Isotope-specific reactions of acetonitrile (CH$_3$CN) with trapped, translationally cold CCl$^+$

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The gas-phase reaction of CCl$^+$ with acetonitrile (CH$_3$CN) is studied using a linear Paul ion trap coupled to a time-of-flight mass spectrometer. This work builds on a previous study of the reaction of CCl$^+$ with acetylene$^4$ and further explores the reactivity of CCl$^+$ with organic neutral molecules. Both of the reactant species are relevant in observations and models of chemistry in the interstellar medium (ISM). Nitriles, in particular, are noted for their relevance in prebiotic chemistry, such as is found in the atmosphere of Titan, one of Saturn’s moons. This work represents one of the first studied reactions of a halogenated carbocation with a nitrile, and the first exploration of CCl$^+$ with a nitrile. Reactant isotopologues are used to unambiguously assign ionic primary products from this reaction: HNCCl$^+$ and C$_2$H$_3^+$. Branching ratios are measured and both primary products are determined to be equally probable. Quantum chemical and statistical reaction rate theory calculations illuminate pertinent information for interpreting the reaction data, including: reaction thermodynamics, a potential energy surface for the reaction, as well as rate constants and branching ratios for the observed products. In particular, the reaction products and potential energy surface stimulate questions regarding the strength and role of the nitrile functional group, which can be further explored with more reactions of this class.

I. INTRODUCTION

Nitriles and nitrogen-containing compounds play a prominent role in the chemical reactions thought to take place in the interstellar medium (ISM). These molecules permeate space: from small cyanides such as HCN and DCN found in the Orion Nebula$^{20-22}$ to larger molecules such as benzonitrile, whose initial discovery in the ISM was relatively recent$^{11}$ Nitriles, defined by their C=O functional group, are of particular interest as pre-biotic molecules and potential precursors of amino acids. Several nitriles have been identified in the atmosphere of Titan using the Ion Neutral Mass Spectrometer on the Cassini spacecraft, and are believed to be important in tholin formation$^{12}$ as well as astrobiology$^{13}$.

Acetonitrile (CH$_3$CN; the neutral reactant in this study) has been found abundantly throughout many regions of space since its initial identification in the ISM in 1971$^{17}$ It has been observed in cold dark clouds$^3$, low-mass protostars$^{10,11}$ and is considered an indicator of the presence of hot cores$^{11,12}$ CH$_3$CN has also been discovered in dust from comet Halley$^{13}$ Hale-Bopp (C/1995 O1$^{14}$ and, more recently, at the surface of comet 67P/Churyumov-Gerasimenko$^{15}$ These cometary identifications can yield critical glimpses into the past conditions and evolutionary history of the Milky Way. Deuterated variants CD$_3$CN and CDH$_2$CN have been identified in hot cores and star-formation regions$^{20}$ and the presence of isotopologues of CH$_3$CN are used to study relative populations of hydrogen and deuterium in some regions of the ISM$^{22}$.

Halogen-containing compounds have also been identified in the ISM, but their role and evolution are less well understood. In particular, chlorine-containing compounds have been found in the ISM in several small molecules (NaCl, AlCl, KCl, HCl)$^{16}$ as well as in CH$_3$Cl$^{24}$ and H$_2$Cl$^+$ (20-22) The only halogenated carbocation to be observed thus far in the ISM is CF$^+$ whereas CCl$^+$ has been predicted to occur, although only in low abundances$^{20,21}$ CCl$^+$ can be produced from reactions of C$^+$ + HCl$^{25}$ and once formed, has been assumed to be predominantly nonreactive. Specifically, CCl$^+$ has been shown to not react with HCN (or CO$_2$, CO, O$_2$, H$_2$O, CH$_4$, H$_2$). However, it has been shown to react with NH$_3$ and H$_2$CO$^{25}$ recent work from our group demonstrated CCl$^+$ reacts with acetylene (C$_2$H$_2$), producing small fundamental carbocations after losing neutral Cl or HCl$^{21}$ Despite this, much remains unknown about the role of halogenated carbocations; it is possible that they have a hitherto underestimated role in astronomical chemistry.

