Published in final edited form as:

Proc Combust Inst. 2011 January ; 33(1): 233–261. doi:10.1016/j.proci.2010.06.063.

A detailed kinetic modeling study of toluene oxidation in a premixed laminar flame

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Abstract

An improved chemical kinetic model for the toluene oxidation based on experimental data obtained in a premixed laminar low-pressure flame with vacuum ultraviolet (VUV) photoionization and molecular beam mass spectrometry (MBMS) techniques has been proposed. The present mechanism consists of 273 species up to chrysene and 1740 reactions. The rate constants of reactions of toluene decomposition, reaction with oxygen, ipso-additions and metatheses with abstraction of phenylic H-atom are updated; new pathways of C₄ + C₂ species giving benzene and fulvene are added. Based on the experimental observations, combustion intermediates such as fulvenallene, naphthol, methylnaphthalene, acenaphthylene, 2-ethynylnaphthalene, phenanthrene, anthracene, 1-methylphenanthrene, pyrene and chrysene are involved in the present mechanism. The final toluene model leads to an overall satisfactory agreement between the experimentally observed and predicted mole fraction profiles for the major products and most combustion intermediates. The toluene depletion is governed by metathese giving benzyl radicals, ipso-addition forming benzene and metatheses leading to C₆H₄CH₃ radicals. A sensitivity analysis indicates that the unimolecular decomposition via the cleavage of a methyl C-H bond has a strong inhibiting effect, while decomposition via C-C bond breaking, ipso-addition of H-atom to toluene, decomposition of benzyl radicals and reactions related to C₆H₄CH₃ radicals have promoting effect for the consumption of toluene. Moreover, flow rate analysis is performed to illustrate the formation pathways of mono- and polycyclic aromatics.

Keywords

Detailed kinetic modeling; Toluene; Premixed laminar flame; PAH

1. Introduction

Aromatic compounds are major components of many practical fuels such as gasoline, diesel and jet fuels, and understanding their combustion kinetics is important in the design of efficient engines and in the abatement of atmospheric pollution [1]. Among the aromatic compounds, toluene is often the largest single aromatic component in gasoline and in premium gasoline the toluene mole fraction is as high as 35% [2]. In addition, toluene can be easily produced from the oxidation of other hydrocarbons and it serves as a key precursor leading to the formation of polyaromatic hydrocarbons (PAH) and soot. The combustion

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chemistry of toluene is also of interest because of the toxicity of toluene [3] and its oxidation compounds.

Despite the great abundance of models concerning the oxidation of toluene [4-10], the lack of toluene flame data prevents the literature models to be validated under flame conditions. Therefore, the toluene degradation chemistry is not so well established under flame conditions and uncertainties still remain in the existing mechanisms. To our knowledge, only three studies were carried out on such purposes, by Lindstedt and Maurice [6], El Bakali et al. [11] and Detilleux and Vandooren [12]. Recently, Li et al. [13] reported a detailed chemical structure of a fuel-rich toluene flame measured with molecular-beam mass spectrometry (MBMS) and tunable synchrotron VUV photoionization techniques. Many intermediates especially radicals and isomers that they identified were neither measured nor evaluated by models previously.

The objective of this work is to develop a comprehensive model for toluene oxidation under flame conditions, based on the newly reported flame data obtained by Li et al. [13]. The improved mechanism will provide a more complete model for toluene combustion. It could improve the understanding of the combustion of gasoline and jet fuels and of the formation of soot precursors which lead to pollutant emissions.

2. Chemical kinetic modeling

Simulations were performed using Chemkin Premix codes [14]. The kinetic scheme developed here is an extension of our mechanism of aromatic compounds combustion [10], the latest version of which has been recently validated using data obtained with a premixed flame containing indane [15]. Table 1 lists the modification and addition made to the latest model and the full mechanism is available as supplementary material.

