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Hydrogen-assisted isomerizations of fulvene to benzene and of larger cyclic aromatic hydrocarbons

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Abstract

The H-assisted isomerization of fulvene to benzene is characterized in detail using quantum chemistry, transition state theory, classical trajectory, and master equation calculations. This multistep isomerization involves 10 transition states, nine of which are found to contribute non-negligibly to the overall kinetics. Calculated temperature- and pressure-dependent rate coefficients are presented for H + fulvene → products, with care taken to quantify uncertainties in the theoretical predictions arising from various aspects of the calculation. The rate coefficients agree with past theoretical work within these estimated uncertainties. This fast isomerization proceeds via a cyclopropylcarbinyl intermediate—a substituted cyclopropyl group adjacent to a radical carbon—that provides a facile route for the carbon bonding rearrangement. Analogous H-assisted isomerization pathways involving cyclopropylcarbinyl intermediates are characterized using quantum chemistry calculations for four second-ring isomers of naphthalene: fulvalene, azulene, 1-methyleneindene, and 2-methyleneindene. These processes, and those for larger polycyclic aromatic hydrocarbons (PAHs), may be characterized in a general way as occurring in five steps: H additions, H shifts, cyclopropylcarbinyl intermediate formation, cyclopropylcarbinyl intermediate ring opening, and H-atom regeneration. Trends in the energetics of each of these steps with respect to PAH size and composition are discussed.
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Keywords: Benzene; Fulvene; Naphthalene; PAH; Theoretical chemical kinetics

1. Introduction

An important chemical bottleneck for the generation of large polycyclic aromatic hydrocarbons (PAHs), and therefore soot, is the formation of the first aromatic ring [1–8], which appears in flames as benzene, phenyl radical, benzyl radical, etc. The chemistry associated with the first ring is complex, as these species may be generated via multiple competing pathways, initiated either by small molecule/small radical additions or by the dehydrogenation of cycloalkanes. The relative importance of the competing pathways has long been debated, and detailed high-level chemical kinetics calculations together with modeling of the chemical structures of laboratory-based flames of representative hydrocarbons have greatly aided in our understanding of the chemistry of the first ring. The use of calculated rate coefficients in detailed reaction mechanisms has allowed the quantification of the relative contributions of the different first-ring-formation pathways for a variety of combustion systems, showing that the relative importance of the different pathways depends on both the fuel structure and the flame conditions [6,9].

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The formation of benzene has been particularly well-studied theoretically, with recent high-level ab initio/transition state theory (TST)/master equation (ME) calculations predicting significant benzene formation from the reaction of two propargyl (C_3H_3) radicals [10], the reaction of propargyl and allyl (C_3H_5) radicals [11], the reaction of C_4H_5 radicals with acetylene [12], and the reaction of methyl and cyclopentadienyl (c-C_5H_5) radicals [13]. The $C_3H_3 + C_3H_3$ reaction is generally important in flames of noncyclic fuels, while contributions from other resonantly stabilized radicals, C_3H_5, *i*-C_4H_5, and c-C_5H_5, can be important when these species are readily formed via fuel destruction [9,14–16].

Fulvene is less thermodynamically stable than benzene by ~30 kcal/mol, and is predicted to be formed alongside benzene in significant amounts as a product of the reactions discussed above. In fact, under many conditions relevant to combustion, fulvene is predicted to be the major product of the c-$C_5H_5 + CH_3$ and $C_3H_3 + C_3H_5$ reactions [11,13]; the self-recombination of C_3H_3 is predicted to produce three times more fulvene than benzene at 1500 K and 1 atm [10]. The isomeric composition of C_6H_6 in flames is important, as benzene promotes sooting more strongly than fulvene in rich environments and is more prone to oxidation than fulvene in lean environments. Despite its importance as a major first-ring product and its relative resistance to sooting and oxidation, fulvene concentrations in flames are typically lower than those for benzene [15–17]. In many combustion chemistry models, the main consumption pathway for fulvene is conversion to benzene via H-assisted isomerization [18]. Whereas the unimolecular (unassisted) isomerization of fulvene to benzene is slow and proceeds only via significant barriers and a high-energy bicyclic intermediate [10,19], hydrogen addition to fulvene stabilizes the subsequent bicyclic intermediate, providing a facile route for isomerization. This important bicyclic intermediate is an example of a cyclopropylcarbinyl radical, which features a three-membered ring adjacent to an alkyl radical C atom. These intermediates can readily open at any of the three participating cyclopropyl bonds and therefore provide a low-energy route for skeletal rearrangements. Reactions involving cyclopropylcarbinyl intermediates are known to be fast [20].

