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## Kinetics and dynamics in the photodissociation of the allyl radical

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The direct observation of the products, kinetics and translational energy release from the photodissociation of the allyl radical,  $C_3H_5$ , upon excitation in the near-uv is reported. A statistical analysis of the data shows that they are in agreement with allene formation being the dominant H-loss reaction channel. © *1997 American Institute of Physics*. [S0021-9606(97)02432-X]

We report the direct observation of the products, kinetics and translational energy release from the photodissociation of the allyl radical,  $C_3H_5$ , upon excitation in the near-uv.

Hydrocarbon radicals appear as chemical intermediates in many reactive environments. Of particular importance for combustion processes or tropospheric chemistry are relatively stable radicals that are converted into more reactive species upon photochemical excitation by radiation present in the particular environment. An example of such a system is the allyl radical, whose spectroscopy has been the subject of earlier studies in our group.<sup>1</sup> A large number of vibronic bands between 250 and 240 nm was identified by resonant multiphoton ionization (MPI) and assigned to the B, C, and D states of allyl, which are strongly coupled to each other. No fluorescence has been observed from these states despite the very large oscillator strength of at least one of them.<sup>2</sup> Time-resolved studies in our group have indicated lifetimes on the sub-100 picosecond scale for these states.<sup>3</sup> Likely fast kinetic processes that would occur in competition with emission include the loss of a hydrogen atom, either prior to, or subsequently to a radiationless transition to a lower-lying electronic state. The elucidation of the dynamics of this reaction is the subject of the this communication. Figure 1 shows the energy diagram for the two most important reaction channels, yielding allene and cyclopropene, with data from Refs. 4 and 5. Allene is the thermodynamically favored product. The reaction to cyclopropene would necessarily involve a cyclization to cyclopropyl radical, followed by hydrogen loss. This reaction would be kinetically favorable. Other possible reactions include the formation of 1-propyne, which is expected to have a higher activation barrier due to an additional, less likely hydrogen shift, or concerted H<sub>2</sub> loss, forming cyclopropenyl radical. They will not be considered in this communication.

The photochemistry of the allyl radical has already attracted some interest due to its importance as a model system, with most prior studies performed in rare gas matrices. When allyl was irradiated with blue light, bands appeared that were assigned to the cyclopropyl radical.<sup>6,7</sup> Irradiation at 254 nm in the presence of bromine atoms, on the other hand, yielded allene, propyne and some smaller fragments.<sup>7</sup> The gas-phase resonance Raman spectrum of the  $C {}^2B_1$  state at 225 nm was consistent with isomerization to cyclopropyl radicals.<sup>8</sup> The isomerization to cyclopropyl has also been the subject of several theoretical investigations.<sup>6,9,10</sup> Nevertheless, the evidence for such a reaction is inconclusive.

In our experiments a molecular beam of allyl radicals was produced by means of supersonic jet flash pyrolysis.<sup>11</sup> The allyl is then excited by pulsed uv-laser radiation into one of several vibronic bands of the  $C^{2}B_{1}$  state. The hydrogen atoms formed after a variable time delay can be detected with very high sensitivity employing Lyman- $\alpha$  radiation at 121.6 nm. If the intensity of the hydrogen signal is monitored as a function of the delay time between pump and probe laser, microcanonical reaction rates k(E) are obtained. Product translational energy distributions can be obtained from the Doppler profiles of the hydrogen fragment absorption spectrum. A statistical analysis of the data can then provide information that could distinguish between the two reaction channels.

The probe technique, vuv laser detection of H atoms formed in chemical reactions, has been used for roughly a decade.<sup>12,13</sup> It has been applied mostly to reactions of stable molecules in cells, although some studies on saturated hydro-carbon radicals have been reported.<sup>14</sup> In those studies, how-ever, the radicals were produced by photolysis, complicating the experiment through interference by higher-order multiphoton processes. Alternatively, photofragment translational spectroscopy has been successfully applied to radical reactions.<sup>15</sup> In the next sections, we show that a combination of H-atom detection with pyrolytic production of radicals yields an amount and quality of information equal to that available from experiments on stable molecules, and permits a study of the photochemistry of medium-sized organic radicals in molecular beams.

