Crossed beam investigation of elementary reactions relevant to the formation of polycyclic aromatic hydrocarbon (PAH)-like molecules in extraterrestrial environments

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Abstract

The reactions of ground state carbon atoms, $C(^3P_j)$, with benzene, C_6H_6, and phenyl radicals, C_6H_5, with methylacetylene, CH_3CCH, were investigated in crossed beam experiments at collision energies of 21.8 and 140 kJ mol^{-1} to investigate elementary reactions relevant to the formation and chemistry of polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial environments. The $C(^3P_j)$ reaction proceeds via complex formation and gives a cyclic, seven-membered C_7H_5 doublet radical plus atomic hydrogen. This pathway has neither an entrance nor exit barrier, and is exothermic. Together with the experimental verification of the carbon versus hydrogen exchange under single collision conditions, the findings have an important impact on the chemistry of aromatic molecules in interstellar clouds and outflow of carbon stars. Even in the coldest molecular clouds ($T = 10$ K), the benzene molecule can be destroyed upon reaction with carbon atoms, whereas they are resistant toward an attack of oxygen and nitrogen atoms. Since the aromatic benzene unit is ubiquitous in extraterrestrial, PAH-like material, our results suggest that PAHs might react with carbon atoms as well. On the other side, the reaction of C_6H_5 radicals with methylacetylene to form phenylmethylacetylene is direct. Since an entrance barrier inhibits the reaction in cold molecular clouds and in the atmospheres of hydrocarbon rich planets like Jupiter and Saturn and satellites such as Titan, this reaction is expected to play a role in PAH synthesis only in high temperature interstellar environments, such as circumstellar outflows of carbon stars. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and PAH cations, anions, radicals, alkyl and oxygen substituted PAHs (Langhoff et al., 1998; Parisel et al., 1992; Lee and Wdowiak, 1993; Jourdain de Muizon et al., 1990; Joblin et al., 1996a, b; Salama and Allamandola, 1993; Szczepanski and Vala, 1993; Mendoza-Gómez et al., 1995; Salama et al., 1994; De Frees et al., 1993; Snow et al., 1998; Le Page et al., 1997; Salama et al., 1995; Beintema et al., 1996; Hudgins and Allamandola, 1997; Hudgins and Sandford, 1998; Schutte et al., 1990), as well as partially hydrogenated (Bernstein et al., 1996) or dehydrogenated PAHs (Pauzat et al., 1997; Ekern et al., 1997), are among the most ubiquitous species presumed to be present in the interstellar medium (ISM). The early postulation of their interstellar importance as the missing link between small carbon clusters C_2–C_5 and amorphous carbon particles boosted a huge scientific research. Today, neutral and/or ionized PAH species are assumed to comprise 10–20% of the interstellar carbon in molecular form, and are suggested as a carrier of unidentified infrared bands (UIRs) at 3030, 2915, 2832, 1612, 1300, 1150 and 885 cm^{-1} (Cook and Saykally, 1998; Moutou et al., 1995; Joblin et al., 1995; Bernstein et al., 1996; Bregman et al., 1993; Allamandola et al., 1989a, b;

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Blanco et al., 1990; Brenner et al., 1992; Colangeli et al., 1992a, b; Duley and Jones, 1990; Duley et al., 1998; Flickinger and Wdowiak, 1990; Flickinger et al., 1991; Robinson et al., 1997; Schlemmer et al., 1994). These UIR bands are observed in emission toward sources in which interstellar dust particles are irradiated with ultraviolet (UV) or visible (VIS) light. The PAH molecule absorbs a UV photon followed by a rapid internal conversion to the ground electronic state. The energy of the UV–VIS photon is distributed randomly among vibrational modes of the PAH species, and the latter then cools by photon emission in the infrared (IR) region of the electromagnetic spectrum. In addition, PAH species could be responsible for some of the diffuse, interstellar absorption bands (DIBs) covering the visible spectrum from 440 nm to the near infrared (Cossart-Magos and Leach, 1990; Salama and Allamandola, 1992; Hudgins and Sandford, 1998), and might have contributed to the IR emission features in the spectrum of comet P/Halley (Joblin et al., 1997; Moreels et al., 1994).

