

LASER FLASH PHOTOLYSIS OF 1-ALKENES AT 193 nm IN THE GAS PHASE: EFFECT OF MOLECULAR SIZE ON THE FORMATION YIELD OF ALLYL RADICAL

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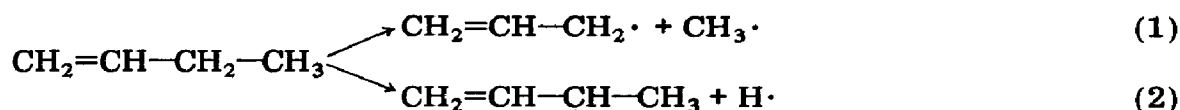
(Received July 17, 1985; in revised form October 18, 1985)

Summary

Allyl radical has been detected as a major product in the photolysis of 1-alkenes ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{R}$) using an ArF excimer laser (193 nm). A broad absorption spectrum was obtained immediately after excitation, indicating the formation of a vibrationally hot radical. This spectrum is gradually sharpened by collisional deactivation. The relaxed spectrum in the presence of high pressure nitrogen is almost the same as that reported by flash photolysis on the microsecond time scale. The relative yields of allyl radical have been estimated by measuring absorbances at the peak (223 nm). In the presence of 800 Torr nitrogen, they decrease as the size of the molecule becomes larger in the order $\text{C}_3\text{H}_6 > 1-\text{C}_4\text{H}_8 > 1-\text{C}_5\text{H}_{10} \gg 1-\text{C}_6\text{H}_{12}$, $4-\text{CH}_3-1-\text{C}_5\text{H}_9$, $1-\text{C}_7\text{H}_{14} \gg 1-\text{C}_8\text{H}_{16} > 1-\text{C}_9\text{H}_{18}$. This size dependence is discussed in terms of a "hot molecule mechanism", namely it is postulated that 1-alkenes are dissociated from hot molecules formed by internal conversion.

1. Introduction

Photolysis of alkenes in the gas phase has been investigated by using conventional vacuum UV light sources [1 - 7], by microsecond flash photolysis [8 - 12] and recently by nanosecond laser photolysis [13 - 15]. Two competing processes have been reported for the photolysis of 1-butene in the wavelength range 124 - 185 nm [1 - 5]:



These are dissociation processes of the C—C bond at the position β to the double bond (process (1)) and of the C—H bond (process (2)). Process (1)

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must be the major reaction in the case of the 193 nm excitation because the ratio of process (1) to process (2) increases as the excitation energy decreases [1 - 5, 8].

Photodissociation via a Rydberg state was proposed from an investigation of the effects of pressure on the photoproducts [4]. However, photodissociation via a hot molecule has been postulated for *cis*-2-hexene, *cis*-2-butene and a number of alkenes [7, 13]. We have recently confirmed this mechanism by direct measurement of dissociation rates [14]. In this paper a hot molecule is defined as a state with high vibrational energy in the electronic ground state.

In this paper we report on the dissociation mechanism of 1-alkenes studied by nanosecond laser photolysis, with discussion from a new standpoint, namely the effect of the molecular size of 1-alkenes on the formation yield of allyl radicals. If the hot molecule mechanism is valid, slower dissociation rates are expected for alkenes with larger molecular sizes. In the presence of foreign gases, the yield of allyl radical is expected to decrease with an increase in the size of the molecule, because reactions via hot molecules are quenched by them. Recently, a similar hypothesis has been proposed on theoretical grounds [6] and a size effect has been predicted for the dissociation yield of alkenes.

Because the excitation energy of the ArF (193 nm) laser (620 kJ mol^{-1}) is sufficiently large to dissociate the C—C bond at the β position ($D_0 \approx 301 \text{ kJ mol}^{-1}$), allyl radicals thus produced have a high internal energy. Vibrationally excited radicals (hot radicals) are detected immediately after pulse irradiation. Collisional deactivation is observed for the allyl radicals, as has been demonstrated for benzyl radicals [16].

