

A crossed beams study of the reaction of carbon atoms, $C(^3P_j)$, with vinyl cyanide, $C_2H_3CN(X^1A')$ —investigating the formation of cyano propargyl radicals

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The chemical dynamics of the reaction of ground state carbon atoms, $C(^3P_j)$, with vinyl cyanide, $C_2H_3CN(X^1A')$, were examined under single collision conditions at collision energies of 29.9 and 43.9 kJ mol^{-1} using the crossed molecular beams approach. The experimental studies were combined with electronic structure calculations on the triplet C_4H_3N potential energy surface (H. F. Su, R. I. Kaiser, A. H. H. Chang, *J. Chem. Phys.*, 2005, **122**, 074320). Our investigations suggest that the reaction follows indirect scattering dynamics *via* addition of the carbon atom to the carbon–carbon double bond of the vinyl cyanide molecule yielding a cyano cyclopropylidene collision complex. The latter undergoes ring opening to form *cis/trans* triplet cyano allene which fragments predominantly to the 1-cyano propargyl radical *via* tight exit transition states; the 3-cyano propargyl isomer was inferred to be formed at least a factor of two less; also, no molecular hydrogen elimination channel was observed experimentally. These results are in agreement with the computational studies predicting solely the existence of a carbon *versus* hydrogen atom exchange pathway and the dominance of the 1-cyano propargyl radical product. The discovery of the cyano propargyl radical in the reaction of atomic carbon with vinyl cyanide under single collision conditions implies that this molecule can be an important reaction intermediate in combustion flames and also in extraterrestrial environments (cold molecular clouds, circumstellar envelopes of carbon stars) which could lead to the formation of cyano benzene (C_6H_5CN) upon reaction with a propargyl radical.

1. Introduction

Resonantly stabilized free radicals (RSFRs) such as the propargyl ($C_3H_3; X^2B_1$) radical are believed to play a crucial role in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot,¹ in the combustion of fuels,² and in the chemical processing of carbon rich circumstellar envelopes.³ Due to the delocalization of the unpaired electron, resonantly stabilized free hydrocarbon radicals are more stable than ordinary radicals and form weaker bonds with stable molecules such as molecular oxygen in combustion flames.^{4–9} These weakly bound complexes are not easily stabilized by collisions at high temperatures.¹⁰ Therefore, RSFRs are relatively unreactive and can reach high concentration in flames. These high concentrations and the relatively fast rates of the corresponding radical–radical reactions make them important in the mechanism of formation of complex hydrocarbons such as the very first aromatic ring species in flames and in the interstellar medium. For instance, Miller and Melius¹¹ as well as Kern and Xie¹² suggested odd-carbon-atom reaction pathways involving the recombination of two propargyl radicals. Electronic struc-

ture calculations imply that the initially formed acyclic collision complex(es) of the recombination of two propargyl radicals can isomerize *via* multiple steps to ultimately form benzene and/or the phenyl radical plus a hydrogen atom.^{13,14} An alternative even–odd carbon-atom sequence could include the reaction of propargyl radicals (C_3H_3) with acetylene (C_2H_2) to yield the cyclopentadienyl radical (C_5H_5). The latter can react in multiple steps to benzene.¹⁵

Nevertheless, reactions of *substituted* propargyl radicals, which in turn could yield *substituted* benzene molecules and cyclopentadienyl radicals *via* reaction with a propargyl radical and acetylene molecule, respectively, have not been included yet in reaction models simulating hydrocarbon flames and the chemistry in circumstellar envelopes such as of IRC + 10216. For instance, the cyano propargyl radical, *i.e.* a propargyl radical in which a hydrogen at the C1 or C3 position is replaced by a cyano (CN) group, could react with propargyl and acetylene to form cyano benzene (C_6H_5CN) and cyano cyclopentadienyl radicals (C_5H_4CN), respectively. However, to validate this proposed route, the first step is to elucidate possible formation routes to the cyano propargyl radical itself. A recent crossed beams study on the reaction of ground state carbon atoms, $C(^3P_j)$, with ethylene, $C_2H_4(X^1A_1)$, suggested that the propargyl radical and atomic hydrogen are the dominating reaction products.¹⁶ Therefore, a reaction of

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carbon atoms with vinyl cyanide (cyano ethylene; C_2H_3CN (X^1A')), *i.e.* a substituted ethylene molecule, is expected to yield cyano propargyl radicals under single collision conditions. Very recently, Su *et al.* investigated this reaction computationally.¹⁷ The authors concluded that cyano propargyl radicals are the sole reaction products under single collision conditions. However, an experimental verification of these computations remains to be carried out. In this paper, we verify the formation routes experimentally and investigate the chemical dynamics of the reaction of ground state carbon atoms, $C(^3P_j)$, with vinyl cyanide, $C_2H_3CN(X^1A')$, under single collision conditions at collision energies of 29.9 and 43.9 kJ mol^{-1} in crossed molecular beams experiments to form cyano propargyl radicals. Finally, we comment on the implication of this reaction in combustion and interstellar chemistry.

