Velocity Map Imaging Study of Ion–Radical Chemistry: Charge Transfer and Carbon–Carbon Bond Formation in the Reactions of Allyl Radicals with C⁺

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Supporting Information

ABSTRACT: We present an experimental and computational study of the dynamics of collisions of ground state carbon cations with allyl radicals, C₃H₅⁺, at a collision energy of 2.2 eV. Charge transfer to produce the allyl cation, C₃H₅⁺⁺, is exoergic by 3.08 eV and proceeds via energy resonance such that the electron transfer occurs without a significant change in nuclear velocities. The products have sufficient energy to undergo the dissociation process C₃H₅⁺⁺ → C₂H₄⁺⁺ + H. Approximately 80% of the reaction products are ascribed to charge transfer, with ~40% of those products decaying via loss of a hydrogen atom. We also observe products arising from the formation of new carbon–carbon bonds. The experimental velocity space flux distributions for the four-carbon products are symmetric about the centroid of the reactants, providing direct evidence that the products are mediated by formation of a C₄H₃⁺⁺ complex living at least a few rotational periods. The primary four-carbon reaction products are formed by elimination of molecular hydrogen from the C₃H₅⁺⁺ complex. More than 75% of the nascent C₄H₃⁺⁺ products decay by C–H bond cleavage to yield a C₄H₂⁺⁺ species. Quantum chemical calculations at the MP2/6-311+g(d,p) level of theory support the formation of a nonplanar cyclic C₄H₅⁺⁺ adduct that is produced when the p-orbital containing the unpaired electron on C⁺ overlaps with the unpaired spin density on the terminal carbon atoms in allyl. Product formation then occurs by 1,2-elimination of molecular hydrogen from the cyclic intermediate to form a planar cyclic C₄H₃⁺⁺ product. The large rearrangement in geometry as the C₄H₃⁺⁺ products are formed is consistent with high vibrational excitation in that product and supports the observation that the majority of those products decay to form the C₄H₂⁺⁺ species.

INTRODUCTION

The study of reactions of ions with stable atoms and molecules occupies an important position in the field of chemical dynamics, devoted to answering the question “Where does the energy go in a chemical reaction?” The quest to understand how chemical reactions occur at the level of the underlying potential energy surface is characterized by the conflicting requirements of more precise specification of the initial conditions of an experiment, i.e., reactant quantum state preparation and product detection, and a desire to expand the chemical diversity of species probed at this level of sophistication. The velocity map imaging (VMI) method has begun to play an important role in this evolution because the signal levels afforded by the detection of all velocity space elements in a single time window, i.e., multiplex advantage, are compatible with products formed in low concentrations.

The development of a reliable, intense source of free radicals, based on supersonic expansion of gas containing an appropriate radical precursor and subsequent pyrolysis in a heated SiC “afterburner”, has made the study of reactions of free radicals in crossed molecular beams possible. Pioneering crossed beam studies of the reactions of free radicals with open-shell atoms have revealed new patterns of reactivity and dynamical signatures, and the rich chemistry observed has been supported by significant theoretical efforts.

Only recently has the subject of the reactions of ions with free radicals received experimental attention. Russell et al. reported a Fourier transform ion cyclotron resonance study of the reactions of benzyl cation with allyl radicals that provided evidence for the formation of new C–C bonds. Ellison and Bierbaum and their co-workers have measured rates of proton transfer from H₃O⁺ to allyl radicals and benzene diradicals in a SIFT (selected ion flow tube) experiment. Most recently, the Viggiano lab showed that reactions of Ar⁺ and O₂⁺ with CH₃ radicals were dominated by charge transfer, consistent with the low ionization energies of free radicals. A recent publication from our laboratory in which an ion beam was crossed by a beam of free radicals produced by pyrolysis and products were detected by VMI, examined both the proton transfer and charge transfer reaction of H₃⁺ with CH₄. The study reported one of the first probes of energy partitioning in ion–radical reactions, examining not only the ubiquitous...
process of charge transfer but also proton transfer, a process that is often governed by both kinematics and dynamics.\textsuperscript{17}

