

The Energy Dependence of Selective Hydrogen Atom Abstraction by H(D) Atoms in the Photolysis of Neopentane–Ethane Mixtures at 77 K

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Selective hydrogen-atom-abstraction reaction by an H or D atom has been studied in a *neo*-C₅H₁₂–C₂H₆ (less than 1 mol%) mixture at 77 K by ESR spectroscopy. The H (or D) atom produced by the photolysis of HI (or DI) reacts with *neo*-C₅H₁₂ and C₂H₆ to form *neo*-C₅H₁₁ and C₂H₅ radicals. In order to obtain H atoms with different kinetic energies, the photolysis was performed with different lights of 313, 254, and 229 nm. The selective formation of the C₂H₅ radical by the reaction of the H (or D) atom with C₂H₆ becomes more effective with the decrease in the energy of the H (or D) atom. The formation of the *neo*-C₅H₁₁ radical by the reaction of the H (or D) atom with *neo*-C₅H₁₂ becomes more effective with the increase in the energy of the H (or D) atom.

The reaction of the H atom is quite important in chemical kinetics as well as in the radiation chemistry of organic compounds. Though extensive results on the reaction of hot H atom have been reported in the gas phase,¹⁾ information on the solid phase at low temperatures is quite scanty at present.

Recently Miyazaki *et al.* found interesting phenomena concerning hydrogen-atom abstraction reactions by the H atom in the solid neopentane-alkane mixtures at 77 K.²⁾ When the H atom is produced at 77 K by the radiolysis of neopentane or by the UV-photolysis of hydrogen halide, the H atom reacts selectively with the solute, resulting in the formation of the solute radical. The H atom produced by the radiolysis or the photolysis has excess kinetic energy. When the wavelength of light is changed in the photolysis of HI, an H atom with a different kinetic energy is produced.

In order to obtain information on the reactivity of an H atom with a differential initial kinetic energy in the solid alkane, the reactions of the H atoms produced by the photolysis of HI in neopentane–ethane mixture are studied here.

Experimental

The D content of deuterium iodide, supplied by Merk Sharp and Dohm, Canada, Ltd., is more than 98%. The other reagents used in this study are the same as those used before.^{2c)}

UV illumination was provided by a medium-pressure mercury lamp with a UV-29 filter, a low-pressure mercury lamp with a UV-25 filter, and a home-made cadmium lamp. The cadmium lamp was made of quartz and kept in an electric furnace at 533 K.³⁾ The emission spectra of the light from the lamps used in the experiment were measured with an emission spectrometer. The emission spectra are shown in Fig. 1. In order to determine the light absorbed by HI, the extinction coefficient (ϵ) of HI was measured. Since neopentane is polycrystalline at 77 K, the extinction coefficient of HI was measured in 3-methylpentane glass at 77 K. ϵ at 254 nm, for example, is 95 mol⁻¹ dm³ cm⁻¹, nearly equal to the reported values of 95 mol⁻¹ dm³ cm⁻¹ in the gas phase⁴⁾ and 127 mol⁻¹ dm³ cm⁻¹ in the liquid solvent.⁵⁾ The absorption spectrum of 0.5 mol% HI is shown in Fig. 1 by the unit of absorbance percentage, where the pass length of light is 0.3 cm.

The free radical formed in the photolysis was measured at 77 K with a JES-3BX ESR spectrometer. The microwave

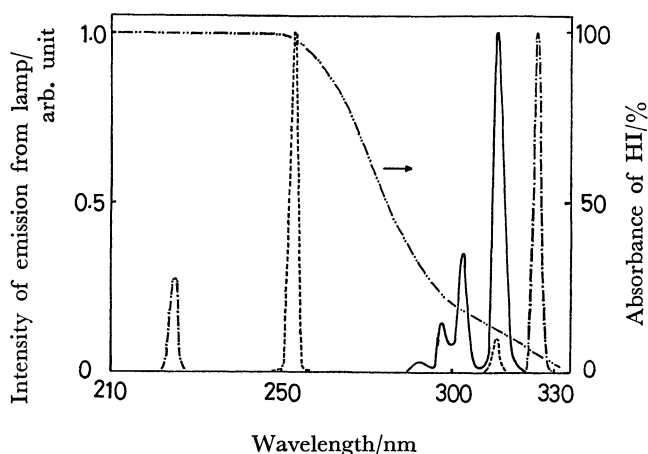


Fig. 1. Emission spectra from lamp and absorbance of HI. Maximum intensity of light from each lamp is normalized to 1.

