Exploring the dynamics of reaction N(2D) + C2H4 with crossed molecular-beam experiments and quantum-chemical calculations

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We conducted the title reaction using a crossed molecular-beam apparatus, quantum-chemical calculations, and RRKM calculations. Synchrotron radiation from an undulator served to ionize selectively reaction products by advantage of negligibly small dissociative ionization. We observed two products with gross formula C2H3N and C2H2N associated with loss of one and two hydrogen atoms, respectively. Measurements of kinetic-energy distributions, angular distributions, low-resolution photoionization spectra, and branching ratios of the two products were carried out. Furthermore, we evaluated total branching ratios of various exit channels using RRKM calculations based on the potential-energy surface of reaction N(2D)+C2H4 established with the method CCSD(T)/6-311 + G(3df,2p)//B3LYP/6-311G(d,p) + ZPE[B3LYP/6-311G(d,p)]. The combination of experimental and computational results allows us to reveal the reaction dynamics. The N(2D) atom adds to the C=C π-bond of ethene (C2H4) to form a cyclic complex c-CH2(N)CH2 that directly ejects a hydrogen atom or rearranges to other intermediates followed by elimination of a hydrogen atom to produce C2H3N; c-CH2(N)CH+H is the dominant product channel. Subsequently, most C2H3N radicals, notably c-CH2(N)CH, further decompose to CH2CN + H. This work provides results and explanations different from the previous work of Balucani et al. [J. Phys. Chem. A, 2000, 104, 5655], indicating that selective photoionization with synchrotron radiation as an ionization source is a good choice in chemical dynamics research.

I. Introduction

Dinitrogen (N2) is the most abundant molecule in the atmosphere but too inert to react with other atmospheric molecules due to the strong N≡N triple bond. In contrast, atomic nitrogen, particularly in an electronic excited state, could react with some atmospheric molecules. The chemistry of nitrogen atoms plays an important role in the atmosphere because nitrogen atoms can be produced from nitrogen-containing molecules, notably N2, by cosmic radiation and lightning. In laboratories nitrogen atoms are producible typically from N2 by various discharge approaches.

Atomic nitrogen with an electronic configuration of 1s22s22p3 has three lowest-lying electronic states 4S, 2D, and 2P. State 2D lies 2.38 eV and 2.57 eV above the ground state 4S.1 Nitrogen atoms in state 2D are believed to be more reactive than in states 4S and 2P based on measurements of rate coefficients of reactions of nitrogen atoms with various molecules.2 A nitrogen atom in state 2D has a radiative lifetime of 17 h,1 which makes feasible the reaction of atomic N(2D) with other molecules in experiments. Thus, most studies on reaction dynamics of nitrogen atoms were devoted to the reactions of 2D nitrogen atoms with H2,2–5 C2H2,12,13 and C2H4.14–16 Reactions started with an insertion mechanism of N(2D) atoms into bonds H–H, C–H, and Si–H to form reaction complexes H–N–H, CH3–N–H and SiH3–N–H, as well as an addition mechanism to the π-bond of CH=CH and CH2=CH2 to form cyclic complexes c-CH(N)CH and c-CH3(N)CH3, respectively. The complexes underwent either direct decomposition or various isomerization processes followed by decomposition. Two product channels SiNH2+2H and SiNH+H2+H were reported for the N(2D)+SiH4 reaction whereas only single channels with the elimination of a hydrogen atom were reported for the reactions of N(2D) with H2, CH4, C2H2 and C2H4.

As for the title reaction N(2D)+C2H4, a part of the doublet potential-energy surface (PES) was established by Takayanagi et al. using the method PMP4(SDTQ)/cc-pVTZ//MP2/cc-pVdz.14 The calculations predicted that the main reaction mechanism is addition of atomic N(2D) onto the C=C π-bond of C2H4 to form a three-membered cyclic complex c-CH3(N)CH2 that undergoes various pathways for elimination.
of hydrogen atoms to form various C\textsubscript{2}H\textsubscript{2}N isomers. The authors calculated product branching ratios of c-CH\textsubscript{2}(N)CH\textsubscript{2} with internal energy 104.3 kcal mol\textsuperscript{-1}, i.e., zero collision energy (E\textsubscript{c}) for reactant N\textsuperscript{(2D)}+C\textsubscript{2}H\textsubscript{4} using Rice–Ramsperger–Kassel–Marcus (RRKM) theory based on the established 
\textit{ab initio} PES.\textsuperscript{14} The calculations predicted that c-CH\textsubscript{2}(N)CH+ exists in the dominant channel with a branching ratio of 0.848. Thermal rate coefficients of reaction N\textsuperscript{(2D)}+C\textsubscript{2}H\textsubscript{4} in the temperature range 225–292 K were measured and expressible as 2.3 \times 10^{-10} e^{-E_{a}/kT} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}; activation energy E\textsubscript{a} equals 1.0 \pm 0.1 kcal mol\textsuperscript{-1}, indicating a small barrier in the entrance channel.\textsuperscript{15}

Balucani et al. conducted the title reaction at E\textsubscript{c} = 8 kcal mol\textsuperscript{-1} in a crossed molecular-beam apparatus equipped with an electron-impact ionizer.\textsuperscript{16} Product ions were observed at mass-to-charge ratios (m/z) 38–41 u. Because the signals at those m/z values have similar TOF spectra and laboratory angular distributions, the ions with m/z = 41 u were assigned to products with gross formula C\textsubscript{2}H\textsubscript{2}N and those ions with m/z = 38–40 u to daughter ions of C\textsubscript{2}H\textsubscript{1}N due to severe dissociative ionization. The authors employed the data recorded at m/z = 40 u for analysis because of large ion signals. The authors, however, might have ignored the possibility that the ions with m/z = 41 u are the isotopic variants of product C\textsubscript{2}H\textsubscript{2}N with loss of two hydrogen atoms, since the signal of m/z = 40 u is much larger than that of m/z = 41 u. If so, the signal of C\textsubscript{2}H\textsubscript{1}N isotomers might overlap with the signal of product C\textsubscript{2}H\textsubscript{3}N at m/z = 41 u. Selective photoionization\textsuperscript{17} can give a solution to this ambiguity.

