FORMATION OF NITRILES IN THE INTERSTELLAR MEDIUM VIA REACTIONS OF CYANO RADICALS, CN($X\,^2\Sigma^+$), WITH UNSATURATED HYDROCARBONS

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ABSTRACT

Crossed molecular beam experiments of cyano radicals, CN($X\,^2\Sigma^+$, $v = 0$), in their electronic and vibrational ground state reacting with unsaturated hydrocarbons acetylene, $C_2H_2(X\,^1\Sigma_g^+)$, ethylene, $C_2H_4(X\,^1A_g)$, methylacetylene, $CH_3CCH(X\,^1A_1)$, allene, $H_2CCCH_2(X\,^1A_1)$, dimethylacetylene, $CH_3CCCH_3(X\,^1A_1')$, and benzene, C_6H_6 ($X\,^1A_{1g}$), were performed at relative collision energies between 13.3 and 36.4 kJ mol^{-1} to unravel the formation of unsaturated nitriles in the outflows of late-type AGB carbon stars and molecular clouds. In all reactions, the CN radical was found to attack the π electron density of the hydrocarbon molecule with the radical center located at the carbon atom; the formation of an initial addition complex is a prevalent pathway on all the involved potential energy surfaces. A subsequent carbon-hydrogen bond rupture yields the nitriles cyanoacetylene, HCCCN ($X\,^1\Sigma^+$), vinyl-cyanide, C_2H_3CN ($X\,^1A'$), 1-methylcyanoacetylene, CH_3CCCN ($X\,^1A_1$), cyanoallene, $H_2CCCH(CN)$ ($X\,^1A'$), 3-methylcyanoacetylene, $HCCCH_2CN(X\,^1A')$, 1,1-cyanomethylallene, $H_2CCC(CN)(CH_3)$ ($X\,^1A'$), and cyanobenzene, C_6H_5CN ($X\,^1A_1$). In case of acetylene and ethylene, a second reaction channel involves a [1, 2]-H atom shift in the initial HCCHCN and H_2CCH_2CN collision complexes prior to a hydrogen atom release to form cyanoacetylene, HCCCN ($X\,^1\Sigma^+$), and vinylcyanide, C_2H_3CN ($X\,^1A'$). Since all these radical-neutral reactions show no entrance barriers, have exit barriers well below the energy of the reactant molecules, and are exothermic, the explicit identification of this CN versus H atom exchange pathway under single collision conditions makes this reaction class a compelling candidate to synthesize unsaturated nitriles in interstellar environments holding temperatures as low as 10 K. This general concept makes it even feasible to predict the formation of nitriles once the corresponding unsaturated hydrocarbons are identified in the interstellar medium. Here HCCCN, C_2H_3CN, and CH_3CCCN have been already observed; since CH_3CCH is the common precursor to $H_2CCCH(CN)/CH_3CCCN$ and the latter isomer has been assigned unambiguously toward TMC-1 and OMC-1, $H_2CCCH(CN)$ is strongly expected to be present in both clouds as well. The formation of iso-nitrile isomers was not observed in our experiments. Since all reactions to HCCNC, C_2H_3NC, CH_3CCNC, $H_2CCCH(NC)$, $H_2CCC(NC)(CH_3)$, and C_6H_5NC are either endothermic or the exit barrier is well above the energy of the reactants, neutral-neutral reactions of cyano radicals with closed shell unsaturated hydrocarbons cannot synthesize isonitriles in cold molecular clouds. However, in outflow of carbon stars, the enhanced translational energy of both reactants close to the photosphere of the central star can compensate this endothermicity, and isonitriles might be formed in these hotter environments as well.

Subject headings: ISM: molecules — methods: laboratory — molecular processes

1. INTRODUCTION

Unraveling the chemical reaction dynamics to form unsaturated nitriles—organic molecules containing the CN group—in cold molecular clouds as well as outflow of late-type AGB carbon stars is of paramount importance to understand the chemical history of extraterrestrial environments and to establish versatile concepts involved in the synthesis of carbon-nitrogen–bearing molecules in the interstellar medium (ISM). To fully resolve this 40 year old mystery, we must first understand the abundances, distribution, and structure of these nitriles together with the physical conditions in their formation zones before elucidating precise mechanisms to synthesize these molecules in extraterrestrial environments.

All hydrogen-deficient nitriles observed so far can be arranged in four groups: cyanopolyynes of the general chemical formula H—(C≡C)$_n$—CN (group 1), methyl substituted cyanopolyynes (CH$_3$—(C≡C)$_n$—CN; group 2), cyanopolyyne radicals ((C≡C)$_n$—CN; group 3), and

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olefinic nitriles containing the C=C moiety together with a CN group (group 4). All cyanopolyynes are ubiquitous in the ISM and hold high fractional abundances of up to 6×10^{-9} relative to hydrogen (Bettens, Lee, & Herbst 1995). The first member of this series, cyanoacetylene, HCCCN ($X\,^1\Sigma^+$), was identified in dark molecular clouds TMC-1 and OCM-1 as well as the carbon star IRC+10216 (CW Leo) (Turner 1971; Morris et al. 1975; Broten et al. 1978; Cernicharo, Guelin, & Kahan 2000). Toward high-intensity IR sources like IRC+10216 (Turner 1987) and massive O-B stars within dense molecular clouds rotational transitions inside vibrationally excited states were observed as well (Wyrowski, Schilke, & Walmsley 1999). Since HCCCN is produced in the early stage of the cyanopolyyne chain growth, it is thought to be the key molecule in the cyanopolyyne formation. More complex cyanopolyynes HC_5N, HC_7N, HC_9N, and $HC_{11}N$ have been observed in TMC-1 (Broten et al. 1984; Bell et al. 1997, 1998). Based on chemical models of the synthesis of polycyanoacetylenes in IRC+10216 and TMC-1 and decreasing fractional abundances of these nitriles with increasing molecular weight down to 10^{-10}, Cherchneff, Glassgold, & Mamon (1993), Bettens et al. (1995), and Ruffle et al. (1997) classified these cyanopolyynes as late time chemistry indicators.

The second group of cyanopolyynes contains only one member, namely 1-methylcyanoacetylene, CH_3CCCN. Broten et al. (1984) identified weak rotational transitions of the latter in TMC-1; Ohishi & Kaifu (1998) confirmed this assignment very recently. A tentative detection was made toward the molecular complex M-0.02-0.07 near the Galactic center (Chin 2000). Compared to the closed shell cyanopolyynes, the radicals C_3N and C_5N (group 3) were identified in TMC-1 and IRC+10216; their fractional abundances are 2 orders of magnitude less than their HC_3N and HC_5N counterparts (Guelin, Neininger, & Cernicharo 1988). Finally, vinylcyanide, C_2H_3CN, is the only olefinic nitrile (group 4) observed so far toward TMC-1 (Ohishi & Kaifu 1998); vibrationally excited C_2H_3CN molecules were detected in SgrB2(N) (Nummelin & Bergman 1999) and toward the star-forming region Orion KL (Schilke et al. 1999).

However, despite these impressive astronomical assignments and line surveys together with calculated fractional abundances, the question "How are nitriles synthesized in various astrophysical environments?" is far from being resolved. Since the average kinetic energy of interstellar species is typically confined to 0.8 kJ mol^{-1} (diffuse clouds) and 0.08 kJ mol^{-1} (dark, molecular clouds), their formation via gas phase reactions under thermodynamical equilibrium conditions must have little or no barrier and involve only two-body collisions. Ternary encounters occur only once in a few 10^9 yr and can be neglected considering mean interstellar cloud lifetimes of 10^6 yr. Therefore, ion-molecule reactions were postulated to play a central role in interstellar reaction networks. Early models of interstellar cloud chemistry suggest that the HCCCNH$^+$ ion is the key intermediate in the formation of the simplest acetylenic nitrile, HCCCN, and its isonitrile isomer, HCCNC, via a dissociative recombination of HCCCNH$^+$ with an electron of the cosmic radiation field (Knight et al. 1986):

$$HCCCNH^+ + e^- \rightarrow HCCCN + H ,$$
$$\rightarrow HCCNC + H . \qquad (1)$$
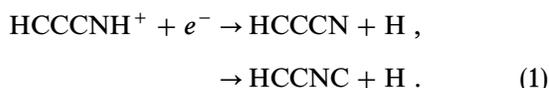
HCCCNH$^+$ itself is thought to be formed via ion-molecule reactions

$$C_2H_2^+ + CN \rightarrow HCCCN^+ + H , \qquad (2)$$
$$C_2H_2^+ + HCN \rightarrow HCCCNH^+ + H , \qquad (3)$$
$$C_3H_3^+ + N(^4S) \rightarrow HCCCNH^+ + H . \qquad (4)$$

If this process is indeed the main route, relative abundances of HCCCN versus HCCNC not far from unity are expected—in strong disagreement with astronomical surveys showing a ratio of 160:1 toward TMC-1 (Kawaguchi 1994; Ohishi, Irvine, & Kaifu 1992). In addition, chemical models including these reaction sequences yield HCCCN fractional abundances orders of magnitudes less than observed (Herbst & Millar 1991). A second shortcoming is the observation of ^{13}C isotopic enrichments in HCCCN isotopomers toward TMC-1 (Takano et al. 1998). A detailed mapping indicates that $H^{13}CCCN$ and $HC^{13}CCN$ have similar intensities, but that $H^{13}CCCN$ versus $HCCC^{13}CN$ shows a ratio of 1.4. If ion-molecule reactions are in charge to form HCCCN, all three isotopomers should be equal since the carbon atoms of c—$C_3H_3^+$ cannot be distinguished. Most importantly, a very recent theoretical ab initio investigation of reaction (4)—the backbone system in these ion-molecule reaction networks—presented unambiguous evidence that this reaction is not feasible in molecular clouds (Takagi et al. 1999). All these data suggest that ion-molecule reactions are not sufficient to explain formation of HCCCN in the ISM. A new mechanism is clearly necessary.