2. Experimental setup and data analysis

The scattering experiments were conducted under single collision conditions in a crossed molecular beams machine at The University of Hawai'i.¹⁸ Pulsed beams of ground state carbon atoms, $C(^3P_j)$, were produced in the primary source chamber by laser ablation of graphite at 266 nm. This was achieved by tightly focusing the fourth harmonic of a Nd:YAG laser (10 mJ per pulse at a repetition rate of 30 Hz) onto a rotating graphite rod. The ablated species were seeded in helium gas (99.9999%; 3040 Torr) released by a Proch-Trickl pulsed valve. After passing a skimmer, a four-slot chopper wheel selected a component of the carbon beam with a peak velocity v_p of either $2356 \pm 19 \text{ ms}^{-1}$ or $2868 \pm 45 \text{ ms}^{-1}$, depending on the required collision energy (Table 1). At these velocities, carbon atoms are only in their 3P electronic ground state. Only at velocities higher than 3000 ms^{-1} , the first electronically excited 1D state of carbon can be populated as well.¹⁹ The ablation beam also contained dicarbon and tricarbon molecules. However, optimizing the pulsed valve–laser delay time and focusing the laser tightly reduced the dicarbon concentrations to less than 2–4% compared to the atomic carbon beam. As a matter of fact, we could not detect any signal from the reaction of dicarbon with vinyl cyanide (section 3). Likewise, tricarbon molecules were found not to react with vinyl cyanide under our experimental conditions. This is consistent with the finding that the reactions of tricarbon with related olefins such as ethylene involve significant entrance barriers.²⁰ Therefore, neither dicarbon nor tricarbon molecules interfered with the scattering signal from the carbon–vinyl cyanide reaction. The atomic carbon beam crossed at a right angle with a pulsed vinyl cyanide (99+%, Aldrich) beam released by a second pulsed valve at a pressure of 550 Torr under well-defined

collision energies of 29.9 ± 0.5 and $43.9 \pm 1.4 \text{ kJ mol}^{-1}$. In order to achieve the desired collision energy, the vinyl cyanide molecules were seeded either in argon (99.9999%, Gaspro) or neon (99.999%, Gaspro) carrier gases at seeding fractions of 3–4% (Table 1). The reactively scattered species were monitored using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules. The detector could be rotated within the plane defined by the primary and the secondary reactant beams to take angular resolved TOF spectra in steps of 2.5° . By integrating the TOF spectra at distinct laboratory angles, we obtained the laboratory angular distribution, *i.e.* the integrated signal intensity of an ion of distinct m/z versus the laboratory angle. Finally, information on the chemical dynamics was extracted by fitting these TOF spectra and the angular distribution in the laboratory frame (LAB) using a forward-convolution routine.²¹ 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.

$$N(v) = v^2 \exp\left[-\left(\frac{v}{\alpha} - S\right)^2\right] \quad (1)$$

3. Results

3.1. Laboratory data

We observed reactive scattering signal at mass-to-charge ratios, m/z , of 64 ($C_4H_2N^+$), 63 (C_4HN^+), and 62 (C_4N^+). Time-of-flight spectra (TOF) for various scattering angles at the most intense mass-to-charge value, *i.e.* $m/z = 63$ (C_4HN^+), are shown in Fig. 1 for both collision energies. At each collision energy investigated, the TOF spectra recorded at mass-to-charge ratios from 64 to 62 are superimposable suggesting that (i) $m/z = 63$ and 62 originate from dissociative ionization of the C_4H_2N parent in the electron impact ionizer and (ii) solely the atomic carbon *versus* atomic hydrogen exchange pathway exists replacing formally a hydrogen by a carbon atom. This channel results in the formation of molecules of the generic formula C_4H_2N plus atomic hydrogen. Based on our signal-to-noise ratio, upper limits of 1–2% can be derived of the molecular hydrogen elimination route; this correlates nicely with previous electronic structure calculations which predict that the molecular hydrogen elimination pathway is absent.¹⁷ Signal at higher masses was not detected suggesting that the dicarbon and tricarbon molecules do not contribute to the reactive scattering signal (section 2).

Table 1 Peak velocities (v_p), speed ratios (S), center-of-mass angles (θ_{CM}), together with the nominal collision energies of the carbon and the vinyl cyanide reactants (E_c). The speed ratio is defined *via* eqn (1) with $\alpha = [(2RT)/m]^{-1/2}$ with m being the mass of the species, R the ideal gas constant, and T the temperature of the beam

Beam	v_p/ms^{-1}	S	E_c/kJmol^{-1}	θ_{CM}
$C_2H_3CN(X^1A')/Ar$	746 ± 3	17.3 ± 0.4	—	—
$C(^3P)/He$	2356 ± 19	3.3 ± 0.1	29.9 ± 0.5	54.4 ± 0.1
$C_2H_3CN(X^1A')/Ne$	861 ± 10	14.9 ± 0.2	—	—
$C(^3P)/He$	2868 ± 45	2.3 ± 0.2	43.9 ± 1.4	53.0 ± 0.2