The merits of photoionization with synchrotron vacuum-ultraviolet (VUV) radiation as an ionization source in studies of unmolecular photodissociation\textsuperscript{17–19} and atom–molecule chemical reactions\textsuperscript{11,20,21} have been described elsewhere. The advantage of negligibly small dissociative photoionization enabled the direct detection of reaction products C\textsubscript{2}H\textsubscript{3}N and C\textsubscript{2}H\textsubscript{2}N which were indistinguishable using electron-impact ionization. The present work corrected the previous experimental results\textsuperscript{16} conducted with electron-impact ionization and explored more deeply the dynamics of the reaction of N\textsuperscript{(2D)}+ethene (C\textsubscript{2}H\textsubscript{4}) using electron-impact ionization. To support the experimental observations, a comprehensive PES was established and RRKM calculations were also performed in the present work.

II. Experiments
The experimental apparatus and procedure have been described elsewhere;\textsuperscript{11,20,21} thus, only a brief description is given here. The crossed molecular-beam apparatus comprised two source chambers, a reaction chamber and a detection chamber. One source chamber equipped with an Even–Lavie valve and a discharge chamber device\textsuperscript{22} served to generate a pulsed beam of nitrogen atoms. A mixture of 3% N\textsubscript{2} and 97% He was supersonically expanded from the Even–Lavie valve with a backing pressure of 104 psi. A discharge was synchronously ignited while a molecular nitrogen pulse passed through the discharge device driven with a high-voltage pulse of ~1 kV and 10 \mu s. The N-atom beam was collimated with two successive skimmers. In the other source chamber, an Even–Lavie valve heated up to 110 °C served to expand supersonically neat ethene at a stagnation pressure of 54 psi. The pulsed molecular ethene beam was collimated with a skimmer. An L-shaped copper panel installed near the reaction region was chilled to 14 K to diminish the background pressure in the reaction region. The cold panel had a hole of diameter 3 mm in each side for penetration of both atomic and molecular beams that intercepted at 90° to each other in the reaction chamber. Nitrogen atoms and ethene had mean velocities of 1750 and 890 m s\textsuperscript{-1}, respectively, giving a collision energy of 4.3 kcal mol\textsuperscript{-1}. Reaction products were scattered into a whole solid angle but only the products flying towards an ion detector were ionized with undulator radiation after a free flight along a path of length 100.5 mm. The undulator radiation had photons with harmonic frequencies in addition to the desired photons with the fundamental frequency. A windowless gas cell installed on the beam line was filled with noble gas to absorb high harmonic photons. An additional optical filter of MgF\textsubscript{2} served to effectively suppress high harmonic photons when the energy of fundamental-frequency photons was less than 10 eV. The filtered VUV beam was focused into a size of diameter \sim 1 mm in the ionization region. The flux was \sim 1 \times 10\textsuperscript{16} photons s\textsuperscript{-1} and the energy resolution (\Delta E/E) was \sim 4%. The photon energy was tunable on adjusting the gap of the undulator for the purpose of selective ionization. Ion optics extracted product cations into a quadrupole mass filter for selection of species with a specific m/z ratio. An ion detector of Daly type counted the selected cations and a multi-channel scaler (MCS) sampled ions into 4000 bins of 1 \mu s. Two trigger-pulse generators operating at 200 Hz synchronized the experimental components. A time-of-flight (TOF) spectrum of a product can be obtained after subtracting the ion flight interval from the total flight duration and a background from the raw signal if necessary. To obtain product TOF spectra at various laboratory scattering angles (\Theta) between the N-atom beam and the detection axis, the source-chamber assembly was rotated from \Theta = -20° to 110°.

III. Computations
The computational details have been described elsewhere;\textsuperscript{11,20,23} thus, only a brief description is given here. We established a comprehensive potential-energy surface for the N\textsuperscript{(2D)}+C\textsubscript{2}H\textsubscript{4} reaction using the method CCSD(T)/6-311+G(3df,2p)//
B3LYP/6-311G(d,p) + ZPE[B3LYP/6-311G(d,p)]. Computations were conducted using a suite of programs Gaussian-03 in a computer equipped with four CPUs and 16 GB of memory. Structures of molecules at stationary and transition states (TS) were optimized at the level of B3LYP/6-311G(d,p); harmonic vibrational frequencies and zero-point energies (ZPE) of molecules at optimized structures were computed also at the same level of theory. In addition to the examination of the number of imaginary vibrational frequency, the calculation of intrinsic reaction coordinate (IRC) served to verify the connection of a transition structure with its reactant and product. Total energies of atomic and molecular species were computed at the level of CCSD(T)/6-311 + G(3df,2p). The same computational method was applied also to molecular cations for the calculations of adiabatic ionization energy (IE). We calculated rate coefficients of individual reaction steps
for the multi-channel dissociation of reaction complex c-CH₃(N)CH₂ with $E_c = 5$ kcal mol⁻¹ using RRKM theory and variational transition state theory (VTST). RRKM theory was applicable to a reaction path with a transition state whereas VTST theory to a barrierless reaction path. The microcanonical rate coefficient $k(E)$ of a reaction step can be expressed as $k(E) = \sum \frac{W_q(E - E^*)}{\sigma^2(E)}$ using RRKM theory; $\sigma$ is a symmetry factor (or reaction path degeneracy), $h$ is the Plank constant, $W_q(E - E^*)$ represents the number of states accessible in a transition structure with a barrier height $E^*$, and $\rho(E)$ denotes the density of states of a reactant with internal energy $E$ in a reaction step. The values of $W_q(E - E^*)$ and $\rho(E)$ were estimated using a direct-count method based on the computed harmonic vibrational frequencies. In the VTST calculations, we calculated $k(E)$ as a function of reaction coordinate $q^*$ assuming each molecular structure optimized along $q^*$ is a pseudo transition state. A minimal rate coefficient could be found along $q^*$ according to the equation $\frac{dk(E)}{dq^*} = 0$. Kinetic master equations $\frac{d\rho}{dt} = \sum k_m[C_i] - \sum k_m[C_j]$ were constructed and solved using stationary-state approximation, where $[C_i]$ and $[C_j]$ are concentrations of species $i$ and $j$ at time $t$ as well as $k_m$ and $k_m$ are microcanonical rate coefficients computed with the RRKM or VTST approach. At $t \to \infty$, product branching ratios can be yielded.

