

THE FORMATION OF C₅H₅ ISOMERS AS POTENTIAL KEY INTERMEDIATES TO POLYCYCLIC AROMATIC HYDROCARBON-LIKE MOLECULES

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ABSTRACT

The reactions of ground-state atomic carbon with three C₄H₆ isomers, dimethylacetylene, 1,2-butadiene, and 1,3-butadiene, are studied at relative collision energies between 19.3 and 48.6 kJ mol⁻¹ in crossed molecular beam experiments to elucidate the reaction products and chemical dynamics to form C₅H₅ isomers—possible precursor radicals to PAH-like species—in the circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars. Our combined experimental and computational studies show that reactions are dominated by the C(³P_j) versus hydrogen atom exchange to form the 1-methylbutatrienyl radical, H₂CCCCCH₃ (*X*²A''), as well as 1- and 3-vinylpropargyl radicals, HCCCCHC₂H₃ (*X*²A'') and H₂CCCC₂H₃ (*X*²A''), under single-collision conditions. The methyl (CH₃) and vinyl radical (C₂H₃) loss channels to yield the propargyl radical C₃H₃ (*X*²B₂) and *n*-C₄H₃ (*X*²A') are only minor pathways. All reactions have no entrance barrier and are dominated by an addition of the carbon atom to the π electron density of the second reactant via a complex-forming reaction mechanism on the triplet potential energy surface (PES). The decomposing complexes are long lived and reside in a deep potential energy well bound by 360–410 kJ mol⁻¹ with respect to the separated reactants. Tight exit transition states of about 20 kJ mol⁻¹ above the products and strong exothermic reactions of 180–240 kJ mol⁻¹ are common features of the involved PESs. These characteristics make the reactions of atomic carbon with C₄H₆ isomers a compelling candidate to form C₅H₅ isomers in the outflow of AGB stars.

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

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), their cations, anions, and radicals, and alkyl- and oxygen-substituted PAHs (Langhoff 1996; Joblin et al. 1996; Salama, Joblin, & Allamandola 1994; Snow et al. 1998; Le Page et al. 1997; Beintema et al. 1996; Hudgins & Allamandola 1997; Hudgins & Sandford 1998), as well as partially hydrogenated or even dehydrogenated PAHs (Pauzat, Talbi, & Ellinger 1997; Ekern et al. 1997), are among the most ubiquitous species thought to be present in the interstellar medium (ISM). These molecules are believed to be the carriers of diffuse, interstellar absorption bands (DIBs) covering the visible spectrum from 440 nm to the near infrared and may contribute to the infrared (IR) emission features in the spectrum of comet P/Halley (Joblin, Boissel, & de Parseval 1997). PAH-like species might be the emitters of unidentified infrared bands (UIRs) observed at 3030, 2915, 2832, 1612, 1300, 1150, and 885 cm⁻¹ (Cook & Saykally 1998; Duley et al. 1998; Robinson, Beegle, & Wdowiak 1997).

However, despite this significance of PAH (-like) molecules in molecular clouds and outflow of carbon-rich stars, experimentally and theoretically well-defined mechanisms to synthesize these species in the gas phase of the interstellar medium have not been elucidated (Allain, Sedlmayr, & Leach 1997; Sagan et al. 1993). All chemical reaction networks modeling PAH formation suggest a stepwise extension of monocyclic rings via benzene, C₆H₆, phenyl, C₆H₅,

and/or C₅H₅ radicals to polycyclic systems (Marinov et al. 1996, 1997, 1998; Melius et al. 1996). However, even the most fundamental data on the formation of these very first cyclic building blocks are lacking. Therefore, we launched a systematic program to study reaction pathways to form these simple, hydrogen-deficient precursors strongly thought to be involved in the formation of PAHs in extra-terrestrial environments on the most fundamental, microscopic level.

What approach is useful to unravel this question? Recent crossed-beam experiments show that the encounters of atomic carbon, C(³P_j), with unsaturated hydrocarbons ethylene, C₂H₄, acetylene (Kaiser, Lee, & Suits 1996a), C₂H₂, allene (Kaiser et al. 1999a; Mebel, Kaiser, & Lee 2000), H₂CCCH₂, methylacetylene, CH₃CCH (Kaiser et al. 1996b; Mebel et al. 2000), propylene (Kaiser et al. 1997), C₃H₆, and benzene (Kaiser et al. 1999a), C₆H₆, are dominated by a carbon versus hydrogen exchange: atomic carbon was incorporated in the molecule, and a hydrogen atom was emitted. This leads to the general reaction scheme



in which C_nH_m represents an unsaturated hydrocarbon molecule. Therefore, if we select reactions of C₄H₆ with atomic carbon, the formation of C₅H₅ isomers is strongly expected. Current chemical models of PAH formation in outflow of carbon stars as well as combustion flames reveal that these C₄H₆ isomers are indeed intermediately formed in these environments (Castaldi et al. 1996). In this paper we report on the reactions of C(³P_j) with C₄H₆ isomers 1,3-butadiene, dimethylacetylene, and 1,2-butadiene (Fig. 1) employing the crossed molecular beam technique and combining this investigation with electronic structure calculations; these quantum mechanical investigations are useful

