

Supplementary description for the paper

**THE OXIDATION OF LARGE ALKYL BENZENES: AN EXPERIMENTAL
AND MODELING STUDY**

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I/ KINETIC PARAMETERS USED IN THE PRIMARY MECHANISM

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OXIDATION OF ALKYL BENZENES**

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IV/ OTHER TESTS OF THE PRESENT *n*-BUTYL BENZENE MODEL

**V/ MODELLING OF PRESENT *n*-BUTYL BENZENE JSR DATA AT 1 ATM USING
THE MODEL OF LAWRENCE LIVERMORE NATIONAL LABORATORY [10]**

I/ KINETIC PARAMETERS USED IN THE PRIMARY MECHANISM

Table S1: internal isomerizations of free radicals.

Pre-exponential factor (A) is mainly based on the changes in the number of internal rotations as the reactant moves to the cyclic transition state. Activation energies have been set equal to the sum of the activation energy for H-abstraction from the substrate by analogous radicals ($E_{\text{H-abstr.}}$, see Table S1a) and the strain energy of the cyclic transition state (E_{ring} , see Table S1b).

$$E = E_{\text{H-abstr.}} + E_{\text{ring}}$$

Table S1a: Activation energy for a H-atom abstraction ($E_{\text{H-abstr.}}$) (kcal mol^{-1})

Abstracted H atom	Primary	Secondary	Secondary benzylic
Abstraction by ROO•	20 ¹	17 ¹	14.5 ¹
Abstraction by •R	13.5	11	6.5
Abstraction by benzylic radical	23.0	21.0	-

¹ If the carbon bearing this H-atom is also linked to an atom of oxygen, $E_{\text{H-abstr.}}$ is decreased by 2 kcal.mol^{-1}

Table S1b: Strain energy of cyclic compounds (E_{ring}) (kcal mol^{-1})

Size of the ring	4	5	6	7	8
Rings containing two O atoms	23.0	15.5	8.5	5.0	4.0
Rings containing zero or one O atom	26.0	6.3	1.0	6.4	9.9

Table S2: Other reactions

Rate constants are expressed in the form $k = A T^b \exp(-E/RT)$, with the units cm^3 , mol, s, cal, by H atoms which can be abstracted. $\bullet R_p$, $\bullet R_s$, $\bullet R_t$ are primary, secondary and tertiary alkyl free radicals.

Table S2a: H-abstraction or beta-scission reactions involving the breaking of a C-H bond

	Primary H-atom			Secondary H-atom			Secondary benzylic H-atom		
	log A	b	E	log A	b	E	log A	b	E
Bimolecular initiation	12.85	0	ΔH_r^*	12.85	0	ΔH_r^*	11.85	0	ΔH_r^*
Oxidation of an alkyl free radical	11.36	0	5000	11.90	0	5000	11.11	0	2500
Oxidation of a benzylic free radical	-	-	-	11.90	0	15200	-	-	-
H-ATOM ABSTRACTION BY									
$\bullet O\bullet$	13.23	0	7850	13.11	0	5200	10.64	0.7	3250
$\bullet H$	6.98	2	7700	6.65	2	5000	4.43	2.5	-1900
$\bullet OH$	5.95	2	450	6.11	2	-770	6.17	2	-1520
$\bullet CH_3$	-1	4	8200	11.0	0	9600	10.70	0	7300
$HO_2\bullet$	11.30	0	17000	11.30	0	15500	3.50	2.6	12400
$\bullet CHO$	4.53	2.5	18500	6.73	1.9	17000	8.75	1.3	15500
$\bullet CH_2OH$	1.52	2.95	14000	1.48	2.95	12000	1.25	2.95	10000
$\bullet OCH_3$	10.73	0	7300	10.86	0	4500	11.94	0	1200
$\bullet OOR$	12.30	0	20000	12.18	0	17500	11.69	0	14550
$\bullet C_2H_5$	11.00	0	13500	11.00	0	11000	0.34	3.5	4140

* ΔH_r is the enthalpy of reaction calculated using THERGAS [19].

Table S2b: Other reactions

	log A	b	E
Addition of an alkylic radical to O₂		See text	
Addition of a benzylic radical to O₂	10.08	0	-2300
Ipsso addition with			
•H	13.76	0	8100
•O	13.23	0	3600
•OH	2.91	2.9	3200
•CH ₃	12.08	0	15900
•HO ₂	11.84	0	11300
C-C β-scission of an alkylic radical			
•CH ₃ + molecule	13.30	0	31000
•R _p + molecule	13.30	0	28700
Benzyl radical + olefin	3.3E13		22500
C-C β-scission of a benzylic radical			
•CH ₃ + molecule	13.11	0	38200
•R _p + molecule	13.11	0	35900
C-O β-scission of an alkylic radical			
•HO ₂ + molecule	12.93	0	26000
C-H β-scission of an alkylic radical			
•H _p + molecule	13.00	0	39000
•H _s + molecule	13.18	0	38000
•H _{allylic} + molecule	13.20	0	34800
C-H β-scission of a benzylic radical			
•H _p + molecule	13.00	0	51500
C-O β-scission of a benzylic radical			
•HO ₂ + molecule	12.93	0	33200
O-O β-scission of a radical			
Alkyl radical •OH + ketone	12.93	0	7500
Benzylic radical •OH + ketone	12.93	0	14700
Cyclic ether formation			
cycle with 3 atoms	11.50	0	16500
cycle with 4 atoms	10.39	0	15250
cycle with 5 atoms	9.32	0	6500
cycle with 6 atoms	8.17	0	1800
•OOR and HO₂• disproportionation	11.30	0	-1300
Combinations of benzylic H-atoms			
with H-atom	14.00	0	0
with •OH radicals	13.17	0	0
with alkyl radicals	13.00	0	0
with •HO ₂ radicals	11.00	0	0

In the case of the addition of a free radical to an oxygen molecule, an additivity method is used to take into account the structure of each considered radical more closely:

$$k = n_p k_p + n_s k_s + n_t k_t + n_q k_q \quad \text{with :}$$

$n_p =$ number of primary groups (CH₃) linked to the carbon with the radical point,

$n_s =$ number of secondary groups (CH₂) linked to the carbon with the radical point,

and :

$$k_p = 8.0 \times 10^{18} T^{-2.5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$k_s = 9.0 \times 10^{18} T^{-2.5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

II/ RULES OF GENERATION OF THE SECONDARY MECHANISM OF THE OXIDATION OF ALKYL BENZENES

Below are presented the generic reaction rules for species formed in the primary mechanism. The generic reaction rules are given for each class of species along with particular cases and an example to illustrate the rule. Note that these rules have been deduced from the rules that already exist for alkanes as the alkyl-benzene molecules can be seen as an alkyl chain linked to a non reactive phenyl ring. The specificities due to the presence of a phenyl ring have been taken in account (presence of benzylic H-atoms as an example).