2. Experimental details

2.1. Materials

1-Butene (98%), 1-pentene (99%), 1-hexene (97%), 4-methyl-1-pentene (98%), 1,5-hexadiene (99%), 1-octene (98%), allyl chloride (98%), allylamine (98%) and allyl alcohol (98%) were purchased from Tokyo Kasei, propylene was purchased from Takachiho Kagaku and 1-heptene (better than 99%) and 1-nonene (99%) were purchased from Aldrich. All these 1-alkenes were purified by trap-to-trap distillation in vacuum and were degassed by performing more than five freeze-pump-thaw cycles before being transferred to an optical cell which was made of Suprasil quartz with an effective path length of 3.7 cm. Nitrogen (Nippon Sanso, stated purity 99.99% or better) and nitric oxide (Takachiho Kagaku, stated purity 98% or better, the major impurity being nitrogen) were used without further purification. UV absorption spectra of all 1-alkenes were measured using a Cary 17 spectrophotometer, to determine the absorption coefficients at 193 nm.

2.2. Flash photolysis

Samples were irradiated using an ArF excimer laser (Lambda Physik EMG-500 or EMG-101E, having a typical pulse energy of about 10 mJ and

a pulse width of 12 ns) at room temperature. Transient species were monitored using a pulsed xenon lamp. The details of the flash photolysis apparatus have been described previously [17]. In this paper, $t = 0$ ns is defined as the time at which 90% of the laser energy is absorbed.

2.3. Product analysis by gas chromatography

After several shots of irradiation from the ArF excimer laser, the products were analysed on an Okura Model GC103 gas chromatograph using a Waters Porapak Q column with a flame ionization detector. Since the product ratios were constant for both a single pulse and repeated irradiation by several shots, secondary photoreactions were disregarded.

3. Results and discussion

3.1. Transient absorption of 1-butene on excitation at 193 nm

Time-resolved absorption spectra of 1-butene (5 Torr) have two peaks as shown in Fig. 1. The peaks at about 220 nm and 216 nm can be safely assigned to the allyl radical [11] and the methyl radical respectively, on the basis of the results of flash photolysis on the microsecond time-scale [18]. All the 1-alkenes irradiated in this study give the same absorption peak at about 220 nm.

As can be seen in Fig. 1, a broad absorption spectrum is obtained immediately after irradiation by a laser pulse (0 ns). This broadness is ascribable to vibrationally excited (hot) states of the radicals. The time-resolved spectra become sharper as time proceeds, namely the absorption intensity at the peak position (about 220 nm) increases until about 1 μ s, as shown in Fig. 2(a). However, the absorptions at the tail region decrease after 100 ns. These changes can be interpreted in terms of collisional deactivation of hot allyl radicals by unexcited 1-butene molecules. When nitrogen (800 Torr) is added to the sample as a foreign gas, the hot radicals with the broad spectra are deactivated more effectively than in the absence of nitrogen; this takes about 200 ns, as shown in Fig. 2(b). The relaxed spectra are essentially the same as those obtained by microsecond flash photolysis [8 - 11]. As is shown in Fig. 1, spectrum f, the absorptions of allyl radicals and methyl radicals are completely quenched within 400 ns by adding 100 Torr nitric oxide as a radical scavenger.

The time-resolved absorption at about 235 nm behaves differently from that above owing to the cooling process of hot allyl radicals. An extra absorption remains as a tail between 230 and 245 nm after collisional relaxation. A difference spectrum between the observed spectrum and the spectrum of allyl radicals obtained by irradiation of propylene (see Fig. 3) reveals an absorption peak at about 235 nm (broken line in Fig. 1, spectrum e). This is due to the α -methallyl radical which is expected to be observed according to process (2). The yield of α -methallyl radical was estimated to be about one tenth that of allyl radical on the basis of the molar extinction coefficients

