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Oxidation, ignition and combustion of toluene: Experimental and detailed chemical kinetic modeling[†]

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The oxidation of toluene was studied in a jet-stirred reactor at 1 atm. New experimental results were obtained over the high temperature range 1000–1375 K, and variable equivalence ratio ($0.5 \le \varphi \le 1.5$). Concentration profiles of reactants, stable intermediates and final products were measured by probe sampling followed by online and off-line GC analyses. These experiments were modeled using a detailed kinetic reaction mechanism (120 species and 920 reactions, most of them reversible). This kinetic scheme was also used to simulate the ignition of toluene–oxygen–argon mixtures and the burning velocities of toluene–air mixtures. The presently proposed mechanism has already been validated by simulating the oxidation of benzene at 0.46 to 10 atm under stirred-reactor conditions, the ignition of benzene–oxygen–argon mixtures and reaction path analyses, based on species rates of reaction, were used to interpret the results. The routes involved in toluene oxidation have been delineated: toluene oxidation proceeds *via* the formation of benzene; benzyl oxidation yields benzaldehyde, that further reacts yielding phenyl whereas benzyl thermal decomposition yields acetylene and cyclopentadienyl; further reactions of cyclopentadienyl yield vinylacetylene.

Introduction

Toluene is present in commercial gasoline, it is also easily formed from the oxidation of hydrocarbons and commercial fuels used in S.I. engines, Diesel engines and aircraft. The emissions of toluene via gasoline evaporation and from combustion are of major concern due not only to its own toxicity but also to the formation of other toxic compounds by oxidation in the troposphere.¹ Only a limited number of kinetic studies dealing with the combustion of toluene have been reported in the literature. Burcat et al.^{2,3} measured the ignition delays of simple aromatics including toluene-oxygen-argon mixtures behind a reflected shock wave. The oxidation of toluene was studied in a turbulent plug flow reactor (PFR) at 1 atm and ~1200 K.⁴⁻⁷ The kinetics of toluene oxidation was also studied in a static reactor by addition of toluene to a reacting $H_2 + O_2$ mixture at 773 K.⁸ Davis *et al.*^{9,10} measured the laminar flame speeds of toluene-air mixtures at 1 atm and proposed a kinetic scheme derived from a previous modeling effort⁷ to simulate toluene-air flame speeds and major species measured in a turbulent PFR. The oxidation of toluene and n-butane-toluene mixtures was studied in a turbulent PFR¹¹ and a kinetic mechanism derived from ref. 7 was proposed. A more comprehensive kinetic modeling of toluene pyrolysis and combustion was presented by Lindstedt and Maurice.

The present paper has two main objectives: (i) to obtain new experimental kinetic results for the oxidation of toluene at 1 atm in a jet-stirred reactor (JSR) over a wide range of equivalence ratio and temperature and (ii) to further validate a detailed chemical kinetic reaction mechanism, already successfully used to simulate benzene oxidation, ignition and combustion, against these new experimental results.

Experimental set-up

The JSR experimental set-up used in this work is similar to that described earlier.^{13,14} It consists of a 40 mm diameter sphere (30.5 cm³) made of fused silica (to prevent wall catalytic reactions). It has four nozzles of 1 mm id for the admission of the gases which achieve the stirring. A nitrogen flow of 100 L h^{-1} is used to dilute the fuel. All the gases are preheated before injection, minimizing temperature gradients inside the JSR. A regulated heating wire of ~ 1.5 kW maintains the temperature of the reactor at the desired working temperature. The reactants are diluted by nitrogen (<50 ppm of O_2 and H₂O; <1000 ppm of Ar; <5 ppm of H₂), and mixed at the entrance of the injectors.¹³ High purity reactants were used: oxygen 99.995% and toluene >99.5%. Toluene was thoroughly sonically degassed before use. A piston pump (Isco 100 DM) was used to deliver toluene to an atomizer-vaporizer assembly maintained at 150 °C. Good thermal homogeneity along the whole vertical axis of the reactor was observed for each experiment by thermocouple (0.1 mm Pt-Pt/Rh 10% located inside a thin-wall silica tube) measurements (typical change ≤ 5 K). The reacting mixtures were probe-sampled by means of a low-pressure sonic quartz probe. The samples $(\leq 30 \text{ Torr} \equiv 4 \text{ kPa})$ were taken at steady temperature and residence time and analyzed on-line by means of a GC-MS (Varian Saturn) and off-line, after collection in 1 L Pyrex bulbs. Low vapor-pressure species were analyzed on-line whereas high vapor-pressure compounds and permanent gases were analyzed off-line. The experiments were performed at steady

[†] Electronic supplementary information (ESI) available: Arrhenius parameters for reactions. See http://www.rsc.org/suppdata/cp/b1/ b110282f/

state, at a constant mean residence time, the reactants flowing continually in the reactor, varying stepwise the temperature of the gases inside the JSR. A high degree of dilution was used (0.15% vol. of fuel), reducing temperature gradients in the JSR and heat release (no flame occurred in the JSR).

