

# Oscillator Strengths of the Ultraviolet Bands of Hot and Relaxed Methallyl, Allyl, and Methyl Radicals

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Absorption spectra of methallyl, allyl, and methyl radicals were measured in the ArF laser flash photolysis of halogenated methanes and olefins, and 2-methyl-1-butene. Broad absorption spectra were detected immediately after excitation, indicating that the radicals carried high internal energy (called “hot” radicals here). The spectra were sharpened with time due to collisions with foreign gases and finally reached equilibrium (spectra in relaxed states). The oscillator strengths ( $f$ ) of methallyl and allyl radicals were found to remain about the same for hot and relaxed states. The values ( $f$ ) in the relaxed states were determined with errors of  $\pm 10\%$  to be 0.14 for the methallyl radical, 0.26 for the allyl radical, and  $1.57 \times 10^{-2}$  (including the partition function) for the methyl radical. The molar extinction coefficients of the allylic radicals were 1.4–1.8 times as great as ones previously reported. Rate constants of collisional relaxation by nitrogen were discussed for seven hot radicals and molecules. Larger species gave greater rate constants. The hot methyl radical relaxed with a rate constant of  $1.0 \times 10^7 \text{ s}^{-1}$  in the presence of 760 Torr of nitrogen, while for the trimethylallyl radical it was 20 times as great as that of the methyl radical.

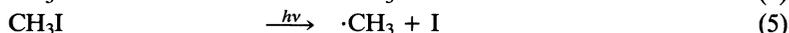
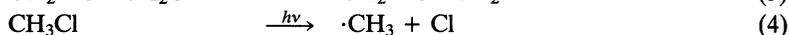
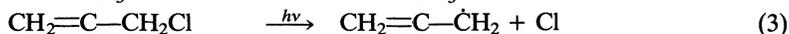
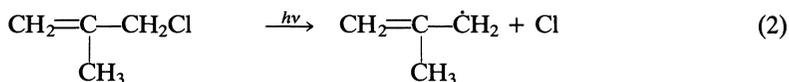
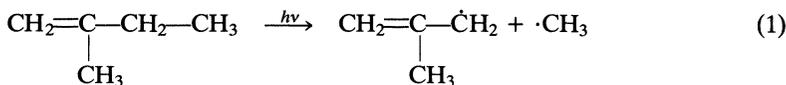
**KEY WORDS:** Oscillator strength; absorption spectrum; methyl radical; methallyl radical; allyl radical; flash photolysis; hot radical.

## INTRODUCTION

Radicals immediately after photodissociation are in highly excited vibrational and rotational states (called “hot” radicals). The hot radicals are collisionally cooled by foreign gases and finally reach equilibrium states (called “relaxed” radicals). The ultraviolet (UV) absorption spectra and molar extinction coefficients of allylic and

methyl radicals have been extensively studied, but most of the work has been concerned with the relaxed states<sup>1-17</sup>. Hot methyl radicals have been investigated in detail on absorption spectra and by collisional dynamics<sup>1,4,6,10,11</sup>. Absorption spectra of hot benzyl and allyl radicals are also studied<sup>18-21</sup>. However, detailed spectroscopic information on large radicals with high internal energy has been limited.

In order to obtain qualitative data concerning hot radicals the following five molecules have been photolysed by an ArF laser in this paper:



Absorption spectra, their molar extinction coefficients, and the rate constants of collisional relaxation of hot radicals have been determined. Allylic radicals were produced by photolysis as shown in Eqns (1), (2), and (3). The absorption spectra of hot radicals are markedly different from those of the relaxed ones. Nevertheless, the oscillator strength is found to remain about the same.

The absorption spectrum of the  ${}^2A'_1 \leftarrow {}^2A''_2$  transition of a methyl radical has been measured and analyzed by Herzberg<sup>1</sup> and Callear and Metcalfe<sup>4</sup>. Many independent studies have been published on the extinction coefficient and the oscillator strength of the UV band<sup>2-10</sup>. The methyl radical can be a good reference for other transient species. These values have been confirmed by photolysing halomethanes in Eqns (4) and (5). We have found that the molar extinction coefficient of the relaxed methyl radical at the peak depends slightly on foreign gases. Although this is a minor effect, it is important when we use the extinction coefficient as a standard.

The rate constants associated with collisional relaxation have been measured for five hot radicals. The rate constants are derived from

overall apparent relaxation. For large radicals, present data are useful for discussing the mechanism of the collisional energy transfer of hot species.

## EXPERIMENTAL

The irradiation light source was an ArF laser (193.2 nm with the FWHM of 0.6 nm, Lambda Physik EMG 500 or EMG 101). The typical pulse width was measured to be 13 ns (FWHM). Olefins with pressures of 0.3–5 Torr were irradiated in an area of  $0.5 \times 3.7 \text{ cm}^2$ . The irradiation energy was 4–10 mJ/cm<sup>2</sup> after correcting absorption and refraction losses of the cell window. Delay times were measured from the end of the laser pulse, i.e. 0 ns was defined as the end of the pulse.

The spectral resolution ( $\Delta\lambda$ ) was 0.4 nm (FWHM) for methyl radical in Figures 1, 2, 4, and 5, and 0.6 nm in Figure 3. Stray light was negligible (<1%) with regard to all wavelengths studied in this paper. The other details have been described elsewhere<sup>22</sup>.

All experiments by the laser photolysis were carried out at room temperature (291–297 K); however, a temperature of 295 K was adopted for calculation of collision times. For each point in time-resolved spectra and for rate constants of collisional relaxation an average of 2–10 sets of data was taken.

Laser energy was measured by using transient absorbance of benzene. Hot benzene is formed immediately after irradiation with the ArF laser light. The lifetime is long enough (longer than 500 ns for pressures of less than 2 Torr) to measure accurately its absorbance at  $t = 0$  ns. The molar extinction coefficient at 230 nm and at  $t = 0$  ns has been determined to be  $3500 \text{ M}^{-1}\text{cm}^{-1}$ <sup>22</sup>. N<sub>2</sub>O actinometry was used to calibrate a Gentec ED 500 power meter. Therefore, molar extinction coefficients of photoproducts could be determined, if the yields were known. The accuracy of the absolute value was estimated to be  $\pm 10\%$  in a single  $\sigma$  by repeated experiments.

