# Experimental and Modeling Study of the Oxidation of Toluene

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ABSTRACT: This paper describes an experimental and modeling study of the oxidation of toluene. The low-temperature oxidation was studied in a continuous flow stirred tank reactor with carbon-containing products analyzed by gas chromatography under the following experimental conditions: temperature from 873 to 923 K, 1 bar, fuel equivalence ratios from 0.45 to 0.91, concentrations of toluene from 1.4 to 1.7%, and residence times ranging from 2 to 13 s corresponding to toluene conversion from 5 to 85%. The ignition delays of toluene–oxygen–argon mixtures with fuel equivalence ratios from 0.5 to 3 were measured behind reflected shock waves for temperatures from 1305 to 1795 K and at a pressure of  $8.7 \pm 0.7$  bar. A detailed kinetic mechanism has been proposed to reproduce our experimental results, as well as some literature data obtained in other shock tubes and in a plug flow reactor. The main reaction paths have been determined by sensitivity and flux analyses. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 37: 25–49, 2005

# INTRODUCTION

Aromatic compounds are present in significant amounts in gasolines ( $\sim$ 35%) and diesel fuels ( $\sim$ 30%) [1]. Nevertheless, detailed chemical kinetic models for the combustion and the oxidation of aromatic compounds are still scarce and are mainly restricted to benzene [2–10]. We have recently published a paper presenting an experimental and modeling study of the oxidation of benzene [11] that we have used as a basis for this work about the oxidation of toluene.

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Toluene is the most important aromatic compound in gasolines (up to 10%), with a research octane number of 120 [1]. Its slow oxidation has been studied experimentally in a flow reactor by Brezinsky et al. [12,13], in a jet-stirred reactor by Dagaut et al. [14], and in a singlepulse shock tube by Sivaramakrishnan et al. [15]. The autoignition of toluene has been studied in a shock tube by Burcat et al. [16] and Pengloan et al. [14,17] and in a rapid compression machine by Roubaud et al. [18]. Diffusion and laminar flames containing toluene have been studied by Hamins and Seshadri [19] and by Davis et al. [20], respectively. Several kinetic mechanisms [2,13,14,21,22] have also been proposed to model these experimental data.

It is worth noting that all the experiments in reactors [12-14] have been performed using a low concentration of toluene ( $\leq 0.15\%$ ) and, consequently, with no noticeable conversion for a temperature lower than 1000 K. The two purposes of this paper then are:

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- To present new experimental data for the oxidation of toluene obtained both in a jet-stirred reactor at atmospheric pressure, at a concentration of toluene from 1.4 to 1.7%, at temperatures from 873 to 923 K, and in a shock tube for temperatures between 1305 and 1795 K at a pressure of  $8.7 \pm 0.7$  bar.
- To propose a new mechanism able to model these experimental results, and also to reproduce literature data obtained in a flow reactor at 1100 K [12] and in different shock tubes [14–16]. Some of our results obtained in a shock tube have already been modeled by Pitz et al. [22], but the predicted ignition delays were too long (at least a factor 3) compared to the experimental delays, particularly at the highest temperatures.

# EXPERIMENTAL RESULTS OF THE OXIDATION OF TOLUENE

A discussion of the experimental results presented here is given later in the text with the comparisons with simulations.

As this experimental study was performed using the same two devices as in our study of the oxidation of benzene, a jet-stirred reactor and a shock tube [11], we shall not recall the experimental procedure here. Toluene (99.8% pure) was provided by Fluka. Oxygen (99.5% pure), argon, and helium (both 99.995% pure) were supplied by Alphagaz-L'Air Liquide.

### Jet-Stirred Reactor

As liquid toluene used for bubbling the flow of carrier gas (helium) to obtain gas-phase toluene needs to be maintained below room temperature (here at 289 K) to avoid the condensation of hydrocarbon before it enters the reactor, the maximum mole fraction was 1.7%, which was much lower than what was used for benzene (4.5%) [11].

This study was performed under the following experimental conditions:

- temperature: 873, 893, and 923 K;
- atmospheric pressure;
- mixtures (helium: toluene: oxygen, in molar percent) were 1.7:17:81.3 and 1.4:28:70.6, respectively, which correspond to two different equivalence ratios ( $\Phi = 0.45$  and 0.9) and lead to conversion of toluene from 5 to 85%.

The equivalence ratio  $\Phi$  is defined as  $\Phi = 9 \times (\%_{toluene} / \%_{oxygen})$  by using as a reference of the total reaction

$$C_7H_8 + 9O_2 = 7CO_2 + 4H_2O$$

The main carbon-containing products analyzed by gas chromatography were carbon monoxide and dioxide, methane, C<sub>2</sub> species (acetylene and ethylene were not separated), allene, propene, 1,3-butadiene, benzene, phenol, ethyl benzene, styrene, benzaldehyde, benzyl alcohol, and bibenzyl. Chromatographs with thermal conductivity detector and hydrogen as carrier gas were used to analyze O2, CO, and CO2 with a Carbosphere packed column. Gas-phase light hydrocarbons (CH<sub>4</sub>, C<sub>2</sub> species, C<sub>3</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>6</sub>) were analyzed on a 30% Squalane on Chromosorb P column with detection by flame ionization detection and nitrogen as carrier gas. The analyses of products containing more than five atoms of carbon were performed by gas chromatography with flame ionization detection by using a HP PONA capillary column and nitrogen as carrier gas, which gave a good separation for the abovementioned products with a limit of detection around  $10^{-5}$  in mole fraction [11]. For each sample, the carbon balance was checked and an agreement was obtained to within 5%. The formation of cyclopentadiene and cresols was not detected.

Tables I and II present all the experimental results obtained in a jet-stirred reactor. Figure 1 displays the evolution of the conversion of toluene, of the formation of the two major primary products, benzene and benzaldehyde, and the production of carbon monoxide, vs. residence time for an equivalence ratio of 0.9 and for a temperature equal to 873 (Fig. 1a), 893 (Fig. 1b), and 923 K (Fig. 1c). This figure shows that the reaction is autoaccelerated with an induction delay time that decreases with temperature. Figures 2 and 3 display the evolution of the conversions of toluene and oxygen and of the formations of all the observed products vs. residence time at 893 K and for an equivalence ratio of 0.45.

#### Shock Tube

As in our previous work [11], the temperature and the pressure of the test gas behind the incident and the reflected shock waves were derived from the value of the incident shock velocity by using ideal one-dimensional shock equations. The onset of ignition was detected by OH radical emission at 306 nm through a quartz window with a photomultiplier fitted with a monochromator at the end of the reaction part. The last pressure transducer was located at the same place along the axis of the tube as the quartz window. The ignition delay time was defined as the time interval between the pressure rise measured by the last pressure transducer due to the arrival of the reflected shock wave and the rise of the optical signal by the photomultiplier up to 10% of its maximum value.

		1.4%	o of Toluene, $\Phi = 0$	0.45		
			Residence	e Time (s)		
Compound	2.5	4	6.5	9	11	13
			Mole F	Fraction		
CH <sub>4</sub>	$2.64 \times 10^{-4}$	$5.17 \times 10^{-4}$	$6.37 \times 10^{-4}$	$6.99 \times 10^{-4}$	$6.99 \times 10^{-4}$	$6.09 \times 10^{-4}$
$C_2H_2 + C_2H_4$	$2.36 \times 10^{-4}$	$3.09 \times 10^{-4}$	$3.02 \times 10^{-4}$	$2.42 \times 10^{-4}$	$2.14 \times 10^{-4}$	$1.24 \times 10^{-4}$
$C_3H_4$	$1.31 \times 10^{-5}$	$2.75 \times 10^{-5}$	$3.24 \times 10^{-5}$	$3.23 \times 10^{-5}$	$2.92 \times 10^{-5}$	$2.44 \times 10^{-5}$
C <sub>3</sub> H <sub>6</sub>	$4.83 \times 10^{-6}$	$6.17 \times 10^{-6}$	$5.3 \times 10^{-6}$	$3.96 \times 10^{-6}$	$3.89 \times 10^{-6}$	$3.08 \times 10^{-6}$
1,3-C <sub>4</sub> H <sub>6</sub>	$1.02 \times 10^{-5}$	$9.23 \times 10^{-6}$	$1.08 \times 10^{-5}$	$7.46 \times 10^{-6}$	$4.99 \times 10^{-6}$	$4.17 \times 10^{-6}$
O <sub>2</sub>	0.279	0.272	0.269	0.224	0.206	0.218
CO	0.014	0.0386	$5.89 \times 10^{-2}$	$6.16 \times 10^{-2}$	$5.94 \times 10^{-2}$	$5.94 \times 10^{-2}$
CO <sub>2</sub>	0.00167	0.0046	0.0148	0.0144	0.0182	0.0207
C7H8	0.00603	0.00422	0.00319	0.00206	0.00224	0.0026
C <sub>6</sub> H <sub>6</sub>	$3.53 \times 10^{-4}$	$5.87  imes 10^{-4}$	$5.9  imes 10^{-4}$	$4.97  imes 10^{-4}$	$5.33  imes 10^{-4}$	$4.08  imes 10^{-4}$
C <sub>8</sub> H <sub>10</sub>	$3.68 \times 10^{-5}$	$5.51 \times 10^{-5}$	$6.79 \times 10^{-5}$	$5.01 \times 10^{-5}$	$4.12 \times 10^{-5}$	_
C <sub>8</sub> H <sub>8</sub>	$2.62 \times 10^{-5}$	$4.43 \times 10^{-5}$	$4.51 \times 10^{-5}$	$3.49 \times 10^{-5}$	$3.1 \times 10^{-5}$	_
C <sub>6</sub> H <sub>5</sub> CHO	$2.28  imes 10^{-4}$	$2.91 \times 10^{-4}$	$2.38  imes 10^{-4}$	$2.45 \times 10^{-4}$	$1.19 \times 10^{-4}$	_
C <sub>6</sub> H <sub>5</sub> OH	$2.3 \times 10^{-4}$	$5.6 \times 10^{-4}$	$5.6  imes 10^{-4}$	$5.93  imes 10^{-4}$	$5.07 \times 10^{-4}$	_
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	$3.05 \times 10^{-5}$	$5.77 \times 10^{-5}$	$2.69 \times 10^{-5}$	_	_	_
C <sub>14</sub> H <sub>14</sub>	$7.97 \times 10^{-5}$	$5.8 \times 10^{-5}$	$3.22 \times 10^{-5}$	_	_	_
		1.79	% of Toluene, $\Phi =$	0.9		
			Residence	e Time (s)		
Compound	2.5	4	6	8	10	12
			Mole F	Fraction		
CH <sub>4</sub>	$2.38 \times 10^{-5}$	$1.24 \times 10^{-4}$	$4.72 \times 10^{-4}$	$7.59 \times 10^{-4}$	$8.95 \times 10^{-4}$	$1.03 \times 10^{-3}$
$C_2H_2 + C_2H_4$	$1.51 \times 10^{-6}$	$2.35 \times 10^{-5}$	$1.97 \times 10^{-4}$	$3.11 \times 10^{-4}$	$3.61 \times 10^{-4}$	$4.13 \times 10^{-4}$
C <sub>3</sub> H <sub>6</sub>	$3.62 \times 10^{-6}$	$4.89 \times 10^{-6}$	$6.72 \times 10^{-6}$	$5.97 \times 10^{-6}$	$5.76 \times 10^{-6}$	$4.94 \times 10^{-6}$
C <sub>3</sub> H <sub>4</sub>	$7.93 \times 10^{-7}$	$6.32 \times 10^{-6}$	$3.32 \times 10^{-6}$	$4.31 \times 10^{-5}$	$4.39 \times 10^{-5}$	$4.5 \times 10^{-5}$
1,3-C <sub>4</sub> H <sub>6</sub>	$3.95  imes 10^{-6}$	$3.52 \times 10^{-6}$	$7.67 \times 10^{-6}$	$1.21 \times 10^{-5}$	$1.17 \times 10^{-5}$	$9.67 \times 10^{-6}$
O <sub>2</sub>	0.167	0.169	0.149	0.131	0.115	0.112
СО	_	_	$1.91 \times 10^{-2}$	$3.03 \times 10^{-2}$	$3.6 \times 10^{-2}$	$3.89 \times 10^{-2}$
CO <sub>2</sub>	_	_	$5.87 \times 10^{-4}$	$5.51 \times 10^{-3}$	$6.1 \times 10^{-3}$	$6.31 \times 10^{-3}$
$\bar{C_7H_8}$	0.0154	0.0122	0.00901	0.00726	0.00587	0.00563
C <sub>6</sub> H <sub>6</sub>	$4.42 \times 10^{-5}$	0.000211	0.000608	0.00846	0.00801	0.000887
C8H10	$2.93 \times 10^{-6}$	$2.95 \times 10^{-5}$	$7.46 \times 10^{-5}$	$9.07 \times 10^{-5}$	$1.05 \times 10^{-4}$	$9.33 \times 10^{-5}$
C <sub>8</sub> H <sub>8</sub>	_	$2.12 \times 10^{-5}$	$5.2 \times 10^{-5}$	$4.81 \times 10^{-5}$	$4.89 \times 10^{-5}$	$6.7 \times 10^{-5}$
C <sub>6</sub> H <sub>5</sub> CHO	$1.28 \times 10^{-5}$	0.000122	0.000205	0.000218	0.000255	0.000211
C6H5OH	$5.27 \times 10^{-6}$	$4.64 \times 10^{-5}$	$2.23 \times 10^{-4}$	$2.9 \times 10^{-4}$	$4.1 \times 10^{-4}$	$4.3 \times 10^{-4}$
C6H5CH2OH	_	_		$4.02 \times 10^{-5}$	_	_
C <sub>14</sub> H <sub>14</sub>	$3.54 \times 10^{-5}$	$9.97 \times 10^{-5}$	$9.72 \times 10^{-5}$	$7.8 \times 10^{-5}$	$2.9  imes 10^{-5}$	$2.28 \times 10^{-5}$