The mechanism was updated in several aspects. The rate constants of the unimolecular (R1 and R2, see Table 1) and bimolecular initiations of toluene (R3) were replaced by values determined by Oehlschlaeger et al. [16-17]. The rate constants of two metatheses (R8 and R9) with abstraction of phenylic H-atom were renewed based on newly published data [18-19]. The rate constants of reactions R7 and R10 were adopted from similar reactions R16 and R19, respectively. The kinetics of reactions of bibenzyl ($C_{14}H_{14}$) and related radicals (R11-R15) were taken from Sakai et al. [20]. The ipso-addition of OH to toluene, forming phenol and methyl radical (R7), was added with the kinetics reported by Seta et al. [18]. The metathesis reaction of toluene with CHO radical (R21) was considered with the rate constant proposed by Mehl et al. [21]. The new formation pathways of $C_4 + C_2$ giving benzene and fulvene proposed by Hansen et al. [22] were used (not shown in Table 1).

To reproduce the formation and consumption of large combustion intermediates, namely methylnaphthalene, acenaphthylene, 2-ethynylnaphthalene, phenanthrene, anthracene, 1-methylphenanthrene, pyrene and chrysene, which were not considered in our previous mechanism [15], reactions proposed by Slavinskaya et al. [23] have been added (not listed in Table 1). Moreover, two new species, fulvenallene ($C_5H_4CCH_2$) and naphthol have been considered based on the experimental observations. Their kinetic schemes are analogous to those of allene (R23-31) and phenol (R32-38), respectively.

Another key feature of the present model is the inclusion of new, theoretically based rate constants of metatheses and ipso-addition of benzene and toluene, namely reactions R4-R6, R16 and R19. The rate constants of these five reactions were determined using *ab initio* calculations, which was performed with the CBS-QB3 method implemented in Gaussian03 [24]. Frequency analysis was used to determine one imaginary frequency for each transition state (TS) with the mode of vibration corresponding to the reaction coordinate. Hindered

rotors were taken into account and barrier heights have been calculated at the B3LYP/6-31G(d,p) level. Tunneling effect was considered for H-transfer from the relation given by Skodje and Truhlar [25]. The kinetic parameters were obtained from transition state theory and by fitting for several temperatures (400–2000 K) with a modified Arrhenius form. The comparisons of these calculated rates with some previous ones are demonstrated in Figs. S1–S4 in the supplementary material.

3. Results and discussion

3.1 Flame chemical structure

The detailed kinetic mechanism was tested by comparing simulated results with experiments performed by Li et al. [13]. The reported experimental temperature profile was used as input for simulations. To account for the perturbations induced by the quartz probe and the thermocouple [26], the temperature profile was shifted 2.5 mm away from the burner surface.

Figure 1 displays the mole fraction profiles of the major species (toluene, O₂, Ar, H₂, H₂O, CO, and CO₂), and a good agreement is observed between predicted and experimental results. Our model slightly underpredicts the production of CO and overpredicts the level of CO₂ in the post-flame zone. However, these differences are within the experimental error which was $\pm 10\%$ for major species, $\pm 25\%$ for intermediates with known photoionization cross sections and about a factor of two for those with estimated cross sections [13].

The mole fraction profiles of common combustion intermediates are shown in Figs. 2–4. Figure 2 presents the mole fraction profiles for species C₃. Our mechanism makes fairly good predictions for the experimental concentrations of methane, ethylene, ketene (C₂H₂O) and allene (aC₃H₄) while it tends to overpredict the peak values of propyne (pC₃H₄), methyl and vinyl radicals. Although not reported by Li et al. [13], mass 42 could contain the contribution of propene (C₃H₆). The modeling result shows that C₂H₂O is the dominant species for mass 42 and the contribution of C₃H₆ is negligible. The model captures well the shape of acetylene (C₂H₂) profile before its maximum value. However, the maximum concentration of C₂H₂ is underpredicted and a tail is observed further than 12.0 mm from the burner surface, which could be due to unidentified issues with the mechanism in the post flame zone. A similar tail was exhibited for predicted C₂H₂ profile in modeling fuel-rich 1,3-butadiene flames by Hansen et al. [22]. For propargyl radical (C₃H₃), the mole fraction profile is fairly predicted when experimental uncertainties are taken into account.

