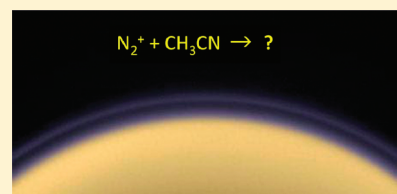


# Low-Temperature Branching Ratios for the Reaction of State-Prepared $\text{N}_2^+$ with Acetonitrile

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**ABSTRACT:** In this work, the primary product branching ratio (BR) for the reaction of state-prepared nitrogen cation ( $\text{N}_2^+$ ) with acetonitrile ( $\text{CH}_3\text{CN}$ ), a possible minor constituent of Titan's upper atmosphere, is reported. The ion–molecule reaction occurs in the collision region of the supersonic nozzle expansion that is characterized by a rotational temperature of  $45 \pm 5$  K. A BR of  $0.86 \pm 0.01/0.14 \pm 0.01$  is obtained for the formation  $\text{CH}_2\text{CN}^+$  and the  $\text{CH}_3\text{CN}^+$  product ions, respectively. The reported BR overwhelmingly favors the formation of  $\text{CH}_2\text{CN}^+$  product channel and is consistent with a simple capture process that is accompanied by a nonresonant dissociative charge transfer reaction. The BRs are independent of the  $\text{N}_2$  rotational levels excited. Apart from providing insights onto the dynamics of the title ion–molecule reaction, the reported BR represents the most accurate available low-temperature experimental measurement for the reaction useful to aid in the accurate modeling of Titan's nitrile chemistry.



## INTRODUCTION

Acetonitrile was first discovered in the atmosphere of Saturn's haze-shrouded moon, Titan, via ground-based midmicrowave submillimeter spectroscopy.<sup>1</sup> A disk-averaged vertical profile mole fraction on the order of  $10^{-8}$  was revealed above 150 km.<sup>2</sup> This profile was found to increase slowly with altitude up to 500 km. In 2004, the Wilson and Atreya<sup>3</sup> model computed a mole fraction of  $1 \times 10^{-5}$  for the neutral  $\text{CH}_3\text{CN}$  at 1100 km; a value that appears close to the  $3 \times 10^{-6}$  value reported by the Vuitton et al.<sup>4</sup> model in 2007.  $\text{CH}_3\text{CN}$  has also been found to be ubiquitous in laboratory experiments simulating Titan's atmosphere.<sup>5–7</sup> Although the reaction of the ground state  $\text{N}(^4\text{S})$  with  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  radicals is speculated to be the most probable origin of CN functional groups in Titan's upper atmosphere, the long radiative lifetime of the  $^2\text{D}$  state of 17 h makes its reaction with other molecules quite feasible.<sup>8</sup> Indeed, of the three low-lying electronic states of atomic nitrogen ( $^4\text{S}$ ,  $^2\text{D}$ , and  $^2\text{P}$ ), the  $^2\text{D}$  is believed to be the most reactive on the basis of the measured rate coefficients of N atoms with various molecules.<sup>9</sup> Therefore, in Titan's upper atmosphere,  $\text{CH}_3\text{CN}$  is most probably formed via the reaction of  $\text{N}(^2\text{D})$  with ethylene ( $\text{C}_2\text{H}_4$ ).

It is interesting to note that the routes leading to the formation of  $\text{CH}_3\text{CN}$  in Titan's atmosphere were not clearly known for a long time owing to limited experimental data. As a result, the possible reaction pathways leading to  $\text{CH}_3\text{CN}$  formation were not included in many pre-Cassini models.<sup>10,11</sup> However, following the pioneering crossed molecular beam (CMB) work on  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_4$  reaction by Balucani et al.,<sup>12,13</sup> recent models appear to accept and include the insertion of  $\text{N}(^2\text{D})$  into  $\text{C}_2\text{H}_4$  as the major route leading to the production of  $\text{CH}_3\text{CN}$ . Balucani et al.<sup>12</sup> show that even in a collision-free environment, this reaction proceeds through the formation of  $\text{C}_2\text{H}_3\text{N}$  intermediates ( $\text{CH}_2\text{CNH}$  and cyclic  $\text{CH}(\text{N})\text{CH}_2$ ) that spontaneously tautomerize to the most stable isomer,  $\text{CH}_3\text{CN}$ . Very recently, Lee et al.<sup>8</sup>

