

The Formation of Nitriles in Hydrocarbon-Rich Atmospheres of Planets and Their Satellites: Laboratory Investigations by the Crossed Molecular Beam Technique

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ABSTRACT

Crossed molecular beam experiments of cyano radicals, $\text{CN}(X^2\Sigma^+)$, reacting with unsaturated hydrocarbons have been performed to investigate synthetic routes to nitriles formation in hydrocarbon-rich atmospheres of planets and their moons. We have verified that all cyano radical reactions with acetylene, ethylene, methylacetylene, allene, benzene, and dimethylacetylene proceed without entrance barrier, have exit barriers well below the energy of the reactant molecules, and are strongly exothermic. The identification of the CN versus H atom exchange channel makes these reactions compelling candidates to synthesize unsaturated nitriles in solar system environments. Some of these nitriles, hitherto unobserved in our solar system, now represent an ideal target to be detected in the future Cassini–Huygens mission to Titan.

I. Introduction

During the past century, the atmospheres of Jupiter, Saturn, Uranus, and Neptune have been investigated with great effort because their atmospheric composition and chemical evolution are expected to reveal key aspects of prebiotic chemistry of Earth.¹ The Voyager I/II missions and ground-based telescopes revealed that the atmospheres of the giant gas planets are composed primarily of the light elements hydrogen and helium;² polyatomic molecules methane (CH_4), ammonia (NH_3), water (H_2O), phosphine (PH_3), carbon monoxide (CO), carbon dioxide

(CO_2), germane (GeH_4), hydrogen sulfide (H_2S) as well as the hydrocarbons ethane (C_2H_6), acetylene (C_2H_2), ethylene (C_2H_4), methylacetylene (CH_3CCH), propane (C_3H_8), and diacetylene (HCCCCH) and the methyl radical ($\cdot\text{CH}_3$) have also been found to be present in trace amounts with mole fractions between 10^{-9} and 10^{-5} .³ Saturn's moon Titan has attracted special attention, because Earth and Titan are believed to have emerged with similar atmospheres from the solar nebula.⁴ Molecular nitrogen (N_2) and methane (CH_4) are the main constituents of Titan's present atmosphere, followed by molecular hydrogen (H_2), nitrogen-bearing molecules, hydrogen cyanide (HCN), dicyan (C_2N_2), and cyanoacetylene (HCCCN), as well as the hydrocarbons acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (CH_3CCH), propane (C_3H_8), and diacetylene (C_4H_2).³ Even though the above-mentioned nitriles—molecules containing a cyano ($-\text{CN}$) group—occur only in trace amounts of a few parts per billion, they are of particular importance because they are thought to be the key intermediates to form biologically relevant molecules. Nitriles can be hydrolyzed and react via multistep synthesis ultimately to amino acids, thus providing one of the basic “ingredients” for life.⁵ As opposed to Earth, however, the surface temperature of Titan is about 94 K—too cold for liquid water to exist—and the chemical evolution has remained frozen at an early stage. As a consequence, the study of the chemistry of Titan's atmosphere offers the unique opportunity to reconstruct the scene of the primordial terrestrial atmosphere and to unveil key concepts about how biologically active molecules and their nitrile precursors were synthesized on proto-Earth.

One of the main basic questions is, how can the nitrile chemistry be initiated in those low-temperature environments? The atmospheres of Titan and the giant gas planets are constantly bombarded with high-energy photons and cosmic ray particles. In the upper layers of Titan's atmosphere, for example, the energy deposition is mainly from strongly ionizing, high-energy electrons from Saturn's magnetosphere and short-wavelength solar ultraviolet photons ($\lambda < 155$ nm). Hence, the ionospheric chemistry is dominated by ion–molecule reactions.⁶ However, longer wavelength photons penetrate down to the stratosphere and photodissociate HCN to yield cyano radicals, $\text{CN}(X^2\Sigma^+)$. Since the cyano radical concentration profile overlaps with atmospheric regions containing unsaturated hydrocarbons such as acetylene, it has been speculated that these radicals react with hydrocarbons to produce unsaturated nitriles via neutral–neutral reactions.⁷ The potential importance of the cyanopolynes ($\text{H}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$) in that environment strongly motivates laboratory studies, the aim of which is to elucidate their routes of formation.

Laboratory data on the reactions of cyano radicals with unsaturated hydrocarbons were lacking for a long time, predominantly due to the experimental difficulty in preparing a large concentration of $\text{CN}(X^2\Sigma^+)$ radicals. Two

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kinds of experimental information are necessary to establish whether these reactions might synthesize nitriles in low-temperature environments: (i) the values of the reaction rate constants and (ii) the reaction products themselves. Recent kinetic studies on CN reactions with acetylene, methylacetylene, and ethylene at temperatures as low as 13 K have proved that these reactions are indeed very fast and hold rate constants in the gas kinetics order (about $10^{-10} \text{ cm}^3 \text{ s}^{-1}$).⁸ Therefore, these experiments have demonstrated that cyano radicals can react at the prevailing temperatures of Jupiter (165 K), Saturn (134 K), Uranus (76 K), and Neptune (57 K). However, in those investigations, only the decay rate of the free radical concentration was monitored, and no information on the identity of the reaction products could be given. Because of this limitation, systematic laboratory studies to identify the reaction products of cyano radical reactions with unsaturated hydrocarbons are required in order to assess, once and for all, whether these routes of nitrile formation are open in the solar system environments.

