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Reaction Dynamics on the Formation of 1- and 3-Cyanopropylene in the Crossed Beams Reaction of Ground-State Cyano Radicals (CN) with Propylene (C_3H_6) and Its Deuterated Isotopologues†

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Crossed molecular beams experiments were utilized to explore the chemical reaction dynamics of ground-state cyano radicals, $CN(X^2\Sigma^+)$, with propylene (CH_3CHCH_2) together with two d_3-isotopologues (CD_3CHCH_2, CH_3CDCD_2) as potential pathways to form organic nitriles under single collision conditions in the atmosphere of Saturn's moon Titan and in the interstellar medium. On the basis of the center-of-mass translational and angular distributions, the reaction dynamics were deduced to be indirect and commenced via an addition of the electrophilic cyano radical with its radical center to the α-carbon atom of the propylene molecule yielding a doublet radical intermediate: CH_3CHCH_2CN. Crossed beam experiments with propylene-*1,1,2*-d_3 (CH_3CDCD_2) and propylene-*3,3,3*-d_3 (CD_3CHCH_2) indicated that the reaction intermediates CH_3CDCD_2CN (from propylene-*1,1,2*-d_3) and CD_3CHCH_2CN (from propylene-*3,3,3*-d_3) eject both atomic hydrogen through tight exit transition states located about 40−50 $kJmol^{-1}$ above the separated products: 3-butenenitrile [H_2CCDCD_2CN] (25%), and *cis*/*trans*-2-butenenitrile [$CD_3CHCHCN$] (75%), respectively, plus atomic hydrogen. Applications of our results to the chemical processing of cold molecular clouds like TMC-1 and OMC-1 are also presented.

1. Introduction

The chemical dynamics of ground-state cyano radicals, $CN(X^2\Sigma^+)$, with unsaturated hydrocarbons are of paramount importance in understanding the formation of nitrogen-bearing polycyclic aromatic hydrocarbons together with their hydrogen deficient precursors such as nitriles from the "bottom up" in the interstellar medium[1] and in hydrocarbon-rich atmospheres of planets and their moons, predominantly of Titan.[2,3] Here, molecular nitrogen (N_2) and methane (CH_4) are the main constituents of Titan's atmosphere followed by hydrogen (H_2), nitrogen bearing molecules such as nitriles, and hydrocarbons.[4−10] Even though the unsaturated hydrocarbon molecules like acetylene (C_2H_2), ethylene (C_2H_4), diacetylene (HCCCCH)), and benzene (C_6H_6) occur only in trace amounts,[11] they are of particular importance because they are thought to be key intermediates to form Titan's organic, aerosol-particle based haze layers.[12−22] Whereas the main source of the cyano radicals has been unambiguously identified as the photolysis of hydrogen cyanide (HCN),[23−28] the underlying dynamics and kinetics of cyano radical reactions and the role in the build-up of complex hydrocarbons have started to emerge only recently.[29]

Because the macroscopic alteration of Titan's atmosphere consists of multiple elementary reactions that are a series of bimolecular encounters between radicals and molecules, a detailed understanding of the mechanisms involved at the microscopic level is crucial to unravel the chemical evolution and processing of Titan's atmosphere. These are experiments under single collision conditions in which particles of one supersonic beam are made to "collide"only with particles of a second beam. Studies of cyano radical reactions with unsaturated hydrocarbons utilizing the crossed molecular beams method provided valuable input data into chemical models of Titan demonstrating the potential of this approach. These were the formation of cyano acetylene (HCCCN), vinyl cyanide (C_2H_3-CN), cyanobenzene (C_6H_5CN), 1-cyanoallene ($H_2CCCHCN$), as well as 1- and 3-cyanomethylacetylene (CH_3CCCN; $HCCCH_2CN$) plus atomic hydrogen from reactions of cyano radicals with acetylene,[29] ethylene,[30] benzene,[31] allene,[32] and methylacetylene,[33] respectively, as studied in our group. Recent kinetics experiments at temperatures as low as 13 K demonstrated nicely that cyano radical reactions with unsaturated hydrocarbons were fast (a few 10^{-10} cm^3 s^{-1}) and proceeded without entrance barriers.[34] However, these experiments monitored only the decay kinetics of the cyano radical, and reaction products could not be sampled. On the other hand, crossed molecular beam experiments can hardly provide temperature dependent rate constants. Therefore, a combination of kinetics experiments with crossed molecular beams data provide a powerful approach to elucidate the rate constants, reaction intermediates, and the nascent products of cyano radical reactions with unsaturated hydrocarbons in hydrocarbon-rich atmospheres of planets and their moons.