Despite the crucial importance of PAH-like species in the interstellar medium, experimentally and theoretically well defined mechanisms to synthesize PAHs in various extraterrestrial environments have been elucidated so far only for the solid state, such as interstellar, carbon rich grains and hydrocarbon rich ices in our solar system (Kaiser and Roessler, 1997). In these ices, PAHs were found to be synthesized via interaction of MeV ions of the galactic cosmic ray particle field. On the other side, chemical reaction networks modeling PAH formation in the gas phase, such as in circumstellar envelopes agree that PAH synthesis should proceed via benzene, C_6H_6, or phenyl radicals, C_6H_5 (Messenger et al., 1998; Allain et al., 1995, 1997; Cherchneff and Barker, 1992; Cadwell et al., 1994). Recent combustion chemistry models adapted to chemistry in outflows of carbon rich stars show that the first aromatic ring is likely formed by recombination of two propargyl radicals, C_3H_3, or reaction of a C_4H_5 radical with acetylene (Kazakov and Frenklach, 1998; Chan et al., 1998; Wang and Cadman, 1998; Cherchneff et al., 1992). Propargyl itself is thought to be synthesized via hydrogen replacement in a reaction of carbene, CH_2, with C_2H_2. However, recent crossed beam experiments show that the encounter of atomic carbon, $C(^3P_j)$, with ethylene, C_2H_4, can synthesize C_3H_3 as well (Kaiser et al., 1996). The latter route seems more plausible, since both reactants, i.e. carbon atoms, as well as ethylene, have been identified in circumstellar shells, whereas the presence of carbene is still questionable. An alternative route to PAH formation in the gas phase of hydrocarbon-rich planetary atmospheres was suggested to proceed via a ring forming reaction of metastable triplet diacetylene, HCCCCH, with 1,3-butadiene, C_2H_3–C_2H_3, to give

C_6H_6 and/or C_8H_6, phenylacetylene (Arrington et al., 1998).

However, to get a complete understanding to the formation and the chemical properties of PAHs in outflows of carbon stars, cold molecular clouds, as well as hydrocarbon rich planetary atmospheres, it is crucial to set up a systematic research program investigating the basic elementary chemical reactions leading to PAH synthesis and their reactions on the most fundamental, microscopic level. In this paper, we present solid laboratory data and employ the crossed molecular beam technique (Balucani et al., 2000). Two reactions are reported on, the first one of atomic carbon, $C(^3P_j)$, with benzene, C_6H_6, and the second one of phenyl radicals, C_6H_5, with methylacetylene, CH_3CCH, to form C_7H_5 and C_9H_8 radicals, respectively:

$$C(^3P_j) + C_6H_6 \rightarrow C_7H_5 + H, \qquad (1)$$

$$C_6H_5 + CH_3CCH \rightarrow C_9H_8 + H. \qquad (2)$$
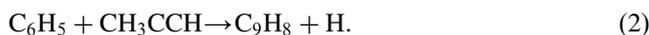
Reaction (1) must be considered as a prototype and model reaction of atomic carbon with the most stable aromatic unit present in each PAH molecule. This unravels the stability of the aromatic skeleton with respect to reactive collisions and compares our findings to the PAH destruction via photochemistry in the ISM (Allain et al., 1995; Bakes and Tielens, 1998; Buch, 1989; Ekern et al., 1998; Jochims et al., 1996, 1994). Reaction (2) investigates the formation of PAH precursors, such as naphthaline formed via phenyl radical intermediates as postulated previously (Messenger et al., 1998; Allain et al., 1997; Cherchneff and Barker, 1992).

2. Crossed molecular beam setup and data analysis

The basic experimental setup, data recording, as well as data processing were described in Balucani et al. (2000). Briefly, the reactive scattering experiments were performed with the 35″ crossed molecular beam machine equipped with a triply differentially pumped universal, electron-impact ionizer detector. The detector is rotatable within the scattering plane of the primary and secondary beams from −25.0 to 72.0°. To generate a stable beam of atomic carbon, the 40–60 mJ, 266 nm output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating carbon rod in the primary source. The ablated species $C(^3P_j)$, C_2, and C_3 are seeded into helium carrier gas. A four-slot chopper wheel located between the skimmer of the primary source and the copper shield, slices a 9 μs segment of the pulsed carbon beam selecting well-defined velocities v_p between 1280 and 3012 ms^{-1} and speed ratios S

between 4.5 and 8.7, respectively. The pulsed carbon beam crosses a second pulsed beam of benzene seeded in neon carrier gas ($v_p = 780 \pm 10$ ms^{-1}; $S = 12.0 \pm 0.2$). Neon was chosen as a carrier gas since the center-of-mass angle of helium seeded benzene reacting with C(^{3}P$_j$) would have been out of the range of our detector; a heavier carrier gas of the secondary beam reduces the velocity of the benzene molecule thus decreasing the center-of-mass scattering angle. For the second set of experiments we generated a pulsed, supersonic beam of phenyl radicals, C$_6$H$_5$, of $v_p = 3100 \pm 30$ ms^{-1}; $S = 8.8 \pm 0.2$ via pyrolysis of a 0.1% helium seeded C$_6$H$_5$NO in a resistively heated silicon carbide tube. This beam interacts with a pulsed, neat methylacetylene beam ($v_p = 850 \pm 10$ ms^{-1}; $S = 9.0 \pm 0.1$) of the secondary source in the interaction region. Time-of-flight (TOF) spectra of reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometer with an electron-impact ionizer in 2.5° steps with respect to the primary beam. To gain information on the reaction dynamics, TOF spectra and the laboratory angular distribution (LAB) are fit using a forward-convolution technique yielding the translational energy flux distribution $P(E_T)$ and angular distribution $T(\theta)$ in the center-of-mass reference frame. This approach initially guesses the angular flux-distribution $T(\theta)$ and the translational energy distribution $P(E_T)$ in the center-of-mass (CM) coordinate system assuming mutual independence. The adjustable parameters are refined stepwise until a good agreement between the simulated and experimental data is achieved.

