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

Diesel fuels are complex blends of hundreds of species, which are mainly hydrocarbons from the distillation of crude oil and also oxygenated molecules used as additives [1, 2]. The main classes of molecules found in closely equal amounts in petroleum based diesel fuels are \( n \)- and \( iso \)-paraffins, naphthenes and aromatic compounds with carbon atom numbers ranging from 10 to 22 (with an average value around 14-15) [1]. Aromatic compounds usually consist of one aromatic ring with one or several side alkyl chains.

This paper focuses on the development of detailed kinetic models for the oxidation of alkylbenzenes actually present in diesel fuel: e.g. \( n \)-decylbenzene (\( \phi \)C\(_{10}\)H\(_{21}\)). For this purpose a new version of the software EXGAS dedicated to the automatic generation of detailed oxidation models has been developed for alkylbenzenes (EXGAS-Akylbenzene\(^1\), called EXGAS in this paper) and validated for the molecules with a C\(_{3-4}\) alkyl chain for which recent experimental data were available [3-10], including new experimental results obtained for \( n \)-hexylbenzene (\( \phi \)C\(_{6}\)H\(_{13}\)) in a jet stirred reactor. To our knowledge, the gas-phase oxidation of this last reactant has never been previously investigated. Simulations using generated models for a series of \( n \)-alkylbenzenes up to \( n \)-decylbenzene have also been performed. Note that due to the lack of data and model for this last compound, it has recently been proposed to use mixtures of \( n \)-propylbenzene and \( n \)-butylbenzene with \( n \)-heptane to simulate \( n \)-decylbenzene ignition [11].

\(^1\) Software EXGAS-Akylbenzenes automatically generates detailed kinetic mechanisms for the oxidation of linear and branched alkanes and mono-alkylbenzenes and is freely available for academic researchers (valerie.warth@univ-lorraine.fr).
DESCRIPTION OF THE KINETIC MODELS

The detailed kinetic mechanisms used in this study have been automatically generated by the computer package EXGAS. This software has already been used for generating mechanisms in the case of alkanes [12-14], alkenes [15], as well as of oxygenated biofuels [16]. We will recall here very shortly its main features which have already been much described and we will present the specificities in the reactions and rate constants which were taken into account and implemented in the system to well represent the behavior of alkylbenzenes. All the mechanisms generated for this study are provided as supplementary material in CHEMKIN format.

General features of EXGAS

The system provides reaction mechanisms made of three parts, in which the pressure dependence of the reactions is only considered in the first one:

- An aromatic reaction base, which consists in the model proposed for ethylbenzene by [17] and which contains 755 reactions.

  This reaction base includes a C_0-C_2 reaction base, a mechanism to model the oxidation of C_3–C_5 unsaturated hydrocarbons, as well as recently up-dated mechanisms for the oxidation of small aromatic compounds, benzene, and toluene.

- A comprehensive primary mechanism, where the only molecular reactants considered are the initial organic compounds and oxygen.

- A lumped secondary mechanism, containing the reactions consuming the molecular products of the primary mechanism, which do not react in the reaction base.

  Thermochemical data for molecules or radicals were automatically calculated and stored according to the CHEMKIN formalism [18]. These data were calculated using software THERGAS [19], based on the group and bond additivity methods [20]. Group data were mainly those proposed by Domalski and Hearing [21] and bond dissociation energies (BDE) were taken from Luo [22]. On the alkyl chain of the molecule, C-H BDEs were 85.4 kcal mol\(^{-1}\), 98.7
kcal mol$^{-1}$, and 100.9 kcal mol$^{-1}$ in the case of the benzylic position, of the secondary C-atoms and of the terminal methyl group, respectively. New data have been used for the enthalpy and the entropy (-4.94 kcal/mol and -10.21 cal/mol/K, respectively, of the C-(Cb)-(C)-(O)-(H) group, allowing us to get better agreement between simulations and experiments). For the enthalpy, this value is close to that proposed by Cohen [23] (i.e. -4.4 kcal/mol).

The kinetic data of isomerizations, combinations and unimolecular decompositions are calculated using software KINGAS [12] based on the thermochemical kinetics methods [20] using the transition state theory or the modified collision theory. The kinetic data, for which the calculation is not possible by KINGAS, are estimated from correlations, which are based on quantitative structure-reactivity relationships and obtained from a literature review [13][15].

**Primary mechanism of the oxidation of alkylbenzenes**

Compared to the case of alkanes, the changes made in the generation of primary mechanisms due to the presence of the aromatic ring have been based on a previous model of the oxidation of $n$-butylbenzene [7]. This model had been manually written, but following the rules taken into account during the automatic generation of mechanisms for the oxidation of alkanes and alkenes by the software EXGAS. The reactions considered in the primary mechanism of alkylbenzenes are given in figure 1. The only type of reactions specific to alkylbenzenes is the ipso-addition of H or O atoms and of small radicals, OH, CH$_3$, and HO$_2$, which consist of the substitution of the alkyl chain by the atom or the radical involved in the reaction. For instance, the ipso-addition of an OH radical to $n$-butylbenzene gives phenol and a $n$-butyl radical. While the primary mechanisms have been generated using rules mainly similar to those proposed in the case of the oxidation of alkanes [12], the encoding of these reactions had to be fully revised to take into account the presence of the aromatic ring in the involved alkylbenzenic species using a new internal representation.

**FIGURE 1**
The primary mechanisms have been generated based on two simple assumptions: (i) the aromatic ring only reacts through ipso-additions which have been shown to be of importance for toluene and ethylbenzene [17], (ii) the reactivity of the resonance stabilized benzylic secondary radicals (see the resonance stabilized radical deriving from \(n\)-hexylbenzene in equation (1)) has been taken equal to that of resonance stabilized allylic secondary radicals [15].

\[
\begin{align*}
\text{Resonance stabilized radical deriving from } n\text{-hexylbenzene}
\end{align*}
\]

(1)

A table summarizing the kinetic data is given in Supplementary material. Most of the correlations used for the calculation of kinetic parameters are derived from correlations proposed for linear alkanes [13] and alkenes [15]. The rate constants for the ipso-additions are those considered by [7], except for that of \(\text{HO}_2\) radicals which was not considered. Since there is no data for this last rate constant, it has been estimated based on that of other radicals.

**Secondary mechanism of the oxidation of alkylbenzenes**

For reducing the number of reactants in the secondary mechanism, the molecules formed in the primary mechanism, with the same molecular formula and the same functional groups, are lumped into one unique species, without distinguishing between the different isomers [12]. The considered species are several types of benzylhydroperoxides, alkyl and alkenylbenzenes, cyclic ethers connected to a benzene ring, benzylic alcohols, benzylic aldehydes and benzylic ketones. Similarly to the case of alkanes [14], the writing of the secondary reactions is made in order to promote the formation of alkyl or benzyl alkyl radicals which contain more than two carbon atoms and which are already included in the primary mechanism or in the aromatic reaction base. Note that these secondary reactions are no more elementary steps and that the formation of molecules included in the aromatic base, such as styrene or benzaldehyde, has been favored. An example of generic secondary reaction is presented in equation (2) for the case of benzylketohydroperoxides, all the isomers of which are written: \(\phi C_5H_{10}(CO)(OOH)\). The
structure represented in equation (2) is just an example.

\[
\phi C_5H_{10}(CO)(OOH) \rightarrow \text{Benzaldehyde} + \cdot\text{OH} + \text{CO} + \cdot\text{C}_4\text{H}_9 \quad (2)
\]

When a molecule not included in the aromatic base, such as C\(_8^+\) benzylaldehydes or benzyloxiranes, obtained by addition on alkenylbenzenes of OH and HO\(_2\) radicals, respectively, is formed, it reacts again in this secondary mechanism. The list of the rules used for generating these secondary reactions is given in Supplementary Material.

**VALIDATIONS OF THE KINETIC MODELS**

The generated models have been tested in the case of the oxidation of \(n\)-propylbenzene and \(n\)-butylbenzene using literature data, and for that of \(n\)-hexylbenzene using newly obtained experimental results. No adjustment has been made to the models obtained using the automatic generator. Despite the simplicity of the assumptions used in the generation of primary mechanisms, the obtained agreement is satisfactory over a wide range of experimental conditions for the three alkylbenzenes for which experimental data are available.