—: Medium-pressure mercury lamp with UV-29 filter; ----: low pressure mercury lamp with UV-25 filter; —·—: cadmium lamp; ·····: absorbance of HI(0.5 mol %) in 3-methylpentane glass at 77 K, where a pass length of light is 0.3 cm.

power levels used did not result in the saturation of the signal of the alkyl radicals.

Results

The emission intensity multiplied by the absorbance of HI in Fig. 1 corresponds to the light absorbed by HI in the photolysis. The most effective lights for the photolysis of HI are 313 nm from the medium-pressure mercury lamp with a UV-29 filter, 254 nm from the low-pressure mercury lamp with a UV-25 filter, and 229 nm from the cadmium lamp. In fact, the photolysis of HI does not occur upon the irradiation with the cadmium lamp with a UV-29 filter, which cuts off the light of 229 nm and transmits only 326 nm.

Figure 2 shows the yield of the C₂H₅ radical in the photolysis of *neo*-C₅H₁₂–HI(0.5 mol %)-C₂H₆ mixtures at 77 K. The relative yield of the C₂H₅ radical was estimated from the peak height of the C₂H₅ radical in the ESR spectrum. In the present work, the peaks which do not overlap with those of other radicals were used for the measurement of the relative yield of the C₂H₅ radical. The yield of the C₂H₅ radical

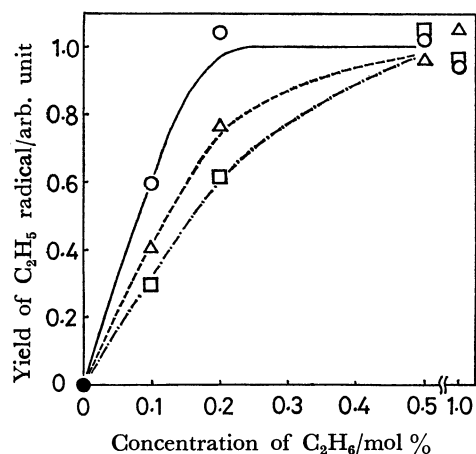


Fig. 2. Yield of C_2H_5 radical against concentration of C_2H_6 in the photolysis of $neo-C_5H_{12}$ -HI(0.5 mol %)- C_2H_6 at 77 K. The plateau yield at high concentration of C_2H_6 is normalized to 1.
 ○: Photolysis at 313 nm; △: photolysis at 254 nm;
 □: photolysis at 229 nm.

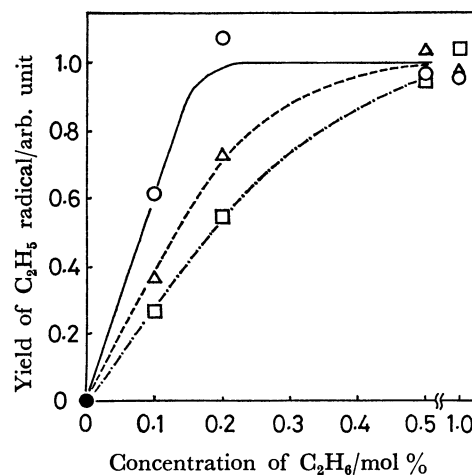


Fig. 4. Yield of C_2H_5 radical against concentration of C_2H_6 in the photolysis of $neo-C_5H_{12}$ -DI(0.5 mol %)- C_2H_6 at 77 K. The plateau yield at high concentration is normalized to 1.
 ○: Photolysis at 311 nm; △: photolysis at 254 nm;
 □: photolysis at 229 nm.

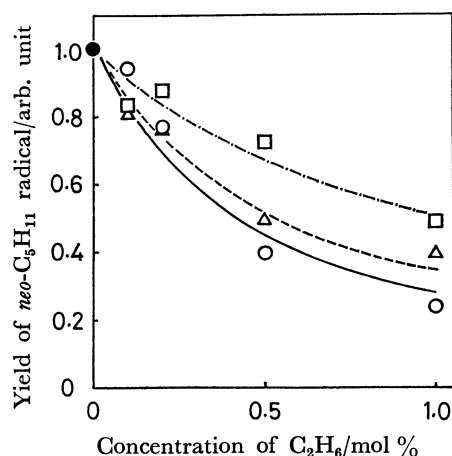


Fig. 3. Yield of $neo-C_5H_{11}$ radical against concentration of C_2H_6 in the photolysis of $neo-C_5H_{12}$ -HI(0.5 mol %)- C_2H_6 at 77 K. The yield in the absence of C_2H_6 is normalized to 1.
 ○: Photolysis at 313 nm; △: photolysis at 254 nm;
 □: photolysis at 229 nm.

