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Internal Energy Dependence of the H + Allene/H + Propyne Product Branching from the Unimolecular Dissociation of 2-Propenyl Radicals

Julie A. Mueller, Johanna L. Miller, and Laurie J. Butler*

The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Fei Qi, Osman Sorkhabi, and Arthur G. Suits

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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This Letter introduces a new technique to probe the competing unimolecular dissociation channels of isomerically-selected hydrocarbon radicals as a function of internal energy in the radical. The crossed laser−molecular beam scattering experiments produce 2-propenyl radicals by photolysis of 2-chloropropene and disperse the radicals by the neutral velocity imparted in the photolysis, thus dispersing them by internal energy in the neutral time-of-flight spectrum. For the unstable radicals, the experiments then measure the branching between the two competing C-H bond fission product channels via tunable vacuum-UV photoionization of the products. Dispersing the neutral products by arrival time at the detector allows us to measure the branching between isomeric product channels as a function of internal energy in the dissociating radical isomer. The data resolve the competition between the unimolecular H + allene and H + propyne product channels from the radical with internal energies from 0 to 18 kcal/mol above the H + propyne barrier. We find that the barrier to H + allene formation from this high-energy C_3H_5 radical is slightly higher than the barrier to H + propyne formation, in agreement with recent theoretical calculations but in sharp contrast to that predicted for the most stable C_3H_5 isomer, the allyl radical. The dominance of the branching to H + propyne formation over H + allene formation for this isomer persists at the higher internal energies in agreement with RRKM predictions that take into account the freezing of the methyl rotor in the H + allene channel and predict a concomitant reduction in the *A* factor for that channel.

Radical intermediates play a key role in a wide range of chemical processes, yet even after decades of the finest research, the reactions of many key isomeric radical intermediates elude direct experimental probes. The experiments reported here photolytically prepare a high-energy C_3H_5 radical isomer, the 2-propenyl radical, and disperse the radicals by their internal energy in a time-of-flight spectrum. The nascent radicals with enough internal energy dissociate and the two energetically allowed C_3H_4 products, allene and propyne, are then detected by tunable photoionization as a function of their neutral flight time, allowing us to measure the change in product branching with internal energy to the two isomeric product channels:

$$H_2C{=}CCH_3 \rightarrow H_2C{=}C{=}CH_2 + H \quad (1)$$

$$H_2C{=}CCH_3 \rightarrow HC{\equiv}CCH_3 + H \quad (2)$$

Based on energetic considerations alone, one expects the primary products of the unimolecular decomposition of the 2-propenyl radical to be a near-equal mixture of allene and propyne. The barrier heights and endothermicities are within 1 kcal mol^{-1} for the two isomeric products, yet we expect branching to H + propyne (reaction 2) to dominate even at the higher internal energies because that reaction channel does not freeze an internal rotor, while the channel forming allene (reaction 1) does. While the experimental results may be understood with statistical transition state theory,[1] these results on the 2-propenyl radical are novel because they show one can resolve the selective unimolecular dissociation channels of a radical which is 19 kcal/mol higher in energy than the most stable C_3H_5 isomer, the allyl radical. The isomerization and unimolecular dissociation of the 2-propenyl radical has received considerable attention in prior studies where it was embedded in C_3H_5 kinetics[2−4] or allyl radical dynamics[5−7] studies. The method presented here opens up a broad spectrum of studies on previously elusive hydrocarbon radical isomers, studies of the competition between the unimolecular reactions of the isomerically selected radicals as a function of internal energy in the radical.

The experiment was carried out in a crossed laser-molecular beam apparatus (End Station I) at the Berkeley Advanced Light Source (ALS),[8] detecting the products with tunable vacuum ultraviolet photoionization 15.2 cm from the crossing of the laser and molecular beam. A full report will appear elsewhere.[9] The photofragment translational spectroscopy method used to investigate the photolysis channels producing the 2-propenyl radicals is similar to prior work on vinyl chloride,[10] except the laser energy was 10 mJ/pulse and the 2-chloropropene beam was produced by a pulsed expansion of a 10% mixture in He through a 1.0 mm diameter orifice heated to near 150 °C. This is the first report of resolving the internal energy dependence of the product branching from a high-energy isomer of a radical in its ground electronic state.