The experiment was carried out in a molecular beam machine equipped with a time-of-flight (TOF) mass spectrometer. The details of the experimental setup will be described in a future publication, the supersonic jet flash pyrolysis source<sup>16</sup> and the formation of the allyl radical<sup>1</sup> have been described previously. Two Nd:YAG pumped dye laser systems were employed, synchronized externally to within better than 2 ns. The first laser excited the allyl radical and induced photolysis. The hydrogen detection was carried out as described by Welge and co-workers.<sup>17</sup> A second laser was frequency tripled in 225 mTorr of Kr to produce Lyman- $\alpha$  radiation around 121.6 nm, exciting H atoms into the 2*p* state. They were ionized by the 364.7 nm dye laser fundamental and detected in the TOF spectrometer. Typically each

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FIG. 1. Schematic diagram of the energetics of the allyl radical for the two most important reaction channels, leading to allene and cyclopropene

data point represents an average of 200 shots.

In Fig. 2, a resonant MPI spectrum of the allyl radical is given, showing the region around the  $C^{2}B_{1}$  state origin. While the pump laser was scanned, the probe laser was kept fixed at 121.6 nm. The masses 41 (allyl, lower trace) and 1 (hydrogen, upper trace) were recorded simultaneously. The spectrum was not corrected for laser power. For each peak in the allyl channel there is a corresponding peak in the hydrogen channel. The transitions into the C-state origin band, as well as into the  $B 9_0^1$  and the  $C 7_0^1$  bands, can be identified. Power studies revealed a quadratic dependence on the pump laser energy for the allyl signal, but a linear dependence for the hydrogen signal, indicating that the hydrogen originates from dissociation of the neutral excited allyl radical rather than from the cation. When the probe laser was blocked no hydrogen was detected. However, the probe laser alone did produce a small background signal, attributable either to hydrogen produced in the pyrolysis source or to photodissociation induced by the vuv light, that was subtracted in the Doppler-spectra discussed below. Although both of the



FIG. 2. Resonant MPI spectrum of the allyl radical (lower trace). The signal recorded simultaneously in the hydrogen mass channel is given in the upper trace. For each resonance in the allyl spectrum there is a corresponding increase in the hydrogen signal.



FIG. 3. Growth curve of the hydrogen signal as a function of the delay time between excitation laser and Lyman- $\alpha$  laser. The curve is fitted with a rise-time of 25 ns, corresponding to a rate  $k(E) = 4 \times 10^7 \text{ s}^{-1}$ . The exponential decay is due to the motion of the hydrogen out of the observation region.

*C*-state bands visible in Fig. 1 were studied in detail, we will concentrate exclusively on the  $C \ 0_0^0$  band.

A microcanonical rate for the H loss can be obtained when the appearance of the hydrogen signal is monitored as a function of the pump-probe delay. Such a delay scan is given in Fig. 3. The hydrogen signal shows a fast risetime, a short plateau around 100 ns, and a decay at longer delay times. The decay is due to the motion of the hydrogen atoms out of the detection region and does not have any physical significance. The rate can be extracted from a fit of the rising edge of the curve. The time constant is 25 ns, yielding  $k(E) = 4 \times 10^7 \text{ s}^{-1}$ . This is close to the limits of the time resolution of our laser system. As mentioned above, timeresolved studies indicate lifetimes of less than 100 ps for the states excited in the present experiments. As we observe hydrogen loss on a nanosecond timescale we conclude that hydrogen is not lost directly from the C state. Presumably, the C state decays via an internal conversion, forming very hot ground state molecules or allyl radicals in the A state. In either case, the timescale of dissociation is long enough to assume that the allyl is completely thermalized before the reaction occurs, and that statistical theories can be applied.