 Table I
 Experimental Results Obtained in a Jet-Stirred Reactor at 893 K and 1 atm

This study was performed under the following experimental conditions (after the reflected shock):

- temperature (T) from 1305 to 1795 K.
- pressure from 8 to 9.5 bar.
- mixtures (argon:toluene:oxygen, in molar percent) were 1.25:22.5:76.25, 1.25:11.25:87.5, 1.25:7.5:91.25, 1.25:3.75:95.0, and 0.5:4.475:

95.025, respectively, which correspond to four different equivalence ratios ( $\Phi = 0.5$ , 1, 1.5 and 3) and to two different concentrations of toluene (1.25% (a graph summarizing the results for 1.25% has already been presented [22]) and a new more dilute condition, 0.5%) and lead to ignition delay times from 3 to 1560 µs.

			Temperatu	ire 873 K			
			R	esidence Time	(s)		
Compound	3	4.4	6	7.5	8.7	11	13
				Mole Fraction			
$CH_4$	$1.14 \times 10^{-5}$	$2.21 \times 10^{-5}$	$4.76 \times 10^{-5}$	$1.07 \times 10^{-4}$	$3.6 \times 10^{-4}$	$5.28 \times 10^{-4}$	$7.15 \times 10^{-4}$
$C_2H_2 + C_2H_4$	$3.22 \times 10^{-7}$	$8.69 \times 10^{-7}$	$2.75 \times 10^{-6}$	$1.35 \times 10^{-5}$	$1.06 \times 10^{-4}$	$2.22 \times 10^{-4}$	$2.66 \times 10^{-4}$
C <sub>3</sub> H <sub>6</sub>	_	_	$4.23 \times 10^{-7}$	$1.59 \times 10^{-6}$	$3.53 \times 10^{-6}$	$3.89 \times 10^{-6}$	$4.06 \times 10^{-6}$
C <sub>3</sub> H <sub>4</sub>	$2.7 \times 10^{-7}$	_	$1.56 \times 10^{-6}$	$4.56 \times 10^{-6}$	$2.13 \times 10^{-5}$	$2.63 \times 10^{-5}$	$3.75 \times 10^{-5}$
$1,3-C_4H_6$	_	_	$4.21 \times 10^{-6}$	$5.05 \times 10^{-6}$	$6.99 \times 10^{-6}$	$7.6 \times 10^{-6}$	$8.22 \times 10^{-6}$
O <sub>2</sub>	0.166	0.167	0.164	0.139	-	0.140	_
co	_	_	_	$4.05 \times 10^{-4}$	$5.21 \times 10^{-4}$	$4.95 \times 10^{-3}$	$1.61 \times 10^{-2}$
$CO_2$	_	_	_	_	_	$7.73 \times 10^{-4}$	$3.47 \times 10^{-3}$
$\bar{C_7H_8}$	0.0161	0.0156	0.0157	0.0137	0.0118	0.00993	0.00856
C <sub>6</sub> H <sub>6</sub>	$2 \times 10^{-5}$	$4.18 \times 10^{-5}$	$8.67 \times 10^{-5}$	$1.69 \times 10^{-4}$	$4.26 \times 10^{-4}$	$4.48 \times 10^{-4}$	$6.65 \times 10^{-4}$
$C_8H_{10}$	_	_	$2.62 \times 10^{-5}$	$3.51 \times 10^{-5}$	$5.74 \times 10^{-5}$	$5.9 \times 10^{-5}$	$6.39 \times 10^{-5}$
$C_8H_8$	_	_	_	$2.2 \times 10^{-5}$	$3 \times 10^{-5}$	$5.19 \times 10^{-5}$	$5.46 \times 10^{-5}$
C <sub>6</sub> H <sub>5</sub> CHO	$2.65 \times 10^{-5}$	$7.9 \times 10^{-5}$	$6.2 \times 10^{-5}$	$1.05 \times 10^{-4}$	$1.79 \times 10^{-4}$	$1.81 \times 10^{-4}$	$2.32 \times 10^{-4}$
C <sub>6</sub> H <sub>5</sub> OH	_	_	_	_	$1.84 \times 10^{-4}$	$3.13 \times 10^{-4}$	$4.54 \times 10^{-4}$
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	_	_	_	_	$2.24 \times 10^{-5}$	_	_
C <sub>14</sub> H <sub>14</sub>	$2.16\times10^{-5}$	$1.16\times 10^{-5}$	$8.19\times10^{-5}$	$9.15  imes 10^{-5}$	$1.26 \times 10^{-4}$	$1.24 \times 10^{-4}$	$1.21 \times 10^{-4}$
			Temperatu	ure 923 K			
				Residence Time	e (s)		
Compound	2.5	4		6	8	10	12
				Mole Fractio	'n		
CH <sub>4</sub>	$4.85 \times 10^{-4}$	$9.55 \times 10^{-10}$	$0^{-4}$ 1.26 x	$< 10^{-3}$ 1.5	$58 \times 10^{-3}$	$1.8 \times 10^{-3}$	$1.76 \times 10^{-3}$
$C_{2}H_{2} + C_{2}H_{4}$	$2.43 \times 10^{-4}$	$5.22 \times 10^{-10}$	$0^{-4}$ 6.45	$< 10^{-4}$ 7.0	$0.3 \times 10^{-4}$	$7.39 \times 10^{-4}$	$7.12 \times 10^{-4}$
C <sub>3</sub> H <sub>6</sub>	$1.27 \times 10^{-5}$	$1.34 \times 10^{-1}$	$0^{-5}$ 6.14	$< 10^{-6}$ 4.1	$19 \times 10^{-6}$	$5.5 \times 10^{-6}$	$3.76 \times 10^{-6}$
C <sub>3</sub> H <sub>4</sub>	$3.82 \times 10^{-5}$	$5.25 \times 10^{-10}$	$0^{-5}$ 4.91	$< 10^{-5}$ 5.3	$37 \times 10^{-5}$	$4.63 \times 10^{-5}$	$4.19 \times 10^{-5}$
1.3-C4H6	$1.92 \times 10^{-5}$	$2.1 \times 1$	$0^{-5}$ 1.23 >	$< 10^{-5}$ 1.5	$57 \times 10^{-5}$	$1.21 \times 10^{-5}$	$1.41 \times 10^{-5}$
02	0.160	_	0.	108	0.113	_	0.111
co	$1.89 \times 10^{-2}$	$3.57 \times 10^{-10}$	$0^{-2}$ 4.62 >	$< 10^{-2}$ 5.	$.4 \times 10^{-2}$	$6.27 \times 10^{-2}$	$6.06 \times 10^{-2}$
CO <sub>2</sub>	$1.69 \times 10^{-3}$	$5.63 \times 10^{-10}$	$0^{-3}$ 8.2 >	$< 10^{-3}$ 2.0	$0.09 \times 10^{-2}$	$1.13 \times 10^{-2}$	$1.42 \times 10^{-2}$
C7H8	0.0095	0.0054	1 0.00	)401 (	0.00387	0.00326	0.00337
C <sub>6</sub> H <sub>6</sub>	0.000648	0.00090	0.00	0945 (	0.00113	0.00111	0.00108
C <sub>8</sub> H <sub>10</sub>	$1.02 \times 10^{-4}$	$1.1 \times 1$	$0^{-4}$ 1.15 >	$< 10^{-4}$ 1.2	$21 \times 10^{-4}$	$1.01 \times 10^{-4}$	$7.96 \times 10^{-5}$
C <sub>8</sub> H <sub>8</sub>	$7.67 \times 10^{-5}$	$7.62 \times 1$	$0^{-5}$ 8.16 >	< 10 <sup>-5</sup> 8.1	$15 \times 10^{-5}$	$6.11 \times 10^{-5}$	$5.86 \times 10^{-5}$
C <sub>6</sub> H <sub>5</sub> CHO	0.000331	0.00026	.00	0018	0.0238	0.000265	0.000138
C <sub>6</sub> H <sub>5</sub> OH	$4.31 \times 10^{-4}$	$6.18 \times 10^{-1}$	$0^{-4}$ 5.67 >	< 10 <sup>-4</sup> 4.9	$91 \times 10^{-4}$	$5.36 \times 10^{-4}$	$7.05  imes 10^{-4}$
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	$4.77 \times 10^{-5}$	$4.54 \times 10^{-10}$	$0^{-5}$ 5.57 >	$< 10^{-5}$ 6.1	$14 \times 10^{-5}$	$7.54 \times 10^{-5}$	$4.67  imes 10^{-5}$
$C_{14}H_{14}$	$1.09 \times 10^{-4}$	$1.14 \times 1$	$0^{-4}$ 1.06 >	< 10 <sup>-4</sup>	_	_	-

Table IIExperimental Results Obtained in a Jet-Stirred Reactor at 1 atm, for 1.7% of Toluene and  $\Phi$  Equal to 0.9

Table III and Fig. 4 present the experimental data thus obtained.

For the five mixtures, ignition delay times  $(\tau)$  decrease when *T* rises and varies exponentially vs. 1000/T. It is also shown that for a given *T*, ignition delay times decrease with the equivalence ratio of the mixture for a given concentration of toluene,

but increase with the concentration of hydrocarbon for a given equivalence ratio. It is worth noting that in the case of benzene [11], ignition delay times decrease when the concentration of hydrocarbon increases. The lower part of Fig. 4 also presents the data obtained by Burcat et al. [16] at  $\Phi = 1$ , at 0.5% of toluene, and at a pressure of 7 bar, which is close to the pressure



Figure 1 Oxidation of toluene in a jet-stirred reactor at  $\Phi = 0.9$ . Comparison between experimental (symbols) and computed (lines) mole fraction of species versus residence time at 873 K (a), 893 K (b), and 923 K (c).

(8.4 bar) used in our experiments, and shows that both series of measurements are in good agreement.

# DESCRIPTION OF THE REACTION MECHANISM

This mechanism, which is available on request, has been written in the CHEMKIN II [23] format and includes three parts:

• A primary mechanism containing 59 reactions, in which only toluene and oxygen are considered as molecular reactants,

- A secondary mechanism including 134 reactions, in which the reactants are the molecular products (apart from benzene) formed by the primary mechanism and styrene.
- The mechanism for the oxidation of benzene which is presented in a previous paper [11] and includes the C<sub>0</sub>-C<sub>6</sub> reaction base, which is also described in recent papers [24,25].

Benzene is an important primary product of the oxidation of toluene. As previously presented [11], its oxidation mechanism contains 135 reactions and includes the reactions of benzene molecules and of



Figure 2 Oxidation of toluene in a jet-stirred reactor at 893 K and at  $\Phi = 0.45$ . Comparison between experimental (symbols) and computed (lines) mole fraction of species versus residence time.

cyclohexadienyl, phenyl, phenylperoxy, phenoxy, hydroxyphenoxy, cyclopentadienyl, cyclopentadienoxy, and hydroxycyclopentadienyl free radicals, as well as the reactions of ortho-benzoquinone, phenol, cyclopentadiene, cyclopentadienone, and vinylketene molecules, which are the primary products obtained.