We would like to stress that the reactions are performed under **single collision conditions**; this means **ONE** atom/radical A of the primary source reacts only with **ONE** molecule BC of the secondary source to form AB + C reaction products. Three body reactions are eliminated, and hence, neither the involved reaction intermediate ABC can be stabilized nor the reaction products AB + C can react with another molecule/atom. This guarantees that the nascent reaction products can be observed. Further, the primary and secondary beams are rotationally and vibrationally cold since both beams are prepared in a supersonic expansion (Scoles, 1988). 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

$$E_C = \tfrac{1}{2}(m_A m_{BC})/(m_A + m_{BC})(v(A)^2 + v(BC)^2).$$

The reactions of C(^{3}P$_j$) with benzene were performed at collision energies between 8 and 60 kJ mol^{-1},

whereas the reaction of phenyl radicals with methylacetylene was investigated at 140 kJ mol^{-1}.

3. Experimental results: laboratory angular distribution (LAB), and TOF spectra

In both crossed beam experiments, the radical/atom versus hydrogen exchange pathway was observed experimentally, and reactive scattering signal was detected at mass to charge ratios $m/e = 89$ [C$_7$H$_5^+$, reaction (1)] and $m/e = 116$ [C$_9$H$_8^+$, reaction (2)]. All TOF spectra observed at lower m/e ratios to $m/e = 84$ [reaction (1)] and $m/e = 108$ [reaction (2)] depict identical patterns. Since they could be fit with the same center-of-mass functions as the parent ions, this result suggests that those m/e ratios come from cracking of the parent ion in the electron-impact ionizer. Finally, no radiative association was found. In reaction (2), we would like to point out that the H atom loss can occur from the CH$_3$ group and/or from the acetylenic hydrogen atom. To discriminate between both possibilities,
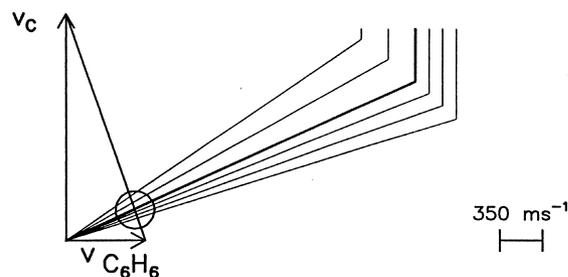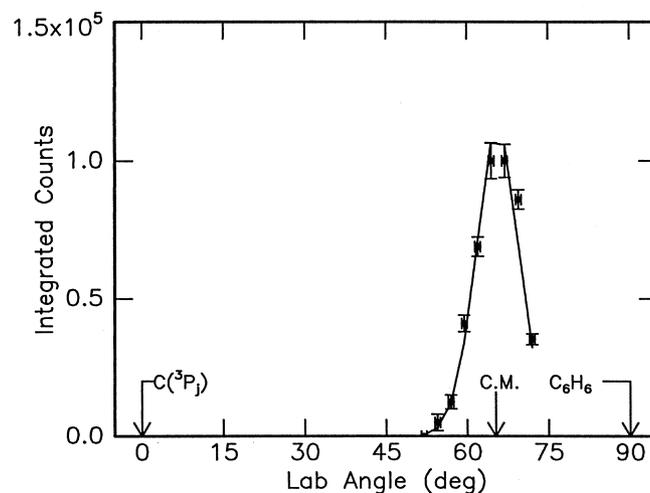

Fig. 1. Laboratory angular distribution for the C$_6$H$_6$ + C(^{3}P$_j$) reaction to C$_7$H$_5$ at a collision energy of 21.8 kJ mol^{-1}.

we complemented our experimental studies and performed crossed beam experiments with partially deuterated methylacetylenes, CD_3CCH and CH_3CCD. These studies prove unambiguously, that under our experimental conditions, the H atom is released from the former acetylenic unit, whereas the CH_3 group is conserved in the reaction. No CH_3 loss was observed.

