

THE ENERGY DEPENDENCE OF SELECTIVE HYDROGEN ATOM ABSTRACTION BY H(D) ATOMS 213
IN THE PHOTOLYSIS OF NEOPENTANE-ETHANE MIXTURES AT 77K

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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 77K 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 77K⁽²⁾. When the H atom is produced at 77K 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.

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EXPERIMENTAL

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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 533K⁽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 77K, the extinction coefficient of HI was measured in 3-methylpentane glass at 77K. ϵ at 254 nm, for example, is $95 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, nearly equal to the reported values of $95 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ in the gas phase⁽⁴⁾ and $127 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ 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 77K with a JES-3B X ESR spectrometer. The microwave 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 C_2H_5 radical in the photolysis of neo- C_5H_{12} -HI (0.5 mol %)- C_2H_6 mixtures at 77K. The relative yield of the C_2H_5 radical was estimated from the peak height of the C_2H_5 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 C_2H_5 radical. The yield of the C_2H_5 radical 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-C₅H₁₁ radical in the photolysis of neo-C₅H₁₂-HI (0.5 mol %) -C₂H₆ mixtures at 77K. The relative yield of the neo-C₅H₁₁ radical was estimated also from the peak height of the neo-C₅H₁₁ 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-C₅H₁₁ radical. The yield in the absence of C₂H₆ is taken as 1.0.

Figures 4 and 5 show the yields of the C₂H₅ and neo-C₅H₁₁ radicals respectively in the photolysis of neo-C₅H₁₂-DI (0.5 mol %) -C₂H₆ mixtures at 77K.

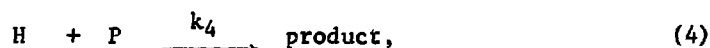
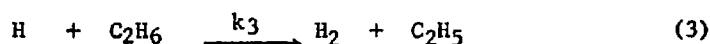
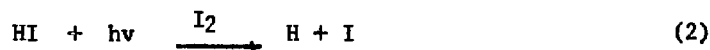
DISCUSSION

Formation of the C₂H₅ Radical. When neo-C₅H₁₂-HI-alkane mixtures are UV-irradiated or neo-C₅H₁₂-alkane mixtures are γ -irradiated at 77K, the alkyl radical from the solute, such as i-C₄H₁₀, C₃H₈, n-C₆H₁₂, and C₂H₆, 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, 2h). 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-C₄H₁₀ and C₂H₆. First, when the neo-C₅H₁₂-i-C₄H₁₀ mixture is γ -irradiated at 4K, only the neo-C₅H₁₁ radical is produced. The selective formation of the C₄H₉ radical is not observed when the irradiated sample is warmed from 4K to 77K, though the C₄H₉ radical is formed in the γ -irradiation at 77K^(2e). Second, when the neo-C₅H₁₂-i-C₄H₉D-2-d₁-HI mixture is irradiated with UV light at 77K, 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 77K, the yield of the C₂H₅ radical decreases upon the addition of i-C₄H₁₀, resulting in the complementary formation of the t-C₄H₉ radical^(2h). Therefore, the C₂H₅ radical is also formed by the selective reaction of the H atom.

Figure 2 shows that the yield of the C_2H_5 radical in the photolysis of neo- C_5H_{12} -HI (0.5 mol %)- C_2H_6 mixtures increases with the increase in C_2H_6 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 C_2H_5 radical can be represented as follows:



where I_2 is the rate of the production of the reactive H atom which reacts with C_2H_6 at high concentrations of C_2H_6 . k is a rate constant. Reaction 4 represents some reaction which competes with Reaction 3. P may be neo- C_5H_{12} and HI. Since I_2 is normalized to 1,

$$k_3 / \{k_4 [P]\} = [C_2H_5] / \{[C_2H_6] (1 - [C_2H_5])\}. \quad (5)$$

Since $[P]$ is constant in the present experiment, $k_3 / \{k_4 [P]\}$ 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, $k_3 / \{k_4 [P]\}$ should be independent of the light sources in the evolution of H from HI.

