Crossed-beam reaction of $C(^3P_j)$ with $C_2H_2(^1\Sigma_g^+)$: Observation of tricarbon-hydride C_3H

R. I. Kaiser, Yuan T. Lee, and Arthur G. Suits[a)]
Department of Chemistry, University of California and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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The reaction between ground state carbon atoms, $C(^3P_j)$, and acetylene, $C_2H_2(^1\Sigma_g^+)$, was studied at an average collision energy of (8.4 ± 0.3) kJ mol^{-1} using the crossed molecular beam technique. The product angular distribution and time-of-flight spectra of $m/z=37$, i.e., C_3H, were recorded. Only $m/z=37$ was detected, but no signal from the thermodynamically accessible $C_3(^1\Sigma_g^+)+H_2(^1\Sigma_g^+)$ channel. Forward-convolution fitting of the results yielded a center-of-mass angular flux-distribution forward scattered in respect to the carbon beam, whereas the translational energy flux distribution peaked at only (5.4 ± 1.2) kJ mol^{-1}, suggesting a simple C–H-bond-rupture to $H+C_3H$. The reaction likely proceeds on the triplet surface with an entrance barrier to the C_3H_2–PES of $<(8.4\pm0.3)$ kJ mol^{-1} via addition of the carbon atom to two bonding π-orbitals located both at C1 or at C1 and C2 of the acetylene molecule. The explicit identification of C_3H product under single collision conditions strongly demands incorporation of atom-neutral reactions in reaction networks simulating chemistry in the interstellar medium, in interstellar shock waves, and in outflows of carbon stars. © *1995 American Institute of Physics.*

I. INTRODUCTION

Chemical reactions of atomic carbon in its electronic ground state $C(^3P_j)$ are of major importance in combustion processes,[1–3] hydrocarbon syntheses,[1–3] and interstellar chemistry.[4–7] In the interstellar medium (ISM), i.e., the matter between the stars of our galaxy, and in the outflow of carbon stars, e.g., IRC+10216,[2,3] isomers of C_3H and C_3H_2, i.e., propynylidyne (*l*inear-C_3H)/cyclopropynylidyne (*c*yclo-C_3H) and cyclopropenylidene/vinylidenecarbene, are among the most abundant molecules, with number densities $\approx10^{-8}$ relative to H_2. Current reaction-networks explain their formation via elaborate, multiple ion–molecule reactions:[8,9]

$$C_2H_2+C^+\rightarrow l/c\text{-}C_3H^++H, \tag{1}$$

$$l/c\text{-}C_3H^++H_2\rightarrow c\text{-}C_3H_3^++h\nu, \tag{2}$$

$$l/c\text{-}C_3H_3^++e\rightarrow l/c\text{-}C_3H_2+H \tag{3}$$

$$\rightarrow l/c\text{-}C_3H+2\,H \tag{4}$$

$$\rightarrow l/c\text{-}C_3H+H_2. \tag{5}$$

This approach, however, neither reproduces column densities, isomer ratios, nor isotope enrichments.[8] In addition, the exact electron density necessary for dissociative recombinations (3–5) can only be estimated within two orders of magnitude. Furthermore, not all cross sections of ion–molecule reactions are experimentally accessible, but rather approximated as Langevin cross sections, i.e., exothermic ion–molecule reactions proceed within orbiting cross section.[10] Recently, however, entrance barriers for several exothermic reactions were determined to ca. 4 kJ mol^{-1} at 293 K.[11] The role of ion–molecule reactions in interstellar formation of some of these species is thus open to question. The possibility of generation of C_3H from neutral reactants, e.g., $C(^3P_j)+C_2H_2(^1\Sigma_g^+)$ has not been considered in the past. This single step mechanism does not require a protracted chain of successive collisions under conditions with reactant number densities between 10^{-3} and 10^{-4} cm^{-3}.

In order to demonstrate the importance of reactions of neutral species, systematic experiments need to be carried out to probe the detailed mechanism and dynamics of such atom–neutral and radical–radical reactions as $C(^3P_j)+C_2H_x$ and $CH(^2\Pi_{1/2})+C_2H_x(x=1,2,3,4)$. In our Communication, we focus on the reaction $C(^3P_j)+C_2H_2(^1\Sigma_g^+)$ studied under single-collision conditions as provided in crossed-beam experiments. These detailed insights in the reaction dynamics reveal possible reaction pathways to C_3H-isomers, valuable information on the C_3H and C_3H_2 potential energy surfaces (PES) as well as hitherto undetermined enthalpy of formations of *l*- and *c*-C_3H.