The potential energy surface (PES) for the H-assisted isomerization of fulvene to benzene was previously characterized by Melius et al. [18], and a rate coefficient for

$$\mathrm{H + fulvene} \rightleftarrows \mathrm{H + benzene} \tag{1a}$$

estimated [21] from this PES has been used in many detailed reaction mechanisms. More recently, the kinetics of H + fulvene was studied at 1 atm using high-level theoretical methods [22], where, in addition to (1a), the authors identified the stabilization reactions

$$\mathrm{H + fulvene\ (+M)} \rightleftarrows \mathrm{methylcyclopentadienyl\ (+M)} \tag{1b}$$
$$\rightleftarrows \alpha\text{-hydrofulvenyl (+M)} \tag{1c}$$
$$\rightleftarrows \beta\text{-hydrofulvenyl (+M)} \tag{1d}$$

to be important under some conditions. A complete pressure-dependent theoretical characterization was not attempted in Ref. [22] and some difficulties in the theoretical application were noted. One goal of the present work is to fully characterize the kinetics of the H-assisted isomerization of fulvene to benzene using ab initio/TST/ME methods [23,24], with nonempirical collisional energy transfer parameters calculated using a recently developed trajectory approach [25,26].

Reaction (1a) converts a five-membered ring into a six-membered one and generates the more thermodynamically-favored benzene from its higher-energy isomer. This reaction is suggestive of reactions of larger aromatic hydrocarbons (PAHs), where the abundance of H atoms in sooting flames may promote the ready interconversion of PAH isomers via analogous cyclopropylcarbinyl radical intermediates and other processes. If sufficiently fast, such processes may promote thermodynamic equilibria among isomeric PAHs and simplify the development of detailed reaction mechanisms for PAH growth. Several H-assisted isomerizations on the $C_{10}H_9$ PES are considered here involving the two-ring species fulvalene, azulene, 1-methyleneindene, 2-methyleneindene, and naphthalene. Although one could attempt detailed chemical kinetics studies for the second ring (and for larger PAHs) of the kind that have proven useful for the first ring, we do not attempt to do so here. Instead, we discuss trends in the expected chemistry of second ring isomerizations and extrapolate to larger PAHs. This perspective may be particularly useful for the development of models of PAH growth, where the large number of similar but different chemical reactions discourages their enumeration.

As noted above, theoretical predictions are increasingly being employed alongside experimental rate determinations in detailed reaction mechanisms. Under favorable circumstances, theoretical rate coefficients now approach what could be called "kinetic accuracy," which may be defined as a factor of ~2. (This term may be compared with the 1990s realization of "chemical accuracy" for theoretical thermochemistry of ~1 kcal/mol, as theoretical predictions began to be considered alongside experimental measurements. A similar situation has recently emerged in kinetics, as advocated by Klippenstein [27] and others.) This value roughly corresponds to: (1) an apparent lower uncertainty limit for computationally practical calculations of real systems, (2) an upper uncertainty

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limit for what can be defined as a useful prediction, and (3) an upper limit on experimental uncertainties for some kinds of kinetics measurements. These three qualitative bounds provide a useful metric for discussing the accuracy of theoretical predictions. Several sources of uncertainty in the present theoretical calculations are identified and discussed in the Supplementary data.

2. Theory

The theoretical kinetics methods used here closely follow the predictive ab initio/TST/ME strategies of Harding, Klippenstein, and Miller [23,24], which have been validated against numerous experimental results over the past several years. This section highlights details of the present application that differ from other recent ones.

