Energy Transfer in the Radiolysis of Neopentane-Alkane Mixture in the Solid Phase at 77 K

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When neopentane containing a small amount of cyclohexane is γ-irradiated at 77 K, the cyclohexyl radical is mainly formed by the energy transfer from neopentane to cyclohexane. The addition of CCl_4, which is an electron scavenger and an excitation acceptor, to the mixture suppresses the formation of the cyclohexyl radical. This fact indicates that the energy transfer is not due to an ion-molecule reaction. When CO_2, which can capture an electron in the neopentane matrix to form CO_2^-, is added to the neopentane–cyclohexane mixture, scarcely any CO_2^- is formed by the irradiation. When ethyl chloride or nitrous oxide is added to the neopentane–cyclohexane mixture, the formation of the cyclohexyl radical is not suppressed, although these additives capture electrons effectively in the solid neopentane. The addition of tetramethylethylene (TME) to the neopentane–cyclohexane–carbon dioxide mixture does not affect the formation of the cyclohexyl radical, although an appreciable amount of TME^+ is formed. These results show that the energy transfer is not due to the ionic process, but to a non-ionic process. The energy transfer is explained by two possible mechanisms, a selective abstraction reaction by the hydrogen atom and an excitation transfer *via* a highly-excited state.

We have previously studied the radiolysis in the solid state in order to elucidate the primary process of radiolysis in the solid state and in order to obtain information about reaction kinetics in the solid state. The quite peculiar phenomena[1–6] we then found could not be explained by applying the mechanism of the radiolysis in the gas and liquid phases to the solid phase.

Therefore, we have indicated that two important problems must be solved in order to elucidate the cause of the peculiar phenomena in the radiolysis of solid hydrocarbons. One problem is the energy transfer in the primary process; the other is how the state of the solid matrix, such as its phase or defects, affects the reaction in the solid phase.

When neopentane containing a small amount of another alkane is γ-irradiated in the solid phase at 77 K, the solute radical is mainly formed by the energy transfer from the γ-irradiated neopentane to the solute.[6] Even if the ionization potential and the energy of the first singlet excited state of the solute are higher than those of neopentane, the solute radical is effectively formed. It was suggested, from the point of view of energetics, that the energy transfer may occur *via* a non-ionic process.[6]

We have here obtained clearer results demonstrating the mechanism of the non-ionic energy transfer in the radiolysis of neopentane containing cyclohexane in the solid phase.

Experimental

The neopentane and cyclopentane supplied by the Tokyo Kagaku Seiki Co. were more than 99.9% pure. Spectrograde cyclohexane and toluene were passed through a 1 m column packed with silica gel and then distilled on a vacuum line before use. The tetramethylethylene supplied by the Tokyo Kagaku Seiki Co. was more than 99.0% pure. The ethane and carbon dioxide supplied by the Takachiho-Shoji Co. were of a high purity and were used without further purification. The carbon tetrachloride was used after distillation on a vacuum line.

Samples were irradiated with γ-rays from a ^{60}Co source at 77 K and at a dose rate of 7.8×10^5 rad/hr. The total dose was 2.0×10^5 rad. The ESR spectra of irradiated samples were measured at 77 K on a JES-3BX ESR spectrometer.

Results and Discussion

Radiolysis of Neopentane Containing Cyclohexane in the Solid Phase at 77 K. When neopentane containing a small amount of cyclohexane is γ-irradiated at 77 K, the cyclohexyl radical is mainly formed, while the formation of the solvent radical is suppressed. The ESR spectra of the irradiated samples were shown in a previous paper.[6] The yields of the cyclohexyl radical are shown in Fig. 1 as a function of the concentration of cyclohexane. Cyclohexane at a concentration of over 0.2% accepts energy efficiently from the irradiated neopentane. When neopentane containing other alkanes, such as ethane, propane, and cyclopentane, is γ-irradiated at 77 K, the energy transfer from neopentane to the solute also occurs efficiently.[6] Since the ionization potential and the first excited state of these alkanes are higher than those of neopentane, a charge transfer from the neopentane cation in a ground state and/or an excitation transfer from neopentane in the first excited state to the solute are impossible. Therefore, we will discuss here whether the energy

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[1] a) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **43**, 1017 (1970). b) T. Miyazaki, T. Yamada, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **44**, 934 (1971).