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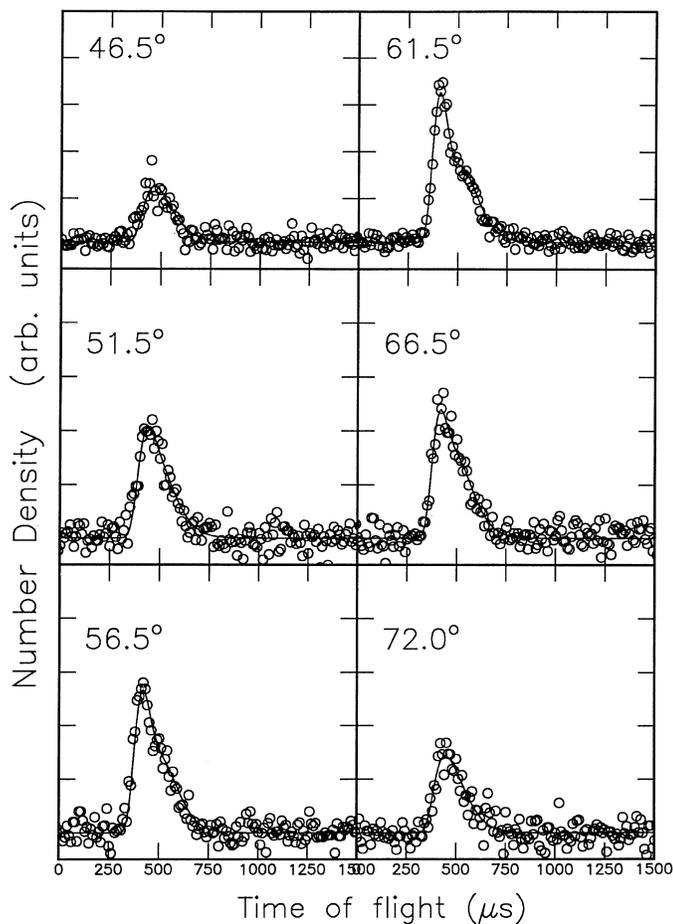


FIG. 3.—Time of flight data of distinct laboratory angles as indicated in Fig. 2. The circles indicate the experimental data, the solid lines the calculated fit.

region of the scattering chamber; experiments were performed at collision energies between 19.3 and 48.6 kJ mol⁻¹. We would like to underline that the experiments are performed at a well-defined *collision energy*, but not at a certain temperature. This is in strong contrast to chemical reactions in, for example, a flow reactor. In our experiments—employing the velocity of both beams and the masses m_A and m_{BC} of the reactants—the collision energy E_C calculates to $E_C = 1/2(m_A \times m_{BC})/(m_A + m_{BC}) \times [v(A)^2 + v(BC)^2]$. Reactively scattered products were detected in the plane defined by two beams using a rotatable detector consisting of a Brink-type electron-impact ionizer, quadrupole mass filter, and a Daly ion detector at distinct laboratory angles between 3° and 72° with respect to the carbon beam. The velocity distribution of the products was recorded using the time of flight (TOF) technique, i.e., recording the time-dependent intensity of ions at one m/e ratio at different laboratory scattering angles. These time of flight spectra are integrated at each angle to obtain the laboratory angular distribution. Information on the chemical dynamics of the reaction was gained by fitting the TOF spectra and the product angular distribution in the laboratory frame (LAB) using a forward convolution routine (Weis 1986). This approach initially assumes an angular flux distribution $T(\theta)$ and the translational energy flux distribution $P(E_T)$ in the center-of-mass system (CM). Laboratory TOF spectra and the laboratory angular distributions were

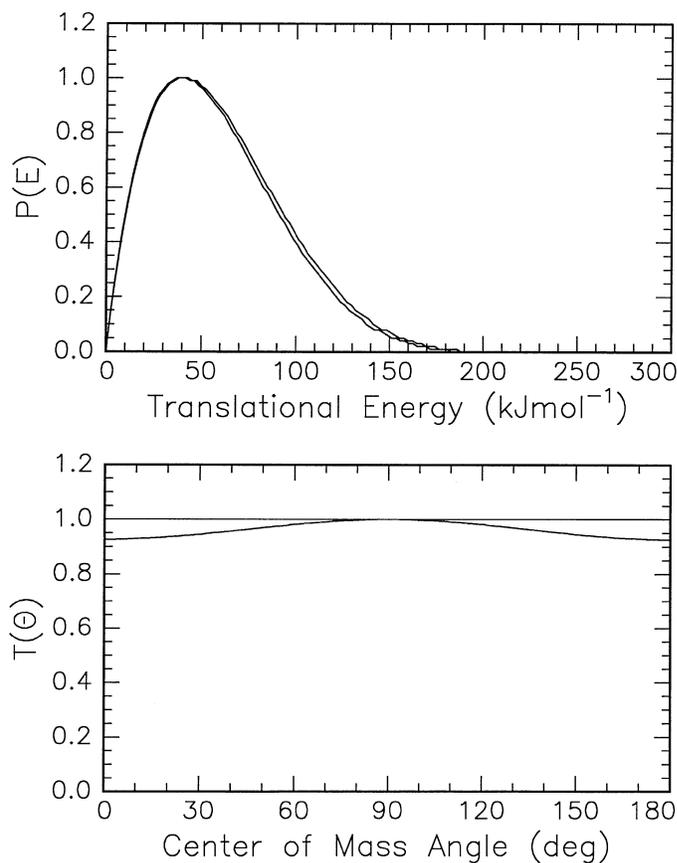


FIG. 4.—Bottom, center-of-mass angular flux distribution and top, translational energy distribution for the reaction $C(^3P_j) + H_2CCCH(CH_3) \rightarrow C_5H_5 + H$ at a collision energy of 20.4 kJ mol⁻¹.

then calculated from these $T(\theta)$ and $P(E_T)$ averaged over the apparatus and beam functions. Best TOF and laboratory angular distributions were achieved by refining adjustable $T(\theta)$ and $P(E_T)$ parameters.