2.1. C_6H_7

Critical points on the C_6H_7 PES were characterized using the QCISD(T)/CBS//M06-2X/6-311++G(d,p) dual level method, where the complete basis set (CBS) limit was extrapolated [28] from cc-pVDZ and cc-pVTZ calculations, and M06-2X is a Minnesota DFT method [29]. The single reference approach is appropriate for the species considered here, which have Q_1 diagnostics [30] less than 0.025, except for the kinetically unimportant b-hydrofulvenyl radical, for which the QCISD(T) method failed and the M06-2X/6-311++G(d,p) energy is reported. The QCISD(T) energies were calculated using MOLPRO [31], and the DFT calculations were carried out using Gaussian [32].

Several additional quantum chemistry calculations were performed to test the reliability of the predicted barrier heights and thermochemistry. CBS extrapolations using larger basis sets (cc-pVTZ and cc-pVQZ) were tested for the H-addition saddle point energies and for the energies of the adducts; the two CBS extrapolations differed by less than 0.01 kcal/mol. The QCISD(T)/CBS//B3LYP/6-311++G(d,p) method, which has been used extensively in past kinetics studies and which is similar to the popular G3B3 and CBS-QB3 methods, was tested for the entire PES. The B3LYP/6-311++G(d,p) method failed to locate a saddle point for addition to form the *tert*-hydrofulvenyl radical; this failure was noted previously for this saddle point [22]. Otherwise, the two dual level methods are in good agreement, differing in their predictions by ~1 kcal/mol for the other H additions and by less than ~0.3 kcal/mol for the other species, except for the H-shift saddle point connecting the methylcyclopentadienyl and *tert*-hydrofulvenyl radicals. For this saddle point, the two dual level methods differ by 7.7 kcal/mol.

Saddle points were identified for the four unique H additions to fulvene, for three H-atom shifts connecting the adducts to one another, for the ring closing and ring opening of the cyclopropylcarbinyl intermediate, and for H loss from the cyclohexadienyl radical. The single-transition-state kinetics for each of these processes was calculated using direct canonical variational (transition state) theory (CVT) [33], as implemented in the computer code POLYRATE [34] interfaced [35] with Gaussian. The dual level method used above to characterize the PES was deemed to be too expensive for the direct CVT calculations, so the following approach was adopted. Several lower-level methods with efficiencies suitable for direct dynamics were tested against the QCISD(T)/CBS//M06-2X/6-311++G(d,p) predictions for the properties of the saddle points. The M06-2X/6-31+G(d,p) method was found to give geometries, frequencies, and energies very close to those of the QCISD(T)/CBS//M06-2X/6-311++G(d,p) method, differing by less than 0.5% for the rotational constants, 3% for the frequencies, and 0.5 kcal/mol for the energies. The resulting M06-2X/6-31+G(d,p) kinetics were then corrected by a Boltzmann factor of the small energy differences in the two methods.

For the four H-addition transition states, significant variational effects were observed, lowering the predicted rate coefficients to as much as one-third of their nonvariational values. The use of curvilinear coordinates [36] to represent harmonic frequencies away from the saddle point was found to be important here, where, for the H-addition reactions, the curvilinear coordinate calculations predicted rate coefficients that are 10–90% larger than those predicted by the more conventional Cartesian coordinate calculations. The principal effect of the use of curvilinear coordinates is to more accurately describe the low-frequency bending modes involving the reactant H atom, for which Cartesian normal modes provide a particularly poor description. This effect may be anticipated in general for H-addition reactions with low barriers.

Tunneling was calculated using the asymmetric Eckart method [37] as implemented in VariFlex [38] and Truhlar's small and large curvature tunneling (SCT [39] and LCT [40]) methods. For the present systems, the SCT method predicted larger tunneling than the LCT method and is therefore preferred [41]. For the four addition reactions, the Eckhart tunneling corrections were similar to the SCT ones and were smaller by only 20% at 300 K. At elevated temperatures the tunneling corrections were small, as predicted by all three methods. Two recent computational studies found that, despite the apparent simplicity of the Eckart model, the SCT and Eckart methods make similar predictions [42,43], in agreement with the

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present work. SCT corrections were used throughout the rest of this work.