II. EXPERIMENT AND DATA PROCESSING

The experiments were performed with a universal crossed molecular beam apparatus described in Ref. 12 in detail. Briefly, a pulsed supersonic carbon beam was generated via laser ablation of graphite at 266 nm.[13] The 30 Hz, (40 ± 2) mJ output of a Spectra Physics GCR 270-30 Nd-YAG laser is focused onto a rotating graphite rod with a 1000 mm focal length UV-grade fused silica lens to a spot of (0.5 ± 0.05) mm diameter. Ablated carbon atoms are subsequently seeded into neon gas released by a Proch–Trickl pulsed valve operating at 60 Hz, 80 μs pulses, and 4 atm backing pressure. Densities of $(0.7\pm0.3)*10^{13}$ C atoms cm^{-3} in the interaction region are achieved. Neither carbon ions C_n^+ nor electronically excited $C(^1D_j)$ or $C(^1S_j)$ atoms could be detected within the detection limits of the quadrupole mass spectrometer.[13] A chopper wheel mounted 40 mm after the laser ablation zone accomplishes selecting a 7 μs segment of the carbon pulse. The pulsed carbon beam with a

[a)]Author to whom correspondence should be addressed.

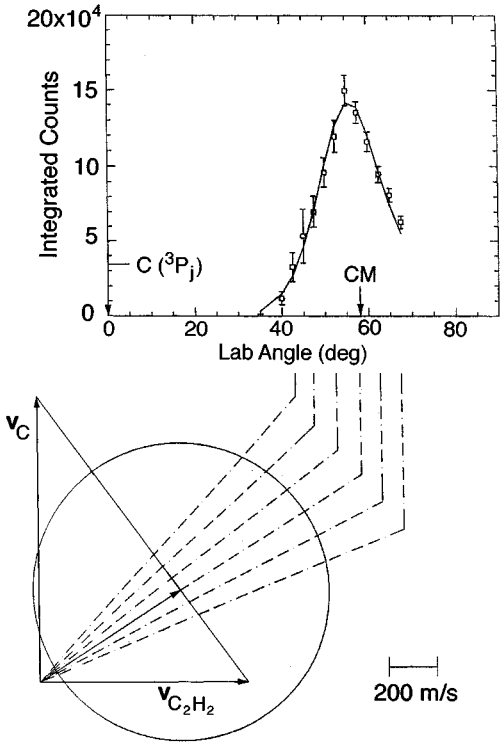

FIG. 1. Lower: Newton diagram for the reaction $C(^3P_j)+C_2H_2(^1\Sigma_g^+)$ at a collision energy of 8.8 kJ mol^{-1}. The circle stands for the maximum center-of-mass recoil velocity of the C_3H-product (see text). Upper: Laboratory angular distribution of product channel at $m/z=37$. Circles and error bars indicate experimental data, the solid line the calculated distribution.

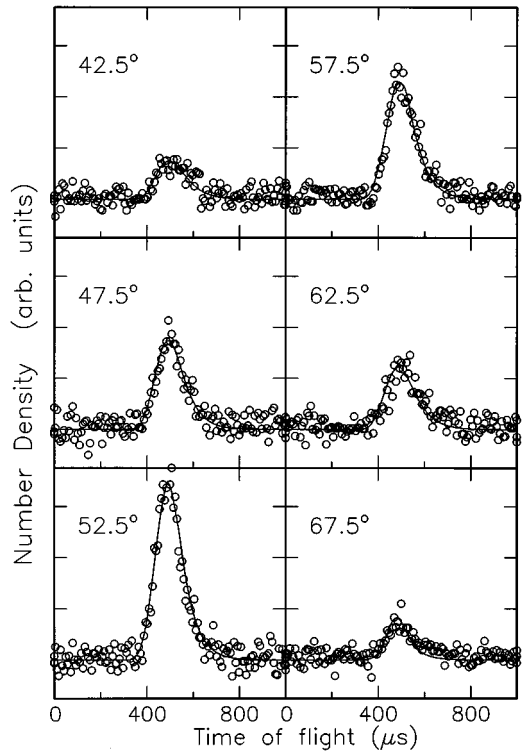

FIG. 2. Time-of-flight data for laboratory angle 42.5, 47.5, 52.5, 62.5, and 67.5°.