We generate the 2-propenyl radicals in the gas phase under collisionless conditions by photodissociating 2-chloropropene at 193.3 nm. Fission of the C−Cl bond generates the 2-propenyl

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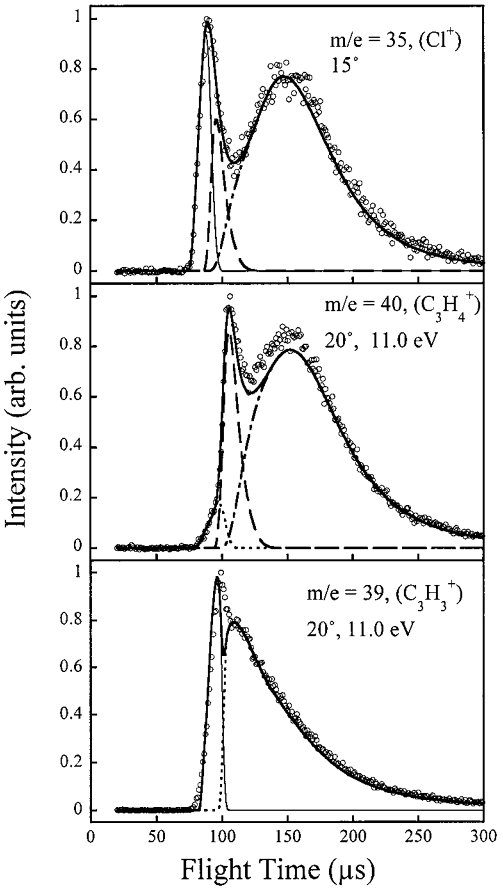

Figure 1. TOF spectra of the Cl atoms from the photolytic precursor to the 2-propenyl radicals (top), the mass 40 (allene/propyne) products at a 20° source angle and 11.0 eV photoionization energy (middle), and the mass 39 products from secondary dissociation of the allene/propyne from HCl elimination in the precursor (bottom). (The bottom frame also includes a daughter ion from the stable mass 41 product from C−Cl fission.) In the middle frame, the predicted arrival times of dissociation products from the low internal energy 2-propenyl radicals from C−Cl fission are shown with dashed line and those from the higher internal energy radicals in dot-dashed line. Both are calculated from the Cl atoms momentum-matched to the radicals that dissociated to give those products, assuming that C−H fission in the radical does not significantly alter the velocity of the mass 40 product from the parent radical's velocity. Thick solid lines in all three spectra are the total fit. The thin solid line in the Cl atom TOF in the top frame and the mass 39 TOF in the bottom frame show the arrival times of the stable 2-propenyl radicals as determined by the mass 41 TOF not shown. To determine the contribution of the stable allene/propyne (dotted line, middle frame) from HCl elimination in the precursor, we used the total $P(E_T)$ derived from the HCl product TOF spectrum (not shown), but first subtracted from it the lower energy portion that we estimated gave allene/propyne unstable to secondary dissociation. We estimated what part of the HCl $P(E_T)$ should be attributed to lower energy portion that produced allene/propyne with enough internal energy to undergo secondary dissociation by fitting the arrival times of the propargyl radicals (dotted line, bottom frame).

radicals with a distribution of internal energies, but radicals with larger internal energies have smaller recoil velocities, so we can disperse both the stable and unstable radicals by the velocity imparted in the photolysis step.[11] We measure the time-of-flight (TOF) spectrum of the Cl atom product from the primary photolysis (Figure 1, top frame) to determine the distribution of energies partitioned to product translation and, by energy conservation,[11] the distribution of internal energies in the nascent 2-propenyl radicals produced. Roughly half of the radicals are produced without enough internal energy to undergo C−H bond fission and so are detected at mass 41. The other half, divided

