

Crossed beam reaction of atomic carbon, $C(3P_j)$, with the propargyl radical, $C_3H_3(X^2B_2)$: Observation of diacetylene, $C_4H_2(X^1\Sigma_g^+)$

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Crossed beam reaction of atomic carbon, $C(^3P_j)$, with the propargyl radical, $C_3H_3(X^2B_2)$: Observation of diacetylene, $C_4H_2(X^1\Sigma_g^+)$

R. I. Kaiser,^{a)} W. Sun,^{b)} A. G. Suits,^{c)} and Y. T. Lee^{d)}

Department of Chemistry, University of California, Berkeley, California 94720 and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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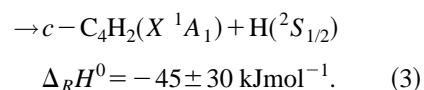
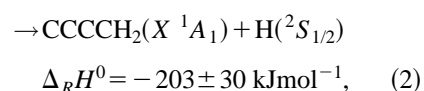
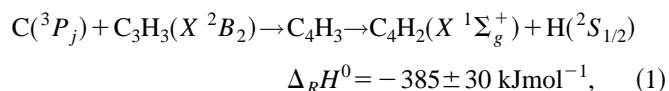
The reaction of ground-state carbon, $C(^3P_j)$, with the propargyl radical, $C_3H_3(X^2B_2)$, is investigated at an average collision energy of 42.0 kJmol^{-1} employing the crossed molecular beams technique and a universal mass spectrometric detector. The laboratory angular distribution and time-of-flight spectra of the C_4H_2 product are recorded at $m/e = 50$. Forward-convolution fitting of our data reveals the formation of diacetylene, $HCCCH$, in its $X^1\Sigma_g^+$ electronic ground state. The reaction dynamics are governed by an initial attack of $C(^3P_j)$ to the π -electron density at the acetylenic carbon atom of the propargyl radical, followed by a [1,2]-hydrogen migration to the n - C_4H_3 isomer. A final carbon–hydrogen bond rupture yields atomic hydrogen and diacetylene through a tight exit transition state located 30 – 60 kJmol^{-1} above the products. This first successful crossed molecular beams study of a reaction between an atom and a free radical marks the beginning of the next generation of crossed beams experiments elucidating the formation of molecular species in combustion processes, chemical vapor deposition, in the interstellar medium, outflows of carbon stars, and hydrocarbon-rich planetary atmospheres via radical–radical reactions. © 1997 American Institute of Physics. [S0021-9606(97)04144-5]

I. INTRODUCTION

The chemical reaction dynamics of atomic carbon in its $C(^3P_j)$ electronic ground state with unsaturated hydrocarbon molecules are of major importance in interstellar chemistry,^{1,2} combustion processes,³ and chemical vapor deposition.⁴ Recently, we initiated these studies in our lab elucidating the chemical dynamics and reaction products of exothermic atom–molecule reactions of $C(^3P_j)$ with acetylene, C_2H_2 , ethylene, C_2H_4 , methylacetylene, CH_3CCH , and propylene, C_3H_6 , employing the crossed beams technique with electron impact ionizer coupled to a quadrupole mass spectrometer. These investigations provided collision energy dependent (8.8 – 45.0 kJmol^{-1}), doubly differential cross sections to both interstellar tricarbon hydride radicals,⁵ $1/c$ - C_3H , and to hitherto unobserved interstellar propargyl⁶ [$C_3H_3(X^2B_2)$], n - $C_4H_3(X^2A')$,⁷ and methylpropargyl⁸ [$C_4H_5(X^2B_2/X^2A'')$] radicals. The explicit identification of this carbon–hydrogen exchange under single collision conditions elucidated the importance of a one-step pathway to free hydrocarbon radicals. This mechanism can be employed further to predict large scale concentrations of unobserved interstellar radicals C_3H_3 , C_4H_3 , and C_4H_5 in extraterrestrial environments.²