Absorption spectra of olefins in the ground state were measured by a Cary 2300 spectrophotometer with a spectral resolution of 0.4 nm. The molar extinction coefficients of the laser light were also confirmed by measuring transmittance of the laser light. They are shown in the units  $\text{M}^{-1}\text{cm}^{-1}$  as follows: methyl chloride, 18.9; methyl iodide, 460; 2-methyl-1-butene, 5930; 1-chloro-2-methyl-2-pentene, 4070; allyl

chloride, 1400; benzene, 4920 with errors of  $\pm 2\%$ . The molar extinction coefficients for the  ${}^1B_{1u} \leftarrow {}^1A_{1g}$  transition of benzene at the peak (200.3 nm) is  $6600 \text{ M}^{-1}\text{cm}^{-1}$ .

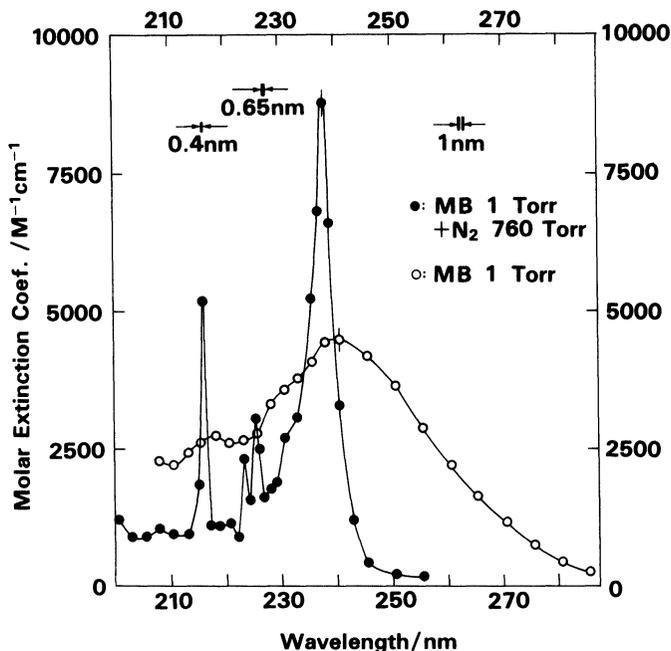
Chemicals (benzene, nitrogen, propane, nitrous oxide, and oxygen) were of the same qualities as those described previously<sup>22</sup>. The following chemicals (with a stated purity and source) were distilled trap to trap: allyl chloride (>98%, Tokyo Kasei), 2-methyl-1-butene (>99%, Tokyo Kasei), methyl iodide (>98%, Kanto Kagaku), and 1-chloro-2-methyl-2-propene (>98%, Tokyo Kasei). Methyl chloride (>99.5%, Takachiho Kagaku Kogyo) was used without further purification.

## RESULTS

### Methallyl radical

This radical was generated by photolysis of 2-methyl-1-butene (MB) and 1-chloro-2-methyl-2-propene (CMP). Both molecules were used for observing the UV absorption spectrum of methallyl radical by Callear and Lee<sup>12</sup>. We will show that the oscillator strength remains about the same for hot and relaxed radicals by assuming the dissociation yield at the  $\beta$  position to be 0.9 (*see below*) under a low pressure.

The absorption spectrum of the hot radical is shown in Figure 1 as open circles. This spectrum is obtained by photolysing 1 Torr of MB and by observing the transients at 10 ns. Secondary decomposition has presumably not occurred at this short delay time. The absorption spectrum due to methyl radical is broad and very weak. The weak intensity suggests that only several per cent of methyl radicals populate the lowest vibrational states (*see under Discussion*). Hot radicals are collisionally relaxed in the presence of 760 Torr of nitrogen and the absorption spectra are sharpened. The spectrum reaches an equilibrated (relaxed) state after 60 ns. Just a small percentage of the absorbance at 60 ns decayed in the next 300 ns due to slow recombination reactions. The peaks in the relaxed spectrum are in good agreement with those measured by microsecond flash photolysis<sup>13</sup>. The strongest peak appears at 238 nm and the smaller peaks are seen at 225 and 223 nm. The peak at 216.4 nm is due to the  ${}^2A'_1 \leftarrow {}^2A'_2$  transition of methyl radical<sup>1</sup>. Table I shows the molar extinction coefficients at the peaks and the apparent oscillator strengths ( $\phi_{\text{MA}} \times f_{\text{obs}}$ ), where  $\phi_{\text{MA}}$  is the formation yield of the methallyl radical.



**Figure 1** Absorption spectra of hot ( $\circ$ ) and relaxed ( $\bullet$ ) methallyl radical. ( $\circ$ ) Obtained at 10 ns after excitation of 1 Torr of 2-methyl-1-butene (MB); ( $\bullet$ ) at 60 ns delay time for 1 Torr of MB in the presence of 760 Torr nitrogen. Molar extinction coefficients are evaluated by assuming that the formation yield of the radical is unity. The spectral resolution is 0.4 ~ 1 nm as indicated. Error bar corresponds to a single  $\sigma$ .

**Table I** Molar extinction coefficients and the oscillator strength  $f$  of the UV transition of methallyl radical.

$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{CH}\dot{\text{C}}\text{H}_2 \end{array}$	$\phi_{\text{MA}} \times \varepsilon_{\text{max}} /$ ( $\text{M}^{-1}\text{cm}^{-1}$ ) ( $\lambda_{\text{max}}/\text{nm}$ )	$\phi_{\text{MA}} \times f^{\text{a}}$	$\phi_{\text{MA}}$	$\varepsilon_{\text{max}}(\text{M}^{-1}$ $\text{cm}^{-1})$	$f$
Hot <sup>b</sup>	4650 (240)	0.13(45.2 ~ 34)	0.9 <sup>c</sup>	5170	0.14
Relaxed <sup>d</sup>	9000 (237.5)	0.064 (46 ~ 39)	0.46 <sup>e</sup>	19500	0.14

<sup>a</sup> Integration wavenumber range ( $/10^3\text{cm}^{-1}$ ).

<sup>b</sup> Observed at 10 ns by photolysis of 2-methyl-1-butene (MB) 1 Torr.

<sup>c</sup> Formation yield of methallyl radical under a low pressure ( $\phi_{\text{MA}}$ , see text).