In contrast to CCl$^+$, laboratory reactions of nitriles have been much more widely studied. Ion cyclotron resonance (ICR) spectrometry has been used to measure reactions with HCN and carbocations$^{26}$, while other ion trap experiments have investigated reactions of CH$_3$CN with multiple carbocations$^{27}$ Selected-ion flow-tube mass spectrometry (SIFT) experiments demonstrated reactivity of CH$_3$CN with O$^+$, H$^+$, D$^+$, HeD$^+$, and HeH$^+$ as well as with C$_2$H$_4^+$ and C$_2$H$_2^+$ (20) However, very few measurements have reported reactions

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of halogenated carbocations with any nitrile. The only reported reaction of this type is the reaction of CF$_3^+$ with CH$_3$CN and benzonitrile, both of which were shown to produce only the adduct.\cite{fischer2009}

The reactions of CF$_3^+$ were executed in a higher pressure regime than that of the current experiment, where reactive intermediates are unable to be stabilized through collisions with background gas. The reactivity of halogenated carbocations with nitriles is in need of further exploration, particularly in a cold, low-pressure environment. This work seeks to understand more about this reaction class by studying the reaction of CCl$_3^+$ + CH$_3$CN in this regime.

The cold, low-pressure environment provided by using a linear Paul ion trap (LIT) is excellent for elucidating ion-neutral chemical reactions.\cite{christiansen2001,smith2003} This experimental setup affords a significant amount of control, including the manipulation of collisional energy,\cite{christiansen2001,smith2003} nuclear spin,\cite{smith2003} and the measurement of isotope,\cite{christiansen2001,smith2003} isotopic,\cite{christiansen2001,smith2003} and quantum state\cite{christiansen2001,smith2003} dependencies. Ions of interest are co-trapped and sympathetically cooled with laser-cooled Ca$^+$, forming a mixed species Coulomb crystal, achieving translationally cold, trapped ions. Furthermore, the addition of a time-of-flight mass spectrometer (TOF-MS) provides detection of ionic reactants and products with high mass resolution – a powerful tool for probing reaction products and kinetics.

The reaction of sympathetically cooled CCl$_3^+$ with CH$_3$CN is studied using our LIT TOF-MS. This work seeks to illuminate the role and reactivity of these novel species in the gas phase under experimental conditions that are approximate to that of the ISM and planetary atmospheres. The primary products are found to be C$_2$H$_3^+$ and HNCCl$^+$, which are unambiguously assigned through the use of isotope substitutions. Computational modeling also supports these product assignments, suggesting a reaction pathway requiring cleavage of the C––N bond of CH$_3$CN in order to form the observed products. Furthermore, the study of CCl$_3^+$ + CH$_3$CN signifies an initial investigation in reactions of halogenated carbocations with nitriles.

II. METHODS

A. Experimental Methods

Reaction data were collected using a LIT radially coupled to a TOF-MS. Detailed descriptions of the apparatus have been outlined previously\cite{christiansen2001,smith2003} and only a brief summary focusing on the specific details relevant to the current experiment will be given here. CCl$_3^+$ was produced using tetrachloroethylene (TCE, C$_2$Cl$_4$) seeded in a pulsed supersonic expansion of rare atomic gas (1.4% C$_2$Cl$_4$ in ~1000 Torr He). The skimmed molecular beam was overlapped with a focused beam (216 nm) from a pulsed dye laser (LIOPTEC LiopStar; 10 ns pulse, 100 μJ/pulse) in the center of the trap. Non-resonant multiphoton ionization of TCE resulted in several fragments, including C$^{35}$Cl$^+$, C$^{37}$Cl$^+$, 35Cl$^+$, 37Cl$^+$, C$_2^+$, and small amounts of C$_2$ $^{35}$Cl$^+$ (hereafter, the more abundant isotope $^{35}$Cl will be referred to as simply Cl, while $^{37}$Cl will be specified when appropriate). Unwanted ions were ejected from the trap by sweeping over resonance frequencies of the specific mass-to-charge ratio ($m/z$) of undesired ions.\cite{ravindran2006} This provided a clean sample of either CCl$_3^+$ or C$^{37}$Cl$^+$ with minimal impurities, as demonstrated in Fig. 1.

After removing unwanted ionization products from the trap, Ca$^+$ was loaded by non-resonantly photoionizing an effusive beam of calcium using the third harmonic of an Nd:YAG (Minilite, 10 Hz, ~ 7 mJ/pulse). The resulting Ca$^+$ ions were Doppler laser cooled by two external cavity diode lasers, forming a Coulomb crystal structure, which sympathetically cooled the co-trapped CCl$_3^+$ ions via the Coulomb interaction. Ca$^+$ ion fluorescence was collected using a microscope objective and focused onto an intensified CCD camera located above the trap, allowing for qualitative visual monitoring of the experiment. The heavier “dark” CCl$_3^+$ ions arrange themselves in outer shells around the Ca$^+$ ions, deforming the fluorescing Coulomb crystal as seen in Fig. 1b. A typical experiment utilized 150-250 CCl$_3^+$ ions trapped with ~ 1000 Ca$^+$ ions, all of which were translationally cold (~10 K).

