

AN AB INITIO INVESTIGATION OF REACTIONS OF CARBON ATOMS, $C(^3P_j)$, WITH C_2H_4 AND C_3H_6 IN THE INTERSTELLAR MEDIUM

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ABSTRACT

The reactions of ground state atomic carbon $C(^3P_j)$ with the two simplest olefines ethylene (C_2H_4) and propylene (C_3H_6) are investigated computationally to explore the formation of carbon-bearing radicals in extraterrestrial environments. The calculations revealed that the reactions proceed on the triplet surface and are initiated by a barrier-less addition of the carbon atom to the π -bond forming three-membered ring adducts cyclopropylidene and methylcyclopropylidene. Both complexes reside in deep potential energy wells and ring-open to allene and cis/trans 1,2-butadiene, respectively. The decomposition of these intermediates is dominated by an H atom loss to form the propargyl radical ($C(^3P_j)/C_2H_4$) as well as 1-, 3-methylpropargyl, and 1,3-butadienyl-2 radicals ($C(^3P_j)/C_3H_6$). Additionally, triplet 1,2-butadiene can lose a CH_3 group to give a propargyl radical. To a minor amount, triplet allene was found to undergo a hydrogen migration followed by fragmentation of the H_2CCHCH complex to acetylene (C_2H_2) and triplet carbene (CH_2). All reaction channels have no entrance barrier, show exit barriers well below the energy of the reactant molecules, and are strongly exothermic. Therefore, binary collisions of carbon atoms with ethylene and propylene present compelling candidates to form (substituted) propargyl radicals even in cold molecular clouds. Since these radicals are suggested to play an important role in the formation of polycyclic aromatic hydrocarbons, all isomers should be incorporated in future chemical models of interstellar clouds and circumstellar envelopes around carbon stars.

Subject headings: astrochemistry — ISM: molecules — molecular processes

1. INTRODUCTION

Atomic carbon is ubiquitous in the interstellar medium (ISM), and the $609 \mu m$ $^3P_1-^3P_0$ transition has proven a valuable probe to detect $C(^3P_j)$ in circumstellar envelopes of evolved stars IRC + 10216 and α Orionis (Keene et al. 1993; van der Veen et al. 1998), in molecular clouds Orion A (Ikeda et al. 1999) and TMC-1 (Flower et al. 1994; Schilke et al. 1995; Maezawa 1999), and toward the protoplanetary nebulae CRL 618 and CRL 2688 (Young 1997). In the last few years, reactions of carbon atoms with unsaturated hydrocarbons have been suggested to form complex, hydrogen-deficient hydrocarbon radicals in extraterrestrial environments (Herbst et al. 1994; Herbst 1995; Bettens & Herbst 1997; Kaiser et al. 1998; Smith & Rowe 2000). Husain and coworkers demonstrated elegantly that binary collisions of $C(^3P_j)$ with alkynes and olefines—molecules with $C \equiv C$ and $C = C$ bonds, respectively—have no entrance barrier, proceed barrierless, and are very fast. Reaction rate constants were determined to be 10^{-10} – $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at room temperature (Haider & Husain 1993; Husain 1993; Clary et al. 1994). In the following years, kinetical studies of $C(^3P_j)$ reactions were extended to astrophysically relevant temperatures as low as 13 K (Smith & Rowe 2000). These investigations unraveled unambiguously that even at very low temperatures of interstellar clouds, binary reactions of carbon atoms with acetylene (Chastaing et al. 1999, 2001), ethylene (Chastaing et al. 1999, 2001), methyl-acetylene (Chastaing et al. 2000, 2001), allene (Chastaing et al. 2000, 2001), and propylene (Chastaing et al. 1999) are rapid and have large rate constants of 2.87 – $4.76 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

However, the ultimate goal of astrochemistry is to predict observational abundances of hitherto unobserved interstellar molecules. Therefore, not only rate constants, but also the reaction products and structural isomers in particular—molecules with the same chemical formula but different connectivities of atoms like the astrophysically important cyclic and linear C_3H radicals—have to be included into detailed reaction networks modeling chemical processes in interstellar clouds and outflow of carbon stars. So far, kinetic experiments investigated solely the disappearance of the reacting carbon atom. No information on reaction products have been provided yet. Therefore, additional laboratory experiments are necessary to supply these complementary data.