The work described above is just the beginning towards

a better understanding of the importance of neutral–neutral reactions in contrast to ion–molecule reactions in the formation of molecules and radicals in extraterrestrial environments. The chemical dynamics of atom–radical as well as radical–radical reactions in the hydrogen deficient C–H system are completely unknown. Both reaction classes, however, are expected to have a profound impact on chemistry in interstellar and hydrocarbon-rich planetary environments at very low temperatures down to 10 K : Reactive encounters between carbon atoms with open shell hydrocarbons such as CH , C_2H , C_2H_3 , and C_3H_3 radicals are thought to resemble prototype reactions proceeding without any barrier in the entrance channel. Therefore, these reactions are strongly expected to form complex species even in the coldest known interstellar clouds where the average kinetic energy of reactant molecules are about 0.08 kJmol^{-1} . In this communication, we present the chemical dynamics of atomic carbon reacting with the propargyl radical to form C_4H_2 isomers diacetylene [reaction (1)], butatrienyldiene [reaction (2)], and/or the cyclic isomer cyclopropenylidenecarbene [reaction (3)]^{9–11}



^{a)}Present address: Academia Sinica, Institute of Atomic and Molecular Sciences, Nankang, Taipei, 11529, Taiwan, ROC; and Department of Physics, Technical University Chemnitz-Zwickau, 09107 Chemnitz, Germany. Electronic mail: kaiser@po.iam.s.sinica.edu.tw

^{b)}Electronic mail: weizhong@leea.cchem.berkeley.edu

^{c)}Electronic mail: agsuits@lbl.gov

^{d)}Present address: Academia Sinica, Institute of Atomic and Molecular Sciences, Nankang, Taipei, 11529, Taiwan, ROC. Electronic mail: ytleee@gate.sinica.edu.tw

II. EXPERIMENT

Investigating the chemical dynamics of radical–radical reactions using the crossed molecular beams technique is quite challenging. Compared to $C(^3P_j)$ reactions with neat hydrocarbons, the secondary neat hydrocarbon beam must be replaced by $\sim 10\%$ beam of the radical precursor seeded in helium. Even assuming an excellent conversion of 10% into radicals, the reactive scattering signal drops by two orders of magnitude to gain a comparable signal to noise ratio to closed shell systems if the reactive scattering cross sections are comparable. The experiment is performed with a universal crossed molecular beam apparatus described in Ref. 12 in detail. Briefly, a pulsed supersonic carbon atom beam is generated via laser ablation of graphite in the primary source chamber.¹³ The 65 mJ 266 nm output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating graphite rod, and ablated carbon atoms are seeded into helium gas. A four slot chopper wheel located between skimmer of the primary source and the interaction region, slices a $9\ \mu\text{s}$ segment of the pulsed carbon beam to select a velocity $v_0 = 2765 \pm 14\ \text{ms}^{-1}$ and a speed ratio $S = 3.0 \pm 0.3$. The pulsed propargyl radical beam is produced in the secondary source region via photodissociation of 10% propargyl bromide precursor seeded in helium carrier gas at 1 atm stagnation pressure. The 80 mJ, 193 nm output of a Lamda Physik Compex 110 excimer laser is focused 5 mm downstream of the pulsed valve nozzle to a rectangle of $1 \times 4\ \text{mm}$. These operation parameters yield a propargyl beam with a velocity $v_0 = 1220 \pm 20\ \text{ms}^{-1}$ and a speed ratio $S = 14.0 \pm 0.5$, i.e., a spread of about $60\text{--}80\ \mu\text{s}$ at 50% of its peak intensity. Time-of-flight spectra of reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometer with an electron-impact ionizer^{14,15} in 5.0° steps with respect to the carbon beam at $m/e = 51$ and $m/e = 50$. To gain information on the reaction dynamics, the time-of-flight (TOF) spectra and the laboratory angular distribution (LAB) are fit using a forward-convolution technique¹⁶ yielding the translational energy flux distribution $P(E_T)$ and angular distribution $T(\theta)$ in the center-of-mass reference frame.

Since both the carbon and propargyl beams are pulsed, extreme care has to be taken to select the correct time delay between the primary and secondary pulsed valve prior to the crossing at 90° in the interaction region. An improper timing would have resulted in reaction of $C(^3P_j)$ with the slow part of the secondary beam containing predominantly propargyl bromide precursor to form C_4H_3 detectable at $m/e = 51$ and $m/e = 50$ as well as Br atoms. Here, we optimize this delay by monitoring the excimer laser correlated integrated intensity of the time-of-flight (TOF) spectra at $m/e = 50$ versus the delay time of the second pulsed valve. Signal at $m/e = 50$ recorded with the excimer laser “off” originates only from reaction of atomic carbon with the propargyl bromide precursor and the fragmentation of the C_4H_3 product in the electron impact ionizer. However, signal with the excimer laser “on” can arise from reaction of carbon atoms with propargyle bromide as well as propargyl radicals. Therefore,