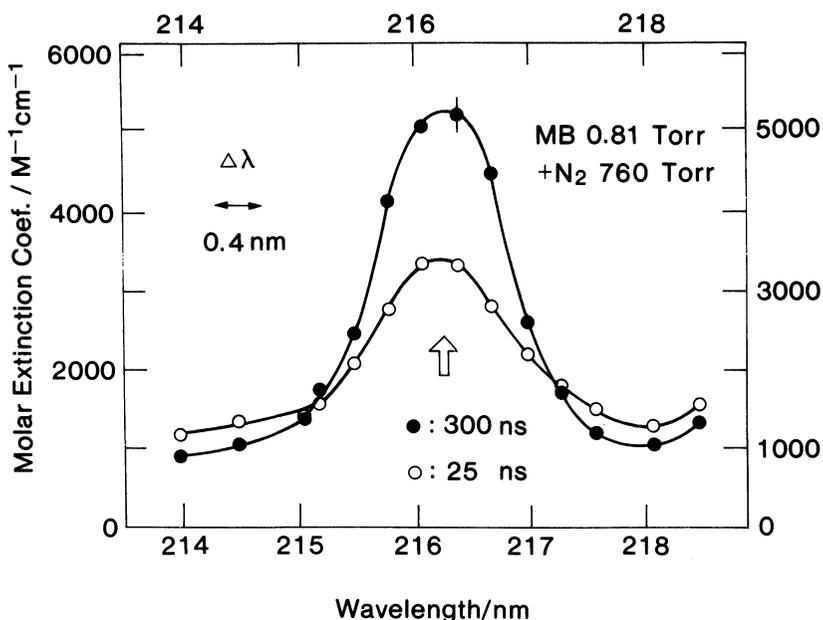
<sup>d</sup> Observed at 60 ns by photolysis of 1 Torr of MB in the presence of 760 Torr nitrogen.

<sup>e</sup>  $\phi_{\text{obs}}^{\text{h}}(\text{CH}_3) = 0.46$  ( $\phi_{\text{MA}}^{\text{h}}$ , see text).

Collin *et al.* have determined the dissociation yield to be 0.9 for MB at the C—C bond of the  $\beta$  position to the double bond. MB was irradiated at 147, 163, 174, and recently 185 nm<sup>23,24</sup>. On irradiation with vacuum ultraviolet (VUV) light at a longer wavelength, yields of minor reactions decrease, minor processes being  $\alpha$ (C—C) and  $\beta$ (C—H) dissociation. Bayrakceken *et al.* have shown that the dissociation ratio of the radical mechanism is  $\beta$ (C—C) :  $\beta$ (C—H) :  $\alpha$ (C—C) = 13 : 1.37 : 1 by microsecond flash photolysis on irradiation with light in the wavelength range of 170–200 nm<sup>16</sup>. The ArF laser light is of long wavelength compared with those used in previous work. Therefore, the formation yield of methallyl radical can be assumed to be the highest, namely, 0.9( $\phi_{MA}^l$ ) under a low pressure (the superscript “l” means low pressure). This yield of 0.9 enables us to evaluate the molar extinction coefficients and the oscillator strength at a low pressure.

It is of interest to measure the yield of methyl radical, because it is expected to be nearly equal to that of methallyl radical. Figure 2 shows spectra of methyl radical in an expanded scale in the presence of 760 Torr of nitrogen. It requires 250 ns to reach a constant level of absorbance at 216.4 nm. The relaxation time of the hot methyl radical is about five times slower than that of the hot methallyl radical. In order to avoid the bimolecular reactions between methyl radicals as well as with methallyl radical, the molar extinction coefficient of the peak is obtained by extrapolation to zero laser power. The band width (FWHM) is 1.36 nm with 0.4 nm spectral resolution. These relaxation times and FWHM are almost the same as those in the case of CH<sub>3</sub>I photolysis (250 ns and 1.3 nm, *see below*). The background of the spectra decays due to collisional cooling of the hot methallyl radical. The molar extinction coefficient of the methyl radical in Figure 2 [ $\phi_{obs}^h(CH_3) \times \epsilon_{max}(CH_3)$ ] is 4250 M<sup>-1</sup>cm<sup>-1</sup> obtained by subtracting the background. The yield under high pressure [ $\phi_{obs}^h(CH_3)$ ] is evaluated to be 0.46 on the basis of the molar extinction coefficient of the methyl radical (9250 M<sup>-1</sup>cm<sup>-1</sup>) obtained from CH<sub>3</sub>I photolysis (*see below*). This value should be almost equal to  $\phi_{MA}^h$ , which is the formation yield of methallyl radical under high pressure. The oscillator strength and the molar extinction coefficients in the presence of 760 Torr nitrogen are evaluated as in Table I using this yield.

The methyl radical is formed by two pathways. The major one is the  $\beta$ (C—C) bond dissociation and the minor one is the  $\alpha$ (C—C) bond dissociation. The value obtained,  $\phi_{MA}^h$ , includes both the processes of



**Figure 2** Time resolved absorption spectra in the wavelength region of the  ${}^2A_2 \leftarrow {}^2A_2'$  transition of the methyl radical. Delay times after an excitation pulse are 25 ns ( $\circ$ ) and 300 ns ( $\bullet$ ) for 0.81 Torr 2-methyl-1-butene in the presence of 760 Torr nitrogen. The spectral resolution is 0.4 nm. Molar extinction coefficients are evaluated on the assumption that the formation yield of the radical is unity.

$\beta(\text{C}-\text{C})$  and  $\beta(\text{C}-\text{H})$  dissociation, because 2-methylallyl, 2-ethylallyl and, presumably, dimethyl allyl radicals show very similar spectra<sup>13</sup>. Fortunately, the yields of  $\alpha(\text{C}-\text{C})$  and  $\beta(\text{C}-\text{H})$  bond dissociation are similar and both of the minor processes are only a small percentage of the  $\beta(\text{C}-\text{C})$  dissociation process<sup>16,23,24</sup>. Therefore, the estimated yield of  $\phi_{\text{MA}}^{\text{h}}$ , which is measured by transient absorption, can be regarded as the same value as that of methyl radical [ $\phi_{\text{obs}}^{\text{h}}(\text{CH}_3)$ ] with a good approximation.

