Stripping dynamics in the reactions of electronically excited carbon atoms, C(^1D), with ethylene and propylene—production of propargyl and methylpropargyl radicals

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The reactions of electronically excited carbon atoms, C(^1D), with ethylene and propylene were studied at three collision energies between 48 and 104 kJmol^{-1} employing the crossed molecular beam technique. Forward-convolution fitting of our data combined with electronic structure calculations suggests that the reactions proceed via stripping dynamics. Extremely short-lived allene and 1,2-butadiene intermediates decompose via atomic hydrogen emission to yield propargyl and methylpropargyl radicals, respectively. These production routes are of potential importance to form benzene, toluene, and *o-/p*-xylenes in circumstellar envelopes of carbon stars and combustion flames. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1428754]

I. INTRODUCTION

The propargyl radical, $C_3H_3(X\ ^2B_1)$, received considerable attention due to its importance in combustion flames,[1] in the interstellar medium (ISM),[2] and in planetary atmospheres.[3] Current models of the chemistry in circumstellar envelopes and oxygen-poor combustion scenarios postulate that soot formation and the synthesis of polycyclic aromatic hydrocarbons (PAHs) are connected.[4] This chemistry is thought to be initiated by recombination of two propargyl radicals to form linear C_6H_6 isomers and after isomerization(s) the first aromatic ring structure, benzene [$C_6H_6(X\ ^1A_{1g})$].[5] An alternative route to form benzene was suggested to involve C_4H_5 radicals reacting with acetylene, $C_2H_2(X\ ^1\Sigma_g^+)$, via various C_6H_7 isomers through an atomic H($^2S_{1/2}$) atom elimination pathway.[6] But despite the importance of C_3H_3 and C_4H_5 radicals, little is known on their formation routes. The reaction of singlet carbene, $CH_2(a\ ^1A_1)$, with acetylene to produce propargyl [reaction (1)] was proposed recently.[7] Alternatively, a unimolecular decomposition of vibrationally excited allene [$H_2CCCH_2(X\ ^1A_1)$] and methylacetylene [$CH_3CCH(X\ ^1A_1)$], reactions (2) and (3),[8] or photodissociation of C_3H_4 isomers revealed that the propargyl radical is the primary product.[9] The very first identification of $C_3H_3(X\ ^2B_1)$ under single collision conditions in the crossed beam reaction of ground-state carbon atoms, C(^3P_j), with ethylene [$C_2H_4(X\ ^1A_g)$][10] together with high level electronic structure calculations[11] demonstrated doubtlessly that $C_3H_3(X\ ^2B_1)$ can indeed be formed in combustion flames and around circumstellar envelopes of carbon stars such as of IRC+10216.[4,12] On the other hand, formation routes to C_4H_5

radicals were assumed to proceed via reaction of the vinyl radical, $C_2H_3(X\ ^2A')$, with acetylene [$C_2H_2(X\ ^1\Sigma_g^+)$].[13] A recent crossed beam study of carbon atoms with propylene, $C_3H_6(X\ ^1A')$, opened a second pathway as two C_4H_5 isomers, namely the 1-, and 3-methylpropargyl radicals, were identified.[14]

$$CH_2(a\ ^1A_1) + C_2H_2(X\ ^1\Sigma_g^+) \rightarrow C_3H_3(X\ ^2B_1) + H(^2S_{1/2}),\tag{1}$$

$$H_2CCCH_2(X\ ^1A_1) \rightarrow C_3H_3(X\ ^2B_1) + H(^2S_{1/2}),\tag{2}$$

$$CH_3CCH(X\ ^1A_1) \rightarrow C_3H_3(X\ ^2B_1) + H(^2S_{1/2}),\tag{3}$$

$$C(^3P_j) + C_2H_4(X\ ^1A_g) \rightarrow C_3H_3(X\ ^2B_1) + H(^2S_{1/2}).\tag{4}$$
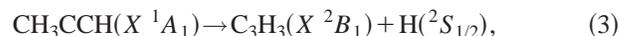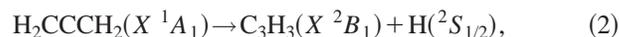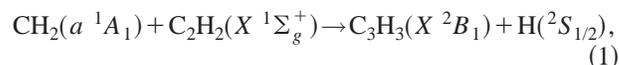
In this paper, we investigate alternative routes to form C_3H_3 and C_4H_5 isomers via reactions of electronically excited carbon atoms C(^1D) with ethylene [$C_2H_4(X\ ^1A_g)$] and propylene [$C_3H_6(X\ ^1A')$] under single collision conditions as provided in crossed molecular beam experiments. Combined with electronic structure calculations on the singlet C_3H_4 and C_4H_6 potential energy surfaces (PESs), detailed information on the reaction dynamics is disclosed and applications to combustion and interstellar chemistry are presented.