The understanding of the reaction mechanisms of $C(^3P_j)$ with unsaturated hydrocarbons and the assignment of the products requires an intimate knowledge of the involved elementary processes at the most fundamental microscopic level employing the crossed molecular beam approach. These experiments are conducted under well-characterized primary and secondary beam conditions with narrow velocity distributions, well-defined interaction angle, and consequently well-defined collision energy (Kaiser et al. 1998). Most important, crossed beam experiments are conducted under single collision conditions precluding subsequent collisions which could modify the primary products or their energy content. This means that in a binary reaction proceeding via a complex, $A + BC \rightarrow [ABC]^* \rightarrow AB + C$, one species A reacts only with one species BC without collisional stabilization or successive reaction of the initially formed $[ABC]^*$ complex (exclusion of three body

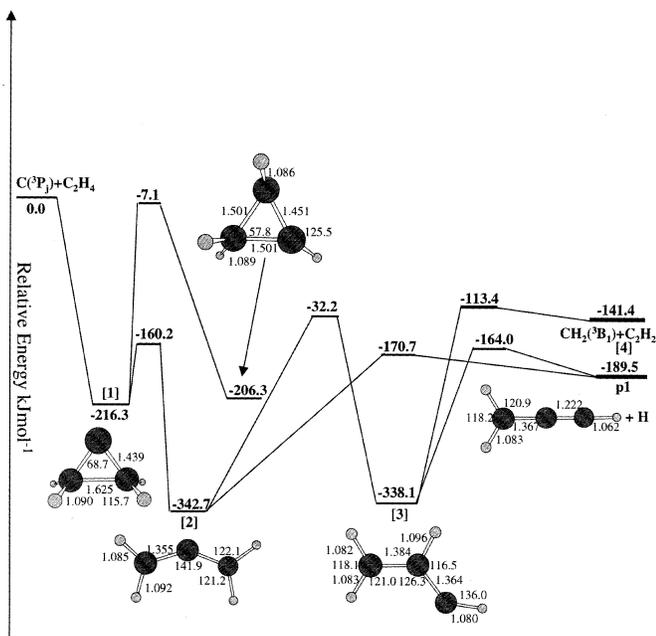


FIG. 1.—Schematic potential energy surface of the reaction of atomic carbon with ethylene. Important bond distances are given in Angstroms, bond angles in degrees.

reactions). This is a crucial requirement because under astrophysical conditions, ternary encounters occur only once in a few 10^9 years and can be neglected considering mean interstellar cloud lifetimes of 10^6 years.

A systematic research program to investigate the reaction products of elementary reactions of atomic carbon with a great variety of unsaturated hydrocarbons on this most fundamental, microscopic level has been engaged recently. During the last five years, crossed beam experiments of $C(^3P_j)$ with acetylene (C_2H_2) (Kaiser, Lee, & Suits 1995, 1996b, 1997a, 1997b, 1999b; Ochsenfeld et al. 1997), methylacetylene (CH_3CCH) (Kaiser et al. 1996c), dimethylacetylene (CH_3CCCH_3) (Huang et al. 2000), the propargyl radical (H_2CCCH) (Kaiser et al. 1997c), the vinyl radical (C_2H_3) (Kaiser et al. 1998), ethylene (C_2H_4) (Kaiser, Lee, & Suits 1996a), propylene (C_3H_6) (Kaiser et al. 1997b), allene (H_2CCCH_2) (Kaiser et al. 1999b; Mebel, Kaiser, & Lee 2000), 1,2-butadiene (Balucani et al. 2001) and 1,3-butadiene (C_4H_6) (Hahndorf et al. 2000), and benzene (C_6H_6) (Kaiser et al. 1999a) have been performed. These experiments provided evidence on the existence of a carbon versus atomic hydrogen exchange pathway (reaction [1]) to form highly unsaturated, cyclic and linear hydrocarbon radicals of significant astrophysical importance such as C_3H and C_3H_2 isomers just to name a few. In the case of acetylene, an elimination of molecular hydrogen to form the tricarbon molecule was observed as well (reaction [2]) (Kaiser et al.