We applied the second method to estimate  $\phi_{\text{MA}}^{\text{h}}$  as follows: in the photolysis of 1-chloro-2-methyl-2-propene (CMP), the weakest  $\beta(\text{C}-\text{Cl})$  bond will dissociate with high yield. Callear and Lee have described this as the best source of methylallyl radical<sup>13</sup>. Assuming that the dissociation yield is unity, the  $\phi_{\text{MA}}^{\text{h}}$  of MB in the presence of 760

Torr of nitrogen is 0.42 by comparing the absorption intensities of methallyl radicals of both systems.

Table II lists three values of  $\phi_{MA}^h$  determined by three different methods. The third one is evaluated on the assumption of invariability of the  $f$  value under the two pressures. The formation yield of methallyl radical ( $\phi_{MA}^h$ ) at high pressure is:

$$\begin{aligned}\phi_{MA}^h &= \phi_{MA}^l \times (\phi_{MA}^h \times f_{MA}^h) / (\phi_{MA}^l \times f_{MA}^l) \\ &= 0.9 \times 0.064 / 0.13 = 0.44\end{aligned}\quad (6)$$

where  $f_{MA}^h$  is the oscillator strength of methallyl radical in the presence of 760 Torr of nitrogen,  $f_{MA}^l$  is the oscillator strength at 1 Torr of MB. The values of  $\phi_{MA}^h \times f_{MA}^h$  and  $\phi_{MA}^l \times f_{MA}^l$  are obtained by integrating the observed spectrum at each pressure.

**Table II** Yields of radicals formed by photolysis of 2-methyl-1-butene (MB) in the presence of 760 Torr nitrogen obtained by three methods.

Radical	Yield	Method of evaluation
Methyl	0.46	$\epsilon_{\text{obs}}(\text{CH}_3) / \epsilon_{\text{max}}(\text{CH}_3)$ = 4250/9250 (FWHM = 1.36 nm)
Methallyl	0.42	$\epsilon_{\text{obs}}(\text{MB}) / \epsilon_{\text{obs}}(\text{CMP})$
Methallyl	0.44	Eqn (6)

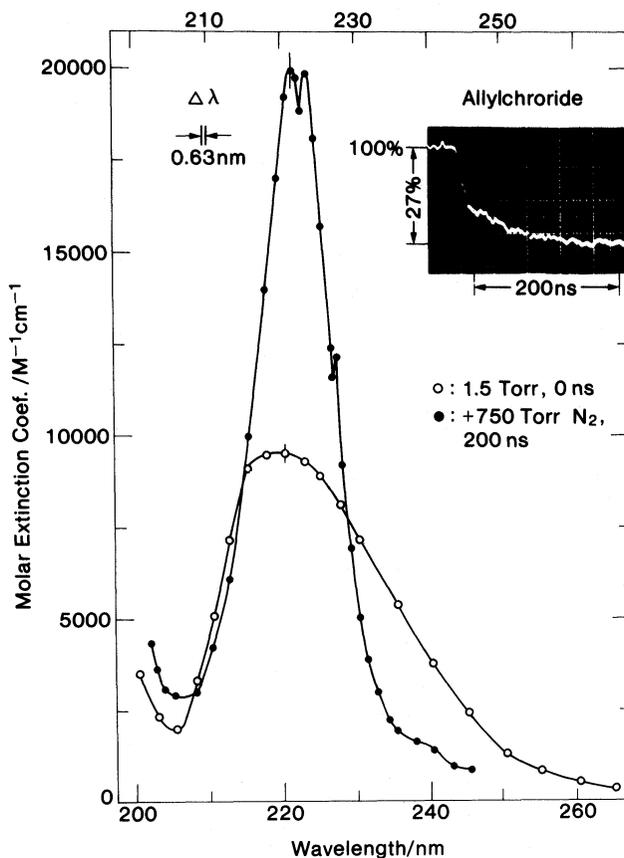
<sup>a</sup> Ratio of molar extinction coefficients at the peak of methallyl radical formed by photolysis of MB and 1-chloro-2-methyl-2-propene (CMP).

The three values obtained in Table II are in good agreement with each other. These findings clearly indicate the following two conclusions:

- (1) The yield of the  $\beta(\text{C}-\text{C})$  bond dissociation is 0.9 under a low pressure, whereas, the yield is reduced to about one-half by adding 760 Torr of nitrogen.
- (2) Although a drastic spectral change is seen between hot and relaxed spectra, the oscillator strength remains unchanged.

### Allyl radical

This radical was obtained by photolysing allyl chloride. Figure 3 shows the absorption spectra of the hot and relaxed allyl radicals. The hot



**Figure 3** Absorption spectra of hot ( $\circ$ ) and relaxed ( $\bullet$ ) allyl radical. ( $\circ$ ) Obtained at 0 ns after excitation of 1.5 Torr allyl chloride; ( $\bullet$ ) at 200 ns delay time for 1.5 or 3.1 Torr allyl chloride in the presence of 760 Torr of nitrogen. Molar extinction coefficients are evaluated on the assumption of the formation yield of unity. The spectral resolution is better than 1 nm. Error bar corresponds to a single  $\sigma$ . The inserted oscillogram is obtained by photolysis of 1.5 Torr allyl chloride in the presence of 760 Torr nitrogen observed at 221.5 nm. The rise curve indicates collisional relaxation by nitrogen.

radical has a peak around 219–220 nm. In the presence of 760 Torr of nitrogen, it takes 200 ns to reach the relaxed spectrum as shown in the inserted oscillogram. This spectrum has a peak around 223 nm and is essentially the same as that found in the literature<sup>12,13</sup>. The absorption peak has been assigned to the Rydberg transition of the

$(b_1)^2(2b_1)^1 2^2B_1 \leftarrow (b_1)^2(a_2)^1 2A_2$ . The direction of the spectral shift is unusual, since a hot spectrum usually shifts to the shorter wavelengths by collisional relaxation. A similar opposite shift (10 nm) has been seen in an Ar matrix, where the absorption peak appears at 213 nm<sup>17</sup>.

The dissociation yield of allyl chloride can be regarded as unity in the presence or absence of the foreign gas nitrogen. Sears and Volman have studied the photochemistry of allyl chloride<sup>25</sup>. They concluded that the assumption of a quantum yield of unity for the dissociation of the C—Cl bond has led to a reasonable account for the product distributions.

We can compare the  $f$  values of the hot and relaxed spectra. They are 0.24 for the hot radical and 0.26 for the relaxed one. The  $f$  value remains about the same as seen for the case of methallyl radical in the previous section.