**Validations for \(n\)-propylbenzene oxidation**

The oxidation of \(n\)-propylbenzene has been previously studied in a jet-stirred reactor (JSR) at temperatures ranging from 750 to 1100 K (1 atm, a residence time of 0.7 s, an inlet fuel mole fraction of 0.1%) [5]. Figure 2 presents a comparison between these experimental data and simulations using a model generated for the oxidation of \(n\)-propylbenzene. It shows that the fuel consumption is very well simulated, as well as the formation of major products such as carbon monoxide and styrene. Satisfactory predictions of other products such as ethylene, formaldehyde, benzene and toluene are also obtained.
Validations for $n$-butylbenzene oxidation

The generated model has been validated against literature data obtained in a rapid compression machine, a shock tube, and 1.06 and 10 atm JSRs.

The auto-ignition of $n$-butylbenzene has been previously experimentally investigated in a rapid compression machine [4, 6] and in a shock tube way [7]. Figure 3 presents a comparison between these experimental data and simulation using a model generated for the oxidation of $n$-butylbenzene. It can be observed that in both cases, the model, tested under the same conditions as in [7], performs as well as this previous model. The agreement is as satisfactory with the rapid compression machine results as with the hand-written model of [7] (see figure S1 in supplementary material), even if the hypothesis of the adiabatic core made by [7] certainly leads to some under-estimation of the delay times at the lowest temperatures. Under shock tube conditions, as with the hand-written model of [7] (see figure S1 in supplementary material), while the agreement is good at atmospheric pressure, it deteriorates with increasing pressure.

Husson et al. [7] have studied the oxidation of $n$-butylbenzene in a JSR at atmospheric pressure in Nancy for a residence time of 2s and an inlet fuel mole fraction of 0.4%. Figure 4 presents the experimental and modeled evolutions with temperature of the reactant and the major product mole fractions. It shows that the model leads to a satisfactory agreement, even better than that obtained by Husson et al. [7] (see figure S2 in supplementary material), since the low-temperature reactivity observed below 800 K is now well reproduced. The oxidation of $n$-butylbenzene has also been studied in a flow reactor at 1 atm [3] and in another JSR at 10 atm (residence time of 1s) [5]. Figure S3 in supplementary material presents the simulated evolutions of reactants and major products in the flow reactor. As shown by this figure, the model slightly underpredicts the fuel consumption, but predicts satisfactorily the formation of the major
products, such as CO, methane, ethylene, benzene, toluene and styrene. Figure S4 in supplementary material presents the simulated evolutions of fuel and formaldehyde mole fractions (a good indicator of the low-temperature reactivity) in JSR. This figure shows that the model reproduces well the fuel consumption and the formaldehyde mole fraction below 800 K, but that the formation of this last compound is overestimated by a factor of 2 above, while a correct agreement was obtained by [7].

FIGURE 4

Note also that figure S5 in supplementary material presents the prediction of the model of Nakamura et al. [10] for the JSR results for n-butylbenzene obtained by Husson et al. [7]. This figure, plotted under the same format as figure 4, shows that this last model overpredicts significantly fuel conversion both below and above 800 K, while the automatically generated model presented here leads to satisfactory predictions. The overprediction of fuel conversion leads to an overprediction of acetaldehyde and propene formation below 800 K, and to deviations in the predictions of small aromatic compound formation above 800 K.

Validations for n-hexylbenzene oxidation – New experimental results

An experimental study of the oxidation of n-hexylbenzene has been performed in a JSR, a type of reactor which has often been used for gas phase kinetic studies [17], and especially to study the n-hexylbenzene oxidation under the same conditions as n-butylbenzene, including the same carbon atom initial mole fraction [7]. Experiments were performed at a constant pressure of 800 Torr (1.06 atm), at a residence time of 2 s, at temperatures ranging from 750 to 1100 K using stoichiometric mixtures. The fuel was diluted in helium (n-hexylbenzene inlet mole fraction of 0.0033). n-Hexylbenzene was provided by Aldrich (purity ≥ 97 %), and helium and oxygen by Messer (purity of 99.999% for He and 99.995% for O₂).

The reactor consists of a quartz sphere (volume = 95 cm³) into which diluted reactant enters through an injection cross located at its center. It is operated at constant temperature and pressure
and it is preceded by an annular preheating zone in which the temperature of the gases is progressively increased up to the reactor temperature before entering inside. Gas mixture residence time inside the annular preheater is very short compared to its residence time inside the reactor. Both the spherical reactor and the annular preheating zone are heated by resistance heaters wrapped around their walls. Despite the exothermicity of the reaction, the temperature gradient in the vessel was lower than 5 K. The fuel flow rate was controlled by a liquid mass flow controller and was mixed with the carrier gas and then evaporated by passing through a single pass heat exchanger, the temperature of which was set above the boiling point of the hydrocarbon. Carrier gas and oxygen flow rates were controlled by gas mass flow controllers. The accuracy of the liquid and gas flow rates was around 0.5%.

The outlet products were analyzed online by gas chromatography. The online analysis of products which are liquid at standard conditions was performed using a heated transfer line between the reactor outlet and the chromatograph sampling gates which were also heated. During the study, the temperature of the transfer line was set to its maximum, 473 K, but it was not high enough to keep all the reaction products in the gas phase. Three gas chromatographs (GC) were used for the quantification of the different species. The first GC, equipped with a Carbosphere packed column, a thermal conductivity detector, and a flame ionization detector (FID), was used for the quantification of O\textsubscript{2}, carbon oxides, and C\textsubscript{1}-C\textsubscript{2} hydrocarbons. Detected in GC-MS, hydrogen, water and formaldehyde were however not quantified. The second GC was fitted with a PlotQ capillary column and a FID, and was used for the quantification of C\textsubscript{1}-C\textsubscript{4} hydrocarbons and of small oxygenated compounds. The third GC was fitted with a HP-5 capillary column and a FID, and was used for the quantification of species with more than five heavy atoms (i.e. carbon and oxygen atoms). The identification and the calibration of light species (e.g. carbon oxides, C\textsubscript{1}-C\textsubscript{4} hydrocarbons) were performed by injecting commercial gaseous mixtures. For other species, the calibration was performed by injecting known amounts
of the pure substances. Based on the repeatability of the experiments, uncertainty estimates on obtained mole fractions were about ± 5\% (measure reading). It was not possible to quantify neither \(n\)-hexylbenzene (\(\phi\text{C}_6\text{H}_{13}\)) nor products heavier than ethylbenzene due to a too low vapor pressure and condensation problem in the transfer line between the reactor and the gas chromatographs.

Figure 5 presents the experimental and computed evolution with temperature of oxygen and the measured products with a mole fraction reaching at least 80 ppm, together with the simulated fuel profile. By comparison with figure 4 made for \(n\)-butylbenzene under the same JSR conditions and with the same content in atoms of carbon in the inlet gas, it can be observed that a close reactivity is experimentally obtained from both fuels above 800K, as well shown by most product mole fractions, but that below this temperature, the reactivity of \(n\)-hexylbenzene is the largest as indicated by the acetaldehyde and styrene mole fractions. The mole fractions of these species also indicate a pronounced negative coefficient (NTC) behavior, more marked than in the case of \(n\)-butylbenzene. Figure 5 also shows that, according to the product formation, the reactivity of \(n\)-hexylbenzene in both temperature ranges is well reproduced by the model.

**FIGURE 5**

**MODELLING ALKYLBENZENES WITH A C\(_6\) ALKYL CHAIN**

As the models generated by EXGAS are able to successfully reproduce many available experimental results for the oxidation of alkylbenzenes from propylbenzene up to \(n\)-hexylbenzene, we have attempted to generate models for a series \(n\)-alkylbenzenes up to \(n\)-decybenzene and to compare the obtained reactivity with that of smaller compounds. Note that similar attempts to model a family of large hydrocarbons of increasing size have already been made in the case of linear C\(_7\) alkanes [14][24].

Table 1 presents the number of species and reactions in all the models generated in this study. In the case of \(n\)-butylbenzene, the generated model is slightly smaller than that manually written.
(2303 reactions) [7]. Note that despite the fact that the aromatic ring is considered as mostly unreactive, the model for a given \( n \)-alkylbenzene (e.g. 5598 reactions in the case of \( n \)-octylbenzene) is significantly larger than that generated for the corresponding \( n \)-alkane (2013 reactions for \( n \)-octane). Due to the presence of the aromatic ring, the symmetry of the molecule is lost, inducing the production of a much larger number of isomers, e.g. 4 radicals are formed from \( n \)-octane by H-abstractions, while 8 are produced from \( n \)-octylbenzene. This large number of involved species and reactions certainly supports the use of model automatic generation methods.