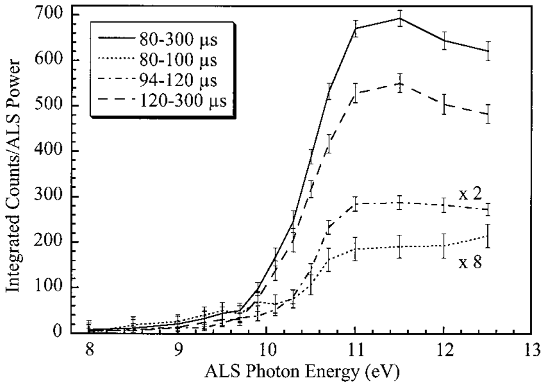

Figure 2. Photoionization efficiency curves for mass 40 products.

almost equally between a group with median internal energy about 3 kcal mol^{-1} above the barrier to H + propyne and a group with higher median internal energy near 15 kcal mol^{-1} above the barrier to H + propyne, can undergo C−H fission to form either allene (eq 1) or propyne (eq 2). The heats of formation of allene and propyne differ only by 1.7 kcal mol^{-1} and the barriers to the reverse reactions are small, so reasoning based on relative barrier heights alone leads one to expect a near equal yield of each from the dissociation of the higher internal energy radicals. (Dissociation of the group of radicals with the lower median internal energy is expected to be sensitive to the small barrier height difference, and so should result in primarily propyne + H.) We can identify the products from the dissociation of both the low internal energy and the higher internal energy 2-propenyl radicals separately by noting that the time of arrival of the C_3H_4 product should differ little from what the arrival time of the 2-propenyl radical would have been if it had not undergone C−H bond fission. The middle frame of Figure 1 shows what the arrival times of the undissociated 2-propenyl radicals would have been (product from low internal energy radicals in dashed line, product from higher internal energy radicals in dot-dashed line, derived by momentum conservation from the Cl atom spectrum) superimposed on the detected mass 40 C−H bond fission product (open circles) from dissociation of the radicals. We identify the mass 40 product isomer for each group by scanning the energy of the VUV photon used to ionize the product through the ionization energies for allene, 9.69 eV, and propyne, 10.38 eV. Figure 2 shows the photoionization efficiency (PIE) curve for all the signal in the mass 40 spectrum and three partial curves which integrate the signal over narrower time windows. The dashed curve in Figure 2 integrates signal over the arrival times of the C_3H_4 products from the dissociation of the low internal energy 2-propenyl radicals and the dot-dashed over the products from the higher internal energy radicals. The similarity of these two partial PIE curves to that of propyne indicates that both the low and high internal energy 2-propenyl radicals undergo C−H bond fission predominantly via fission at the vinylic C−H bond, eq 2, rather than via cleavage of the methyl C−H bond, eq 1. (The spectrum in the middle frame in Figure 1 also shows a contribution in dotted line at the fastest arrival times from mass 40 products from HCl elimination in the photolytic precursor. Many of the mass 40 products from HCl elimination are lost to secondary dissociation, yielding primarily H + propargyl (Figure 1, bottom frame).)[12] However, because some of the stable mass 40 products from HCl elimination underlie the mass 40 from dissociation of the 2-propenyl radical, note that our branching analysis below assumes that propyne and allene from the HCl elimination channels are equally likely to be formed with enough internal energy to undergo secondary dissociation.)

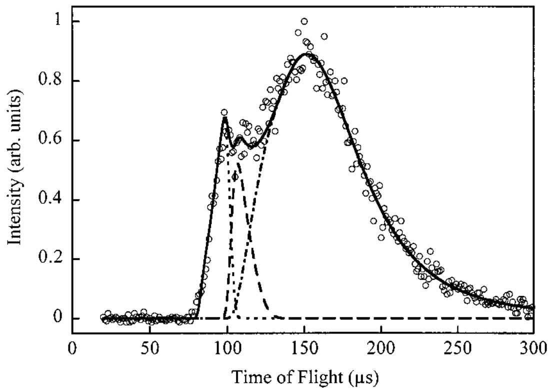

Figure 3. TOF spectrum of the mass 40 (allene) products from the unimolecular dissocation of 2-propenyl radicals. The data were taken at a 20° source angle and 10.0 eV photoionization energy with narrow (2.2%) ALS bandwidth. The arrival times of allene from the unimolecular dissociation of the low internal energy 2-propenyl radicals from C−Cl fission is shown in short-dashed line (calculated from the $P(E_T)$ in short-dashed line in Figure 4) and from the higher internal energy radicals in dot-dashed line. The dotted line contribution is from stable but vibrationally excited allene/propyne from HCl elimination.