Both the laboratory product angular distributions and the calculated curves are depicted in Figs. 1 and 2, together with the most probable Newton diagram. Figs. 3 and 4 show the corresponding TOF spectra for selected angles. The LAB distribution of reaction (1) peaks close to the center-of-mass (CM) angle and is extremely narrow. It extends only about 25° within the scattering plane, indicating that this reaction is only weakly exothermic and/or that a large fraction of energy channels into the internal energy of the products. Reaction (2) gives a different behavior. Here, the LAB distribution does not show a maximum at the CM angle of 8.2°, but more forward scattered with respect to the phenyl radical beam (closer to the C_6H_5 beam) at 6.5°. The LAB distribution is even narrower and ranges from only 3.5 to 11.5°. We like to recall
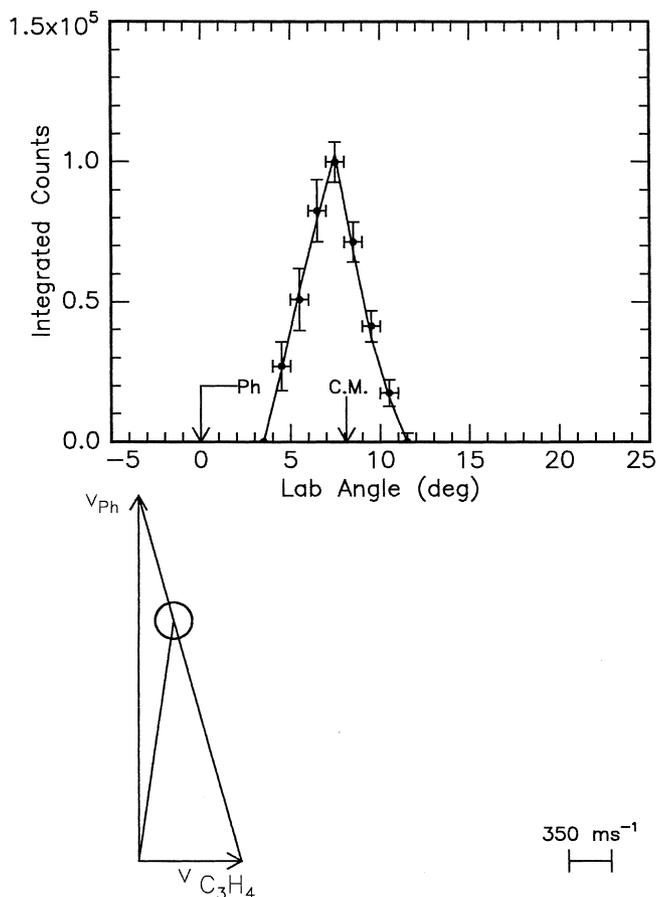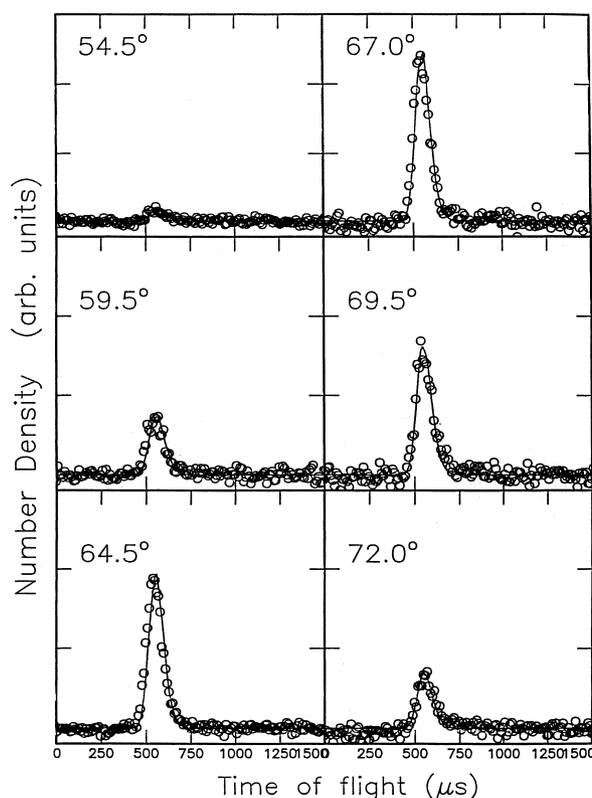