Here, we expand our previous studies and elucidate the reaction dynamics of cyano radicals with propylene ($CH_3CH{=}CH_2$) in a crossed molecular beams experiment. Earlier investigations of the cyanopropylene system and of the relevant C_4H_6N and C_4H_5N potential energy surfaces (PES) are meager. In 1964, Pearson et al. identified the 2-cyano-2-propyl radical intermediate for the first time via electron spin resonance.[35] This radical has also been characterized by electronic structure calculations.[36] Sims and Smith followed the kinetics of the reaction of cyano radicals with propylene down to temperatures as low as 15 K and deduced that the reaction had no entrance barrier and proceeded close to gas kinetics with rate constants of a few 10^{-10} cm^3 s^{-1}.[37] Very recently, Pilling and co-workers monitored the hydrogen atom yield in the reactions of cyano

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radicals with unsaturated hydrocarbons, among them propylene, at 298 and 195 K.[38] Coupled with electronic structure calculations, the authors suggested that the cyano radical adds without entrance barrier to the carbon−carbon double bond of the propylene molecule followed by an emission of a hydrogen atom. According to these calculations, a second channel was found to be the formation of the methyl radical plus vinyl cyanide, with a branching ratio of the atomic hydrogen versus methyl loss of about 49% versus 51%.

In the present crossed beam experiments, by utilizing partially deuterated reactants propylene-*1,1,2*-d_3 (CH_3CDCD_2) and propylene-*3,3,3*-d_3 (CD_3CHCH_2), we aim to extract to what extent the hydrogen atom is emitted from the vinyl group and/or from the methyl group. This allows us to obtain branching ratios of the reaction products and to identify important reaction intermediates. Finally, we compare the reaction dynamics and extracted branching ratios with the related reaction of cyano radicals with methylacetylene, in which two distinct isomers, i.e., 1- and 3-cyanomethylacetylene (CH_3CCCN; $HCCCH_2CN$), were identified as the primary reaction products at a branching ratio of about 1.[32] Note that in 2007, propylene was also identified toward the cold molecular cloud TMC-1 with column densities of 4×10^{13} molecules cm^{-2}.[39] This corresponds to fractional abundances of 4×10^{-9} with respect to molecular hydrogen, i.e., the same order of magnitude of ubiquitous interstellar molecules such as cyclopropenylidene (c-C_3H_2).[40] The authors noted that although propylene could play an important role in the chemistry of the interstellar medium, gas phase chemical models have largely ignored this molecule, predominantly because information on the reaction products are lacking. So far, only the reaction of astrophysically relevant ground-state carbon atoms with propylene yielding 1- and 3-methylpropargyl products plus atomic hydrogen, has been studied under single collision conditions.[33] Therefore, we hope that our experimental investigation of the cyanopropylene system will also aid to develop more comprehensive models of the chemical evolution of cold molecular clouds involving propylene reactant molecules.

2. Experimental Section

The experiments were carried out in a crossed molecular beam machine at The University of Hawai'i under single collision conditions.[41] A pulsed supersonic cyano radical beam, $CN(X^2\Sigma^+)$, is generated in situ in the primary source chamber via laser ablation of graphite at 266 nm at pulse energies of 20 mJ and subsequent reaction of the ablated species with neat nitrogen gas (99.9999%; Gaspro) which also acts as seeding gas.[42] After passing a skimmer, a four-slot chopper wheel selected a part of the cyano radical beam with a peak velocity, v_p, of 1573 ± 27 ms^{-1} and a speed ratio, *S*, of 3.0 ± 0.3. This radical beam intersected pulsed propylene [CH_3CHCH_2, Aldrich; 99+ %], propylene-*3,3,3*-d_3 [CD_3CHCH_2, CDN; 99+ % D], and propylene-*1,1,2*-d_3 [CH_3CDCD_2, CDN; 99+ % D] beams released by a second pulsed valve (propylene and propylenes-d_3) under a well-defined collision energy of 25.5 ± 1.3 kJ mol^{-1} (cyanopropylene) in the interaction region. Peak velocities of the secondary beams were 835 ± 25 ms^{-1} (propylene) and 765 ± 20 ms^{-1} (propylenes-d_3) at speed ratios of 12.5 ± 1.0 (propylene) and 8.0 ± 0.4 (propylenes-d_3). We should indicate that besides the cyano radical, the primary beam also contains carbon atoms as well as dicarbon and tricarbon molecules. However, we have shown recently that tricarbon molecules have a significant entrance barrier upon reacting with unsaturated hydrocarbon molecules.[43] Therefore, even if tricarbon is in the beam, it does not react with propylene under our experimental conditions. Dicarbon molecules and carbon atoms have masses of 24 and 12 amu, respectively, compared to 26 amu for the cyano radical. Therefore, carbon and dicarbon molecules lead to reaction products which are lower in mass than those formed in the reaction of cyano radicals with propylene.

