

Supplemental Material:

Experimental and Kinetic Modeling Study of the Pyrolysis and Oxidation of 1,5-Hexadiene: The Reactivity of Allylic Radicals and Their Role in the Formation of Aromatics

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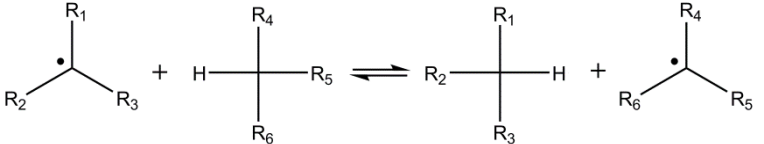
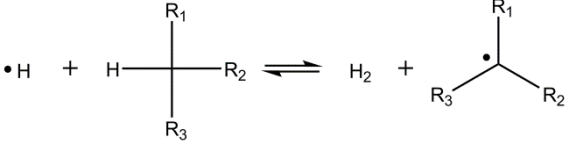
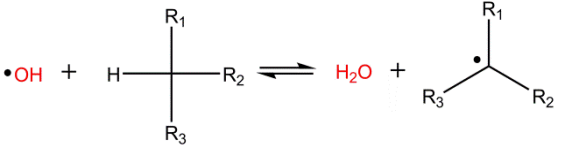
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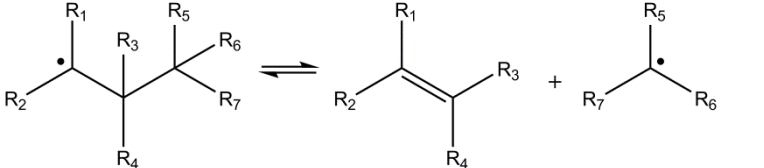
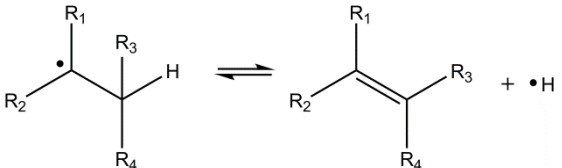
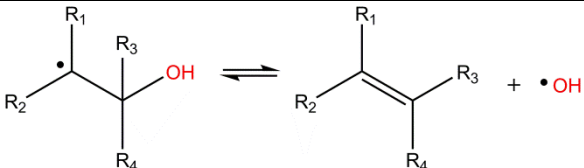
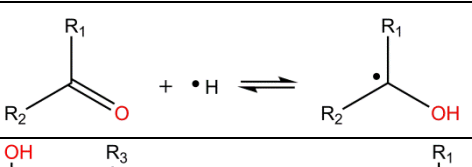
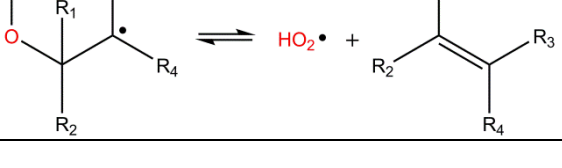
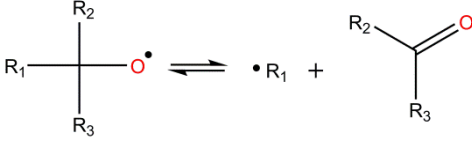
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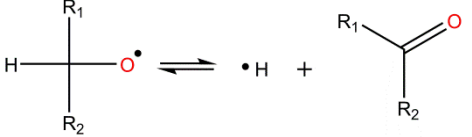
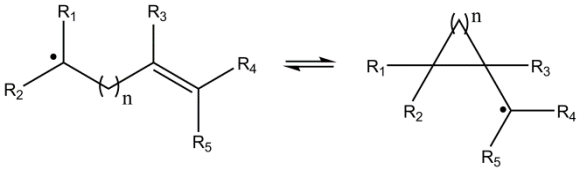
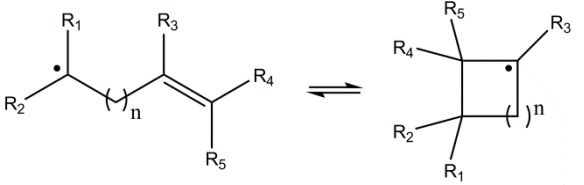
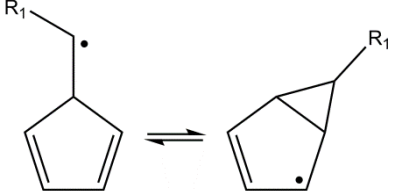
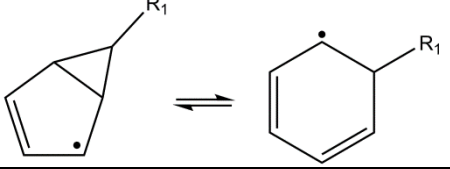
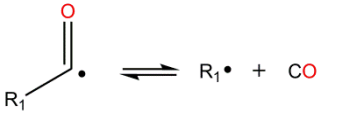
Reaction families and rate rules considered in Genesys for this work