Fig. 3. Time-of-flight data of distinct laboratory angles for the $C_6H_6 + C(^3P_j)$ reaction to C_7H_5 at a collision energy of 21.8 kJ mol^{-1}. The dots indicate the experimental data, the solid lines the calculated fit.
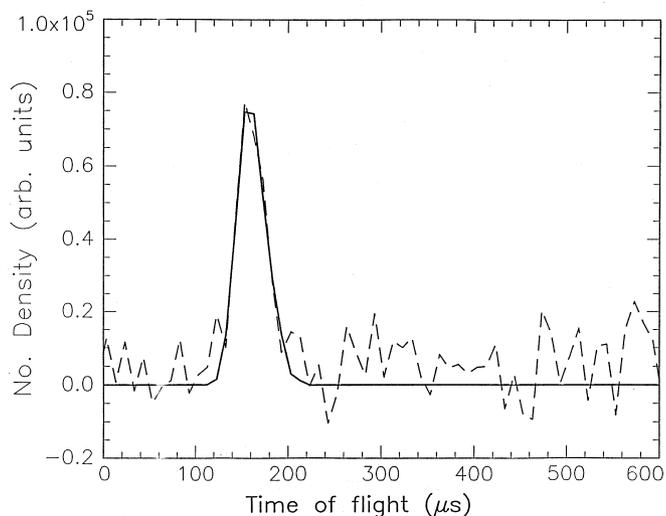

Fig. 2. Laboratory angular distribution for the $C_6H_5 + CH_3CCH$ reaction to C_9H_8 at a collision energy of 141 kJ mol^{-1}.

Fig. 4. Time-of-flight data at the center-of-mass angle for the $C_6H_5 + CH_3CCH$ reaction to C_9H_8 at a collision energy of 141 kJ mol^{-1}. The dashed line indicates the experimental data, the solid lines the calculated fit.

that if the energetics of the product isomers are well separated, it is possible to identify the actual product isomer (Balucani et al., 2000). However, since the enthalpies of formation of distinct C_7H_5 isomers differ only by about 20 kJ mol^{-1} (Kaiser et al., 1999), we cannot resolve this issue at this point (cf Discussion).

4. Experimental results: energetical information from the $P(E_T)$ distributions

Figs. 5 and 6 depict the center-of-mass translational energy flux distributions for reactions (1) and (2). Both reactions show a very different behavior. The $P(E_T)$ for the $C_6H_6 + C$ reaction peaks at zero translational energy suggesting that the decomposing C_7H_6 complex fragments without an exit barrier. Further, the maximum of the translation energy distribution extends to 37–45 kJ mol^{-1}. On the other hand, the flux distribution of reaction (2) peaks well away from zero at 60–70 kJ mol^{-1}, and the high energy cutoff of this $P(E_T)$ is at 160 kJ mol^{-1}. Adding 10–15 kJ mol^{-1} to this data does not influence the fit. As stated above, the high energy cutoff of the translational energy E_{max} can be used to identify the nature of the product iso-

mer. Here, E_{max} is simply the sum of the reaction exothermicity plus the collision energy. Hence, we find that reaction (1) and (2) are exothermic by about 15–23 and 19–34 kJ mol^{-1}.