Phenomenological temperature- and pressure-dependent rate coefficients and product branching fractions were calculated using the thermochemistry and single-transition-state kinetics discussed above and the Klippenstein–Miller ME, described elsewhere [23] and available in a recent version of VariFlex. As noted previously for this reaction [22], the chemically significant eigenvalues corresponding to equilibration of the *tert*-hydrofulvenyl, cyclopropylcarbinyl, and methylcyclopentadienyl radicals merge into the continuum of internal energy relaxation eigenvalues at some temperatures and pressures. We employed the well-reduction strategies of Miller and Klippenstein (personal communication, 2011) at temperatures and pressures where these issues were identified.

The single-exponential-down model [44] was used to describe collisional stabilization and activation in the ME. Results for the bath gas Kr are presented here; results for other heavy atomic and diatomic baths are likely to be very similar to those for Kr, with differences within the accuracy of our approach for predicting collisional energy transfer parameters [26]. The required parameters for the single exponential down model are the temperature-dependent exponential range parameter, α, and the Lennard–Jones collision parameters, $r_{LJ} \equiv 2^{1/6}\sigma_{LJ}$ and ε_{LJ}. These parameters were calculated using classical trajectory simulations of target–bath gas collisions. Details of the trajectory strategies for calculating α have been given elsewhere [25,26]. A full-dimensional potential energy surface was used with universal hydrocarbon–Kr parameters taken from those for $CH_4 + Kr$ [45]. This approach was validated against full-dimensional direct dynamics trajectory calculations for C_2 and C_3 systems [46].

The Lennard–Jones collision parameters were obtained in a new but simple way from trajectory calculations. A small ensemble was prepared corresponding to zero impact parameter collisions with random initial relative orientations. The center-of-mass separation of the target and the bath gas was monitored, and the values of the center-of-mass distance and the interaction energy at the maximum target–bath interaction energy along each trajectory were recorded. These values were averaged over the ensemble and assigned to r_{LJ} and ε_{LJ}.

Collision parameters were calculated for the three adducts most likely to be stabilized: the methylcyclopentadienyl, α-hydrofulvenyl, and β-hydrofulvenyl radicals. The trajectory calculations predicted very similar collision parameters for these three wells, with $r_{LJ} = 4.5$ Å and $\varepsilon_{LJ} = 230\ cm^{-1}$ for Kr. The ensemble-averaged values of α were also similar for the three complexes, differing by less than 25% for 500–2500 K. A single set of energy transfer parameters was therefore employed for all the wells in this system, with $\alpha(T) = 333\ (T/300\ K)^{0.7}\ cm^{-1}$ for 300–2500 K.

2.2. $C_{10}H_9$

The M06-2X/6-311++G(d,p) method was used to calculate geometries, frequencies, and energies for stationary points associated with second ring H-assisted isomerizations. High-level energy corrections were not pursued. The accuracy of this approach may be validated by comparing the energies predicted by the M06-2X/6-311++G(d,p) method with those of the dual level method discussed above for the C_6H_7 PES. Agreement is good, with the M06-2X method predicting higher H-addition barriers by only 0.4 kcal/mol, on average, and lower energies for the two saddle points associated with the cyclopropylcarbinyl intermediate by ~1 kcal/mol. Larger differences were found for the H-shift barriers, with an average difference of 4 kcal/mol. These errors are likely suitable for the present study of trends for the larger PAHs.

3. Results and discussion

3.1. H + fulvene H + benzene and other products

The calculated PES for Eq. (1) is shown in Fig. 1 and is in very good agreement with the BAC-MP4 PES of Melius et al. [18]. In a more recent theoretical study [22], this PES was characterized using CBS-QB3 as part of a much larger work, and some details were not provided. Qualitatively, the previous CBS-QB3 energies appear to be in very good agreement with the present work (based on Fig. 14 of Ref. [22]). The principal differences in the present and recent [22] high-level PESs are the present higher barrier height for the

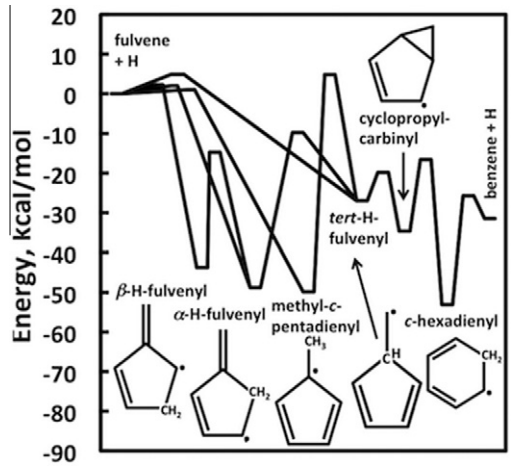

Fig. 1. Potential energy diagram for H + fulvene.