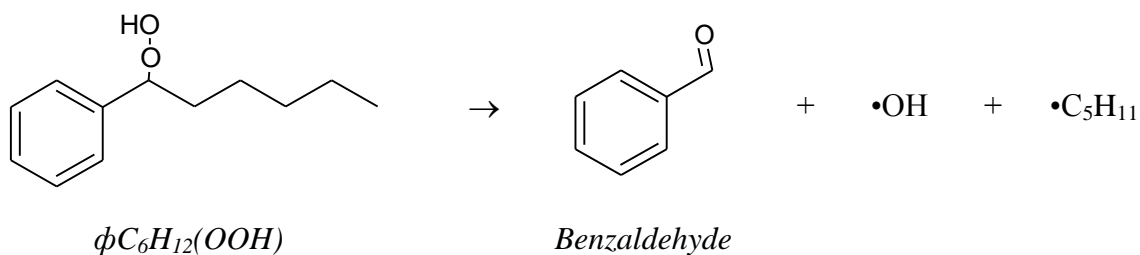
The kinetic data are also provided in the following paragraphs (highlighted in green at the end of the different rules).

a. Generic decomposition rules of degenerate branching agents

Branching agents are species with hydroperoxy groups (R-OOH). Due to the weakness of the O-O bond in the hydroperoxy group, this type of species decomposes by a breaking of this bond. The decomposition leads to the formation of an $\bullet\text{OH}$ and a $\text{RO}\bullet$ radicals. To simplify, very reactive $\text{RO}\bullet$ radicals are not written and it is considered that they decompose directly to smaller species that are already in the primary mechanism or in the aromatic reaction base. The kinetic parameters are those of the reaction of decomposition through the breaking of the O-O bond.

α . R(OOH) species (hydroperoxides): $\phi\text{C}_n\text{H}_{2n}(\text{OOH})$

Example with a C_6 side chain:



Generic rule:

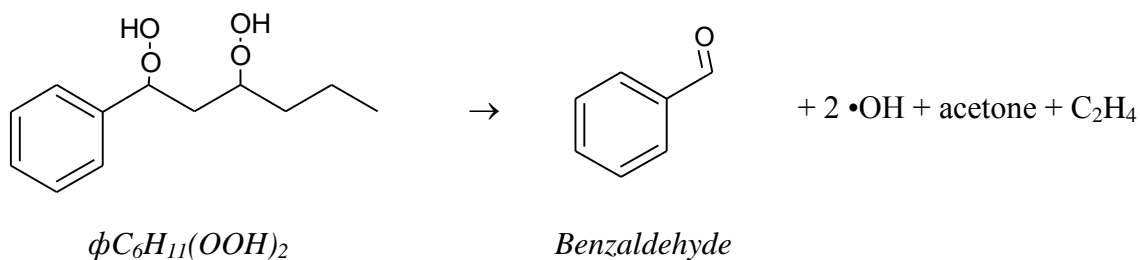
If $n > 2$



$$k = 1.5 \cdot 10^{16} \exp(-43000/RT) \text{ s}^{-1}$$

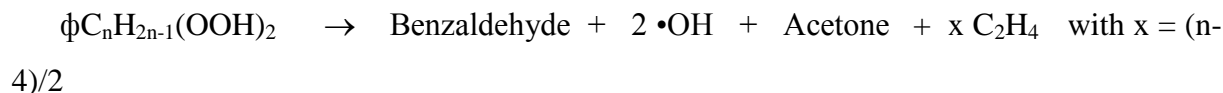
β . $R(OOH)_2$ species (di-hydroperoxides): $\phi C_n H_{2n-1} (OOH)_2$

Example with a C_6 side chain: $\phi C_6 H_{11} (OOH)_2$

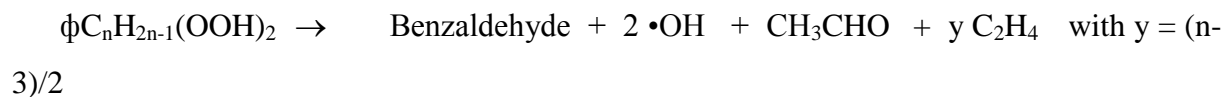


Generic rule:

If n is even ($n \geq 4$)



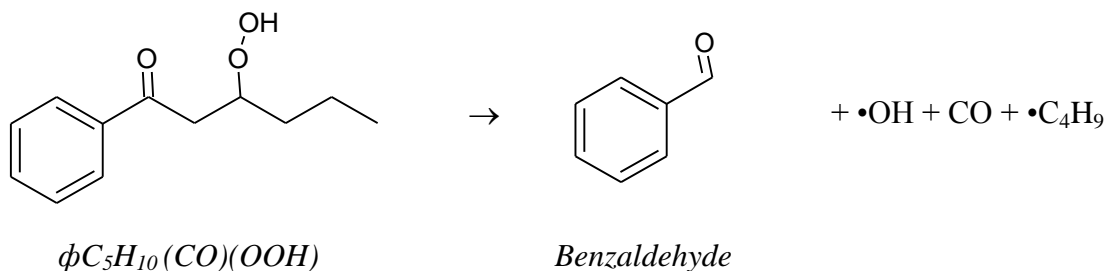
If n is odd ($n \geq 3$)



$$k = 3 \cdot 10^{16} \exp(-43000/RT) \text{ s}^{-1}$$

γ . $R(CO)(OOH)$ species: $\phi C_{n-1} H_{2n-2} (CO)(OOH)$

Example with a C_6 side chain: $\phi C_5 H_{10} (CO)(OOH)$



Generic rules:

