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Branching Fractions of the CN + C₃H₆ Reaction Using Synchrotron Photoionization Mass Spectrometry: Evidence for the 3-Cyanopropene Product

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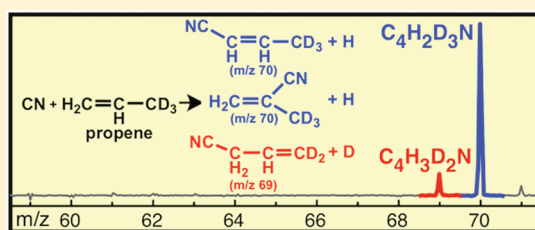
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ABSTRACT: The gas-phase CN + propene reaction is investigated using synchrotron photoionization mass spectrometry (SPIMS) over the 9.8–11.5 eV photon energy range. Experiments are conducted at room temperature in 4 Torr of He buffer gas. The CN + propene addition reaction produces two distinct product mass channels, C₃H₃N and C₄H₅N, corresponding to CH₃ and H elimination, respectively. The CH₃ and H elimination channels are measured to have branching fractions of 0.59 ± 0.15 and 0.41 ± 0.10 , respectively. The absolute photoionization cross sections between 9.8 and 11.5 eV are measured for the three

considered H-elimination coproducts: 1-, 2-, and 3-cyanopropene. Based on fits using the experimentally measured photoionization spectra for the C₄H₅N mass channel and contrary to the previous study (*Int. J. Mass. Spectrom.* **2009**, *280*, 113–118), where it was concluded that 3-cyanopropene was not a significant product, the new data suggests 3-cyanopropene is produced in significant quantity along with 1-cyanopropene, with isomer branching fractions from this mass channel of 0.50 ± 0.12 and 0.50 ± 0.24 , respectively. However, similarities between the 1-, 2-, and 3-cyanopropene photoionization spectra make an unequivocal assignment difficult based solely on photoionization spectra. The CN + CH₂CHCD₃ reaction is studied and shows, in addition to the H-elimination product signal, a D-elimination product channel (m/z 69, consistent with CH₂CHCD₂CN), providing further evidence for the formation of the 3-cyanopropene reaction product.



INTRODUCTION

Along with rate coefficients, product branching fractions are important data to understand and predict the evolution of a chemical system. A good example of where these data provide for practical models is in understanding the chemical processes in the atmosphere of Saturn's largest moon, Titan, where the temperature is in the 90–200 K range. Understanding the rich hydrocarbon chemistry responsible for Titan's optically opaque atmosphere has engaged many scientists. Due to the CASSINI mission in particular, modeling studies can now be compared to directly measured data.¹ The validity of these models depends on the accuracy of the experimental data contained within them; experimentally determined kinetic data and product branching fractions are, therefore, vital.²

Several research teams have measured rate coefficients for numerous CN radical-hydrocarbon reactions, at Titan-relevant temperatures, and these data are incorporated into modeling studies.^{2–5} Single-collision crossed molecular beam methods have provided detailed complementary information about the reaction dynamics and product yields for radical-neutral reactions, including the cyano reaction systems.^{6–8} H-atom laser-induced

fluorescence detection schemes have also been recently employed at low temperature to measure the H-atom elimination branching channels for a number of radical-hydrocarbon reactions.^{9–12} In addition, our research program has been active using synchrotron photoionization with multiplexed mass spectrometry to measure the major products from reactions of Titan-relevant radicals (e.g., C₂H, CH, and CN) with hydrocarbons.^{13–18}

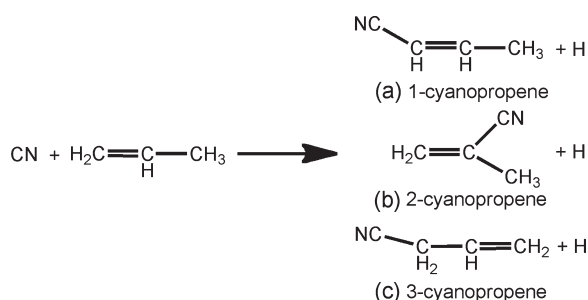
Previously we reported the measurement of CN + propene product branching fractions using the synchrotron photoionization mass spectrometry (SPIMS) technique.¹⁷ The reported product channels were consistent with complex-forming CN addition to propene followed by either CH₃ or H-atom elimination. The CH₃ elimination coproduct was found to be solely cyanoethene, whereas for the H-atom elimination channel there are three plausible cyanopropene isomers: 1-, 2-, and 3-cyanopropene. The structures of these three C₄H₅N isomers are depicted in Scheme 1. Based on fits of experimental data to simulated photoionization spectra,

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Scheme 1



1- and 2-cyanopropene were reported to be the dominant species contributing to the $\text{C}_4\text{H}_5\text{N}$ mass channel and 3-cyanopropene was assigned a <15% contribution. Since this report, several subsequent papers have investigated this reaction.