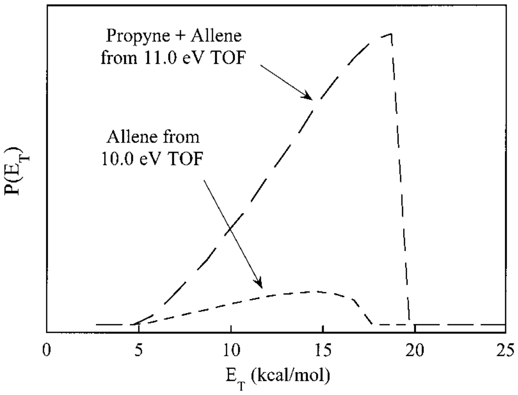

Figure 4. The partial $P(E_T)$ shown in short-dashed line, our prediction for the distribution of radicals that dissociated to allene products, adequately fits the partial TOF spectrum of the mass 40 (allene) products at 10.0 eV photoionization energy in Figure 3, while using a constant fraction of the overall distribution of radicals produced from the precursor photolysis (long-dashed line) in this energy range does not. The partial $P(E_T)$ was calculated assuming that the branching to the H + allene channel depends on the internal energy in the radical as predicted with RRKM calculations.

To get a quantitative measure of how the branching between the H + propyne versus H + allene products changes as a function of internal energy in the radical, we retook the spectrum in the middle frame of Figure 1 at a 10.0 eV photoionization energy in order to detect only the allene products. The 10 eV spectrum is shown in Figure 3. The ratio of mass 40 products (corrected for kinematic factors) from C−H fission from the group of lower internal energy radicals (dashed line) to the group of higher internal energy radicals (dot-dashed line) changed from 0.84 in the 11 eV spectrum to 0.42 in the 10.0 eV spectrum where only allene products are detected. Thus the quantum yield of allene in the C−H bond fission reaction is 2.0 (+0.05/−0.15) times higher for the higher internal energy radicals. This is in very good agreement with the change in branching as a function of internal energy predicted from RRKM calculations[13] (see below). Taking the yield of allene in C−H bond fission processes from the lower internal energy radicals to be 10.3(±2)% (estimated with RRKM theory, see below), the experimental yield of allene from the higher internal energy radicals deduced from how the relative signal intensities changed is then $\phi_1 = 21(\pm 4)\%$. Fitting the 10 eV spectrum in Figure 3 also shows that one can resolve the internal energy dependence of the product branching even within the distribution of radicals produced with energies ranging from 0 kcal to 10 kcal mol^{-1} above the H + propyne C−H bond fission barrier. Figure 4 shows the translational energy distribution (short-dashed line) of the 2-propenyl radicals that should dissociate to H + allene derived from weighting the number of radicals produced photolytically (long-dashed line) at each internal energy (also shown in Figure 4, and derived from the Cl atom TOF spectrum) with the $k_1/(k_1 + k_2)$ ratio of RRKM rate constants[13] for each channel. To identify which kinetic energy release produces radicals with an internal energy just above the barrier to H + propyne, we use the arrival time of the fastest mass 40 product from C−Cl fission in the precursor. We thus identify 18.4 kcal mol^{-1} in kinetic energy as producing 2-propenyl radicals with internal energies at the barrier to propyne + H. (This should be roughly interpreted as 2-propenyl radicals from the most probable internal energy in the photolytic precursor. At the nozzle temperature used, the mean internal energy in the precursor is 1.2 kcal mol^{-1}, so significant dissociation is expected to be observed, and is, for radicals from photolysis events that partitioned a kcal mol^{-1} more into kinetic energy. Our energy resolution is thus about 3 kcal mol^{-1}.) Comparing the fits to the 10 eV spectrum shows that using the RRKM prediction for how the branching to the H + allene channel changes with internal energy to predict the $P(E_T)$, short dashed line in Figure 4, of the radicals that dissociated to H + allene gives the good fit to the spectrum shown in short-dashed line in Figure 3, while using a branching ratio that is constant to internal energies 10 kcal mol^{-1} above the barrier gives an obviously bad fit between 100 and 120 μs. Thus it is clearly experimentally determined that the barrier to H + allene is slightly higher than that to H + propyne, in agreement with recent G2(B3LYP) calculations.[2]