4. RESULTS

4.1. Reactive Scattering Signal

The laboratory angular distribution and distinct TOF spectra of the C_5H_5 product recorded at mass to charge $m/e = 65$ from the reaction of atomic carbon with 1,2-butadiene at a collision energy of 20.4 kJ mol⁻¹ are shown as typical examples of our data in Figures 2 and 3. For all isomers, the $C(^3P_j)$ versus hydrogen atom exchange pathway was observed, and reactive scattering signal was recorded at $m/e = 65$ ($C_5H_5^+$) to $m/e = 60$ (C_5^+) at all collision energies. In the case of 1,3-butadiene, H atom loss can be from C1 or C2, or both. To narrow these possibilities, we performed this experiment with partially deuterated 1,3-butadiene, $D_2CCHCHCD_2$, as well and observed data at $m/e = 69$ ($C_5D_4H^+$), 68 ($C_5D_4^+$ and/or $C_5D_3H_2^+$), 67 ($C_5D_3H^+$), and 66 ($C_5D_3^+$ and/or $C_5D_2H_2^+$). This indicates that at least the carbon versus H atom exchange channel to form C_5D_4H ($m/e = 69$) exists. Since $m/e = 68$ can originate from fragmentation of $m/e = 69$ or from D atom loss, we cannot resolve at the present stage whether a D atom emission occurs. To solve this question, we have to fit the TOF spectra at $m/e = 69$ and 68. Nevertheless, the identification of the C_5H_5 alone under single-collision conditions as present in our experiments and in outflow of carbon stars

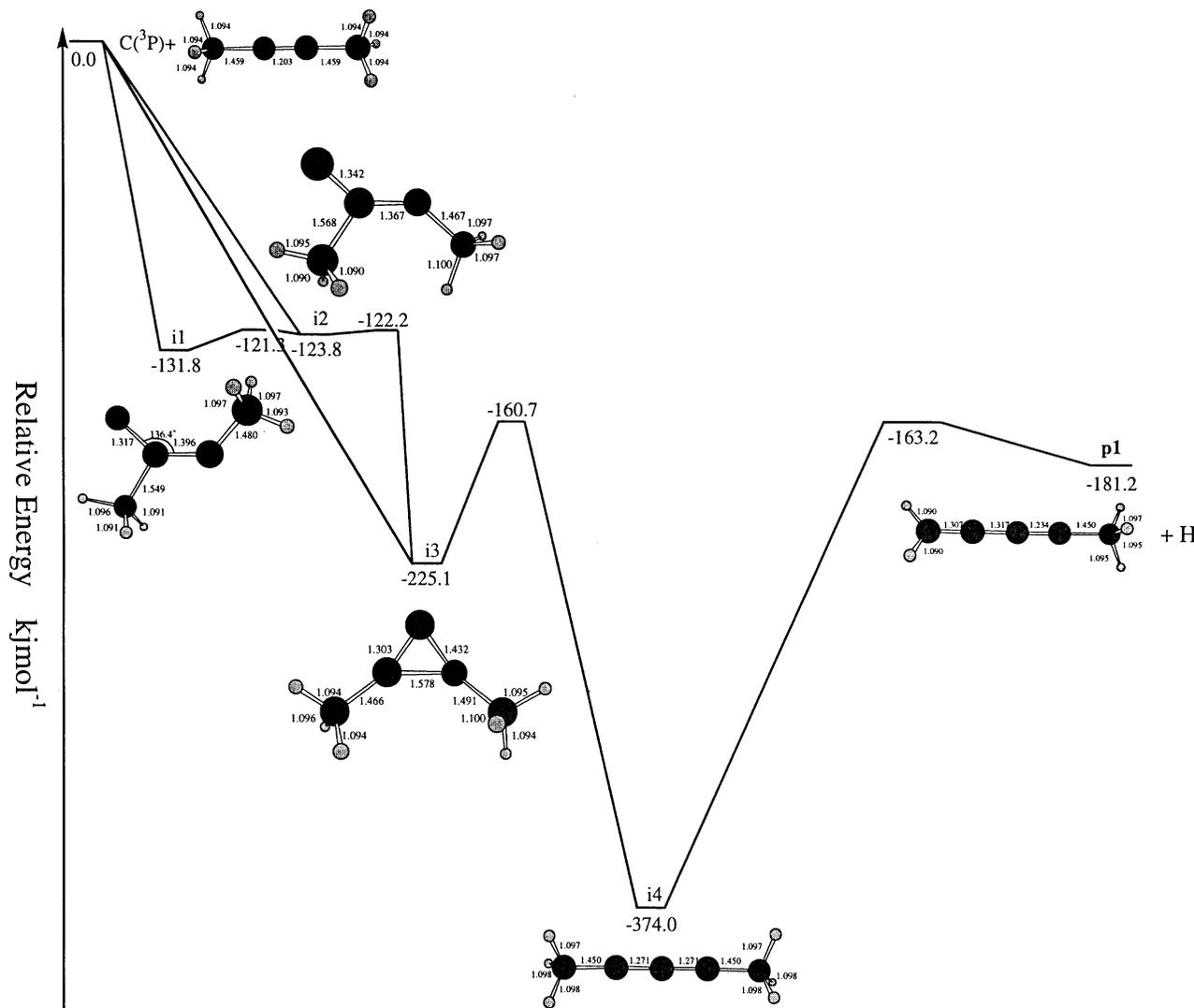


FIG. 5.—Schematic representation of the C₅H₆ potential energy surface relevant in the C(³P_j) + CH₃CCCH₃ reaction. Adapted from Huang et al. (2001). Important bond distances are given in angstrom units and bond angles in degrees.

strongly outlines the potential contribution of these neutral-neutral reactions to the formation of PAH precursor in extraterrestrial environments. Most important, the pattern of TOF data at all lower m/e ratios down to 60 are identical and could be fitted with the same center-of-mass functions as of $m/e = 65$. This means that all lower masses originate from dissociative ionization in the electron impact ionizer. No radiative association channel to C₅H₆ was noticed. Therefore, we must conclude that the rotationally and vibrationally excited reactive intermediates do not survive under our experimental single-collision conditions and hence not in outflow of carbon stars.