If $n \geq 3$



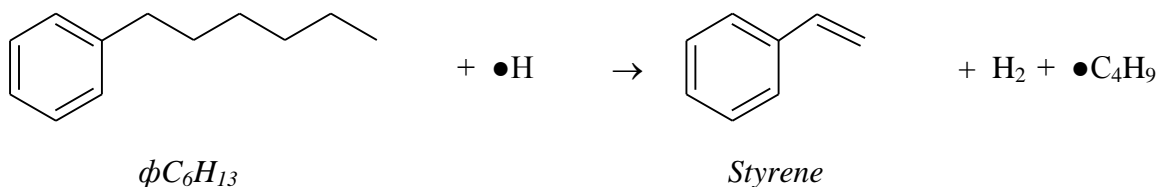
$$k = 1.5 \cdot 10^{16} \exp(-43000/RT) \text{ s}^{-1}$$

b. Generic consuming rules of alkyl- and alkenyl-benzenes by H-atom abstraction

In the case of H-atom abstractions, kinetic data are dependant of the number and the nature of abstractable H-atoms. These two parameters are indicated along with the reaction rules. Note that correlations enabling the determination of kinetic constants of H-atom abstractions are already implemented in the software EXGAS as they are the same as those used in the case of alkanes and alkenes.

α . Reaction $\phi C_n H_{2n+1}$ (alkyl-aromatics) + $\bullet R'$ ($\bullet R' = H\bullet, \bullet O\bullet, OH\bullet, HO_2\bullet, C_2H_5\bullet$)

Example with a C_6 side chain: $\phi C_6 H_{13}$



Generic rules:

If $n \geq 3$



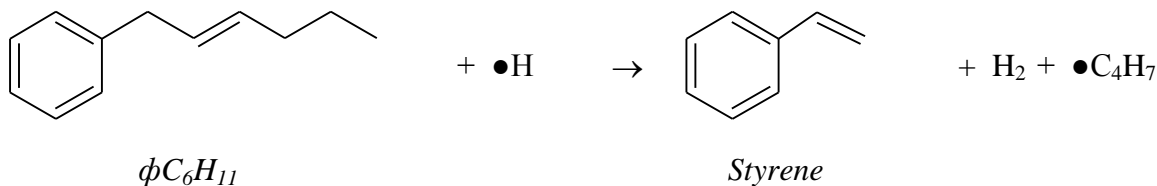
Particular case $n=1$

Toluene (already in the toluene reaction base)

For all $n \geq 2$: k is that for the abstraction of 2 benzylic H, 3 primary alkylic H and $2n-4$ secondary alkylic H

β . Reaction $\phi C_n H_{2n-1}$ (unsaturated alkyl-aromatics) + $\bullet R'$ ($\bullet R' = H\bullet, \bullet O\bullet, OH\bullet, HO_2\bullet, C_2H_5\bullet$)

Example with a C₆ side chain: ϕC_6H_{11}

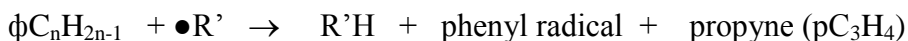


Generic rules:

If $n > 4$

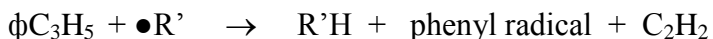


Particular case $n=4$



(thus the unrealistic formation of $\bullet C_2H_3$ is avoided)

Particular case $n=3$



If $n \geq 4$: k is that for the abstraction of 2 benzylic H, $2n-8$ secondary alkylic H and 2 secondary allylic H

If $n=4$: k is that for the abstraction of 2 benzylic H and 2H secondary alkylic H

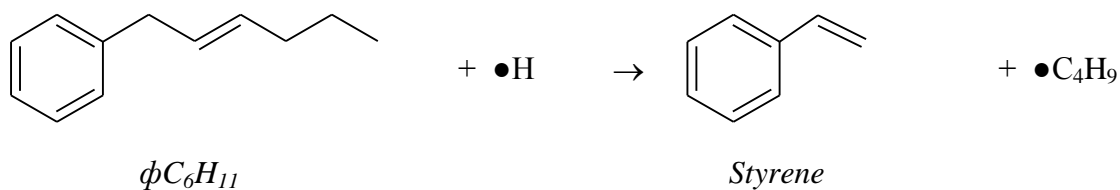
If $n=3$: k is that for the abstraction of 2 benzylic H

c. Generic consuming rules of alkenyl-benzenes by a radical addition on the double bond

When adding a radical to a double bond there is two possible reactions as there are two addition sites. The new radical which is considered to decompose directly into species already considered in the primary mechanism or in the toluene reaction base. To simplify, the two reactions are the same (duplicate reactions) with two sets of kinetic parameters which can differ if the two addition sites are not the same (the addition can occur on a secondary or on a tertiary radical carbon atom).

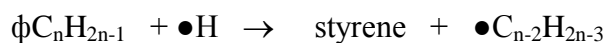
α . Reaction of addition of $\bullet\text{H}$ on ZH (unsaturated alkyl-aromatics)

Example with a C_6 side chain: $\phi\text{C}_6\text{H}_{11}$



Generic rules:

If $n \geq 3$



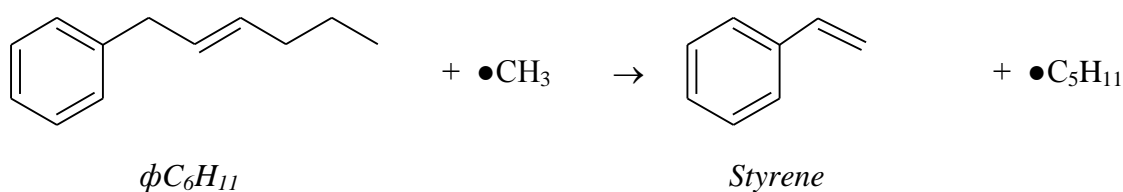
2 DUPLICATE reactions

$1.32 \cdot 10^{13}$	0.0	1560	(addition on secondary C)
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$1.32 \cdot 10^{13}$	0.0	3260	(addition on tertiary C)
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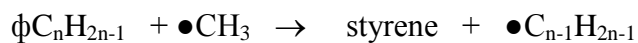
β . Reaction of addition of $\bullet\text{CH}_3$ to ZH (unsaturated alkyl-aromatics)