Figure 3 summarizes the mole fraction profiles of C₄–C₇ and three oxygenated species. The predicted peak values of the two C₄H₄ isomers, vinylacetylene (vC₄H₄) and butatriene (tC₄H₄) reveals that vC₄H₄ is dominant for mass 52, which is in agreement with experimental observations. The modeled maximum concentration of 1,3-butadiene (1,3-C₄H₆) is located about 1.6 mm downstream compared to the corresponding experimental value, which could result from measurement uncertainties since the reaction path analysis identified the reaction of cyclopentadienyl radicals (C₅H₅#) with OH radicals to be the major formation route of 1,3-C₄H₆ and C₅H₅# is well predicted. Besides C₅H₅#, the model performs well at predicting the mole fraction profiles of benzene (C₆H₆#), phenyl (C₆H₅#), and benzyl radicals (C₇H₇). With the formation pathways proposed by Hansen et al. [22], fulvene (fC₆H₆) mole fraction is underpredicted by a factor of ten. The predicted mole fraction profile of fulvenallene, which is well reproduced in another low pressure fuel-rich toluene flame [12] using the present model (see Fig. S5 in supplemental material), is one-fifth of the experimental one. However, the experimental error cannot be ruled out since the photoionization cross sections of fulvene and fulvenallene are estimated [13].

For the oxygenated species, the formation of benzylalcohol ($C_6H_5CH_2OH$) is fairly predicted while that of phenol (C_6H_5OH) tends to be underpredicted across the flame zone. However, measurement uncertainties cannot be ruled out, especially since both $C_6H_5\cdot$ and benzyl radicals, their major sources, are well captured by the present model. There is a big difference (3.8 mm) between the predicted and measured locations of the peak concentration of benzaldehyde (C_6H_5CHO). The experimental C_6H_5CHO profile is obtained by subtracting contributions of three C_8H_{10} species [13], a process that could introduce larger experimental error. Our mechanism makes fairly good reproduction of the mole fraction profiles including that of benzaldehyde in a CH_4 /toluene doped flame [11] (see Figs. S6 and S7 in supplemental material), which gives some confidence in the model's predictions.

Figure 4 compares the predicted mole fraction profiles of C_8 - C_{14} species with the measurements. The mono- and polycyclic aromatics such as indenyl radical (C_9H_7), naphthalene ($C_{10}H_8$) and phenanthrene ($pC_{14}H_{10}$) are predicted accurately and reasonable predictions are made for ethylbenzene (eC_8H_{10}) and methylnaphthalene ($C_{11}H_{10}$). Contributions from styrene (sC_8H_8) are underpredicted by a factor of more than two, which could be resulted from measurement uncertainties since the current model make good predictions for sC_8H_8 in both pure toluene [12] and CH_4 /toluene [11] flames (see Figs. S5 and S7 in supplemental material). For mass 106, Li et al. assigned the threshold 8.47 eV to the ionization of *p*-xylene [13]. However, *o*-xylene ($o-C_8H_{10}$), which is an isomer and has close ionization energy to *p*-xylene ($p-C_8H_{10}$), could contribute to this threshold. The predicted peak concentration of *o*-xylene is five times larger than that of *p*-xylene and the experimental profile of C_8H_{10} compounds is fairly captured by that of *o*-xylene. Hence, *o*-xylene is assigned as the dominant contributor to this threshold. For C_8H_9 (mass 105), the two isomers, 4-methylbenzyl (not considered in the model) and 1-phenylethyl (C_8H_9) radicals were not distinguished experimentally [13]. However, another isomer, *o*-methylbenzyl ($o-C_8H_9$) radical which has close ionization energy could also contribute to mass 105. The predicted *o*- C_8H_9 profile is in good agreement with the experimental C_8H_9 profile, indicating *o*- C_8H_9 is the dominant species. Three species, indane (C_9H_{10}), 2-ethynylphenol (not considered in the model) and benzofuran (C_8H_6O) were reported to contribute to mass 118 [13]. However, the predicted maximum mole fraction of indane (3.0×10^{-8}) is much smaller than the experimental peak value of mass 118 (6.6×10^{-5}). Since the indane mechanism made correct predication for indane and indene for both premixed flame and jet-stirred reactor results [15], we deem it more reasonable to attribute mass 118 to benzofuran (bC_8H_6O). For mass 144, it could contain the contribution of both 1,2,3,4-tetrahydro-1-methylene-naphthalene (not considered in the model) and naphthol ($C_{10}H_8O$).