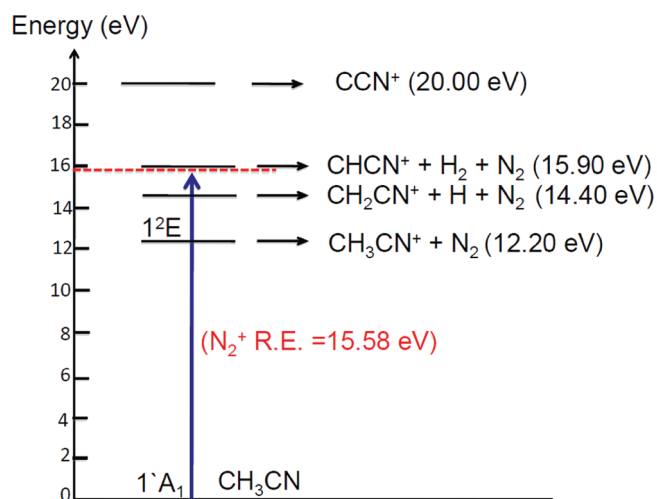
reinvestigated the dynamics of this reaction in a CMB apparatus that is equipped with synchrotron vacuum-ultraviolet (VUV) radiation. This strategy provides a selective photoionization scheme that eliminates the ambiguity associated with the identification of product ions using the electron impact ionization strategy employed by Balucani et al. Augmented by high-level quantum-chemical calculations, the work of Lee et al. shows that a  $\text{N}(^2\text{D})$  atom adds to the  $\text{C}=\text{C}$   $\pi$ -bond of  $\text{C}_2\text{H}_4$  to form a dominant cyclic complex  $c\text{-CH}_2(\text{N})\text{CH}_2$  that directly ejects a H atom or rearranges to other intermediates, followed by the elimination of a H atom to produce  $\text{C}_2\text{H}_3\text{N}$ . Lee et al. attributes the formation of  $m/z$  41 product ions in the Balucani et al. work as due to isotopic variants of the product  $\text{C}_2\text{H}_2\text{N}$ ; however, both Balucani et al. and Lee et al. are in agreement that  $\text{CH}_3\text{CN}$  is produced as the most stable isomer with a possibility of subsequent multiple isomerization processes.

Although the possible role of  $\text{CH}_3\text{CN}$  and other related cyano compounds in Titan's ion–molecule reactions has not received much attention in the past, we seek to report on the low-temperature product BR of  $\text{N}_2^+$  reaction with  $\text{CH}_3\text{CN}$  as an initial attempt toward understanding the fate of other closely related nitrile constituents in Titan's  $\text{N}_2^+$ -initiated ion–molecule reactions. Utilizing the selected ion flow tube (SIFT) technique, Wincel et al.<sup>14</sup> reported room temperature rate coefficient and product BRs for the reaction of  $\text{N}_2^+$  cation with  $\text{CH}_3\text{CN}$ . To our knowledge, for a period of more than 20 years, no experiments on  $\text{N}_2^+$  reaction with  $\text{CH}_3\text{CN}$  have been undertaken, and the existing BRs are largely in error because of the use of inaccurate dissociation thresholds for  $\text{CH}_3\text{CN}^+$  cation and the possible involvement of electronically excited  $\text{N}_2^+$  cations. We will expand on this in our discussion of our measured BRs.

