

# Pericyclic reactions in ether biofuels

Juan-Carlos Lizardo-Huerta, Baptiste Sirjean\*, Pierre-Alexandre Glaude,  
René Fournet

*Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, 1 rue Grandville BP 20451 54001  
Nancy Cedex, France*

Received 3 December 2015; accepted 8 July 2016  
Available online 26 July 2016

## Abstract

Unimolecular decompositions of acyclic ethers through a pericyclic mechanism, i.e., alcohol elimination, have been shown to play a crucial role in the high-temperature combustion of these compounds. The production of new fuels derived from biomass has led to a renewed interest into the combustion chemistry of ethers. A large fraction of ethers produced as potential biofuels features a cyclic structure. The pericyclic reactions in these cyclic structures, with or without a lateral alkyl group, remains unknown. In this work, we performed a systematic theoretical study on the pericyclic reactions in acyclic and cyclic ethers. Envisaged concerted reactions includes the classical alcohol formation and a H<sub>2</sub> eliminations that was recently shown to play a non negligible role in the thermal decomposition of tetrahydrofuran (Verdicchio et al., 2015). Theoretical calculations performed in this work demonstrated that H<sub>2</sub> elimination in acyclic ethers is negligible. In the case of cyclic ethers (tetrahydrofuran and tetrahydropyran), the branching ratio of the unimolecular pericyclic reactions strongly depends on the presence of a lateral alkyl group bonded to the carbon atom in position 2. If an alkyl group is present, the alcohol formation is favored through an *exo* 4-center rearrangement, that we newly defined in this work. If no lateral alkyl group is available in position 2, *endo* alcohol formation and H<sub>2</sub> eliminations are equivalently important. Reaction rate rules were established to include pericyclic decomposition reactions in detailed chemical kinetic models of ether combustion.  
© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

**Keywords:** Theoretical kinetics; Quantum chemistry; Biofuel; Ethers

## 1. Introduction

Ethers have attracted a great interest as promising transportation fuels produced from biomass [1]. Ether compounds that can be used as addi-

tives or biofuels can be divided into two categories: acyclic and cyclic ethers. Acyclic ethers, dimethyl ether (DME: (CH<sub>3</sub>)<sub>2</sub>O) and its derivatives, are well-known octane improvers produced from alcohols. Cyclic ethers, either saturated or unsaturated furans, are mostly produced from catalytic treatments of lignocellulosic biomass. The potential of these compounds have led to a large number of studies aiming to unravel their combustion chemistry at the molecular level. Tran et al. [2] listed all the

\* Corresponding author. Fax: +33 38 332 2975.

E-mail address: [baptiste.sirjean@univ-lorraine.fr](mailto:baptiste.sirjean@univ-lorraine.fr)  
(B. Sirjean).

detailed kinetic models available for these compounds in their 2012 review. Since then, a kinetic mechanism on dibutyl ether (DBE:  $(C_4H_9)_2O$ ) has been published [3], and new versions of published combustion kinetic models of ethers are proposed regularly in the literature [4–6]. Those studies showed that unimolecular eliminations are crucial in the high temperature combustion chemistry of acyclic ethers (larger than DME).

Danby and Freeman first detected ethanol as a product of diethyl ether (DEE:  $(C_2H_5)_2O$ ) thermal decomposition in 1958 [7], and ascribed its formation to the reaction