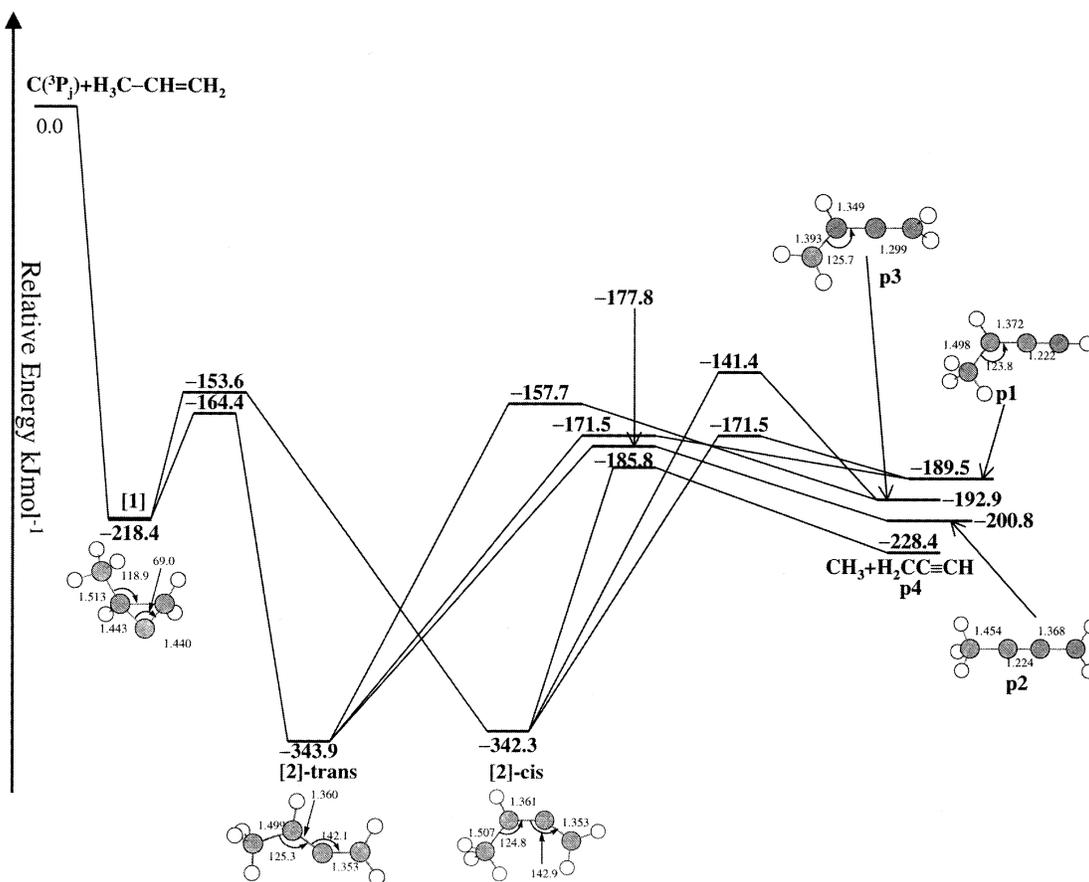
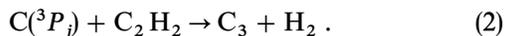
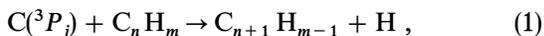


FIG. 2.—Schematic potential energy surface of the reaction of atomic carbon with propylene. Important bond distances are given in Angstroms, bond angles in degrees.

2001; P. Casavecchia 2001, private communication):



However, even sophisticated crossed beam studies experienced two inherent difficulties. First, if distinct structural isomers are formed, it has not been feasible yet to investigate the production of those molecules contributing only a few percent or less to the reactive scattering signal. Second, fragmentation of carbon-carbon bonds and the loss of, for example, a methyl group (CH_3) are difficult to detect with the electron impact ionizer—quadrupole mass spectrometric detector because of the background from the parent molecule. Although these channels might represent only minor pathways, their reaction products are possibly of significant astrophysical interest. We have to recall that the majority of interstellar molecules have been detected via radio astronomy; for example, $c-C_3H_2$, is ubiquitous in the ISM and holds high fractional abundances up to 10^{-8} relative to hydrogen. If, for example, the second astronomically detected isomer, vinylidenecarbene $CCCH_2$, is only a minor reaction product of let us say 1%, it cannot be observed in crossed beam experiments. However, an astronomical observation of fractional abundances as low as 10^{-10} could be feasible. Therefore, to get a complete picture of the reaction products of neutral-neutral reactions involving atomic carbon, the reactions of $C(^3P_j)$ with ethylene and propylene were investigated computationally (see Figs. 1 and 2). These results were then compared to recent crossed molecular beams experiments.