The C<sub>0</sub>–C<sub>6</sub> reaction base was constructed from a review of the recent literature and is an extension of our previous C<sub>0</sub>–C<sub>2</sub> reaction base [26,24]. This C<sub>0</sub>–C<sub>2</sub> reaction base includes the reactions of radicals or molecules including carbon, hydrogen, and oxygen atoms and containing less than three carbon atoms. The kinetic data used in this base were taken from the literature and are mainly those proposed by Baulch et al. [27] and Tsang and Hampson [28]. The C<sub>0</sub>–C<sub>6</sub> reaction base includes reactions involving C<sub>3</sub>H<sub>2</sub>···, ·C<sub>3</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>4</sub> (allene and propyne), ·C<sub>3</sub>H<sub>5</sub> (three isomers), C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>2</sub>, ·C<sub>4</sub>H<sub>3</sub> (two isomers), C<sub>4</sub>H<sub>4</sub>, ·C<sub>4</sub>H<sub>5</sub> (five isomers), C<sub>4</sub>H<sub>6</sub> (1,3-butadiene, 1,2-butadiene, methylcyclopropene, 1-butyne, and 2-butyne), as well as the formation of benzene [24,25]. Pressure-dependent rate constants follow the formalism proposed by Troe [29], and efficiency coefficients have been included. This reaction base was constructed in order to model experimental results obtained in a jet-stirred reactor for methane and ethane [26]; profiles in laminar flames of methane, acetylene, and 1,3-butadiene [24]; and shock tube autoignition delays for acetylene, propyne, allene, 1,3-butadiene [24], 1-butyne, and 2-butyne [25].

Specific heats, heats of formation, and entropies of the molecules or radicals considered have been calculated using software THERGAS [30], based on the group and bond-additivity methods proposed by Benson [31], and stored as 14 polynomial coefficients, according to the CHEMKIN II formalism [23]. Table IV presents the names, the formulae, and the heats of formation of the 25 aromatic species that are not included in the mechanism for the oxidation of benzene [11]. It must be kept in mind that the precision obtained by using group additivity methods to estimate



Figure 3 Oxidation of toluene in a jet-stirred reactor at 893 K and at  $\Phi = 0.45$ . Comparison between experimental (symbols) and computed (lines) mole fraction of species versus residence time.

heats of formation is around 2 kcal  $mol^{-1}$  for molecules and 4 kcal  $mol^{-1}$  for radicals [31].

The primary and secondary mechanisms for the oxidation of toluene are presented in Table V, as well as the references related to the kinetic data used. These mechanisms have been constructed using as a basis those proposed by Emdee et al. [2] and Lindstedt and Maurice [21], but in order to be more comprehensive to model experimental results around 900 K, e.g. termination steps of resonance-stabilized radicals have been considered in more detail.

#### **Primary Mechanism**

The primary mechanism includes the reactions of toluene molecules and of benzyl, methylphenyl, peroxybenzyl, alcoxybenzyl, and cresoxy free radicals.

Unimolecular decompositions (1 and 2, numbers referring to Table V) of toluene molecules give either benzyl radicals and  $\cdot$ H atoms or phenyl and methyl radicals. Two rather different expressions for the rate constant of the reaction involving the breaking of a C—C bond have been published. Pamidimukkala et al.

Com (me	position ole %)						Compo (mole	osition e %)					
C <sub>7</sub> H <sub>8</sub>	O <sub>2</sub>	$P_1$ (atm)	$V \text{ (m s}^{-1})$	$P_5$ (atm)	<i>T</i> <sub>5</sub> (K)	au (µs)	$C_7H_8$	O <sub>2</sub>	$P_1$ (atm)	$V \text{ (m s}^{-1})$	$P_5$ (atm)	<i>T</i> <sub>5</sub> (K)	au (s)
1.25	11.25	0.2631	794	8.28	1305	1553	1.25	7.5	0.246	824	8.60	1418	179
		0.2237	838	8.25	1419	90			0.2237	847	8.47	1486	86
$\Phi$	$\dot{P} = 1$	0.1974	847	8.51	1456	59	$\Phi =$	1.5	0.2395	847	9.07	1486	111
		0.2092	847	9.01	1456	66			0.2158	857	8.44	1515	63
		0.2395	857	9.43	1474	50			0.2263	862	9.00	1530	54
		0.2118	862	8.48	1488	57			0.2105	872	8.65	1560	40
		0.2368	867	8.50	1513	17			0.1974	877	8.25	1576	25
		0.2105	872	8.69	1528	18			0.1934	882	8.22	1591	32
		0.2237	882	8.42	1558	13			0.2066	887	8.92	1608	19
		0.1974	893	8.72	1578	4			0.1842	909	8.51	1675	5
		0.1842	914	8.70	1656	3							
							1.25	3.75	0.1987	862	8.28	1563	128
1.25	22.5	0.2585	824	9.18	1311	203			0.1887	893	8.68	1660	37
		0.246	833	9.00	1335	170	Φ=	= 3	0.1802	909	8.88	1712	25
$\Phi$	= 0.5	0.2385	857	9.45	1398	56							
		0.2368	857	9.40	1398	51	0.5	4.475	0.2526	843	8.84	1569	119
		0.2131	862	8.60	1411	38			0.2329	862	8.68	1633	38
		0.2239	872	9.33	1438	23	$\Phi = 1$	1.006	0.1974	888	7.97	1720	7
		0.1974	872	8.23	1438	26			0.1974	909	8.52	1795	5
		0.2237	872	9.33	1438	36							
		0.2105	882	9.08	1465	19							
		0.2010	898	9.14	1509	6							
		0.1776	898	8.06	1509	8							
		0.1868	909	8.77	1539	5							

Table III Mixture Compositions, Shock Conditions, and Ignition Delays for Toluene

*Note:*  $P_1$  is the pressure of the mixture before the shock. V the speed of the incident wave.  $P_5$  and  $T_5$  are pressure and temperature behind the reflected shock wave.  $\tau$  is the ignition delay time.

[58] proposed  $k = 8.9 \times 10^{13} \exp(-143750/T) \text{ s}^{-1}$ , which was the value used by Lindstedt and Maurice [21], while Rao and Skinner [45] gave,  $k = 1.4 \times$  $10^{16} \exp(-197600/T)$  s<sup>-1</sup> at 4 bar, which is a pressure close to the average value of the data that we have used for the validations in shock tubes. We have based our rate constant on this last expression, which is more consistent with thermochemistry (the energy of the broken C–C bond is around 100 kcal  $mol^{-1}$  according to Benson [31]), but multiplying the A factor by 7 to obtain a better agreement with the experiments performed in a flow reactor at  $\Phi = 1.4$ . Rao and Skinner [45] have shown that these unimolecular initiations display an important fall-off effect at 1600 K, for pressures below 2 bar. That should be taken into account for further modeling at higher temperature or lower pressure. The initiations with oxygen molecules (3) have also been considered, with a rate constant calculated as recommended by Ingham et al. [46] for alkylbenzenes.

The addition of  $\cdot$ H atoms to toluene molecules leads to the formation of benzene and methyl radicals (4), the addition of  $\cdot$ O $\cdot$  atoms gives  $\cdot$ H atoms and cresoxy radicals (5), and the addition of  $\cdot$ OH radicals produces  $\cdot$ H atoms and benzyl alcohol (6). We have considered fewer addition reactions than Lindstedt and Maurice [21], who proposed two possible additions with  $\cdot$ OH radicals and three with  $\cdot$ O $\cdot$  atoms, but we have written only the most probable channels for which a satisfactory evaluation of the rate constant could be found. In the case of the addition of  $\cdot$ OH radicals, the best data available were proposed by Baulch et al. [39] for the formation of an adduct between 200 and 300 K. We have preferred to use the same value as that proposed for the formation of phenol from benzene [11].

An important part of the reactions of toluene molecules involves the formation of the resonancestabilized benzyl radicals by unimolecular (1) and bimolecular (3) initiations and by metatheses with H-abstraction (7–24). Because of the high stability of benzyl radicals, metatheses are considered for a wide range of radicals, especially resonance-stabilized radicals, which are present in important concentration. The radicals taken into account are then  $\cdot$ H,  $\cdot$ O,  $\cdot$ OH,  $\cdot$ HO<sub>2</sub>,  $\cdot$ CH<sub>3</sub>,  $\cdot$ C<sub>2</sub>H<sub>3</sub>,  $\cdot$ C<sub>3</sub>H<sub>5</sub> (allyl),  $\cdot$ nC<sub>4</sub>H<sub>5</sub>,  $\cdot$ iC<sub>4</sub>H<sub>5</sub>,



**Figure 4** Autoignition delays of toluene in a shock tube from 7 to 9.5 bar. Semilog plot of experimental (symbols) and computed (lines) ignition delays as a function of temperature behind the reflected shock wave for different equivalence ratios at 1.25% of toluene (a) and for different toluene concentrations at  $\Phi = 1$  (b). The experimental results obtained by Burcat et al. [16] at  $\Phi = 1$  and at 0.5% of toluene is shown in (b), together with the related computed line.

 $\cdot C_5H_5$  (cyclopentadienyl),  $\cdot C_6H_5$  (phenyl),  $\cdot C_6H_5O$  (phenoxy),  $\cdot C_6H_4CH_3$  (methyl phenyl),  $\cdot OC_6H_4CH_3$  (cresoxy),  $C_6H_5CH_2OO$  (peroxybenzyl),  $C_6H_5CH_2O$ . (alcoxybenzyl), and HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>. (hydroxybenzyl) radicals. In order to be as comprehensive as possible, we have also considered the formation of methyl phenyl radicals by abstraction of phenylic H-atoms (25–29). These reactions were not considered by previous authors [2,13,14,21,22].

Benzyl radicals can decompose by beta-scission as proposed by Colket and Seery [35] (30,31), react with oxygen molecules (32,33), or by termination reactions with other radicals (34–39). Two reactions with oxygen are possible, the formation of peroxybenzyl radicals (32), which is important at low temperature, and the production of  $\cdot$ O $\cdot$  atoms and alcoxybenzyl radicals (33). Benzyl radicals can combine with  $\cdot$ OH,  $\cdot$ CH<sub>3</sub>,  $\cdot$ HO<sub>2</sub>, and benzyl radical, to give benzyl alcohol, ethylbenzene, benzylhydroperoxide, and biben**Table IV**Names, formulae, and heats of formation for<br/>aromatic species involved in Table V. The heats of<br/>formation have been calculated by the softwareTHERGAS [30] at 298 K in kcal  $mol^{-1}$ 

	$\Delta H_{\mathrm{f}}$ (298 K	()
Molecules		
Toluene ( $C_6H_4CH_3$ )	11.9	
Benzaldehyde (C <sub>6</sub> H <sub>5</sub> CHO)	-6.0	
Benzyl hydroperoxide (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OOH)	-8.2	
Cresols (HOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )	-30.1	
Benzyl alcohol (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH)	-24.0	
Ethyl benzene ( $C_6H_5CH_2CH_3$ )	7.1	
Styrene ( $C_6H_5CH=CH_2$ )	35.2	
Bibenzyl ( $C_6H_5CH_2CH_2C_6H_5$ )	34.1	
Stilbene ( $C_6H_5CH=CHC_6H_5$ )	58.1	
Hydroxy benzaldehyde (HOC <sub>6</sub> H <sub>4</sub> CHO)	-51.5	
Radicals		
Benzyl ( $\cdot C_6H_5CH_2$ )	49.4	
Methyl phenyl ( $\cdot C_6 H_4 C H_3$ )	73.1	
Peroxy benzyl ( $\cdot C_6H_5CH_2O_2$ )	26.9	
Alcoxy benzyl (·C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)	27.3	
Cresoxy ( $\cdot OC_6H_4CH_3$ )	5.3	
Benzoyl ( $\cdot C_6H_5CO$ )	26.0	
Hydroxy benzyls (·HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )	6.9	
Hydroxy benzyls ( $\cdot C_6H_5CHOH$ )	9.3	
Hydroxy alcoxybenzyl (·HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> O)	-15.5	
Hydroxy benzoyl (·HOC <sub>6</sub> H <sub>4</sub> CO)	-16.7	
Hydroxy peroxybenzyl (·HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> O <sub>2</sub> )	-15.8	
$C_8H_9$ (· $C_6H_5CHCH_3$ )	40.4	
$C_8H_9-1$ (· $C_6H_5CH_2CH_2$ )	55.9	
$C_8H_7$ (· $C_6H_5C=CH_2$ )	81.6	
$C_{14}H_{13}$ (· $C_{6}H_{5}CHCH_{2}C_{6}H_{5}$ )	67.4	

zyl, respectively. The reactions with  $\cdot$ O· atoms, which are important at high temperature, lead to phenyl radicals and formaldehyde molecules (34) or to  $\cdot$ H atoms and benzaldehyde molecules (35). For the rate constant of this last channel, we use a value of  $1 \times 10^{14}$ cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, while Hippler et al. [38] proposed  $4 \times 10^{14}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and Linstedt and Maurice [21] have used  $3.5 \times 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

The reactions of methyl phenyl radicals (40–47) have been adapted from those proposed for phenyl radicals [11] and includes reactions with oxygen molecules to give either  $\cdot$ O $\cdot$  atoms and cresoxy radicals or methyl radicals and benzoquinone molecules and termination steps with other radicals.