The reactively scattered products were probed using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules at 80 eV at an emission current of 2 mA. The detector could be rotated within the plane defined by the primary and the secondary reactant beams to take angular resolved TOF spectra. By integrating the TOF spectra at the laboratory angles and correcting for the day-to-day intensity fluctuations of the cyano radical beam, we could obtain the laboratory angular distribution, which depicted the integrated signal intensity of an ion of distinct *m*/*z* versus the laboratory angle. Information on the chemical dynamics was gained by fitting these TOF spectra and the angular distribution in the laboratory frame (LABORATORY) using a forward-convolution routine.[24−26] This approach initially assumed an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then calculated from these center-of-mass functions. Because previous kinetics studies of cyano radical reactions with propylene showed the absence of an entrance barrier to reaction,[37,38] we included an energy dependent cross section, $\sigma(E_c) \sim E_C^{-1/3}$ with the collision energy E_C.[44] Due to the low signal counts, we had to record up at least 2×10^6 TOF spectra to obtain a reasonable signal-to-noise ratio of the reactively scattered species. This limited us to carry out the experiments with the deuterated propylene reactants only at the corresponding center-of-mass angles.

3. Results

3.1. Laboratory Data. In case of the cyano radical (26 amu)−propylene (42 amu) system, we recorded reactive scattering signal at mass to charge ratios at $m/z = 67$ ($C_4H_5N^+$) (Figure 1) and $m/z = 66$ ($C_4H_4N^+$). TOF spectra recorded at the lower *m*/*z* ratio showed identical pattern and could be fit with identical center-of-mass functions as those data taken at $m/z = 67$. This finding indicates that signal at $m/z = 66$ originated from dissociative ionization of the C_4H_5N reaction product in the electron impact ionizer of the detector. This experimental finding alone verifies that in the reaction of the cyano radical with propylene, the cyano radical versus atomic hydrogen exchange channel is open. Figure 2 depicts the laboratory angular (LABORATORY) distribution of the ion counts at $m/z = 67$ ($C_4H_5N^+$). This distribution is relatively broad and spreads over about 50° in the scattering plane defined by both supersonic beams. Besides the atomic hydrogen loss, we also attempted to check for a possible methyl group (CH_3) loss channel. This was achieved by monitoring ion counts at $m/z = 53$ ($C_3H_3N^+$). However, the signal at $m/z = 53$ can also originate from reaction of ground-state carbon atoms (12 amu) with propylene (42 amu). As a matter of fact, the number densities of the carbon atoms are one order of larger than the cyano radicals; therefore, it was not feasible to monitor the methyl group loss pathway in the cyanopropylene system. However, experiments are on the way utilizing photolysis of cyanogen as a cyano radical beam source and monitoring the methyl radical via REMPI detection schemes.[45]

Because we have identified the atomic hydrogen elimination channel, it is important to elucidate the position of the hydrogen