In an initial attempt to probe the rich chemistry of bond formation reactions that may occur between ions and hydrocarbon-based free radicals, we have examined collisions of the ground state carbon cation with allyl radical in this paper. The specific reactions observed in this study are the following:

\[
\begin{align*}
C^+(3P) + C_3H_5 & \rightarrow C_3H_4^+ + C \quad \Delta H^o = -3.08 \text{ eV} \\
& \rightarrow C_3H_4^+ + H + C \quad \Delta H^o = +0.62 \text{ eV} \\
& \rightarrow c-C_4H_3^+ + H_2 \quad \Delta H^o = -7.20 \text{ eV} \\
& \rightarrow n-C_4H_3^+ + H_2 \quad \Delta H^o = -7.49 \text{ eV} \\
& \rightarrow c-C_4H_2^+ + H + H_2 \quad \Delta H^o = -1.91 \text{ eV} \\
& \rightarrow n-C_4H_2^+ + H + H_2 \quad \Delta H^o = -3.55 \text{ eV}
\end{align*}
\]

Both charge transfer and carbon–carbon bond formation processes occur, each of which forms products with sufficient internal energy to cleave a C–H bond in the most highly internally excited parent ions. The reaction exoergicity for (1) is calculated from standard enthalpies of formation taken from the literature.\textsuperscript{18} The reaction exoergicities for (2), (3a,b), and (4a,b) are estimated from \textit{ab initio} calculations described in a later section of this paper. The prefixes \textit{c} and \textit{n} denote cyclic and open-chain products, respectively.

\section*{EXPERIMENTAL METHOD}

The crossed beam experimental arrangement has been described in our previous publications.\textsuperscript{19,20} The charged and neutral reactant beams intersect in a grounded region of space electrostatically shielded by electrodes with a cylindrical “curtain” design similar to that described by Wester and co-workers.\textsuperscript{21} Reaction products are ejected from the collision volume by a short electrical pulse that initiates the VMI detection process. A series of aperture lenses held at appropriate potentials provides the electrostatic fields that satisfy the velocity mapping condition and correct for the chromatic aberration that arises from the finite thickness of the collision volume. The products travel along a 0.6 m drift space, strike a pair of microchannel plates (MCPs) mounted in a chevron configuration, and produce an image that is displayed on a phosphor screen. The MCPs are gated with an appropriately delayed pulse that is correlated with the flight time of product ions. A charge-coupled device (CCD) camera records this image and sends the digital output to a laboratory computer via a USB interface. The shielded volume in which the beams intersect is maintained at a pressure \(2 \times 10^{-7} \text{ Torr}\) with both beams running. The ion detector is differentially pumped with a turbomolecular pump.

The free radical source is based on the afterburner design described above. A pulsed solenoid valve injects a 1\% mixture of 1,5-hexadiene (Aldrich) in He carrier gas at a total pressure of 3 atm into a 1 mm diameter SiC tube 25 mm in length heated by 45 W of dc power. The flow from the pyrolysis region is sonic under these operating conditions.\textsuperscript{22} Experiments were carried out to ensure that all product ions were formed from \(\text{C}_3\text{H}_5\) radicals produced pyrolytically rather than from undissociated precursor species. The internal temperature of the allyl radicals is estimated to be approximately 500 ± 100 K, on the basis of results from a recent synchrotron radiation study of the threshold photoelectron spectroscopy of radicals produced from a continuous pyrolytic source with similar heating parameters.\textsuperscript{23} The internal energy contribution to the system from the radical beam is thus considered to be small, on the order of 0.05 eV, consistent with the results of crossed beam studies of allyl radicals with oxygen atoms.\textsuperscript{5}

The ion beam is produced by electron impact on a 10\% mixture of CO in He in the ion source described in the literature,\textsuperscript{24} and employed in previous studies from our lab.\textsuperscript{19,20} This method is known to produce carbon cations in the ground (\(3P\)) electronic state with excited state contamination below 1\%.\textsuperscript{25,26} The ion beam is extracted from the source and is momentum-analyzed, focused, and decelerated to its terminal energy at the collision center, which is maintained at ground potential as described previously. The energy width of the ion beam is \(\sim 0.2 \text{ eV}\) full width half-maximum (fwhm).

\section*{RESULTS}

Velocity map images for all products are determined as described in previous publications.\textsuperscript{19,20} Figure 1 shows raw velocity map images for charge transfer (\(m/e = 41\)) and dissociative charge transfer (\(m/e = 40\)) products, reactions 1 and 2, at a collision energy of 2.2 eV. Figure 2 shows the ion...
result is consistent with the preeminence of charge transfer as a major channel in much of gas phase ion chemistry. Approximately 40% of the nascent charge transfer products dissociate to form C4H3+ + H2, consistent with the fact that nearly 6 eV is accessible to the C4H3+ product. Perhaps more surprising is the fact that of the remaining reaction products formed by carbon–carbon bond formation, only ~20% of those products survive as C4H3+.

