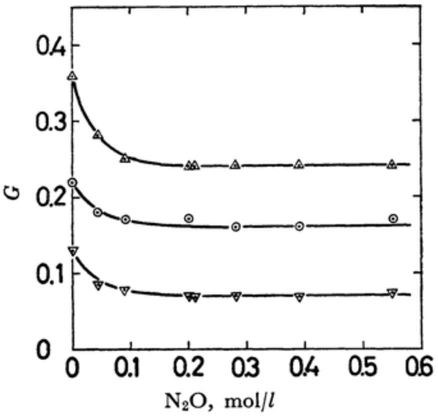

Fig. 2. Yields of methane, propylene and propane from N_2O - *n*-hexane solution.

—⊙— CH_4, —▽— C_3H_6
—△— C_3H_8

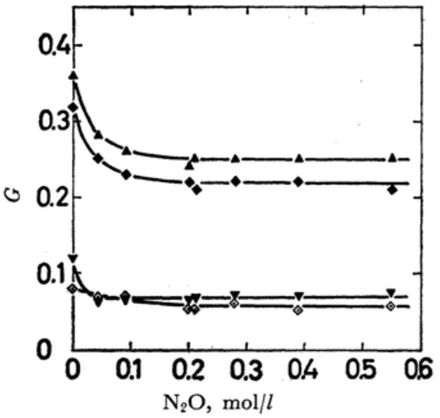

Fig. 3. Yields of ethylene, ethane, 1-butene and *n*-butane from N_2O - *n*-hexane solution.

—▼— C_2H_4, —▲— C_2H_6,
—◈— 1-C_4H_8, —◆— *n*-C_4H_{10}

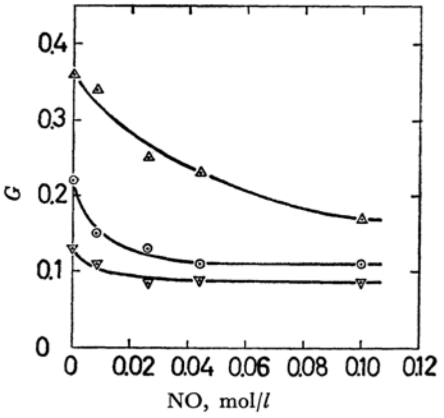

Fig. 4. Yields of methane, propylene and propane from NO - *n*-hexane solution.

—⊙— CH_4, —▽— C_3H_6,
—△— C_3H_8

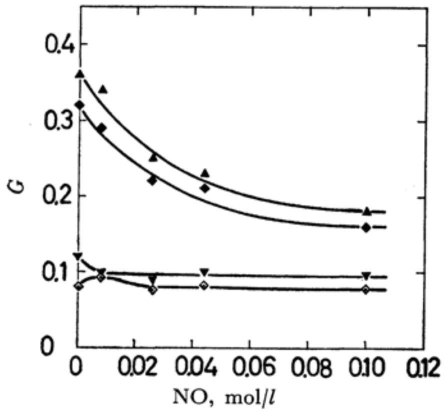

Fig. 5. Yields of ethylene, ethane, 1-butene and *n*-butane from NO - *n*-hexane solution.

—▼— C_2H_4, —▲— C_2H_6,
—◈— 1-C_4H_8, —◆— *n*-C_4H_{10}

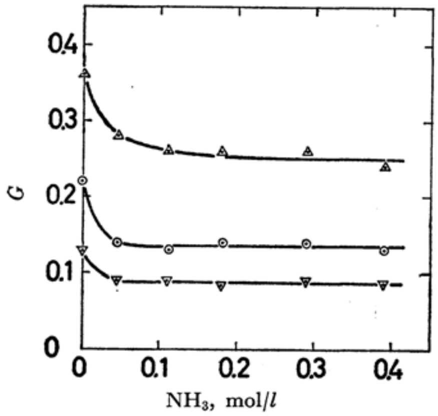

Fig. 6. Yields of methane, propylene and propane from NH_3 - *n*-hexane solution.