Example with a C_6 side chain: $\phi\text{C}_6\text{H}_{11}$



Generic rules:

If $n \geq 3$



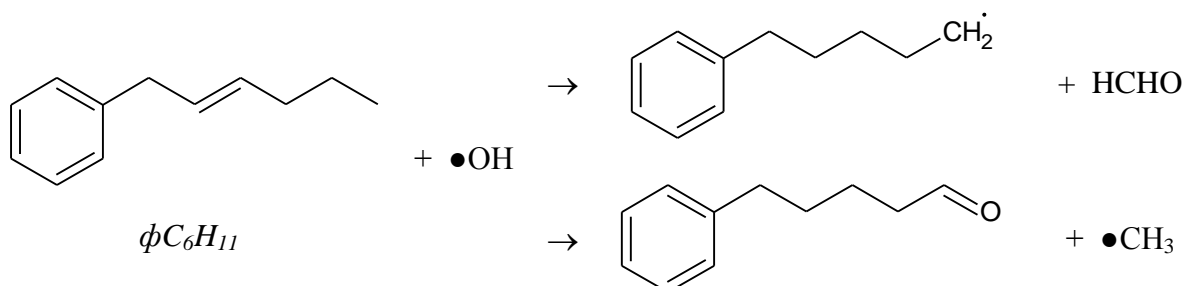
2 DUPLICATE reactions

$1.69 \cdot 10^{11}$	0.0	7400	(addition on secondary C)
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$9.64 \cdot 10^{10}$	0.0	8000	(addition on tertiary C)
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γ. Reaction of addition of •OH on ZH (unsaturated alkyl-aromatics)

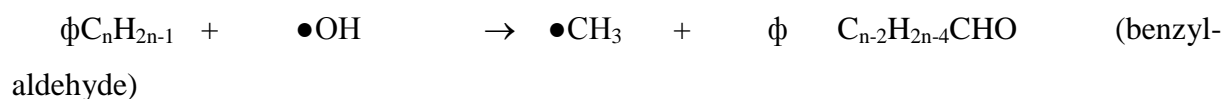
Example with a C₆ side chain: φC₆H₁₁



Two reactions are considered here to better account for the reality as the decomposition of the intermediate radical can occur through the breaking of a bond in the ring side or of a bond in the other side.

Generic rules:

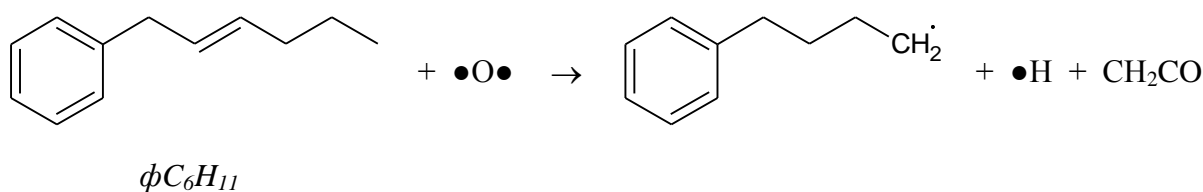
For any n



$$1.4 \cdot 10^{12} \quad 0.0 \quad -1040 \quad (A, n, E_a, \text{ respectively})$$

δ. Reaction of addition of •O• to ZH (unsaturated alkyl-aromatics)

Example with a C₆ side chain: φC₆H₁₁



Generic rules:

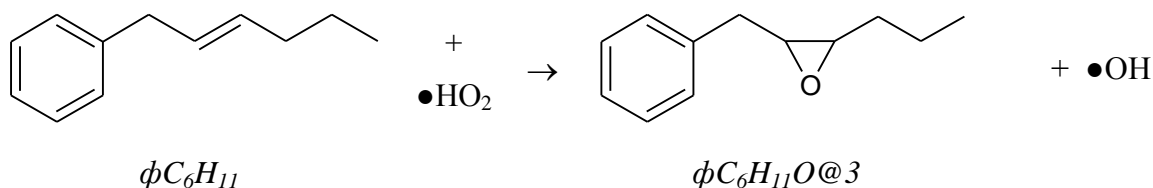
For any n



$$1.2 \cdot 10^5 \quad 2.56 \quad -1130 \quad (A, n, E_a, \text{ respectively})$$

ε. Reaction of addition of •HO₂ to ZH (unsaturated alkyl-aromatics)

Example with a C₆ side chain: φC₆H₁₁



Generic rules:

For any n



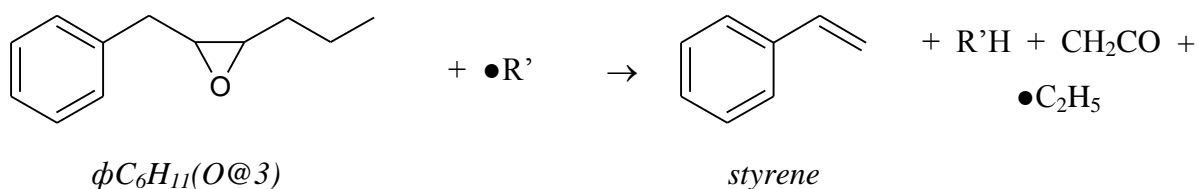
1.0*10¹² 0.0 14200 (A, n, Ea, respectively)

d. Generic consuming rules of cyclic ethers

It is considered that cyclic ethers react with radicals via H-atom abstraction reactions. The new radical is not written and its decomposition into small species (already in the primary mechanism or in the toluene reaction base) is directly written. Three membered ring cyclic ethers are considered separately from the others with a larger ring (four, five and six membered ring cyclic ethers) as they behave slightly differently.