The yield of the C_2H_5 radical in the photolysis of neo- C_5H_{12} -DI (0.5 mol %)- C_2H_6 mixtures is shown in Fig. 4. The amount of the C_2H_5 radical increases with the increase in the C_2H_6 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 C_2H_5 radical in the photolysis of DI. The $k_3 / \{k_4 [P]\}$ 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

TABLE 1

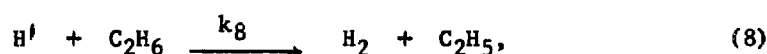
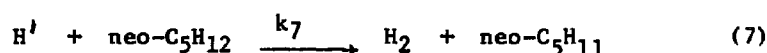
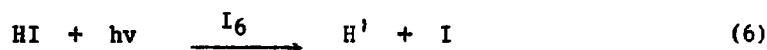
RATE CONSTANT FOR HYDROGEN-ATOM ABSTRACTION REACTION BY THE H(D)
ATOM AT 77K.

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

D atom increases with the decrease in the kinetic energy of the D atom. It is noted that the $k_3/(k_4[P])$ value and its energy dependence for the D atom are similar to those for the H atom. 218

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 77K^(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 77K. 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 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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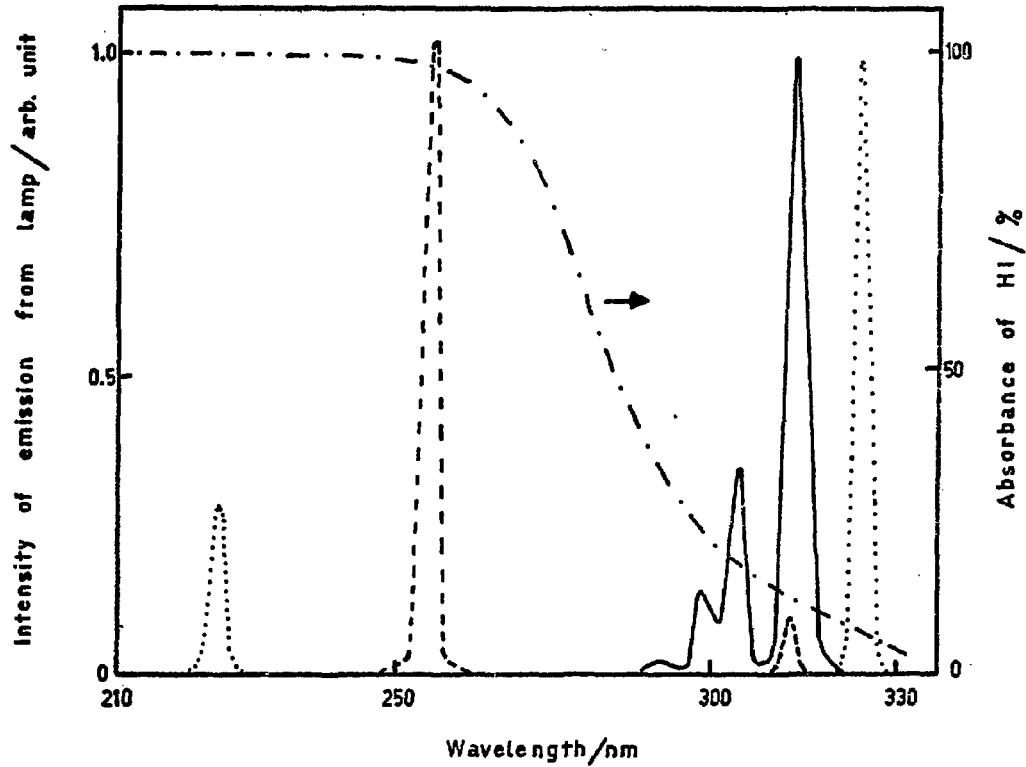


Figure 1: Emission spectra from lamp and absorbance of HI. Maximum intensity of light from each lamp is normalized to 1.

