

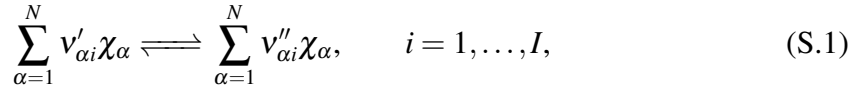
Appendix. Supplementary material

S.1 Steady-state and partial-equilibrium model equations

The sections that follow summarise the development of the steady-state and partial-equilibrium model equations used in this work. The exposition and the production and loss notation closely follows that used in a number of related works [see for example 5–7, 9, 13].

S.1.1 General reaction equations

A general set of chemical reactions can be written in the form



where χ are the chemical species and $v'_{\alpha i}$ and $v''_{\alpha i}$ are the forward and reverse stoichiometric coefficients of species α in reaction i . The rate of progress q_i can be written as

$$q_i = k_i \prod_{j=1}^N c_j^{v'_{ji}} - \frac{k_i}{K_{ci}} \prod_{j=1}^N c_j^{v''_{ji}}, \quad (\text{S.2})$$

where k_i is the forward rate constant, K_{ci} is the equilibrium constant of reaction i and c_j is the concentration of species j . The net production rate $\dot{\omega}_{\alpha}$ of species α is given as

$$\dot{\omega}_{\alpha} = \sum_{i=1}^I (v''_{\alpha i} - v'_{\alpha i}) q_i. \quad (\text{S.3})$$

S.1.2 Production and loss terms

The net production rate $\dot{\omega}_{\alpha}$ can be manipulated by substituting Eq. (S.2) into Eq. (S.3) to separate the terms responsible for the production and consumption of species α

$$\dot{\omega}_{\alpha} = \sum_{i=1}^I (v''_{\alpha i} - v'_{\alpha i}) \left(k_i \prod_{j=1}^N c_j^{v'_{ji}} - \frac{k_i}{K_{ci}} \prod_{j=1}^N c_j^{v''_{ji}} \right), \quad (\text{S.4})$$

$$\begin{aligned} &= \sum_{i=1}^I \left(v''_{\alpha i} k_i \prod_{j=1}^N c_j^{v'_{ji}} + v'_{\alpha i} \frac{k_i}{K_{ci}} \prod_{j=1}^N c_j^{v''_{ji}} \right) \\ &\quad - \sum_{i=1}^I \left(v'_{\alpha i} k_i \prod_{j=1}^N c_j^{v'_{ji}} + v''_{\alpha i} \frac{k_i}{K_{ci}} \prod_{j=1}^N c_j^{v''_{ji}} \right). \end{aligned} \quad (\text{S.5})$$

Assuming that all reactions are first order with respect to all species in the forward and reverse reactions, Eq. (S.5) can be rearranged to give

$$\dot{\omega}_{\alpha} = P_{\alpha} - L_{\alpha} c_{\alpha}, \quad (\text{S.6})$$

where P_α and L_α are the production and loss terms of species α

$$P_\alpha = \sum_{i=1}^I P_\alpha^{(i)}, \quad \text{where} \quad P_\alpha^{(i)} = v''_{\alpha i} k_i \prod_{j=1}^N c_j^{v_j^{(i)}} + v'_{\alpha i} \frac{k_i}{K_{ci}} \prod_{j=1}^N c_j^{v_j''}, \quad (\text{S.7})$$

$$L_\alpha = \sum_{i=1}^I L_\alpha^{(i)}, \quad \text{where} \quad L_\alpha^{(i)} = v'_{\alpha i} k_i \prod_{\substack{j=1 \\ j \neq \alpha}}^N c_j^{v_j^{(i)}} + v''_{\alpha i} \frac{k_i}{K_{ci}} \prod_{\substack{j=1 \\ j \neq \alpha}}^N c_j^{v_j''}. \quad (\text{S.8})$$

In order to assist the analysis in the following sections, it is useful to introduce the terms

$$P_{\alpha,\beta} = \sum_{i \in \mathbf{R}_{\beta \rightarrow \alpha}} P_{\alpha,\beta}^{(i)}, \quad \text{where} \quad P_{\alpha,\beta}^{(i)} = v''_{\alpha i} k_i \prod_{\substack{j=1 \\ j \neq \beta}}^N c_j^{v_j^{(i)}} + v'_{\alpha i} \frac{k_i}{K_{ci}} \prod_{\substack{j=1 \\ j \neq \beta}}^N c_j^{v_j''}. \quad (\text{S.9})$$

$\mathbf{R}_{\beta \rightarrow \alpha}$ is the set of reactions that produce species α from species β . The term $P_{\alpha,\beta}$ is a pseudo first-order rate coefficient such that $P_{\alpha,\beta} c_\beta$ gives rate of production of species α from species β under the first-order assumption made above and under the provision that species α and β are on different sides of the reaction equation.¹

The loss term is a pseudo first-order rate coefficient and has a connection with the lifetime τ_α of species α

$$\tau_\alpha = \frac{1}{L_\alpha}, \quad (\text{S.10})$$

which has been shown to be related to the time for which a short-lived species is present in a reaction system [13].

S.1.3 Approximations based on timescale separation

In the analysis that follows, we assume a closed constant-volume isothermal system with N species and I chemical reactions. A material balance over the system yields

$$\frac{dc_\alpha}{dt} = P_\alpha - L_\alpha c_\alpha, \quad \alpha = 1, \dots, N, \quad (\text{S.11})$$

where the right hand side describes the net production rate of species α and follows from Eq. (S.6), and c is the solution vector containing the molar concentrations of the species.

Steady-state approximation

The steady-state approximation decomposes Eq. (S.11) into the following equations

$$0 \approx P_\alpha - L_\alpha c_\alpha, \quad \alpha \in \mathbf{S}_{\text{ss}}, \quad (\text{S.12})$$

$$\frac{dc_\alpha}{dt} = P_\alpha - L_\alpha c_\alpha, \quad \alpha \notin \mathbf{S}_{\text{ss}}, \quad (\text{S.13})$$

¹Under these restrictions, $(v'_{\alpha i}, v'_{\beta i}, v''_{\alpha i}, v''_{\beta i}) = (0, 1, 1, 0)$ or $(1, 0, 0, 1)$.

where S_{ss} denotes a subset of species that evolve rapidly relative to the other species in the system. The underlying assumption is that these species reach a local steady-state, such that the left hand side of Eq. (S.12) tends to zero over timescales much smaller than the timescales of Eq. (S.13). Tikhonov's theorem [11, 12] states that the solution of Eqs. (S.12) and (S.13) approaches the solution of Eq. (S.11) as the left hand side of (S.12) tends to zero.