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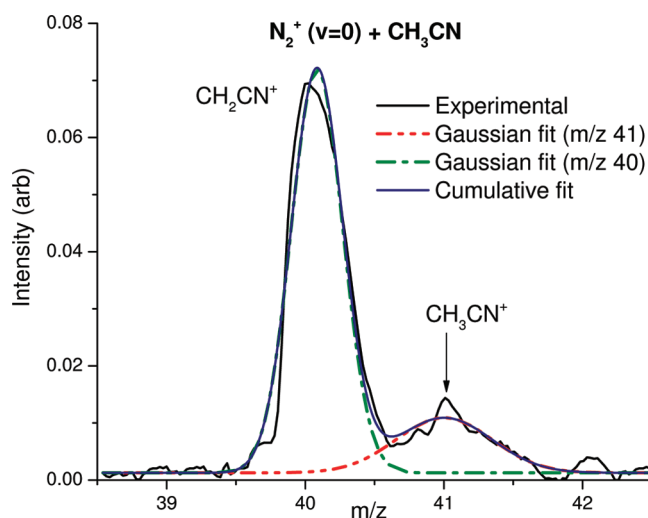
**Figure 1.** Energy diagram showing the possible dissociation channels of acetonitrile cation in a charge transfer reaction involving  $\text{N}_2^+$  cation with a total recombination energy of 15.58 eV.

Figure 1 shows some of the energetically allowed ionization and fragmentation pathways for  $\text{CH}_3\text{CN}$ . According to He I photoelectron spectroscopy<sup>15</sup> and threshold electron-secondary ion coincidence<sup>16</sup> technique, the two low-lying electronic states of the  $\text{CH}_3\text{CN}^+$  primary ion are  $^2\text{E}$  and  $^2\text{A}_1$  (which represent the ground and the first excited state of the cation, respectively). The  $\text{CH}_3\text{CN}^+$  in the  $^2\text{E}$  state corresponds to the ion in which a  $\pi_{\text{CN}}$  electron is removed, and  $\text{CH}_3\text{CN}^+$  in the  $^2\text{A}_1$  state represents the ion that has the  $\sigma_{\text{CN}}$  electron state removed.<sup>17,18</sup> The dipole moment of  $\text{CH}_3\text{CN}(\text{A}_1)$ ,  $\text{CH}_3\text{CN}^+(^2\text{E})$ , and  $\text{CH}_3\text{CN}^+(^2\text{A}_1)$  are 3.89, 2.58, and 0.02 D, respectively.<sup>16</sup> Since the interaction energy of an ion–molecule reaction involving a polar molecule is strongly influenced by the dipole moments,<sup>19</sup> the vanishing dipole moment associated with the  $^2\text{A}_1$  state leads to a corresponding decrease in the reaction cross section for this state as compared with the more dipolar  $^2\text{E}$  state. In addition, ion–molecule reactions are relatively disadvantageous for the  $^2\text{A}_1$  state, since the C–H bond of  $\text{CH}_3\text{CN}^+(^2\text{E})$  is weaker than that of  $\text{CH}_3\text{CN}^+(^2\text{A}_1)$ . According to Figure 1, the lowest energy values associated with the production of  $\text{CH}_2\text{CN}^+$ ,  $\text{CHCN}^+$ , and  $\text{CCN}^+$  are 14.4, 15.9, and 20.0 eV,<sup>20</sup> respectively.

Studies on acetonitrile molecular cation dissociation have also been carried out using several mass spectrometric techniques. Using mass-analyzed ion kinetic energy spectrometry, Choe<sup>21</sup> has, for example, obtained the kinetic energy distribution for the H-loss channel that leads to the formation of  $\text{CH}_2\text{CN}^+$  product ion and performed density functional theory calculations to investigate the isomerization and dissociation pathways of the ground state  $\text{CH}_3\text{CN}^+$  cation. In this experiment, only the H loss product was observed, in agreement with the previous experimental results. The present work, to some extent, seeks to expand on the previous room temperature BR measurements by Wincel et al.,<sup>14</sup> using state-prepared  $\text{N}_2^+$  cations under low-temperature molecular beam conditions where primary ion–molecule reactions initiated by ground vibrational state  $\text{N}_2^+$  ions prevail.