Several gas chromatographs (GC), equipped with capillary columns (Poraplot U, Molecular Sieve 5A, DB5ms, DB-624, Plot Al₂O₃/KCl, Carboplot P7), a thermal conductivity detector (TCD) and flame ionization detector (FID), were used for stable species measurements. Compound identifications were made *via* GC/MS analyses of the samples. An ion trap detector operating in electron impact ionization mode (GC/MS Varian Saturn) was used. CH₂O and CO₂ were measured by FID after hydrogenation on a Pt/H₂ catalyst connected to the exit of the GC column. A good repeatability of the measurements and a good carbon balance ($\pm 10\%$) were obtained in the present experiments. The uncertainties of the present results obtained by GC analyses were in the range 5–10%.

Modeling

The kinetic modeling of the JSR experiments was performed using the PSR computer code¹⁵ that calculates species concentrations from the balance between the net rate of production of each species by chemical reaction and the difference between the input and output flow rates of species. These rates are computed from the kinetic reaction mechanism and the rate constants of the elementary reactions calculated at the experimental temperature, using the modified Arrhenius equation:

$$k = AT^b \exp(-E/RT)$$

The ignition delays were modeled using the Senkin computer program.¹⁶ The ignition delays were computed assuming constant volume under reflected shock-wave conditions.

The toluene–air burning velocities at 298 K, Su, were computed using the Premix computer package.¹⁷ Care was taken in the calculations to reach the final solution (no evolution of Su when the number of mesh points is increased).

The kinetic scheme used in the present study is based on the comprehensive mechanism developed for the reduction of NO, in simulated reburning conditions, by natural gas blends, methane, ethane, ethylene, acetylene, propane, propene, n-butane and isobutane¹⁹ and the oxidation of buta-1,3-diene.²⁰ The same kinetic scheme has been used to successfully simulate the oxidation of benzene in a JSR at 1-10 atm and in a microreactor at 0.46 atm, the ignition of benzene-oxygen-argon mixtures under reflected shock wave conditions, flame speeds of benzene-air mixtures and low-pressure benzene flame structures.²¹ Also, the oxidation of n-propylbenzene was successfully modeled using the same kinetic scheme.²² The reaction mechanism used here consisted of 120 species and 920 reversible reactions. This mechanism, including references and thermochemical data, is available from the authors. The rate constants for the reverse reactions were computed from the forward rate constants and the appropriate equilibrium constants, $K_c = k_{\text{forward}}/k_{\text{reverse}}$, calculated using thermochemical data.^{21–23} The pressure dependences of unimolecular reactions and of some pressure-dependent bimolecular reactions were taken into account when information was available (i.e., k(P,T)). First-order local sensitivity analyses, $S_{i,j} = \partial \ln(\text{mole}$ fraction of $i)/\partial \ln(k_i)$, were performed as well as reaction rates analyses by computation of rates of consumption (ROC) and rates of production (ROP) for every species.

The proposed kinetic scheme has a strong hierarchical structure. Since most of the present mechanism has been presented in detail in previous papers, only the reaction submechanism for the oxidation of toluene is presented here (Table 1). This sub-mechanism represents an updated version of that used in the prediction of benzene formation in previous work dealing with the oxidation of unsaturated hydrocarbons.^{20,26} It follows a general oxidation scheme⁷ that also served as a basis in previous modeling efforts.^{9,11,12} The initiation reactions for the oxidation of toluene include C–C and C–H bond cleavage,

$$Toluene \rightleftharpoons C_6H_5 + CH_3 \tag{730}$$

$$Toluene \rightleftharpoons C_6H_5CH_2 + H \tag{731}$$

and a reaction with molecular oxygen (732).

The kinetics of reaction (730) was taken from Emdee.⁷ The rate constant of reaction (731) consistent with the recommendation of Baulch et al.²⁷ was taken from Müller-Markgraf and Troe.²⁹ Reaction (730) was not measured directly ; only estimates were derived either from experimental measurements where reaction (731) dominates, or from kinetic modeling. Brouwer *et al.*²⁸ studied the kinetics of the decomposition of toluene in a shock-tube at 1450-1900 K. They measured k(731) in excellent agreement with most of the recent kinetic studies^{29–32} and in agreement with data evaluations.²⁷ The ratio k(730)/k(731) was estimated by Brouwer *et al.*²⁸ and by Braun-Unkhoff *et al.*³⁰ who studied the decomposition of toluene at high temperature (1380-1700 K) and moderate pressure (1.5-6 atm). Both concluded that reaction (731) dominates with k(730)/k(731) in the range 0.1–0.3²⁸ and ≤ 0.2 .³⁰ These results are in excellent agreement with the values of k(730) and k(731) used here since k(730)/k(731) = 0.07 at 1400 K and 0.27 at 1800 K. Consequently, the rate constants used here for reactions (730) and (731) are fully consistent with literature data (see Table 2). However, more information regarding the pressure and temperature dependences of these reactions would be helpful.

