

Laser-induced fluorescence studies of C₃ formation and isomerization in the 193 nm photolysis of allene and propyne

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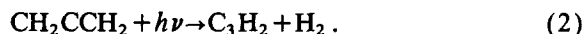
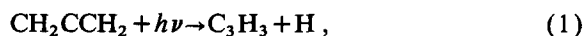
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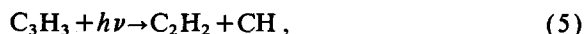
The quantum state distributions of the C₃ radical from the UV multiphoton dissociation of allene and propyne in a pulsed molecular beam have been measured. The observed distributions for both molecules are identical and are much colder than a phase space model would predict, implying that direct dissociation is occurring in one step and isomerization in another. It is concluded that both allene and propyne undergo internal conversion from the S₁ state to the vibrationally excited S₀ ground state of allene followed by molecular elimination of H₂. The observed C₃ is then produced by molecular elimination of H₂ from the secondary photolysis of C₃H₂.

1. Introduction

In the previous work on the 193 nm laser photolysis of allene, Jackson et al. used angle-resolved time-of-flight measurements of the fragments to study the primary processes involved in the photodissociation of this molecule [1]. The two primary processes identified are the elimination of hydrogen atom and hydrogen molecule,



Secondary photolysis of the C₃H₃ radical results in the following products:



while the photolysis of the C₃H₂ radical yields



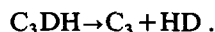
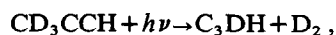
Angle-resolved time-of-flight measurement of the fragments identifies the product channels, as well as

the recoil velocity distributions of the products, but only in rare cases does it give the internal energy distributions of the products. However, laser-induced fluorescence (LIF) measurements yield information about the internal energy distributions of the products, and one can only infer the velocity distribution. In addition, since the LIF technique can only be applied to those fragments that fluoresce, it cannot be used to detect all of the products of the primary and secondary photolysis processes. In the above dissociation scheme two of the products, namely the CH and C₃ radicals, can be studied using the LIF technique, and with it one should be able to obtain complementary information about the reaction pathways during dissociation.

On the other hand, propyne is the geometrical isomer of allene. Studying the photochemistry of two geometrical isomers, such as the case of allene and propyne, should provide additional information about the potential surfaces for both species. Photoexcitation of each of the geometrical isomers will result in a Franck-Condon transition to different parts of the excited potential surface. If dissociation occurs in one vibration, the products formed and the dynamics of their formation should be different even though the available energy is the same. Internal conversion to the ground state surface of the excited geometrical isomers will result in the formation of

highly vibrationally excited molecules with excitation energies considerably higher than the 60–66 kcal/mol barrier for isomerization between allene and propyne [2–4]. The energy of these photoexcited molecules is also considerably higher than the barriers for 1,2 and 1,3 hydrogen migration, as well as for the cyclization reaction to form cyclopropene. Therefore, these reactions should also be possible [2]. The three types of reactions mentioned above are prototypical for many organic reactions, and the information that we obtain on how the reactions occur when one starts from different parts of the potential surface will be important in furthering our understanding of these processes in chemical reactions.

The present work is also important in understanding the formation of C_3 radicals in comets. Earlier work by Stief on the photolysis of propyne at 123.6 nm showed that C_3 could be produced with one photon by the following two-step process [5]:



This is one of the mechanisms that have been proposed for forming C_3 via a one-photon process [6]. In a later paper we will evaluate the relative importance to C_3 formation in comets of this mechanism and the mechanism discussed in the present Letter.

In the present Letter, we will describe the experiments that use the LIF technique to probe the internal energy distribution of the C_3 fragments produced in the 193 nm multiphoton dissociation of allene and propyne.