4.2. Laboratory Angular Distributions

Figure 2 depicts a typical laboratory angular distribution (LAB) together with the most probable Newton diagram of the C₅H₅⁺ ion at $m/e = 65$ recorded from the reaction of atomic carbon radical with 1,2-butadiene at a collision energy of 20.4 kJ mol^{-1} . The peaking of all LAB distributions at the center-of-mass angle and a forward-backward symmetric shape are common features. Both findings suggest that the reaction advances via a complex-forming reaction mechanism (indirect reactive scattering dynamics).

Furthermore, all distributions are found to be very broad and extend up to 60° in the scattering plane. These results and the C₅H₅ + H product mass ratio of 65 suggest that the center-of-mass translational energy distributions, $P(E_T)$ s, peak away from zero and hence that the reaction has an exit barrier.

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

The center-of-mass translational energy distributions, $P(E_T)$ s, are of great help in unraveling the chemical reaction dynamics. A typical $P(E_T)$ of the C₅H₅⁺ ion at $m/e = 65$ from the reaction of atomic carbon with 1,2-butadiene at a collision energy of 20.4 kJ mol^{-1} is shown in Figure 4. First, we investigate the maximum translation energy E_{max} of all distributions. Since E_{max} is the sum of the reaction exothermicity plus the relative collision energy in our crossed-beam experiments, a subtraction of the collision energy from the experimentally determined E_{max} yields the reaction exothermicity and hence—in the most favorable case—an identification of the isomer product. Here, the best-fit center-of-mass functions give experimental reaction exothermicities of $190 \pm 25 \text{ kJ mol}^{-1}$ (dimethylacetylene), $214 \pm 15 \text{ kJ}$

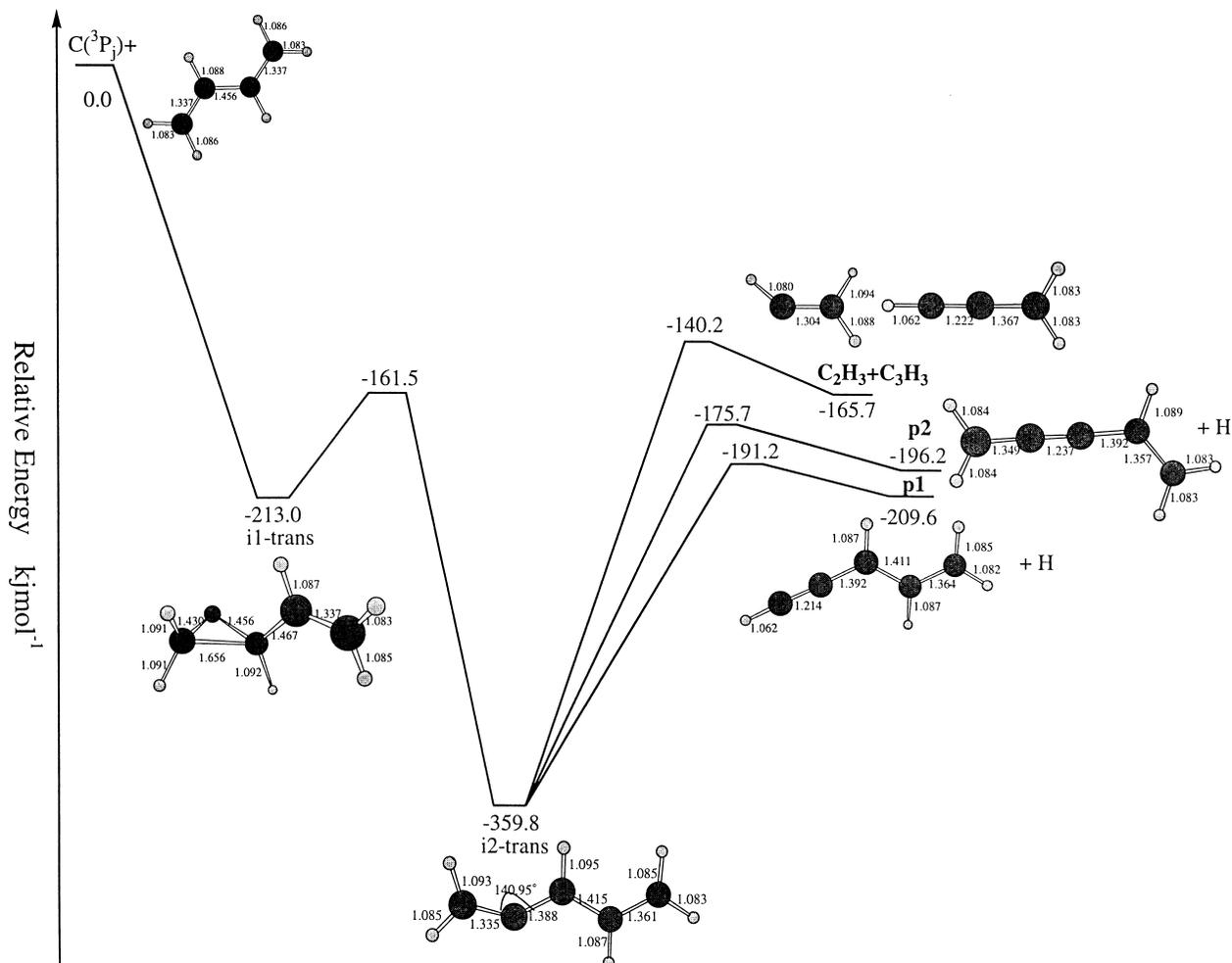


FIG. 6.—Schematic representation of C_5H_6 potential energy surface relevant in the $C(^3P_j) + C_2H_3-C_2H_3$ reaction. *Part 1*: Reaction of trans 1,3-butadiene. *Part 2*: Reaction of cis 1,3-butadiene. Adapted from Hahndorf et al. (2001). Important bond distances are given in angstrom units and bond angles in degrees.