II. EXPERIMENT

Reactive scattering experiments are performed with the 35″ crossed molecular beam machine.[15] Briefly, the 30 Hz, 40 mJ output of a Nd:YAG laser is focused onto a rotating carbon rod, and ablated carbon atoms are seeded into helium released by a pulsed valve. A four slot chopper wheel selects

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a 9.0 μs segment of the fast part of the carbon beam with velocities of 4900 ± 150 ms^{-1} (ethylene experiment), 3100 ± 95 ms^{-1}, and 3580 ± 100 ms^{-1} (propylene experiments) with speed ratios between 2.2 and 2.6. The carbon source was characterized previously:[16] At velocities less than about 3000 ms^{-1}, the beam contains only the ground-state carbon C(^3P_j)[16] and at higher velocities both ground state and the first electronically excited-state C($^3P_j/^1D$);[14] even faster segments yielded exclusively C(^1D).[17] These pulsed carbon beams cross a second continuous ethylene or propylene beam of velocities of 844 ± 10 ms^{-1} and 775 ± 10 ms^{-1} at 90° in the interaction region of the scattering chamber at relative collision energies E_C of 104 ± 6 kJmol^{-1} (C$_2$H$_4$–C), 48 ± 3 kJmol^{-1} (C$_3$H$_6$–C), and 63 ± 3 kJmol^{-1}.

Reactively scattered products are detected in the plane defined by both beams employing a rotatable detector with a Brink-type electron-impact ionizer, quadrupole mass filter, and a Daly ion detector at distinct laboratory angles. Velocity distributions of the products are taken recording time-of-flight (TOF) spectra at each angle. Information on the chemical dynamics of the reactions were gained by fitting the TOF spectra and the product angular distribution in the laboratory frame (LAB) using a forward-convolution routine.[18] This procedure initially assumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). The $P(E_T)$ is chosen as a parameterized function

$$P(E_T) = (E_T - B)^p * (E_{av} - E_T)^q. \tag{1}$$

The B-parameter is related to the exit barrier with $B=0$ for a simple bond rupture without an exit-barrier. Peaking at a finite value E_p and for $B \neq 0$, the first argument in (1) governs the energy difference of E_p and the low energy tail where $E_T \rightarrow 0$, whereas the second argument describes a decaying function from E_p to the high energy tail. $T(\theta)$ is defined as a sum of three Legendre-polynomials $P_1(\cos \theta)$ with coefficients a_1

$$T(\theta) = \sum_{l=0}^{2} a_l * P_l(\cos \theta). \tag{2}$$

Laboratory TOF spectra and the laboratory angular distributions were then calculated from $T(\theta)$ and $P(E_T)$ accounting for the transformation Jacobian and averaging over the apparatus and beam functions. Best fits of the TOF and laboratory angular distributions were achieved by refining adjustable $T(\theta)$ and $P(E_T)$ parameters of Eqs. (1) and (2). To account for the experimental uncertainties in the velocities of the beams, speed ratios, and the laboratory angular distributions, the parameters of the best fit $T(\theta)$ and $P(E_T)$ functions were varied systematically to gain upper and lower limits of the center-of-mass functions within the error limits.

III. ELECTRONIC STRUCTURE CALCULATIONS

The geometries of the reactants, products, various intermediates, and transition states for the title reaction were optimized using the hybrid density functional B3LYP method, i.e., Becke's three-parameter nonlocal exchange functional[19] with the nonlocal correlation functional of Lee, Yang, and
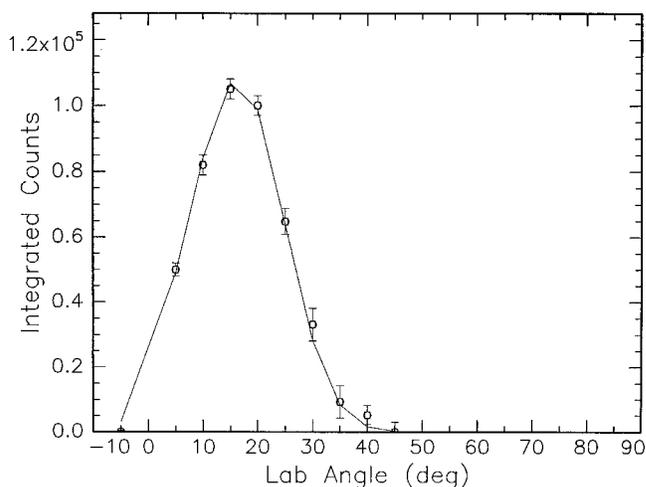
FIG. 1. Laboratory angular distribution of the C$_3$H$_3$ product at $m/e=39$. Circles and 1σ error bars indicate experimental data, the solid line the calculated distribution.

Parr,[20] and the 6-311G(d,p) basis set.[21] Vibrational frequencies, calculated at the B3LYP/6-311G(d,p) level, were used for characterization of stationary points and zero-point energy (ZPE) corrections. All the stationary points were positively identified for minimum or transition state. The relative energies were refined using the G2M(RCC,MP2) method,[22] which approximates the coupled cluster[23] CCSD(T)/6-311+G($3df,2p$) energies with B3LYP/6-311G(d,p) ZPE corrections. The GAUSSIAN 98[24] and MOLPRO 2000[25] programs were employed for the potential energy surface computations. The accuracy of our calculations is expected to be about ±5 kJmol^{-1}.