Table S 1 k [bimolecular - $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$; unimolecular - s^{-1}] = $A T^n \exp(-E_a/RT)$ where $R = 8.314 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

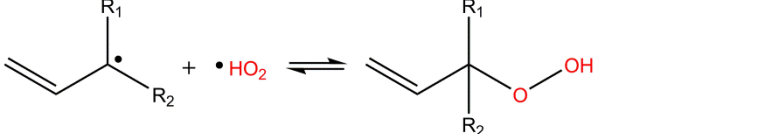
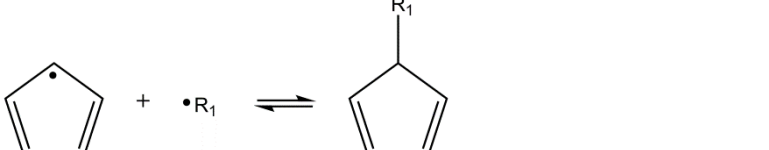
Reaction family	Comment	Kinetic parameters			Ref	
		<i>A</i>	<i>n</i>	<i>E_a</i>		
Hydrogen abstraction						
<i>Intermolecular</i>						
by C• from C-H			Group additivity		[1, 2]	
		H abstr from C(=O)-H by CH ₃	2.5e-6	3.6	18.1	[3]
by H• from C-H			Group additivity		[4]	
		H abstr from C(=O)-H	7.15e-1	2.4	6.6	[3]
by •OH from C-H		R ₁ , R ₂ , R ₃ alkyl chains or H atoms	Rate rules for alkanes		[5, 6]	
		R ₁ , R ₂ H atoms R ₃ C=C	7.80e-1	2.3	-5.7	[7]
		R ₁ H atom R ₂ alkyl chain R ₃ C=C	7.50e-2	2.4	-3.9	[7]
		R ₁ H atom R ₂ OH R ₃ alkyl chain	1.15e-2	2.6	-8.7	[7]
		R ₁ H atom R ₂ OH R ₃ C=C	2.55e-2	2.6	-13.3	[7]
		H abstr from C(=O)-H	6.13e-2	2.7	-19.2	[3]

