Crossed beam reaction of the cyano radical, CN($X\,^2\Sigma^+$), with methylacetylene, CH₃CCH ($X\,^1A_1$): Observation of cyanopropyne, CH₃CCCN ($X\,^1A_1$), and cyanoallene, H₂CCCHCN ($X\,^1A'$)

L. C. L. Huang, N. Balucani,[a] Y. T. Lee, and R. I. Kaiser[b]
Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Rd.,
107 Taipei, Taiwan, Republic of China

Y. Osamura
Department of Chemistry, Rikkyo University, 3-34-1-Nishi-ikebukuro, Toshima-ku, Tokyo, 171, Japan

The chemical dynamics to form cyanopropyne, CH₃CCCN ($X\,^1A_1$), and cyanoallene, H₂CCCHCN ($X\,^1A'$), via the neutral–neutral reaction of the cyano radical, CN ($X\,^2\Sigma^+$), with methylacetylene, CH₃CCH ($X\,^1A_1$), is investigated under single collision conditions in a crossed molecular beam experiment at a collision energy of 24.7 kJ mol⁻¹. The laboratory angular distribution and time-of-flight spectra of the C₄H₃N products are recorded at $m/e = 65$, 64, 63, and 62. The reaction of d_3-methylacetylene, CD₃CCH ($X\,^1A_1$), with CN radicals yields reactive scattering signal at $m/e = 68$ and $m/e = 67$ demonstrating that two distinct H(D) atom loss channels are open. Forward-convolution fitting of the laboratory data reveal that the reaction dynamics are indirect and governed by an initial attack of the CN radical to the π electron density of the β carbon atom of the methylacetylene molecule to form a long lived CH₃CCHCN collision complex. The latter decomposes via two channels, i.e., H atom loss from the CH₃ group to yield cyanoallene, and H atom loss from the acetylenic carbon atom to form cyanopropyne. The explicit identification of the CN vs H exchange channel and two distinct product isomers cyanoallene and cyanopropyne strongly suggests the title reaction as a potential route to form these isomers in dark molecular clouds, the outflow of dying carbon stars, hot molecular cores, as well as the atmosphere of hydrocarbon rich planets and satellites such as the Saturnian moon Titan. © *1999 American Institute of Physics.* [S0021-9606(99)01831-0]

I. INTRODUCTION

The chemical dynamics of CN($X\,^2\Sigma^+$) radical reactions with unsaturated hydrocarbons are of fundamental relevance to the atmospheric chemistry in Saturn's moon Titan.[1] Its atmospheric composition is dominated by N₂ and CH₄ together with minor components of C₂H₆, C₃H₈, C₂H₂, HCN, HC₃N, CH₃CCH, and C₂N₂.[2] Here, Titan's cyano chemistry is thought to be closely related to the prebiotic nitrogen chemistry on proto Earth[3] and very likely initiated by photolyses of HCN and C₂N₂ by the solar radiation field to generate reactive CN radicals in their $^2\Sigma^+$ electronic ground state. Pioneering kinetic studies of the CN($X\,^2\Sigma^+$) radical reactions with unsaturated hydrocarbons C₂H₂ and C₂H₄ at temperatures as low as 25 K demonstrated explicitly that these reactions proceed without entrance barrier. Further, rate constants k of these reactions are of the order of the gas kinetic values ($k = 10^{-9} - 10^{-10}$ cm³ s⁻¹),[4] clearly underlining that CN radicals could react with unsaturated hydrocarbons in Titan's atmosphere. Since however these studies measure rate coefficient via the decay kinetics of CN($X\,^2\Sigma^+$) without details on chemical dynamics and most

important the reaction products, further investigations of this reaction class are clearly necessary to unravel the photochemically driven chemical models of Titan's atmosphere.[5]