mol^{-1} (1,3-butadiene), and 190 ± 20 $kJ\ mol^{-1}$ (1,2-butadiene). The latter data is very insensitive to the high-energy cutoff, and extending the tail to 270 $kJ\ mol^{-1}$ does not change the fit significantly. Furthermore, the peak position of the $P(E_T)$ yields an order of magnitude of the barrier height in the exit channel. Our $P(E_T)$ s show distribution maxima between 20 and 50 $kJ\ mol^{-1}$, implicating in all cases a significant geometry as well as electron density change from the fragmenting intermediate to the final products (tight exit transition state). We would like to stress that these reactive intermediates are covalently bound molecules from reaction of the unsaturated hydrocarbon with the carbon atom. Under the experimental single-collision conditions, the lifetimes of these intermediates are on the order of 1 ps, and a third-body collision cannot stabilize these internally excited short-lived species in our experiments. In the case of partially deuterated butadiene the TOF at $m/e = 69$ could be fitted with kinematics of an H atom loss and a single $P(E_T)$ showing identical patterns as the translational energy distribution of 1,3-butadiene. However, at $m/e = 68$, two contributions of a D atom loss ($C_5D_3H_2^+$) and fragmentation of the H atom loss isomer to $C_5D_4^+$ are necessary to fit our data. These results show clearly the formation of at least two distinct C_5H_5 isomers in the reaction of atomic carbon with 1,3-butadiene.

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

In this paragraph we interpret the center-of-mass angular distributions of the crossed-beam data (Levine & Bernstein 1987). This information represents the angular-dependent flux distribution an observer would see if he moved with the center-of-mass velocity dwelling in the center of mass of the system. In our experiments, we define the direction of the carbon beam as $\theta = 0^\circ$ and that of the hydrocarbon beam to $\theta = 180^\circ$. Our best-fit functions show that all reactions proceed via indirect scattering dynamics through a collision complex. All distributions are symmetric around 90° and isotropic (“flat”). These symmetric shapes underline that the lifetimes of the complexes are longer than their rotational period, which is on the order of 1 ps. We stress that, in principle, all these reactive intermediates can be stabilized in denser media such as circumstellar envelopes close to the star’s photosphere.

5. DISCUSSION

5.1. Reaction (1): $C(^3P_j) + CH_3CCCH_3$

In this paper, we present a combined experimental crossed-beam and theoretical ab initio investigation to expose the chemical reaction dynamics of the reaction of $C(^3P_j)$ with dimethylacetylene. Figure 5 depicts a simplified