## EXPERIMENTAL SECTION

The  $\text{N}_2^+ + \text{CH}_3\text{CN}$  ion–molecule reaction was carried out using a modified ion imaging apparatus that has been described in



**Figure 2.** Time-of-flight spectrum of  $\text{CH}_2\text{CN}^+$  and  $\text{CH}_3\text{CN}^+$  product ions from the reaction of  $\text{N}_2^+ (v^+ = 0)$  with acetonitrile. The solid black line is the experimental data, and the Gaussian fitting is shown as indicated in the legend.

detail elsewhere.<sup>22,23</sup> A supersonic molecular beam consisting of  $\sim 1\%$   $\text{CH}_3\text{CN}$  (stated purity  $>99\%$ ) and  $\text{N}_2$  ( $\sim 1\text{--}5\%$ ) seeded in helium was introduced into the ionization chamber of our modified differentially pumped ion imaging apparatus at a backing pressure of  $\sim 500$  Torr. Briefly, the reactant  $\text{N}_2^+$  ions were produced via a 2 + 1 resonance enhanced multiphoton ionization (REMPI) scheme.<sup>24</sup> In this scheme, two photons of the 202 nm laser light are used to excite the ground state  $\text{N}_2$  molecule to the intermediate  $a'' \Sigma_g^+$  Rydberg state. Absorption of an additional photon from the same laser pulse allows the production of  $\text{N}_2^+$  ions. The  $a'' \Sigma_g^+$  Rydberg state possesses a ground state  $\text{N}_2^+$  core and has been shown to ionize exclusively via  $\Delta v = 0$ .<sup>16</sup> Furthermore, under identical conditions in gas mixtures containing argon, no  $\text{Ar}^+$  was observed. Charge transfer from  $\text{N}_2^+ (v^+ = 1)$  is known to be efficient, confirming the absence of vibrationally excited  $\text{N}_2^+$  from this REMPI process. A simulation of the REMPI spectrum gave a rotational temperature of  $45 \pm 5$  K. Although we do not measure the translational temperature in the collision region, it is unlikely to be significantly different from the rotational temperature. The tunable 202 nm light used to prepare the  $\text{N}_2^+$  ions was generated by frequency-tripling of the output of a tunable, narrow-line width ( $<0.075 \text{ cm}^{-1}$ ) OPO laser system (Spectra-Physics MOPO HF). The MOPO HF was pumped by the third harmonic of a seeded Nd:YAG laser operating at 10 Hz. Approximately 50 mJ/pulse of horizontally polarized 607 nm light with a 10 ns pulse width was produced. The MOPO output was then doubled in an angle-tuned KDP crystal and then, finally, frequency-tripled in a BBO crystal to produce vertically polarized 202 nm light. The tripled light was then focused with a 16 cm lens into the ionization chamber, where the reactions of  $\text{N}_2^+$  ions with  $\text{CH}_3\text{CN}$  took place.

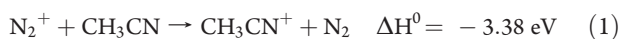
Newly born ions were extracted and accelerated from the ionization chamber by appropriately pulsing extractor and the repeller lens plates. The ions were then focused onto the microchannel-plate detector (MCP), mass selected, and the time-of-flight signal was recorded and averaged by an oscilloscope before being acquired by a computer. The areas of the TOF peaks were fitted using

Gaussian functions, and the product BRs were calculated after baseline subtraction and correction for the  $^{13}\text{C}$  contribution.

## RESULTS AND DISCUSSION

Figure 2 shows the mass spectrum associated with the reaction of state-prepared  $\text{N}_2^+$  cation with neutral  $\text{CH}_3\text{CN}$  at 202 nm. Here, we neglect the  $\text{N}_2^+$  peak and show only the H-loss and charge transfer product ion peaks at  $m/z$  40 and 41, respectively. To obtain the BR, the area under each peak was determined after fitting the peaks using Gaussian functions as shown. It should be mentioned here that the BRs obtained by a direct integration of the peak areas were not very different from that obtained by fitting with Gaussians. We therefore choose to report the BR obtained using the Gaussian fitting because it gives a more consistent BR, since it eliminates the uncertainty brought about by the tailing of the peaks at higher masses. Within our uncertainty, no dependence on  $\text{N}_2^+$  rotational level was observed over the small region populated at 45 K.