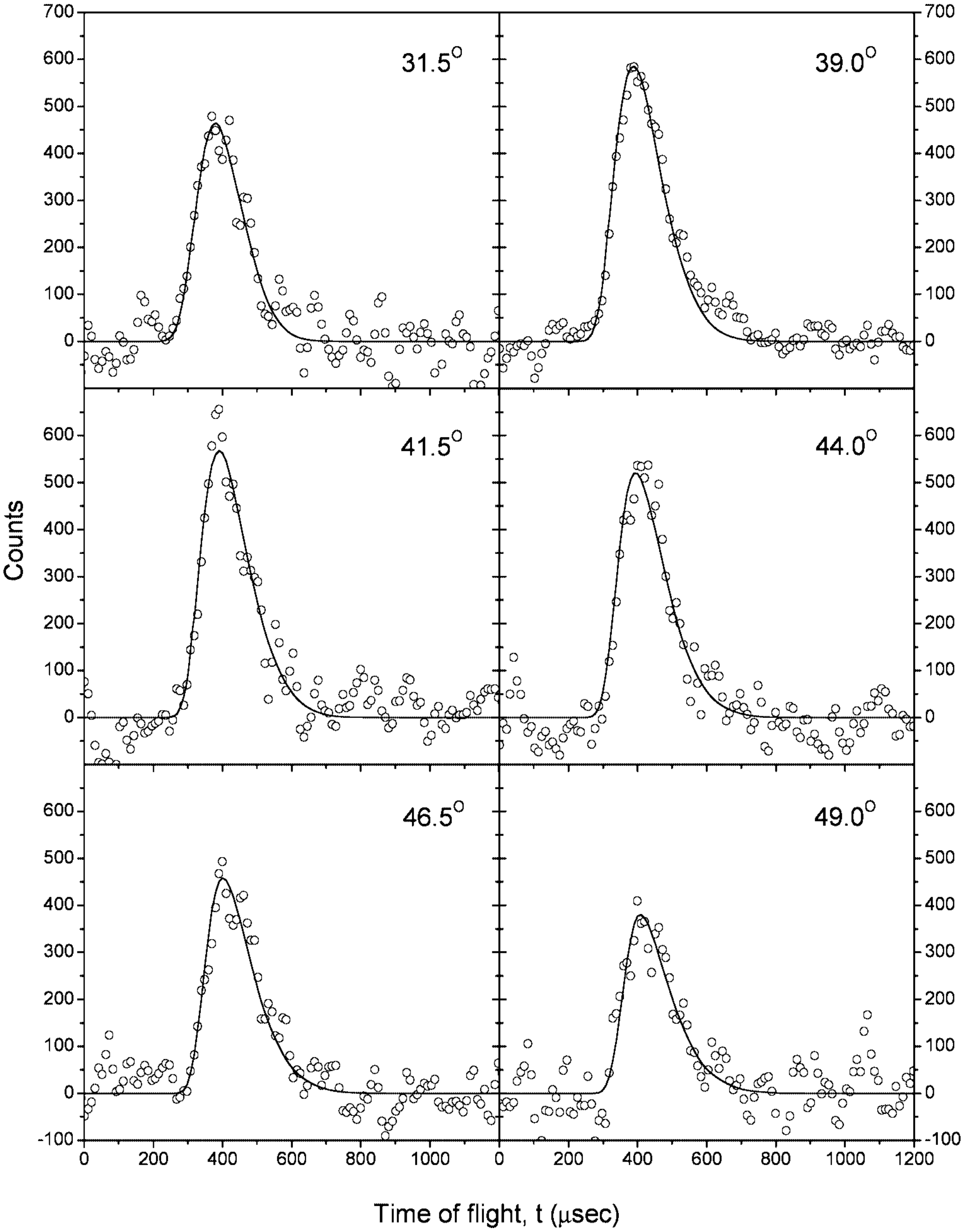

Figure 1. Selected time-of-flight data recorded at mass-to-charge (*m*/*z*) of 67 ($C_4H_5N^+$) in the reaction of cyano radicals with propylene at a collision energy of 25.5 ± 1.3 kJ mol^{-1}. The open circles are the experimental data; the solid lines, the fits. Intensities are relative intensities and have been scaled for identical data accumulation times.

loss (does it come from the methyl and/or vinyl group?) and to extract branching ratios. Therefore, we conducted crossed beams studies of the cyano radicals with propylene-*3,3,3-d*$_3$ (CD_3CHCH_2) and propylene-*1,1,2-d*$_3$ (CH_3CDCD_2). In both cases, an atomic hydrogen loss should lead to a product of the gross formula $C_4H_2D_3N$, which can be observable via its ion at *m*/*z* = 70. Note that the competing deuterium elimination ($C_4H_3D_2N$) can only lead to signal at *m*/*z* = 69. In both CD_3CHCH_2 and CH_3CDCD_2 systems, we were able to monitor signal at *m*/*z* = 70 (Figure 3). This indicates that hydrogen atoms are emitted from the vinyl group (in CD_3CHCH_2) *and* also from the methyl group (CH_3CDCD_2). However, it is important to stress that, on the basis of the time-of-flight spectra recorded at the center-of-mass angle, the signal at *m*/*z* = 70 originating from the CH_3CDCD_2 is less intense compared to the CD_3CHCH_2 reactant. Consequently, we can conclude that two hydrogen elimination pathways exist: from the vinyl group and from the methyl group. We recall that the use of partially deuterated reactants only allowed us to record TOF spectra at the corresponding center-of-mass angles due to the low signal counts and the costs of these chemicals.

3.2. Center of Mass Translational Energy, *P*(*E*$_T$), and Angular Distribution, *T*(*θ*). A sensible fit of the TOF data (Figure 1) and LABORATORY distribution (Figure 2) of signal at *m*/*z* = 67 ($C_4H_5N^+$) was obtained with a one-channel fit resulting in reaction product(s) of the molecular formula C_4H_5N plus a hydrogen atom. Best fits of the center-of-mass translational energy distribution, *P*(*E*$_T$), were accomplished with distributions extending to a maximum translational energy release, E_{max}, of 130 ± 8 kJ mol^{-1}. We recall that that the high energy cutoff resembles the sum of the absolute of the reaction energy and the collision energy. Therefore, we can subtract the collision energy from E_{max} to compute the reaction energy to be −103 ± 8 kJ mol^{-1}. Also, the *P*(*E*$_T$) is very broad and depicts an obvious distribution maximum far away from zero translational energy, i.e., of about 40−50 kJ mol^{-1}. This suggests that

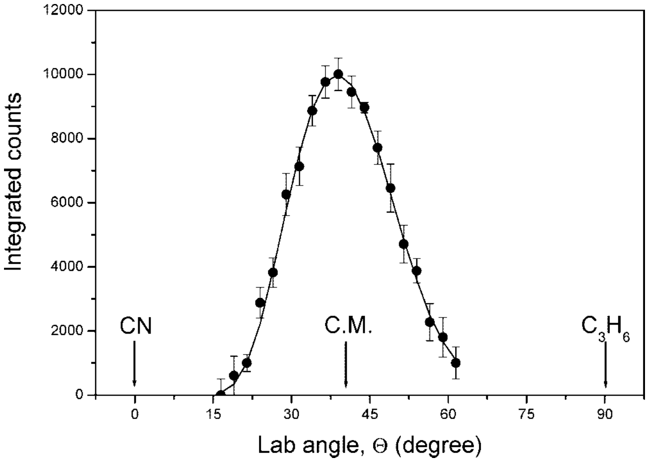

Figure 2. Laboratory angular distribution of ion counts recorded at mass-to-charge (*m*/*z*) of 67 ($C_4H_5N^+$) in the reaction of cyano radicals with propylene at a collision energy of 25.5 ± 1.3 kJ mol^{-1}. The circles are the experimental data; the solid lines, the fits. C.M. defines the center-of-mass angle.