by HO ₂ • from C-H	$\text{HO}_2\cdot + \text{H}-\begin{matrix} \text{R}_1 \\ \\ \text{C} \\ \\ \text{R}_3 \end{matrix}-\text{R}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_3 \end{matrix}-\text{R}_2$	R ₁ , R ₂ , R ₃ alkyl chains or H atoms	Rate rules for alkanes			[8]
		R ₁ , R ₂ or R ₃ OH	1.23e-11	5.26	31.3	[9]
		R ₁ , R ₂ or R ₃ C=C	7.68e-2	4.4	56.7	[10]
		H abstr from C(=O)-H	1.18e-10	4.9	15.4	[3]
by O ₂ from C-H	$\text{O}_2 + \text{H}-\begin{matrix} \text{R}_1 \\ \\ \text{C} \\ \\ \text{R}_3 \end{matrix}-\text{R}_2 \rightleftharpoons \text{HO}_2\cdot + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_3 \end{matrix}-\text{R}_2$		1.00e7	0.0	ΔH _r	[11, 12]
<i>Intramolecular</i>						
by C• from C-H	$\begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_2 \end{matrix}-\text{H} + \begin{matrix} \text{H} \\ \\ \text{C} \\ \\ \text{R}_4 \end{matrix}-\text{R}_3 \rightleftharpoons \begin{matrix} \text{H} \\ \\ \text{C} \\ \\ \text{R}_4 \end{matrix}-\text{H} + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_2 \end{matrix}-\text{R}_3$		Group additivity + rate rule A = function of # hindered rotors in TS E _a = ring strain in TS + activation energy analogous bimolecular reaction			[1, 2, 13, 14]
by R-O-O• from C-H	$\begin{matrix} \text{O} \\ \\ \text{O}\cdot \\ \\ \text{R}_1 \end{matrix}-\text{C}(\text{R}_2)-\text{H} + \begin{matrix} \text{H} \\ \\ \text{C} \\ \\ \text{R}_4 \end{matrix}-\text{R}_3 \rightleftharpoons \begin{matrix} \text{O} \\ \\ \text{O} \\ \\ \text{R}_1 \end{matrix}-\text{C}(\text{R}_2)-\text{H} + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_2 \end{matrix}-\text{R}_3$	Formation of an alkyl radical	Rate rules for alkanes			[15]
		Formation of an allylic radical	2.24e6	1.29	59.6	[16]
by R-O-O• from O-H	$\begin{matrix} \text{O} \\ \\ \text{O}\cdot \\ \\ \text{R}_1 \end{matrix}-\text{C}(\text{R}_2)-\text{CH}_2-\text{OH} + \begin{matrix} \text{H} \\ \\ \text{C} \\ \\ \text{R}_4 \end{matrix}-\text{R}_3 \rightleftharpoons \begin{matrix} \text{O} \\ \\ \text{O} \\ \\ \text{R}_1 \end{matrix}-\text{C}(\text{R}_2)-\text{CH}_2-\text{OH} + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_2 \end{matrix}-\text{R}_3$	Analogy with 2-peroxy-2-methylpropan-1-ol	2.91e12	-0.23	93.3	[17]
by cyclopentadienyl from C-H through 3-membered transition state	$\text{Cyclopentadienyl}\cdot + \text{H}-\begin{matrix} \text{R}_1 \\ \\ \text{C} \\ \\ \text{R}_3 \end{matrix}-\text{R}_2 \rightleftharpoons \text{Cyclopentadiene} + \begin{matrix} \text{R}_1 \\ \\ \text{C}\cdot \\ \\ \text{R}_3 \end{matrix}-\text{R}_2$	Analogy with methyl-cyclopentadienyl	2.20e-3	4.91	169.0	[18]
β-scission / radical addition						

Intermolecular						
$\bullet\text{C-C-C} \rightleftharpoons \text{C=C} + \bullet\text{C}$			Group additivity			[19]
$\bullet\text{C-C-H} \rightleftharpoons \text{C=C} + \bullet\text{H}$			Group additivity			[20]
$\bullet\text{C-C-OH} \rightleftharpoons \text{C=C} + \bullet\text{OH}$		Analogy with 2-hydroxy-ethyl to ethene plus OH	3.00e13	0.0	112.1	^a
$\bullet\text{C-O-H} \rightleftharpoons \text{C=O} + \bullet\text{H}$		Analogy with acetaldehyde plus H to 1-hydroxy-ethyl	1.10e8	0.0	44.7	^a
$\bullet\text{C-C-O-O-H} \rightleftharpoons \text{C=C} + \text{HO}_2\bullet$			Rate rules for alkanes			[15]
$\bullet\text{O-C-C} \rightleftharpoons \text{C=O} + \bullet\text{C}$		R ₁ alkyl Analogy with 2-oxy-propane	6.00e13	0.22	59.0	^a
		R ₁ C=C Analogy with allyloxy	2.70e14	0.00	100.0	[21]

