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Probing Centrifugal Barriers in Unimolecular Dissociation of the Allyl Radical

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Time-resolved photoionization of the hydrogen atom product from the allyl radical, C_3H_5, dissociation with 115 kcal/mol total energy provides information on the unimolecular dissociation dynamics. Vibrationally hot ground-state allyl radicals in both low and high *J*-states are prepared by electronic excitation to selected rovibrational states of *C*-state allyl followed by internal conversion. The measured dissociation rates and kinetic energy release are independent of the allyl parent rotational energy and suggest that centrifugal effects are unimportant in allyl radical dissociation at 115 kcal/mol.

The allyl radical, C_3H_5, is probably the best-understood polyatomic radical and its dissociation dynamics has been studied extensively.[1−10] The allyl radical is stable in the electronic ground state but becomes reactive upon electronic excitation and subsequent fast internal conversion, for which a 22 ± 1 ps lifetime was measured for the *C* electronically excited state.[6] Three-state conical intersections[11] may play an important role in the nonadiabatic dynamics that follow electronic excitation to the coupled *B*, *C*, and *D* electronic states to form hot ground-state radicals that dissociate on the ground-state surface. The most favorable reaction channel[4] in unimolecular dissociation dynamics of allyl is unimolecular hydrogen loss forming predominantly allene over a barrier of 60 kcal/mol.[12] In one recent experimental study, Szpunar et al. used photofragment translational spectroscopy to disperse highly vibrationally and rotationally energized allyl radicals produced by secondary photolysis of allyl iodide by their internal energy.[1,2] They found a considerable fraction of allyl radicals with internal energies up to 15 kcal/mol above the barrier that did not dissociate. The authors suggested that a centrifugal barrier characterized by a near-zero impact parameter for hydrogen loss from allyl to produce allene and the small reduced mass of the system are responsible for the increased stability of rotationally hot allyl radicals toward dissociation. If confirmed, the effect would represent a remarkable example of *J*-dependent dynamics in a polyatomic molecule. We suspect that similar effects could be important in the dissociation of other alkyl radicals.[13,14]

In the work described here, we extend our earlier studies[3,15] and measure the dissociation rate of vibrationally hot allyl ground-state radicals with selected *low* and *high* angular momentum. On the basis of the conjecture from Szpunar et al. that the dissociation probability for the allyl radical in low *J*-states is highest, we would expect a reduced dissociation rate for allyl prepared in high *J*-states. The experimental apparatus is an improved version of one described previously.[15] We generate an internally cold allyl radical by supersonic jet flash pyrolysis[16] of allyl iodide. Figure 1 shows the energetics of the pump−probe experiments. Pulsed ultraviolet laser excitation prepares the *C*-state allyl radical selected according to K_a' which, following internal conversion under collision-free conditions, produce angular momentum-selected ground state radicals that dissociate to form mainly allene and a hydrogen atom. The hydrogen atoms are then ionized by 1+1′ REMPI via the 1s−2p transition in the source of a linear time-of-flight mass spectrometer, in which double channel plates detect the resulting hydrogen ions. A modified ion source in the time-of-flight mass spectrometer combined with high precision high-voltage power supplies (ISEG Spezialelektronik SHQ) and improved stability of the dye lasers (Radiant Dyes NarrowScan) lead to a 25-fold increase in signal-to-noise ratio compared to our earlier experiments on the allyl radical.[3,15]

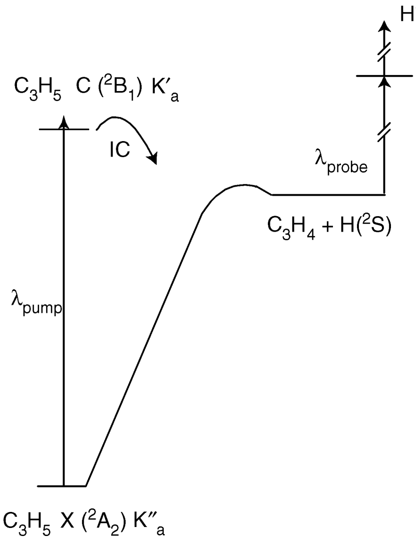

Figure 1. Schematic energy level diagram for the pump−probe experiments. The electronically excited allyl radicals decay nonradiatively to form hot ground-state radicals that dissociate into $C_3H_4 + H$.