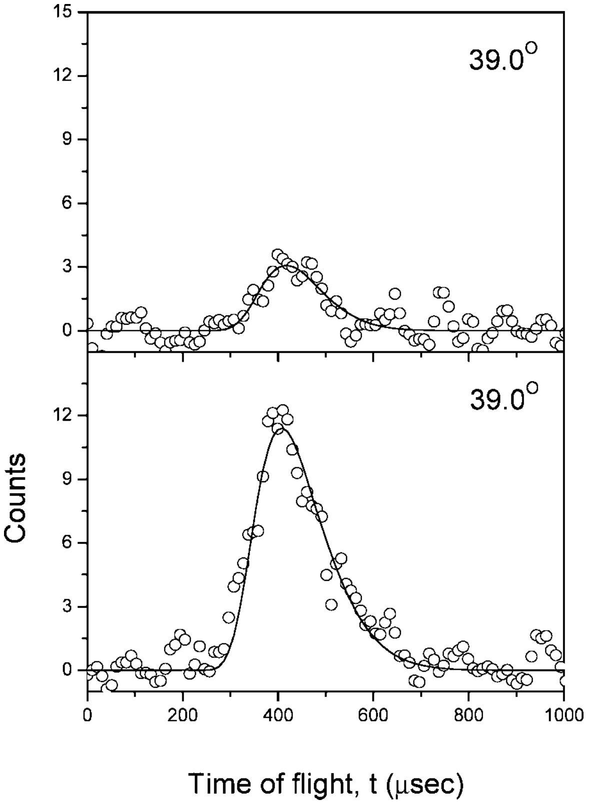

Figure 3. Time of flight spectra of mass-to-charge (*m*/*z*) of 70 ($C_4H_2D_3N^+$) recorded during the reactions of cyano radicals with propylene-*3*,*3*,*3*-d_3 (CD_3CHCH_2) (lower) and propylene-*1*,*1*,*2*-d_3 (CH_3CDCD_2) (upper). The open circles are the experimental data; the solid lines, the fits. Intensities are relative intensities; data accumulation times for reactions of cyano radicals with propylene-*3*,*3*,*3*-d_3 (CD_3CHCH_2) (lower) and propylene-*1*,*1*,*2*-d_3 (CH_3CDCD_2) (upper) are identical.

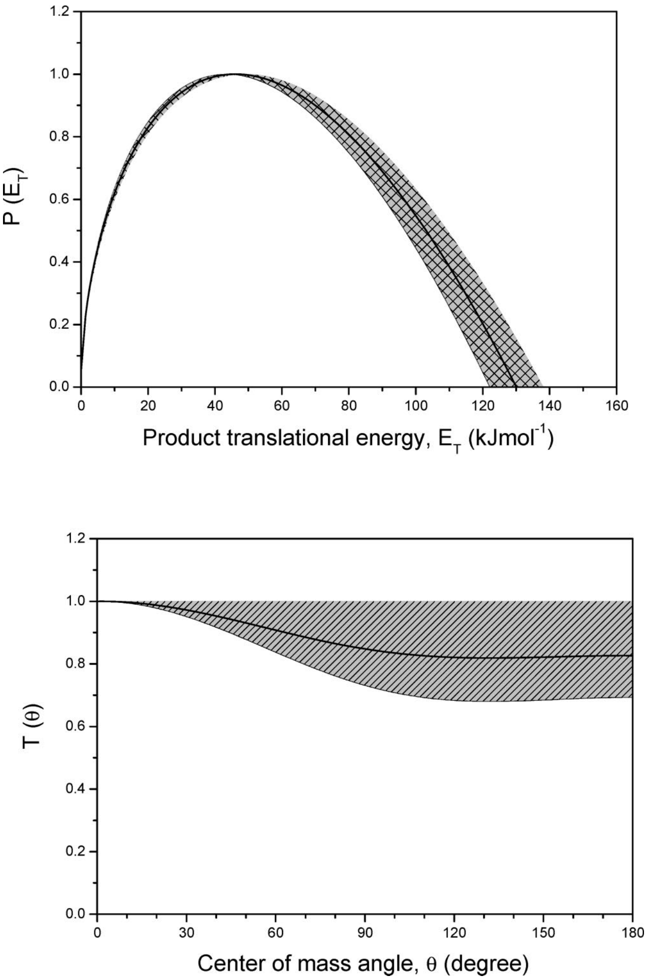

Figure 4. Center-of-mass translational (upper) and angular distributions (lower) of the C_4H_5N product(s) formed in the reaction of cyano radicals with propylene. The hatched areas account for the experimental error limits of the laboratory angular distribution as well as the peak velocity and speed ratio; the solid line presents the "best fit" holding the lowest χ^2 parameter of the fitting routine. Data in Figure 3 could be fit with identical center of mass angular (Figure 3, top and bottom) and translational energy (Figure 3, bottom); however, to fit the time-of-flight recorded during the reactions of cyano radicals with propylene-*1*,*1*,*2*-d_3 (CH_3CDCD_2), the center-of-mass translational energy distribution had to be cut by about 40 kJ mol^{-1}; also, the distribution maximum of the $P(E_T)$ shifted downward to about 30 kJ mol^{-1}.

the exit barrier(s) is (are) likely to be tight.[44] By integrating the center-of-mass translational energy distribution and accounting for the available energy, we can also compute that the average fraction of available energy channeling into the translational degrees of freedom is 43 ± 4%.