The crossed molecular beam method is a powerful experimental technique to provide this complementary piece of information. The complex networks of chemical processes occurring in the planetary atmospheres consist of a series of elementary reactions, most of which are bimolecular collisions between a radical or an atom and a closed-shell species. A detailed experimental knowledge of the elementary processes involved at a fundamental microscopic level is therefore desirable, even if we want simply to assess the nature of the primary reaction products. Experiments under single-collision conditions are essential to achieve this, because in a binary collision involving CN radicals and the molecules of a generic hydrocarbon, RH, where an intermediate is formed, i.e., $\text{CN}(X^2\Sigma^+) + \text{RH} \rightarrow [\text{RHCN}]^* \rightarrow \text{RCN} + \text{H}$, a cyano radical will react only with one single hydrocarbon molecule, and the stabilization of the $[\text{RHCN}]^*$ intermediate and/or successive reaction of the primary products will be avoided. Only this requirement can guarantee that the real primary reaction products are identified. Three-body collisions may occur in dense planetary atmospheres, and the reaction intermediate complexes $[\text{RHCN}]^*$ might be stabilized or, since these transient species are often radicals, might react, leading to more complex molecules. Therefore, information on the identity of these species is vital as well to get a global picture under realistic, "planetary scale" reaction conditions.

In this Account, we review recent progress on crossed molecular beam studies of the reactions of cyano radicals with the unsaturated hydrocarbons acetylene, ethylene, methylacetylene, dimethylacetylene, allene, and benzene. Most of these hydrocarbons have already been identified in hydrocarbon-rich atmospheres of planets and their moons; allene has not yet been observed in any solar system body, but recent data from the European Infrared Satellite Observatory (ISO) derived upper limits for their mole fractions of about 5×10^{-9} . Additionally, recent photochemical models predict that allene should exist in Titan, Jupiter, and Saturn.⁹

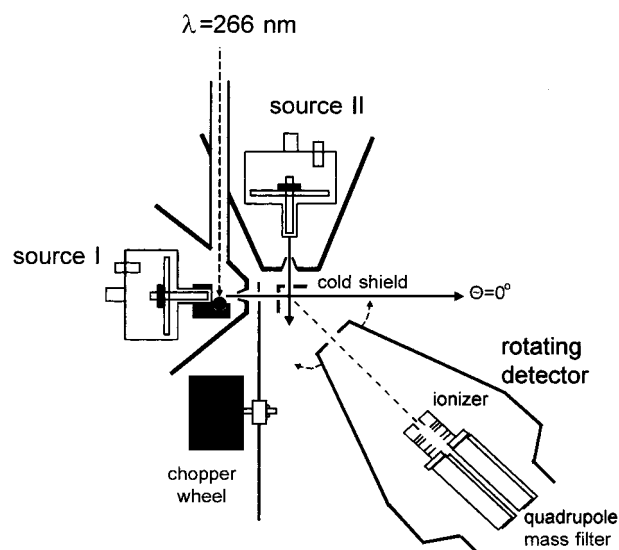


FIGURE 1. Schematic top view of the crossed molecular beam apparatus. The two pulsed beam source chambers are visible in the top and left parts; in the case of the CN beam source (source I), the carbon rod holder and the incident laser beam are also sketched. The chopper wheel, the cold shield, and a sketch of the detector outer chamber are also shown.

II. The Crossed Molecular Beam Approach

The crossed molecular beam (CMB) method with mass-spectrometric detection¹⁰ is a versatile technique to study elementary reactions under single-collision conditions, thus permitting the elucidation of the chemical dynamics and—in the case of polyatomic reactions—the primary products. In contrast to bulk experiments, where reactants are mixed, the main advantage of a crossed beam experiment is the capability to confine the radicals in a separate, supersonic beam; this implies that the radicals will collide only with the molecules of a second beam at a specific collision energy and crossing angle, therefore ensuring the observation of the consequences of well-defined molecular encounters. All the experiments reported here were performed by using the 35" crossed molecular beam machine (Figure 1).¹¹ The apparatus consists of two source chambers fixed at a crossing angle of 90° , a large stainless steel scattering chamber, and an ultra-high-vacuum tight, rotatable, differentially pumped quadrupole mass spectrometric (QMS) detector ($<8 \times 10^{-13}$ mbar). In the primary source, a pulsed supersonic cyano $\text{CN}(X^2\Sigma^+)$ radical beam is generated in situ by laser ablation of graphite at 266 nm and subsequent seeding of the liberated species in molecular nitrogen which also acts as a reactant.¹² The cyano radical beam passes through a skimmer into the main chamber. The supersonic expansion freezes the diatomic radicals in their ground vibrational level and lowest rotational levels. A chopper wheel selects a slice of molecules with well-defined velocity which reach the interaction region. At this point, the cyano radicals collide with the second pulsed beam of the unsaturated hydrocarbon at typical collision energies in the range $15.0\text{--}31.0 \text{ kJ mol}^{-1}$. Reactively scattered species are probed at different laboratory angles by the QMS,

which is preceded by an electron impact ionizer; the velocity distributions for the different ionized species are obtained by recording the time-of-flight (TOF) distributions at each selected mass-to-charge ratio (m/e). Since the electron impact ionizer and the QMS compactly reside in the rotating detector chamber, this setup allows the intensity of distinct m/e to be recorded as a function of the flight time at different laboratory angles in the scattering plane defined by the two crossing beams. Despite the triply differential pumping setup of the detector chambers, molecules desorbing from wall surfaces lying on a straight line to the electron impact ionizer cannot be avoided. Their mean free path is of the order of 10^3 m, compared to maximum dimensions of the detector chamber of about 1 m. To reduce this background, a copper plate attached to a two-stage closed cycle helium refrigerator is placed right before the collision center and cooled to 4.5 K. In this way, the ionizer views a cooled surface which traps all species with the exception of hydrogen and helium.