velocity $v=(1177\pm3)$ m s^{-1} and speed ratio $S=(6.4\pm0.05)$ and continuous acetylene beam [$v=(866\pm7)$ m s^{-1}, $S=(9.3\pm0.1)$, (563 ± 6) Torr backing pressure] pass through skimmers with apertures of 1.0 mm and 0.58 mm and cross at 90° in the interaction region.

The scattered species were monitored using a triply differentially pumped detector consisting of a Brink-type electron-impact-ionizer,[14] quadrupole mass-filter, and a Daly ion detector[15] in 2.5° steps between 7.5° and 67.5° with respect to the carbon beam. The electron energy was optimized to 200 eV with an emission current of 8.5 mA.

Information on the reaction dynamics is extracted from the TOF-spectra and the laboratory angular distribution by using a forward-convolution technique.[18] This iterative approach initially guesses the angular flux distribution in the center-of-mass (COM) coordinate system, $T(\theta_c)$, and the translational energy flux distribution in the COM system, $P(E_T)$ assumed to be independent of each other, and convolutes over the experimental parameters to obtain simulations of the experimental result.

III. RESULTS AND DISCUSSION

The thermochemistry of $C(^3P_j)+C_2H_2(^1\Sigma_g^+)$ opens two energetically accessible product channels, i.e., C_3H+H and C_3+H_2. Reaction to C_3 in its $^1\Sigma_g^+$ electronic ground state is exothermic by 129 kJ mol^{-1}, and has to proceed via intersystem crossing from the initial triplet to singlet surface. Unfortunately, the C_3H enthalpies of formation and relative stabilities of linear–cyclic isomers are not known. Simple additivity rules estimate $C(^3P_j)+C_2H_2(^1\Sigma_g^+)\rightarrow C_3H+H$ to be exothermic 69 kJ mol^{-1}. Nevertheless, this value is not consistent with the acetylenic like C–H bond of C_3H as determined via FTIR spectroscopy:[17] the dissociation energy of the C–H bond $C_3H\rightarrow C_3(^1\Sigma_g^+)+H(^2S_{1/2})$ is calculated to be 372 kJ mol^{-1}, lower than typical aliphatic carbon–hydrogen bond strengths of 400 kJ mol^{-1}. Alternative reaction enthalpies are obtained by imposing different C–H bond dissociation energies of model hydrocarbons, and yield reaction enthalpies to $C_3H+H(^2S_{1/2})$ between -114 (C–H bond in ethane) and -253 kJ mol^{-1} (C–H bond in acetylene). These exothermicities allow calculation of the maximum recoil velocities of the C_3H-fragment, shown as a limit circle in the kinematic diagram Fig. 1, assuming no rotational and vibrational excitation of the C_3H product.

Reactive scattering signal was observed only at $m/z=37$, i.e., C_3H (Fig. 2); no $C_3(^1\Sigma_g^+)+H_2(^1\Sigma_g^+)$-channel was detected. Time-of-flight spectra for several scattering angles are shown in Fig. 2. Reaction of carbon with acetylene-dimers to $C_2H_3+C_3H$ does not contribute to the signal within the detection limits of the experimental setup because the signal intensity scales linearly with the C_2H_2 number density in the interaction region. The laboratory angular distribution (Fig. 1) peaks at 55° near the center-of-mass angle at $\theta_{COM}=(58.8\pm0.8)°$. The product distribution was fitted with a center-of-mass angular flux distribution $T(\theta_C)$ forward scattered with respect to the carbon beam (Fig. 3) and a center-of-mass translational energy flux distribution $P(E_T)$ peaking at only (5.4 ± 1.2) kJ mol^{-1}, indicating nearly a