—⊙— CH_4, —▽— C_3H_6,
—△— C_3H_8

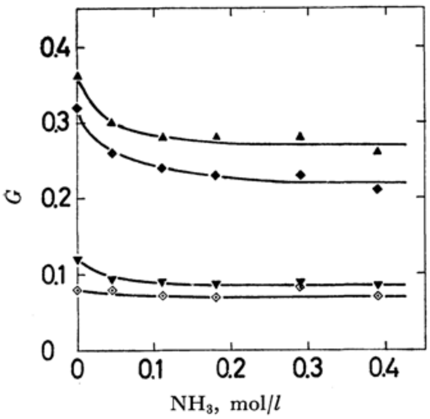

Fig. 7. Yields of ethylene, ethane, 1-butene and *n*-butane from NH_3 - *n*-hexane solution.

—▼— C_2H_4, —▲— C_2H_6,
—◈— 1-C_4H_8, —◆— *n*-C_4H_{10}

TABLE 1. YIELDS OF FRAGMENT PRODUCTS IN THE RADIOLYSIS OF LIQUID *n*-HEXANE WITH AND WITHOUT ADDITIVES

Product[a]	*n*-C_6H_{14}	*n*-C_6H_{14} + N_2O		*n*-C_6H_{14} + NO	
	G_0	G_A	ΔG_A	G_B	ΔG_B
H_2	4.11[b] 4.78[c]	2.15	1.96[d] 2.63[e]		
CH_4	0.22	0.16	0.06	0.11	0.11
C_2H_4	0.12	0.07	0.05	0.10	0.02
C_2H_6	0.36	0.25	0.11	0.18	0.18
C_3H_6	0.13	0.07	0.06	0.09	0.04
C_3H_8	0.36	0.24	0.12	0.17	0.18
1-C_4H_8	0.08[b] 0.18[c]	0.06	0.02[f] 0.12[g]	0.08	0.10[g]
n-C_4H_{10}	0.32	0.22	0.10	0.16	0.16

a C₅ products were not detected.
b *G*-Values without correction of dose dependence.
c Initial *G*-values.
d Calculated from $G_0(H_2)=4.11$.
e Calculated from $G_0(H_2)=4.78$.
f Calculated from $G_0(1\text{-}C_4H_8)=0.08$.
g Calculated from $G_0(1\text{-}C_4H_8)=0.18$.

TABLE 2. YIELDS OF FRAGMENT PRODUCTS IN THE RADIOLYSIS OF LIQUID *n*-HEXANE WITH ADDITIVES

Product	*n*-C_6H_{14}+(NO+N_2O)[a]			*n*-C_6H_{14}+NH_3	
	G_C	ΔG_C	ΔG_{BC}	G_D	ΔG_D
H_2				3.99[b]	0.12[c]
CH_4	0.10	0.12	0.01	0.14	0.08
C_2H_4	0.08	0.04	0.02	0.08	0.04
C_2H_6	0.15	0.21	0.03	0.27	0.09
C_3H_6	0.06	0.07	0.03	0.09	0.04
C_3H_8	0.14	0.22	0.03	0.25	0.11
1-C_4H_8	0.05	0.13[d]	0.03	0.07	0.01[e] 0.11[d]
n-C_4H_{10}	0.13	0.19	0.03	0.22	0.10

a NO concentration: 0.09 mol/*l*,
  N_2O concentration: 0.48 mol/*l*.
b NH_3 concentration: 0.48 mol/*l*.
c Calculated from $G_0(H_2)=4.11$.
d Calculated from $G_0(1\text{-}C_4H_8)=0.18$.
e Calculated from $G_0(1\text{-}C_4H_8)=0.08$.

of nitric and nitrous oxide (it is not shown in a figure), and G_D in that of ammonia (Figs. 6 and 7), and the yields of the fragment products in the absence of the additives are represented by G_0. Defining ΔG_A, ΔG_B, ΔG_C, ΔG_D and ΔG_{BC} by the relationships $G_0-G_A=\Delta G_A$, $G_0-G_B=\Delta G_B$, $G_0-G_C=\Delta G_C$, $G_0-G_D=\Delta G_D$ and $G_B-G_C=\Delta G_{BC}$ respectively, one obtains the values in Tables 1 and 2.