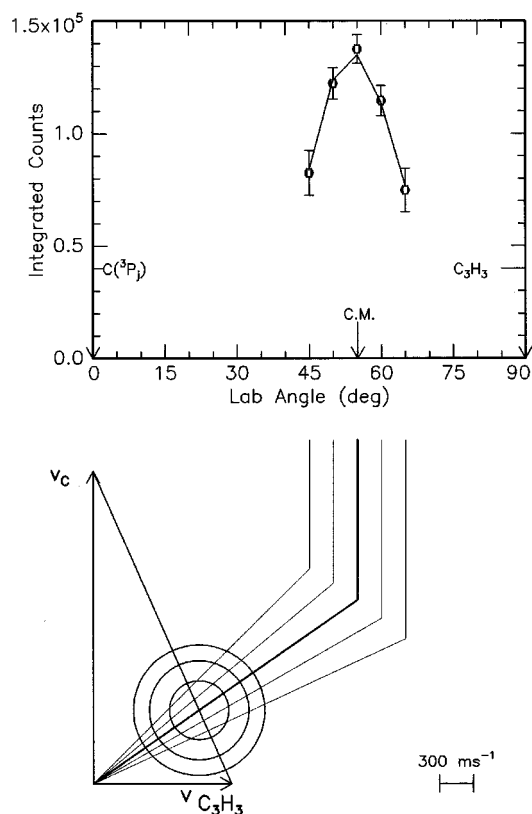


FIG. 1. Lower: Newton diagram for the reaction $C(^3P_j) + C_3H_3$ at a collision energy of $42.0\ \text{kJmol}^{-1}$. The circle stands for the maximum center-of-mass recoil velocity in the center-of-mass reference frame of C_4H_2 isomers. From outer to inner: Diacetylene, butatrienylidene, and cyclopropenylidenecarbene. Upper: Laboratory angular distribution of C_3H_3 at $m/e = 50$. Circles and 1σ error bars indicate experimental data, the solid line the calculated distribution. C.M. designates the center-of-mass angle of 55.0° .

a correct time delay should show no signal at $m/e = 50$ with the excimer laser “off”, but only with the excimer laser “on”. Further, the laser “on” TOFs at the correct delay time should show no intensity at $m/e = 51$. This optimization procedure results in triggering the second pulsed valve between 7 and $15\ \mu\text{s}$ prior to the primary pulsed valve.

III. RESULTS

Reactive scattering signal was only observed at $m/e = 50$, i.e., C_4H_2 , cf. Figs. 1 and 2; no signal was detected at $m/e = 51$, unconditionally supporting the absence of propargyl bromide reacting with atomic carbon in our experimental conditions. The LAB distribution of the C_4H_2 product (Fig. 1) peaks at 55° near the center-of-mass angle of $55 \pm 1^\circ$, but shows a slight forward shape with respect to the carbon beam if we compare intensities at 45° and 50° with those at 55° and 60° , respectively. Due to the limiting signal to noise ratio, no data could be obtained at angles smaller than 45° and larger than 65° . Best fits of our data as shown in Fig. 3 yield translational energy distributions $P(E_T)$ s extending to $300\text{--}420\ \text{kJmol}^{-1}$, whereas the total available energy gives $427 \pm 30\ \text{kJmol}^{-1}$ to form the diacetylene isomer, cf. reaction (1). Finally, the $P(E_T)$ s depict a maximum about

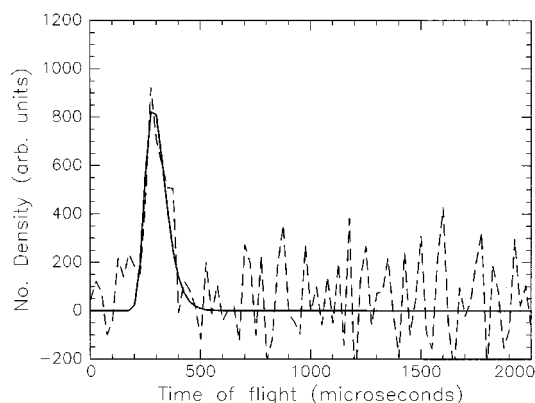


FIG. 2. Time-of-flight data at the center-of-mass angle of 55.0° . The dashed line indicates the experimental data, the solid line the fit.