Based on recent low-temperature laboratory measurements of CN radical reactions with C_2H_2 and C_2H_4 (Sims et al. 1992, 1993a, 1993b, 1994a, 1994b; Smith, Sims, & Rowe 1997), it was postulated that bimolecular rapid neutral-neutral reactions between the cyano radical and unsaturated hydrocarbons might produce the simplest members of interstellar nitriles HCCCN and C_2H_3CN in the outflow of the circumstellar envelope surrounding the carbon star IRC+10216 (Cherchneff & Glassgold 1993; Millar & Herbst 1994; Doty & Leung 1998), hot molecular cores (Ruffe et al. 1997; Millar, Macdonald, & Gibb 1997), and dark molecular clouds such as TMC-1 (des Forets et al. 1991; Suzuki et al. 1992):

$$CN(X\,^2\Sigma^+) + C_2H_2(X\,^1\Sigma_g^+) \rightarrow$$
$$HCCCN(X\,^1\Sigma^+) + H(^2S_{1/2}), \qquad (5)$$
$$CN(X\,^2\Sigma^+) + C_2H_4(X\,^1A_g) \rightarrow C_2H_3CN(X\,^1A') + H(^2S_{1/2}) . \qquad (6)$$
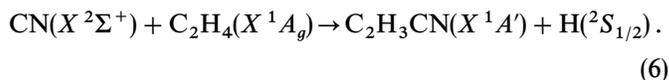
The rate constants of both reactions increase as the temperature decreases, reaching a maximum of 5×10^{-10} cm^3 s^{-1} at 30 K that is, they are on the order of gas phase collisions. These studies monitored only the decay kinetics of the CN radical, and hence reaction products could not be determined explicitly and the reaction mechanism only speculated. This shortcoming has made a call for a systematic experimental investigation at the microscopic level where the primary reaction products and the reaction mechanism can be identified under single collision conditions.

The present paper fills this gap and presents for the first time a concise study of bimolecular reactions of cyano radicals CN in their $^2\Sigma^+$ electronic and vibrational ground state with unsaturated hydrocarbons, employing the crossed

molecular beams approach (Lee 1988; Lee et al. 1969); see reactions (7)–(12):

$$CN(X\,^2\Sigma^+) + C_2H_2(X\,^1\Sigma_g^+) \to HCCCN(X\,^1\Sigma^+) + H(^2S_{1/2}),$$
(7)

$$CN(X\,^2\Sigma^+) + C_2H_4(X\,^1A_g) \to C_2H_3CN(X\,^1A') + H(^2S_{1/2}),$$
(8)

$$CN(X\,^2\Sigma^+) + CH_3CCH(X\,^1A_1)$$
$$\to CH_3CCCN(X\,^1A_1) + H(^2S_{1/2}),$$
$$\to HCCCN(X\,^1\Sigma^+) + CH_3(X\,^2A_2''),$$
$$\to H_2CCCH(CN)(X\,^1A') + H(^2S_{1/2}),\quad (9)$$

$$CN(X\,^2\Sigma^+) + H_2CCCH_2(X\,^1A_1)$$
$$\to H_2CCCH(CN)(X\,^1A') + H(^2S_{1/2}),$$
$$\to HCCCH_2CN(X\,^1A') + H(^2S_{1/2}),\quad (10)$$

$$CN(X\,^2\Sigma^+) + CH_3CCCH_3(X\,^1A_1')$$
$$\to H_2CCC(CN)(CH_3)(X\,^1A') + H(^2S_{1/2}),$$
$$\to CH_3CCCN(X\,^1A_1) + CH_3(X\,^2A_2''),\quad (11)$$

$$CN(X\,^2\Sigma^+) + C_6H_6(X\,^1A_{1g}) \to C_6H_5CN(X\,^1A_1) + H(^2S_{1/2}).$$
(12)
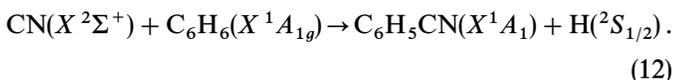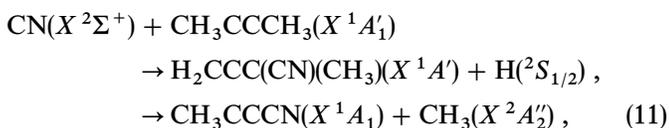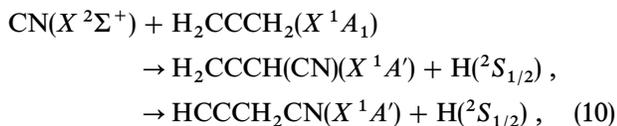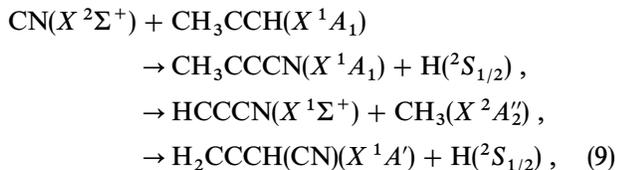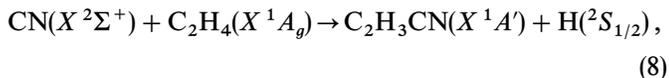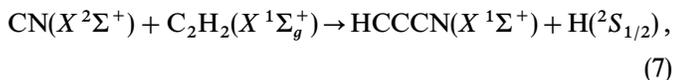
Reactions (7), (8), and (12) represent CN binary collisions with the simplest, neutral closed shell alkyne (acetylene), olefine (ethylene), and aromatic molecule (benzene) to form astronomically observed cyanoacetylene, HCCCN, and vinylcyanide, C_2H_3CN, together with hitherto unobserved cyanobenzene, C_6H_5CN. The study of binary encounters of (9) and (10) unravel the reaction products of cyano radicals with two C_3H_4 isomers, methylacetylene and allene. Reaction products, involved intermediates, and triply differential reaction cross sections will be investigated systematically in laboratory experiments under well-defined experimental conditions. This study establishes a detailed database of these reaction products and short-lived intermediates—a crucial input to future chemical models on the formation of nitriles in cold molecular clouds and outflow of carbon stars.

2. EXPERIMENTAL PROCEDURE, DATA PROCESSING, AB INITIO CALCULATIONS

The upgraded 35″ universal crossed molecular beam machine and the supersonic cyano radical, $CN(X\,^2\Sigma^+, v = 0)$, source have been described in Balucani et al. (1999a) and Kaiser et al. (1999) in detail. Briefly, the 30 Hz pulsed 266 nm output of a Spectra Physics GCR -270-30 Nd:YAG laser is focused on a rotating carbon rod. Carbon species are ablated at 30 mJ per pulse and seeded into neat nitrogen carrier gas which acts as a reactant as well. These operation conditions form cyano radicals in their electronic $^2\Sigma^+$ and vibrational ground state ($v = 0$). After the pulsed CN beam passes the skimmer, a four-slot chopper wheel selects a 9.0 μs segment of this pulse with velocities between 1000 and 1990 ms^{-1} and speed ratios between 4.0 and 8.0. The beam segment and the second pulsed supersonic hydrocarbon beam cross at 90° under a well-defined collision energy in the interaction region. The resulting collision energies range between 13.3 and 36.4 kJ mol^{-1} depending on the initial beam velocities. Reactively scattered products are moni-

tored in the collision plane using a rotatable triply differentially pumped quadrupole mass spectrometer with a Brink-type electron-impact ionizer in the time-of-flight (TOF) mode, i.e., recording the time-dependent intensity of ionized products at specific mass to charge ratios (m/e) at different laboratory scattering angles. The ultimate pressure in the ionizer region is less than 8×10^{-13} torr. Information on the reaction dynamics is then gained by fitting the TOF spectra and the product angular distribution in the laboratory reference frame using a forward-convolution routine; see Vernon (1981) and Weiss (1986) for details.

The theoretical investigations have been performed using hybrid Hartree-Fock/Density Functional Theory with the Gaussian 98 program (Frisch et al 1998). Becke's (Becke 1993) three-parameter hybrid functional and the correlation functional of Lee, Yang, & Parr (1988) (B3LYP) have been employed in conjunction with the $6-311+G^{**}$ basis set for geometry optimizations and computation of the harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs). Energies given are corrected for the ZPVE unless stated otherwise.

3. RESULTS

3.1. Reactive Scattering Signal

The CN radical versus H atom exchange dominates reactions (7)–(12); reactive scattering signal was detected at mass to charge ratios $m/e = 51$ (C_3HN^+, reaction [7]), $m/e = 53$ ($C_3H_3N^+$, reaction [8]), $m/e = 65$ ($C_4H_3N^+$, reactions [9] and [10]), $m/e = 79$ ($C_5H_5N^+$, reaction [11]), and $m/e = 103$ ($C_7H_5N^+$, reaction [12]). The observation of these product masses under well-defined single collision conditions strongly emphasizes the potential significance of these reactions to synthesize nitriles in interstellar environments. In addition, TOF spectra of lower m/e ratios down to $m/e = 50$ (reactions [7] and [8]), $m/e = 62$ (reactions [9] and [10]), $m/e = 74$ (reaction [11]), and $m/e = 98$ (reaction [12]) were taken at selected angles as well. Since these spectra depict identical patterns and could be fitted with the same center-of-mass functions as the parent ion, those lower masses originate from dissociative ionization in the electron impact ionizer. It should be emphasized that no radiative association channel to any adduct was found in our experiments. This finding emphasizes explicitly that the internally excited intermediate survives neither under experimental single collision conditions nor in the interstellar medium. Nevertheless, denser planetary atmospheres or cometary comae could provide a third-body reaction to divert the excess energy and to stabilize these intermediates (see § 4).

3.2. Laboratory Angular Distributions

In general, all our laboratory angular distributions peak in the vicinities of the center-of-mass angles and are quite narrow, spreading over only 32°–45° in the scattering plane defined by the two intersecting beams. Since the quadrupole mass spectrometer by itself cannot distinguish among the possible product isomers (molecules with the same chemical formula but different atomic arrangements such as cyanoacetylene HCCCN and isocyanoacetylene HCCNC), a deeper understanding of the underlying chemical reaction dynamics—that is, an investigation of the chemical reaction on the microscopic level—is needed to determine which product isomer is actually formed. One of the crucial points in a chemical reaction is the exother-

micity of a reaction since it determines the total amount of energy available to the system (Kaiser et al. 1998). We find that cyanoacetylene (HCCCN; reaction [7]), vinyl-cyanide (C_2H_3CN, reaction [8]), 1,1-cyanomethylallene ($CH_3CNCCCH_2$, reaction [11]), and cyanobenzene (C_6H_5CN, reaction [12]) are synthesized. Reactions (9) and (10) represent a particular problem, since both energetically accessible isomers cyanoallene ($H_2CCCH(CN)$) and 1-methylcyanoacetylene (CH_3CCCN) are only separated by about 15–20 kJ mol^{-1}. Due to the velocity spread of both primary and secondary beams, these isomers cannot be discriminated based on their limiting Newton circles. For reaction (9), we repeated the crossed beam experiments with the partially deuterated methylacetylene, CD_3CCH, and found an H atom as well as a D atom loss channel, i.e., detection of $m/e = 68$ of $C_4D_3N^+$ and $m/e = 67$ of $C_4D_2HN^+$. This strongly indicates that the two isomers are both formed in this reaction; see § 4.