Propagation reactions proceed *via* H-atom abstraction by atoms and radicals yielding benzyl. The kinetics of reactions (732) and (733) were recently measured by Eng *et al.*³³ We used their kinetic results here. The rate constant for reaction (734) was derived from a fit to the available measurements.³³ The kinetics of reaction (735) is from Hoffman *et al.*;³⁴ that of reaction (736) is from Hippler *et al.*³⁵ The kinetics of reactions (738) and (739) were obtained from a fit to the NIST data review.³⁶ For reaction (740), we used the rate expression proposed previously.⁷ The addition of H-atom to toluene yields benzene and methyl; the kinetics was measured by Robaugh and Tsang.³⁷

Benzyl radicals decompose thermally and react with molecular oxygen, O (751, 752), OH (750) and HO₂ (742). Reaction (748) yields benzoxy that thermally decomposes producing benzaldehyde (749). The kinetics of reactions (745) and (746) were taken from Colket and Seery³⁸ whereas for the other reactions, we used previously proposed rate constants.⁷ Benzyl alcohol is formed by OH addition to benzyl. The reaction with atomic oxygen yields phenyl and formaldehyde. The oxidation of benzyl alcohol yields benzaldehyde. The addition of H-atoms to benzyl alcohol yields benzene. Benzaldehyde forms C₆H₅CO by thermal decomposition and reactions with atoms and radicals that proceed by Hatom abstraction. The reactions of benzaldehyde with OH and H yield HCO. Benzoyl decomposes and reacts with oxygen and HO₂. Phenyl reactions with oxygen, OH and HO₂ yield phenoxy. Although the reaction with O₂ might yield H and C₆H₄O₂ as a minor route, only reaction (709) was included in this reaction scheme, since C₆H₄O₂ was not detected in these experiments. More direct kinetic investigations of these reactions are needed. Phenyl reactions with C₂H, ethylene, acetylene and diacetylene yield larger aromatics. Phenoxy radicals decompose, yielding two important intermediates: cyclopentadienyl and phenol. The further reactions of these species, yielding other important intermediates, will be discussed in the next section.

Table 1 Reaction sub-set used in the present study. The Arrhenius parameters are given in units of s^{-1} , cm^3 , mol^{-1} , cal

