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Fragmentation of the Excited Isobutane Ion Produced by Charge Transfer from the Nitrogen Molecule Ion

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The radiolysis of the N_2-*iso*C_4H_{10} (0.0153 mol/mol of N_2) mixture has been studied by using such ion scavengers as ammonia and sulfur hexafluoride. It was found that the $C_3H_7^+$ ion is formed by the fragmentation of the excited isobutane ion produced by the charge transfer from the nitrogen ion. Although nitrogen is an effective quencher of the excited ion, the yield of the $C_3H_7^+$ ion is constant over the pressure range from 0.66 to 130 atm. It has been concluded that the excited isobutane ion produced by the charge transfer with 5 eV excess energy decomposes very fast and that it can not be deactivated by nitrogen of 130 atm, while it has been reported by other authors that the excited isobutane ion with 1.2 eV excess energy can be deactivated below 1 atm. This difference in the characters of the excited isobutane ions can be explained by the previously-proposed mechanism of the fragmentation.

The fragmentation of the excited ion has been explained by the quasi-equilibrium theory,[1] which is based on the fundamental assumption that the randomization of excitation energy among oscillators occurs before the dissociation of the excited ion.

We concluded in a previous study[2] of the effect of density in the radiolysis of butanes that excited ions can be classified into two types, M^{+*} and M^{+**}. The M^{+*} ion decomposes slowly and can be collisionally deactivated by an increase in the pressure. The M^{+**} ion decomposes in a time of one vibration and can not be deactivated even in the liquid phase. In order to obtain further details on the mechanism, studies[3,4] have been made of the ionic fragmentation in the liquid-phase radiolysis of hydrocarbons, and the following new mechanism of the fragmentation of M^{+**} ion has been proposed[5]: The M^{+**} ion is the electronically-excited ion, and the electronic excitation energy spreads over all the C–C bonds in a molecule prior to its fragmentation. The ion decomposes instantaneously in one vibration at a bond where the mean excitation energy per C–C bond exceeds its bond energy.

The present work studies the effect of pressure on the fragmentation of the excited isobutane ion produced by the charge transfer from the nitrogen ion; the previously-proposed mechanism of the fragmentation is confirmed.

Experimental

The isobutane was supplied by the Takachiho-Shoji Co.; its gas chromatographic analysis showed the presence of $5\times10^{-4}\%$ C_2H_6 as an impurity. The ammonia and sulfur hexafluoride were both of high purity and were used without further purification. The nitrogen was 99.99% pure.

The samples were irradiated with γ rays from ^{60}Co at a dose rate of 2.26×10^5 rad/hr and with a total dose of 1.13×10^5 rad at room temperature. The energy absorbed in nitrogen was measured by Fricke dosimetry.

The reaction at a nitrogen pressure of 0.66 atm was carried out in a 350 cc glass cylinder, while those at nitrogen pressures above 1 atm were carried out in a stainless-steel autoclave (45 cc). The products were analyzed by a Hitachi K 53 gas chromatograph equipped with a flame ionization detector (activated alumina column, 2 m, 100°C).

Results and Discussion

Sensitization by Nitrogen. The *G*-value of propane in the radiolysis of N_2(100 atm)-*iso*C_4H_{10} (0.0153 mol/mol of N_2) mixtures amounts to 46 if the value is expressed by the number of product molecules per 100 eV directly absorbed on isobutane. Since the $G(C_3H_8)$ value is 2—3 in the radiolysis of pure isobutane,[2] it may be reasonable to consider that most of the propane in the radiolysis of N_2-*iso*C_4H_{10} mixtures is formed by the sensitization of nitrogen. A similar sensitization was previously

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[1] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

[2] T. Miyazaki, *J. Phys. Chem.*, **71**, 4282 (1967).