**TABLE 1**

Figure 6a presents simulations performed under atmospheric jet-stirred reactor conditions for the studied series of alkylbenzenes (\( \text{C}_n\text{H}_{2n+1} \) with \( 3 < n < 10 \), named here \( \text{C}_n \)) for stoichiometric mixtures containing the same carbon atom content as under the conditions of figures 4 and 5, e.g. an inlet mole fraction of 0.0025 for \( \text{C}_8 \). It can be observed that the low-temperature reactivity observed below 800 K steadily increases when the size of the alkyl chain increases, with no low-temperature reactivity observed for \( n \)-propylbenzene. For all the other compounds, a very well marked negative temperature coefficient zone can be observed around 800 K. This increase of reactivity is much more pronounced than what was observed by Biet et al. [14] in the case of \( \text{C}_7 \) alkanes under similar conditions, for which an increase of the alkyl chain of 7 atoms of carbon led to a conversion increase of only 25%. In figure 6, an increase of the alkyl chain of 6 atoms of carbon (from \( n \)-butylbenzene to \( n \)-decylbenzene) leads to an increase of the low-temperature maximum conversion of about a factor of 4, due to the decreasing influence of the aromatic ring. However for compounds larger than \( \text{C}_9 \), the increase of reactivity with the size of the alkyl chain starts to be more limited. Simulations under these condition for \( \text{C}_8 \) (fig 6b and c) confirm the important low temperature reactivity, with a large formation of CO, ethylene, styrene, large alkenes, and aldehydes observed below 800 K.
In order to explain this change in the low-temperature reactivity according to the studied alkylbenzene, a flow rate analysis has been performed at 610 K (the temperature of the maximum of the low-temperature reactivity for \textit{n}-butylbenzene) under the conditions of figure 6. As shown in Table 2, alkylbenzenes are mainly consumed by abstractions of alkylic and benzylic H-atoms, with the ratio between both channels being almost equal for C4, but of a factor larger than 2 in favor of alkylic H-atoms in the case of C8. Due to the thermochemistry of this addition, benzylic radicals react much less easily than alkylic radicals by addition to oxygen to give branching agents. Benzylic radicals derived from C4 react then mainly by combinations with methyl or HO$_2$ radicals, and by oxidation to give butenylbenzenes and the unreactive HO$_2$ radicals, even if the activation energy of this reaction (15.2 kcal/mol, see Table S2a in supplementary material) is relatively high. This explains the very low reactivity of C4, for which the promoting influence of a third channel of fuel consumption, ipso-additions, especially those with HO$_2$ radicals, has an important role to promote reactivity, even if its contribution to the total fuel consumption is only of 2%.

When the size of the alkyl chain increases, isomerizations of benzylic radicals to give secondary alkylic radicals through 6-membered ring transition states start to be possible. Due to their low activation energy (see Table S1b in supplementary material), these isomerizations compete significantly with the other channels consuming benzylic radicals as shown in Table 2. Already in the case of C6, the isomerizations of benzylic to alkylic radicals account for 32.8% of benzylic radical consumption. Note that about 90% of alkylic radicals react by addition to oxygen promoting the formation of well known branching agents, keto-hydroperoxydes. Isomerizations of benzylic radicals into alkylic radicals explained why the consumption of alkylic radicals by addition to oxygen is larger than their formation, as shown in Table 2. When the size of the alkyl...
chain increases, the part of isomerization in the consumption of benzylic radicals keeps on increasing, while that of the inhibiting oxidation keeps on decreasing. Therefore, there are three effects promoting reactivity when the size of the alkyl chain increases, (i) the lower contribution of the formation of benzylic radicals by H-abstractions, (ii) the easiest isomerizations of benzylic radicals to give alkylic radicals, and (iii) the easiest isomerizations of peroxy radicals obtained from alkylic radicals. In the case of C$_7$+ alkanes or of $n$-alkylbenzenes above C9, the limited increase of conversion when the size of the reactant increases, is only due to this last effect.

Above 800K, the formation of benzylic radicals for the fuel consumption still accounts for a significant part which is decreasing with the size of the alkyl chain. However, at this temperature, these radicals react mostly by $\beta$-scissions to give styrene and alkyl radicals (more than 90%). The activation energy of this $\beta$-scission is higher by more than 10 kcal/mol than that of the decomposition of alkylic radicals (see Table S2b in supplementary material). This explains why at a given temperature above 800 K the reactivity of $n$-alkylbenzenes up to C5 increases when the size of the alkyl chain increases, and does not change for heavier compounds. The reactivity of C3 is by far the lowest since in this case the alkyl radical is a methyl radical with an activation energy still 2.3 kcal/mol higher than for the formation of larger alkyl radicals, and with the largest contribution of the formation of benzylic radicals in the fuel consumption.

CONCLUSION

A new version of software EXGAS dedicated to alkylbenzenes has been developed and used to automatically generate the first models for a series of $n$-alkylbenzenes with a C$_3$-C$_{10}$ alkyl chain. For the three first compounds of the series, the models allow a satisfactory simulation of existing experimental data, as well as of new ones especially obtained in a atmospheric jet-stirred reactor for $n$-hexylbenzene. Simulations for the largest compounds lead to the prediction of a significantly enhanced reactivity, especially below 800 K, when the size of the alkyl chain
increases. This is well explained by a smaller influence of the formation of benzylic radicals in the largest fuels.

ACKNOWLEDGEMENTS

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2 SUPPLEMENTARY MATERIAL

1/ Additional description

2/ A zip directory containing the 8 mechanisms for \(n\)-propylbenzene up to \(n\)-decylbenzenes.
REFERENCES


### Table 1: Numbers of species and reactions in the generated mechanisms.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of species</th>
<th>Number of reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylbenzene</td>
<td>238</td>
<td>1657</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>262</td>
<td>1871</td>
</tr>
<tr>
<td>Pentylbenzene</td>
<td>357</td>
<td>2475</td>
</tr>
<tr>
<td>Hexylbenzene</td>
<td>465</td>
<td>3226</td>
</tr>
<tr>
<td>Heptylbenzene</td>
<td>621</td>
<td>4260</td>
</tr>
<tr>
<td>Octylbenzene</td>
<td>815</td>
<td>5598</td>
</tr>
<tr>
<td>Nonylbenzene</td>
<td>1059</td>
<td>7260</td>
</tr>
<tr>
<td>Decylbenzene</td>
<td>1353</td>
<td>9302</td>
</tr>
</tbody>
</table>

### Table 2: Flow rate analysis (in %) at 610 K under the conditions of figure 6.

<table>
<thead>
<tr>
<th>Types of reaction</th>
<th>Butyl benzene</th>
<th>Hexyl benzene</th>
<th>Octyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel consumption</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ipso addition</td>
<td>2.0</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Alkylic H-abstraction</td>
<td>48.1</td>
<td>61.4</td>
<td>67.7</td>
</tr>
<tr>
<td>Benzylic H-abstraction</td>
<td>49.9</td>
<td>37.5</td>
<td>31.7</td>
</tr>
<tr>
<td><strong>Consumption/formation for alkyl radicals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; addition</td>
<td>88.7</td>
<td>119.4</td>
<td>112.0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>11.4</td>
<td>3.6</td>
<td>7.6</td>
</tr>
<tr>
<td><strong>Benzylic radicals consumption</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; addition</td>
<td>38.6</td>
<td>51.4</td>
<td>38.9</td>
</tr>
<tr>
<td>Oxidation</td>
<td>30.4</td>
<td>6.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Isomerization</td>
<td>0</td>
<td>32.8</td>
<td>38.0</td>
</tr>
<tr>
<td>Combination</td>
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<td>6.2</td>
<td>11.5</td>
</tr>
<tr>
<td>β-scission</td>
<td>8.1</td>
<td>1.8</td>
<td>2.0</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Color figures in electronic versions only.

Figure 1: Algorithm of comprehensive generation of primary mechanisms for the oxidation of alkylbenzenes.

Figure 2: Oxidation of \( n \)-propylbenzene in a jet-stirred reactor under stoichiometric conditions (points are experiments [4] and lines simulations).

Figure 3: Auto-inflammation of \( n \)-butylbenzene in (a) a rapid compression machine (\( \Phi = 0.4 \) at \( P_{TDC} \) from 14.3 to 18.3 bar, \( \Phi = 0.5 \) at \( P_{TDC} \) from 17.2 to 23.2 bar and \( \Phi = 1 \) at \( P_{TDC} \) from 13.4 to 17.9 bar) and (b) a shock tube (stoichiometric mixture) (points are experiments [4, 6] and lines simulations).

Figure 4: Major products of the oxidation of \( n \)-butylbenzene in a jet-stirred reactor (points are experiments [7] and lines simulations).