Reactio	n ^a	A	b	Ε	Ref. b
Reactio	ns pertaining to this toluene sub-mechanism				
675	$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O13 + OH$	3.00×10^{13}	0.0	0	7
676	$C_5H_5 + OH \rightleftharpoons C_5H_4OH + H$	9.00×10^{13}	0.0	0	а
677	$C_5H_5 + OH \rightleftharpoons C_4H_6 + CO$	4.00×10^{14}	0.0	4500	14
678	$C_5H_5 + H(+M) \rightleftharpoons CPD(+M)$	1.00×10^{14}	0.0	0	9
	Low pressure limit:	0.44×10^{51}	-18.28	12 994	9
(70	Troe centering, F_c : $a = 0.068$; $T^{***} = 400$; $T^* = 4136$; $T^{**} = 5500$	2 10 1061	12.2	40.010	9,40
6/9	$C_5H_4O + H \rightleftharpoons nC_4H_5 + CO$	2.10×10^{13}	-13.3	40 810	b
681	$C_5\Pi_5 + O \rightarrow rC \Pi_4 O + \Pi_5 O = 0$	3.81×10^{14}	0.0	20	c
682	$C_{2}H_{2}O(3) \approx nC_{4}H_{2} + CO$	2.00×10^{11} 2.51 × 10 ¹¹	0.0	43 900	а 7
683	$C_{\epsilon}H_{4}OH \Rightarrow C_{\epsilon}H_{4}O + H$	2.01×10^{13}	0.0	48 000	7
684	$C_{SH_4O} \rightarrow CO + C_4H_4$	1.00×10^{12}	0.0	53 000	14
685	$CPD + O_2 \rightleftharpoons C_5 H_5 + HO_2$	2.00×10^{13}	0.0	25 000	7
686	$CPD + HO_2 \rightleftharpoons C_5H_5 + H_2O_2$	2.00×10^{12}	0.0	11 660	7
687	$CPD + OH \rightleftharpoons C_5H_5 + H_2O$	3.43×10^9	1.2	-447	7
688	$CPD + H \rightleftharpoons C_5H_5 + H_2$	2.19×10^{8}	1.8	3000	7
689	$CPD + H \rightleftharpoons C_3H_3 + C_2H_4$	$2.00 imes 10^{14}$	0.0	10 000	d
708	$C_6H_6 + iC_4H_5 \rightleftharpoons C_6H_5 + C_4H_6$	2.00×10^{12}	0.0	15000	h
709	$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	2.09×10^{12}	0.0	7470	7
710	$C_6H_5 + HO_2 \rightleftharpoons C_6H_5O + OH$	5.00×10^{13}	0.0	1000	e
711	$C_6H_5 + OH \rightleftharpoons C_6H_5O + H$	5.00×10^{13}	0.0	0	f
712	$C_6H_5 + C_2H \rightleftharpoons C_6H_5C_2H$	3.00×10^{8}	0.0	1391	g
713	$C_6H_5 + C_2H_4 \rightleftharpoons Styrene + H$	1.43×10^{8}	1.2	3540	36
714	$C_6H_5 + C_2H_2 \rightleftharpoons C_6H_5C_2H + H$	1.00×10^{13}	0.0	7647	h
715	$C_6H_5 + C_4H_2 \rightleftharpoons C_6H_5C_2H + C_2H$	2.00×10^{13}	0.0	0	i
716	$C_6H_5 + C_4H_4 \rightleftharpoons C_6H_5C_2H + C_2H_3$	1.00×10^{13}	0.0	7647	h
717	$C_6H_5O \rightleftharpoons C_5H_5 + CO$	8.00×10^{13}	0.0	55 400	J
/18	$C_6H_5O + H + M \rightleftharpoons C_6H_5OH + M$	2.50×10^{11}	0.0	0	9
	Low pressure limit:	0.10×10^{55}	-21.84	13880	9
720	The centering, F_c : $a = 0.043$; $T^{***} = 304$; $T^* = 60000$; $T^{**} = 5900$	1.40×10^{16}	0.0	00.800	9,40 7
730	Toluene $\rightarrow C_6 H_5 + C H_3$	1.40×10^{15}	0.0	99 800	20
732	Toluene $\leftarrow C_6 \Gamma_5 C \Gamma_2 + \Gamma$ Toluene $+ O \rightarrow C H C H + HO$	3.00×10^{14}	0.0	00 194 43 062	29
732	Toluene + $HO \rightarrow C H CH + HO$	3.00×10^{14}	0.0	43 002	30
734	Toluene + $OH \Rightarrow C_2H_2CH_2 + H_2O_2$	1.00×10^{13}	0.0	2180	36
735	Toluene + $O \Rightarrow C_1 H_2 C H_2 + O H_2$	6.30×10^{11}	0.0	2100	36
736	Toluene + $H \rightleftharpoons C_6 H_5 C H_2 + H_2$	1.26×10^{14}	0.0	8364	36
737	Toluene + H \rightleftharpoons C ₆ H ₂ + CH ₂	2.40×10^{13}	0.0	5123	37
738	Toluene + CH ₃ \rightleftharpoons C ₆ H ₅ CH ₂ + CH ₄	8.88×10^{10}	0.0	8754	36
739	Toluene + $C_2H_5 \rightleftharpoons C_6H_5CH_2 + C_2H_6$	1.01×10^{11}	0.0	9514	36
740	Toluene + $C_6H_5 \rightleftharpoons C_6H_5CH_2 + C_6H_6$	2.10×10^{12}	0.0	4400	7
741	Toluene + $nC_4H_5 \rightleftharpoons C_6H_5CH_2 + C_4H_6$	4.00×10^{12}	0.0	7500	14
742	Toluene + $C_2H_3 \rightleftharpoons C_6H_5CH_2 + C_2H_4$	4.00×10^{12}	0.0	7500	14
743	$nC_4H_5 + aC_3H_4 \rightleftharpoons Toluene + H$	2.00×10^{11}	0.0	3700	36
744	$nC_4H_5 + pC_3H_4 \rightleftharpoons Toluene + H$	6.32×10^{11}	0.0	3700	36
745	$C_6H_5CH_2 \rightleftharpoons C_4H_4 + C_3H_3$	2.00×10^{14}	0.0	83 600	38
746	$C_6H_5CH_2 \rightleftharpoons C_5H_5 + C_2H_2$	6.03×10^{13}	0.0	70000	38
747	$C_6H_5CH_2 + O_2 \rightleftharpoons C_6H_5HCO + OH$	6.31×10^{12}	0.0	43 000	5
748	$C_6H_5CH_2 + HO_2 \rightleftharpoons C_6H_5CH_2O + OH$	3.16×10^{12}	0.0	0	5
749	$C_6H_5CH_2O \rightleftharpoons C_6H_5HCO + H$	1.30×10^{14}	0.0	1100	5
750	$C_6H_5CH_2 + OH \rightleftharpoons C_6H_5CH_2OH$	2.00×10^{13}	0.0	0	30
751	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5HCO + H$	1.58×10^{13}	0.0	0	5
752	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5 + CH_2O$	1.00×10^{13}	0.0	0	0
/53	$C_6H_5CH_2 + C_3H_3 \equiv 1 \text{ oluene} + C_3H_2$	1.00×10^{12}	0.0	0	0
/54	$C_6H_5CH_2 + C_6H_5OH \equiv \text{foluene} + C_6H_5O$	1.05×10^{14}	0.0	9500	/
/55	$C_6H_5CH_2OH + O_2 \rightarrow C_6H_5HCO + HO_2 + H$	2.00×10^{12}	0.0	41 400	/
750	$C_6H_5CH_2OH + OH \rightarrow C_6H_5HCO + H_2O + H$	8.43×10 1.20 × 10 ¹³	0.0	2383	7
759	$C_{6}\Pi_{5}C\Pi_{2}O\Pi + \Pi \leftarrow C_{6}\Pi_{6} + C\Pi_{2}O\Pi$	1.20×10 2.11 × 10 ¹¹	0.0	0500	7
750	$C_{6}\Pi_{5}C\Pi_{2}O\Pi + C_{6}\Pi_{5}C\Pi_{2} \rightarrow C_{6}\Pi_{5}\Pi_{5}\Pi_{5}\Pi_{5}U + Iolucle + \Pi$	2.11×10 1.40×10^{12}	0.0	9300	7
759	$C_{6}H_{2}OH + C_{6}H_{5} \rightarrow C_{6}H_{5}HCO + C_{6}H_{6} + H$	1.40×10^{15} 3.98×10^{15}	0.0	4400 83 701	36
761	$C_{0}H_{2}HCO \leftarrow C_{0}H_{2}CO + HO_{2}$	1.02×10^{13}	0.0	30 000	50 12
762	$C_0H_2HCO + HO_2 \approx C_0H_2CO + HO_2$	1.02×10^{12} 2.00 $\times 10^{12}$	0.0	11 665	r ŀ
763	$C_{H_2}H_{CO} + OH \equiv C_{H_2}C_{O} + H_{2}O_{2}$	1.71×10^9	1.2		7
764	$C_{H_2}H_{CO} + OH \equiv C_2H_2OH + H_{CO}$	1.71×10^{13}	0.0	5123	14
765	$C_{\epsilon}H_{\epsilon}HCO + O \Rightarrow C_{\epsilon}H_{\epsilon}CO + OH$	9.04×10^{12}	0.0	3080	7
766	$C_{\alpha}H_{\beta}HCO + H \Rightarrow C_{\alpha}H_{\beta}CO + H_{2}$	5.00×10^{13}	0.0	4928	, 7
767	$C_{\alpha}H_{\beta}HCO + H \Rightarrow C_{\alpha}H_{\alpha} + HCO$	1.20×10^{13}	0.0	5148	, 7
	0 0				