The Cartesian flux profiles shown in Figures 1 and 2 were processed by inverse Abel transformation to extract proper product velocity and kinetic energy distributions. We have employed the BASEX program\textsuperscript{18} for this purpose. The transformed data may then be expressed in barycentric polar coordinates \( u \) and \( \theta \), given by the following expressions:

\[
u = (u_x^2 + u_y^2)^{1/2}
\]
\[
\theta = \tan^{-1}(u_y/u_x)
\]

The relationship between Cartesian and polar flux intensity is then simply found from the following relationship:

\[
I_{\text{pol}}(u, \theta) = u^2 P(u_x, u_y)
\]

Product angular and kinetic energy distributions are computed by integrating the flux distributions over recoil speed and scattering angle, respectively. The angle-averaged relative translational energy distribution of products, \( P(E_t') \), is given by the following expression:

\[
\langle P(E_t') \rangle_\theta = \int_0^{\pi} d\theta \sin \theta u P(u_x, u_y)
\]

Integration over specific angular regions provides a means to assess how energy disposal may depend on scattering angle. Even in the case of a collision complex that lives at least several rotational periods, one might expect the angular distribution to be coupled to the recoil energy distribution, especially when hydrogen atoms are ejected, but the quality of the data reported here are insufficient to justify such an analysis.

The total energy accessible to the reaction products is defined as

\[
E_{\text{total}} = E_T + E_{\text{int}} - \Delta H
\]

where \( E_T \) is the initial relative kinetic energy, \( E_{\text{int}} \) is the total internal energy of the reactants, and \( \Delta H \) is reaction exoergicity. As we noted earlier, the neutral reactants are formed with relatively low internal energy below 0.1 eV.\textsuperscript{5}

The product kinetic energy distributions for the charge transfer processes (1) and (2) are shown in Figure 3, and Figure 4 shows the corresponding distributions for the carbon–carbon bond formation processes (3a,b) and (4a,b). Apparent structure in the distributions is within the error limits shown on the figures, reflective of the low signal levels in these experiments. The red curves shown in the plots are simply to guide the eye. The kinetic energy distributions for charge transfer are consistent with electron transfer occurring on a time scale sufficiently short that the velocities of the C3H5+ reactants and C4H3+ products are the same. The distributions for carbon–carbon bond formation are strongly peaked at low kinetic energy, consistent with disposal of a small fraction of the available energy into product translation. The kinetic energy distributions for the primary C4H3+ products resemble those for the dissociation products C4H3+ + H, although less total energy is accessible to the latter products. This fact is reflected in the

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**Figure 2.** Top panel: velocity map image for C3H5+ bond formation products at a collision energy of 2.2 eV. The kinematic Newton diagram appropriate for this collision energy is superimposed on the image. The circle describes the maximum C3H5+ product center of mass speed allowed by the total available energy, the sum of collision energy and reaction endoergicity. Bottom panel: same as above, for C4H3+ bond formation products at a collision energy of 2.2 eV.
Formation of \( \text{C}_4\text{H}_2^+ + \text{H}_2 + \text{H} \) is a three-body process. We have estimated the kinetic energy for formation of the \( \text{C}_4\text{H}_2^+ \) product shown in Figure 4b by assuming that this product is formed by ejection of a hydrogen atom from the \( \text{C}_4\text{H}_3^+ \) product with small kinetic energy. Thus, the velocity of the nascent \( \text{C}_4\text{H}_2^+ \) product is essentially equal to that of the parent \( \text{C}_4\text{H}_3^+ \) precursor. This procedure is well-established and has been validated in the literature.\(^{29–31}\)

**COMPUTATIONAL STUDIES**

The experimental velocity map image for the formation of the \( \text{C}_4\text{H}_3^+ \) product is symmetric with respect to the centroid of the collision system, providing evidence that the approaching reactants form a long-lived \( \text{C}_4\text{H}_3^+ \) reactive intermediate from which product formation occurs by ejection of two hydrogen atoms. Computations described in this section will show that that spin-allowed elimination of molecular hydrogen is likely the preferred route for \( \text{C}_4\text{H}_3^+ \) production. The nature of the interaction of the \( \text{C}^+(2\text{P}) \) reactant with the \( \pi \)-type molecular orbitals of the allyl radical provides qualitative justification for the role of a \( \text{C}_4\text{H}_5^+ \) intermediate living at least a few rotational periods and formed by the approaching reactants. The singly occupied molecular orbital (SOMO) of allyl is nonbonding, with a node on the central carbon atom and out-of-phase \( p \)-orbitals on the terminal carbon atoms. The incoming \( \text{C}^+ \) reactant may approach the allyl radical perpendicular to the plane of the carbon atoms, and overlap of the wave function for the single 2p-electron on \( \text{C}^+ \) with the SOMO produces a nonplanar cyclobutyl ring system.