Figure 5: Major products of the oxidation of \( n \)-hexylbenzene in a jet-stirred reactor (points are experiments and lines simulations).

Figure 6: Figure 6: (a) computed evolution of the fuel conversion for the oxidation of a serie of \( n \)-alkylbenzenes (\( \text{C}_6\text{H}_5\text{C}_n\text{H}_{2n+1}: \text{C}_n \), with \( n \) from 3 to 10) under the conditions of figure 4 and 5, (b) and (c) mole fraction profiles of some important products formed from \( n \)-octylbenzene (C8) under these conditions.
Figure 1: Algorithm of comprehensive generation of primary mechanisms for the oxidation of alkylbenzenes.
Figure 2: Oxidation of \( n \)-propylbenzene in a jet-stirred reactor under stoichiometric conditions (points are experiments [5] and lines simulations).
Figure 3: Auto-ignition of \( n \)-butylbenzene in (a) a rapid compression machine \( (\Phi = 0.4 \) at \( P_{\text{TDC}} \) from 14.3 to 18.3 bar, and \( \Phi = 1 \) at \( P_{\text{TDC}} \) from 13.4 to 17.9 bar) and (b) a shock tube (stoichiometric mixture) (points are experiments [4, 6] and lines simulations).
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Figure 6: (a) computed evolution of the fuel conversion for the oxidation of a series of \( n \)-alkylbenzenes (C6H5CnH2n+1: Cn, with n from 3 to 10) under the conditions of figure 4 and 5. (b) and (c) mole fraction profiles of some important products formed from \( n \)-octylbenzene (C8) under these conditions.
Answers to reviewers for paper PROCI-S-13-00005

We thank the three referees for their helpful comments.

For the comments of Reviewer #1:

The paper describes the automated construction of kinetic models for the oxidation of a series of normal-alkyl benzenes (1-benzenes). The foundation for the work on the large molecules is other similarly indirect modeling studies on n-propyl benzene and n-butyl benzene. The authors use these systems and previously produced kinetic models as a template for the larger alkyl benzenes which have not been studied to date. A perfectly stirred reactor data set for the oxidation of n-hexyl benzene is measured at 1 atm, from 500-1100K to verify the apparent accuracy of the model input parameters. The models are then used to suggest that as the n-alkyl chain of the alkyl benzene increases, the magnitude of the low temperature reactivity increases, which would be as one expects.

At present, the paper is not very novel, more another implementation of reaction rate rules for another molecule, in n-hexyl benzene. There is nothing very special about the measurements, the quality of the model reproductions, which are quite poor in places, or the overall conclusions that are drawn. The paper is quite brief and short on important detail regarding the model description. Later much of what is needed is presented as 15 pages of supplemental material. As this is the central content of the paper, the model parameter derivations should be discussed and evaluated to high detail with regard uncertainty in the manuscript itself. If this cannot be done, my view is that the paper's message cannot be sufficiently communicated with the restrictions of PROCI.

Our rebuttal has thoroughly answered to this criticism about the lack of novelty of this paper. We will not repeat that here.

Specific comments requiring redress:

Comment 1:
For a paper that is mostly about kinetic modelling, it is inadequate that not one reaction rate constant (the model consists of very many ) and a justification for its choice appears in the text. It is not clear what, if any, the fundamental meaning of the kinetic model parameters is. There are fifteen pages of supplemental material that do provide some of this description -this should be in the text, as it is the contribution and main substance of the paper. The reader needs to get some information of how "true" the important assignments are likely to be -this is not provided at present.

As explained in the rebuttal, we disagree that the 15 pages of Supp. Mat. is the central content of the paper. The text gives the physico-chemical bases on which rely the reaction generation rules and related kinetic data. What is presented in Supp. Mat. is just a data-base explicitly giving all the details of the rules and values of the rate constants and we would prefer it to remain in Supp. Mat., knowing that the main features concerning these kinetic data are given in the text in pages 5-7.

Comment 2
The same remark is true of the very important thermochemical parameters. The authors should state what the estimated reaction enthalpies or bond energies are that allow them to assign their assumptions regarding hydrogen abstraction and bond scissions, one or two lines would be sufficient. Specific justifications are required for the rate constant assignments to the two C-H bond sites closest to the ring.

To give more detail about thermochemical data, we have added in page 4-5 the following sentence: “Group data were mainly those proposed by Domalski and Hearing [20] and bond dissociation
energies (BDE) were taken from Luo [21]. On the alkyl chain of the molecule, C-H BDEs were 85.4 kcal mol\(^{-1}\), 98.7 kcal mol\(^{-1}\), and 100.9 kcal mol\(^{-1}\) in the case of the benzylic position, of the secondary C-atoms and of the terminal methyl group, respectively., as well as new ref. [20] and [21].

Comment 3:
Figure 3 and page 8, it is normal to plot ignition delay on a logarithmic y-axis so that the detail of the comparison of measurement to simulation can be discerned.

As explained in the rebuttal, we think that the deviation between experiments and model can be better seen, when possible, in a linear y-axis, which is mostly used in the literature for RCM results. We prefer to keep figure 3 unchanged.

The simulations of the "model" model [6] should be included to verify the statement on top page 8. Please provide details of the simulation -adiabatic core, volume expansion or adiabatic core, constant volume. Which "assumption" of [6] (same authors as this study) is referred to as being in error?

To make the point clearer about RCM simulation, we have corrected the sentence in page 8: “The agreement is satisfactory in the rapid compression machine, even if the hypothesis of the adiabatic core made by [7]”.

Comment 4:
Again Figure 3 (b), the simulations of the model model should be presented to communicate that the essential details of the kinetic systems have been transcribed to the automated models produced in this work.

A comparison of data and simulations using the model of Husson et al. has already been published, but a comparison with the ignition data (rapid compression machine and shock tube) of figure 3 is presented again as Supp. Mat. in the same format as this figure is displayed in this text (see new figure S1). We have modified our text accordingly: “The agreement is as satisfactory with the rapid compression machine results as with the hand-written model of [7] (see figure S1 in supplementary material), even if the hypothesis of the adiabatic core made by [7] certainly leads to some under-estimation of the delay times at the lowest temperatures. Under shock tube conditions, as with the hand-generated model of [7] (see new figure S1 in supplementary material), while the agreement is good at atmospheric pressure, it deteriorates with increasing pressure.”.

Comment 5:
Same comment to figure 2 and figure 4, we must demonstrate that the models are consistent or where they are different.

A comparison of data and simulations using the model of Husson et al. has already been published, but a comparison with the JSR data of figure 4 is presented again as Supp. Mat. in the same format as this figure is displayed in this text (see new figure S2). We have modified our text accordingly: “It shows that the model leads to a satisfactory agreement, even better than that obtained by Husson et al. [7] (see new figure S2 in supplementary material)”. Concerning figure 2, we do not have older model for propylbenzene.

Comment 6:
Also, the authors don't need to include the data in their paper, but please provide some explanation for the omission of other works on the model molecules.
of n-propyl benzene and n-butyl benzene, there are nice data sets from the laboratories of Brezinsky, Glassman, Ju/Won, Hanson, Dagaut and probably others. This is important as Figs 2-4 do not show the present work to do a very good job, so is this a problem with the data or with the model?

This paper already presents validations for a wide range of reactors: jet-stirred reactors (JSR) at 2 pressures (a comparison with the data of Dagaut et al. at 10 bar is presented in Supp. Mat.), RCM and shock tube. As announced in the rebuttal, we have included a comparison with the data of Brenzinsky in a flow tube, a type of reactor which is not in the previous list. New figure S3 has been added in Supplementary material, as well as the corresponding text in page 8: “Figure S3 in supplementary material presents the simulated evolutions of reactants and major products in the flow reactor. As shown by this figure, the model slightly underpredicts the fuel consumption, but predicts satisfactorily the formation of the major products, such as CO, methane, ethylene, benzene, toluene and styrene.”.

Comment 7:
For a mechanistic study such as this, it is unfortunate that the heavier fuel type molecules could not be extracted. A statement of uncertainty for the original measurements to this study should be made. It seems odd that benzene cannot be reproduced but styrene can, can this be explained?

As explained in the rebuttal, concerning uncertainty on hexylbenzene JSR results, it is written on page 10: “Based on the repeatability of the experiments, uncertainty estimates on obtained mole fractions were about ± 5% (measure reading).”. Also, in figure 5, benzene seems to be as well reproduced as styrene.