3.3. Center-of-Mass Translational Energy Distributions, $P(E_T)$

To get additional information on the chemical reaction dynamics we must investigate the center-of-mass translational energy distributions in detail. Three properties of the translational energy distributions are worth investigating. First, the maximum translation energy E_{max} can be utilized to identify the product isomer. Since E_{max} is simply the sum of the reaction exothermicity plus the relative collision energy in our crossed beam experiments, a subtraction of this collision energy from the experimentally determined E_{max} yields the reaction exothermicity. The values of E_{max} determined from the best-fit functions together with the calculated reaction energies support the assignment of the product isomers of the previous section. Second, in favorable cases, the peak position of the $P(E_T)$ can give the order of magnitude of the barrier height in the exit channel. Our $P(E_T)$'s show maxima between 15 and 45 kJ mol^{-1}, implicating in all cases a significant geometry as well as electron density change from the fragmenting intermediate to the final products. These complexes represent covalently bound intermediates from reaction of the unsaturated hydrocarbon with the CN radical. In our crossed beams experiments, the lifetime of these intermediates is on the order of 1 ps. Due to our single collision conditions, a third-body collision cannot stabilize these internally excited short-lived species. In denser planetary atmospheres, however, a three-body reaction can divert this excess energy and might supply a stable radical reaction product in addition to the closed shell nitriles. The structure of these important reaction intermediates in planetary chemistry will be identified in the next sections.

3.4. Center-of-Mass Angular Distributions, $T(\theta)$

The angular information of the crossed beam data is of crucial importance to elucidate the chemical reaction dynamics (Levine & Bernstein 1987; Miller, Safron, & Herschbach 1967; Miller 1969). These functions represent the angular-dependent flux distribution an observer would see if he moves with the center of mass velocity dwelling in the center of mass of the system. Here the direction of the CN beam is defined as $\theta = 0°$, and that of the hydrocarbon beam to $\theta = 180°$. A multitude of shapes of the flux distributions is feasible; see detailed discussion in Balucani et al. (2000b). Our best-fit functions show that all reactions

(7)–(12) proceed via indirect scattering dynamics and involve a collision complex. Reactions (8) and (10)–(12) depict symmetric distributions, and the lifetime of the complex is longer than the rotational period which is often in the order of a picosecond. We would like to stress again that in principle, all these collision complexes can be isolated in denser media such as the atmosphere of Saturn's moon Titan. They are radicals and therefore they will react with other molecules sooner or later. In reaction (7) and (9), the distributions show an asymmetry and hint to the formation of osculating complexes.

4. DISCUSSION

4.1. Reaction (1): $CN + C_2H_2$

A combined experimental crossed beam approach and theoretical ab initio investigation is employed to unravel the chemical reaction dynamics of the CN/C_2H_2 system. This study presents for the first time a complete C_3H_2N potential energy surface (PES) compared to previous limited studies by Fukuzawa & Osamura (1997) and Woon & Herbst (1997). Figure 1 displays a simplified doublet C_3H_2N PES and feasible exit channels to C_3HN isomers omitting all unobserved high-energy isomers and isocyano intermediates/products; see Huang et al. (2000) for a complete PES. The CN radical attacks the π electron density of two perpendicular π molecular orbitals without entrance barrier to form the cis and trans cyanovinyl radicals HCCHCN (Balucani et al. 2000a; Huang, Lee, & Kaiser 1999a). Both initial collision complexes are stabilized by 242 kJ mol^{-1} with respect to the separated reactants. Due to the low barrier of interconversion of the cis to the trans form of only 14 kJ mol^{-1} and the inherent ultrafast inversion rate constant ($k = 2.5$–2.6×10^{13} s^{-1}), the initial concentration of the cis versus trans population is unity. Both complexes show a C—H bond cleavage to form cyanoacetylene, HCCCN, and a hydrogen atom. RRKM calculations show that 15% of the collision complexes depict a [1, 2] H atom migration via a barrier of 177 kJ mol^{-1} forming the doublet H_2CCCN radical. This intermediate is stabilized by 288 kJ mol^{-1} with respect to the reactants, represents the global minimum of the C_3H_2N PES, and decays via H atom emission to the HCCCN isomer. The experimentally derived reaction exothermicity to HCCCN of 80–100 kJ mol^{-1} is in agreement with the theoretical data of 94 kJ mol^{-1}. A detailed investigation shows that no isocyanoacetylene isomer, HCCNC, is formed, as its formation is endothermic by 13 kJ mol^{-1}. Likewise, no H atom abstraction by CN to form HCN plus C_2H or HNC plus C_2H is energetically feasible in cold molecular clouds, as both reactions are endothermic by 23 and 83 kJ mol^{-1} and must pass barriers of 41 and 96 kJ mol^{-1}. We like to point out, however, that in the outer atmosphere of old dying carbon stars such as IRC+10216 the enhanced kinetic energy of the reactants in the tail of the Maxwell-Boltzmann distribution might be sufficient to overcome the barriers to form the HCCNC isomer or HNC/HCN in these high-temperature environments.

4.2. Reaction (2): $CN + C_2H_4$

Analogous to the previous reaction, the CN radical attacks the π molecular orbital of the C_2H_4 molecule; see Figure 2. This pathway is barrierless as well and forms a C_s symmetric 1-cyanoethyl-2 radical, CH_2CH_2CN, which is
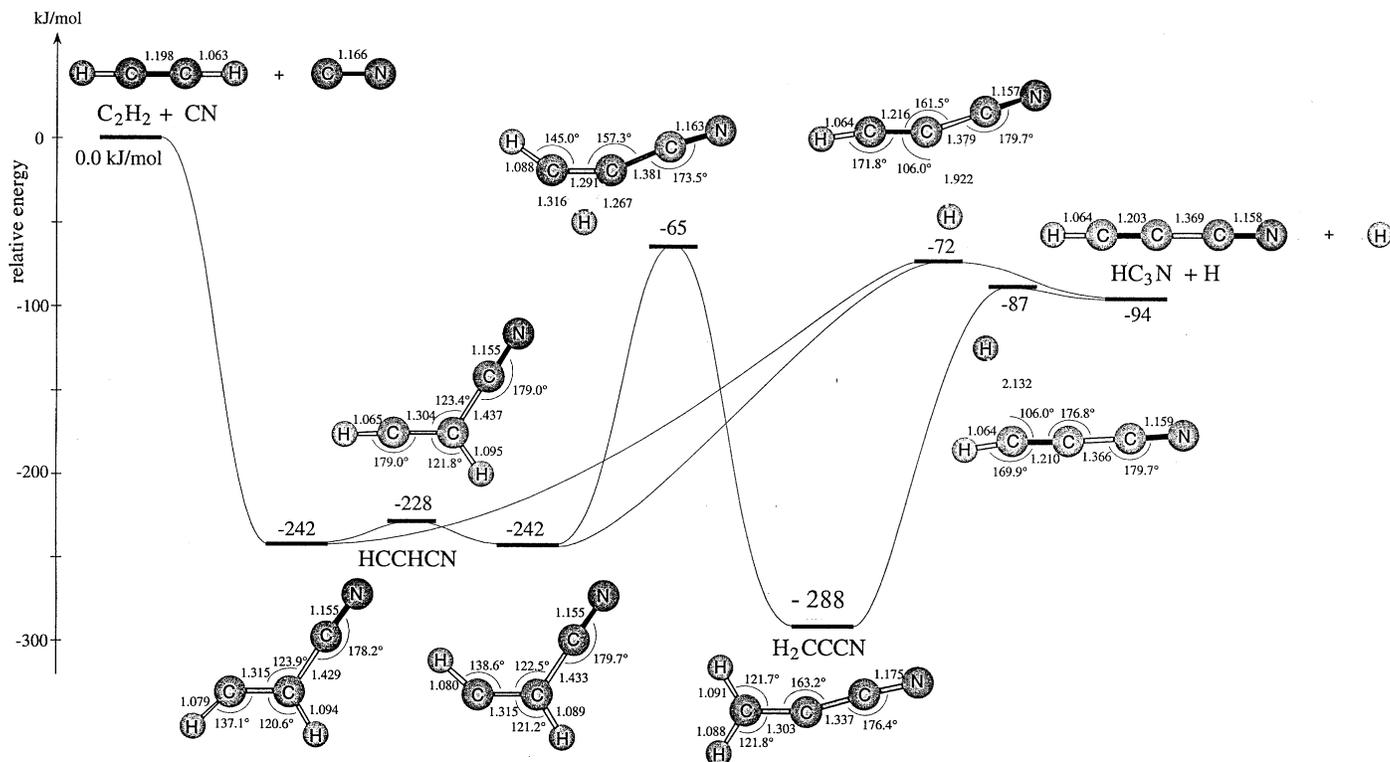
FIG. 1.—Schematic representation of the C_3H_2N potential energy surface relevant in the $CN + C_2H_2$ reaction. Adapted from Huang et al. (2000). Important bond distances are given in angstrom units and bond angles in degrees.