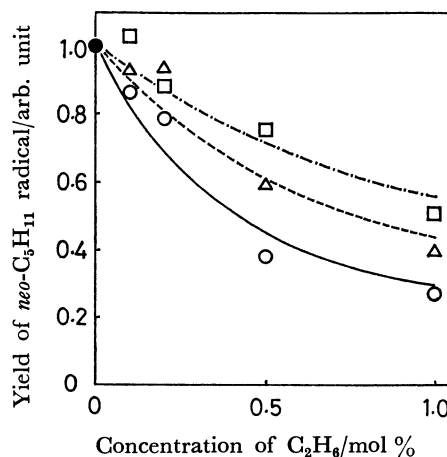


Fig. 5. Yield of $neo-C_5H_{11}$ radical against concentration of C_2H_6 in the photolysis of $neo-C_5H_{12}$ -DI(0.5 mol %)- C_2H_6 at 77 K. The yield in the absence of C_2H_6 is normalized to 1.
 ○: Photolysis at 313 nm; △: photolysis at 254 nm;
 □: photolysis at 229 nm.

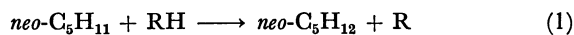
increases with the increase in the C_2H_6 concentration and reaches a plateau at a high concentration of C_2H_6 . The plateau yield is taken as 1.0.

Figure 3 shows the yield of the $neo-C_5H_{11}$ radical in the photolysis of $neo-C_5H_{12}$ -HI(0.5 mol %)- C_2H_6 mixtures at 77 K. The relative yield of the $neo-C_5H_{11}$ radical was estimated also from the peak height of the $neo-C_5H_{11}$ radical in the ESR spectrum. The peak which does not overlap with those of the other radicals was used for the measurement of the yield of the $neo-C_5H_{11}$ radical. The yield in the absence of C_2H_6 is taken as 1.0.

Figures 4 and 5 show the yields of the C_2H_5 and $neo-C_5H_{11}$ radicals respectively in the photolysis of $neo-C_5H_{12}$ -DI(0.5 mol %)- C_2H_6 mixtures at 77 K.

Discussion

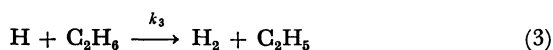
Formation of the C_2H_5 Radical. When $neo-C_5H_{12}$ -HI-alkane mixtures are UV-irradiated or $neo-C_5H_{12}$ -alkane mixtures are γ -irradiated at 77 K, the alkyl radical from the solute, such as $i-C_4H_{10}$, C_3H_8 , $c-C_6H_{12}$, and C_2H_6 , is produced in a much higher yield than would be expected from the concentration of the solute. The reaction mechanism for the selective formation of the alkyl radical has been reported in detail in previous papers.^{2a-d,2b} The formation of the alkyl radical by the radical site migration (Reaction 1) can be neglected for the following reasons:



where RH represents the solute, such as $i-C_4H_{10}$ and C_2H_6 . First, when the $neo-C_5H_{12}$ - $i-C_4H_{10}$ mixture is

γ -irradiated at 4 K, only the *neo*-C₅H₁₁ radical is produced. The selective formation of the C₄H₉ radical is not observed when the irradiated sample is warmed from 4 K to 77 K, though the C₄H₉ radical is formed in the γ -irradiation at 77 K.^{2a)} Second, when the *neo*-C₅H₁₂-*i*-C₄H₉D-2-*d*₁-HI mixture is irradiated with UV light at 77 K, the selective formation of the HD molecule and the *t*-C₄H₉ radical is observed, though the H₂ molecule and the *t*-C₄H₉ radical should be formed by the mechanism of the radical-site migration. Thus, the formation of the *t*-C₄H₉ radical is not due to the radical-site migration, but to the selective hydrogen-atom abstraction by the H atom. The other experimental evidence for the selective reaction of the H atoms has been presented in the previous papers.^{2b,d)} When *neo*-C₅H₁₂-C₂H₆-*i*-C₄H₁₀-HI mixtures are UV-irradiated at 77 K, the yield of the C₂H₅ radical decreases upon the addition of *i*-C₄H₁₀, resulting in the complementary formation of the *t*-C₄H₉ radical.^{2b)} Therefore, the C₂H₅ radical is also formed by the selective reaction of the H atom.