- : 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 77K, where a pass length of light is 0.3 cm.

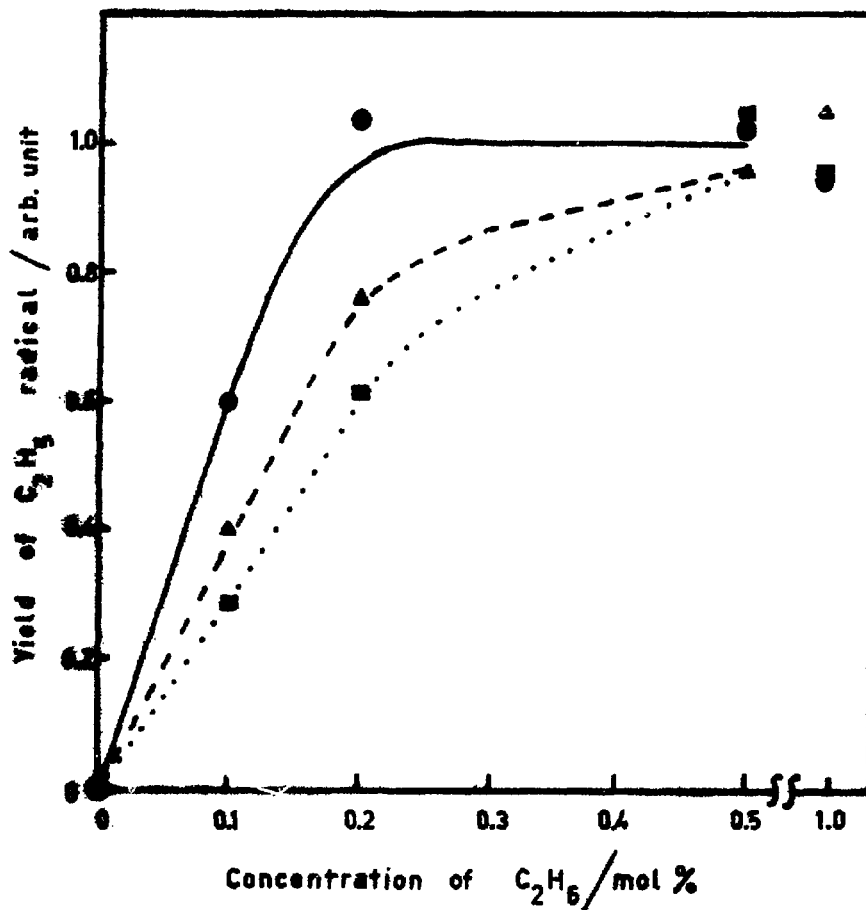


Figure 2: Yield of C₂H₅ radical against concentration of C₂H₆ in the photolysis of neo-C₅H₁₂-HI(0.5 mol%)-C₂H₆ at 77K. The plateau yield at high concentration of C₂H₆ is normalized to 1.

- : Photolysis at 313 nm;
- ▲ : Photolysis at 254 nm;
- : Photolysis at 229 nm.