**IV. Results and analysis**

Different from the work of Balucani et al., we observed two reaction products with gross formula C₂H₃N at $m/z = 41$ u and C₂H₂N at 40 u. To verify our assignments, Fig. 1 presents the TOF spectra of both species with $m/z = 41$ and 40 u recorded at $\Theta = 44^\circ$ with photoionization energies 10.8, 11.7, and 15.1 eV. The species of $m/z = 41$ u has two features peaking around 90 and 160 μs but the species of $m/z = 40$ u has a single feature peaking around 100 μs in TOF distributions. The distinct TOF distributions indicate the presence of two reaction products; the two features of $m/z = 41$ u are ascribed to product C₂H₃N and the single feature of $m/z = 40$ u to product C₂H₂N. The species with $m/z = 40$ u (C₂H₂N) has a TOF distribution insensitive to photoionization energy in the range of 10.8–15.1 eV, indicating that the dissociative ionization from product C₂H₃N to C₂H₂N⁺ is negligible compared with the ion signal of product C₂H₂N in this energy range. In contrast, the TOF distribution of species with $m/z = 41$ u varies with photoionization energy; the TOF distribution has two apparent features with photon energies at 10.8 and 11.7 eV but becomes similar to that of $m/z = 40$ u at 15.1 eV. The variation of TOF distributions is attributed to the contribution of isotopic variants of product C₂H₂N to the signal of $m/z = 41$ u. Based on the natural abundances 1.1 $\times$ 10⁻² of ¹³C, 3.66 $\times$ 10⁻³ of ¹⁵N and 1.5 $\times$ 10⁻⁴ of ²H atoms, the isotopic ratio of 41 u to 40 u of C₂H₂N is expected to be about 0.026 because C₂H₂N has two carbon, two hydrogen and one nitrogen atoms. Fig. 1 shows that the peak signals of $m/z = 40$ u (C₂H₂N) recorded with photoionization energies 10.8, 11.7 and 15.1 eV are about 5, 7.4 and 20 counts per 10³ pulses, respectively. Therefore, isotopic variants of C₂H₂N will have about 0.13, 0.19 and 0.52 counts per 10³ pulses contributing to the peak signals of $m/z = 41$ u recorded with photons at 10.8, 11.7 and 15.1 eV, respectively. Because product C₂H₂N has a yield much greater and an ionization threshold higher than that of product C₂H₃N (vide infra), the isotopic contribution of C₂H₂N to $m/z = 41$ u becomes more significant when photoionization energy is much larger than the ionization threshold $\sim$ 10 eV of C₂H₃N. The TOF distributions of both species of $m/z = 40$ and 41 u become similar in appearance with photoionization energy larger than 15 eV, which accounts for the observation of Balucani et al. using electron-impact ionization.

Fig. 2 exhibits Newton diagrams associated with two-dimensional product velocity contours for the reactions of N(²D) + C₂H₄ to C₂H₃N + H and to C₂H₃N + 2H. In the laboratory frame, the flight direction of nitrogen atoms is defined as $\theta = 0^\circ$ and of ethene as $\theta = 90^\circ$. $\Theta_{cm} \approx 46^\circ$ is the flight direction of the center of masses (c.m.) of the reaction system. In the c.m. frame, the incident direction of nitrogen atoms is defined as $\theta = 0^\circ$ and the opposite direction, i.e., the incident direction of ethene, as $\theta = 180^\circ$. The scattering directions of reaction products C₂H₃N and C₂H₂N are called forward, sideways and backward for $\theta$ scanning from 0° through 90° to 180°. A simulation program served to mimic TOF spectra of products using forward convolution of initial guess c.m. kinetic-energy and angular distributions with experimental parameters. The transformation of signals from the laboratory frame to the c.m. frame was detailed in ref. 11. From the best fit to the experimental TOF spectra detected at various laboratory angles, angle-specific kinetic-energy distributions $P(E; \theta)$ and an angular distribution $P(\theta)$ of products in the c.m. frame are derivable. $E_i$ denotes the total kinetic energy of two
Fig. 2 Newton diagrams and two-dimensional product velocity contours for the reactions of N(D) + C2H4 → C2H3N + H and N(D) + C2H4 → C2H3N + 2H. Dashed lines denote the detection axes at laboratory angles 15°–70°.

momentum-matched products. The kinetic-energy distribution at any θ value is derivable by interpolation.

Fig. 3 presents the TOF spectra of species with m/z = 41 u from Θ = 15° to 70° using photoionization energies 9.6 eV and 11.7 eV which are below and above, respectively, the ionization threshold ~10 eV of product C2H2N. The data with Θ larger than 70° incur interference of impurities in the ethene beam and thus are omitted here. With photoionization energy 9.6 eV, the feature along with simulation is assigned to product C2H3N with loss of a hydrogen atom. Energy 9.6 eV, the feature along with red-line simulation is assigned to product C2H3N with loss of a hydrogen atom. Because hydrogen atoms are too elusive to be detected in the present work, we assume a two-body dissociation process with a product mass ratio of 40:2 to simulate the TOF spectra of product C2H2N. Fig. 7 exhibits P(Ei) distributions at seven θ angles and the P(θ) distribution derived from the best simulation as shown in Fig. 6; the P(Ei) and P(θ) distributions were employed also to simulate the blue components of m/z = 40 u shown in Fig. 3. Fig. 8 presents the low-resolution photoionization spectrum of product C2H2N; ion signals were detected at Θ = 44° and integrated from 60 μs to 240 μs in the flight time. Arrows indicate the adiabatic ionization energies of isomers CH3NC and CH2CN. The combination of product TOF spectra (Fig. 1, 3 and 6) and product photoionization spectra (Fig. 5 and 8) clearly indicates that there are two distinct products with gross formula C2H3N and C2H2N observed in the present work. Fig. 9 presents the doublet PES established for the N(D) + C2H4 reaction including various exit channels. The green and red paths are not calculated in the work of Takayanagi et al. Thick solid lines denote some likely pathways leading to products C2H3N + H and C2H2N + 2H. CH3NCH, CH2CHNH and CH2CNH have symmetry C3v and thus have cis- and trans-conformers according to the geometry of skeletons CNCH, CCNH, and CCNH, respectively, as shown in Fig. 9.