5. Experimental results: angular information from $T(\theta)$ distributions

The shapes of the flux distributions $T(\theta)$ contain important information to investigate the chemical reaction dynamics of a bimolecular reaction (Balucani et al., 2000). In these graphs, the direction of the atomic/radical species are defined as 0°, and of the hydrocarbon beam to 180°. First, the $T(\theta)$ of the $C(^3P_j)$ reaction exhibits a flat flux profile symmetric around 90°. This 'forward–backward' behavior is characteristic for a bimolecular reaction $A + BC \rightarrow AB + C$, which goes through an $[ABC]^*$ complex (indirect scattering dynamics) which holds a lifetime larger than its rotation period (Balucani et al., 2000). The reaction of the phenyl radical shows a striking difference. Here, the angular flux distribution is asymmetric around 90° and shows predominant flux only in the forward direction. One fit was achieved in which the flux peaks at
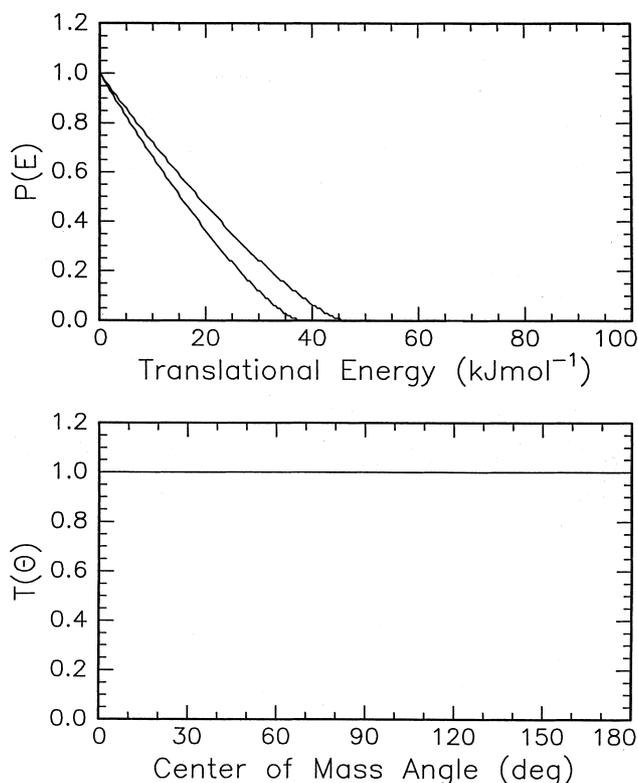
Fig. 5. Center-of-mass functions for the $C_6H_6 + C(^3P_j)$ reaction to C_7H_5 at a collision energy of 21.8 kJ mol^{-1}.
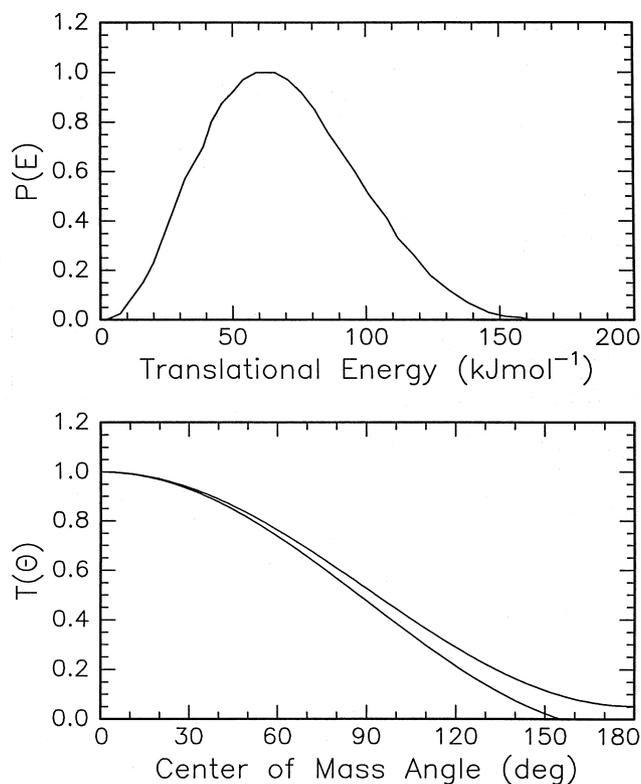
Fig. 6. Center-of-mass functions for the $C_6H_5 + CH_3CCH$ reaction to C_9H_8 at a collision energy of 141 kJ mol^{-1}.
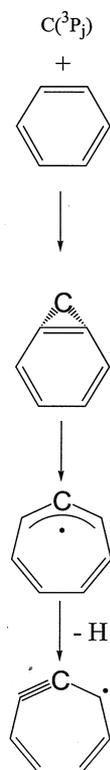
C(^{3}P$_j$)

+

Fig. 7. Schematic representation of the reaction for the reaction C$_6$H$_6$ + C(^{3}P$_j$). See text for details.

0° and is zero at angles larger than 150°. Within the error limits, a minor intensity at these larger angles can fit the data as well and does not influence the fit. This strongly suggests the reaction is 'direct' and proceeds via a very short-lived, highly rovibrationally excited intermediate with a lifetime in the order of a sub pico second.

6. Discussion: C(^{3}P$_j$) + C$_6$H$_6$ reaction

The translational energy flux distribution together with the maximum available energy suggest the formation of the 1,2-didehydrocycloheptatrienyl radical (cf Fig. 7 and Kaiser et al., 1999). Initially, the C(^{3}P$_j$) attacks the π-electron density of the benzene molecule without an entrance barrier to form a long-range, weakly bound triplet complex. This intermediate ring opens to cyclohepta-2,4,6-trienylidene and decomposes barrier-less via the C—H bond cleavage to the 1,2-didehydrocycloheptatrienyl radical and atomic hydrogen. The $P(E_T)$ peaks at zero kinetic energy, and, hence, verifies that the homolytic bond rupture proceeds without an exit barrier. Further, the forward–backward symmetric center-of-mass angular distribution suggests that the cyclohepta-2,4,6-trienylidene intermediate lives longer than its rotational period.