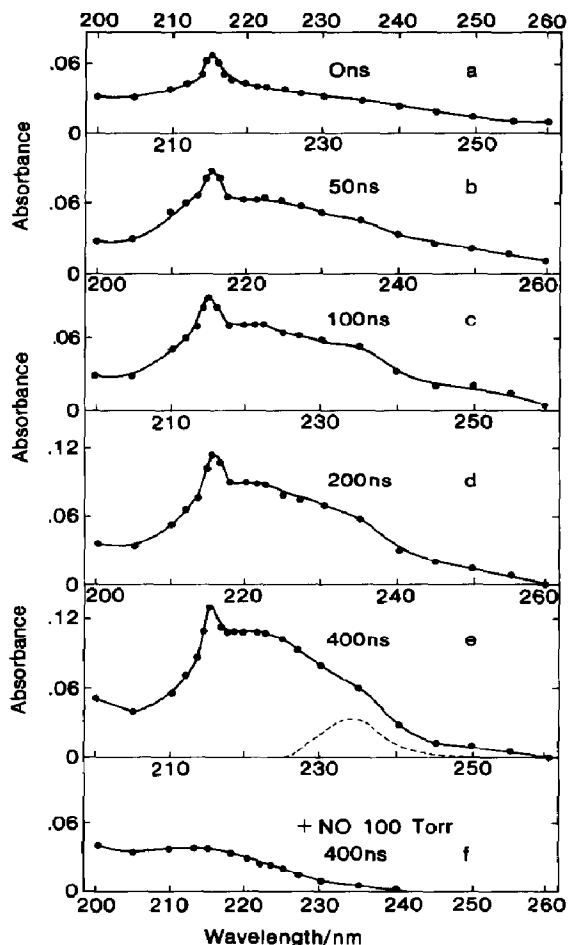
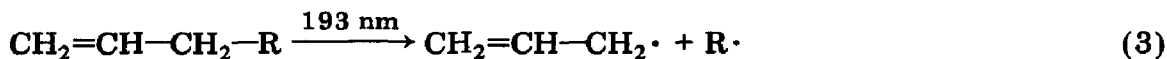


Fig. 1. Time-resolved absorption spectra obtained after excitation of 1-butene (5 Torr) using an ArF excimer laser (193 nm; 8 mJ). The broken line in spectrum e was obtained by subtracting the allyl radical spectrum (Fig. 3) from that at 400 ns. Spectrum f shows the disappearance of radicals when 100 Torr nitric oxide is added as a radical scavenger.

for the allyl radical [11] ($\epsilon_{\max}(223 \text{ nm}) = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and the α -methallyl radical ($\epsilon_{\max}(238 \text{ nm}) = 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [12]. This value is reasonable because the ratio of α -methallyl to allyl is extrapolated to be about 0.1 at 193 nm from previous results, namely 0.46 at 147 nm [2], 0.24 at 174 nm [3], 0.17 at 185 nm [4] and 0.17 upon excitation with light of wavelength longer than 185 nm [8].

3.2. Molecular size dependence of allyl-radical formation

Various 1-alkenes were photolysed using an ArF excimer laser. Time-resolved absorption spectra of propylene are shown in Fig. 3, as an example. All the 1-alkene compounds studied give the same allyl-radical absorption peak at about 220 nm and have dynamical behaviour similar to that of 1-butene. The major process is



where R is H, CH₃, C₂H₅, *n*-C₃H₇, *i*-C₃H₇, *n*-C₄H₉, *n*-C₅H₁₁ or *n*-C₆H₁₃.

We now explain how to estimate the relative yields of allyl radical by nanosecond laser photolysis. At low pressures, the absorption intensity at a fixed wavelength (*e.g.* 223 nm) may not be directly proportional to the concentration of the allyl radical, because higher vibrational temperatures are accompanied by dissociation, as shown in Figs. 1 and 3. In order to

