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Excitation Transfer in the Radiolysis of Solid Alkane Mixtures at 77 K

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The radiolysis of isobutane–propane (less than 5 mol %) or neopentane–alkane (5 mol%) mixtures has been studied at 77 K by means of ESR spectroscopy. When these alkane mixtures are γ-irradiated, the solute radicals are mainly formed by energy transfer from γ-irradiated isobutane or neopentane to the solutes. It is discussed whether the energy transfer is due to a proton transfer, a positive-charge transfer, or an excitation transfer, and it is concluded, for the following reasons, that the energy tranfser is probably due to the excitation transfer and that the excitation transfer may occur *via* highly-excited states of isobutane or neopentane; (i) The ionization potentials and the energies of the first singlet-excited states of the some additives are higher than those of isobutane or neopentane. (ii) The decrease in the solvent radical yields and the increase in the solute radical yields upon the addition of the solutes to the isobutane or neopentane amount approximately to 2—2.5 G-units. (iii) The yields of hydrogen increase sharply upon the addition of cyclopentane in the radiolysis of solid neopentane. (iv) It was concluded in previous studies that the formation of the solvent radical in the radiolysis of solid isobutane is due to the fragmentation of excited isobutane produced directly by γ-irradiation.

It was reported in previous studies that, while the fragmentation of excited ions plays an important role in the radiolysis of isobutane in the gas¹⁾ and liquid²⁾ phases, the fragmentation of excited molecules is an important process in the solid phase at 77 K.³⁾ It was found that the physical conditions of the matrix appreciably affects the radiolysis in the solid phase; this is the case for isobutane,⁴⁾ phenylacetate,⁵⁾ and succinic

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1) T. Miyazaki, *J. Phys. Chem.*, **71**, 4282 (1967).

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

3) a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **42**, 1164 (1969). b) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **43**, 1017 (1970). c) T. Miyazaki, T. Yamada, T. Wakayama, K. Fueki, and Z. Kuri, *ibid*, **44**, 934 (1971).

4) a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, *ibid*, **42**, 2086 (1969). b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970). c) Y. Saitake, T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **44**, 301 (1971).

5) Y. Noro, M. Ochiai, T. Miyazaki, A. Torikai, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 63 (1970).

acid.[6)]

Then, 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 is the problem of the extent to which the formation of an exciton plays an important role; the other is how the state of the solid matrix, such as the phase and the defects, affects the fate of the exciton.

It was previously concluded that, in the radiolysis of solid isobutane at 77 K,[3)] C–H bond rupture occurs by way of the fragmentation of an excited isobutane molecule produced directly by γ-irradiation. This conclusion is based on the following observation:

i) The yields of the C_4H_9 radical in the radiolysis of polycrystalline isobutane are not changed by the presence of conventional electron scavengers, such as phenyl iodide, ethyl iodide, nitrous oxide, and sulfur hexafluoride.

ii) The yields of the C_4H_9 radical do not increase upon the photobleaching of toluene anions in the γ-irradiated isobutane–toluene (5 mol/100 mol of *i*-C_4H_{10}) mixture in the polycrystalline state.

iii) The yields of the C_4H_9 radical do not increase upon the photo-bleaching of electron trapped in the γ-irradiated isobutane–methylcyclohexane (4 mol/100 mol of *i*-C_4H_{10}) mixture in the glassy state or upon the photobleaching of benzene anions in the γ-irradiated isobutane–methylcyclohexane (4 mol/100 mol of *i*-C_4H_{10})–benzene (5 mol/100 mol of *i*-C_4H_{10}) mixture in the glassy state.

iv) The yields of H_2 in the radiolysis of glassy isobutane are not changed at all by the presence of conventional electron scavengers, such as nitrous oxide and sulfur hexafluoride.

Since the yields of the C_4H_9 radical and H_2 decrease upon the addition of CCl_4 or toluene, it was suggested that the migration of an exciton to the solutes may be an important process in the radiolysis of solid isobutane. The role of the exciton was also studied by the measurement of the luminescence from eleven kinds of alkanes containing toluene (2 mol %) during γ-irradiation at 77 K.[7)]

In this paper we will report clearer results suggesting the excitation transfer in the radiolysis of isobutane and neopentane in the solid phase.

