

Formation of astrochemically relevant molecular ions: Reaction of translationally cold CCl^+ with benzene in a linear ion trap

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(Received 26 August 2021; accepted 19 January 2022; published 3 February 2022)

The gas-phase ion-neutral reaction of CCl^+ + benzene (C_6H_6) is investigated using a linear Paul ion trap coupled to a time-of-flight mass spectrometer. Low collision energies are achieved by sympathetically cooling CCl^+ reactant ions with cotrapped laser-cooled Ca^+ . The observed products include the astrochemically relevant carbocations C_7H_5^+ , C_5H_3^+ , and C_3H_3^+ , as well as $\text{C}_3\text{H}_2\text{Cl}^+$. Branching ratios of these products are measured, and C_7H_5^+ , a carbon-growth species, is favored. Complementary electronic structure calculations provide thermodynamic limits for the reaction and allow for assignment of reaction products to specific structural isomers. Only one exoergic isomer is identified for each observed product with the exception of C_7H_5^+ where many identified structural isomers are exoergic. The results from this Letter broaden our understanding of the reactivity and possible role of CCl^+ and C_6H_6 in interstellar chemistry. Furthermore, this Letter provides insight into a potential pathway to larger carbocations that may be precursors to more complex polycyclic aromatic hydrocarbons.

DOI: [10.1103/PhysRevA.105.L020801](https://doi.org/10.1103/PhysRevA.105.L020801)

Rich chemistry takes place in regions that we still know relatively little about, such as areas of the interstellar medium (ISM) and planetary atmospheres. This chemistry is slowly being understood through a multidisciplinary effort focused on laboratory and theoretical studies as well as physical measurements from new space exploration missions [1–13]. Within this larger effort, ion-neutral reactions have been identified as requiring more experimental exploration especially at lower temperatures [4]. This is because ion-neutral reactions are known to have much faster rates than neutral-neutral reactions and, thus, are predicted to have a more prominent role in the chemistry present in these remote areas [4,14]. Of particular interest are the ion-neutral reaction pathways that lead to carbon molecular weight growth and perhaps to polycyclic aromatic hydrocarbons (PAHs). Interest in PAHs is fueled by their ubiquity in, and importance to, the chemistry of many regions of the ISM [5,15–21]. Interest has also been due to speculation that PAHs could be the carriers for the diffuse interstellar bands, the mostly unidentified absorption features seen towards reddened stars and other extraterrestrial objects [5,13]. Only C_{60}^+ has been confirmed as a carrier, but the PAH hypothesis has fueled many spectroscopic and kinetic studies of potential PAH carriers and formation reactions [5,10,13]. The spectroscopy of several PAHs has been well understood, but it remains to be demonstrated exactly how they form. A promising pathway involves additions of small ions to small aromatics (including benzene) [1,4–7,12,14]. Much work remains to investigate reactions within this category before a clear picture of this process can emerge. This requires exploration of candidate reactions to define their dynamics and potential role in such a process. Controlled, low-temperature and pressure terrestrial kinetics and dynamics experiments

can reproduce the conditions of the remote areas of the ISM and beyond, providing a clearer understanding of the complex reaction pathways and mechanisms in these environments.

Here, we report on the ion-neutral reaction of CCl^+ + C_6H_6 , measured in a low-temperature and pressure regime. C_6H_6 has been identified in the atmosphere of Jupiter, Saturn, and Titan (one of Saturn's moons) [2,3,8,9] and has been tentatively identified in interstellar and circumstellar environments using midinfrared spectroscopy [22,23]. Benzene's participation in ISM chemistry is established, including reactivity with highly abundant atomic species, such as H, O, C, and N^+ [1,24–29]. So far, CCl^+ has not been considered a primary player in interstellar chlorine chemistry because its abundance is uncertain and was thought to be primarily inert to many (but not all) interstellar species [30–34]. Only recently has the reactivity of CCl^+ been illuminated through experimental efforts by our group. Specifically, its reactivity has been demonstrated with astrochemically relevant molecules acetylene and acetonitrile at low collision energies [35,36]. These studies support the hypothesis that CCl^+ has a hitherto underrepresented role in the chemistry that is occurring in the ISM. Potential abundances and plausible locations of CCl^+ are inferred with the aid of measured reactions and rate constants as well as predictions and models of chemistry involving CCl^+ . Thus, we believe CCl^+ to be an important molecule to study, even preceding a definite conclusion regarding its abundance in the ISM. The main ionic products from the reaction presented here include C_7H_5^+ , C_3H_3^+ , C_5H_3^+ , and $\text{C}_3\text{H}_2\text{Cl}^+$ of which C_3H_3^+ has been identified and the rest have been speculated to exist in various areas in the ISM and beyond [2,37–40]. Importantly, the reaction results in a carbon growth pathway that could be consequential to chemistry in the ISM, planetary atmospheres, and other remote areas.