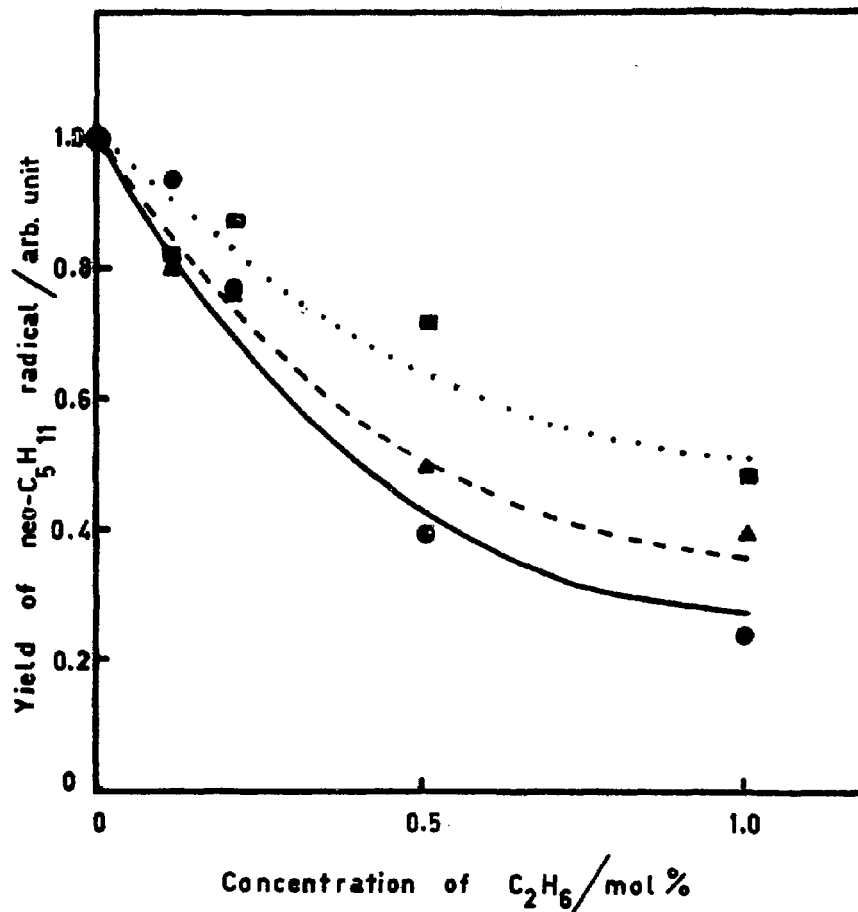


Figure 3: Yield of neo-C₅H₁₁ radical against concentration of C₂H₆ in the photolysis of neo-C₅H₁₂-HI(0.5 mol%)-C₂H₆ at 77K. The yield in the absence of C₂H₆ is normalized to 1.

- : Photolysis at 313 nm;
- ▲ : Photolysis at 254 nm;
- : Photolysis at 229 nm.