$30\text{--}60\text{ kJmol}^{-1}$, demonstrating a repulsive carbon-hydrogen bond rupture to result in a tight exit transition state.

The center-of-mass angular flux distribution $T(\theta)$ is slightly forward scattered with respect to the carbon beam. This finding implies (a) one microchannel to C_4H_2 through a complex holding a lifetime comparable to its rotational period (osculating complex) or (b) two microchannels giving an isotropic as well as a forward scattered contribution. Finally, the weak $T(\theta)$ polarization results from a poor coupling between the initial \mathbf{L} and final orbital angular momentum \mathbf{L}' with $L' < 0.15\text{--}0.2 L$ indicating that most of the total angular momentum channels into rotational excitation of the C_4H_2 product.

IV. DISCUSSION

Figure 4 displays a schematic energy level diagram of

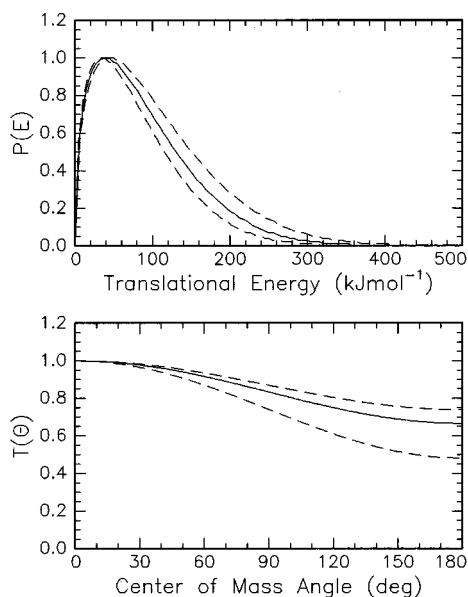


FIG. 3. Lower: Center-of-mass angular flux distribution for the reaction $\text{C}(^3P_j) + \text{C}_3\text{H}_3$. Upper: Center-of-mass translational energy flux distribution for the reaction $\text{C}(^3P_j) + \text{C}_3\text{H}_3$. Solid lines represent the best fit, dashed lines limit the range of acceptable fits within 1σ error bars.

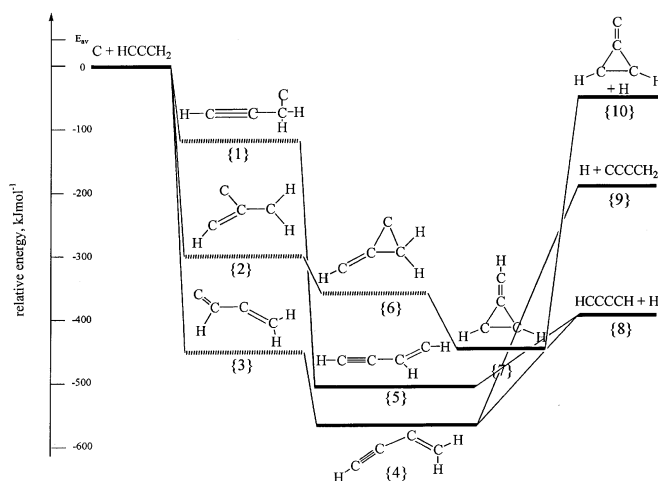


FIG. 4. Schematic energy level diagram for the reaction $\text{C}(^3P_j) + \text{C}_3\text{H}_3$. Solid dashed lines: No *ab initio* calculations have been performed on these structures. E_{av} indicates the total available energy.

