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Selective Formation of Solute Radicals in the Radiolysis of Neopentane-Cyclopentane Mixtures at 4 and 77 K as Studied by Capillary Gas Chromatography and ESR Spectroscopy

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Synopsis. The dimer yields in the radiolysis of the *neo*-C_5H_{12}-*cyclo*-C_5H_{10} (1 mol%) mixtures at 77 and 4 K have been measured by capillary gas chromatography. Analysis of the results indicates that cyclopentyl radicals are produced selectively at 77 K, while their selective formation is suppressed at 4 K. This result coincides well with the data obtained by ESR spectroscopy.

When neopentane containing a small amount of other alkane is γ-irradiated at 77 K, solute alkyl radicals are formed selectively.[1] H atoms, produced by the radiolysis of neopentane, abstract hydrogen atoms much more efficiently from the alkane solute than the neopentane solvent to form the solute radicals selectively.[2] This phenomenon was also found in several solid alkanes.[3] The selective formation of radicals was studied by ESR spectroscopy which can only detect trapped reaction intermediates. Since it has been generally accepted that the radiation effect is not selective, the selective formation of the solute radicals should be verified by the product analysis which gives information about overall radiation effects.

Recently the selective formation of the $C_{10}H_{21}$ radicals in the radiolysis of the *n*-$C_{10}D_{22}$-*n*-$C_{10}H_{22}$ mixtures was verified by the analysis of dimer products.[4]

Here, we report the results on dimer products in the radiolysis of the neopentane-cyclopentane mixtures as measured by a capillary gas chromatography, and compare them with the results of ESR measurement.

Experimental

The details of the experimental procedure were described in a previous paper.[5] Neopentane and cyclopentane were the same as those used previously.[5] In order to cool the sample completely, helium gas at 400 mmHg was sealed in a cell for the γ-irradiation at 4 K. The total dose for experiments on product analysis at 4 and 77 K was fixed at 0.24 Mrad. The dose rate of γ-rays was 0.14 Mrad h^{-1}.

Product analysis was performed by means of Varian Aerograph 1440 and 3700 gas chromatographs with a FID detector. The capillary column (25 m×1.25 mm) was coated with squalane. A typical chromatogram of the heavy products in the radiolysis of neopentane was shown in a previous paper.[5]

The radicals produced in the irradiated samples were measured with a JEOL ESR spectrometer at microwave power levels of 200 μW at 77 K and 10 μW at 4 K.

Results and Discussion

When pure neopentane is γ-irradiated at 77 K, neopentyl radicals are the main radicals observed by ESR spectroscopy.[2] Figure 1A shows the ESR spectrum of the *neo*-C_5H_{12}-*cyclo*-C_5H_{10} (1 mol%) mixture γ-irradiated at 77 K. The spectrum consists of the spectrum of cyclopentyl radicals, denoted by arrows (↑), and that of neopentyl radicals, denoted by arrows (↑). The relative yield of the cyclopentyl radicals, measured by a double integration of the spectrum, amounts to 26% of the total radical yields, which is much higher than the concentration (1 mol%) of cyclopentane in the mixture. The selective formation of the solute radicals was reported previously by Miyazaki *et al.*[1] Figure 1B shows the ESR spectrum of the *neo*-C_5H_{12}-*cyclo*-C_5H_{10} (1 mol%) mixture containing He, γ-irradiated at 4 K and measured at 4 K. It is seen that cyclopentyl radicals are not observed at all, but neopentyl radicals, denoted by arrows (⇡), are formed, exclusively.[6,7]

In order to measure the dimer products in the radiolysis of the *neo*-C_5H_{12}-*cyclo*-C_5H_{10} mixture by gas chromatography, 2,2,5,5-tetramethylhexane (bineopentyl), neopentylcyclopentane, and bicyclopentyl were synthesized and their structures were determined by ^{13}C NMR spectroscopy. The chromatographic retention of the radiolysis products was compared with that of the

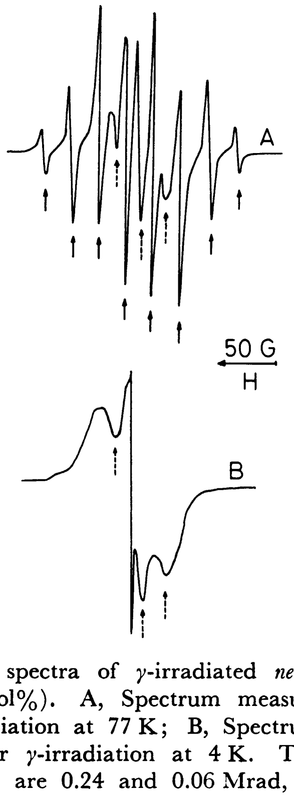
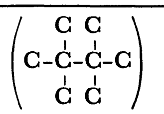
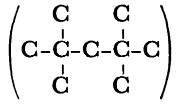
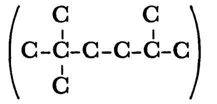
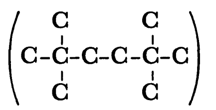
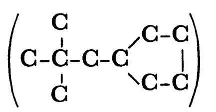
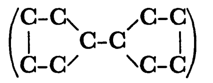


Fig. 1. ESR spectra of γ-irradiated *neo*-C_5H_{12}-cyclo-C_5H_{10} (1 mol%). A, Spectrum measured at 77 K after γ-irradiation at 77 K; B, Spectrum measured at 4 K after γ-irradiation at 4 K. Total doses at 77 and 4 K are 0.24 and 0.06 Mrad, respectively.