Kaiser and co-workers reported crossed molecular beam experiments at 25.5 kJ mol^{-1} collision energy where detection of a product at mass-to-charge (m/z) 67 ($\text{C}_4\text{H}_5\text{N}^+$) verified that the H-atom elimination channel is active at the higher collision energy.¹⁹ To determine if the H loss originates from the methyl or the vinyl group of the CN adduct complex, Kaiser and co-workers investigated reactions with two deuterated propene isotopomers: propene-3,3,3- d_3 ($\text{CH}_2=\text{CHCD}_3$) and propene-1,1,2- d_3 ($\text{CD}_2=\text{CDCH}_3$). For both isotopomers, product signal at m/z 70 ($\text{C}_4\text{H}_2\text{D}_3\text{N}^+$) was observed, indicating that H elimination channels occur in each case, with m/z 70 appearing less intense for CN + propene-1,1,2- d_3 than for CN + propene-3,3,3- d_3 . This result supports multiple H-elimination product channels, with the eliminated hydrogen originating from either the methyl group or the vinyl group of propene. Ultimately, from the product isotopic distributions, Kaiser and co-workers inferred elimination branching fractions of $75 \pm 8\%$ *cis/trans*-2-butenenitrile (1-cyanopropene) for CN + propene-3,3,3- d_3 and $25 \pm 5\%$ 3-butenenitrile (3-cyanopropene) for CN + propene-1,1,2- d_3 .

A subsequent computational investigation also examined the CN + propene reaction by implementing RRKM calculations to predict the product branching fractions for a range of collision energies (0–10 kcal/mol).²⁰ With yields depending on the structural form of the CN + propene adduct, in all cases the CH_3 loss channel was found to dominate and the less-dominant H elimination channel was made up of 3- and 1-cyanopropene. The study concluded that the formation of 2-cyanopropene was unlikely to occur to a significant extent. Predictions for product branching ratios were found to be sensitive to the barrierless entrance channel because the CN radical species can add directly to either of the unsaturated carbons of propene, forming a primary or secondary radical intermediate. A stabilized cyclic CN-addition complex, which has the cyano group simultaneously bound to two carbons with the radical positioned on the cyano-group carbon, was also found to be a possible intermediate species; this cyclic intermediate then isomerizes into the aforementioned primary or secondary radical intermediate. Predicted branching fractions, for example, at 0 kcal/mol collision energy occurring via the secondary radical intermediate (i.e., addition of CN to the CH_2 carbon of propene) were predicted to be 0.12 for 1-cyanopropene + H, 0.18 for 3-cyanopropene + H, and 0.70 for cyanoethene + CH_3 . Increasing the collision energy to 5 kcal/mol for the same addition channel shifts the fractionation to 0.16 for 1-cyanopropene + H, 0.26 for 3-cyanopropene + H, and 0.57

for cyanoethene + CH_3 . In contrast to our previous conclusions,¹⁷ these calculations predict 3-cyanopropene to be generated in detectable quantities and the 2-cyanopropene to be negligible.

Because both recent investigations conclude 3-cyanopropene should be produced in detectable quantities, we have reinvestigated the CN + propene reaction with significant additions to our previous study. The new synchrotron photoionization mass spectrometry (SPIMS) results performed here benefit from improved mass resolution. More importantly, in the initial study, we calculated the reference photoionization spectra of the three cyanopropene isomers ($\text{C}_4\text{H}_5\text{N}$), whereas in this paper we measure experimental photoionization spectra for all three isomers, using these basis functions to fit the isomer branching fractions of $\text{C}_4\text{H}_5\text{N}$ from the CN + propene reaction. However, as will be described, it is not possible to make conclusive assignments based solely on this methodology. Therefore, we also measure product mass spectra from the CN + propene-3,3,3- d_3 reaction. Deuterium elimination from the CD_3 group of propene-3,3,3- d_3 is measured from this reaction, which supports the formation of 3-cyanopropene.