We obtained average kinetic-energy release ⟨Ei⟩ and fraction f1 of available energy (E ava) in translation based on ⟨Ei⟩ = \int Ei P(Ei; θ) dEi and f1 = ⟨Ei⟩/E ava. Table 1 lists the values of E ava, ⟨Ei⟩, and f1 for product channels C2H3N + H and C2H2N + 2H. The E ava values of the most-probable isomeric channels c-CH3(N)CN + H and CH2CN + 2H were adopted for the calculations of ⟨Ei⟩ and f1. Table 2 summarizes the adiabatic ionization energies of six isomers of C2H2N and three isomers of C2H3N. The difference between calculated and experimental IE values is within ±0.3 eV for CH3CN, CH3NC, c-CH3(N)CN and CH2CN; thus, the other calculated IE values might be reliable. Table 3 summarizes total branching ratios of various two-body dissociation channels predicted by RRKM and VTST calculations with E2 = 5 kcal mol−1; branching of secondary dissociation is beyond the present calculations.

V. Discussion

Ignoring the initial angular momenta of reactants supersonically cooled, the total angular momentum J of a reaction system equals approximately the orbital angular momentum \( \tilde{L} \) of a two-particle collision system, i.e., \( J \approx \tilde{L} \).
reduced mass, $\bar{b}$ is an impact parameter, and $\bar{v}_{\text{rel}}$ is the relative velocity between two colliding reactants. Parameter $b$ is perpendicular to and randomly polarized about axis $\bar{v}_{\text{rel}}$. The opacity function $P(b)$, a reaction probability as a function of $b$, governs the dynamics of a two-particle collision. The spatial distribution of reaction products has a symmetric axis along vector $\bar{v}_{\text{rel}}$ in the c.m. frame. For a direct reaction with a transient complex, the product angular distribution is dynamically controlled and typically forward–backward asymmetric.\textsuperscript{30} In contrast, for a reaction with a persisting (long-lived) complex the original memory in dynamics becomes obscure and the angular distribution approaches forward–backward symmetric due to rotation of the reaction complex before decomposition.\textsuperscript{30,31}
Since the reactivity of nitrogen atoms in states $^4S$ and $^2P$ are typically much smaller than in state $^2D$ and the population of nitrogen atoms in state $^2P$ is less than in state $^2D$, reactions of $\text{N}(^4S)$ and $\text{N}(^2P)$ atoms with ethene are neglected here. Although the rate coefficient of $\text{N}(^2P)$ was close to $\text{N}(^2D)$ reactions with $\text{C}_2\text{H}_4$, the deactivation process of $\text{N}(^2P)$ was determined to be the spin-allowed quenching process $\text{N}(^2P) + \text{C}_2\text{H}_4(\text{S}_0) \rightarrow \text{N}(^4S) + \text{C}_2\text{H}_4(\text{T}_1)$. The $\text{N}(^2D) + \text{C}_2\text{H}_4$ reaction starts with the addition of atomic $\text{N}(^2D)$ to the $\pi$-bond of ethene to form $c$-$\text{CH}_2(\text{N})\text{CH}_2$ through a small barrier at the entrance channel. Sato et al. reported an activation energy $E_a = 1.0 \pm 0.1 \text{ kcal mol}^{-1}$ for this reaction. Takayanagi et al. reported a classical barrier height $3.2 \text{ kcal mol}^{-1}$ for this addition process using a computational method CASSCF/cc-pVDZ; the barrier height was reduced to $1.6 \text{ kcal mol}^{-1}$ with a correction of CASMP2 calculations but the location of the potential maximum shifted toward the reactant side. The reaction complex $c$-$\text{CH}_2(\text{N})\text{CH}_2$ subsequently undergoes either direct dissociation or a series of isomerization processes followed by decomposition mainly to $\text{C}_2\text{H}_3\text{N} + \text{H}$ and $\text{C}_2\text{H}_2\text{N} + 2\text{H}$ at exit channels (vide infra). The mechanism of atomic $\text{N}(^2D)$ inserting into bond $\text{C}–\text{H}$ of ethene is negligible because of a significant entrance barrier that is $13 \text{ kcal mol}^{-1}$ at the CASSCF(5,5)/cc-pVDZ level of theory.

A Reaction $\text{N}(^2D) + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{N} + \text{H}$

Based on the PES shown in Fig. 9, the following lists some likely product channels for elimination of a hydrogen atom.

$$\text{N}(^2D) + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CN} + \text{H} \quad \Delta H^\circ = -107.6 \text{ kcal mol}^{-1}$$

(1)

$$\rightarrow \text{CH}_3\text{NC} + \text{H} \quad \Delta H^\circ = -84.2 \text{ kcal mol}^{-1}$$

(2)

$$\rightarrow \text{CH}_2\text{CNH} + \text{H} \quad \Delta H^\circ = -79.8 \text{ kcal mol}^{-1}$$

(3)

$$\rightarrow c$-$\text{CH}_2(\text{N})\text{CH} + \text{H} \quad \Delta H^\circ = -60.2 \text{ kcal mol}^{-1}$$

(4)

$$\rightarrow \text{CH}_2\text{NCH} + \text{H} \quad \Delta H^\circ = -51.4 \text{ kcal mol}^{-1}$$

(5)

$$\rightarrow c$-$\text{CH}(\text{NH})\text{CH} + \text{H} \quad \Delta H^\circ = -27.0 \text{ kcal mol}^{-1}$$