[2] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970).

[3] T. Miyazaki, Y. Fujitani, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **44**, 984 (1971).

[4] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **44**, 2619 (1971).

[5] M. Fukaya, T. Wakayama, T. Miyazaki, Y. Saitake, and Z. Kuri, 14th Japanese Conference on Radiation Chemistry, Sept. 1971, Sapporo, Japan; This Bulletin, **46**, 1036 (1973).

[6] T. Miyazaki, T. Wakayama, M. Fukaya, Y. Saitake, and Z. Kuri, 14th Japanese Conference on Radiation Chemistry, Sept. 1971, Sapporo, Japan; This Bulletin, **46**, 1030 (1973).

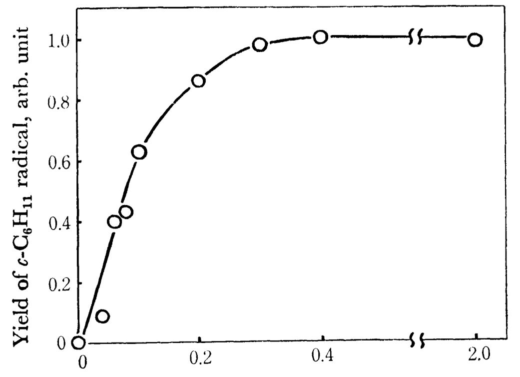

Fig. 1. Formation of cyclohexyl radical as a function of the concentration of cyclohexane in the radiolysis of solid neopentane at 77 K.

transfer is due to an ionic process, such as an ion-molecule reaction and a positive charge transfer *via* an excited ion, or to a non-ionic process.

Ion-Molecule Reaction. Willard *et al.* proposed that the solvent radical may be formed by the ion-molecule reaction in the radiolysis of 3-methylpentane in the solid phase.[7] According to this mechanism, the formation of the solute radical in the radiolysis of neopentane containing alkane may be represented as follows:

$$\text{neo-}C_5H_{12} \rightsquigarrow C_5H_{12}^+ + e^- \tag{1}$$

$$C_5H_{12}^+ + \text{neo-}C_5H_{12} \longrightarrow C_5H_{13}^+ + C_5H_{11}\cdot \tag{2}$$

$$C_5H_{12}^+ + RH \longrightarrow C_5H_{13}^+ + R\cdot \tag{3}$$

$$C_5H_{13}^+ + e^- \longrightarrow C_5H_{12} + H \tag{4}$$

$$H + H \longrightarrow H_2 \tag{5}$$

where RH represents some alkane as a solute. In the previous paper,[6] it was suggested that, for the following reasons, these reactions seem unlikely.

First, when neopentane containing cyclopentane is γ-irradiated at 77 K, the cyclopentyl radical is mainly formed. If the formation of the cyclopentyl radical is due to Reaction (3), neither the amounts of the $C_5H_{13}^+$ ion nor the yields of hydrogen (Reactions (4) and (5)) change upon the addition of cyclopentane. The experimental results, however, show that the yields of hydrogen increase sharply upon the addition of cyclopentane.

Second, the ion-molecule reaction between a neopentane parent ion and an ethane molecule (Reaction (3)) is expected to be endothermic.