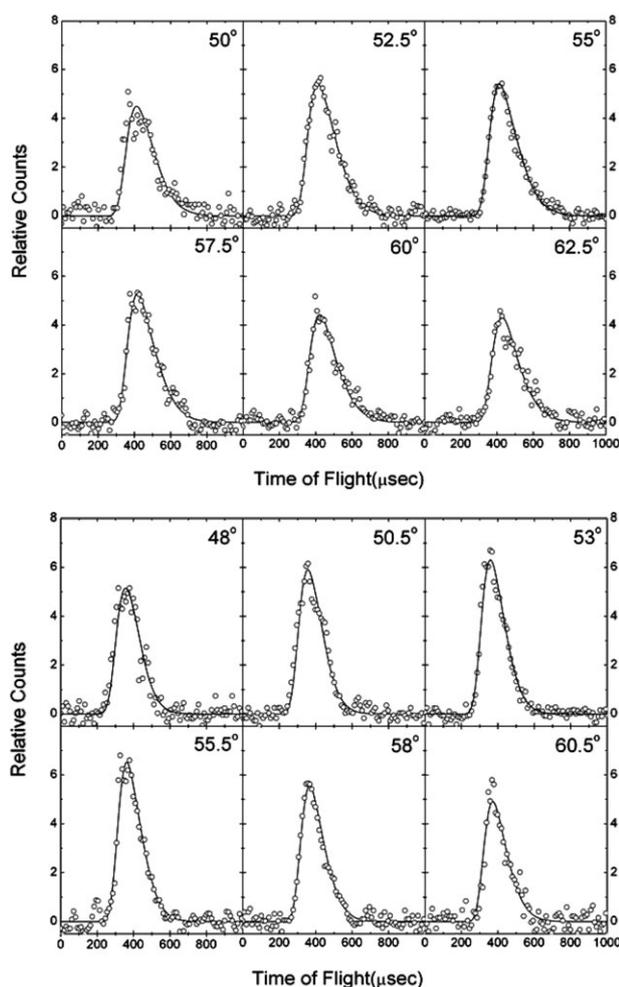


Fig. 1 Selected time-of-flight data for $m/z = 63$ (C_4HN^+) recorded at collision energies of 29.9 kJ mol^{-1} (top) and 43.9 kJ mol^{-1} (bottom) at various laboratory angles. The circles indicate the experimental data, the solid lines the calculated fit.

Summarized, the interpretation of the TOF data alone implies the existence of a carbon *versus* atomic hydrogen replacement channel leading to C_4H_2N isomer(s) under single collision conditions at both collision energies.

The most probable Newton diagrams of the reactions of carbon atoms with vinyl cyanide together with the laboratory angular distributions (LAB) of the C_4H_2N isomer(s) recorded at the most intense mass-to-charge ratio of $m/z = 63$ (C_4HN^+) are depicted in Fig. 2. Note that the overall shape of the LAB distribution barely changes by increasing the collision energy from $29.9 \pm 0.5 \text{ kJ mol}^{-1}$ to $43.9 \pm 1.4 \text{ kJ mol}^{-1}$. Within the error limits, both distributions peak at the center-of-mass angles of the reactions (Table 1).

3.2. Center-of-mass translational energy, $P(E_T)$ s, and angular distributions, $T(\theta)$ s

For both collision energies, the translational energy distributions in the center-of-mass frame, $P(E_T)$, are shown in Fig. 3. Best fits of the TOF spectra and of the LAB distributions were acquired with only a single channel fit, *i.e.* only one center-of-mass translational energy distribution at each collision energy.

These $P(E_T)$ s extended to a maximum translational energy, E_{max} , of 249 and 276 kJ mol^{-1} at collision energies of 29.9 ± 0.5 and $43.9 \pm 1.4 \text{ kJ mol}^{-1}$, respectively. Considering that the co-product is a light hydrogen atom, the high energy cutoffs are relative insensitive to adding or cutting 10 kJ mol^{-1} . Since the maximum available translational energy is the sum of the collision energy and the reaction energy release, E_{max} can be utilized to compute the energetics of the carbon plus vinyl cyanide reaction. Averaging over both collision energies, the reaction to form C_4H_2N isomer(s) under single collision conditions was found to be exoergic by $226 \pm 10 \text{ kJ mol}^{-1}$. In the most favorable case, the most probable translational energy gives information on the order-of-magnitude of the barrier height in the exit channel, *i.e.* the atomic hydrogen loss pathway(s).³ Here, both $P(E_T)$ s show maxima around $35\text{--}45 \text{ kJ mol}^{-1}$. This finding indicates that an exit barrier and hence a tight exit transition state might be involved in the atomic hydrogen elimination channel(s). Finally, the center-of-mass translational energy distributions assist to derive the fraction of total energy available channeling into the translational modes of the products. The averaged fraction of the available energy released into translation was found to be $30 \pm 2\%$ independent of the collision energy. This order of magnitude indicates that the reaction dynamics are indirect and that the reaction proceeds *via* C_4H_3N intermediate(s).²²

