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# Elementary reactions of the phenyl radical, $C_6H_5$, with $C_3H_4$ isomers, and of benzene, $C_6H_6$, with atomic carbon in extraterrestrial environments

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**Abstract.** Binary collisions of ground state carbon atoms, $C(^3P_j)$, with benzene, $C_6H_6(X^1A_{1g})$, and of phenyl radicals, $C_6H_5(X^2A_1)$, with methylacetylene, $CH_3CCH(X^1A_1)$, were investigated in crossed beam experiments, ab initio calculations, and via RRKM theory to elucidate the underlying mechanisms of elementary reactions relevant to the formation of polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial environments. The reactions of phenyl radicals with allene, $H_2CCCH_2$, and with cyclopropene, cyc-$C_3H_4$, as well as the reaction of benzyl radicals, $C_6H_5CH_2$, with acetylene, HCCH, were also investigated theoretically. The $C(^3P_j)$ atom reacts with benzene via complex formation to a cyclic, seven membered $C_7H_5$ doublet radical plus atomic hydrogen. Since this pathway has neither an entrance nor an exit barrier and is exoergic, the benzene molecule can be destroyed by carbon atoms even in the coldest molecular clouds. On the other hand, the reaction of phenyl radicals with methylacetylene has an entrance barrier; at high collision energies, the dynamics are at the boundary between an osculating complex and a direct pathway. Statistical calculations on the phenyl plus methylacetylene reaction demonstrate dramatic energy/temperature dependencies: at lower temperatures, the bicyclic indene isomer is the sole reaction product. But as the temperature increases to 2000 K, formation of indene diminishes in favor of substituted acetylenes and allenes, such as PhCCH, $PhCCCH_3$, $PhCHCCH_2$, and $PhCH_2CCH$. Also, direct H-abstraction channels become accessible, forming benzene and $C_3H_3$ radicals, including propargyl. Similar conclusions were reached for the reactions of phenyl radicals with the other $C_3H_4$ isomers, as well as for the benzyl + acetylene reaction. The strong temperature dependence emphasizes that distinct product isomers must be included in reaction networks modeling PAH formation in extraterrestrial environments.

**Key words.** astrochemistry – ISM: atoms – ISM: molecules – ISM: jet and outflows

## 1. Introduction

Chemical reaction networks modeling the formation of polycyclic aromatic hydrocarbon (PAH)-like species in circumstellar envelopes of carbon rich asymptotic giant branch (AGB) stars suggest that benzene, $C_6H_6$, phenyl radicals, $C_6H_5$, and/or possibly $C_5H_5$ radicals are crucial reaction intermediates (Messenger et al. 1998; Allain et al. 1997; Cherchneff & Barker 1992). The most favorite synthetic route postulated so far involves stepwise PAH formation. Here, the collision of phenyl radicals with acetylene molecules is followed by a second reactive encounter of the radical intermediate with an acetylene molecule to form a naphthalene-like PAH species via ring closure (Kazakov & Frenklach 1998). However, a crucial drawback of all such chemical models is the lack of well-defined experimental data. While rate constants for phenyl radicals reacting with olefins and alkynes range between $10^{-12}$ and $10^{-14}$ $cm^3$ $s^{-1}$ at temperatures up to 1100 K and entrance barriers were determined to be 25–43 kJ $mol^{-1}$, reaction products are purely speculative (Yu & Lin 1995a; Yu & Lin 1995b; Duncan & Trotman-Dickenson 1962; Fahr & Stein 1989; Herzler & Frank 1992). Obviously, the products of the reaction of phenyl with molecular hydrogen as studied by Lin and coworkers should be benzene and atomic hydrogen (Yu & Lin 1995a), but the problem is more complex if unsaturated hydrocarbons are the reactants.

Therefore, a detailed and complete understanding of the formation of PAH-like molecules requires a systematic research program to investigate the basic elementary chemical reactions on the most fundamental, microscopic level. In this paper we present ab initio and RRKM studies on two important systems investigated very recently in crossed molecular beam experiments of atomic carbon, $C(^3P_j)$, with benzene, $C_6H_6(X^1A_{1g})$ (reaction 1), and the phenyl radical,

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$C_6H_5(X^2A_1)$, with methylacetylene, $CH_3CCH(X^1A_1)$ (reaction 2). The first system represents a prototype reaction of atomic carbon with the basic aromatic unit present in PAH molecules. This probes the stability of benzene with respect to reactive collisions. The second reaction investigates the previously postulated formation of potential PAH precursors via phenyl radicals. In addition to these combined experimental and theoretical studies, the reactions of phenyl radicals with allene, $H_2CCCH_2$, and with cyclopropene, cyc-$C_3H_4$, as well as the reaction of benzyl radicals, $C_6H_5CH_2$, with acetylene, $C_2H_2$, were investigated theoretically using RRKM theory and Master Equation analyses, to investigate the dependence of the results to the isomeric form of the $C_3H_4$ coreactant, and to other formation channels of the $C_9H_9$ intermediate.