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

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

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

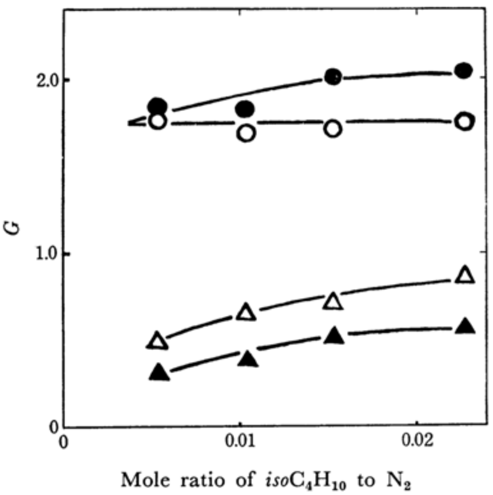

Fig. 1. Effect of increasing concentration of isobutane on the nitrogen sensitization at constant nitrogen pressures of 0.66 and 100 atm.
—●— C_3H_8 at 0.66 atm of N_2
—○— C_3H_8 at 100 atm of N_2
—▲— C_3H_6 at 0.66 atm of N_2
—△— C_3H_6 at 100 atm of N_2

found in the radiolysis of the N_2 - n-C_4H_{10} system.[6] Therefore, the G-values of products are expressed in this paper by the number of product molecules per 100 eV absorbed on nitrogen. The effect of an increase in the concentration of isobutane on the yields of propane above a 0.0153 mol ratio of isobutane suggests that the sensitization by nitrogen may be completed above this concentration (Fig. 1).

Mechanism of Nitrogen Sensitization. The ionic processes of the sensitization were studied by using ammonia as a scavenger of the carbonium ion and sulfur hexafluoride as an electron scavenger. The effect of ammonia on the radiolysis of N_2 (100 atm) - $isoC_4H_{10}$ (0.0153 mol/mol of N_2) - SF_6 (0.003 mol/mol of N_2) mixtures is shown in Fig. 2. Since the neutralization reaction of the stable butane ion ($C_4H_{10}^+$) is suppressed by the presence of sulfur hexafluoride, the reactions of the excited butane ion, such as reactions (3) and (4), can be studied by the addition of ammonia.[3,4] The marked decrease in propane and the increase in propylene upon the addition of ammonia is due to the following reactions of the $C_3H_7^+$ ion with ammonia:

$$N_2 \rightsquigarrow N_2^+ + e \qquad (1)$$

$$N_2^+ + i\text{-}C_4H_{10} \rightarrow C_4H_{10}^{+**} + N_2 \qquad (2)$$

$$C_4H_{10}^{+**} \rightarrow C_3H_7^+ + CH_3 \qquad (3)$$

$$C_3H_7^+ + i\text{-}C_4H_{10} \rightarrow C_3H_8 + C_4H_9^+ \qquad (4)$$

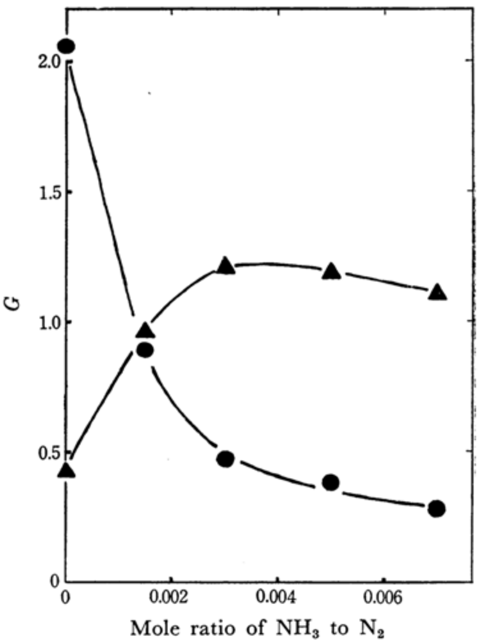

Fig. 2. Effect of ammonia on the radiolysis of N_2(100 atm)-$isoC_4H_{10}$(0.0153 mol/mol of N_2)-SF_6 (0.003 mol/mol of N_2) mixtures.
—●— C_3H_8 —▲— C_3H_6