The shapes of the center-of-mass angular flux distributions, $T(\theta)$, of the atomic hydrogen loss pathway(s) (Fig. 4) provide valuable information on the reaction dynamics. Most importantly, both distributions depict intensity over the complete angular range from 0 to 180° . This finding suggests that the chemical dynamics are indirect, and that the reaction of atomic carbon with vinyl cyanide proceeds *via* formation of C_4H_3N complex(es). At both collision energies, the distributions are forward-backward symmetric suggesting that the lifetime of the decomposing complex is longer than its rotational period. The weak polarization of the center-of-mass angular distributions can be readily rationalized in terms of total angular momentum conservation and angular momentum disposal.²³ In the present case, large reactive impact parameters lead to complex formation; also, the light, departing hydrogen atom cannot carry away a significant orbital angular momentum. This result suggests an insignificant final orbital angular momentum and hence a preferential channeling of the total angular momentum into rotational excitation of the C_4H_2N product(s). As the collision energy is increased to $43.9 \pm 1.4 \text{ kJ mol}^{-1}$, the $T(\theta)$ can—within the error limits—also be fit with a slightly forward scattered distribution. We find an intensity ratio at the poles of $T(0^\circ)/T(180^\circ) = 1.3 \pm 0.2$. The trend—a forward-backward symmetric angular distribution at lower collision energy and a forward-scattered distribution at higher energy—is characteristic of an osculating complex.²³ By identifying the decomposing complex(es) and taking into account the intensity ratio at the poles, we can also estimate its lifetime (section 4).

4 Discussion

The center-of-mass translational energy distributions suggests that the reaction to form C_4H_2N radical(s) plus atomic

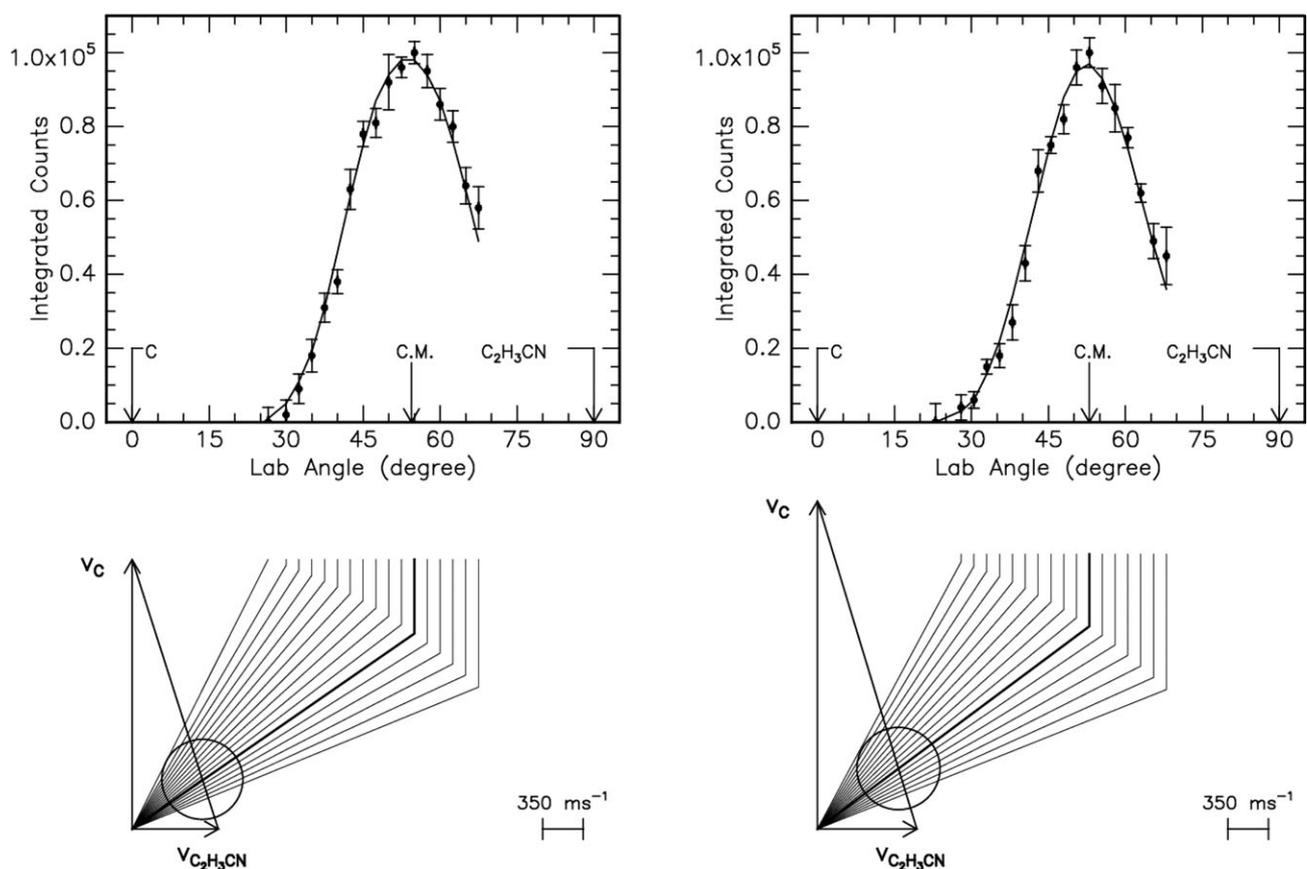


Fig. 2 Newton diagrams for the reaction of carbon atoms with vinyl cyanide at two collision energies of 29.9 kJ mol^{-1} (left) and 43.9 kJ mol^{-1} (right) together with the corresponding laboratory angular distribution of the $\text{C}_4\text{H}_2\text{N}$ radical(s) recorded at $m/z = 63$ (C_4HN^+). Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions. The vectors in the Newton diagram define the velocities of the carbon and vinyl cyanide reactant beams. The inserted circle centered at the center-of-mass stands for the maximum center-of-mass recoil velocity of the cyano propargyl radicals.