The crossed beam technique addresses fundamental aspects of reaction mechanisms at the microscopic level. Only recently, technological improvements in the unstable species beam production and vacuum technology have allowed the study of elementary reactions of practical interest, such as those reported here. The observables of this technique contain some basic information. Every species can be ionized at the typical electron energy used in the ionizer, and therefore, it is possible to determine the mass and the gross formula of all the possible species produced from the reactions by simply selecting different m/e in the QMS. Even though some problems, such as dissociative ionization and background noise, limit the method, the advantages with respect to spectroscopic techniques are obvious, since the applicability of the latter needs as a prerequisite the knowledge of the optical properties of the products. Another important aspect is that, by measuring the product velocity distributions, one can immediately derive the amount of the total energy available to the products and, therefore, the enthalpy of reaction of the reactive collision. This is of great help when different structural isomers with different enthalpies of formation can be produced.

For a more detailed physical interpretation of the reaction mechanism, it is necessary to transform the laboratory (LAB) data into the center-of-mass (CM) system using a forward-convolution routine.¹³ This procedure initially assumes trial angular, $T(\theta)$, and translational energy, $P(E_T)$, distributions in the CM reference frame. Laboratory TOF spectra and angular distributions are then calculated from $T(\theta)$ and $P(E_T)$ and averaged over the apparatus and beam functions. The procedure is repeated until a satisfying fit of the LAB distributions is achieved; the CM functions so determined are called "the best-fit CM functions". The ultimate output is the generation of a product flux contour map which reports the intensity of the reactively scattered products as a function of the CM scattering angle, θ , and product velocity, u , and which is given by $I(\theta, u) \approx P(u)T(\theta)$. The function $I(\theta, u)$ is called

the reactive *differential cross section*. The contour map can be seen as the *image* of the reaction and contains all the information on the scattering process.

III. Results and Discussion

In this section we report our experimental findings for the six different reactions of CN radicals with the unsaturated hydrocarbons listed in the Introduction. We have selected these reactive systems for different reasons: the reactions with C_2H_2 and C_2H_4 are the prototypes for the two classes of reactions CN + alkynes and CN + alkenes, and thus are expected to reveal key concepts for reactions with the higher members of the same series. The reactions with methylacetylene and dimethylacetylene were selected to observe the effect of the H-substitution with one or two alkyl groups. Binary collisions with allene, when compared to the reaction with its isomer methylacetylene, are expected to reveal effects due to the specificity of the CN attack. Finally, the reaction with benzene is the prototype for the series of reactions of CN with aromatic hydrocarbons; in this respect we recall that polycyclic aromatic hydrocarbons are believed to be widely spread in the universe and that the stability of the aromatic rings toward the chemical attack of atoms and radicals has been the subject of extensive debate. Some details on the experimental results and on what we have learned from them are given here only for the reaction CN + ethylene. The purpose is to show the peculiarity and the potential of the experimental method. A survey of the experimental findings obtained for the other reactions with special attention to the implications in the chemistry of the atmosphere of Titan will be briefly given.

The Reaction CN + C_2H_4 .¹⁴ The reaction CN + ethylene was found to be very fast in the whole range of temperatures investigated by means of kinetic techniques.^{8,15} Quite interestingly, from the comparison of the rate constants for the reactions CN + C_2H_4 , CN + C_2H_2 , and CN + $H_2C=C=CH_2$, it was inferred that all of these reactions proceed through the addition of CN to the π systems, leading to the formation of nitriles and atomic hydrogen, rather than through H-atom abstraction, leading to the formation of HCN and alkenyl/alkynyl radicals.¹⁵ Once we have disregarded a significant occurrence of the pathway leading from CN + C_2H_4 to HCN and vinyl radical, we still have to face the problem of individualizing the structure of the formed nitrile. In the case of the present reaction, three possible isomers of gross formula C_3H_3N could be formed by the reaction, namely cyanoethylene, $CH_2=CH(CN)$, isocyanoethylene, $CH_2=CH(NC)$, and triplet cyanomethylcarbene, $CH_3-C=C=N$ (see Figure 2a). The energetics of the reaction channels leading to the three possible isomers are very different, and this has allowed us to establish which isomer is really formed under our experimental conditions and, presumably, in the atmosphere of Titan.