EXPERIMENTAL METHODS

Details of the multiplexed SPIMS apparatus used in these experiments are described in several recent articles.^{14,16,21} The recent addition of an orthogonal acceleration time-of-flight mass spectrometer affords significantly higher resolution mass spectra ($m/\Delta m > 1500$) compared to the magnetic-sector spectrometer used in the previous CN + propene study.¹⁷

The experiment comprises a reaction flow tube coupled to a photoionization mass spectrometer. The flow tube is a 62 cm long quartz tube with 1.05 cm inner diameter. The gas pressure within the reaction tube is typically 4 Torr (533 kPa) with a total gas flow of 100 sccm. At room temperature, these conditions correspond to a gas flow velocity of 4 m s^{-1} . The He buffer gas, CN radical precursor (ICN, $\sim 1 \times 10^{13} \text{ molecules cm}^{-3}$), and reaction gas (propene, $9 \times 10^{14} \text{ molecules cm}^{-3}$) are supplied to the reaction flow via separate mass-flow controllers. The pressure within the reaction flow-tube is maintained at 4 Torr (533.3 Pa) using a butterfly valve that throttles a Roots pump. At room temperature (298 K) the total flow density is $1.3 \times 10^{17} \text{ molecules cm}^{-3}$. Within the flow-tube, radical reactions are initiated by photolysis of ICN using a pulsed excimer laser operating on KrF (248 nm), generating CN radicals uniformly throughout the reactor. The photolysis fluence is typically $\sim 15 \text{ mJ cm}^{-2}$ and the initial CN concentration is approximately $10^{11} \text{ molecules cm}^{-3}$. At $\sim 30 \text{ cm}$ along the flow tube, a $650 \mu\text{m}$ diameter pinhole allows a small portion of the gas mixture to escape into a vacuum chamber. This gas is sampled by a skimmer creating a beam of molecules that is subsequently intersected by the quasi-continuous vacuum-ultraviolet (VUV) synchrotron radiation. Ions formed in this region are then detected as a function of their mass-to-charge (m/z) ratio using a 50 kHz pulsed orthogonal-acceleration time-of-flight mass spectrometer. All detected ions are time-tagged relative to the excimer laser pulse and accumulated in a multi-channel scaler. In this way, complete mass spectra are collected as a function of reaction time. The excimer laser is operated at 4 Hz, allowing sufficient time between laser pulses to completely refresh the gas mixture before the next laser pulse. The photon energy of the synchrotron radiation can also be scanned, in this study from 9.8–11.5 eV in steps of 0.025 eV, and this ultimately provides a three-dimensional data set of time-resolved mass

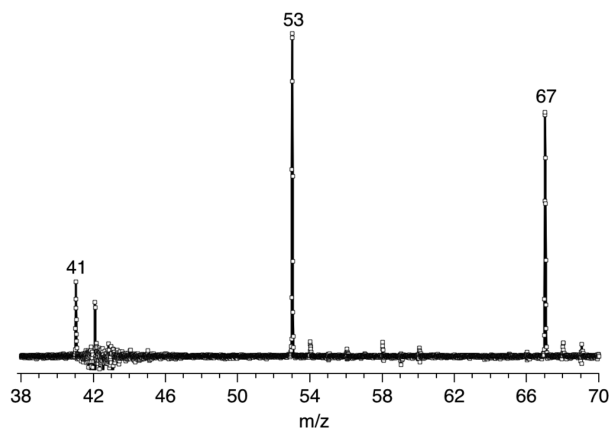


Figure 1. Mass spectrum of the products of the CN + C₃H₆ reaction, integrated over 9.8–11.5 eV photon energy and 0–80 ms after pulsing of the photolysis laser.

spectra and photoionization energy. All data are normalized for variations in the ALS photocurrent using a NIST-calibrated photodiode (SXUV-100, International Radiation Detectors, Inc.). All data reported here were acquired at 298 K.

Reagent gases were used without further purification: Propene-*d*₃ (CH₂=CHCD₃; 98%, Cambridge Isotope Laboratories) and undeuterated propene (≥99%, Sigma-Aldrich). Cyanopropene isomers were obtained from commercial vendors and used without further purification: 1-cyanopropene (mixture of *cis* and *trans*, 99%, Sigma-Aldrich), 2-cyanopropene (99%, Sigma-Aldrich), and 3-cyanopropene (98%, Sigma-Aldrich).