hydrogen is exoergic by $226 \pm 10 \text{ kJ mol}^{-1}$. This reaction energy correlates—within the error limits—with the computed values to form the 1-cyano propargyl (C_5 ; $\text{X } ^2\text{A}''$) and the 3-cyano propargyl (C_{2v} ; $\text{X } ^2\text{B}_1$) radicals, *i.e.* $-212 \pm 5 \text{ kJ mol}^{-1}$ and $-227 \pm 5 \text{ kJ mol}^{-1}$ at the B3LYP/6-311G(d,p) level of theory (Fig. 5). Since the reaction energies differ by only 15 kJ mol^{-1} , it is not feasible to decide to what extent the 1-cyano

and 3-cyano propargyl radical are formed. Consequently we will combine our experimental results with the computed potential energy surfaces to solve this question (Fig. 5).¹⁷

What reaction dynamics can be proposed to correlate the structures of the 1- and 3-cyano propargyl radical product(s) with the carbon atom and vinyl cyanide reactants? The chemical dynamics can be rationalized by proposing an initial addition of the carbon atom to the carbon–carbon double bond of the vinyl cyanide reactant forming a cyano cyclopropylidene intermediate (**i1**) which is stabilized by 218 kJ mol^{-1} with respect to the separated reactants. This cyclic intermediate can ring open *via* a barrier of only 32 kJ mol^{-1} to the *cis/trans* cyano allene isomer (**i2**). Compared to the cyclic isomer, the cyano allene molecules are more stable by about 165 kJ mol^{-1} . Recall that this addition–ring opening sequence is similar to that found in the reaction of atomic carbon with the related ethylene¹⁶ and propylene molecules.²⁴ The *cis/trans* cyanoallene molecule can undergo atomic hydrogen elimination to form either the 1-cyano propargyl radical (**p1**) or the 3-cyanopropargyl radical (**p2**) *via* tight exit transition states located about 12 and 23 kJ mol^{-1} , respectively, above the products. Since the transition state to **p1** is lower in energy by about 10 kJ mol^{-1} and is also less tight (imaginary frequencies were computed to be 619 (*trans*) cm^{-1} and 658 (*cis*) cm^{-1})

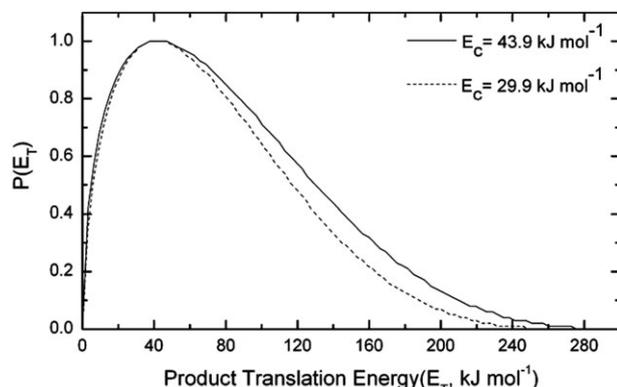


Fig. 3 Center-of-mass translational energy flux distributions for the reaction of carbon atoms with vinyl cyanide at two collision energies.

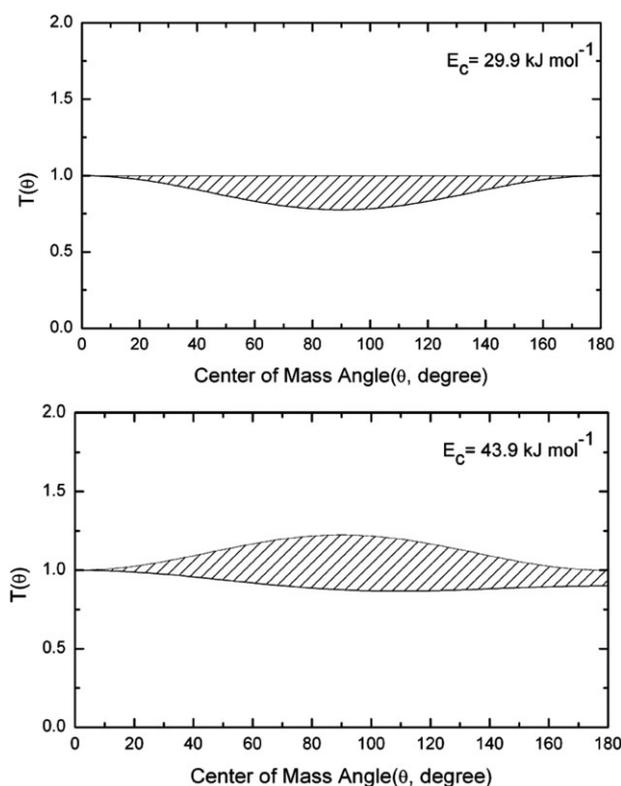


Fig. 4 Center-of-mass angular distributions for the reaction of carbon atoms with vinyl cyanide at two collision energies. The hashed regions define the uncertainties of the distributions.