bound by 232 kJ mol^{-1} (Balucani et al. 2000a). About 40% of all initial collision complexes show C—H bond rupture via a tight exit transition state located 16 kJ mol^{-1} above the products to form vinylcyanide, C_2H_3CN, and atomic hydrogen. The remaining 60% undergo a [1, 2] H atom shift via a 136 kJ mol^{-1} barrier to yield CH_3CHCN prior to an H atom release and formation of vinylcyanide. Based on our center-of-mass angular distributions, the lifetime of the fragmenting complexes must be longer than its rotational period to account for the symmetric $T(\theta)$ distribution. The
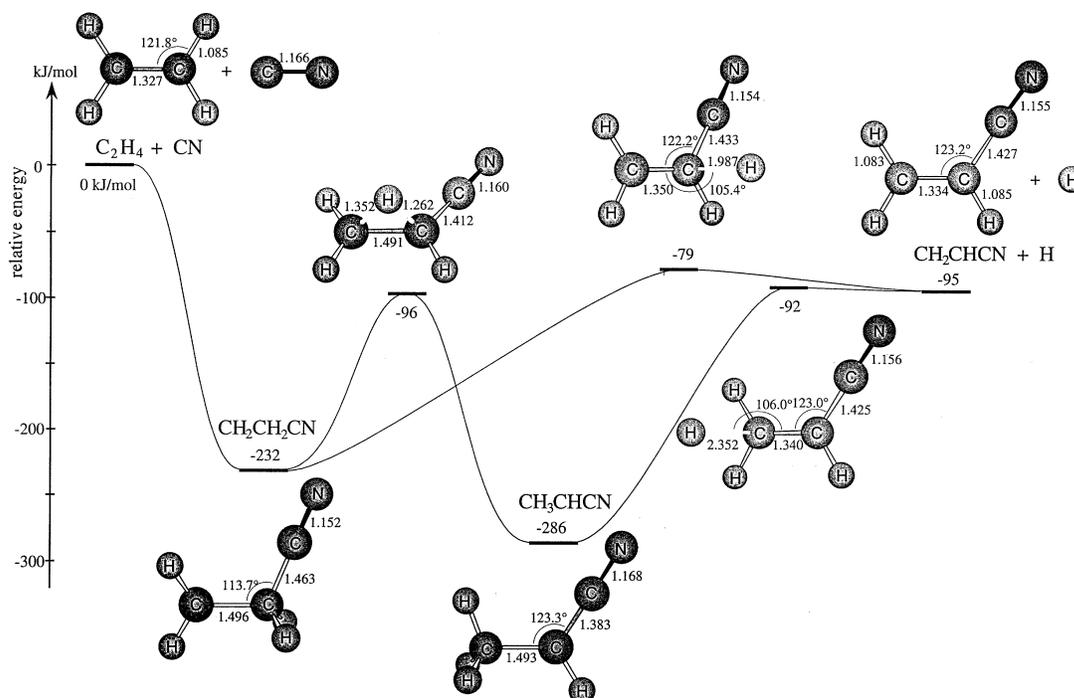
FIG. 2.—Schematic representation of the C_3H_4N potential energy surface relevant in the $CN + C_2H_4$ reaction. Adapted from Balucani et al. (2000a). Important bond distances are given in angstrom units and bond angles in degrees.

reaction energy to the C_2H_3CN of 90–100 kJ mol^{-1} as derived from our center-of-mass translational energy distributions agrees with tabulated literature data. The vinylisocyanide isomer is less stable by 99 kJ mol^{-1}; it was not found to be formed under our experimental conditions. In strong analogy to the HCCNC molecule, formation of vinylisocyanide, C_2H_3NC, is endothermic by 4 kJ mol^{-1} and cannot occur in cold interstellar clouds. An H atom abstraction by CN to form HNC is exothermic by 22 kJ mol^{-1}, but the barrier of 12 kJ mol^{-1} is too high for interstellar physical conditions. Although the H atom abstraction to form HCN and C_2H_3 is exothermic by 82 kJ mol^{-1} and has no barrier, this channel could not be detected in our experiments due to the high detector background at $m/e = 27$. Preliminary variational RRKM calculations show that HCN formation is less that 10% compared to formation of vinylcyanide (J. Peters 2000, private communication). Therefore, we conclude that the CN radical attacks preferentially the π molecular orbital compared to the σ bond.

4.3. Reaction (3): CN + CH₃CCH

The crossed molecular beam studies of the CN radical reacting with methylacetylene and the solid identification of the C_4H_3N product(s) demonstrated clearly the existence of a CN versus H atom exchange (Huang et al. 1999b; Balucani et al. 2000b). Our isotopic investigation of the reaction of CN with CD_3CCH combined with the explicit detection

of D and H atom loss ($m/e = 68$ and $m/e = 67$) further suggests the existence of two distinct reaction products. Based on these findings and the indirect (complex-forming) reactive scattering dynamics as extracted from the center-of-mass angular distributions, the reaction of the $CN(X\,^2\Sigma^+)$ radical with methylacetylene proceeds via a C_3H_4CN complex (Fig. 3). Here $CN(X\,^2\Sigma^+)$ attacks the π electron density at the C1 carbon of the methylacetylene to form cis/trans C_3H_4CN complex without entrance barriers. Both intermediates are stabilized by 253 and 252 kJ mol^{-1} with respect to the reactants; a cis/trans isomerization barrier of about 17 kJ mol^{-1} is located well below the total available energy of the reaction, and structures are expected to be populated equally. We would like to emphasize that the addition to the C1 position at expense of the C2 atom is based on the enhanced spin density of the C1 and a simultaneous steric hindrance of the methyl group to attack the C2 position. After the CN addition, the C_3H_4CN complexes can fragment via H atom emission through two distinct channels to $CH_3CCCN + H$ (channel 1) and $H_2CCCHCN + H$ (channel 2). Both isomers are formed in equal amounts. The exit transition state of the first pathway is found to be slightly higher than the transition state of the second channel, lying about 19 and 7–8 kJ mol^{-1} above the products. The shape of our velocity flux contour map already suggested the existence of an exit barrier. Further, the reaction exothermicities are calculated to be 106 and 94 kJ mol^{-1} for the first and second channel, respectively. As
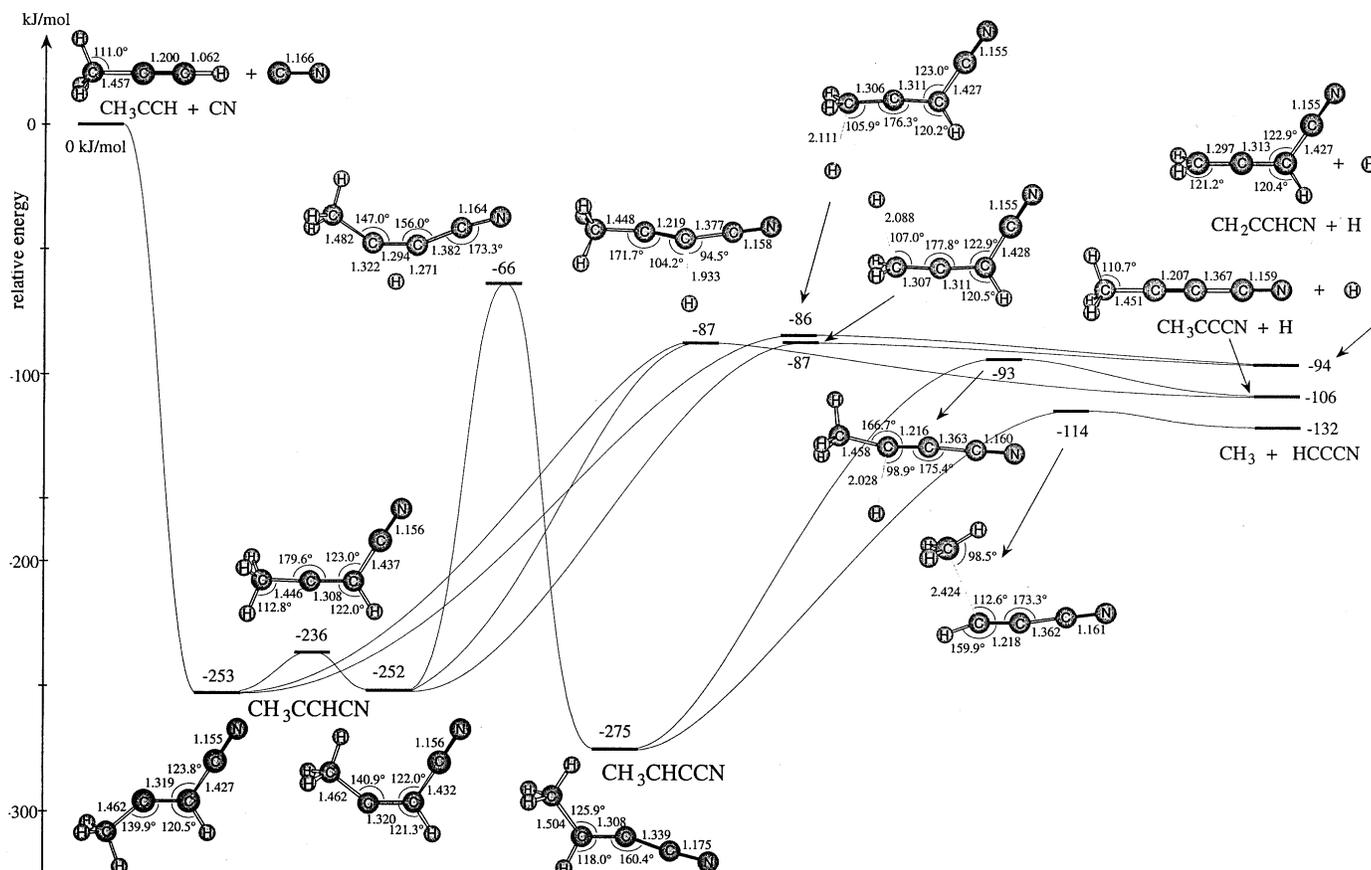
FIG. 3.—Schematic representation of the C_4H_4N potential energy surface relevant in the CN + CH_3CCH reaction. Adapted from Huang et al. (1999b). Important bond distances are given in angstrom units and bond angles in degrees.

in all reactions discussed above, formation of isonitriles is irrelevant in cold interstellar clouds since the reactions to form CH_3CCNC and $H_2CCCH(NC)$ are endothermic by 8 and 6 kJ mol^{-1}, respectively.

