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PROGRESS IN DETAILED KINETIC MODELING OF THE COMBUSTION OF OXYGENATED COMPONENTS OF BIOFUELS

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Abstract

Due to growing environmental concerns and diminishing petroleum reserves, a wide range of oxygenated species has been proposed as possible substitutes to fossil fuels: alcohols, methyl esters, acyclic and cyclic ethers. After a short review the major detailed kinetic models already proposed in the literature for the combustion of these molecules, the specific classes of reactions considered for modeling the oxidation of acyclic and cyclic oxygenated molecules respectively, are detailed.

Keywords

Biofuel; combustion; gas-phase oxidation; detailed kinetic models; alcohol; ester; ether; furan

I. INTRODUCTION

As traditional fossil fuels are considered to be largely responsible for important atmospheric degradations, there is an increasing interest to shift from hydrocarbon fossil fuels to bio-fuels. It has been shown that the presence of additional oxygenated compounds could reduce the formation of soot in diesel engines [1], but may also promote the formation of some toxic pollutants, such as aldehydes [2][3]. To better assess the effect of the presence of these new molecules in fuels on the engine efficiency and the pollutants formation, it is necessary to develop well validated detailed kinetic models for the combustion and the oxidation of the oxygenated components of biofuels. In order to be used in a predictive way, these detailed kinetic models need to include a large number of elementary reactions [4]. Before writing such detailed kinetic models, the types of involved reacting species have to be defined. The first part of this paper focuses then on the identification of the main types of oxygenated molecules present in the fuels which can be obtained from biomass. A second part reviews the major detailed kinetic models already proposed in the literature for the combustion of potential oxygenated components of biofuels and of molecules representative of them. Finally, a third and a fourth part describe the specific classes of reactions considered in detailed kinetic models for the combustion of acyclic and cyclic oxygenated molecules, respectively.

II. SUMMARY OF THE MAIN COMPONENTS OF THE FUELS DERIVED FROM BIOMASS AND WAYS TO OBTAIN THEM

The major difficulty in developing biofuels is to transform the very large and very oxygenated molecules present in biomass (e.g. carbohydrates, such as cellulose and starch, are large polymer chains assembled from thousand of sugar units which each contains 6 carbon atoms and a similar number of oxygen atoms) into molecules suitable to be used as fuels for engines, (e.g. small molecules including from 5 to 20 carbon atoms and very few oxygen atoms) [5]. A review of the ways to obtain transportation fuel from biomass has been recently published [6]. A method widely proposed is to partially oxidize biomass to produce a 'syngas' (a mixture of mainly carbon monoxide and hydrogen) [7] which can thereafter feed a catalytic process (Fisher-Tropsch synthesis) to produce a liquid fuel. This latter, made of linear saturated hydrocarbons, can easily be used in diesel engines [8]. However, as shown in figure 1, many types of oxygenated molecules (see Table 2 for their main chemical and physical properties) considered as potential additives to gasoline or diesel fuel can be obtained through a wide range of processes involving fermentation or catalytic reactions [9]:

- Alcohols; methanol can be obtained from 'syngas' [10], while ethanol, propanol, or butanol can be obtained through the fermentation of sugars or starches which can be produced from very common crops, such as sugar cane or corn [11][12]. Ways to produce alcohols from cellulose [13][14] or algae [15] have also been proposed. Alcohols are the most usually blended with gasoline. Heavier alcohols such as *n*-butanol have a higher energy density, a higher boiling point and a lower solubility in water than ethanol (see table 2) which should facilitate their use in spark ignition engines.
- Fatty acid methyl and ethyl esters, which are obtained through the transesterification of vegetal oils or animal fat with methanol or ethanol, respectively. Vegetal oils mainly include triglycerides (98%), with small amounts of mono and diglycerides. The main fatty acids in rapeseed and soybean oils oleic (C18:1 monounsaturated) and linoleic (C18:2 omega-6 polyunsaturated) acids [16]. Methyl esters can be blended in any proportion with diesel fuel obtained from petroleum [11].
- Acyclic ethers (see formulae in Table 1), such as dimethyl ether, which can be obtained from methanol or directly from 'syngas', and which has been proposed as an efficient alternative fuel for use in a diesel engine [17], or ethyl *ter*-butyl ether, which can be obtained by reaction of ethanol with isobutene and which is a common additive to gasoline [18].
- Cyclic ethers (see formulae in Table 1) of the family of furans, such as 2,5-dimethylfuran, which can be obtained from fructose which is enzymatically produced from starch [19]. Saturated cyclic ethers such as methyl- or dimethyl-tetrahydrofurans, which can be obtained from carbohydrates or cellulosic biomass by a catalytic process [20], are also considered. These cyclic ethers could be valuable substitutes to fossil fuels for transportation. As shown in Table 2, compared to ethanol, 2,5-dimethylfuran has a higher energy density, a higher boiling point, and is not soluble in water [19].