These systematic studies were initiated very recently in crossed molecular beams experiments under single collision conditions.[6] Huang *et al.* demonstrated that in the reaction of CN($X\,^2\Sigma^+$) with the simplest closed shell molecule containing a carbon carbon triple bond, acetylene C₂H₂, a CN vs H exchange forms cyanoacetylene, HCCCN, which has been clearly identified in Titan's atmosphere. Fueled by these findings, we present in this communication the first results from crossed molecular beams experiments on the reaction of CN($X\,^2\Sigma^+$) with methylacetylene combined with electronic structure calculations. The substitution of an acetylenic H atom by a CH₃ group might open a second reaction channel besides the loss of an acetylenic H atom, i.e., reactions (1a) and (1b), and hence could give the first experimental verification of the potential existence of two structural isomers in Titan's atmosphere,

$$\text{CH}_3\text{CCH} + \text{CN} \rightarrow \text{CH}_3\text{CCCN} + \text{H}, \tag{1a}$$

$$\rightarrow \text{H}_2\text{CCCHCN} + \text{H}. \tag{1b}$$

II. EXPERIMENT AND DATA ANALYSES

The experiments are performed with the 35″ crossed molecular beams machine.[7] Briefly, a pulsed supersonic cy-

---

[a] Visiting scientist. Permanent address: University of Perugia, Dipartimento di Chimica, 06123 Perugia, Italy.
[b] Author to whom correspondence should be addressed. Also at Department of Physics, Technical University Chemnitz-Zwickau, 09107 Chemnitz, Germany. Electronic mail: kaiser@po.iams.sinica.edu.tw
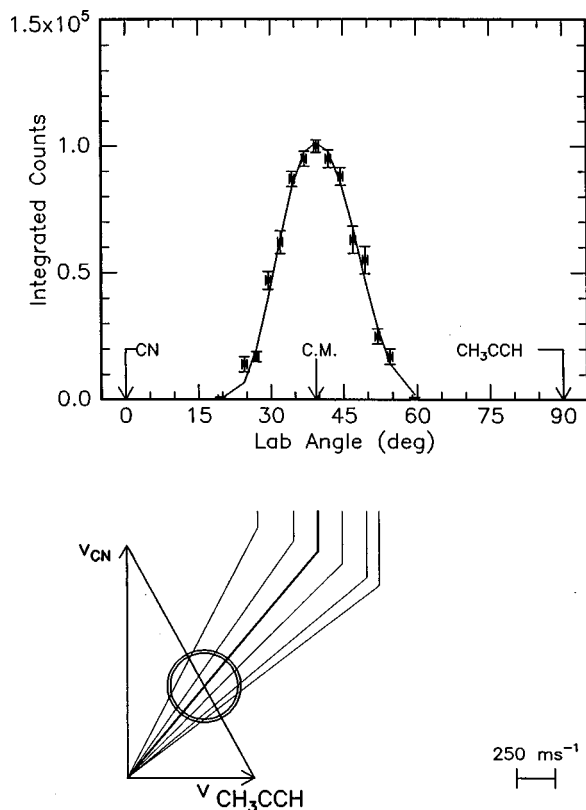
FIG. 1. (Lower) Newton diagram for the reaction $CN(X\,^2\Sigma^+)+CH_3CCH$ at a collision energy of 24.7 kJ mol^{-1}. The two Newton circle stand for the maximum center-of-mass recoil velocities of the CH_3CCCN and $H_2CCCHCN$ products. (Upper) Laboratory angular distribution of the C_4H_3N product. Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions.

