

Table S1: Reactions modified in the secondary mechanisms of toluene.

Reactions	A	n	E _a	References	n ^o
Reactions modified in the secondary mechanism toluene					
C6H5CHO+CH3=C6H5CO+CH4	2.0x10 ⁻⁶	5.6	2.5	estimated ^a	(24)
C6H5CHOH=C6H5CHO+H	2.0x10 ¹³	0.0	36.3	estimated ^b	(25)
bibenzyl+H=C6H6+C8H9-1	5.6x10 ⁸	1.43	5.65	estimated ^c	(26)
bibenzyl+OH=C6H5OH+C8H9-1	7.8x10 ²	2.88	3.2	estimated ^d	(27)
C14H13+O2= stilbene+HO2	1.6x10 ¹²	0.00	15.2	estimated ^e	(28)
C14H13+OOH=>R2OH+C6H5CHO+benzyl C14H13 is C6H5•CHCH2C6H5	8.2x10 ⁴	2.20	-5.13	estimated ^f	(29)
Added submechanism for stilbene (C6H5CHCHC6H5)					
stilbene+H=>C6H6+C2H2+C6H5	5.7x10 ⁸	1.43	5.65	estimated ^c	(30)
stilbene+OH=C6H5OH+C6H5C2H2	7.8x10 ²	2.88	3.2	estimated ^d	(31)
stilbene+OH=C6H5CHO+benzyl	1.0x10 ¹³	0.0	5.9	estimated ^g	(32)
Added submechanism for phenylbenzyl ether (C6H5OCH2C6H5)					
C6H5CH2O+toluene=C6H5OCH2C6H5+CH3	7.8x10 ²	2.88	3.22	estimated ^d	(33)
C6H5O+benzyl=C6H5OCH2C6H5	1.0x10 ¹¹	0.0	0.00	estimated ⁱ	(34)
C6H5OCH2C6H5+H=C6H5CH2O+C6H6	8.5x10 ¹²	0.0	5.81	Estimated ^h	(35)
C6H5OCH2C6H5+OH=>C6H5+C6H5CHO+H2O	3.5x10 ⁹	1.0	0.87	estimated ^j	(36)
C6H5OCH2C6H5+H=>C6H5+C6H5CHO+H2	1.95x10 ⁶	2.37	5.81	estimated ^c	(37)
C6H5OCH2C6H5+O=>C6H5+C6H5CHO+OH	4.2x10 ¹¹	0.0	0.00	estimated ^j	(38)
Added submechanism for methylphenylbenzylether (To1OCH2C6H5)					
OC6H4CH3+benzyl=To1OCH2C6H5	1.0x10 ¹¹	0.0	0.00	estimated ⁱ	(39)
C6H4CH3+C6H5CH2O=To1OCH2C6H5	1.0x10 ¹¹	0.0	0.00	estimated ⁱ	(40)
To1OCH2C6H5+H=toluene+C6H5CH2O	8.5x10 ¹²	0.0	5.81	Estimated ^h	(41)
To1OCH2C6H5+OH=>C6H4CH3+C6H5CHO+H2O	8.7x10 ¹¹	1.0	0.87	estimated ^j	(42)
To1OCH2C6H5+H=>C6H4CH3+C6H5CHO+H2	4.9x10 ⁶	2.37	5.81	estimated ^c	(44)
To1OCH2C6H5+O=>C6H4CH3+C6H5CHO+OH	1.0x10 ¹²	0.0	0.00	estimated ^j	(44)
Added submechanism for ethylphenylphenol (PhenolC2H4bz)					
bibenzyl+OH=PhenolC2H4bz+H	1.7x10 ¹³	0.0	10.6	estimated ^k	(45)
C6H4OH+C8H9-1=PhenolC2H4bz	1.0x10 ¹¹	0.0	0.00	estimated ⁱ	(46)
HOC6H4CH2+benzyl=PhenolC2H4bz	1.0x10 ¹¹	0.0	0.00	estimated ⁱ	(47)
PhenolC2H4bz+OH=>styrene+C6H5O+H2O	8.7x10 ⁹	1.0	0.87	estimated ^j	(48)
PhenolC2H4bz+H=>styrene+C6H5O+H2	4.9x10 ⁶	2.37	5.81	estimated ^c	(49)
PhenolC2H4bz+O=>styrene+C6H5O+OH	1.0x10 ¹²	0.0	0.0	estimated ^j	(50)
Added submechanism for 1-butenylbenzene (C6H5C4H7)					
benzyl+C3H5=C6H5C4H7	5.0x10 ¹²	0.00	0.00	estimated ⁱ	(51)
C6H5C4H7+OH=>benzyl+pC3H4+H2O	5.2x10 ⁹	1.0	0.87	estimated ^j	(52)
C6H5C4H7+H=>benzyl+pC3H4+H2	2.9x10 ⁶	2.37	5.81	estimated ^c	(53)
C6H5C4H7+O=>benzyl+pC3H4+OH	6.3x10 ¹¹	0.0	0.0	estimated ^j	(54)
C6H5C4H7+OH=>benzyl+pC3H4+H2O	3.0x10 ⁶	2.0	-1.52	estimated ^e	(55)
C6H5C4H7+H=>benzyl+pC3H4+H2	5.4x10 ⁴	2.5	-1.9	estimated ^e	(56)
C6H5C4H7+O=>benzyl+pC3H4+OH	8.8x10 ¹⁰	0.7	3.25	estimated ^e	(57)