Table 1 (continued)

Reaction ^a		A	b	Ε	Ref. ^b
768	$C_6H_5HCO + CH_3 \rightleftharpoons C_6H_5CO + CH_4$	2.77×10^{3}	2.8	5773	7
769	$C_6H_5HCO + C_6H_5 \rightleftharpoons C_6H_5CO + C_6H_6$	$7.01 imes 10^{11}$	0.0	4400	7
770	$C_6H_5CO \rightleftharpoons C_6H_5 + CO$	$3.98 imes 10^{14}$	0.0	29 401	7
771	$C_6H_5CO + O_2 \rightleftharpoons C_6H_5O + CO_2$	$3.00 imes 10^{10}$	0.0	2870	14
772	$C_6H_5CO + HO_2 \rightarrow C_6H_5 + CO_2 + OH$	$2.00 imes 10^{13}$	0.0	0	14
Other i	mportant reactions				
6	$H + O_2 = OH + O$	1.85×10^{14}	0.0	16812	1
25	HCO + M = H + CO + M	1.85×10^{17}	-1.0	17000	m
30	$HCO + O_2 = CO + HO_2$	2.11×10^{9}	1.1	-620	36
48	$CH_3 + O_2 = CH_2O + OH$	$4.38 imes 10^{11}$	0.0	14656	36
98	$CH_3O + M = CH_2O + H + M$	4.88×10^{15}	0.0	22773	n
112	$CH_2O + OH = HCO + H_2O$	1.72×10^{9}	1.2	-447	0
114	$CH_2O + H = HCO + H_2$	1.26×10^{8}	1.6	2170	р
116	$CH_2O + CH_3 = HCO + CH_4$	4.09×10^{12}	0.0	8843	27
160	$C_2H_2 + O_2 = HCCO + OH$	2.00×10^{8}	1.5	30 100	q
167	$C_2H_2 + O = CH_2 + CO$	1.98×10^4	2.6	656	r
168	$C_2H_2 + O = HCCO + H$	4.62×10^{4}	2.6	656	r
229	$HCCO + O_2 = CO_2 + CO + H$	$1.40 imes 10^9$	1.0	0	q
245	$CH_2OH + O_2 = CH_2O + HO_2$	2.17×10^{14}	0.0	4690	S
565	$C_4H_6 = C_2H_4 + C_2H_2$	1.00×10^{14}	0.0	75000	36
587	$C_4H_6 + O \rightarrow OC_4H_6$	3.00×10^{13}	0.0	80	t
589	$OC_4H_6 \rightarrow C_2H_4 + CH_2CO$	5.00×10^{14}	1.0	78000	k
634	$C_4H_4 + OH = iC_4H_3 + H_2O$	2.00×10^{7}	2.0	2000	q
636	$C_4H_4 + O = aC_3H_4 + CO$	3.00×10^{13}	0.0	1810	u
640	$C_4H_4 + CH_3 = iC_4H_3 + CH_4$	1.66×10^{1}	3.7	9499	v
644	$iC_4H_3 + O_2 = CH_2CO + HCCO$	1.00×10^{12}	0.0	0	q
898	$C_2H_2 + H = C_2H_3$	4.53×10^{14}	-0.7	2688	1
901	$C_2H_3 + O_2 = CH_2O + HCO$	1.85×10^{23}	-3.3	3892	W

