

# Evidence of a Surprising Channeling of Ring-Opening Energy to the H<sub>2</sub> Product in the H + c-C<sub>3</sub>H<sub>6</sub> → H<sub>2</sub> + C<sub>3</sub>H<sub>5</sub> Abstraction Reaction

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The product energy disposal in the abstraction reaction H + c-C<sub>3</sub>H<sub>6</sub> → H<sub>2</sub>(*v'*, *j'*) + C<sub>3</sub>H<sub>5</sub> at 1.6 eV collision energy has been characterized by quantum-state-selective, Doppler-resolved REMPI detection of the H<sub>2</sub>(*v'*, *j'*) product. The H<sub>2</sub>(*v'*, *j'*) product is observed with total energy, translational plus rotational plus vibrational, in excess of the total available energy if the C<sub>3</sub>H<sub>5</sub> product is a cyclopropyl radical, but the total H<sub>2</sub>(*v'*, *j'*) energy matches the total available energy if the C<sub>3</sub>H<sub>5</sub> product is allyl. This implies ring-opening of cyclopropyl to allyl concerted with abstraction and the deposition of a large fraction of the ring-opening energy into the H<sub>2</sub>(*v'*, *j'*) product. Such behavior is unprecedented and entirely unexpected. Calculations indicate that both direct H-by-H abstraction and H-addition/H<sub>2</sub>-elimination should occur too quickly to allow the isomerization to occur before product separation. Even if ring-opening did occur, the appearance of the total isomerization energy in the H<sub>2</sub> product would seem dynamically forbidden. The reaction must follow an unanticipated and surprising path.

## Introduction

The cyclopropyl and allyl radicals are well-characterized isomers of the species C<sub>3</sub>H<sub>5</sub>. The allyl radical is the more stable of the two by 1.11(2) eV,<sup>1</sup> so the cyclopropyl radical is thermodynamically unstable but the 0.95(8)-eV<sup>2,3,4</sup> activation energy for isomerization makes it kinetically stable under most conditions. In particular, there are no examples of reactions of the type A + c-C<sub>3</sub>H<sub>6</sub> → HA + C<sub>3</sub>H<sub>5</sub> in which the production of allyl occurs concerted with formation of the HA product. For example, the reactions of Cl<sup>5</sup> and F<sup>6,7</sup> yield cyclopropyl quantitatively. However, there is evidence that in the very exoergic F reaction isomerization of an energized cyclopropyl radical product occurs after the atom-transfer reaction.<sup>6</sup>

Very recently, the isomerization of cyclopropyl to allyl has been observed in the unimolecular reaction of photoexcited cyclopropyl iodide<sup>8</sup> and cyclopropyl cyanide,<sup>9</sup> where the total energy far exceeds the 0.95(8)-eV barrier to ring-opening, and even here the appearance of allyl occurs only because of an unusual double curve-crossing or the production of a very highly excited intermediate. In these cases, the photofragment separation involves heavy-atom motion that is on the same time scale as the ring-opening, so the product isomerization and product separation can easily be concerted.

Here we report evidence that the hydrogen abstraction reaction, H + c-C<sub>3</sub>H<sub>6</sub> → H<sub>2</sub>(*v'*, *j'*) + C<sub>3</sub>H<sub>5</sub>, at 1.6 eV collision energy results in a cyclopropyl ring-opening to allyl that is concerted with the production of H<sub>2</sub>, despite the fact that the H-by-H abstraction reaction can and should occur on a time scale much shorter than that of the ring-opening. Further, we

find that a large fraction of the 1.11(2)-eV energy made available by the isomerization to allyl can appear in the H<sub>2</sub> product, indicating a surprisingly effective channeling of energy into the H<sub>2</sub> product.

Our group has previously measured the rovibrational state distributions of the H<sub>2</sub> products of reactions of the type H + RH → H<sub>2</sub>(*v'*, *j'*) + R for reactions involving linear, cyclic, and branched alkanes of up to six carbon atoms.<sup>10–13</sup> Cyclopropane differs from the other alkane reactants studied by relatively high C–H bond energy and higher activation energy for hydrogen abstraction.<sup>14</sup> However, these differences are small in comparison to the total energy available to the reaction at the high collision energy, 1.6 eV, at which the reactions are studied. As a result, it is expected that, as with the other H + RH reactions, this reaction proceeds by a direct abstraction, making the relatively slow cyclopropyl radical ring-opening inconsequential in the production of H<sub>2</sub>.