Comment 8:
The authors conclude that the extent of low temperature reactivity steadily increases with the size of the alkyl chain. This feature is a matter of debate presently, shock tube ignition delay data of Oehlschlaeger indicates a commonality of reactivity for constant carbon-concentration systems for normal alkanes beyond a certain size, apparently contradicting the conclusion of Biet et al. (authors of the present manuscript). So, some discussion and error analysis on the kinetic terms producing this conclusion would be of interest.

As explained in the rebuttal, actually there is a discussion between the Nancy and Livermore teams in the case of large alkanes to know if there is a small reactivity increase when increasing the chain length of the reactants. This was not fully settled by the experimental results of Oehlschlaeger. But this is a different story, since here the reactivity increase at low temperature when increasing the chain length of the reactants is not small, but it is more than a factor of 4 from propylbenzene to decylbenzene. This is due to the influence of the aromatic ring which becomes more limited when the size of the species increases. To make this point clearer, we have added in page 12: “leads to an increase of the low-temperature maximum conversion of about a factor of 4, due to the decreasing influence of the aromatic ring.”.

For the comments of Reviewer #2:

Comments 1:

p.4: The enthalpy is close, but not the same as the value of Cohen. How did you choose this value? Why? I assume that there must have been a reason not to just adopt the Cohen number, so this value is important (if not, then why not take the Cohen number). Give a reference or explanation.
To make this point clearer, we have completed the sentence of page 4-5: “New data have been used for the enthalpy and the entropy (-4.94 kcal/mol and -10.21 cal/mol/K, respectively, of the C-(Cb)-(C)-(O)-(H) group, allowing us to get better agreement between simulations and experiments.”

Comments 2:
I am not sure how to understand the “favoritism” in the case of the mechanism development. Is it done to keep the mechanism at a reasonable size? Also, the example scheme on p. 6 does not add up: how can you make these fragments from the ketohydroperoxide shown? You need a complicated rearrangement for this to happen. Or is this the point that even though this reaction is not physically possible, but the mechanism still goes along this pathway? Please explain.

The reaction in the scheme of page 6 is not an elementary reaction, but a lumped one aiming producing species already included in the reaction base or in the primary mechanism. This technique is the same as that used by Biet and al. [13] in the case of alkanes. To make that clearer, we have added in page 6: “Note that these secondary reactions are no more elementary steps and that the formation of molecules included in the aromatic base, such as styrene or benzaldehyde, has been favored. An example of generic secondary reaction is presented in equation (2) for the case of benzylketohydroperoxides, all the isomers of which are written: $\phi C_5H_{10}(CO)(OOH)$. The structure represented in equation (2) is just an example.”.

Comment 3:
Fig. 3: auto-inflammation ---> auto-ignition

This has been corrected.

Comments 4:
How was the pressure dependence of the reactions treated? Please add to the manuscript a description.

Pressure dependence of the reactions is only taken into account in the reaction base. To make that clearer we have added in page 4: “The system provides reaction mechanisms made of three parts, in which the pressure dependence of the reactions is only considered in the first one”.

Comment 5:
How does the mechanism compare to the LLNL mechanism?

As announced in the rebuttal, an attempt of simulation has been performed in the case of butylbenzene JSR results using the LLNL model. New figure S5 in Supplementary Material has been added to presents this comparison and is described by the new text in page 9: “Note also that figure S5 in supplementary material presents the prediction of the model of Nakamura et al. [10] for the JSR results for n-butylbenzene obtained by Husson et al. [7]. This figure, plotted under the same format as figure 4, shows that this last model overpredicts significantly fuel conversion both below and above 800 K, while the automatically generated model presented here leads to satisfactory predictions. The overprediction of fuel conversion leads to an overprediction of acetaldehyde and propene formation below 800 K, and to deviations in the predictions of small aromatic compound formation above 800 K.”.
For the comments of Reviewer #3:

We thank this referee for his very positive comments.

The most serious one is in the Abstract where it says "a new type of primary reaction, ipso-addition".

We are sorry for our misleading sentence in the abstract about ipso-additions which has been corrected as follows: "They involve a new type of generic primary reaction for EXGAS mechanisms, ipso-addition,"

On page 8 the authors' claim that the reactivity below 800K is now well reproduced - nothing much happens below 800K as can be seen in Fig 4 so what does this statement mean? What are they claiming to have accomplished?

In page 8, figure 4 shows a small fuel conversion as well as production of acetaldehyde, styrene and propene, which could not be seen with the previous model of Husson (see new Supp. Mat.).

Also on page 8 the authors' state that a JSR is a good instrument for studying reactions at the same conditions. Same conditions as what?

It should be read "same conditions as for n-butylbenzene", this has been corrected.

I did wonder, since it is stated in this paper without reference, if diesel fuel actually does have any significant concentration of alkylated benzenes with side chains as long as C10.

Note that Ref [1] proposes n-decylbenzene as a component in a diesel surrogate fuel, we have also added the following description of new ref [10] page 3: "Note that due to the lack of data and model for this compound, it has recently been proposed to use mixtures of n-propylbenzene and n-butylbenzene with n-heptane to simulate n-decylbenzene ignition".
THE OXIDATION OF LARGE ALKYLBENZENES: AN EXPERIMENTAL AND MODELING STUDY

Frédérique Battin-Leclerc*, Valérie Warth, Roda Bounaceur, Benoît Husson, Olivier Herbinet, Pierre-Alexandre Glaude

Laboratoire Réactions et Génie des Procédés, UMR 7274 CNRS - Université de Lorraine, 1 rue Grandville, 54000 Nancy

Colloquium : Reaction kinetics

Details of the word count (Method 1):

Text: 3878, 24 References: 454, 2 tables: 250, 6 figures: 1663

TOTAL = 6231

2 supplementary files:

Color figures in electronic versions only

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THE OXIDATION OF LARGE ALKYLBENZENES: AN EXPERIMENTAL AND MODELING STUDY

Frédérique Battin-Leclerc*, Valérie Warth, Roda Bounaceur, Benoit Husson, Olivier Herbinet, Pierre-Alexandre Glaude

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This paper describes the first development of detailed kinetic models for the alkylbenzenes actually present in diesel fuels. Thanks to a new version of the software EXGAS dedicated to alkylbenzenes, the first detailed models for the oxidation of alkylbenzenes with an alkyl chain containing more than 4 atoms of carbon have been automatically generated. These models are based on an aromatic reaction base consisting of a recent ethylbenzene detailed kinetic model. They involve a new type of generic primary reaction for EXGAS mechanisms, ipso-addition, and new generic rules for the estimation of kinetic parameters involved in primary and secondary mechanisms. The existing experimental data on the oxidation of \( n \)-propylbenzene and \( n \)-butylbenzene, as well as new results on the oxidation of \( n \)-hexylbenzene obtained in a jet-stirred reactor from 500 to 1100 K under 1 atm, have been successfully modeled. Simulations well reproduce the more important low temperature reactivity which is observed for \( n \)-hexylbenzene compared to \( n \)-butylbenzene. This new tool has been also used to numerically investigate the behavior of alkylbenzenes from \( n \)-propylbenzene up to \( n \)-decylbenzene. Simulations using this model show an important enhancement of low-temperature reactivity when the alkyl chain in the compounds increases. Flow rate analyses show that this significant increase is due to an influence of resonance stabilized benzylic radicals obtained from the reactant by H-abstractions on the carbon atom neighboring the ring.

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Keywords: detailed kinetic models, hexylbenzene, decylbenzene, oxidation, jet-stirred reactor.

INTRODUCTION

Diesel fuels are complex blends of hundreds of species, which are mainly hydrocarbons from the distillation of crude oil and also oxygenated molecules used as additives [1, 2]. The main classes of molecules found in closely equal amounts in petroleum based diesel fuels are \( n \)- and \( iso \)-paraffins, naphthenes and aromatic compounds with carbon atom numbers ranging from 10 to 22 (with an average value around 14-15) [1]. Aromatic compounds usually consist of one aromatic ring with one or several side alkyl chains.

This paper focuses on the development of detailed kinetic models for the oxidation of alkylbenzenes actually present in diesel fuel: e.g. \( n \)-decylbenzene (\( \phi C_{10}H_{21} \)). For this purpose a new version of the software EXGAS dedicated to the automatic generation of detailed oxidation models has been developed for alkylbenzenes (EXGAS-Akylbenzene\(^1\), called EXGAS in this paper) and validated for the molecules with a \( C_{3-4} \) alkyl chain for which recent experimental data were available [3-10], including new experimental results obtained for \( n \)-hexylbenzene (\( \phi C_6H_{13} \)) in a jet stirred reactor. To our knowledge, the gas-phase oxidation of this last reactant has never been previously investigated. Simulations using generated models for a series of \( n \)-alkylbenzenes up to \( n \)-decylbenzene have also been performed. Note that due to the lack of data and model for this last compound, it has recently been proposed to use mixtures of \( n \)-propylbenzene and \( n \)-butylbenzene with \( n \)-heptane to simulate \( n \)-decylbenzene ignition [11].