RESULTS AND DISCUSSION

Kinetically resolved mass spectra for the CN + propene reaction were gathered in steps of 0.025 eV in synchrotron photon energy over the 9.8–11.5 eV photon range. A product mass spectrum integrated over this entire photon energy range is shown in Figure 1. The spectrum is background-corrected by subtracting the averaged signal during the 20 ms prior to the excimer laser pulse. Figure 1 shows the most intense product peak appearing at *m/z* 53, consistent with C₃H₃N formation from CN addition to propene followed by CH₃ elimination. The plausible C₃H₃N species is cyanoethene. This conclusion is supported by the observed 10.91 eV onset of *m/z* 53 in the data and in agreement with computational predictions.^{10,17,20} The prominent peak at *m/z* 67 corresponds to C₄H₅N, indicative of CN addition to propene followed by H elimination. As stated previously, there are three species that might plausibly contribute to this mass channel: 1-cyanopropene (NC–CH=CHCH₃), 2-cyanopropene (CH₂=C(CN)CH₃), and 3-cyanopropene (CH₂=CHCH₂CN). The presence of iso-cyano isomers is ruled out on the basis of their comparatively lower adiabatic ionization energies (AIEs).¹⁷ In the following sections we discuss isomer assignments for this product channel. The *cis/trans* isomers for the 1- and 2-cyanopropene species are not distinguishable at the photoionization resolution of these experiments. The small sharp peak at about *m/z* 42 is an artifact of the background subtraction of the prelaser propene signal. Also apparent in Figure 1 is a peak at *m/z* 41, which likely arises from dissociative ionization of another product, as discussed below.

C₄H₅N Isomers. We measured absolute photoionization spectra for the three commercially available C₄H₅N isomers that are

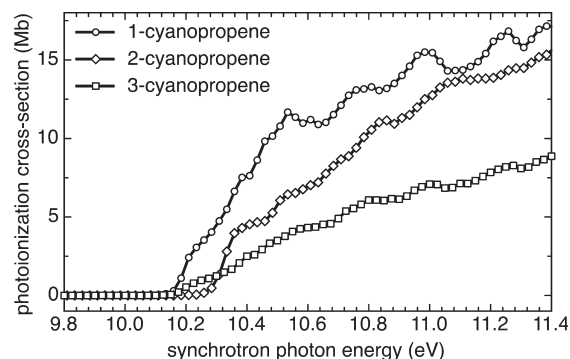


Figure 2. Absolute photoionization curves of three C₄H₅N isomers: 1-cyanopropene (circles), 2-cyanopropene (diamonds), and 3-cyanopropene (squares).

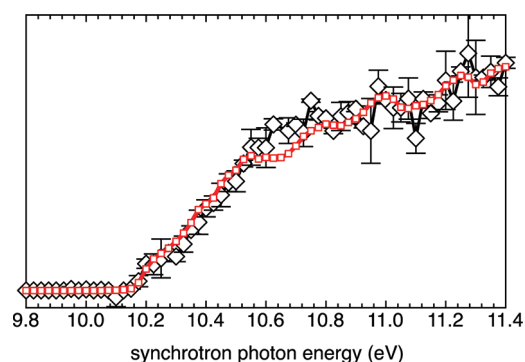


Figure 3. Photoionization spectrum of C₄H₅N⁺ (*m/z* 67) from the CN + propene reaction (diamonds) and the fitted curve (squares) corresponding to Fit 1 in Table 1 in the text.

considered for the *m/z* 67 mass channel, shown together in Figure 2. The observed onsets of 2-cyanopropene (10.3 ± 0.04 eV) and 3-cyanopropene (10.2 ± 0.04 eV) are in good agreement with the reported AIE values from threshold photoelectron measurements, 10.34 and 10.20 eV, respectively.²² 1-Cyanopropene has a measured vertical ionization energy of 10.23 eV,²³ in good accord with the measured onset in Figure 2 of 10.19 ± 0.04 eV. The 1- and 3-cyanopropene species have similar ionization onsets and there are similarities in all three spectra. As will be discussed below, this makes it difficult to uniquely fit these spectra to the *m/z* 67 photoionization spectrum from the CN + propene reaction. Also notable in Figure 2 is that, ~1 eV above threshold, the ionization cross sections can differ by as much as a factor of 2. Some evidence of the different ionization properties of these cyano isomers, particularly the gradual onset in the case of 3-cyanopropene, has been noticed before,²² but the cause of the differences in cross section is not clear.