2. THEORETICAL METHODS

The geometries of the reactants, products, relevant intermediates, and transition states were optimized using the hybrid density functional B3LYP method, i.e., Becke's three-parameter non-local exchange functional (Becke 1992) with the non-local correlation functional of Lee, Yang, and Parr (Lee, Yang, & Parr 1988) and the 6-311G(d, p) basis set. Vibrational frequencies, calculated at the B3LYP/6-311G(d,p) level, were used for characterization of stationary points and zero-point energy (ZPE) correction. All the stationary points were positively identified for minimum or transition state. In some cases, geometries and frequencies were recalculated at the MP2/6-311G(d,p) and CCSD(T)/6-311G(d,p) level (Purvis & Bartlett 1982). In order to obtain more reliable energies, we used the G2M(RCC,MP2) method (Mebel, Morokuma, & Lin 1995), a modification of the Gaussian-2 [G2(MP2)] approach. The GAUSSIAN 98 (Frisch et al. 1998), MOLPRO 98 (Werner et al. 1998), and ACES-II (Stanton et al. 1997) programs were employed for the potential energy surface computations. Finally, we predicted the branching ratios of the reactions via RRKM theory at zero-pressure conditions, cf. Chang et al. (1998) for a systematic description.

3. RESULTS AND DISCUSSIONS

3.1. Reaction $C(^3P_j) + C_2 H_4$

Our results indicate that $C(^3P_j)$ attacks the π -orbital of the C_2H_4 molecule barrierless to form a triplet cyclopropylidene intermediate [1]. This addition complex is

deeply bound by $216.3 \text{ kJ mol}^{-1}$ with respect to the reactants and ring opens to triplet allene [2]. An alternative isomerization of [1] via hydrogen migration to cyclopropene can be excluded considering a barrier height of $209.2 \text{ kJ mol}^{-1}$ compared to 56.1 kJ mol^{-1} of the ring opening. Species [2] either ejects a hydrogen atom to yield the propargyl radical **p1** or undergoes a 1,2-H shift to vinylmethylene [3], which in turn gives the propargyl radical **p1** plus H. All transition states involved are lower than the energy of the separated reactants and are accessible energetically. The overall reaction to **p1** was found to be exothermic by $189.5 \text{ kJ mol}^{-1}$. The propargyl radical is determined to be a nearly exclusive product of the $C(^3P) + C_2 H_4$ reaction. Detailed RRKM calculations show that 93% of propargyl comes from fragmentation of triplet allene [2] and 7% from vinylmethylene [3]. A minor pathway (2%) was found to be a decomposition of [4] to $CH_2(^3B_1) + C_2 H_2$; this reaction is exothermic by $141.4 \text{ kJ mol}^{-1}$. The channels leading to C_3H_2 isomers and molecular hydrogen cannot compete.

These results correlate very nicely with recent crossed beam experiments (Kaiser et al. 1996a). Only the atomic carbon versus hydrogen atom replacement was observed; no molecular hydrogen elimination could be sampled. In strong agreement with our electronic structure calculations, a forward-convolution fitting of the experimental data yielded compelling evidence on the formation of the propargyl radical. The reaction dynamics inferred from the experimental data indicate two microchannels, both initiated by attack of the carbon atom to the π -orbital of the ethylene molecule via a loose, reactant like transition state located at the centrifugal barrier. The initially formed triplet cyclopropylidene complex [1] undergoes ring opening to triplet allene and decomposes via hydrogen emission through a tight transition state to the propargyl radical. A second, direct microchannel arises from A-like rotations of the cyclopropylidene complex, followed by ring opening and H-atom elimination.

Both experimental and computational approaches are highly complementary: the crossed beam experiments could not identify the minor contribution from a decomposing vinylmethylene intermediate [3] as well as formation of $CH_2(^3B_1) + C_2 H_2$, whereas our theoretical investigation fails to account for the direct reaction mechanism via triplet allene complexes rotating around their A axis. This is a typical example of synergistic information based on a combined crossed beam and theoretical study of an elementary reaction relevant to chemistry in the interstellar medium.