ano $CN(X\,^2\Sigma^+)$ radical beam is generated in the primary source *in situ* via laser ablation of graphite at 266 nm and seeding the ablated carbon in neat nitrogen carrier gas released by a Proch–Trickl pulsed valve.[8] The Spectra Physics GCR 270-30 Nd-YAG laser operates at 30 Hz, and 30 mJ per pulse are focused onto a rotating graphite rod. A chopper wheel selects a 9 μs segment of the CN beam with a velocity $v_0=1560\pm30$ ms^{-1} and speed ratio $S=6.8\pm0.5$. A second, pulsed methylacetylene, CH_3CCH, beam ($v_0=840\pm10$ ms^{-1}, $S=8.9\pm0.5$, 505 Torr backing pressure) crosses the CN beam perpendicular in the interaction region at a collision energy of 24.7 ± 0.9 kJ mol^{-1} and center-of-mass (CM) angle of $39.6\pm0.8°$. A second set of experiments is performed by replacing the CH_3CCH beam by CD_3CCH at the same backing pressure. Reactively scattered species are monitored using a triply differentially pumped detector consisting of a Brink-type electron-impactionizer, quadrupole mass-filter, and a Daly ion detector[9] recording time-of-flight spectra (TOF) in 2.5° steps between 7.5° and 72.0° with respect to the CN beam. By integrating those TOF spectra at different laboratory angles and correcting for the CN beam intensity drift the laboratory angular distribution (LAB) is obtained. In the case of the CD_3CCH experiments, TOF spectra are only taken at center-of-mass angle. Information on the reaction dynamics is derived from the TOF spectra and the LAB distribution by using a forward-convolution
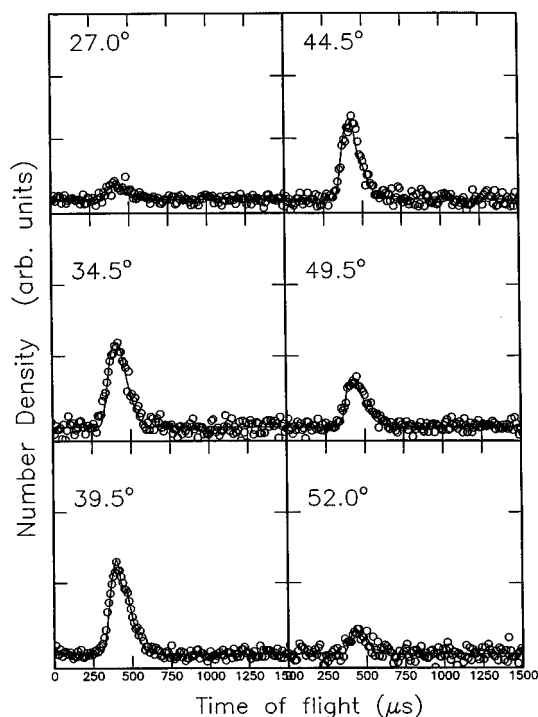

FIG. 2. Selected time of flight data for $m/e=62$ of distinct laboratory angles as indicated in Fig. 1. The circles indicate the experimental data, the solid lines the calculated fit.

technique.[10] This approach initially guesses the angular flux-distribution $T(\theta)$ and the translational energy distribution $P(E_T)$ in the center-of-mass (CM) coordinate system assuming mutual independence. The final outcome is the generation of a velocity flux contour map $I(\theta,u)\sim P(u)*T(\theta)$ in the center-of-mass frame showing the intensity as a function of angle θ and velocity u. This map serves as an image of the title reaction and contains the basic information of the scattering process.

III. RESULTS

We observe scattering signal at $m/e=65$ ($C_4NH_3^+$), 64 ($C_4NH_2^+$), 63 (C_4NH^+), and 62 (C_4N^+; cf. Fig. 1). Time-of-flight spectra (TOF) for several scattering angles are shown in Fig. 2; data accumulation range from 1 h to 6 h times at
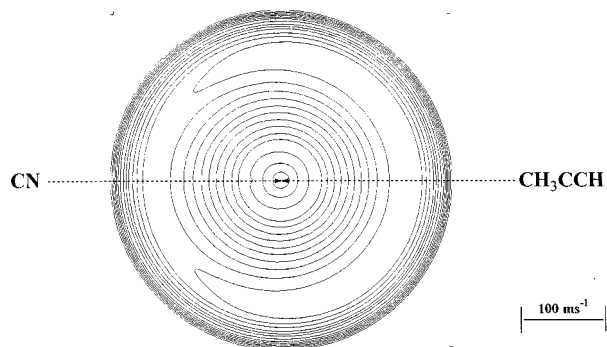