3.2 Ways of toluene consumption

Figures 5 and 6 present sensitivity and flux analysis for the consumption of toluene at a temperature of 1510 K and 78.9% conversion. The sensitivity result displayed in Fig. 5 (C_0 - C_2 reactions are not shown except for $O_2 + H = OH + O$ which has the most important promoting effect) indicates that the unimolecular decomposition via cleavage of a methyl C-H bond has a strong inhibiting effect on toluene consumption, while decomposition via C-C breaking, ipso-addition, decomposition of benzyl radicals and reactions related to $C_6H_4CH_3$ radicals have promoting effect. These results are consistent with the conclusion that the formation of benzyl and $C_6H_4CH_3$ radicals have respective inhibiting and promoting effect deduced from the results obtained in a jet-stirred reactor at 893 K [10].

As shown in Fig. 6, the major route of toluene consumption in the flame is metatheses by H, OH and CH_3 to produce the resonance-stabilized benzyl radicals. Besides reverse reaction to toluene, benzyl radicals are mainly consumed through two pathways, thermal decomposition to C_2H_2 and $C_5H_5\cdot$ and addition of O-atom to give C_6H_5CHO . Benzyl radicals are also an important source of benzylalcohol by OH termination and ethylbenzene through

combination with CH_3 radical. Moreover, benzyl radicals can decompose to $\text{C}_5\text{H}_5\text{CCH}$ which further reacts yielding $\text{C}_5\text{H}_4\text{CCH}_2$.

Two less important channels, ipso-addition forming benzene and metatheses giving $\text{C}_6\text{H}_4\text{CH}_3$ radicals account for 11.6% and 11.2% of the toluene consumption, respectively. The flow rate analysis identifies the ipso-addition of H-atom as the major formation pathway of benzene. The importance of this reaction was confirmed by Dagaut et al. [9], El Bakali et al. [11] and Detilleux and Vandooren [12]. In a low-pressure CH_4 /toluene flame, El Bakali et al. reported that toluene was mainly consumed by H-abstraction reactions with H and OH and by elimination of CH_3 [11], which is in good agreement with the conclusion given by Dagaut et al. [9] who studied the toluene oxidation in a jet-stirred reactor at 1 atm. Besides producing benzene and benzyl radical, Detilleux and Vandooren concluded that unimolecular decomposition yielding $\text{C}_6\text{H}_5\#$ and CH_3 radicals was another significant consumption channel for toluene combustion in rich conditions [12]. However, all the three groups did not pay attention to the role of $\text{C}_6\text{H}_4\text{CH}_3$ radicals. In our model, reaction of $\text{C}_6\text{H}_4\text{CH}_3$ radicals with oxygen molecule producing *ortho*-benzoquinone ($\text{OC}_6\text{H}_4\text{O}$) and CH_3 radicals plays a more significant role than the reaction $\text{C}_6\text{H}_5\# + \text{O}_2 = \text{OC}_6\text{H}_4\text{O} + \text{H}$ for the formation of $\text{OC}_6\text{H}_4\text{O}$ which can decompose further to 2,4-cyclopentadien-1-one ($\text{C}_5\text{H}_4\text{O}\#$) and finally to CO and C_4H_4 . Besides $\text{OC}_6\text{H}_4\text{O}$, cresoxy radical ($\text{OC}_6\text{H}_4\text{CH}_3$) is another product of the reaction of $\text{C}_6\text{H}_4\text{CH}_3$ radicals with O_2 . Da Silva et al. [1] studied the reaction pathways for $\text{C}_6\text{H}_4\text{CH}_3 + \text{O}_2$ systems and concluded that the dominant products were methyl-dioxo-hexadienyl radicals and $\text{OC}_6\text{H}_4\text{CH}_3 + \text{O}$. They proposed that α -quinone methide (α -QM) was a significant intermediate in toluene combustion [27]. However, α -QM was neither experimentally identified by Li et al. [13] nor reported by El Bakali et al. [11]. In the present mechanism, α -QM was not included. In addition, $\text{C}_6\text{H}_4\text{CH}_3$ is an important source of α -xylene as mentioned above. Other minor pathways of toluene degradation are thermal decomposition giving $\text{C}_6\text{H}_5\#$ and CH_3 , and ipso-addition of O-atom leading to the formation of $\text{OC}_6\text{H}_4\text{CH}_3$, most of which converts to $\text{C}_6\text{H}_6\#$, C_2H_2 , C_3H_3 , aC_3H_4 and C_4H_4 by releasing CO.

