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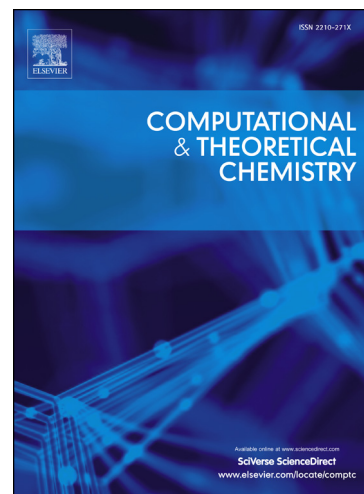
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Reaction Mechanisms and Kinetics of the Isomerization Processes of Naphthalene Peroxy Radicals

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Abstract

The isomerization processes of naphthalene peroxy radicals $[\text{C}_{10}\text{H}_8\text{-OH}]^{\bullet}\text{-O}_2$ into bicyclic peroxy or oxy hydroperoxide radicals via ring closure and intramolecular hydrogen transfers have been studied computationally using density functional theory, along with various exchange-correlation functionals and an extremely large basis set. The calculated energy profiles have been supplemented with calculations of kinetic rate constants under atmospheric pressure and in the fall-off regime, using transition state theory (TST) and statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The cyclisation of the R1-2OO-*syn* peroxy radical into the R1-2,9OO-*syn* bicyclic peroxy radical through formation of an O–O bridge is endothermic and reversible. Both from a thermodynamic and kinetic view points, the two most favorable processes for the R1-2OO-*syn* peroxy radical are ring closure into the R1-2,9OO-*syn* bicyclic peroxy radical species, and conversion through hydrogen transfer into the R1-P2O1-*syn* oxy hydroperoxide radical. Among all studied reaction channels, the latter process is the kinetically most competitive one. Also, in view of the computed rate constants, the R1-2OO-*syn* peroxy radical appears to be chemically much more reactive than the R1-4OO-*syn* species. All in all, the atmospheric oxidation mechanisms of naphthalene appear at this reaction stage to be quite different from that of benzene and its derivatives.

Keywords: Naphthalene, oxidation processes, energy barriers, rate constants, isomerization processes, reaction mechanisms.

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