The currently reported results, however, indicate that this is not the case and that the mechanism of the reaction is unlikely to be either direct abstraction or an ordinary H-addition/H<sub>2</sub>-elimination. We present product H<sub>2</sub>(*v'*, *j'*) Doppler profiles from the H + c-C<sub>3</sub>H<sub>6</sub> reaction that show that the production of allyl radical is required to provide the energy observed in the H<sub>2</sub> product and that this allyl production is a major reaction channel.

## Experimental Methods

The experimental apparatus that was used has been described previously.<sup>11</sup> In brief, a 10:1 mixture of HI and cyclopropane with a total backing pressure of 220 Torr expands through a pulsed nozzle into the source region of a REMPI/TOF apparatus. A 266-nm pulsed laser beam intersects the molecular beam, photolyzing HI to produce H atoms with a collision energy of 1.6 eV. These H atoms react with cyclopropane to make H<sub>2</sub>.

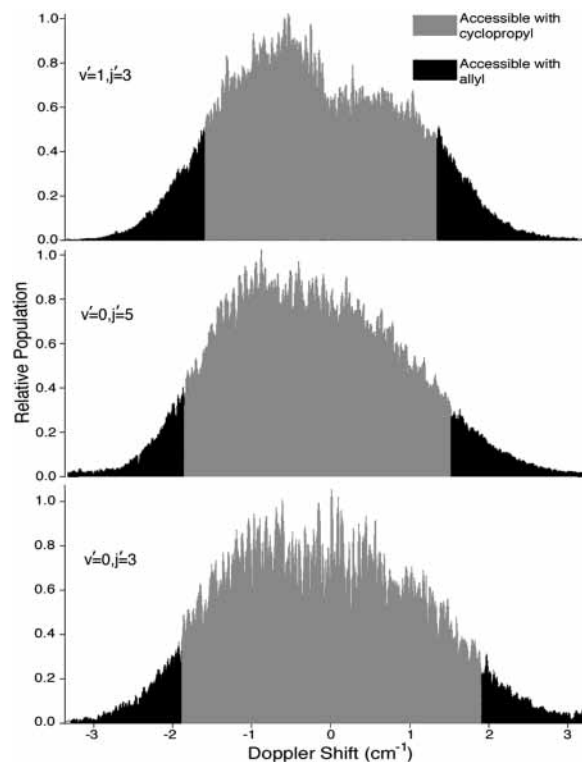
The H<sub>2</sub>(*v'*, *j'*) product is ionized at ~205 nm by a 2 + 1 REMPI scheme using the frequency-tripled output of a pulsed

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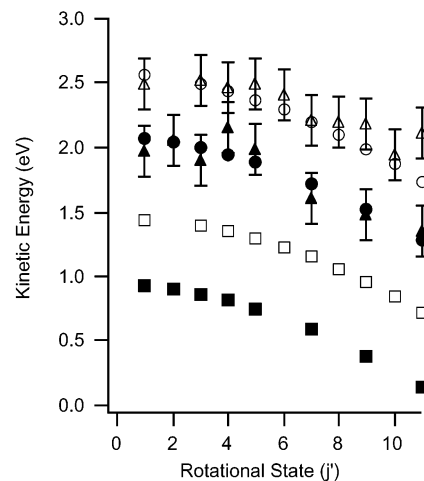
**Figure 1.** Doppler profiles of three rovibrational states of product  $\text{H}_2$  from  $\text{H} + \text{c-C}_3\text{H}_6$ . Lightly shaded areas denote population energetically accessible by direct abstraction, and darkly shaded areas show additional energy accessible with added energy from ring-opening.

dye laser. The 5-ns REMPI pulse follows the 5-ns photolysis pulse by 20 ns, a time delay that ensures single-collision conditions. The resulting  $\text{H}_2^+$  ions are collected and detected by a Wiley–McLaren-type time-of-flight mass spectrometer<sup>15</sup> operating with a Daly detector.<sup>16</sup> For each  $\text{H}_2(v', j')$  REMPI transition associated with a specific rovibrational state, a frequency scan is taken over the Doppler-broadened line profile.