This simple picture may be justified with rigorous calculations. A computational study of nine isomers of \( \text{C}_4\text{H}_5^+ \) reported by Cunje et al.\(^{32}\) has identified a number of isomerization pathways among linear and cyclic structures and offers us a starting point for understanding possible routes to \( \text{C}_4\text{H}_3^+ \) products from a \( \text{C}_4\text{H}_5^+ \) structure assembled from the reactants. Our calculations, performed via the MP2 method with the 6-11+g(d,p) basis set in Gaussian 03,\(^{33}\) produced structures of reactants, products, reactive intermediates, and transition states connecting selected \( \text{C}_4\text{H}_3^+ \) intermediates. An intrinsic reaction coordinate (IRC) calculation for each transition state (TS) verified that the TS in question connected the appropriate intermediates. Details of the structures obtained by the computations are reported in the Supporting Information for this article.

A potential energy surface scan showed, as expected, that the preferred carbon cation approach is perpendicular to the plane defined by the three carbon atoms of the allyl radical, with the \( \text{C}^+ \) \( p \)-orbital oriented in a plane parallel to the allylic framework. This approach geometry allows the electron density on the carbon cation to overlap the unpaired spin densities on the terminal carbon atoms of allyl, forming a four-membered ring. This species corresponds to structure 13 of Cunje et al.\(^{32}\). The carbon atom framework of this intermediate is non-coplanar, forming a butterfly-shaped structure. The calculations also showed that the carbon cation does not attack the unpaired spin density presented by a terminal carbon on allyl to produce an open-chain intermediate.

Figure 5 summarizes the results of these \textit{ab initio} calculations, as detailed in the Supporting Information. Figure 5a shows the formation pathway for the cyclic isomer of \( \text{C}_4\text{H}_3^+ \). Figure 5b illustrates the pathway for forming open-chain \( \text{C}_4\text{H}_3^+ \) products. The terminal carbon atoms of the allyl radical are labeled \( \text{C}_1 \) and \( \text{C}_2 \), the central carbon is denoted \( \text{C}_0 \), and the approaching images shown in Figure 2, where the velocity space circle defining the maximum speed for the \( \text{C}_4\text{H}_2^+ \) products is smaller than for \( \text{C}_4\text{H}_3^+ \) products. However, the images for both products fall cleanly within the circles defining the respective thermodynamic limits, whether the products are cyclic or open chain. Kinetic energy release data alone are insufficient to distinguish between these two isomeric forms.
A recent study of the photoelectron spectra of neutral C4H5+ radicals32 demonstrated that C4H5+ ions may exist as open-chain isomers in addition to the cyclic species identified by Cunje et al.32 This observation motivated us to search for reactive pathways between C+ and allyl radicals that form open-chain products and result in elimination of hydrogen atoms or molecules.

The calculations revealed that the cyclic intermediate IM1 may also undergo a series of rearrangements that ultimately leads to a linear isomer of C4H3+. Figure 5b illustrates the processes involved. Attack of C4 on C2, with an activation barrier of 0.44 eV, followed by cleavage of the C4−C1 bond produces an intermediate IM2 that is best described as a distorted methylene cyclopropane ring system. The C2−C3 bond, which is abnormally long in IM2, 1.71 Å, ultimately cleaves over a small barrier (∼0.08 eV) to form an open-chain intermediate, denoted IM3, that lies nearly 3 eV below IM1 and IM2 and is the lowest energy structure in the pathway for producing open-chain products. Hydrogen atom migration in IM3 from C2 to C1 over a 1.53 eV barrier forms IM4, which corresponds to structure 4 in the work of Cunje et al.32 The calculations indicate that 1,4-elimination of H2 over a 3.68 eV barrier leads to the linear H2CCCCH isomer of C4H3+. This product is ∼0.9 eV more stable than the cyclic C4H3+ product, but the long sequence of rearrangements that precedes its formation, with the tight transition state associated with the high barrier for H2 elimination, suggests that this pathway is significantly less probable than simple elimination of H2 from IM1.

In support of this hypothesis, rate constants for isomerization of selected intermediates that control the branching between cyclic and open-chain C4H3+ products were computed with the statistical Rice–Ramsperger–Kassel–Marcus prescription35 using the vibrational frequencies for the relevant intermediates and transition states connecting them. At the total energy available to nascent products, the rate of passage over the barrier controlling 1,4-elimination of molecular hydrogen across the C1−C4 bond in IM4 is ∼1011 s−1, approximately an order of magnitude slower than the 1,2-elimination of H2 from IM1 to form cyclic products. This information provides a strong argument that the most likely isomer of C4H3+ formed in the present experiments is the cyclic product. The results of these rate constant calculations are reported in the Supporting Information.