![FIG. 1. a) TOF traces demonstrating before and b) after cleaning using secular excitations. After cleaning, only Ca$^+$ ($m/z$ 40, $m/z$ 42, and $m/z$ 44) and CCl$_3^+$ ($m/z$ 47) remain in quantities greater than ~ 5 ions. Also included on the left is a false-color CCD image of fluorescing Ca$^+$ ions, the resulting Coulomb crystal is deformed primarily in the center section by the heavier CCl$_3^+$ ions. The crystal appears truncated because it expands slightly beyond the CCD camera frame.](image)
After CCl⁺ and Ca⁺ ions were loaded, neutral CH₃CN (9-10% CH₃CN or CD₃CN in N₂) was leaked into the vacuum chamber (2 × 10⁻⁹ Torr gas pressure at 300 K) for a set duration of time using a pulsed leak-valve scheme. The measurements of gas partial pressures in the chamber were recorded using a Bayard-Alpert hot cathode ionization gauge. The opening of the leak valve (LV) defined the zero-time point; the LV remained open for 0, 10, 30, 60, 90, 120, 150, 180, 210, 240, or 330 s before ejecting the ions into the TOF-MS. This process was repeated about 10 times for every time step and measured ion numbers from each mass were averaged over each time step. The average number of reactant and product ions were then normalized by the initial CCl⁺ numbers and plotted against time, forming a reaction curve. These reaction curves were then used to determine the relevant rate constants. Reaction curves were collected in the same manner for isotopologues C³⁷Cl⁺ and CD³CN, such that all four possible combinations of isotopologues were used. The chemical formula of each mass peak was confirmed by examining the shift in mass spectra as a result of isotopic substitution (see section III.B). In addition, all of the ionic species were tracked via TOF-MS traces. The total number of ions were compared for each time point to ensure that the numbers were constant throughout the experiment; this ruled out systematic losses of ions from the trap. Figures illustrating conservation of charge over each reaction are given with more context in the supplementary material.

B. Computational Methods

Several theoretical methods were used to explore the potential energy surface for the reaction of CCl⁺ + CH₃CN. In a previous study, the M06-2X/aug-cc-pVTZ level of theory was found to produce accurate geometries and electronic energies, vibrational frequencies, and moments of inertia were from the CCSD(T)/CBS//MP2/aug-cc-pVTZ model chemistry calculations. Microscopic rate constants were calculated via Rice-Ramsperger-Kassel-Marcus (RRKM) theory, on the basis of rigid-rotor harmonic-oscillator sums and densities of state. For barrierless ion-molecule reactions, association rate coefficients were set at the ADO theory value, with the restricted Gorin model then applied to fit an effective transition state structure. Energy grained master equation simulations were performed in order to predict the CCl⁺ + CH₃CN reaction products. These calculations featured energy grains of 10 cm⁻¹ and a single exponential down collisional energy transfer model, with the average energy in deactivating collisions set at 200 cm⁻¹. Simulations comprised 10¹⁰ trajectories, and in each case a reaction was predicted to be complete within less than the time required for one bath-gas collision (i.e., effectively collisionless). Simulations were performed at a pressure of 2 × 10⁻⁹ Torr N₂, with temperature varied between 40 and 400 K in order to examine predicted rates from atmospheric down to astrochemically relevant conditions.

III. RESULTS & DISCUSSION

For the sake of clarity, the reaction thermodynamics will be discussed with the concluded chemical formula assignments in Section III.A followed by experimental support in Section III.B. Finally, in Section III.C the modeled potential energy surface, branching ratios, and rate constants of the reaction are discussed.

A. Reaction thermodynamics

Overall, the reaction of CCl⁺ + CH₃CN forms the primary ionic products C₂H₄⁺ and HNCCl⁺, which proceed to react with excess CH₃CN to form the secondary product protonated acetonitrile (CH₃CNH⁺). This model is illustrated in Fig. 2.
Neutral CH$_3$CN was introduced into the vacuum chamber as a room temperature gas (300 K). Therefore, when reacting with translationally cold CCl$^+$ ($\sim$ 10 K), the calculated collision energy for the reaction is $\sim$ 15 meV (160 K). This provides a narrow upper limit to the reaction energetics. The observed products are all significantly exothermic and well below the upper limit provided by the calculated collision energy, as shown by Equations 1-4 [CCSD(T)/CBS//CCSD/aug-cc-pVTZ; accurate within 0.04 eV].

