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Reactions of Ions in the Radiolysis of Liquid Propane

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The reactions of ions, especially fragmentation of excited ions and the subsequent reactions of fragment ions in the radiolysis of liquid propane have been investigated by the use of charge scavengers such as sulfur hexafluoride (SF_6) and ammonia (NH_3). It has been confirmed that the fragment ions are produced by the dissociation of the excited parent ion prior to the parent ion-electron recombination. The yields of $C_2H_5^+$ and $C_3H_7^+$ have been measured by the use of the reaction, $RH^+ + NH_3 \rightarrow R + NH_4^+$, with the results $G \gtrsim 0.28$ and ~ 1.1 respectively. These ions neutralize with electrons to form ethylene or propylene. The hydride ion transfer reaction between $C_2H_5^+$ and propane may be competing with the neutralization of $C_2H_5^+$ by electron in the absence of an additive. The yields of fragment ions are compared in the radiolysis of several saturated hydrocarbons.

Studies of ionic reactions in the liquid-phase radiolysis of some branched saturated hydrocarbons using charge scavengers such as SF_6 and NH_3 were reported previously.[1,2] Some of the significant results found were (1) the fragmentation of excited molecular ions still occurs in the liquid phase, (2) the fragment ion (such as $t\text{-}C_4H_9^+$ and $s\text{-}C_3H_7^+$) neutralizes with an electron to form an olefin molecule, and (3) the hydride ion transfer reaction may not be so fast as in the gas phase. The present report of the radiolysis of liquid propane shows a similar pattern of ionic reactions. Koob and Kevan[3,4] studied extensively the liquid-phase

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[1] K. Tanno, T. Miyazaki, K. Shinsaka and S. Shida, *J. Phys. Chem.*, **71**, 4290 (1967).

[2] K. Tanno, S. Shida and T. Miyazaki, *ibid.*, **72**, 3496 (1968).

[3] R. D. Koob and L. Kevan, *Trans. Faraday Soc.*, **64**, 706 (1968).

[4] R. D. Koob and L. Kevan, *ibid.*, **64**, 422 (1968).

radiolysis of propane by the use of deutrated propane and a radical scavenger (oxygen). However, we have employed a different technique to detect the ionic species, that is, proper use of charge scavengers.

Experimental

The propane supplied by Takachiho Shoji Co. was purified by gas chromatography and trap-to-trap distillations to reduce hydrocarbon impurities less than 10 ppm. SF_6 (>98%) (Matheson Co.) and NH_3 Takachiho Shoji Co.) of high purity were used without further purification. Propane was irradiated in Pyrex glass ampoules 5 mm in diameter fitted with break seals. Mole fraction of the gas-phase propane was less than 5% of the total in the ampoule. Samples were kept at $4°\pm1°C$ during irradiation in an ice-water mixture. Irradiations were carried out by ^{60}Co γ-rays, at a dose rate of 7.1×10^{19} eV/g hr. The total doses were 3.55×10^{20} eV/g. Other experimental details were described previously.[2] G Values reported here are based on the energy absorbed by propane only.

Results and Discussion

In Fig. 1 is shown the effect of SF_6 on the yield of ethane, ethylene and propylene. Other radiolytic yields are $G(H_2)=4.8$ and $G(CH_4)=0.68$ without SF_6, and $G(H_2)=2.5$ and $G(CH_4)=0.56$ with 4 mol% SF_6. The G values of fragment products obtained in the present work without an additive are somewhat smaller than those obtained by Koob and Kevan.[4]

An appreciable increase in the ethane yield is observed upon the addition of SF_6, while the yields of ethylene and propylene decrease rapidly. This phenomenon suggests the definite contribution of ionic reactions to the formation of these products. A similar increase in an alkane and the decrease in an olefin product yield upon the addition of an electron scavenger has also been observed in the radiolysis of liquid isobutane and isopentane where $G(C_3H_8)$ or $G(C_4H_{10})$ increases upon the addition of SF_6[2] or CCl_4.[5]

