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Selective Hydrogen Atom Abstraction by Hydrogen Atoms in Photolysis of Cyclohexane-Pentane Mixtures at 77 K

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Synopsis. The reaction of H atoms, produced by the photolysis of HI, has been studied in *c*-C_6H_{12}–*n*-C_5H_{12} mixtures at 77K. H atoms in *c*-C_6H_{12} matrix react more effectively with solute *n*-C_5H_{12} than with solvent *c*-C_6H_{12}, while H atoms in *n*-C_5H_{12} matrix react more effectively with solute *c*-C_6H_{12} than with solvent *n*-C_5H_{12}.

Recently, quite interesting phenomena have been reported concerning the hydrogen atom abstraction reaction by H atoms in the solid alkane at 77 K.[1] When H atoms are produced at 77 K by the photolysis of a hydrogen halide or the radiolysis of a solvent alkane, such as neopentane, the H atoms react selectively with the solute alkane which exists in the neopentane matrix as an additive. The experimental bases of the selective hydrogen atom abstraction reaction by H atoms were described fully in a previous paper.[1b] The same selective reaction has been found also in the matrices of 2,2,3,3-tetramethylbutane, isobutane, and cyclopropane.[1c] The selective hydrogen atom abstraction reaction by H atoms has proposed new problems in reaction kinetics in the solid phase at 77 K. When H atoms are hot, we must assume that they migrate a long distance at 77 K through the alkane crystal without losing their kinetic energies. When H atoms are thermal, we must assume that the activation energy for the hydrogen atom abstraction reaction is nearly zero in the alkane matrix at 77 K, though the value amounts to 7—10 kcal/mol in the gas phase.[2,3]

The previous examples of this reaction have the following characteristics: H atoms react selectively with the solute alkane, denoted as B, in the solvent alkane, denoted as A, where the combination of B in A is fixed. The selective reaction was not observed in the reverse combination, *i.e.* A in B. Here we will report a new type of combination in the case of cyclohexane and normal pentane mixtures. When A contains a small amount of B, H atoms react selectively with B. On the contrary, when B contains A, H atoms react selectively with A.

Experimental

Experimental procedures were identical with those described in the previous studies.[1] Cyclohexane, >99.7 mol%, and pentane, >99 mol%, were passed through a 1-m column packed with freshly activated alumina and then distilled on a vacuum line before use. UV illumination was provided by a Toshiba medium-pressure mercury lamp at 77 K. The esr measurement was done at 77 K on a JES-ME-3 esr spectrometer.

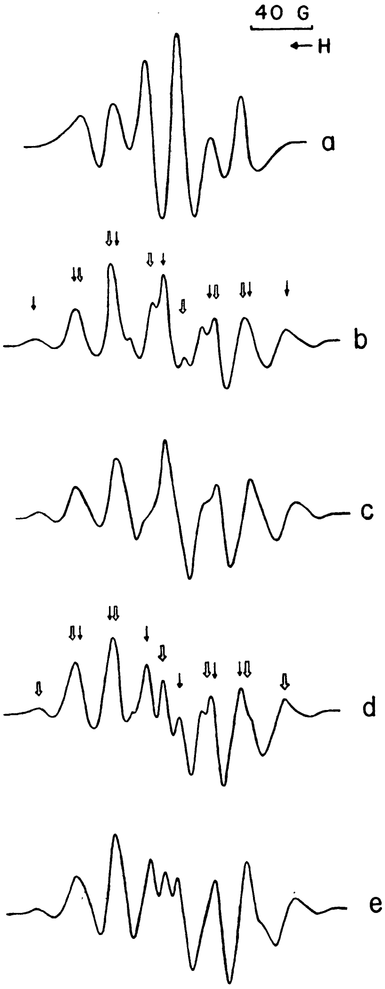

Fig. 1. a: ESR spectrum of UV-illuminated *c*-C_6H_{12}–HI (0.5 mol %) at 77 K. b: ESR spectrum of UV-illuminated *c*-C_6H_{12}–*n*-C_5H_{12} (5%)–HI (0.5%) at 77 K. c: ESR spectrum of UV-illuminated *n*-C_5H_{12}–HI (0.5%) at 77 K. d: ESR spectrum of UV-illuminated *n*-C_5H_{12}–*c*-C_6H_{12} (5%)–HI(0.5%) at 77 K. e: Simulated ESR spectrum of a mixture of C_5H_{11} radicals (60%) and *c*-C_6H_{11} radicals (40%). The relative sensitivities of the spectrometer for a, b, c, and d are approximately the same. The microwave power is 0.2 mW and the modulation width is 5 G. The area of double integration of the first-derivative ESR signal of each radical was used for simulation of the mixed spectra of the two radicals.

