**Supplementary Information**

**Description of Chemical Reaction Mechanism**

The current polycyclic aromatic hydrocarbon (PAH) growth mechanism contains reactions that can occur at any given kinetic Monte Carlo (kMC) step, depending on the structure of the molecule. Figures 1 and 2 illustrate example reaction pathways followed by the reactions implemented in the current PAH growth model. Tables 1 and 2 enumerate the reaction rates used for the constituent reactions of the pathways. Importantly, these reaction pathways are not an exhaustive list, but are meant to provide an idea of how PAHs may grow as a result of different reactions. Due to the mixing of these reactions, many more reaction pathways are possible.

Figure 1a shows the growth of benzene to naphthalene via the hydrogen abstraction, acetylene addition (HACA) mechanism. The mechanism utilizes chemical rate constants derived from work by Kislov et al. [1]. The growth model also includes the addition reactions of the vinyl radical ($C_2H_3$) and ethylene ($C_2H_4$). These reactions are alternative addition reactions involving 2 carbons, which also lead to growth through the HACA mechanism shown in Figure 1. The growth model includes the ring closures depicted by R15 and R16, creating 5- and 6-membered rings at zig zag and armchair sites, respectively. The armchair and zig zag closure reactions utilize rates derived from Kislov et al. [1]. Figure 1b depicts 5- and 6-membered ring closures at bay sites, which utilize rates derived from Raj et al. [2] and Violi [3].

Figure 2 shows additional reaction pathways that have been translated into the PAH growth model which form several different moieties. These pathways include the 5-membered ring migration pathway proposed by Frenklach et al. [4], shown in Figure 2a; the addition of propargyl sequentially to form biphenyl, shown in Figure 2b; the formation of indene through addition of methyl radicals and acetylene, shown in Figure 2c; the formation of phenanthrene by reaction with the cyclopentadienyl radicals, shown in Figure 2c; the addition of benzene and phenyl radicals to PAHs and subsequent ring closures involving attached benzyl groups, shown in Figure 2d. All of the elementary steps of these reactions are expected to mix in simulations, exploring complex reaction pathways beyond those illustrated.
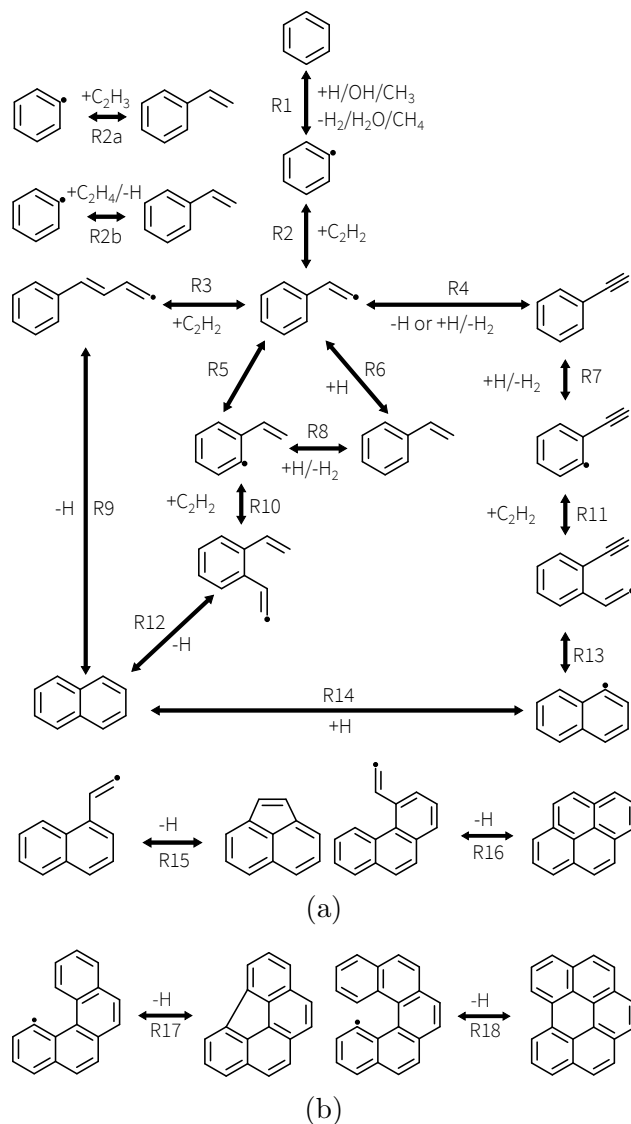
Figure 1: The reaction network of the HACA mechanism: (a) benzene growth to naphthalene and 5- and 6-membered ring closure at zig zag and armchair sites (b) 5- and 6-membered ring closure at bay sites.
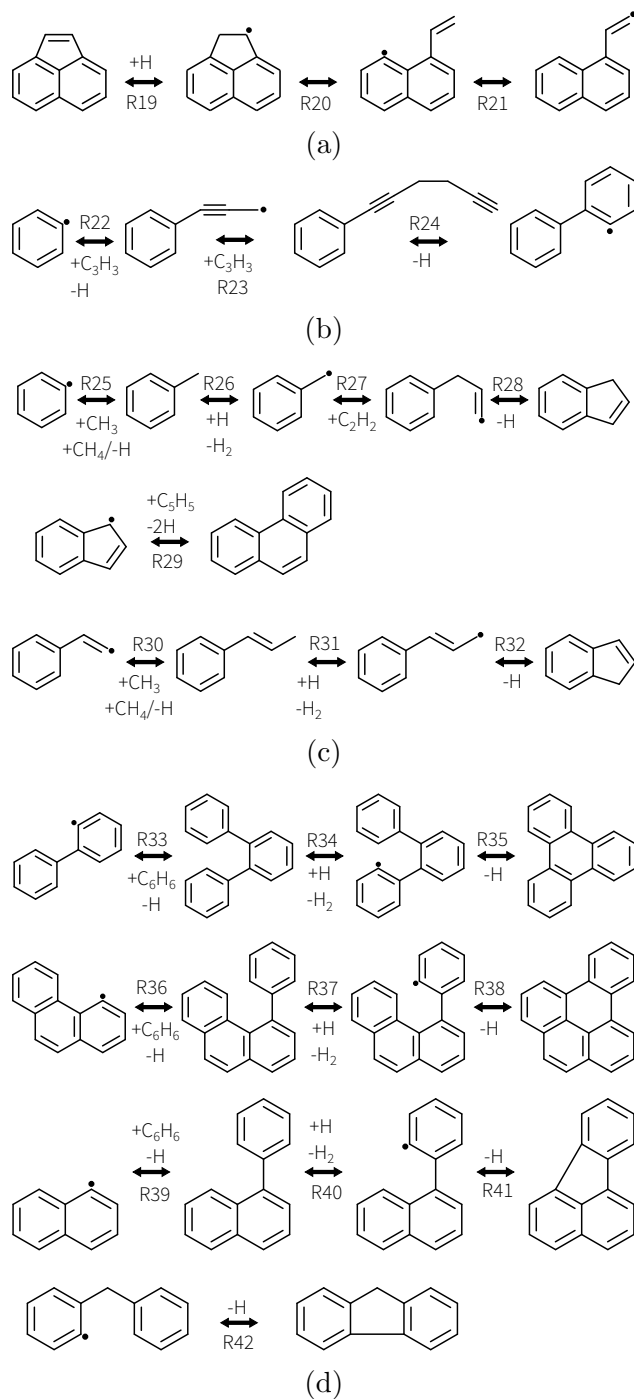
Figure 2: Additional reaction pathways in the PAH growth model: (a) 5-membered ring migration (b) propargyl addition to biphenyl (c) formation of indene and reaction with cyclopentadienyl radicals to phenanthrene (d) benzene and phenyl addition and ring closures.