3.3 Formation of mono-/polycyclic aromatics

Many mono- and polycyclic hydrocarbons such as benzene, phenylacetylene, styrene, ethylbenzene, indene, naphthalene, methylnaphthalene, phenanthrene, pyrene and chrysene, were experimentally observed in the toluene flame. Li et al. attributed the formation of many aromatic intermediates to the so-called HACA (hydrogen abstraction carbon addition) mechanism [13]. The formation routes of some aromatic species will be discussed from the present simulation results.

Benzene formation pathways were recently reviewed by Hansen et al. [28] and they concluded that the contributions of these channels were dependent on the fuel structure. In the current model, benzene formation is governed by the ipso-addition of H-atom to toluene, and the reaction $\text{OC}_6\text{H}_4\text{CH}_3 = \text{C}_6\text{H}_6\# + \text{H} + \text{CO}$, while in CH_4 /toluene flame [11], the reaction $\text{C}_6\text{H}_5\# + \text{H} = \text{C}_6\text{H}_6\#$ was found to be more significant than the decomposition of $\text{OC}_6\text{H}_4\text{CH}_3$. According to the rate of production analysis, ethylbenzene is mainly formed via the radical combination of benzyl and CH_3 radicals. By H-abstraction, ethylbenzene can convert to 1-phenylethyl radical. Most of styrene comes from the decomposition of 1-phenylethyl radical. The addition of OH to indenyl radicals which was the major source of styrene in indane flame [15] is also an important route for styrene production. The main reactions involved in the formation of phenylacetylene are (a) the decomposition of 1-phenylvinyl radical by breaking a C-H bond, (b) the ipso-addition of C_2H radical to benzene and (c) the addition of phenyl radical to C_2H_2 .