FIG. 3. Velocity flux contour map in the center-of-mass reference frame for the reaction $CN(X\,^2\Sigma^+)+CH_3CCH$ at a collision energy of 24.7 kJ mol^{-1}. The contour lines connect data points with an identical flux.
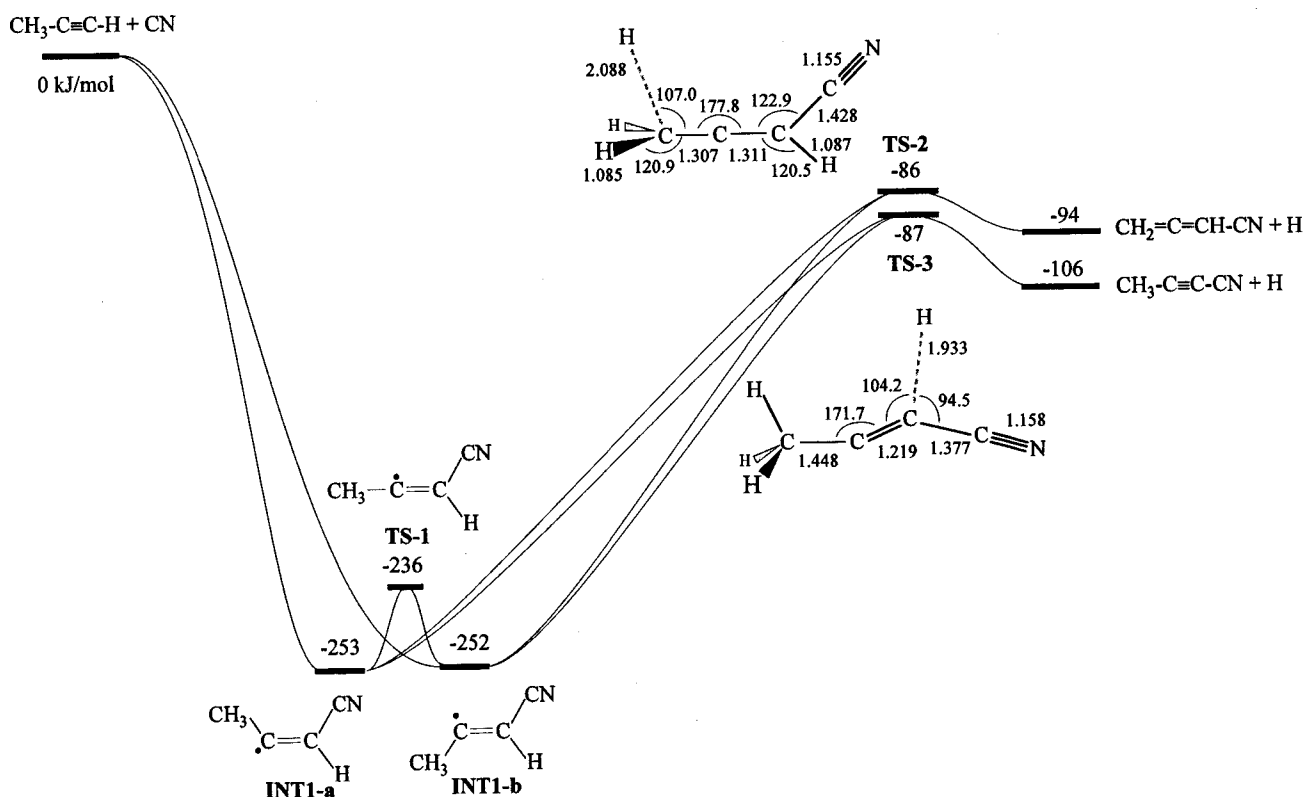
FIG. 4. Potential energy surface for the reaction of CN($X\,^2\Sigma^+$) with CH_3CCH. Calculations were performed employing B3LYP density functional theory using 6-311G(d,p) basis set.

each angle. TOF spectra recorded at all mass to charge ratios reveal identical patterns and could be fit with identical $T(\theta)$ and $P(E_T)$ distributions. This demonstrates that the CN vs H exchange to C_4NH_3 is the only reaction channel since $C_4NH_3^+$ fragments to $m/e = 64-62$ in the electron impact ionizer of the detector. Mass-to-charge ratios higher than 65 are not observed. The $CN+CD_3CCH$ reaction was studied to examine if the H(D) atom is released from the methyl or acetylenic group of the methylacetylene molecule. The resolution of the quadrupole mass spectrometer is chosen so that one mass unit could be separated and no mass leaking occurs. Our TOF spectra recorded at the center of mass angle shown reactive scattering signal at $m/e = 68$ ($C_4D_3N^+$; a H atom loss) as well as $m/e = 67$ ($C_4D_2NH^+$; D atom loss). Integration of TOFs at $m/e = 68$ and 67 and correcting for the distinct mass combination of both products yields a ratio of the D atom vs the H atom loss channel of about one.