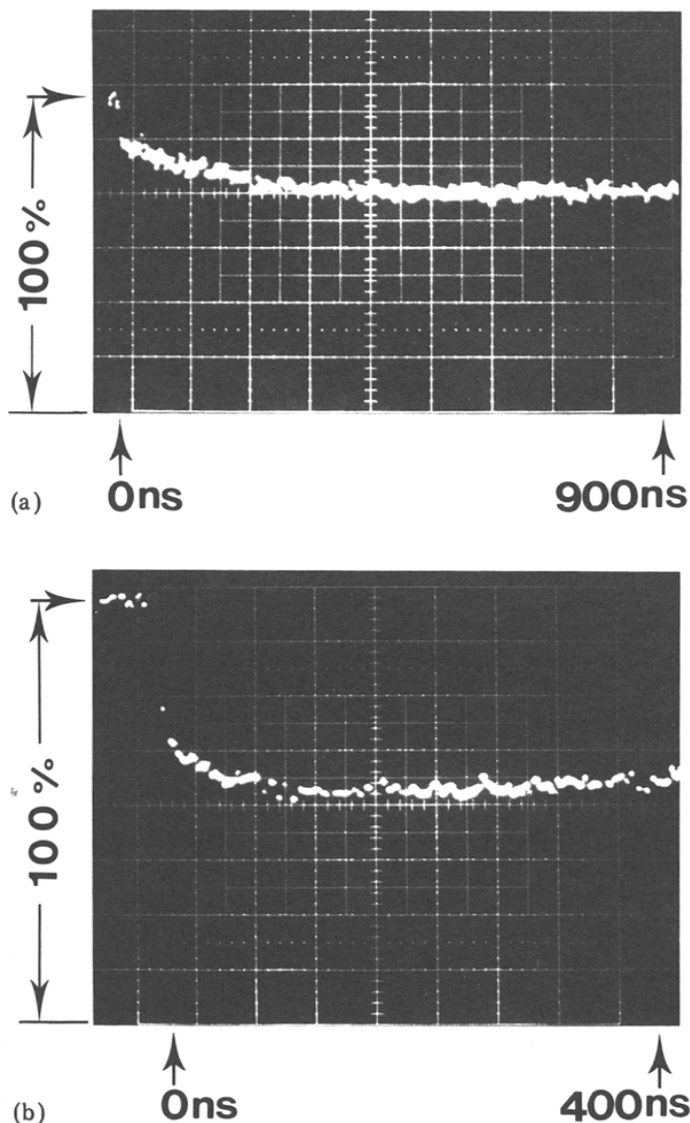


Fig. 2. Time profile of the transient absorption observed at 223 nm after excitation of 1-butene using an ArF excimer laser. (a) 1-Butene (5 Torr): relaxation process of hot allyl radicals, which takes about 1 μ s. (b) 1-Butene (5 Torr) and nitrogen (800 Torr): the hot allyl radicals are relaxed within 200 ns. The decay in (b) is due to recombination processes.

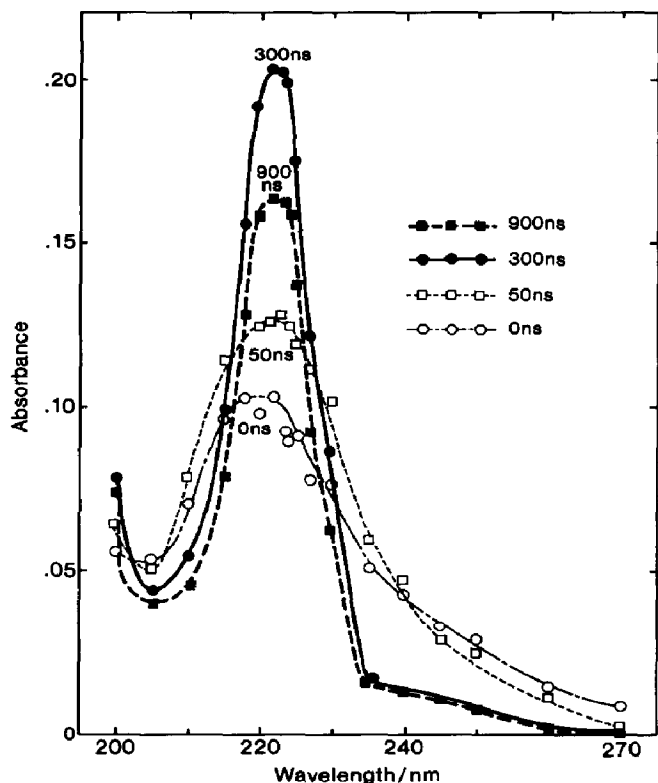


Fig. 3. Transient absorption spectra of allyl radicals obtained after irradiation of propylene (20 Torr) using an ArF excimer laser (15 mJ). The increases in absorbance indicate collisional relaxation processes until about 300 ns, and the decreases indicate that recombination processes take place afterwards.

obtain the relative yield of allyl radical, 800 Torr nitrogen should be added. The allyl radical then relaxes to an equilibrium temperature within a few hundred nanoseconds. The equilibrium temperatures thus reached are sufficiently close to room temperature for the relative yield to be obtained by simply measuring the absorption at the fixed wavelength.