RRKM calculations, including rotation, for both the direct loss of hydrogen from hot allyl radicals, and H loss subsequently to cyclization were performed. For the pathway yielding cyclopropene, we assumed that cyclization occurs fast and that hydrogen loss is the rate determining step. From a statistical viewpoint, this assumption is justified by the large amount of excess energy available for the reaction. The activation energies  $E_A$  were calculated from the thermochemical data given in Fig. 1, assuming reverse barriers of  $\sim$  5 kcal/mol. All frequencies were calculated with the aid of the GAUSSIAN 94 program package<sup>18</sup> on the MP4(SDQ) 6-31 G\* level.<sup>19</sup> The frequencies were scaled by a factor of 0.94 in order to match the experimentally known frequencies of the allyl radical.8 The details of the calculation will be reported in a full account of this work. This procedure yielded rate constants of  $k(E) = 2.6 \times 10^9 \text{ s}^{-1}$  for the reaction from allyl $\rightarrow$ allene, and  $6 \times 10^9$  s<sup>-1</sup> for the reaction from cyclopropyl->cyclopropene, both calculated rates overshooting the experimentally observed reaction rates considerably. However, under our conditions there would be excess energies of 59.1 and 36.6 kcal/mol for the allyl→allene and cyclopropyl-cyclopropene reaction present in the system, making the effect of anharmonicity non-negligible. In order to mimic the effect of anharmonicity, we employed an additional scaling factor obtained in the following way: Ab *initio* frequencies were used to calculate heat capacities  $C_n$ of allene and propene. The calculated values were then compared to data obtained from an extrapolation of experimental values.<sup>20</sup> When the molecular frequencies were scaled by an additional factor of 0.71, a good fit to the extrapolated  $C_n$ data around 3000 K was obtained. As will be discussed below, the vibrational temperature of the allyl radical can be calculated to be around 4000 K. However, experimental data to check the extrapolation are only reported up to 1500 K, leading probably to unreliable predictions at temperatures higher than 3000 K. Nevertheless, another set of RRKM calculations was then performed in which the ab initio frequencies were multiplied by an additional factor of 0.71 to simulate the effects of anharmonicity. Under these conditions rate constants  $k(E) = 9.5 \times 10^7 \text{ s}^{-1}$  and  $8 \times 10^8 \text{ s}^{-1}$  for the allyl-allene and cyclopropyl-cyclopropene reaction were obtained. A RRKM calculation for the isomerization of allyl to cyclopropyl, assuming a reverse barrier of 16.6 kcal/mol obtained from *ab initio* calculations,<sup>21</sup> yielded a value of  $k(E) = 2 \times 10^{10} \text{ s}^{-1}$ , confirming the assumption that hydrogen loss is the rate determining step. We note that the value for allene formation is within a factor of 2 of the experimental data, while the rate calculated for cyclopropene formation is too fast by a factor of 30.

Information on the product energy distribution can be obtained from Doppler profiles of the hydrogen spectrum. A representative Doppler profile, recorded at a pump-probe delay of 100 ns, is depicted in Fig. 4. It is fitted well by a Gaussian with a full width at half maximum (FWHM) of  $4.1 \text{ cm}^{-1}$ , implying a speed distribution which is close to Maxwellian. Part of the halfwidth is due to the laser bandwidth of  $0.4 \text{ cm}^{-1}$  in the vuv and the fine-structure splitting of the  ${}^{2}P_{3/2}$  and the  ${}^{2}P_{1/2}$  states of hydrogen, which are 0.4 cm<sup>-1</sup> apart. A deconvolution of the band yielded a Doppler broadening  $\delta \nu$  of 4.0 cm<sup>-1</sup>. From the formula given in the literature<sup>22</sup> a translational temperature  $T_T$ =4583 K is calculated. Using the expression  $\langle E_T \rangle = 3/2$  RT and correcting for the mass of the hydrogen fragment, a corresponding translational energy release of 13.9 kcal/mol is obtained. For the reaction forming allene, the excess energy is 59.1 kcal/ mol, meaning that 23% would have been released as translational energy if this channel were to be dominant. This is within the range of values typical for predissociative hydrogen loss in unsaturated hydrocarbons, if compared with, e.g., ethylene  $(18\%)^{23}$  or methyl substituted benzenes and pyrazines (10%-15%).<sup>24</sup> For a reaction forming cyclopropene, the lower excess energy of 36.6 kcal/mol would mean that 37% is released as translational energy, a fraction significantly higher than in the above mentioned examples. For