## 2. Reaction (1): $C(^3P_j) + C_6H_6(X^1A_{1g})$

The detailed study of the $C_7H_6$ potential energy surface (PES) at the B3LYP/6-311+G(d,p) hybrid density functional theory (DFT) level (Becke 1992; Lee et al. 1988) suggests the formation of the 1,2-didehydrocycloheptatrienyl radical (Fig. 1) (Bettinger et al. 2000; Hahndorf et al. 2002). Initially, the $C(^3P_j)$ atom interacts with benzene at positions with large $\pi$-electron density. This step has no entrance barrier and forms a rather weakly bound ($-63$ kJ mol$^{-1}$) triplet complex. Absolute rate measurements by Haider and Hussain (1993) yielded a rate coefficient $k(300\ \mathrm{K},\ 0.01\ \mathrm{bar}) = 4.8 \times 10^{-10}$ cm$^3$ s$^1$, nearly identical to the collision limit and therefore clearly supporting the lack of an entrance barrier. The initially formed metastable bicyclic intermediate opens via a very low barrier, only about 4 kJ mol$^{-1}$, to give triplet cyclohepta-2,4,6-trienylidene ($-294$ kJ mol$^{-1}$ with respect to the separated reactants) and then decomposes without barrier via C–H bond cleavage to yield the 1,2-didehydrocycloheptatrienyl radical plus atomic hydrogen. Alternatively, an intersystem crossing in the vicinity of the initial triplet complex might result in singlet bicyclo[4.1.0] hepta-2,4-diene-7-ylidene ($-152$ kJ mol$^{-1}$ with respect to the separated reactants). From a ring opening reaction singlet cyclohepta-1,2,4,6-tetraene ($-376$ kJ mol$^{-1}$ with respect to the separated reactants) is obtained, which also can loose an H atom without barrier to yield the 1,2-didehydrocycloheptatrienyl radical.

Our recent crossed beam data support these conclusions (Kaiser et al. 1999). First, the center-of-mass translation energy distribution peaks at zero kinetic energy thus verifying that the homolytic bond rupture proceeds without exit barrier. Secondly, the forward-backward symmetric center of mass flux contour map suggests that the reaction proceeds via a $C_7H_6$ complex, which undergoes C–H bond rupture and which lives longer than its rotational period. Our results underline further that the thermodynamically more stable $C_7H_5$ benzocyclopropenyl radical is not formed as a major product since this reaction is exoergic by 45.2 kJ mol$^{-1}$, clearly incompatible with our experimental data. This dynamic preference of the potential energy surface underlines the importance of investigating the detailed chemical reaction dynamics rather than focussing solely on the reaction exothermicity as done in existing chemical reaction networks of PAH formation.

In addition to the electronic structure calculations and crossed beam experiments, the kinetics of the $C_6H_6/C(^3P_j)$ system were quantified by RRKM-based Master Equation analysis (Hahndorf et al. 2002) using the URESAM-3 program suite (Vereecken et al. 1997). The calculations carried out verify our experimental findings and reveal that for reaction conditions comparable to those in the interstellar medium ($T < 100$ K, near-zero pressure), the chemically activated triplet $C_7H_6$ adduct isomerizes rapidly to triplet cyclohepta-2,4,6-trienylidene, and finally dissociates mainly to the cyclic seven-membered 1,2-didehydrocycloheptatrienyl radical plus atomic hydrogen. The formation of other $C_7H_5$ species is less favorable, though dissociation to the bicyclic $C_7H_5$ isomer is expected to occur for a minor fraction, roughly less than 5%. The calculated product distribution is not sensitive to the relative energies of the intermediates and isomerization transition states, but the ratio of the two main products depends strongly on the relative energy of their exit channels. Accurate quantum chemical determination of these relative energies proved difficult, but the experimental observations allow us to optimize the energy difference used. While re-dissociation of the initially formed $C_7H_6$ adduct to the reactants is negligible at 10 K, this fraction is expected to increase at higher temperatures (about 10% at 1500 K, and approaching 50% at 2500 K), leading to a slight negative temperature dependence of the total rate coefficient. This enhances the small negative temperature dependence attributable to the barrier-free initial addition reaction. The combined lifetime of the series of activated $C_7H_6$ intermediates at these low temperatures is about 60 ms; this accounts for the forward-backward symmetric flux distribution at lower collision energies as found experimentally. Our results for this reaction in low-pressure conditions and temperatures below 2500 K can be summarized by the Arrhenius expression $k_{\mathrm{C+C6H6}} = 4.2 \times 10^{-10} \exp(1\ \mathrm{J\ mol^{-1}}/RT)$ cm$^3$ s$^1$ with 1,2-didehydrocycloheptatrienyl + H as the dominant product, and less than 5 % of bicyclic $C_7H_5$ + H.