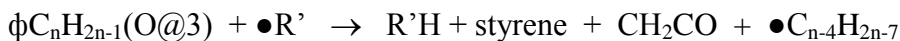
α. Three membered ring cyclic ethers φC_nH_{2n-1}(O@3) + •R'

Example with a C₆ side chain: φC₆H₁₁(O@3)

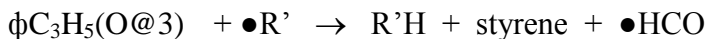


Generic rules:

If $n \geq 5$



Particular case $n=3$



Particular case $n=4$

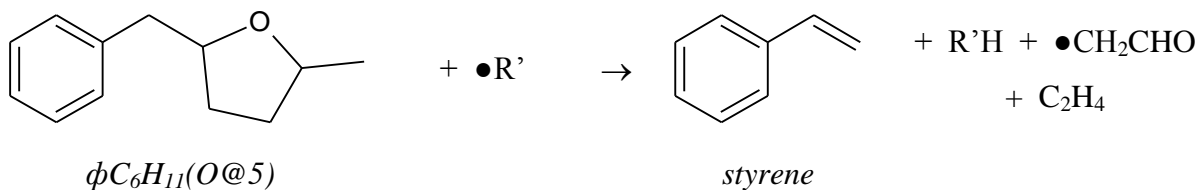


If $n \geq 3$: k is that for the abstraction of 3 primary alkylic H, $2n-6$ secondary alkylic H and 2 benzylic H

$n=2$: kinetic parameters are in the toluene reaction base

β . Cyclic ethers $\phi C_n H_{2n-1} (O@N) + \bullet R'$, with $N = 4, 5$ or 6

Example with a $\phi C_6 H_{11}$ five membered ring cyclic ether



Generic rules:

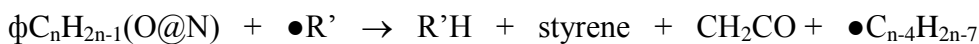
If $n = 3$



If $n = 4$



If $n \geq 4$:



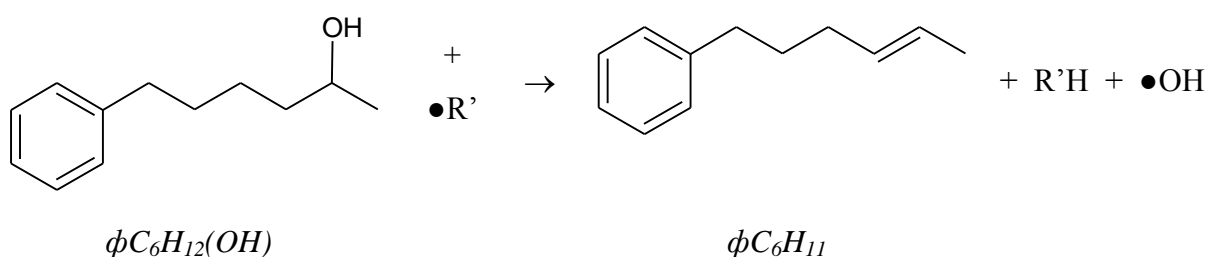
k is that for the abstraction of 3 primary alkylic H, $2n-6$ secondary alkylic H and 2 benzylic H

e. Generic consuming rules of saturated alcohols

It is considered that alcohols react by H-atom abstraction. The new radical is not written as its decomposition into smaller species already in the primary mechanism or in the toluene reaction base is directly written.

α . H-atom abstraction from an alcohol $\phi C_n H_{2n}(OH)$ by $\bullet R'$

Example with a C_6 side chain:



Generic rules:

For any n



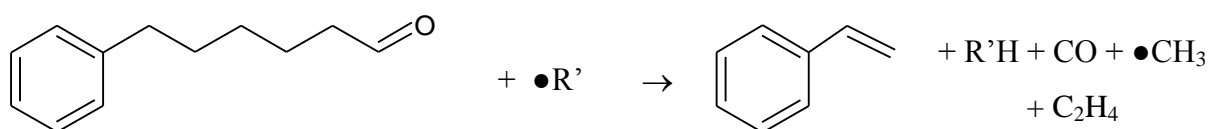
If $n \geq 3$: k is that for the abstraction of 3 primary alkylic H, $2n-5$ secondary alkylic H and 2 benzylic H

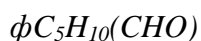
f. Generic decomposition rules of aldehydes

It is considered that aldehydes react by H-atom abstraction. The new radical is not written as its decomposition into smaller species already in the primary mechanism or in the toluene reaction base is directly written.

α . H-atom abstraction from $\phi C_{n-1} H_{2n-2}(CHO)$ by $\bullet R'$

Example with a C_6 side chain:





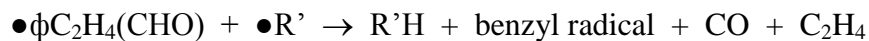
styrene

Generic rules:

If n even (n ≥ 4)



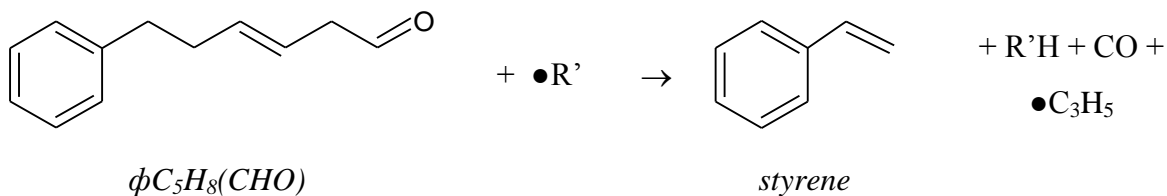
Particular case n=3



If n > 2: k is that for the abstraction of 1 aldehydic H, 2n-4 secondary alkylic H and 2 benzylic H

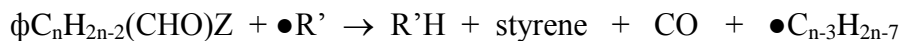
β . H-atom abstraction from $\phi C_{n-1}H_{2n-4}(CHO)Z$ by $\bullet R'$

Example with a C₆ side chain:

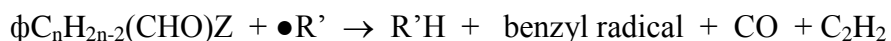


Generic rules:

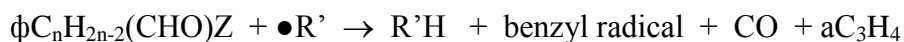
if n ≥ 5



Particular case n=3



Particular case n=4



If n ≥ 3: k is that for the abstraction of 1 aldehydic H, 2n-6 secondary alkylic H and 2 allylic H

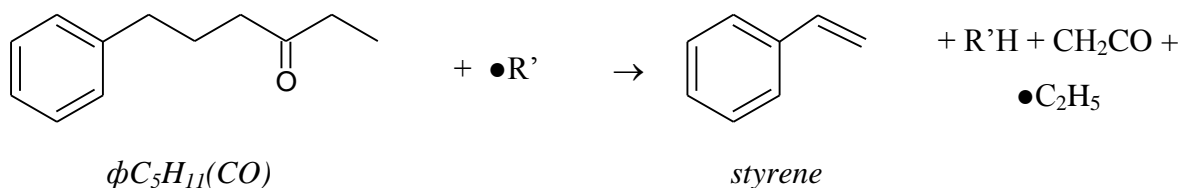
If n=3: k is that for the abstraction of 1 aldehydic H

g. Generic decomposition rules of ketones

It is considered that ketones react by H-atom abstraction. The new radical is not written as its decomposition into smaller species already in the primary mechanism or in the toluene reaction base is directly written.