Third, though the proton-transfer reaction of polar molecules has been found by means of the mass spectrometer, the reaction cannot be detected in any alkane systems except for methane and ethane. The reaction seems to become more difficult as the molecular weight of alkane increases.[8] It has been reported, from a study of the high-pressure mass spectrometry of propane, that the protonated alkane ion was not detected at all, but only a clustered parent ion.[9]

In the present study we have obtained clear results which support the previous suggestion. Carbon tetrachloride, which is an electron scavenger and an excitation acceptor,[1,10] was added to the neopentane-cyclohexane mixture. If Reactions (1)—(3) occur in the solid phase, CCl_4 will capture the electron (Reaction (6)) and prolong the lifetime of the cation:

$$e^- + CCl_4 \longrightarrow Cl^- + CCl_3\cdot \tag{6}$$

Therefore, the ion-molecule reaction (3) should be promoted by the addition of CCl_4, as has been observed in the radiolysis of liquid neopentane.[11] The effect of CCl_4 on the formation of the cyclohexyl radical is shown in Fig. 2. The formation of the cyclohexyl radical, however, is suppressed by the addition of CCl_4. The formation of solute radicals in the radiolysis of neopentane containing ethane or cyclopentane is also suppressed by the addition of CCl_4. Since carbon tetrachloride does not react with the neopentane cation in the liquid phase,[12,13] it may be a source of difficulty that carbon tetrachloride disturbs the ion-molecule reaction (3). Therefore, Reactions (1)—(3) are not responsible for the formation of solute radicals in the radiolysis of neopentane containing alkane.

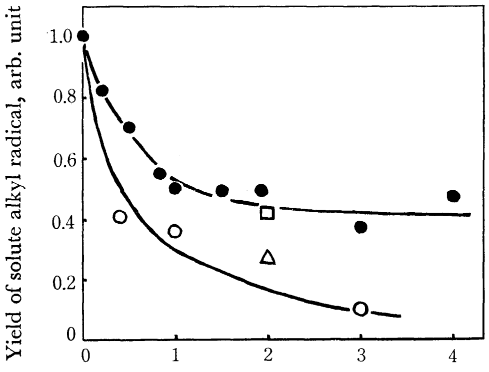

Fig. 2. Effect of CCl_4 on the formation of solute alkyl radical in the radiolysis of neopentane containing alkane at 77 K.
●—●: cyclo-C_6H_{11} in the radiolysis of neo-C_5H_{12}—cyclo-C_6H_{12} (2%).
○—○: cyclo-C_6H_{11} in the radiolysis of neo-C_5H_{12}—cyclo-C_6H_{12} (0.4%).
△: C_2H_5 in the radiolysis of neo-C_5H_{12}—C_2H_6(2%).
□: cyclo-C_5H_9 in the radiolysis of neo-C_5H_{12}—cyclo-C_5H_{10} (2%).

Positive Charge Transfer. Hamill *et al.* proposed that a charge transfer in the irradiated 3-methylpentane glass may occur *via* the excited state of the solvent cation.[14] According to this mechanism, the formation

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[7] a) M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1968). b) D. Timm and J. E. Willard, *ibid.*, **73**, 2403 (1969).

[8] F. P. Abramson and J. H. Futrell, *ibid.*, **71**, 3791 (1967).

[9] L. W. Sieck, S. Searles, and P. Ausloos, *J. Chem. Phys.*, **54**, 91 (1971).

[10] P. K. Ludwig and C. D. Amata, *J. Phys. Chem.*, **72**, 3725 (1968).

[11] A. A. Scala, S. G. Lias, and P. J. Ausloos, *J. Amer. Chem. Soc.*, **89**, 3677 (1967).

[12] J. A. Stone and G. Matsushita, *Can. J. Chem.*, **49**, 3287 (1971).

[13] G. J. Collin and P. Ausloos, *J. Amer. Chem. Soc.*, **93**, 1336 (1971).