Second, the center-of-mass angular distribution, $T(\theta)$, aids us to gather additional data on the reaction dynamic. Figure 4 shows that the angular flux distribution depicts intensity over the complete angular range from 0° to 180°. Best fits could be achieved with a slightly forward-scattered (with respect to the cyano radical beam) distribution; on the basis of the χ^2 parameter in the fitting routine and a visual inspection of the TOF spectra and LABORATORY distribution, an isotropic fit only yielded a slightly worse fit. These findings indicate that the reaction proceeds via a C_4H_6N reaction intermediate via indirect scattering dynamics. On the basis of the best fit functions, the lifetime of this intermediate is comparable to its rotational period.[30]

We also comment on the center-of-mass functions utilized to fit the data obtained in the CN−CD_3CHCH_2 and CN−CH_3CDCD_2 systems (Figure 3). Most importantly, signal at m/z = 70 ($C_4H_2D_3N^+$) for each system could be fit with a single channel using identical center-of-mass angular distributions as obtained from the cyanopropylene system. However, the center-of-mass translational energy distributions depict interesting features. Considering the reaction of cyano radicals with propylene-*3*,*3*,*3*-d_3 (CD_3CHCH_2), the TOF at m/z = 70

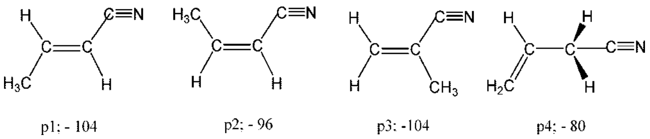

Figure 5. Reaction energies in kJ mol^{-1} of distinct product channels leading to C_4H_5N isomers plus atomic hydrogen. Reaction energies were taken from refs 38 and 46: **p1**, *trans*-2-butenenitrile; **p2**, *cis*-2-butenenitrile; **p3**, 2-propenenitrile; **p4**, 3-butenenitrile..

($C_4H_2D_3N^+$), i.e., the atomic hydrogen elimination loss from the vinyl group, could be fit with an identical $P(E_T)$ as obtained for the C_4H_5N product formed in the cyanopropylene reaction. However, to fit the time-of-flight recorded during the reactions of cyano radicals with propylene-*1,1,2-d*$_3$ (CH_3CDCD_2), at m/z = 70 ($C_4H_2D_3N^+$), i.e., the atomic hydrogen loss from the methyl group, the center-of-mass translational energy distribution had to be cut by up to 40 kJ mol^{-1}; also, the distribution maximum of the $P(E_T)$ shifted downward to about 30 kJ mol^{-1}; this suggests a reaction energy of −73 ± 8 kJ mol^{-1}. Summarized, our findings suggest that the atomic hydrogen elimination from the vinyl group (propylene-*3,3,3-d*$_3$ (CD_3-$CHCH_2$), and from the methyl group (propylene-*1,1,2-d*$_3$ (CH_3CDCD_2) may lead to two distinct $C_4H_2D_3N$ isomers.

4. Discussion

The experiments helped us to derive the energetics of the reaction in the cyanopropylene system of −103 ± 8 kJ mol^{-1} to form a product of the gross formula C_4H_5N together with atomic hydrogen. These data can be compared now with energies obtained for four different product isomers (Figure 5). Within the error limits, the experimentally determined reaction energy can relate to the formation of three isomers: **p1**, *trans*-2-butenenitrile; **p2**, *cis*-2-butenenitrile; **p3**, 2-methyl-2-propenenitrile. This presents a tricky problem. On the basis of the CN−C_3H_6 reaction alone, we cannot exclude contributions of the less stable 3-butenenitrile product (**p4**). Consequently, we have to combine these data and energetics with those obtained from atomic hydrogen elimination pathways from the vinyl (propylene-*3,3,3-d*$_3$ (CD_3CHCH_2) and from the methyl group (propylene-*3,3,3-d*$_3$ (CH_3CDCD_2) providing two distinct $C_4H_2D_2N$ isomers (section 3.2).