Primary products:

$$\text{CCl}^+ + \text{CH}_3\text{CN} \rightarrow \text{C}_2\text{H}_3^+ + \text{NCCl}$$

$$\Delta E = -1.17 \text{ eV}$$

$$\text{CCl}^+ + \text{CH}_3\text{CN} \rightarrow \text{HNCCI}^+ + \text{C}_2\text{H}_2$$

$$\Delta E = -2.09 \text{ eV}$$

Secondary products:

$$\text{C}_2\text{H}_3^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{C}_2\text{H}_2$$

$$\Delta E = -1.41 \text{ eV}$$

$$\text{HNCCI}^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{NCCl}$$

$$\Delta E = -0.48 \text{ eV}$$

These calculated limits assume the lowest energy isomers. For example, in Eqns. 2 and 3, the C$_2$H$_3^+$ energy refers to that of the non-classical “bridge” isomer (see Fig. 2 or PRD2 in Fig. 4). This non-classical isomer is where the third H hovers between the two carbons, as opposed to the “classical” or “Y” structure (H$_2$C$_2$H$^+$, see PRD3). Other possible isomeric products are discussed in Section III C.

B. Reaction Measurements

Curves that are produced from the reaction of CCl$^+$ + CH$_3$CN are shown in Fig. 3. Here, CCl$^+$ ($m/z$ 47; blue) reacts to form two primary products: C$_2$H$_3^+$ ($m/z$ 27; green) and HNCCI$^+$ ($m/z$ 62; black). The reduction of the CCl$^+$ population (blue) is concurrent with the growth of C$_2$H$_3^+$ (green) and HNCCI$^+$ (black). Both of the primary product populations then reduce over time as the secondary product CH$_3$CNH$^+$ ($m/z$ 42; red) population grows from reactions with excess CH$_3$CN. CH$_3$CNH$^+$ is confirmed as a second order product because its maximum slope coincides with the maximum number of primary products. Experimental reaction rates are determined by fitting the reaction data to a pseudo-first order model. These curve fits are shown as lines in Fig. 3. Details of these fits are provided in the supplementary material.
products. An additional process occurs in reactions involving CD$_3$CN, which produces a small amount of a tertiary product m/z 45, assigned to CD$_3$CN$^+$. This tertiary process occurs possibly by either from H-D swapping or from contributions from a small number of contaminant ions remaining from the initial ion loading scheme (any given contaminant constitutes ≤ 5% of 150-250 initial CCl$^+$ numbers). The isotopologue reaction curves are plotted in the supplementary material. Extrapolated rate constants and branching ratios from these reaction curves are provided in Tables II.

The measured rate constants for primary products of CCl$^+$ + CH$_3$CN are reported in Table I. The Langevin capture model is a natural starting place for the analysis of experimental reaction rate constants, as it is the simplest and most general approach for predicting reaction rate constants in this regime. Notably temperature-independent, this theory estimates the likelihood of collisions between an ion and a neutral nonpolar molecule. The Langevin rate constant was found to be $k = 1.11 \times 10^{-9} \text{cm}^3/\text{s}$, 3.6 times smaller than the total reaction rate constant. This underestimation is most likely due to the polar nature of neutral CH$_3$CN, which is not accounted for in Langevin theory. Average dipole orientation (ADO) theory expands on Langevin theory to account for the polarity of the neutral reactant and should show closer agreement with the measured total reaction rate constant. This is reflected in the fact that CH$_3$CN has a rather large dipole-locking constant (c) of ~0.25, leading to $k_{ADO, unsub} = 3.74 \times 10^{-9} \text{cm}^3/\text{s}$ (calculated with the reduced mass of unsubstituted reactants). Our measured total reaction rate constant for CCl$^+$ + CH$_3$CN, $3.8 \pm 0.7 \times 10^{-9} \text{cm}^3/\text{s}$ (see Table I), reflects good agreement with ADO theory. This agreement testifies to the high degree of efficiency of the CCl$^+$ + CH$_3$CN reaction, where effectively every ion-molecule collision results in the formation of new reaction products, with little reformation of the reactants (vide infra). The high reactivity of CCl$^+$ toward acetonitrile stands in stark contrast to much of the previous work on the reaction kinetics of this ion with neutral molecules.