$\bullet\text{O}-\text{C}-\text{H} \rightleftharpoons \text{C}=\text{O} + \bullet\text{H}$		R_1 or R_2 $\text{C}=\text{C}$. Analogy with allyloxy	1.17e10	1.00	77.6	[21]
Intramolecular						
exo-addition			Group additivity + rate rule A = function of # hindered rotors in TS Ea = ring strain in TS + activation energy analogous bimolecular reaction			[13, 19]
endo-addition			Group additivity + rate rule A = function of # hindered rotors in TS Ea = ring strain in TS + activation energy analogous bimolecular reaction			[13, 19]
endo-addition forming bicyclic species		Analogy with methyl-cyclopentadienyl	3.20e11	0.17	18.4	[18]
ring-enlargement		Analogy with hexadienyl	8.50e11	0.41	69.9	[18]
α-scission						
$\text{C}-\text{C}(=\text{O})\bullet \rightleftharpoons \text{C}\bullet + \text{CO}$		Analogy with acetyl radical	3.30e12	0.62	72.4	^a
Concerted reactions						

$\bullet\text{O}-\text{O}-\text{C}-\text{C}-\text{H} \rightleftharpoons \text{HO}_2\bullet + \text{C}=\text{C}$			Rate rules for alkanes			[15]
Formation of cyclic ethers from hydroperoxyl-alkyl radicals			Rate rules for alkanes			[15]
$\bullet\text{O}-\text{O}-\text{C}-\text{OH} \rightleftharpoons \text{HO}_2\bullet + \text{C}=\text{O}$		Analogy with alpha-hydroxy-ethylperoxy	2.60e8	1.13	44.5	[22]
Sigmatropic hydrogen shift of 5-alkyl-1,3-cyclopentadiene to 1-alkyl-1,3-cyclopentadiene		Analogy with methyl-cyclopentadiene	7.03e8	1.20	103.8	[23]
Sigmatropic hydrogen shift of 1-alkyl-1,3-cyclopentadiene to 2-alkyl-1,3-cyclopentadiene		Analogy with methyl-cyclopentadiene	1.65e7	2.10	105.0	[23]
Oxygen addition on carbon-centered radicals						
$\text{C}\bullet + \text{O}_2 \rightleftharpoons \text{C}-\text{O}-\text{O}\bullet$		$\text{R}_1, \text{R}_2, \text{R}_3$ alkyl chains or H atoms	Rate rules for alkanes			[15]
		$\text{R}_1 \text{ C}=\text{C}$	5.78e1	1.59	4.5	[24]
		$\text{R}_1 \text{ OH}$	4.05e7	-0.31	-1.4	[9]
Recombination / scission						
$\text{C}-\text{O}-\text{O}-\text{H} \rightleftharpoons \text{CO}\bullet + \bullet\text{OH}$		Analogy with allylhydroperoxide	3.35e10	0.60	-8.8	[21]

$C\cdot + HO_2\cdot \rightleftharpoons C-O-O-H$		Analogy with allylhydroperoxide	$1.59e20$	-1.50	179.3	$[21]$
Recombination of cyclopentadienyl with carbon-centered radicals		Analogy with cyclopentadienyl plus methyl	$8.34e9$	-0.70	-2.1	$[23]$

^a CBS-QB3 calculations

Sensitivity analysis with respect to the allyl radical

Supplementary to 1,5-hexadiene, benzene and 1,3-cyclopentadiene, a sensitivity analysis with respect to the allyl radical mole fraction has been performed. The results at fuel-rich oxidation conditions ($\phi=2.0$) at 850K, 950K and 1050K are presented in Figure S 1. Similar to the 1,5-hexadiene mole fraction sensitivity analysis, the allyl radical mole fraction is sensitive to reactions occurring during the initial decomposition of 1,5-hexadiene at low temperatures and to reactions part of the secondary chemistry at higher temperatures. A positive sensitivity coefficient for the addition of a hydrogen atom or a hydroxyl radical to 1,5-hexadiene with the formation of a secondary radical is caused by the subsequent formation of an allyl radical through C-C β -scission. The competing hydrogen addition to 1,5-hexadiene with the formation of a primary radical has a negative sensitivity coefficient as no allyl radical is formed in further reactions. In oxidation conditions, the primary consumption pathways of the allyl radicals involve reaction with hydroperoxy radicals. Pathways in which hydroperoxy radicals are consumed hence have a positive sensitivity coefficient with respect to the allyl radical mole fraction.