Experimental

The ethane, propane, and isobutane were supplied by the Takachiho Shoji Co. and were of a high purity; the isobutane was more than 99.7% pure. The cyclopentane, methylcyclopentane, *n*-hexane, and cyclohexane supplied by the Tokyo Kagaku Seiki Co. were more than 99.0% pure. They were passed through a 30-cm column packed with activated alumina and were used after distillation on a vacuum line. The neopentane was more than 99.9% pure.

Samples were sealed into a quartz cell and irradiated at 77 K with γ-rays from Co-60 at a dose rate of 7.6×10^5 rad/hr. The total doses were 3.8×10^5 rad for the ESR measurements and 1.0×10^7 rad for the product analysis. The ESR spectra of irradiated samples were measured at 77 K on a JES-3BX ESR spectrometer. H_2 and CH_4 were analyzed by a gas burette connected to a Toepler pump and a copper oxide furnace kept at 240°C.

Results

Figure 1a shows the ESR spectrum of γ-irradiated pure isobutane, which is assigned to an isobutyl radical. Figure 1b shows the ESR spectrum of γ-irradiated isobutane containing 4.8 mol% propane. It may be seen from Figures 1a and 1b that there is a drastic difference in the spectra. The spectra in Fig. 1b represent those assigned to two species; the main spectrum is ascribed to the *i*-C_3H_7 radical.

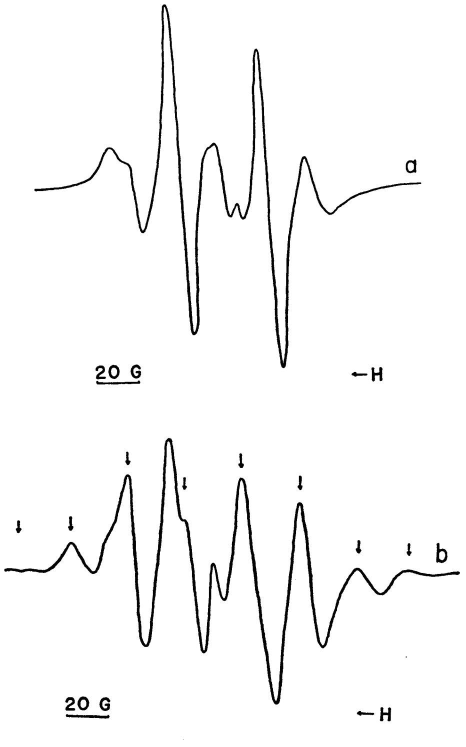

Fig. 1. a) ESR spectrum of γ-irradiated isobutane at 77 K. b) ESR spectrum of γ-irradiated isobutane–propane(4.8 mol%) at 77 K. The arrows indicate signals of C_3H_7 radical.

When pure neopentane is γ-irradiated at 77 K, *t*-C_4H_9 and *neo*-C_5H_{11} radicals are formed; their ESR spectra are shown in Fig. 2a.[8)] The spectrum of eight narrow lines is ascribed to the *t*-C_4H_9 radical. The spectrum of three broad lines is ascribed to the *neo*-C_5H_{11} radical. When neopentane containing a small amount of alkane is γ-irradiated at 77 K, a solute radical and a neopentyl radical are formed, while the *t*-C_4H_9 radical disappears completely. The ESR spectra of γ-irradiated neopentane–ethane, propane,

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[6)] a) T. Miyazaki, S. Okada, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **43**, 1907 (1970). b) T. Miyazaki, Y. Fujitani, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **44**, 984 (1971).

[7)] T. Miyazaki, Y. Saitake, M. Fukaya, T. Wakayama, and Z. Kuri, Japanese Conference on Radiation Chemistry, Sapproo, Japan, Sept. 1971.