3.2. Reaction $C(^3P_j) + C_3 H_6$

The computations reveal that the carbon atom adds to the π -orbital of propylene without entrance barrier. This pathway forms a methylcyclopropylidene intermediate [1] on the triplet surface. Species [1] resides in a deep potential energy well of $218.4 \text{ kJ mol}^{-1}$ with respect to the reactants and ring opens to cis/trans triplet 1,2-butadiene [2]. This intermediate shows four decomposition pathways: atomic hydrogen loss to 1- and 3-methylpropargyl (**p1** and **p2**), 1,3-butadienyl-2 (**p3**), and ejection of a methyl group to form the propargyl radical (**p4**). All reactions are highly exothermic by 189.5, 200.8, 192.9, and $228.4 \text{ kJ mol}^{-1}$, respectively. Similar to the reaction of atomic carbon with ethylene, all transition states and exit barriers lie lower than the energy of the separated reactants. Detailed RRKM calculations

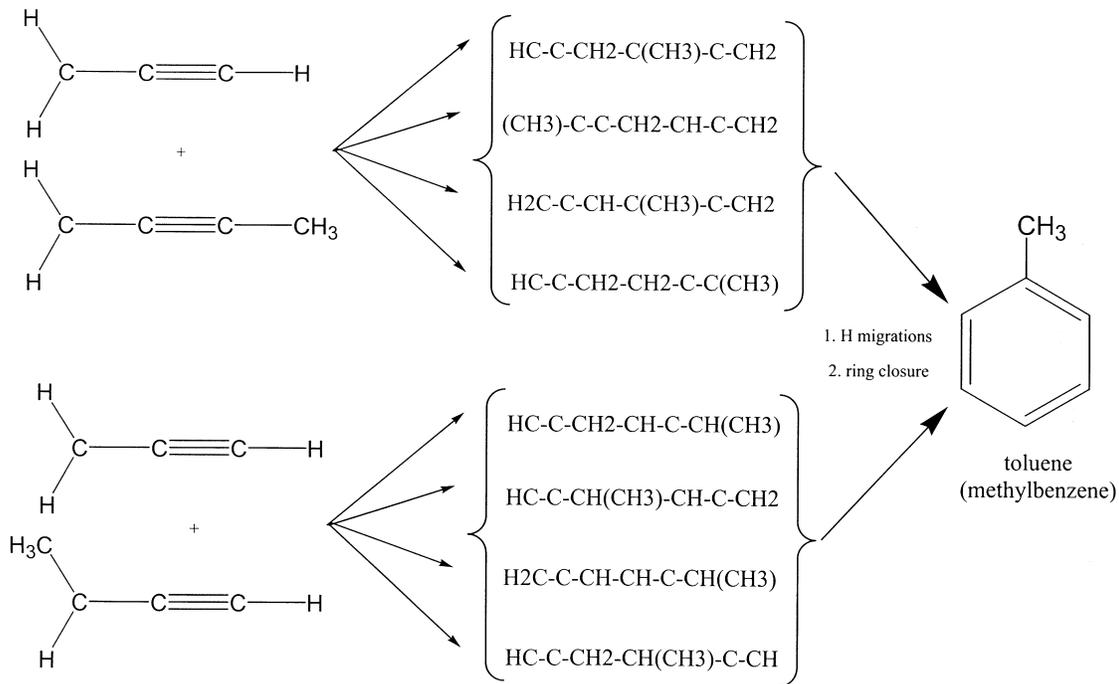


FIG. 3.—Schematic presentation of the role of propargyl and methylpropargyl isomers in the formation of methylbenzene (toluene) via various chain intermediates.