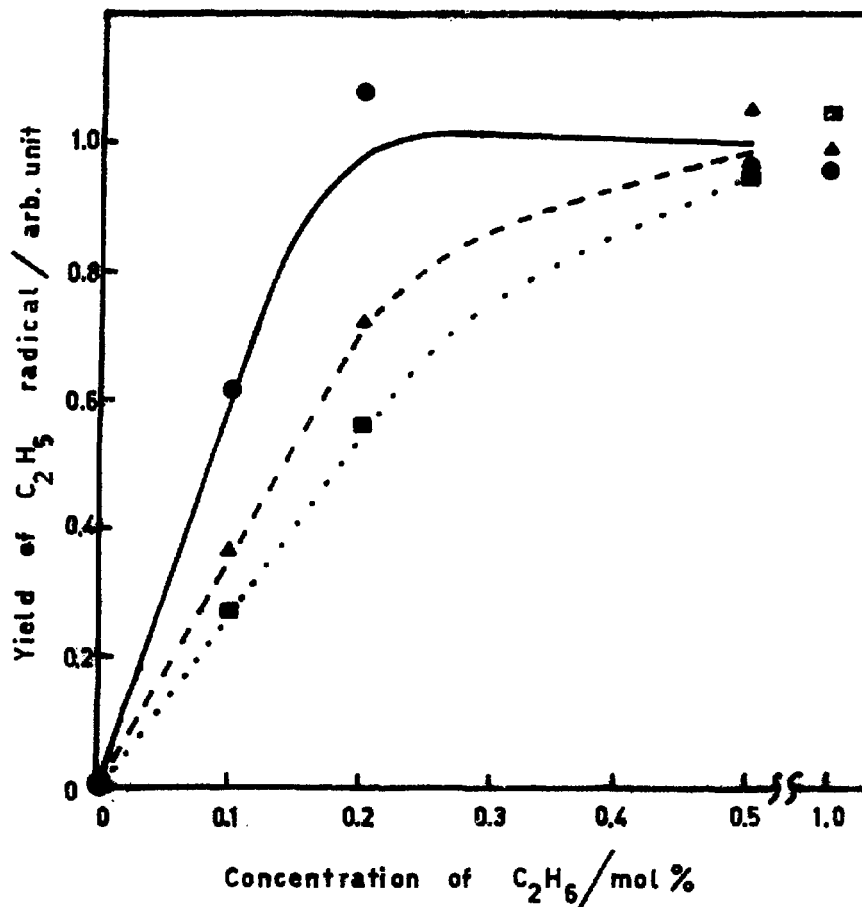


Figure 4: Yield of C₂H₅ radical against concentration of C₂H₆ in the photolysis of neo-C₅H₁₂-DI(0.5 mol%)-C₂H₆ at 77K. The plateau yield at high concentration is normalized to 1.

- : Photolysis at 311 nm;
- ▲ : Photolysis at 254 nm;
- : photolysis at 229 nm.

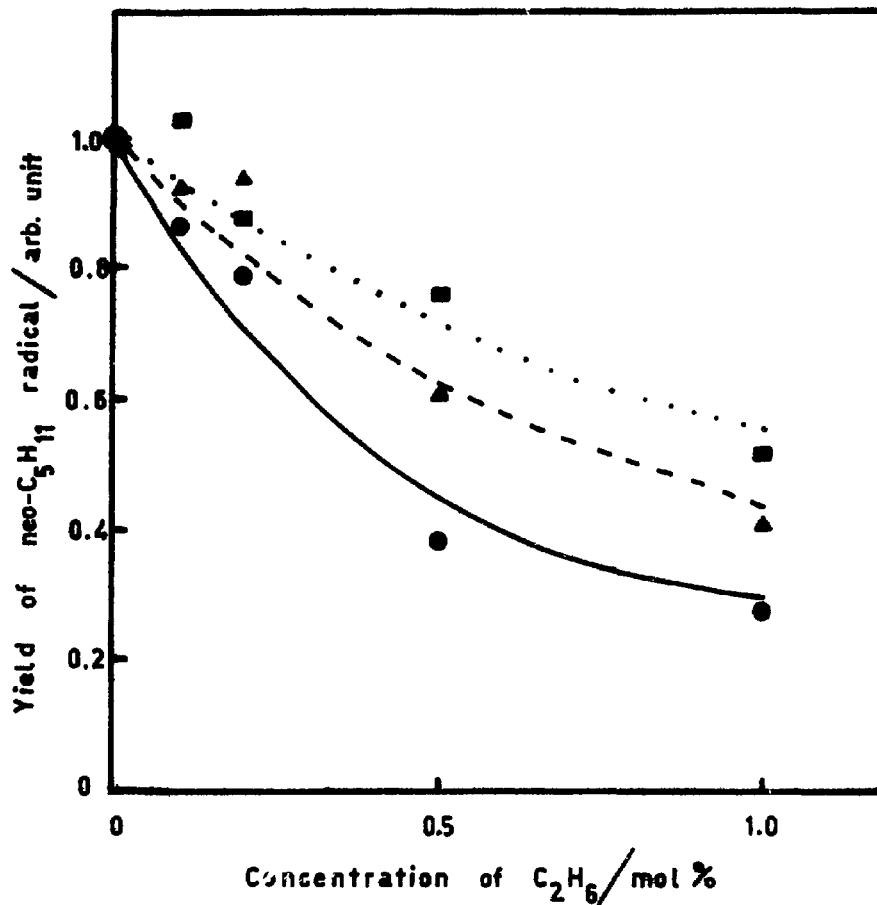


Figure 5: Yield of neo-C₅H₁₁ radical against concentration of C₂H₆ in the photolysis of neo-C₅H₁₂-DI(0.5 mol%)-C₂H₆ at 77K. The yield in the absence of C₂H₆ is normalized to 1.