## Results and Discussion

Figure 1 shows Doppler profiles for the  $\text{H}_2(v', j')$  product of the  $\text{H} + \text{c-C}_3\text{H}_6 \rightarrow \text{H}_2(v', j') + \text{C}_3\text{H}_5$  reaction. The maximum Doppler shifts observed are limited to  $\text{H}_2$  with translational energy equal to the total available energy less the  $\text{H}_2$  internal energy. (The line width of the REMPI probe beam is less than  $0.1 \text{ cm}^{-1}$  and causes immeasurable broadening on the scale of Doppler widths observed,  $\sim 5 \text{ cm}^{-1}$ .) Figure 1 shows that a significant fraction, about 15%, of the  $\text{H}_2$  product of this reaction appears with translational energy that exceeds that allowed for the cyclopropyl radical coproduct. This maximum energy is equal to the collision energy, 1.6 eV, minus the  $\Delta H$  of reaction, 0.09 eV. The vibrational and rotational energy of the  $\text{c-C}_3\text{H}_6$  reactant, cooled in the molecular-beam expansion, must be much less than the thermal energy of the sample at 300 K before expansion, which is approximately 0.15 eV. As a result, the contribution of the  $\text{c-C}_3\text{H}_6$  reactant's internal energy to the total available energy is negligible.

The observed  $\text{H}_2(v', j')$  Doppler profiles have maximum velocities that imply an available energy that is 1.1 eV higher than that associated with the cyclopropyl radical coproduct. This matches the 1.11(2)-eV energy that would be made available if the coproduct were allyl rather than cyclopropyl. We propose that ring-opening from cyclopropyl to allyl occurs before the



**Figure 2.** Observed and calculated maximum  $\text{H}_2$  product kinetic energies for the  $\text{H} + \text{c-C}_3\text{H}_6 \rightarrow \text{H}_2(v', j') + \text{C}_3\text{H}_5$  reaction. Open triangles and solid triangles are observed values for the product in rotational states in  $v' = 0$  and  $v' = 1$ , respectively. Open and solid circles are the calculated maxima for  $v' = 0$  and  $v' = 1$ , respectively, with the allyl radical as the coproduct ( $\Delta H = -1.11 \text{ eV}$ ). Open and solid squares are the  $v' = 0$  and  $v' = 1$  maxima for the cyclopropyl radical as the coproduct ( $\Delta H = 0.09 \text{ eV}$ ).

$\text{H}_2$  product becomes energetically isolated from the alkyl radical coproduct, thereby making the additional energy available.

The relation between the observed maximum  $\text{H}_2(v', j')$  kinetic energy and the maximum  $\text{H}_2(v', j')$  kinetic energy expected for the production of the allyl coproduct is shown in Figure 2. The agreement is excellent, being within the experimental uncertainty for 17 of the 18  $v', j'$  product states for which we have taken data.

Computational studies on the ring-opening of cyclopropyl to allyl yield an energy release of 1.39 eV,<sup>17,18</sup> significantly above the experimental value of 1.11(2) eV.<sup>1</sup> Our results place a lower bound on the energy difference that is in agreement with the experimental value but do not exclude the higher theoretical value. If the experimental value is correct, then our results indicate that all of the energy released in the ring-opening is accessible to the  $\text{H}_2$  product. If the theoretical value is correct, then our results indicate that 90% of the energy is accessible to the  $\text{H}_2$  product. In either case, the result is startling. In the photodissociation of cyclopropyl iodide,<sup>8</sup> where the production of allyl has been recently demonstrated, no more than 80% of the theoretical ring-opening energy appears in the translation of the products, the only degree of freedom other than the allyl rotations and vibrations. In the photodissociation of cyclopropyl cyanide,<sup>9</sup> no more than 40% of this energy is available to translation and CN rotation/vibration.