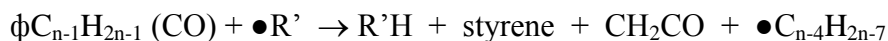
α . H-atom abstraction from $\phi C_{n-1}H_{2n-1} (CO)$ by $\bullet R'$

Example with a C_6 side chain:



Generic rules:

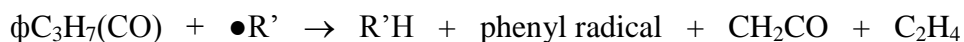
If $n \geq 5$



Particular case $n=3$



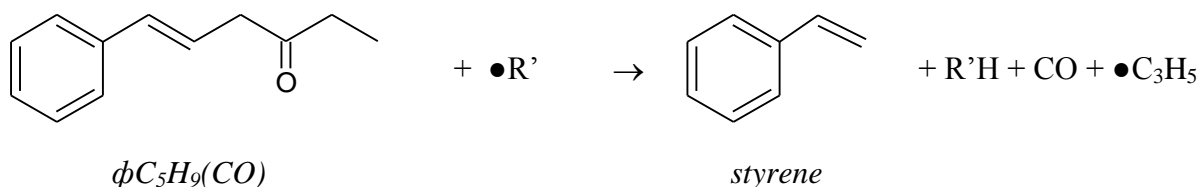
Particular case $n=4$



If $n \geq 3$: k is that for the abstraction of 2 benzylic H, $2n-6$ secondary alkylic H and 3 primary alkylic H

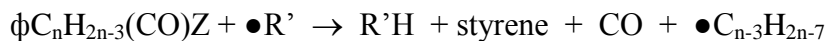
β . H-atom abstraction from $\phi C_{n-1}H_{2n-3} (CO)Z$ by $\bullet R'$

Example with a C_6 side chain:



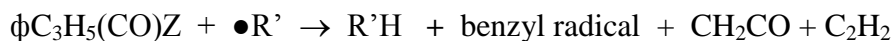
Generic rules:

If $n \geq 5$



Particular case $n=3$ (already in the toluene reaction base)

Particular case $n=4$



If $n \geq 4$: k is that for the abstraction of 2 allylic H, 3 primary alkylic H, 2 allylic H and $2n-8$ secondary alkylic H

f $n=3$: k is that for the abstraction of 3 secondary vinylic H*

III/ MODELING USING THE PREVIOUS MODEL OF HUSSON ET AL. [7]

a/ ignition data

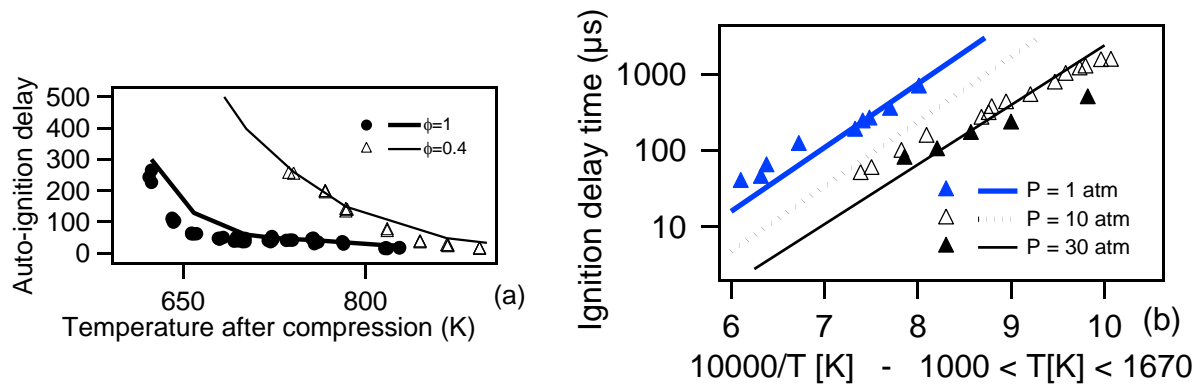


Figure S1: Auto-ignition of *n*-butylbenzene in (a) a rapid compression machine ($\Phi = 0.4$ at P_{TDC} from 14.3 to 18.3 bar, and $\Phi = 1$ at P_{TDC} from 13.4 to 17.9 bar) and (b) a shock tube (stoichiometric mixture) (points are experiments [4, 7] and lines with the model of [7]).