The measured photoionization spectrum for the *m/z* 67 product channel resulting from the reaction of CN + propene is shown in Figure 3. It is worth noting that the photoionization spectrum of *m/z* 67 reported here is essentially the same as that reported in ref 17 except that the reduction of signal after 11.1 eV is not observed in the current trace. It is possible this was due to a fluctuation in the CN precursor concentration in the previous experiments; in the present experiments, the ICN concentration in the flow was carefully monitored and the data in Figure 2 are the average of two photoionization scans. The error bars in

Table 1. Fitted Isomer Branching Fractions for the C_4H_5N Product Channel of the CN + Propene Reaction^a

fit	C_4H_5N isomer			S
	1-cyanopropene	2-cyanopropene	3-cyanopropene	
1	0.50 ± 0.12	0	0.50 ± 0.24	0.158
2	0.76 ± 0.12	0.24 ± 0.14	0 ^b	0.169

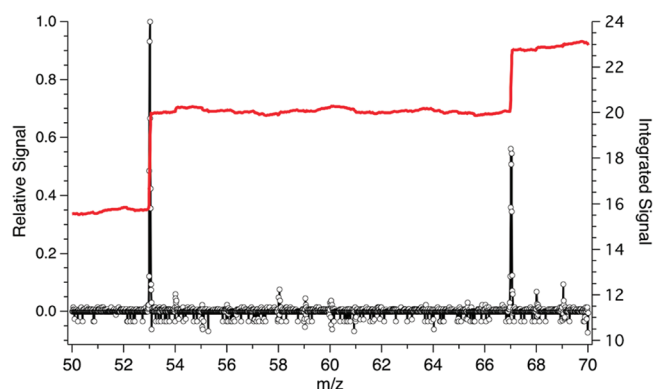
^a Uncertainties represent 2σ from the fit. ^b In this fit, the weighting of the 3-cyanopropene is fixed at zero.

Figure 3 are 1σ about the mean value. To determine product branching fractions, the reference photoionization spectra in Figure 2 were incorporated into a fitting procedure to assign the individual weighting coefficients for each isomer that best reproduces the measured photoionization spectrum curve in the CN + propene reaction. The fitting routine was executed using the Levenberg–Marquardt algorithm. The fitting found the best fit of weighting terms to be an isomeric composition of 1-cyanopropene and 3-cyanopropene with branching fractions of 0.50 ± 0.12 and 0.50 ± 0.24 , respectively, and the weighting constant for 2-cyanopropene hits the lower limit of zero. The resulting branching fraction values are provided in Table 1, where S is the sum of the squared residuals and is labeled Fit 1. The simulated trace using these fitting parameters is shown compared to the experimental data in Figure 3.

If the 3-cyanopropene weighting coefficient is fixed at 0, the best fit yields branching fractions of 0.76 ± 0.12 for 1-cyanopropene and 0.24 ± 0.14 for 2-cyanopropene with a S value of 0.169, shown as fit 2 in Table 1. These two fits yield similar S values (0.158 vs 0.169), and the closeness of these values renders it difficult to conclusively assign the product branching ratios from these data. In fact, a difficult situation exists with this system of C_4H_5N product isomers because the photoionization spectrum of the 1-cyanopropene is rather well reproduced as a linear combination of the other two isomers. At the signal-to-noise level and energy resolution of the experimental data, it is difficult to reach definitive conclusions other than to say that 1-cyanopropene is very likely to be formed from this H-elimination product channel and that, based solely on these data, neither 2-cyanopropene nor 3-cyanopropene can be unequivocally ruled out.

The CN + propene computational studies of Huang et al.²⁰ concluded that 2-cyanopropene is not formed in significant quantities. This lends support to fit 1 (i.e., the exclusive production of 1- and 3-cyanopropene). To gain further insight into the product distributions, the H and D loss product channels from the CN + propene- d_3 reaction were studied. As described below, this additional experiment provides further support for fit 1 over fit 2.