The exploration of cold and controlled reactions is a vibrant and growing field [41–44]. Our experimental apparatus

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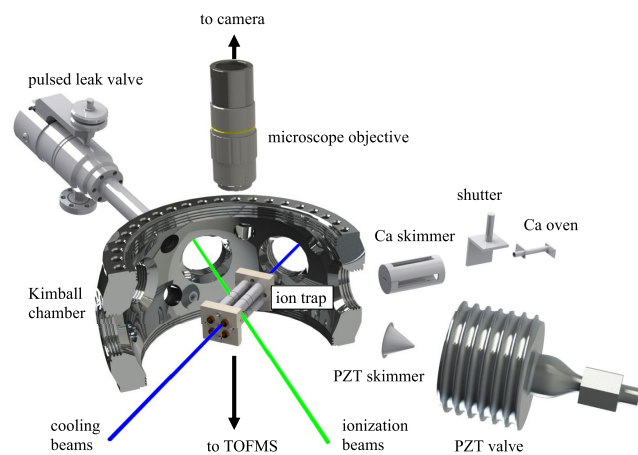


FIG. 1. Schematic of the linear Paul ion trap coupled to a time-of-flight-mass spectrometer (LIT-TOF-MS) used for measuring the reaction of $\text{CCl}^+ + \text{C}_6\text{H}_6$. CCl^+ ions are produced by nonresonant photoionization and sympathetically cooled by the cotrapped laser-cooled Ca^+ . Approximately 2×10^{-10} Torr neutral C_6H_6 (11% in helium, 300 K) is leaked into the vacuum chamber via a pulsed leak valve scheme for a set duration (0, 10, 90, 170, 240, or 320 s). After each reaction step, the resulting ions are then ejected into the TOF-MS, giving highly resolved mass spectra for each time step. Reproduced with permission from Schmid *et al.* Ref. [59]

shown in Fig. 1 allows for the exploration of ion-neutral interactions under cold conditions [45–49]. The setup is composed of a LIT-TOF-MS. While the ultrahigh vacuum environment of the apparatus is denser than the sparsest regions of space, it mimics the single-collision conditions of space in which three-body reactions are extremely unlikely. This apparatus also allows for controlled reactions between translationally cold, trapped ions, and neutral reactant gas over long interrogation times. Low collision energies (here 8 meV or ~ 93 K) are achieved by direct laser cooling of Ca^+ , which sympathetically cools the translational motion of the cotrapped CCl^+ reactant ions. The cold conditions combined with the TOF-MS provide excellent mass resolution enabling clear chemical formula assignments from the resulting mass spectra. The significant energetic constraints on the reaction and identified chemical formulas enable more facile comparison to calculations at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory, allowing for accurate determination of the thermodynamic limits of the reaction (within 0.04 eV). Whereas temperature conditions in the ISM vary widely (from a few Kelvin to 10^6 Kelvin), we aim to understand reactions in the coldest conditions that we can achieve. This combination of experimental and computational tools allows for a clearer view of the chemistry of the important, and yet unexplored, reaction of $\text{CCl}^+ + \text{C}_6\text{H}_6$ under conditions comparable to various remote areas of space.

Kinetic data for the reaction of $\text{CCl}^+ + \text{C}_6\text{H}_6$ are shown in Fig. 2. As the reaction progressed, the majority of the trapped CCl^+ reacted away into four products: C_3H_3^+ (m/z 39), C_5H_3^+ (m/z 63), $\text{C}_3\text{H}_2\text{Cl}^+$ (m/z 73), and C_7H_5^+ (m/z 89). These