^a Nomenclature: C₅H₅, cyclopentadienyl; C₅H₅O: 1,3-cyclopentadienonyl; C₅H₄OH, hydroxycyclopentadienyl; C₄H₆, buta-1,3-diene; CPD; cyclopenta-1,3-diene; C₅H₄O, cyclopentadienone; nC₄H₅, buta-1,3-dienyl; C₄H₄, vinylacetylene; C₆H₆, benzene; iC₄H₅, buta-2,3-dienyl; C₆H₅, phenyl; C_6H_5O , phenoxy; $C_6H_5C_2H$, phenylacetylene; $C_6H_5CH_2$, benzyl; aC_3H_4 , allene; pC_3H_4 , propyne; C_3H_3 , propargyl; C_6H_5HCO , benzaldehyde; C₆H₅CH₂O, benzoxy; C₆H₅CH₂OH; benzyl alcohol; C₆H₅CO, phenylformyl; C₆H₅OH, phenol. ^b Ref.: (a) Based on ref. 7; (b) M. U. Alzueta, P. Glarborg and K. Dam-Johansen, Int. J. Chem. Kinet., 2000, 32, 498; (c) X. Zhong and J. W. Bozzelli, J. Phys. Chem. A, 1998, 102, 3537; (d) Based on ref. 32; (e) D. A. Bittker, Combust. Sci. Technol., 1991, 79, 49; (f) J. A. Miller and C. F. Melius, Combust. Flame, 1992, 91, 21; (g) Y. Tan and P. Frank, P., Proc. Combust. Inst., 1996, 26, 1105; (h) E. Heckmann, H. Hippler and J. Troe, Proc. Combut. Inst., 1996, 26, 543; (i) M. Frenklach, D. W. Clary, W. C. Gardiner, Jr. and S. E. Stein, Proc. Combust. Inst., 1984, 20, 887; (j) S. Olivella, A. Sole and A. Garcia-Raso, J. Phys. Chem., 1995, 99, 10549; (k) This work; (l) D. L. Baulch, L. J. Cobos, R. A. Cox, C. Esser, C. P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker and J. Warnatz, J. Phys. Chem. Ref. Data, 1992, 21, 411; (m) R. S. Timonen, E. Ratajczak, D. Gutman and A. F. Wagner, J. Phys. Chem., 1987, 91, 5325; (n) P. J. Wantuck, R. C. Oldenborg, S. L. Baughcum and K. R. Winn, Proc. Combust. Inst., 1989, 22, 973; (o) W. Tsang and R. F. Hampson, J. Phys. Chem. Data, 1986, 15, 1087; (p) T. K. Choudhury and M. C. Lin, Combust. Sci. Technol., 1989, 64, 19; (q) J. A. Miller and C. F. Melius, Combust. Flame, 1992, 91, 21; (r) K. Mahmud and A. Fontijn, J. Phys. Chem., 1987, 91, 1918; (s) H. Grotheer, G. Riekert, D. Walter and Th. Just, J. Phys. Chem., 1988. 92, 4028; (t) R. J. Cvetanovic, J. Phys. Chem. Ref. Data, 1987, 16, 261; (u) R. P. Lindstedt and G. Skevis, Proc. Combust. Inst., 1996, 26, 703; (v) P. Dagaut and M. Cathonnet, Combust Sci. Technol., 1998, 140, 225; (w) J. W. Bozzelli and A. M. Dean, J. Phys. Chem., 1993, 97, 4427.

Results and discussion

The oxidation of toluene in a JSR at 1 atm

The oxidation of toluene was studied at equivalence ratios of 0.5, 1 and 1.5, at residence times, τ , of respectively 0.07, 0.1 and 0.12 s. From these experiments, molecular species concentration profiles were obtained for O₂, H₂, CO, CO₂, CH₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, aC₃H₄ (allene) and pC₃H₄ (pro-

pyne), 1,3-C₄H₆, vinylacetylene, cyclopentadiene, benzaldehyde, benzene, dibenzyl, styrene, and toluene by probe sampling and GC analysis. The products detected are in agreement with the experimental results obtained in previous PFR studies.^{4,6} The present data were used to propose a detailed chemical kinetic reaction mechanism for the oxidation of toluene. Figs. 1 to 3 present the results obtained at 1 atm for $\varphi = 0.5$, 1 and 1.5, respectively.

Table 2 Comparison of available kinetic data for toluene decomposition (731). The Arrhenius parameters are given in units of s^{-1} , cm³, mol⁻¹, cal

A	Ε	Temperature/K	<i>k</i> (730)/ <i>k</i> (731)	Ref.
3.10×10^{15}	89 205	920-2200		27
2.82×10^{15}	88 887	1450–1900	0.1 to 0.3	28
2.00×10^{15}	88 194	1500-1900	0.1	29
3.60×10^{15}	89 427	1380-1700	≤0.2	30
1.82×10^{16}	91 779	300-1200		31
6.31×10^{15}	90 344	1100-1900	_	32
3.00×10^{15}	88 194	1000-2000	0.07 to 0.3	This work



Fig. 1 Toluene oxidation in a JSR at 1 atm. The initial conditions were: toluene, 0.15%; O_2 , 2.70%, N_2 , 97.15%; $\tau = 0.07$ s; $\varphi = 0.5$. Experimental data (symbols) are compared to computations (lines and small symbols).

The experimental results show that besides CO, H_2 and CO_2 , the major intermediate products are acetylene, benzene, methane, ethylene, formaldehyde, vinylacetylene, and benzaldehyde. The minor products are propyne, cyclopentadiene, allene, buta-1,3-diene, ethane, styrene, and dibenzyl. As can be seen from these figures, overall the proposed model fairly well represents the experimental data. However, it should be noticed that the model over-predicts the formation of acetylene, dibenzyl and benzaldehyde at low fuel conversion.

The kinetic scheme proposed recently⁹ was also tested against the present data. As can be seen from Fig. 4, the present experimental data are poorly represented by the model: The



Fig. 2 Toluene oxidation in a JSR at 1 atm. The initial conditions were: toluene, 0.15%; O_2 , 1.35%, N_2 , 98.5%; $\tau = 0.10$ s; $\varphi = 1.0$. Experimental data (symbols) are compared to computations (lines and small symbols).