b/ JSR data

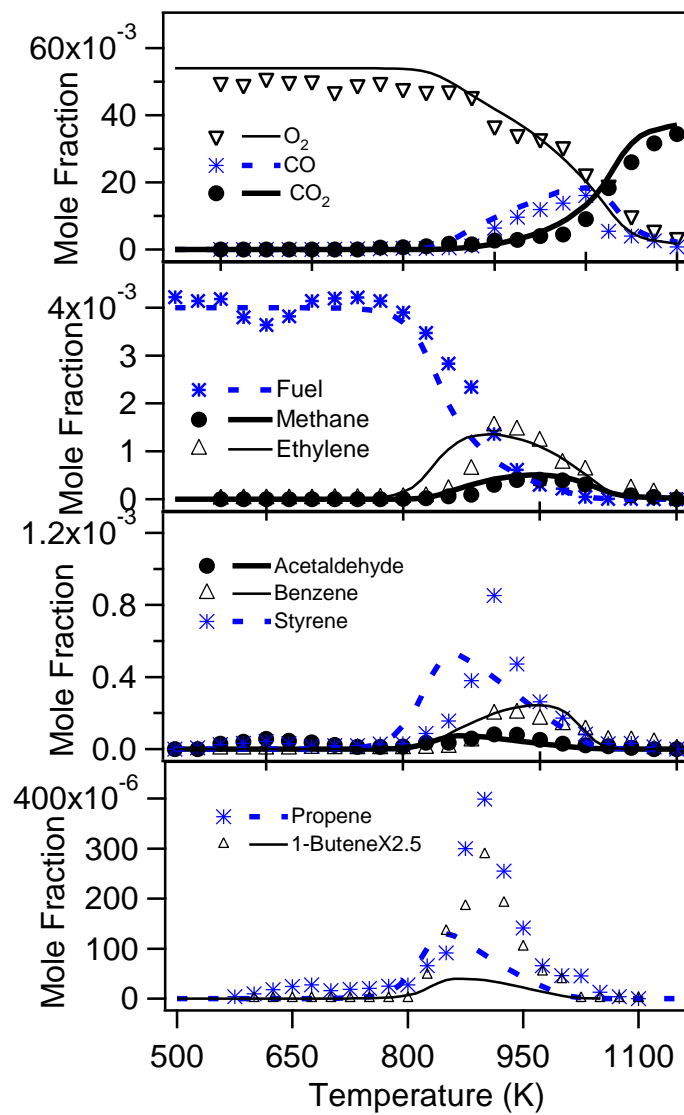


Figure S2: Major products of the oxidation of *n*-butylbenzene in a jet-stirred reactor (points are experiments [7] and lines simulations with the model of [7]).

IV/ OTHER TESTS OF THE PRESENT *n*-BUTYL BENZENE MODEL

a/ FLOW REACTOR DATA AT 1 ATM [3]

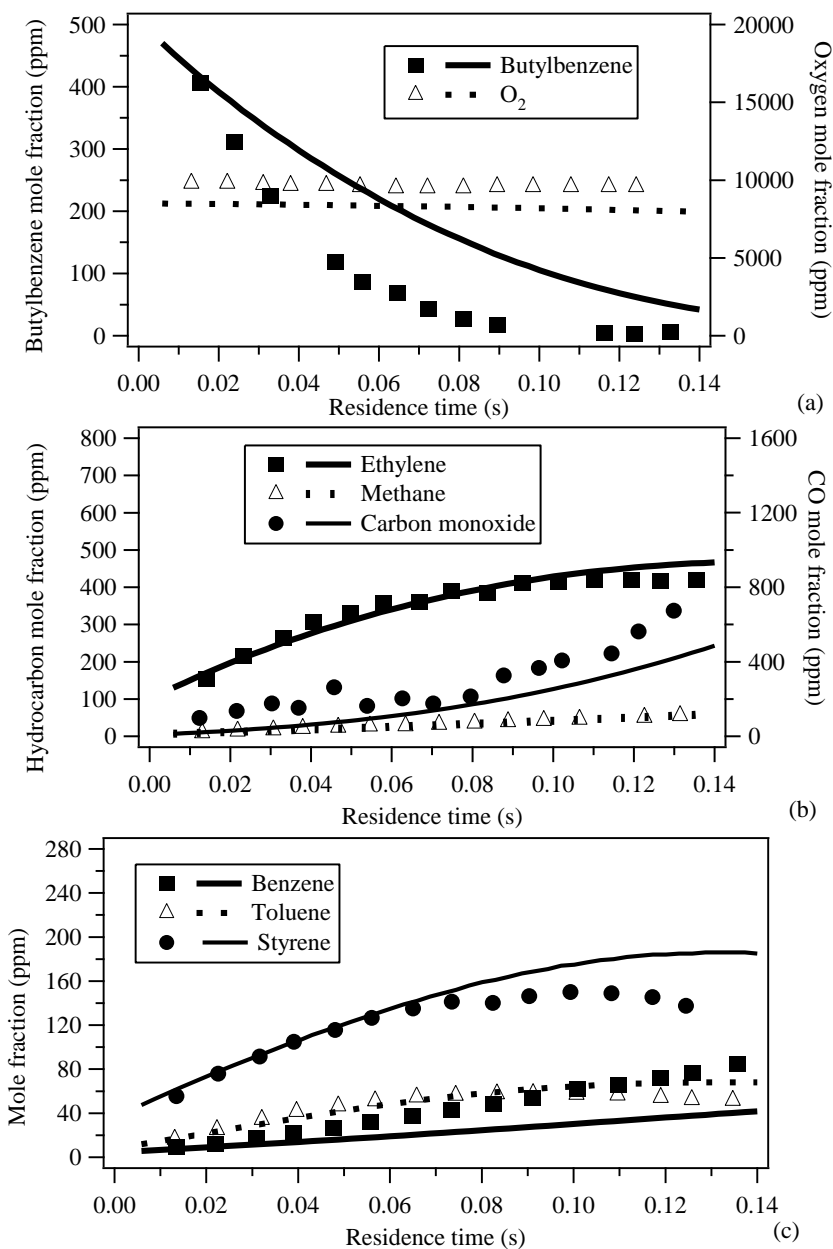


Figure S3: Mole fractions of fuel and of main products during the oxidation of *n*-butylbenzene in a flow reactor at 1060 K, P= 1atm and $\Phi = 0.98$, with an initial concentration of hydrocarbon of 620 ppm (points are experiments [3] and lines simulations with the present automatically generated model).

a/ JSR DATA AT 10 ATM [6]