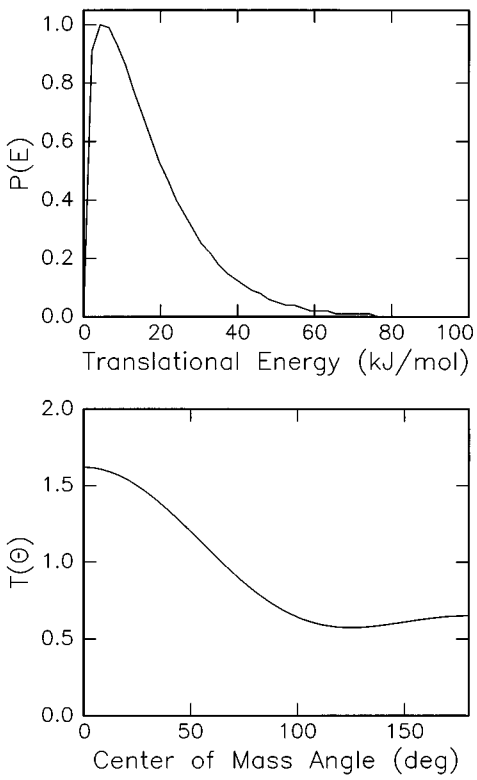

FIG. 3. Lower: Center-of-mass angular flux distribution for the reaction $C(^3P_j)+C_2H_2(^1\Sigma)$ at a collision energy of 8.8 kJ mol^{-1}. Upper: Center-of-mass translational energy flux distribution for the reaction $C(^3P_j)+C_2H_2$ $(^1\Sigma)$ at a collision energy of 8.8 kJ mol^{-1}.

simple barrierless C–H bond rupture process to C_3H.

The energy diagram in Fig. 3 outlines four different reaction pathways: insertion of $C(^3P_j)$ in the C–H-bond of an acetylene molecule leads to triplet-propargylene (1) on the *A* or *B* surface (point group C_2; $\Delta G_f°=551$ kJ mol^{-1},[18] whereas addition of the electrophile carbon atom to carbon centers on C1- and C2-atoms in C_2H_2 forms triplet-cyclopropenylidene (3) (point group C_1; $\Delta G_f°=706$ kJ mol^{-1};[19–25] A surface). The final pathways (4)/(5) involve attack of two perpendicular C-2*p*-orbitals to both perpendicular π-MOs on C1 yields triplet-*cis/trans* propendiylidene (4)/(5) (point group C_s; $\Delta G_f°$ (*trans*)=779 kJ mol^{-1}, $\Delta G_f°$ (*cis*) 859 kJ mol^{-1},[19–25] A'' surface). Finally, matrix studies via FTIR spectroscopy show transformation of (4)/(5) to triplet-vinylidenecarbene (2) (point group C_{2v}; $\Delta G_f°=727$ kJ mol^{-1} [19–25]) upon heating the argon matrix from 10 K to 36 K, implying a barrier less than 1 kJ mol^{-1} for [2,1]-H-migration in propenediylidene.

Insertion of $C(^3P_j)$ into the C–H bond is expected to involve a significant entrance barrier. To our knowledge, no insertion of a triplet-species into a C–H–bond has been reported yet with a barrier less than our (8.4±0.3) kJ mol^{-1} collision energy; typical entrance barriers range between 20 and 100 kJ mol^{-1}.[26] Additionally, reaction via triplet-propargylene (1) should yield a forward–backward-symmetric $T(\theta_C)$ due to the deep well of the collision complex in respect to the reactants and $H+C_3H$ products.

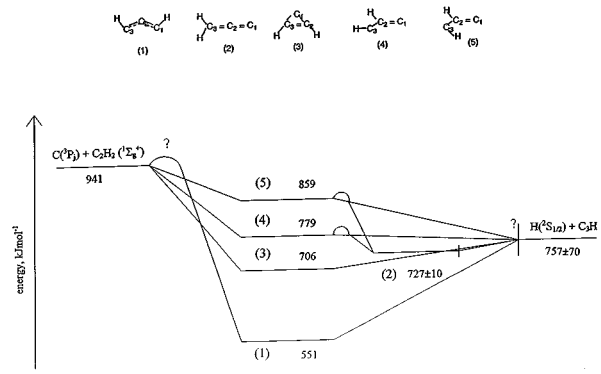

FIG. 4. Energy level diagram for the reaction $C(^3P_j)+C_2H_2(^1\Sigma_g^+)$: (1) triplet-propargylene, (2) triplet-vinylidenecarbene, (3) triplet-cyclopropenylidene, (4) triplet-trans propenediylidene, (5) triplet-cis propenediylidene. The reacting carbon atom is designed as C_1.

