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PENTANE MIXTURES AT 77 K**

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SELECTIVE HYDROGEN ATOM ABSTRACTION BY HYDROGEN ATOMS IN PHOTOLYSIS OF CYCLOHEXANE-NORMAL PENTANE MIXTURES AT 77 K

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ABSTRACT

The reaction of H atoms, produced by the photolysis of HI, has been studied in $c\text{-C}_6\text{H}_{12}$ - $n\text{-C}_5\text{H}_{12}$ mixtures at 77 K. H atoms in $c\text{-C}_6\text{H}_{12}$ matrix react more effectively with solute $n\text{-C}_5\text{H}_{12}$ than solvent $c\text{-C}_6\text{H}_{12}$, while H atoms in $n\text{-C}_5\text{H}_{12}$ matrix react more effectively with solute $c\text{-C}_6\text{H}_{12}$ than solvent $n\text{-C}_5\text{H}_{12}$.

INTRODUCTION

Recently quite interesting phenomena have been reported on the hydrogen atom abstraction reaction by H atoms in the solid alkane at 77 K^(4,5,8). When H atoms are produced at 77 K by the photolysis of hydrogen halide or the radiolysis of the solvent alkane, such as neopentane, the H atoms react selectively with the solute alkane which exists in neopentane matrix as an additive. The experimental bases of the selective hydrogen atom abstraction reaction by H atom were described fully in a previous paper⁽⁴⁾. The selective reaction has been found also in the matrices of 2,2,3,3-tetramethylbutane, isobutane, and cyclopropane besides neopentane⁽⁵⁾. The selective hydrogen atom abstraction reaction by H atoms has proposed new problems in a 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 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^(3,7).

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 the 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^(4,5,8). Cyclohexane, >99.7 mol%, and normal 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.

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RESULTS AND DISCUSSION

Figure 1 is the esr spectrum obtained by UV-illumination of $c\text{-C}_6\text{H}_{12}\text{-HI}$ (0.5 mol%) at 77 K. The spectrum is consistent with the reported spectrum for cyclohexyl radical^(2,6) H atom produced by the photolysis of HI abstracts hydrogen atom from cyclohexane to produce cyclohexyl radical. When $c\text{-C}_6\text{H}_{12}$ containing $n\text{-C}_5\text{H}_{12}$ (5 mol%) and HI (0.5 mol%) is illuminated at 77 K by ultraviolet light, quite different esr spectrum is obtained (Figure 2). Figure 3 shows the esr spectrum obtained by the photolysis of $n\text{-C}_5\text{H}_{12}\text{-HI}$ (0.5 mol%) at 77 K H atom produced by the photolysis of HI abstracts H atom from $n\text{-C}_5\text{H}_{12}$ to produce C_5H_{11} radical. The spectrum of Figure 3 is ascribed to pentyl radical⁽¹⁾. It is clear that the spectrum of Figure 2 contains largely the spectrum due to C_5H_{11} radical. The spectrum of Figure 2 is ascribed to a mixture of C_5H_{11} radical, indicated by \downarrow , and $c\text{-C}_6\text{H}_{11}$ radical, indicated by \ddagger . Therefore H atom produced by the photolysis of HI in cyclohexane react effectively with solute $n\text{-pentane}$ to form C_5H_{11} radical.

When $n\text{-C}_5\text{H}_{12}$ containing $c\text{-C}_6\text{H}_{12}$ (5 mol%) and HI (0.5 mol%) is illuminated at 77 K by ultraviolet light, esr spectrum of Figure 4 is obtained. The spectrum is different from that of Figure 3 which is obtained by the photolysis of $n\text{-C}_5\text{H}_{12}\text{-HI}$ (0.5 mol%). The simulated spectrum of a mixture of C_5H_{11} radical (60%) and $c\text{-C}_6\text{H}_{11}$ radical (40%) is shown in Figure 5. The spectrum of Figure 4 is approximately similar to that of Figure 5. \ddagger and \downarrow in Figure 4 represent C_5H_{11} and $c\text{-C}_6\text{H}_{11}$ radicals respectively. Therefore H atom produced by the photolysis of HI in $n\text{-C}_5\text{H}_{12}$ react effectively with the solute cyclohexane to form cyclohexyl radical.