\(^1\) Software EXGAS-Akylbenzenes automatically generates detailed kinetic mechanisms for the oxidation of linear and branched alkanes and mono-alkylbenzenes and is freely available for academic researchers (valerie.warth@univ-lorraine.fr).
DESCRIPTION OF THE KINETIC MODELS

The detailed kinetic mechanisms used in this study have been automatically generated by the computer package EXGAS. This software has already been used for generating mechanisms in the case of alkanes [12-14], alkenes [15], as well as of oxygenated biofuels [16]. We will recall here very shortly its main features which have already been much described and we will present the specificities in the reactions and rate constants which were taken into account and implemented in the system to well represent the behavior of alkylbenzenes. All the mechanisms generated for this study are provided as supplementary material in CHEMKIN format.

General features of EXGAS

The system provides reaction mechanisms made of three parts, in which the pressure dependence of the reactions is only considered in the first one:

- An aromatic reaction base, which consists in the model proposed for ethylbenzene by [17] and which contains 755 reactions.
  This reaction base includes a C_0-C_2 reaction base, a mechanism to model the oxidation of C_3-C_5 unsaturated hydrocarbons, as well as recently up-dated mechanisms for the oxidation of small aromatic compounds, benzene, and toluene.
- A comprehensive primary mechanism, where the only molecular reactants considered are the initial organic compounds and oxygen.
- A lumped secondary mechanism, containing the reactions consuming the molecular products of the primary mechanism, which do not react in the reaction base.

Thermochemical data for molecules or radicals were automatically calculated and stored according to the CHEMKIN formalism [18]. These data were calculated using software THERGAS [19], based on the group and bond additivity methods [20]. Group data were mainly those proposed by Domalski and Hearing [21] and bond dissociation energies (BDE) were taken from Luo [22]. On the alkyl chain of the molecule, C-H BDEs were 85.4 kcal mol$^{-1}$, 98.7
kcal mol$^{-1}$, and 100.9 kcal mol$^{-1}$ in the case of the benzylic position, of the secondary C-atoms and of the terminal methyl group, respectively. New data have been used for the enthalpy and the entropy (-4.94 kcal/mol and -10.21 cal/mol/K, respectively, of the C-(Cb)-(C)-(O)-(H) group, allowing us to get better agreement between simulations and experiments). For the enthalpy, this value is close to that proposed by Cohen [23] (i.e -4.4 kcal/mol).

The kinetic data of isomerizations, combinations and unimolecular decompositions are calculated using software KINGAS [12] based on the thermochemical kinetics methods [20] using the transition state theory or the modified collision theory. The kinetic data, for which the calculation is not possible by KINGAS, are estimated from correlations, which are based on quantitative structure-reactivity relationships and obtained from a literature review [13][15].

**Primary mechanism of the oxidation of alkylbenzenes**

Compared to the case of alkanes, the changes made in the generation of primary mechanisms due to the presence of the aromatic ring have been based on a previous model of the oxidation of $n$-butylbenzene [7]. This model had been manually written, but following the rules taken into account during the automatic generation of mechanisms for the oxidation of alkanes and alkenes by the software EXGAS. The reactions considered in the primary mechanism of alkylbenzenes are given in figure 1. The only type of reactions specific to alkylbenzenes is the ipso-addition of H or O atoms and of small radicals, OH, CH$_3$, and HO$_2$, which consist of the substitution of the alkyl chain by the atom or the radical involved in the reaction. For instance, the ipso-addition of an OH radical to $n$-butylbenzene gives phenol and a $n$-butyl radical. While the primary mechanisms have been generated using rules mainly similar to those proposed in the case of the oxidation of alkanes [12], the encoding of these reactions had to be fully revised to take into account the presence of the aromatic ring in the involved alkylbenzenic species using a new internal representation.

**FIGURE 1**
The primary mechanisms have been generated based on two simple assumptions: (i) the aromatic ring only reacts through ipso-additions which have been shown to be of importance for toluene and ethylbenzene [17], (ii) the reactivity of the resonance stabilized benzylic secondary radicals (see the resonance stabilized radical deriving from \(n\)-hexylbenzene in equation (1)) has been taken equal to that of resonance stabilized allylic secondary radicals [15].

\[
\text{(1)}
\]

A table summarizing the kinetic data is given in Supplementary material. Most of the correlations used for the calculation of kinetic parameters are derived from correlations proposed for linear alkanes [13] and alkenes [15]. The rate constants for the ipso-additions are those considered by [7], except for that of HO\(_2\) radicals which was not considered. Since there is no data for this last rate constant, it has been estimated based on that of other radicals.

**Secondary mechanism of the oxidation of alkylbenzenes**

For reducing the number of reactants in the secondary mechanism, the molecules formed in the primary mechanism, with the same molecular formula and the same functional groups, are lumped into one unique species, without distinguishing between the different isomers [12]. The considered species are several types of benzylhydroperoxides, alkyl and alkenylbenzenes, cyclic ethers connected to a benzene ring, benzylic alcohols, benzylaldehydes and benzylketones. Similarly to the case of alkanes [14], the writing of the secondary reactions is made in order to promote the formation of alkyl or benzylic radicals which contain more than two carbon atoms and which are already included in the primary mechanism or in the aromatic reaction base. Note that these secondary reactions are no more elementary steps and that the formation of molecules included in the aromatic base, such as styrene or benzaldehyde, has been favored. An example of generic secondary reaction is presented in equation (2) for the case of benzylketohydroperoxides, all the isomers of which are written: \(\phi C_7H_{10} (CO)(OOH)\). The
The generated models have been tested in the case of the oxidation of \( n \)-propylnbenzene and \( n \)-butylbenzene using literature data, and for that of \( n \)-hexylnbenzene using newly obtained experimental results. No adjustment has been made to the models obtained using the automatic generator. Despite the simplicity of the assumptions used in the generation of primary mechanisms, the obtained agreement is satisfactory over a wide range of experimental conditions for the three alkylbenzenes for which experimental data are available.

**Validations for \( n \)-propylnbenzene oxidation**

The oxidation of \( n \)-propylnbenzene has been previously studied in a jet-stirred reactor (JSR) at temperatures ranging from 750 to 1100 K (1 atm, a residence time of 0.7 s, an inlet fuel mole fraction of 0.1%) [5]. Figure 2 presents a comparison between these experimental data and simulations using a model generated for the oxidation of \( n \)-propylnbenzene. It shows that the fuel consumption is very well simulated, as well as the formation of major products such as carbon monoxide and styrene. Satisfactory predictions of other products such as ethylene, formaldehyde, benzene and toluene are also obtained.
Validations for \textit{n}-butylbenzene oxidation

The generated model has been validated against literature data obtained in a rapid compression machine, a shock tube, and 1.06 and 10 atm JSRs.

The auto-ignition of \textit{n}-butylbenzene has been previously experimentally investigated in a rapid compression machine [4, 6] and in a shock tube way [7]. Figure 3 presents a comparison between these experimental data and simulation using a model generated for the oxidation of \textit{n}-butylbenzene. It can be observed that in both cases, the model, tested under the same conditions as in [7], performs as well as this previous model. The agreement is as satisfactory with the rapid compression machine results as with the hand-written model of [7] (see figure S1 in supplementary material), even if the hypothesis of the adiabatic core made by [7] certainly leads to some under-estimation of the delay times at the lowest temperatures. Under shock tube conditions, as with the hand-written model of [7] (see figure S1 in supplementary material), while the agreement is good at atmospheric pressure, it deteriorates with increasing pressure.

Husson et al. [7] have studied the oxidation of \textit{n}-butylbenzene in a JSR at atmospheric pressure in Nancy for a residence time of 2s and an inlet fuel mole fraction of 0.4%. Figure 4 presents the experimental and modeled evolutions with temperature of the reactant and the major product mole fractions. It shows that the model leads to a satisfactory agreement, even better than that obtained by Husson et al. [7] (see figure S2 in supplementary material), since the low-temperature reactivity observed below 800 K is now well reproduced. The oxidation of \textit{n}-butylbenzene has also been studied in a flow reactor at 1 atm [3] and in another JSR at 10 atm (residence time of 1s) [5]. Figure S3 in supplementary material presents the simulated evolutions of reactants and major products in the flow reactor. As shown by this figure, the model slightly underpredicts the fuel consumption, but predicts satisfactorily the formation of the major
products, such as CO, methane, ethylen, benzene, toluene and styrene. Figure S4 in supplementary material presents the simulated evolutions of fuel and formaldehyde mole fractions (a good indicator of the low-temperature reactivity) in JSR. This figure shows that the model reproduces well the fuel consumption and the formaldehyde mole fraction below 800 K, but that the formation of this last compound is overestimated by a factor of 2 above, while a correct agreement was obtained by [7].