Ellis et al. [59] have shown that the peroxybenzyl radical isomerization and decomposition makes a substantial contribution to the formation of benzaldehyde at 773 K. The kinetic data for this channel (48) have been calculated according to the method proposed by Warth et al. [48] for peroxy alkyl radicals. A-factor has been derived from the change in the number of

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ReactionsAn $E_a$ ReferencesPRIMARY MECHANISM<br/>Reactions of Toluene MoleculesUmimolecular inititationToluene = Benzyl + H $1.0 \times 10^{15}$ 0.088.9HIPPLER90 [32]Toluene = C<sub>6</sub>H<sub>5</sub> + CH<sub>3</sub>Bimolecular inititationToluene + O<sub>2</sub> = Benzyl + HO<sub>2</sub> $2.1 \times 10^{12}$ 0.038.6Estimated<sup>a</sup>AdditionsToluene + H = C<sub>6</sub>H<sub>6</sub> + CH<sub>3</sub> $5.8 \times 10^{13}$ 0.08.1BAULCH94 [27]Toluene + H = C<sub>6</sub>H<sub>6</sub> + CH<sub>3</sub>Toluene + H = C<sub>6</sub>H<sub>6</sub> + CH<sub>3</sub> $5.8 \times 10^{13}$ 0.03.6TAPPE89 [33]

$Toluene = C_6H_5 + CH_3$	$1.0 \times 10^{17}$	0.0	97.0	Estimated <sup>a</sup>	(2)
Bimolecular inititiation					
$Toluene + O_2 = Benzyl + HO_2$	$2.1 \times 10^{12}$	0.0	38.6	Estimated <sup>b</sup>	(3)
Additions					
$Toluene + H = C_6H_6 + CH_3$	$5.8 \times 10^{13}$	0.0	8.1	BAULCH94 [27]	(4)
$Toluene + O = OC_6H_4CH_3 + H$	$1.7 \times 10^{13}$	0.0	3.6	TAPPE89 [33]	(5)
$Toluene + OH = HOC_6H_4CH_3 + H$	$1.3 \times 10^{13}$	0.0	10.6	Estimated <sup>c</sup>	(6)
	Metatheses				
Metatheses with abstraction of a benzylic H-atom					
Toluene + H = Benzyl + H <sub>2</sub>	$1.2 \times 10^{14}$	0.0	8.4	HIPPLER90	(7)
Toluene + O = Benzyl + OH	$6.3 \times 10^{11}$	0.0	0.0	HOEEMANN90[34]	(8)
Toluene + $OH = Benzyl + H_2O$	$5.2 \times 10^{9}$	1.0	0.87	BAULCH94	(9)
$Toluene + HO_2 = Benzyl + H_2O_2$	$4.0 \times 10^{11}$	0.0	14.0	BAULCH94	(10)
$Toluene + CH_3 = Benzyl + CH_4$	$1.6 \times 10^{12}$	0.0	11.1	COLKET94 [35]	(11)
$Toluene + C_2H_3 = Benzyl + C_2H_4$	$4.0 \times 10^{12}$	0.0	8.0	COLKET94	(12)
$Toluene + C_3H_5 = Benzyl + C_3H_6$	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup>d</sup>	(13)
Toluene + $C_3H_3$ = Benzyl + $pC_3H_4$	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup>d</sup>	(14)
Toluene + $iC_4H_5$ = Benzyl + 1,3-C <sub>4</sub> H <sub>6</sub>	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup>d</sup>	(15)
Toluene + $nC_4H_5$ = Benzyl + 1,3-C <sub>4</sub> H <sub>6</sub>	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup>d</sup>	(16)
Toluene + $C_5H_5$ = Benzyl + $C_5H_6$	$1.6 \times 10^{12}$	0.0	11.1	Estimated <sup>d</sup>	(17)
Toluene + $C_6H_5$ = Benzyl + $C_6H_6$	$7.9 \times 10^{13}$	0.0	12.0	HECKMANN96 [36]	(18)
Toluene + $C_6H_5O = Benzyl + C_6H_5OH$	$1.6 \times 10^{11}$	0.0	15.1	Estimated <sup>d</sup>	(19)
Toluene + $C_6H_4CH_3$ = Benzyl + Toluene	$7.9 \times 10^{13}$	0.0	12.0	Estimated <sup>e</sup>	(20)
Toluene + $OC_6H_4CH_3 = Benzyl + HOC_6H_4CH_3$	$1.6 \times 10^{11}$	0.0	15.1	Estimated <sup>d</sup>	(21)
Toluene + $C_6H_5CH_2OO = Benzyl + C_6H_5CH_2OOH$	$4.0 \times 10^{11}$	0.0	14.0	Estimated <sup>f</sup>	(22)
Toluene + $C_6H_5CH_2O = Benzyl + C_6H_5CH_2OH$	$1.6 \times 10^{11}$	0.0	11.1	Estimated <sup>d</sup>	(23)
Toluene + $HOC_6H_4CH_2 = Benzyl + HOC_6H_4CH_3$	$1.6 \times 10^{11}$	0.0	15.1	Estimated <sup>d</sup>	(24)
Metatheses with abstraction of a phenylic H-atom					( )
Toluene + H = $C_6H_4CH_3 + H_2$	$6.0 \times 10^{8}$	1.0	16.8	Estimated <sup>c</sup>	(25)
Toluene + O = $C_6H_4CH_3 + OH$	$2.0 \times 10^{13}$	0.0	14.7	Estimated <sup>c</sup>	(26)
Toluene + OH = $C_6H_4CH_3 + H_2O$	$1.6 \times 10^{8}$	1.42	1.45	Estimated <sup>c</sup>	(27)
Toluene + HO <sub>2</sub> = $C_6H_4CH_3 + H_2O_2$	$4.0 \times 10^{11}$	0.0	28.9	Estimated <sup>c</sup>	(28)
Toluene + $CH_3 = C_6H_4CH_3 + CH_4$	$2.0 \times 10^{12}$	0.0	15.0	Estimated <sup>c</sup>	(29)
Reaction	ns of Benzyl Rad	licals			(-)
Decompositions by beta-scission	2				
$Benzyl = C_5H_5 + C_2H_2$	$6.0 \times 10^{13}$	0.0	70.0	COLKET94	(30)
$Benzyl = C_3H_3 + C_4H_4$	$2.0 \times 10^{14}$	0.0	83.6	COLKET94	(31)
Reactions with oxygen molecule					
$Benzyl + O_2 = C_6H_5CH_2OO$	$4.6 \times 10^{11}$	0.0	-0.38	FENTER94 [37]	(32)
$Benzyl + O_2 = C_6H_5CH_2O + O$	$6.3 \times 10^{12}$	0.0	40.0	LINSTEDT96 [21]	(33)
Termination reactions					( )
$Benzyl + O = C_6H_5 + HCHO$	$3.5 \times 10^{13}$	0.0	0.0	EMDEE92 [2]	(34)
$Benzyl + O = C_6H_5CHO + H$	$1.0  imes 10^{14}$	0.0	0.0	Estimated <sup>g</sup>	(35)
$Benzyl + OH = C_6H_5CH_2OH$	$2.0 \times 10^{13}$	0.0	0.0	HIPPLER90' [38]	(36)
$Benzyl + HO_2 = C_6H_5CH_2OOH$	$5.0 \times 10^{12}$	0.0	0.0	HIPPLER90'	(37)
$etC_6H_5 = Benzvl + CH_3$	$6.1 \times 10^{15}$	0.0	75.1	BAULCH92 [39]	(38)
2Benzyl = Bibenzyl	$2.5 \times 10^{11}$	0.4	0.0	MULLER88 [40]	(39)
Reactions o	f Methyl Phenyl	Radicals			. /
Reactions with oxygen molecule	5 5				
$C_6H_4CH_3 + O_2 = OC_6H_4CH_3 + O_2$	$2.6 \times 10^{13}$	0.0	6.1	Estimated <sup>h</sup>	(40)

 Table V
 Primary and Secondary Mechanism for the Oxidation of Toluene

Continued

No.

(1)

Table	V	Continued

Reactions	Α	n	$E_{\rm a}$	References	No.
$C_6H_4CH_3 + O_2 = OC_6H_4O + CH_3$	$3.0 \times 10^{13}$	0.0	9.0	Estimated <sup>h</sup>	(41)
Termination reactions					
$C_6H_4CH_3 + H = Toluene$	$1.0  imes 10^{14}$	0.0	0.0	Estimated <sup>i</sup>	(42)
$C_6H_4CH_3 + H = Benzyl + H$	$1.0 \times 10^{13}$	0.0	0.0	MILLER92 [41]	(43)
$C_6H_4CH_3 + O = OC_6H_4CH_3$	$1.0 \times 10^{14}$	0.0	0.0	Estimated <sup>h</sup>	(44)
$C_6H_4CH_3 + OH = HOC_6H_4CH_3$	$1.0 \times 10^{13}$	0.0	0.0	Estimated <sup>h</sup>	(45)
$C_6H_4CH_3 + CH_3 = Xylene$	$1.2 \times 10^{6}$	1.96	-3.7	Estimated <sup>j</sup>	(46)
$C_6H_4CH_3 + HO_2 = OC_6H_4CH_3 + OH$	$5.0  imes 10^{12}$	0.0	0.0	Estimated <sup>h</sup>	(47)
Reactions of Pe	roxybenzyl Radi	cals			
Isomerisation-decomposition reactions					
$C_6H_5CH_2OO = C_6H_5CHO + OH$	$3.4 \times 10^{9}$	1.0	37.5	Estimated <sup>k</sup>	(48)
Combination reactions					
$C_6H_5CH_2OO + H = C_6H_5CH_2OOH$	$1.0 \times 10^{14}$	0.0	0.0	Estimated <sup>i</sup>	(49)
Dispropotionnation reactions					
$C_6H_5CH_2OO + HO_2 = C_6H_5CH_2OOH + O_2$	$2.0 \times 10^{11}$	0.0	0.0	Estimated <sup>1</sup>	(50)
$2C_{6}H_{5}CH_{2}OO = C_{6}H_{5}CH_{2}OH + C_{6}H_{5}CHO + O_{2}$	$1.4 \times 10^{10}$	0.0	-0.72	Estimated <sup>1</sup>	(51)
$C_{6}H_{5}CH_{2}OO + C_{6}H_{5}CH_{2}OO = 2C_{6}H_{5}CH_{2}O + O_{2}O_{5}OO = 2C_{6}H_{5}CH_{2}O + O_{2}O_{5}OO = 0$	$6.3 \times 10^{10}$	0.0	-0.72	Estimated <sup>1</sup>	(52)
Reactions of Ale	coxy Benzyl Rad	icals			(==)
Decomposition by beta-scission					
$C_6H_5CH_2O = H + C_6H_5CHO$	$2.0 \times 10^{13}$	0.0	27.5	Estimated <sup>m</sup>	(53)
$C_6H_5CH_2O = C_6H_5 + HCHO$	$2.0 \times 10^{13}$	0.0	27.5	Estimated <sup>m</sup>	(54)
Reactions with oxygen	2.0 × 10	0.0	27.0	Lotinuted	(31)
$C_{4}H_{5}CH_{2}O + O_{2} = HO_{2} + C_{4}H_{5}CHO$	$6.0 \times 10^{10}$	0.0	16	Estimated <sup>n</sup>	(55)
$\mathbf{R} = \mathbf{R} = \mathbf{R} + \mathbf{C}_2 = \mathbf{R} + \mathbf{C}_2 + $	Cresoxy Radical	ls	1.0	Lotinuted	(55)
CO elimination with rearrangement	cresoxy Rudied	15			
$OC_2H_4CH_2 = H + C_2H_2 + CO_2$	$3.0 \times 10^{11}$	0.0	43.8	Estimated <sup>0</sup>	(56)
$OC_{2}H_{4}CH_{2} = H + C_{4}H_{2} + C_{2}H_{2} + C_{0}$	$3.0 \times 10^{11}$	0.0	43.8	Estimated <sup>0</sup>	(50)
$OC_{2}H_{4}CH_{2} = C_{2}H_{2} + C_{2}H_{4} + CHO$	$1.5 \times 10^{11}$	0.0	43.8	Estimated <sup>0</sup>	(58)
Termination reactions	1.5 × 10	0.0	45.0	Estimated	(50)
$OC_2H_1CH_2 + H = HOC_2H_1CH_2$	$1.0 \times 10^{14}$	0.0	0.0	Estimated <sup>i</sup>	(50)
		0.0	0.0	Estimated	(37)
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Reactions of Benzaldehyde	Molecules and L	Jerived R	adicals		$\langle \langle 0 \rangle$
$C_6H_5CHO = C_6H_5CO + H$	$4.0 \times 10^{13}$	0.0	83.7	GRELA86 [42]	(60)
$C_6H_5CHO + O_2 = C_6H_5CO + HO_2$	$7.0 \times 10^{11}$	0.0	39.5	Estimated	(61)
$C_6H_5CHO + H = C_6H_6 + R_5CHO$	$5.8 \times 10^{13}$	0.0	8.1	Estimated <sup>p</sup>	(62)
$C_6H_5CHO + H = C_6H_5CO + H_2$	$4.0 \times 10^{13}$	0.0	3.2	Estimated <sup>q</sup>	(63)
$C_6H_5CHO + O = C_6H_5CO + OH$	$6.0 \times 10^{12}$	0.0	1.8	BAULCH94	(64)
$C_6H_5CHO + OH = C_6H_5CO + H_2O$	$7.8 \times 10^{12}$	0.0	0.0	BAULCH94	(65)
$C_6H_5CHO + HO_2 = C_6H_5CO + H_2O_2$	$3.0 \times 10^{12}$	0.0	11.0	Estimated <sup>q</sup>	(66)
$C_6H_5CHO + CH_3 = C_6H_5CO + CH_4$	$2.0 \times 10^{-6}$	5.6	1.5	Estimated <sup>q</sup>	(67)
$C_6H_5CHO + C_2H_5 = C_6H_5CO + C_2H_6$	$1.3 \times 10^{12}$	0.0	7.5	Estimated <sup>q</sup>	(68)
$C_6H_5CHO + C_3H_5 = C_6H_5CO + C_3H_6$	$1.3 \times 10^{12}$	0.0	11.5	Estimated <sup>r</sup>	(69)
$C_6H_5CHO + iC_4H_5 = C_6H_5CO + 1,3-C_4H_6$	$1.3 \times 10^{12}$	0.0	11.5	Estimated <sup>r</sup>	(70)
$C_6H_5CHO + nC_4H_5 = C_6H_5CO + 1,3-C_4H_6$	$1.3 \times 10^{12}$	0.0	7.5	Estimated <sup>r</sup>	(71)
$C_6H_5CHO + C_5H_5 = C_6H_5CO + C_5H_6$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(72)
$C_6H_5CHO + C_6H_5 = C_6H_5CO + C_6H_6$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(73)
$C_6H_5CHO + Benzyl = Toluene + C_6H_5CO$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(74)
$C_6H_5CHO + C_6H_5O = C_6H_5CO + C_6H_5OH$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(75)
$C_6H_5CHO + OC_6H_4CH_3 = C_6H_5CO + HOC_6H_4CH_3$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(76)
$C_6H_5CHO + HOC_6H_4CH_2 = C_6H_5CO + HOC_6H_4CH_2$	$1.3 \times 10^{11}$	0.0	11.5	Estimated <sup>r</sup>	(77)
$C_{6}H_{5}CO = C_{6}H_{5} + CO$	$4.0 \times 10^{14}$	0.0	29.5	SOLLY71 [43]	(78)
Reactions of Benzvl Hydroprero	xide Molecules :	and Deriv	ed Radicals	,	(, )
$C_6H_5CH_2OOH = C_6H_5CH_2O + OH$	$1.5 \times 10^{16}$	0.0	42.0	Estimated <sup>s</sup>	(79)
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Table V Continued