## 3. Reaction (2): $C_6H_5(X^2A_1) + CH_3CCH(X^1A_1)$

Our combined crossed beam B3LYP-DFT6-311+G(d,p) quantum chemical investigation shows that the $C_6H_5$ radical interacts with methylacetylene via its $\pi$ molecular orbital with a barrier of about 18 kJ mol$^{-1}$ to form a trans $C_6H_5$–HCC–$CH_3$ intermediate RAD1 (Fig. 2) (Vereecken et al. 2002a). The more favorable attachment to the C1 carbon compared to the C2 atom is based on the sterical hindrance of a phenyl radical attack of the C2 position. This screening effect of the methyl group was observed experimentally in the reactions of methylacetylene with CN radicals. At our collision energy of 140 kJ mol$^{-1}$, RAD1 is highly rovibrationally excited, very short lived, and emits a hydrogen atom to form phenylmethylacetylene, $CH_3CCC_6H_5(X^1A')$. The experimentally determined reaction exothermicity of 19 – 34 kJ mol$^{-1}$ (Kaiser et al. 2000a) is in reasonable agreement with bond energy increment estimates (about 25 kJ mol$^{-1}$) and our ab initio result (12 kJ mol$^{-1}$). Although the acetylenic C–H bond

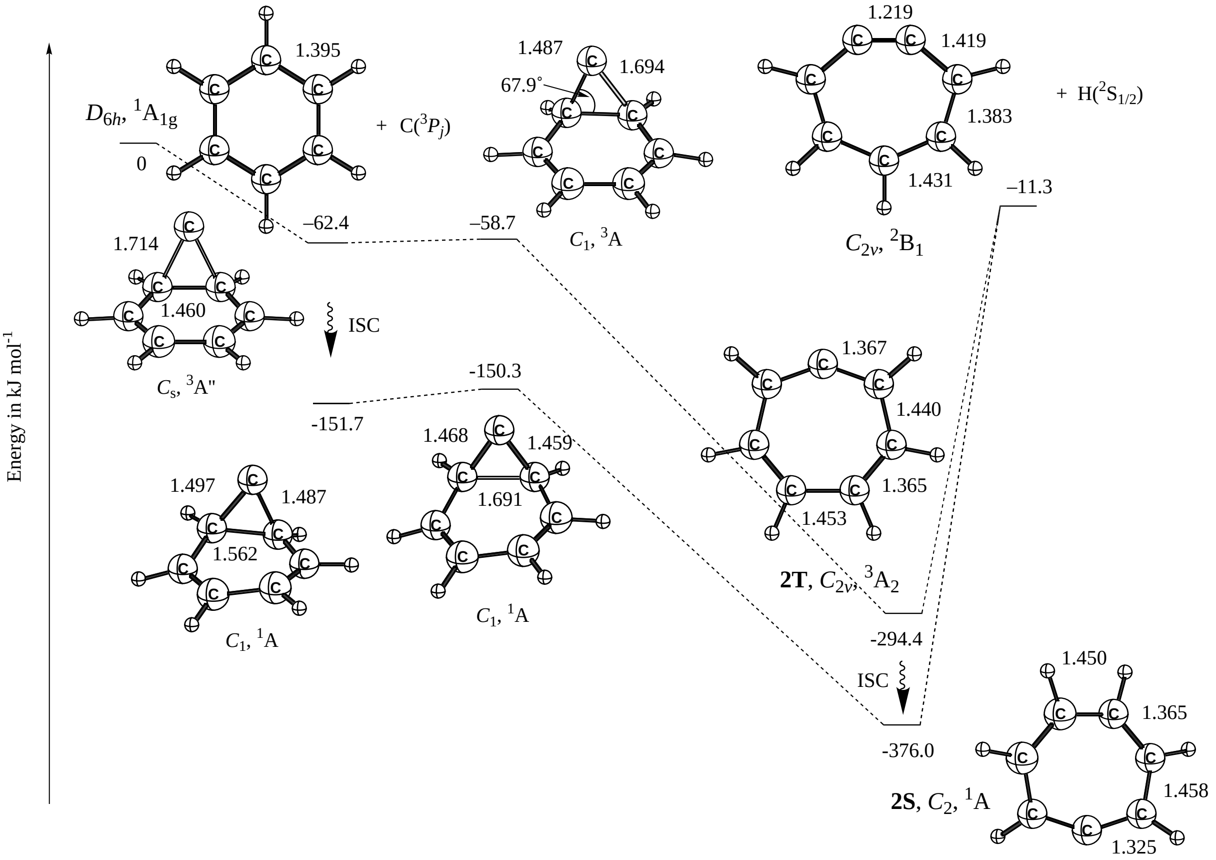

**Fig. 1.** Schematic energy level diagram for the $C(^3P_j)$ + $C_6H_6$ reaction as computed at the B3LYP/6-311+G(d.p) level of theory. Important bond lengths are given in angstrom.

is about 120 kJ $mol^{-1}$ stronger than the aliphatic C–H bond, the latter is not broken. Since the shape of the flux contour map suggests that the reaction is on the boundary between an osculating complex and a direct pathway, the trans $CH_3CCH(C_6H_5)$ intermediate must be very short lived to result in (almost) direct scattering dynamics. Therefore, the time scale is too short for energy transfer from the newly formed carbon-carbon $\sigma$ bond to the C–H bond of the $CH_3$ group. Consequently the methyl group is not affected at our collision energy of 140 kJ $mol^{-1}$. Note that the similar experiment of cyano (CN) and ethynyl ($C_2H$) radicals with methylacetylene resulted in cleavages of the acetylenic as well as the aliphatic C–H bonds. These experiments were performed at collision energies of around 20 kJ $mol^{-1}$, which is low enough for a long lived complex behavior (indirect scattering dynamics) and an energy transfer channeling into the aliphatic C–H-bond cleavage reaction coordinate. These findings underline the crucial importance of chemical dynamics in understanding the formation of the phenylmethylacetylene product.