In order to obtain the fraction of solute radical yield to the total radical yield, the esr spectrum in the photolysis of $c\text{-C}_6\text{H}_{12}\text{-}n\text{-C}_5\text{H}_{12}\text{-HI}$ mixture is compared with the simulated spectrum of the mixture of $c\text{-C}_6\text{H}_{11}$ and C_5H_{11} radicals. The formations of the solute radicals in $c\text{-C}_6\text{H}_{12}$ and $n\text{-C}_5\text{H}_{12}$ matrices are shown in Figure 6 and 7 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 $c\text{-C}_6\text{H}_{12}$ matrix react more effectively with solute $n\text{-C}_5\text{H}_{12}$ than solvent $c\text{-C}_6\text{H}_{12}$ (Figure 6), while H atoms in the $n\text{-C}_5\text{H}_{12}$ matrix react more effectively with solute $c\text{-C}_6\text{H}_{12}$ than solvent $n\text{-C}_5\text{H}_{12}$ (Figure 7). The solute alkane may form some active site in the solid alkane at 77 K and be subjected selectively to H atom attack.

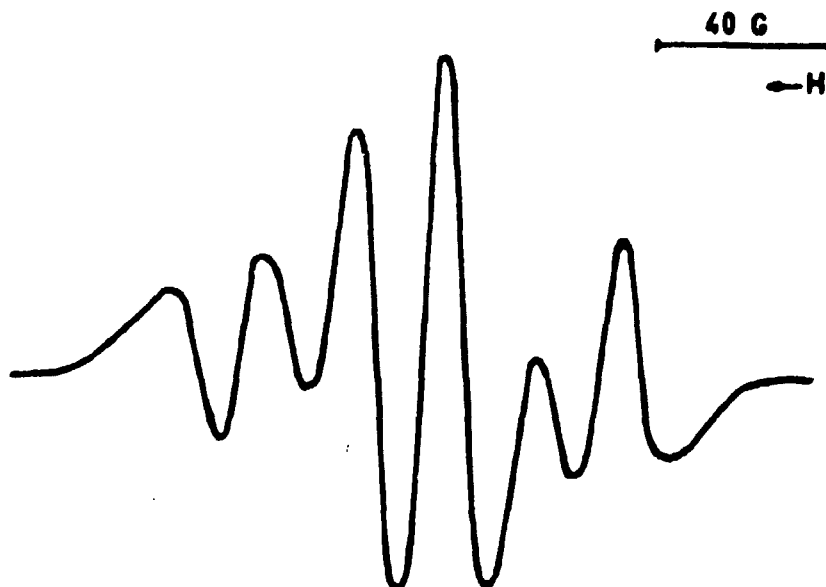


Figure 1 — ESR spectrum of UV-illuminated $c\text{-C}_6\text{H}_{12}\text{-HI}$ (0.5 mol%) at 77 K.

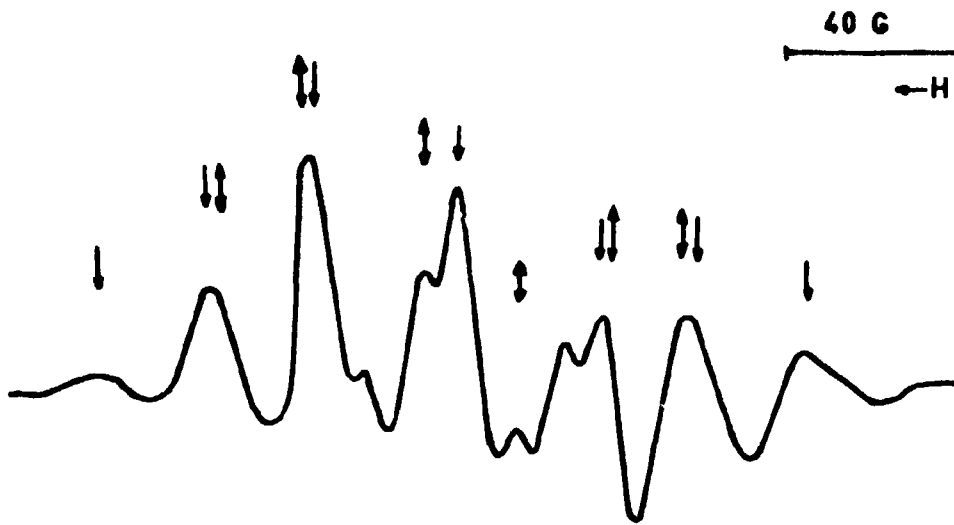


Figure 2 — ESR spectrum of UV-illuminated $c\text{-C}_6\text{H}_{12}\text{-}n\text{-C}_5\text{H}_{12}$ (5% HI (0.5%)) at 77 K.



Figure 3 — ESR spectrum of UV-illuminated $n\text{-C}_3\text{H}_{12}\text{-HI}$ (0.5%) at 77 K.