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Table 1: Chemical rates for reactions included in the HACA portion of the PAH growth model. The source "CR" refers to a reverse rate computed using thermodynamic equilbrium.

| Reaction and Number(s) | Forward Rate | | | | Reverse Rate | | | |
|---|---|---|---|---|---|---|---|---|
| | A | n | $E_a$ | Source | A | n | $E_a$ | Source |
| Units: A = [s$^{-1}$] for unimolecular reactions, [cm$^3$s$^{-1}$mol$^{-1}$] for bimolecular reactions; $E_a = \frac{\text{kcal}}{\text{mol}}$ | | | | | | | | |
| **Hydrogen Abstraction, Acetylene/Carbon Addition** | | | | | | | | |
| **H Abstraction by H** e.g. R1, R6, R8, R14, R26, R31, R34, R37, R40 | 6.46E+07 | 1.86 | 15.98 | [1] | 9.23E+04 | 2.39 | 5.82 | [1] |
| **H Abstraction by OH** e.g. R1, R6, R8, R14, R26, R31, R34, R37, R40 | 8.65E+02 | 3.04 | 3.68 | [1] | 5.59E+00 | 3.57 | 8.66 | [1] |
| **H Abstraction by CH$_3$** e.g. R1, R6, R8, R14, R26, R31, R34, R37, R40 | 8.65E+02 | 3.04 | 3.68 | [1] | 5.59E+00 | 3.57 | 8.66 | [1] |
| **Acetylene Addition** e.g. R2, R3, R10 | 3.29E+06 | 2.05 | 3.16 | [1] | 2.48E+15 | 0.01 | 46.06 | [1] |
| **Vinyl (C2H3) Addition** e.g. R2a | 1.50E+22 | -2.6 | 6.28 | [5] | 7.10E+21 | -1.67 | 118.73 | CR |
| **Ethylene (C2H4) Addition** e.g. R2b | 2.51E+12 | 0 | 6.2 | [5] | 4.84E+20 | -2.17 | 13.66 | CR |
| **Isomerization - Ethenyl to Acetyl** e.g. R4 | 7.18E+10 | 1.02 | 38.67 | [1] | 1.06E+09 | 1.53 | 5.63 | [1] |
| **Isomerization - Ethenyl to Acetyl by H** e.g. R4 | 1.65E+11 | 0.49 | 10.63 | [1] | 6.99E+08 | 1.32 | 87 | [1] |
| **Hydrogen Transfer** e.g. R5 | 5.90E+10 | 0.55 | 27.57 | [1] | 2.32E+10 | 0.69 | 25.93 | [1] |
| **6-Membered Ring Closure** e.g. R9 | 3.61E+09 | 0.6 | 3.64 | [1] | 3.91E+17 | -1.51 | 67.91 | CR |
| **6-Membered Ring Closure** e.g. R12 | 5.14E+12 | 0.06 | 2.13 | [1] | 4.16E+20 | -2.05 | 66.35 | CR |
| **6-Membered Ring Closure** e.g. R13 | 9.95E+11 | 0.05 | 5.4 | [1] | 2.22E+12 | 0.74 | 62.4 | CR |
| **5-Membered Ring closure - Zig Zag** e.g. R15 | 2.88E+11 | 0.23 | 17.03 | [1] | 6.67E+12 | 0.43 | 15.54 | CR |
| **6-Membered Ring closure - Armchair** e.g. R16 | 1.91E+09 | 1.14 | 1.63 | [1] | 3.29E+11 | 1.24 | 26.43 | CR |
| **Ring Closures at Bay Sites** | | | | | | | | |
| **5-Membered Ring Closure - Bay** e.g. R17 | 3.86E+11 | 0.21 | 17.7 | [3] | 6.67E+12 | 0.43 | 15.54 | CR |
| **6-Membered Ring Closure - Bay** e.g. R18 | 1.11E+11 | 0.66 | 23.99 | [2] | 3.29E+11 | 1.24 | 26.43 | CR |