Reactions	Α	n	Ea	References	No.
Reactions of Cresol Molecules at	nd Derived Rad	dicals			
$HOC_6H_4CH_3 + O_2 = OC_6H_4CH_3 + HO_2$	$1.0 \times 10^{13}$	0.0	38.9	Estimated <sup>t</sup>	(80)
$HOC_6H_4CH_3 + O_2 = HOC_6H_4CH_2 + HO_2$	$2.1 \times 10^{12}$	0.0	39.7	Estimated <sup>b</sup>	(81)
$HOC_6H_4CH_3 + H = C_6H_5OH + CH_3$	$5.8 \times 10^{13}$	0.0	8.1	Estimated <sup>p</sup>	(82)
$HOC_6H_4CH_3 + H = OC_6H_4CH_3 + H_2$	$1.2 \times 10^{14}$	0.0	12.4	Estimated <sup>t</sup>	(83)
$HOC_6H_4CH_3 + O = OC_6H_4CH_3 + OH$	$1.3 \times 10^{13}$	0.0	2.9	Estimated <sup>t</sup>	(84)
$HOC_6H_4CH_3 + OH = OC_6H_4CH_3 + H_2O$	$1.4 \times 10^{8}$	1.4	-0.96	Estimated <sup>t</sup>	(85)
$HOC_6H_4CH_3 + HO_2 = OC_6H_4CH_3 + H_2O_2$	$1.0 \times 10^{12}$	0.0	10.0	Estimated <sup>t</sup>	(86)
$HOC_6H_4CH_3 + CH_3 = OC_6H_4CH_3 + CH_4$	$1.8 \times 10^{11}$	0.0	7.7	Estimated <sup>t</sup>	(87)
$HOC_6H_4CH_3 + C_6H_5 = OC_6H_4CH_3 + C_6H_6$	$4.9 \times 10^{12}$	0.0	4.4	Estimated <sup>t</sup>	(88)
$HOC_6H_4CH_3 + C_5H_5 = OC_6H_4CH_3 + C_5H_6$	$4.9 \times 10^{11}$	0.0	9.4	Estimated <sup>t</sup>	(89)
$HOC_6H_4CH_3 + C_3H_5 = OC_6H_4CH_3 + C_3H_6$	$4.9 \times 10^{11}$	0.0	9.4	Estimated <sup>t</sup>	(90)
$HOC_6H_4CH_3 + iC_4H_5 = OC_6H_4CH_3 + 1,3-C_4H_6$	$4.9 \times 10^{11}$	0.0	9.4	Estimated <sup>t</sup>	(91)
$HOC_6H_4CH_3 + C_6H_5O = OC_6H_4CH_3 + C_6H_5OH$	$4.9 \times 10^{11}$	0.0	9.4	Estimated <sup>t</sup>	(92)
$HOC_6H_4CH_3 + H = HOC_6H_4CH_2 + H_2$	$1.2 \times 10^{14}$	0.0	8.4	Estimated <sup>p</sup>	(93)
$HOC_6H_4CH_3 + O = HOC_6H_4CH_2 + OH$	$6.3 \times 10^{11}$	0.0	0.0	Estimated <sup>p</sup>	(94)
$HOC_6H_4CH_3 + OH = HOC_6H_4CH_2 + H_2O$	$5.2 \times 10^{9}$	1.0	0.87	Estimated <sup>p</sup>	(95)
$HOC_6H_4CH_3 + HO_2 = HOC_6H_4CH_2 + H_2O_2$	$4.0 \times 10^{11}$	0.0	14.0	Estimated <sup>p</sup>	(96)
$HOC_6H_4CH_3 + CH_3 = HOC_6H_4CH_2 + CH_4$	$1.6 \times 10^{12}$	0.0	11.1	Estimated <sup>p</sup>	(97)
$HOC_6H_4CH_3 + C_3H_5 = HOC_6H_4CH_2 + C_3H_6$	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup><i>p</i></sup>	(98)
$HOC_6H_4CH_3 + C_3H_3 = HOC_6H_4CH_2 + pC_3H_4$	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup><i>p</i></sup>	(99)
$HOC_6H_4CH_2 + iC_4H_5 = HOC_6H_4CH_2 + 13-C_4H_6$	$1.6 \times 10^{12}$	0.0	15.1	Estimated <sup><i>p</i></sup>	(100)
$HOC_{0}H_{4}CH_{2} + nC_{4}H_{5} = HOC_{0}H_{4}CH_{2} + 1.3 C_{4}H_{6}$	$1.6 \times 10^{12}$	0.0	11.1	Estimated <sup><i>p</i></sup>	(100)
$HOC_{\varepsilon}H_{4}CH_{2} + C_{\varepsilon}H_{\varepsilon} = HOC_{\varepsilon}H_{4}CH_{2} + C_{\varepsilon}H_{\varepsilon}$	$1.0 \times 10^{11}$	0.0	15.1	Estimated <sup>P</sup>	(101)
$HOC_{2}H_{4}CH_{2} + C_{2}H_{5} = HOC_{2}H_{4}CH_{2} + C_{5}H_{6}$	$7.0 \times 10^{13}$	0.0	12.0	Estimated <sup>P</sup>	(102)
$HOC_{6}H_{4}CH_{3} + C_{6}H_{5} - HOC_{6}H_{4}CH_{2} + C_{6}H_{6}$	$1.5 \times 10^{11}$	0.0	15.1	Estimated <sup>p</sup>	(103)
$HOC_{6}H_{4}CH_{2} + C_{6}H_{5}CH_{2} - HOC_{6}H_{4}CH_{2} + C_{6}H_{5}CH_{4}CH_{2}$	$1.0 \times 10^{13}$ 7.9 × 10 <sup>13</sup>	0.0	12.0	Estimated <sup>p</sup>	(10+)
$HOC_{14}CH_{2} + C_{14}CH_{2} - HOC_{14}CH_{2} + HOC_{14}CH_{2}$	$1.9 \times 10^{11}$	0.0	12.0	Estimated <sup>p</sup>	(105)
$HOC_{6}H_{4}CH_{3} + C_{6}H_{4}CH_{3} - HOC_{6}H_{4}CH_{2} + HOC_{6}H_{4}CH_{3}$	$1.0 \times 10^{11}$	0.0	14.0	Estimated <sup>p</sup>	(100)
$HOC_{6}H_{4}CH_{2} + C_{6}H_{5}CH_{2}OO = HOC_{6}H_{4}CH_{2} + C_{6}H_{5}CH_{2}OO H$	$4.0 \times 10^{11}$	0.0	14.0	Estimated <sup>P</sup>	(107)
$HOC_{6}H_{4}CH_{3} + C_{6}H_{5}CH_{2}O = HOC_{6}H_{4}CH_{2} + C_{6}H_{5}CH_{2}OH_{$	$1.0 \times 10$	0.0	0.29	Estimated <sup>#</sup>	(100)
$HOC_{6}H_{4}CH_{2} + O_{2} = HOC_{6}H_{4}CH_{2}OO$	$4.0 \times 10^{12}$	0.0	-0.38	Estimated <sup>11</sup>	(109)
$HOC_{6}H_{4}CH_{2} + O_{2} = HOC_{6}H_{4}CH_{2}O + O_{4}O_{4}O_{4}O_{4}O_{4}O_{4}O_{4}O_{4}$	$0.3 \times 10^{14}$	0.0	40.0	Estimated	(110)
$HOC_6H_4CH_2 + H = HOC_6H_4CH_3$	$1.0 \times 10^{12}$	0.0	0.0	Estimated <sup>2</sup>	(111)
$HOC_6H_4CH_2 + HO_2 = HOC_6H_4CH_2OOH$	$5.0 \times 10^{12}$	0.0	0.0	Estimated <sup><math>n</math></sup>	(112)
$HOC_6H_4CH_2 + CH_3 = C_6H_5OH + C_2H_4$	$5.0 \times 10^{-10}$	0.0	0.0	Estimated <sup>*</sup>	(115)
$HOC_6H_4CH_2OO = HOC_6H_4CHO + OH$	$3.4 \times 10^{-1}$	1.0	37.5	Estimated <sup>2</sup>	(114)
$HOC_6H_4CH_2O = H + HOC_6H_4CHO$	$2.0 \times 10^{13}$	0.0	27.5	Estimated <sup>1</sup>	(115)
$HOC_6H_4CH_2O = C_6H_4OH + HCHO$	$2.0 \times 10^{10}$	0.0	27.5	Estimated	(110)
$HOC_6H_4CH_2O + O_2 = OOH + HOC_6H_4CHO$	$6.0 \times 10^{13}$	0.0	1.6	Estimated	(117)
$HOC_6H_4CHO + H = HOC_6H_4CO + H_2$	$4.0 \times 10^{13}$	0.0	3.2	Estimated <sup>y</sup>	(118)
$HOC_6H_4CHO + O = HOC_6H_4CO + OH$	$6.0 \times 10^{12}$	0.0	1.8	Estimated <sup>y</sup>	(119)
$HOC_6H_4CHO + OH = HOC_6H_4CO + H_2O$	$7.8 \times 10^{12}$	0.0	0.0	Estimated <sup>y</sup>	(120)
$HOC_6H_4CHO + HO_2 = HOC_6H_4CO + H_2O$	$3.0 \times 10^{12}$	0.0	11.0	Estimated <sup>y</sup>	(121)
$HOC_6H_4CHO + CH_3 = HOC_6H_4CO + CH_4$	$2.0 \times 10^{-6}$	5.6	1.5	Estimated <sup>y</sup>	(122)
$HOC_6H_4CO = C_6H_5O + CO$	$4.0 \times 10^{14}$	0.0	29.5	Estimated <sup>z</sup>	(123)
Reactions of Benzyl Alcohol Molecu	les and Derived	d Radic	als	1	
$C_6H_5CH_2OH + O_2 = HO_2 + C_6H_5CHOH$	$1.4 \times 10^{12}$	0.0	34.0	Estimated <sup><i>b</i></sup>	(124)
$C_6H_5CH_2OH + O_2 = HO_2 + C_6H_5CH_2O$	$2.0 \times 10^{14}$	0.0	41.4	EMDEE92	(125)
$C_6H_5CH_2OH + H = C_6H_6 + CH_2OH$	$5.8 \times 10^{13}$	0.0	8.1	Estimated <sup>p</sup>	(126)
$C_6H_5CH_2OH + H = C_6H_5CHOH + H_2$	$8.0 \times 10^{13}$	0.0	6.4	Estimated <sup>aa</sup>	(127)
$C_6H_5CH_2OH + O = C_6H_5CHOH + OH$	$4.2 \times 10^{11}$	0.0	-2.0	Estimated <sup>aa</sup>	(128)
$C_6H_5CH_2OH + OH = C_6H_5CHOH + H_2O$	$3.9 \times 10^{9}$	1.0	-1.1	Estimated <sup>aa</sup>	(129)
$C_6H_5CH_2OH + HO_2 = C_6H_5CHOH + H_2O_2$	$2.7 \times 10^{11}$	0.0	12.0	Estimated <sup>aa</sup>	(130)