Taking the recombination energy of  $\text{N}_2^+$  cation to be 15.58 eV and considering the associated dissociation thresholds of  $\text{CH}_3\text{CN}^+$  cation as presented in Figure 1, the only primary product channels that are energetically possible in a charge transfer reaction involving  $\text{N}_2^+$  with  $\text{CH}_3\text{CN}$  are (i) nondissociative CT, leading to the formation of the  $\text{CH}_3\text{CN}^+$  parent cation, and (ii) dissociative CT resulting in the formation of  $\text{CH}_2\text{CN}^+$  as an H-loss product of the nascent parent cation. This is, indeed, consistent with our TOF data, as opposed to the Wincel et al.<sup>14</sup> experimental results in which the  $\text{H}_2$  loss product was also observed as a significant channel. As shown by eqs 1 and 2, the CT and H-loss channels are exoergic by 3.38 and 1.19 eV, respectively, and  $\text{H}_2$  loss is endoergic.



In the Wincel experiment, the  $\text{N}_2^+$  ions were prepared by electron bombardment of gas mixtures of  $\text{CH}_3\text{CN} + \text{M}$  ( $\text{M} = \text{Ar}, \text{H}_2, \text{N}_2, \text{CO}, \text{CO}_2$ , and  $\text{CH}_4$  at pressures ranging from 0.01 to 0.4 Torr and temperatures between 305 and 345 K). This method of preparing  $\text{N}_2^+$  cations resulted in the formation of long-lived excited ions of  $\text{N}_2^+$  ion that reacted with  $\text{CH}_3\text{CN}$ , forming  $\text{CH}_2\text{CN}^+$  product ions. Under low-temperature conditions, a direct loss of  $\text{H}_2$  from the ground state  $\text{CH}_3\text{CN}^+$  cation may be hindered by the presence of a barrier. Moreover, reaction 3 is endoergic by 0.33 eV. Our low-temperature conditions preclude the occurrence of CT reactions that either have a significant barrier or are endoergic; therefore, the chemically relevant CT reactions involving  $\text{N}_2^+$  cation with  $\text{CH}_3\text{CN}$  must be exoergic and proceed without entrance barrier. This is also the case in Titan's low-temperature conditions, where either endoergic reactions or those that have a significant entrance barrier are essentially blocked. Our reported low-temperature BR measurements are therefore consistent with a characteristic barrierless exoergic CT reaction that is dictated by attractive, long-range forces.

Presented in Table I is a summary of the BRs of the product channels formed in a CT reaction between  $\text{N}_2^+$  with  $\text{CH}_3\text{CN}$ . For comparison and to facilitate discussion, the room temperature BRs from Wincel et al. work are also listed in Table 1. Our low temperature technique gives a BR of 0.86/0.14 for the

**Table 1. BRs for the Formation of Various Product Ion Channels Observed upon the Reaction of  $\text{N}_2^+$  ( $\nu = 0$ ) with  $\text{CH}_3\text{CN}^a$**

reference	product ion/channel	BR
Wincel et al. (1988) (SIFT technique)	$\text{CH}_3\text{CN}^+ + \text{N}_2$	0.15
	$\text{CH}_3\text{CN}^+ + \text{H} + \text{N}_2$	0.65
	$\text{CH}_3\text{CN}^+ + \text{H}_2 + \text{N}_2$	0.20
present work	$\text{CH}_3\text{CN}^+ + \text{N}_2$	$0.14 \pm 0.01$
	$\text{CH}_2\text{CN}^+ + \text{H} + \text{N}_2$	$0.86 \pm 0.01$

<sup>a</sup>The branching ratios are an average of at least six independent measurements under similar conditions with  $\pm 2\sigma$  error.