Figure 2 shows that the yield of the C₂H₅ radical in the photolysis of *neo*-C₅H₁₂-HI(0.5 mol %)-C₂H₆ mixtures increases with the increase in C₂H₆ and reaches a plateau at high concentrations. Since the plateau value is normalized to 1 in Fig. 2, the amounts of the reactive H atoms produced by the photolysis of HI with three different lights are normalized to the same value. The reaction mechanism for the formation of the C₂H₅ radical can be represented as follows:



where I_2 is the rate of the production of the reactive H atom which reacts with C₂H₆ at high concentrations of C₂H₆. k is a rate constant. Reaction 4 represents some reaction which competes with Reaction 3. P may be *neo*-C₅H₁₂ and HI. Since I_2 is normalized to 1,

$$k_3/\{k_4[\text{P}]\} = [\text{C}_2\text{H}_5]/\{[\text{C}_2\text{H}_6](1 - [\text{C}_2\text{H}_5])\}. \quad (5)$$

Since [P] is constant in the present experiment, $k_3/\{k_4[\text{P}]\}$ represents the relative reactivity of Reaction 3 and is summarized in the third column in Table 1. When hydrogen iodide absorbs ultraviolet light, the H atom produced by the photolysis obtains excess kinetic energy. The energetics of the dissociation process is a little complicated by the possibility that iodine atoms can be formed in two electronic states, the ground or the first-excited state.⁶⁾ It is assumed here, however, that most of the iodine atoms are in the ground state and that the average initial energy of the hydrogen atom is the difference between the energy of light and the bond energy of HI. The average excess energy is shown in the second column in Table 1. The relative reactivity of the selective hydrogen-atom abstraction reaction increases with the decrease in the kinetic energy of the H atom. If the reactive H atom is a thermal H atom, $k_3/\{k_4[\text{P}]\}$ should be independent of the light sources in the

TABLE 1. RATE CONSTANT FOR HYDROGEN-ATOM ABSTRACTION REACTION BY THE H(D) ATOM AT 77 K

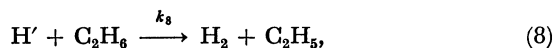
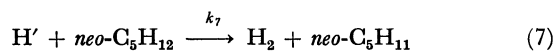
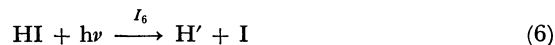
Wave length of photolysis nm	Excess energy of the hydrogen atom kcal/mol	$k_3/\{k_4[\text{P}]\}^a$	k_8/k_7
<i>neo</i> -C ₅ H ₁₂ -HI(0.5 mol %)-C ₂ H ₆			
313	20	1500	250
254	41	1100	190
229	54	600	100
<i>neo</i> -C ₅ H ₁₂ -DI(0.5 mol %)-C ₂ H ₆			
313	20	1600	250
254	41	900	130
229	54	500	80

a) The unit of concentration is the mole fraction. See text.

evolution of H from HI.

The yield of the C₂H₅ radical in the photolysis of *neo*-C₅H₁₂-DI(0.5 mol %)-C₂H₆ mixtures is shown in Fig. 4. The amount of the C₂H₅ radical increases with the increase in the C₂H₆ concentration and reaches a plateau at a high concentration. The same mechanism as in Reactions 2, 3, and 4 can be applied to the formation of the C₂H₅ radical in the photolysis of DI. The $k_3/\{k_4[\text{P}]\}$ value for the D atom, as estimated from Eq. 5, is shown in Table 1. The relative reactivity of the selective hydrogen-atom abstraction by the D atom increases with the decrease in the kinetic energy of the D atom. It is noted that the $k_3/\{k_4[\text{P}]\}$ value and its energy dependence for the D atom are similar to those for the H atom.

Formation of the *neo*-C₅H₁₁ Radical. Figure 3 shows that the yield of the *neo*-C₅H₁₁ radical in the photolysis of *neo*-C₅H₁₂-HI(0.5 mol %)-C₂H₆ mixtures decreases upon the addition of C₂H₆, while that of the C₂H₅ radical increases (Fig. 2). Since the *neo*-C₅H₁₁ radical does not react with C₂H₆ in the solid phase at 77 K,^{2e)} the dependence of the *neo*-C₅H₁₁-radical yield upon C₂H₆ may be due to a competitive reaction between *neo*-C₅H₁₂ and C₂H₆ for the H atom.



where I_6 is the rate of the production of the reactive H atom, which produces the *neo*-C₅H₁₁ radical in the absence of C₂H₆. The two reactive hydrogen atoms in Reactions 2 and 6 will be compared below. Since I_6 is normalized to 1 in Fig. 3, the following equation is obtained:

$$\frac{1}{[\text{neo-C}_5\text{H}_{11}]} = 1 + \frac{k_8[\text{C}_2\text{H}_6]}{k_7[\text{neo-C}_5\text{H}_{12}]} \quad (9)$$

The average values of k_8/k_7 , obtained from the kinetic plots of $1/[\text{neo-C}_5\text{H}_{11}]$ and $[\text{C}_2\text{H}_6]/[\text{neo-C}_5\text{H}_{12}]$, are shown in the last column in Table 1. k_8/k_7 decreases with the increase in the energy of the H atom. Thus, the formation of the *neo*-C₅H₁₁ radical becomes more favorable with the increase in the energy of the H atom.