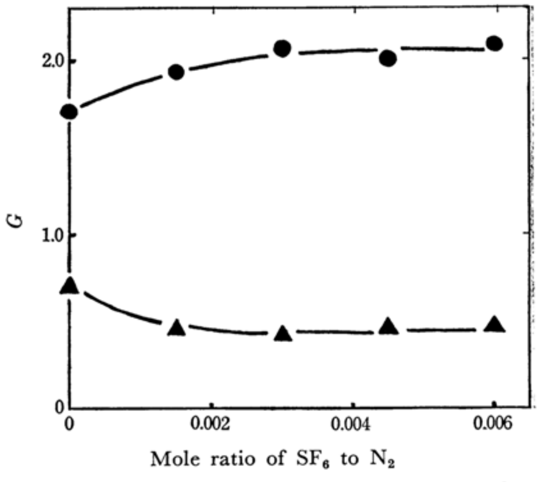

Fig. 3. Effect of sulfur hexafluoride on the radiolysis of N_2(100 atm)-$isoC_4H_{10}$(0.0153 mol/mol of N_2) mixtures.
—●— C_3H_8 —▲— C_3H_6

$$C_3H_7^+ + NH_3 \rightarrow C_3H_6 + NH_4^+ \qquad (5)$$
$$\searrow C_3H_7NH_3^+ \qquad (6)$$

The similar phenomenon was also observed in the gas-phase radiolysis of the n-butane-ammonia system.[7] Since the ionization potential of nitrogen is 15.6 eV, and since that of isobutane is 10.6 eV,

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[6] T. Miyazaki, S. Arai, S. Shida and S. Sunohara, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[7] T. Miyazaki and S. Shida, This Bulletin, **38**, 2114 (1965).

the $C_4H_{10}^{+**}$ ion formed by the charge transfer from the nitrogen ion has an excitation energy of 5 eV, much higher than the bond energy of the C–C bond (0.61 eV).

The effect of sulfur hexafluoride on the radiolysis of N_2(100 atm) - *iso*C_4H_{10}(0.0153 mol/mol of N_2) mixtures is shown in Fig. 3. Propane increases upon the addition of sulfur hexafluoride, while propylene decreases. The results in Table 1, however, show that propylene does not decrease upon the addition of sulfur hexafluoride in the nitrogen sensitization at 10 and 40 atm, while propane increases. Therefore, the variations in the yields of propane and propylene upon the addition of sulfur hexafluoride may be due to the different mechanisms. One possible mechanism of the slight increase in propane may be as follows:

TABLE 1. EFFECT OF PRESSURE OF NITROGEN ON THE FRAGMENTATION OF ISOBUTANE$^{a)}$

	Pressure of N_2, atm					
	0.66	10	40	70	100	130
	iso$C_4H_{10}^{b)}$ system					
C_3H_8	2.01	2.15	2.26	2.22	1.71	1.88
C_3H_6	0.51	0.42	0.55	0.70	0.71	0.89
	iso$C_4H_{10}^{b)}$-$SF_6^{c)}$ system					
C_3H_8	2.08	2.36	2.46	2.41	2.06	2.11
C_3H_6	0.60	0.49	0.52	0.45	0.42	0.51
	iso$C_4H_{10}^{a)}$-$SF_6^{c)}$-$NH_3^{d)}$ system					
C_3H_8	0.79	0.87	0.89	0.89	0.47	0.52
C_3H_6	0.99	1.19	1.28	1.35	1.21	1.02

a) Yields are expressed as the number of product molecules per 100 eV absorbed in nitrogen.
b) Concentration of *iso*C_4H_{10} is 0.0153 mol/mol of N_2.
c) Concentration of SF_6 is 0.003 mol/mol of N_2.
d) Concentration of NH_3 is 0.003 mol/mol of N_2.

$$N_2 \rightsquigarrow N_2^+ + e \qquad (1)$$

$$ \rightsquigarrow N_2^* \qquad (7)$$

$$N_2^+ + e \rightarrow N_2,\ 2N \text{ or } N_2^* \qquad (8)$$

$$N_2^+ + i\text{-}C_4H_{10} \rightarrow C_4H_{10}^{+**} + N_2 \qquad (2)$$

$$e + SF_6 \rightarrow SF_6^- \qquad (9)$$

If the recapture of electrons by nitrogen (reaction (8)) is notable even at 10 atm of nitrogen, the reaction (8) is retarded in the presence of sulfur hexafluoride by reaction (9) and reaction (2) is facilitated.