2. Experimental

The experimental apparatus used in this work is the same as described in ref. [7]. Fig. 1 is a schematic diagram of the experimental setup. The $C_3(X^1\Sigma_g^+)$ radicals were produced via the two-photon photodissociation at 193 nm of allene or propyne after supersonic expansion of the neat gases in a pulsed molecular beam. A Newport BV100 pulsed valve with a 0.5 mm orifice was used to form the supersonic jet. The photolysis laser (Lambda Physik EMG101) was focused 20 nozzle diameters down-

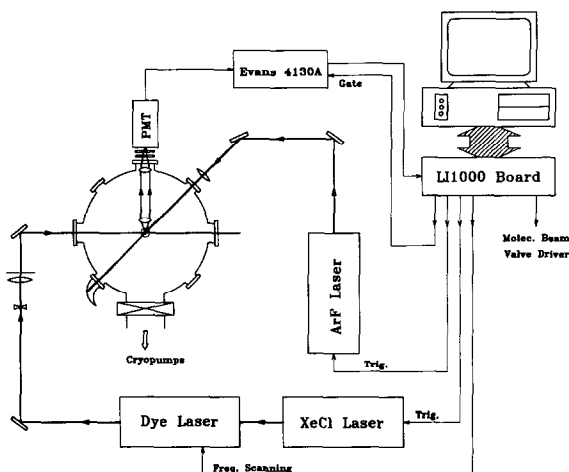


Fig. 1. The schematic diagram of the experiment setup.

stream from the molecular beam nozzle at a 90° angle to the molecular beam. The $C_3(X^1\Sigma_g^+)$ radicals produced were subsequently probed by pumping the $\Delta v=0$ sequence of the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition using a XeCl-excimer-pumped dye laser (Lambda Physik EMG101/FL2002, DPS in dioxane). The dye laser beam was also fixed at a 90° angle to the direction of the molecular beam expansion, but it was about 26 nozzle diameter downstream from the nozzle. The fluorescence from the $A^1\Pi_u$ state was collected by a lens, filtered with an interference filter (Corion P10-486, centered at 486 nm with a fwhm of 10 nm), and then focused onto the photocathode of a photomultiplier tube (EMI 9789QB). The signal from the photomultiplier tube was fed into an Evans 4130A gated integrator whose analog output was digitized by a Laser Interfaces LI-1000 data acquisition system which was also used for controlling the experiment and storing the experimental data inside an IBM compatible personal computer.

Allene was obtained from PCR with a purity of 95%. Propyne was obtained from American Tokyo Kasei with a minimum purity of 98%. Both gases were used without further purification. The isomer purity of these gases was checked using FTIR spectrometry. The analysis showed that the propyne impurity in the allene sample was only 1.7% and the allene impurity in the propyne sample was 2.4%.

3. Results and discussion

LIF spectra of the 000 and 010 vibrational states of $C_3(X^1\Sigma_g^+)$ radicals were observed in the photodissociation of allene. No LIF signals were detected from the 020 and 100 vibrational states of this radical. In the photodissociation of propyne, the LIF signal was much weaker than it was from allene; therefore, only the LIF spectrum of the 000 vibrational state could be observed with a reasonable signal-to-noise ratio. Typical LIF spectra that were observed for the $C_3(A^1\Pi_u(000) \leftarrow X^1\Sigma_g^+(000))$ and the $C_3(A^1\Pi_u(010) \leftarrow X^1\Sigma_g^+(010))$ transitions from the 193 nm photolysis of allene are shown in figs. 2 and 3, respectively. The LIF spectrum of the $C_3(X^1\Sigma_g^+, 000)$ state produced in the photodissociation of propyne is also shown in fig. 2 for comparison. These spectra were assigned according to the line positions measured by Gausset et al. [8].