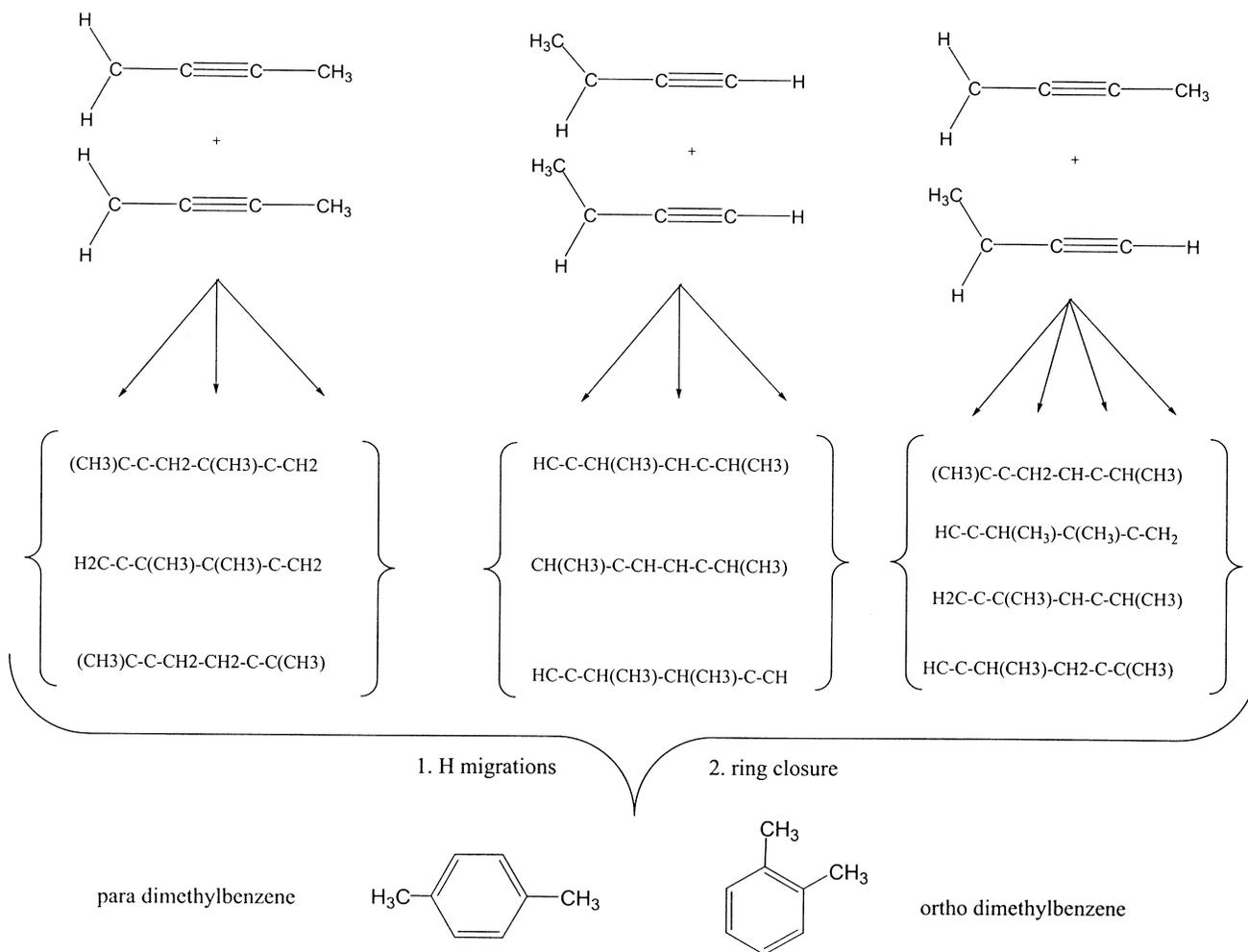


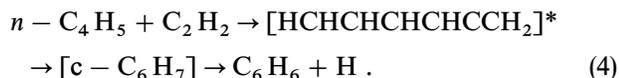
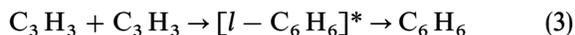
FIG. 4.—Schematic presentation of the role of methylpropargyl isomers in the formation of ortho- and para-dimethylbenzene via various chain intermediates.

depict branching ratios of 30–32:10–12:40–43:16–17 to yield **p1**, **p2**, **p3**, and **p4** slightly depending on the collision energy in the 0–45 kJ mol⁻¹ range.

The computational results complement the crossed beam data on the reaction between ground state carbon atoms and propylene (Kaiser et al. 1997b). Forward-convolution fitting of the experimental data suggested that the reaction proceeded on the lowest ³A surface via an initial addition of the carbon atom to the π-orbital to form a triplet methylcyclopropylidene collision complex followed by ring opening to triplet 1,2-butadiene. Within 0.3–0.6 ps, triplet 1,2-butadiene decomposed through carbon-hydrogen bond rupture to atomic hydrogen and methylpropargyl radicals. Due to the inherent high background, no methyl loss pathway was observed experimentally.