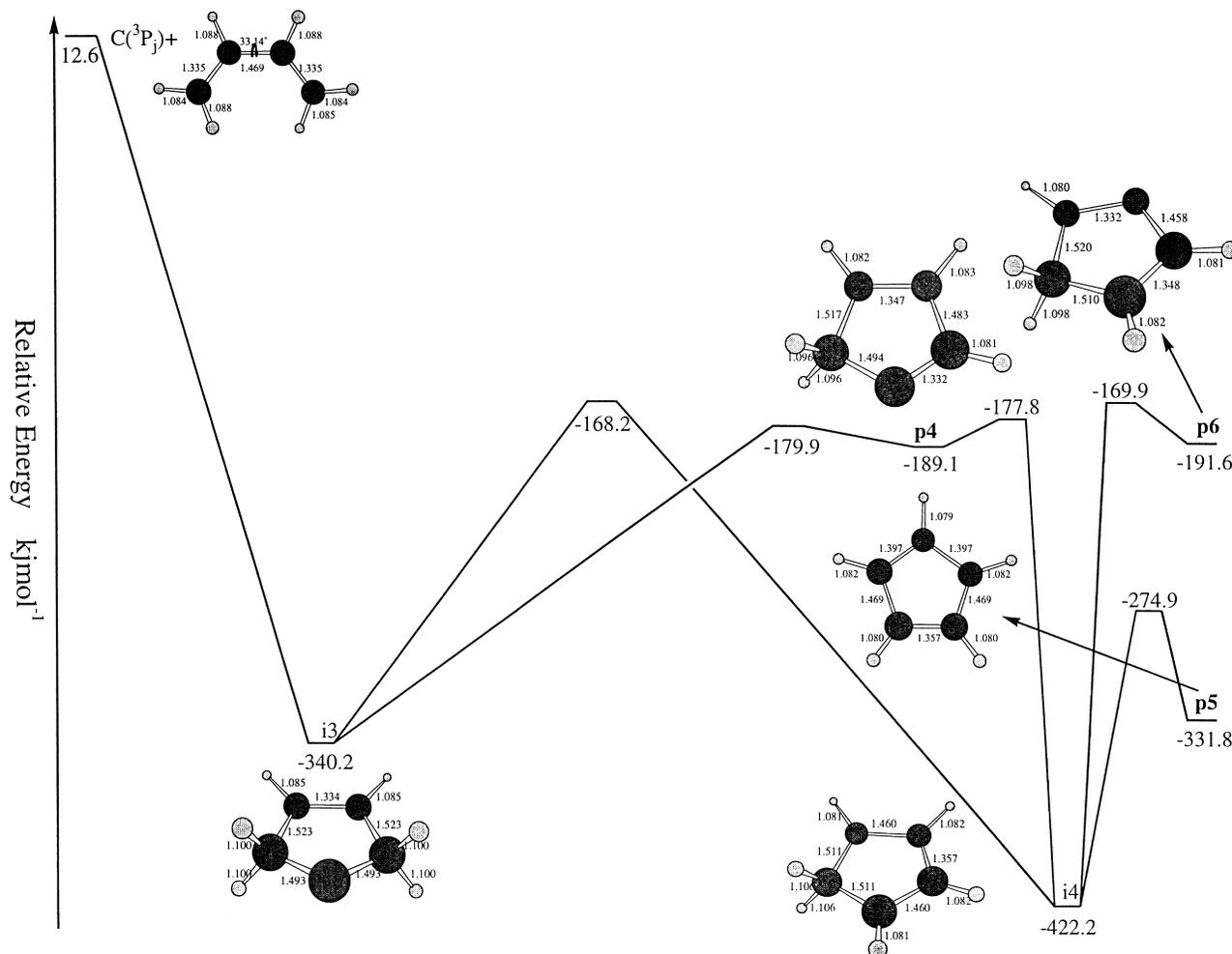


FIG. 6.—Continued

triplet C₅H₆ potential energy surface (PES); see Huang et al. (2001) for a complete PES. Our results show that atomic carbon is not inserted in any C—H or C—C single bond but rather attacks the π electron density of the carbon-carbon triple bond. This pathway has no entrance barrier and gives a dimethylcyclopropenylidene intermediate **i3** in one step via an addition to C1 and C2 of the acetylenic bond or through an addition to only one carbon atom yielding short-lived cis/trans dimethylpropenediylidene intermediates **i1** and **i2** (both C_s point group), respectively, followed by ring closure to **i3**. The attack of the carbon-carbon triple bond is in strong analogy to the reactions of atomic carbon with acetylene and methylacetylene studied earlier in our group (Kaiser et al. 1996a, 1997; Mebel et al. 2000). The cyclic intermediate **i3** ring opens to a dimethylpropargylene radical **i4** (D_{3d} point group); **i4** is the lowest in energy of this part of the triplet C₅H₆ potential energy surface, is stabilized by 374 kJ mol⁻¹ with respect to the separated reactants, and fragments to atomic hydrogen and 1-methylbutatrienyl radical **p1**, H₂CCCCCH₃ (*X*^{2A'}), via a tight exit transition state located about 18 kJ mol⁻¹ above the products. Our experimental exothermicity of 190 ± 25 kJ mol⁻¹ is in strong agreement with the calculated data of 181 kJ mol⁻¹. Likewise, the theoretical prediction of a tight exit transition state is well reflected in a translational energy distribution peaking away from zero. Furthermore, no CH₃ elimination channel is present.

5.2. Reaction (2): C(³P_j) + C₂H₃-C₂H₃

Our calculations depict that the 1,3-butadiene can exist in a trans or cis form; the latter is energetically less favored by 12 kJ mol⁻¹. Both isomers can be interconverted via a 23.5 kJ mol⁻¹ high barrier. In our molecular beam, more than 99.6% of the 1,3-butadiene exists in the energetically more stable trans form. In strong analogy to the previous reaction, atomic carbon is not inserted but interacts with the unsaturated bond via addition without entrance barrier. This pathway forms a triplet vinylcyclopropylidene complex **i1-trans**; see Figure 6 (Hahndorf et al. 2001). The initial collision complex undergoes ring opening to a long-lived vinyl-substituted triplet allene molecule **i2-trans**, which is stabilized by 359.8 kJ mol⁻¹ with respect to the reactants. This complex shows three reaction pathways. Our experimental isotopic studies combined with micro-canonical transition state theory identify two distinct H atom loss channels to form 1- and 3-vinylpropargyl radicals, HCCCHC₂H₃ (*X*^{2A''}), **p1**, and H₂CCCC₂H₃ (*X*^{2A''}), **p2**, through tight exit transition states located about 20 kJ mol⁻¹ above the products; the branching ratio of the 1-versus 3-vinylpropargyl radical is about 8:1. Both reactions are strongly exothermic by 209.6 and 196.2 kJ mol⁻¹. This is in good agreement with our experimental data of 215 ± 15 kJ mol⁻¹. A minor channel of less than 10% is the formation of a vinyl, C₂H₃ (*X*^{2A'}), and propargyl radical C₃H₃ (*X*^{2B₂}).