The rotational distributions of these vibrational

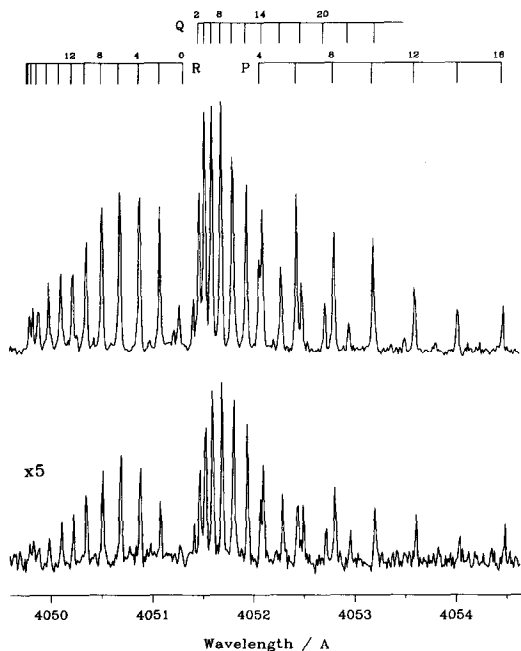


Fig. 2. Typical LIF spectra of the 000 band of $C_3(X^1\Sigma_g^+)$ formed in the 193 nm photolysis of allene and propyne. The top spectrum was obtained using 930 Torr of allene behind the nozzle while the bottom spectrum was obtained using 900 Torr of propyne. The energy of the photolysis laser was 5 mJ/pulse (attenuated with copper screen).

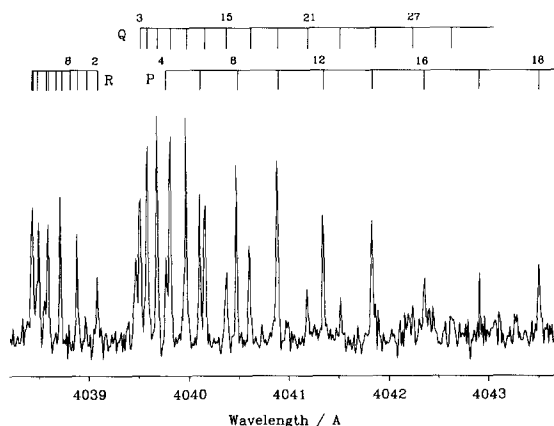
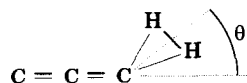


Fig. 3. A typical LIF spectrum of the 010 band of $C_3(X^1\Sigma_g^+)$ obtained in the 193 nm photolysis of allene.

states were calculated by measuring the peak areas under each individual rotational line, normalized to the probe laser intensity, and then correcting for the transmittance of the interference filter and the rotational line strength. To ensure that the observed LIF signals were not saturated by the probe laser, the dependence of the LIF signal on the probe laser intensity was measured. The intensity of the probe laser was always attenuated with a set of neutral density filters into the linear range before any LIF spectra were taken. The measured rotational distribution of the 000 vibrational state of the $C_3(X^1\Sigma_g^+)$ radical formed in the photolysis of allene is shown in fig. 4, along with two calculated distributions based upon the impulse model and phase-space theory, respectively. It is clear from this figure that the rotational distribution predicted by the impulse model is a better fit to the observed distribution than that calculated from the phase-space theory. In the impulse model calculations it was assumed that the C_3 radical is formed via direct processes from the C_3H_2 radical which is produced via a minor channel in the primary dissociation process [1]. The geometry of the excited state of C_3H_2 that undergoes the impulsive dissociation is assumed to be like that shown below:



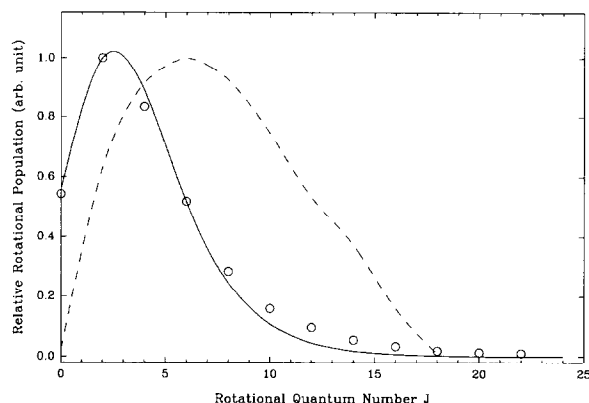


Fig. 4. The relative rotational population of the $C_3(X' \Sigma_g^+, 000)$ state formed in the 193 nm photolysis of allene. The calculated populations from (---) phase space theory and (—) impulsive model are also plotted for comparison. (O) Experimental data.