[14] W. H. Hamill, "Ionic Process in Irradiated Organic Solids," a chapter in "Radical Ions," E. T. Kaiser and L. Kevan, Eds., John Wiley and Sons, New York, N. Y., 1968.

of the solute radical in the radiolysis of neopentane containing cyclohexane may be represented as follows:

$$\text{neo-C}_5\text{H}_{12} \rightsquigarrow \text{C}_5\text{H}_{12}{}^{+*} + \text{e}^- \qquad (7)$$

$$\text{C}_5\text{H}_{12}{}^{+*} + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{C}_5\text{H}_{12} + \text{C}_6\text{H}_{12}{}^+ \qquad (8)$$

$$\text{C}_6\text{H}_{12}{}^+ + \text{e}^- \longrightarrow \text{C}_6\text{H}_{11}\cdot + \text{H} \qquad (9)$$

where $C_5H_{12}{}^{+*}$ represents an excited cation. Though the information on the excited ion is very scanty at present, we will point out some drawbacks to this mechanism.

First, carbon dioxide captures an electron in the solid phase to form $CO_2{}^-$ (Reaction (10)), and its formation can be easily detected by ESR spectroscopy:

$$\text{e}^- + \text{CO}_2 \longrightarrow \text{CO}_2{}^- \qquad (10)$$

If Reaction (7) occurred in the radiolysis of neopentane, $CO_2{}^-$ should be formed upon the addition of CO_2. Since cyclohexane traps the mobile excited cation in Reaction (8), it is expected that the electron may be more easily captured by CO_2 in the presence of cyclohexane, as has been discussed in connection with the radiolysis of 3-methylpentane.[14,15] The yields of $CO_2{}^-$ in the radiolysis of neopentane–cyclohexane–CO_2 (2%) mixture are shown in Fig. 3. The yields of $CO_2{}^-$ are quite small, contrary to the expectation based on Reactions (7), (8), (9), and (10). The G-values of $CO_2{}^-$ are only 0.04—0.01, although the yields of the cyclohexyl radical amount to 2 G-units in the radiolysis of the neopentane–cyclohexane(3%)–CO_2(2%) mixture and cyclohexane captures a large amount of active species. There is a possibility that CO_2 is not dissolved into the neopentane matrix and that it cannot capture an electron in this matrix. This possibility is, however, obviated by the following experimental results. When tetramethylethylene is added to the neopentane–CO_2 (2%) mixture, an appreciable amount of $CO_2{}^-$ is formed (Fig. 3).

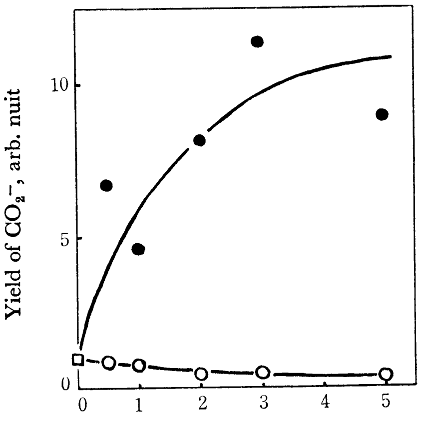

Fig. 3. Effect of solute on the formation of $CO_2{}^-$ in the radiolysis of neopentane containing CO_2 (2%) at 77 K.
●—●: Yields of $CO_2{}^-$ in the presence of tetramethylethylene.
○—○: Yields of $CO_2{}^-$ in the presence of cyclohexane.
□: Yields of $CO_2{}^-$ in the absence of the solute.

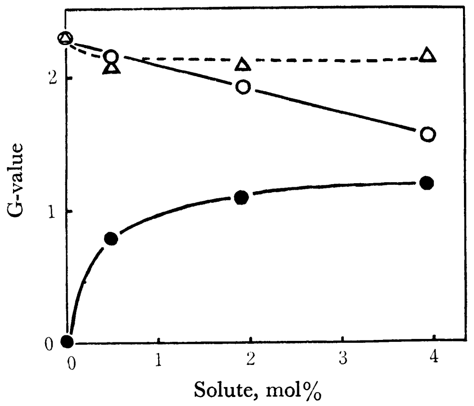

Fig. 4. Effect of C_2H_5Cl and N_2O on the formation of cyclohexyl radical in the radiolysis of neopentane–cyclohexane (2%) mixture at 77 K.
○—○: cyclohexyl radical upon the addition of C_2H_5Cl.
●—●: ethyl radical upon the addition of C_2H_5Cl.
△—△: cyclohexyl radical upon the addition of N_2O.