4.4. *Reaction* (4): $CN + H_2CCCH_2$

The CN radical interacts with the π electron density without entrance barrier to give two possible $H_2CCCH_2(CN)$ intermediates which are stabilized by 219/216 kJ mol^{-1} with respect to the reactants; see Figure 4 (Balucani et al. 2000b). An addition of the CN radical to the central carbon atom of the allene molecule does not take place: if the CN radical forms the new carbon-carbon single bond to the central carbon atom, the intermediate would undergo ring closure followed by hydrogen elimination and formation of a cyanopropene molecule. This pathway, however, is endothermic by about 11 kJ mol^{-1}, and hence energetically not accessible in our crossed beam experiments and in the interstellar medium. The initially formed $H_2CCCH_2(CN)$ complex loses a hydrogen atom either at the CH_2 or CH_2CN group. The transition state energies are 41 and 68 kJ mol^{-1} below the reactants, respectively. So both H loss channels from CH_2 side and CH_2CN side are feasible. The reaction to the cyanoallene isomer, $H_2CCCHCN$, together with atomic hydrogen is exothermic by 86 kJ mol^{-1}. These theoretical data are in strong agreement with our experimental range of the reaction exothermicity of 85–90 kJ mol^{-1}, and we conclude that the cyanoallene isomer is formed in our experiments as well as in cold molecular clouds. Our RRKM calculations show that the energetically less stable $HCCCH_2(CN)$ isomer is formed to about 20%. The formation of the corresponding isocyanide isomers $H_2CCCHNC$ and $HCCCH_2(NC)$ are

endothermic by 14 and 40 kJ mol^{-1} and hence cannot take place in dark molecular clouds.

4.5. *Reaction* (5): $CN + CH_3CCCH_3$

The dimethylacetylene molecule shows analogous chemical reaction dynamics toward reaction of the CN radical as acetylene and methylacetylene (Balucani et al. 1999a). With the radical center located at the carbon atom, the cyano radical, $CN(X\ ^2\Sigma^+)$, attacks the π-orbital of the dimethylacetylene molecule barrierless to form cis and trans 1-cyano-2-buten-3-yl, $CNCH_3CCCH_3$, collision complexes which are stabilized by 236 and 241 kJ mol^{-1} with respect to the reactants; see Figure 5. The fast RRKM rate constant of $k = 2.86 \times 10^{13}$ s^{-1} of the cis-trans isomerization of both 1-cyano-2-buten-3-yl radicals strongly suggests that the chemical reaction dynamics are invariant on the initial concentration of the cis versus trans intermediates. The transition states of the H atom loss channel are located only 6–7 kJ mol^{-1} above the products. This finding is verified by the center-of-mass translational energy distributions $P(E_T)$ showing a flux distribution maximum of 15–25 kJ mol^{-1}. We would like to point out that we were unable to detect the methyl group elimination channel due to the low signal-to-noise ratio of the reactive scattering signal and the unfavorable kinematic relationship of the products. However, the calculated branching ratios show that this channel should be dominant, yielding a branching ratio of the CH_3 versus H loss of about 360 at our collision energy. If we go to 0 kJ mol^{-1} collision energy, i.e., approaching the very cold regions of the interstellar medium, this ratio increases to about 650. For this system, the reaction to the isonitrile isomer CH_3CCNC is exothermic by 36 kJ mol^{-1}, but formation of $CH_2CCCH_3(NC)$ endothermic by 14 kJ mol^{-1}.
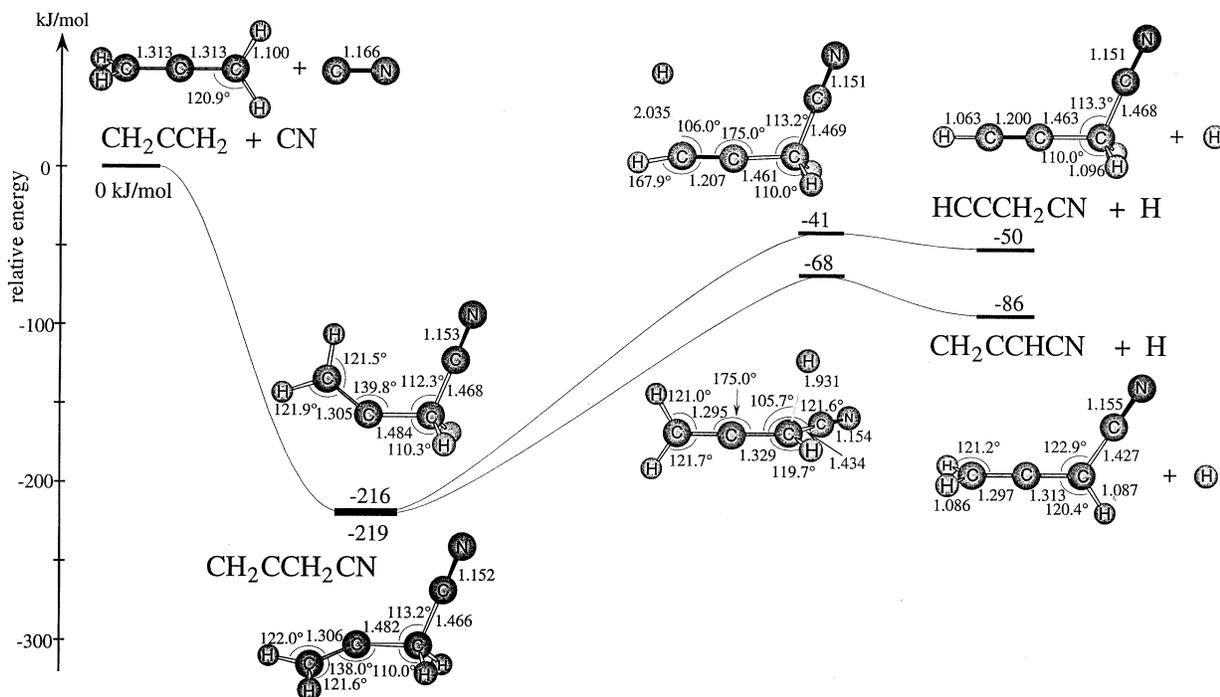
FIG. 4.—Schematic representation of the C_4H_4N potential energy surface relevant in the CN + H_2CCCH_2 reaction. Adapted from Balucani et al. (2000b). Important bond distances are given in angstrom units and bond angles in degrees.
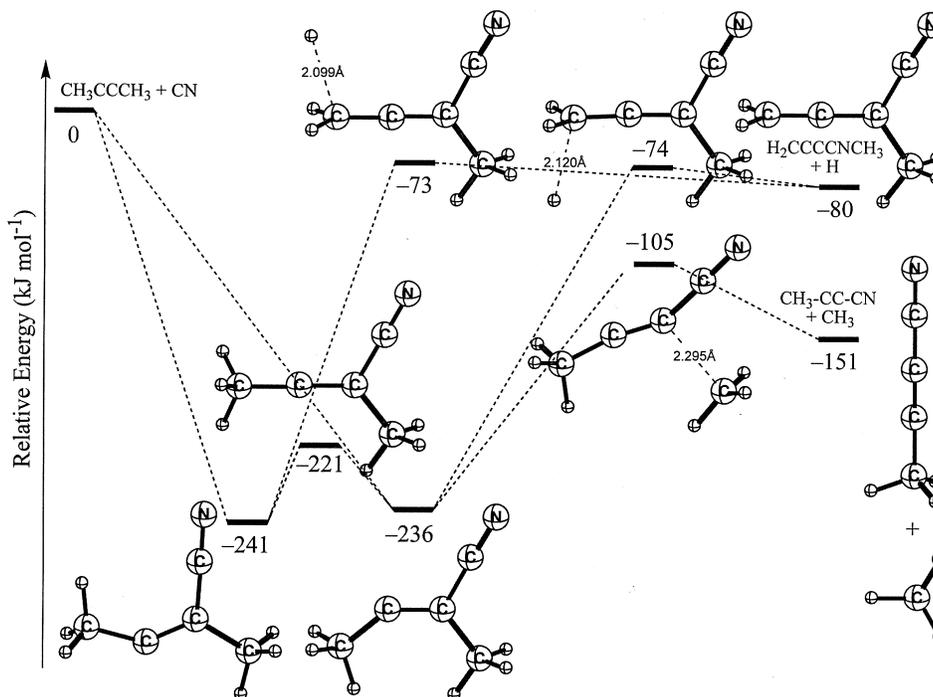
Fig. 5.—Schematic representation of the C_5H_6N potential energy surface relevant in the CN + CH_3CCCH_3 reaction. Adapted from Balucani et al. (1999b). Important bond distances are given in angstrom units.

4.6. Reaction (6): CN + C_6H_6

Similar to all other systems studied in our lab, the reaction of the cyano radical with benzene, C_6H_6, is initially dominated by long-range dispersion forces (Balucani et al. 1999a). The reaction is barrierless and is governed by an initial attack of the CN radical to form a C_s symmetric C_6H_6CN collision complex; see Figure 6. The collision complex is bound by 165 kJ mol^{-1} with respect to the reactants and undergoes C—H bond rupture through a tight exit transition state located 33 kJ mol^{-1} above the products to form a hydrogen atom and the cyanobenzene isomer, C_6H_5CN. Detailed energy and angular momentum conservation consideration demonstrate that the 90 kJ mol^{-1} less stable C_6H_5NC isomer is not formed in the reaction. Although the reaction is exothermic by about 5 kJ
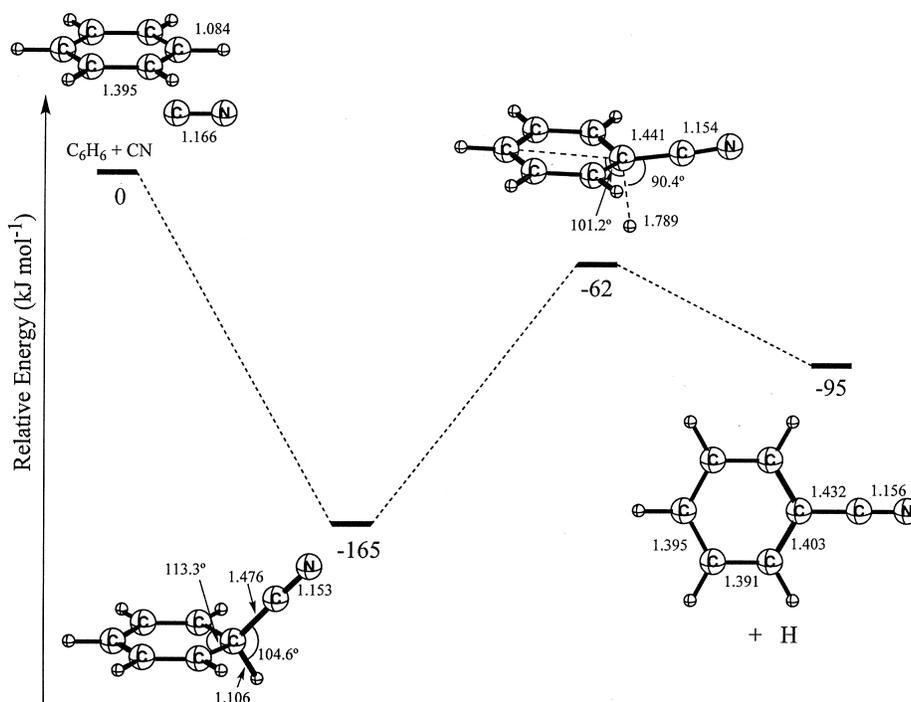
Fig. 6.—Schematic representation of the C_7H_6N potential energy surface relevant in the CN + C_6H_6 reaction. Adapted from Balucani et al. (1999a). Important bond distances are given in angstrom units and bond angles in degrees.

mol^{-1}, the exit barrier is located 38 kJ mol^{-1} above the energy of the separated reactants and hence cannot be passed in cold molecular clouds.