The LAB distribution of the C_4H_3N product shows a peak at 35.5° very close to the center-of-mass angle of 35.6°. The distribution is broad and lies within about 40° in the scattering plane defined by both the CN and CH_3CCH beams. This strongly suggests that a significant amount of the total available energy is released into translation of the H and C_4H_3N. In addition, the $P(E_T)$ and hence velocity flux contour map should show a maximum very well away from zero. In our experiments, optimum fits of the LAB distribution and TOF spectra are reached with $P(E_T)$s extending to 90–130 kJ mol^{-1}. If we account for the relative collision energy of 24.7 kJ mol^{-1}, the title reaction to form H and C_4H_3N must be exothermic by 65–105 kJ mol^{-1}. In addition,

the velocity flux contour map shows a maximum corresponding to a translational energy release in the CM frame of about 20–32 kJ mol^{-1} suggesting a tight exit transition state from the decomposing complex to the products.

The velocity flux contour map of the heavy fragment shows further an almost isotropic, slightly forward-scattered distribution with respect to the CN beam, Fig. 3. The peak extends to a broad plateau between 30° and 90°. Both results show that the title reaction follows indirect scattering dynamics via a C_4H_4N complex whose lifetime is of the order of its rotational period. The weak $T(\theta)$ polarization results from a poor coupling between the initial $\mathbf{L}$ and final orbital angular momentum $\mathbf{L}'$ indicating that most of the total angular momentum channels into rotational excitation of the product.

IV. DISCUSSION

Our crossed molecular beams studies of the CN radical reacting with methylacetylene and the solid identification of the C_4H_3N product(s) demonstrated clearly with the existence of a CN vs H atom exchange. Our isotopic studies of the reaction of CN with CH_3CCD combined with the explicit detection of D and H atom loss ($m/e = 68$ and $m/e = 67$) suggest further the existence of two distinct reaction products. The chemical dynamics of the first channel proceed via emission of the acetylenic hydrogen atom and maintenance of the methyl group to form the cyanopropyne; channel two shows a carbon–deuterium bond rupture of the aliphatic C–D bond at the CD_3 group together with a D atom release yielding cyanoallene. Based on these findings and the indi-

rect (complex forming) reactive scattering dynamics as extracted from the velocity flux contour map, the reaction of the $CN(X\,^2\Sigma^+)$ radical with methylacetylene very likely proceeds via a C_3H_4CN complex. Here, $CN(X\,^2\Sigma^+)$ attacks the π electron density at the β-carbon of the methylacetylene to form a C–C σ bond and a radical center at the α carbon atom. The addition to the β position at expense of the α C atom is likely based on the enhanced spin density of the α C and a simultaneous steric hindrance of the methyl group to attack the β position. After CN addition, the C_3H_4CN complex can fragment via H atom emission through two distinct channels to conserve the acetylenic structure (channel 1) and to form an allenic unit (channel 2).

Our *ab initio* calculations support the experimental findings, cf. Fig. 4. The *cis/trans* C_3H_4CN complex(es), INT1-a and INT1-b $(X\,^2A')$ can form without entrance barrier. Both are stabilized by 254 and 252 $kJ\,mol^{-1}$ with respect to the reactants; an interconversion barrier TS-1 between both isomers is located well below the total available energy, and hence both *cis* and *trans* structures are expected to be populated. The C_3H_4CN intermediate can fragment to CH_3CCH+H (channel 1) and $H_2CCCHCN+H$ (channel 2). The exit transition state of the first pathway TS-3 is found to be slightly tighter than the transition state of the second channel TS-2 lying about 19 and 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. These data are in close agreement with our experimentally derived exothermicities of 70–105 $kJ\,mol^{-1}$. Finally, we point out the milder sideways scattering as evident from the velocity flux contour map compared to the $CN+C_2H_2$ reaction. In the latter, the HCC≡H bond angle is about 109.8° and the H–CCN angle ~92.8° to account for the sideways peaking. In the present experiment, the C—H angles in the exit transition states are 94.5° and 104.2° (TS-3) and 107.0° (TS-2). These findings, together with energetically accessible C–H low frequency bending and wagging modes, should be reflected in a sideways peaking of the velocity flux contour map as well. The existence of a second reaction channel and the corresponding C–H bond cleavage of the methyl group very likely smears out the expected stronger sideways peaking as found in the $CN+C_2H_2$ reaction.