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H-shift saddle point connecting the methylcyclopentadienyl and *tert*-hydrofulvenyl radicals as well as the present identification of an H-addition saddle point for forming the methylcyclopentadienyl radical, which could not be located at the level of theory used in the earlier study [22].

The energy barriers for H addition are small and are 1.0, 2.1, 2.2, and 4.9 kcal/mol for the methylcyclopentadienyl, α-hydrofulvenyl, β-hydrofulvenyl, and *tert*-hydrofulvenyl adducts, respectively. The latter three adducts are connected to one another by energetically accessibly H-atom shifts. The H-atom shift connecting the methylcyclopentadienyl and *tert*-hydrofulvenyl radicals, however, has a higher barrier energy, with the threshold for this process above that of the reactants. This tight transition state therefore inhibits further isomerization and subsequent formation of benzene from the methylcyclopentadienyl adduct. The other adducts can readily interconvert with the *tert*-hydrofulvenyl radical. As discussed in detail by Melius et al. [18], the *tert*-hydrofulvenyl radical contains the $^{\bullet}CH_2{-}CHR{-}CH{=}CH{-}$ moiety, which can readily close to a cyclopropylcarbinyl ([3.1.0]bicyclo) radical. The resulting substituted cyclopropyl group can open via low barriers at any of its three bonds. The barrier for closing to the cyclopropylcarbinyl intermediate is only 15 kcal/mol, and the barrier for opening to the cyclohexadienyl radical is only 18 kcal/mol, both of which are readily superable by the activated C_6H_7 complex. H-loss from the cyclohexadienyl radical proceeds via a low-energy loose transition state and regenerates the catalytic H atom forming benzene.

Calculated temperature- and pressure-dependent rate coefficients are shown in Fig. 2. The high-pressure limit for fulvene + H (cf. Fig. 2a) is the sum of the four H-addition rates, as the assumption in this limit is that the initial adducts are immediately stabilized with no benzene formed. In contrast, benzene + H is the only product in the collisionless (zero pressure) limit, as the absence of collisions prevents stabilization. Product branching is strongly dependent on pressure, which is a general result for reactions featuring an activated complex and one or more low-energy bimolecular product channels, such as this one. What is unexpected, perhaps, is that the *total* rate coefficient is also a function of pressure. This pressure dependence arises for two reasons. First, the H-shift transition state connecting the methylcyclopentadienyl and *tert*-hydrofulvenyl radicals is sufficiently high that the methylcyclopentadienyl radical cannot be converted to benzene in significant amounts, even at the highest temperature considered here, 2500 K. The contribution to the total rate coefficient from the methylcyclopentadienyl adducts therefore goes to zero as the pressure is decreased to zero. Second, the tight transition states in the benzene exit channel associated with the cyclopropylcarbinyl intermediate are partially rate limiting for benzene formation but are not accessed (and so are not rate limiting) when the adducts are stabilized. These transition states, therefore, have no effect in the high-pressure-limit but lower the collisionless rate coefficient by as much as a factor of 2 at 2500 K. The effect of these late transition states on the total rate coefficient is negligible below 1000 K, even at zero pressure.

