# Experimental and semi-detailed kinetic modeling study of decalin oxidation and pyrolysis over a wide range of conditions

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**Abstract**

Decalin is the simplest polycyclic alkane (polynaphtenic hydrocarbon) found in liquid fuels (jet fuels, Diesel). In order to better understand the combustion characteristics of decalin, this study provides new experimental data for its oxidation in a jet-stirred reactor. For the first time, stable species concentration profiles were measured in a jet-stirred reactor at a constant mean residence time of 0.1 s and 0.5 s at respectively 1 and 10 atm, over a range of equivalence ratios ($\phi = 0.5$–1.5) and temperatures (750–1350 K). The oxidation of decalin under these experimental conditions was modeled using a semi-detailed chemical kinetic reaction mechanism (11,000 reactions involving 360 species) derived from a previously proposed scheme for the ignition of the same fuel in a shock-tube. The proposed mechanism that includes both low- and high-temperature chemistry shows reasonably good agreement with the present experimental data set. It can also represent well decalin pyrolysis and oxidation data available in the literature. Reaction path analyses and sensitivity analyses were conducted to interpret the results.
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## 1. Introduction

Decalin and other polycyclic alkanes are present in synthetic liquid fuels (e.g., coal to liquid) and could be obtained from natural gas through other synthesis processes [1]. Also, the use of heavier petroleum feed-stocks (oil sand, tar sand) will increase the fractions of polycyclic alkanes in fuels [2]. Recently, the production of second-generation biofuels, including naphtenics, from lignin was described [3], opening new sources of polycyclic alkanes which have been reported to reduce the emissions of Diesel engines particulates [1]. Decalin was previously proposed to represent polycyclic alkanes in liquid fuels surrogates [4]. Therefore, experimental and computational results were published for the pyrolysis and oxidation of decalin [4–7]. However, these studies showed there is a lack of detailed data (e.g., species concentration profiles versus temperature or reaction time) for decalin

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oxidation. Such data are essential to validate a kinetic model and improve the description of the combustion of practical liquid fuels by using better surrogate mixtures.

Based on the above mentioned considerations, the goal of this study was twofold: (1) obtain archival experimental data on the oxidation of decalin over a wide range of conditions, (2) use the present data along with literature data for decalin pyrolysis and ignition to validate a kinetic reaction mechanism at high temperatures.

## 2. Experimental

The jet stirred reactor (JSR) has been described previously [8,9]. The reactor consists of a 4 cm diameter fused silica sphere equipped with four nozzles of 1 mm i.d. Prior to the injectors, the reactants were diluted with nitrogen and mixed. The reactants were high-purity oxygen (99.995% pure) and high-purity decalin (40/60 *cis/trans* decalin >99% pure from Aldrich, CAS 91-17-8). The reactants were preheated before injection to minimize temperature gradients inside the reactor. A piston pump (Isco 100 DM, Isco, Lincoln, NE, USA) was used to deliver the fuel to an atomizer-vaporizer assembly maintained at 573 K. The experiments were performed at steady state. The reactants were continually flowing in the reactor whereas the temperature of the gases inside the JSR was increased stepwise.

Good thermal homogeneity along the vertical axis of the reactor (gradients of ~1 K/cm) was observed during the experiments by thermocouple measurements (0.1 mm Pt–Pt/Rh-10%, located inside a thin-wall silica tube). The reacting mixtures were sampled by a movable fused silica low pressure sonic probe connected to analyzers via a deactivated heated line maintained at 523 K. They were analyzed online and off-line after collection in 1 L Pyrex bulbs. The analyses were performed using gas chromatographs (GC) equipped with capillary columns (DB-5ms, CP-Al$_2$O$_3$-KCl, Poraplot-U, and Carboplot-P7), a thermal conductivity detector and a flame ionization detector; uncertainties on concentrations were ca. 15%. A GC–MS (Varian Saturn 4) operating with electron ionization (70 eV) was used for online products identification.

## 3. Kinetic scheme

The semi-detailed kinetic sub-mechanism for the description of the high temperature pyrolysis and oxidation of decalin is summarized in Table 1. The lumped reaction scheme of decalin decomposition (R1–R25) has already been discussed [5]. The further decomposition and/or oxidation of the smaller radicals and molecules involved are

already considered in the whole oxidation mechanism for hydrocarbon fuels up to C$_{16}$. The overall kinetic scheme is based on hierarchical modularity and is constituted by 360 species involved in about 11,000 reactions [4,10]. Thermochemical data for most species were obtained from the CHEMKIN thermodynamic database [11,12]. Unavailable thermodynamic data were estimated using the group additivity method [13]. Due to the symmetry of decalin's structure, H-abstraction reactions from decalin yield to the formation of three C$_{10}$H$_{17}$ radicals. Successive isomerization and decomposition reactions can form eight different decalyl radicals (see Fig. 1a). Decalin contains 16 secondary and 2 tertiary H atoms. The rate constants for the lumped H abstraction reactions on decalin (R5) are simply derived by using analogy rules [14] and referring to the rate parameters of the equivalent abstraction of 20 secondary H atoms.[1] Similarly, reactions R22 and R29 refer to 20 and 16 secondary H-atoms respectively. At high temperatures, the successive isomerization and decomposition reactions of the decalyl radicals are very complex and require the use of automated techniques for the determination of reaction paths and product fractions. As already discussed [5], the high-temperature decomposition path of decalin was originally performed by using the MAMA software described previously [15,16]. To support and illustrate the need for a lumped reaction mechanism, it was already observed that a detailed description of the decomposition and isomerization involved in the radical paths of decalin decomposition would require more than 75,000 reactions and 5500 species. It is evident, from these extremely large number of species and reactions, that the results of a kinetic generator are of no practical use in the obtained detailed form.

Apart from the modifications in the relative decomposition paths of decalyl radicals (R9–R18), the major difference between the reaction mechanism of Table 1 and the previous mechanism [5] is the addition of a lumped molecular reaction path which, through four and six center molecular reactions, can form several different cyclo-alkene species. This molecular reaction path, with an activation energy of 78.5 kcal/mol, contributes to the larger formation of aromatic species at lower pressure and higher temperatures. Figure 1b shows some of the possible species involved in concerted paths and grouped in the ODECA lumped olefinic species (reaction R19). Successive molecular decomposition reactions of

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[1] It is assumed that tertiary H-atoms react two times faster than secondary H-atoms.