Therefore, a reaction via triplet-propargylene (1) can likely be ruled out.

The forward peaking $T(\theta_C)$ in respect to the carbon beam suggests the reaction proceeds in a direct fashion via triplet-cyclopropenylidene (3), vinylidenecarbene (2), or tiplet-*cis/trans* propenediylidene (4/5) with a life-time of less than one rotational period. The initially formed C_3H_2-collision complex has to perform a prolate rotation around the principal axis with the leaving hydrogen and the added carbon atom on opposite sites in order to explain the backward-peaking of the C_3H-product in respect to the acetylene-beam. Due to the low reduced mass of 0.974 amu in the exit channel to C_3H+H, angular momentum conservation demands C_3H to be strongly rotationally excited: hydrogen–bond rupture at C2 in *cis/trans*-propenediylidene (4/5) fulfills this condition and could populate high rotational levels of *l*-C_3H-product. Likewise, bond-rupture at C2 in *cis*-propenediylidene (5) might excite rotational levels as can be treated as a linear combination of the doubly degenerate bending mode of *l*-C_3H. Alternatively, rearrangement of (4/5) to triplet-vinylidenecarbene (2), followed by C–H–bond cleavage, fulfills the angular momentum criterion. Finally, an anisotropic exit potential in the triplet-cyclopropenylidene (3) PES could populate rotational levels of *c*-C_3H after C–H–bond cleavage. The poor coupling between the initial and final orbital angular momenta in this system accounts for the weakly polarized $T(\theta_C)$ (Fig. 3).

At the present stage, we cannot identify the reaction pathway unambiguously. However, future experiments will increase the center-of-mass collision energy to ≈50 kJ mol^{-1}. Within orbiting limits, the additional collision energy should reduce the maximum impact parameter and result in a less polarized center-of-mass angular flux-distribution. Further, reactions of $C(^3P_j)$ with deuterated acetylene C_2D_2 and methyl-acetylene CH_3C_2H shift the reduced mass from 0.974 amu (C_3H+H), to 1.897 amu (C_3D+D) to 10.673 amu (CH_3+C_3H). Under these conditions, for the C_3H product, the increased reduced mass and, hence, final orbital momentum can reduce the rotational excitation. Finally, *ab-initio* calculations on the equilibrium geometry of (1)–(5) and the transition-state frequencies are in

preparation. Comparisons of the complex-lifetimes elucidated via the osculating complex model and RRKM-based reaction rate constants should identify the collision complex unambiguously.

Although atom-neutral reactions have been discussed for over a decade to influence interstellar column densities,[4–6] they are only slowly being incorporated into interstellar reaction networks, predominantly owing to assumed order-of magnitude advantage of ion-molecule rate constants vs atom-neutral reactions [$k(C^+ + C_2H_2) = (2.6 \pm 0.3) * 10^{-9}$ cm^3 s^{-1},[22] $k(C(^3P_j) + C_2H_2) = (2.0 \pm 0.1) * 10^{-10}$ cm^3 s^{-1},[27] both at 293 K]. The ratio of $C(^3P_j)$ to singly ionized carbon ranges from 30 to 250[28] in interstellar clouds and outflow of carbon stars, however, clearly undermining the order-of-magnitude rate constant advantage of ion–molecule reactions as compared to atom–molecule reactions. Typically, molecules as well as atoms in molecular clouds hold equilibrium translational temperatures of 10−20 K. Although the collision energy in our experiments are close to 1000 K, theoretical calculations as well as bulk[27] and crossed beam experiments[29] indicate the $C(^3P_j) + C_2H_2$ reaction proceeds without entrance barrier within orbiting limits,[10] i.e., a rising cross section with decreasing translational energy. Additionally, the temperature in outflow of carbon stars range between 100 and 5500 K. Hence, formation of interstellar C_3H via $C(^3P_j) + C_2H_2$ yields a more realistic approach than postulated ion molecule reactions (1)–(2) and (4)–(5).

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