Astrobiology – the final frontier in chemical reaction dynamics

Ralf I. Kaiser[1] and Nadia Balucani[2]

[1]*Department of Chemistry, University of York, York YO10 5DD, UK*
e-mail: rik1@york.ac.uk
[2]*Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy*
e-mail: deneb@impact.dyn.unipg.it

Abstract: Crossed-beam experiments on the reactions of cyano $CN(X^2\Sigma^+)$ and ethinyl $C_2H(X^2\Sigma^+)$ radicals with the unsaturated hydrocarbons acetylene, ethylene, methylacetylene allene and benzene have been carried out under single-collision conditions to investigate synthetic routes to form nitriles, polyynes and substituted allenes in hydrocarbon-rich atmospheres of planets and their moons. All reactions were found to proceed without an entrance barrier, to have exit barriers well below the energy of the reactant molecules and to be strongly exothermic. The predominant identification of the radical versus atomic hydrogen exchange channel makes these reactions compelling candidates for the formation of complex organic chemicals – precursors to biologically important amino acids – in Solar system environments and in the interstellar medium.

Received 31 July 2001

Key words: astrobiology, amino acids, crossed-beam experiments, laboratory studies, nitriles, polyynes and prebiotic ozone.

Introduction

Astrobiology investigates how life began and evolved, whether live exists elsewhere in the universe, and the future of life on Earth and beyond (Morrison 2001). These topics alone demonstrate clearly the strong interdisciplinarity of this field and the tremendous challenges that lie ahead of us. Various approaches can be applied to plunge into this endeavour ranging from astronomical observations of Earth-like (habitable) planets, via the search for potential artefacts and traces of extraterrestrial life, to an actual identification of the ingredients of DNA- and RNA-based life as we know it (amino acids, sugars and phosphates). Cutting-edge laboratory experiments present a unique opportunity to address the hitherto unresolved puzzle of how these ingredients and their precursors might have been formed abiotically in extraterrestrial environments. Once the prebiotic synthetic routes to form these molecules have been exposed in laboratory experiments, we can then predict where amino acids, sugars and phosphates (or their precursors) can be formed, searched for and, ultimately, observed spectroscopically (via telescopes) or *in situ* (via space missions).

In this paper, we review recent developments in laboratory experiments to investigate how astrobiologically important molecules might have been formed in our Solar system. Here, understanding the organic chemistry of the atmosphere of Saturn's moon Titan is of crucial importance to unravelling the origin and chemical evolution of biologically important molecules in our Solar system. The atmospheric chemistry of Titan is strongly related to astrobiological problems and serves as a model for prebiotic chemistry and the origins of life on Earth (Clarke & Ferris 1995, 1997; Raulin *et al.* 1998). In fact, analogously to proto Earth, Titan's atmosphere is dense (1.6 atm) and consists mainly of molecular nitrogen (N_2) and trace amounts of hydrocarbons methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (CH_3-CCH), propane (C_3H_8), diacetylene (HCCCCH), nitriles – molecules containing a cyano (-CN) group – hydrogen cyanide (HCN), cyanomethane (CH_3CN), dicyan (NCCN), cyanoacetylene (HCCCN), and presumably solid-phase dicyanoacetylene (NCCCCN), as well as two oxygen-bearing species: carbon monoxide (CO) together with carbon dioxide (CO_2) (Letourneur & Coustenis 1993; Clarke & Ferris 1997; Raulin *et al.* 1990; Hidayat *et al.* 1997, 1998; Tanguy *et al.* 1990; Raulin *et al.* 1998; Lara *et al.* 1991; Clarke & Ferris 1997; Griffith *et al.* 1998; Karkoschka 1994; Lunine *et al.* 1998). Photochemical models proposed pathways to even larger, more complex species such as triacetylene (C_6H_2) and tetraacetylene (C_8H_2) (Yung *et al.* 1984). It was the detection of nitriles (in trace amounts of a few parts per billion) to trigger the interest of exobiologists in the evolution of simple organic chemistry in Titan. In fact, even though nitriles occur only in trace amounts, these species are thought to be *the* key intermediates in the formation of biologically relevant molecules in Solar system environments, since through hydrolysis and multi-step reactions they lead ultimately to amino acids and thus provide one of the basic 'ingredients' for life (Brack 1998; Raulin *et al.* 1999). As opposed to Earth, however, the
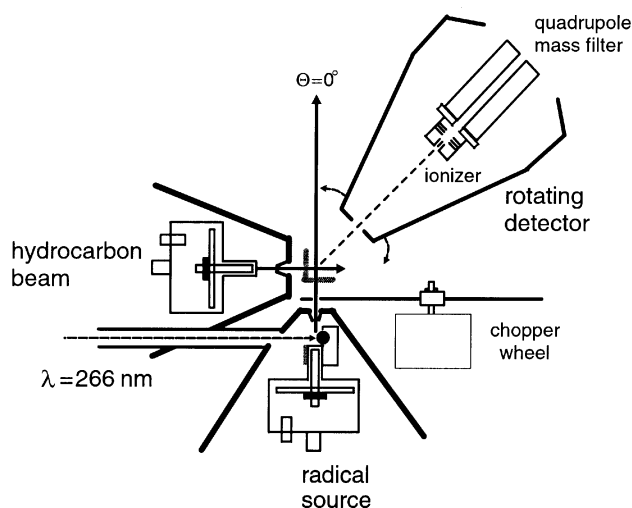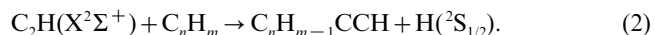
Fig. 1. Schematic representation of the experimental set-up with a radical source, a hydrocarbon source and the rotating detector.

