A model of tetrahydrofuran low-temperature oxidation based on theoretically calculated rate constants

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ABSTRACT

The first detailed kinetic model of the low-temperature oxidation of tetrahydrofuran has been developed. Thermochemical and kinetic data related to the most important elementary reactions have been derived from ab initio calculations at the CBS-QB3 level of theory. A comparison of the rate constants at 600 K, obtained from these calculations with values estimated using recently published rate rules for alkanes, sometimes show differences of several orders of magnitude for alkylperoxy radical isomerizations, HO_2-eliminations, and oxirane formations. The new model satisfactorily reproduces previously published ignition delay times obtained in a rapid-compression machine and in a shock tube, as well as numerous product mole fractions measured in a jet-stirred reactor at low to intermediate temperatures and in a low-pressure laminar premixed flame. To highlight the most significant reaction pathways, flow-rate and sensitivity analyses have been performed with this new model.

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1. Introduction

It is now well established that the use of traditional fossil fuels is largely responsible for current environmental issues such as climate change. An efficient way to reduce CO_2 emissions while still making use of internal combustion engine technology and of the infrastructures build around liquid fuel usage is to shift from hydrocarbon fossil fuels to biofuels. Unlike first-generation biofuels whose synthesis is in competition with agricultural food production, second generation biofuels are produced from other types of biomass, such as lignocellulosic biomass, which is not part of the food chain [1]. Acquiring a thorough understanding of the combustion chemistry and emission levels is a crucial prerequisite before any type of bio derived molecule can be considered as fuel for wide use in engines.

Biomass contains a variety of substituted five- and six-membered cyclic components, and strategies are being developed to transform biomass into suitable transportation fuels that retain these structures. Saturated cyclic ethers of the family of tetrahydrofuran (THF) can be obtained from carbohydrates or cellulosic

biomass by catalytic processes [2]. Thanks to their heating values being close to that of gasoline, these ethers have the potential to become promising bio-fuels for internal combustion engines [3]. Initial engine tests for this family of compounds showed satisfactory performances, with power outputs and emissions close to that of unleaded fuels [4].

THF and other saturated cyclic ethers are also well-known primary products of the low-temperature oxidation of alkanes [5]. Consequently, any improvement of the understanding of the low-temperature oxidation of these cyclic oxygenated compounds will also help to improve model predictions of alkane oxidation.

Two kinetic models for the high-temperature THF oxidation can be found in the literature. The first detailed reaction mechanism containing 71 species and 484 reactions was proposed by Dagaut et al. [6] in 1998. This model was validated against experimental data obtained in a shock tube and in a jet-stirred reactor, respectively (covering a temperature range from 800 to 1800 K, pressures (*p*) from 202 to 1013 kPa and equivalence ratios (*φ*) from 0.5 to 2). More recently, Tran et al. [3] published a detailed reaction mechanism for THF oxidation that contains 255 species and 1723 reactions. The rate expressions of the most important reactions were calculated with ab initio methods. This last model was validated for pressures from 6.7 to 8550 kPa and equivalence ratios ranging from 0.5 to 2 against species profiles measured in a low-pressure

Fig. 1. Potential energy surfaces of the low-temperature reactions of (a) the tetrahydrofuran-2-peroxy (α-ROO) and (b) tetrahydrofuran-3-peroxy (β-ROO) radicals calculated in the present work. The values are 0 K energies in kcal mol^{-1} relative to the initial peroxyl radicals. The corresponding results from Antonov et al. [9] are given in parentheses.

premixed flame, adiabatic laminar burning velocity measurements for an atmospheric pressure premixed flame, and ignition delay times measured in a shock tube. The two previous kinetic models do not include low-temperature oxidation pathways, i.e. the formation and consumption of tetrahydrofuranylperoxy radicals.

Three experimental studies of the low-temperature oxidation of THF have recently been published. In 2014, Uygun et al. [7] studied THF ignition delay times in a shock tube for temperatures ranging from 691 to 1100 K, at 2.0 and 4.0 MPa for stoichiometric mixtures. In 2015, Vanhove et al. reported ignition delay times measured in a