The strict assignment of the carbon versus hydrogen exchange channel and the exothermicity of the reaction together with the absence of any entrance, as well as the exit barrier have strong implications to chemistry in interstellar environments. First, benzene molecules in interstellar clouds at temperatures as low as 10 K can react with atomic carbon; the six-membered aromatic ring is not conserved in this reaction, but opens up to a seven-membered, highly unsaturated C$_7$H$_5$ species. This finding is in strong contrast to reactions of atomic oxygen, O(^{3}P$_j$); this reaction has an entrance barrier of about 15–20 kJ mol^{-1} preventing any reaction in cold environments. Likewise, the reactive encounter of atomic nitrogen, N(^{4}S), is expected to have an entrance barrier as well, and cannot happen in cold molecular clouds either. We demonstrated recently in our laboratory that the reaction of interstellar cyano radicals, CN, with benzene is exothermic
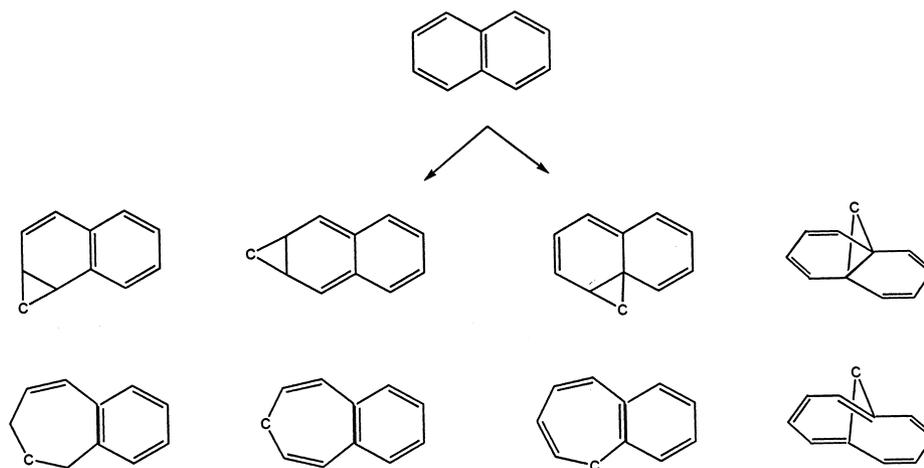

Fig. 8. Suggested intermediates and products in the reaction of C(^{3}P$_j$) with naphthalene as a typical example. As the PAH becomes increasingly complex, various sites can be attached.

and proceeds barrier-less as well (Balucani et al., 2000). But in this reaction, the CN versus H exchange conserves the aromatic ring, and cyanobenzene, C_6H_5CN is formed. Second, since the aromatic benzene unit is common in PAHs, we suggest that atomic carbon might react in interstellar environments with PAH molecules under ring extension as well, whereas PAHs are inert to oxygen and nitrogen atoms. Fig. 8 shows typical examples of PAH molecules reacting with atomic carbon and possible intermediates; these experiments are under development in our group. It is noteworthy that this chemistry has a profound effect on the spectroscopic properties of the PAH molecules. Although in larger PAHs such as coronene, a large aromatic unit still exists even upon reaction with atomic carbon, the infrared emission features toward sources in which interstellar dust particles are irradiated with UV light will change. This might yield a better fit to some UIR features than previous assignments. Likewise, it is important to investigate the diffuse interstellar bands once the spectroscopic properties of the PAH–$C(^3P_j)$ reaction products have been assigned. We would like to suggest that the $C(^3P_j) + C_6H_6$ reaction might be a strong alternative to the $C_2H + C_6H_6$ collision in a stepwise growth of PAHs in the outflow of carbon rich stars. Detailed model studies suggest that the latter is feasible only in a very narrow temperature window between 800 and 1200 K, whereas an attack of atomic carbon shows no temperature restrictions. Further, a subsequent radical–radical reaction of C_7H_5 with C_2H can proceed without a barrier and leads to a stepwise growth of PAH precursors. Finally, our C_7H_5 isomer might present an important tracer of benzene molecules: unlike C_6H_6, the C_7H_5 radical has a permanent dipole moment of 1.7 D (Kaiser et al., 1999), which makes it accessible to radio astronomical observation.

7. Discussion: $C_6H_5 + CH_3CCH$ reaction

The unpaired electron of the phenyl radical is localized on one carbon atom and lies in the molecular plane. C_6H_5 can then interact with one π molecular orbital to attack the α and/or β carbon atom of the CH_3CCH molecule to form C_6H_5–CH_3CCH intermediates (cf Fig. 9). Since the isotopic studies clearly indicate the loss of an acetylenic H atom, we infer a preferential formation of the *cis/trans* $CH_3CCH(C_6H_5)$ intermediate. This might be rationalized in terms of the screening effect by the CH_3 group of the α carbon atom, which was already found experimentally in the reactions of methylacetylene with CN radicals (Balucani et al., 2000) and atomic carbon. Both *cis*- and *trans*-isomers can then emit a hydrogen atom to form phenylmethylacetylene, $CH_3CCC_6H_5$. The experimen-