All the reaction pathways of indene in this mechanism were adopted from [15]. The production of indene occurs via the combination of H-atom and indenyl radical which comes from the reaction of C_4H_2 and $C_5H_5\#$. While the indane mechanism has been validated in our recent work [15], the reaction $C_4H_2 + C_5H_5\# \Rightarrow$ indenyl does not include pressure fall-off effects, which needs further investigation. Modeling shows that at low temperatures, naphthalene is mainly formed by the combination of benzyl and propargyl radicals, while at high temperatures (> 1000 K), the combination of cyclopentadienyl radicals is the major source. This is opposite to the conclusion obtained in non-premixed flame by McEnally and Pfefferle [29]. Previously, Lindstedt et al. [30] also considered the naphthalene formation pathways involving $C_5H_5\# + C_5H_5\#$, $C_6H_5\# + C_4H_4$, benzyl + C_3H_3 and ethenylphenyl radical ($p\text{-}C_8H_7$) + C_2H_2 reactions. By modeling the experimental data of low-pressure cyclopentene flame performed by Lamprecht et al. [31], Lindstedt et al. [32] concluded that the addition of C_2H_2 to $p\text{-}C_8H_7$ was the dominant formation path of naphthalene. Compared the rates estimated by Lindstedt et al. [30] and those collected by Slavinskaya and Frank [23] who evaluated the data reported over the last 30 years from 12 independent work groups, both show close rates for reaction $C_8H_7 + C_2H_2$ while the rate of reaction $C_5H_5\# + C_5H_5\#$ given by the latter is about 18 times than that of the former at 1100 K. In both [15] and this work, we used the same rate constant for reactions of naphthalene, involving $C_5H_5\# + C_5H_5\# =$ naphthalene and benzyl + $C_3H_3 =$ naphthalene + $2H$ as those gathered in [23]. In the fact that in [15] and the current work, both $C_5H_5\#$ and naphthalene were fairly well predicted, leading us to think these reactions and their rate constants are reasonable. However, further confirmation is still needed. Based on theoretical calculation, Kislov and Mebel [33] proposed that pentafulvalene was the dominant product of $C_5H_5\#$ recombination at $T > 1500$ K and naphthalene was a minor product. However, the calculated ionization energy of pentafulvalene is 7.81 eV (B3LYP/6-311G(d,p), [24]) and only one threshold at 8.18 eV was reported experimentally for mass 128 [13], indicating that scarce pentafulvalene is formed in the flame.

The formation of naphthyl from H-abstraction of naphthalene is an important route in the molecular growth process. The reactions of naphthyl with CH_3 radicals are responsible for the formation of methylnaphthalene. Phenanthrene ($C_{14}H_{10}$) production proceeds mostly through the reaction of naphthalene with C_4H_2 via HACA sequence. The major consumption routes of phenanthrene involve decomposition reactions leading to acenaphthylene and C_2H_2 , isomerization to give anthracene, and O/OH addition to form ethynylnaphthalene. In addition to phenanthrene, the reactions of indenyl with propargyl radicals and of naphthalene with C_2H radicals exhibit noticeable contribution for the ethynylnaphthalene production. Moreover, pyrene and chrysene can be originated from the addition (via HACA sequence) of C_2H_2 to acenaphthylene, and of C_4H_2 to phenanthrene, respectively.

4. Conclusion

A detailed toluene combustion model has been developed by updating the oxidation kinetics of toluene and evaluating a low-pressure premixed laminar flame. The predictions by the present mechanism are in reasonable agreement with the experimental results for both major products and combustion intermediates. On the basis of the predicted mole fraction profiles, some chemical structures are reassigned. The results indicate that toluene consumption mainly proceeds via the formation of benzene, benzyl, and $C_6H_4CH_3$ radicals. Benzene formation is governed by ipso-addition of H-atom to toluene and decomposition of $OC_6H_4CH_3$ radicals. At low temperature ($T < 1000$ K), naphthalene is mainly formed by the combination of benzyl and propargyl radicals, while at high temperature ($T > 1000$ K), combination of two cyclopentadienyl radicals is the major source of this biaromatic species.

Furthermore, the key reaction pathways of other aromatics are identified by rate production analysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors thank Prof. Fei Qi and Mr. Yuyang Li for providing data and for helpful discussions. This work performed by CNRS-Nancy University was funded by the European Commission through the “Clean ICE” Advanced Research Grant of the European Research Council. The portion of this work supported by Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy and Contract DE-AC52-07NA27344.

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Fig. 1.

Experimental (symbols) and predicted (lines) mole fraction profiles of major species toluene, O_2 , Ar, H_2 , H_2O , CO, and CO_2 , along with the experimental temperature profile applied in the simulations.

Fig. 2. Experimental (symbols) and predicted (lines) mole fraction profiles of (a) CH_3 and CH_4 ; (b) C_2H_2 , C_2H_3 and C_2H_4 ; (c) $\text{C}_2\text{H}_2\text{O}$ (ketene), C_3H_3 (propargyl) and C_3H_6 (propene); (d) aC_3H_4 (allene) and pC_3H_4 (propyne).