Previous work<sup>6,7</sup> involving the abstraction of hydrogen from cyclopropane by atomic fluorine shows that the HF product does not receive any additional energy from cyclopropyl ring-opening. Although the cyclopropyl radical coproduct isomerizes to give the allyl radical, the allyl radical retains all of the ring-opening energy because the isomerization occurs after the reaction that produces HF. This result is in agreement with an abstraction mechanism that is fast relative to the ring-opening. Previous kinetic studies<sup>19,20</sup> of the abstraction of hydrogen from cyclopropane by atomic hydrogen have dismissed the possibility of cyclopropyl ring-opening affecting the  $\text{H}_2$  product because of the relatively slow rate of ring-opening compared to the rate of further hydrogen abstraction.

Rate calculations indicate that the time scale for cyclopropyl ring-opening is indeed far longer than that of the direct hydrogen

abstraction. RRKM calculations by Arnold et al.<sup>8</sup> and RRK calculations that we have carried out indicate that the ring-opening of the cyclopropyl radical to the allyl radical with an internal energy of 1.6 eV, the maximum available, occurs on a time scale of  $10^{-11}$  s. In contrast, QCT calculations<sup>21</sup> indicate that the direct  $H + RH \rightarrow H_2 + R$  reaction at a collision energy of 1.6 eV occurs in about  $10^{-14}$  s, 1000 times faster. Because the ring-opening cannot occur before the  $H_2$  product has departed, a direct abstraction mechanism is not sufficient to account for the observed high-energy product.

Our experimental results then suggest that the reaction must occur through a reaction that is not direct but rather involves an H-addition/ $H_2$ -elimination mechanism. However, the slow rate of the ring-opening process renders this an unsatisfactory mechanism as well. Our RRK calculations show that  $H_2$  is eliminated from a  $c\text{-C}_3\text{H}_6\text{-H}$  complex with 1.6 eV of total energy in about  $10^{-12}$  s with all modes active, which is still 10 times faster than ring-opening. It is unlikely that all of the modes are indeed active, so this is an upper limit on the time scale of  $H_2$  elimination, making the participation of ring-opening even less likely.

The reaction must involve an unexpected mechanism, one in which the  $H + c\text{-C}_3\text{H}_6$  collision energy is somehow efficiently channeled into the ring-opening reaction coordinate to drive that process, and the energy released by the ring-opening subsequently drives the  $H_2$  elimination. The evidence of this unusual path does not mean that the reaction does not proceed through the expected direct abstraction or H-addition/ $H_2$ -elimination mechanisms as well. The quantitative contribution of different pathways to product formation cannot be determined from our measurements. However, about 15% of the total  $H_2$  product appears above the energetic limit for  $H_2 + \text{cyclopropyl}$ , as shown in Figure 1, so whatever the mechanism that leads to  $H_2 + \text{allyl}$ , it is a major reaction path. The measured rovibrational state distributions of the  $H_2(v', j')$  product support this conclusion but are outside the scope of this letter and will be reported elsewhere. The angular distribution of the  $H_2$  product could help determine the relative contributions of the direct and indirect pathways. We plan to make these measurements in the future using a new experimental apparatus now under development in our laboratory. Theoretical calculations of the reaction path, which should be very accurate for this reaction, are likely to provide additional insight into the dynamics of the reaction, and such calculations are anticipated.<sup>22</sup>

Whatever the path, there is some mechanism that dynamically couples the motion of the light H atoms that leads to  $H_2$  formation and the motion of the heavy C atoms needed to effect cyclopropyl ring-opening. This suggests that there could be other

product channels in the reaction of  $H + \text{cyclopropane}$ . The production of  $\text{CH}_3 + \text{C}_2\text{H}_4$  is exoergic by 0.76 eV, and  $\text{CH}_4 + \text{C}_2\text{H}_3$  is exoergic by 0.49 eV. Such products would be expected if the addition of H to  $c\text{-C}_3\text{H}_6$  leads to the formation of the isopropyl or *n*-propyl radicals.<sup>23</sup> Experiments aimed at detecting these other products will be important, and we are planning to attempt to observe the methyl and vinyl radicals in our laboratory. If these channels are observed, then it is clear that even the simplest reaction of cyclopropane is quite rich in its dynamics, and even if these channels are not important, the results reported here show that the dynamics of this reaction are surprisingly complicated.

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