III. DETAILED KINETIC MODELS FOR THE COMBUSTION OF POTENTIAL OXYGENATED COMPONENTS OF BIOFUELS

Table 3 summarizes the major detailed kinetic models which have been published for the combustion of oxygenated molecules which are considered as potential components of fuels. For each model, the conditions under which they have been validated are detailed. Mixtures have not been considered.

All the experimental results used for model validation have been obtained for pressures below 10 bar, the major part being measured close to atmospheric pressure, and for equivalence ratios from 0.2 to 4, the major part being measured close to stoichiometry. More experimental studies are certainly needed in order to enable model validations under a wider range of conditions, especially under pressures closer to those usually observed in engines.

The family of molecules for which the largest number of models has been proposed is alcohols. Note that the major part of these studies has been recently performed. The experimental investigations related to alcohols, apart from one for *n*-hexanol [71], have all been performed at temperature above 770 K. This is mostly due to a lack of reactivity of these compounds at lower temperatures. However in a mixture with more reactive species, such as some of those included in gasoline (e.g. linear alkanes), alcohols could certainly react at lower temperature by reactions which are not considered in the present models. The two alcohols, the behaviors of which have been the more investigated, are ethanol and butanols (mainly *n*-butanol). Concerning *n*-butanol, the best validated model is the recent one by Harper et al. [67], but improvements are still needed for modeling some experimental data such as those obtained in a jet-stirred reactor [61].

A fair number of models have recently been published about the combustion of methyl esters. A model has also been proposed for the oxidation of dimethylcarbonate [72]. The most studied species is methyl butanoate, even if its small size prevents it to have a chemistry representative of the large molecules present in biodiesel [80]. However even for this small ester, zones of shadow remain to fully explain its lack of low-temperature reactivity [80]. Most work deals with saturated esters, with very few studies dedicated to unsaturated ones, even if unsaturated esters are the most abundant esters in biodiesel. Note that very few experimental studies can be used to test the predictions of the models proposed for heavy esters representative of those included in biodiesel. This is true to such an extent that several models have been proposed without possibility to be validated at the time of their development. The experimental investigations related to methyl esters have all been performed at temperatures from 550 K. The evolution with temperature of the reactivity of methyl esters from methyl hexanoate exhibits a marked negative temperature coefficient behavior. As illustrated in figure 2 in the case of methyl decanoate, this behavior, well known for alkanes [120], consists in a temperature zone where the reactivity decreases with temperature. As shown in figure 2a, this behavior is well predicted by the current models. These models can also reproduce the formation of products specific to esters, e.g. cyclic ethers with an ester function or unsaturated esters, such as heptenoate as shown in figure 2b. Note that, mainly due to the availability of experimental results, no validation of model of the combustion of esters including more than 5 atoms of carbons has been published for flame or ignition (in shock tube or rapid compression machine) conditions. While many models have been proposed for methyl esters, only a very few studies concern ethyl esters [80][82].

A large number of models have also been published about the combustion of acyclic ethers, but a large part of this work has been made before 2000. This is due to the fact that these compounds have been considered as octane boosters well before the need for using biofuels

has been seriously considered [106]. The first ether which has been proposed as anti-knock fuel additive is MTBE (its use has been recently reduced due to environmental problems [121]), followed soon by ETBE. This explains why a significant number of models have been written for the oxidation of these two ethers. While acyclic ethers can also exhibit a low-temperature reactivity [106], most of the proposed models have been validated using experimental results obtained for temperatures above 800 K.

Only two models have been proposed for cyclic ethers, one for tetrahydrofuran by Dagaut et al. [116], and a very recent one by Tian et al. [117] for furan.

Note that some recent models can be very large: the model of Harper et al. [67] for the oxidation of *n*-butanol consists in 263 species and 3381 reactions and that of Herbinet et al. [89] for the oxidation of methyl palmytate includes 30425 reactions for 4442 species.

IV. SPECIFIC REACTION CLASSES CONSIDERED FOR MODELING THE OXIDATION OF ACYCLIC OXYGENATED COMPONENTS OF BIOFUELS

The kinetic study of the oxidation of acyclic oxygenated compounds is advanced enough for a system of automatic generation of mechanism (EXGAS) [122] to be able to produce validated detailed kinetic models for the oxidation of the three types of acyclic saturated molecules present in biofuels: ethers [109], alcohols [27] and methyl esters (EXGAS-ALKANES-ESTERS¹) [84]. The used rules of generation are based on the chemical conclusions which can be derived from the analysis of the mechanisms listed in Table 3.