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Table	V	Continue
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eactions	Α	n	Ea	References	No.
$C_6H_5CH_2OH + CH_3 = C_6H_5CHOH + CH_4$	$1.1\times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(131
$C_6H_5CH_2OH + C_3H_3 = C_6H_5CHOH + pC_3H_4$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(132
$C_6H_5CH_2OH + C_3H_5 = C_6H_5CHOH + C_3H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(133
$C_6H_5CH_2OH + iC_4H_5 = C_6H_5CHOH + 1,3-C_4H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(134
$C_6H_5CH_2OH + nC_4H_5 = C_6H_5CHOH + 1,3-C_4H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(135
$C_6H_5CH_2OH + C_5H_5 = C_6H_5CHOH + C_5H_6$	$1.1 \times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(136
$C_6H_5CH_2OH + C_6H_5 = C_6H_5CHOH + C_6H_6$	$5.2 \times 10^{13}$	0.0	10.0	Estimated <sup>aa</sup>	(137
$C_6H_5CH_2OH + C_6H_5O = C_6H_5CHOH + C_6H_5OH$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(138
$C_6H_5CH_2OH + Benzyl = C_6H_5CHOH + Toluene$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(139
$C_6H_5CH_2OH + C_6H_4CH_3 = C_6H_5CHOH + C_6H_5CH_2OH$	$5.2 \times 10^{13}$	0.0	10.0	Estimated <sup>aa</sup>	(140
$C_6H_5CH_2OH + OC_6H_4CH_3 = C_6H_5CHOH + HOC_6H_4CH_3$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(141
$C_6H_5CH_2OH + HOC_6H_4CH_2 = C_6H_5CHOH + HOC_6H_4CH_3$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(142
$C_6H_5CH_2OH + C_6H_5CH_2O = C_6H_5CHOH + C_6H_5CH_2OH$	$1.1 \times 10^{11}$	0.0	9.1	Estimated <sup>aa</sup>	(143
$C_6H_5CHOH = C_6H_5CHO + H$	$2.0 \times 10^{14}$	0.0	23.3	Estimated <sup>bb</sup>	(144
Reactions of Ethylbenzene Molec	cules and Deriv	ed Radica	ls		
$etC_6H_5 = C_8H_9 + H$	$4.3 \times 10^{14}$	0.0	83.6	Estimated	(146
$etC_6H_5 + O_2 = C_8H_9 + HO_2$	$1.4 \times 10^{12}$	0.0	34.0	Estimated <sup><i>b</i></sup>	(147
$etC_6H_5 + O_2 = C_8H_9 - 1 + HO_2$	$1.2 \times 10^{13}$	0.0	49.0	Estimated <sup>aa</sup>	(148
$etC_6H_5 + H = C_6H_6 + C_2H_5$	$5.8 \times 10^{13}$	0.0	8.1	Estimated <sup>aa</sup>	(149
$etC_6H_5 + H = C_8H_9 + H_2$	$8.0 \times 10^{13}$	0.0	6.4	Estimated <sup>aa</sup>	(150
$etC_6H_5 + O = C_8H_9 + OH$	$3.9 \times 10^9$	1.0	-1.1	Estimated <sup>aa</sup>	(151
$etC_6H_5 + OH = C_8H_9 + H_2O$	$1.2 \times 10^{14}$	0.0	8.4	Estimated <sup>aa</sup>	(152
$etC_6H_5 + HO_2 = C_8H_9 + H_2O_2$	$2.7 \times 10^{11}$	0.0	12.0	Estimated <sup>aa</sup>	(153
$etC_6H_5 + CH_3 = C_8H_9 + CH_4$	$1.1 \times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(154
$etC_6H_5 + C_3H_5 = C_8H_9 + C_3H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(155
$etC_6H_5 + iC_4H_5 = C_8H_9 + 1,3-C_4H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(156
$etC_6H_5 + nC_4H_5 = C_8H_9 + 1,3-C_4H_6$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(157
$etC_6H + C_5H_5 = C_8H_9 + C_5H_6$	$1.1 \times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(158
$etC_6H_5 + C_6H_5O = C_8H_9 + C_6H_5OH$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(159
$etC_6H_5 + Benzyl = C_8H_9 + Toluene$	$1.1 \times 10^{12}$	0.0	13.1	Estimated <sup>aa</sup>	(160
$etC_6H_5 + OC_6H_4CH_3 = C_8H_9 + HOC_6H_4CH_3$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(161
$etC_6H_5 + HOC_6H_4CH_2 = C_8H_9 + HOC_6H_4CH_3$	$1.1 \times 10^{11}$	0.0	13.1	Estimated <sup>aa</sup>	(162
$etC_6H_5 + H = C_8H_9 - 1 + H_2$	$2.8 \times 10^{7}$	2.0	7.7	Estimatedee	(163
$etC_6H_5 + O = C_8H_9-1 + OH$	$5.1 \times 10^{13}$	0.0	7.8	Estimated <sup>ee</sup>	(164
$etC_6H_5 + OH = C_8H_9 - 1 + H_2O$	$2.7 \times 10^{6}$	2.0	0.4	Estimated <sup>ee</sup>	(165
$etC_6H_5 + HO_2 = C_8H_9 - 1 + H_2O_2$	$6.0 \times 10^{11}$	0.0	17.0	Estimated <sup>ee</sup>	(166
$etC_6H_5 + CH_3 = C_8H_9 - 1 + CH_4$	0.3	4.0	8.2	Estimated	(167
$C_8H_9 = H + Styrene$	$3.1 \times 10^{13}$	0.0	50.7	MULLER88	(168
$C_8H_9-1 = H + Styrene$	$1.6 \times 10^{13}$	0.0	34.8	Estimated	(169
$C_8H_9-1 = C_2H_4 + C_6H_5$	$7.1 \times 10^{14}$	0.0	43.5	EBERT78 [44]	(170
$C_8H_9 + O_2 = HO_2 + Styrene$	$7.0 \times 10^{11}$	0.0	15.0	Estimated <sup>gg</sup>	(171
$C_8H_9-1+O_2 = HO_2 + Styrene$	$1.5 \times 10^{12}$	0.0	5.0	Estimated <sup>gg</sup>	(172
$C_8H_9 + HO_2 = OH + C_6H_5CHO$	$5.0 \times 10^{12}$	0.0	0.0	Estimated	(173
$C_8H_9-1 + HO_2 = OH + HCHO + Benzyl$	$5.0 \times 10^{12}$	0.0	0.0	Estimated	(174
Reactions of Styrene Molecule	$2 \circ 10^{13}$	Radicals	57.0	E	(175
Styrene + $O_2$ = H $O_2$ + $C_6H_5C_2H_2$	$2.0 \times 10^{13}$	0.0	57.9	Estimated <sup>m</sup>	(1/5
Styrene + $O = C_6 H_5 + C H_2 C H O$	$5.0 \times 10^{\circ}$	1.45	0.9	Estimated <sup>m</sup>	(1/0
Styrene + $OH = Benzyl + HCHO$	$1.4 \times 10^{12}$	0.0	0.0	Estimated <sup>m</sup>	(17)
Styrene + $OH = C_6H_5CHO + CH_3$	$2.8 \times 10^{12}$	0.0	0.0	Estimated""	(178
Styrene + H = $C_6H_5C_2H_2 + H_2$	$0.0 \times 10^{-5}$	2.53	9.2	Estimated <sup>nn</sup>	(179
$\text{Styrene} + \text{OH} = \text{C}_6\text{H}_5\text{C}_2\text{H}_2 + \text{H}_2\text{O}$	$1.5 \times 10^{\circ}$	2.0	0.4	Estimated""	(180
Styrene + $CH_3 = C_8H_7 + CH_4$	$3.3 \times 10^{15}$	0.0	15.5	Estimated""	(181
$C_8H_7 + O_2 = C_6H_5CO + HCHO$	$4.5 \times 10^{10}$	-1.39	1.0	Estimated"	(182

Continued

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Table V Co	ontinued
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Reactions	Α	n	$E_{a}$	References	No.
Reactions of	Bibenzyl Molecule	s and Derive	ed Radicals		
$Bibenzyl = C_{14}H_{13} + H$	$1.0 \times 10^{14}$	0.0	83.0	HIPPLER90'	(183)
Bibenzyl + $O_2 = C_{14}H_{13} + HO_2$	$2.8  imes 10^{12}$	0.0	35.0	Estimated <sup>b</sup>	(184)
Bibenzyl + H = $C_{14}H_{13} + H_2$	$1.6  imes 10^{14}$	0.0	6.4	Estimated <sup>aa</sup>	(185)
$Bibenzyl + O = C_{14}H_{13} + OH$	$8.4  imes 10^{11}$	0.0	-2.0	Estimated <sup>aa</sup>	(186)
Bibenzyl + OH = $C_{14}H_{13} + H_2O$	$7.0 \times 10^{9}$	1.0	-1.1	Estimated <sup>aa</sup>	(187)
Bibenzyl + $HO_2 = C_{14}H_{13} + H_2O_2$	$5.4  imes 10^{11}$	0.0	12.0	Estimated <sup>aa</sup>	(188)
$Bibenzyl + CH_3 = C_{14}H_{13} + CH_4$	$2.2 \times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(189)
Bibenzyl + $C_3H_5 = C_{14}H_{13} + C_3H_6$	$2.2 \times 10^{12}$	0.0	9.1	Estimated <sup>aa</sup>	(190)
Bibenzyl + $C_6H_5O = C_{14}H_{13} + C_6H_5OH$	$2.2 \times 10^{11}$	0.0	9.1	Estimated <sup>aa</sup>	(191)
$Bibenzyl + Benzyl = C_{14}H_{13} + Toluene$	$2.2 \times 10^{11}$	0.0	9.1	Estimated <sup>aa</sup>	(192)
$C_{14}H_{13} = Stilbene + H$	$7.1 \times 10^{14}$	0.0	30.0	EBERT78	(193)

The rate constants are given at 1 atm ( $k = AT^n \exp(-E_a/RT)$ ) in cc, mol, s, kcal units. Reference numbers are given in brackets when they appear for the first time. This mechanism should be used together with our mechanism for the oxidation of benzene [11].

<sup>*a*</sup> Rate constant taken equal to that proposed by Rao et al. [45] multiplied by 10.

<sup>b</sup> The rate constant of this bimolecular initiation with oxygen molecule has been calculated as proposed by Ingham et al. [46]: A is taken equal to  $n \times 7 \times 10^{11}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, where *n* is the number of benzylic hydrogen atoms abstractable, and the activation energy to the reaction enthalpy.

<sup>c</sup> Rate constant taken equal to that of the similar reaction in the case of benzene [11].

<sup>*d*</sup> Rate constant taken equal to that of the H-abstraction with methyl radicals proposed by Colket et al. [35] with A divided by 10 for cyclic radicals and with an activation energy 4 kcal mol<sup>-1</sup> higher for resonance stabilized radicals.

<sup>e</sup> Rate constant taken equal to that of the H-abstraction with phenyl radicals proposed by Heckmann et al. [36].

<sup>f</sup> Rate constant taken equal to that of the H-abstraction with HO<sub>2</sub> radicals proposed by Baulch et al. [27].

<sup>g</sup> This rate constant is that proposed by Hippler et al. [38] with the A-factor divided by 4.

<sup>*h*</sup> Rate constant taken equal to that of the similar reaction in the case of phenyl radicals [11].

Rate constant taken equal to that of the recombination of H atoms with alkyl radicals as proposed by Allara et al. [47].

<sup>*j*</sup> Rate constant taken equal to that of the similar reaction in the case of phenyl radicals by Rao et al. [45].