## 4. Reactions of $C_6H_5$ + $C_3H_4$ isomers, and $C_6H_5CH_2$ + $C_2H_2$

In addition to our experiments, we studied the kinetics of the reaction of phenyl radicals with three $C_3H_4$ isomers methylacetylene, allene, and cyclopropene, as well as the reaction of benzyl + acetylene, employing the RRKM-based Master Equation analysis and the URESAM-3 program suite (Vereecken et al. 1997). Besides direct hydrogen abstraction channels, there are several addition channels leading to chemically activated intermediates. The subsequent reactions of these intermediates proceed over the highly complicated $C_9H_9$ potential energy surface (PES), involving dozens of intermediates interconnected by hydrogen and phenyl shifts as well as ring opening and closure reactions (Vereecken et al. 2002a). The potential energy surface was characterized at the B3LYP-DFT level of theory with various basis sets, supported by CCSD(T) and QCISD(T) calculations for selected structures and transition states. The detailed temperature and pressure dependence of the rate coefficient and product distribution can be found in

**Table 1.** Modified Arrhenius expressions for the rate coefficients $k(T) = A \cdot T^n \cdot \exp(-E_A/kT)$, including addition and H-abstraction channels, and corrections for redissociation of the adducts to the initial reactants. The fits agree with the theoretical predictions within a factor of 2 for the indicated temperature range.

| Reaction | Temp. range, K | $A$, $cm^3\ s^{-1}$ | $n$ | $E_A$, kJ $mol^{-1}$ |
|---|---|---|---|---|
| $C_6H_5$ + $HCCCH_3$ | 20-4000 | $1.794\times10^{-18}$ | 2.074 | 12.856 |
| $C_6H_5$ + $H_2CCCH_2$ | 30-4000 | $1.025\times10^{-19}$ | 2.522 | 13.249 |
| $C_6H_5$ + $cycC_3H_4$ | 30-4000 | $1.156\times10^{-19}$ | 2.499 | 2.210 |
| $C_6H_5CH_2$ + HCCH | 20-4000 | $3.452\times10^{-14}$ | 0.451 | 54.651 |