(6)

where, $\Delta H^\circ$ denotes a reaction enthalpy computed at 0 K. The numbering of reaction paths (or product channels) is based on the order of reaction enthalpy. Available energy $E_{\text{ava}}$ of a reaction can be calculated based on $E_{\text{ava}} = E_c - \Delta H^\circ$. The RRKM and VTST calculations predicted that reactions (1)–(6) have branching ratios $\sim 0.042, 0.023, 0.869, 0.044$, and $\sim 0$, respectively. Although reaction (1) produces the most stable isomer $\text{CH}_3\text{CN}$ (acetonitrile), the multiple isomerization processes as shown in Fig. 9 results in almost no yield to this reaction.
product. Fig. 9 indicates that reaction complex \(-\text{CH}_2(\text{N})\text{CH}_2\) might directly eject a hydrogen atom through TS10 to produce \(-\text{CH}_2(\text{N})\text{CH}(\text{2H-azirine})\) (reaction 4a). In addition, one of hydrogen atoms of \(-\text{CH}_2(\text{N})\text{CH}_2\) might migrate to the nitrogen atom to form \(-\text{CH}_2(\text{NH})\text{CH}\) that subsequently ejects the hydrogen atom through TS9 to produce \(-\text{CH}_2(\text{NH})\text{CH}\) (reaction 4b). Reactions (4a) and (4b) were predicted to have branching ratios 0.819 and 0.05, respectively, by RRKM calculations.

\(-\text{CH}_2(\text{NH})\text{CH}\) can rupture the \(\text{CH}_2-\text{NH}\) bond to form \(\text{cys-CH}_2\text{CNH}\) that subsequently decomposes to \(\text{CH}_2\text{CNH}+\text{H}\) through TS18 (reaction 3). Because of large dissociation energy, the decomposition from \(-\text{CH}_2(\text{NH})\text{CH}\) to \(-\text{CH}(\text{NH})\text{CH}+\text{H}\) (reaction 6) was predicted to be negligible by RRKM calculations. \(-\text{CH}_2(\text{N})\text{CH}_2\) can rearrange also to \(\text{cis-CH}_3\text{NCH}\) through TS12 followed by decomposition to \(\text{CH}_3\text{NC}+\text{H}\) (reaction 2). Takayanagi et al. ignored reactions (2) and (5) that were predicted to have non-negligible branching ratios by RRKM calculations.

Table 1

<table>
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<tr>
<th>Product channels</th>
<th>(\text{C}_2\text{H}_3\text{N}+\text{H})</th>
<th>(\text{C}_2\text{H}_2\text{N}+2\text{H})</th>
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<tr>
<td>(E_{av})/kcal mol(^{-1})</td>
<td>64.5</td>
<td>18.2</td>
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<td>(&lt;E&gt;/kcal mol(^{-1})</td>
<td>23.1</td>
<td>7.3 (^b)</td>
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<td>(f_i) (%)</td>
<td>35.8</td>
<td>40.1</td>
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\(^a\) The \(E_{av}\) values of the most-probable isomeric channels \(-\text{CH}_2(\text{N})\text{CH}+\text{H}\) and \(\text{CH}_3\text{CN}+2\text{H}\) were adopted for the calculations of \(<E>/\text{av}\>\) and \(f_i\). \(^b\) The \(<E>/\text{av}\>\) value of the channel \(\text{CH}_2\text{H}_2\text{N}+2\text{H}\) was derived based on an assumption of a two-body dissociation process with a product mass ratio of \(40:2\).

Table 2

<table>
<thead>
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<th>Species</th>
<th>Theoretical IE(^a)/eV</th>
<th>Experimental IE(^b)/eV</th>
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</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CN})</td>
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<td>12.20 (\pm) 0.01</td>
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<tr>
<td>(\text{CH}_3\text{NC})</td>
<td>11.2</td>
<td>11.53 (\pm) 0.04</td>
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<td>(-\text{CH}_2(\text{N})\text{CH})</td>
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<td>10.1</td>
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<td>N/A</td>
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<tr>
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<td>(\text{CHNCH})</td>
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</table>

\(^a\) The present values calculated at the level of CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p) + ZPE[B3LYP/6-311G(d,P)].

\(^b\) Quoted from NIST Chemistry WebBook: http://webbook.nist.gov/chemistry.
The maximal kinetic-energy release is in good agreement with the energetic limit of reaction (4) and the ionization threshold of C\(_2\)H\(_3\)N is in good agreement with the IE of CH\(_2\)NCH from reaction (5). Thus, isomers c-CH\(_2\)(N)CH and CH\(_2\)NCH might have contributions to product C\(_2\)H\(_3\)N although the TOF distributions of product C\(_2\)H\(_3\)N shown as the red curves in Fig. 3 have no significant change with the increase of photon energy from 9.6 eV to 11.7 eV. Since atomic hydrogen carrier energy carries no internal energy, the distribution of internal energy (E\(_{\text{int}}\)) of product C\(_2\)H\(_3\)N can be derived directly based on \(P(E_{\text{int}}) = P(E_{\text{ava}} - E_0)\). c-CH\(_2\)(N)CH, if produced alone, will have average internal energy 41.4 kcal mol\(^{-1}\) (1.80 eV), which might cause a red shift in the ionization threshold to some extent. c-CH\(_2\)(N)CH\(_2\) was calculated to have moments of inertia \(I_A = 19.130\) uÅ\(^2\), \(I_B = 23.107\) uÅ\(^2\), and \(I_C = 35.506\) uÅ\(^2\). The present RRKM calculations indicate that reaction complex c-CH\(_2\)(N)CH\(_2\) has a decay rate \(\sim 4.52 \times 10^{12} \text{ s}^{-1}\) corresponding to a lifetime of 0.022 ps that is shorter than rotational periods 13.4, 16.2 and 24.8 ps of c-CH\(_2\)(N)CH\(_2\) with \(L = 1\) along principal axes \(a, b\) and \(c\), respectively. In the theoretical study of reaction N(2D) + H\(_2\) → NH + H, the angular distribution of NH was nearly forward-backward symmetric with a slight bias towards backward scattering at low collision energy. Deviations from symmetry arise when small impact parameters (small \(L\) values) were favored, as then reactions favored backward scattering in hydrogen-atom elimination. This argument is applicable also to the present result of backward-biased angular distribution. TS10 in the dominant reaction path (4a) has the leaving hydrogen atom to be recoiled preferentially into the backward hemisphere. Rotational periods become 0.40, 0.48 and 0.74 ps for \(L = 47\) along principal axes \(a, b\) and \(c\), respectively; this \(L\) value is calculated with \(b = 1.636\) Å estimated from the equilibrium structure of c-CH\(_2\)(N)CH\(_2\). Thus, products could be scattered into the forward and backward hemispheres for large \(L\) values. The angular distribution behaves forward-backward (or sideways) peaking when products are recoiled preferentially perpendicular (or parallel) to \(L\) based on a statistical model. The angular distribution behaves nearly isotropic when products are recoiled into a wide angular range with respect to vector \(L\). The contribution from internally-excited C\(_2\)H\(_3\)N (e.g., c-CH\(_2\)(N)CH) to C\(_2\)H\(_2\)N\(^+\) by dissociative photoionization is negligible herein based on the following reasons. First, the enthalpy of reaction c-CH\(_2\)(N)CH → CH\(_2\)CN\(^+\) + H + e\(^-\) was calculated to be 12.2 eV; thus, product c-CH\(_2\)(N)CH requires internal energy at least 50.7 kcal mol\(^{-1}\) (2.2 eV), which is larger than the barrier height 43.6–43.9 kcal mol\(^{-1}\) of isomerization and the enthalpy 46.3 kcal mol\(^{-1}\) of dissociation c-CH\(_2\)(N)CH → CH\(_2\)CN + H, to undergo this dissociative ionization process with photon energy 10 eV. Second, Fig. 1 indicates that the species with \(m/z = 40\) u has a TOF distribution insensitive to the photoionization energy from 15.1 to 10.8 eV (even down to 10.2 eV but not shown therein) and quite different from that of the species with \(m/z = 41\) u. Third, the bimodal feature of \(m/z = 41\) u in TOF distributions at scattering angles near \(\Theta_{\text{cm}}\) remains as the photoionization energy is below the appearance threshold 10 eV of species with \(m/z = 40\) u; Fig. 3 presents the TOF spectra of \(m/z = 41\) u recorded at 9.6 eV. Fourth, Fig. 8 indicates that the appearance threshold of C\(_2\)H\(_2\)N\(^+\) is in good agreement with the ionization energy of CH\(_2\)CN. Accordingly, the signal observed at \(m/z = 40\) u is attributed mainly to product C\(_2\)H\(_2\)N rather than a daughter ion of product C\(_2\)H\(_3\)N.