Equation (S.12) can be written as

$$L_\alpha c_\alpha - \sum_{\beta \in S_{ss}} P_{\alpha,\beta} c_\beta = P_\alpha - \underbrace{\sum_{\beta \in S_{ss}} P_{\alpha,\beta} c_\beta}_{=: b_\alpha}, \quad \alpha \in S_{ss}. \quad (\text{S.14})$$

A key insight is that Eq. (S.14) is linear in the concentrations of the species in S_{ss} if S_{ss} is chosen such that no more than one species from S_{ss} appears on any side of a reaction. To see this, we note that under the given constraint, L_α is not a function of c_α (see Eq. (S.8)) and $P_{\alpha,\beta}$ is not a function of c_α or c_β (see Eq. (S.9) and note that $P_{\alpha,\beta}$ describes the *production* of species α , such that species α is not a reactant). Furthermore, b_α does not depend on the species in S_{ss} because the second term introduced on the right hand side of Eq. (S.14) is designed to exactly subtract those dependencies from P_α .

Under these constraints, Eq. (S.14) can be written as a linear system

$$M_{ss} c_{ss} = b_{ss}, \quad (\text{S.15})$$

where c_{ss} is a vector of the molar concentrations of the species in the set S_{ss} ,

$$M_{ss} = \begin{bmatrix} L_{\alpha_1} & -P_{\alpha_1,\alpha_2} & \cdots & -P_{\alpha_1,\alpha_{N_{ss}}} \\ -P_{\alpha_2,\alpha_1} & L_{\alpha_2} & \cdots & -P_{\alpha_2,\alpha_{N_{ss}}} \\ \vdots & \vdots & \ddots & \vdots \\ -P_{\alpha_{N_{ss}},\alpha_1} & -P_{\alpha_{N_{ss}},\alpha_2} & \cdots & L_{\alpha_{N_{ss}}} \end{bmatrix} \quad \text{and} \quad b_{ss} = \begin{bmatrix} b_{\alpha_1} \\ b_{\alpha_2} \\ \vdots \\ b_{\alpha_{N_{ss}}} \end{bmatrix},$$

where α_i , $i = 1, \dots, N_{ss}$ is an enumeration of the species in the set S_{ss} and

$$b_\alpha = P_\alpha - \sum_{\beta \in S_{ss}} P_{\alpha,\beta} c_\beta. \quad (\text{S.16})$$

Equation (S.15) can be solved for the concentrations of the species in the set S_{ss} . The concentrations of the remaining species must be solved by integrating Eq. (S.13). The solutions of these equations must be tightly coupled in order to obtain accurate results. This approach that allows the reduction of the dimension of the set of ODEs from N to $N - N_{ss}$, reducing the computational cost of the problem.

Several authors have investigated the application of the steady-state approximation to different systems [8, 10, 12, 13]. Its application to slow-forming species can produce significant errors, whereas good results can be achieved given appropriate selection of fast-forming species. The chemical lifetime of a species seems to be the best predictor to determine whether it can be approximated or not by the steady-state assumption [12].

Partial-equilibrium approximation

The partial-equilibrium approximation decomposes Eq. (S.11) into two equations

$$\frac{dc_\alpha}{dt} = P_\alpha - L_\alpha c_\alpha, \quad \alpha \in S_{\text{peq}}, \quad (\text{S.17})$$

$$\frac{dc_\alpha}{dt} = P_\alpha - L_\alpha c_\alpha, \quad \alpha \notin S_{\text{peq}}, \quad (\text{S.18})$$

where S_{peq} denotes a subset of species whose concentrations are controlled by a set of reactions that rapidly approach equilibrium, R_{peq} . These should be reversible reactions where the forward and reverse rates are large and approximately equal, and where at least one species in the reaction (a reactant, a product or one of each) belongs to S_{peq} .

The terms in Eq. (S.17) can be further decomposed

$$\frac{dc_\alpha}{dt} = (P_\alpha^{\text{peq}} + P_\alpha^{\text{neq}}) - (L_\alpha^{\text{peq}} + L_\alpha^{\text{neq}}) c_\alpha, \quad \alpha \in S_{\text{peq}}, \quad (\text{S.19})$$

where P_α^{peq} and L_α^{peq} denote the contribution from reactions in R_{peq} (and P_α^{neq} and L_α^{neq} denote contributions from the remaining reactions) to P_α and L_α , such that

$$0 \approx P_\alpha^{\text{peq}} - L_\alpha^{\text{peq}} c_\alpha, \quad \alpha \in S_{\text{peq}}. \quad (\text{S.20})$$

Under constraints analogous to those described in relation to Eq. (S.14), Eq. (S.20) can be used to obtain a linear system for c_{peq}

$$M_{\text{peq}} c_{\text{peq}} = b_{\text{peq}}, \quad (\text{S.21})$$

where c_{peq} is a vector of the molar concentrations of the species in the set S_{peq} ,

$$M_{\text{peq}} = \begin{bmatrix} L_{\alpha_1}^{\text{peq}} & -P_{\alpha_1, \alpha_2}^{\text{peq}} & \cdots & -P_{\alpha_1, \alpha_{N_{\text{ss}}}}^{\text{peq}} \\ -P_{\alpha_2, \alpha_1}^{\text{peq}} & L_{\alpha_2}^{\text{peq}} & \cdots & -P_{\alpha_2, \alpha_{N_{\text{ss}}}}^{\text{peq}} \\ \vdots & \vdots & \ddots & \vdots \\ -P_{\alpha_{N_{\text{ss}}}, \alpha_1}^{\text{peq}} & -P_{\alpha_{N_{\text{ss}}}, \alpha_2}^{\text{peq}} & \cdots & L_{\alpha_{N_{\text{ss}}}}^{\text{peq}} \end{bmatrix} \quad \text{and} \quad b_{\text{peq}} = \begin{bmatrix} b_{\alpha_1}^{\text{peq}} \\ b_{\alpha_2}^{\text{peq}} \\ \vdots \\ b_{\alpha_{N_{\text{ss}}}}^{\text{peq}} \end{bmatrix},$$

where α_i , $i = 1, \dots, N_{\text{peq}}$ is an enumeration of the species in the set S_{peq} ,

$$b_\alpha^{\text{peq}} = P_\alpha^{\text{peq}} - \sum_{\beta \in S_{\text{peq}}} P_{\alpha, \beta}^{\text{peq}} c_\beta, \quad (\text{S.22})$$

and P_α^{peq} , L_α^{peq} and $P_{\alpha, \beta}^{\text{peq}}$ are defined as special cases of Eqs. (S.7), (S.8) and (S.9)

$$P_\alpha^{\text{peq}} = \sum_{i \in R_{\text{peq}}} P_\alpha^{(i)}, \quad (\text{S.23})$$

$$L_\alpha^{\text{peq}} = \sum_{i \in R_{\text{peq}}} L_\alpha^{(i)}, \quad (\text{S.24})$$

and

$$P_{\alpha,\beta}^{\text{peq}} = \sum_{i \in \mathbf{R}_{\text{peq}} \cap \mathbf{R}_{\beta \rightarrow \alpha}} P_{\alpha,\beta}^{(i)}, \quad (\text{S.25})$$

where the sum over reactions $i \in \mathbf{R}_{\text{peq}} \cap \mathbf{R}_{\beta \rightarrow \alpha}$ should be understood as a sum over the subset of reactions in \mathbf{R}_{peq} that produce species α from species β .