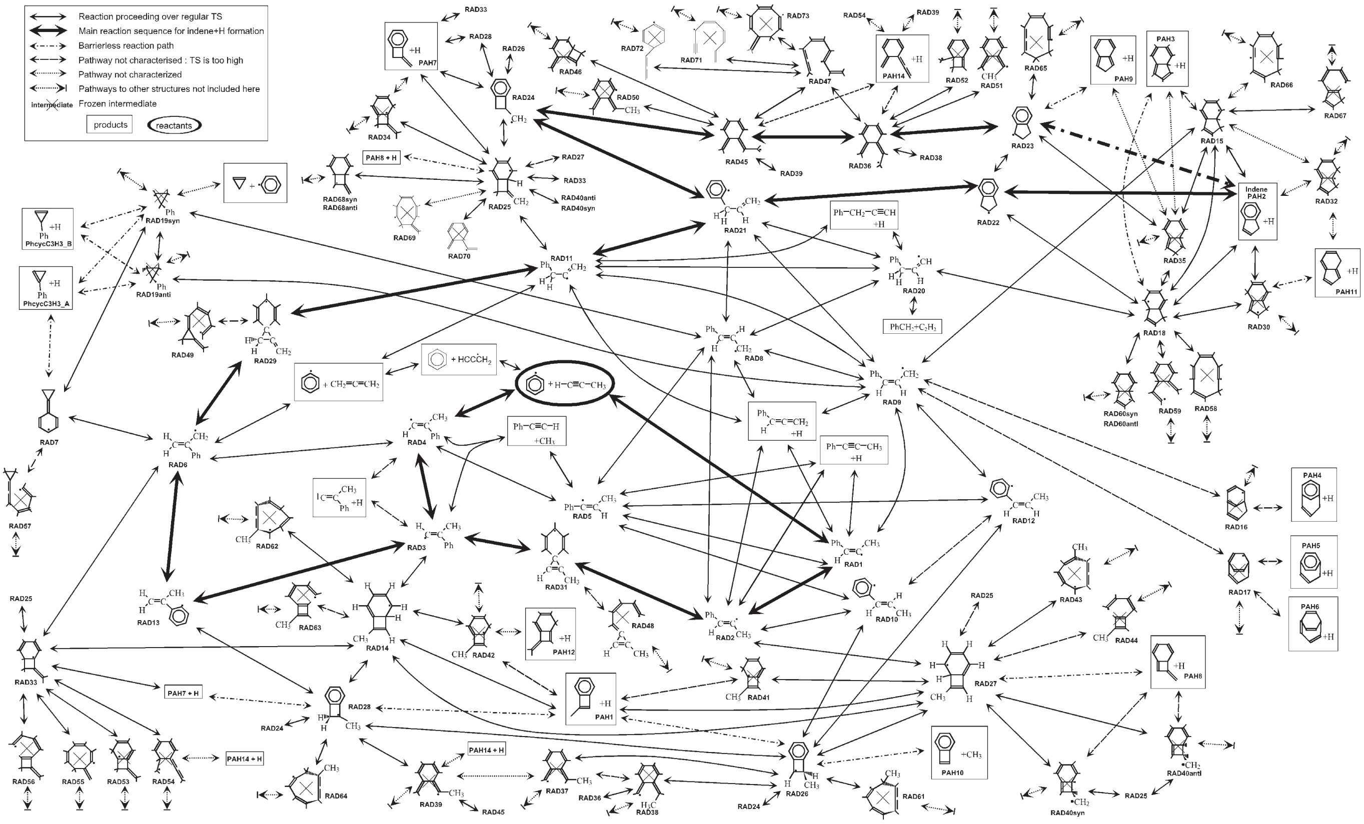

**Fig. 2.** Schematic reaction mechanism for the $C_6H_5$+$CH_3CCH$ reaction. Stationary points and transition states were optimized at the B3LYP density functional theory level with the 6-31G* and 6-311+G** basis sets. The thick arrows constitute the dominant reaction steps in the formation of indene+H, while most of the other products are formed from intermediates along this path.

Vereecken et al. (2002b, 2003); we limit ourselves here to a short discussion of the main results at near-zero pressures. For use in kinetic models, modified Arrhenius expressions for the total rate coefficients of the reactions studied here are given in Table 1, while the product distributions are depicted in Figs. 3–6. All results given here are corrected for redissociation of the initial adducts to the original reactants.