TABLE 1. RELATIVE YIELDS OF DIMER PRODUCTS IN THE RADIOLYSIS OF NEOPENTANE AT 77 K AND 4 K[a)]

Product[b)]		neo-C_5H_{12} 77 K	neo-C_5H_{12}-$cyclo$-C_5H_{10} (1 mol%) 77 K	neo-C_5H_{12}-$cyclo$-C_5H_{10} (1 mol%) 4 K
2233TeMC_4		—	—	0.23
2244TeMC_5		0.03	0.04	—
225TMC_6		0.05		0.02
C_9H_{18}[c)]		0.19	0.20	0.15
bineopentyl		1.0	1.0	1.0
$C_{10}H_{22}$		0.08	0.07	0.08
neopentylcyclopentane		—	0.63	0.07
bicyclopentyl		—	0.13	0.003

a) Yield of bineopentyl is taken as 1. G-values of bineopentyl at 77 and 4 K are approximately 0.3. b) T, Te, and M represent tri, tetra, and methyl, respectively. For example, 2233TeMC_4 means 2,2,3,3-tetramethylbutane. c) C_9H_{18} represents a mixture of isomers. (*cf.* Ref. 5)

synthesized one. The relative yields of dimer products are shown in Table 1. Bineopentyl, neopentylcyclopentane and bicyclopentyl are all formed in the radiolysis of the neo-C_5H_{12}-$cyclo$-C_5H_{10}(1 mol%) mixture at 77 K. In the radiolysis at 4 K, however, the formation of neopentylcyclopentane and bicyclopentyl is suppressed drastically, but bineopentyl is still a main product.

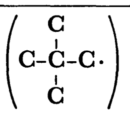
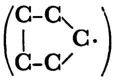
The relative yields of neopentyl and cyclopentyl radicals can be estimated from the dimer yields by the following assumptions: (1) the dimer formation is due to the recombination of radicals; (2) neopentyl and cyclopentyl radicals have the same dispropotionation-combination rate constant ratio, k_d/k_c. Then, the relative yields of neopentyl and cyclopentyl radicals can be obtained as follows:[8)]

$$\text{Yield of } neo\text{-}C_5H_{11} = 2 \times (\text{bineopentyl yield}) + (\text{neopentylcyclopentane yield})$$

$$\text{Yield of } cyclo\text{-}C_5H_9 = 2 \times (\text{bicyclopentyl yield}) + (\text{neopentylcyclopentane yield})$$

The relative yields of neopentyl and cyclopentyl radicals in the radiolysis of the neo-C_5H_{12}-$cyclo$-C_5H_{10} (1 mol%) mixture at 77 and 4 K are summarized in Table 2. Since k_d/k_c for secondary radicals, such as cyclopentyl radicals, may be larger than that for primary radicals, such as neopentyl radicals,[9)] the relative yields of the cyclopentyl radicals may be somewhat underestimated. The radical yields obtained by the product analysis coincide well with those by ESR spectroscopy. The yields of cyclopentyl radicals at 77 K are much higher than expected from the mole fraction of cyclopentane in the mixture. Thus, it has been confirmed from product analysis as well as ESR measurement that the cyclopentyl radicals, *i.e.*, solute radicals, are selectively formed in the radiolysis of the neo-C_5H_{12}-$cyclo$-C_5H_{10} (1 mol%) mixture at 77 K.

TABLE 2. RELATIVE YIELDS OF NEOPENTYL AND CYCLOPENTYL RADICALS IN THE RADIOLYSIS OF neo-C_5H_{12}-$cyclo$-C_5H_{10} (1 mol%) AT 77 AND 4 K[a)]

Radicals		77 K Prod. Anal.[b)]	77 K ESR[c)]	4 K Prod. Anal.[b)]	4 K ESR[c)]
neo-C_5H_{11}		1.00	1.00	1.00	1.00
$cyclo$-C_5H_9		0.33	0.35	0.03	<0.05

a) Yield of neo-C_5H_{11} radicals is taken as 1.00. b) Yield of radicals were obtained by analysis of dimer products. c) Yield of radicals were obtained by ESR measurements. The ratio of concentration of $cyclo$-C_5H_9 radicals to that of neo-C_5H_{11} radicals did not change after annealing the γ-irradiated sample to 77 K.

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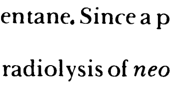
7) The ESR spectrum in the radiolysis of the neopentane system at 4 K is independent of an irradiation dose in the range of 0.06—0.24 Mrad. (*cf.* Ref. 5 and 6).

8) Isobutene is one of the main stable products in the radiolysis of neopentane. Since a product of  was not formed in the radiolysis of neo-C_5H_{12}-$cyclo$-C_5H_{10} at 77 K, the reaction of free radicals with stable producs, such as isobutene, may play a minor role.

9) a) B. Tilquin, J. Allaet, and P. Claes, *J. Phys. Chem.*, **78**, 462 (1974); b) P. Tilman, P. Claes, and B. Tilquin, *Radiat. Phys. Chem.*, **15**, 465 (1980).