In spite of this remaining challenge and the quanitification of the initial INT1-a and INT1-b ratios, we have demonstrated that the neutral–neutral reaction of cyano radicals, $CN(X\,^2\Sigma^+)$, with methylacetylene, CH_3CCH, leads to the formation of two C_4H_3N isomers, i.e., cyanopropyne, CH_3CCCN, and cyanoallene, H_2CCHCN. This solid proof of the reaction products means that the title reaction should be included in reaction networks modeling the chemistry in Titan's atmosphere. Since neither isomer has been identified in Titan so far, our results offer a unique task for the NASA-ESA Cassini–Huygens mission to Titan.[11] The spacecraft Huygens mission will carry an IR mapping spectrometer as well as a quadrupole mass spectrometer capable of identifying these isomers in Titan's atmosphere.[12]

In addition to solar system chemistry, the title reaction offers a strong synthetic route to interstellar CH_3CCCN identified in dark molecular clouds as well as in the outflows of dying carbon stars[13–16] and should encourage astronomers to search for the hitherto unobserved second isomer, cyanoallene. Since the CN vs H exchange channel offers a versatile route to form highly unsaturated nitriles, reactions of CN with ethylene, allene, and benzene are in progress to setup a systematic data base of reaction products to be incorporated into prospective models of interstellar as well as planetary environments.

ACKNOWLEDGMENTS

[1] D. W. Clarke and J. P. Ferris, Origins Life Evol. Biosphere **27**, 225 (1997). ESA Special Publication SP-338 (1992) Symposium on Titan.

[2] B. Letourner and A. Coustenis, Planet. Space Sci. **41**, 393 (1993).

[3] T. Owen *et al.* in Huygens: Science, Payload and Mission, ESA Sp-1177 (1997), p. 51.

[4] I. R. Sims *et al.*, Chem. Phys. Lett. **211**, 461 (1993); I. W. M. Smith, I. R. Sims, and B. R. Rowe, Chem.-Eur. J. **3**, 1925 (1997); B. R. Rowe and D. C. Parent, Planet. Space Sci. **43**, 105 (1995).

[5] F. Raulin *et al.*, Adv. Space Res. **22**, 353 (1998).

[6] L. H. C. Huang, Y. T. Lee, and R. I. Kaiser, J. Chem. Phys. **110**, 7119 (1999).

[7] Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, Rev. Sci. Instrum. **40**, 1402 (1969); R. I. Kaiser *et al.*, J. Chem. Phys. (submitted).

[8] D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713 (1989).

[9] G. O. Brink, Rev. Sci. Instrum. **37**, 857 (1966); N. R. Daly, *ibid.* **31**, 264 (1960).

[10] M. S. Weis, Ph.D. thesis, University of California, Berkeley, 1986.

[11] D. W. Clarke and J. P. Ferris, Icarus **115**, 119 (1995).

[12] M. Khlifi and F. Raulin, Spectrochim. Acta A **A47**, 171 (1991); F. Raulin *et al.*, Adv. Space Res. **22**, 353 (1998).

[13] I. Cherchneff and A. E. Glassgold, Astrophys. J. Lett. **419**, L41 (1993).

[14] T. J. Millar and E. Herbst, Astron. Astrophys. **288**, 561 (1994); S. D. Doty and C. M. Leung, Astrophys. J. Lett. **502**, 898 (1998); I. Cherchneff, A. E. Glassgold, and G. A. Mamon, *ibid.* **410**, 188 (1993).

[15] D. P. Ruffle *et al.*, Mon. Not. R. Astron. Soc. **291**, 235 (1997); T. J. Millar, G. H. Macdonald, and A. G. Gibb, Astron. Astrophys. **325**, 1163 (1997).

[16] E. Herbst *et al.*, Mon. Not. R. Astron. Soc. **268**, 335 (1994).