FIGURE 4

Note also that figure S5 in supplementary material presents the prediction of the model of Nakamura et al. [10] for the JSR results for n-butylbenzene obtained by Husson et al. [7]. This figure, plotted under the same format as figure 4, shows that this last model overpredicts significantly fuel conversion both below and above 800 K, while the automatically generated model presented here leads to satisfactory predictions. The overprediction of fuel conversion leads to an overprediction of acetaldehyde and propene formation below 800 K, and to deviations in the predictions of small aromatic compound formation above 800 K.

Validations for n-hexylbenzene oxidation – New experimental results

An experimental study of the oxidation of n-hexylbenzene has been performed in a JSR, a type of reactor which has often been used for gas phase kinetic studies [17], and especially to study the n-hexylbenzene oxidation under the same conditions as n-butylbenzene, including the same carbon atom initial mole fraction [7]. Experiments were performed at a constant pressure of 800 Torr (1.06 atm), at a residence time of 2 s, at temperatures ranging from 750 to 1100 K using stoichiometric mixtures. The fuel was diluted in helium (n-hexylbenzene inlet mole fraction of 0.0033). n-Hexylbenzene was provided by Aldrich (purity ≥ 97 %), and helium and oxygen by Messer (purity of 99.999% for He and 99.995% for O₂).

The reactor consists of a quartz sphere (volume = 95 cm³) into which diluted reactant enters through an injection cross located at its center. It is operated at constant temperature and pressure.
and it is preceded by an annular preheating zone in which the temperature of the gases is progressively increased up to the reactor temperature before entering inside. Gas mixture residence time inside the annular preheater is very short compared to its residence time inside the reactor. Both the spherical reactor and the annular preheating zone are heated by resistance heaters wrapped around their walls. Despite the exothermicity of the reaction, the temperature gradient in the vessel was lower than 5 K. The fuel flow rate was controlled by a liquid mass flow controller and was mixed with the carrier gas and then evaporated by passing through a single pass heat exchanger, the temperature of which was set above the boiling point of the hydrocarbon. Carrier gas and oxygen flow rates were controlled by gas mass flow controllers. The accuracy of the liquid and gas flow rates was around 0.5%.

The outlet products were analyzed online by gas chromatography. The online analysis of products which are liquid at standard conditions was performed using a heated transfer line between the reactor outlet and the chromatograph sampling gates which were also heated. During the study, the temperature of the transfer line was set to its maximum, 473 K, but it was not high enough to keep all the reaction products in the gas phase. Three gas chromatographs (GC) were used for the quantification of the different species. The first GC, equipped with a Carbosphere packed column, a thermal conductivity detector, and a flame ionization detector (FID), was used for the quantification of O₂, carbon oxides, and C₁-C₂ hydrocarbons. Detected in GC-MS, hydrogen, water and formaldehyde were however not quantified. The second GC was fitted with a PlotQ capillary column and a FID, and was used for the quantification of C₁-C₄ hydrocarbons and of small oxygenated compounds. The third GC was fitted with a HP-5 capillary column and a FID, and was used for the quantification of species with more than five heavy atoms (i.e. carbon and oxygen atoms). The identification and the calibration of light species (e.g. carbon oxides, C₁-C₄ hydrocarbons) were performed by injecting commercial gaseous mixtures. For other species, the calibration was performed by injecting known amounts
of the pure substances. Based on the repeatability of the experiments, uncertainty estimates on obtained mole fractions were about ± 5% (measure reading). It was not possible to quantify neither \( n \)-hexylbenzene (\( \varphi C_6H_{13} \)) nor products heavier than ethylbenzene due to a too low vapor pressure and condensation problem in the transfer line between the reactor and the gas chromatographs.

Figure 5 presents the experimental and computed evolution with temperature of oxygen and the measured products with a mole fraction reaching at least 80 ppm, together with the simulated fuel profile. By comparison with figure 4 made for \( n \)-butylbenzene under the same JSR conditions and with the same content in atoms of carbon in the inlet gas, it can be observed that a close reactivity is experimentally obtained from both fuels above 800K, as well shown by most product mole fractions, but that below this temperature, the reactivity of \( n \)-hexylbenzene is the largest as indicated by the acetaldehyde and styrene mole fractions. The mole fractions of these species also indicate a pronounced negative coefficient (NTC) behavior, more marked than in the case of \( n \)-butylbenzene. Figure 5 also shows that, according to the product formation, the reactivity of \( n \)-hexylbenzene in both temperature ranges is well reproduced by the model.

**FIGURE 5**

**MODELLING ALKYLBENZENES WITH A C\(_6\) ALKYL CHAIN**

As the models generated by EXGAS are able to successfully reproduce many available experimental results for the oxidation of alkylbenzenes from propylbenzene up to \( n \)-hexylbenzene, we have attempted to generate models for a series \( n \)-alkylbenzenes up to \( n \)-decal benzene and to compare the obtained reactivity with that of smaller compounds. Note that similar attempts to model a family of large hydrocarbons of increasing size have already been made in the case of linear C\(_{7+}\) alkanes [14][24].

Table 1 presents the number of species and reactions in all the models generated in this study. In the case of \( n \)-butylbenzene, the generated model is slightly smaller than that manually written
(2303 reactions) [7]. Note that despite the fact that the aromatic ring is considered as mostly unreactive, the model for a given \( n \)-alkylbenzene (e.g. 5598 reactions in the case of \( n \)-octylbenzene) is significantly larger than that generated for the corresponding \( n \)-alkane (2013 reactions for \( n \)-octane). Due to the presence of the aromatic ring, the symmetry of the molecule is lost, inducing the production of a much larger number of isomers, e.g. 4 radicals are formed from \( n \)-octane by H-abstractions, while 8 are produced from \( n \)-octylbenzene. This large number of involved species and reactions certainly supports the use of model automatic generation methods.

**TABLE 1**

Figure 6a presents simulations performed under atmospheric jet-stirred reactor conditions for the studied series of alkylbenzenes (\( \text{C}_6\text{H}_5\text{C}_n\text{H}_{2n+1} \) with \( 3 < n < 10 \), named here C\( n \)) for stoichiometric mixtures containing the same carbon atom content as under the conditions of figures 4 and 5, e.g. an inlet mole fraction of 0.0025 for C8. It can be observed that the low-temperature reactivity observed below 800 K steadily increases when the size of the alkyl chain increases, with no low-temperature reactivity observed for \( n \)-propylbenzene. For all the other compounds, a very well marked negative temperature coefficient zone can be observed around 800 K. This increase of reactivity is much more pronounced than what was observed by Biet et al. [14] in the case of C\( 7+ \) alkanes under similar conditions, for which an increase of the alkyl chain of 7 atoms of carbon led to a conversion increase of only 25%. In figure 6, an increase of the alkyl chain of 6 atoms of carbon (from \( n \)-butylbenzene to \( n \)-decylbenzene) leads to an increase of the low-temperature maximum conversion of about a factor of 4, due to the decreasing influence of the aromatic ring. However for compounds larger than C9, the increase of reactivity with the size of the alkyl chain starts to be more limited. Simulations under these condition for C8 (fig 6 b and c) confirm the important low temperature reactivity, with a large formation of CO, ethylene, styrene, large alkenes, and aldehydes observed below 800 K.
In order to explain this change in the low-temperature reactivity according to the studied alkylbenzene, a flow rate analysis has been performed at 610 K (the temperature of the maximum of the low-temperature reactivity for \( n \)-butylbenzene) under the conditions of figure 6. As shown in Table 2, alkylbenzenes are mainly consumed by abstractions of alkylcic and benzylic H-atoms, with the ratio between both channels being almost equal for C4, but of a factor larger than 2 in favor of alkylcic H-atoms in the case of C8. Due to the thermochemistry of this addition, benzylic radicals react much less easily than alkylcic radicals by addition to oxygen to give branching agents. Benzylic radicals derived from C4 react then mainly by combinations with methyl or \( \text{HO}_2 \) radicals, and by oxidation to give butenylbenzenes and the unreactive \( \text{HO}_2 \) radicals, even if the activation energy of this reaction (15.2 kcal/mol, see Table S2a in supplementary material) is relatively high. This explains the very low reactivity of C4, for which the promoting influence of a third channel of fuel consumption, ipso-additions, especially those with \( \text{HO}_2 \) radicals, has an important role to promote reactivity, even if its contribution to the total fuel consumption is only of 2%.