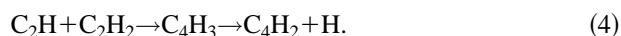
the title reaction. Five reaction pathways on the ground-state doublet surface are theoretically feasible. Defining the acetylenic carbon atom of the propargyl radical as C1, the central C atom as C2, the olefinic as C3, and the attacking one as C4, these are addition to C3, C2, or C1 forming the C_4H_3 isomers {1}, {2}, and {3}, as well as $\text{C}(^3P_j)$ insertion into the acetylenic C-H bond yielding *n*- C_4H_3 (X^2A') {4} or insertion into an olefinic C-H bond to form the iso C_4H_3 (X^2A') isomer {5}. Hereafter, [1,4]-H migration in {3}→{4}, a [3,4]-H migration in {1}→{5}, ring closure of {2}→{6} followed by a [3,4]-H migration to {7} are theoretically possible. A final C-H bond rupture in {4} or {5} could form diacetylene {8}, and a C-H cleavage in {4} can yield butatrienylidene {9}. Comparing the scattering range with limit circles of the C_4H_2 isomers and analyzing the high energy cutoff of the $P(E_T)$ strongly suggest that *c*- C_4H_2 {10} is not the major contribution. Therefore, we restrict the discussion on C_4H_2 isomers to diacetylene {8} and butatrienylidene {9}.

The crucial question to be answered is the nature of the decomposing C_4H_3 complex, i.e., {4} and/or {5}. The forward peaked center of mass angular distribution requires that the attacking $\text{C}(^3P_j)$ and the leaving H atom must be located on opposite sites of the rotation axis of the fragmenting C_4H_3 . A detailed analyses of the principal rotational axes of {4} and {5} employing *ab initio* geometries from Refs. 17 and 18 clearly shows that {5} must rotate around its A axis to account for this $T(\theta)$ shape. The final C-H bond cleavage, however, would yield a linear diacetylene molecule, rotating about its internuclear axis. Due to the vanishing moment of inertia around the A axis, this rotation is energetically not accessible, and {5} can be safely excluded as the fragmenting C_4H_3 complex. The same argument strictly eliminates a decomposing {4} excited to A-like rotations, but rotations around the B/C axes contribute to the observed $T(\theta)$, leading to diacetylene {8} in the final C-H bond rupture excited to B-like rotations. The preferred olefinic bond cleavage in {4} as compared to the acetylenic one goes hand in hand with

olefinic C–H bonds about 60–80 kJmol^{−1} weaker than acetylenic ones.

Based on our data alone, we cannot distinguish between a single insertion process into the acetylenic C1–H bond, or an initial addition to C1 followed by a hydrogen migration to yield {4}. Keeping in mind that C(³P_j) insertions are symmetry-forbidden and are expected to hold an entrance barrier, and comparing our findings with the chemical dynamics of atomic carbon reacting with C₂H₂ and CH₃CCH, we find that C(³P_j) does not insert into C–H bonds, but rather attacks preferentially the carbon atom with the highest π -electron density, in our system the acetylenic C1. Further, acceptable impact parameters leading to reaction support the chemical dynamics. Here, attack to the olefinic C3 atom is expected to proceed almost perpendicular to the C₃H₃ molecular plane. The acetylenic C1–C2 bond, however, shows almost cylindrical symmetry, and in plane as well as out of plane approach geometries can lead to a C₄H₃ intermediate. We conclude that the reaction between atomic carbon and propargyl radical is initiated by an attack to the C1 atom yielding {3}, followed by a hydrogen migration to {4} and a final bond rupture to form atomic hydrogen and diacetylene {8}.

Besides the chemical reaction dynamics, these results are of fundamental importance to interstellar as well as solar system chemistry as in Titan's stratosphere,¹⁹ the Jovian atmosphere²⁰ as well as Neptune, Uranus, Saturn, and Triton.²¹ Since C₃H₃ can be formed through reaction of atomic carbon with C₂H₄ and photodissociation of C₃H₄ isomers,²² the title reaction is strongly suggested to be included in chemical reaction networks modeling these extra-terrestrial environments. Further, reaction of C(³P_j) with C₃H₃ provides an alternative pathway to diacetylene hitherto thought to be solely synthesized via reaction (4)^{23,24}



Future investigations of reactions (1)–(3) will focus on the existence of a second isomer as detected around the circumstellar envelope of IRC+10216 and toward TMC-1,^{25,26} CCCCH₂, by replacing HCCCH₂ by HCCCD₂. Despite this open question, the present work clearly demonstrates that the investigation of the chemical reaction dynamics of radical–radical as well as atom–radical reactions employing the crossed molecular beam technique is technologically feasible and extendible to other systems. For example, preliminary reactive scattering experiments on the interaction of C(³P_j) with the vinyl radical, C₂H₃, show laser correlated signal at $m/e=38$, i.e., ubiquitous interstellar C₃H₂²⁷—boldly to go where no one has gone before...

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