

An experimental and theoretical kinetic study of the reaction of OH radicals with tetrahydrofuran

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Abstract

Tetrahydrofuran (C₄H₈O, THF) and its alkylated derivatives of the cyclic ether family are considered to be promising future biofuels. They appear as important intermediates during the low-temperature oxidation of conventional hydrocarbon fuels and of heavy biofuels such as long-chain fatty acid methyl esters. The reaction of tetrahydrofuran with OH radicals was investigated in a shock tube, over a temperature range of 800–1340 K and at pressures near 1.5 bar. Hydroxyl radicals were generated by the rapid thermal decomposition of tert-butyl hydroperoxide, and a UV laser absorption technique was used to monitor the mole fraction of OH radicals. High-level CCSD(T)/cc-pV(D,T)Z//MP2/aug-cc-pVDZ quantum chemical calculations were performed to explore the chemistry of the THF + OH reaction system. Our calculations reveal that the THF + OH (R1) reaction proceeds via either direct or indirect H-abstraction from various sites, leading to the formation of tetrahydrofuran-2-yl (THF-R2) or tetrahydrofuran-3-yl (THF-R3) radicals and water. Theoretical kinetic analysis revealed that both channels are important under conditions relevant to combustion. To our knowledge, this is the first direct experimental and theoretical kinetic study of the reaction of tetrahydrofuran with OH radicals at high temperatures. The following theoretical rate expressions (in units of cm³mol⁻¹s⁻¹) are recommended for combustion modeling in the temperature range 800–1350 K:

$$k_1(T) = 4.11 \times 10^4 \left(\frac{T}{\text{K}}\right)^{2.69} \exp\left(-\frac{1316.8 \text{ K}}{T}\right) \quad (\text{THF} + \text{OH} \rightarrow \text{Products})$$

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$$k_2(T) = 6.93 \times 10^{11} \left(\frac{T}{\text{K}}\right)^{0.41} \exp\left(\frac{-106.8 \text{ K}}{T}\right) \quad (\text{THF} + \text{OH} \rightarrow \text{THF-R2} + \text{H}_2\text{O})$$

$$k_3(T) = 4.12 \times 10^3 \left(\frac{T}{\text{K}}\right)^{3.02} \exp\left(\frac{456.9 \text{ K}}{T}\right) \quad (\text{THF} + \text{OH} \rightarrow \text{THF-R3} + \text{H}_2\text{O})$$

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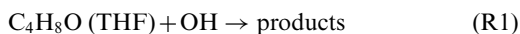
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1. Introduction

The use of biofuels as an alternative to fossil fuels as part of the future energy portfolio has become an intriguing area of research in recent years. Many innovative methods have been proposed for the production of biofuels from biomass [1–8]. Among the many choices of biofuels, tetrahydrofuran (THF) and its alkylated derivatives have attracted the attention of researchers because of their advantages over other biofuels such as ethanol [9–11]. These fuels of the THF family have a lower heating value (LHV) of about 29 MJ L^{-1} , comparable to gasoline (31.6 MJ L^{-1}), while the LHV for ethanol is 21.3 MJ L^{-1} [12]. THF-derived fuels also have a higher energy density and lower water affinity than ethanol, making them promising biofuels for internal combustion engines. Moreover, these cyclic ethers are observed as important intermediates during the combustion of conventional and heavy biofuels such as fatty acid methyl esters [13–15]. The mechanism for the formation of cyclic ethers via the hydroperoxy alkyl radical ($\bullet\text{QOOH}$) during the low-temperature oxidation of hydrocarbon fuels is well established [16]. Among cyclic ethers, the five-membered cyclic ethers, of which tetrahydrofurans are an example, are by far the most abundant oxygenated products [13,14]. Subsequent reactions of these ethers play an important role in the overall reactivity of a fuel. A

better understanding of the gas phase kinetics and oxidation of these cyclic ethers under combustion-relevant conditions is therefore crucial.

The reactions of cyclic ethers with OH radicals are important due to the abundance of hydroxyl radicals in the combustion systems. While some studies [9,11,17–19] have focused on the initial steps in the pyrolysis of THF, and while a number of experimental and modeling studies have aimed to understand the ignition and oxidation behavior of THF at high temperatures [12,20–24], so far no experimental or theoretical works have investigated hydrogen abstraction of THF by OH radicals (R1).



Dagaut et al. [20] have used an estimated rate expression for R1, $k_1(T) = 5.5 \times 10^6 T^2 \exp(844 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, to construct a detailed kinetic model for THF that consists of 71 species and 484 reactions. This kinetic model successfully reproduces their shock tube ignition delay times and jet-stirred reactor oxidation data for THF over a wide range of experimental conditions ($T=800\text{--}1800 \text{ K}$, $p=2\text{--}10 \text{ atm}$ and $\varphi=0.5\text{--}2$). Most recently, Tran et al. [21] have reported data from shock tube and premixed flame during the com-

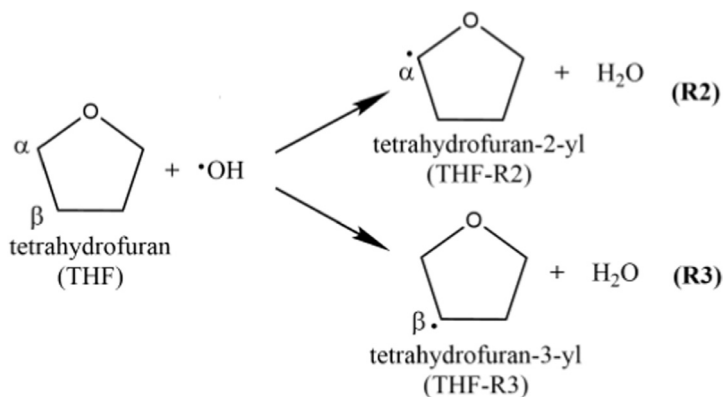


Fig. 1. Possible H-abstraction channels of THF by OH radicals.

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