Another possible mechanism of the increase in propane may be as follows: As an excited agron reacts with sulfur hexafluoride,[8] a highly-excited nitrogen molecule may react with sulfur hexafluoride in a similar fashion to form the nitrogen molecule ion; therefore, the yield of N_2^+, that is, that of $C_4H_{10}^{+**}$, increases upon the addition of sulfur hexafluoride:

$$N_2^* + SF_6 \rightarrow N_2^+ + SF_6^- \qquad (10)$$

Effect of Pressure on the Fragmentation of the Excited Butane Ion. The yields of the $C_3H_7^+$ ion are obtained by using the results in Table 1 and the following relationship[4]:

$$G(C_3H_7^+) = G(C_3H_8) \text{ in the } N_2\text{-}iso C_4H_{10}\text{-}SF_6 \text{ system}$$
$$- G(C_3H_8) \text{ in the } N_2\text{-}iso C_4H_{10}\text{-}SF_6\text{-}NH_3 \text{ system}$$

$G(C_3H_7^+)$ shows a constant value of 1.55, even if the pressure of nitrogen varies from 0.66 to 130 atm (Fig. 4). In the mass spectrum of isobutane upon the bombardment of electrons with 14—15 eV energy, the fraction of $C_3H_7^+$ amounts to 65% of all the ions.[9] Taking $W(N_2)$ as 36.3 eV, it may be expected that $G(C_3H_7^+)=1.79$ in the fragmentation of isobutane by nitrogen sensitization. The $G(C_3H_7^+)$ obtained in the sensitization is obviously in agreement with the mass spectrometric value.

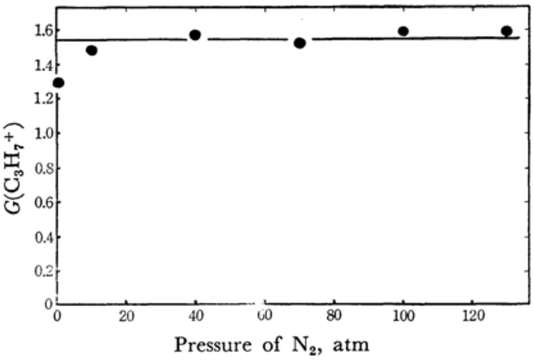

Fig. 4. Effect of pressure of nitrogen on the yields of $C_3H_7^+$ ion formed by the fragmentation of excited isobutane ion.

It has been reported[10] that nitrogen acts as an efficient quencher of the fragmentation of the excited butane ion which is formed by the photoionization at 1048 A (11.8 eV), and that the quenching cross section of nitrogen is a seventh that of butane. As is shown in Fig. 4, the yield of the $C_3H_7^+$ ion is constant and the following deactivation reaction of the excited isobutane ion does not occur, even at 130 atm of nitrogen:

$$C_4H_{10}^{+**} + N_2 \rightarrow C_4H_{10}^+ + N_2 \qquad (11)$$

It may be concluded that the excited isobutane ion with 5 eV excess energy decomposes very fast, probably in the period of one vibration, before the collisons with nitrogen. On the contrary, Ausloos *et al.*[9] reported that the excited isobutane ion with 1.2 eV excess energy decomposes slowly and is

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[8] H. Hotop and A. Niehaus, *J. Chem. Phys.*, **47**, 2506 (1967).

[9] S. G. Lias and P. Ausloos, *ibid.*, **48**, 392 (1968).

[10] P. Ausloos and S. G. Lias, *ibid.*, **45**, 524 (1966).

collisionally deactivated by isobutane of 0.033 atm, which corresponds to a nitrogen pressure of 0.23 atm.

This large difference in the rates of fragmentation of the excited isobutane ions can be explained by the following proposed mechanism[5]: When the ion is highly excited and when the mean excitation energy per C–C bond exceeds its bond energy, the excited ion decomposes in one vibration. When the ion is little excited and when the mean excitation energy per C–C bond does not exceed its bond energy, the excited ion decomposes slowly according to the quasi-equilibrium theory. Since there are three C–C bonds in the isobutane ion, the mean excitation energy per C–C bond of the ion with 5 eV excess energy will be 1.7 eV, higher than the C–C bond energy (0.61 eV), and that of the ion with 1.2 eV excess energy will be 0.4 eV. Consequently, the former excited ion may decompose quickly, in one vibration, while the latter may do so more slowly because of the time lag needed for the accumulation of the excitation energy in a particular bond.