One important difference between the partial-equilibrium and steady-state approximations is that the terms in the partial-equilibrium equations (Eqs. (S.23)–(S.25)) are defined in terms of a subset of the reactions. One consequence of this is that the partial-equilibrium equations, Eqs. (S.18) and (S.20), are less tightly coupled than the steady-state equations, Eqs. (S.12) and (S.13).

S.2 Steady-state and partial-equilibrium reactions and species

Tables S.1–S.3 list the reactions and species used in steady-state and partial-equilibrium approximations in Sections 4.1–4.3 of the main text.

Table S.1: Reactions used for the steady-state and partial-equilibrium approximations of naphthalene (A_2) growing from benzene (A_1). Reactions above the midline (1–20) are used in the partial-equilibrium approximation. All reactions (1–28) are used in the steady-state approximation. The treatment of reactions 21–28 in the partial-equilibrium approximation is explained in Section S.2.1. Rates taken from ABF mechanism [1].

| No. | Reaction | | | | |
|-----------------|---------------------------|------------|----------------------|---------------------|----------|
| 1 | A_1 | + H | \rightleftharpoons | A_1^\bullet | + H_2 |
| 2 | A_1 | + OH | \rightleftharpoons | A_1^\bullet | + H_2O |
| 3 | A_1^\bullet | + H + (M) | \rightleftharpoons | A_1 | + (M) |
| 4 | A_1^\bullet | + C_2H_2 | \rightleftharpoons | A_1C_2H | + H |
| 5 | A_1^\bullet | + C_2H_2 | \rightleftharpoons | $A_1C_2H_2$ | |
| 6 | A_1C_2H | + H | \rightleftharpoons | $A_1C_2H_2$ | |
| 7 | A_1C_2H | + C_2H | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | + H |
| 8 | A_1C_2H | + H | \rightleftharpoons | $A_1C_2H^\bullet$ | + H_2 |
| 9 | A_1C_2H | + OH | \rightleftharpoons | $A_1C_2H^\bullet$ | + H_2O |
| 10 | $A_1C_2H^\bullet$ | + H + (M) | \rightleftharpoons | A_1C_2H | + (M) |
| 11 | A_1 | + C_2H | \rightleftharpoons | A_1C_2H | + H |
| 12 | $A_1C_2H_3$ | + H | \rightleftharpoons | $A_1C_2H_3^\bullet$ | + H_2 |
| 13 | $A_1C_2H_3$ | + OH | \rightleftharpoons | $A_1C_2H_3^\bullet$ | + H_2O |
| 14 | $A_1C_2H_3^\bullet$ | + H + (M) | \rightleftharpoons | $A_1C_2H_3$ | + (M) |
| 15 | A_1^\bullet | + C_2H_4 | \rightleftharpoons | $A_1C_2H_3$ | + H |
| 16 | A_1^\bullet | + C_2H_3 | \rightleftharpoons | $A_1C_2H_3$ | |
| 17 | A_1 | + C_2H_3 | \rightleftharpoons | $A_1C_2H_3$ | + H |
| 18 | $A_1C_2H_3$ | + H | \rightleftharpoons | $A_1C_2H_2$ | + H_2 |
| 19 | $A_1C_2H_3$ | + OH | \rightleftharpoons | $A_1C_2H_2$ | + H_2O |
| 20 | $A_1C_2H^\bullet$ | + C_2H_2 | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | + H |
| 21 [†] | $A_1C_2H_2$ | + C_2H_2 | \rightleftharpoons | A_2 | + H |
| 22 [†] | $A_1C_2H_3^\bullet$ | + C_2H_2 | \rightleftharpoons | A_2 | + H |
| 23 [†] | A_1^\bullet | + C_4H_4 | \rightleftharpoons | A_2 | + H |
| 24 [†] | $A_1C_2H^\bullet$ | + C_2H_2 | \rightleftharpoons | A_2^\bullet | |
| 25 [†] | $A_1(C_2H)C_2H_2^\bullet$ | + H | \rightleftharpoons | A_2^\bullet | |
| 26 | A_2 | + H | \rightleftharpoons | A_2^\bullet | + H_2 |
| 27 | A_2 | + OH | \rightleftharpoons | A_2^\bullet | + H_2O |
| 28 | A_2^\bullet | + H + (M) | \rightleftharpoons | A_2 | + (M) |

[†] Indicates reactions contributing to Eq. (S.30). See Section S.2.1.

Species sets:

$S_{ss} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet, A_1C_2H_3, A_1C_2H_3^\bullet, A_1(C_2H)C_2H_2^\bullet, A_2^\bullet, A_2\}$.

$S_{peq} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet, A_1C_2H_3, A_1C_2H_3^\bullet, A_1(C_2H)C_2H_2^\bullet\}$.

$S_{ss} \setminus S_{peq} = \{A_2^\bullet, A_2\}$.

Table S.2: Reactions used for the steady-state and partial-equilibrium approximations of phenanthrene (A_3) growing from naphthalene (A_2). Reactions above the mid-line (1–14) are used in the partial-equilibrium approximation. All reactions (1–19) are used in the steady-state approximation. The treatment of reactions 15–19 in the partial-equilibrium approximation is explained in Section S.2.1. Rates taken from ABF mechanism [1].

