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Effect of Matrix on the Formation of Solvent Radicals in the Radiolysis of Alkanes in the Solid State at 77 K

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The effect of the matrix on the radiolysis of 2,3-dimethylbutane, neopentane, 2,2-dimethylbutane, and isobutane in the solid state has been studied at 77 K by means of ESR spectroscopy. Though only the $\cdot CH_2CH(CH_3)CH(CH_3)_2$ radical is formed by the γ-irradiation of 2,3-dimethylbutane in the I crystal, the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical is formed by the γ-irradiation of 2,3-dimethylbutane in the II crystal. Though the t-C_4H_9 and *neo*-C_5H_{11} radicals are formed by the γ-irradiation of pure neopentane, the formation of radicals is affected appreciably by the addition of a small amount of alkanes. When neopentane containing ethane, *etc.* is γ-irradiated, the solute radical is mainly formed by energy transfer form the γ-irradiated neopentane to the solute. Most of the solutes have a spherical molecular structure like that of neopentane or are smaller than neopentane. When neopentane containing 3-methylpentane, *etc.* is γ-irradiated, only the neopentyl radical is formed. The molecular structures of the solutes are very different from that of neopentane. The formation of the solvent radical in the radiolysis of 2,2-dimethylbutane is affected by the addition of 3-methylpentane or methylcyclohexane. The formation of the butyl radical in the radiolysis of isobutane is also changed drastically by addition of alkanes. It is concluded that the formation of solvent radicals in the radiolysis of solid alkane is appreciably affected by the conditions of the matrix.

It has previously been found that the isobutyl radical is formed by the radiolysis of isobutane in the polycrystalline state, while the t-C_4H_9 radical is formed in the transparent solid state.[1] The study of the radiolysis of isobutane-2-d_1 showed that the phase change affects the primary process of the C–H bond rupture in the radiolysis of solid isobutane.[2] The phase effect was also reported in the radiolyses of phenyl acetate[3] and disodium succinate[4] in the solid state. Recently it was found in the radiolysis of solid succinic acid that the $G(CO+H_2)$ from the powder is much higher than that from the single crystal. It was suggested that the exciton produced by the γ-irradiation of solid succinic acid migrates to a surface or a defect of the powder and thus produces CO and H_2.[5] It was also been reported that, in the radiolysis of alkanes at 77 K, solvent radicals are formed by the fragmentation of excited molecules produced directly by γ-irradiation.[6]

Therefore, we have proposed that two important problems must be solved in order to elucidate the mechanism of the solid-phase radiolysis. One is the problem of the extent to which the formation of an exciton plays an important role: the other is how the condition of the matrix affects the reaction in the solid phase. Here we will report about the latter problem in the radiolyses of 2,3-dimethylbutane, neopentane, 2,2-dimethylbutane, and isobutane in the solid phase.

Experimental

The isobutane was more than 99.7% pure. The neopentane was more than 99.9% pure. The 2,3-dimethylbutane and 2,2-dimethylbutane were more than 99.0% pure and were passed through a 30-cm column packed with activated alumina. They were used after distillation on a vacuum line. The additives, such as ethane, propane, *n*-hexane, cyclohexane, and methylcyclohexane, were the same as those which had been used before.[6d] The additives, such as *n*-pentane, *n*-octane, isooctane, and *trans*-decaline, were Tokyo Kagaku Seiki's guaranteed reagents. The *n*-heptane, *n*-decane, *n*-hexadecane, isopentane, cyclooctane, adamantane, and carbon tetrachloride were Nakarai Chemicals' guaranteed reagents. The *n*-butane and nitrous oxide were supplied by Takachiho Shoji Co. and were of a high purity. The 3-methylpentane (Aldrich Chemical Co.) was washed with concentrated sulfuric acid. After this treatment the specimen was separated from the sulfuric acid solution by distillation.

Samples were sealed into a silica 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 dose was 3.8×10^5 rad. The ESR spectra of the irradiated samples were measured at 77 K on a JES-3BX ESR spectrometer.

Results and Discussion

Effect of Phase on the Formation of Radicals in the Radiolysis of 2,3-Dimethylbutane at 77 K. Recently Adachi, Suga, and Seki have reported a calorimetric

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[1] a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **42**, 2086 (1969). b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970).