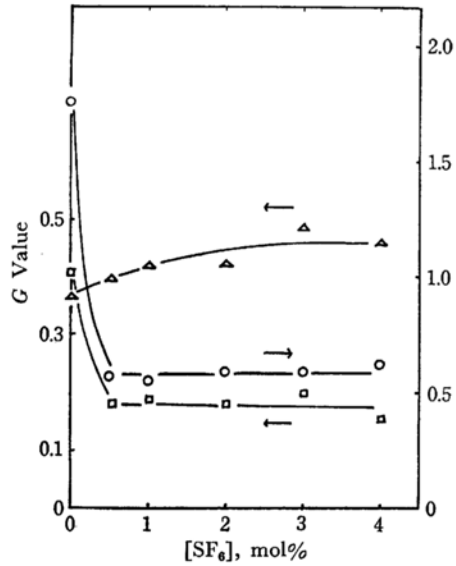

Fig. 1. Effect of SF_6 in the radiolysis of liquid propane.
△ C_2H_6, □ C_2H_4, ○ C_3H_6

A possible mechanism of the ionic reactions for the formation of ethylene is

$$C_3H_8 \rightsquigarrow C_2H_5^+ + CH_3 \tag{1}$$

$$C_2H_5^+ + e^- \rightarrow C_2H_4 + H \tag{2}$$

$$C_3H_8^+ + e^- \rightarrow C_2H_4 + CH_4 \tag{3}$$

Ethylene is formed by neutralization with an electron of $C_2H_5^+$ as well as the parent ion such as reaction (3). We reported the formation of an olefin molecule by neutralization of a fragment carbonium ion in the radiolysis of several liquid hydrocarbons.[1,2] A part of $C_2H_5^+$ may form ethane by the hydride ion transfer reaction with propane, competing with the neutralization reaction (2).

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \tag{4}$$

The decrease in ethylene yield caused by SF_6 is due to the capture of electrons by SF_6.

$$e^- + SF_6 \rightarrow SF_6^- \tag{5}$$

The increased yield of ethane upon the addition of SF_6 may be explained by the fact that the neutralization of $C_2H_5^+$ is delayed and that the hydride ion transfer reaction (reaction (4)) becomes predominant in place of the neutralization of $C_2H_5^+$. The decrement of ethylene exceeds the increment of ethane, because the ethylene formation by both reactions (2) and (3) is prevented by SF_6, while ethane formation is promoted only by reaction (4).

Although the possibility that SF_6 promotes the H_2^- transfer reaction could not be denied,

$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_6^+ \tag{6}$$

the extent of reaction (6), if any, is estimated to be smaller than that of reaction (4), if one considers the result of gas-phase radiolysis of propane[6] or the mass spectral data,[7] where the relative abundance of $C_2H_5^+$ greatly exceeds that of $C_2H_4^+$. Actually Koob and Kevan[3] infrerred that the degree of reaction (6) is about half as much smaller than that of reaction (4) in the liquid-phase radiolysis of propane at 35°C. However, the following explanation for the increased yield of ethane could not be entirely excluded.

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[5] A. A. Scala and P. Ausloos, *J. Chem. Phys.*, **47**, 5129 (1967).

[6] L. I. Bone, L. W. Sieck and J. H. Futrell, "The Chemistry of Ionization and Excitation," ed. by G. R. A. Johnson and G. Scholes, Taylor and Francis, Ltd., London (1967), pp. 223—235.

[7] American Petroleum Institute Research Project 44

$$C_2H_5^+ + SF_6^- \rightarrow C_2H_5 + SF_6 \qquad (7)$$

$$C_2H_5 + C_3H_8 \rightarrow C_2H_6 + C_3H_7 \qquad (8)$$

Thus, following reaction (5), SF_6^- neutralizes with $C_2H_5^+$ to lead to the formation of ethyl radicals which then abstract hydrogen atom of propane to form ethane. Detailed discussion on this point was given in a previous paper.[2] We tentatively prefer reaction (4) for the increase in the ethane yield upon the addition of SF_6.