| No. | Reaction | | | | |
|-----------------|---------------------------|-------------|----------------------|-------------------|----------|
| 1 | A_2 | $+ H$ | \rightleftharpoons | A_2^\bullet | $+ H_2$ |
| 2 | A_2 | $+ OH$ | \rightleftharpoons | A_2^\bullet | $+ H_2O$ |
| 3 | A_2^\bullet | $+ H + (M)$ | \rightleftharpoons | A_2 | $+ (M)$ |
| 4 | A_2^\bullet | $+ C_2H_2$ | \rightleftharpoons | $A_2C_2H_2$ | |
| 5 | A_2^\bullet | $+ C_2H_2$ | \rightleftharpoons | A_2C_2H | $+ H$ |
| 6 | A_2 | $+ C_2H$ | \rightleftharpoons | A_2C_2H | $+ H$ |
| 7 | A_2C_2H | $+ H$ | \rightleftharpoons | $A_2C_2H_2$ | |
| 8 | $A_2C_2H_2$ | $+ H$ | \rightleftharpoons | A_2C_2H | $+ H_2$ |
| 9 | $A_2C_2H_2$ | $+ OH$ | \rightleftharpoons | A_2C_2H | $+ H_2O$ |
| 10 | A_2C_2H | $+ H$ | \rightleftharpoons | $A_2C_2H^\bullet$ | $+ H_2$ |
| 11 | A_2C_2H | $+ OH$ | \rightleftharpoons | $A_2C_2H^\bullet$ | $+ H_2O$ |
| 12 | $A_2C_2H^\bullet$ | $+ H + (M)$ | \rightleftharpoons | A_2C_2H | $+ (M)$ |
| 13 | A_2C_2H | $+ C_2H$ | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | $+ H$ |
| 14 | $A_2C_2H^\bullet$ | $+ C_2H_2$ | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | $+ H$ |
| 15 [†] | $A_2C_2H^\bullet$ | $+ C_2H_2$ | \rightleftharpoons | A_3^\bullet | |
| 16 [†] | $A_2(C_2H)C_2H_2^\bullet$ | $+ H$ | \rightleftharpoons | A_3^\bullet | |
| 17 | A_3 | $+ H$ | \rightleftharpoons | A_3^\bullet | $+ H_2$ |
| 18 | A_3 | $+ OH$ | \rightleftharpoons | A_3^\bullet | $+ H_2O$ |
| 19 | A_3^\bullet | $+ H + (M)$ | \rightleftharpoons | A_3 | $+ (M)$ |

[†] Indicates reactions contributing to Eq. (S.30). See Section S.2.1.

Species sets:

$$S_{ss} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet, A_3^\bullet, A_3\}.$$

$$S_{peq} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet\}.$$

$$S_{ss} \setminus S_{peq} = \{A_3^\bullet, A_3\}.$$

Table S.3: Reactions used for partial-equilibrium approximation of phenanthrene (A_3) growing from benzene (A_1). Reactions above the midline (1–12) are used in the partial-equilibrium approximation. The treatment of reactions 13–17 is explained in Section S.2.1. Rates taken from ABF mechanism [1].

| No. | Reaction | | |
|-----------------|-------------------|--------------------|---|
| 1 | A_1 | $+H$ | $\rightleftharpoons A_1^\bullet + H_2$ |
| 2 | A_1 | $+OH$ | $\rightleftharpoons A_1^\bullet + H_2O$ |
| 3 | A_1^\bullet | $+H+(M)$ | $\rightleftharpoons A_1 + (M)$ |
| 4 | A_1^\bullet | $+C_2H_2$ | $\rightleftharpoons A_1C_2H + H$ |
| 5 | A_1^\bullet | $+C_2H_2$ | $\rightleftharpoons A_1C_2H_2$ |
| 6 | A_1C_2H | $+H$ | $\rightleftharpoons A_1C_2H_2$ |
| 7 | A_1C_2H | $+C_2H$ | $\rightleftharpoons A_1(C_2H)C_2H_2 + H$ |
| 8 | A_1C_2H | $+H$ | $\rightleftharpoons A_1C_2H^\bullet + H_2$ |
| 9 | A_1C_2H | $+OH$ | $\rightleftharpoons A_1C_2H^\bullet + H_2O$ |
| 10 | $A_1C_2H^\bullet$ | $+H+(M)$ | $\rightleftharpoons A_1C_2H + (M)$ |
| 11 | A_1 | $+C_2H$ | $\rightleftharpoons A_1C_2H + H$ |
| 12 | $A_1C_2H^\bullet$ | $+C_2H_2$ | $\rightleftharpoons A_1(C_2H)C_2H_2 + H$ |
| 13 | A_1 | $+A_1^\bullet$ | $\rightleftharpoons P_2 + H$ |
| 14 | P_2 | $+H$ | $\rightleftharpoons P_2^\bullet + H_2$ |
| 15 [†] | P_2^\bullet | $+C_2H_2$ | $\rightleftharpoons A_3 + H$ |
| 16 [†] | A_1 | $+A_1C_2H^\bullet$ | $\rightleftharpoons A_3 + H$ |
| 17 [†] | A_1^\bullet | $+A_1C_2H$ | $\rightleftharpoons A_3 + H$ |

[†] Indicates reactions contributing to Eq. (S.30). See Section S.2.1.

Species sets:

$$S_{\text{peq}} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet, A_1(C_2H)C_2H_2^\bullet\}.$$

This process is only treated using the partial-equilibrium approximation.

Table S.4: *Jump processes, reactions and species for the KMC model. For each process, reactions above the midline are used in the partial-equilibrium approximation; all reactions (above and below the line) are used in the steady-state approximation. Reactions below the midline are used to calculate the overall rate of the process. See Section S.2.2. Rates taken from ABF mechanism [1].*