The scattering experiments were performed at collision energies (E_c) of 15.3 and 21.0 kJ mol⁻¹. We were able to observe scattered products at different mass-to-charge

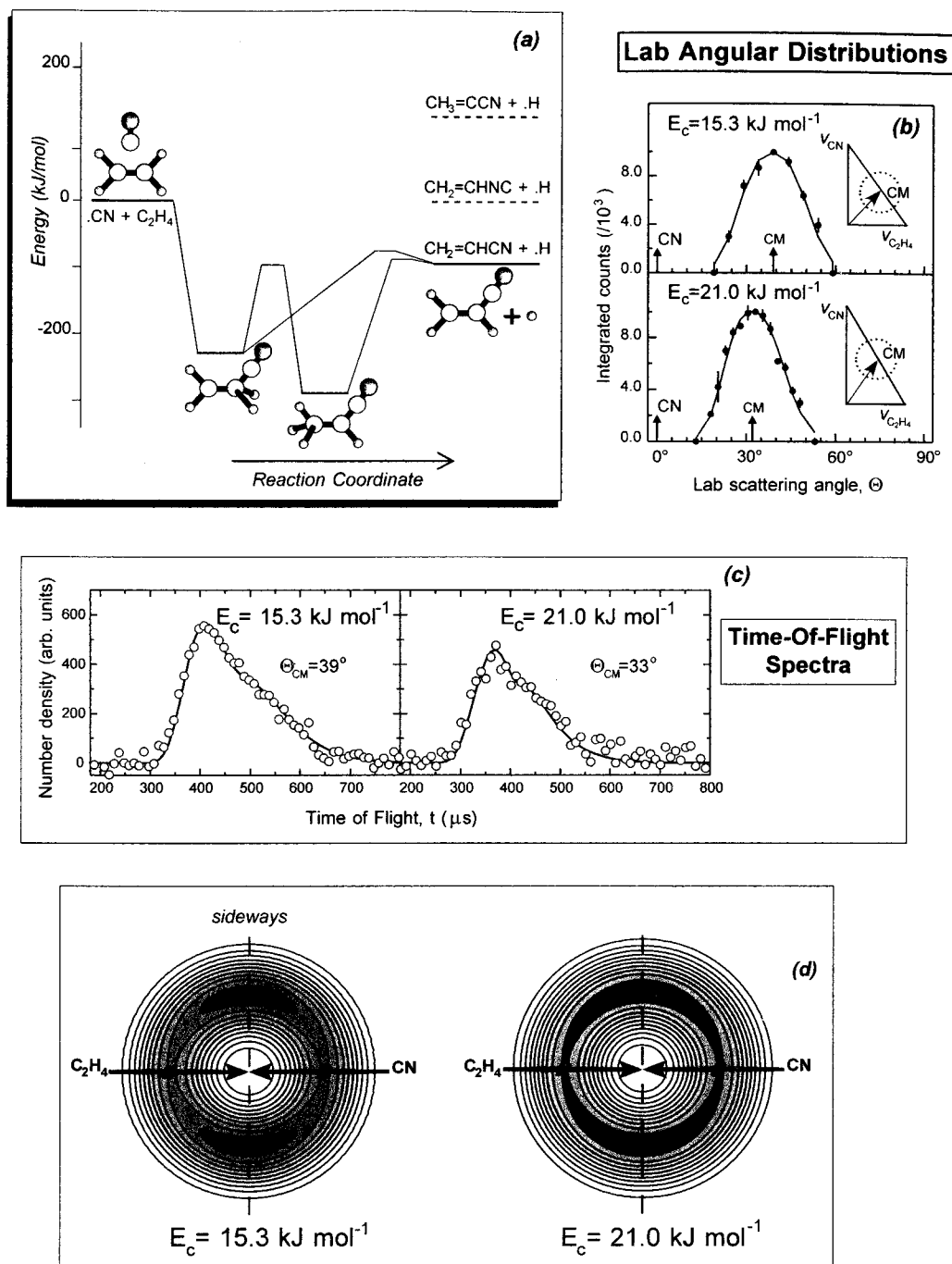


FIGURE 2. (a) Schematic potential energy surface for the $\text{CN}(\chi^2\Sigma^+)$ + C_2H_4 system. (b) Laboratory angular distributions of the $m/e = 50$ ion (C_3N^+) at two collision energies of 15.3 and 21.0 kJ mol^{-1} , together with the corresponding Newton diagrams. (c) TOF spectra of the $m/e = 50$ ion at the center-of-mass angles of 39° and 33° for the lower and higher collision energies, respectively. (d) CM flux contour plots of the $\text{C}_2\text{H}_3\text{CN}$ product for both collision energies. Lines connect points with identical intensities.

ratios from 53 to 50, which correspond to the ions $\text{C}_3\text{H}_3\text{N}^+$, $\text{C}_3\text{H}_2\text{N}^+$, C_3HN^+ , and C_3N^+ . However, the LAB distributions recorded at all m/e revealed identical patterns and could be fit with the same CM functions. This unambiguously indicates that the only product really formed under our experimental conditions has a gross formula $\text{C}_3\text{H}_3\text{N}$ and that it partly fragments to $\text{C}_3\text{H}_2\text{N}^+$, C_3HN^+ , and C_3N^+ in the electron impact ionizer because of dissociative ionization. A signal at $m/e = 54$, corresponding to a possible stable reaction adduct of formula $\text{C}_3\text{H}_4\text{N}$, was not observed. Due to the high background signal at $m/e = 27$,

we could not detect the reaction products HCN/HNC deriving from the possible H abstraction reaction channel.