Notes: The rate constants are given at 1 atm ($k = AT^n \exp(-E_a/RT)$) in cm³, mol, s, kcal units.

a: Rate constant taken equal to that proposed by Baulch *et al.* [32] for acetaldehyde.

b: -factor taken equal to that proposed Heyberger *et al.* [33] and activation energy estimated using the Evans-Polyanyi correlation proposed by Sirjean *et al.* [35] for β -scissions of alkyl radicals.

c: Rate constant taken equal to that theoretically calculated with CBS-QB3 method with Gaussian03 [16] by Tian *et al.* [21], with when needed A-factor multiplied by a factor taking into account the number abstractable H atoms.

d: Rate constant taken equal to that of the similar reaction of toluene proposed by Seta *et al.* [34].

e: Rate constant taken equal to that proposed by Touchard *et al.* [35] in the case of allylic radicals.

f: Rate constant taken equal to that used for the similar reaction of benzyl radicals [25].

g: Rate constant taken equal to that of the similar reaction for ethylene proposed by Baulch *et al.* [32].

h: Rate constant taken equal to that proposed by Manion and Louw [36] for the same reaction for phenol.

i: Rate constants of unimolecular initiations or combinations calculated using software KINGAS [29].

j: Rate constant taken equal to that of the similar reaction in the case of toluene [19] with A-factor multiplied by a factor taking into account the number abstractable H atoms.

k: Rate constant taken equal to that of the similar reaction in the case of toluene [19].

Validation of the mechanism on benzene and toluene data (JSR):

► Benzene (experimental data from Da Costa et al. [20])

Operating conditions:

- (1) $T = 923 \text{ K}$ $\Phi = 1.9$ $x_{\text{benzene}} = 0.04$ $\tau = 1.6 - 8.8 \text{ s}$ $P = 800 \text{ Torr}$
(2) $T = 923 \text{ K}$ $\Phi = 3.6$ $x_{\text{benzene}} = 0.045$ $\tau = 1.6 - 8.8 \text{ s}$ $P = 800 \text{ Torr}$