surface temperature of Titan is about 94 K and even in the upper stratosphere the temperature does not exceed 170 K. In these conditions, water is mainly in the solid state and the absence of liquid water certainly prevents the evolution of biochemistry as we know it. On the other hand, exactly because of the absence of a biosphere, Titan provides us with the opportunity to investigate a chemical environment close enough to the primitive terrestrial atmosphere and, therefore, to understand how complex organic molecules can originate from simple parent molecules, such as CH_4 and N_2. To fully describe the prebiotic organic chemistry in the atmospheres of Titan and Earth comprehensively, we have to address two questions. First, we have to figure out how nitriles can be formed in the reducing atmospheres of Titan. Secondly, it is crucial to understand how these precursors could have been protected in the atmospheres of Titan and proto-Earth from the destructive, Solar ultraviolet radiation field. This brings us to the hitherto unanswered question how diacetylene (HCCCCH) and related molecules are formed in these environments. We recall that diacetylene is thought to play a key role in atmospheric chemistry since this molecule probably serves as an ultraviolet radiation shield in planets and their moons. In analogy to ozone protecting Earth from ultraviolet photons today, diacetylene could have absorbed the destructive range of the ultraviolet spectrum in Titan and proto-Earth to preserve their lower atmospheric layers and surfaces (Zwier *et al.* 1996).

From the point of view of the chemist, the basic questions to be solved are if and how nitriles and polyynes can be formed in that low-temperature environment. To address this question we have to take into consideration that the atmospheres of Titan and proto-Earth have been constantly bombarded with high-energy photons and cosmic ray particles for the last 4.5 Gyr. In the upper atmospheric layers, the energy deposition is mainly from strongly ionizing high-energy electrons from planetary magnetospheres and short-wavelength solar ultraviolet photons ($\lambda < 155$ nm). Hence, ion–molecule reactions dominate in these regions (Fox & Yelle 1997; Ewan *et al.*

1998; Nagy & Cravens 1998). However, longer-wavelength photons penetrate the stratosphere and can photodissociate the gaseous species which are present at that altitude, notably HCN and C_2H_2 the photodissociation products of which are the cyano $CN(X^2\Sigma^+)$ and ethynyl $C_2H(X^2\Sigma^+)$ radicals, respectively. Since the ethynyl and cyano radical concentration profiles overlap with atmospheric regions containing unsaturated hydrocarbons such as acetylene, it has been speculated that these radicals react with unsaturated hydrocarbons via neutral–neutral reactions to produce unsaturated nitriles and polyynes through the generalized schemes (1) and (2) (Seki *et al.* 1996; Lorenz *et al.* 1997; Yung *et al.* 1984):

$$CN(X^2\Sigma^+) + C_nH_m \rightarrow C_nH_{m-1}CN + H(^2S_{1/2}), \qquad (1)$$

$$C_2H(X^2\Sigma^+) + C_nH_m \rightarrow C_nH_{m-1}CCH + H(^2S_{1/2}). \qquad (2)$$

In addition to chemical models, significant help comes from a series of laboratory experiments that mimic Titan's atmospheric chemistry. In different research groups N_2/CH_4 gas mixtures have been irradiated with different energy sources (for recent work see Coll *et al.* 1999) and the gas- and solid-phase products analysed. Several limitations of these methods, such as wall effects, affect their validity and it has been suggested recently to reduce the complexity of the problem by carrying out laboratory experiments that mimic only part of the chemical scheme of the models (Gazeau *et al.* 2000). In particular, to judge the importance of single chemical reactions used in the models, it is necessary to acquire experimental information on the following aspects:

(i) can the suggested reactions take place at low temperatures?

(ii) are the suggested nitriles and polyynes the main products of the considered reactions? and

(iii) what are the reaction mechanisms of product formation?

While the answer to the first question usually comes from a kinetic investigation of a reactive system, the second and the third questions find a proper answer if we apply more sophisticated techniques that allow one to investigate each reaction at a microscopic level. For instance, recent state-of-the-art kinetic studies on $CN(X^2\Sigma^+)$ and $C_2H(X^2\Sigma^+)$ radical reactions with unsaturated hydrocarbons down to temperatures as low as 13 K suggest that these reactions are very fast and hold rate constants of the order of gas kinetics of about 10^{-10} cm^3 s^{-1} (Rowe & Parent 1995; Smith *et al.* 1997; Chastaing *et al.* 1998). In all of these experiments slightly negative temperature dependences, i.e. acceleration at decreasing temperatures, were recorded, suggesting the absence of any entrance barrier. However, since in this kind of experiment only the decay kinetics of the radicals is monitored, missing information concerning the nature of the reaction products represents a major drawback. This limitation clearly indicates the need for novel and systematic laboratory studies to identify the primary reaction products. This paper fills that gap and reviews recent accomplishments on reactions of cyano and ethynyl radicals with unsaturated hydrocarbons, disclosing ultimately the intermediates involved and the primary reaction products. This

was made possible by the application of the crossed molecular beam (CMB) technique with mass spectrometric detection. This technique allows one to consider selectively the reaction of CN or C_2H with molecules of interest in Titan's atmosphere and to fully characterize them. The advantages of this experimental technique – well known in the field of chemical kinetics – strongly motivate its extension to the study of reactions of interest in astrochemistry, as already shown in Kaiser *et al.* (1997, 2000, 2001a) and Balucani *et al.* (2000a). This paper is organized as follows. Section 2 outlines the experimental approach, i.e. the crossed molecular beam technique, and the information that can be obtained from these studies. Section 3 focuses on the experimental results from reactions of cyano and ethynyl radicals with acetylene, ethylene, methylacetylene, allene, and benzene. All of these molecules except allene have already been identified in hydrocarbon-rich atmospheres of planets and partly in their moons. A short summary and outlook will be given in the final section.