Fig. 3. Experimental (symbols) and predicted (lines) mole fraction profiles of (a) vC_4H_4 (vinylacetylene), tC_4H_4 (butatriene) and 1,3- C_4H_6 (1,3-butadiene); (b) $\text{C}_5\text{H}_5\#$ (cyclopentadienyl) and $\text{C}_6\text{H}_5\#$ (phenyl); (c) $\text{C}_6\text{H}_6\#$ (benzene), fC_6H_6 (fulvene), $\text{C}_5\text{H}_4\text{CCH}_2$ (fulvenallene) and C_7H_7 (benzyl); (d) $\text{C}_6\text{H}_5\text{OH}$ (phenol), $\text{C}_6\text{H}_5\text{CHO}$ (benzaldehyde) and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (benzylalcohol).

Fig. 4. Experimental (symbols) and predicted (lines) mole fraction profiles of (a) $s\text{C}_8\text{H}_8$ (styrene), $e\text{C}_8\text{H}_{10}$ (ethylbenzene), $o\text{-C}_8\text{H}_{10}$ (o-xylene) and $p\text{-C}_8\text{H}_{10}$ (p-xylene); (b) $1\text{-C}_8\text{H}_9$ (1-phenylethyl), $o\text{-C}_8\text{H}_9$ (o-methylbenzyl) and C_9H_7 (indenyl); (c) C_9H_{10} (indane), $b\text{C}_8\text{H}_6\text{O}$ (benzofuran), and $\text{C}_{10}\text{H}_8\text{O}$ (naphthol); (d) C_{10}H_8 (naphthalene), $\text{C}_{11}\text{H}_{10}$ (methylnaphthalene) and $p\text{C}_{14}\text{H}_{10}$ (phenanthrene).

Fig. 5. Sensitivity analysis for the conversion of toluene at a distance of 7.8 mm from the burner, corresponding to temperature of 1510 K and 78.9% conversion of toluene.

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Table 1

Modified and added reactions used in the present study. $k = A T^n \exp(-E_a/RT)$, units are mol, s, cm³ and kcal.