IV. RESULTS

A. Laboratory data

Reactive scattering signal was detected at mass to charges $m/e=39$ (C$_3$H$_3^+$), 38 (C$_3$H$_2^+$), 37 (C$_3$H$^+$), and 36 (C$_3^+$) in the C–C$_2$H$_4$ system and at $m/e=53$–48 (C$_4$H$_5^+$–C$_4^+$) (C–C$_3$H$_6$ experiments), cf. Figs. 1 and 2 for selected data sets. TOF spectra at the fragment mass to charge regions 38–36 and 52–48 show identical patterns compared to $m/e=39$ and 53, respectively. This suggests that these signals originate in cracking of the parent in the ionizer. Therefore, only an atomic hydrogen elimination pathway is observable in both reactions. The molecular hydrogen ejection is absent within our detection limits ($<1\%$). We would like to stress that a possible methyl group elimination could not be investigated; the detection of the C$_3$H$_3$ counter fragment in the C–C$_3$H$_6$ system failed due to the inherent high background at $m/e=39$ from electron impact dissociation of the propylene reactant in the ionizer.

TOF spectra at distinct angles can be integrated to yield the laboratory angular distribution (LAB). A typical set of data is shown in Fig. 1 for the C–C$_2$H$_4$ reaction at m/e $=39$ (C$_3$H$_3^+$). All LAB distributions are very broad and extend 65°–55° in the scattering plane as defined by both beams. This result suggests that the energy release into the