4. ASTROPHYSICAL IMPLICATIONS

The explicit identification of the propargyl radical and three C₄H₅ isomers 1-methylpropargyl, 3-methylpropargyl, and 1,3-butadienyl-2 under single collision conditions represents an important route to form key C3 and C4 hydrocarbon radicals. These species are thought to be involved in the formation of the first aromatic ring molecule, benzene (C₆H₆), in circumstellar envelopes (Westmoreland et al. 1989; Millar & Melius 1992). Previous chemical models of polycyclic aromatic hydrocarbon (PAH) and benzene growth in these environments focussed solely on the role of the propargyl radical and a *n*-C₄H₃ isomer (1,3-butadienyl-1; HCCHCHCH₂) which was not detected in our experiment to yield benzene via an initial radical-radical recombination, followed by H shifts, a ring closure, and H ejection (C₄H₅ reaction only) (Millar & Melius 1992; Wang & Frenklach 1994):



Previously, neither the 1-methylpropargyl nor 3-methylpropargyl radicals has been contemplated to form aromatic, six-membered rings and/or their derivatives. However, the assignment of both methylpropargyl isomers holds far reaching consequences for the formation of the first very first methyl substituted aromatic ring in circumstellar envelopes of carbon stars and post asymptotic giant branch stars. Based on the dimerization pathways of two propargyl isomers (Millar & Melius 1992; Morter et al. 1994), we can predict that the reaction of propargyl with methylpropargyl radicals leads ultimately to toluene—the simplest methyl-substituted benzene ring (Fig. 3). Here the initial addition step to form four distinct linear C₇H₈ isomers is strongly expected to proceed without entrance barrier since both reactants are radicals. Followed by two hydrogen migration and ring closure, toluene (methylbenzene) can be formed. Likewise, the recombination of methylpropargyl isomers as identified in our investigation is strongly predicted to yield dimethyl-substituted benzene isomers (Fig. 4). Most important, these reaction pathways are isomer selective and produce only ortho-dimethylbenzene and para-dimethylbenzene, but no

meta-dimethylbenzene. Hence, updated reaction networks modeling the formation of aromatic molecules and especially PAHs in circumstellar envelopes should include especially 1- and 3-methylpropargyl isomers (synthesis of toluene and dimethylbenzenes), but not only the *n*-C₄H₅ radical which is expected to produce solely benzene. Based on the results, the spectra of the *Infrared Space Observatory* taken toward CRL 618 should be reinvestigated: Cernicharo et al. detected benzene in the circumstellar shell of CRL 618 (Cernicharo et al. 2001), but our investigations suggest that toluene as well as ortho- and para-dimethylbenzene should be present as well.

5. SUMMARY

The reactions of atomic carbon, C(³P_{*j*}), with ethylene (C₂H₄) and propylene (C₃H₆) were investigated computationally to examine the reaction products of atom-neutral collisions relevant to the formation of carbon-bearing molecules in interstellar clouds and outflow of carbon stars. Both reactions proceed on the triplet surface and are initiated by a barrierless addition of the carbon atom to the π-bond forming three-membered ring adducts cyclopropylidene and methylcyclopropylidene. These complexes reside in deep potential energy wells and ring-open to allene and cis/trans 1,2-butadiene, respectively. The decomposition of both complexes is dominated by an H atom loss to form the propargyl radical (C(³P_{*j*})/C₂H₄) as well as 1-, 3-methylpropargyl, and H₂CCH=C=CH₂ radicals (C(³P_{*j*})/C₃H₆); in addition, triplet 1,2-butadiene complexes can lose CH₃ groups to give propargyl radicals. To a minor amount, triplet allene was found to undergo a hydrogen migration followed by fragmentation to acetylene (C₂H₂) and triplet carbene (CH₂). All reaction channels have no entrance barrier, show exit barriers well below the energy of the reactant molecules, and are strongly exothermic. Therefore, the reactions of atomic carbon with ethylene and propylene represent compelling candidates to form (substituted) propargyl radicals even in cold molecular clouds. The potential energy surfaces of the latter are of fundamental importance to infer applications to chemistry in circumstellar envelopes. Close to the atmosphere of the central stars, the intermediates involved can be stabilized via a third-body reaction or react even further. Since all radical products and intermediates are suggested to play an important role in the formation of polycyclic aromatic hydrocarbons, our findings strongly demand the incorporation of these isomers in prospective chemical models of interstellar clouds and circumstellar envelopes around carbon stars. The temperature-dependent rate constants of the title reactions have been explored (Chastaing et al. 1999), branching ratios are now known, the potential energy surfaces have been investigated, and both reaction explored in crossed beam experiments.

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