The isotope substituted total reaction rate constants (also in Table I) agree fairly well with the measured rate constant for CCl$^+$ + CH$_3$CN, but do trend faster, between $5.4 - 6.4 \times 10^{-9} \text{cm}^3/\text{s}$, compared to the unsubstituted total reaction rate constant. This trend is not precisely captured by ADO theory, which predicts a very small (≤ 5%) reduction in the rate constant for both C$^{37}$Cl$^+$ and CD$_3$CN substitutions. There is precedence for the trend of increased rate constant upon isotope substitution. Indeed, recently, this inverse kinetic isotope effect has been observed using a similar apparatus and Coulomb crystal environment by monitoring the charge exchange reaction between Xe$^+$ and NH$_3$ or ND$_3$. This effect, which was suggested to be due to intramolecular vibrational redistribution (IVR) occurring at a faster rate, and to a higher density of states in the deuterated ammonia. It is possible that we are observing a similar effect here. It should be emphasized that we use a Bayard-Alpert hot cathode ionization gauge to measure the partial pressure of CH$_3$CN gas in the chamber. While sensitivity factors for the gases used in this study have been previously measured, they are not well characterized at pressures of $10^{-9} - 10^{-10}$ Torr (current regime). This systematic uncertainty is difficult to quantify, and is not reflected in our reported uncertainties. For this reason, we do not make a definitive assessment as to whether we are observing an inverse kinetic isotope effect. Instead, more significance is placed on the determination of branching ratios (see Table II) and assignments of chemical formulas and structures of observed reaction products, rather than to individual rate constant measurements.

**TABLE I. Rate constants for isotopological variations of CCl$^+$ + CH$_3$CN primary products. ‘X’ represents a hydrogen or deuterium, and corresponds to the neutral reactant.**

| Reactants       | C$_2$X$_3^+$ | XNCCI$^+$ | total       |
|-----------------|-------------|-----------|-------------|
| CCl$^+$ + CH$_3$CN | 1.6 ± 0.5   | 2.2 ± 0.5 | 3.8 ± 0.4   |
| C$^{37}$Cl$^+$ + CH$_3$CN | 2.9 ± 0.7   | 3.0 ± 0.7 | 5.9 ± 0.3   |
| CCl$^+$ + CD$_3$CN  | 2.4 ± 0.5   | 3.0 ± 0.5 | 5.4 ± 0.3   |
| C$^{37}$Cl$^+$ + CD$_3$CN | 2.9 ± 0.8   | 3.4 ± 0.8 | 6.3 ± 0.3   |

**TABLE II. Branching ratios for primary products by isotopological variations of CCl$^+$ + CH$_3$CN reaction.**

| Reactants       | Branching Ratio |
|-----------------|-----------------|
| CCl$^+$ + CH$_3$CN | 0.43 ± 0.16     |
| C$^{37}$Cl$^+$ + CH$_3$CN | 0.50 ± 0.17     |
| CCl$^+$ + CD$_3$CN  | 0.44 ± 0.11     |
| C$^{37}$Cl$^+$ + CD$_3$CN | 0.46 ± 0.17     |

The branching ratios shown in Table II are nearly 50% for each of the primary products; here reported as the rate of the C$_2$H$_3^+$ production over the sum of both primary product rate constants. If all products branched from the same final step of the potential energy surface (see Fig. III), the more exothermic product, HNCCI$^+$, might be expected to be favored. However, as will be discussed in section IV, the potential energy surface is much more complex, with the existence of branching pathways, as well as multiple isomers of products. This necessitates an energy grained master equation approach to obtain quantitative branching ratio predictions.

Secondary reactions with excess CH$_3$CN are comprised of a proton transfer from either C$_2$H$_3^+$ or HNCCI$^+$ forming CH$_3$CNH$^+$. Analysis of the kinetics for these reactions is more straightforward, and the relative proton...
affinities of the neutral molecules guide our expectations for the stability of the products. CH$_3$CN has a larger proton affinity than either NCCl or C$_2$H$_2$ (see supplementary material for calculated values), and thus both primary products transfer a proton to neutral CH$_3$CN to form the secondary product CH$_3$CNH$^+$. Reaction dynamics predicted by relative proton affinities has precedence in ion-neutral gas-phase chemistry, and bounds on proton affinities have been determined by examining which proton transfers do or do not take place. In addition, these reactions are both energetically favorable, as per the reaction thermodynamics reported in Eqns. (3-4). As for the relative rate constants calculated for the second order reactions, ADO theory predicts a slightly larger rate constant for the C$_2$H$_3^+ + $ CH$_3$CN reaction ($4.3 \times 10^{-9}$ cm$^3$/s) due to its smaller reduced mass as compared to HNCCI$^+ + $ CH$_3$CN ($3.5 \times 10^{-9}$ cm$^3$/s). This trend is consistent with the reported experimental reaction rate constants in Table III. Overall, there is reasonable agreement within the experimental uncertainty between the ADO calculated rate constants and those measured experimentally.