The best signal-to-noise ratio was achieved at $m/e = 50$, and so the complete set of final measurements were carried out at this value. In panel b of Figure 2, the LAB product angular distributions together with the most probable Newton diagrams showing the kinematics of the reactive collisions are reported. The TOF spectra taken in the vicinity of the CM position angle (Θ_{CM}) are shown in panel c for the lower (left) and higher (right) collision energies. The solid lines superimposed on the experimen-

tal results are the calculated curves when using the best-fit CM functions which generate the product flux contour maps reported in panel d of Figure 2. Both laboratory angular distributions have a peak close to Θ_{CM} and show about the same intensity in the backward and forward directions (with respect to the CN radical beam direction). Also, they are quite wide, with scattered products extending for about 45° . The Θ_{CM} time-of-flight spectra show some structure with definite shoulders. The limiting circles shown in the Newton diagrams of panel b have been drawn assuming that all the available energy is released as product translational energy in the case that cyanoethylene is the formed product. The Newton circles delimit—through the total energy and linear momentum conservation rules—the LAB angular range within which the products can be scattered. If we compare this limit with the experimentally determined scattering range of the still unidentified $\text{C}_3\text{H}_3\text{N}$ isomers, the substantial coincidence of the angular ranges indicates that $\text{C}_2\text{H}_3\text{CN}$ must be formed in significant amounts. This suggestion becomes more clear if we move to the CM reference frame. The two best-fit $P(E_T)$ values (not reported here explicitly, but implicitly shown in the product flux contour maps) are characterized by a maximum value of translational energy, $E_{T(\text{max})}$, of about $100\text{--}110\text{ kJ mol}^{-1}$ (note that if we extend or cut the high-energy tails of the best-fit $P(E_T)$ values by $10\text{--}15\text{ kJ mol}^{-1}$, the quality of the fit does not change significantly). Since the energy conservation rule states that $E_{T(\text{max})} \leq E_c - \Delta H_{\text{react}}^\circ$, once we account for the relative collision energies of 15.3 and 21.0 kJ mol^{-1} , the CN/H exchange reaction turns out to be exothermic by about $90\text{--}100\text{ kJ mol}^{-1}$. The thermochemistry of the channels leading to the possible $\text{C}_3\text{H}_3\text{N}$ isomers and atomic hydrogen is very different, as recently derived by electronic structure ab initio calculations.²⁰ The exothermicity of the reaction channel leading to cyanoethylene, $\text{C}_2\text{H}_3\text{CN}$, and $\text{H}(^2\text{S})$ was found to be -95.0 kJ mol^{-1} (the recommended experimental value is -90 kJ mol^{-1}), in contrast to the values $+4.0$ and $+113\text{ kJ mol}^{-1}$ calculated for the reaction channels leading to the two other possible isomers, isocyanoethylene, $\text{C}_2\text{H}_3\text{NC}$, and triplet cyanomethylcarbene, CH_3CCN , respectively. In conclusion, from the energy cutoff of the product translational distributions, we can establish that it is the thermodynamically more stable cyanoethylene isomer that mainly formed from the $\text{CN} + \text{C}_2\text{H}_4$ reaction. Taking into account the exothermicity of the $\text{C}_2\text{H}_3\text{CN} + \text{H}$ formation channel, the fraction of the total available energy channeled into the product translational energy is about $30\text{--}35\%$; this percentage, together with the $P(E_T)$ peak far from $E_T = 0$, might indicate that a modest exit barrier is present.

Other important suggestions can be derived from the angular part of the differential cross section. At both collision energies, the $I(\theta)$ and $I(\theta, u)$ values are forward–backward symmetric with respect to $\theta = 90^\circ$, as is well visible in the contour maps of panel d of Figure 2. This finding suggests that the reaction follows indirect scattering dynamics; i.e., the reaction is proceeding through the formation of a bound intermediate. The lack of signal

at $m/e = 54$ means that this bound intermediate is not stable enough to reach the detection region, having rapidly fragmented because of its high energy content. Quite interestingly, besides being symmetric, the angular distributions show a mild peak in the “sideways” direction ($\theta = 90^\circ$); this experimental finding suggests some geometrical constraints in the decomposing $\text{C}_2\text{H}_4\text{CN}$ intermediate which define a specific orientation of the H atom emission.