where the mechanism of formation of ethylene and ethanol was unknown but probably first order. In 1963, Laidler and McKenney proved that the formation of the products of reaction (1) occurred from a molecular elimination in DEE [8] and subsequently proposed a rate constant with an activation energy of  $83.8 \text{ kcal mol}^{-1}$  and a frequency factor of  $2.75 \times 10^{18} \text{ s}^{-1}$ . Fifteen years later, Foucaut and Martin [9] measured a rate constant of  $1.0 \times 10^{13} \text{ s}^{-1} \exp(-62.2 (\text{kcal mol}^{-1})/RT)$  between 763 and 798 K. Large discrepancies can be observed between these rate parameters and those proposed by Laidler and McKenney. A comparison of the two rate constants at 800 K, where the experimental temperature bounds are the closest, ultimately leads to a factor of 2.9 (Foucaut and Martin's rate is higher than Laidler and McKenney). In 2008, Yasunaga et al. [10] studied the pyrolysis of ethyl tert-butyl ether (ETBE:  $C_2H_5-O-C(CH_3)_3$ ) behind reflected shock waves and showed that the 4-center elimination of alcohol is dominant in the initial decomposition steps of ETBE. They calculated the high-pressure rate constant for this pericyclic reaction, using quantum chemistry, at the MP4/cc-pVTZ//MP2/cc-pVTZ level of theory. It can be noted that no treatment of internal rotors was reported by the authors. The computed kinetic parameters of this reaction were subsequently used for reaction (1) in an experimental and modeling study on DEE pyrolysis and combustion [11]. Their computed rate constant was reported to be approximately three times higher than that of Foucaut and Martin. Very recently, Al Rashidi et al. [12] calculated the high-pressure limit rate constant for the 4-center pericyclic elimination of butanol in dibutylether using CBS-QB3 and G4 level of theory. Internal rotations were treated using the approximation of Pitzer and Gwinn [13], based on relaxed scans performed at the B3LYP/6-31+G(d,p) level of theory. The lowest critical energy computed by these authors is  $67.7 \text{ kcal mol}^{-1}$  (G4 at 0 K) which is  $7.7 \text{ kcal mol}^{-1}$  higher than the one calculated by Yasunaga et al. (MP4/cc-pVTZ//MP2/cc-pVTZ at 0 K). The total high-pressure limit rate constant calculated by Al Rashidi et al. at 800 K

is  $3.56 \times 10^{-6} \text{ s}^{-1}$ , which is lower by a factor of 28 compared to the value reported by Foucaut and Martin.

The role of the pericyclic elimination of alcohol in cyclic ether has almost not been studied in the literature. In the case of unsaturated cyclic ethers, i.e., furan derivatives, this kind of elimination seems not to be possible. In our work on 2,5-dimethylfuran (2,5-DMF), no 4-center elimination transition state was optimized at the B3LYP/cbsb7 level of theory despite our attempts [14]. In the case of saturated cyclic ethers, three studies can be mentioned. Moshhammer et al. [15] proposed a detailed chemical kinetic model to simulate the combustion of 2-methyltetrahydrofuran (2-MTHF) in flames. In their model, eliminations reaction from the fuel are included, leading to the formation of formaldehyde and butene, acetaldehyde and propene or acetone and ethylene. No detail was given for the determination of these reactions and their associated kinetic parameters. Verdicchio et al. [16] theoretically explored the unimolecular decomposition of tetrahydrofuran (THF) and envisaged a molecular elimination, similar to the one presented in reaction (1)



where the cyclic structure of THF leads to the formation of but-3-en-1-ol, an unsaturated alcohol. This elementary step involves a bicyclic transition state structure, where the H-atom bonded to the carbon 3 is transferred on the oxygen atom. A computed energy barrier of  $80.4 \text{ kcal mol}^{-1}$  was reported by the authors for reaction (2) at the CBS-QB3 level of theory. Verdicchio et al. also reported an original  $H_2$  elimination reaction in THF leading to a zwitterionic  $C_4H_6O$  cyclic species that further isomerizes to 2,3-dihydrofuran. It was shown, in this study, that the  $H_2$  elimination is competitive with the pericyclic rearrangement yielding the unsaturated alcohol. Tran et al. [17] proposed a combustion and pyrolysis kinetic model for tetrahydropyran (THP) that included unimolecular decomposition reactions of the fuel based on analogies with the work of Verdicchio et al. [16]. They calculated a high-pressure limit rate constant at the CBS-QB3 level of calculation (including 1-DHR treatment of internal rotors), and reported a computed rate constant of  $4.20 \times 10^5 \text{ T}^{2.6} \exp(-73.3 (\text{kcal mol}^{-1})/RT) \text{ s}^{-1}$ . The fitted activation energy of  $73.3 \text{ kcal mol}^{-1}$  is lower than the similar pericyclic reaction in THF by  $7 \text{ kcal mol}^{-1}$ . These authors did not envisaged the  $H_2$  elimination reaction in their model. It can be noted that no pericyclic reaction is included in the kinetic models of THP combustion proposed by Labbe et al. [18] and that Dagaut et al. [19] considered lumped molecular elimination in their mechanism, based on experiments performed on THF.

Download English Version:

<https://daneshyari.com/en/article/6478022>

Download Persian Version:

<https://daneshyari.com/article/6478022>

[Daneshyari.com](https://daneshyari.com)