Major Product Channels. The relative abundance of the CH_3 and H elimination channels observed in the mass spectrum is also examined to establish branching ratios for these two distinct product mass channels (m/z 53 and 67, respectively). Figure 4 shows the mass spectrum in the region of these two ions acquired at photon energies 11.025–11.05 eV. The integrated signal ratio of these two ions is 1.000:0.698 for m/z 53 and 67, respectively. For quantitative comparison of these product channels the signal must be adjusted by the respective photoionization cross sections and instrumental mass discrimination effects.^{21,24} Here, 14 Mb ($1 \text{ Mb} = 1 \times 10^{-18} \text{ cm}^{-2}$) is used for m/z 53, corresponding to the approximated cross section over the 11.025–11.05 eV range

**Figure 4.** Mass spectrum integrated over 0–80 ms and 11.025–11.05 eV for the CN + propene reaction (black) and the integrated signal (red).

for cyanoethene,¹⁷ and a value of 11 Mb is used for m/z 67 based on the branching fractions for 1- and 3-cyanopropene predicted by fit 1 (Table 1) and the absolute photoionization cross sections presented in Figure 2. After normalization for the photoionization cross-section, the signals are then corrected based on their mass-dependent sampling efficiencies inherent in the experiment ($m/z^{0.66}$). This empirical mass dependent detection-efficiency correction was validated by recording mass spectra of a calibration gas containing known concentrations of H_2 , Ar, Kr, and Xe, for which absolute cross-section measurements are known. After correcting the measured signal in this manner, the relative branching fractions are found to be 0.59 ± 0.15 for m/z 53 and 0.41 ± 0.10 for m/z 67 with uncertainties estimated to be $\pm 25\%$ arising primarily from the uncertainty in the photoionization cross sections.

For comparison, a similar calculation is made using the branching fractions predicted by Fit 2. In this case the average photoionization cross-section for the isomeric distribution in the m/z 67 channel increased to 14.6 Mb and, as a result, the relative fractions change to 0.65 ± 0.16 for m/z 53 and 0.35 ± 0.09 for m/z 67. In both cases, the loss of CH_3 radicals dominates the fragmentation in CN + propene.

The branching ratio for m/z 53 and m/z 67, using the photoionization cross section for m/z 67 with the isomer composition from fit 1, reconciles well with the work of Gannon et al. who measured H atom product yields using LIF techniques.¹⁰ For the title reaction they report H atom yields at 0.478 ± 0.045 at 2 Torr and 0.392 ± 0.050 at 5 Torr. Linearly interpolating these measurements to 4 Torr yields 0.420 ± 0.050 . This agreement between the two studies further supports the assignments resulting from fit 1. The RRKM calculations of Huang et al. also predict CH_3 to dominate over H elimination with the ratio sensitive to the initial CN adduct complex and the collision energy.²⁰

Apparent also in Figure 1 is a signal at m/z 41. From the title reaction, the possibility of a $HCN + C_3H_5$ product (mass 41) deserves discussion. A recent article by Suits and co-workers²⁵ reports results for the CN + 1-pentene reaction using a crossed molecular beam experiment with collision energies within the 5–9 kcal/mol range. In this study they see evidence for a significant H-abstraction channel that concurrently gives rise to a resonantly stabilized C_5H_9 radical species. In light of their CN + 1-pentene result, further examination of H-abstraction in the CN + propene reaction is warranted, where the analogous channel would produce the resonantly stabilized allyl radical (C_3H_5).

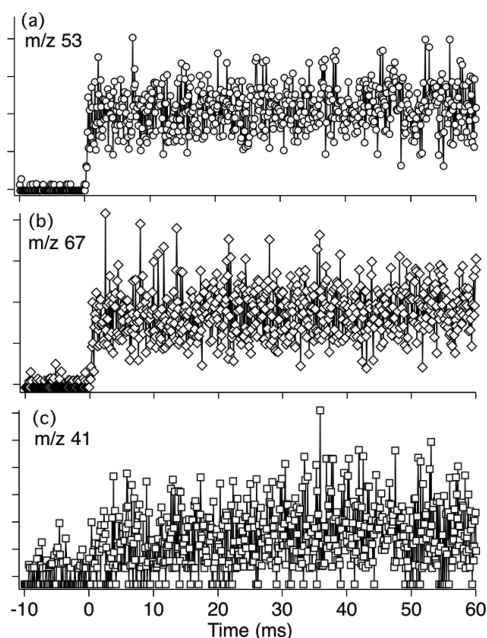


Figure 5. Time traces for the (a) m/z 53, (b) m/z 67, and m/z 41 (c) signals integrated over 9.8–11.5 eV. The time binning is 100 microseconds.