<sup>k</sup> The kinetic data for this isomerization of a peroxy radical have been calculated state according to the method proposed by Warth et al. [48] for peroxyalkyl radicals (see text).

<sup>1</sup> Rate constant taken equal to that the disproportionation of peroxyalkyl radicals as proposed by Warth et al. [48].

<sup>*m*</sup> For these beta-scissions involving the breaking of a C–C or a C–H bond, A-factor is an average value for beta-scissions [49] and activation energies have been estimated from thermochemistry and to obtain the best results for simulations.

<sup>n</sup> Rate constant taken equal to that of the similar reaction in the case of ethoxy radicals as proposed by Baulch et al. [39].

<sup>*o*</sup> The global rate constant has been taken equal to that the decomposition of phenoxy radicals to give carbon monoxide and cyclopentadienyl radicals, as proposed by Franck et al. [50].

<sup>*p*</sup> Rate constant taken equal to that of the similar reaction in the case of toluene.

<sup>*q*</sup> Rate constant estimated from the parameters proposed for acetaldehyde by Warnatz [51] (for  $\cdot$ H atoms), by Baulch et al. [26] (for  $\cdot$ HO<sub>2</sub> and  $\cdot$ CH<sub>3</sub> radicals), and by Holhein et al. [52] (for  $\cdot$ C<sub>2</sub>H<sub>5</sub> radicals) with an activation energy 1 kcal mol<sup>-1</sup> lower due to the resonance stabilization of the obtained radical.

<sup>*r*</sup> Rate constant taken equal to that of the H-abstraction with ethyl radicals with A divided by 10 for cyclic radicals and with an activation energy 4 kcal mol<sup>-1</sup> higher for resonance-stabilized radicals.

<sup>3</sup> Rate constant taken equal to that the decomposition of hydroperoxide molecules as proposed by Sahetchian et al. [53].

<sup>t</sup> Rate constant taken equal to that of the similar reaction in the case of phenol [11].

<sup>*u*</sup> Rate constant taken equal to that of the similar reaction for benzyl radicals.

<sup>v</sup> Rate constant taken equal to that of the combination calculated using software KINGAS [54] based on thermochemical kinetics methods [31]. Activation energies of recombination are taken to be zero and A factors are estimated from modified collision theory [48].

<sup>w</sup> Rate constant taken equal to that of the similar reaction for benzyl peroxy radicals.

<sup>x</sup> Rate constant taken equal to that of the similar reaction for benzyl alcoxy radicals.

<sup>y</sup> Rate constant taken equal to that of the similar reaction for benzaldehyde.

 $^{z}$  Rate constant taken equal to that of the similar reaction for  $\cdot C_{6}H_{5}CO$  radicals.

<sup>*aa*</sup> Rate constant taken equal to that of the similar reaction in the case of toluene with A multiplied by 2/3 (for benzyl alcohol and ethyl benzene) and by 4/3 (for bibenzyl) to take into account the number abstractable H atoms and with an activation energy 2 kcal mol<sup>-1</sup> lower due OH substitution (for benzyl alcohol) or to the abstraction of secondary H atoms instead of primary ones (for ethyl benzene and bibenzyl).

<sup>bb</sup> Rate constant taken equal to that of the similar reaction in the case of  $C_2H_5O$  radicals proposed by Heicklen et al. [55].

<sup>cc</sup> Rate calculated using software KINGAS [54].

<sup>dd</sup> Rate constant taken equal to that the bimolecular initiation of alkanes as proposed by Warth et al. [48].

<sup>ee</sup> Rate constant taken equal to that the abstraction of three primary alkylic H atoms as proposed by Warth et al. [48].

<sup>ff</sup> Rate constant taken equal to that the beta-scission of an alkenyl radicals involving the abstraction of an allylic H-atoms [49].

<sup>gg</sup> Rate constant taken equal to that the oxidation of allylic radicals (for  $C_6H_5CHCH_3$  radicals) as proposed by Touchard et al. [56] or of alkylic radicals (for  $C_6H_5CH_2CH_2$  radicals) as proposed by Warth et al. [48].

<sup>hh</sup> Rate constant taken equal to that of the similar reaction in the case of 1,3-butadiene [24] with A divided by 2 to take into account the number of double bonds.

<sup>*ii*</sup> Rate constant taken equal to that of the similar reaction in the case of  $\cdot C_2 H_3$  radicals proposed by Mebel et al. [57].

internal rotations as the reactant moves to the transition state. The activation energy has been set equal to the sum of the activation energy for the abstraction of an allylic secondary hydrogen atom by a peroxy radical (14.5 kcal mol<sup>-1</sup> [49]) and the strain energy of a fourmembered cyclic transition state (23 kcal mol<sup>-1</sup> [31]). Linstedt and Maurice [21] have also considered this reaction with an *A*-factor of  $1 \times 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and an activation energy of 28.7 kcal mol<sup>-1</sup>. We have also considered the termination with H-atoms (49) and the disproportionations of these radicals with  $\cdot$ HO<sub>2</sub> radicals and with themselves (50–52).

Alcoxy benzyl radicals can react with oxygen to give benzaldehyde and  $\cdot$ HO<sub>2</sub> radicals (55) or by betascission. Two beta-scissions are possible, the first involving the breaking of a C–H bond (53) with an enthalpy of reaction of 15.9 kcal mol<sup>-1</sup>, the second involving the breaking of a C–C bond (54) with an enthalpy of reaction of 23.6 kcal mol<sup>-1</sup>. We have used the same activation energy for both channels, since we found the simulations to be much deteriorated if we allowed the activation energies to be different.

Like phenoxy radicals [11], cresoxy radicals can react by CO elimination (56–58) or combine with Hatoms (59). CO elimination (56–58) would lead to the formation of  $\cdot$ C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub> radicals, but Emdee et al. [2] proposed a fast rearrangement of this species to give  $\cdot$ H atoms and benzene (56). We propose here that betascissions from this radical can also lead to the opening of the ring and to the formation of small linear unsaturated species (57,58).

#### Secondary Mechanism

Apart from the additions of H-atoms, which lead to •CHO radicals and benzene (62), the reactions of benzaldehyde molecules involve the formation of the resonance-stabilized benzoyl radicals by unimolecular (60) and bimolecular (61) initiations and by metatheses with H-abstraction (63–77). Benzoyl radicals decompose to produce phenyl radicals and carbon monoxide (78).

Benzyl hydroperoxide molecules can easily decompose by rupture of the O–OH bond (79), and a rate constant can be estimated by analogy with that proposed for alkyl hydroperoxide molecules [53]. This reaction leads to the formation of ·OH and alcoxy benzyl radicals.

Apart from the additions of H-atoms, which lead to methyl radicals and phenol (82), the reactions of cresol molecules involve the formation of two resonance-stabilized radicals,  $\cdot OC_6H_4CH_3$  (cresoxy) and HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>·, by bimolecular initiations (80 and 81, respectively) and by metatheses with H-abstraction (83-92 and 93-108, respectively). For the formation of  $HOC_6H_4CH_2$ · radicals, the rate parameters are deduced from those used from toluene and for the formation of cresoxy radicals from those used for phenol. The reactions deriving from  $HOC_6H_4CH_2$ · radicals (109–123) are deduced from the major steps deriving from benzyl radicals.

Apart from the additions of H-atoms, which lead to  $\cdot$ CH<sub>2</sub>OH radicals and benzene (126) and the bimolecular initiation (125) leading to benzyl alcoxy and  $\cdot$ HO<sub>2</sub> radicals, the reactions of benzyl alcohol molecules involve the formation of the resonancestabilized  $\cdot$ C<sub>6</sub>H<sub>5</sub>CHOH radicals by bimolecular initiation (124) and by metatheses with H-abstraction (127–143).  $\cdot$ C<sub>6</sub>H<sub>5</sub>CHOH radicals can decompose to hydrogen atoms and benzaldehyde (144).

In the case of ethylbenzene molecules, the additions of H-atoms lead to  $\cdot C_2H_5$  radicals and benzene (149). Unimolecular (146) and bimolecular initiation (147) and metatheses with H-abstraction (150– 162) involve the formation of the resonance-stabilized  $\cdot C_6H_5CHCH_3$  radicals. We have also considered the formation of  $\cdot C_6H_5CH_2CH_2$  radicals by bimolecular initiation (148) and by metatheses with H-abstraction (163–167). Both radicals lead to the formation of styrene, by decompositions involving the breaking of a C—H bond (168–169) or by reaction with oxygen molecules (171,172) or combine with  $\cdot$ HO<sub>2</sub> radicals (173,174) to give hydroperoxide molecules, which quickly decompose.  $\cdot C_6H_5CH_2CH_2$  radicals can also decompose to give ethylene and phenyl radicals (170).

In the case of styrene molecules, the reactions have been derived from those proposed for 1,3-butadiene [24] and include a bimolecular initiation (175), additions of  $\cdot$ O· atoms (176) and  $\cdot$ OH radicals (177) to the double bond, and metatheses with H-abstraction involving the formation of  $\cdot$ C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub> radicals (178, 181), which can react with oxygen molecules to give formaldehyde and benzoyl radicals (182).

In the case of bibenzyl molecules, we have only considered the formation of the resonance-stabilized  $\cdot C_6H_5CHCH_2C_6H_5$  radicals by unimolecular (183) and bimolecular (184) initiation and by metatheses with H-abstraction (185–192).  $\cdot C_6H_5CHCH_2C_6H_5$  radicals can decompose to hydrogen atoms and stilbene (193). The formation of stilbene from the recombination of benzyl radicals has been proposed by Hippler et al. [32].

# COMPARISON BETWEEN COMPUTED AND EXPERIMENTAL RESULTS

Simulations were performed using the CHEMKIN II software [23]. We have tried to reproduce the

experimental data described in this paper (jet-stirred reactor and shock tube), but to extend the validity of the proposed mechanism, we have also attempted to model results of the literature obtained in other shock tubes in a wider pressure range (from 2.4 to above 600 bar) [14–16] and in a flow tube [12,13]. The mechanism presented here before has been used for all the different performed simulations.

# **Perfectly Stirred Reactor**

Figures 1 to 3 display comparisons between the experimental (symbols) and computed (lines) results for some of the experiments performed in a jet-stirred reactor. Figures 1 and 2 show that our mechanism leads to an acceptable agreement for the conversion of toluene and the formation of the two major primary products, benzene and benzaldehyde, and for that of carbon monoxide, under all the conditions studied, apart from that the modeled increase in the concentration of benzene is steeper than the experimental one for an equivalence ratio of 0.9 and the formation of carbon monoxide is underestimated by a factor 2 at 893 K and for an equivalence ratio of 0.45. As an example of the agreement obtained, Figs. 2 and 3 present the simulated profiles of oxygen and products at 893 K and for an equivalence ratio of 0.45; the same kind of agreement can be obtained in other conditions. Conversion of oxygen and the formations of minor primary products, phenol, benzyl alcohol, and ethylbenzene are also correctly reproduced. Bibenzyl is systematically overestimated, irrespective of residence time, which is probably indicative of a condensation problem for this compound before it enters the trap. As regards the nonprimary products, the formation of styrene, allene, carbon dioxide, and methane are satisfactorily reproduced, while the production of C<sub>2</sub> compounds is underpredicted at short residence times and correctly modeled at long residence times. At 893 K, at an equivalence ratio of 0.45 and a residence time of 4 s, C<sub>2</sub> compounds contain 52% acetylene and 48% ethylene. The profiles of propene and butadiene are seriously underpredicted whatever the residence time.

#### **Shock Tubes**

Computed results for our shock tube appear in Fig. 4. It is worth noting that the experimental OH emission at 306 nm is related to the electronically exited OH population and is not directly proportional to OH radical concentration. Nevertheless, previous work [24] has shown a correct agreement between the shapes of the profiles of experimental emission and calculated OH concentration during the rise of the signal, which is

the important part of the curve for the determination of ignition delays. Both experimentally and theoretically, the ignition delay is determined at 10% of the maximum OH peak. Modeled results reproduce the systematic trends of the measurements, including variations in ignition delay times with temperature, equivalence ratio, and concentration of toluene. While the global agreement is better than that obtained with the mechanism of Pitz et al. [22], it deteriorates when temperature increases, for the most concentrated mixtures, 1.25% of toluene and  $\Phi$  equal to 0.5 or to 1. In these cases, computed times can be up to three times longer than the experimental values. This could be due to the fact that the dilution of the mixtures (76.25% of Ar for the most concentrated mixture) is low enough for non-ideal processes starting to occur. That could explain why the agreement is correct in stoichiometric mixtures at 0.5 of toluene and not at 1.25% of toluene as shown in Fig. 4b.