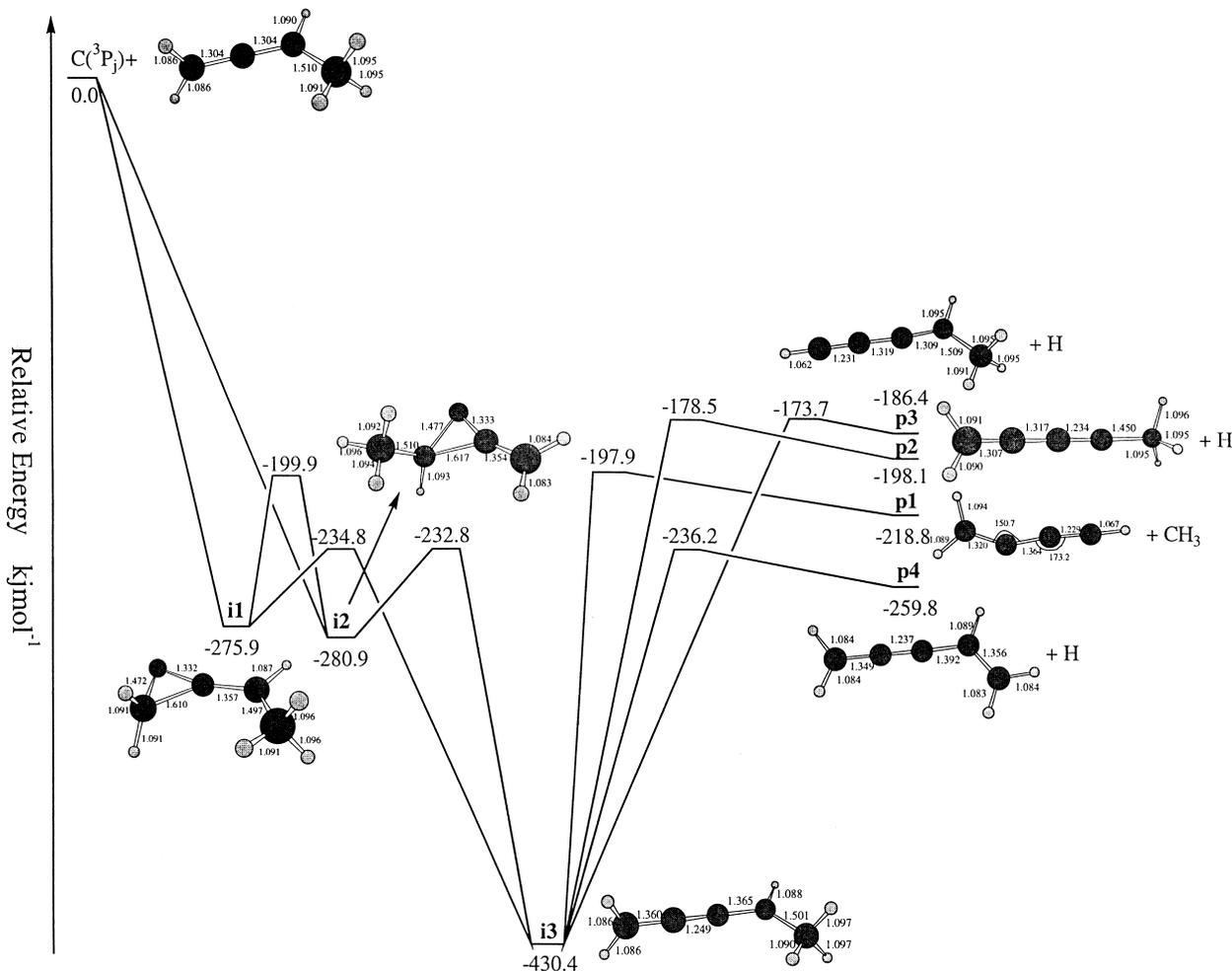


FIG. 7.—Schematic representation of the C_5H_6 potential energy surface relevant in the $C(^3P_j) + H_2CCCH(CH_3)$ reaction. Adapted from N. Balucani et al. (2001, in preparation). Important bond distances are given in angstrom units and bond angles in degrees.

The reader has to keep in mind that our experiments are performed under single-collision conditions; this means that upon a feasible, collision-induced cis-trans isomerization no third-body reaction partner is present. However, in the outflow of carbon stars—close to the photosphere of the central star—this ternary reaction might happen. Therefore, we investigated computationally the product branching ratios for the case when the cyclic intermediate $i3$ is formed in the reaction of the carbon atom with cis 1,3-butadiene; see Figure 6. The results show that $i3$ produces 95.6% of $p4$ and only 4.4% of cyclopentadienyl $p5$.

5.3. Reaction (3): $C(^3P_j) + H_2CCCH(CH_3)$

Similar to the reaction of $C(^3P_j)$ with the 1,3-butadiene isomer, the carbon atom reacts with the olefinic bond in 1,2-butadiene without barrier; see Figure 7. Since the double bonds are not identical, two distinct intermediates can be formed. An attack to C1/C2 yields a tricyclic intermediate $i1$, whereas interaction with C2/C3 forms an $i2$ collision complex. The intermediates are stabilized by 275.9 and 280.9 kJ mol^{-1} , respectively. Both structures can isomerize via a barrier located 199.9 kJ mol^{-1} below the reactants. A common pathway of $i1$ and $i2$ is a ring opening via barriers of about 41 and 48 kJ mol^{-1} to give a triplet methylbutatriene radical $i3$, which is the lowest in energy of this

part of the triplet C_5H_6 PES ($-430.4 \text{ kJ mol}^{-1}$). This intermediate can fragment via H atom or methyl group emission to form the isomers $p1$ – $p4$ in strong exothermic reactions. Our microcanonical transition state calculations show branching ratios of 71.8:2.3:1.4:24.5 for $p4:p3:p2:p1$.

6. ASTROPHYSICAL IMPLICATIONS

Our combined crossed molecular beam experiments and ab initio calculations on the reactions of carbon atoms with three C_4H_6 isomers, dimethylacetylene, 1,2-butadiene, and 1,3-butadiene, are governed by the $C(^3P_j)$ versus hydrogen atom exchange mechanism to form the 1-methylbutatrienyl radical, $H_2CCCCCH_3$ (X^2A'), as well as 1- and 3-vinylpropargyl radicals, $HCCCHC_2H_3$ (X^2A'') and $H_2CCCC_2H_3$ (X^2A''), under single-collision conditions. The methyl (CH_3) and vinyl radical (C_2H_3) loss channels to yield the propargyl radical C_3H_3 (X^2B_2) and $n\text{-}C_4H_3$ (X^2A') are only minor contributors. All reactions have no entrance barrier and are dominated by an addition of the carbon atom to the π electron density via a complex-forming reaction mechanism on the triplet PES. The decomposing complexes are long lived and reside in a deep potential energy well bound by 360–410 kJ mol^{-1} with respect to the reactants. Tight exit transition states of about 20 kJ mol^{-1} above the products and strong exothermic reactions of 180–240 kJ mol^{-1} are common features on the