Let us consider first the reaction of the cyano radical with propylene-*1,1,2-d*$_3$ (CH_3CDCD_2). The electrophilic cyano radical can add with its radical center located at the carbon atom to the carbon−carbon double bond of the propylene molecule. This can lead to two reaction intermediates **i1** and **i2** (Figure 6). Intermediate **i1** can lose a hydrogen atom, as observed experimentally, leading to a 3-butenenitrile-*2,3,3-d*$_3$ species (**D3-p4**). On the other hand, a hydrogen loss from the methyl group in intermediate **i2** cannot lead to any of the energetically accessible, partially deuterated product isomers **p1**−**p4**. Note that in propylene, α, β, and γ (methyl group) have charges of −0.42, 0.0, and −0.41.[32] On the basis of the sterical hindrance of the β-attack and the enhanced electron density at the α-carbon atom, the radical center should attack the $=CD_2$ unit of the propylene molecule forming a doublet radical intermediate **i1**. The latter can lose a hydrogen atom from the methyl group, leading to 3-butenenitrile-*2,3,3-d*$_3$. The experimentally determined reaction energy of −73 ± 8 kJ mol^{-1} is an close agreement for the data obtained from ref 46 to be −80 kJ mol^{-1}; note that the exact reaction energies to form the partially deuterated samples are unknown; however, they can be estimated reliably by accounting for the differences in zero point vibrational energies to be about −78 kJ mol^{-1} to form 3-butenenitrile-*2,3,3-d*$_3$ plus atomic hydrogen. Therefore, we can conclude that the reaction of the cyano radical with propylene-*1,1,2-d*$_3$ leads via addition of the cyano group following indirect scattering dynamics through a doublet radical intermediate. The latter decomposes via a tight exit transition state (3.1/3.2) located 30−40 kJ mol^{-1} above the separated 3-butenenitrile-*2,3,3-d*$_3$ (**D3-p4**) plus atomic hydrogen products.

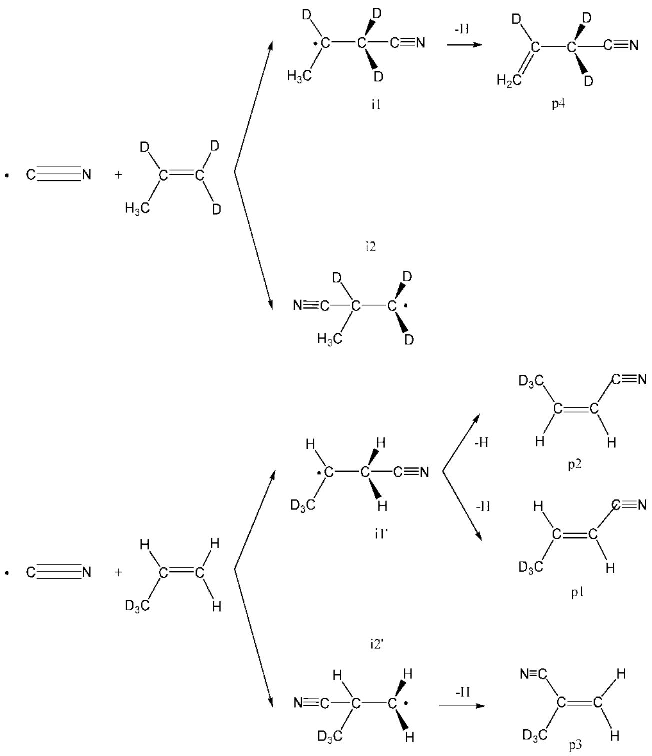

Figure 6. Schematic representation of the reaction of cyano radicals with propylene-*1,1,2-d*$_3$ (CH_3CDCD_2) (top) and propylene-*3,3,3-d*$_3$ (CD_3CHCH_2) (bottom).

We can turn our attention now to the reaction of the cyano radical with propylene-*3,3,3-d*$_3$ (CD_3CHCH_2). The change in the position of the deuterium atoms from the 1,1,2 to the 3,3,3 positions does not influence the preferential attack of the cyano radical to the α-carbon atom of propylene-*3,3,3-d*$_3$, leading to intermediate **i1′**. An elimination of a hydrogen atom leads to *cis*/*trans*-2-butenenitrile-*1,1,1-d*$_3$ (**p1**/**p2**) via a tight exit transition state of about 40−50 kJ mol^{-1} (section 3.2). Recall that this tight exit transition state was predicted on the basis of the center-of-mass translational energy distribution. In other words, the reversed addition of a hydrogen atom to *cis*/*trans*-2-butenenitrile-*1,1,1-d*$_3$ has an entrance barrier of the same order-of-magnitude.[47] Also, the experimentally derived reaction energies correlate—corrected for the zero point vibrational energies of—nicely with the reaction energies of −96 and −104 kJ mol^{-1}, as obtained from the NIST database and from a previous theoretical study.[38] We emphasize that in case of the propylene-*3,3,3-d*$_3$ reaction, we cannot elucidate explicitly to what extent the cyano group in intermediate **i1′** migrates from the α to the β carbon atom. Here, previous studies on the cyanoethylene system[30] suggested that the cyano group can migrate from one carbon atom to the other; this process involves tri- and/or tetracyclic reaction intermediates. Effectively, this could lead to a defacto attachment of the cyano group to the β carbon atom of the propylene molecule via multiple steps although this carbon atom has the lowest charge in propylene and a direct attack on the β-position is not favorable. The decomposition of **i2′** could result in formation of partially deuterated **p3**. Recall that, on the basis of the energetics alone, **p3** could not be ruled out.