(1) At an equivalence ratio of 1.9

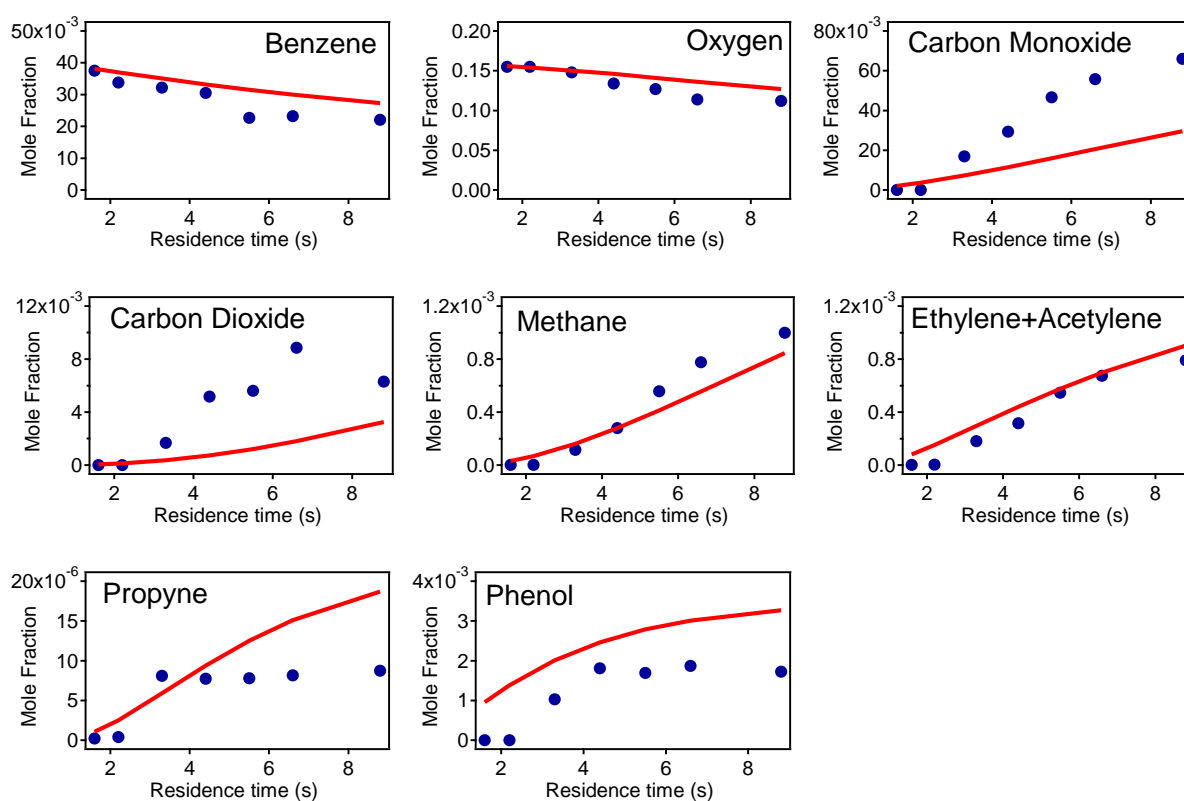


Figure 1: Oxidation of benzene in a Jet-Stirred Reactor ($T = 923 \text{ K}$; $\phi = 1.9$; $P = 800 \text{ Torr}$; $\tau = 1.6-8.8$; $x_{\text{benzene}} = 0.04$). Points \bullet are experiments [20], lines are simulations with the mechanism presented in the attached paper.

(2) At an equivalence ratio of 3.6

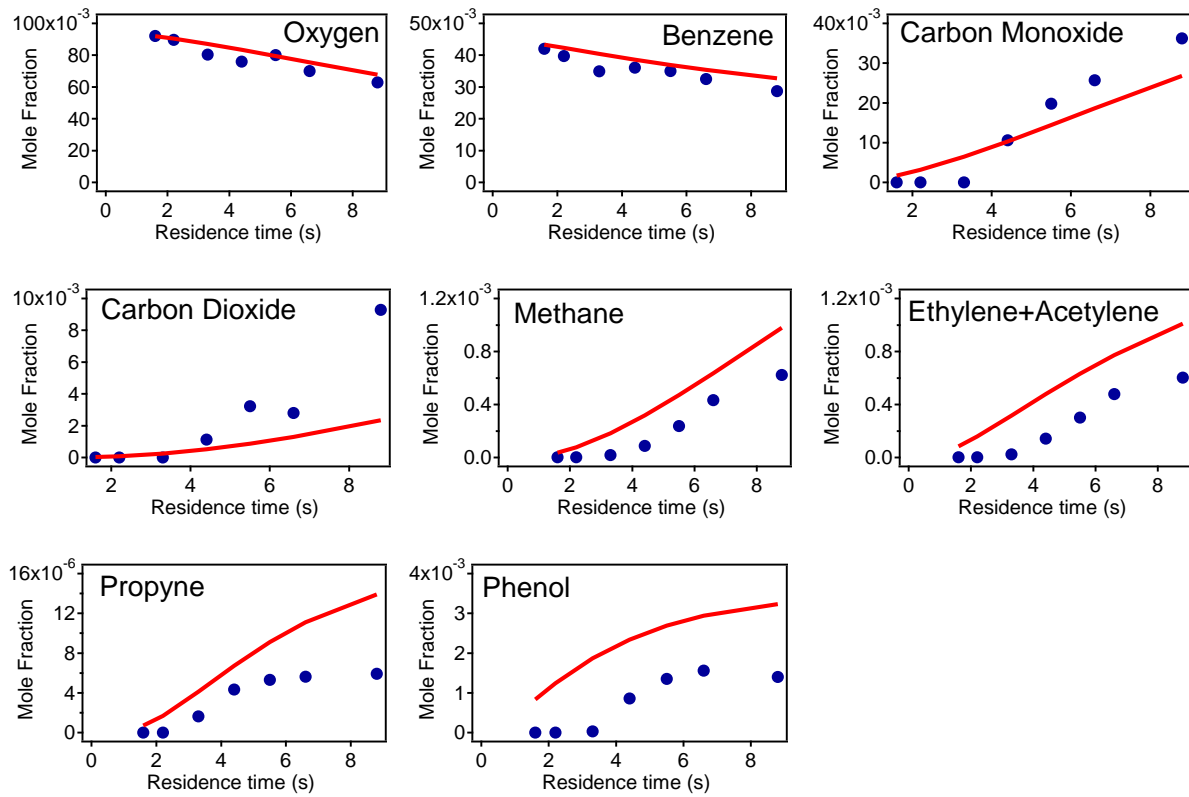


Figure 2: Oxidation of benzene in a Jet-Stirred Reactor ($T = 923\text{K}$; $\phi = 3.6$; $P = 800$ Torr; $\tau = 1.6\text{-}8.8$; $x_{\text{benzene}} = 0.045$). Points \bullet are experiments [20], lines are simulations with the mechanism presented in the attached paper.