All the experimental findings gain full support from extensive ab initio calculations performed on the $\text{C}_3\text{H}_4\text{N}$ potential energy surface (PES), which revealed the structure of possible intermediate and product isomers.¹⁴ In panel a of Figure 2, a simplified sketch of the doublet $\text{C}_3\text{H}_4\text{N}$ PES is given where the minimum energy path leading to the most stable product $\text{C}_2\text{H}_3\text{CN}$ is shown. The unpaired electron is mainly localized on the carbon atom of the CN radical; this makes it the more reactive end of the diatomic species. The radical attacks the π cloud of ethylene; the addition pathway is barrier-less and forms a C_s -symmetric 1-cyanoethyl-2 radical, Figure 2a. As shown by the ab initio calculations, there is an alternative reaction pathway in which the CN radical attacks ethylene on the N side. Even though this approaching geometry involves the lone-pair electrons on the N atom rather than the unpaired electron of carbon, the potential energy surface indicates attractiveness, and there is no transition state for the formation of a bound (-139 kJ mol^{-1}) 1-isocyanoethyl-2 radical, $\text{CH}_2\text{CH}_2\text{NC}$. Isomerization pathways from the cyano to the isocyano ethyl radical were found to be accessible to the system, but what is really relevant here is that the formation of the products isocyanoethylene and atomic hydrogen can be achieved only through exit barriers of more than 10 kJ mol^{-1} ; this theoretical finding accounts well for the lack of the experimental observation of the isocyano product isomer. In contrast, the 1-cyanoethyl-2 radical can fragment to cyanoethylene and atomic hydrogen through a transition state which is easily accessible, being located at -79 kJ mol^{-1} with respect to the reactant asymptotes. Alternatively, the initial addition intermediate can isomerize through a 1,2-H atom shift to a more stable 2-cyanoethyl-2 radical intermediate which is the global minimum of the potential energy surface (the H atom shift from the central carbon atom to the terminal carbon atom produces a structure with a methyl group and allylic conjugation). This second intermediate can, in turn, fragment to cyanoethylene and atomic hydrogen via a loose exit transition state. Interestingly, both structures of the transition states leading from the two bound intermediates to the products resemble the kind of geometry which is necessary to observe the sideways scattering we have seen in our experiments. The attack of CN at one of the $\sigma\text{C-H}$ bonds is also predicted to be an accessible channel: the H atom abstraction to form HCN and C_2H_3 is exothermic by 52.5 kJ mol^{-1} and has no barrier.¹⁴ The H atom abstraction which forms HNC is exothermic by 22 kJ mol^{-1} , but the barrier of 12 kJ mol^{-1} makes this reaction channel quite improbable (we recall that the two products HCN/HNC,

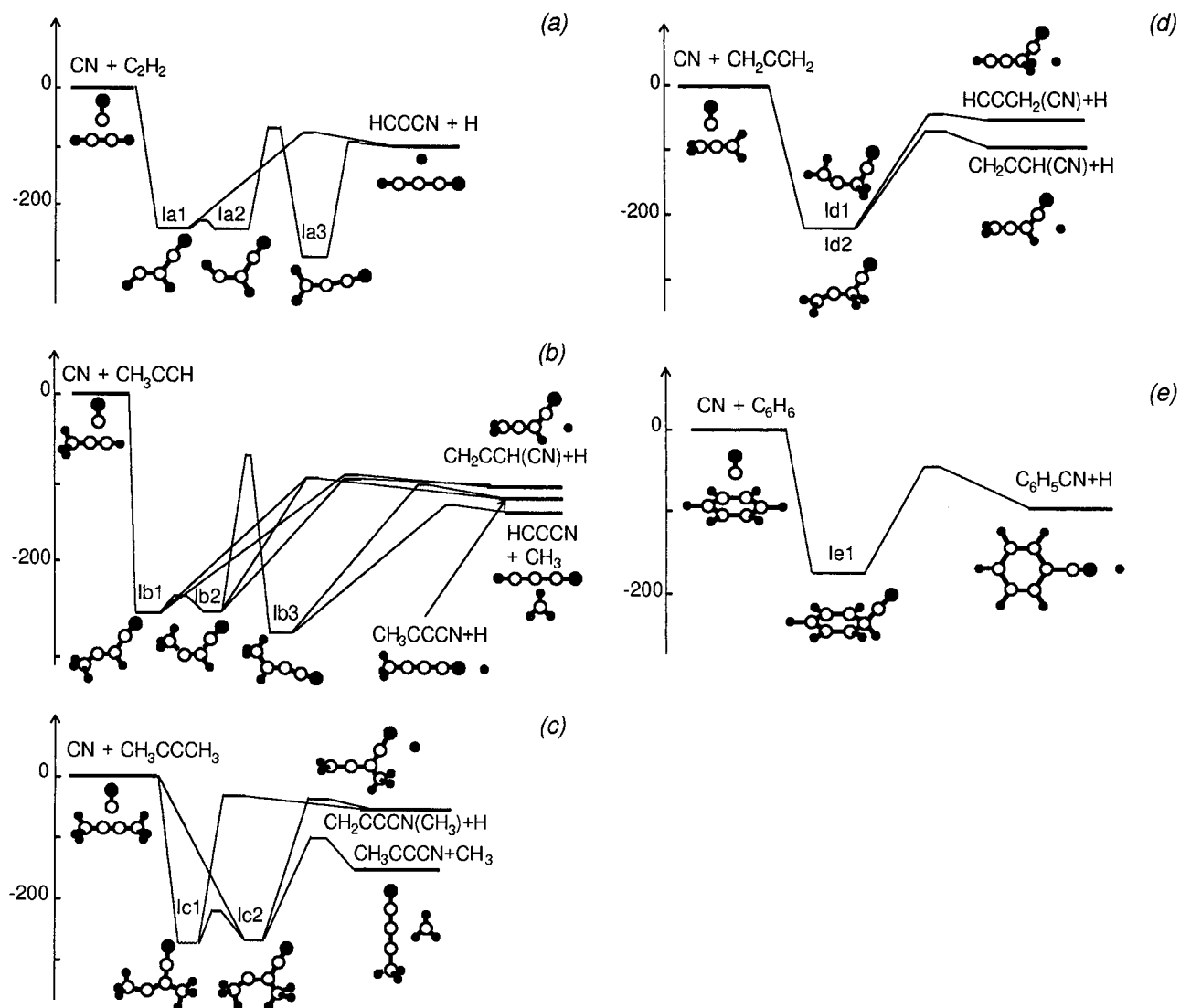


FIGURE 3. Schematic potential energy surfaces for the (a) $\text{CN}(X^2\Sigma^+) + \text{C}_2\text{H}_2$, (b) $\text{CN}(X^2\Sigma^+) + \text{CH}_3\text{CCH}$, (c) $\text{CN}(X^2\Sigma^+) + \text{CH}_3\text{CCCH}_3$, (d) $\text{CN}(X^2\Sigma^+) + \text{H}_2\text{CCCH}_2$, and (e) $\text{CN}(X^2\Sigma^+) + \text{C}_6\text{H}_6$ systems.