In the case of addition of nitrous oxide, nitrogen was produced as shown in Fig. 1. When the concentration of nitrous oxide increased, $G(N_2)$

increased corresponding to the decrease of $G(H_2)$, though both $G(N_2)$ and $G(H_2)$ tended to level off at high concentration of nitrous oxide. This is the same as in the case with other hydrocarbons.3,4) In the case of pure *n*-hexane, the yields of hydrogen and 1-butene decreased with increasing dose. These dose dependences would be attributable to the addition of H atoms to the unsaturated products, especially hexenes.2) In the case of cyclohexane,3) almost all H radicals scavengable by unsaturated products appear to be produced through neutralization. Therefore, assuming that it is the case with *n*-hexane, ΔG_2 (H_2) in Table 1, the true decrease of $G(H_2)$ at high concentration of nitrous oxide would be closer to 2.63 than 1.96, and $\Delta G_A(1\text{-}C_4H_8)$ would be closer to 0.12 than 0.02.

Discussion

Mechanism of C-C Bond Rupture. For simplicity, initial processes and subsequent reactions in the radiolysis of liquid *n*-hexane are represented schematically as follows; ionization with dissociation will be discussed later on.

Initial ionization and excitation:

$$AH \begin{cases} \rightsquigarrow AH^+ + e^- & (1) \\ \rightsquigarrow AH^* & (2) \end{cases}$$

Neutralization:

$$AH^+ + e^- \begin{cases} \longrightarrow R + S & (3) \\ \longrightarrow M + N & (4) \end{cases}$$

Neutral decomposition:

$$AH^* \begin{cases} \longrightarrow R + S & (5) \\ \longrightarrow M + N & (6) \end{cases}$$

where AH denotes *n*-hexane, R and S denote radicals scavengable by a radical scavenger, and M and N denote molecular products unaffected by a radical scavenger.

It has been reported that nitrous oxide captures a thermal electron by the reaction (7),12) and that it is not reactive to free radicals.13,14)

$$N_2O + e^- \rightarrow N_2 + O^- \qquad (7)$$

The charge transfer from $n\text{-}C_6H_{14}^+$ to N_2O appears improbable because of lower ionization potential of $n\text{-}C_6H_{14}$ (10.54 eV15)) than that of N_2O (12.9 eV16)), and so the decrements of product yields due to added N_2O may be considered to be the portion produced through the reaction (3) or (4). It is known that nitric oxide is very reactive to free radicals.10) Though there is a possibility of a charge transfer from $n\text{-}C_6H_{14}^+$ to NO because of the lower ionization potential of NO (9.4±0.2 eV17)) than that of $n\text{-}C_6H_{14}$, it would be neglected9) at such a low concentration (less than 1.3 mol%). So the decrements of product yields due to added NO may be considered to be the portion produced through the radicals in the reaction (3) or (5). In the coexistence of N_2O and NO, the decrements of product yields may be considered to be the portion produced through the reaction (3), (4) or (5).