[2] Y. Saitake, T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **44**, 301 (1971).

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

[4] a) H. M. Vyas, J. Janecka, and M. Fujimoto, *Can. J. Chem.*, **48**, 2804 (1970). b) M. Fujimoto and W. A. Seddon, *ibid*, **48**, 2809 (1970).

[5] 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).

[6] a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid*, **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). d) T. Miyazaki, T. Wakayama, M. Fukaya, Y. Saitake, and Z. Kuri, *ibid*, **46**, 1030 (1973).

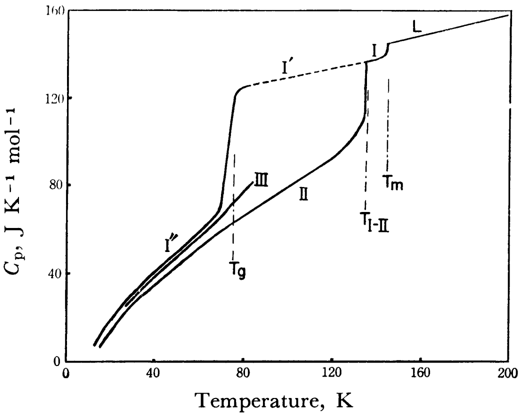

Fig. 1. The heat capacity curves of 2,3-dimethylbutane measured by Adachi *et al.*[7]
L, the liquid; I, the crystal–I; I′, the supercooled crystal–I; I″, the glassy crystal–I; II, the crystal–II; III, the crystal–III:
T_m, the melting point (145 K); T_{I-II}, the phase transition temperature between crystal–I and II (136 K); T_g, the glass transition temperature (76 K).

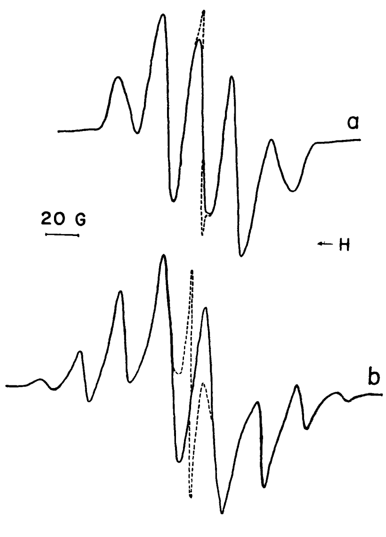

Fig. 2. a) ESR spectrum of γ-irradiated 2,3-dimethylbutane in crystal–I at 77 K.
b) ESR spectrum of γ-irradiated 2,3-dimethylbutane in crystal–II at 77 K.
Dotted lines represent the spectra of trapped electrons which are easily bleached by illumination with visible light.

study of 2,3-dimethylbutane in the solid state.[7] The heat-capacity curves measured by them are shown in Fig. 1. 2,3-Dimethylbutane has three crystalline phases: a high-temperature form (the I crystal) which is stable at temperatures between 136 K to 145 K, a low-temperature form (the II crystal) which is stable below 126 K, and a metastable intermediate phase (the III crystal).[8] When 2,3-dimethylbutane is cooled repidly at 77 K, it forms a supercooled crystal (I′ in Fig. 1), which is a transparent solid.[9] When the supercooled I crystal is warmed to some temperature lower than 136 K and then cooled to 77 K, and when annealing is repeated several times, it forms a II crystal.

The ESR spectrum of γ-irradiated 2,3-dimethylbutane in the supercooled I crystal at 77 K is shown in Fig. 2a. The spectrum consists of five lines, with a splitting of 22 G, which is approximately consistent with the reported value of 21 G for the $\cdot CH_2CH(CH_3)CH_3$ radical.[10] The spectrum may be assigned to the $\cdot CH_2CH(CH_3)CH(CH_3)_2$ radical which is formed by the rupture of a primary C–H bond.