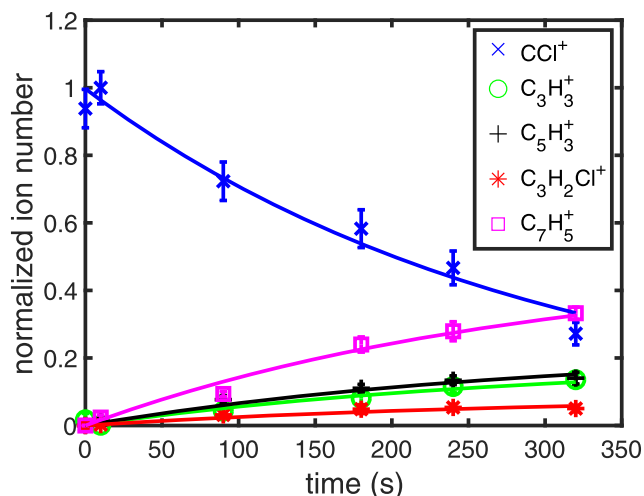


FIG. 2. Rate reaction data (points) and fits (curves) for pseudo-first-order reaction of $\text{CCl}^+ + \text{C}_6\text{H}_6$. CCl^+ (blue \times) reacts with excess C_6H_6 resulting in first-order products C_3H_3^+ (green \circ), C_5H_3^+ (black $+$), $\text{C}_3\text{H}_2\text{Cl}^+$ (red $*$), and C_7H_5^+ (magenta \square).

observed products were used to construct a reaction model in order to fit the reaction data and extract reaction rates and product branching ratios (see Table I). Under our experimental conditions, C_6H_6 is in excess, allowing for the use of a pseudo-first-order kinetic model, which includes a set of differential equations (given in the Supplemental Material (SI) [50]) used to fit the experimentally observed ion numbers as a function of time (resulting fits shown as solid lines in Fig. 2). Notably, in this reaction, the majority of CCl^+ reacted away, although in the time frame of our experiments some remained. This timescale was chosen mainly because the principal focus of the study was to determine the primary products and their branching fractions as opposed to measuring subsequent reactions of the primary products with benzene. The products shown here can be identified as primary products by the profile of the number of ions measured as a function of time. These product ions have the largest growth rate when the CCl^+ numbers are at their greatest, and continue to grow while the CCl^+ is in the trap. This holds true for data taken at early time points as shown in the SI [50]. Additionally, secondary ion products are not detected in the trap, and the total number of ions (summed over products and reactants) does not change over the course of a reaction, which implies that all ion products are detected (Data showing the conservation of ion number during a reaction can be found in the SI [50]).

TABLE I. Branching ratios for the primary products of CCl^+ and C^{37}Cl^+ reacting with C_6H_6 . The numbers are given as percentages and uncertainties are derived from the 90% confidence interval from the pseudo-first-order model fits.

Reactants	C_3H_3^+	C_5H_3^+	$\text{C}_3\text{H}_2\text{Cl}^+$	C_7H_5^+
$\text{CCl}^+ + \text{C}_6\text{H}_6$	19(2)	23(2)	9(1)	49(4)
$\text{C}^{37}\text{Cl}^+ + \text{C}_6\text{H}_6$	24(2)	18(1)	11(1)	46(4)

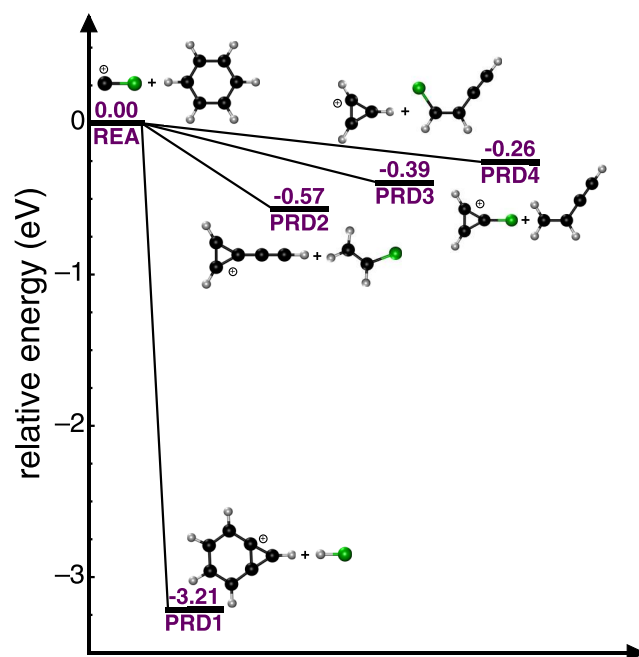


FIG. 3. Energetic limits for the reaction of $\text{CCl}^+ + \text{C}_6\text{H}_6$ going to four different products, $\text{C}_7\text{H}_5^+ + \text{HCl}$, $\text{C}_5\text{H}_3^+ + \text{C}_2\text{H}_3\text{Cl}$, $\text{C}_3\text{H}_2\text{Cl}^+ + \text{C}_4\text{H}_4$, and $\text{C}_3\text{H}_2\text{Cl}^+ + \text{C}_4\text{H}_4$. All products are exoergic with respect to the reactants at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory. The bare “+” denotes infinite distance between the ion-neutral pair and the inscribed “+” symbol corresponds to the ion of the ion-neutral pair.