1320   J. Chem. Phys., Vol. 116, No. 4, 22 January 2002

Kaiser *et al.*
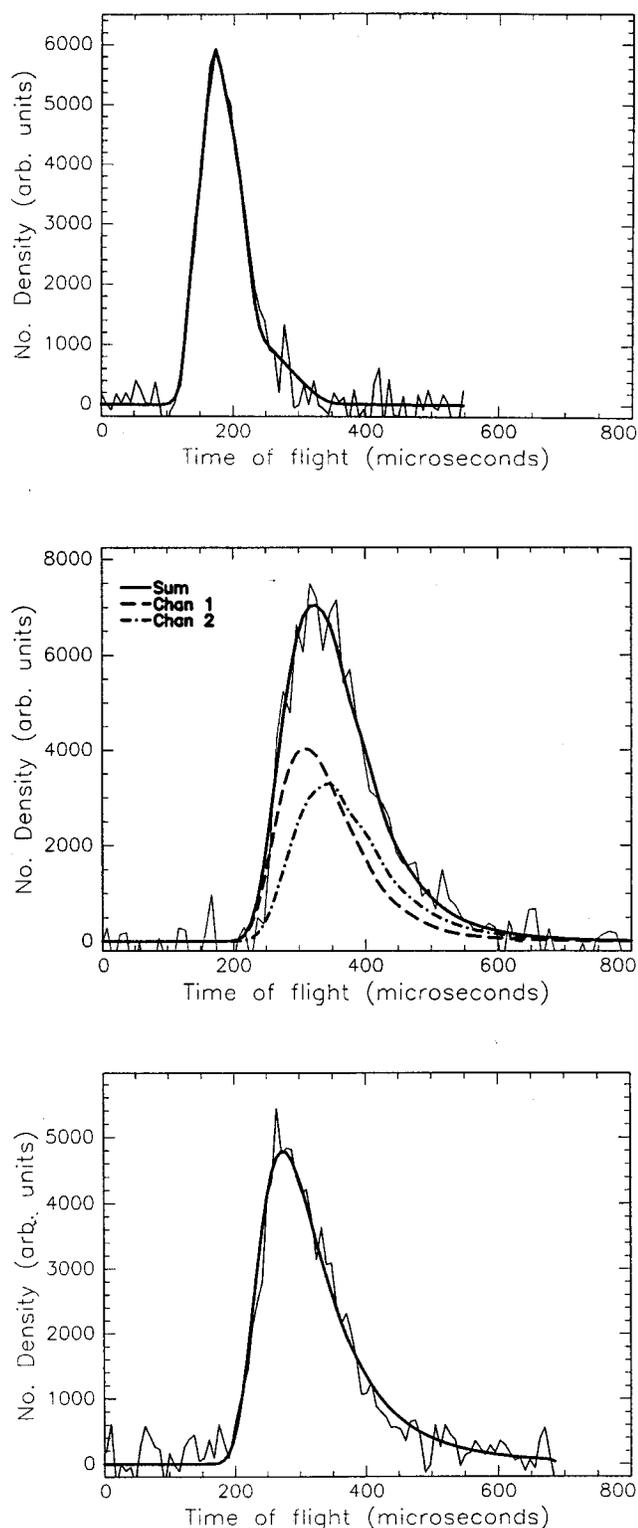
FIG. 2. Top: Time-of-flight spectra for the reaction $C(^1D) + C_2H_4(X\ ^1A_g)$ at $m/e = 39$ recorded at a collision energy of 104 kJmol^{-1} at a laboratory angle of 20.0°. The thin solid line represents the experimental data, thick solid line the fit. Middle: Time-of-flight spectra for the reaction $C(^3P_j) - C(^1D) + C_3H_6(X\ ^1A')$ at $m/e = 53$ recorded at a collision energy of 48 kJmol^{-1} at a laboratory angle of 37.5°. The thin solid line represents the experimental data, dashed and dashed–dotted lines the calculated distributions for $C(^3P_j)$ and $C(^1D)$, and the solid line the sum of the fit. Bottom: Time-of-flight spectra for the reaction $C(^1D) + C_3H_6(X\ ^1A')$ at $m/e = 53$ recorded at a collision energy of 63 kJmol^{-1} at a laboratory angle of 37.5°.
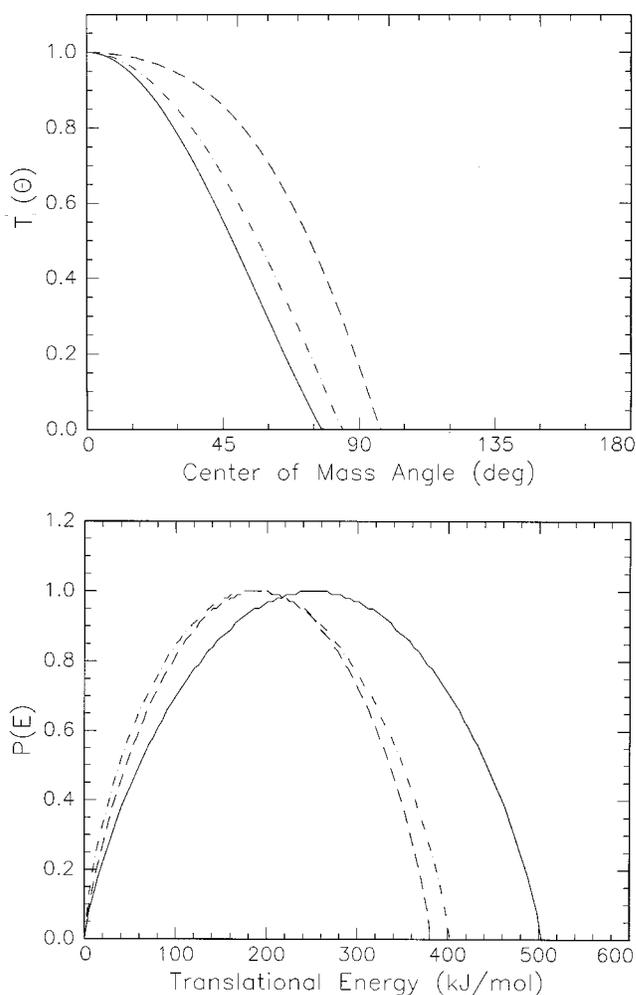
FIG. 3. Best fit center-of-mass angular flux distributions (top) and translational energy distributions (bottom) for the reactions $C(^1D) + C_2H_4(X\ ^1A_g)$ at $m/e = 39$ recorded at a collision energy of 104 kJmol^{-1} (solid lines), $C(^1D) + C_3H_6(X\ ^1A')$ at $m/e = 53$ recorded at a collision energy of 48 kJmol^{-1} (dashed lines), and $C(^1D) + C_3H_6(X\ ^1A')$ at $m/e = 53$ recorded at a collision energy of 63 kJmol^{-1} (dashed–dotted lines).