Deviations could be expected because of recombination reactions and/or spectral overlap. These are disregarded because they give only a minor contribution to the spectral intensities, for the following reasons. Firstly, recombination reactions for allyl-allyl and allyl-alkyl radicals reduce the concentration of allyl radical. The recombination rate constant of allyl radicals has been determined to be $1.1 \times 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ ($\epsilon_{\text{max}}(223 \text{ nm}) = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [15]. When the reaction rate for allyl-alkyl radicals is assumed to be the same as that for allyl-allyl radicals, the quantity of allyl radicals remaining after 200 ns is estimated to be 95% of the concentration at $t = 0 \text{ ns}$, for the case of 1-butene. Secondly, the absorption spectra of alkyl radicals overlap with those of allyl radicals, and their intensities depend on the kind of alkyl radicals. However, the molar extinction coefficients are about $500 \text{ M}^{-1} \text{ cm}^{-1}$ [19] which is less than 4% of that of the allyl radical at

223 nm. The actual absorbance is negligibly small in our experiments. The yield of α -alkylallyl radicals resulting from β -C-H dissociation is of the order of 10%, as discussed in Section 3.1; their contribution to the absorbance at 223 nm is estimated to be less than 5%.

The relative formation yields of allyl radical are summarized in Table 1, and they decrease significantly with increasing molecular size in the order $C_3H_6 > 1-C_4H_8 > 1-C_5H_{10} \gg 1-C_6H_{12}$, $4-CH_3-1-C_5H_9$, $1-C_7H_{14} \gg 1-C_8H_{16} > 1-C_9H_{18}$.

TABLE 1

Relative yield of the allyl-radical formation $CH_2=CH-CH_2-R \xrightarrow{193 \text{ nm}} CH_2=CH-CH_2\cdot + R\cdot$

<i>R</i>	<i>Molecule</i>	<i>Pressure</i> ^a (Torr)	<i>Absorbance</i> ^b	<i>Relative yield</i> ^c
H	Propylene	38.0	0.329	1.00
CH ₃	1-Butene	16.2	0.325	0.98
C ₂ H ₅	1-Pentene	12.6	0.301	0.91
<i>n</i> -C ₃ H ₇	1-Hexene	12.4	0.077	0.23
<i>i</i> -C ₃ H ₇	4-Methyl- 1-pentene	11.9	0.074	0.22
<i>n</i> -C ₄ H ₉	1-Heptene	7.6	0.076	0.23
<i>n</i> -C ₅ H ₁₁	1-Octene	8.7	0.031	0.09
<i>n</i> -C ₆ H ₁₃	1-Nonene	7.3 ^d	0.019	0.06
CH ₂ CH=CH ₂	1,5-Hexadiene	4.8	0.577	0.88 (1.75 ^e)
Cl	Allyl chloride	4.5	0.323	0.98
NH ₂	Allylamine	3.4	0.166	0.50
OH	Allyl alcohol	5.9	0.075	0.23

^aThe pressure of each sample was adjusted to an absorbance of 0.3 cm^{-1} at the wavelength (193 nm) of the laser line. Nitrogen was added as a foreign gas (the total pressure was 800 Torr) in order to relax hot radicals within 200 ns.

^bAbsorbance at 223 nm and at 200 ns.

^cNormalized by the propylene absorbance.

^dExtrapolated value because of the low vapour pressure (6 Torr).

^eDissociation of 1,5-hexadiene produces two allyl radicals.