[8)] B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

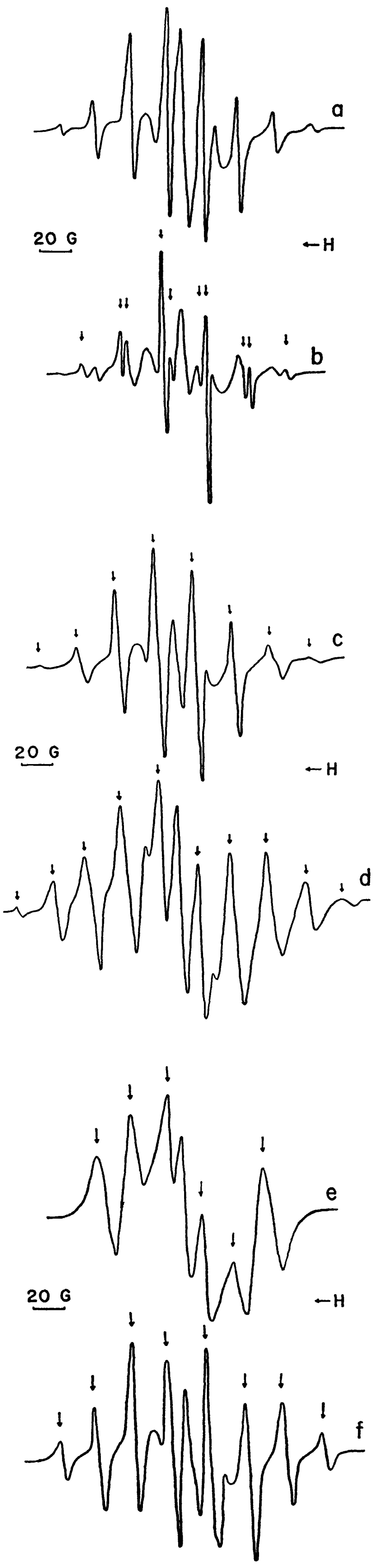
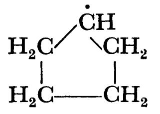
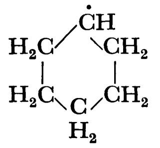


Fig. 2. ESR spectra of γ-irradiated neopentane and neopentane-alkane mixtures at 77 K. The arrows indicate signals of solute alkane radicals.
a) pure neopentane. b) neopentane-ethane (4.8 mol%). c) neopentane-propane(4.9 mol%). d) neopentane-methylcyclopentane(4.9 mol%). e) neopentane-cyclohexane(6.5 mol%). f) neopentane-cyclopentane(4.7 mol%)

Table 1. Formation of solute radical in the radiolysis of neopentane containing alkane at 77 K

Solute alkane	Solute radical	Splitting, Gauss This work	 Other work
Ethane	$\cdot CH_2CH_3$	$\alpha^{a)}$: 22.9 $\beta^{a)}$: 27.1	$\alpha^{a)}$: 22.4[b)] $\beta^{a)}$: 26.9[b)]
Propane	$CH_3\dot{C}HCH_3$	24.1	24.8[c)]
2,3-dimethylbutane	$\cdot CH_2CH(CH_3)$-$CH(CH_3)_2$	22.7	22[d)]
Cyclopentane		23.7	23.8[c)]
Cyclohexane		21.4	21[e)]

a) Splittings by α-proton and β-proton are represented by α and β respectively.
b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
c) P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).
d) M. Fukaya, T. Wakayama, T. Miyazaki, Y. Saitake, and Z. Kuri, This Bulletin, **46**, 1036 (1973).
e) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

methylcyclopentane, cyclohexane, and cyclopentane systems are shown in Figs. 2b, c, d, e, and f respectively. When neopentane containing a small amount of isobutane, 2,3-dimethylbutane, or n-hexane is γ-irradiated, solute radicals are mainly formed also. The structures and splittings of the solute radicals formed in the radiolysis of neopentane-alkane mixtures are shown in Table 1. The splittings of the radicals formed by other methods are also shown there.

The effect of propane on the formation of radicals in the radiolysis of solid isobutane is shown in Fig. 3. The i-C_4H_9 radical decreases sharply upon the addition

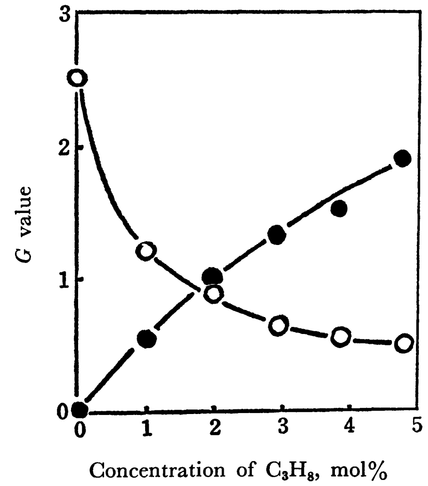


Fig. 3. Effect of propane on the formation of isobutyl radical in the radiolysis of isobutane at 77K.
○: i-C_4H_9 radical ●: i-C_3H_7 radical