### Methyl radical

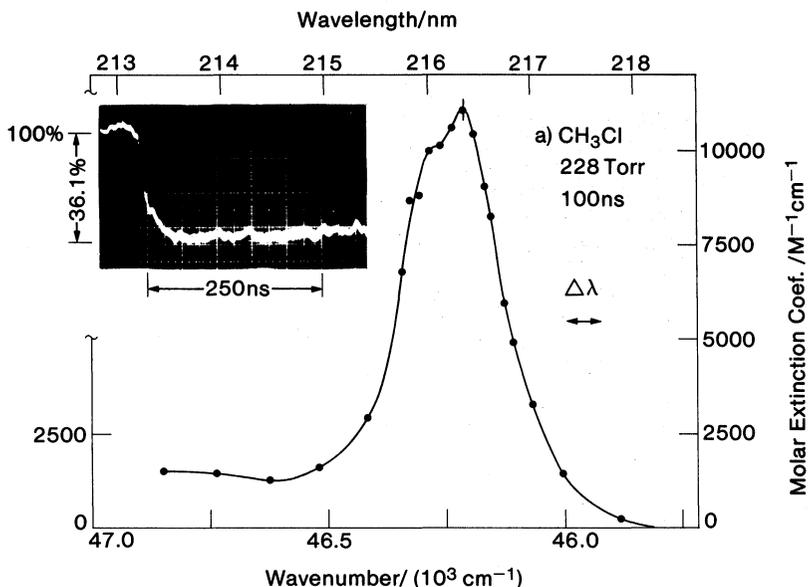
The absorption spectrum of the  $2A_1' \leftarrow 2A_2''$  transition was detected by photolysis showing Eqns (1) and (2) and in Figures 4 and 5. They are in good agreement with those in the literature<sup>1-7</sup>. Because of low spectral resolution (0.4 nm),  $R(215.76 \text{ nm})$  and  $(Q + P)$  (216.36 nm) were not fully separated in the relaxed spectra (at 100 ns in Eqn (1) and 250 ns in Eqn (2)). Transient absorbance obeyed Lambert-Beer's law up to absorbance of 0.15 for our band-pass (0.4 nm) at the central wavelength.

Molar extinction coefficients are determined on the basis of the dissociation yield of unity as being dealt with in the Discussion. The coefficients at the peak are  $1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{CH}_3\text{Cl}$  system and  $0.94 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{CH}_3\text{I}$  system. They are in good agreement with those in the literature (*see* Table IV). However, the bandwidth (FWHM) varies from a system to the other, i.e. 1.15 nm for the  $\text{CH}_3\text{Cl}$  and 1.3 nm for the  $\text{CH}_3\text{I}$  system in this paper.

The oscillator strength is obtained by integrating the relaxed spectra in Figure 1.

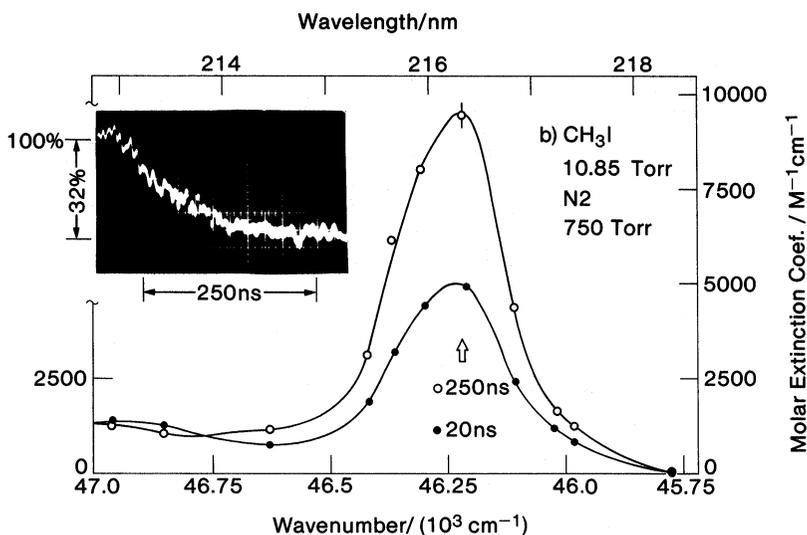
$$f_{00} = Q \times 4.32 \times 10^{-9} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \epsilon(\tilde{\nu}) d\tilde{\nu} = (1.57 \pm 0.16) \times 10^{-2}$$

where  $\tilde{\nu}_1 = 46\,000 \text{ cm}^{-1}$ ,  $\tilde{\nu}_2 = 45\,750 \text{ cm}^{-1}$ .  $Q$  is the partition function and is 1.11 at 298 K.



**Figure 4** Absorption spectrum of methyl radical formed by 193-nm photolysis of 228 Torr methyl chloride. Observed at 100-ns delay time with spectral resolution of 0.4 nm. The inserted oscillogram was obtained at 216.4 nm. The rise and decay curve is caused by fast collisional relaxation and slow radical recombination processes. An error bar at the peak indicates a single  $\sigma$  obtained by several measurements.

Four  $f$  values and two spectra with the molar extinction coefficients have been reported since the pioneering work by van den Berg *et al.*<sup>2</sup> as listed in Table IV. They did not presumably take into account the partition function for two old values ( $1.02 \times 10^{-2}$ ,  $1.0 \times 10^{-2}$ )<sup>3,4</sup>. It may not be easy to compare with the results by Glänzer *et al.*<sup>6</sup>, because they obtained them at a high temperature of 1400 K. Parks *et al.*<sup>5</sup> and Adachi *et al.*<sup>7</sup>, reported spectra and molar absorption coefficients. We can obtain two  $f$  values by integrating their spectra. The present oscillator strength can be compared with three other values:  $1.37 \times 10^{-24}$ ,  $1.75 \times 10^{-2}$  (from Parks *et al.*)<sup>5</sup>, and  $1.5 \times 10^{-2}$  (from Adachi *et al.*)<sup>7</sup>. All the integrated values ( $f_{00}$ ) are in agreement within the stated errors. Recently, Macpherson *et al.* have accurately determined the molar extinction coefficient by ArF laser flash photolysis<sup>10</sup>. This is practically the same as our value.