3.3. Dissociation mechanism

The effect of the molecular size on the relative dissociation yield can be reasonably interpreted if alkenes dissociate from hot molecules. This mechanism was originally suggested by Chesick [7] in 1966 on the basis of the pressure dependence of photoproducts in steady state experiments. Recently, we have succeeded in directly measuring the photodissociation rates of the C-C bond at the β position of alkenes by nanosecond laser photolysis [14]. At low pressures, the rate constants for 2,3,3-trimethyl-1-butene (TMB) and 2,3-dimethyl-2-pentene (DMP) were determined to be $4 \times 10^7 \text{ s}^{-1}$ and $2 \times 10^7 \text{ s}^{-1}$ respectively. These rate constants are larger by three orders of magnitude than the rate constant for the fluorescence decay

(about 7 ps) estimated from the oxygen quenching data [20]. This result is also a good indication that the major photodissociation proceeds through hot molecules for the 1-alkenes examined here.

Based on this mechanism, we can explain the pressure dependence of the yield as follows. It is reasonable to assume that in a hot molecule all the absorbed energy is randomized over a large number of internal degrees of freedom immediately after rapid internal conversion. On the basis of statistical rate theory, it takes a long time for a carbon-carbon bond in a large molecule with many vibrational modes to dissociate and to produce an allyl radical. For this reason the dissociation reaction of a large molecule is expected to be quenched more effectively by foreign gases.

Let us examine the possibility of formation of allyl radicals by a predissociation process, which means a pressure-independent process in this paper. Allylic radicals have actually been detected from tetramethylethylene (TME) and DMP via both hot molecules and predissociation [21]. The rate constants of the formation of allylic radicals from S_0^{**} are $1.4 \times 10^7 \text{ s}^{-1}$ for TME and $2.0 \times 10^7 \text{ s}^{-1}$ for DMP. The Stern-Volmer plots reach a plateau at pressures higher than 400 Torr nitrogen. These results indicate that the slow process (via hot molecules) is quenched in the presence of 800 Torr nitrogen. Therefore, the reaction products will be detected only via predissociation in the presence of 800 Torr nitrogen.

On the basis of RRKM theory the rate constants for the reaction from hot molecules can be estimated by the Whitten-Rabinovitch procedure [22] with the semiloose activated complex model I of Dorer and Rabinovitch [23]. The reaction rate constant of 1-hexene is estimated to be about $2 \times 10^8 \text{ s}^{-1}$ and that of 1-heptene is estimated to be about $3 \times 10^7 \text{ s}^{-1}$. These rate constants are presumably reliable to a factor of 3, because the calculated rate constants reproduce our direct observations for the 2-methyl-1-alkene series 2-methyl-1-butene to 2-methyl-1-nonene [21].

In the presence of 800 Torr nitrogen, we found that products via predissociation are only detected from 1-alkenes containing more than seven carbon atoms (1-heptene). The relative yield of 1-hexene (about 20%) probably arises from a contribution of predissociation processes. The RRKM rate constant ($k \approx 6 \times 10^{10} \text{ s}^{-1}$) for 1-butene can still be slower than its decay rate constant from the electronically excited state (S_2). The fluorescence lifetime of 1-butene is much shorter than that of TME (7 ps), because the fluorescence yield of 1-butene is about 3% of that of TME [20]. Therefore the above discussion is applicable to molecules containing as few as four carbon atoms (1-butene).

The relative yield of allyl radicals from 1,5-hexadiene is as high as that for 1-pentene. This finding suggests that the dissociation rate constant of 1,5-hexadiene is comparable with that of 1-pentene. This is reasonable because the dissociation energy of the β carbon-carbon bond of 1,5-hexadiene is 262 kJ mol^{-1} , which is 87% of that of 1-butene [24]. (ΔH_f° for 1,5-hexadiene is estimated to be $84.43 \text{ kJ mol}^{-1}$ and ΔH_f° for the allyl radical is estimated to be $173.2 \text{ kJ mol}^{-1}$.) However, we could not explain the

relatively abrupt decrease in the yields of allyl radicals in going from C_5 to C_6 and from C_7 to C_8 . Direct measurement of the dissociation rate constants will give more detailed information.

3.4. Major reaction paths in the photochemistry of 1-butene

The scheme in Fig. 4 is suggested from the results of nanosecond flash photolysis and product analysis and from the above discussion. 1-Butene excited to the S_2 electronic state ($\pi\pi^*$) at 193 nm is transferred to the hot ground state by rapid internal conversion. This hot 1-butene molecule self-dissociates to a hot allyl radical and a hot methyl radical. These hot radicals are deactivated to the relaxed state by collisional relaxation and recombine to give the final products, namely ethane, 1,5-hexadiene and 1-butene.