compared to the transition state connecting *cis/trans* cyanoallene and **p2** (805 i cm^{-1}), we would expect a preferential formation of the 1-cyano propargyl isomer in the decomposi-

tion of *cis/trans* cyanoallene. In addition, a detailed study of the rotational axis (see below) suggests lifetimes of the decomposing *cis/trans* cyanoallene complexes of about 2–6 ps, *i.e.* a timescale on which the energy randomization is likely to be complete. The C1 atom holds two hydrogen atom, but only one hydrogen atom is connected to C3; therefore, if the energy randomization is complete, hydrogen atom elimination from the C1 position is statistically favorable compared to an ejection from the C3 atom. In conclusion, the 1-cyano propargyl isomer is expected to be the dominant reaction product compared to the 3-cyano propargyl isomer. This has also been confirmed in recent RRKM calculations on this system which suggest a branching ratio of about 5 : 1 from *cis/trans* **i2**.¹⁷

It should be noted that the existence of an exit barrier in the atomic hydrogen elimination correlates nicely with our experimental finding of $P(E_T)$ s peaking well away from zero translational energy. Considering the resonance structures of the 1- and 3-cyano propargyl radicals, the reversed reaction, *i.e.* a hydroatom addition to the 1- and 3-cyano propargyl radicals, we see that the hydrogen atom has to add to the carbon-carbon triple bond to form the *cis/trans* cyanoallene intermediate. As seen in related potential energy surfaces, the reaction of a hydrogen atom to an acetylenic bond is always correlated with a barrier and therefore a tight exit transition state.²¹ Secondly, the proposed reaction mechanism of an indirect reaction also gains support from the derived $T(\theta)$ which suggested the involvement of a reaction intermediate to form the cyano propargyl radicals plus atomic hydrogen (section 3). The deep potential energy well of about 380 kJ mol^{-1} in which the cyanoallene intermediates reside can also account for the experimentally found forward-backward symmetric center-of-mass angular distributions indicating a lifetime of the decomposing complex which is longer than its rotational

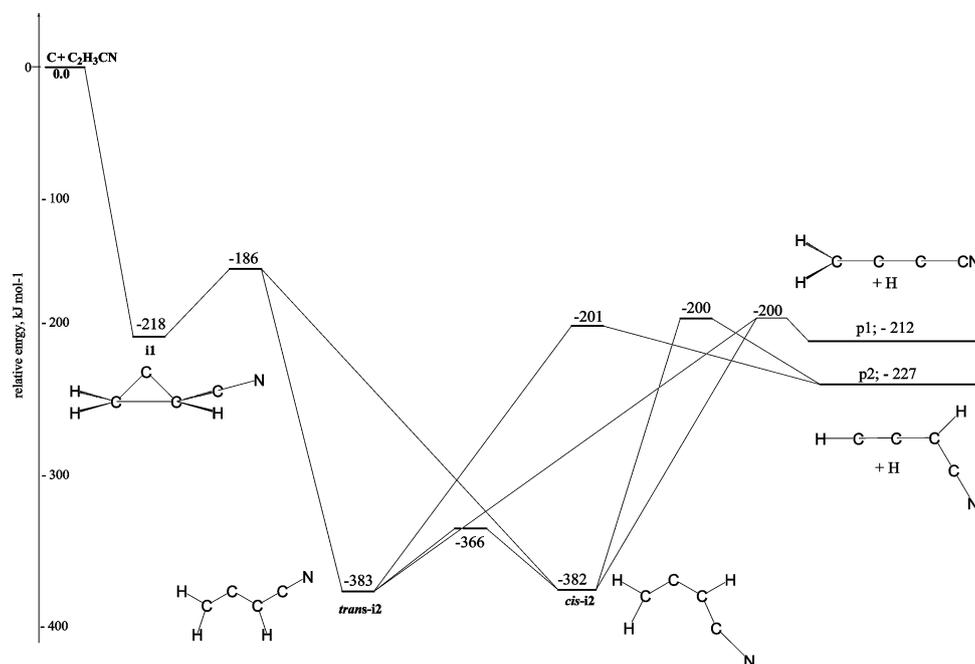


Fig. 5 Relevant stationary points on the triplet $\text{C}_4\text{H}_3\text{N}$ potential energy surface of the reaction of atomic carbon with vinyl cyanide adapted from ref. 17.