| Jump process | Intermediate reactions | | | | | |
|--|---------------------------|---------------------|-------------------|----------------------|---------------------|---------|
| | 1 | A_1 | $+H$ | \rightleftharpoons | A_1^\bullet | $+H_2$ |
| | 2 | A_1 | $+OH$ | \rightleftharpoons | A_1^\bullet | $+H_2O$ |
| | 3 | A_1^\bullet | $+H+(M)$ | \rightleftharpoons | A_1 | $+(M)$ |
| | 4 | A_1^\bullet | $+C_2H_2$ | \rightleftharpoons | A_1C_2H | $+H$ |
| | 5 | A_1^\bullet | $+C_2H_2$ | \rightleftharpoons | $A_1C_2H_2$ | |
| | 6 | A_1C_2H | $+H$ | \rightleftharpoons | $A_1C_2H_2$ | |
| | 7 | A_1C_2H | $+C_2H$ | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | $+H$ |
| | 8 | A_1C_2H | $+H$ | \rightleftharpoons | $A_1C_2H^\bullet$ | $+H_2$ |
| | 9 | A_1C_2H | $+OH$ | \rightleftharpoons | $A_1C_2H^\bullet$ | $+H_2O$ |
| | 10 | $A_1C_2H^\bullet$ | $+H+(M)$ | \rightleftharpoons | A_1C_2H | $+(M)$ |
| | 11 | A_1 | $+C_2H$ | \rightleftharpoons | A_1C_2H | $+H$ |
| | 12 | $A_1C_2H_3$ | $+H$ | \rightleftharpoons | $A_1C_2H_3^\bullet$ | $+H_2$ |
| | 13 | $A_1C_2H_3$ | $+OH$ | \rightleftharpoons | $A_1C_2H_3^\bullet$ | $+H_2O$ |
| | 14 | $A_1C_2H_3^\bullet$ | $+H+(M)$ | \rightleftharpoons | $A_1C_2H_3$ | $+(M)$ |
| Free-edge ring growth $A_1 \longrightarrow A_2$ | 15 | A_1^\bullet | $+C_2H_4$ | \rightleftharpoons | $A_1C_2H_3$ | $+H$ |
| | 16 | A_1^\bullet | $+C_2H_3$ | \rightleftharpoons | $A_1C_2H_3$ | |
| | 17 | A_1 | $+C_2H_3$ | \rightleftharpoons | $A_1C_2H_3$ | $+H$ |
| | 18 | $A_1C_2H_3$ | $+H$ | \rightleftharpoons | $A_1C_2H_2$ | $+H_2$ |
| | 19 | $A_1C_2H_3$ | $+OH$ | \rightleftharpoons | $A_1C_2H_2$ | $+H_2O$ |
| | 20 | $A_1C_2H^\bullet$ | $+C_2H_2$ | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | $+H$ |
| | 21 [†] | $A_1C_2H_2$ | $+C_2H_2$ | \longrightarrow | A_2 | $+H$ |
| 22 [†] | $A_1C_2H_3^\bullet$ | $+C_2H_2$ | \longrightarrow | A_2 | $+H$ | |
| 23 [†] | A_1^\bullet | $+C_4H_4$ | \longrightarrow | A_2 | $+H$ | |
| 24 [†] | $A_1C_2H^\bullet$ | $+C_2H_2$ | \longrightarrow | A_2^\bullet | | |
| 25 [†] | $A_1(C_2H)C_2H_2^\bullet$ | $+H$ | \longrightarrow | A_2^\bullet | | |
| $S_{ss} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet,$ $A_1C_2H_3, A_1C_2H_3^\bullet, A_1(C_2H)C_2H_2^\bullet, A_2^\bullet, A_2\}.$ | | | | | | |
| $S_{peq} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet,$ $A_1C_2H_3, A_1C_2H_3^\bullet, A_1(C_2H)C_2H_2^\bullet\}.$ | | | | | | |
| $S_{ss} \setminus S_{peq} = \{A_2^\bullet, A_2\}.$ | | | | | | |

Continued on next page

Table S.4 – continued from previous page

| Jump process | Intermediate reactions | | | | | |
|--|---------------------------|-------------------|-------------------|----------------------|---------------------|------------|
| Free-edge ring desorption ¹ $A_2 \longrightarrow A_1$ | 1 | A_2 | + H | \rightleftharpoons | A_2^\bullet | + H_2 |
| | 2 | A_2 | + OH | \rightleftharpoons | A_2^\bullet | + H_2O |
| | 3 | A_2^\bullet | + H + (M) | \rightleftharpoons | A_2 | + (M) |
| | 4 [‡] | A_2 | + H | \longrightarrow | $A_1C_2H_2$ | + C_2H_2 |
| | 5 [‡] | A_2 | + H | \longrightarrow | $A_1C_2H_3^\bullet$ | + C_2H_2 |
| | 6 [‡] | A_2 | + H | \longrightarrow | A_1^\bullet | + C_4H_4 |
| | 7 [‡] | A_2^\bullet | | \longrightarrow | $A_1C_2H^\bullet$ | + C_2H_2 |
| | 8 [‡] | A_2^\bullet | | \longrightarrow | $A_1(C_2H)C_2H_2$ | + H |
| Free-edge ring growth $A_2 \longrightarrow A_3$ | 1 | A_2 | + H | \rightleftharpoons | $A_2^\bullet + H_2$ | |
| | 2 | A_2 | + OH | \rightleftharpoons | A_2^\bullet | + H_2O |
| | 3 | A_2^\bullet | + H + (M) | \rightleftharpoons | A_2 | + (M) |
| | 4 | A_2^\bullet | + C_2H_2 | \rightleftharpoons | $A_2C_2H_2$ | |
| | 5 | A_2^\bullet | + C_2H_2 | \rightleftharpoons | A_2C_2H | + H |
| | 6 | A_2 | + C_2H | \rightleftharpoons | A_2C_2H | + H |
| | 7 | A_2C_2H | + H | \rightleftharpoons | $A_2C_2H_2$ | |
| | 8 | $A_2C_2H_2$ | + H | \rightleftharpoons | A_2C_2H | + H_2 |
| | 9 | $A_2C_2H_2$ | + OH | \rightleftharpoons | A_2C_2H | + H_2O |
| | 10 | A_2C_2H | + H | \rightleftharpoons | $A_2C_2H^\bullet$ | + H_2 |
| | 11 | A_2C_2H | + OH | \rightleftharpoons | $A_2C_2H^\bullet$ | + H_2O |
| | 12 | $A_2C_2H^\bullet$ | + H + (M) | \rightleftharpoons | A_2C_2H | + (M) |
| | 13 | A_2C_2H | + C_2H | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | + H |
| | 14 | $A_2C_2H^\bullet$ | + C_2H_2 | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | + H |
| 15 [†] | $A_2C_2H^\bullet$ | + C_2H_2 | \longrightarrow | A_3^\bullet | | |
| 16 [†] | $A_2(C_2H)C_2H_2^\bullet$ | + H | \longrightarrow | A_3^\bullet | | |
| $S_{ss} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet, A_3^\bullet, A_3\}$. $S_{peq} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet\}$. $S_{ss} \setminus S_{peq} = \{A_3^\bullet, A_3\}$. | | | | | | |
| Free-edge ring desorption ¹ $A_3 \longrightarrow A_2$ | 1 | A_3 | + H | \rightleftharpoons | A_3^\bullet | + H_2 |
| | 2 | A_3 | + OH | \rightleftharpoons | A_3^\bullet | + H_2O |
| | 3 | A_3^\bullet | + H + (M) | \rightleftharpoons | A_3 | + (M) |
| | 4 [‡] | A_3^\bullet | | \longrightarrow | $A_2C_2H^\bullet$ | + C_2H_2 |
| | 5 [‡] | A_3^\bullet | | \longrightarrow | $A_2(C_2H)C_2H_2$ | + H |