**Figure 5** Time-resolved absorption spectra obtained by photolysis of 10.85 Torr methyl iodide in the presence of 750 Torr nitrogen at delay time of 20 ns (●) and 250 ns (○). The rise curve in the inserted oscillogram shows collisional relaxation of hot methyl radical.

## DISCUSSION

### Invariability and comparison of $f$ values

The oscillator strength of allylic radicals was found to be essentially the same for hot and relaxed radicals in spite of the large difference in their spectra. The  $f$  value is calculated by the following equation;

$$f = 4.32 \times 10^{-9} \int_0^{\infty} \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (7)$$

On the other hand, Eqn (8) holds, if the electronic transition moment is the same from each vibrational level in the ground electronic state<sup>26-28</sup>.

$$\int \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} = \text{const.} \quad (8)$$

The factor  $1/\tilde{\nu}$  can be taken out from the integral in Eqn (8), because it only has a small effect on the integral. Tables I and III indicate that the  $f$  values of the relaxed spectra remain about the same between the hot

**Table III** Molar extinction coefficients and the oscillator strength of the  $2^2B_1 \leftarrow 2^2A_2$  transition of allyl radical.

$\text{CH}_2\dot{\text{C}}\text{HCH}_2$	$\epsilon_{\text{max}}(\text{M}^{-1}\text{cm}^{-1})(\lambda_{\text{max}})$	Bandwidth ( $\text{cm}^{-1}$ )	$f_{\text{obs}}^{\text{a}}$
Hot <sup>a</sup>	9500 (220)	5400	0.24
Relaxed <sup>c</sup>	20200 (223)	2400	0.26
(d)	15000 (223)	2750	0.14

<sup>a</sup> Integration range  $\tilde{\nu} \geq 48600 \text{ cm}^{-1}$ .

<sup>b</sup> Observed at 0 ns by photolysis of 1.5 Torr of allylchloride.

<sup>c</sup> Obtained at 200 ns by photolysis of 1.5 and 3.1 Torr of allyl chloride in the presence of 760 Torr of nitrogen.

<sup>d</sup> Photolysis of 1-butene in the presence of 400 Torr nitrogen<sup>15</sup>.

and relaxed spectra. Therefore, the electronic transition moment from each vibrational level is about the same.

This finding for  $f$  values can be applied to estimate concentrations of hot radicals. Although molar extinction coefficients vary by 2–4 times when pressures of foreign gases are changed from 0 to 760 Torr, the integration of spectra allows us to determine concentrations. Then we can make Stern–Volmer plots of the primary radical concentration *versus* the pressure of added gases in the nanosecond laser photolysis of olefins<sup>29</sup>.

**Table IV** Molar extinction coefficients ( $\lambda_{\text{max}}$ ) of methyl radical for the electronic transition of the  $2^2A'_1 \leftarrow 2^2A''_2$  and the oscillator strength ( $f$ ) of the 0–0 band.

$\epsilon_{\text{max}}(10^4 \text{ M}^{-1}\text{cm}^{-1})$	$\lambda(\text{nm})^{\text{a}}$	$f_{00}(b)^{\text{c}}(\times 10^{-2})$	Ref. (Method)
1.02	b	$1.2 \pm 0.2^{\text{d}}$	2 (FP)
$1.02 \pm 0.06$	b	$1.0^{\text{d}}$	3 (FP)
$0.96 \pm 0.11$	b	$1.37 \pm 0.15$	4 (FP)
$0.84 \pm 0.16$	0.6	$1.75^{\text{e}}$	5 (FP)
$0.18 \pm 0.06$ (1400 K)	1.6	1.6	6 (ST)
$0.95 \pm 0.04$	0.06	$1.5^{\text{e}}$	7 (FP)
$1.10 \pm 0.1$	0.4	$1.57 \pm 0.15$	this work (LFP)
$1.01 \pm 0.070$	b	f	8 (FP)
$0.90 \pm 0.08$	0.4, 0.6	f	9 (FP)
$1.08 \pm 0.029^{\text{g}}$	0.6	f	10 (LFP)

<sup>a</sup> Spectral resolution.

<sup>b</sup> Photographic method with high resolution (about 0.1 nm ?).

<sup>c</sup> Taking into account the partition function except for where marked d.

<sup>e</sup> Integration of their spectra by us.

<sup>f</sup> No spectrum was given.

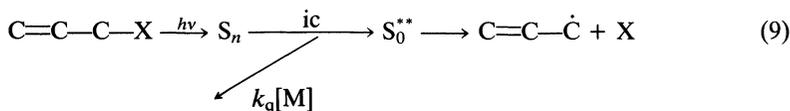
<sup>g</sup> Error  $2\sigma$ .

LFP, laser flash photolysis; FP, microsecond flash photolysis; MS, modulation spectrometry; ST, shock tube experiments.

The present  $f$  values, as well as the molar extinction coefficients of allylic radicals are 1.4–1.8 times as great as those obtained by van den Bergh *et al.*<sup>15</sup> and Bayrakceken *et al.*<sup>16</sup> These differences may be caused by secondary decomposition of methallyl radical on irradiation with a pulse of long duration and observation at a long delay time. They studied MB by microsecond flash photolysis and discussed molar extinction coefficients on the basis of the ratio of absorbance of the methyl relative to that of the methallyl radical. Callear *et al.* obtained the ratio of 2 : 1 by using an excitation pulse of 30  $\mu\text{s}$  and described it as abnormally low<sup>13</sup>. Bayrakceken *et al.* obtained the high ratio of 1 : 1.3 with a pulse duration of 10  $\mu\text{s}$  and evaluated the molar extinction coefficient of methallyl radical to be 13 200  $\text{M}^{-1}\text{cm}^{-1}$ . Our result is 1 : 2 with a 10-ns pulse. Therefore, the molar extinction coefficients of methallyl radical should be much higher than those by Bayrakceken *et al.*, when it is determined on the basis of the methyl radical.

In the case of the allyl radical, the present value of 20 200  $\text{M}^{-1}\text{cm}^{-1}$  is 30% higher than that in the literature<sup>15</sup>, which has also been determined on the basis of the molar extinction coefficient of the methyl radical. A bandwidth (FWHM) of 2750  $\text{cm}^{-1}$  is wider than the present value (2400  $\text{cm}^{-1}$ ). These differences imply that the system had not been equilibrated and/or was at a high temperature. The methyl radical was in a hot and/or non-equilibrated state. The molar extinction coefficients of the hot methyl radical should be smaller than those at room temperature. Tulloch *et al.* have measured the bimolecular rate constant of allyl radical by ArF laser flash photolysis and suggested that the molar absorption coefficients in the literature were too small<sup>30</sup>.