RN ^a	Reaction	A	n	E _a	Ref.
<i>Modified reactions</i>					
R1.	Toluene = benzyl + H	2.09E15	0.0	87.51	[16]
R2.	Toluene = C ₆ H ₅ # + CH ₃	2.66E16	0.0	97.88	[16]
R3.	Toluene + O ₂ = benzyl + HO ₂	2.18E7	2.5	46.045	[17]
R4.	Toluene + H = C ₆ H ₆ # + CH ₃	5.67E8	1.43	5.65	<i>b</i>
R5.	Toluene + H = benzyl + H ₂	2.92E6	2.372	5.81	<i>b</i>
R6.	Toluene + CH ₃ = benzyl + CH ₄	3.91E0	3.76	6.98	<i>b</i>
R7.	Toluene + H = C ₆ H ₄ CH ₃ + H ₂	1.22E8	2.031	15.88	<i>c</i>
R8.	Toluene + OH = C ₆ H ₄ CH ₃ + H ₂ O	1.36E4	2.7	0.6196	[18]
R9.	Toluene + HO ₂ = C ₆ H ₄ CH ₃ + H ₂ O ₂	9.2E12	0.0	28.81	[20]
R10.	Toluene + CH ₃ = C ₆ H ₄ CH ₃ + CH ₄	2.07E0	3.861	13.3	<i>c</i>
R11.	2Benzyl = bibenzyl	5.01E12	0.0	0.454	[20]
R12.	Bibenzyl = C ₁₄ H ₁₃ # + H	1.0E16	0.0	83.66	[20]
R13.	Bibenzyl + H = C ₁₄ H ₁₃ # + H ₂	5.4E4	2.5	-1.9	<i>d</i>
R14.	Bibenzyl + benzyl = C ₁₄ H ₁₃ # + toluene	2.2E12	0.0	9.1	[20]
R15.	C ₁₄ H ₁₃ # = stilbene + H	7.94E15	0.0	51.864	[20]
R16.	C ₆ H ₆ # + H = C ₆ H ₅ # + H ₂	1.22E8	2.031	15.88	<i>b</i>
R17.	C ₆ H ₆ # + OH = C ₆ H ₅ # + H ₂ O	1.36E4	2.7	0.6196	[18]
R18.	C ₆ H ₆ # + HO ₂ = C ₆ H ₅ # + H ₂ O ₂	9.2E12	0.0	28.81	<i>e</i>
R19.	C ₆ H ₆ # + CH ₃ = C ₆ H ₅ # + CH ₄	2.07E0	3.861	13.3	<i>b</i>
<i>Added reactions</i>					
R20.	Toluene + OH = C ₆ H ₅ OH# + CH ₃	7.83E2	2.884	3.2193	[18]
R21.	Toluene + CHO = benzyl + HCHO	3.77E13	0.0	23.787	[21]
R22.	Benzyl = C ₅ H ₅ CCH + H	3.16E15	0.0	85.205	[6]
R23.	C ₆ H ₅ C ₂ H ₂ + H = C ₆ H ₅ #C ₂ H + H ₂	1.0E13	0.0	0.0	[6]
R24.	C ₆ H ₅ C ₂ H ₂ + OH = C ₆ H ₅ #C ₂ H + H ₂ O	1.0E13	0.0	0.0	[6]
R25.	C ₅ H ₅ CCH = C ₅ H ₅ # + C ₂ H	4.2E15	0.0	125.0	<i>f</i>
R26.	C ₅ H ₅ CCH + H = C ₅ H ₅ # + C ₂ H ₂	2.0E10	0.0	0.0	[6]
R27.	C ₅ H ₅ CCH + H = C ₄ H ₄ + C ₃ H ₃	6.0E10	0.0	0.0	[6]
R28.	C ₅ H ₅ CCH + OH = C ₅ H ₅ # + CH ₂ CO	4.3E11	0.0	-0.8	<i>f</i>
R29.	C ₅ H ₄ CCH ₂ = C ₅ H ₅ CCH	2.5E12	0.0	59.0	<i>f</i>
R30.	C ₅ H ₄ CCH ₂ + H = C ₅ H ₅ CCH + H	8.5E12	0.0	2.0	<i>f</i>
R31.	C ₅ H ₄ CCH ₂ + OH = C ₅ H ₅ # + CH ₂ CO	2.0E12	0.0	-0.2	<i>f</i>
R32.	Naphthyl + OH = naphthol	1.0E13	0.0	0.0	<i>g</i>
R33.	Naphthol + H = naphthoxy + H ₂	1.2E14	0.0	12.4	<i>g</i>
R34.	Naphthol + O = naphthoxy + OH	1.3E13	0.0	2.9	<i>g</i>
R35.	Naphthol + OH = naphthoxy + H ₂ O	1.4E8	1.4	-0.96	<i>g</i>

RN ^a	Reaction	A	n	E _a	Ref.
R36.	Naphtol + HO ₂ = naphtoxy + H ₂ O ₂	1.0E12	0.0	10.0	^g
R37.	Naphtol + CH ₃ = naphtoxy O + CH ₄	1.8E11	0.0	7.7	^g
R38.	Naphtoxy + H = naphtol	1.0E14	0.0	0.0	^g

^a Note: RN represents reaction number;

^b rate constants are calculated theoretically with CBS-QB3 method with Gaussian03 [24];

^c rate constants taken equal to the values calculated theoretically with CBS-QB3 method with Gaussian03 [24] for similar reactions of benzene;

^d Rate constant estimated by using the correlations proposed by Heyberger et al. [34] in the case of alkenes;

^e rate constant taken equal to the value proposed for reaction R9;

^f rate constants estimated by analogy with the values for C₃H₄ (allene and propyne);

^g rate constants estimated by analogy with the values for phenol.