To account for the production of C\(_2\)H\(_3\)N + 2H, we calculated the following five isomeric channels as shown in Fig. 9.

\[
\text{N}(2\text{D}) + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2\text{N} + 2\text{H} \quad \Delta H^\circ = -13.9 \text{ kcal mol}^{-1}
\]

(7)

\[
\rightarrow \text{CH}_2\text{NC} + 2\text{H} \quad \Delta H^\circ = 8.9 \text{ kcal mol}^{-1}
\]

(8)

\[
\rightarrow \text{HCCNH} + 2\text{H} \quad \Delta H^\circ = 18.9 \text{ kcal mol}^{-1}
\]

(9)

\[
\rightarrow \text{bent-CH}_2\text{CN} + 2\text{H} \quad \Delta H^\circ = 36.6 \text{ kcal mol}^{-1}
\]

(10)

\[
\rightarrow \text{c-CH(N)CH + 2H} \quad \Delta H^\circ = 40.5 \text{ kcal mol}^{-1}
\]

(11)

\[
\text{bent-CH}_2\text{CN and cyclic-CH(N)CH (c-CH(N)CH)} \text{ can be produced from successive elimination of two hydrogen atoms from the same and from different carbon atoms, respectively, of reaction complex c-CH}_2\text{(N)CH}_2\]. Only reaction (7) is energetically accessible in the present work. C\(_2\)H\(_3\)N can also be produced by elimination of a hydrogen molecule as the following three reactions.

\[
\text{N}(2\text{D}) + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2\text{N} + \text{H}_2 \quad \Delta H^\circ = -115.2 \text{ kcal mol}^{-1}
\]

(12)

\[
\rightarrow \text{CH}_2\text{NC} + \text{H}_2 \quad \Delta H^\circ = -92.4 \text{ kcal mol}^{-1}
\]

(13)

\[
\rightarrow \text{CHNCH} + \text{H}_2 \quad \Delta H^\circ = -53.0 \text{ kcal mol}^{-1}
\]

(14)

The production of C\(_2\)H\(_3\)N by elimination of a hydrogen molecule cannot satisfactorily account for the experimental observations based on the following reasons. First, a reaction like (12)–(14) having a large exothermicity and a large exit barrier typically recoils products into large translational energy; however, Fig. 7 indicates that the maximal kinetic-energy

<table>
<thead>
<tr>
<th>Labels</th>
<th>Products</th>
<th>Branching ratios(^a) (%)</th>
<th>Branching ratios(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_2)CN + H</td>
<td>0.03</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>CH(_2)NC + H</td>
<td>4.18</td>
<td>N/C</td>
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<tr>
<td>3</td>
<td>CH(_2)CNH + H</td>
<td>2.28</td>
<td>N/C</td>
</tr>
<tr>
<td>4</td>
<td>c-CH(_2)(N)CH + H</td>
<td>86.91 (= 81.93(^\circ) + 4.98(^\circ))</td>
<td>84.8</td>
</tr>
<tr>
<td>5</td>
<td>CH(_2)NCH + H</td>
<td>4.40</td>
<td>N/C</td>
</tr>
<tr>
<td>6</td>
<td>c-CH(N)CH+H</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>7</td>
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<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>8</td>
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<td>N/C</td>
</tr>
<tr>
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<td>2.17</td>
<td>N/C</td>
</tr>
<tr>
<td>10</td>
<td>CH(_2)NCH + H</td>
<td>0.99</td>
<td>N/C</td>
</tr>
<tr>
<td>11</td>
<td>CH(_2)N + CH(_2)</td>
<td>0.34</td>
<td>~0</td>
</tr>
<tr>
<td>12</td>
<td>CH(_2)CN + CH(_2)</td>
<td>0.98</td>
<td>~0</td>
</tr>
</tbody>
</table>

\(^a\) Calculated at \(E_0 = 5\) kcal mol\(^{-1}\) in the present work. \(^b\) Calculated at \(E_0 = 0\) kcal mol\(^{-1}\) by Takayanagi et al. (ref. 14); N/C denotes “Not Considered”. For reaction (4a). For reaction (4b).
release is near the energetic limit of reaction (7). Second, if products from reactions (12)-(14) have small kinetic energy release like that in Fig. 7, C2H2N will be predicted to have a large internal energy and have a considerable red shift in the ionization threshold; however, Fig. 8 indicates that the ionization threshold of C2H2N is in good agreement with the ionization energy of CH2CN (cyanomethyl). Product CH2CN from reaction (7) has an average internal energy merely 10.9 kcal mol\(^{-1}\) (0.47 eV). Third, reactions (12)-(14) have negligible branching ratios based on RRKM calculations. Thus, reaction (7) is the most likely channel for the production of C2H2N.