Kinetic data for the reaction of $\text{C}^{37}\text{Cl}^+ + \text{C}_6\text{H}_6$ was also measured (see the SI [50] for reaction curves), and this reaction was used as a mechanism for the identification of chlorinated products in order to refine molecular formula assignments. Indeed, only one observed mass product changed when the heavier C^{37}Cl^+ was used, $m/z\ 73 \rightarrow 75$, confirming its assignment as $\text{C}_3\text{H}_2\text{Cl}^+$. Overall, we can be certain that the products were composed only of the atoms in the reactants (that is, C, H, or Cl) because we begin our reactions with a clean sample of either CCl^+ or C^{37}Cl^+ (see methods section in the SI [50] for details). Product assignments are further supported by computational modeling discussed below. Although it is not the focus of the current Letter, it should be noted that the rate of reaction for C^{37}Cl^+ is twice as fast as that for CCl^+ , indicating that a kinetic isotope effect may be at play here, driving the faster rate.

Branching ratios for each of the observed products were obtained by dividing the separate product growth rates by the CCl^+ loss rate (see Table I). Branching of the $\text{CCl}^+ + \text{C}_6\text{H}_6$ reaction favored the C_7H_5^+ product by about 50% compared to the other observed products. Additionally, we confirmed conservation of trapped ions by monitoring the total ion number as a function of trap time. These data were collected for the reactions of CCl^+ and C^{37}Cl^+ with C_6H_6 and are provided in the SI [50]. The lowest-energy structural isomers for each product channel are plotted in Fig. 3 with additional isomers for each channel given in the SI [50]. The product isomers presented for each observed mass in Fig. 3 are

significantly more exoergic relative to the reactants at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory and may all be formed. It is assumed that a reaction complex forms as the reaction proceeds, particularly, because the $\text{C}_3\text{H}_2\text{Cl}^+$ and C_7H_5^+ products have constituents of both reactants. From such a reaction complex, various steps may be required before fragmentation into the experimentally observed products. Ideally, a potential energy surface would be used to connect the reactants and products and would yield a more rigorous comparison to experimental branching ratios. This would be a large undertaking. Even without a calculated potential energy surface, we are able to demonstrate which isomers contribute to observed experimental products. This is because of the tight energetic constraints of our cold experimental conditions ($\sim 93\ \text{K}$, $8\ \text{meV}$). This assumes a room-temperature rovibrational distribution of the reactants and products. Although we conducted an exhaustive computational search for all possible isomers of each mass channel and corresponding neutral, some higher-energy isomers may not have been found.

Only one ion-neutral pair was found to be exoergic for the $\text{C}_3\text{H}_2\text{Cl}^+ + \text{C}_4\text{H}_4$ and $\text{C}_5\text{H}_3^+ + \text{C}_2\text{H}_3\text{Cl}$ products shown as PRD4 and PRD2, respectively, in Fig. 3. Because these ions are energetically favorable, and the other closest available isomers are $> 200\ \text{meV}$ higher in energy, it should be straightforward to assign the $m/z\ 73$ product to the PRD4 isomer of $\text{C}_3\text{H}_2\text{Cl}^+$ and the $m/z\ 63$ product to the PRD2 isomer of C_5H_3^+ . For $\text{C}_3\text{H}_2\text{Cl}^+ + \text{C}_4\text{H}_4$, the lowest-energy pair for this product is shown as PRD3 in Fig. 3. The only energetically favorable ion for this channel is the cyclopropenyl cation ($c\text{-C}_3\text{H}_3^+$) shown in Fig. 3, which we assign to the $m/z\ 39$ product. The assignment of $m/z\ 39$ to $c\text{-C}_3\text{H}_3^+$ is consistent with the observed ions not continuing to react with C_6H_6 in the experiment. The reaction of $c\text{-C}_3\text{H}_3^+$ with C_6H_6 is known to be very slow compared to the linear propargyl isomer, further supporting this assignment [14]. A few neutral $\text{C}_4\text{H}_3\text{Cl}$ isomers are energetically favorable for this channel. However, because the neutral is not trapped in our experiments, it is not possible to know its exact identity.