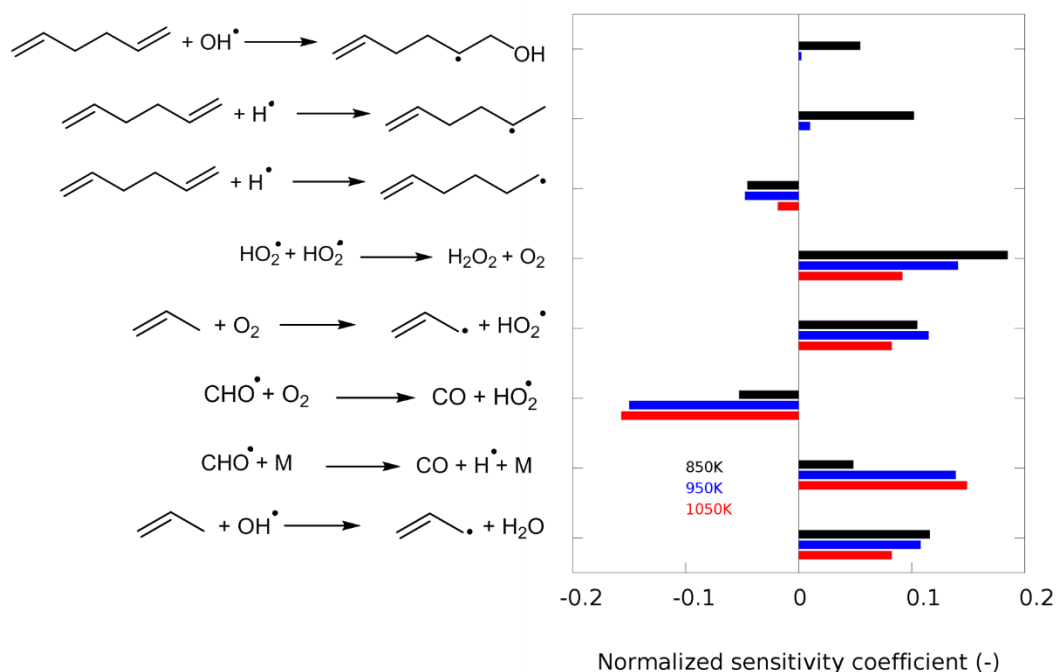


Figure S 1 Sensitivity coefficients for allyl radical mole fraction in 1,5-hexadiene oxidation ($\phi=2.0$). Operating conditions correspond to $P=0.107$ MPa, $F_V=4.06 \cdot 10^{-5} \text{ m}^3 \text{ s}^{-1}$, $x_{1,5\text{-hexadiene},0}=0.008$, $T = 800\text{K}$ (black), 900K (blue), and 1000K (red).

Comparison to the propene pyrolysis model by Wang et al.

The model performance of the kinetic model developed for the pyrolysis of propene by Wang et al. [25] (CSM model) has been compared to the model performance of the kinetic model developed in this work for the pyrolysis of 1,5-hexadiene. The results are shown in Figure S 2. Although the model is developed for the pyrolysis of propene, it can well describe the pyrolysis products of 1,5-hexadiene. In general, the main product yields of the small products are well described by both models. The performance of the kinetic model in this work is better for hydrogen gas, propene, propadiene and 1-butene mole fractions. However, the CSM model seems to perform better to predict the ethane, ethyne and 2-butene mole fractions. The ethyne mole fraction in this work can be improved by re-evaluation of the reaction from a vinyl radical to ethyne and a hydrogen atom. Towards the performance for the mole fractions of the cyclic products and aromatics formed from 1,5-hexadiene, our kinetic model clearly demonstrates improved performance. The mole fraction trends as a function of temperature are better reproduced by this kinetic model compared to the CSM model. The mole fractions of cyclic C₆ species, like cyclohexene and 1,3-cyclohexadiene, are clearly under predicted by the CSM model, while a quantitative agreement is obtained with our model. The CSM model predicts the trend of the benzene mole fraction quite good, but a better agreement is obtained with the model developed in this work. Furthermore, the mole fractions of all heavier aromatics, like toluene, ethyl-benzene, styrene and naphthalene, are under predicted by the CSM model.

To conclude, although the CSM model was developed for the pyrolysis of propene, it leads to good predictions of the mole fractions of the small products of 1,5-hexadiene pyrolysis. However, the model performance of the kinetic model developed in this work, more accurately predicts the mole fractions of heavier, cyclic and aromatic products.”