A quite different ESR spectrum is, however, obtained by the γ-irradiation of 2,3-dimethylbutane in the II crystal form at 77 K (Fig. 2b). The spectrum consists of eight lines, with a splitting of 24 G. The spectrum may be assigned to the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical which is formed by the rupture of a tertiary C–H bond, or to the C_3H_7 radical which is formed by the rupture of a C–C bond. The yield of H_2 in the radiolysis of 2,3-dimethylbutane in the II crystal at 77 K is the same as that in the radiolysis of 2,3-dimethylbutane in the I crystal. The spectrum of eight lines coincides well with that of the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical which is produced by H-atom abstraction from 2,3-dimethylbutane during the UV illumination of a 2,3-dimethylbutane-hydrogen iodide mixture at 77 K in the II crystal.[11] Therefore, it is probable that the solvent radical of γ-irradiated 2,3-dimethylbutane in the II crystal may be the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical.

The following two conclusions are obtained from the results of the radiolysis of 2,3-dimethylbutane at 77 K. First, in the previous studies of the effect of the phase on the radiolysis of solid isobutane[1,2] the phase change was caused by the addition of alkane and the phase change was not ascertained by the calorimetric measurements. The present results for the radiolysis of solid 2,3-dimethylbutane, however, clearly show that quite different radicals are formed in the two different phases, as determined by calorimetric measurement.

Second, it was proposed that, in the radiolysis of isobutane,[1b] the phase effect on the formation of the solvent radical may be explained by the cage effect. The present results, however, show that the phase effect on the radiolysis of solid 2,3-dimethylbutane cannot be explained by the cage effect. In effect, since the C–C bond of the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical is formed by sp^2-hybrid orbitals, two CH_3 groups and $CH(CH_3)_2$ group constitute a planar structure. Therefore, a structural rearrangement of C–C bonds would be necessary for the formation of the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical from the 2,3-dimethylbutane molecule, while such a change would not be necessary for the formation of the $\cdot CH_2CH(CH_3)CH(CH_3)_2$ radical. Therefore, it would be expected from the hypothesis of the cage effect that the for-

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[7] K. Adachi, H. Suga, and S. Seki, This Bulletin, **44**, 78 (1971).

[8] Unfortunately, the crystal structures of crystal–I, II and III are unknown at present. X-Ray analysis of these crystals is desirable in future.

[9] The terms "glass" or "glassy state" were often used in the previous studies by the present authors.[1,2,5,6] These terms, however, mean only that the solid is in the transparent state.

[10] P. B. Ayscough and H. E. Evans, *J. Phys. Chem.*, **68**, 3066 (1964).

mation of the C–C bonds may be suppressed in the II crystal, which is more rigid than the I crystal (i.e., the plastic crystal). The experimental results, however, show that the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical is formed only in the II crystal.

The phenomenon that different solvent radicals are formed selectively by the change in the phase is quite mysterious for us. When a solvent radical is formed by H-atom abstraction from 2,3-dimethylbutane during the UV illumination of a 2,3-dimethylbutane-hydrogen iodide mixture at 77 K, the $\cdot CH_2CH(CH_3)CH(CH_3)_2$ radical is formed in the I crystal, while the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical is formed in the II crystal.[11] Therefore, the effect of the phase on the H-atom abstraction reaction is similar to the effect on the radiolysis. The results suggest that the matrix of 2,3-dimethylbutane itself possesses a selectivity for the formation of the solvent radical.

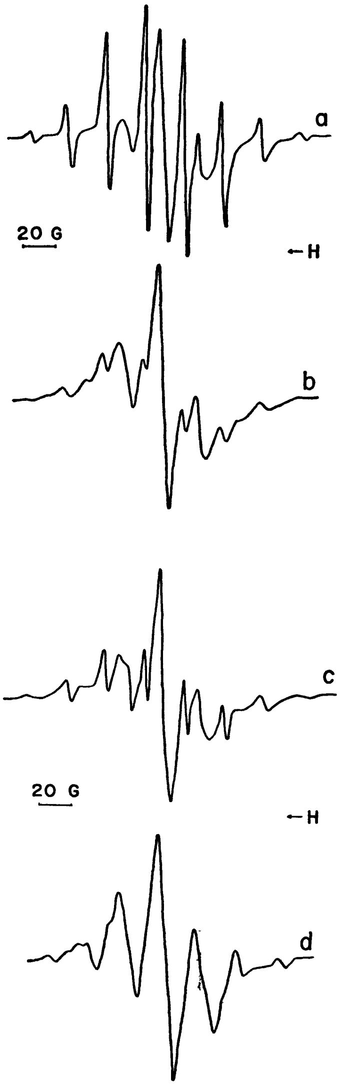
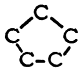
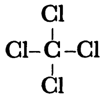
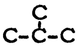
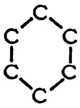
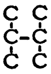
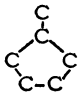
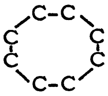
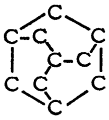
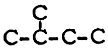
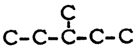
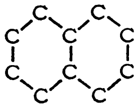
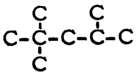