Ignition delay times behind reflected shock waves have been also measured by Burcat et al. [16] for pressures between 2.4 and 7 bar and by Pengloan et al. [14,17] at 1.1 bar. Figures 4b and 5a show that our mechanism allows us to reproduce the results obtained by Burcat et al. [16] very accurately, whatever the pressure. The agreement in the case of the results of Pengloan et al. [14,17] deteriorates slightly, but is still acceptable.

Sivaramakrishnan et al. [15] have measured the consumption of the organic reactant and the formation of carbon monoxide, benzene, and acetylene during the oxidation of toluene behind reflected shock wave in a single pulse shock tube at a pressure in excess of 600 bar and in a temperature range from 1250 to 1450 K. Figure 6 shows that our mechanism is able to correctly reproduce these results, apart from the formation of carbon monoxide and acetylene at the highest temperatures. As Sivaramakrishnan et al. [15] consider that the residence time in the reaction zone was between  $1.5 \pm 0.1$  ms, we have used a value of 1.5 ms in our simulations.

#### **Flow Reactor**

Brezinsky et al. [12] have studied the oxidation of toluene in a flow reactor at 1180 K, at atmospheric pressure, with nitrogen as bath gas, for a concentration of toluene of 1400 ppm and for two equivalence ratios, 0.63 and 1.4. Figures 7 and 8 display comparisons between the experimental (symbols) and computed (lines) results at  $\Phi$  equal to 0.63 and 1.4, respectively, and show that a globally correct agreement can be observed in both cases. The model can satisfactorily reproduce the consumption of toluene and the



**Figure 5** Autoignition delays of toluene in a shock tube at 1.1 and 2.4 bar. Semilog plot of experimental (symbols) and computed (lines) ignition delays as a function of temperature behind the reflected shock wave for the experimental results obtained by Burcat et al. [16] at 2.4 bar for different mixtures (a) and those of Pengloan et al. [14,17] at 1.1 bar, at 0.4% of toluene and different equivalence ratios (b).



**Figure 6** Oxidation of toluene in a shock tube at 613 bar and  $\Phi = 5$ . Comparison between experimental (symbols) and computed (lines) concentration of species versus temperature at an estimated residence time of 1.5 ms and an initial concentration of toluene of 14 ppm [15].

formation of benzene, benzaldehyde, ethyl benzene, styrene, cresols ethylene, methane, and carbon monoxide. The production of phenol is well simulated at  $\Phi$ equal to 1.4, while it is strongly overestimated for the longest residence times at  $\Phi$  equal to 0.63. The formation of acetylene is correctly simulated at  $\Phi$  equal to 0.63, while it is overestimated by a factor around 2 at  $\Phi$  equal to 1.4. The production of benzyl alcohol is overestimated by a factor around 2 in both cases.

Our model leads to a global agreement similar to that obtained by Lindstedt and Maurice [21]; but it is worth noting that unlike these authors, we have not found it necessary to introduce a time shift, just as in our previous modeling of the oxidation of benzene [11] in the same apparatus.

# ANALYSIS OF THE MECHANISM AND DISCUSSION

The fluxes and sensitivity analyses presented hereafter have been performed with the mechanism described previously and the accuracy of conclusions derived from them can only reflect the accuracy of the proposed reaction channels and of the used thermodynamic and kinetic data.

Figures 9a and 10 present sensitivity and fluxes analysis computed in a jet-stirred reactor at 893 K, Figs. 9b and 11 present sensitivity and fluxes analysis computed in a flow reactor at 1180 K, and Figs. 9c and 12 present sensitivity and fluxes analysis computed in a shock tube. As already shown in previous studies [11,24,25], Fig. 9c demonstrates the determinant role for ignition delays of the branching reaction between ·H atoms and oxygen molecules.

# Main Reaction Pathways of Toluene Molecules

In all cases, toluene reacts by four main channels, metatheses by H  $\cdot$  and  $\cdot$ O  $\cdot$  atoms, OH  $\cdot$ , methyl, HO<sub>2</sub>  $\cdot$ , phenoxy, and cresoxy radicals to form benzyl radicals (7–11, 21, 23 (reaction numbers refer to Table V)), metatheses by OH· radicals to form methylphenyl radicals (27), addition of  $\cdot O \cdot$  atoms to give cresoxy radicals and H $\cdot$  atoms (5), and addition of H $\cdot$  atoms to form benzene and methyl radicals (4). In a perfectly stirred reactor at 893 K, metatheses giving benzyl radicals account for 61% of the toluene consumption, while 18% is due to the addition of .O. atoms, 14% to metatheses giving methylphenyl radicals, and 7% to the addition of H. atoms. This last channel is favored when equivalence ratio or temperature increases, while the ratio between the three other channels does not depend much on temperature or equivalence ratio. In a shock tube



Figure 7 Oxidation of toluene in a flow reactor at 1180 K and at  $\Phi = 0.63$  [12]. Comparison between experimental (symbols) and computed (lines) mole fraction of species versus residence time.

at 1800 K, 30% of toluene also decomposes to phenyl and methyl radicals (2).

Figure 9 shows that, in all cases, the metatheses leading to the formation of the resonance-stabilized benzyl radicals have a strong inhibiting effect, while the metathesis involving to the production of methylphenyl radicals has a promoting effect, as these radicals mainly react through branching step with oxygen molecules to give  $\cdot O \cdot$  atoms and cresoxy radicals. The important sensitivity coefficient of these reactions shows that it is important to take them into account in the mechanism.

In a flow tube at  $\Phi = 1.4$ , the decomposition of benzyl radicals to phenyl and methyl radicals has an important promoting effect, while it contributes for only 6% of the consumption of toluene. The rate constant that we use for this reaction allows us considerably to improve our simulations in these conditions, both for the conversion of toluene and for the formation of products deriving from methyl radicals, methane, and ethylbenzene.

At 893 K, the main ways of production of propene and 1,3-butadiene, which are strongly underestimated in our simulations, are the metatheses of allyl and i-C<sub>4</sub>H<sub>5</sub> radicals with toluene. The formation of these radicals derives from the decomposition of C<sub>5</sub> cyclic compounds, such as cyclopentadienyl radicals or cyclopentadienone, which are still not well understood.



Figure 8 Oxidation of toluene in a flow reactor at 1190 K and at  $\Phi = 1.4$  [12]. Comparison between experimental (symbols) and computed (lines) mole fraction of species versus residence time.

# **Reactions Deriving from the Formation** of Benzyl Radicals

In all cases, benzyl radicals react mainly by termination steps with  $\cdot O \cdot$  atoms and with  $OH \cdot$ , methyl, and  $HO_2 \cdot$  radicals and with themselves (34–39). In a perfectly stirred reactor, the major recombination is that with  $HO_2 \cdot$  radicals producing benzylhydroperoxide molecules, which rapidly yield alcoxybenzyl radicals (79), which decompose to produce benzaldehyde and H· atoms (53) or formaldehyde and phenyl radicals (54). As it enables the very stable benzyl radicals to be transformed into the reactive H· atoms, the recombination of benzyl and HO<sub>2</sub>· radicals is the reaction with the strongest accelerating effect at 893 K.

The reactions of phenyl and derived radicals are not presented in great detail in Figs. 10–12, because



**Figure 9** Sensitivity analyses related to (a) the conversion of toluene in a jet-stirred reactor, at 893 K and a residence time of 4 s, (b) the mole fraction of carbon monoxide in a flow reactor [12] at 1180 K and a residence time of 0.02 s, and (c) the mole fraction of hydroxyl radicals in a shock tube at  $\Phi = 1$ , 8.7 bar and 0.5% of toluene and a residence time corresponding to 50% conversion of toluene (for the clarity of the figure, only reactions, with an absolute value of the sensitivity coefficient above a given threshold depending on the studied reactor, are shown).



Figure 10 Oxidation of toluene in a jet-stirred reactor at 893 K. Flux analysis at  $\Phi = 0.5$  and a residence time of 4 s.





Figure 12 Oxidation of toluene in a shock tube at 1800 K. Flux analysis at  $\Phi = 1, 8.7$  bar and 0.5% of toluene and a residence time corresponding to 50% conversion of toluene.

they are similar to what was observed during our previous study of the oxidation of benzene [11]. They react mainly with oxygen molecules to give benzoquinone, which yields cyclopentadienone by CO elimination or phenoxy radicals, which lead to phenol at 893 K and to cyclopentadienyl radicals by CO elimination at 1180 and 1800 K. As the production of benzoquinone occurs mainly through the formation of peroxyphenyl radicals, it decreases with temperature. At 1180 K, cyclopentadienyl radicals react mainly with oxygen molecules to produce C<sub>4</sub>H<sub>4</sub>O and carbon monoxide, while at 1800 K, it yields 1,3-butadiene and carbon monoxide. From 1180 K, the major recombination is that with  $\cdot$ O· atoms yielding benzaldehyde and H· atoms (35). Figure 9 shows that the rate constant of this reaction is a sensitive parameter under the experimental conditions of the flow reactor. The recombination giving phenyl radicals and formaldehyde is less important (36). Benzaldehyde reacts mainly by metatheses with OH-radicals to give benzoyl radicals (65), which decompose to produce phenyl radicals and carbon monoxide (78).

The recombination of benzyl radicals giving bibenzyl is important at 893 K, but decreases with temperature, while the recombination of benzyl radicals with methyl radicals to form ethylbenzyl is optimum at 1180 K and that with OH· radicals to produce benzyl alcohol is favored at 1800 K. Ethylbenzene reacts mainly by metatheses with H· atoms and OH· radicals to form the resonance-stabilized  $\cdot C_6H_5CHCH_3$ radicals (150, 152), which decompose to give styrene and H· atoms (168). At 1180 K,  $\cdot C_6H_5CH_2CH_2$  radicals are formed (163, 164) and lead to the production of styrene (169) and of ethylene and phenyl radicals (170).

At 893 K, 2% of benzyl radicals react with oxygen molecules to give peroxybenzyl radicals (32), which isomerize and decompose to give benzaldehyde and H-atoms (48). At 1800 K, 13% of benzyl radicals decompose to give cyclopentadienyl radicals and acetylene (30).

# **Reactions Deriving from the Formation** of Cresoxy Radicals

At 893 K, resonance-stabilized cresoxy radicals react mainly by disproportionation with  $\cdot$ HO<sub>2</sub> radicals (80) or by H-abstraction with phenol to form cresols (92). The reaction of cresoxy and ·HO<sub>2</sub> radicals is the reaction with the strongest inhibiting effect at 893 K. According to our simulations, cresols should have been important primary products under our experimental conditions; the fact that we have not observed them could be due to condensation problems for these compounds before the entrance of the trap, as in the case of bibenzyl. It is also worth noting that the rate constants of the reactions involved in the formation and the consumption of cresols are mostly estimated and that, at this low temperature, there are large uncertainties concerning the reactions forming or consuming O atoms. At higher temperatures, cresols are mainly formed by recombination between H. atoms and cresoxy radicals

The abstractions of the hydroxylic H-atom by  $\cdot O_{\cdot}$  (84) atoms and OH $\cdot$  (85) and  $\cdot HO_2$ , at 893 K, radicals (86) to give back cresoxy radical are important reactions of cresols accounting for 75% of their consumption at 893 K. This is due to the fact that cresoxy radicals are resonance stabilized. Cresols can also react by abstraction of the benzylic H-atoms by H $\cdot$  (93) and  $\cdot O \cdot$  (94) atoms and OH $\cdot$  (95) radicals to form hydroxybenzyl radicals, which can recombine with  $\cdot HO_2$  radicals (112) and ultimately lead to the production of hydroxybenzaldehyde or carbon monoxide and cyclopentadienone.

Cresoxy radicals can also react by CO elimination to give benzene and H $\cdot$  atoms (56), acetylene, vinylacetylene, and H $\cdot$  atoms (57) or allene and propargyl radicals (58). The importance of these reactions, which are responsible for most of the formation of acetylene and allene at 893 K, increases with temperature.

#### CONCLUSION

This paper presents new experimental results for the oxidation of toluene in a jet-stirred reactor at temperatures from 873 to 923 K and in a shock tube between 1305 and 1795 K and proposes a detailed mechanism able to reproduce these data, but also previously published experiments in others shock tubes [14–17] and in a flow reactor [12,13].

The reactions of importance in this mechanism have been determined by using flux and sensitivity analyses. Amongst them, the reactions of cresols, styrene, and related radicals are yet very uncertain and should be subject of studies for specialists of elementary reactions to progress toward a better modeling of the oxidation of aromatic compounds.

Despite the uncertainties in the chemistry of some species, the mechanism proposed here constitutes a first basis in the further development of models for the oxidation of other aromatic compounds, such as xylenes or methylnaphthalenes. It could also be included in a wider model to reproduce the oxidation and autoignition of surrogate fuel mixtures (e.g. *n*-heptane–toluene mixtures), but that should be done carefully at low temperature as this model has not been validated below 893 K.

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