both having $m/e = 27$, could not be detected in our experiments). Preliminary variational RRKM calculations show that HCN formation can account for up to 10% compared to formation of vinylcyanide, and therefore, the suggestion previously made that the CN radical preferentially attacks the π molecular orbital rather to the σ bond is fully confirmed. When applied to the channel leading to $\text{C}_3\text{H}_3\text{N}$ isomers and H, the RRKM approach indicates that cyanoethylene is the only isomer formed and that about 40% of it formed from the fragmentation of the first intermediate and 60% from the decomposition of the second intermediate.

The Reactions $\text{CN} + \text{C}_2\text{H}_2$,¹⁶ CH_3CCH ,¹⁷ and CH_3CCCH_3 .¹⁸

By combining our experimental results with the ab initio electronic structure calculations of the relevant stationary points, as shown in the previous section for the reaction $\text{CN} + \text{C}_2\text{H}_4$, we have been able to unravel the chemical reaction dynamics of $\text{CN} +$ acetylene (i) and methyl-substituted acetylene, that is methylacetylene (ii) and dimethylacetylene (iii). In Figure 3a–c, a simplified sketch of the doublet potential energy surface is shown together

with feasible exit channels; for simplicity, the unobserved isomers have been omitted, but the CN/CH_3 displacement channels are shown in the case of methyl-substituted acetylene. In the three cases, the CN radical interacts with the π electronic cloud without entrance barrier and forms the cis and trans isomers of the corresponding addition intermediates Ia1 (i), Ib1 (ii), and Ic1 (iii). The intermediates in the cis and trans forms (Ia2, Ib2, and Ic2) are characterized by deep wells (about -240 , -250 , and -240 kJ mol^{-1} with respect to the separated reactants in the three cases, respectively). Due to the low barrier of interconversion between the cis and trans forms (10 – 20 kJ mol^{-1}), the initial concentration of the cis versus trans population is unity. These intermediates can undergo C–H bond cleavages, leading to (i) cyanoacetylene, HCCCN, (ii) cyanomethylacetylene, CH_3CCCN , and cyanoallene, $\text{CH}_2\text{CCH}(\text{CN})$, and (iii) $\text{CH}_2\text{CCCN}(\text{CH}_3)$. In the case of reaction with acetylene, RRKM estimates have shown that a fraction (15%) of the initial addition intermediates can isomerize through 1,2-H atom migration to Ia3 (the global minimum of the $\text{C}_3\text{H}_3\text{N}$ PES, -288 kJ mol^{-1}), which, in turn, decays

via H atom emission to the same product, HCCCN.¹⁷ The experimental findings are in perfect agreement with the suggested picture, as it is summarized in the PES sketch of Figure 3a. Our investigation has shown that neither isocyanoacetylene isomer, HCCNC, nor HCN/HNC products are energetically feasible under our experimental conditions and, presumably, in the atmosphere of Titan.

Quite interestingly, in the case of reaction with methylacetylene, both product isomers, cyanomethylacetylene and cyanoallene, are formed in the same amounts, as evidenced by experiment with deuterated methylacetylene.^{17,19} As in all reactions discussed above, formation of isonitriles is not favored, since the reaction channels leading to CH₃CCNC and H₂CCCH(NC) are endothermic by 8 and 6 kJ mol⁻¹, respectively.

Also in the case of the reaction with dimethylacetylene, we were unable to detect the methyl group elimination channel due to the low signal-to-noise ratio of the reactive scattering signal.¹⁸ Quite interestingly, we have observed the occurrence of the CN/H exchange channel, and we have established that the departing H is one of those of the methyl group at the opposite end of the original dimethylacetylene molecule (see Figure 3c); that is, the formed product is the 1-cyano-1-methylallene. We recall that RRKM calculations of the branching ratio showed that the channel leading to CH₃ and cyanomethylacetylene is by far the most dominant (the branching ratio of the CH₃ versus H loss is about 360 at our collision energy).¹⁸