The C_3 radical is formed by molecular detachment of H_2 from the C_3H_2 molecule, and as it dissociates it pushes against the end carbon atom. The center of mass of the H_2 has to push on the end of this carbon atom in order to obtain enough angular momentum to explain the observed rotational distribution. The phase-space model overestimates the amount of energy that goes into rotation because there is no dynamical constraint built into the model. The models for the rotational distribution suggest that the dissociation is a direct one, and that the excited state of C_3H_2 that produces C_3 only lives for a very short time.

The Boltzmann plot of the rotational distribution of the 010 band of $C_3(X' \Sigma_g^+)$ is shown in fig. 5. The rotational distribution of the 000 band is also shown in fig. 5 for comparison. The rotational distribution of the 010 band is similar to the one of the 000 band. This is in agreement with the result of the modeling that suggests the photodissociation of C_3H_2 occurs in an impulsive manner. The frequency of the C_3 bending vibration [8] is only 63.1 cm^{-1} which is extremely small and, as a result, the 010 state is almost as linear as the 000 state. Thus very little change is expected in the rotational distribution of C_3 . The integrated intensity of the 000 band is about five times the integrated intensity of the 010 band. We can not convert this to a relative vibrational population because the Franck-Condon factor for this transition is unknown.

The C_3 spectra in fig. 2 obtained from the pho-

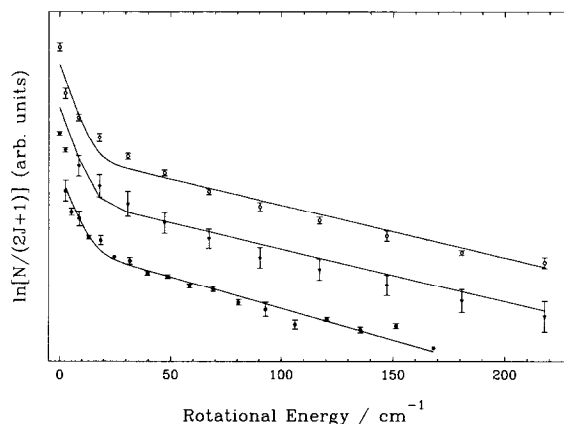


Fig. 5. The Boltzmann plots of the observed $C_3(X' \Sigma_g^+)$ rotational distributions formed in the two-photon photolysis of allene and propyne. (O) $C_3(000)$ from allene, (∇) $C_3(000)$ from propyne, (\bullet) $C_3(010)$ from allene.

Table 1
Comparison of the LIF signal size of C_3 from allene (CH_2CCH_2) and propyne (CH_3C_2H)

Peaks	Allene ^{a)}	Propyne ^{b)}	Ratio (%) of propyne to allene
Q(2)	9179	1162	12.6
Q(4)	13877	1669	12.0
Q(6)	14497	2124	14.6
Q(8)	14588	2203	15.1
Q(10)	11218	2008	17.9
R(2)	8304	769	9.3
R(4)	8797	1183	13.3
R(6)	9061	1356	14.9
R(8)	8204	1119	13.6
R(10)	6249	849	13.6
average = $13.7 \pm 2.1\%$			

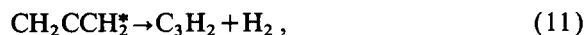
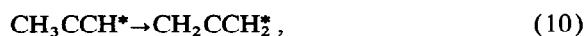
^{a)} For allene, $\sigma_{193 \text{ nm}} \approx 6.6 \times 10^{-19} \text{ cm}^2$, propyne impurity = 1.7%.

^{b)} For propyne, $\sigma_{193 \text{ nm}} \approx 1.2 \times 10^{-18} \text{ cm}^2$, allene impurity = 2.4%.