5. ASTROPHYSICAL IMPLICATIONS

Our crossed molecular beam experiments of ground state cyano radicals with unsaturated hydrocarbons acetylene, ethylene, methylacetylene, allene, dimethylacetylene, and benzene are dominated by the CN versus H atom exchange pathway to form unsaturated nitriles HCCCN ($X^1\Sigma^+$), vinylcyanide, C_2H_3CN (X^1A'), 1-methylcyanoacetylene, CH_3CCCN (X^1A_1), cyanoallene, $H_2CCCH(CN)$ (X^1A'), 3-methylcyanoacetylene, $HCCCH_2CN(X^1A')$, 1,1-cyanomethylallene, $CH_2CC(CN)(CH_3)(X^1A')$ and cyanobenzene, C_6H_5CN (X^1A_1) under single collision conditions. All involved potential energy surfaces and chemical dynamics show common features. First, all reactions are barrierless, dominated by long-range attractive forces in the entrance channel, and governed by indirect scattering dynamics via formation of a collision complex. 30%–40% of the total available energy channels into the translational degrees of freedom of the nitrile and atomic hydrogen. Further, $CN(X^2\Sigma^+)$ attacks the π electron density, with the radical center located at the carbon atom. This generally observed pathway yields intermediates stabilized by 232–288 kJ mol^{-1} with respect to the separated reactants. Due to aromaticity of the benzene reactant, the C_6H_6CN complex resides in a shallower potential energy well of only 165 kJ mol^{-1}. In both the C_2H_2 and C_2H_4 reaction, a [1, 2] H shift in the initial collision complex goes via a 137–177 kJ mol^{-1} barrier to a complex stabilized by 288–286 kJ mol^{-1}. All complexes can decompose in exothermic reactions (73–106 kJ mol^{-1}) via H atom elimination through transition states located 3–32 kJ mol^{-1} above the products. Since these reactions show no entrance barriers, have exit barriers well below the energy of the reactants, and are exothermic, the explicit identification of this CN versus H atom exchange pathway under single collision conditions identifies this reaction class as an important route to synthesize unsaturated nitriles in cold interstellar clouds holding temperatures as low as 10 K as well as outflow of AGB stars. Therefore, although the collision energies in the crossed beam experiments are above those in cold clouds, our combination with electronic structure calculations shows once and for all that single collision neutral-neutral reactions are a strong alternative to hitherto postulated reaction chains of ion-molecule reactions to form complex nitrogen-bearing molecules in the ISM. For example, Seki et al. (1996) determined in bulk experiments at 293 K the reaction rate constant of CN radicals with diacetylene, HCCCCH, to 4.2×10^{-10} cm^3 s^{-1}; since this reaction has no entrance barrier (Fukuzawa, Osamura, & Schaefer 1998), the cyano versus H atom exchange pathway postulates the formation of interstellar cyanodiacetylene via reaction (13) as confirmed in ab initio calculations:

$$HCCCCH + CN \rightarrow HCCCCCN + H . \qquad (13)$$

Most importantly, our experiments unravel the hitherto unexplained abundances of HC_3N isomers. Here the isomers cyanoacetylene, HCCCN, isocyanoacetylene, HCCNC, and HNCCC have been identified in the ISM (Fukuzawa & Osamura 1997). Among them the thermodynamically most stable HCCCN isomer has the largest abundance; both metastable HCCNC and

HNCCC molecules were identified in the cold molecular cloud TMC-1 and the outflow of the carbon star IRC+ 10126. A recent line survey toward the Taurus molecular cloud TMC-1 yielded observed abundance ratios of [HCCCN]:[HCCNC]:[HNCCC] = 1000:8:1 (Ohishi & Kaifu 1998). Ion-molecule reaction networks and high-level electronic structure calculations (Osamura et al. 1999) suggest a recombination of interstellar $HCCCNH^+$ ions with an electron from the cosmic radiation followed by an isomerization from HCCCNH to HCCNCH and H atom emission. This reaction sequence yields ratios of [HCCCN]:[HCCNC]:[HNCCC] = 240:8:1. Although this mechanism can explain satisfactorily the abundances of both metastable isomers quantitatively, the majority of the HCCCN molecules cannot be produced via ion-molecule reactions. As established in our crossed beam experiments, binary, reactive collisions between neutral cyano radicals and neutral acetylene molecules can represent the missing interstellar HCCCN source.

We wish to point out that the formation of isonitrile isomers was not observed in our experiments. All reactions to HCCNC, C_2H_3NC, CH_3CCNC, $H_2CCCH(NC)$, and $H_2CCCCH_3(NC)$ are endothermic by 13 kJ mol^{-1}, 4 kJ mol^{-1}, 8 kJ mol^{-1}, and 6 kJ mol^{-1}; see Table 1 and Figure 7. Although the formation of C_6H_5NC is exothermic by about 5 kJ mol^{-1}, the exit barrier of the final carbon-hydrogen bond rupture is 38 kJ mol^{-1} above the energy of the separated reactants. The PES of reaction (11) to form $CH_3CCNC + CH_3$ shows similar features: despite an exothermic reaction of -36 kJ mol^{-1}, the exit barrier is located 9 kJ mol^{-1} above the reactants. Therefore, in cold molecular clouds, the average translational energy of the reactants of 0.08 kJ mol^{-1} can neither compensate for the reaction endoergicity nor promote overcoming the exit barrier. However, in circumstellar envelopes of carbon stars close to the photosphere, the enhanced translational energy of the reactants can overcome the endoergicity, and isonitriles might be formed in these high-temperature environments.

The versatile concept of a CN versus H exchange as established in our study makes it even feasible to predict the formation zones of nitriles in the ISM once the corresponding unsaturated hydrocarbons are identified in the interstellar medium. Here HCCCN, C_2H_3CN, and CH_3CCCN have been already observed in extraterrestrial environments (see § 1). Since methylacetylene, CH_3CCH, is the common precursor to $H_2CCCH(CN)$ and CH_3CCCN (reaction [9]) and CH_3CCCN has been already assigned in TMC-1 (Broten et al. 1984; Ohishi & Kaifu 1998), $H_2CCCH(CN)$ is strongly expected to be present in TMC-1 as well. A search for this isomer is currently underway (Chin et al. 2000). Our investigation of this reaction shows that the ratio of 1-methylcyanoacetylene versus cyanoallene should be unity (Huang et al. 1999b). Any observed deviation from this ratio, for example an enhanced fractional abundance of cyanoallene could hint to a second formation mechanism, i.e., the reaction of allene with cyano radicals. A second isomer, $HCCCH_2CN$, which can only be formed via reaction of CN and allene, can map the allene abundances as well. Therefore, an astronomical mapping of these isomers will help to unravel the distribution of the allene molecule which itself shows no pure rotational spectrum. Our findings should encourage further an actual search for the hitherto unobserved cyanobenzene molecule, C_6H_5CN.

TABLE 1

REACTION ENERGIES OF CN RADICALS AND UNSATURATED HYDROCARBONS TO
ISONITRILE ISOMERS

Reaction	Reaction Energy (kJ mol^{-1})
$C_2H_2(X\,^1\Sigma_g^+) + CN(X\,^2\Sigma^+) \rightarrow HCCNC(X\,^1\Sigma^+) + H(^2S_{1/2})$	13
$C_2H_4(X\,^1A_g) + CN(X\,^2\Sigma^+) \rightarrow C_2H_3NC(X\,^1A') + H(^2S_{1/2})$	4
$CH_3CCH(X\,^1A_1) + CN(X\,^2\Sigma^+) \rightarrow CH_3CCNC(X\,^1A_1) + H(^2S_{1/2})$	8
$\rightarrow HCCNC(X\,^1\Sigma^+)CH_3$	25
$\rightarrow H_2CCCHNC(X\,^1A') + H(^2S_{1/2})$	6
$H_2CCCH_2(X\,^1A_1) + CN(X\,^2\Sigma^+) \rightarrow H_2CCCHNC(X\,^1A') + H(^2S_{1/2})$	14
$\rightarrow HCCCH_2NC(X\,^1A') + H(^2S_{1/2})$	40
$CH_3CCCH_3(X\,^1A_1') + CN(X\,^2\Sigma^+) \rightarrow CNCH_3CCCH_2(X\,^1A') + H(^2S_{1/2})$	14
$\rightarrow CH_3CCN(X\,^1A_1) + CH_3$	-36^a
$C_6H_6(X\,^1A_{1g}) + CN(X\,^2\Sigma^+) \rightarrow C_6H_5NC(X\,^1A_1) + H(^2S_{1/2})$	-5^b

[a] Exit barrier: 9 kJ mol^{-1}.
[b] Exit barrier: 30 kJ mol^{-1}.

FIG. 7.—Structures of isonitrile isomers. Important bond distances are given in angstrom units and bond angles in degrees.