formation of  $\text{CH}_2\text{CN}^+$  and  $\text{CH}_3\text{CN}^+$  product ions, respectively. According to high-resolution photoelectron spectroscopy, the ionization potential of acetonitrile is  $12.20 \pm 0.02$  eV.<sup>15</sup> As expected, a collision encounter between  $\text{N}_2^+$  cation with  $\text{CH}_3\text{CN}$  produces the parent  $\text{CH}_3\text{CN}^+$  cation as one of the possible primary product channel. Theoretical calculations<sup>21,25–27</sup> have shown that upon ionization, the  $\text{CH}_3\text{CN}^+$  cation can rearrange to a more stable keteneimine cation ( $\text{CH}_2\text{CNH}^+$ ) as well as to other isomers such as  $\text{CH}_3\text{NC}^+$  and  $\text{CH}_2\text{NCH}^+$ .  $\text{CH}_2\text{CNH}^+$  is more stable than  $\text{CH}_3\text{CN}^+$  cation by 2.4 eV;<sup>27</sup> however, although energetically favorable, the interconversion of  $\text{CH}_3\text{CN}^+$  to  $\text{CH}_2\text{CNH}^+$  through a 1,3 H-shift involves an isomerization barrier of 0.73 eV.<sup>26,27</sup>

Our TOF data presented in Figure 2 provide little direct structural and isomeric information that would provide deeper dynamical insights into the charge transfer reaction involving acetonitrile and  $\text{N}_2^+$ . Furthermore,  $\text{CH}_3\text{CN}^+$  has been found to react with  $\text{CO}_2$  and  $\text{COS}$  through proton transfer (PT) and CT, respectively.<sup>27</sup> The  $\text{CH}_2\text{CNH}^+$  isomer, on the other hand, is unreactive. This provides some indication that there may be a barrier to H loss from  $\text{CH}_2\text{CNH}^+$  isomer. The nascent  $\text{CH}_3\text{CN}^+$  is formed with an internal energy of 3.38 eV; hence, as indicated by the measured BR (0.05), it is expected to undergo rapid dissociation to form the H-loss product as discussed further below.

Our BR data presented in Table 1 indicate that a CT reaction between  $\text{N}_2^+$  cation and  $\text{CH}_3\text{CN}$  overwhelmingly favors the formation of the H-loss product channel. Compared with the work of Wincel et al.,<sup>14</sup> our BR ratio for this channel is substantially higher (0.86 versus 0.65). As mentioned earlier, the  $\text{H}_2$ -loss channel is endoergic. Although the Wincel et al. experiment included vibrationally excited  $\text{N}_2^+$  reactant ions, our supersonic beam/REMPI preparation leads to the exclusive formation of the ground vibration state of  $\text{N}_2^+$ .<sup>22</sup> Hence, the BR in the present study is higher than in Wincel et al., because no  $\text{H}_2$ -loss product ion is formed in this case. Separate studies by Ascenzi et al.<sup>26</sup> and Tachikawa et al.<sup>16</sup> have shown that the PT from  $\text{CH}_3\text{CN}^+$  to  $\text{CH}_3\text{CN}$  to form  $\text{CH}_3\text{CNH}^+$  involves a direct collision process. The  $\text{CH}_3\text{CN}^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{CH}_2\text{CN}$  reaction is fast and exoergic by 0.65 eV. The ion yield dependence on the photon energy of the protonated acetonitrile is, indeed, very similar to that of  $\text{CH}_3\text{CN}^+$ .<sup>26</sup> A careful scrutiny of our TOF data presented in Figure 2 seems to indicate a possible appearance of  $m/z$  42, but even at slightly higher acetonitrile concentrations, we did not observe any quantifiable protonated  $\text{CH}_3\text{CNH}^+$  species. The fact that we do not observe any protonated acetonitrile or other higher masses in our TOF spectrum is indicative of the inherent capability of our apparatus to measure primary BRs of



product channels that are predominantly formed in primary ion–molecule reaction involving  $\text{N}_2^+$  and  $\text{CH}_3\text{CN}$ .