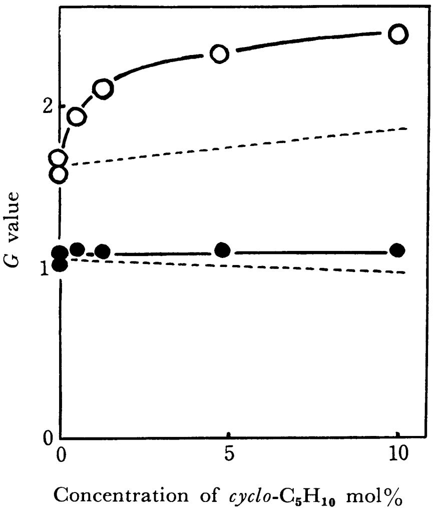


Fig. 4. Effect of cyclopentane on the radiolysis of neopentane in the solid phase at 77 K.
○: H_2 ●: CH_4

of propane, while the C_3H_7 radical increases complementally. The sum of $G(C_3H_7)$ and $G(i\text{-}C_4H_9)$ decreases slightly upon the addition of 1 mol% propane. It is uncertain whether this result is due to experimental errors or to some characteristic phenomena upon the addition of C_3H_8.

The yields of H_2 and CH_4 in the radiolysis of *neo*-C_5H_{12}-*cyclo*-C_5H_{10} mixtures in the solid are shown in Fig. 4.

Discussion

The C_4H_9 radical decreases sharply upon the addition of propane in the radiolysis of isobutane, while the C_3H_7 radical increases complementally (Fig. 1b and Fig. 3). Since the electron fraction of propane is smaller than 0.04 in the experimental concentration, the results represent some type of energy transfer from γ-irradiated isobutane to propane. Since the electron fraction of the solutes is about 0.05 in the radiolysis of neopentane-solute mixtures, the formation of solute radicals also represents the energy transfer from γ-irradiated neopentane to the solute (Fig. 2). We will discuss here whether the energy transfer is due to a proton transfer, a positive-charge transfer, or an excitation transfer.

Proton-transfer Reaction in γ-irradiated Alkane Mixtures in the Solid Phase. Willard *et al.* proposed that the solvent radical may be formed by the proton-transfer reaction in the radiolysis of 3-methylpentane in the solid phase.[9] According to this mechanism, the formation of the solute radical in the radiolysis of neopentane (or isobutane) may be represented as follows:

$$neo\text{-}C_5H_{12} \rightsquigarrow C_5H_{12}^+ + e^- \qquad (1)$$

$$C_5H_{12}^+ + C_5H_{12} \longrightarrow C_5H_{11}\cdot + C_5H_{13}^+ \qquad (2)$$

$$C_5H_{12}^+ + RH \longrightarrow R\cdot + C_5H_{13}^+ \qquad (3)$$

where RH represents an alkane as a solute. These mechanisms, however, seem unlikely because for the following three reasons: i) Though the proton-transfer reaction of polar molecules has been found in 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.[10] Recently it has been reported, from a study of the high-pressure mass spectrometry of propane, that the protonated alkane ion ($C_3H_9^+$) was not detected at all, but only a clustered parent ion ($(C_3H_8)_2^+$).[11] The formation of a clustered parent ion was also reported in the high-pressure mass spectrometry of butane.[12]

ii) Only the fragmentation of the parent ion ($C_4H_{10}^+$ or $C_5H_{12}^+$) has been observed in the radiolysis of isobutane and neopentane in the liquid phase.[2,13,14] The existence of the parent ion (*cyclo*-$C_5H_{10}^+$ or *cyclo*-$C_6H_{12}^+$) has been also shown in the radiolysis of cyclopentane or cyclohexane in the liquid phase.[15]

Since the proton-transfer reaction between *neo*-$C_5H_{12}^+$ and *neo*-C_5H_{12} (Reaction (2)) does not occur in the liquid phase, Reaction (2) may be endothermic; in it the heat of reaction is taken as ΔH_2 kcal/mol. Therefore, the heat of hydrogen-transfer reaction between $C_5H_{12}^+$ and C_2H_6 (Reaction (4)) may be expected to be $\Delta H_2+3.7$ kcal/mol:

$$neo\text{-}C_5H_{12}^+ + C_2H_6 \longrightarrow C_5H_{13}^+ + C_2H_5\cdot \qquad (4)$$

Therefore, Reaction (4) is also endothermic and its occurrence may be more difficult than that of Reaction (2).