Second, since the efficiency of electron capture by carbon dioxide is relatively small, we have used more efficient electron scavengers, such as ethyl chloride and nitrous oxide. Figure 4 shows the effects of ethyl chloride and nitrous oxide on the formation of the cyclohexyl radical in the radiolysis of the neopentane–cyclohexane (2%) mixture at 77 K. When ethyl chloride captures an electron, it produces the ethyl radical by dissociative electron attachment. The yields of the ethyl radical, which represent the amounts of electrons captured by ethyl chloride, are also shown in the figure. The yields of the cyclohexyl radical decrease gradually upon the addition of ethyl chloride, while the yields of the ethyl radical increase sharply upon the addition of a small amount of ethyl chloride. The decreases in the yields of the cyclohexyl radical are much smaller than the yields of the ethyl radical at the concentrations of 0.5 and 2% ethyl chloride. It has been reported that nitrous oxide can efficiently capture an electron in the radiolysis of solid neopentane at 77 K.[16] According to the product analysis, the $G(N_2)$ in the radiolysis of neopentane containing nitrous oxide (4%) at 77 K was about 0.5, suggesting that nitrous oxide captures an electron in the solid neopentane at 77 K. The yields of the cyclohexyl radical do not decrease at all upon the addition of nitrous oxide. Therefore, the neutralization reaction does not participate in the formation of the cyclohexyl radical in the radiolysis of neopentane containing cyclohexane at 77 K.

Third, Fig. 5 shows the effect of tetramethylethylene (TME) on the formation of the cyclohexyl radical in the radiolysis of the neopentane–cyclohexane(1%)–CO_2 (2%) mixture at 77 K. Though an appreciable amount of TME^+ is formed upon the addition of TME, and though $G(TME^+)$ amounts approximately to 1—1.5 at 2% of TME, the yields of cyclohexyl radical do not decrease at all. Therefore, the charge transfer reaction does not participate in the formation of cyclohexyl radical.

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15) M. Shirom, R. F. C. Claridge, and J. E. Willard, *J. Chem. Phys.*, **47**, 286 (1967).

16) J. Lin and F. Williams, *J. Phys. Chem.*, **72**, 3707 (1968).

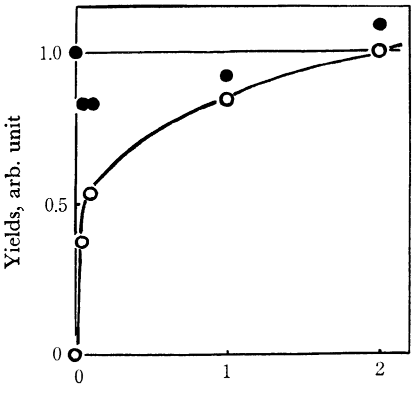

Fig. 5. Effect of TME on the formation of cyclohexyl radical in the radiolysis of neopentane–cyclohexane (1%)–CO_2(2%) mixture at 77 K.
●: yield of cyclohexyl radical.
○: yields of TME^+.

Fourth, since the neopentane parent ion is quite unstable and decomposes in the period of one vibration in the gas[17] and liquid phases,[13,18,19] the excited ion may decompose before charge transfer.

From the present discussions, it seems to be difficult to explain the energy transfer in the radiolysis of solid neopentane by the ionic processes. In the present poor state of knowledge of the radiolysis in the solid phase, we cannot decide the true mechanism of the energy transfer. We will try, however, to explain the energy transfer by two possible non-ionic processes as a basis for further study.