The experimental method

The main advantage of the CMB technique is that it allows one to study binary (elastic, inelastic and reactive) collisions under well-defined conditions. In fact, in contrast to a bulk experiment, the colliding species are confined into distinct beams that cross each other at a specific angle and collision energy; in other words, the species of each beam are made to collide only with the molecules of the other beam and the products formed fly undisturbed towards the detector. This allows us to observe the consequences of a single molecular collision, preventing secondary collisions and wall effects. A schematic view of the experimental apparatus is shown in Fig. 1. Briefly, two supersonic pulsed beams of the reactants – well collimated in angle and velocity – are crossed at 90° under single-collision conditions in a large scattering chamber kept below 10^{-7} mbar. The angular and velocity distributions of the reaction products are recorded by an ultra-high-vacuum (8×10^{-13} mbar) electron-impact ionizer followed by a quadrupole mass filter. The whole detector unit can be rotated in the plane of the two beams around their intersection axis ($\Theta = 0°$ represents the direction of the radical beam and $\Theta = 90°$ represents that of the hydrocarbon beam). The velocity of reactants and products is derived using time-of-flight (TOF) analysis.

The measurable quantities determined by this technique contain basic information. Any species can be ionized in the electron impact ionizer that precedes the mass filter and, in principle, it is possible to determine the mass (and the gross formula) of all the products of a bimolecular reaction by varying the mass-to-charge ratio, m/e, in the mass filter. Therefore, despite some problems (such as dissociative ionization and background noise), which restrict the sensitivity of the method, the use of mass spectrometric detection is advantageous if compared with spectroscopic techniques. Their applicability, in fact, requires knowledge of the optical properties of the products, while, in many cases, their nature itself is unknown. A considerable advantage with respect to common

flow reactors coupled with a mass spectrometer is the possibility to measure product angular and velocity distributions, which allows one to directly derive the total amount of energy available to the products and, therefore, the energetics of the reaction. This is crucial when more isomers with the same gross formula, but different enthalpy of formation, can be produced.

For a more detailed physical interpretation of the reactive encounter it is necessary to transform the laboratory (LAB) data into the center-of-mass (CM) system using a forward-convolution routine. 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 $P(E_T)$, taking into account the transformation Jacobian and the averaging over the apparatus and beam functions. The procedure is repeated until a satisfying fit of the LAB distributions is achieved and 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 $I(\theta, u) = P(u) \times T(\theta)$ ($P(u)$ is easily obtained from the best-fit $P(E_T)$ and vice versa). The function $I(\theta, u)$ is called the reactive differential cross-section and fully describes the dynamics of the reactive collision.

In summary, by measuring angular and velocity distributions of the possible products from bimolecular reactions, the CMB technique allows us to: (a) identify the primary reaction products; (b) determine the branching ratios of competing reaction channels; (c) untangle the microscopic reaction mechanisms; (d) quantify the product energy release; and hence to (e) gain information on the underlying potential energy surface (PES), which governs the transformation from reactants to products. The crossed-beam technique, used successfully over a number of years in the study of numerous elementary reactions, has more recently been applied to the study of some reactions of importance in astrophysics, such as the reactions of carbon atoms (Kaiser *et al.* 2001a; Kaiser & Mebel 2001), electronically excited nitrogen atoms (Balucani *et al.* 2000b,c), OH radicals (Alagia *et al.* 1993, 1996), and C_2 and C_3 (Kaiser *et al.* 2001b). Here, we have exploited the capability of producing pulsed supersonic beams of cyano (CN) and ethynyl (C_2D) radicals, from *in situ* reactions of the species formed by laser ablation of a carbon rod with the carrier and reactant gases N_2 and D_2, respectively (Kaiser & Suits 1995; Kaiser *et al.* 1999). In the following paragraph we report our results on the reaction of cyano radicals with acetylene in some details to illustrate the unprecedented capabilities of the experimental method. Hereafter, results obtained for the other reactions of CN and C_2H are compiled.