**Table III.** Rate constants for isotope variations of CCl$^+$ + CH$_3$CN secondary products. ‘X’ represents a hydrogen or deuterium from CH$_3$CN, and corresponds to the isotopologue used. Rates are in units of $\times 10^{-9}$ cm$^3$/s, and reported statistical uncertainty is the calculated 90% confidence interval.

| Reactants          | C$_3$NCH$^+$        |
|--------------------|---------------------|
| C$_2$H$_3^+ + $ CH$_3$CN | 4.2 ± 1.7          |
| HNCCI$^+ + $ CH$_3$CN | 4.1 ± 1.2          |
| C$_2$H$_3^+ + $ CH$_3$CN | 6.2 ± 2.0          |
| HNCCI$^{15}$Cl$^+ + $ CH$_3$CN | 3.8 ± 1.1         |
| C$_2$D$_3^+ + $ CD$_3$CN | 6.0 ± 1.5          |
| DNCCI$^+ + $ CD$_3$CN  | 4.4 ± 0.9          |
| C$_2$D$_3^+ + $ CD$_3$CN | 6.2 ± 2.3          |
| DNCCI$^{15}$Cl$^+ + $ CD$_3$CN | 5.9 ± 1.9         |

**C. Modelling the CCl$^+$ + CH$_3$CN reaction**

The potential energy surface shown in Fig. 4 represents a few plausible reaction pathways of the CCl$^+$ + CH$_3$CN reaction. It is a result of quantum chemical calculations and is comprised of equilibrium structures that bridge the reactants and the observed products. The experimental conditions are cold and very low pressure, which therefore means that there is no quenching of the internal energy of any of the intermediate low energy structures. Furthermore, the stationary points along this reaction pathway are all exothermic with respect to the reactants, such that the reaction complex can sample all these intermediary states until it leaves the surface irreversibly. It is useful to consider the potential energy surface not only because it is an accessible way to explore the pathways to eventual exothermic products presented, but also because it provides a basis for the quantitative master equation-based kinetic modeling presented below. For clarity, the non-hydrogens will be numbered C1, C2, N3, C4, C5, as marked on INT1 in Fig. 4.

In the presented potential energy surface, CCl$^+$ and CH$_3$CN initially form the adduct INT1 as a bond is formed between N3 and C4. This structure then undergoes various changes in its bond lengths and angles isomerizing into the lower energy INT2 structure. INT2 can isomerize into INT4, which can dissociate without a barrier into PRD1 (HNCCI$^+ + $ HC$_2$H), PRD2 (C$_2$H$_3^+ + $ NCCI; where C$_2$H$_3^+$ is the non-classical bridge structure), or PRD4 (HNCCI$^+ + $ H$_2$C$_2$; where H$_2$C$_2$ is the vinylidene isomer of C$_2$H$_2$). Determining the exact chemical identity of the C$_2$H$_2$ isomer is beyond the scope of this study; while the m/z of ionic products is known based on the mass spectra, neutral products are speculative since they cannot be observed experimentally.

INT2 can also isomerize to INT3, which leads to the barrierless dissociation into PRD3, the classical ‘Y’ C$_2$H$_4^+$ structure and NCCI. The isomerization barrier between the two isomers of C$_2$H$_3^+$ has been the subject of rigorous computational and experimental studies, and was found to be 4.8 meV as calculated at the CBS-APNO level of theory. Regardless of which isomer is produced in this reaction, both isomers are energetically allowed, with exothermicity larger than the isomerization barrier. Therefore, either C$_2$H$_3^+$ isomer may be the experimentally observed cation.

All of the outlined products are exothermic with respect to the reactants and there are only submerged barriers in the potential energy surface. This indicates that both products are likely to form, which is perhaps reflected in the experimentally observed branching ratios being equal. This observation is tested below through RRKM theory/master equation kinetic modeling.