Fig. 3. ESR spectra of γ-irradiated neopentane and neopentane-alkane mixture at 77 K.
a) pure neopentane b) neopentane–3-methylpentane (4.5 mol%) c) neopentane–isooctane (4.8 mol%) d) neopentane–*n*-butane (6.2 mol%)

Effect of the Addition of Alkanes on the Formation of Radicals in the Radiolysis of Neopentane at 77 K. When pure neopentane is γ-irradiated at 77 K in the solid phase, the ESR spectrum of the radicals is as is shown in Fig. 3a.[12] 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 quite different ESR spectrum is obtained. The effects of the addition of alkanes may be classified into two types. Type A is as follows: when neopentane containing ethane *etc.* is γ-irradiated, the solute radical is mainly formed by excitation transfer from the γ-irradiated neopentane to the solute. The details of Type A were reported in a previous study.[6] Type B is as follows: when neopentane containing 3-methylpentane, *etc.* is γ-irradiated, only a neopentyl is formed, while the formation of the t-C_4H_9 radical and the solute radical is suppressed. A small quantity of solute radicals, however, seems to be formed in a few cases. The ESR spectra of γ-irradiated neopentane containing 3-methylpentane, isooctane, and *n*-butane are shown in Figs.

Table 1. Effects of additives on the radiolysis of solid neopentane at 77 K

		Additives				
		Alkanes				Other
Type A	○	C-C	●		●	 $Cl-\overset{Cl}{\underset{Cl}{C}}-Cl$
	○	C-C-C				
		C-C-C-C-C-C				
	●	 $C-\overset{C}{C}-C$	●			
	●	 $\overset{C}{\underset{C}{C}}-\overset{C}{\underset{C}{C}}$				
Type B		C-C-C-C				N_2O
		C-C-C-C-C				
		C-C-C-C-C-C				
		n-$C_{10}H_{22}$	●			 CH
		n-$C_{16}H_{34}$				
		 $C-\overset{C}{C}-C-C$				
		 $C-C-\overset{C}{C}-C-C$				
		 $C-\overset{C}{\underset{C}{C}}-C-\overset{C}{C}-C$				

●: spherical molecules
○: Its size is smaller than that of neopentane.

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[11] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, unpublished results.

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

3b, c, and d respectively. A small amount of the t-C_4H_9 radical is formed in the radiolysis of neopentane containing isooctane (Fig. 3c).

The effects of various alkanes on the radiolysis of neopentane are classified in Table 1. Most of the alkanes of Type A have approximately spherical molecular structures, like that of neopentane, or are smaller than neopentane. The molecular structures of the additives of Type B, however, are very different from that of neopentane. Although adamantane is spherical like neopentane, it is larger than that of neopentane.

Since the information on the radiolysis of solid alkane is very scanty at present, it is difficult to explain why the effects of alkane mixtures fall into two types. The phenomena may be related to the behavior of an exciton formed by γ-irradiation, the local crystalline structure near the additive, or some such thing.

It is noted that when neopentane containing 4 mol% nitrous oxide is γ-irradiated at 77 K, only the *neo*-C_5H_{11} radical is formed. Lin and Williams ascribed this phenomenon to the electron-scavenging effect of nitrous oxide.[13] Since the solvent radical may be formed by the fragmentation of an excited neopentane molecule,[6] and since a decrease in the t-C_4H_9 radical is also observed upon the addition of alkanes, it is possible that nitrous oxide acts similarly to the addition-effect of alkanes in the radiolysis of solid neopentane.