Table 2: Chemical rates for additional reactions included in the PAH growth model. The source "CR" refers to a reverse rate computed using thermodynamic equilbrium.

| Reaction and Number(s) | Forward Rate | | | | Reverse Rate | | | |
|---|---|---|---|---|---|---|---|---|
| | A | n | Ea | Source | A | n | Ea | Source |
| Units: A = [s$^{-1}$] for unimolecular reactions, [cm$^3$s$^{-1}$mol$^{-1}$] for bimolecular reactions; $E_a = \frac{\text{kcal}}{\text{mol}}$ | | | | | | | | |
| **5-Membered Ring Migration** | | | | | | | | |
| **5-Membered Ring Hydrogenation** e.g. R19 | 8.41E+08 | 1.49 | 0.99 | [4] | 1.00E+10 | 0.22 | 25.54 | [4] |
| **5-Membered Ring Opening - Hydrogenated** e.g. R20 | 1.00E+10 | -0.22 | 23.22 | [4] | 5.04E+06 | 0.74 | 6.57 | [4] |
| **Hydrogen Transfer** e.g. R21 | 1.22E+06 | 1 | 8.01 | [4] | 3.22E+06 | 0.93 | 7.38 | [4] |
| **Propargyl Addition and Formation of Biphenyl** | | | | | | | | |
| **Propargyl Addition** e.g. R22 | 3.00E+12 | 0 | 0 | [6] | 3.39E+17 | -1.06 | -0.94 | [6] |
| **Propargyl Addition and Ring Closure to Biphenyl** e.g. R23 + R24 | 3.00E+12 | 0 | 0 | [6] | 3.39E+17 | -1.06 | -0.94 | [6] |
| **Formation of Indene and Phenanthrene** | | | | | | | | |
| **Methyl Addition** e.g. R25,R30 | 2.82E+44 | -9.36 | 14.31 | [5] | 1.03E+22 | -1.8 | 106.82 | CR |
| **Acetylene Addition to Methyl** e.g. R27 | 3.20E+11 | 0 | 7 | [5] | 2.48E+15 | 0.01 | 46.06 | [1] |
| **Ring Closure - Propenyl Chain** e.g. R28,R32 | 2.88E+11 | 0.23 | 17.03 | [1] | 6.67E+12 | 0.43 | 15.54 | CR |
| **Indene to Phenanthrene** e.g. R29 | 5.00E+12 | 0 | 8 | [5] | 1.00E+19 | -1.05 | -15.56 | CR |
| **Benzene, Phenyl Addition and Ring Closures** | | | | | | | | |
| **Benzene Addition** e.g. R33,R36,R39 | 2.22E+83 | -20.79 | 46.89 | [5] | 1.79E+22 | -2.45 | 23.59 | CR |
| **Phenyl Addition** e.g. R33,R36,R39 (Analogous) | 2.00E+26 | -3.9 | 6.32 | [5] | 7.06E+21 | -1.56 | 119.01 | CR |
| **6-Membered Ring Closure** e.g. R35,R38 | 1.11E+11 | 0.66 | 23.99 | [1] | 3.29E+11 | 1.24 | 26.43 | CR |
| **5-Membered Ring Closure** e.g. R41,R42 | 3.86E+11 | 0.21 | 17.7 | [1] | 6.67E+12 | 0.43 | 15.54 | CR |

## References

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