translational degrees of the products is large. Finally, the LAB distributions depict distribution maxima in the "forward" directions with respect to the carbon beam at 15.0°, 35.0°, and 27.5° compared to the center-of-mass angles of 21.9°±0.8° (C–C$_2$H$_4$), 41.2°±0.5° (C–C$_3$H$_6$), and 37.3° ±0.9° (C–C$_3$H$_6$). These data suggest either indirect scattering dynamics through osculating complexes or direct reaction mechanisms.

B. Center-of-mass functions

The center-of-mass translational energy and angular distributions are presented in Fig. 3. In case of the C–C$_2$H$_4$ system, fits of the TOF spectra and LAB distribution could be achieved with one channel assuming that the scattering signal of $m/e = 39$ emerges from the reaction of $C(^1D)$ only. The reaction with C$_3$H$_6$ is more complex: At lower collision energy, the experimental data must be fit with two channels arising from reactions of ground-state carbon and electronically excited carbon. As the collision energy rises, a reasonable fit could be achieved with a primary beam consisting
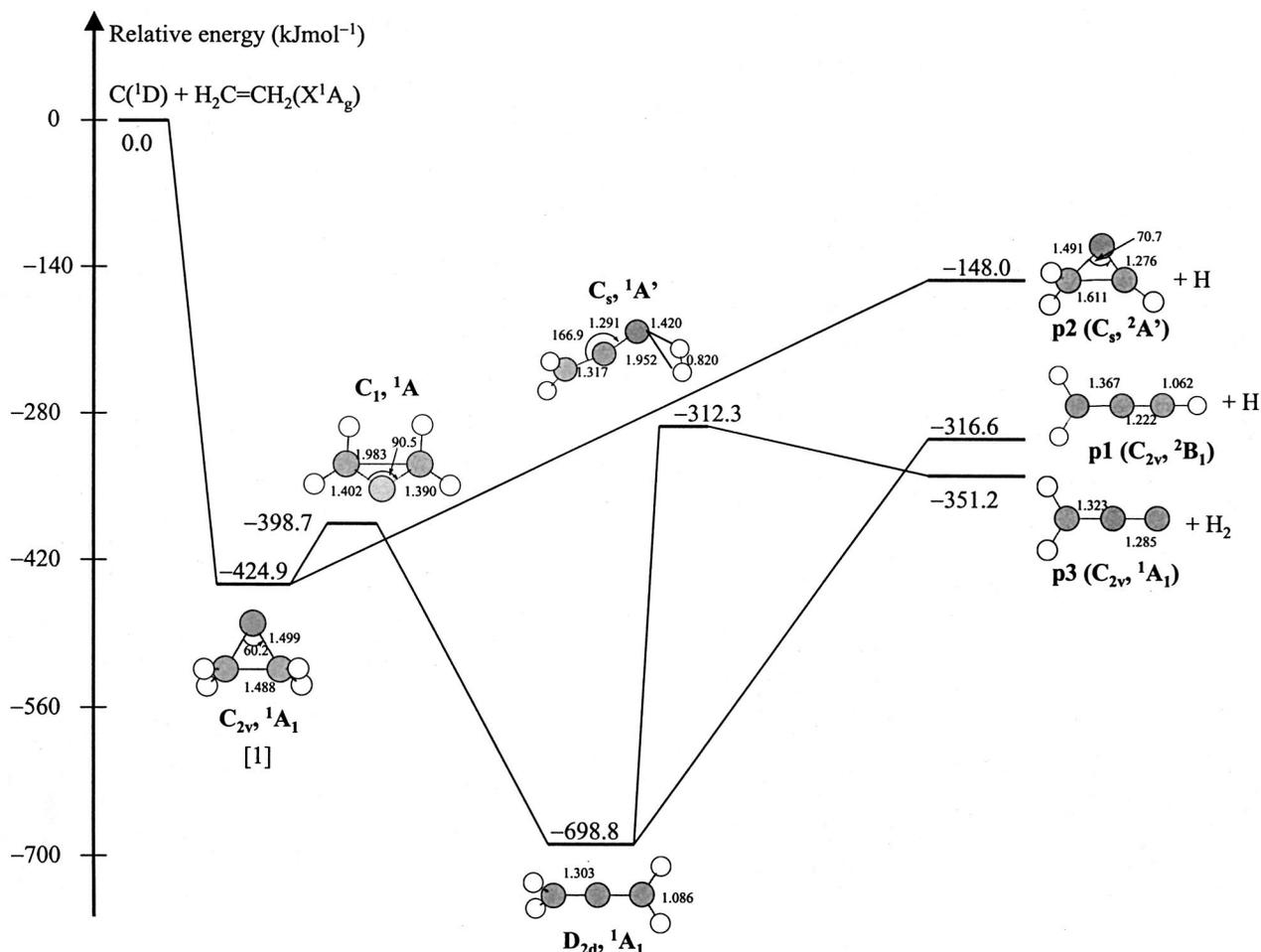
FIG. 4. Schematic representation of the singlet C_3H_4 potential energy surface and structures of reactants, potentially involved singlet C_3H_4 collision complexes, and products. Bond lengths are given in Angstrom, bond angles in degrees.

solely of C(^1D). The reaction dynamics of ground-state carbon atoms with propylene were discussed extensively in Ref. 14, and we limit the discussion to those pathways arising from electronically excited carbon atoms.

Best fits of TOF spectra and LAB distributions of the C(^1D)+C_2H_4 and C(^1D)+C_3H_6 reactions were achieved with $P(E_T)$s extending to the maximum translational energy $E_{max}=500$ kJmol^{-1} (C_2H_4), 380 kJmol^{-1} (C_3H_6), and 400 kJmol^{-1} (C_3H_6). Extending or cutting the fits by up to 50 kJmol^{-1} does not change the fit. These limits can be investigated to calculate the reaction energies. Here, the maximum available energy is simply the sum of the reaction exothermicity plus the collision energy; if we subtract the latter from E_{max}, experimental exothermicities of 396 kJmol^{-1} (C_2H_4) and 332–337 kJmol^{-1} (C_3H_6) are obtained.

We compare now our experimental data with the theoretically predicted reaction energies to form the propargyl (−317 kJmol^{-1}) and the less stable cyclopropen-1-yl radical (−148 kJmol^{-1}) (Fig. 4). This suggests that at least the thermodynamically most stable propargyl isomer is formed in our experiment.[26] The computations on the C_4H_6 PES indicate that the formation of the 1-methylpropargyl (CH$_3$CCCH$_2$), 3-methylpropargyl [HCCCH(CH$_3$)], and 1,3-butadienyl-2 radicals (H$_2$CCHCH$_2$) are exothermic by 328,

317, and 320 kJmol^{-1} (Fig. 5). Since all three energies are very close to our experimental data of 332–337 kJmol^{-1}, we cannot assign the C_4H_5 isomer(s) formed in the crossed beam experiment now, but the chemical reaction dynamics remain to be ascertained. Nevertheless, these energetics present solid evidence that our primary beam contains carbon in its first electronically excited C(^1D) state; the reactions with ground-state carbon, C(^3P_j) are 122 kJmol^{-1} less exothermic. Finally, it is worth to mention that all three $P(E_T)$s peak far away from zero translational energy at about 240–280 kJmol^{-1} (C_2H_4) and 180–200 kJmol^{-1} (C_3H_6). The averaged fraction of energy released into translational motion of the products is about 55%–65%.