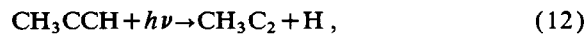
tolysis of allene and propyne look very similar to each other, and a Boltzmann-type plot of the data also shown in fig. 5 confirms that they are essentially the same within experimental errors. A comparison in table 1 of the relative signal intensities of the spectra obtained under identical experimental conditions for both molecules on the same day shows that the average ratio of the signal sizes of propyne to allene is 13.7%. If the photodissociation mechanism for both

molecules is exactly the same, the signal intensity for the propyne signal should have been twice that of the allene signal because the absorption cross section for propyne is twice as big as allene's (table 1). It was first thought that the small C_3 signal from propyne was due to an allene impurity in the propyne sample used for the experiments. The amount of allene impurity in propyne is only 2.4% which proves this is not the case because the observed signal is too large. Thus to explain the almost identical C_3 spectra from allene and propyne photolysis at 193 nm it must be concluded both form primary radicals which can undergo secondary photolysis in an identical manner. The most reasonable way to explain this observation is that some of the excited propyne isomerizes to excited allene before dissociation and this excited allene then dissociates to produce the observed C_3 radical.

The similarity in the C_3 rotational distributions from the photodissociation of propyne and allene suggests that the mechanism for the C_3 formation in the 193 nm photolysis of propyne can be described as follows:



The yield of C_3 from propyne relative to that from allene was 13.7%, but since 2.4% of this is due to the allene impurity, the true relative yield is 11.3%. Seki and Okabe have recently reported quantum yields in the 193 nm photodissociation of propyne [9]. Their results indicate that 81%–91% of the primary processes goes through the following two channels:



The quantum yield for reaction (12), Φ_{12} , is 0.7 ± 0.1 and for reaction (13), Φ_{13} , is 0.11 ± 0.01 . The fact that the hydrogen atom comes from the carbon atom with the highest C–H bond energy suggests, as they pointed out in their paper, that the excited state involved in reaction (12) decomposes in a time short compared to the time required to redistribute the energy. Compared to reaction (12),

certain amount of rearrangement must occur for reaction (13) to take place. It is therefore not surprising that the quantum yield for reaction (13) is considerable less than reaction (12). Similarly, since reaction (10) requires a 1,3 hydrogen atom shift rather than a 1,2 hydrogen atom shift, its quantum yield should be less than the quantum yield for reaction (13). We, therefore, suggest that about 10% of the excited propyne molecules undergo internal conversion to the highly vibrationally excited regions of the S_0 ground state of allene. Based upon these arguments, the quantum yield for the production of $C_3H_2 + H_2$ could be of the order of 0.01, if only 11% of the $CH_2CCH_2^*$ formed by initial conversion decomposes to form C_3 . The C_3H_2 radicals produced in the primary process can then absorb a second photon and produce the products shown in reactions (6)–(8). Only one of these reactions leads to C_3 formation so that the quantum yield for the production of C_3 should be much less than the quantum yield for the production of C_3H_2 .

The quantum yield ratio of C_3 from propyne to that from allene ($=0.07$) can be approximately given by the total C_3 LIF signal from propyne to that from allene (0.14 from table 1) times the absorption cross section ratio of 0.55. The quantum yield for the C_3 production from allene has to be less than 0.11 which is the quantum yield for the production of C_3H_2 in reaction (2). This in turn implies that the $\Phi(P)$ is less than 0.007, which is in agreement with the earlier value derived using the results of Seki and Okabe [9].

4. Conclusions

Laser-induced fluorescence studies of the photolysis of allene have confirmed that C_3 is produced in the 193 nm laser photolysis of allene. The observed rotational distributions suggest that the photodissociation of the vibrationally excited intermediate C_3H_2 occurs within one vibration. Similar experiments with propyne have been used to show that the molecular dissociation channel that produces the $C_3H_2 + H_2$ occurs via fast internal conversion from the excited state followed by molecular elimination on the vibrationally excited ground state surface. The relative quantum yields for the production of C_3 from

allene and propyne have been used to estimate an upper limit to the quantum yield for the production of C_3 radical from propyne of 0.007, which is completely consistent with the recent results of Seki and Okabe [9].

Acknowledgement

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