The same conclusion can be obtained also from the results in the radiolysis of an ethane-neopentane mixture in the liquid phase.[6] It has been shown that the proton-transfer reaction between $C_2H_6^+$ and *neo*-C_5H_{12} (Reaction (5)) does not occur:

$$C_2H_6^+ + neo\text{-}C_5H_{12} \longrightarrow C_2H_5 + C_5H_{13}^+ \qquad (5)$$

Reaction (5) is expected to be an endothermic reaction and the heat of its reaction is taken to be ΔH_5 kcal/mol. The heat of Reaction (4) may, then, be expected to be ΔH_5+30 kcal/mol. Therefore, the occurrence of Reaction (4) may be more difficult than that of Reaction (5).[17,18]

iii) When neopentane containing cyclopentane

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

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

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

[12] T. A. Milne, J. E. Beachey, and F. T. Greene, Annual Conference on Mass Spectrometry and Applied Topics, 17th ASTM Committee, E-14, Dallas Tex., U. S. A., May, 1969.

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

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

[15] P. Ausloos, A. A. Scala, and S. G. Lias, *ibid.*, **89**, 3677 (1967).

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

[17] Neopentane has a solid phase transition at 140 K (J. G. Aston and G. H. Messerly, *J. Amer. Chem. Soc.*, **58**, 2354 (1936); E. O. Stejskal, D. E. Woessner, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **31**, 55 (1959)), but it has no phase transition near 77 K. The reaction (4) is not facilitated at 77 K by the phase transition.

(5 mol%) is γ-irradiated at 77 K, the cyclopentyl radical is mainly formed (Fig. 2f). If the formation of the cyclopentyl radical is due to Reaction (3), the amounts of the $C_5H_{13}^+$ ion do not change upon the addition of cyclopentane. $C_5H_{13}^+$ ion may produce a H atom or a H_2 molecule upon neutralization with an electron:

$$C_5H_{13}^+ + e^- \longrightarrow C_5H_{12} + H\cdot \qquad (6)$$

$$\searrow C_5H_{11}\cdot + H_2 \qquad (7)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (8)$$

Therefore, it may be expected from Reactions (1)—(3) and (6)—(8) that the yields of hydrogen do not change upon the addition of cyclopentane if the proton-transfer reaction is responsible for the formation of the cyclopentyl radical. The experimental results, however, show that the yields of hydrogen increase sharply upon the addition of cyclopentane in the radiolysis of solid neopentane (Fig. 4). This result suggests that the C–H bond rupture of cyclopentane is accelerated by the energy transfer from γ-irradiated neopentane to cyclopentane.

Positive-charge Transfer in the γ-irradiated Alkane Mixtures in the Solid Phase. *Isobutane Containing Propane*: Though a positive-charge transfer is generally proposed in the γ-irradiated alkane mixtures in the liquid phase,[16,19] such a mechanism (Reactions (7)—(10)) cannot be adopted here for the following two reasons:

$$C_4H_{10} \rightsquigarrow C_4H_{10}^+ + e^- \qquad (7)$$

$$C_4H_{10}^+ + e^- \longrightarrow C_4H_9\cdot + H\cdot \qquad (8)$$

$$C_4H_{10}^+ + C_3H_8 \longrightarrow C_4H_{10} + C_3H_8^+ \qquad (9)$$

$$C_3H_8^+ + e^- \longrightarrow C_3H_7\cdot + H\cdot \qquad (10)$$

i) As has been described in the Introduction, the C_4H_9 radical is not formed by the neutralization reaction between the butane cation and the electron.

ii) Though the gas-phase ionization potentials may be different from the condensed-phase ionization potentials, the charge-transfer reaction in the liquid alkane mixtures can be discussed by using the gas-phase ionization potentials.[16,19] The ionization potential of an alkane ion is always higher than that of a charge acceptor. Therefore, the relative magnitude of the gas-phase ionization potentials of alkanes may hold even in the condensed phase. Since the ionization potential of isobutane is lower than that of propane (Table 2), it is impossible for a charge transfer from the isobutane cation in a ground state to propane to occur.