**TABLE 2**

When the size of the alkyl chain increases, isomerizations of benzylic radicals to give secondary alkylcic radicals through 6-membered ring transition states start to be possible. Due to their low activation energy (see Table S1b in supplementary material), these isomerizations compete significantly with the other channels consuming benzylic radicals as shown in Table 2. Already in the case of C6, the isomerizations of benzylic to alkylcic radicals account for 32.8% of benzylic radical consumption. Note that about 90% of alkylcic radicals react by addition to oxygen promoting the formation of well known branching agents, keto-hydroperoxydes. Isomerizations of benzylic radicals into alkylcic radicals explained why the consumption of alkylcic radicals by addition to oxygen is larger than their formation, as shown in Table 2. When the size of the alkyl...
chain increases, the part of isomerization in the consumption of benzylic radicals keeps on increasing, while that of the inhibiting oxidation keeps on decreasing. Therefore, there are three effects promoting reactivity when the size of the alkyl chain increases, (i) the lower contribution of the formation of benzylic radicals by H-abstractions, (ii) the easiest isomerizations of benzylic radicals to give alkylic radicals, and (iii) the easiest isomerizations of peroxy radicals obtained from alkylic radicals. In the case of C\textsubscript{7+} alkanes or of \textit{n}-alkylbenzenes above C9, the limited increase of conversion when the size of the reactant increases, is only due to this last effect.

Above 800K, the formation of benzylic radicals for the fuel consumption still accounts for a significant part which is decreasing with the size of the alkyl chain. However, at this temperature, these radicals react mostly by $\beta$-scissions to give styrene and alkylic radicals (more than 90%). The activation energy of this $\beta$-scission is higher by more than 10 kcal/mol than that of the decomposition of alkylic radicals (see Table S2b in supplementary material). This explains why at a given temperature above 800 K the reactivity of \textit{n}-alkylbenzenes up to C5 increases when the size of the alkyl chain increases, and does not change for heavier compounds. The reactivity of C3 is by far the lowest since in this case the alkyl radical is a methyl radical with an activation energy still 2.3 kcal/mol higher than for the formation of larger alkylic radicals, and with the largest contribution of the formation of benzylic radicals in the fuel consumption.

**CONCLUSION**

A new version of software EXGAS dedicated to alkylbenzenes has been developed and used to automatically generate the first models for a series of \textit{n}-alkylbenzenes with a C\textsubscript{3}-C\textsubscript{10} alkyl chain. For the three first compounds of the series, the models allow a satisfactory simulation of existing experimental data, as well as of new ones especially obtained in a atmospheric jet-stirred reactor for \textit{n}-hexylbenzene. Simulations for the largest compounds lead to the prediction of a significantly enhanced reactivity, especially below 800 K, when the size of the alkyl chain
increases. This is well explained by a smaller influence of the formation of benzylic radicals in the largest fuels.

ACKNOWLEDGEMENTS

This study was supported by SAUDI-ARAMCO. The authors are grateful to C.K. Westbrook for initiating this study.

2 SUPPLEMENTARY MATERIAL

1/ Additional description

2/ A zip directory containing the 8 mechanisms for \( n \)-propylbenzene up to \( n \)-decylbenzenes.
REFERENCES


**Table 1:** Numbers of species and reactions in the generated mechanisms.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of species</th>
<th>Number of reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylbenzene</td>
<td>238</td>
<td>1657</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>262</td>
<td>1871</td>
</tr>
<tr>
<td>Pentylbenzene</td>
<td>357</td>
<td>2475</td>
</tr>
<tr>
<td>Hexylbenzene</td>
<td>465</td>
<td>3226</td>
</tr>
<tr>
<td>Hexylbenzene</td>
<td>621</td>
<td>4260</td>
</tr>
<tr>
<td>Octylbenzene</td>
<td>815</td>
<td>5598</td>
</tr>
<tr>
<td>Nonylbenzene</td>
<td>1059</td>
<td>7260</td>
</tr>
<tr>
<td>Decylbenzene</td>
<td>1353</td>
<td>9302</td>
</tr>
</tbody>
</table>

**Table 2:** Flow rate analysis (in %) at 610 K under the conditions of figure 6.

<table>
<thead>
<tr>
<th>Types of reaction</th>
<th>Butyl benzene</th>
<th>Hexyl benzene</th>
<th>Octyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel consumption</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ipso addition</td>
<td>2.0</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Alkyllic H-abstraction</td>
<td>48.1</td>
<td>61.4</td>
<td>67.7</td>
</tr>
<tr>
<td>Benzylic H-abstraction</td>
<td>49.9</td>
<td>37.5</td>
<td>31.7</td>
</tr>
<tr>
<td><strong>Consumption/formation for alkyl radicals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ addition</td>
<td>88.7</td>
<td>119.4</td>
<td>112.0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>11.4</td>
<td>3.6</td>
<td>7.6</td>
</tr>
<tr>
<td><strong>Benzylic radicals consumption</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ addition</td>
<td>38.6</td>
<td>51.4</td>
<td>38.9</td>
</tr>
<tr>
<td>Oxidation</td>
<td>30.4</td>
<td>6.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Isomerization</td>
<td>0</td>
<td>32.8</td>
<td>38.0</td>
</tr>
<tr>
<td>Combination</td>
<td>18.6</td>
<td>6.2</td>
<td>11.5</td>
</tr>
<tr>
<td>β-scission</td>
<td>8.1</td>
<td>1.8</td>
<td>2.0</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Color figures in electronic versions only.

Figure 1: Algorithm of comprehensive generation of primary mechanisms for the oxidation of alkylbenzenes.

Figure 2: Oxidation of \(n\)-propylbenzene in a jet-stirred reactor under stoichiometric conditions (points are experiments [4] and lines simulations).

Figure 3: Auto-inflammation of \(n\)-butylbenzene in (a) a rapid compression machine (\(\Phi = 0.4\) at \(P_{TDC}\) from 14.3 to 18.3 bar, \(\Phi = 0.5\) at \(P_{TDC}\) from 17.2 to 23.2 bar and \(\Phi = 1\) at \(P_{TDC}\) from 13.4 to 17.9 bar) and (b) a shock tube (stoichiometric mixture) (points are experiments [4, 6] and lines simulations).

Figure 4: Major products of the oxidation of \(n\)-butylbenzene in a jet-stirred reactor (points are experiments [7] and lines simulations).

Figure 5: Major products of the oxidation of \(n\)-hexylbenzene in a jet-stirred reactor (points are experiments and lines simulations).

Figure 6: (a) computed evolution of the fuel conversion for the oxidation of a series of \(n\)-alkylbenzenes (\(C_6H_5CnH_{2n+1}: C_n\), with \(n\) from 3 to 10) under the conditions of figure 4 and 5, (b) and (c) mole fraction profiles of some important products formed from \(n\)-octylbenzene (\(C_8\)) under these conditions.
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Click here to download Supplemental Material: Revised additional description.pdf
Click here to download Supplemental Material: meca-Nonylbenzene.txt
Click here to download Supplemental Material: meca-Propylbenzene.txt
Reactant \( (C_6H_5C_nH_{2n+1}) \)

**Initiations**
- Unimolecular initiations
- Bimolecular initiations

\( R \cdot \)

**Propagations**
- Ipso-additions to the benzene ring
- \( O_2 \) additions
- \( \beta \)-scissions
- Isomerizations
- Cyclic ether decompositions
- Oxidations to alkenylbenzene s+ \( HO_2 \)
- H-abstractions of alkylic and benzylic H-atoms

\( R' + \text{primary species} \)

**Terminations** *(important for benzylic radicals)*
- Combinations
- Disproportionations

\( \text{Primary species} \)
Figure 3b
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The graph shows the relationship between delay times (μs) and 10000/T [K] for different pressures. The pressure levels are represented as follows:

- Blue triangles: P = 1 atm
- Black triangles: P = 30 atm
- Dotted line: P = 10 atm

The plot indicates that delay times increase as the inverse of temperature increases, suggesting an inverse relationship. The temperature range is 1000 < T[K] < 1670.
Figure 4

Click here to download high resolution image