Integrating the hydrogen ion signal for 80 laser shots as a function of pump laser wavelength gives the action spectrum. Figure 2 shows the action spectrum at a $\Delta t = 50$ ns pump−

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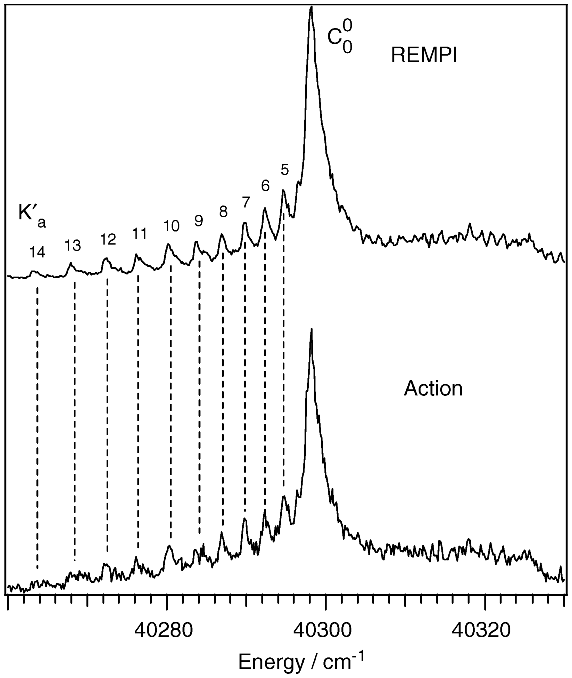

Figure 2. REMPI spectrum of allyl and action spectrum recorded simultaneously at a time delay $\Delta t = 50$ ns in the $m/z = 41$ and $m/z = 1$ mass channel. The ^{Q}P-branch is rotationally resolved in K_a (see ref 17).

probe delay time in the energy region of the *C*-state, together with the REMPI spectrum of allyl recorded simultaneously in the $C_3H_5^+$ ($m/z = 41$) mass channel. For each resonance in the REMPI spectrum we find a corresponding resonance in the action spectrum, confirming that the hydrogen is lost from neutral allyl. We previously analyzed the rovibronic band envelopes of allyl[17] to obtain the assignments of the spectra summarized in Figure 2. The allyl radical is a near prolate top with a large change in the *A* rotational constant upon electronic excitation leading to a long series of *K*-subband heads in the ^{Q}P branch. The spectra in Figure 2 show that the type A, ^{Q}P-branch subband heads are well resolved for K_a' quantum numbers up to at least 14. Though the spectrum is not resolved in *J*, the requirement that $J \geq K_a$ provides a measure of *J*-selection in the electronic excitation. This partially rotationally resolved spectrum allows us to prepare allyl radicals that, following internal conversion to the ground electronic state, are vibrationally hot with 115 kcal/mol total energy but with selected low or high angular momentum.

Monitoring the total flux of hydrogen atoms as a function of the time delay between excitation and probe lasers gives the appearance time of the hydrogen atom. From these transients the unimolecular dissociation rate $k(E,J)$ is obtained. Figure 3 shows the time-delayed scans obtained following excitation to the $K_a' < 5$ and $K_a' = 13$ subband heads of *C*-state allyl origin band. Excitation to $K_a' = 13$ compared to $K_a' < 5$ increases *J* by at least 9. The signal curve has a fast instrument-limited rise up to a time delay of ≈6 ns followed by a slow increase in signal amplitude up to a maximum at ≈45 ns pump−probe delay. At longer delay times the signal decays as the hydrogen atom leaves the detection volume. We fitted the data with three exponentials convoluted with a 6 ns fwhm Gaussian corresponding to the cross-correlation of the two laser pulses. We obtain a rate constant $k_{\text{fast}} > 1 \times 10^8$ s^{-1} for the initial fast rise of the signal and a rate constant $k_{\text{slow}} = (2.82 \pm 0.81) \times 10^7$ s^{-1} for excitation to the $K_a' < 5$ subband. The k_{fast} obtained from fitting the $K_a' = 13$ scan is still instrument limited $> 1 \times 10^8$ s^{-1} and $k_{\text{slow}} = (2.85 \pm 0.83) \times 10^7$ s^{-1} remains essentially unchanged compared to the $K_a' < 5$ scan.

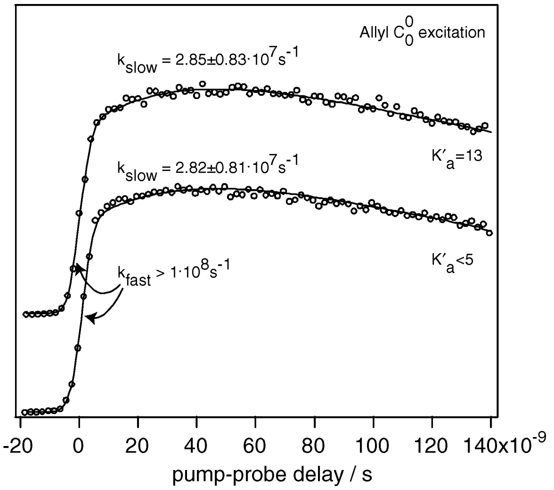

Figure 3. Appearance of the hydrogen atom signal following excitation to the $K_a' < 5$ and $K_a' = 13$ subband heads of *C*-state allyl.