Laboratory results

The reaction of cyano radicals with acetylene

The CN/C_2H_2 system is alleged to be one of the most important steps in the formation of cyanopolyynes in different environ-
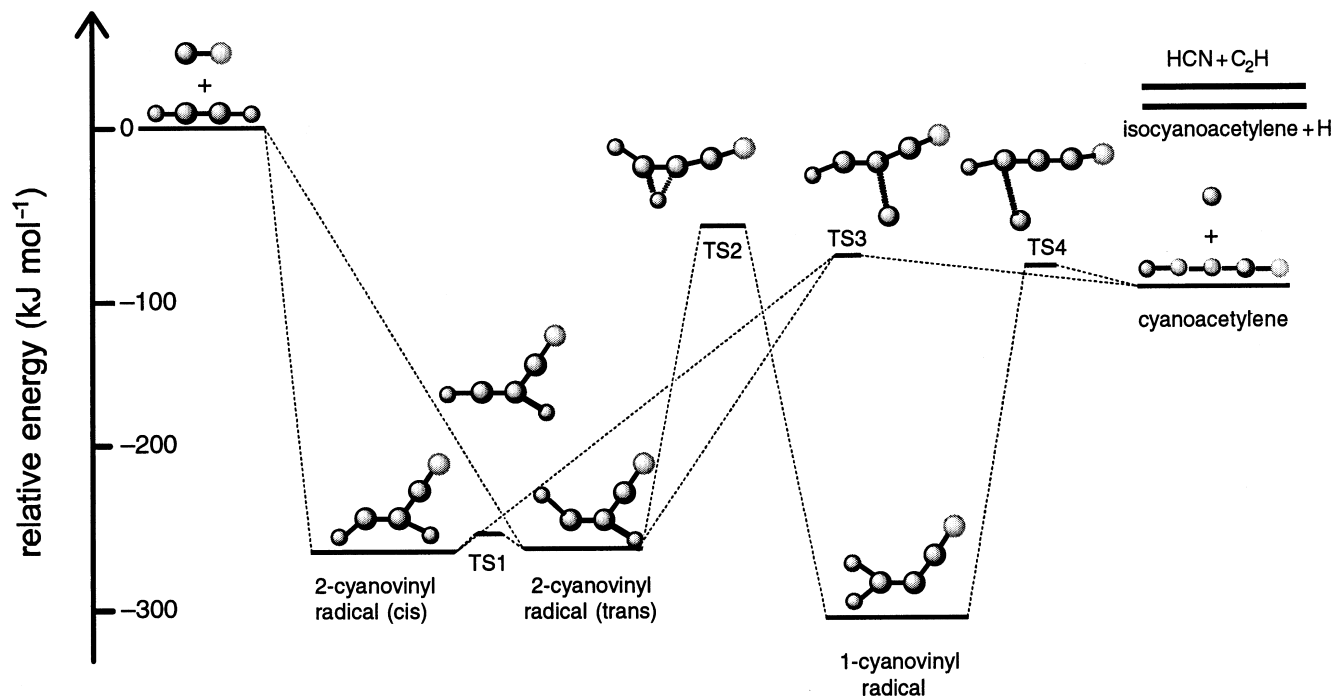
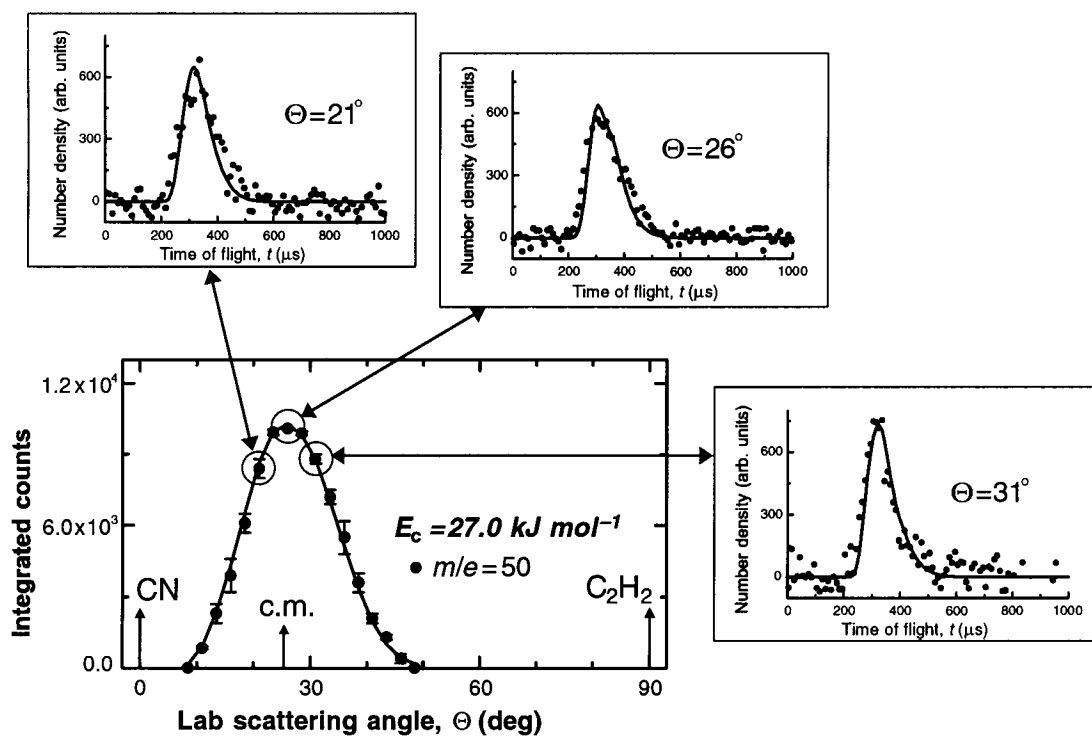**Fig. 2.** Schematic potential energy surface of the reaction of cyano radicals with acetylene.