Effects of the Addition of Alkane on the Formation of Radicals in the Radiolysis of 2,2-Dimethylbutane at 77 K. The ESR spectrum of γ-irradiated pure 2,2-dimethylbutane in the solid state is shown in Fig. 4a. The spectrum consists mainly of three lines, with a splitting of 23 G, which is consistent with that of 23 G for the $\cdot CH_2C(CH_3)_2CH_3$ radical. The spectrum may be assigned to the $\cdot CH_2C(CH_3)_2CH_2CH_3$ radical.

When 2,2-dimethylbutane containing 5 mol% of 3-methylpentane is γ-irradiated at 77 K, the spectrum of the triplet decreases, while the very small peaks on both sides of the triplet are not affected by the addition of 3-methylpentane. Therefore, the spectrum of γ-irradiated 2,2-dimethylbutane containing 3-methylpentane consists of five lines, as is shown in Fig. 4b. The assignment of the quintet ESR spectrum is not possible at present. A similar effect is also observed upon the addition of methyl-cyclohexane.

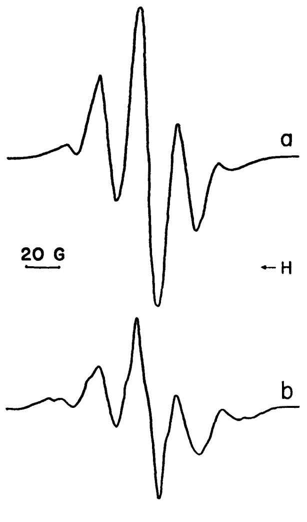
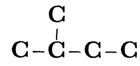
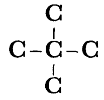
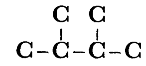
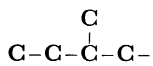
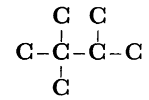
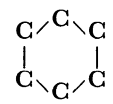
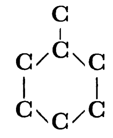


Fig. 4. a) ESR spectrum of γ-irradiated pure 2,2-dimethylbutane at 77 K.
b) ESR spectrum of γ-irradiated 2,2-dimethylbutane-3-methylpentane (4.9 mol%) at 77 K.

Effect of the Addition of Alkane on the Formation of Radicals in the Radiolysis of Isobutane at 77 K. When pure isobutane is γ-irradiated at 77 K in the solid state, the isobutyl radical is formed,[6a,b] while a quite different ESR spectrum is obtained in the radiolysis of isobutane containing a small amount of alkane at 77 K.[1] The effects of the addition of alkanes on the radiolysis of solid isobutane may be classified into two types. When isobutane containing propane is γ-irradiated at 77 K, the propyl radical is mainly formed, while the formation of the isobutyl radical is suppressed. As was discussed in a previous study,[6d] the exciton by the γ-irradiation of isobutane migrates to propane to produce the propyl radical. We could not, however, find any other alkanes which behave like propane in the radiolysis of solid isobutane.

When isobutane containing other alkanes is γ-irradiated at 77 K, the formation of the isobutyl radical is suppressed without the solute radical appearing, while the t-C_4H_9 radical is formed as has been shown in the previous reports.[1]

TABLE 2. EFFECTS OF ADDITIVES ON THE RADIOLYSIS OF SOID ISOBUTANE AT 77 K

	Alkanes as additives
Type A	○ C–C–C
Type B	C–C–C–C–C C–C–C–C–C–C C–C–C–C–C–C–C  $C-\overset{C}{\overset{\vert}{C}}-C-C$  $C-\overset{C}{\overset{\vert}{\underset{\underset{C}{\vert}}{C}}}-C$  $C-\overset{C}{\overset{\vert}{C}}-\overset{C}{\overset{\vert}{C}}-C$  $C-C-\overset{C}{\overset{\vert}{C}}-C-C$  $C-\overset{C}{\overset{\vert}{\underset{\underset{C}{\vert}}{C}}}-\overset{C}{\overset{\vert}{C}}-C$  

○: Its size is smaller than that of isobutane.

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[13] J. Lin and F. Williams, *J. Phys. Chem.*, **72**, 3707 (1968).

The effects of various alkanes on the radiolysis of isobutane are shown in Table 2. It may be noted that propane is smaller than isobutane, while the other alkanes of Type B are larger than isobutane.

It may be concluded that the radiolysis of alkane in the solid phase is appreciably affected by the condition of the matrix. The effect is characteristic of the solid phase; further studies are desired for the elucidation of the solid kinetics.