Because the reactions of cyano radicals with propylene-*3,3,3-*d_3 and propylene-*1,1,2-*d_3 molecules identify at least two distinct isomers leading to *cis/trans*-2-butenenitrile-*1,1,1-*d_3 and -3-butenenitrile-*2,3,3-*d_3, we estimate now the branching ratios to form these isomers via hydrogen atom loss from the methyl and vinyl group, respectively. It shall be recalled that that, to derive accurate branching ratios,[48] it is important to gather the fragmentation ions arising from dissociative ionization of the parents in the electron impact ionizer. Also, it is important to have a laboratory angular distribution of both reaction channels available.[36] However, in cases of isotopically labeled experiments, we have shown that if the laboratory angular distributions have a similar pattern, i.e., for reaction channels that have comparable available energies, it is feasible to utilize the TOF spectra recorded at the center of-mass angles for the parent ions to estimate the branching ratios within 10%.[49] On the basis of these considerations, the branching ratios of the channels can be estimated considering the signal of $m/z = 70$ ($C_4H_2D_3N^+$) recorded during the reactions of cyano radicals with propylene-*3,3,3-*d_3 (CD_3CHCH_2) and propylene-*1,1,2-*d_3 (CH_3CDCD_2) (Figure 4). This leads to about 75 ± 8% *cis/trans*-2-butenenitrile-*1,1,1-*d_3 and to 25 ± 5% *cis/trans*-3-butenenitrile-*2,3,3-*d_3. Considering the energetics of the reaction, this branching ratio agrees very well with the formation of the thermodynamically more stable product **p1/p2**. Also, we should point out that, to lose a hydrogen atom from the methyl group in **i1**, the energy has to "flow" from the initially activated carbon−carbon bond at the α-carbon atom over three bonds—compared to only one bond to form **p1/p2** —to cleave the carbon−hydrogen bond in the methyl group. The fact that this pathway and product **p3** is observable experimentally indicates that the lifetime of the reaction intermediate is long enough to allow this energy redistribution to occur. Note that a previous theoretical study did not investigate the formation of this product isomer. However, Pilling et al. predicted that the cyano radical attacks without entrance barrier the α-carbon atom of the propylene molecule leading to intermediate **i1** which is stabilized by 233 kJ mol^{-1} with respect to the separated reactants. Also, the computations suggest a tight exit transitions state to form **p1** + H. Finally, it is attractive to compare the cyanopropylene reaction with the related reaction of cyano radicals with methylacetylene studied previously in our group at a similar collision energy.[33] Isotopic studies with methylacetylene-d_3, CD_3CCH, provided explicit evidence on the formation of two product isomers cyanomethylacetylene-d_3 (CD_3CCCN) and cyanoallene-d_2 ($D_2CCC(CN)H$) via a radical intermediate $CD_3CC(CN)H$. Similar to the cyanopropylene system, the formation of the cyanomethylacetylene-d_3 (CD_3CCCN) and cyanoallene-d_2 ($D_2CCC(CN)H$) isomers is triggered by an addition of the cyano group to the α carbon atom of the hydrocarbon molecule forming a $CD_3CC(CN)H$ intermediate; the decomposition to the experimentally detected cyanomethylacetylene-d_3 (CD_3CCCN) and cyanoallene-d_2($D_2CCC(CN)H$) isomers required an energy "flow" form the initially chemically activated bond over two and four bonds, respectively.

5. Conclusions and Summary

Here, we conducted crossed molecular beams experiments to explore the chemical reaction dynamics of ground-state cyano radicals, $CN(X^2\Sigma^+)$, with propylene (CH_3CHCH_2) together with two d_3-isotopologues (CD_3CHCH_2, CH_3CDCD_2). On the basis of the center-of-mass translational and angular distributions, the reaction dynamics were inferred to be indirect and commenced via an addition of the electrophilic cyano radical with its radical center to the α-carbon atom of the propylene molecule yielding a doublet radical intermediate (CH_3CHCH_2CN). Crossed beam experiments with propylene-*1,1,2-*d_3 (CH_3CDCD_2) and propylene-*3,3,3-*d_3 (CD_3CHCH_2) suggested that the reaction intermediates CH_3CDCD_2CN (from propylene-*1,1,2-*d_3) and CD_3CHCH_2CN (from propylene-*3,3,3-*d_3) eject both atomic hydrogen through tight exit transition states forming two distinct isomers: 3-butenenitrile [H_2CCDCD_2CN] (25%), and *cis/trans*-2-butenenitrile [$CD_3CHCHCN$] (75%), respectively, plus atomic hydrogen. Because propylene has been detected recently in the cold molecular cloud TMC-1 and the title reactions are barrierless and exoergic, we can predict that both 2- and 3-butenenitrile should be formed and detectable in these environments and also in the atmospheres of hydrocarbon-rich planets and moons such as Saturn's satellite Titan.

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