We previously assigned the two rate constants to competing pathways in the unimolecular dissociation of allyl at 115 kcal/mol[15] on the basis of isotopic labeling experiments. Direct cleavage of the central C−H bond in allyl leads to allene formation whereas a hydrogen shift from allyl to 1-propenyl or 2-propenyl followed by hydrogen loss produces allene or propyne. On the basis of RRKM modeling, we assigned k_{fast} to direct dissociation forming allene with a calculated rate constant of 4×10^8 s^{-1}. We cannot exclude a small change in the k_{fast} rate constant for $K_a' < 5$ compared to $K_a' = 13$ excitation because the signal rise is instrument limited. Nevertheless, the short lifetime, even for high-*J* radicals, stands in sharp contrast to the conjecture of Szpunar et al.,[1] that these radicals could be long-lived, although the experiments are not completely comparable. They observed allyl radicals that are stable 48 μs after primary dissociation of allyl-d_2 iodide and concluded that both the barrier to allyl radical direct dissociation and the barrier to isomerization are increased by centrifugal effects. We suggest that centrifugal barriers do not play an important role in the unimolecular dissociation of energized allyl radicals with 115 kcal/mol excess energy as the measured rate constants remain essentially unchanged for dissociation of rotationally cold and warm allyl radicals.

We also obtained Doppler profiles by scanning the probe laser while detecting the total H-atom photofragment flux at a pump−probe delay $\Delta t = 50$ ns that corresponds to maximum signal intensity. The Doppler lines shapes are independent of the polarization vector of the excitation laser that was aligned parallel to the time-of-flight axis in all the measurements reported here. The Doppler profiles shown in Figure 4 are an average of 10 individual probe laser scans. For excitation to both the $K_a' < 5$ and $K_a' = 13$ levels of *C*-state allyl the measured Doppler profiles have a near Gaussian shape with a fitted fwhm of 3.98 ± 0.05 cm^{-1}. A large centrifugal barrier for direct dissociation of allyl to produce allene and hydrogen would be expected to lead to a change in the translational energy distribution for allyl-derived hydrogen atoms deriving from high versus low-*J* radicals. Most of the parent rotational energy should appear in allene angular momentum and not orbital angular momentum $\mu|v_{\text{rel}}|b$ because of the near-zero impact parameter *b* and the small reduced mass μ for the C−H bond fission, which would, in turn, require that $|v_{\text{rel}}|$ should increase to form rotationally colder allene product and the translational

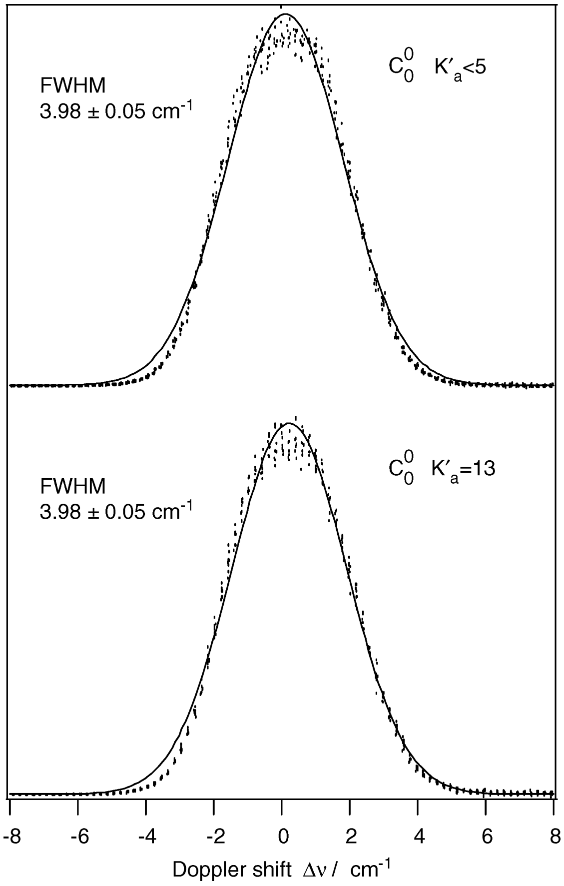

Figure 4. Doppler profiles obtained following excitation to the *C*-state $K_a' < 5$ levels (top) and $K_a' = 13$ subband head (bottom).

energy distribution should peak at higher energies for $K_a' < 5$ excitation than for $K_a' = 13$. The Doppler profiles obtained for $K_a' < 5$ and for $K_a' = 13$ excitation, however, are identical. This observation is consistent with the unchanged dissociation rates and suggests that centrifugal effects are unimportant for allyl radical unimolecular dissociation at 115 kcal/mol.

An angular-momentum-selected experiment finds no discernible difference between photodissociation dynamics of high and low-*J* allyl radicals. Although we cannot exclude that species with *J* substantially higher than was accessible in this experiment could show different behavior, we consider it unlikely that a centrifugal barrier is the principal explanation for the long-lived population of radicals reported by Szpunar et al.[1]

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