- : Photolysis at 313 nm;
- ▲: Photolysis at 254 nm;
- : Photolysis at 229 nm.

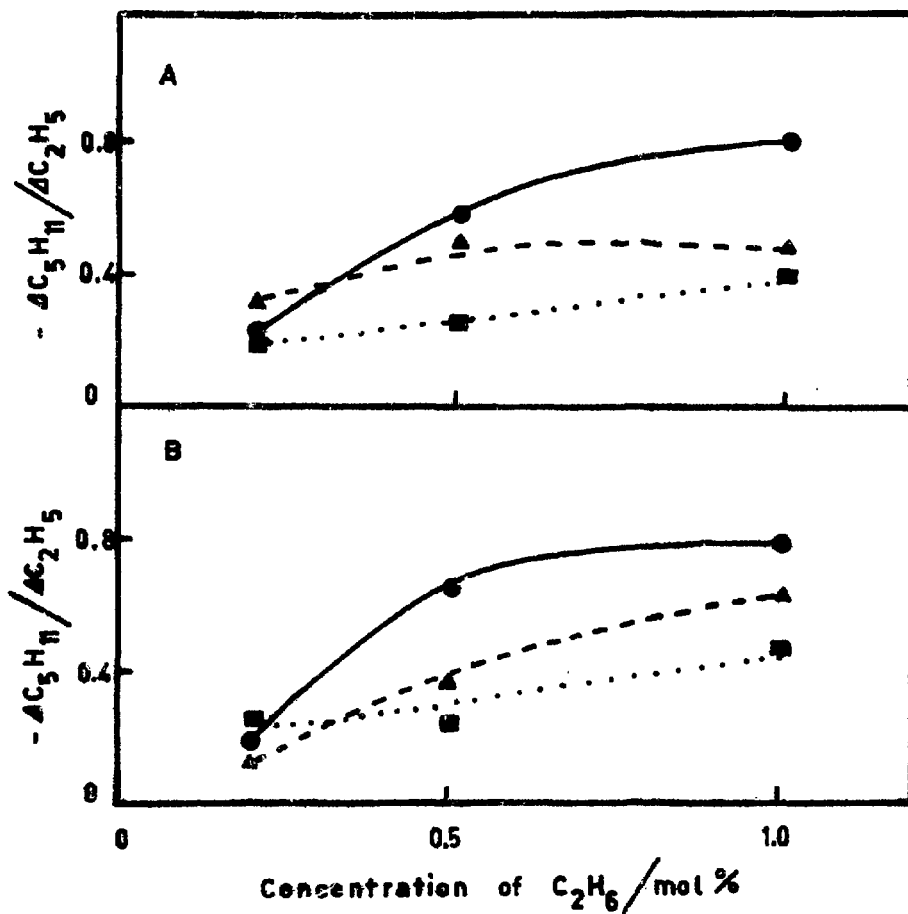


Figure 6: The ratio of decrement of neo-C₅H₁₁ radical yield ($-\Delta C_5H_{11}$) to increment of C₂H₅ radical yield (ΔC_2H_5) against concentration of C₂H₆. Figures A and B are neo-C₅H₁₂-HI(0.5 mol%)-C₂H₆ system and neo-C₅H₁₂-DI(0.5 mol%)-C₂H₆ system respectively.

- : Photolysis at 313 nm;
- ▲ : Photolysis at 254 nm;
- : Photolysis at 229 nm.