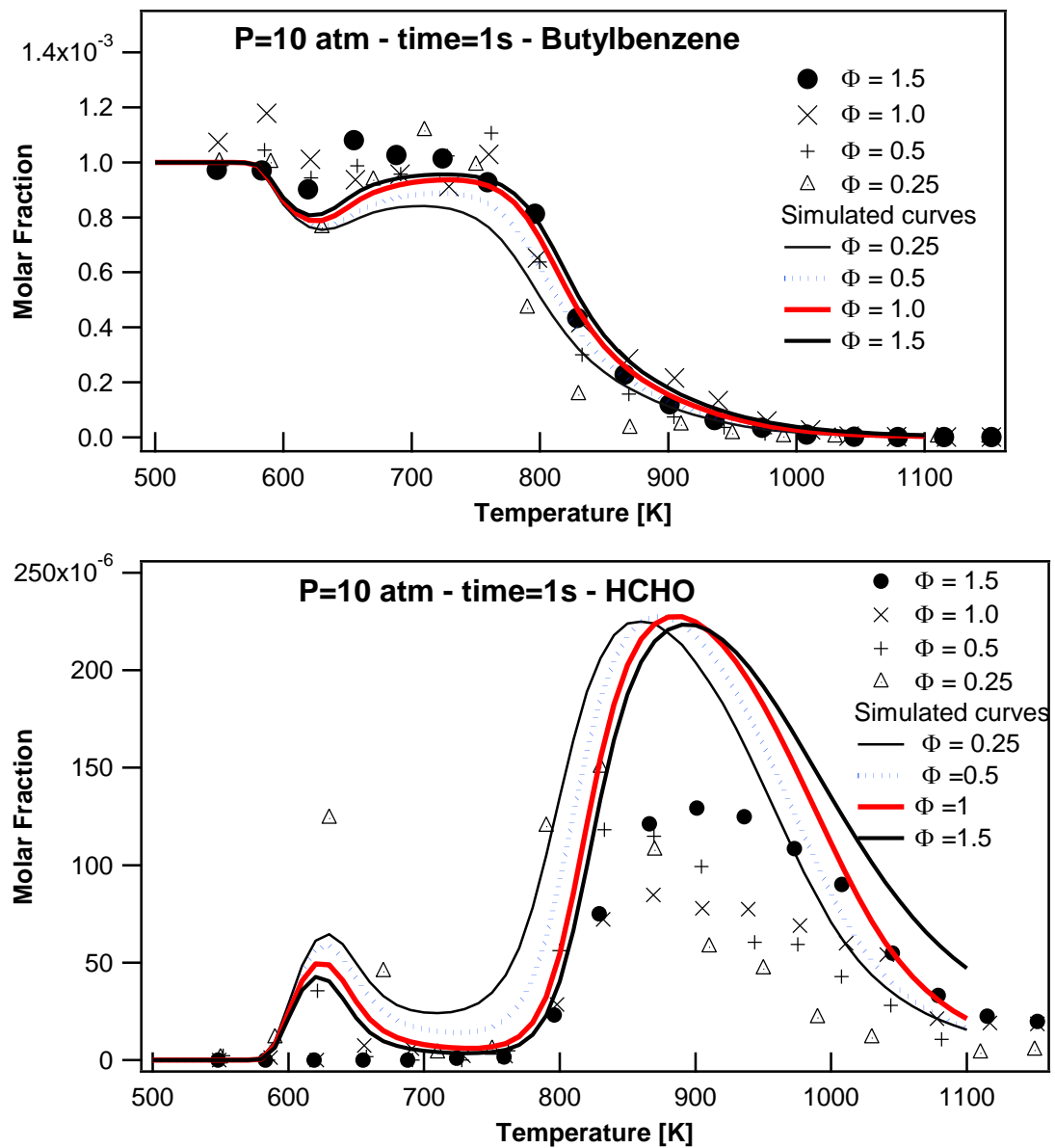


Figure S4: Mole fractions of fuel and of formaldehyde during the JSR oxidation of *n*-butylbenzene at 10 atm (equivalence ratios of $\Phi = 0.25, 0.5, 1$ and 1.5 , inlet *n*-butylbenzene mole fraction of 1000 ppm, residence time of 1 s) (points are experiments [6] and lines simulations with the present automatically generated model).

V/ MODELLING OF PRESENT *n*-BUTYLBENZENE JSR DATA AT 1 ATM USING THE MODEL OF LAWRENCE LIVERMORE NATIONAL LABORATORY [10]

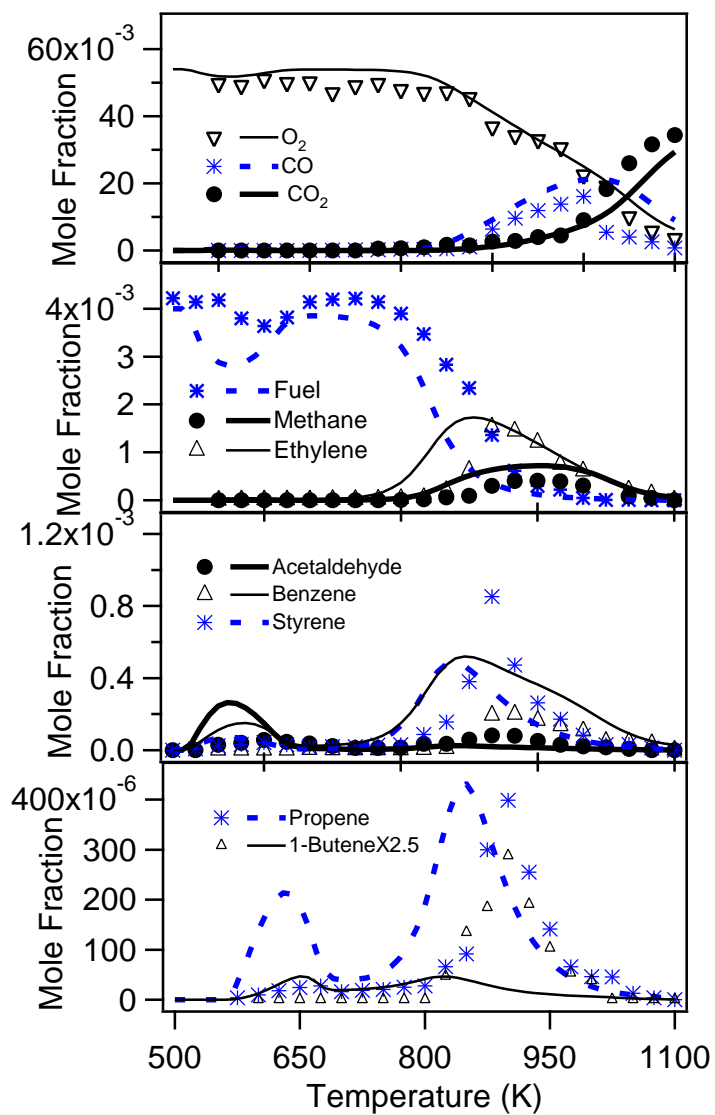


Figure S5: Major products of the oxidation of *n*-butylbenzene in a jet-stirred reactor (points are experiments [6] and lines simulations with the model of [10]).