Fig. 3 Toluene oxidation in a JSR at 1 atm. The initial conditions were: toluene, 0.15%; O_2 , 0.675%, N_2 , 99.175%; $\tau = 0.12$ s; $\varphi = 1.5$. Experimental data (symbols) are compared to computations (lines and small symbols).

predicted reactivity is much higher than in the experiments, the maximum mole fractions of acetylene, ethylbenzene, benzaldehyde and styrene are over-predicted whereas those of formaldehyde, methane, benzene, ethylene and vinylacetylene are underpredicted. No ethane, propyne and allene are predicted since these species were not considered in the scheme.⁹

Sensitivity analyses and reaction path analyses, through species reaction rate of production (ROP) and rate of consumption (ROC) computations, have been used to elaborate the proposed mechanism and interpret the results. These computations show that the kinetics of toluene oxidation, in the present experimental conditions, is mainly sensitive to a limited num-



Fig. 4 Toluene oxidation in a JSR at 1 atm. The initial conditions were: toluene, 0.15%; O_2 , 1.35%, N_2 , 98.5%; $\tau = 0.10$ s; $\varphi = 1.0$. Experimental data (symbols) are compared to computations (lines and small symbols) using the kinetics scheme and the thermochemical data of Davis *et al.*⁹

ber of reactions pertaining to the toluene oxidation submechanism and to reactions of simple intermediates. At 1300 K, in stoichiometric conditions (conditions of Fig. 2), toluene computed mole fractions are mostly sensitive to reaction (6), S = -0.4, to reactions of toluene with H (S(731) = 0.45, S(736) = 0.16, S(737) = -0.46) and to thermal decomposition, S(746) = -0.33.

According to this modeling, the oxidation of toluene proceeds according to the scheme depicted in Fig. 5. The size of the arrows indicates the importance of the reaction In stoichiometric conditions and low fuel conversion (1080 K), toluene mostly reacts with OH (ROC(734) = -0.43), O₂ (ROC (732) = -0.29) and HO₂ (ROC(733) = -0.10) whereas reactions with H and O atoms are of minor importance.

At higher fuel conversion (1300 K), toluene reacts with H (ROC(734) = -0.24; ROC(736) = -0.40) and OH (ROC (737) = -0.28). Benzyl, predominantly formed by reaction (736), mostly recombines with H-atoms to yield toluene, ROC(-731) = -0.59, and decomposes: ROC(746) = -0.22. Its reaction with HO₂ yields benzoxy and OH (ROC(748) = -0.05). Benzoxy, formed in reaction (748), decomposes into benzaldehyde and H (749). Benzaldehyde predominantly reacts by thermal decomposition (ROC (760) = -0.37) and H-atom abstraction (ROC(763) = -0.20; ROC(766) = -0.23). C₆H₅CO thermally decomposes, yielding phenyl and CO (770). Benzene, mostly formed in (737), mainly reacts with O (ROC(703) = -0.64) and OH (ROC(701) = -0.26). Phenyl predominantly reacts with O_2 , yielding phenoxy, ROC(709) = -0.79. Phenoxy, mostly formed by reactions (703) and (709), ROP(703) = 0.51 and ROP(709) = 0.45, decomposes via (717) yielding cyclopentadienyl and CO. More kinetic information is still needed for this reaction. At this stage, the original aromatic ring has disappeared. Cyclopentadienyl, is mostly formed by reactions (717), $ROP(C_5H_5) = 0.587$, and (746), $ROP(C_5H_5) = 0.3$. It reacts with O (ROC(681) = -0.20; ROC(680) = -0.05), H (ROC (678) = -0.13),HO₂ (ROC(675) = -0.19) and OH $(ROC(676) = -0.17; ROC(677) = -0.14). C_5H_4O$ mostly decomposes via (683) yielding vinylacetylene and CO. C_5H_4OH , formed in reaction (676), decomposes thermally via (683) yielding C₅H₄O. Cyclo-1,3-pentadiene mostly reacts with O_2 (ROC(685) = -0.19), H (ROC(688) = -0.39) and OH (ROC(687) = -0.24). At this stage, cyclic species have been converted into linear products. Vinylacetylene, mostly formed by decomposition of C5H4O (684), predominantly reacts with OH (ROC(634) = -0.43), O (ROC(636) = -0.22)

-0.22) and CH₃ (ROC(640) = -0.09). iC₄H₃ mostly reacts with molecular oxygen (644), yielding ketene and ketenyl. Acetylene is mostly formed by decomposition of benzyl (ROP(746) = 0.26), butadienyl (ROP(613) = 0.34), and vinyl, ROP(898) = 0.3. The oxidation of acetylene by O and O₂ mainly yields HCCO: ROC(167) = -0.12; ROC(168) =-0.28; ROC(160) = -0.52. Ethylene is mainly produced from the decomposition of ethyl, ROP(894) = 0.43, and also from the buta-1,3-diene oxidation submechanism: ROP(565) = 0.110.11 and ROP(589) = 0.16. Ethylene is mostly consumed by reaction with O, OH, and CH₃. Butadiene is almost exclusively formed in reaction (677). It mostly decomposes via (565), ROC(565) = -0.21, and oxidizes, ROC(587) = -0.25. Methane is formed by reaction of methyl radicals with H_2 , CH₂O and C₄H₄. It is mostly consumed by reaction with OH (71%) and O (29%). Methyl is mostly produced by H-atom displacement reaction of H with toluene (67%) and mostly recombines (25%), yielding ethane. A smaller fraction reacts with H_2 (16%), yielding methane, and O_2 , yielding $CH_2O + OH$ and $CH_3O + O$ (15%). Ethane, almost exclusively formed by recombination of methyl, predominantly reacts with OH (44%), H (31%), O (15%), and CH₃ (9%). Allene is mostly produced by the oxidation of vinylacetylene by Oatoms (636). It mostly isomerizes (47%), yielding propyne, that in turn is mostly oxidized by reactions with O and OH, yielding HCCO, CH₂CO, and C₃H₃.