In contrast to the other products, there are several possible exoergic isomers that could be assigned to the HCl loss product C_7H_5^+ . The lowest-energy isomer, shown in Fig. 3 as PRD1, is much more exoergic than any of the other possible products. The increased number of viable isomers and the exoergic nature of the products might give insight into why this channel is experimentally favored. There may be submerged barriers to some of the energetically favorable isomers of C_7H_5^+ that would complicate this simplistic interpretation. Thus, a full potential-energy surface and kinetic modeling of this reaction would be enlightening and could be of broad interest to the question of PAH production. We hope that others will continue with these efforts.

There are no experiments with which we can directly compare our results and predicted products. Similar products have been seen before for reactions of $\text{C}^+ + \text{C}_6\text{H}_6$ using ion cyclotron resonance mass spectrometry and a crossed molecular beam apparatus over collision energies of $0.02\text{--}12\ \text{eV}$ [14,51–54]. However, because of the difference in ionization energies between the two reactants, the main product measured was C_6H_6^+ and constituted a branching of 67–85%. The C_7H_5^+ product was observed, but with only a modest

branching of up to 10% [54]. This is in contrast to our observation of $\text{CCl}^+ + \text{C}_6\text{H}_6$, where C_7H_5^+ constitutes 50% of the products. The shared carbon growth product between the two reactions is intriguing and even more so that branching to C_7H_5^+ in the reaction with CCl^+ is more heavily favored. Of course, it is likely that the differences in these reactions are, at least, partially attributed to the presence of the chlorine atom. The high electronegativity of chlorine likely impacts the distribution of electron density in the reaction complex in which case, the energy landscape of the reaction dramatically changes. Further computational work and reaction studies of this type, including with other halogenated carbocations and C_6H_6 , may illuminate a possible mechanism for this carbon growth.

The experimentally favored HCl loss channel product C_7H_5^+ must be formed by the addition of the carbon atom from CCl^+ to the ring of C_6H_6 . This reaction could provide another mechanism for growth of carbonaceous species and possibly PAH formation in low-temperature and pressure environments. As discussed above, because so many of the possible C_7H_5^+ isomers are exoergic with respect to the reactants, it is difficult to pinpoint which C_7H_5^+ isomer is formed in this reaction. However, this represents an intriguing step to uncovering a possible new pathway to larger carbonaceous species, which might be consequential to chemistry taking place in the ISM, planetary atmospheres, or other environments. Hopefully, this Letter will inspire further experimental and theoretical studies towards understanding additional pathways to complex organic molecules and carbon molecular weight growth.

From this and other reaction studies, CCl^+ itself has a growing basis for consideration as an astrochemically relevant molecule. Whereas a positive identification in the ISM is yet

to be achieved, its potential to participate in interstellar chemistry via reactions with other interstellar molecules has been demonstrated [34–36]. In fact, a high-resolution rotational spectrum of CCl^+ has recently been measured by Asvany *et al.* [55], and it can be expected that the question of whether it exists in the ISM be answered in the near future.

This Letter has outlined the reaction of CCl^+ with C_6H_6 and shows a pathway to multiple astrochemically relevant carbocations, C_3H_3^+ , C_5H_3^+ , and C_7H_5^+ , as well as $\text{C}_3\text{H}_2\text{Cl}^+$. With the aid of computational work, only one possible exoergic product for each channel was identified, except in the case of C_7H_5^+ in which several viable exoergic isomers exist. The reactants and products each comprise definite or possible participants in ISM chemistry, and the formation of the favored product C_7H_5^+ may illuminate a new pathway to molecular weight growth of carbonaceous species. This could have possible implications for the creation of complex organic molecules and perhaps PAHs in the ISM, planetary atmospheres, and other extraterrestrial environments. The complex chemistry connecting smaller carbocations to larger PAHs is still being understood, and more reaction studies with various molecules are required to fully understand the progression from small carbocations to complex molecules like C_{60}^+ . We believe this reaction contributes to this important open question and presents a very intriguing first step to carbon growth at colder temperatures from CCl^+ reacting with the abundant C_6H_6 .

This work was supported by the National Science Foundation (Grants No. PHY-1734006 and No. CHE-1900294) and the Air Force Office of Scientific Research (Grant No. FA9550-20-1-0323).

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