The Reactions CN + CH₂CCH₂¹⁹ and C₆H₆.²⁰ In the case of the reaction with allene, once again the CN radical interacts with the π electron density without entrance barrier to give *cis/trans* intermediates Id1 and Id2 (-233 kJ mol⁻¹ with respect to the reactants) (see Figure 3d). The addition of the CN radical to the central carbon of the allene molecule is not an active reaction pathway: if the CN radical formed a new carbon-carbon single bond to the central carbon atom, the intermediate would undergo ring closure and then hydrogen elimination, forming cyanopropene. This pathway, however, is endothermic by about 11 kJ mol⁻¹, and hence energetically not accessible or at least very unfavorable under the conditions of our experiments and of planetary atmospheres. The initially formed complexes lose a hydrogen atom at either the CH₂ or CH₂CN group (both pathways are feasible because of the energy of the relative transition states). The channel leading to the cyanoallene isomer, HCCCH₂CN, together with atomic hydrogen was found to be exothermic by 86 kJ mol⁻¹. This value matches well with the experimentally derived exothermicity (85–90 kJ mol⁻¹), suggesting that the cyanoacetylene isomer is mainly formed in our experiments as well as in cold molecular clouds. Indeed, RRKM calculations have shown that the other isomer, HCCCH₂(CN), can account for up to 20% of the total reaction yield.¹⁹

Additionally, the interaction of the CN radical with benzene is initially dominated by long-range dispersion forces, as observed for the reaction with alkenes and alkynes.²⁰ The addition reaction Ie1 is barrier-less and correlates with the intermediate Ie1 (see Figure 3e), which is

bound by 165 kJ mol⁻¹ with respect to the reactants. This intermediate undergoes a C–H bond rupture through a tight exit transition state located 33 kJ mol⁻¹ above the products, leading to the cyanobenzene isomer, C₆H₅CN, and atomic hydrogen. From our experimental findings, we could exclude the possibility that the less stable C₆H₅–NC isomer is significantly formed in the reaction.

In summary, in all the reactions investigated, the CN/H exchange channel is open, and products with a multiple C–C bond and a –CN group are formed. No isonitrile isomers were observed in our experiments: all the reaction channels leading to these isomers are either endothermic by a few kilojoules per mole, or the relative exit barriers are 5–30 kJ mol⁻¹ above the energy of the separated reactants.²¹ We note that, in cold planetary atmospheres, the translation energy of the reactants cannot open these channels as well. However, if the cyano radical is vibrationally excited, this excess energy might be used to compensate for the reaction endothermicity.

IV. Conclusions

In this Account, we have reported unprecedented information on the chemical dynamics, involved complexes, and products of the cyano radical reactions, CN(X²Σ⁺), with the unsaturated hydrocarbon molecules acetylene (C₂H₂), ethylene (C₂H₄), methylacetylene (CH₃CCH), dimethylacetylene (CH₃CCCH₃), allene (H₂CCCH₂), and benzene (C₆H₆). In all these cases, the CN/H exchange channel was found to be accessible, and the primary products were identified to be cyanoacetylene (HCCCN), vinylcyanide (C₂H₃CN), 1-cyanomethylacetylene (CH₃CCCNCN), cyanoallene (H₂CCCH(CN)), 1-cyano-1-methylallene (CH₂CCCNCN(CH₃)), cyanobenzene (C₆H₅CN), and 3-cyanomethylacetylene (CH₂(CN)CCH). These reaction channels have no entrance barrier, show an exit barrier well below the energy of the reactant molecules, are exothermic, and proceed through the formation of bound intermediates. All these findings fully confirm that this reaction class is a compelling candidate to explain the presence of unsaturated nitriles in hydrocarbon-rich atmospheres of solar system planets and their moons. In Titan, for example, cyanoacetylene has been identified unambiguously, and we can now state that the neutral-neutral reaction of cyano radicals with acetylene can well account for its presence. The observation of a cyano radical versus a hydrogen atom exchange pathway in all reactions studied leads to the conclusion that unobserved nitriles CH₃CCCNCN, C₂H₃CN, H₂CCCH(CN), CH₂(CN)CCH, and C₆H₅CN could be present, at least in the atmosphere of Titan, because of a significant abundance of their precursors. The detection of these molecules is now a task for the NASA–ESA Cassini–Huygens mission to Titan.²² The spacecraft Huygens will carry an infrared mapping spectrometer as well as a quadrupole mass spectrometer capable of identifying these isomers in Titan's atmosphere.

Besides the reaction products, we have identified several intermediates that could be stabilized in the dense atmospheres of the giant gas planets and their satellites,

where three-body collisions can divert the excess internal energy with which they are formed. These intermediates are doublet radicals and hence very reactive, even at the low temperatures prevailing in the outer solar system. Hitherto, no chemical reaction network of planetary environments has considered the chemistry of these radicals, but they could play a significant role in the stepwise growth to larger molecules or even in aerosol production.

What we have exposed here is the very first step toward a comprehensive and systematic understanding of the fundamental elementary processes involved in the chemistry of hydrocarbon-rich planetary atmospheres. Since the experimental data can be employed to set up a systematic database of reaction products and predict the formation of hitherto unobserved gas-phase molecules, future spectroscopic surveys in the framework of the Cassini-Huygens mission to Titan and analytical devices for upcoming space missions can be designed. This provides a crucial link between laboratory experiments and applied space exploration. These applications of the crossed beam method to planetary chemistry problems have just begun to scratch the surface. Many interesting problems remain to be studied, such as the role of ethynyl radicals, C_2H -($X^2\Sigma^+$),²³ in the formation of substituted polyynes and their derivatives to name a typical example. The very first reaction of this important radical—which is isoelectronic with the cyano species—with methylacetylene has been investigated very recently.²³ In the coming century, laboratory experiments of the kind we have presented here combined with planetary space mission data will undoubtedly unravel the complex chemical processes prevailing in planetary atmospheres of our solar system.

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