► Toluene (experimental data from Bounaceur et al. [19])

Operating conditions:

$T = 923 \text{ K}$

$\Phi = 0.9$

$x_{\text{toluene}} = 0.017 \tau = 2.5 - 12 \text{ s}$

$P = 800 \text{ Torr}$

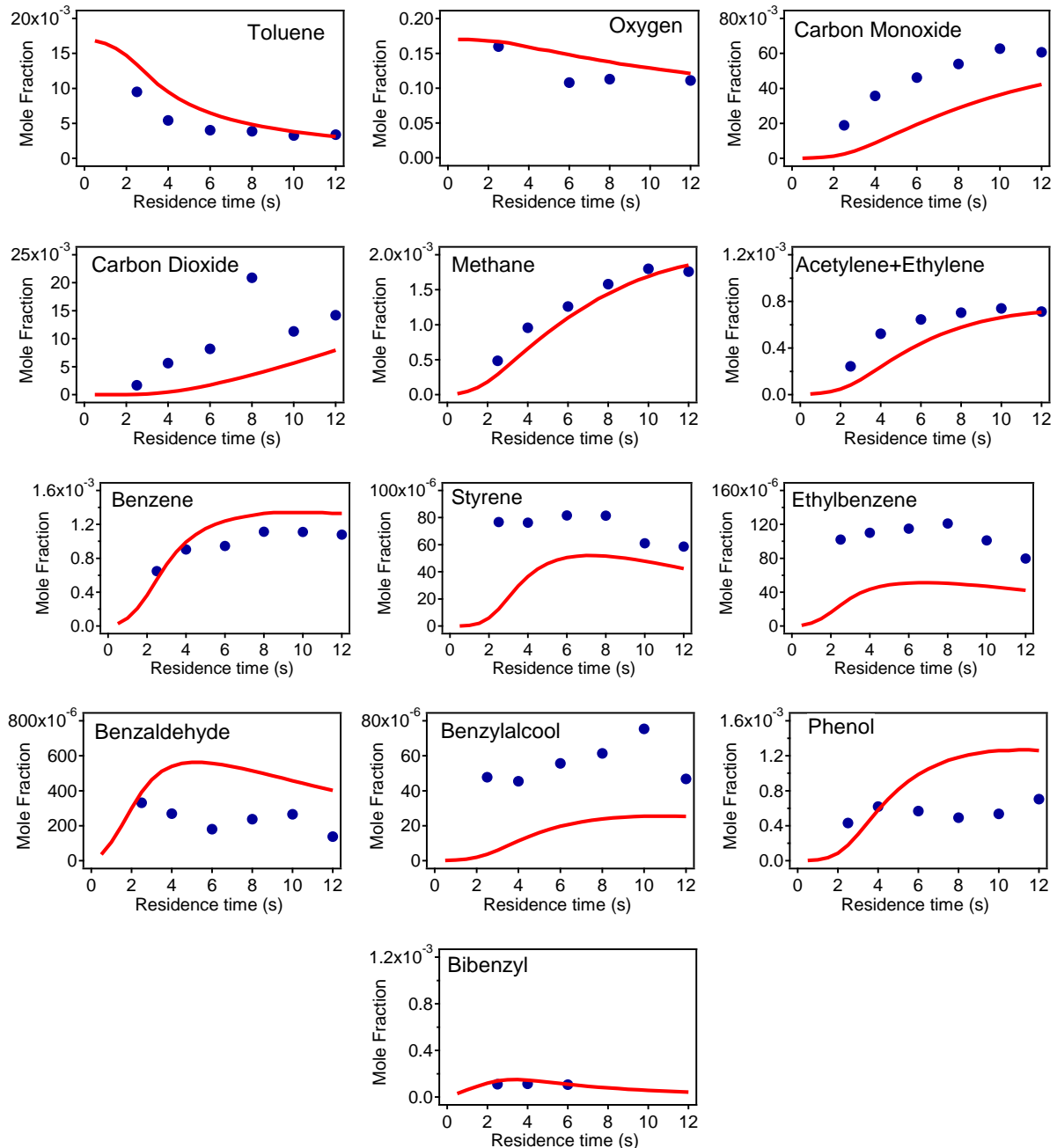


Figure 4: Oxidation of toluene in a Jet-Stirred Reactor ($T = 923 \text{ K}$; $\phi = 0.9$; $P = 800 \text{ Torr}$; $\tau = 2.5-12$; $x_{\text{toluene}} = 0.017$). Points \bullet are experiments [19], lines \sim are simulations with the mechanism presented in the attached paper.

REFERENCES

References until [31] are those given in the main text.

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