For the reaction of phenyl radicals with methylacetylene, $C_6H_5$+$CH_3CCH$, at low temperatures and near-zero pressures, the dominant initial reaction step is addition of the phenyl radical to the triple bond in $HCCCH_3$, followed by extensive isomerization of the initially formed and chemically activated adduct, and finally a dissociation step. There are several parallel multiple isomerization pathways, all linked to one another. At these low temperatures, below ≤500 K, the predominant final products are indene and atomic hydrogen (see Figs. 2 and 3), formed after a highly exothermic (105–120 kJ mol$^{-1}$) isomerization sequence of at least 9 steps. All of the transition states involved are sufficiently low in energy: the highest barrier in the sequence lies about 50 kJ mol$^{-1}$ below the energies of the separated reactants. The initial addition of $C_6H_5$ to methylacetylene is the bottleneck for indene formation at the relatively low temperatures of the interstellar medium (see Table 1), with an entrance barrier of over 10 kJ mol$^{-1}$. At increasing temperatures, direct H-abstraction leading to benzene +2-propynyl (propargyl) becomes the dominant channel, in part due to increasing redissociation of the initial adducts to the original reactants making the addition channel less effective. Indene formation becomes a minor channel at temperature above 1000 K, with the remaining fraction consisting of substituted acetylene, allene, and methylacetylene: PhCCH + $CH_3$, $PhCHCCH_2$ + H, and $PhCCCH_3$ + H in roughly 2:2:1 ratios. The product distributions depicted in Fig. 3 are calculated assuming rapid energy randomization throughout the adduct; at very high temperatures above 3000 K, dynamic effects could lead to non-statistical product distributions favoring dissociation channels with hydrogen elimination closer to the addition site. These results are in full agreement with our crossed beam experiment simulating the high "temperature" environments close to the photosphere of the AGB stars (which can reach temperatures of up to 4000 K), where the initial adduct was found to be extremely short-lived, resulting in the formation of $PhCCCH_3$ + H.

The analogous reaction of phenyl radicals with allene, $C_6H_5$ + $H_2CCCH_2$, has a comparable product distribution (see Fig. 4), with predominant formation of indene + H at lower temperatures. The number of isomerization steps required for this transformation is significantly smaller than in the case of phenyl + propyne, about 3–5 depending on the entrance channel. Therefore the rigid isomerization transition states can compete longer with the loose dissociation transition states at increasing temperatures, extending the temperature range in which significant indene-formation is observed. Again, direct H-abstraction leading to benzene +2-propynyl becomes