Fig. 3. Laboratory angular distribution of $m/e = 50$ obtained from the reaction of cyano radicals with acetylene; c.m. depicts the center-of-mass angle. Selected TOF spectra are shown as well.

ments, such as planetary atmospheres and the interstellar medium. Its potential importance has been confirmed by kinetic studies, which have found this reaction to be very fast over a large range of temperatures (Rowe & Parent 1995; Smith *et al.* 1997; Chastaing *et al.* 1998). However, as already outlined, the nature of the reaction products could not be established. A tentative assignment was made by comparing

the rate constants for the reactions $CN + C_2H_2$, $CN + C_2H_4$ and $CN + CH_2 = CH-C \equiv CH$. In this way, it was speculated that all of these reactions proceed through the addition of CN to the π bond(s), 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. Two possible isomers of the gross formula C_3HN can be
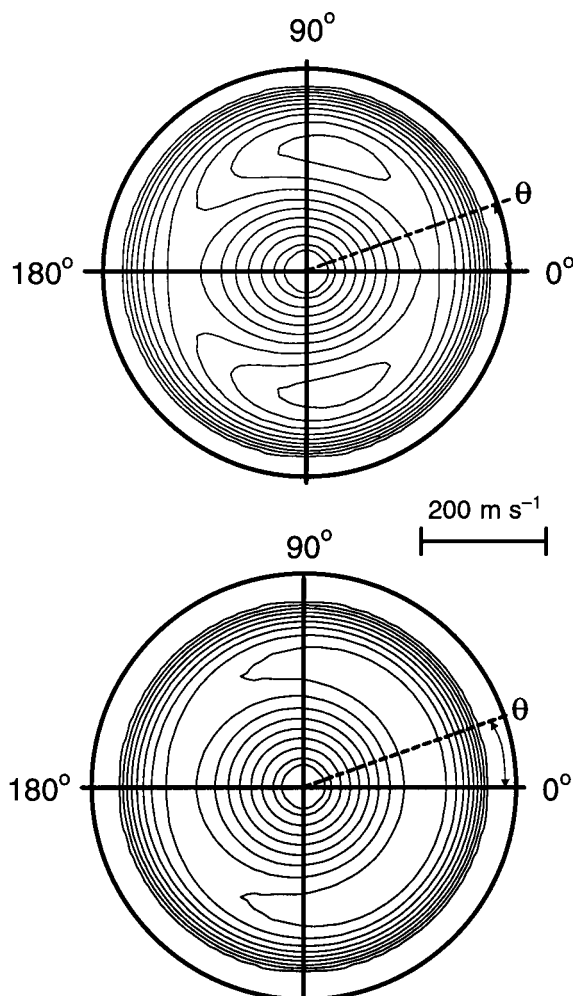
Fig. 4. Flux contour plots of the HC$_3$N product of the reaction of cyano radicals with acetylene at lower (top) and higher (bottom) collision energy.

formed by H-atom displacement in the reaction CN + C$_2$H$_2$, namely cyanoacetylene, HCCCN, and isocyanoacetylene, HCCNC (see Fig. 2). Between the two, cyanoacetylene is the one favoured by thermochemical considerations. Interestingly, cyanoacetylene – effectively detected in Titan's atmosphere and in the interstellar medium – is the simplest member of the cyanopolyacetylene family, and the CN + C$_2$H$_2$ reaction is used in most of the recent models to account for HCCCN formation. Therefore, in addition to rate constant measurements, it is crucial to prove that HCCCN is the actual reaction product if we want to assess the validity of the models that have used this assumption.

In order to establish this, scattering experiments were performed at two different collision energies (E_c) of 21.1 and 27.0 kJ mol^{-1}. We were able to observe scattered products at two different mass-to-charge ratios, 51 and 50, which correspond to the ions C$_3$HN$^+$ and C$_3$N$^+$, respectively. However, the LAB distributions recorded at the two m/e values revealed identical patterns and could be fitted with the same CM functions. This indicates unambiguously that the only product really formed under our experimental conditions has the gross formula C$_3$HN and that it partly fragments to C$_3$N$^+$ in the

electron-impact ionizer because of dissociative ionization. A signal at $m/e = 52$ corresponding to a possible stable reaction adduct of the formula C$_3$H$_3$N was not observed. The lack of a signal at $m/e = 52$ means that this bound intermediate is not stable enough to reach the detection region, i.e. it fragments rapidly because of its high energy content.

Because of the best signal-to-noise ratio, the complete set of final measurements were carried out at $m/e = 50$. In Fig. 3 the LAB product angular distribution at $E_c = 27.0$ kJ mol^{-1} together with selected TOF spectra are reported. The solid lines superimposed on the experimental results are the calculated curves when using the CM best-fit functions that generate the product flux contour maps reported in the Fig. 4. Both laboratory angular distributions have a peak close to the centre-of-mass position angle, 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 35°. The limiting circles shown in the contour maps of Fig. 4 have been drawn assuming that all the available energy is released as product translational energy in the case where cyanoacetylene is the product formed. If we compare this limit with the maximum speed of the C$_3$HN product(s) determined experimentally, the substantial coincidence indicates that HCCCN must be a significant product. The two best-fitting $P(E_T)$s (implicitly shown in the product flux contour maps, see Huang *et al.* (2000) for details) are characterized by a maximum value of translational energy, $E_{T(max)}$, of about 100–130 kJ mol^{-1} (note that by extending or cutting the high-energy tails of the best-fitting $P(E_T)$s by 10 kJ mol^{-1} the quality of the fit does not change significantly.) Since the energy conservation rule states that $E_{T(max)} \leqslant E_c - \Delta H°_{reaction}$, once we account for the relative collision energies the CN/H exchange reaction turns out to be exothermic by about 90 ± 10 kJ mol^{-1}. The thermochemistry of the channels leading to the two possible C$_3$HN isomers and atomic hydrogen is very different as derived recently by electronic structure *ab initio* calculations (Huang *et al.* 2000). The reaction energies of the channel leading to cyanoacetylene and atomic hydrogen was found to be -94.0 kJ mol^{-1} in contrast to the value of $+13.0$ kJ mol^{-1} calculated for the channel leading to the isocyanoacetylene isomer. In conclusion, from the energy cut-off of the product translational distributions we can establish that the thermodynamically more stable cyanoacetylene isomer is by far the main product from the CN + C$_2$H$_2$ reaction.