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Results and Discussion

Figure 1a is the ESR spectrum obtained by UV-illumination of c-C_6H_{12}–HI (0.5 mol%) at 77 K. The spectrum is consistent with the reported spectrum for cyclohexyl radical.[4] The H atom produced by the photolysis of HI abstracts the hydrogen atom from cyclohexane to produce a cyclohexyl radical. When c-C_6H_{12} containing n-C_5H_{12} (5 mol%) and HI (0.5 mol %) is illuminated at 77 K by ultraviolet light, quite a different esr spectrum is obtained (Fig. 1b). Figure 1c shows the esr spectrum obtained by the photolysis of n-C_5H_{12}–HI (0.5 mol %) at 77 K. The H atom produced by the photolysis of HI abstracts the H atom from n-C_5H_{12} to produce a C_5H_{11} radical. The spectrum of Fig. 1c is ascribed to a pentyl radical.[5] It is clear that the spectrum of Fig. 1b contains largely the spectrum due to the C_5H_{11} radical. The spectrum of Fig. 1b is ascribed to a mixture of C_5H_{11} radicals, indicated by ↓, and c-C_6H_{11} radicals, indicated by ⇩. Therefore the H atoms produced by the photolysis of HI in cyclohexane react effectively with solute pentane to form C_5H_{11} radicals.

When n-C_5H_{12} containing c-C_6H_{12} (5 mol %) and HI (0.5 mol %) is illuminated at 77 K by ultraviolet light, the esr spectrum of Fig. 1d is obtained. This spectrum is different from that of Fig. 1c which is obtained by the photolysis of n-C_5H_{12}–HI (0.5 mol %). The simulated spectrum of a mixture of C_5H_{11} radical (60%) and c-C_6H_{11} radical (40%) is shown in Fig. 1e. The spectrum of Fig. 1d is approximately similar to that of Fig. 1e. ⇩ and ↓ in Fig. 1d represent C_5H_{11} and c-C_6H_{11} radicals respectively. Therefore H atoms produced by the photolysis of HI in n-C_5H_{12} react effectively with the solute cyclohexane to form cyclohexyl radicals.

In order to obtain the ratio of the solute radical yield to the total radical yield, the esr spectrum in the photolysis of c-C_6H_{12}–n-C_5H_{12}–HI mixture is compared with the simulated spectrum of the mixture of c-C_6H_{11} and C_5H_{11} radicals. The formations of the solute radicals in c-C_6H_{12} and n-C_5H_{12} matrices are shown in Fig. 2 and 3 respectively. In both cases the fraction of solute radical yield is much higher than the concentration of the solute. Therefore, it is concluded that H atoms in the c-C_6H_{12} matrix react more effectively with solute n-C_5H_{12} than with solvent c-C_6H_{12} (Fig. 2), while H atoms in the n-C_5H_{12} matrix react more effectively with solute c-C_6H_{12} than with solvent n-C_5H_{12} (Fig. 3).

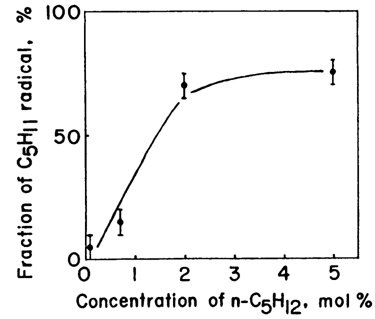

Fig. 2. Formation of solute pentyl radical in the photolysis of c-C_6H_{12}–HI (0.5 mol %) against concentration of n-C_5H_{12}.

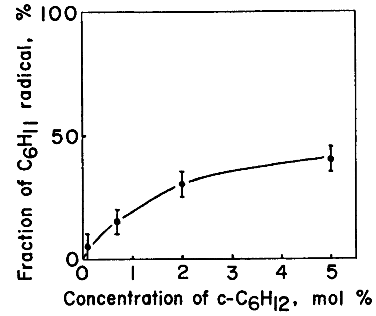

Fig. 3. Formation of solute cyclohexyl radical in the photolysis of n-C_5H_{12}–HI (0.5 mol %) against concentration of c-C_6H_{12}.

The solute alkane may form some active sites in the solid alkane at 77 K and be subjected selectively to H atom attack.

References

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