At a pressure of 760 Torr nitrogen, the yield of methallyl radical is reduced to about one-half. This decrease is qualitatively expected on the basis of the dissociation mechanism of olefin. Olefin dissociates from hot ground state after internal conversion<sup>29,31</sup>. As indicated in Eqn (9), the reaction intermediate is  $S_0^{**}$ . The RRKM reaction rate constant for 2-methyl-1-butene can be estimated as 1.4  $\text{ns}^{-1}$  at a dissociation energy of 73 kcal/mol<sup>32</sup>. The collision occurs with nitrogen once in 0.081 ns.

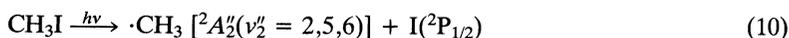


The dissociation reaction will compete with collisional deactivation of  $S_0^{**}$  by nitrogen.

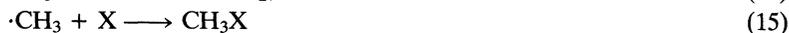
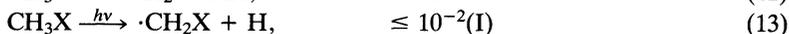
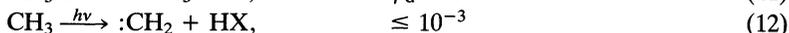
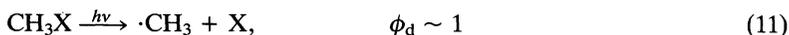
The dissociation yield has not been reported in the case of CMB. High yield is expected for photodissociation, because a similar molecule, such as allyl chloride, dissociates with a yield of unity. CMB may dissociate directly and partly by Eqn (9). Since the RRKM dissociation rate constant is estimated to be two orders of magnitude higher than that of MB, the yield will be reduced just a little even by adding 760 Torr nitrogen. As a result, the assumption of a dissociation yield of unity leads to a reasonable conclusion for the yield of methallyl radical, as seen in Table II.

### Formation yield of methyl radical

A high value for the dissociation yield is expected on the basis of the absorption spectra of halomethane<sup>33-37</sup>. The broad absorption band of  $\text{CH}_3\text{Cl}$  in the range 160–200 nm has been assigned to the transition to an antibonding orbital localized on the C—Cl bond ( $\sigma^*(\text{C—Cl}) \leftarrow 3p$ )<sup>33</sup>. The ArF laser light (193 nm) pumps the antibonding orbital and presumably induces direct dissociation ( $\phi_d = 1$ ). Methyl iodide predissociates from a Rydberg state ( $6s \leftarrow 5p$ ) according to van Veen *et al.*<sup>34</sup>, as follows:



they detected the  $\text{CH}_3$  radical which is selectively excited in the  $v_2''$  mode. Further details of the photolysis are discussed as follows:



Eqns (12)–(14) are known to be minor ones upon excitation at 184.9 nm and the yields are inserted<sup>35</sup> in the equations. Some of these are important at wavelengths shorter than the Hg resonance line. The

trapping yield of methyl radical by Eqn (18) is quite high: higher than 0.81 or  $\text{CH}_3\text{Cl}$  and then 0.9 for  $\text{CH}_3\text{I}$  on irradiation with 184.9-nm light<sup>35</sup>. Hence,  $\phi_d$  is higher than these values. Product analysis for  $\text{CH}_3\text{Cl}$  at 163 nm gives a  $\phi_d$  value of  $0.86 \sim 1.01$ <sup>36</sup>.

Although the hot methyl radical is 10 times more reactive than the relaxed one<sup>38,39</sup>, the radical–molecule reactions of Eqns (17) and (18) will be considerably slower than the competing radical–radical reactions of Eqns (15) and (16)<sup>40</sup>. Therefore, important decay processes in the time range of a few hundred nanoseconds are a combination of Eqns (15) and (16).

The inserted oscillogram in Figure 4 shows that the absorbance of methyl radical rapidly increases and slowly decays. The initial increase ( $< 40$  ns) is due to collisional relaxation. The slow decay can be explained in terms of the recombination reactions as follows: the recombination reaction of methyl radical has been extensively studied. The rate constant ( $k_M$ ) of  $1.95 \times 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$  is used here<sup>10</sup>. When the recombination rate constant between the methyl radical and the chlorine atom is assumed to be the same, the concentration of methyl radical at  $t_1$  decreases to  $\{1 + 3k_M(t_2 - t_1)[\text{Me}](t = t_1)\}^{-1}$  at  $t_2$ . In the oscillogram, the pressure of the methyl radical,  $[\text{Me}]$ , is 0.088 Torr (if  $\phi_d = 1$ ) at  $t_1 = 50$  ns and decreases by 8% at  $t_2 = 250$  ns. The calculated value is 9%. Therefore, the decay processes after 50 ns in Figure 4 can be explained in terms of the recombination processes under the assumption of  $\phi_d = 1.0$ .

### Collisional relaxation of hot radicals

Absorption intensities of the methyl radical increased with time (Figures 4, 5 and the time-resolved spectra in Figure 2). The rise curves are due to an increase of the population of the vibrationally ground state of the  ${}^2A_2''$  state of the methyl radical. Rotational relaxation does not contribute largely to the change of the absorbance at 216.4 nm, because the bandwidth in the  $\text{CH}_3\text{I}$  and 760-Torr system remains almost the same in the time-resolved spectra at 20 ns (a non-relaxed state) and 250 ns (the relaxed state). Time-of-flight (TOF) study of  $\text{CH}_3\text{I}$  with the 193-nm laser light indicates that the umbrella mode ( $\nu_2''$ ) is selectively excited in the photofragment of the methyl radical<sup>34</sup>. No rotational excitation has been observed in the infrared fluorescence detected with 500 ns time resolution at 0.225 Torr of  $\text{CH}_3\text{I}$  and on

266-nm excitation<sup>37</sup>. The present time-resolved spectra are consistent with the TOF studies.