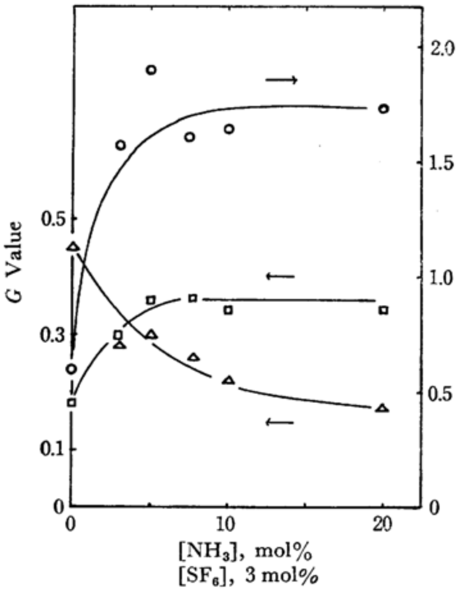

Fig. 2. Effect of NH_3 in the presence of SF_6 in the radiolysis of liquid propane.
△ C_2H_6, □ C_2H_4, ○ C_3H_6

The increased yield of ethylene and the decreased yield of ethane caused by NH_3 added together with SF_6 (Fig. 2) is undoubtedly attributed to the proton transfer from $C_2H_5^+$ to NH_3.

$$C_2H_5^+ + NH_3 \rightarrow C_2H_4 + NH_4^+ \qquad (9)$$

Proton transfer reactions between several carbonium ions and NH_3 have been reported.[8,9] The G increment of ethylene at higher concentrations of NH_3 is 0.17, while the G decrement of ethane is 0.28. A plausible explanation for the difference is that the condensation reaction occurs between $C_2H_5^+$ and NH_3 which does not lead to the formation of ethylene.

$$C_2H_5^+ + NH_3 \rightarrow C_2H_5NH_3^+ \qquad (10)$$

Ward and Hamill[10] reported the similar condensation reactions between several carbonium ions and methyl alcohol. If reaction (10) is assumed, $G(C_2H_5^+) \gtrsim 0.28$ may be estimated from the decrement of ethane at 20 mol%NH_3 allowing for the possibility that $C_2H_5^+$ cannot be captured completely even at 20 mol% NH_3.

Propylene is formed in the absence of an additive as

$$C_3H_7^+ + e^- \rightarrow C_3H_6 + H \qquad (11)$$

The occurrence of the reaction may be supported by the fact that the yield of propylene increases with the addition of NH_3 in the presence of SF_6 (Fig. 2). The increase is due to the proton transfer from $C_3H_7^+$ to NH_3.

$$C_3H_7^+ + NH_3 \rightarrow C_3H_6 + NH_4^+ \qquad (12)$$

Reaction (12) seems to be very efficient, because 5 mol% NH_3 is sufficient enough to capture almost all of $C_3H_7^+$ as seen in Fig. 2. The G increment of propylene is 1.12, and $G(C_3H_7^+) \approx 1.1$ is estimated.

$C_3H_7^+$ can be formed from the decomposition of the excited parent ion as well as the secondary reaction such as reaction (4). In the xenon-sensitized radiolysis of propane in the gas phase,[6] $C_3H_7^+$ produced by the secondary reaction (hydride ion transfer reactions of fragment ions with propane) was estimated as much as 0.91 in M/N yield. However, in the liquid phase, the yield of the fragment ions which undergo the secondary reaction to produce $C_3H_7^+$ is estimated not to greatly exceed $G(C_2H_5^+) \approx 0.28$, so $C_3H_7^+$ may be formed directly from the decomposition of the parent ion in the liquid phase.

We have so far investigated the ionic reactions in the radiolysis of several staurated hydrocarbons and were able to measure the approximate yields of the fragement carbonium ions. The results is summarized in Table 1. The yield of fragment ions differs from one hydrocarbon to another. A simplified theoretical treatment has been proposed by Miyazaki *et al.*[11] to explain the difference and they obtained the qualitative agreement with the experiment. In any case, there seem to be two factors governing the fragment ion formation prior to the parent ion-electron recombination in the radiolysis of liquid saturated hydrocarbons. The two factors are (1) the heat of formation of a carbonium ion from the parent ion and (2) the number of atoms in the hydrocarbon, that is, the number of degrees of vibrational freedom.