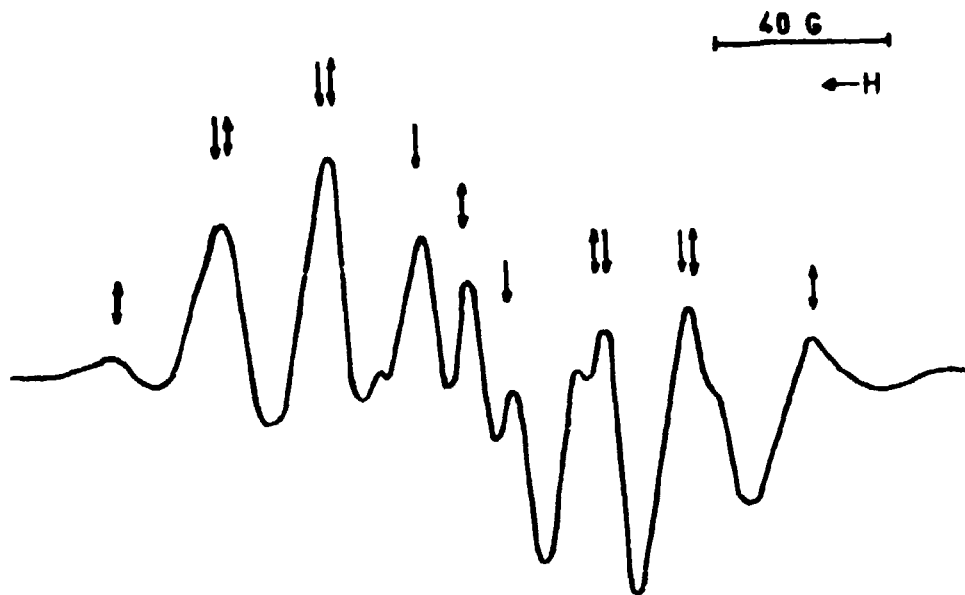


Figure 4 - ESR spectrum of UV-illuminated $n\text{-C}_5\text{H}_{12}$ - $c\text{-C}_6\text{H}_{12}$ (5%)-HI (0.5%) at 77 K.

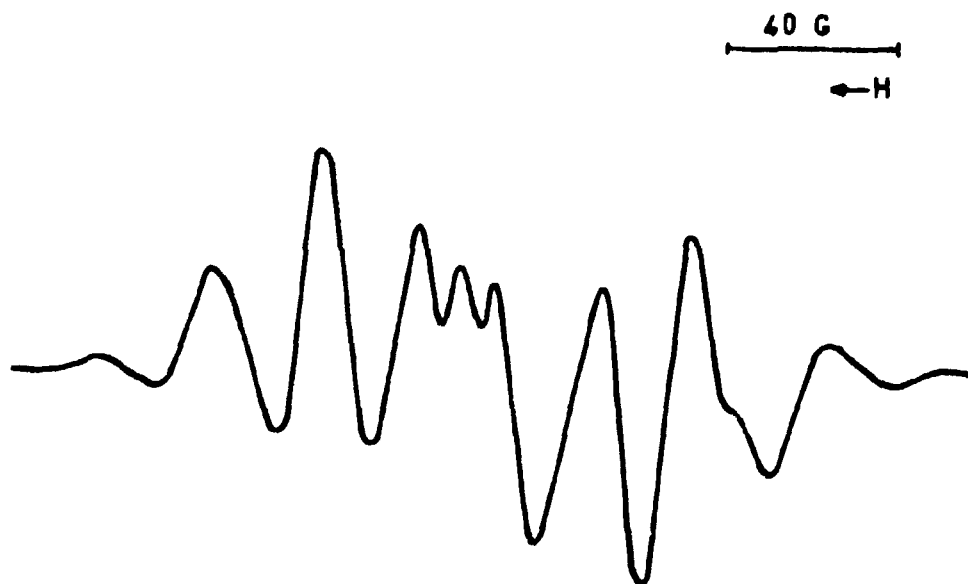


Figure 5 - Simulated esr spectrum of a mixture of C_5H_{11} radical (60%) and $c\text{-C}_6\text{H}_{11}$ radical (40%).
Relative sensitivities of spectrometer for 1, 2, 3, and 4 are approximately the same.