Continued on next page

Table S.4 – continued from previous page

| Jump process | Intermediate reactions | | | | | |
|---|------------------------|-------------------|---------------------|----------------------|-------------------|------------|
| Armchair ring growth $A_3 \longrightarrow A_4$ | 1 | A_3 | + H | \rightleftharpoons | A_3^\bullet | + H_2 |
| | 2 | A_3 | + OH | \rightleftharpoons | A_3^\bullet | + H_2O |
| | 3 | A_3^\bullet | + H + (M) | \rightleftharpoons | A_3 | + (M) |
| | 4 | A_3^\bullet | + C_2H_2 | \rightleftharpoons | $A_3C_2H_2$ | |
| | 5 | A_3^\bullet | + C_2H_2 | \rightleftharpoons | A_3C_2H | + H |
| | 6 | A_3 | + C_2H | \rightleftharpoons | A_3C_2H | + H |
| | 7 | A_3C_2H | + H | \rightleftharpoons | $A_3C_2H_2$ | |
| | 8 [†] | A_3^\bullet | + C_2H_2 | \longrightarrow | A_4 | + H |
| | 9 [†] | A_3C_2H | + H | \longrightarrow | A_4 | + H |
| | 10 [†] | $A_3C_2H_2$ | | \longrightarrow | A_4 | + H |
| $S_{ss} = \{A_3^\bullet, A_3C_2H_2, A_3C_2H, A_4\}$. $S_{peq} = \{A_3^\bullet, A_3C_2H_2, A_3C_2H\}$. $S_{ss} \setminus S_{peq} = \{A_4\}$. | | | | | | |
| Armchair desorption $A_4 \longrightarrow A_3$ | 1 [‡] | A_4 | + H | \longrightarrow | A_3^\bullet | + C_2H_2 |
| | 2 [‡] | A_4 | + H | \longrightarrow | A_3C_2H | + H |
| | 3 [‡] | A_4 | + H | \longrightarrow | $A_3C_2H_2$ | |
| Ring condensation $A_1 \longrightarrow A_3$ | 1 | A_1 | + H | \rightleftharpoons | A_1^\bullet | + H_2 |
| | 2 | A_1 | + OH | \rightleftharpoons | A_1^\bullet | + H_2O |
| | 3 | A_1^\bullet | + H + (M) | \rightleftharpoons | A_1 | + (M) |
| | 4 | A_1^\bullet | + C_2H_2 | \rightleftharpoons | A_1C_2H | + H |
| | 5 | A_1^\bullet | + C_2H_2 | \rightleftharpoons | $A_1C_2H_2$ | |
| | 6 | A_1C_2H | + H | \rightleftharpoons | $A_1C_2H_2$ | |
| | 7 | A_1C_2H | + C_2H | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | + H |
| | 8 | A_1C_2H | + H | \rightleftharpoons | $A_1C_2H^\bullet$ | + H_2 |
| | 9 | A_1C_2H | + OH | \rightleftharpoons | $A_1C_2H^\bullet$ | + H_2O |
| | 10 | $A_1C_2H^\bullet$ | + H + (M) | \rightleftharpoons | A_1C_2H | + (M) |
| | 11 | A_1 | + C_2H | \rightleftharpoons | A_1C_2H | + H |
| | 12 | $A_1C_2H^\bullet$ | + C_2H_2 | \rightleftharpoons | $A_1(C_2H)C_2H_2$ | + H |
| | 13 | A_1 | + A_1^\bullet | \rightleftharpoons | P_2 | + H |
| | 14 | P_2 | + H | \rightleftharpoons | P_2^\bullet | + H_2 |
| | 15* | P_2^\bullet | + C_2H_2 | \longrightarrow | A_3 | + H |
| | 16* | A_1 | + $A_1C_2H^\bullet$ | \longrightarrow | A_3 | + H |
| | 17* | A_1^\bullet | + A_1C_2H | \longrightarrow | A_3 | + H |
| $S_{peq} = \{A_1^\bullet, A_1C_2H_2, A_1C_2H, A_1C_2H^\bullet, A_1(C_2H)C_2H_2^\bullet\}$. Process treated with partial-equilibrium approximation only. | | | | | | |

Continued on next page

Table S.4 – continued from previous page

| Jump process | | Intermediate reactions | | | | |
|--|-----------------|------------------------|------------|----------------------|---------------------|------------|
| | 1 | A_2 | + H | \rightleftharpoons | $A_2^\bullet + H_2$ | |
| | 2 | A_2 | + OH | \rightleftharpoons | A_2^\bullet | + H_2O |
| | 3 | A_2^\bullet | + H + (M) | \rightleftharpoons | A_2 | + (M) |
| | 4 | A_2^\bullet | + C_2H_2 | \rightleftharpoons | $A_2C_2H_2$ | |
| | 5 | A_2^\bullet | + C_2H_2 | \rightleftharpoons | A_2C_2H | + H |
| | 6 | A_2 | + C_2H | \rightleftharpoons | A_2C_2H | + H |
| | 7 | A_2C_2H | + H | \rightleftharpoons | $A_2C_2H_2$ | |
| | 8 | $A_2C_2H_2$ | + H | \rightleftharpoons | A_2C_2H | + H_2 |
| | 9 | $A_2C_2H_2$ | + OH | \rightleftharpoons | A_2C_2H | + H_2O |
| Five-member | 10 | A_2C_2H | + H | \rightleftharpoons | $A_2C_2H^\bullet$ | + H_2 |
| ring growth at | 11 | A_2C_2H | + OH | \rightleftharpoons | $A_2C_2H^\bullet$ | + H_2O |
| zig-zag | 12 | $A_2C_2H^\bullet$ | + H + (M) | \rightleftharpoons | A_2C_2H | + (M) |
| $A_2 \longrightarrow A_2R_5$ | 13 | A_2C_2H | + C_2H | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | + H |
| | 14 | $A_2C_2H^\bullet$ | + C_2H_2 | \rightleftharpoons | $A_2(C_2H)C_2H_2$ | + H |
| | 15 [†] | A_2^\bullet | + C_2H_2 | \longrightarrow | A_2R_5 | + H |
| | 16 [†] | A_2C_2H | + H | \longrightarrow | A_2R_5 | + H |
| | 17 [†] | $A_2C_2H_2$ | | \longrightarrow | A_2R_5 | + H |
| $S_{ss} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet, A_2R_5\}$. $S_{peq} = \{A_2^\bullet, A_2C_2H_2, A_2C_2H, A_2C_2H^\bullet, A_2(C_2H)C_2H_2^\bullet\}$. $S_{ss} \setminus S_{peq} = \{A_2R_5\}$. | | | | | | |
| Five-member | 1 [‡] | A_2R_5 | + H | \longrightarrow | A_2^\bullet | + C_2H_2 |
| ring desorption ¹ | 2 [‡] | A_2R_5 | + H | \longrightarrow | A_2C_2H | + H |
| $A_2R_5 \longrightarrow A_2$ | 3 [‡] | A_2R_5 | + H | \longrightarrow | $A_2C_2H_2$ | |

¹ The rates of the desorption processes are independent of the concentration of intermediate PAH species, and can therefore be evaluated without a steady-state or partial-equilibrium approximation.