If the product yields due to a reaction (*n*) which is one of the above reactions (1) to (6) are represented by $G_{(n)}$, one obtains the following relationships.

$$G_{(5)} + G_{(6)} = G_A, \quad G_{(3)} + G_{(4)} = \Delta G_A,$$
$$G_{(6)} = G_C, \quad G_{(4)} = \Delta G_{BC}$$

Further, defining radical yields and molecular yields due to neutralization by $G_{R\alpha}$ and $G_{M\alpha}$, and those yields due to the other processes by $G_{R\beta}$ and $G_{M\beta}$ respectively, one obtains the following relationships from the above.

$$G_{R\alpha} = \Delta G_A - \Delta G_{BC}, \quad G_{M\alpha} = \Delta G_{BC},$$
$$G_{R\beta} = G_A - G_C, \quad G_{M\beta} = G_C$$

Now, $G_{R\alpha}$, $G_{M\alpha}$ $G_{R\beta}$ and $G_{M\beta}$ are evaluated from the values in Tables 1 and 2, and the results are shown in Tables 3 and 4.

From the reaction (4), the following relationships are expected with regard to molecular yields in neutralization process.

$$G_{M\alpha}(C_2H_4) = G_{M\alpha}(C_4H_{10}),$$
$$G_{M\alpha}(C_2H_6) = G_{M\alpha}(C_4H_8),$$
$$G_{M\alpha}(C_3H_8) = G_{M\alpha}(C_3H_6)$$

The values in Table 3 approximately agree with

TABLE 3. VALUES OF $G_{R\alpha}$ AND $G_{M\alpha}$, AND RATIOS (%) OF THESE YIELDS TO G_0

Product	From neutralization			
	$G_{R\alpha}$	%	$G_{M\alpha}$	%
CH_4	0.05	22.7	0.01	4.5
C_2H_4	0.03	25.0	0.02	16.7
C_2H_6	0.08	22.2	0.03	8.3
C_3H_6	0.03	23.1	0.03	23.1
C_3H_8	0.09	25.0	0.03	8.3
$1\text{-}C_4H_8$	0.09[a]	50.0	0.03	16.7
$n\text{-}C_4H_{10}$	0.07	21.9	0.03	9.4
		$G_{R\alpha}+G_{M\alpha}$	%[b]	
H_2		2.63[c]	55.0	

a Calculated from $G_0(1\text{-}C_4H_8)=0.18$.
b Calculated from $((G_{R\alpha}+G_{M\alpha})/G_0)\times 100$.
c Calculated from $G_0(H_2)=4.78$.

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TABLE 4. VALUES OF $G_{R\beta}$ AND $G_{M\beta}$, AND RATIOS (%) OF THESE YIELDS TO G_0

Product	From the other processes than neutralization			
	$G_{R\beta}$	%	$G_{M\beta}$	%
CH_4	0.06	27.3	0.10	45.5
C_2H_4	0[a]	0	0.08	66.7
C_2H_6	0.10	27.8	0.15	41.7
C_3H_6	0.01	7.7	0.06	46.2
C_3H_8	0.10	27.8	0.14	38.9
1-C_4H_8	0.01	5.6	0.05	27.8
n-C_4H_{10}	0.09	28.1	0.13	40.6
		$G_{R\beta}+G_{M\beta}$	%[b]	
H_2		2.15[c]	45.0	

a By considering an experimental error.
b Calculated from $((G_{R\beta}+G_{M\beta})/G_0)\times 100$.
c Calculated from $G_0(H_2)=4.78$.

this expectation. According to the values in Table 4, yields of saturated products in $G_{M\beta}$ are larger than those of unsaturated products of the same carbon numbers. This appears to suggest that not only the reactions (2), (5) and (6) but also the following reactions (8), (9) and (10) may occur.

$$AH \rightsquigarrow AH^{+*} + e^- \qquad (8)$$

$$AH^{+*} \rightarrow R^+ + S \qquad (9)$$

$$R^+ + AH \rightarrow RH + A^+ \qquad (10)$$

where AH^{+*} denotes an ion decomposing before neutralization, and the reaction (10) denotes a hydride-ion transfer. For example, as for $G_{M\beta}$ (C_3 products), the reactions (9) and (10) indicate the following reactions (9a) and (10b) respectively. As a result, $G_{M\beta}(C_3H_8)$ would be larger than $G_{M\beta}(C_3H_6)$.

$$n\text{-}C_6H_{14}^{+*} \rightarrow C_3H_7^+ + C_3H_7 \qquad (9a)$$

$$C_3H_7^+ + n\text{-}C_6H_{14} \rightarrow C_3H_8 + C_6H_{13}^+ \qquad (10b)$$

The values in Tables 3 and 4 suggest that processes other than neutralization may play rather an important role than neutralization process in the C-C bond rupture in the radiolysis of liquid *n*-hexane.