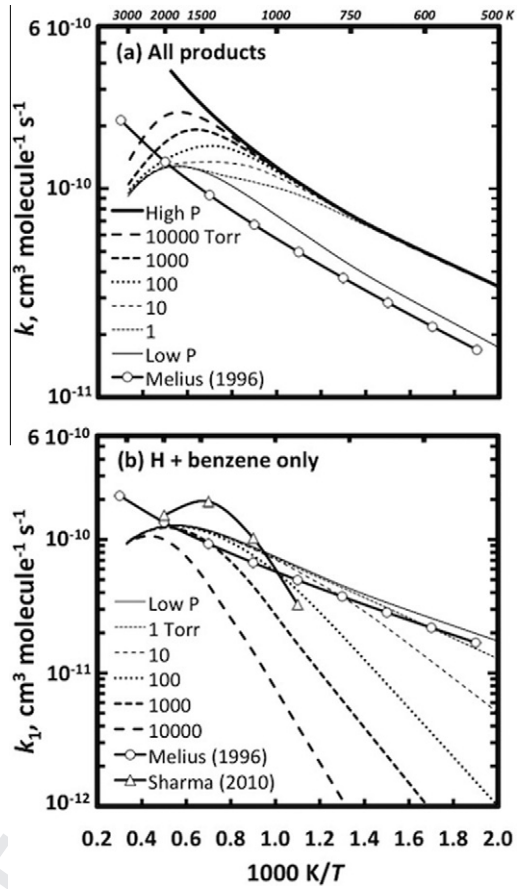

Fig. 2. Predicted rate coefficients for H + fulvene in 1–10,000 Torr Kr (a) for all products and (b) for H + benzene. Also shown are the previous estimates based on the Melius et al. [18,21] potential energy surface and the previous calculation of Sharma et al. [22] for 1 atm N_2.

The rate coefficient for benzene formation is shown in Fig. 2b. The present prediction in this regime is in excellent agreement with both the previous estimate [21] and the recent high-level calculations [22], which differs from the present result by less than a factor of two at 1 atm. Furthermore, the product branching fractions calculated at 1 atm are very close to those reported by Sharma et al. Benzene + H is the major product above ~1000 K, even at high pressures, although

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nonnegligible contributions from collisional stabilization of the methylcyclopentadienyl, α-hydrofulvenyl, and β-hydrofulvenyl adducts may be found for conditions relevant to combustion (cf. Fig. 3).

The excellent agreement between the present and previous [22] high-level theoretical treatments is encouraging, as both calculations involve many steps, some different—but equally reasonable—choices were made for some of these steps, and the effect of uncertainties in each step on the overall kinetics is not necessarily easy to anticipate. The principal differences between the two studies are: (1) the earlier study included an estimate for the methylcyclopentadienyl adduct H-addition rate, whereas here it was calculated; (2) the CVT/SCT kinetics employed here are in principle more accurate than the simpler methods used previously; and (3) the earlier study used a constant value of 600 cm^{-1} for the collisional energy transfer parameter, whereas here this value was calculated and varies from 500 to 1500 cm^{-1} for 500–2500 K.

A detailed uncertainty analysis for the present calculations is given as Supporting information, where it is shown that the present theoretical predictions approach chemical accuracy (~60%) for temperatures above ~500 K and have uncertainties of a factor of four at room temperature. Notably, the two high-level theoretical predictions and the previous estimate agree within this uncertainty. The present calculated rate coefficients are provided as Supporting information.

3.2. H-assisted isomerizations of second ring species

Next, we discuss H-assisted isomerizations involving second-ring species with similar reaction pathways as discussed in Section 3.1 for the first ring. Reaction (1a) proceeds via five steps: (1) H-atom addition, (2) H-atom shifts to generate the cyclopropylcarbinyl precursor, (3) closure of the cyclopropyl group to generate the cyclopropylcarbinyl intermediate, (4) opening of the cyclopropyl group at a different C—C bond to effect the desired skeletal rearrangement, and (5) H loss to form benzene. One can identify analogous steps in larger PAHs by identifying the presence of fulvene-like structural elements, and we have done so for four higher-energy isomers of naphthalene: azulene, 1-methyleneindene, 2-methyleneindene, and fulvalene. Mechanisms for conversion of these $C_{10}H_8$ isomers to naphthalene via H-assisted isomerization and involving cyclopropylcarbinyl intermediates are shown schematically in Fig. 4. Some pathways share common cyclopropylcarbinyl intermediates, and one of the pathways involves two such intermediates. (Note that the species formed via the reaction of two c-C_5H_5 radicals followed by the loss of an H atom is the same species that is formed via H addition to fulvalene, and that cyclopropylcarbinyl intermediates therefore play an important role incorporating five-membered rings into PAHs [18,22]. Likewise, the reaction of indenyl radicals with CH_3 may involve the reaction pathways shown in Fig. 4 for the H-assisted isomerizations of 1- and 2-methyleneindene, even if neither of these parent species is themselves formed in significant amounts in flames.)