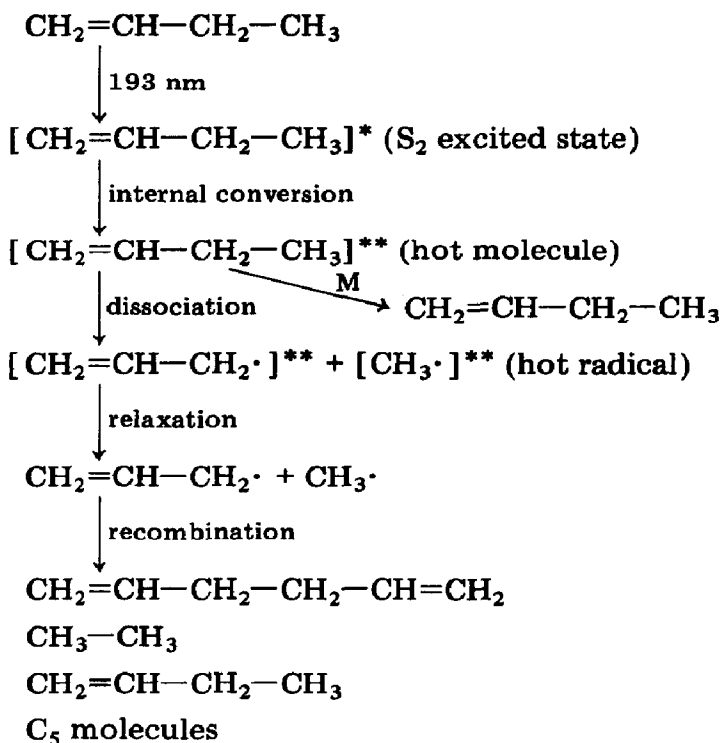


Fig. 4. Possible reaction paths of the 1-butene photolysis for excitation at 193 nm.

After irradiating the sample containing 5 Torr 1-butene with several photolysis shots, many products were detected by gas chromatography. The important photoproducts were ethane, ethylene, propylene, 1,5-hexadiene and a few C_5 compounds. These products have been detected in conventional photolysis experiments [1 - 5].

The effects of added gases support the hot molecule mechanism. The yields of the products are suppressed by 200 Torr nitrogen to about 50% of those in the absence of nitrogen. Nitric oxide is known as a radical scavenger. Addition of 50 Torr nitric oxide markedly decreases the yields of ethane, C_5

compounds and 1,5-hexadiene to 10% of those in the absence of nitric oxide. Therefore these products are presumably formed via radical species.

Ethylene and propylene are not affected by nitric oxide and their mechanism of formation is not very clear at the present stage. Propylene molecules may be formed from a hot state by a molecular dissociation process, because the yield is decreased by nitrogen. The yield of ethylene is unchanged on adding nitrogen. Therefore, it is suggested that ethylene is formed neither via hot molecules nor via radicals, but by direct molecular fragmentation.

3.5. Olefins with Cl, NH₂ or OH substituents

As shown in Table 1, a clear substituent effect is observed (Cl > NH₂ > OH). It is reasonable that allyl chloride is most easily dissociated, since the dissociation energy of the C—Cl bond is much smaller than the dissociation energies of C—N and C—O. The dissociation mechanisms of these three compounds may not be the same as the mechanism discussed above, because the characters of their excited states are different from those of other alkenes. Direct dissociation probably contributes to the dissociation of allyl chloride.

4. Conclusions

On the basis of the following two observations, it is strongly suggested that the major dissociation process of 1-alkenes is via hot molecules. (a) In the presence of 800 Torr nitrogen, the relative yields of allyl-radical formation decrease as the size of the 1-alkene molecule becomes larger. (b) The yields of the dissociation products (e.g. 1,5-hexadiene) decrease upon increasing the pressure of a foreign gas.

Acknowledgments

We thank Professor N. Nishi and Mr. T. Okuyama for lending us their gas chromatograph.

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