

## Quantum Chemical and Kinetic Study of the Oxidation Mechanisms of Naphthalene Initiated by Hydroxyl Radicals. I. The OH Addition Pathway

Abolfazl Shiroudi<sup>a</sup>, Michael S. Deleuze<sup>b</sup>, Sébastien Canneaux<sup>c</sup>

<sup>a</sup> Theoretical Chemistry and Molecular Modelling, Hasselt University, Agoralaan Gebouw D, B-3590 Diepenbeek, Belgium; e-mail: abolfazl.shiroudi@uhasselt.be;

<sup>b</sup> Theoretical Chemistry and Molecular Modelling, Hasselt University, Agoralaan Gebouw D, B-3590 Diepenbeek, Belgium; e-mail: michael.deleuze@uhasselt.be;

<sup>c</sup> University of Lille1 Sciences and Technologies, 59655 Villeneuve d'Ascq Cedex, France; e-mail: sebastien.canneaux@univ-lille1.fr

### Abstract

The oxidation mechanisms of naphthalene by OH radicals under inert (He) conditions and at temperatures smaller than 410 K (Figure 1) have been studied [1] using Density Functional Theory along with various exchange-correlation functionals. Comparison is made with benchmark CBS-QB3 theoretical results. Kinetic rate constants were estimated by means of Transition State Theory (TST) and statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Effective rate constants have been calculated according to a steady state analysis using a two-step model. Comparison with experiment confirms that, on the OH addition reaction pathway leading to 1-naphthol, the first bimolecular reaction step has an effective negative activation energy around -1.5 kcal/mol, whereas this step is characterized by a positive activation energy around 1 kcal/mol on the OH addition reaction pathway leading to 2-naphthol.

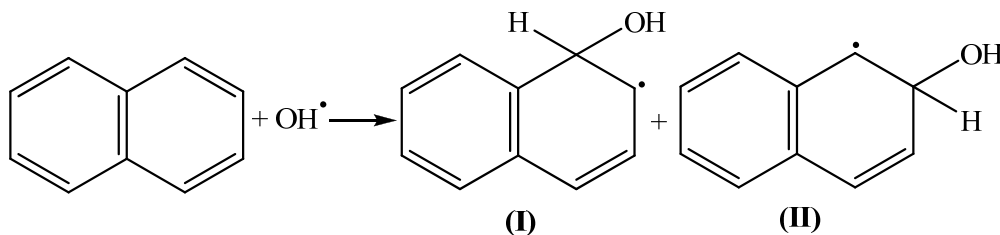


Figure 1: OH• addition upon naphthalene

The calculated branching ratios indicate that, at temperatures lower than 410 K, the most abundant product resulting from the oxidation of naphthalene by OH radicals must be 1-naphthol. The regioselectivity of the reaction decreases with increasing temperatures and decreasing pressures. The RRKM calculations demonstrate that the TST approximation breaks down at ambient pressure for the first bimolecular reaction steps. Pressures larger than 100000 bar are indeed required for restoring within 5 % accuracy the validity of this approximation for all the reaction channels that are involved in the OH• addition pathway. The computed structures, bond orders and free energy profiles demonstrate that all reaction steps involved in the oxidation of naphthalene by OH radicals satisfy Leffler-Hammond's principle. Nucleus independent chemical shift indices and natural bond orbital analysis also show that the computed activation and reaction energies are largely dictated by alterations of aromaticity, and, to a lesser extent, by anomeric and hyperconjugative effects.

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References:

[1] A. Shiroudi, M.S. Deleuze and S. Canneaux, *J. Phys. Chem. A*, **118** (2014) 4593.