The calculated H-addition, H-shift, cyclopropylcarbinyl ring opening and ring closing, and H-loss pathways for the species shown in Fig. 4 are provided as Supplementary data. Here, we summarize trends in the calculated energetics for each of the steps in such a way as to suggest extrapolations to larger PAHs. Notably, the saddle points and intermediates related to the cyclopropylcarbinyl intermediates are *not* directly hindered by the presence of additional rings. The intermediates may appear strained in the two-dimensional representations in Fig. 4, but they are in fact not significantly hindered in three

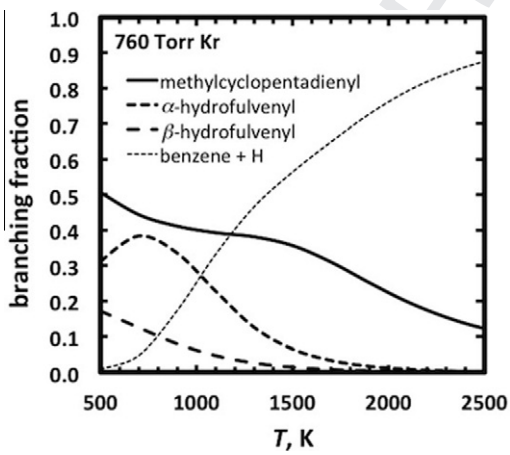

Fig. 3. Predicted product branching fractions for H + fulvene at 760 Torr Kr.

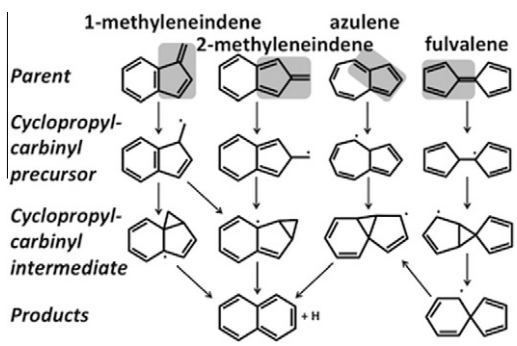

Fig. 4. Reaction scheme showing H-assisted isomerizations of $C_{10}H_8$ species via cyclopropylcarbinyl intermediates.

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dimensions (cf. Supplementary Fig. S4). This property in part explains the general importance of these intermediates [20] and was emphasized already by Melius et al. [18] for processes similar to the ones discussed here. Although the additional rings do not directly block these routes, one may expect some effect from differences in the local environments of the cyclopropylcarbinyl intermediates, and trends in the energetics for the five H-assisted isomerization steps identified above are discussed next for the second-ring isomers.

3.2.1. Steps 1 and 2: H additions and H shifts

As discussed above, H may readily add to fulvene at any C atom but one adduct (methylcyclopentadienyl) is blocked from further isomerization to benzene by a large H-shift barrier. A similar situation arises in the two-ring species. The barriers for H-addition are typically less than 5 kcal/mol, with additions to C atoms in six- and seven-membered rings and to tertiary carbon atoms somewhat less favored than additions to methylene carbons and to five-membered rings. H-atom addition to directly the tertiary C atom to form the cyclopropylcarbinyl precursor is often the least favored addition, such that more favored routes often involve additions to nearby carbon atoms followed by H shifts (cf. Supplementary Fig. S2). The resulting activated complexes typically have 30–60 kcal/mol of internal energy, which is similar to what was found for H addition to fulvene. This internal energy allows the system to readily undergo some, but not all, H shifts. For the systems studied here, H shifts around five-membered rings have barriers of only ~20 kcal/mol, whereas those involving six- or seven-membered rings or methylene carbons have higher barriers of >30 kcal/mol, which are close to or greater than the typical H-addition activation energies. As a general rule, we conclude that H-atom additions to the five-membered rings participating in the isomerizations may readily produce the cyclopropylcarbinyl precursors, whereas H-atom additions elsewhere do not. 1-Methyleneindene is an exception, as this isomer is only slightly less stable than naphthalene and H-addition does not provide enough activation energy to overcome any of the H-shift thresholds.