Selective Abstraction Reaction by the Hydrogen Atom. The formation of the solute radical in the radiolysis of neopentane may be explained by the selective abstraction reactions:

$$\text{neo-}C_5H_{12} \rightsquigarrow C_5H_{12}^* \quad (11)$$

$$C_5H_{12}^* \longrightarrow C_5H_{11}\cdot + H \quad (12)$$

$$H + H \text{ or } R\cdot \longrightarrow H_2 \text{ or } RH \quad (13)$$

$$H + C_5H_{12} \longrightarrow C_5H_{11}\cdot + H_2 \quad (14)$$

$$H + C_2H_6 \longrightarrow C_2H_5\cdot + H_2 \quad (15)$$

where $C_5H_{12}^*$ and $R\cdot$ represent an excited neopentane molecule and some radical respectively. If the H atom in these reactions is a hot hydrogen atom, the rate constant of Reaction (14) is a little larger than that of Reaction (15) in the gas phase.[20] Therefore, it cannot be expected that the ethyl radical is formed selectively in the radiolysis of neopentane containing a small amount of ethane. If the H atom is a thermal hydrogen atom, Reaction (15) cannot occur at 77 K because of its high activation energy. Therefore, we must assume that the reaction of the hydrogen atom in the crystalline neopentane is quite different from that in the gas and liquid phases, and that the H-atom reacts selectively with ethane with a low activation energy at 77 K.

It has been reported recently that H-atom abstraction reaction by a thermal methyl radical occurs with low activation energy in the solid phase.[21] Recently we have found that the hot hydrogen atom produced by the photolysis of hydrogen iodide reacts selectively with solute alkane in the neopentane matrix at 77 K.[22] The result, which cannot be explained by this mechanism, is that the yields of solvent radicals in the radiolysis of neopentane or isobutane decrease below 50% of the initial yields upon the addition of an additive.

Excitation Transfer via *a Highly-excited State.* According to the mechanism of the excitation transfer, the reaction scheme may be represented as follows:

$$\text{neo-}C_5H_{12} \rightsquigarrow C_5H_{12}^* \quad (11)$$

$$C_5H_{12}^* \longrightarrow C_5H_{11}\cdot + H \quad (12)$$

$$\searrow C_4H_9\cdot + CH_3\cdot \quad (16)$$

$$C_5H_{12}^* + RH \longrightarrow C_5H_{12} + RH^* \quad (17)$$

$$RH^* \longrightarrow R\cdot + H \quad (18)$$

Reaction (17) is the excitation transfer to other alkane. Since an appreciable quantity of solute radicals is formed by the addition of ethane, propane, and cyclopentane, whose first excited states are higher than that of neopentane, the excitation transfer may occur *via* the highly-excited state.

The excitation transfer has also been proposed in the radiolysis of isobutane[1] and polyethylene[23] in the solid phase. From the calculation, it was suggested that the excitation transfer is possible in the alkane.[24]

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[17] H. D. Beckey, *Z. Naturforsch.*, **A16**, 505 (1961).

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

[19] J. A. Ward and W. H. Hamill, *J. Amer. Chem. Soc.*, **89**, 5116 (1967).

[20] R. J. Carter, W. H. Hamill, and R. R. Williams, *ibid.*, **77**, 6457 (1955).

[21] a) E. D. Sprague and F. Williams, *ibid.*, **93**, 787 (1971). b) A. Campion and F. Williams, *ibid.*, **94**, 7633 (1972).

[22] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, to be published.

[23] R. H. Partridge, *J. Chem. Phys.*, **52**, 2491 (1970).

[24] T. Miyazaki, This Bulletin, **46**, 329 (1973). The equation (1) in the paper is misprinted and should be corrected as $u = -3f(ea_0)^2 \cdot R/\Delta E \cdot \Omega/r^3$.