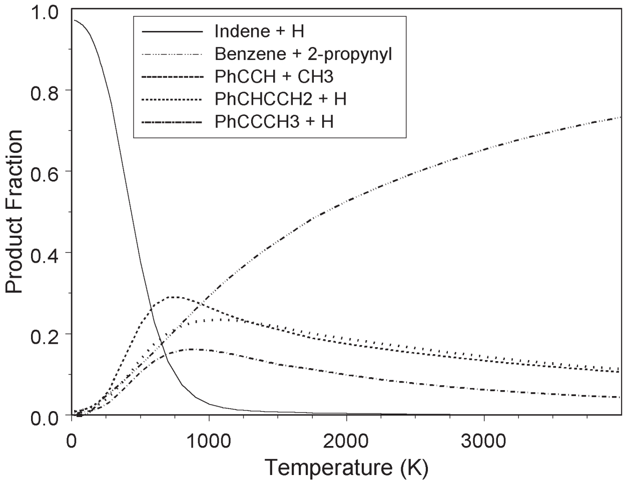

**Fig. 3.** Product distribution of the phenyl + propyne reaction, corrected for redissociation to the reactants.

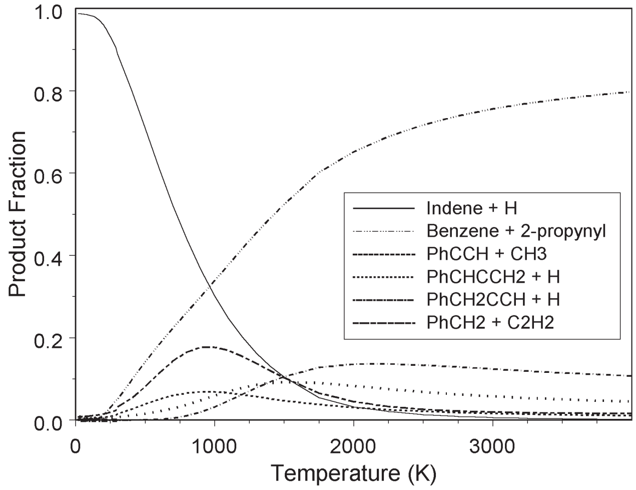

**Fig. 4.** Product distribution of the phenyl + allene reaction, corrected for redissociation to the reactants.

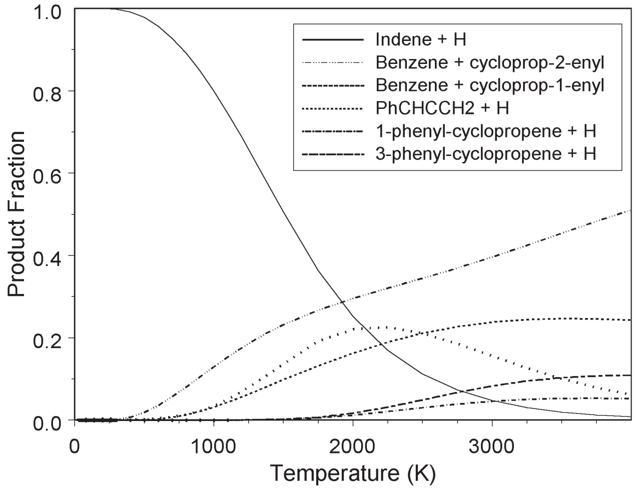

**Fig. 5.** Product distribution of the phenyl + cyclopropene reaction, corrected for redissociation to the reactants.

the dominant channel at higher temperatures above 1000 K, with the remaining fraction consisting of PhCCH + $CH_3$, $PhCHCCH_2$ + H, $PhCH_2CCH$ + H, and benzyl ($PhCH_2$) + acetylene in varying amounts depending on the temperature. Again, indene formation at the lower temperatures of the interstellar medium is hindered mainly by the barriers in the initial addition step of the reaction (see Table 1). Cyclopropene, the highest-energy stable $C_3H_4$ isomer has a significantly different reaction mechanism, dominated mainly by the energy released after the opening of the strained three-membered ring following phenyl addition. As a result, the barrier to reaction is significantly lower, and formation of indene + H remains a major channel up to almost 2000 K (see Fig. 5). Direct H-abstraction resulting in cyclic $C_3H_3$ species + benzene, and increasing hydrogen atom elimination from the chemically activated $PhCHCHCH_2$ intermediate leads to an increasing contribution of the $PhCHCCH_2$ + H product at increasing temperatures. At temperatures above 2500 K, we predict significant fractions of phenyl-substituted cyclopropene being formed. Given the relatively high relative energies of these products, it is likely that for these temperatures direct dynamics become more important, similar to what was observed in the crossed beam measurements for the phenyl+ methylacetylene reaction, resulting in non-statistical energy distributions with increased phenyl versus H substitution on the addition site. At this moment we are unable to properly account for these effects, making the predicted product distribution at higher temperatures less accurate. Finally, we studied the benzyl ($C_6H_5CH_2$) + acetylene reaction. This reaction has a very high barrier of over 50 kJ $mol^{-1}$, and is therefore of minor importance in the lower temperatures of the interstellar medium. Indene is the dominant product for temperatures up to 2500 K (see Fig. 6), with formation of (substituted) allenes and acetylenes at higher temperatures.

## 5. Astrophysical implications

Our investigations emphasize that both reactions studied experimentally and theoretically are dominated by the atom/radical versus hydrogen exchange pathways. These form the 1,2-didehydrocycloheptatrienyl radical ($C_7H_5$, reaction 1), and phenylmethylacetylene ($C_9H_8$, reaction 2), in slightly exothermic reactions. The thermodynamically most stable bicyclic $C_7H_5$ radical (exothermic by 35 kJ $mol^{-1}$, reaction 1) and indene (exothermic by 105–120 kJ $mol^{-1}$, reaction 2) are only minor reaction products under our experimental conditions (Fig. 7). Our statistical transition state calculations reveal an extraordinary temperature dependence of the products of reaction (2) in extraterrestrial environments. Whereas at high temperatures ($\geq$1500 K) the formation of the phenylmethylacetylene isomer dominates, low temperatures of 100 K yield the thermodynamically most stable bicyclic indene isomer exclusively. This finding correlates nicely with the reactions of the phenyl radical with the allene and cyclopropene isomers. Our statistical calculations suggest once more that at lower temperatures, the bicyclic indene molecule presents the dominating reaction product; as the temperature increases, the phenylallene and phenyl-cyclopropene products become more pronounced. In addition, hydrogen abstraction channels, which lead to