**DISCUSSION**

This study of a prototype ion–radical reaction has revealed that charge transfer is a dominant reactive pathway in such systems. However, a significant fraction, nearly 40%, of those products are formed with sufficient internal energy to result in dissociation by C−H bond cleavage. As is often observed in charge transfer processes, the electron transfer occurs on a very short time scale and at long range, resulting in energy resonance, in which the relative kinetic energies of reactant and products are unchanged.

The present study also shows that new chemical bonds, specifically new carbon–carbon bonds, may be formed, and 20% of the reaction products are formed this way. Qualitatively, the fact that the SOMO of allyl has the same b1 symmetry as the p-orbital of C+, suggests that the formation of a four-membered ring intermediate occurs with reasonable cross section. *Ab initio* calculations confirm this picture and suggest that elimination of molecular hydrogen from this cyclic
intermediate is a plausible route for formation of the \( \text{C}_4\text{H}_3^+ \) products. This conclusion is bolstered by statistical rate constant calculations showing that the cyclic product is formed at least an order of magnitude more rapidly than the open-chain product.

It has been established that 1,2-elimination of \( \text{H}_2 \) from chemically activated ions often results in significant kinetic energy,\(^{16}\) consistent with results reported here. In reactions 3a and 3a, the energy available to products is over 10 eV, and although the most probable kinetic energy release is observed to be \( \sim 1 \text{ eV} \), product recoil distribution is quite broad and is compatible with a significant fraction of products carrying away energy in translation. We have noted that the formation of open-chain isomers of \( \text{C}_4\text{H}_3^+ \), shown in Figure 5b, occurs over an even larger barrier. The 1,4-elimination process requires nearly 4 eV of energy and results in an exit channel barrier of almost 2 eV. Although we have commented that the tight transition state associated with this barrier limits the rate of the open-chain isomer, a small contribution from this product may contribute to the width of the kinetic energy distribution.

Despite the large width of the kinetic energy distribution, the most probable four-carbon products are highly internally excited and undergo dissociation by \( \text{C}–\text{H} \) bond cleavage. The dramatic change in geometry as the nonplanar cyclic \( \text{C}_4\text{H}_3^+ \) product eliminates \( \text{H}_2 \) and forms planar \( \text{C}_4\text{H}_4^+ \) results in a large amount of internal excitation in the ring, which, via rapid intramolecular vibrational redistribution, results in significant \( \text{C}–\text{H} \) bond cleavage. In the present case, the majority (\( \sim 80\% \)) of the nascent four-carbon products undergo dissociation. Not only does the large energy available to the products contribute to this high level of dissociation, but also the likely partitioning of this energy in internal excitation of the nascent products, revealed by the \textit{ab initio} calculations as a plausible mechanism for such high vibrational excitation, is critical to understanding the decay dynamics.

\section*{CONCLUSIONS}

The present study demonstrates that the reactions of ions with free radicals add to the richness of ion–neutral chemistry. In conjunction with charge transfer reactions that are of special importance in this class of reactions because of the low ionization potentials of free radicals, bond formation reactions of the type reported here may play an important role in ionic systems.

These low signal level experiments have been made possible by the VMI detection method, and their interpretation has been facilitated by quantum chemical calculations of the structures of key reactive intermediates. Additional experimental studies, supported with \textit{ab initio} calculations of the structures of important intermediates and the transition states that connect them, now appear to be feasible, and we look forward to learning new lessons in chemical reactivity as a consequence.

\section*{ASSOCIATED CONTENT}

\textbf{Supporting Information}
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b05699. Computed structures and energies of reaction products, intermediates, and transition states; energy dependent rate constants for isomerizations of reactive intermediates through appropriate transition states (PDF)

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\textbf{Notes}

The authors declare no competing financial interest.

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\section*{REFERENCES}


(4) Guo, Y.; Mebel, A. M.; Zhang, F.; Gu, X.; Kaiser, R. I. Crossed Molecular Beam Studies of the Reactions of Allyl Radicals, \( \text{C}_3\text{H}_4(X^1\text{A}_1) \) With Methylacetylene (\( \text{CH}_3\text{CCH}(X^1\text{A}_1) \)), Allene (\( \text{H}_2\text{CCCH}(X^1\text{A}_1) \)), and Their Isotopomers. J. Phys. Chem. A 2007, 111, 4914–4921.