The experiments revealed that 2-propenyl radicals undergo C−H fission preferentially at the vinylic H, not the methyl H, despite similar endothermicities. A simple model qualitatively rationalizes the observed selectivity. Of the two nearly isoenergetic reactions, the one that occurred is the one that did not require losing a free internal rotation of a methyl group. If the 2-propenyl radical undergoes C−H fission at the methyl H, the molecule loses a free internal rotation as the allene double bond develops, while in the H + propyne channel it does not. One can use RRKM theory[1,13] to obtain a more quantitative prediction of how the branching between the H + allene and H + propyne channels changes as a function of internal energy in the 2-propenyl radical. We use the frequencies of the radical and transition state complexes and relevant moments of inertia[14] calculated by Davis, Law, and Wang[2] to calculate RRKM rate constants for the reactions in eqs 1 and 2. Because the zero-point-corrected barrier to reaction 1, 38.1 kcal mol^{-1}, is 1 kcal mol^{-1} higher than the barrier to reaction 2, we expect the group of dissociating 2-propenyl radicals with the lower internal energies to favor propyne products for barrier energy reasons alone. This expectation is borne out by fitting the 10 eV TOF spectrum, which reveals the internal energy dependence of the product branching even within the low internal energy group of dissociating radical as shown in Figures 3 and 4. However, even for the higher internal energy radicals, propyne formation dominates. Experimentally, we found that the quantum yield of allene from the higher internal energy group of radicals, with median internal energy 15 kcal mol^{-1} above the H + propyne barrier, is 2.0 (+0.05/−0.15) times higher than the quantum yield of allene from the lower internal energy group of radicals. The RRKM calculations, appropriately averaged over the internal energy distributions for the two groups of radicals, adequately predict the observed change in branching, predicting a ratio of 2.2. Calibrating the experimental yield for the higher internal energy group of radicals with the RRKM yield predicted for the lower internal energy radicals, we find experimentally that only 21% of the 2-propenyl radicals with median internal energy kcal mol^{-1} above the barrier to H + propyne give H + allene products. Because the barriers to the two dissociation channels are similar, any attempt to predict the outcome of the experiment based on relative barrier heights or endothermicities alone would not give the observed preference for propyne + H products at these higher internal energies. The preference for the H + propyne products in this system is thus a nice example of the general effect on rate constants from the tightening of the transition state when a methyl rotor is frozen.

These experimental results are particularly exciting as they show one can investigate the unimolecular dissociation channels of a selected high-energy radical isomer. Identifying the internal energy of the radical that resulted in a particular product relies on the velocity of the product not being significantly altered from that of the radical parent, as is the case for C−H fission in the radical. While we showed here that the 2-propenyl radical dissociates primarily to propyne + H, with the fraction of the minor H + allene channel increasing with increasing internal energy, the unimolecular dissociation of the lowest energy C_3H_5 isomer, the allyl radical, is quite different.[2−7] That radical should form exclusively H + allene at the lowest dissociative internal energies if recent calculations[2,5] of the isomerization barrier to 2-propenyl radical is correct. Likewise, a yet higher-energy C_3H_5 radical, the 1-propenyl radical, should undergo primarily C−C bond fission at the lowest dissociative internal energies. We are pursuing those experiments now with the same experimental technique pioneered here.

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