^{‡/‡} Reversible reactions whose forward and reverse contributions are split between jump processes. The reactions are still treated as reversible for the purpose of solving Eq. (S.14) for c_{ss} .

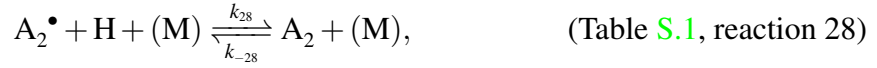
* Reactions treated as irreversible. The reverse rates were observed to be negligible.

^{†/‡/*} Reactions used to calculate the overall rate of each jump process. See Section S.2.2.

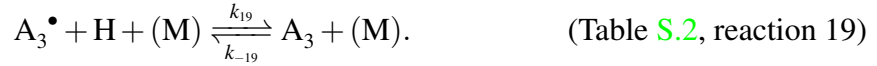
S.2.1 Treatment of non-partial-equilibrium reactions

The partial-equilibrium approximations in this work operate on a subset of reactions that exclude the formation of naphthalene (A_2 , Table S.1) and phenanthrene (A_3 , Tables S.2 and S.3). The concentrations of A_2 and A_3 must be calculated separately.

The concentrations of A_2 and A_3 are controlled by the final reactions in Tables S.1 and S.2



and



An algebraic relationship between the concentrations c_{A_2} and $c_{A_2^\bullet}$, and c_{A_3} and $c_{A_3^\bullet}$ can be derived by applying a steady-state or partial-equilibrium approximation to each of these sets of reactions [see for example 3]. In this work, a partial-equilibrium approximation is used to derive the following relationships

$$c_{A_2^\bullet} = c_{A_2} \left(\frac{k_{26}c_H + k_{27}c_{OH} + k_{-28}}{k_{-26}c_{H_2} + k_{-27}c_{H_2O} + k_{28}c_H} \right), \quad (\text{S.26})$$

$$c_{A_3^\bullet} = c_{A_3} \left(\frac{k_{17}c_H + k_{18}c_{OH} + k_{-19}}{k_{-17}c_{H_2} + k_{-18}c_{H_2O} + k_{19}c_H} \right). \quad (\text{S.27})$$

In the case of the ODE-based simulations (Sections 4.2 and 4.3), the concentrations of species in the set $\alpha \notin S_{\text{peq}}$ are calculated by solving Eq. (S.18). The concentrations of the main PAH products, A_2 and A_3 , are treated as a special case and are calculated using Eqs. (S.26) and (S.27) in conjunction with solving equations of the same form as Eq. (4) to find the total concentration of each species and its corresponding radical

$$c_{A_2} + c_{A_2^\bullet} \approx \int_0^t P_{A_2}^{\text{neq}} + P_{A_2^\bullet}^{\text{neq}} dt, \quad (\text{S.28})$$

$$c_{A_3} + c_{A_3^\bullet} \approx \int_0^t P_{A_3}^{\text{neq}} + P_{A_3^\bullet}^{\text{neq}} dt, \quad (\text{S.29})$$

where

$$P_\alpha^{\text{neq}} = \sum_{i \in R_{\text{neq}}} P_\alpha^{(i)}, \quad (\text{S.30})$$

is the production of species α due to the reactions in the set R_{neq} and $P_{\alpha}^{(i)}$ is defined as per Eq. (S.7). The reactions in R_{neq} contributing to Eqs. (S.28) and (S.29) are marked with a dagger (\dagger) in Tables S.1–S.3. Note that Table S.3, reaction 17 has a dependency on the concentration of P_2^{\bullet} . This is evaluated using the relationship

$$c_{P_2} = \frac{k_{13}c_{A_1}c_{A_1^{\bullet}} + k_{-14}c_{P_2^{\bullet}}c_{H_2}}{k_{-13}c_H + k_{14}c_H} \quad (\text{S.31})$$

$$c_{P_2^{\bullet}} = \frac{k_{14}c_{P_2}c_H}{k_{-14}c_{H_2} + k_{15}c_{C_2H_2}} \quad (\text{S.32})$$

arising from the application of a steady-state approximation to Table S.3, reactions 13–15.

The rationale behind the special treatment of A_2 and A_3 is that it avoids the need to solve tightly coupled ODEs for the non-partial-equilibrium PAH species. This reduces the computational complexity of the method, so is desirable in the context of our objective to develop a computationally efficient model.

S.2.2 Calculation of KMC jump process rates

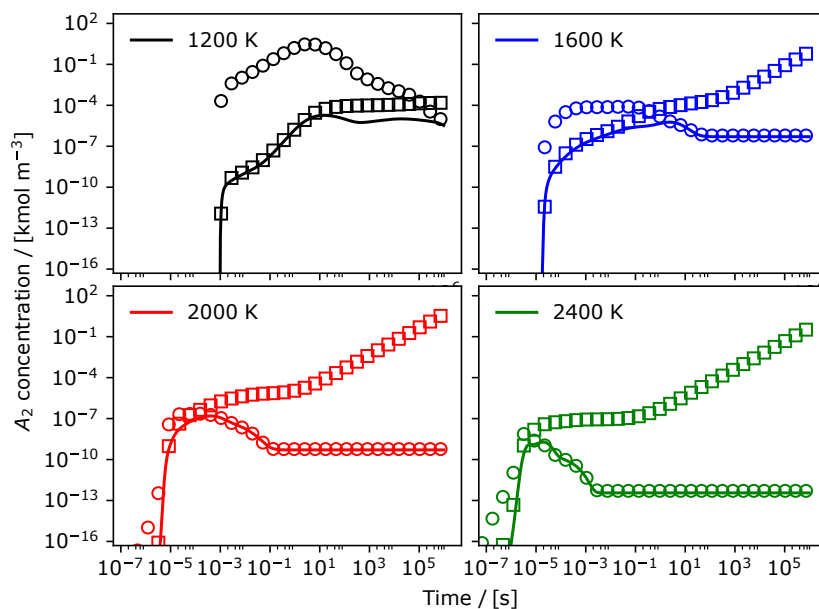
The KMC model calculates the concentrations of A_2 , A_2R_5 , A_3 and A_4 by performing a kinetic Monte Carlo simulation using the jump processes in Table S.4. The temperature and small-molecule concentrations (up to and including benzene, A_1) are imposed as boundary conditions. For each jump process, the concentrations of the (PAH) species in either S_{ss} or S_{peq} are calculated by solving Eq. (S.15) for c_{ss} or Eq. (S.21) for c_{peq} , depending on the choice of method. In both cases, the rates of the jump processes are calculated by evaluating the rates of the reactions marked \dagger , \ddagger and $*$ in Table S.4.