To the best of our knowledge, there are no previous measurements for reactions of CCl$^+$ with any nitriles with which to compare the current results. It does appear to be significant that the elucidated potential energy surface requires cleaving of the C≡N bond of CH$_3$CN. However, this is perhaps unsurprising given that once a bond is formed between the two reactants, more electron density will be pulled toward the more electronegative chlorine group. This is demonstrated in the first step of the PES, when INT1 (see Fig. 4) is formed. Two C-N bonds are of importance to this discussion: the C2-N3 bond, which originated from CH$_3$CN, and the C4-N3 bond, where the carbon from CCl$^+$ attaches to the terminal nitrogen of CH$_3$CN. The shift of electron density from the C2-N3 bond to the C4-N3 and C4-C5 bonds occurs in this first steps of this potential energy surface. On this surface, the shift of electron density between stationary points INT1 and TS1 (Fig. 4) suggests the C≡N functional group pairs with Cl over CH$_3$, stabilizing the complex with respect to the reactants. This is perhaps
FIG. 4. Potential energy surface for CCl\textsuperscript{+} + CH\textsubscript{3}CN, depicting equilibrium geometries connecting the reactants (REA) to the products (PRD1, PRD2, PRD3, and PRD4). In REA, PRD1, PRD2, PRD3, and PRD4, the bare ‘+’ denotes infinite distance between the ion-neutral pair, while the symbol indicates the ion of the ion-neutral pair. Geometries were calculated at MP2/aug-cc-pVTZ level, with CCSD(T)/CBS//MP2/aug-cc-pVTZ energies. ‘INT’ refers to intermediate states, while ‘TS’ indicates transition states. Asterisk denotes a step with a very shallow well (depending on the level of theory), which is discussed in detail in the supplementary material.

intuitive, as the highly electronegative Cl atom pulls electron density towards itself, forming a strong bond, further assisted by the electron donating methyl group of CH\textsubscript{3}CN.

All products that are observed in this study are possibly a result of this shift and subsequent cleavage. Using the \textsuperscript{13}CH\textsubscript{3}CN isotopologue as the neutral reactant could possibly provide more convincing experimental evidence of the C≡N bond cleaving mechanism, however, the cost of the reagent was prohibitive. While unsuccessful attempts were made to find a reaction pathway that did not cleave this C≡N bond, this did not constitute an exhaustive search of the PES. Regardless of whether a reaction pathway without cleavage of the C≡N bond exists, this theoretical mechanism is interesting in its own right.

To gain further insight into the CCl\textsuperscript{+} + CH\textsubscript{3}CN reaction, RRKM theory / master equation simulations were conducted on the basis of the potential energy surface reported in Fig. 4 (with PRD4 excluded). Predicted rate constants are plotted in Fig. 5 for the overall reaction and for formation of the PRD1 - PRD3 products as a function of temperature. Here, the overall rate constants reflect the ADO theory rates less any reverse dissociation of the ion-molecule complex back to the reactants. Also included in Fig. 5 is the experimental measurement made here and the ADO theory capture rate constants.

Fig. 5 indicates that the total rate constant is in good agreement with the experimental value, which in turn is similar to the ADO capture value. This reflects the high efficiency of the CCl\textsuperscript{+} + CH\textsubscript{3}CN reaction, which leads almost exclusively to new products. This is in turn attributed to both the low barriers for CH\textsubscript{3}CNCCl\textsuperscript{+} isomerization and the availability of dissociation channels for the subsequent isomers at below the reactant energy. Only at temperatures of around 300 K and above is the reverse dissociation channel significant, resulting in the predicted rate coefficients to fall below the upper limit set by ADO theory.

Branching between the C\textsubscript{2}H\textsubscript{3}\textsuperscript{+} and HNCCl\textsuperscript{+} product ions is approximately 50:50, again in accord with the experiments. Interestingly, product PRD3 is predicted to be the dominant pathway to C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}, suggesting that it is formed in the classical, yet slightly higher-energy, vinylium form. This result is attributed to transition states TS2 and TS3 throttling the reaction flux from
FIG. 5. Theoretical (RRKM/ME) rate constants for the CCl\(^+\) + CH\(_3\)CN reaction as a function of temperature. Values are included for the overall reaction (total) and for the formation of product ions HNCCI\(^+\) (PRD1) and C\(_2\)H\(_5\)\(^+\) (PRD2 + PRD3). Included for comparison are the experimental measurements (at the effective temperature of 160 K) and the ADO theory capture rate constants.