Fig. 9 presents four pathways for the production of CH2CN + 2H from the spontaneous dissociation of products CH3CN, CH2CNH, and Ch3(N)CH.

\[
\begin{align*}
\text{CH}_3\text{CN} & \rightarrow \text{CH}_2\text{CN} + \text{H} & \Delta H^\circ & = 93.7 \text{ kcal mol}^{-1} \\
\text{CH}_3\text{CNH} & \rightarrow \text{CH}_2\text{CN} + \text{H} & \Delta H^\circ & = 65.9 \text{ kcal mol}^{-1} \\
\text{c-Ch}_3(\text{N})\text{CH} & \rightarrow \text{CH}_3\text{CN} \rightarrow \text{CH}_2\text{CN} + \text{H} & \Delta H^\circ & = 46.3 \text{ kcal mol}^{-1} \\
\text{c-Ch}_2(\text{N})\text{CH} & \rightarrow \text{CH}_2\text{CNH} \rightarrow \text{CH}_2\text{CN} + \text{H} & \Delta H^\circ & = 46.3 \text{ kcal mol}^{-1}
\end{align*}
\]

CH3CN and CH2CNH can decompose to CH2CN + H without barriers. In contrast, c-Ch3(N)CH needs isomerization to CH3CN and CH2CNH through TS22 and TS23, respectively, before decomposition to CH2CN + H. TS22 lies 2.4 kcal mol\(^{-1}\) and TS23 2.7 kcal mol\(^{-1}\) below asymptote CH2CN + H, which makes reactions (4') and (4''), possible. We suggest that reactions (4') and (4'') are more important than reactions (1') and (3') since reaction (4) is much more dominant than reactions (1) and (3) by RRKM calculations. This suggestion coincides with the experimental finding that the channel C2H2N + 2H is about 5.7 times the branching ratio of the channel C2H2N + H. CH2NCH can rearrange to c-Ch3(N)CH through TS24 and subsequently undergoes reactions (4') and (4''); this reaction path has a possible contribution only to the products with E\(_z\) less than 10.9 kcal mol\(^{-1}\) because of the large isomerization barrier (TS24) lying 7.3 kcal mol\(^{-1}\) above asymptote CH2CN + H.

C. Branching ratios

Branching ratios for channel C2H2N + H to channel C2H2N + 2H was estimated to be 15:85 from the c.m. ion signals of products C2H2N and C2H2N recorded with photoionizing energy 11.7 eV on assuming both products have the same detection efficiency. The contribution of isotopomers of C2H2N to the signal of m/z = 41 u was removed. It might not be quantitatively accurate enough in the present analysis without a calibration of detection efficiency (e.g. ionization cross sections) but the channel C2H2N + 2H should be doubtless greater than the channel C2H2N + H in branching. RRKM calculations predict that reaction (4) is overwhelmingly dominant among two-body dissociation channels. Thus, most of nascent C2H2N products, notably c-Ch3(N)CH, are suggested to further decompose to CH2CN + H in order to rationalize the experimental branching ratios. Other energetically accessible product channels unobserved in experiments are listed below.

\[
\begin{align*}
\text{N}^{(2}\text{D}) + \text{C}_2\text{H}_2 & \rightarrow \text{CH}_3 + \text{HCN} & \Delta H^\circ & = -111.6 \text{ kcal mol}^{-1} \\
\rightarrow \text{CH}_3 + \text{HNC} & & \Delta H^\circ & = -98.1 \text{ kcal mol}^{-1} \\
\rightarrow \text{CH}_2\text{N} + \text{CH}_2 & & \Delta H^\circ & = -29.0 \text{ kcal mol}^{-1} \\
\rightarrow \text{C}_2\text{H}_3 + \text{NH} & & \Delta H^\circ & = -22.4 \text{ kcal mol}^{-1}
\end{align*}
\]

Although reactions (15) and (16) have large exothermicities, Fig. 9 indicates that the multi-isomerization processes with large barriers diminish the dissociation probability. Reactions (17) and (18) have small exothermicities and thus lose competition based on RRKM calculations.

D Comparison with previous works

In the experimental part, we explicitly observed two products C2H2N and C2H2N using selective photoionization. In contrast, Balucani \textit{et al}. claimed that they observed product C2H2N at m/z = 40 u using electron-impact ionization.\(^{16}\) Fig. 1 and 3 indicate that the contribution of isotopic variants of C2H2N to m/z = 41 u increases and the TOF distribution of m/z = 41 u becomes similar to that of m/z = 40 u with the increase of photoionization energy, which accounts for the reason why Balucani \textit{et al}. misrecognized the species of m/z = 40 u as daughter ions of the species with m/z = 41 u. In another words, what they reported are the results of product C2H2N rather than C2H2N. On the other hand, the forward-biased angular distribution reported by Balucani \textit{et al}.\(^{16}\) at E\(_c\) = 8 kcal mol\(^{-1}\) differs from the present result having a slight bias to the backward part at E\(_c\) = 4.3 kcal mol\(^{-1}\). The collision-energy dependence of product angular distributions was observed also in the reaction of N\((2\text{D}) + \text{C}_2\text{H}_2 \rightarrow \text{HCCN} + \text{H}\), the angular distribution of HCCN was isotropic at E\(_c\) = 3.1 kcal mol\(^{-1}\) and became forward preferred at E\(_c\) = 9.5 kcal mol\(^{-1}\). Balucani \textit{et al}.\(^{13}\) indicated that at low collision energy the lifetime of a persistent reaction complex (or intermediate) is longer than its rotational period but at high collision energy the lifetime of an osculating complex is comparable to its rotational period and an oscillating model\(^{30,32}\) is applicable. Accordingly, the collision-energy effect can account for the difference between the present work and Balucani’s \textit{et al}. in product angular distributions.