To get deeper insights into the dynamics leading to the formation of  $m/z$  40 as the dominant channel, we invoke some other closely related photochemistry and theoretical studies of the ground state  $\text{CH}_3\text{CN}^+$  cation. Using the mass-analyzed ion kinetic energy spectrometry technique, Choe<sup>21</sup> investigated the unimolecular dissociation of the acetonitrile molecular cation and obtained the kinetic energy distribution for the H-loss product channel. In addition to these experiments, Choe, together with other workers,<sup>16</sup> has performed density functional theory calculations to investigate isomerization and dissociation of  $\text{CH}_3\text{CN}^+$  cation. According to theoretical calculations,<sup>21</sup> there are three possible isomers of  $m/z$  40 that are likely upon the dissociation of the ground state  $\text{CH}_3\text{CN}^+$  cation ( $c\text{-C}_2\text{H}_2\text{N}^+$ ,  $\text{CH}_2\text{CN}^+$ , and  $\text{CH}_2\text{NC}^+$ ). RRKM model calculations based on the obtained potential energy surface predict that  $\text{CH}_3\text{CN}^+$  cation interconverts to  $\text{CH}_2\text{CNH}^+$  and  $\text{CH}_2\text{NCH}^+$ , followed by dissociation to a cyclic  $\text{C}_2\text{H}_2\text{N}^+$  via another cyclic  $\text{C}_2\text{H}_3\text{N}^+$  intermediate near the threshold. The kinetic energy distribution for the H-loss product ion in Choe's experiment seems broader and different from the typical statistical distribution associated with a process. One possibility for this large kinetic energy release is a considerable reverse barrier, which is common in some direct bond cleavage reactions, to produce cations with aromatic stability.<sup>28,29</sup> Our experiments do not provide any direct insight into the role of these intermediates in the H-loss process.

Let us consider the BRs in light of Titan's ionospheric chemistry and the associated  $\text{N}_2^+$ -induced ion–molecule reactions. It has been pointed out that nitriles in Titan's atmosphere<sup>30,31</sup> are more abundantly formed at higher altitudes. In these regions,  $\text{N}_2$  is more frequently ionized or dissociated by the magnetospheric electrons from Saturn's rapidly rotating magnetosphere and EUV irradiation than at the lower altitudes.<sup>32–34</sup> To this end, the determination of accurate BRs of  $\text{N}_2^+$  ion–molecule reactions with trace nitrile compounds such as  $\text{CH}_3\text{CN}$  is important to model Titan's nitrile ionospheric chemistry accurately. The high proton affinities of nitriles such as  $\text{CH}_3\text{CN}$  allow them to be effectively protonated by the ubiquitous protonated hydrocarbon ions (such as  $\text{C}_2\text{H}_5^+$ ) in Titan's reducing ionosphere. Therefore, the accurate low-temperature BRs determined in the current study, if incorporated in Titan's models, will assist in the accurate modeling of nitrile chemistry and may ultimately give some insights into the haze formation mechanisms. It is instructive to mention here that future incorporation of BRs involving the reactions of vibrationally excited states of  $\text{N}_2^+$  with  $\text{CH}_3\text{CN}$  would also be important, since these states may also be populated by  $\text{N}_2$  ionization in Titan's ionosphere, albeit at much lower concentrations as compared with the ground vibrational state.

## CONCLUSIONS

This work reports the BRs of the reaction of state-prepared  $\text{N}_2^+$  ion with  $\text{CH}_3\text{CN}$  as a possible minor nitrile constituent of Titan's upper atmosphere. The ion–molecule reaction is performed in the collision region of the supersonic nozzle that is characterized by a rotational temperature of  $45 \pm 5$  K. A BR of 0.86:0.14 is obtained for the formation of  $\text{CH}_2\text{CN}^+$  and  $\text{CH}_3\text{CN}^+$  product ions, respectively. The reported BRs suggest that a CT reaction between ground state  $\text{N}_2^+$  ions overwhelmingly favors the formation of H-loss product channel from the nascent  $\text{CH}_3\text{CN}^+$  parent cation. This observed BR is suggestive

of a simple capture process, followed by an efficient dissociative CT of the nascent  $\text{CH}_3\text{CN}^+$  parent cation. On the basis of the accurate dissociation thresholds of the parent  $\text{CH}_3\text{CN}^+$  cation and the low-temperature conditions under which this ion–molecule reaction is carried out, the reported BR represent the most accurate available experimental measurement, which should be useful in the accurate modeling of Titan's ionospheric chemistry.

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