TABLE 2

Reaction Energies of CN Radicals and Unsaturated Hydrocarbons to HCN and HNC Formation

Reaction	Reaction Energy (kJ mol^{-1})
$C_2H_2(X\,^1\Sigma_g^+) + CN(X\,^2\Sigma^+) \rightarrow HCC + HCN$	23
$\rightarrow HCC + HNC$	83
$C_2H_4(X\,^1A_g) + CN(X\,^2\Sigma^+) \rightarrow C_2H_3 + HCN$	-82
$\rightarrow C_2H_3 + HNC$	-22
$CH_3CCH(X\,^1A_1) + CN(X\,^2\Sigma^+) \rightarrow CH_3CC + HCN$	22
$\rightarrow H_2CCCH + HCN$	-170
$\rightarrow CH_3CC + HNC$	82
$\rightarrow H_2CCCH + HNC$	-110
$H_2CCCH_2(X\,^1A_1) + CN(X\,^2\Sigma^+) \rightarrow H_2CCCH + HCN$	-162
$\rightarrow H_2CCCH + HNC$	-102
$CH_3CCCH_3(X\,^1A_1') + CN(X\,^2\Sigma^+) \rightarrow CH_3CCCH_2 + HCN$	-176
$\rightarrow CH_3CCCH_2 + HNC$	-118
$C_6H_6(X\,^1A_{1g}) + CN(X\,^2\Sigma^+) \rightarrow C_6H_5 + HCN$	-74
$\rightarrow C_6H_5 + HCN$	-16

Similar to allene, benzene has no permanent dipole moment and cannot be mapped in the microwave region of the electromagnetic spectrum. However, the benzene unit is the key "brick" in the structure of polycyclic aromatic like species in the ISM. Therefore, cyanobenzene can act as tracer molecule to search for unobserved interstellar benzene. Preliminary models including reaction (12) into chemical reaction networks of IRC+10216 depict fractional abundances of about 10^{-9}–10^{-10}. An observational attempt is currently in progress.

Further investigation of this reaction class will focus on the role of the H atom abstraction reaction to HCN and/or HNC. As outlined above, the H atom abstraction from acetylene is endothermic and cannot proceed in cold molecular clouds; see Table 2 and Figure 8. A CN radical approaching to the hydrogen atom of ethylene from the N side has a transition state for the hydrogen abstraction forming HNC and C_2H_3 located 12 kJ mol^{-1} above the