In the computational part, we established a more complete potential-energy surface than the work of Takayanagi \textit{et al}.\(^{14}\) for the N\((2\text{D}) + \text{C}_2\text{H}_2\) reaction. Takayanagi \textit{et al}. ignored the cis-trans isomerization processes of intermediates CH2CHNH and CH4CNH, the dissociation pathways leading to CH2NC + H (reaction 2), CH2NCH + H (reaction 5), CH2NC + H2 (reaction 13), CHNC + H (reaction 14) and CH3 + NCH (reaction 15), and the secondary dissociation pathways leading to various isomers of C2H2N + 2H. The complements (color lines in Fig. 9) make a satisfactory explanation possible for the experimental observations as addressed in the above sections. For instance, the ionization threshold of product C2H2N is in good agreement with the IE of CH2NCH, indicating that reaction (5), in addition to
reaction (4), might have a contribution to product C\textsubscript{2}H\textsubscript{3}N. Furthermore, channel C\textsubscript{2}H\textsubscript{2}N+2H is about 5.7 times the branching of channel C\textsubscript{2}H\textsubscript{3}N+H, indicating that most of primary product c-CH\textsubscript{2}(N)CH from reaction (4) further decomposes to CH\textsubscript{2}CN+H, consistent with quantum-chemical calculations. In the part (black lines in Fig. 9) similar to the work of Takayanagi \textit{et al.},\textsuperscript{14} the energies of intermediates and products relative to reactant N(\textsuperscript{2}D)+C\textsubscript{2}H\textsubscript{4} differ from the present computational values within \pm 3 kcal mol\textsuperscript{-1} except for intermediate CH\textsubscript{2}CHNH (vide infra). Some of the molecular structures computed in the present work differ from those reported by Takayanagi \textit{et al.} mainly on molecular conformations. Fig. 10 presents the optimized structures of molecules situating on reaction path (3) leading to product CH\textsubscript{2}CN+H computed with two methods of B3LYP/6-311G(d,p) (upper path) and MP2/cc-pVDZ (lower path). The molecular structures of B3LYP/6-311G(d,p) correspond to the stationary and transition states of reaction path (3) shown in Fig. 9. The connection of a transition structure with its reactant and product was verified with the calculation of IRC. On the other hand, the lower path of Fig. 10 shows the results of method MP2/cc-pVDZ same as those of Takayanagi \textit{et al.} but with some corrections; the same notations as those of Takayanagi \textit{et al.} were adopted in the lower path. For instance, c-CH\textsubscript{2}(NH)CH presented in the upper path of Fig. 10 has a conformation with dihedral angle \angle HCNH \approx -127.7^\circ but Takayanagi \textit{et al.} reported another conformer M2 that has \angle HCNH \approx -15.0^\circ. M2 cannot correlate directly with TS1 without the two additional structures shown in a bracket. M3’ and TS1’ differ from M3 and TS11 reported by Takayanagi \textit{et al.} M3’ (TS11’) has a reflection operator bisecting the methyl group and has a point group C\textsubscript{s} but M3 (TS11) has a point group C\textsubscript{1}. Moreover, M3 is likely an electronic excited state lying \approx 17 kcal mol\textsuperscript{-1} above cis-CH\textsubscript{2}CHNH.

**VI. Conclusions**

This work explored the dynamics of reaction of atomic N in state \textsuperscript{2}D with ethene (C\textsubscript{2}H\textsubscript{4}) at collision energy \(E\textsubscript{c} = 4.3 \text{ kcal mol}^{-1}\) by interrogating product channels C\textsubscript{2}H\textsubscript{3}N+H and C\textsubscript{2}H\textsubscript{2}N+2H. We measured kinetic-energy distributions, angular distributions, and photoionization spectra of products C\textsubscript{2}H\textsubscript{3}N and C\textsubscript{2}H\textsubscript{2}N. Furthermore, we established a comprehensive doublet PES for the N(\textsuperscript{2}D)+C\textsubscript{2}H\textsubscript{4} reaction and calculated branching ratios of various product channels at \(E\textsubscript{c} = 5 \text{ kcal mol}^{-1}\) using RRKM and VTST approaches. The combination of experimental and theoretical results unveils the reaction mechanisms. The N(\textsuperscript{2}D) atom adds to the C=\text{C} \pi\text{-bond of ethene to form a cyclic complex c-CH\textsubscript{2}(N)CH\textsubscript{2} that subsequently undergoes various dissociation pathways. c-CH\textsubscript{2}(N)CH\textsubscript{2} mainly ejects one of the hydrogen atoms to produce c-CH\textsubscript{2}(N)CH+H with a branching ratio 0.87 predicted by RRKM calculations. Most of c-CH\textsubscript{2}(N)CH further decompose to CH\textsubscript{2}CN+H following isomerization to CH\textsubscript{3}CN or CH\textsubscript{2}CNH, which rationalizes the experimental branching ratios of 15:85 for channel C\textsubscript{2}H\textsubscript{3}N+H to channel C\textsubscript{2}H\textsubscript{2}N+2H. The angular distribution of C\textsubscript{2}H\textsubscript{3}N has a propensity to the backward part, implying that c-CH\textsubscript{2}(N)CH\textsubscript{2} is a short-lived complex compared with its rotational period. Measurements of kinetic-energy release and ionization thresholds allowed us to identify product C\textsubscript{2}H\textsubscript{3}N as a mixture of c-CH\textsubscript{2}(N)CH and CH\textsubscript{2}CNH as well as product C\textsubscript{2}H\textsubscript{2}N as CH\textsubscript{2}CN. The present work corrects the previous work of Balucani \textit{et al.}, elucidating the merits of selective photoionization with synchrotron radiation as an ionization source.
Acknowledgements

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