INT2 to a similar extent. Once TS2 is overcome, dissociation to PRD1 outcompetes all other channels (including PRD2), due to its low energy and high entropy. Following TS3, INT3 prefers to dissociate further to PRD3 than to isomerize back to INT2, presumably due to the loose forward dissociation being highly favored in terms of entropy.

**IV. CONCLUSION AND OUTLOOK**

The gas-phase reaction of CCl\(^+\) + CH\(_3\)CN is presented, with primary products C\(_2\)H\(_5\)\(^+\) and HNCCI\(^+\) formed in approximately equal yields, and both channels producing a CH\(_3\)CNH\(^+\) secondary product. The LIT TOF-MS used in this study enables experimental conditions of low pressures and collisional energies, limiting the reaction dynamics to exothermic pathways without quenching the internal energy of the reaction complex. In addition, the high mass resolution afforded by the TOF-MS yields methodical product identification that is supported by isotope substitution and quantum chemical calculations. The presented potential energy surface pathways indicate a series of equilibrium structures shifting electron density from the original CH\(_3\)CN C≡N bond to the new C≡N bond formed with the carbon of CCl\(^+\). The experimental rate constants were reported and compared to Langevin and ADO theory capture rates, as well as to detailed master equation / RRKM theory-based simulations of the reaction kinetics / RRKM theory-based simulations on a multiple-channel multiple-well potential energy surface. ADO theory, which includes the polarity of the neutral reactant, is in good agreement with the observed experimental primary product rate constants. The master equation modeling indicates that reaction is highly efficient, with the total rate constant predicted to approach the capture rate constant. Moreover, these calculations reproduce the experimentally observed branching fractions between the primary ionic products C\(_2\)H\(_5\)\(^+\) and HNCCI\(^+\). Although CCl\(^+\) has been predicted to not react with several neutrals, here, we see this is not the case, which is consistent with the previously observed reactions with C\(_2\)H\(_2\). This study presents the first example of this class of gas-phase reactions to be studied in a regime more closely comparable to that of the ISM (namely low pressure and temperature), and should aid in predicting the behavior of halogenated carbocations and nitriles in this region.

Future studies could further characterize CH\(_3\)CN with analogous reactions of various halogenated carbocations such as the astrochemically relevant ion CF\(^+\). In theory, a reaction of CF\(^+\) with CH\(_3\)CN would behave similarly, and the even more electronegative fluorine might be expected to reproduce chlorine’s behavior here. This would be particularly relevant to verify, as the presence CF\(^+\) in the ISM is more firmly established. It would also be interesting to study the effects of various functional groups (possibly more electron donating or withdrawing) attached to the C≡N in lieu of the methyl of CH\(_3\)CN. For example, benzonitrile C\(_6\)H\(_5\)(CN) with its attached phenyl group could help stabilize intermediates or primary products and thus possibly shift the observed reaction rates. Studying the reaction of CCl\(^+\) with various substituted nitriles might help elucidate a trend in nitrile reactivity in this low pressure and cold regime. Overall, probing the relative C≡N bond strength across nitriles might contribute to the understanding and predictions of the formation and reactivity of the nitriles present throughout the ISM. Although further isotope
tagging is necessary to absolutely verify the experimental reaction mechanism, the computational results are suggestive, and open questions for the role and reactivity of the C≡N bond in nitriles.

For the LIT-TOFMS apparatus, future directions also include the integration of a traveling wave Stark decelerator to expand control over the internal and external energies of polar neutral molecules. The ability to slow molecules down into the millikelvin regime allows the elucidation of whether quantum mechanical effects to play a greater role ion-neutral chemical dynamics. In this way, it presents an opportunity to both understand this class of reactions at a fundamental level, as well as further our understanding of ISM chemistry.

**SUPPLEMENTARY MATERIAL**

See supplementary material for expanded experimental results, including: plots of averaged total ion reaction times, details of reaction curve fits, and reaction data, as well as curves for isotopologue substituted reactions. See also for computational results in more detail: the full potential energy surface, geometries and energies for reaction limits at CCSD(T)/CBS//CCSD/aug-cc-pVTZ level of theory, and geometries and energies for reaction limits at MP2/aug-cc-pVTZ level of theory.

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**DATA AVAILABILITY**

The data that support the findings of this study are available in the supplementary material and from the corresponding author upon reasonable request.

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