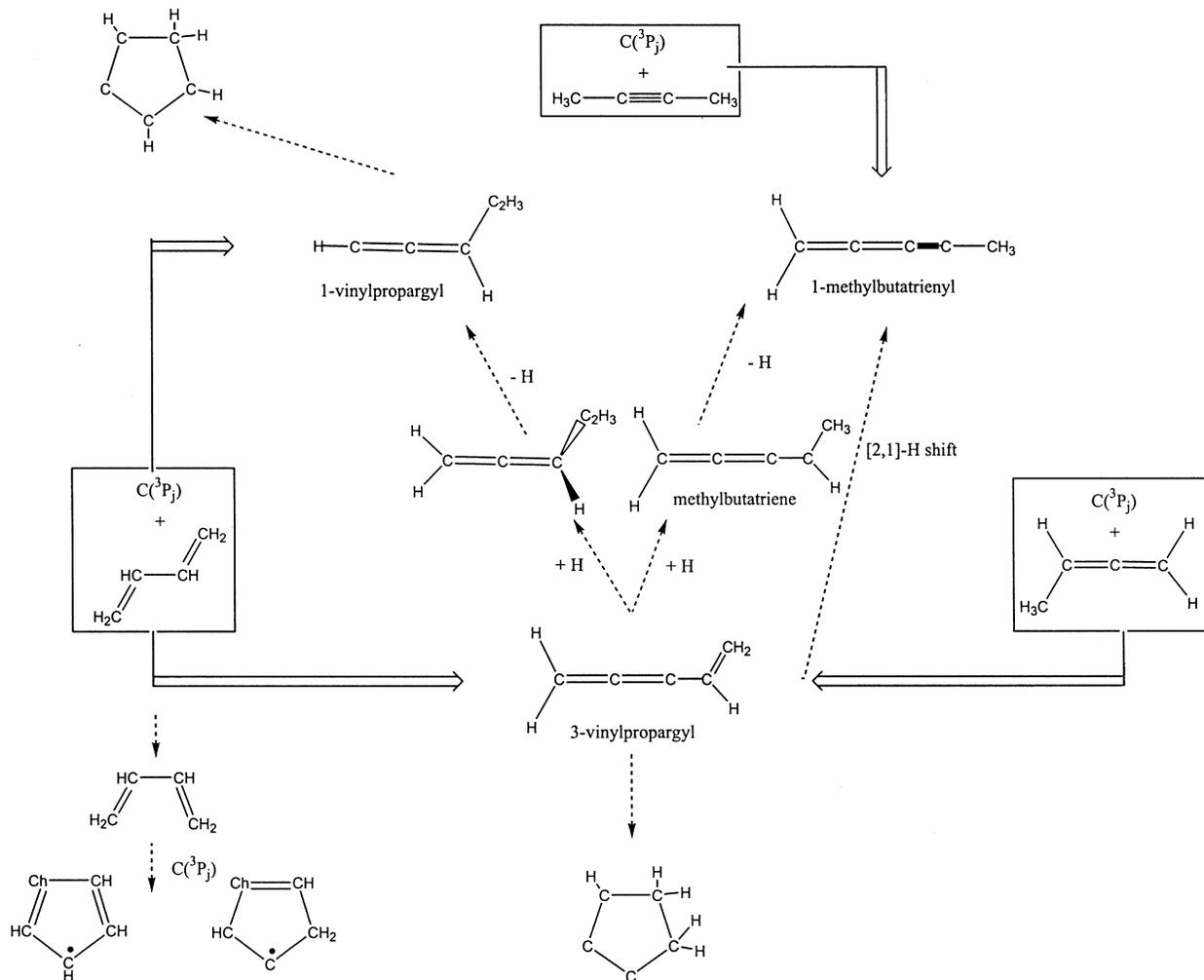


FIG. 8.—Schematic representation of possible conversions of experimentally detected C₅H₅ isomers via H addition–H elimination, cyclization, and H migration.

involved PESs. These characteristics make the reactions of atomic carbon with C₄H₆ isomers a compelling candidate to form C₅H₅ isomers in the outflow of asymptotic giant branch (AGB) stars.

Although our experiments do not verify the formation of the cyclic C₅H₅ radical cyclopentadienyl under single-collision conditions, we have to keep in mind that, in denser environments of the carbon star, additional three-body encounters are feasible. First, we demonstrated that a *cis/trans* isomerization of 1,3-butadiene in high-temperature environments leads to a cyclic C₅H₅ isomer and to a minor amount to cyclopentadienyl. The predominant cyclic radical can isomerize via an H atom addition-elimination process in the circumstellar envelope to the cyclopentadienyl radical; see Figure 6. Second, all identified C₅H₅ chain radicals can be interconverted; see Figure 8: a [2,1] H shift in the 3-vinylpropargyl radical leads to 1-methylbutatrienyl. An H addition to the terminal carbon atom in the 3-vinylpropargyl radical gives singlet methylbutatriene, which can decompose via H atom emission to 1-methylbutatrienyl. Finally, an H addition to the terminal carbon atom in 1-vinylpropargyl followed by a carbon-hydrogen bond rupture at the C3 atom yields the 3-vinylpropargyl radical. Most important, both vinylpropargyl radicals can undergo a collision-induced ring closure to form cyclic C₅H₅ isomers; see Figures 6 and 8. Both isomers can isomerize via H atom addition/

elimination and H migration sequences to form the cyclopentadienyl radical in circumstellar envelopes of carbon stars. Therefore, our combined crossed-beam and computational investigation on the reactions of atomic carbon with C₄H₆ isomers together with ternary isomerizations/H addition-elimination sequences demonstrated explicitly that cyclopentadienyl radicals, one of the precursors to form PAHs in outflow of carbon-rich AGB stars, can be synthesized.

Finally, we would like to point out that our experimental collision energies are roughly equivalent to 1800–4500 K, i.e., those temperatures that exist close to the photospheres of the carbon stars. Supported by our electronic structure calculations, we can conclude that even an extrapolation of the reaction products to interstellar temperatures as low as 10–100 K is feasible since the reactions have no entrance barrier and are exothermic and all involved transition states are well below the energy of the separated reactants.

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