The shape of the $T(\theta)$s correlate nicely with the forward peaking of the LAB distribution. All center-of-mass angular distributions show primarily flux in the forward hemisphere with respect to the primary beam. These distributions peak at 0° and depict no intensity at angles larger than 70° (C_2H_4) and 85°–100° (C_3H_6). The latter system deserves particular attention. With rising collision energy, the forward scattering increases slightly from 100° to 85°. These data strongly suggest that the reaction proceeds via direct reaction dynamics (stripping mechanism) within a time scale of less than 0.1 ps. In the following discussion we will discriminate if the poten-
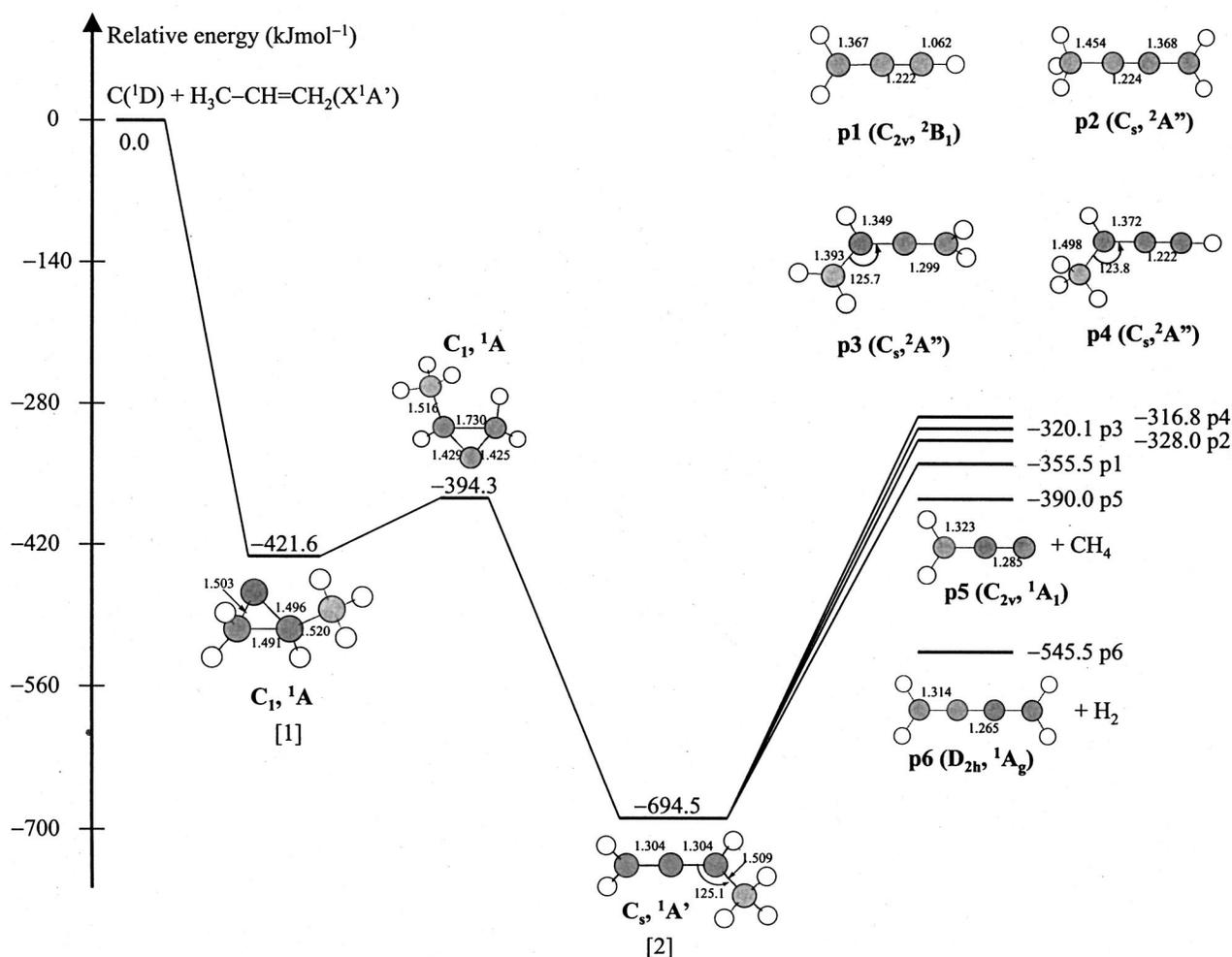
FIG. 5. Schematic representation of the singlet C_4H_6 potential-energy surface and structures of reactants, potentially involved singlet C_4H_6 collision complexes, and products. Bond lengths are given in Angstrom, bond angles in degrees.

tial energy surface (PES) involves highly rovibrationally excited collision complex(es) in a very shallow potential energy well, or only a transition state along the reaction coordinate without a bound intermediate. All $T(\theta)s$ reveal further that the initial and final angular momenta $\mathbf{L}$ and $\mathbf{L}'$ are strongly correlated.