Other important suggestions can be derived from the angular part of the differential cross section. At both collision energies, $T(\theta)$ and $I(\theta, u)$ show more intensity in the forward direction ($\theta = 0°$) as is clearly visible in the contour maps of Fig. 4. The product intensity observed over the whole angular range suggests that the reaction follows indirect scattering dynamics via a C$_3$H$_2$N complex formation. The scattering preference for the forward (with respect to the CN beam direction taken as $\theta = 0°$) hemisphere implies that the complex lifetime is comparable to its rotational period. The availability of the first experimental results at the microscopic level (Huang *et al.* 1999) has stimulated the *ab initio* calculations of the
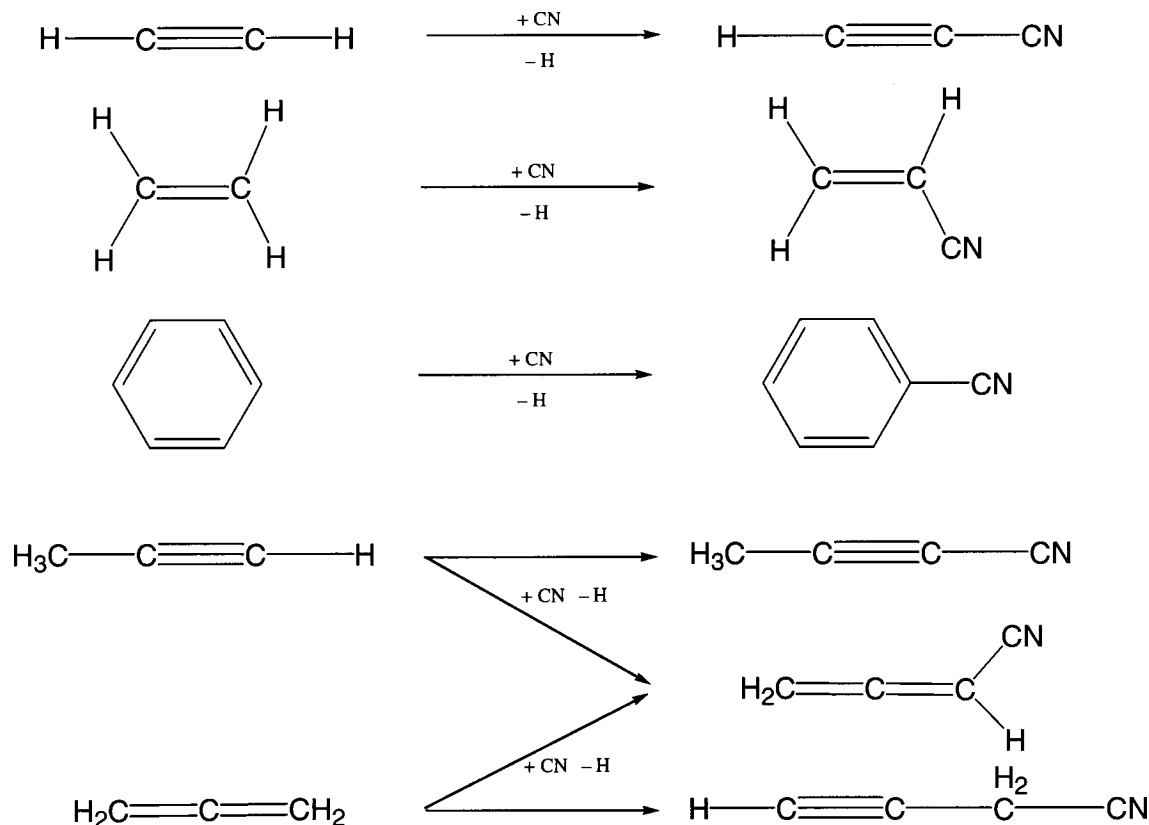
Fig. 5. Products of cyano radical reactions with various unsaturated hydrocarbons.

stationary point electronic structures along the C_3H_2N potential energy surface (Huang *et al.* 2000). The Rice–Ramsberger–Kassel–Marcus (RRKM) theory has also been applied using the *ab initio* results along the possible different reaction pathways to predict the product branching ratio. By comparing our experimental results and RRKM predictions we now have a clear picture of the reaction mechanism and the basic characteristics of the important reaction of cyano radicals with acetylene.

The unpaired electron is localized in the σ-symmetric $^2\Sigma^+$-orbital of the carbon atom and therefore CN attacks the π_s/π_y-orbital of the acetylene molecule via a loose transition state with no entrance barrier. This process forms a deeply bound (242 kJ mol^{-1}) C_s symmetric trans or *cis* 1-cyanovinyl-2 radical intermediate, HCCHCN on the $^2A'$ surface, (cf. Fig. 2). Both the *cis* and *trans* forms can isomerize easily via TS1 located only 14 kJ mol^{-1} above the initial collision complexes. Since the isomerization barrier lies well below the total available energy, the *cis* and *trans* forms are expected to be present in equal amounts. The CN radical can also attack the acetylene molecule with its N-side without an entrance barrier. This approach, however, was not found to be efficient at leading to the isocyanoacetylene product because of significant barriers (~ 30 kJ mol^{-1}) along that reaction pathway (for details see Huang *et al.* 2000); however, the initial addition complex can rearrange to 2-cyanovinyl radicals. The *cis/trans* C_3H_2N intermediates can undergo either an H-atom elimination to form cyanoacetylene through the transition state TS3 (-72 kJ mol^{-1}) or depict a 1,2 H-atom shift through the