energy of the reactants; see Figure 9; this barrier inhibits the reaction in molecular clouds. When the CN radical reacts with ethylene, methylacetylene, allene, and dimethylacetylene, all potential energy surfaces are attractive on the B3LYP level of theory. The formation of HCN and the hydrocarbon radicals is found to be exothermic by 82, 170, 162, and 176 kJ mol^{-1} without energy barriers; see Table 2 and Figures 9, 10, 11, 12, and 13. We like to point out that in the case of benzene, the barrier involved is lower than the energy of the reactants. Therefore, these processes can form HCN even in coldest molecular clouds holding temperatures as low as 10 K. If the cyano radical approaches the H atom of allene, methylacetylene, dimethylacetylene, or allene with its N side, our calculations show the formation of loosely bound van der Waals complexes which are about 10 kJ mol^{-1} more stable than the separated reactants. Due to the smaller polarizibility of ethylene, the intermolecular forces are found to be too weak to form this van
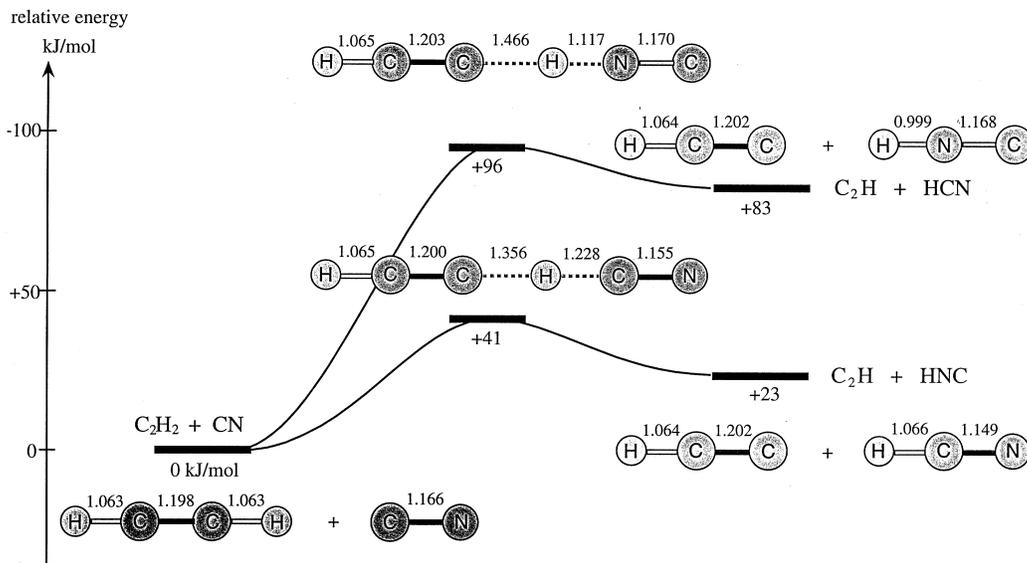
Fig. 8.—Schematic representation of the H abstraction channel in the reactions of CN($X\,^2\Sigma^+$, $v = 0$) radicals with acetylene, $C_2H_2(X\,^1\Sigma_g^+)$. Important bond distances are given in angstrom units and bond angles in degrees.
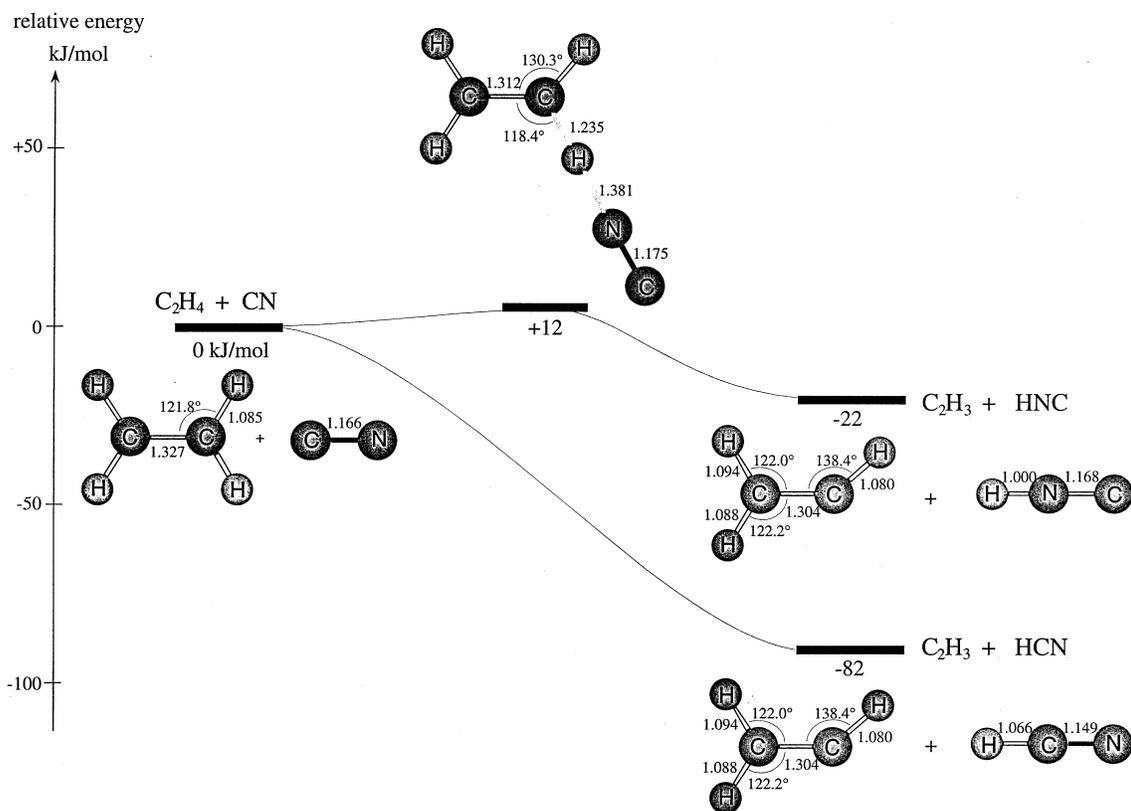
FIG. 9.—Schematic representation of the H abstraction channel in the reactions of CN($X\,^2\Sigma^+$, $v = 0$) radicals with ethylene, $C_2H_4(X\,^1A_g)$. Important bond distances are given in angstrom units and bond angles in degrees.
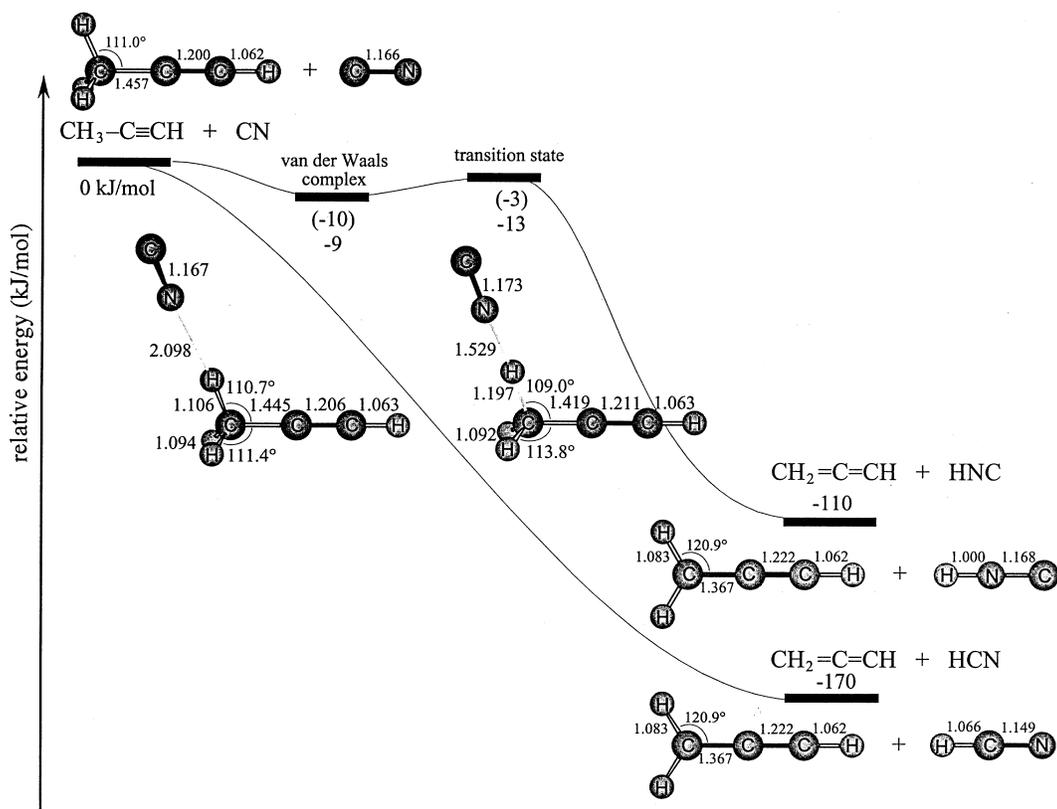
FIG. 10.—Schematic representation of the H abstraction channel in the reactions of CN($X\,^2\Sigma^+$, $v = 0$) radicals with methylacetylene, CH_3CCH ($X\,^1A_1$). Important bond distances are given in angstrom units and bond angles in degrees.
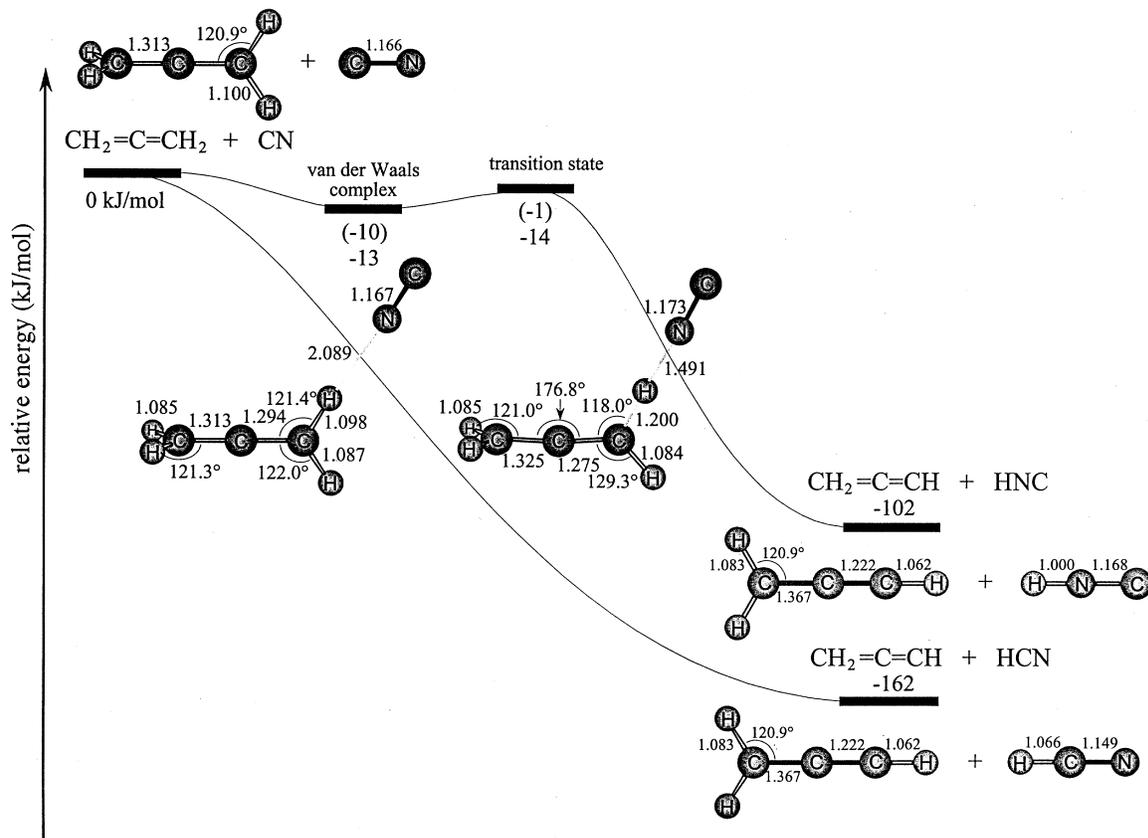
Fig. 11.—Schematic representation of the H abstraction channel in the reactions of CN($X\,^2\Sigma^+$, $v = 0$) radicals with allene, $H_2CCCH_2(X\,^1A_1)$. Important bond distances are given in angstrom units and bond angles in degrees.
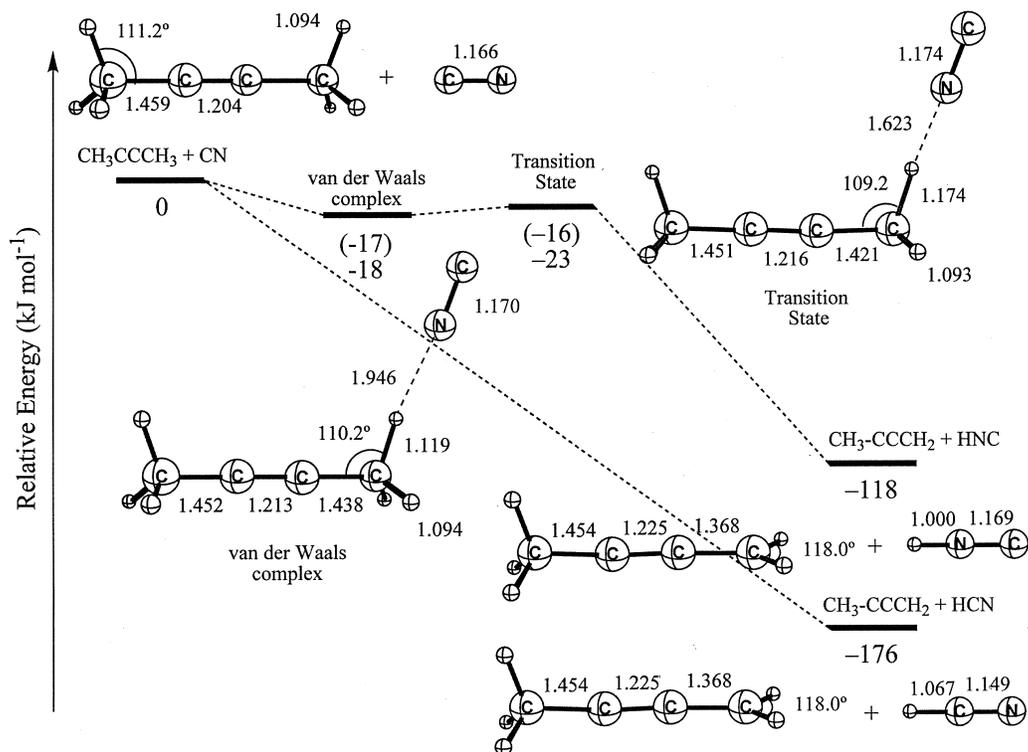
Fig. 12.—Schematic representation of the H abstraction channel in the reactions of CN($X\,^2\Sigma^+$, $v = 0$) radicals with dimethylacetylene, $CH_3CCCH_3(X\,^1A_1')$. Important bond distances are given in angstrom units and bond angles in degrees.
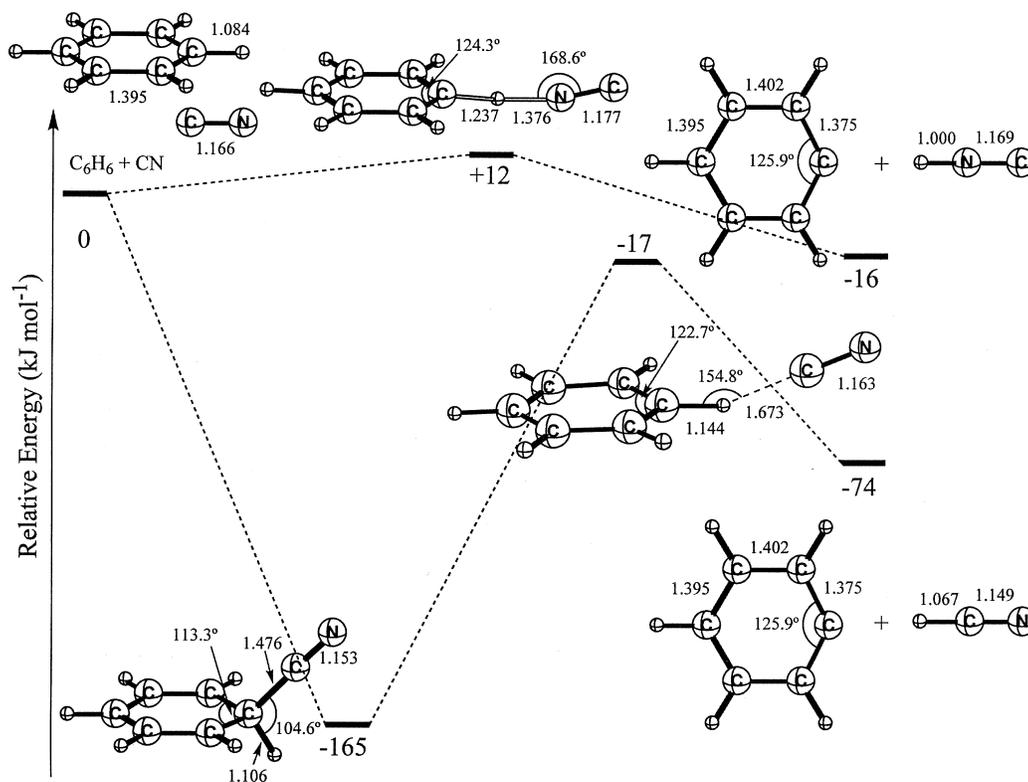
FIG. 13.—Schematic representation of the H abstraction channel in the reactions of $CN(X\,^2\Sigma^+, v = 0)$ radicals with benzene, C_6H_6 ($X\,^1A_{1g}$). Important bond distances are given in angstrom units and bond angles in degrees.

der Waals complex. In all cases, the barrier from these complexes to HNC plus the hydrocarbon radical formation is slightly below the reactants. Therefore, HNC can be formed in dense molecular clouds. Note that the classical barriers (i.e., without ZPVE correction) for HNC formation with respect to the van der Waals complexes are given for C_3H_4, CH_3CCCH_3, and C_6H_6. As the van der Waals complexes correspond to very shallow energy minima on the potential energy surfaces, the ZPVE are overestimated for these species. This results in negative barriers if the ZPVE correction is applied to the absolute energies. These effects have to be investigated further. In addition, absolute rate constants and branching ratios between the nitrile, HNC, and HCN formation are desirable. These task will be completed in the near future (J. Peters 2000, private communication).

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