C. The singlet C_3H_4 and C_4H_6 ab initio potential energy surfaces

The calculated potential energy diagram for the $C(^1D) + C_2H_4$ reaction is illustrated in Fig. 4. The reaction starts with a barrier-less addition of the attacking carbon atom to the double C=C bond of ethylene to produce the singlet cyclopropylidene intermediate,[1] 425 kJmol^{-1} below the reaction. Cyclopropylidene undergoes a ring opening leading to allene[2] via a barrier of 26 kJmol^{-1}. The barrier height obtained by the present G2M(RCC,MP2) calculations is slightly higher than the CCSD(T)/TZ2P//B3LYP/TZP value of 18.8 kJmol^{-1} value reported by Bettinger et al.[27] Allene resides in a deep potential well, 699 kJmol^{-1} lower in energy than $C(^1D) + C_2H_4$, and can eliminate hydrogen atom to yield the propargyl radical $p1$, $H_2CCCH(X\ ^1B_1)$, without exit barrier or molecular hydrogen producing

$H_2CCC(X\ ^1A_1)$, $p2$, via a barrier of 387 kJmol^{-1}. The transition state for the H_2 elimination lies 312 kJmol^{-1} below the reactants, while the $C(^1D) + C_2H_4 \rightarrow H_2CCCH(X\ ^2B_1) + H$ and $C(^1D) + C_2H_4 \rightarrow H_2CCC(X\ ^1A_1) + H_2$ reactions are computed to be exothermic by 317 and 351 kJmol^{-1}, respectively.

The reaction of $C(^1D)$ with propylene (Fig. 5) also starts with the addition of the carbon atom to the double C=C bond with formation of methylcyclopropylidene. The relative energy of this intermediate with respect to $C(^1D) + C_3H_6$ is 422 kJmol^{-1}, very similar to the energy of cyclopropylidene relative to $C(^1D) + C_2H_4$. Then, the ring opening takes place yielding the 1,2-butadiene intermediate. Both the barrier height (27 kJmol^{-1}) and the relative energy of 1,2-butadiene (695 kJmol^{-1}) are close to the barrier for the ring opening in cyclopropylidene and the energy of allene, respectively. Four decomposition channels of 1,2-butadiene have been considered here. A loss of the hydrogen atom from $C(CH_3)-H$ gives the 1-methylpropargyl radical $p2$, 328 kJmol^{-1} below the reactants. An H elimination from the methyl group produces the 1,3-butadienyl-2 radical $p3$, 320 kJmol^{-1} lower in energy than $C(^1D) + C_3H_6$. A hydrogen splitting from the CH_2 group yields 3-methylpropargyl $p4$ with overall reaction

exothermicity of 317 kJmol^{-1}. Finally, a cleavage of the C–CH$_3$ bond results in the propargyl ($p1$) and methyl radicals and the calculated heat of the C(^1D)+C$_3$H$_6$ →H$_2$CCCH($^2B_1$)+CH$_3$($^2A_2''$) reaction is 356 kJmol^{-1}. Thus, H$_2$CCCH($^2B_1$)+CH$_3$($^2A_2''$) are the most exothermic reaction products. All the four dissociation channels depict no exit barriers.

V. DISCUSSION

A. The reaction pathway

Our crossed beam experiments and electronic structure data were combined to unravel the underlying chemical dynamics on the reaction of C(^1D) with ethylene and propylene. These considerations strongly suggest that C(^1D) initially adds to the olefinic bond of ethylene and propylene to form cyclopropylidene, c-C$_3$H$_4$(X $^1A_1$) (Fig. 4) and methylcyclopropylidene, c-C$_3$H$_3$CH$_3$ (X ^1A) (Fig. 5). No evidence of an insertion of the carbon atom into any C–H or C–C was found. This can be likely attributed to the larger cone of acceptance of the olefinic π-bonds compared to the σ-bonds. The three-membered intermediates were found to ring open in a symmetry-allowed concerted reaction to form allene, H$_2$CCCH$_2$(X $^1A_1$), and 1,2-budadiene, H$_2$CCCH(CH$_3$)(X $^1A'$), respectively. The electronic structure calculations suggest that allene and 1,2-butadiene are strongly bound and reside in potential energy well of 699 and 695 kJmol^{-1} with respect to the reactants. Despite this strongly bound intermediates which would imply indirect scattering dynamics with forward–backward symmetric angular distributions, the experimental data demonstrate forward scattered products and typical stripping mode behavior in the spectator limit dominated by attractive interaction of both reactants and large impact parameters leading to the reaction. However, no reaction pathway was found which connects the C(^1D)–C$_2$H$_4$ and C(^1D)–C$_3$H$_6$ reactants directly via a single transition state in each reaction to the H–C$_3$H$_3$ and H–C$_4$H$_5$ products. Therefore we have to conclude that the allene and 1,2-butadiene complexes are highly rovibrationally excited, and do not experience the deep potential energy well. Therefore, the C(^1D) simply ''picks up'' the hydrocarbon unit and transports it into the ''forward'' direction after ring opening; the H atom must recoil in the backward direction to account for angular momentum conservation. This is strongly documented in our experimental data as a significant correlation of the initial and final angular momentum **L** and **L**$'$ was found. Based on these findings, the reaction occurs in a time scale of less than about 0.1 ps. This results in an incomplete energy randomization in the decomposing complexes H$_2$CCCH$_2$ and H$_2$CCCH(CH$_3$)—as verified experimentally—in a significant fraction of available energy channeling into translational energy of the products (55%–65%). The direct nature of both reactions is reflected in the center-of-mass translational energy distributions peaking well away from zero. Since the potential energy surfaces document no exit barrier for the H atom loss pathways, any indirect dynamics should have resulted in $P(E_T)s$ peaking at zero or at least close to zero translational energy.