FIG. 4. Doppler profile of the hydrogen atom after excitation into the  $C_0^0$ band of allyl. The full line represents a Gaussian fit with a FWHM of 4 cm<sup>-1</sup> after deconvolution. This corresponds to an expectation value of 13.6 kcal/mol for the translational energy release.

both reaction channels, the hydrocarbon fragment would contain a large amount of internal excitation, in agreement with an indirect dissociation process in which the molecule undergoes a large geometry change before entering the exit channel.<sup>25</sup> This geometry change is certainly more pronounced for the formation of the cyclic product, cyclopropene, making it surprising if the formation of cyclopropene were to be accompanied by a translational energy release about twice as high as is typical for similar compounds.

An approach to calculate the product translational energy release was described by Quack.<sup>26</sup> He suggested the use of a distribution function

$$P(E_T) = C\rho_p (E - E_T) E_T^n \tag{1}$$

with *n* being an adjustable parameter, 0 < n < 3,  $\rho_n$  being the rovibrational density of states of the product and C a normalization constant, to mimic the more accurate phase space and adiabatic channel model behavior. The parameter n reflects to some extent the tightness of the transition state as well as the extent to which the reaction behaves statistically. We employed the following simplified procedure: The expression

$$\langle E_T \rangle = \int_0^E E_T P(E_T) dE = \frac{\int_0^E \rho_P(E - E_T) E_T^{n+1} dE_T}{\int_0^E \rho_P(E - E_T) E_T^n dE_T}$$
(2)

with the denominator being the normalization constant, was used to find a value for n that could reproduce our experimentally derived  $\langle E_T \rangle$  of 13.9 kcal/mol. We found n to be around 2.4 for the allyl-allene reaction, and 4.5 for the cyclopropyl-cyclopropene reaction. With scaled frequencies ( $\times 0.71$ ) the *n* values increases to n = 2.7 and n = 5.3, respectively. Thus the value of n necessary to fit the experimentally observed translational energy release for the reaction leading to cyclopropene is well outside the range observed to be consistent with statistical behavior.<sup>26</sup> For comparison, we calculated n values for hydrogen-loss from

cycloheptatriene and substituted benzenes,<sup>13,24</sup> forming (substituted) benzyl radicals, and obtained values of  $n \approx 2$ .

In their work on the decomposition of toluene into benzyl and hydrogen Park *et al.*<sup>24</sup> applied the principle of detailed balance<sup>27</sup> to their data, and showed that the vibrational temperature of the energized educt molecule is similar to the translational temperature of the hydrogen. Using the formula from Ref. 24 a vibrational temperature  $T_{vib}$  of 4249 K is calculated for allyl, and 3482 K for cyclopropyl. When scaled frequencies are employed the  $T_{vib}$  come out about 200 K lower. Under the assumption that the principle of detailed balance is valid for our system, the translational temperature of the hydrogen atom of 4583 K agrees reasonably well with the vibrational temperature expected for the allyl—allene reaction. The difference of 500 K is probably also due to the contributions of the reverse barrier. The agreement is less satisfying for the cyclopropyl—cyclopropene reaction.

In conclusion, the statistical analysis of the data suggests that the experimental observations are in better agreement with allene formation as the principal hydrogen-loss channel, rather than cyclopropene formation. However, at present, the latter possibility cannot be ruled out completely. Experiments on isotopically labeled precursors are currently underway, which may provide a definitive answer. It can be assumed that, barring isotopic scrambling, allene formation comes from hydrogen loss at the central carbon atom, while cyclopropene formation corresponds to hydrogen loss at one of the terminal carbon atoms.

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