tally determined reaction exothermicity of 19–34 kJ mol^{-1} is in good agreement with data obtained by bond energy increments of about 25 kJ mol^{-1} (Lide, 1993). We would like to point out that although the acetylenic C—H bond is stronger by about 120 kJ mol^{-1} as compared to the aliphatic one, the latter one is not broken in our experiments. This underlines that the chemical dynamics are of crucial importance to understand formation of the phenylmethylacetylene product. Since the shape of the $T(\theta)$ suggests that the reaction is direct, the *cis/trans* $CH_3CCH(C_6H_5)$ intermediates are very short-lived to result in direct scattering dynamics. This is supported by the large fraction of 45–55% of the available energy channeling into the translational degrees-of-freedom. Related complex-forming reactions of $C(^3P_j)$ and CN radicals with unsaturated hydrocarbons yield only fractions of 30–35%. Since the lifetime of the *cis/trans* intermediate is very low, this timescale must be too short for energy transfer from the initially newly formed carbon–carbon σ bond to the C—H bond of the CH_3 group, and the methyl group stays unaffected at our collision energy of 140 kJ mol^{-1}. We would like to stress that in a similar experiment of CN with methylacetylene, we found cleavages of the acetylenic, as well as aliphatic C—H bond; these experiments were performed at collision energies around 20 kJ mol^{-1} — low enough for a long-lived complex behavior (indirect scattering dynamics) and an energy transfer channeling into the reaction coordinate of aliphatic C—H-bond cleavage.

Although our experiments cannot investigate the existence of a small entrance barrier to the reaction, recent bulk experiments of phenyl radicals with unsaturated hydrocarbons suggest barriers between 15 and 35 kJ mol^{-1}. If this order-of-magnitude can be verified in currently ongoing *ab initio* calculations, the reaction of phenyl radicals with alkynes and olefines cannot
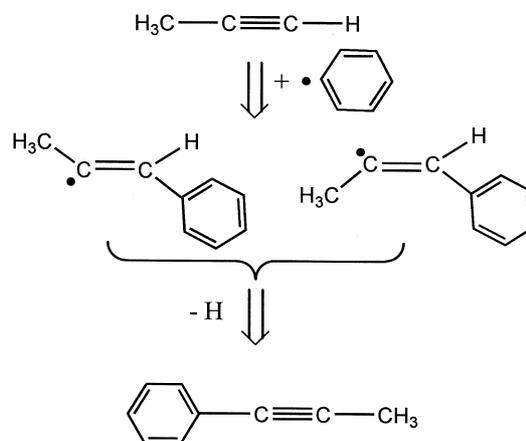

Fig. 9. Schematic representation of the reaction for the reaction $C_6H_5 + CH_3CCH$. See text for details.

play a role in the formation of PAHs in cold molecular clouds or hydrocarbon-rich atmospheres of Jupiter, Saturn, and Titan, since the entrance barrier inhibits the reaction. However, temperatures close to the photosphere of carbon stars can reach up to 4000 K, and the reactions can play a role in these environments. If we extend previously postulated reaction pathways, we suggest that the reaction of phenyl radicals with methylacetylene might be involved in the formation of methyl substituted naphthalene molecules.

8. Summary and conclusion

We investigated two elementary reactions, those of atomic carbon, $C(^3P_j)$ with benzene, C_6H_6, and the phenyl radical, C_6H_5, with methylacetylene, relevant to the chemistry of polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial environments employing the crossed molecular beam technique under single collision conditions. The atom-closed shell reaction to a cyclic, seven-membered C_7H_5 doublet radical proceeds via complex formation, has neither an entrance nor exit barrier, and is exothermic. These features together with the experimental verification of the carbon versus hydrogen exchange pathway under single collision conditions, has a profound impact on the chemistry of aromatic molecules in extraterrestrial environments. Even in the coldest molecular clouds, the aromaticity of the benzene molecule can be destroyed upon reaction with carbon atoms, whereas they are resistant toward an attack of oxygen and nitrogen atoms. Since the benzene unit is present in all PAH molecules as well, atomic carbon is likely to react with these species as well, thus changing the chemical and spectroscopic properties of PAHs in interstellar environments. We would like to point out that in PAHs, not only benzoid units exist, but ethylenic (C=C) and butadienic (C=C–C=C) as well. Therefore, future studies will focus on the reactivity of these reaction centers towards an attack of atomic carbon; nevertheless, either reaction pathway will lead to some sort of PAH, either PAHs with seven-membered rings, exo-cyclopropane derivatives, or hydrogen deficient PAH molecules. On the other side, the reaction of C_6H_5 radicals with methylacetylene to form phenylmethylacetylene is expected to play a role in PAH synthesis only in high temperature interstellar environments. Here, an entrance barrier inhibits the reaction in cold molecular clouds and in the atmospheres of hydrocarbon-rich planets and their satellites. Since our results are obtained under single collision conditions without involved stabilization of the involved reaction intermediate and no subsequent reaction of the reaction products, both crossed beam reactions are performed under realistic pressure/density regimes, which can be applied to the interstellar medium as well.

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