We try now to identify the reaction products. The experi-

mental and theoretical reaction energies as obtained in the C(^1D)–C$_2$H$_4$ system to form C$_3$H$_3$ isomers plus atomic hydrogen strongly suggest that at least the thermodynamically most stable propargyl isomer, C$_3$H$_3$(X $^2B_1$), is formed upon C–H bond rupture in the highly rovibrationally excited allene intermediate.[28] The time scale of this reaction of <0.1 ps suggests that H atom migrations do not take place. However, we cannot rule out that the cyclopropen-1-yl isomer which can be synthesized via H atom loss from a loosely bound, rotationally and vibrationally excited cyclopropylidene structure, might represent an additional product. This C$_3$H$_3$ isomer is about 168 kJmol^{-1} less stable than the propargyl radical. In case of the reaction of electronically excited carbon atoms with propylene, the situation is more complicated as the reaction energies suggest the formation of 1-methylpropargyl (CH$_3$CCCH$_3$), 3-methylpropargyl [HCCCH(CH$_3$)], and/or 1,3-butadienyl-2 radicals (H$_2$CCHCH$_2$). However, the direct reaction dynamics and short time scale of the reaction makes it unlikely that the energy gets completely randomized and hence can channel via three bonds into the C–H bond of the methyl group. Therefore, the 1,3-butadienyl-2 radicals (H$_2$CCHCH$_2$) might be ruled out, and the 1-methylpropargyl (CH$_3$CCCH$_2$) and 3-methylpropargyl [HCCCH(CH$_3$)] radicals are the likely reaction products. However, we like to stress that a possible methyl group elimination could take place as well. Finally, we like to discuss alternative exit channels. The experiments did not detect any H$_2$ (C$_2$H$_4$–C$_3$H$_6$) or CH$_4$ (C$_3$H$_6$) loss pathways. Although these reactions are strongly exothermic (cf. Figs. 4 and 5), the short time scale of the reaction likely inhibits a complete energy randomization and hence a channeling of energy into the reaction coordinate of the H$_2$ and CH$_4$ losses.

B. Comparison with bulk reactions

Previous information on the C(^1D)–C$_2$H$_4$-system was derived from radioactive tracer studies of ^{11}C($^1D_2$) recoil atom reactions with ethylene and ethylene–neon mixtures under bulk conditions.[29] These bulk studies suggested an addition of thermal ^{11}C(^1D) atoms to the olefinic double bond to singlet cyclopropylidene followed by ring opening to form allene. The vibrationally excited molecule could be stabilized via a third body collision to allene. The postulation of an allene intermediate is fully supported by our crossed beam experiments.

VI. CONCLUSIONS

The reactions of electronically excited carbon atoms, C(^1D), with two olefins, ethylene and propylene, were investigated employing the crossed molecular beam technique. Both reactions proceed via direct stripping dynamics via an initial addition of the carbon atom to the π-orbital to form cyclopropenyl and methylcyclopropenyl intermediates which ring open to highly rovibrationally, short lived allene and 1,2-budadiene intermediates, respectively. These structures were found to decompose via atomic hydrogen emission to give the propargyl radical C$_3$H$_3$(X $^2B_1$) (C$_2$H$_4$ reaction) and 1-methylpropargyl and 3-methylpropargyl isomers (C$_3$H$_6$ re-

action). The identification of two methylpropargyl isomers holds far reaching consequences for the formation of the first methyl substituted aromatic ring in circumstellar envelopes of carbon stars and combustion flames. Previously, the dimerization of two propargyl radical has been postulated as a route to form benzene.[5] Based on this reaction pathway, the radical–radical reaction of propargyl with 1-methylpropargyl or 3-methylpropargyl might form toluene via isomerization of the initial chain intermediates; likewise a recombination of two methylpropargyl radicals is anticipated to give *o*- and *p*-xylenes (*o*- and *p*-dimethylbenzenes); the formation of m-xylene is not possible.[30] These processes are currently under investigation.

ACKNOWLEDGMENTS

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