transition state TS2 (-65 kJ mol^{-1}), leading to the 1-cyanovinyl radical which is the absolute minimum of the potential energy surface. This intermediate can also decompose to cyanoacetylene plus atomic hydrogen through the transition state TS4 (-87 kJ mol^{-1}). Two high-energy singlet cyanovinylidene ($+115$ kJ mol^{-1}) and singlet isocyanovinylidene ($+227$ kJ mol^{-1}) isomers are also stable isomers (not discussed here). Since our maximum collision energy is limited to 27 kJ mol^{-1}, none of the vinylidenes is relevant to our experiments. Finally, a direct H-atom abstraction to form HCN or HNC is endothermic by 23 and 83 kJ mol^{-1}, respectively, and involves transition states located 41 and 96 kJ mol^{-1} above the reactants. Therefore, these pathways are not accessible either. We have already commented on the fact that our experimental data are consistent with the formation of the most stable isomer cyanoacetylene; however, by using just the experimental results we cannot exclude a small contribution from the HCCNC formation channel – we have employed RRKM calculations to tackle this problem. This procedure shows that HCCCN is the only reaction product and that only about 15% of it is formed after the rearrangement of *cis/trans* 2-cyanovinyl intermediates into a 1-cyanovinyl radical. In conclusion, the reaction mechanism for the $CN + C_2H_2$ reaction – the prototype of the class of reactions $CN + H\text{-}(C\equiv C)_n$-H – is relatively simple. Amongst the possible approaches, the addition of the CN radical to the triple bond on the C side is favoured; the dissociation of the *cis/trans* forms of the addition intermediates leads to the cyanoacetylene product and atomic hydrogen.
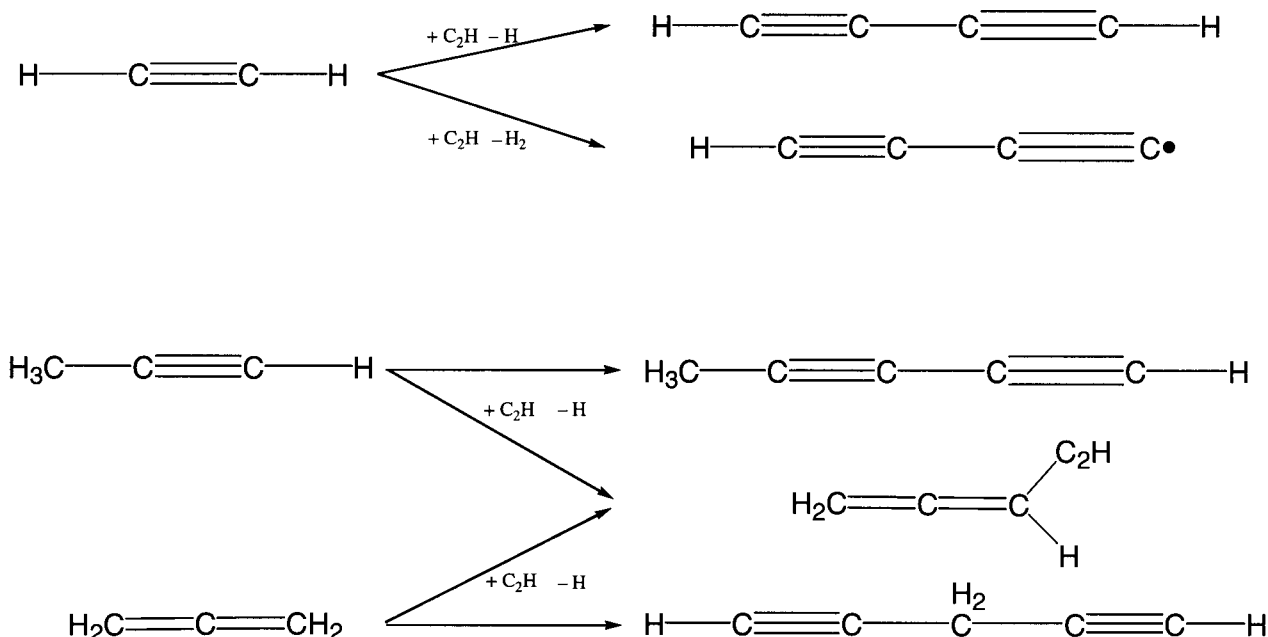
Fig. 6. Products of ethynyl radical reactions with various unsaturated hydrocarbons.

The reactions of cyano radicals with ethylene, acetylene, allene and benzene

We now compile briefly the underlying dynamics of the other CN reactions studied; for a detailed description, the original literature is referred to (Balucani *et al.* 1999, 2000d; Huang *et al.* 1999, 2000). The reactions of cyano radicals with closed-shell unsaturated hydrocarbons are all initiated by addition of the radical reactant to the double or triple bond of the hydrocarbon molecule with subsequent complex formation. In all cases, this kind of approach has no entrance barrier. The initial collision complex(es) either loses an H atom to form the reaction product(s) or undergoes isomerization (*cis/trans*, H-atom migration) prior to decomposition; all transition states involved are below the energy of the reactant molecules. The overall reactions to form the nitrile reaction products as shown in Fig. 5 are exothermic; no isonitriles were identified, and competing H abstraction channels were found to be only of minor importance. Under the single-collision conditions of the present experiments the lifetime of all complexes that are formed with extremely high internal excitation is of the order of a few picoseconds. Hence these intermediates fragment before they can be detected. However, in the denser atmosphere of Titan, three-body collisions would have a profound impact on the atmospheric chemistry and could divert the internal energy, thus stabilizing these intermediates.