As observed in the H + fulvene reaction, H additions that are not readily connected to cyclopropylcarbinyl precursors may result in stabilization of the adducts at low temperatures and/or high pressures.

3.2.2. Steps 3 and 4: Formation and then re-opening of the cyclopropylcarbinyl intermediate

The cyclopropylcarbinyl precursors are typically the highest-energy adducts, with low barriers for closing to the cyclopropylcarbinyl intermediates. The ring-closing barriers vary from 5 to 15 kcal/mol, and the thresholds for these processes are 13–31 kcal/mol (20 kcal/mol for fulvene) below the reactants. The cyclopropylcarbinyl intermediates themselves have energies of 20–50 kcal/mol (35 kcal/mol for fulvene) below the reactants. Ring opening is similar to ring closing, with thresholds that are 8–40 kcal/mol (17 kcal/mol for fulvene) below the reactants. The quantitative effect of the barriers for cyclopropylcarbinyl intermediate ring closing and opening is not straightforward to anticipate without detailed calculations. As discussed above for fulvene, such bottlenecks must be accounted for when making quantitative predictions as they may be partially rate limiting. For the present qualitative discussion, we estimate that these barriers are not likely to significantly hinder isomerization.

Each cyclopropylcarbinyl intermediate may open at any of the three participating cyclopropyl bonds, and it is interesting to compare the competing ring opening processes for the second ring cyclopropylcarbinyl intermediates. For the cyclopropylcarbinyl intermediate associated with azulene in Fig. 4, ring opening to azulene is favored and is nearly barrierless, ring opening to the five-membered ring has a barrier of 8 kcal/mol, and ring opening to the six-membered ring has a barrier of 18 kcal/mol. The isomerization of fulvalene to naphthalene may therefore involve an excursion to the azulene region of the PES. This trend is general, where opening to the thermodynamically favored six-membered rings is typically less favored than opening to five- and seven-membered rings.

3.2.3. Step 5: H loss

Regeneration of H atoms proceeds via low-energy loose transition states and is not expected to be rate limiting.

Overall, the predicted energetics of H-assisted isomerizations of second ring species is very similar to those for fulvene. There are two important rate-determining aspects of the PES. First, the rate is controlled by the number of "active" H-atom additions that are readily connected to the cyclopropylcarbinyl precursor via low-energy H shifts. These adducts are typically those resulting from H-atom additions to C atoms in the fulvene-like five-membered ring participating in the isomerization. Second, the isomerization may be somewhat hindered by high threshold energies for the cyclopropylcarbinyl ring closing and ring opening steps; this effect is expected to be less important for the higher-energy parent isomers. The energetic thresholds of H-assisted isomerizations of second-ring species are similar to those for the first ring and are largely independent of the local environment, which suggests useful extrapolations may be made to larger hydrocarbons. Exploratory calculations of analogous reactions of third ring

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species support this conclusion, although the barriers for H-addition appear to be higher for the larger species, which may limit the importance of these reactions in larger PAHs. In general, one may anticipate rate coefficients for H-assisted isomerization of the higher-energy $C_{10}H_8$ isomers (and for similar processes in larger PAHs) to approach that for fulvene isomerization discussed in Section 3.1.

4. Conclusions

A detailed ab initio/TST/ME calculation was carried out for the H-assisted isomerization of fulvene to benzene. The predicted results agree with an earlier estimate and with a recent high-level calculation within the estimated theoretical uncertainty, which has been characterized in detail here. The energetics of analogous pathways involving the conversion of four two-ring $C_{10}H_8$ species to naphthalene was also discussed. The presence of an additional spectator ring was found to not directly hinder the H-assisted isomerizations, and one may expect similarly rapid H-assisted isomerizations for larger PAHs, although the importance of such processes may be reduced somewhat due to slower H-addition initiation reactions. The present results provide some support for the use of thermodynamic constraints in describing the relative populations of PAH isomers in detailed reaction mechanisms of PAH growth.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2012.06.165.

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