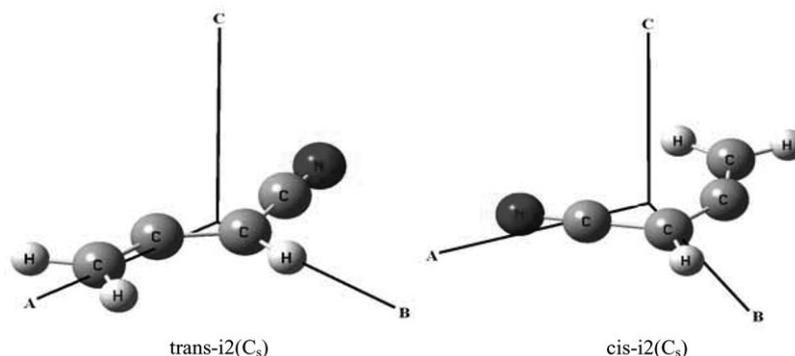


Fig. 6 Structure of the *cis* (right) and *trans* (left) cyanoallene intermediates together with the principal rotational axes.

period. We would like to discuss briefly a potential alternative reaction pathway to form the 1- and 3-cyanopropargyl radicals. The cyanoallene intermediates can undergo also hydrogen shifts to form cyano vinylmethylene intermediates, *i.e.* HCCHCHCN and H₂CCHCCN. However, since the transition state of the hydrogen migration is located about 20 kJ mol⁻¹ higher than the transition state of the hydrogen atom elimination to form the cyano propargyl radicals, the hydrogen migration is likely to be less significant accounting only to only 10% for the formation of the propargyl radicals.

Having proposed the *cis/trans* cyanoallene intermediate as the primary intermediate, which decomposes to form the 1-cyanopropargyl radical plus atomic hydrogen, we attempt now to estimate the lifetime of cyanoallene at the collision energy of 43.9 kJ mol⁻¹. Recall that at this collision energy, cyanoallene can be classified—within the error limits—as an osculation complex (section 3.2.).²⁵ Here, the rotational period of the cyanoallene complex can act as a clock in the molecular beam experiment and can be used to estimate the lifetime τ of the decomposing complex. The osculating model relates the intensity ratio of $T(\theta)$ at both poles to τ via eqn (2)

$$I(180^\circ)/I(0^\circ) = \exp\left(-\frac{t_{\text{rot}}}{2\tau}\right) \quad (2)$$

where t_{rot} represents the rotational period with:

$$t_{\text{rot}} = 2\pi I_i / L_{\text{max}} \quad (3)$$

I_i represents the moment of inertia of the complex rotating around the i -axis ($i = A, B, C$), and L_{max} the maximum orbital angular momentum. Using the *ab initio* geometries of the *cis/trans* cyano allene intermediates¹⁷ we can compute the moments of inertia (Table 2). Taking the maximum impact parameter to be in the order of 1.5 Å estimated from the hard sphere model of a reaction having no entrance barrier,²⁶ the reduced mass of the reactants of 9.8×10^{-3} kg, and the relative velocity of the reactants of 2993 ms⁻¹, a maximum orbital angular momentum of 3.3×10^{-33} kg m² s⁻¹ is obtained. We can compare the estimated lifetimes with the lifetimes of decomposing complexes in related reactions of carbon atoms with unsaturated hydrocarbons.^{3,21} The absolute value of τ depends on the rotation axis, *i.e.* B, C vs. A. Qualitatively speaking, reactions involving intermediates having lifetimes of less than 1 ps such as the related reaction of carbon atoms with propylene²³ are expected to depict a stronger asymmetry and

hence an enhanced forward-peaking than seen in our experimental findings. Our data show only a moderately peaked center-of-mass angular distribution at 43.9 kJ mol⁻¹. Therefore, rotations of the *cis/trans* cyano allene intermediate about the A axis can be likely eliminated, and rotations around the B- and/or C-axis should dominate.

5. Comparison with the reactions of C(³P_i) with ethylene (C₂H₄), propylene (C₃H₆), and 1,3-butadiene (C₄H₆)

It is interesting to compare the present findings with the reactions of ethylene,¹⁶ propylene,²³ and 1,3-butadiene²⁷ studied recently using crossed molecular beams. Here, the reaction dynamics and potential energy surfaces involved in the formation of (substituted) propargyl radicals show common features. All reactions are dictated by indirect scattering dynamics; about 30–35% of the total available energy channels into the translational degrees of freedom. The carbon atom adds to the π electron density. This yields (substituted) cyclopropylidene intermediates which are stabilized by 210–220 kJ mol⁻¹ with respect to the reactants. These cyclic intermediates undergo ring opening through barriers of between 30 and 50 kJ mol⁻¹ to form (substituted) *cis/trans* allene intermediates on the triplet surface. The latter are bound by 340–380 kJ mol⁻¹ compared to the separated reactants. The

Table 2 Moments of inertia, rotational times, and estimated lifetimes of the triplet *cis* and *trans* cyanoallene intermediates. The location of the principal axes of the rotating *cis/trans* cyanoallene intermediates is shown in Fig. 6