Similar to the treatment of the non-partial-equilibrium reactions in the ODE-based simulations (see Section S.2.1), the KMC model uses Eqs. (S.26) and (S.27) to calculate A_2 and A_3 in conjunction with tracking the total concentrations $c_{A_2} + c_{A_2^{\bullet}}$ and $c_{A_3} + c_{A_3^{\bullet}}$. Likewise, Eqs. (S.31) and (S.32) are used to calculate the concentration of P_2^{\bullet} in order to evaluate the rate of the phenyl addition (Table S.4, reaction 15).

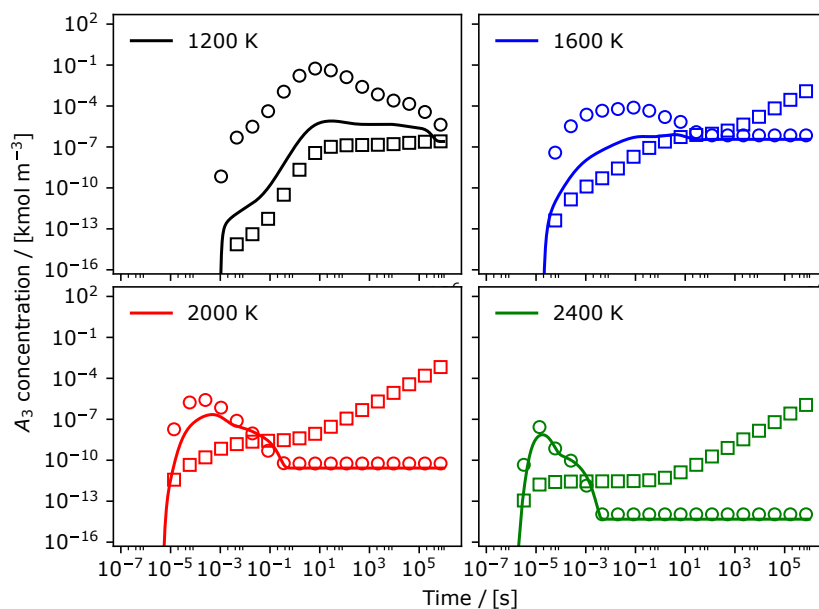
The mechanism in Table S.4 can be generalised (not shown here) to describe the growth of arbitrarily-sized PAHs. See for example the work by Frenklach and co-workers [3, 4] and Celnik et al. [2].

S.3 Effect of ring condensation reactions

Figure S.1 shows the concentrations of A_2 and A_3 calculated using the partial-equilibrium approximation without the inclusion of ring condensation reactions (Fig. 2 process (iii) in the main text) versus reference solutions calculated using the full ABF mechanism in a closed isothermal system. For comparison, we also show data calculated using the steady-state approximation. The figure shows that given long enough, good agreement is seen between the steady-state approximation and the reference solutions. Comparison with Fig. 5 (in the main text) shows that both the improved treatment of reactions during the induction period and the inclusion of process (iii) in the partial-equilibrium approximation are important to achieve agreement with the reference data for A_3 at early times.



(a) Naphthalene (A_2).



(b) Phenanthrene (A_3).

Figure S.1: Simulations of the reaction of ethylene in a closed isothermal system, initially at an equivalence ratio of 5.0, to form naphthalene (A_2 , top panels) and phenanthrene (A_3 , bottom panels). Solid lines show the results of simulations using the full ABF mechanism. Circles show the concentration of each species calculated using the steady-state approximation. Squares show the concentration of each species calculated using the partial-equilibrium approximation. Neither approximation includes process (iii).

References

- [1] J. Appel, H. Bockhorn, and M. Frenklach. Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C2 hydrocarbons. *Combustion and Flame*, 121(1-2):122–136, 2000. doi:10.1016/S0010-2180(99)00135-2.
- [2] M. Celnik, A. Raj, R. West, R. Patterson, and M. Kraft. Aromatic site description of soot particles. *Combustion and Flame*, 155(1-2):161–180, 2008. doi:10.1016/j.combustflame.2008.04.011.
- [3] M. Frenklach. On surface growth mechanism of soot particles. *Symposium (International) on Combustion*, 26(2):2285–2293, 1996. doi:10.1016/S0082-0784(96)80056-7.
- [4] M. Frenklach, C. A. Schuetz, and J. Ping. Migration mechanism of aromatic-edge growth. *Proceedings of the Combustion Institute*, 30(1):1389–1396, 2005. doi:10.1016/j.proci.2004.07.048.
- [5] D. A. Goussis. Quasi steady state and partial equilibrium approximations: Their relation and their validity. *Combustion Theory and Modelling*, 16(5):869–926, 2012. doi:10.1080/13647830.2012.680502.
- [6] E. Hesstvedt, Ö. Hov, and I. S. A. Isaksen. Quasi-steady-state approximations in air pollution modeling: Comparison of two numerical schemes for oxidant prediction. *International Journal of Chemical Kinetics*, 10(9):971–994, 1978. doi:10.1002/kin.550100907.
- [7] L. Jay, A. Sandu, F. Potra, and G. Carmichael. Improved quasi-steady-state-approximation methods for atmospheric chemistry integration. *SIAM Journal on Scientific Computing*, 18(1):182–202, 1997. doi:10.1137/S1064827595283033.
- [8] C. K. Law. *Combustion Physics*. Cambridge University Press, 2006. doi:10.1017/CBO9780511754517.
- [9] T. Løvas, D. Nilsson, and F. Mauss. Automatic reduction procedure for chemical mechanisms applied to premixed methane/air flames. *Proceedings of the Combustion Institute*, 28(2):1809–1815, 2000. doi:10.1016/S0082-0784(00)80583-4.
- [10] N. Peters and B. Rogg. *Reduced Kinetic Mechanisms for Applications in Combustion Systems*. Springer-Verlag Berlin Heidelberg, 1993. doi:10.1007/978-3-540-47543-9.
- [11] A. Tikhonov. Systems of differential equations containing small parameters for derivatives. *Mat. Sb.*, 31 (73)(3):575–586, 1952. In Russian.
- [12] T. Turányi and A. S. Tomlin. *Analysis of Kinetic Reaction Mechanisms*. Springer, Berlin, Heidelberg, 2015. doi:10.1007/978-3-662-44562-4.
- [13] T. Turányi, A. S. Tomlin, and M. J. Pilling. On the error of the quasi-steady-state approximation. *Journal of Physical Chemistry*, 97(1):163–172, 1993. doi:10.1021/j100103a028.