The computational study by Huang et al.²⁰ notes that there are three distinct H-abstraction pathways for CN + propene to directly yield HCN + C₃H₅ and explores the thermodynamics of these pathways using CCSD(T) calculations. They find all these H-abstraction barriers to be less than 2.2 kcal/mol with abstraction from the methyl group to have the lowest barrier at 1.1 kcal/mol. Among C₃H₅ isomers, the allyl + HCN abstraction channel is the most stable, with an energy of -37.7 kcal mol⁻¹ relative to the reactants.²⁰ Both Gannon et al.¹⁰ and Huang et al.²⁰ also find an alternative addition–elimination pathway leading to allyl + HCN, and although these pathways remain below the energy of the reactants, relatively high barriers from the adduct make them unlikely to be competitive with H and CH₃ elimination channels from the same intermediates.

A previous attempt to detect the allyl radical from this reaction found no evidence to support this direct channel, but with the new TOF-MS detection configuration, the substantial increase in mass resolution allows us to clearly resolve m/z 41 at higher photon energies (where the radical has a larger photoionization cross-section) even in the presence of very large propene signal. The allyl radical has an AIE of 8.13 eV.^{26–28} However, the m/z 41 signal we observe has an onset in the 9.805–9.91 eV region. The time trace of the m/z 41 signal, integrated over 9.8–11.5 eV, is shown in Figure 5, along with the time traces of the m/z 53 and m/z 67 channels for comparison, and the mass 41 signal does not appear to decay like a radical should.²⁹ Thus, the m/z 41 signal is not consistent with a direct H-abstraction channel of the CN + propene reaction. In other experiments, Fischer and co-workers have reported in a VUV synchrotron photoionization study that the allyl radical undergoes significant dissociative photoionization above 10.5 eV with the appearance of a C₃H₃⁺ (mass 39) fragment occurring above 10 eV.³⁰ It was shown in that study that C₃H₃⁺ + H₂ is a dominant allyl dissociative ionization channel and that at ~ 10.5 eV the C₃H₃⁺ (m/z 39) signal should be approximately equal in intensity to the C₃H₅⁺ ion signal. Up to

Scheme 2

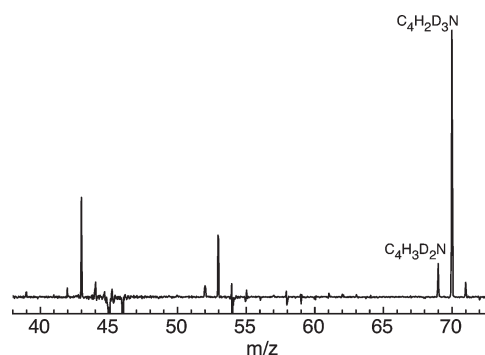
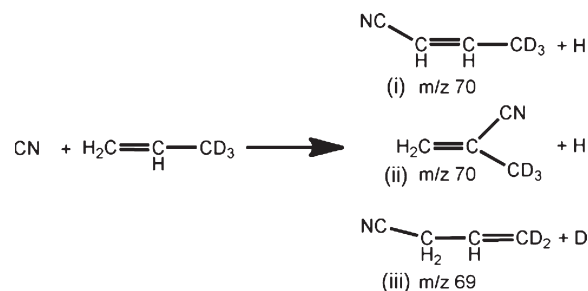


Figure 6. Mass spectrum of the CN + (3,3,3)-propene-*d*₃ reaction integrated over 0–80 ms and 9.8–11 eV photon energy.

11.5 eV we do not detect the C₃H₃⁺ fragment ion in the mass spectrum (Figure 1). In other experiments where the allyl radical was created by the 193 nm photolysis of allyl chloride and definitively detected at 8.3 eV photon energy, we do observe dissociative ionization of allyl radical to form C₃H₃⁺, in agreement with Fischer et al.

With the kinetic trace of the m/z 41 signal inconsistent with a radical product and the lack of observable C₃H₃⁺ above 10.5 eV, it does not appear that this signal results from an allyl + HCN product channel from the title reaction. It is rather suspected to be due to dissociative ionization of a higher mass species, perhaps C₃H₅I formed in side reactions.