TABLE 2. ENERGIES OF FIRST ELECTRONIC EXCITED STATE AND IONIZATION POTENTIALS OF ALKANES

	Energies of first electronic excited state,[a)] eV	Ionization potentials,[b)] eV
C_2H_6	9.3	11.65
C_3H_8	9.0	11.07
i-C_4H_{10}	7.7	10.57
cyclo-C_5H_{10}	8.3	10.53
neo-C_5H_{12}	7.9	10.35
cyclo-C_6H_{12}	7.8	9.88

a) J. W. Raymonds and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

b) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

If the energy transfer in the γ-irradiated *i*-C_4H_{10}–C_3H_8 mixture is due to a charge-transfer reaction, we will have to introduce a mechanism of a charge-transfer *via* the excited state of the solvent cation, as has been suggested by Hamill *et al.*[20] Since our information about the excited cation produced by γ-irradiation is very scanty at present, the energy transfer *via* the excited cation and its chemical reaction cannot be discussed in detail. There are, however, some drawbacks to this mechanism. First, the yields of the excited alkane ion may amount only to 20% of the total alkane ions.[21,22] The *G*-value of the excited ion is likely to be 0.8 if we take the *G*-value for ion-pair production as the gas-phase value of about 4. This value is much smaller than the decrement (G∼2.0) in the *i*-C_4H_9 radical or the increment (G∼1.9) in the C_3H_7 radical upon the addition of propane in the radiolysis isobutane (Table 3). Second, a migration of the excited isobutane ion is considered to be rather difficult, for the toluene cation was not observed at 77 K in the γ-irradiated isobutane containing toluene.[3b)] Third, supposing the excited isobutane ion is formed, it may decompose in the period of one vibration because of the fact that the C–C bond of the isobutane ion is very weak.[2,21] It is highly unlikely, judging from the mass spectrum of isobutane, that the *i*-C_4H_9 radical is formed by the fragmentation of an excited isobutane ion:

$$i\text{-}C_4H_{10}^{+*} \longrightarrow i\text{-}C_4H_9\cdot + H^+ \qquad (11)$$

Neopentane Containing Alkanes: When neopentane containing ethane, propane, cyclopentane, or methylcyclopentane is γ-irradiated at 77 K, ethyl, propyl, cyclopentyl, or methylcyclopentyl radicals are mainly formed respectively (Fig. 2). Since these additives have higher ionization potentials than that of neopentane (Table 2), it is not possible that a charge transfer from the neopentane cation in a ground state to the additive occurs. The yields of the solute radicals amount to approximately 2.5 *G*-units (Table 3),

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[18] The possibility of Reaction (4) was diminished by the recent experiments (M. Ito, T. Miyazaki, Y. Saitake, and Z. Kuri, Japanese Conferrence on Radiation Chemistry, Osaka, Japan, Oct. 1972). The addition of CCl_4, which is an efficient electron scavenger and an excitation quencher, to the *neo*-C_5H_{12}–C_2H_6 mixture suppresses the formation of C_2H_5 radical in the solid radiolysis. If the formation of C_2H_5 radical is due to the Reaction (4), the yield of C_2H_5 radical should not decrease upon the addition of CCl_4.

[19] a) J. Hardwick, *J. Phys. Chem.*, **66**, 2132 (1962). b) T. Kudo and S. Shida, *ibid*, **71**, 1971 (1967). c) J. A. Stone, *Chem. Commun.*, **1968**, 1677.

[20] 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.

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

[22] R. H. Partridge, *ibid.*, **52**, 2491 (1970).

TABLE 3. YIELDS OF RADICALS IN THE γ-IRRADIATED ALKANE AT 77 K[a)]