The absorption intensity of the 0–0 transition of methyl radical at  $t = 0$  ns is about 30% of the relaxed spectrum. The initial population of the  $\nu'' = 0$  levels has been analyzed to be only 6.7% by van Veen *et al.*<sup>34</sup>. The difference from the TOF experiment is presumably caused by an overlap of hot band absorption on the wavelength at the 0–0 transition and by collisional relaxation within the laser pulse width. A weak absorption was detectable at 226.6 nm in our experiments, where the transition  ${}^2A_2'(0) \leftarrow {}^2A_2''[\nu_2''(n=2)]$  is expected and the TOF studies suggest 30% population in the  $\nu_2''(n=2)$  level.

An increase of absorbance in Figure 5 is due to collisional relaxation into the  $\nu'' = 0$  level. The relaxation rate constants are listed in Table VI. The constants ( $k_M^r$ ) are evaluated by the following equation:

$$k_M^r = [M]^{-1}\{k_{\text{obs}}^r - k_{\text{MI}}^r[\text{MI}]\},$$

where  $[M]$  is a pressure of a foreign gas and  $[\text{MI}]$  is that of methyl iodide. Observed rate constants ( $k_{\text{obs}}^r$ ) include a contribution of the parent molecules of methyl iodide ( $k_{\text{MI}}^r[\text{MI}]$ ).

Two papers have been published concerning collisional relaxation of hot methyl radical. Callear *et al.*<sup>11</sup> measured them for the first time by microsecond flash photolysis of diazomethane. The collisional relaxation rate relative to He is as follows: He : Ar : CH<sub>4</sub> : C<sub>2</sub>H<sub>6</sub> : SF<sub>6</sub> = 1 : 1.85 : 13.9 : 17.2 : 19.3. The present ratio is in good agreement with that in common foreign gases. But the present rate constants are about four times as small as those obtained by Callear *et al.*<sup>11</sup> The reason for the difference was not clear. Another relaxation ratio of the hot methyl radical has been evaluated on the basis of the reaction activities as shown in Table V<sup>39</sup>. It also shows a similar tendency with the present results.

The rise time is expected to be 20 ns in the system with 228 Torr of CH<sub>3</sub>Cl, if CH<sub>3</sub>Cl has the same relaxation time as that of CH<sub>3</sub>I. The absorbance in the oscillogram of Figure 4 reaches a maximum at 50 ns, which is consistent with the above expectation. The initial rise is due to collisional population to the  $\nu'' = 0$  level.

The half-width of the methyl radical in the relaxed spectrum depends on the foreign gas. In the case of nitrogen as the foreign gas, the bandwidth (FWHM) is 1.30–1.36 nm (Figures 2 and 4); however, it is 1.14–1.20 nm in the cases of CH<sub>3</sub>Cl (Figure 4) and CH<sub>3</sub>I–C<sub>2</sub>H<sub>6</sub> (200

**Table V** Collisional relaxation rates of hot methyl radical<sup>a</sup>.

Added gas	$k_M(10^4\text{Torr}^{-1}\text{s}^{-1})$	Ratio <sup>b</sup>	Ratio <sup>c</sup>	Ratio <sup>d</sup>
Ar	$1.33 \pm 0.13$	1	1.85	0.36
N <sub>2</sub>	$1.28 \pm 0.05$	1	—	0.86
C <sub>2</sub> H <sub>6</sub>	$13.7 \pm 2$	10.5	17.5	—
CH <sub>3</sub> I	$22.2 \pm 1$	17	—	9.6

<sup>a</sup> Measured at 295 K. Errors in  $k_M$  were single  $\sigma$ .

<sup>b</sup> Normalized by  $k_M$  of Ar.

<sup>c</sup> Ref. 11.

<sup>d</sup> Ref. 39.

Torr) systems. The efficiency of the rotational excitation may be slightly different. As a result, the molar extinction coefficient at the central wavelength depends on a foreign gas. This effect is important when using the molar extinction coefficient as a reference, and so we need to select the foreign gas.

Table VI shows rate constants of collisional relaxation by nitrogen for several radicals. The third column lists the relaxation times evaluated by using the rate constants in the presence of 760 Torr nitrogen. The time for the methyl radical is 100 ns and for the trimethyl radical it is 5 ns. Larger radicals tend to have shorter relaxation times, and this tendency is expected on the basis of many studies of collisional relaxation of neutral hot molecules: hot benzene<sup>22</sup>, hot azurene<sup>41</sup>, and

**Table VI** Collisional relaxation times of hot species.

Hot	$k_r/10^4\text{s}^{-1}\text{Torr}^{-1}$	$\tau_r(760\text{ Torr})/\text{ns}$
$\cdot\text{CH}_3$	$1.3 \pm 0.05$	100
$\text{C}=\text{C}-\text{C}\cdot$	$2.1 \pm 0.1$	65
$\text{C}=\text{C}-\text{C}\cdot$ 	$7.5 \pm 0.4$	18
$\text{C}=\text{C}=\text{C}\cdot$ 	$25 \pm 0.6$	5
 CH <sub>2</sub> <sup>a</sup>	8	16
 ** <sup>b</sup>	1.75	75
 ** <sup>c</sup>	7.4	18

<sup>a</sup> Ref. 20.

<sup>b</sup> Hot benzene with initial energy of 6.4 eV<sup>22</sup>.

<sup>c</sup> Hot hexafluorobenzene (6.4 eV).<sup>44</sup>

hot cycloheptatriene<sup>42,43</sup>. Although it is not simple to discuss the relaxation rate constants for all hot species, including neutral molecules, some scatters are of interest. Benzene and the benzyl radical show rather long relaxation times compared with those of hexafluorobenzene<sup>44</sup> and the trimethylallyl radical. These results suggest that the transferring energy per collision depends on the density of the vibrational mode and/or mode of the frequency. The lowest vibrational frequency of benzene is  $404\text{ cm}^{-1}$ ; on the other hand, it is  $120\text{ cm}^{-1}$  for hexafluorobenzene and of the order of  $20\text{ cm}^{-1}$  for the trimethylallyl radical.

We have found a size effect on the formation yield of allylic radical in the presence of 760 Torr nitrogen<sup>21</sup>. The relative yields decrease as the size of the parent molecule becomes larger. We know in this paper that the efficiency of collisional relaxation is also higher for larger sized molecules. This finding indicates that the low yield from large-sized molecules is caused by a slow dissociation rate constant, as well as by efficient collisional relaxation of the intermediate "hot" molecule.

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