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The oxidation of large alkylbenzenes: An experimental and modeling study

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Abstract

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 2 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 also been 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 a decreasing influence of resonance stabilized benzylic radicals obtained from the reactant by H-abstractions on the carbon atom neighboring the ring.

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1. 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

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alkylbenzenes actually present in diesel fuel: e.g., *n*-decylbenzene ($\varphi\text{C}_{10}\text{H}_{21}$). 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-alkylbenzene¹, 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 ($\varphi\text{C}_6\text{H}_{13}$) 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 or *n*-butylbenzene with *n*-heptane to simulate *n*-decylbenzene ignition [11].

2. Description of the kinetic model

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 general features and we will present the specificities in the reactions and rate constants that were taken into account and implemented in the software to well represent the behavior of alkylbenzenes. All the mechanisms generated for this study are provided as [Supplementary material](#) in CHEMKIN format.

2.1. General features of EXGAS

EXGAS 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 $\text{C}_0\text{--}\text{C}_2$ reaction base, a mechanism to model the oxidation of $\text{C}_3\text{--}\text{C}_5$ unsaturated hydrocarbons, as well as recently updated 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, that do not react in the reaction base.

Thermochemical data for molecules or radicals are automatically calculated and stored according to the CHEMKIN formalism [18]. These data are calculated using software THERGAS [19], based on the group and bond additivity methods [20]. Group data are mainly those proposed by Domalski and Hearing [21] and bond dissociation energies (BDE) are taken from Luo [22]. On the alkyl chain of the molecule, C–H BDEs are 85.4, 98.7, 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, leading to a 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 of the fuel are calculated using software KINGAS [12] using the transition state theory or the modified collision theory [20]. The kinetic data, for which the calculation is not possible by KINGAS, are estimated from correlations based on quantitative structure–reactivity relationships and obtained from a literature review [13,15].

2.2. 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 EXGAS automatic generation of mechanisms for the oxidation of alkanes and alkenes. The reactions considered in the primary mechanism of alkylbenzenes are given in Fig. 1. The only type of reactions specific to alkylbenzenes is the ipso-addition of H or O atoms and of small radicals, OH, CH₃, and HO₂. This reaction consists in 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

¹ Software EXGAS-Alkylbenzenes 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).

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