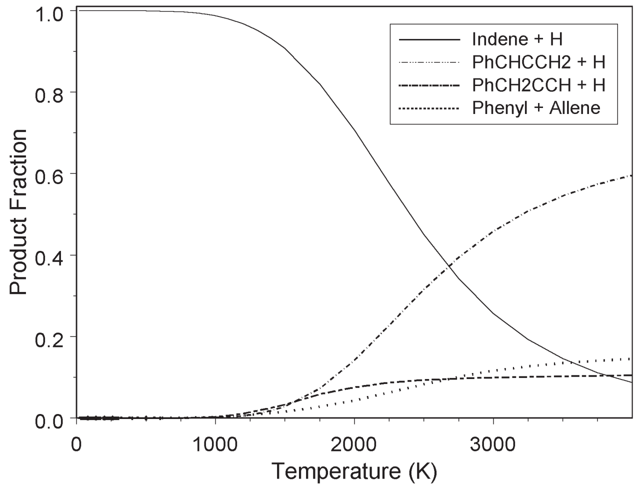

**Fig. 6.** Product distribution of the benzyl + acetylene reaction, corrected for redissociation to the reactants.

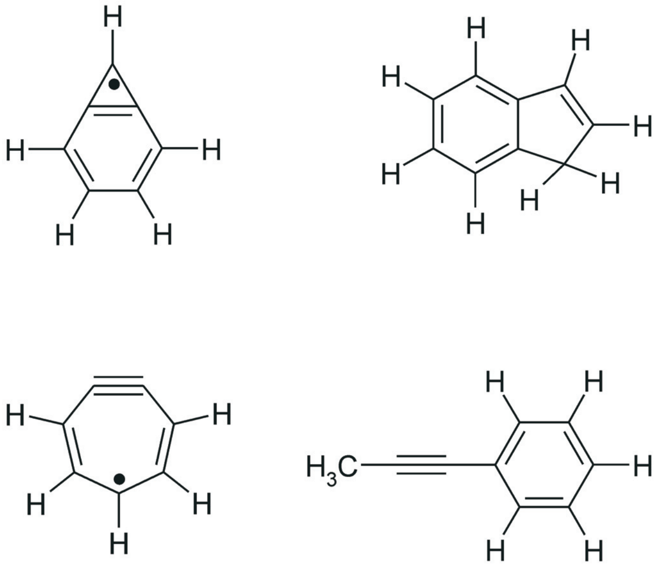

**Fig. 7.** Thermodynamically most stable isomers of the C($^3P_j$)/$C_6H_6$ (top left) and $C_6H_5$/ $CH_3CCH$ (top right) system and the actual 1,2-didehydrocycloheptatrienyl (bottom, left) and phenylmethylacetylene (bottom, right) reaction products under crossed-molecular beams conditions.

various $C_3H_3$ isomers, also open up. Note that the propargyl isomer, $HCCCH_2$, has been suggested as the key intermediate to form benzene and/or phenyl radicals in outflow of carbon stars. The reaction product of the C($^3P_j$)/$C_6H_6$ system does not depend markedly on the temperature.

The actual contribution of the title reactions to formation of PAH-like species and their precursors must be tested in future models investigating the chemistry in cold molecular clouds and in circumstellar envelopes of evolved carbon stars. In both environments, the kinetic temperature of the reactants differ strongly and range from only 10 K (molecular clouds) up to a few 1000 K close to the photosphere of the dying carbon stars. Our crossed beam experiments simulated the conditions in high temperature circumstellar environments, whereas our RRKM calculations covered a broad temperature range to account for cold clouds as well as for carbon stars. Our detailed findings are of paramount importance for chemical models of PAH formation in outflow regions of carbon rich AGB stars. First, similar to solar system environments (Kaiser et al. 2000b) prospective reaction networks should consider distinct product isomers; a simple "guess" and inclusion of the thermodynamically most stable reaction product is not sufficient. Second, the chemical reaction dynamics should be taken into account since the production of thermodynamically unfavorable reaction products is the direct effect of the dynamics and potential energy surfaces involved. Third, the strong temperature dependence of the isomer products under extraterrestrial reaction conditions requires incorporation of temperature dependent branching ratios to particular isomers in these chemical models. However, the higher the complexity of any astrophysically relevant molecular system, the more difficult experimental investigations become. Therefore, it is extremely useful to understand simple, prototype systems and to develop versatile concepts first before attempting to unravel the chemical reactivity of complicated molecules. The chemical reactivity of PAHs and/or PAH-like species can be taken as a typical example. The reactivity of benzene, which has been observed recently toward the preplanetary nebula CRL618 (Cernicharo et al. 2001), is of model character for the larger PAHs comprised of benzenoid building blocks. Our investigations show unambiguously that the C($^3P_j$)/$C_6H_6$ reaction has no entrance barrier, forms a cyclic, seven membered $C_7H_5$ doublet radical, and is exothermic. Hence even in the coldest molecular clouds, the six-membered benzene ring can be enlarged upon reaction with carbon atoms. This finding is in strong contrast to the atomic oxygen, O($^3P_j$), reactions, which have entrance barriers of about 15–20 kJ mol$^{-1}$ preventing any reaction in cold environments. Likewise, the reaction of atomic nitrogen, N($^4S$), is also expected to have an entrance barrier, and cannot happen in cold molecular clouds either. This underlines the special ability of atomic carbon to incorporate into aromatic hydrocarbon molecules under expansion of the cyclic structure. The situation can be more diverse, since more complex PAHs contain not only benzenoid units but also posses ethylenic (C=C) and butadienic (C=C–C=C) structures as found in anthracene and phenanthrene. The reactions of these more complex aromatic systems will be investigated in the future.

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