Figure 5 shows the dependence of the *neo*-C₅H₁₁ radical yield upon C₂H₆ in the photolysis of *neo*-C₅H₁₂-DI(0.5 mol %)-C₂H₆ mixtures. The yield decreases upon the addition of C₂H₆, while that of the C₂H₅ radical increases (Fig. 4). The same kinetics as in Reactions 6–8 and Eq. 9 can be applied to the formation of the *neo*-C₅H₁₁ radical by the D atom. The k_8/k_7 ratio for the D atom is shown in Table 1. k_8/k_7 decreases with the increase in the energy of the D atom.

Now, Reactions 8 and 7 will be compared with Reactions 3 and 4. Since the concentration of P in $k_3/\{k_4[P]\}$ is represented by a mole fraction, $[P]=1$ if P corresponds only to *neo*-C₅H₁₂. In this case, however, the experimental values of k_3/k_4 for the H and D atoms are not equal to k_8/k_7 , but about 6 times as large as k_8/k_7 (Table 1). Thus, Reaction 4 must contain some reaction other than Reaction 7.

The ratio of the decrement in the *neo*-C₅H₁₁-radical yield ($-\Delta C_5H_{11}$) to the increment in the C₂H₅-radical yield (ΔC_2H_5) is shown in Fig. 6 as a function of the C₂H₆ concentration. Since the reliability of the $-\Delta C_5H_{11}$ value at 0.1 mol % is low, the value at 0.1 mol % is omitted in the figure. If Reaction 4 represents only a reaction between H (or D) and *neo*-C₅H₁₂, the $-\Delta C_5H_{11}/\Delta C_2H_5$ ratio should be constant at all concentrations of C₂H₆. Figure 6 shows, however, that the ratio is not constant. In fact, this ratio changes more remarkably with the decrease in the energy of the H (or D) atom. Some of the reactive H (or D) atoms which react with C₂H₆ do not react with *neo*-C₅H₁₂, and the role of these H (or D) atoms increases with the decrease in the energy of the H (or D) atom. Therefore, the H atoms in Reaction 2 represent all the hydrogen atoms which react with C₂H₆, while the H' atoms in Reaction 6 represent only the hydrogen atoms which can react with *neo*-C₅H₁₂.

It is concluded from the energy dependence of the formation of the C₂H₅ radical that H (or D) atoms with different excess energies play an important role in the selective hydrogen-atom abstraction reaction and that the selective reaction occurs more easily with the decrease in the excess energy of the H (or D) atom. The hydrogen atoms with small excess energies migrate through the neopentane matrix at 77 K. The atoms neither react with neopentane nor are deactivated during their migration. These results seem to contradict a kinetic theory of a hot-atom reaction in the gas phase. The reactions in the solid phase, however, may be different from those in the gas phase. Further

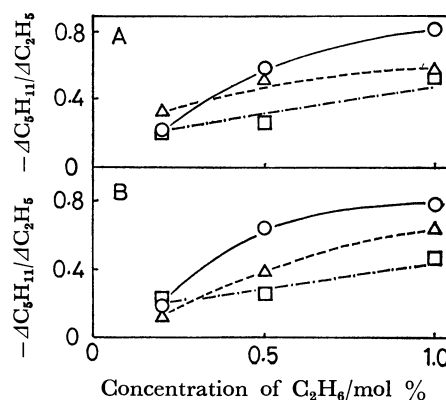


Fig. 6. The ratio of decrement of *neo*-C₅H₁₁ radical yield ($-\Delta C_5H_{11}$) to increment of C₂H₅ radical yield (ΔC_2H_5) against concentration of C₂H₆. Figures A and B are *neo*-C₅H₁₂-HI(0.5 mol %)-C₂H₆ system and *neo*-C₅H₁₂-DI(0.5 mol %)-C₂H₆ system respectively.

○: Photolysis at 313 nm; △: photolysis at 254 nm; □: photolysis at 229 nm.

studies of the reaction and the deactivation process of the hot H atom in the solid phase are now under way.

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