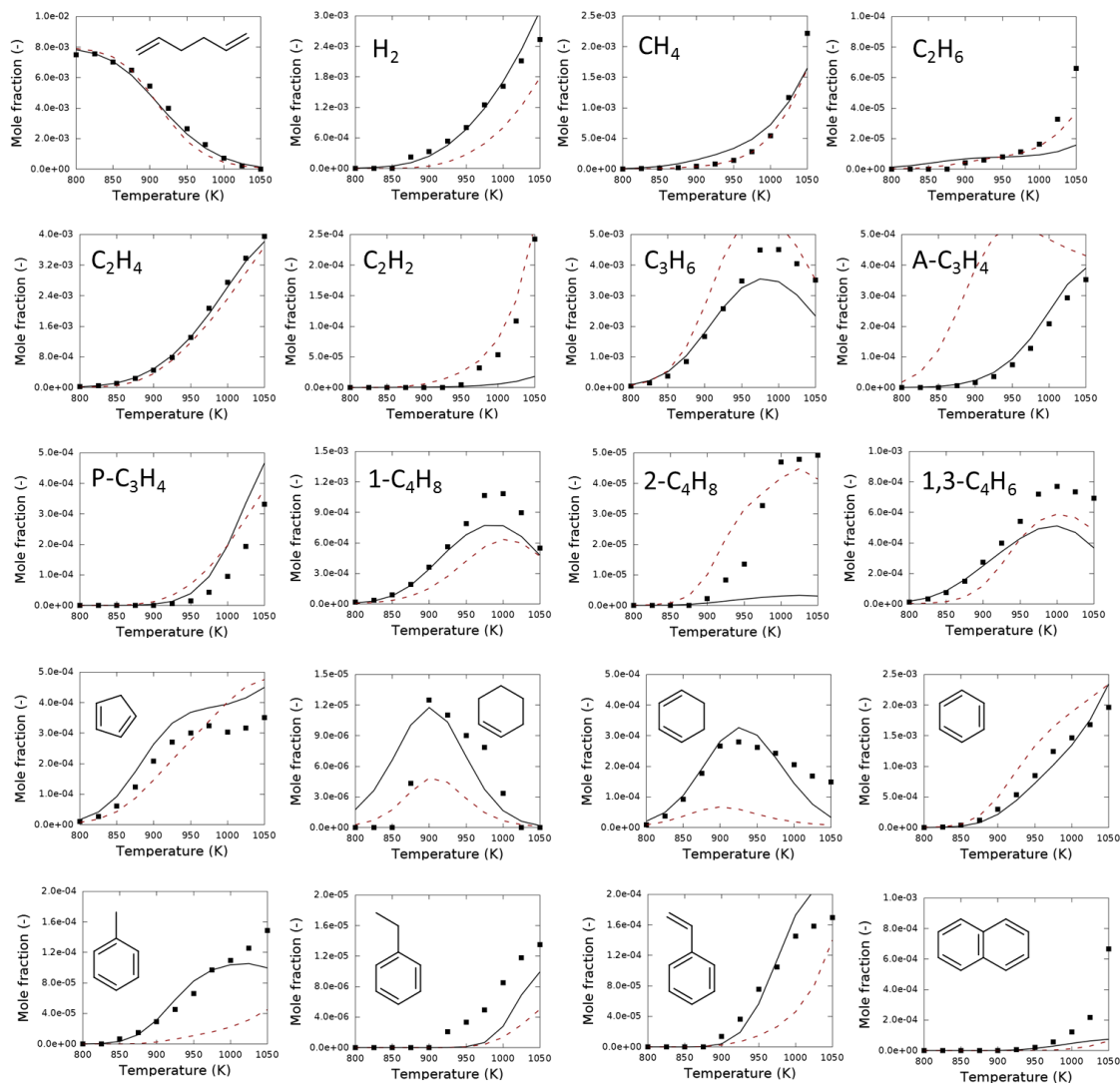


Figure S 2. Comparison of the simulated mole fractions of the main species during 1,5-hexadiene pyrolysis with experimental data (dots). Kinetic models used for simulations are the new kinetic model (black full lines) and the CSM model by Wang et al. (red dashed lines)

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