Higher compounds are formed: ethylbenzene, styrene and dibenzyl. Ethylbenzene is produced by recombination of methyl and benzyl. Dibenzyl is produced by recombination of benzyl radicals. Styrene is almost entirely formed by decomposition of 1-phenylethyl, derived from ethylbenzene degradation. Formaldehyde formation is due to the oxidation of methyl (48), vinyl (901) and hydroxymethyl (245). It mostly reacts with H (114, 36%), OH (112, 38%) and CH₃ (116, 13%) by H-atom abstraction. Formyl decomposes (25, 70%) and reacts with molecular oxygen (30, 30%), yielding CO, H and HO₂. The fuel is mostly consumed by H and OH. Atomic hydrogen is mostly formed by reactions (25) and (229) whereas OH radicals are mostly formed by reaction (6).

The ignition of toluene-oxygen-argon mixtures

The ignition delays of toluene-oxygen-argon mixtures has been measured by Burcat et al.3 over a wide range of experimental conditions (0.5 to 1.5% mol of fuel, 4.48-13.45% mol of oxygen, equivalence ratio ranging from 0.33 to 1 and temperature, T_5 , in the range 1339–1797 K) in reflected shock wave conditions. The pressure behind the reflected shock wave, P_5 , was in the range 1.95–8.85 atm). As can be seen from Fig. 6a, the model tends to predict longer ignition delays than measured although the computed overall activation energy fits the experiments well. Fig. 6b presents a comparison of the kinetic modeling and the ignition delay measured by Pengloan et al.³³ Very good agreement between the data and the modeling was obtained. Sensitivity analyses (Fig. 7) indicate that the ignition delays are mostly sensitive to the kinetics of a limited number of reactions. Increasing the rate of reactions (6), (676), (709), (732), (746), (748), and (751) reduces the computed ignition delays by production of radicals. Conversely, increasing the rate of reactions (-731), (734), and (736), that act as chain-terminating steps or consume H and OH (active radicals) to produce less reactive species such as benzyl which is resonantly stabilized, increases the computed ignition delays.

The toluene-air burning velocities

The proposed kinetic scheme was also tested at higher temperature by modeling laminar burning velocities of atmospheric toluene–air flames at 298 K. The data of Davis *et al.*⁹ obtained for benzene–air and toluene–air flames were used





Fig. 6 Comparison between experimental (symbols) and computed ignition delays of toluene–oxygen–argon mixtures. (a) The data were taken from Burcat *et al.*³ The initial mole fractions were (A): 0.01495 toluene, 0.1345 O₂, 0.85055 Ar; (D): 0.00497 toluene, 0.0448 O₂, 0.95023 Ar; P₅ = 2.5 atm. (b) The data of Pengloan *et al.*³³ were used. The initial mole fractions were $\varphi = 0.5$: 0.4% toluene and 7.2% oxygen; $\varphi = 1:0.4\%$ toluene and 3.6% oxygen; $\varphi = 1.5$: 0.4% toluene

here. The authors measured the burning velocities using their counter-flow flame technique, extrapolating the data to zerostretch conditions *via* linear and non-linear fits with an uncertainty of ~ 2 cm s⁻¹. Fig. 8 compares the predictions of the model with the experimental flame speeds over a wide range of equivalence ratio. The symbols represent the data obtained using a non-linear extrapolation to zero-stretch. One can observe that the agreement between this model and experiment is generally good for both benzene–air and toluene–air flame speeds. Sensitivity analyses showed that burning velocities of toluene–air flames are mostly sensitive to the kinetics of $H + O_2 OH + O$, followed in importance by reactions pertain-



Fig. 7 Sensitivity spectrum for the ignition of a toluene–oxygen– argon (mixture A). The sensitivity coefficients are relative to reaction (6).



Fig. 8 Benzene–air and toluene–air burning velocities at 298 K and atmospheric pressure. Comparison between the experimental data of Davis *et al.*^{9,10} (large symbols) and this modeling (line).

ing to the CO-sub-mechanism, phenoxy and cyclopentadienyl reactions.

Conclusion

The oxidation of toluene has been studied in a JSR over the temperature range 1000–1375 K, for equivalence ratios ranging from 0.5 to 1.5. Molecular species concentration profiles were obtained by probe sampling and GC analysis. These experiments were simulated using a detailed kinetic reaction mechanism already validated for the oxidation of benzene over a wide range of conditions (0.46–10 atm, $0.19 \le \phi \le 1.5$, 950–1350 K). Overall, the proposed kinetic model represents well the present set of data, in contradiction with previously proposed kinetic mechanisms.^{7,9} The kinetic modeling was used to delineate the main reactions involved in the oxidation of toluene, confirming the general reaction mechanism proposed earlier.⁷ Modeling of the ignition of toluene–oxygen–argon mixtures and of the burning velocities of toluene–air mixtures was also successfully performed using the proposed scheme.

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