The internal energy distribution functions of excited parent ions were determined experimentally for only propane and *n*-butane.[12] However, if one assumes that the amount of the internal energy and its distribution of the excited parent ions do not differ greatly from one hydrocarbon to another,

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8) T. Miyazaki and S. Shida, This Bulletin, **38**, 2114 (1965).

9) T. Miyazaki and S. Shida, *ibid.*, **39**, 2344 (1966).

10) J. A. Ward and W. H. Hamill, *J. Am. Chem. Soc.*, **89**, 5116 (1967).

11) T. Miyazaki, K. Tanno and S. Shida, This Bulletin, **42**, 362 (1969).

12) W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961).

TABLE 1. THE *G* VALUES OF FRAGMENT IONS IN THE LIQUID-PHASE RADIOLYSIS OF SATURATED HYDROCARBONS*

Fragment ion	Saturated hydrocarbon					
	CCC	C CCC	C CCCC	C CCC C	CC CCCC	C C CCCCC C
$C_2H_5^+$	0.28 (30)	—	0.1 (19)	—	—	—
$C_3H_7^+$	1.1 (8)	1.15 (14)	0.23 (19)	—	0.5 (17)	—
$C_4H_9^+$	—	—	0.12 (20)	1.0 (8)	— —	0.36 (13)

* The values presented here, except for propane, are taken from Refs. 1 and 2. In the parentheses are shown the heat of formation of the fragment ion formed from the parent molecular ion in kcal/mol, taken from Ref. 13 or F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York (1957)

the smaller the number of bonds in a hydrocarbon, the greater the energy partitioned per one bond. If these two conditions are favorably satisfied, relatively high values of fragment ions may be obtained, for example, such as $G(C_3H_7^+)=1.1$ and 1.15 for propane and isobutane, and $G(C_4H_9^+)=1.0$ for neopentane.

The $C_4H_9^+$ is formed in the radiolysis of neopentane as well as isopentane, but in different yields. Both hydrocarbons have the same number of degrees of vibrational freedom. However, the heat of formation by reaction (13) is 20 kcal/mol,[13] while only 8 kcal/mol[13] is required for reaction (14).

$$\textit{iso}\text{-}C_5H_{12}^+ \rightarrow C_4H_9^+ + CH_3 \qquad (13)$$
$$\Delta H = 20\ \text{kcal/mol}$$

$$\textit{neo}\text{-}C_5H_{12}^+ \rightarrow \textit{t}\text{-}C_4H_9^+ + CH_3 \qquad (14)$$
$$\Delta H = 8\ \text{kcal/mol}$$

Naturally the latter case gives the larger yield of $C_4H_9^+$. The C–C bond energy of a parent ion of a branched hydrocarbon is generally greatly weaker than that of a straight-chain alkane. Although we have not measured, except propane, the yield of fragment ions produced by the C–C bond rupture in the radiolysis of straight-chain alkanes, the yield of fragment ions may be expected smaller, if present, in the radiolysis of straight-chain alkanes such as *n*-pentane and *n*-hexane.

Reactions (15) and (16) require almost the same heat of formation.[13]

$$\textit{iso}\text{-}C_4H_{10}^+ \rightarrow \textit{sec}\text{-}C_3H_7^+ + CH_3 \qquad (15)$$
$$\Delta H = 14\ \text{kcal/mol}$$

$$\textit{iso}\text{-}C_8H_{18}^+ \rightarrow \textit{t}\text{-}C_4H_9^+ + C_4H_9 \qquad (16)$$
$$\Delta H = 13\ \text{kcal/mol}$$

However, if one compares the values in Table 1, $G(\textit{sec}\text{-}C_3H_7^+)$ exceeds $G(\textit{t}\text{-}C_4H_9^+)$. This may be because that the number of degrees of the vibrational freedom of C_4H_{10} is much smaller than that of C_8H_{18}, and that the energy partitioned per C–C bond is larger in the case of isobutane.

The authors wish to thank Dr. T. Miyazaki of Nagoya University for valuable suggestions.

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[13] J. L. Franklin and F. W. Lampe, *Trans. Faraday Soc.*, **57**, 1449 (1961).