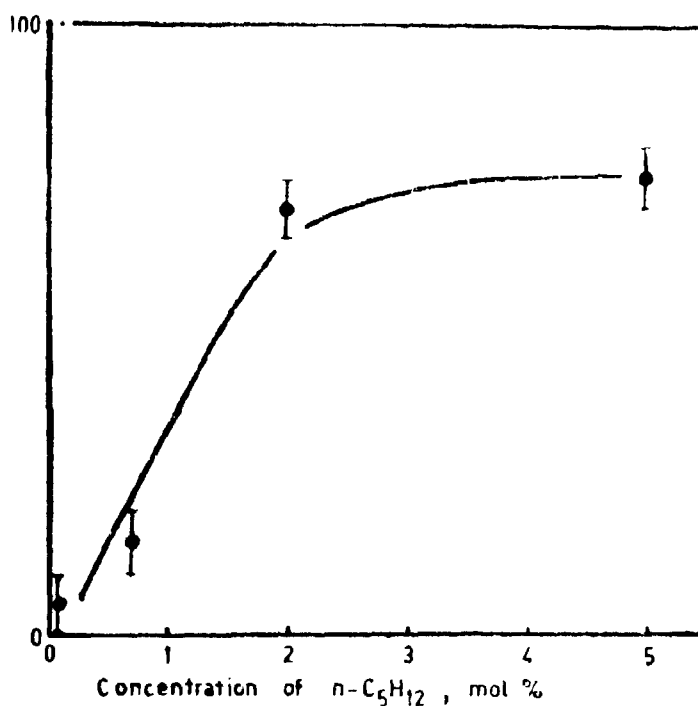


Figure 6 - Formation of solute pentyl radical in the photolysis of $c\text{-C}_6\text{H}_{12}\text{-HI}$ (0.5 mol%) against concentration of $n\text{-C}_5\text{H}_{12}$.

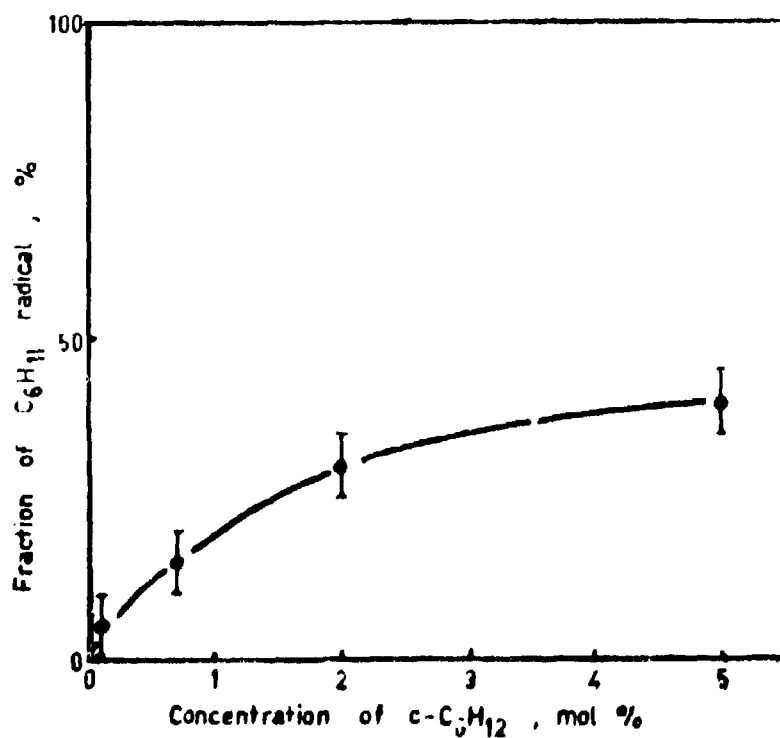


Figure 7 - Formation of solute cyclohexyl radical in the photolysis of $n\text{-C}_5\text{H}_{12}\text{-HI}$ (0.5 mol%) against concentration of $c\text{-C}_6\text{H}_{12}$.

RESUMO

A reação dos átomos de H, produzidos na fotólise do HI, foi estudada no sistema $c\text{-C}_6\text{H}_{11}\text{-}n\text{-C}_5\text{H}_{12}$ à 77° K. Os átomos de H na matriz $c\text{-C}_6\text{H}_{12}$ reagem mais eficientemente com o soluto $n\text{-C}_5\text{H}_{12}$ do que com o solvente $c\text{-C}_6\text{H}_{12}$, enquanto que os átomos de H na matriz $n\text{-C}_5\text{H}_{12}$ reagem mais eficientemente com o soluto $c\text{-C}_6\text{H}_{12}$ do que com o solvente $n\text{-C}_5\text{H}_{12}$.

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