CN + Propene-*d*₃ (CH₂CHCD₃). To further investigate the possible formation of 3-cyanopropene we turned to the CN + propene-3,3,3-*d*₃ reaction. As shown in Scheme 2, following the reaction schemes of Huang et al.,²⁰ the 3-cyanopropene product should be the only isomer directly formed from a D-elimination process, yielding (iii in Scheme 2) CD₂=CHCH₂CN (m/z 69), whereas the H-elimination isomers will appear at m/z 70. The m/z 70 species could be either (i) 1-cyanopropene-*d*₃ or (ii) 2-cyanopropene-*d*₃.

A background-subtracted product mass spectrum, accumulated over 9.8–11 eV photon energy, is shown in Figure 6, with peaks present at both m/z 70 (C₄H₂D₃N) and m/z 69 (C₄H₃D₂N). A low signal-to-noise photoionization spectrum (not shown) suggests that the m/z 69 channel has an onset between 10.2–10.3 eV, as expected for the cyanopropene isomers. The peak at m/z 70 is much stronger and the photoionization spectrum of this mass channel is shown in Figure 7. According to the crossed molecular beam study of Gu et al. the production of 1-cyanopropene-*d*₃ + H from the CN + propene-3,3,3-*d*₃ reaction forms in a relative yield of 3:1 over corresponding D-loss channels.¹⁹

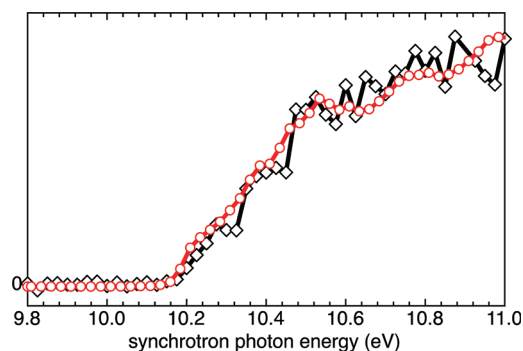


Figure 7. Photoionization spectrum (m/z 70; diamonds) from the CN + propene- d_3 reaction compared to the measured photoionization spectrum of (undeuterated) 1-cyanopropene (circles).

The results here appear to be in good accord with these findings assuming that the photoionization cross-section is not dramatically changed by deuteration. The studies of Person and Nicole have shown that several undeuterated and deuterated hydrocarbons, including propene, have similar photoionization spectra to their undeuterated counterparts.³¹ The appearance of the D-loss channel, attributable to 3-cyanopropene, is also predicted by the computational study of Huang et al.²⁰ The predicted branching fractions depend on the collision energy and the structure of the CN-adduct complex, but H-elimination is predicted in the computational study to dominate over D-elimination (i.e., 1-cyanopropene- d_3 should dominate over 3-cyanopropene- d_2), regardless of entrance channel. Also, kinetic isotope effects alter the predicted product branching fraction values compared to the undeuterated case.

Figure 7 depicts the photoionization spectrum of m/z 70 and it contains an overlay of the measured undeuterated 1-cyanopropene photoionization spectrum for comparison. Both have similar onsets and the same general shape versus photon energy. Considering that the photoionized electron emanates from the $C=C \pi$ system, the similarities seem reasonable and suggest that the isomer responsible for the m/z 70 signal is predominantly 1-cyanopropene- d_3 , with little contribution from 2-cyanopropene- d_3 . If it is assumed that the 3-cyanopropene- d_2 and 1-cyanopropene- d_3 species have the same photoionization cross sections as their undeuterated counterparts over this photon energy range, the resulting normalization ratio is 2.5:1 (for 1- and 3-cyanopropene), based on the measured photoionization cross-section values. The branching fractions for H-loss and D-loss for the CN + CH_2CHCD_3 reaction are then estimated to be 0.75 and 0.25, respectively. This result agrees well with the branching fraction reported by Gu et al.¹⁹ in crossed beam studies of the same reaction at higher collision energy.

CONCLUSION

The CN + propene reaction is reinvestigated using SPIMS at room temperature and 4 Torr. The dominant product channel is found to be $C_2H_3CN + CH_3$ and there is also a significant $C_4H_5N + H$ channel. 1-Cyanopropene is the dominant C_4H_5N isomer arising from H-elimination but not the exclusive contributor to this product mass channel. Contrary to our previous report, we find that 3-cyanopropene is likely to also be produced in significant quantities. Although we cannot unequivocally rule out the contribution of 2-cyanopropene based purely on the

measured photoionization spectrum of the C_4H_5N m/z 67 channel, product isotopic ratios from CN + propene- d_3 experiments provide further evidence against significant 2-cyanopropene production.

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