	$I_A/\text{kg m}^2$	$I_B/\text{kg m}^2$	$I_C/\text{kg m}^2$
<i>trans</i> Cyano allene	1.77×10^{-46}	3.45×10^{-45}	3.63×10^{-45}
<i>cis</i> Cyano allene	5.32×10^{-46}	2.51×10^{-45}	3.04×10^{-45}
	$t_{\text{rot}}(\text{A})/\text{ps}$	$t_{\text{rot}}(\text{B})/\text{ps}$	$t_{\text{rot}}(\text{C})/\text{ps}$
<i>trans</i> Cyano allene	0.15	2.96	3.12
<i>cis</i> Cyano allene	0.45	2.15	2.61
	$\tau(\text{A})/\text{ps}$	$\tau(\text{B})/\text{ps}$	$\tau(\text{C})/\text{ps}$
<i>trans</i> Cyano allene	0.28	5.64	5.93
<i>cis</i> Cyano allene	0.85	4.09	4.96

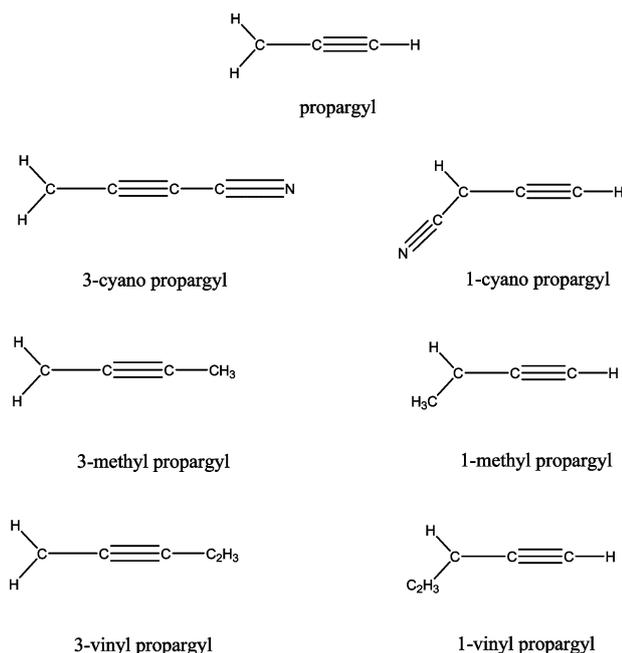


Fig. 7 Structures of the 1- and 3-(substituted) propargyl radicals formed in the reactions of ground state carbon atoms with (substituted) ethylene molecules (see text for details). The position of the radical center is defined as C1.

fate of the triplet allene complexes is governed by hydrogen atom loss channels to (substituted) propargyl radicals *via* exit transition states located about 10–35 kJ mol⁻¹ above the products. Most of the initial angular momentum channels into rotational excitation of the products. The existence of an exit barrier is documented in the center-of-mass translation energy distributions; here, all $P(E_T)$ s peak around 20–50 kJ mol⁻¹. Finally, the exoergicities to form the C₃H₂R (R = CH₃, C₂H₃, H, CN) products are very similar and fall between 190 and 220 kJ mol⁻¹; in all reactions investigated, the 1-substituted propargyl radical was found to be formed systematically in higher yields compared to the 3-substituted isomer with ratios of 3 : 1 (propylene), 8 : 1 (1,3-butadiene), and 5 : 1 (vinyl cyanide).

6. Conclusions

We investigated the chemical dynamics of the reaction of ground state carbon atoms, C(³P₁), with vinyl cyanide, C₂H₃CN(X ¹A'), at collision energies of 29.9 kJ mol⁻¹ and 43.9 kJ mol⁻¹ utilizing a crossed molecular beams setup. Our investigations suggest that the reaction follows indirect scattering dynamics *via* an addition of the carbon atom to the carbon–carbon double bond of the vinyl cyanide molecule yielding a cyano cyclopropylidene collision complex. The latter isomerizes *via* ring opening to *cis/trans* triplet cyano allene. The triplet cyano allene molecule was identified to be the decomposing complex which fragmented preferentially to the 1-cyano propargyl radical *via* tight exit transition states; the 3-cyano propargyl isomer was suggested to be formed at least a factor of two less. These results are in agreement with a previous computational study of this reaction suggesting that

only a carbon *versus* hydrogen atom replacement channel is open. RRKM calculations carried out in the same study predict branching ratios of the 1-cyano propargyl *versus* 3-propargyl radical of about 5 : 1.¹⁷ The explicit identification of the cyano propargyl radical in the reaction of atomic carbon with vinyl cyanide suggests that this species can be an important reaction intermediate in combustion flames and also in extraterrestrial environments (cold molecular clouds, circumstellar envelopes of carbon stars). In denser environments, this radical may react with a propargyl radical to form—after various isomerization step—a cyano benzene molecule *via* a three body collision. This could present a potential important alternative route to form cyano benzene in dense media alongside the previously suggested pathway involving bimolecular collisions of cyano radicals with benzene under single collision conditions.²⁸ Likewise, the triplet cyano allene intermediate may undergo stabilization and intersystem crossing upon collision with a third body, for instance in denser planetary atmospheres and high pressure combustion systems. The synthesis of cyano allene *via* a three body reaction in this way could present a valid route to cyano allene, in addition to accepted mechanism involving reactions of cyano radicals with allene and methylacetylene; the latter reactions were found to yield cyano allene solely under single collision conditions.²⁹

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