The reactions ethynyl radicals with acetylene, methylacetylene and allene

The reactions of ethynyl were found to proceed in a similar way to the cyano ones (Kaiser *et al.* 2001a,b; Stahl *et al.* 2001a,b), leading to the formation of (substituted) diacetylenes and allenes (Fig. 6). In each reaction, the ethynyl radical adds barrier less to the double or triple bond followed either by H-atom emission or H shift prior to fragmentation. In the case of

the C_2H/C_2H_2 system, an additional H_2 elimination pathway to form the butadiynyl radical (HCCCC) was identified. Since all of the reactions are exothermic and all the barriers involved range below the energy of the separated reactants, these systems are of crucial importance in the formation of highly hydrogen deficient species in planetary atmospheres.

Conclusions and outlook

The crossed molecular beam technique has proven to be an elegant method of unravelling the chemical reaction dynamics, complexes involved and product isomers of neutral–neutral reactions of cyano and ethynyl radicals with the unsaturated hydrocarbon molecules acetylene (C_2H_2), ethylene (C_2H_4), methylacetylene (CH_3CCH), allene (H_2CCCH_2) and benzene (C_6H_6). We have inferred useful information on the feasibility of these reactions in extraterrestrial environments. The reactions have no entrance barriers and are all exothermic. Since the involved transition states range well below the energy of the separated reactants, these reactive collisions can occur even in low-temperature environments such as in cold molecular clouds and in the atmospheres of planets and their moons. We have also identified the underlying reaction mechanism. All reactions proceed via an initial addition of the radical to alkenes, alkynes and aromatic species. This is followed either by a hydrogen emission or – in the case of the C_2H_2 and C_2H_4 reactions – by an additional hydrogen migration prior to H-atom loss. The reaction sequence of a radical addition followed by H-atom loss is expected to be generalized and can be extended to predict the reactivity of hitherto not investigated reactions of cyano and ethynyl radicals. The C_2H/C_2H_2 system deserves particular attention as a minor amount (1%) of molecular hydrogen elimination was also observed.

We have identified 11 reaction products, among them nitriles, polyynes, substituted allenes and radicals (Figs 5, 6). The reactions of cyano and ethynyl radicals with acetylene form cyanoacetylene (HCCCN) and diacetylene (HCCCCH), respectively, which have been both observed in the interstellar medium and in the atmosphere of Titan. Furthermore, the formation of the butadiynyl radical (HCCCC) was unravelled. The explicit assignment of reaction pathways is unique to crossed-beam experiments. As radicals are extremely reactive, bulk experiments subjecting gas mixtures to discharges and coupling this set-up to a gas-chromatography-mass spectrometer (GC-MS) cannot identify open-shell reaction products. Thus important information can be lost, and detailed crossed-beam experiments are clearly desired. The reactions of $CN(X^2\Sigma^+)$ with ethylene and benzene yielded vinylcyanide (C_2H_3CN) and cyanobenzene (C_6H_5CN), which have not yet been detected in the atmosphere of Titan so far. However, vinylcyanide was observed toward hot molecular cores and cold clouds. Most importantly, our investigations yielded data on distinct reactivities of structural isomers. Here, the reactions of cyano and ethynyl radicals with methylacetylene and allene gave three distinct isomers each: CH_3CCCN, $H_2CCCH(CN)$ and $HCCCH_2(CN)$ (CN systems) as well as $CH_3-CCCCH$, $H_2CCCH(C_2H)$ and $HCCCH_2(C_2H)$ (C_2H system). These isomers have different spectroscopic properties, photochemical activities and distinct chemical reactivities to form ultimately amino acids in liquid environments. Among them, only CH_3CCCN and CH_3CCCCH have been detected in cold molecular clouds. The explicit experimental identification of unsaturated nitriles, polyynes and allenes hitherto unobserved in Titan makes these molecules a unique target for the NASA–ESA Cassini–Huygens mission to Titan. The spacecraft Huygens will carry an infrared (IR) mapping spectrometer as well as a quadrupole mass spectrometer capable of identifying closed-shell isomers in the atmosphere of Titan. Also, the crossed-beam method is unique in identifying unstable reaction intermediates. All intermediates are doublet radicals, rovibrationally excited, and hence highly reactive in planetary atmospheres. Although under the experimental single-collision conditions the gas is too rarefied to allow three-body collisions, the collision-induced stabilization of the intermediates is possible in the atmosphere of Titan. Notably, these free radicals have unknown spectroscopic properties and could make them responsible for the orange colour of the upper atmospheric layers.

The present work is only the very first step towards a comprehensive and systematic understanding of the fundamental elementary processes involved in the chemistry of hydrocarbon-rich planetary atmospheres. Our experiments explicitly identified synthetic routes to nitriles – precursor molecules to amino acids – and polyacetylene – often dubbed as 'prebiotic ozone'. The experimental data can be employed to set up a systematic database of reaction products and can predict the formation of hitherto unobserved gas-phase molecules in Titan and in the framework of the Cassini–Huygens mission. The applications of the crossed-beam method to planetary chemistry problems have just begun to scratch the surface. Many interesting problems remain to be studied. 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. This is of crucial importance as the planetary modelling community and the correct outcome of their (photo)chemical reaction networks of planetary and satellite atmospheres depend on input data into these models (rate constants, reaction products, isomers, intermediates). Sophisticated, cutting-edge laboratory experiments are crucial to providing these data – now and in the future.

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