γ-Irradiated system	G(solvent radical)	G(solute radical)
i-C_4H_{10}	2.5	0
i-C_4H_{10}-C_3H_8 (4.8%)	0.5	1.9
neo-C_5H_{12}	2.3	0
neo-C_5H_{12}-C_2H_6 (4.8%)	0.9	0.9
neo-C_5H_{12}-C_3H_8 (4.9%)	0.4	1.3
neo-C_5H_{12}-*cyclo*-C_5H_{10} (4.7%)	0.9	2.0
neo-C_5H_{12}-C_6H_{12}[b)] (4.9%)	0.3	2.3
neo-C_5H_{12}-*cyclo*-C_6H_{12} (6.5%)	0.2	2.6
neo-C_5H_{12}-n-C_6H_{14} (4.8%)	0.5	2.4

a) G value of the radicals were determined by assuming $G(\text{radical})=1.6$ for the radicals produced in the γ-irradiated 3-methylpentane at 77 K. (M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1963)) The errors of radical yields are about 20%. When neopentane-alkane mixtures are irradiated, neopentyl and solute radicals are formed. A standard ESR spectrum of neopentyl radical was obtained by the γ-irradiation of neopentane containing N_2O. (*cf.* J. Lin and F. Williams, *J. Phys. Chem.*, **72**, 3707 (1968)). The yields of neopentyl radical were obtained from the height of central peak in the ESR spectrum and the standard spectrum of neopentyl radical. The yields of solute radical was obtained by subtracting the yields of neopentyl radical from the total radical yields.

b) C_6H_{12} represents methylcyclopentane.

which may be much higher than the yields of the mobile excited cations. Even if the excited neopentane cation is formed, it may decompose in the period of one vibration[13,14] before transferring its charge to the additive.

Excitation-transfer Reaction in γ-irradiated Alkane Mixtures in the Solid Phase. It seems from the above discussions that the energy transfer from γ-irradiated isobutane or neopentane to the solutes cannot be ascribed to the ionic processes, although the possibility of a transfer *via* the excited cation cannot be excluded completely. The excitation transfer reaction may be responsible for the energy transfer in the radiolysis of an alkane mixture, as in the radiolysis of the i-C_4H_{10}–CCl_4 (or $C_6H_5CH_3$) system:[3)]

$$neo\text{-}C_5H_{12} \rightsquigarrow C_5H_{12}^* \tag{12}$$

$$C_5H_{12}^* \longrightarrow C_4H_9\cdot + CH_3\cdot \tag{13}$$

$$\searrow C_5H_{11}\cdot + H\cdot \tag{14}$$

$$C_5H_{12}^* + RH \longrightarrow C_5H_{12} + RH^* \tag{15}$$

$$RH^* \longrightarrow R\cdot + H\cdot \tag{16}$$

where $C_5H_{12}^*$ represents an excited molecule. CH_3 radicals are not observed by ESR spectroscopy, although their formation is expected from Eq. (13). This is because the CH_3 radical may migrate in the neopentane matrix even at 77 K and may recombine with other CH_3 radicals or H atoms.

When the i-C_4H_{10}–C_3H_8 or *neo*-C_5H_{12}–C_2H_6, C_3H_8, or i-C_4H_{10} systems are γ-irradiated at 77 K, solute radicals are mainly formed. As is shown in Table 2, it is impossible for an excitation transfer from isobutane or neopentane in the first excited state to the solute alkanes to occur. Therefore, the excitation transfer may occur by way of the highly-excited states of isobutane or neopentane.

Yields of Hydrogen in the Radiolysis of Neopentane Containing Cyclopentane at 77 K in the Solid Phase. The effect of cyclopentane on the yields of H_2 and CH_4 in the radiolysis of neopentane at 77 K in the solid phase is shown in Fig. 4. The yields of H_2 increase sharply upon the addition of a small amount of cyclopentane, while the yields of CH_4 are not affected. The broken line indicates the yields which may be expected when the energy transfer between neopentane and cyclopentane does not occur.

Since the cyclopentyl radical is the main radical formed in the radiolysis of the solid neopentane–cyclopentane (5 mol %) system (Fig. 2f), the large yields of H_2 upon the addition of cyclopentane may be due to an excitation transfer from highly-excited neopentane to cyclopentane (*cf.* Reactions (12)—(16)). Since the increase in H_2 becomes approximately constant above 2 mol % of cyclopentane, the excitation transfer occurs entirely below this concentration. The increase in the cyclopentyl radical shows the same concentration dependency in the radiolysis of the solid neopentane–cyclopentane mixture.[23)] Though it is expected from the ESR study that the yields of the CH_3 radical decrease upon the addition of cyclopentane (*cf.* Reactions (13) and (15)), the yields of CH_4 do not decrease. Therefore, methane may be formed mainly *via* a non-radical process, such as molecular detachment from neopentane.

[23)] M. Fukaya, T. Miyazaki, and Z. Kuri, unpublished results.