The O^- produced in the reaction (7) appears to react predominantly with N_2O,[3] and the resulting O_2^- probably abstracts H^+ from *n*-$C_6H_{14}^+$ as follows.

$$N_2O + O^- \rightarrow N_2 + O_2^- \qquad (11)$$

$$n\text{-}C_6H_{14}^+ + O_2^- \rightarrow C_6H_{13} + HO_2 \qquad (12)$$

This speculation for the proton scavenging efficiency of O_2^- has been adopted to explain the different effects of N_2O and SF_6 in the radiolysis of liquid neopentane.[18] Thus, at sufficiently high concentration of N_2O, the yield of isobutene, which is formed from *t*-$C_4H_9^+$, was nearly equal to those in the absence of N_2O and in the presence of CH_3NH_2 as a proton scavenger, while in the presence of SF_6 as an electron scavenger,[6] however, the yield decreased to about a quarter of that in the absence of SF_6. This result seems to indicate the dual character of N_2O as an electron scavenger and a proton scavenger.

Effect of Added Ammonia. As shown in Table 2, ΔG_D, *i. e.*, the decrease of product yields due to added ammonia, approximately agrees with ΔG_A, *i. e.* the decrease due to added nitrous oxide. This phenomenon appears to suggest that ammonia influenced the same process in the radiolysis of liquid *n*-hexane as nitrous oxide did. Taking into consideration the similalities[19] of basic data with respect to the formation of hydrogen in the radiolysis between *n*-hexane and cyclohexane, nearly the same yield of hydrogen in the presence and absence of ammonia ($G_D(H_2)=3.99$ and $G_0(H_2)=4.11$) appears to be able to be explained by the proton transfer from *n*-$C_6H_{14}^+$ to NH_3 as has been done in the case of cyclohexane.[7,8] This proton transfer reaction (13) is exothermic by 38 kcal/mol.

$$n\text{-}C_6H_{14}^+ + NH_3 \rightarrow C_6H_{13} + NH_4^+ \qquad (13)$$

If ammonia suppresses the neutralization processes (3) and (4) by the proton scavenging, the effect of added ammonia would be similar to that of added nitrous oxide. On the other hand, the ionization potential of ammonia (10.52 eV[15]) is approximately the same as that of *n*-hexane (10.54 eV[15]), and so there is every possibility of the charge transfer from *n*-$C_6H_{14}^+$ to NH_3. It cannot, however, be decided which reaction, the proton transfer or the charge transfer, is the real cause of the decreases of product yields due to added ammonia.

We wish to thank Dr. Shin Sato for his helpful discussions.

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[18] K. Tanno, T. Miyazaki and S. Shida, unpublished. See also Ref. 5.

[19] *G*(H) from *n*-hexane is 2.0[20] and that from cyclohexane is 2.0,[21] C-H bond dissociation energy of *n*-hexane is 93.2 kcal/mol[22] and that of cyclohexane is 94 kcal/mol,[7] the rate constant for hydrogen abstraction from *n*-hexane by hydrogen atoms is 4.9×10^9 cc·mol^{-1} sec^{-1} at 23°C[23] and that from cyclohexane is 6.6×10^9 cc mol^{-1} sec^{-1} at 23°C,[23] and the ionization potential of *n*-hexane is 10.54 eV[15] and that of cyclohexane is 10.3 ± 0.2 eV.[24]

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