The aim of this part is to present the specific classes of reactions and kinetic parameters which are considered by this system in the case of these oxygenated molecules. While EXGAS can also generate mechanism for unsaturated reactants (e.g. for unsaturated esters [82]), the reactions of unsaturated molecules will not be presented here.

As shown in figure 3, the presence of the oxygen atoms in an organic molecule involves first a difference in the bond dissociation energies (BDEs) compared to what is observed in hydrocarbon molecules. In the EXGAS software, the thermochemical data are computed using THERGAS [125] based on the group additivity rules developed by Benson [126] and on BDEs mostly proposed by Tsang [127] and Luo [128]. In the case of esters, the BDEs of the C-H, C-O and C-C bonds close to the ester function were updated from the values proposed by El-Nahas et al. [129].

Before describing more closely the involved reaction classes, let us recall that EXGAS [122] provides reaction mechanisms made of three parts:

* A *comprehensive primary mechanism* including all the reactions of the molecular reactants, the initial organic compounds and oxygen, and of the derived free radicals.

The primary mechanism includes:

- Molecular reactions which will be described further in the text,
- Unimolecular and bimolecular initiation steps
(e.g. $C_3H_7OH \Rightarrow \bullet CH_2OH + \bullet C_2H_5$; $C_3H_7OH + O_2 \Rightarrow \bullet CH_2CH_2CH_2OH + \bullet OOH$),
- Reactions leading to alkenes from alkyl radicals
 - Decompositions by beta-scission

¹Software EXGAS-ALKANES-ESTERS automatically generates detailed kinetic mechanisms for the oxidation of linear and branched alkanes, and linear methyl esters and is freely available for academic researchers (valerie.warth@ensic.inpl-nancy.fr).

(e.g. $\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \Rightarrow \bullet\text{CH}_2\text{OH} + \text{C}_2\text{H}_4$),

- Oxidations to form the conjugated alkene and $\bullet\text{OOH}$

(e.g. $\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \Rightarrow \text{CH}_2=\text{CHCH}_2\text{OH} + \bullet\text{OOH}$),

– Additions of alkyl and hydroperoxyalkyl radicals on a molecule of oxygen,

(e.g. $\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \Rightarrow \bullet\text{OOCH}_2\text{CH}_2\text{CH}_2\text{OH}$;

$\text{HOOCH}_2\text{CH}_2\text{CHOH}\bullet + \text{O}_2 \Rightarrow \text{HOOCH}_2\text{CH}_2\text{CHOHOO}\bullet$),

– Intramolecular isomerizations of alkyl and peroxy radicals involving a cyclic transition state,

(e.g. $\bullet\text{OOCH}_2\text{CH}_2\text{CH}_2\text{OH} \Rightarrow \text{HOOCH}_2\text{CH}_2\text{CHOH}\bullet$):

– Decompositions of hydroperoxyalkyl and di-hydroperoxyalkyl radicals to form cyclic ethers, alkenes, aldehydes or ketones (oxohydroperoxyalkanes),

(e.g. $\text{HOOCH}_2\text{CH}_2\text{CHOH}\bullet \Rightarrow \text{cyclic-HOC}_3\text{H}_5\text{O} + \bullet\text{OH}$),

(e.g. $\text{HOOCH}_2\text{CH}_2\text{COH}(\text{OOH})\bullet \Rightarrow \text{HOOCH}_2\text{CH}_2\text{C}(=\text{O})\text{OH} + \bullet\text{OH}$),

– Metathesis reactions to abstract an H atom from the initial reactant

(e.g. $\bullet\text{OH} + \text{C}_3\text{H}_7\text{OH} \Rightarrow \text{H}_2\text{O} + \bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$),

– Termination steps:

- Combinations of two free radicals

(e.g. $\text{CH}_3\bullet + \text{OH}\bullet \Rightarrow \text{CH}_3\text{OH}$),

- Disproportionations of peroxy radicals with $\bullet\text{OOH}$

(e.g. $\bullet\text{OOCH}_2\text{CH}_2\text{CH}_2\text{OH} + \bullet\text{OOH} \Rightarrow \text{HOOCH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2$),

* A C_0 - C_2 reaction base (core mechanism), including all the reactions involving radicals or molecules containing less than three carbon atoms; but including oxygenated species. The fact that no generic rule can be derived for the generation of the reactions involving very small compounds makes the use of this reaction base necessary. This core mechanism is common to all the generated mechanisms, whatever the reactant.

* A lumped secondary mechanism, containing the reactions consuming the molecular products of the primary mechanism which do not react in the reaction base [130].

For the shortness of this paper, we will not detail the reaction classes involved in the secondary mechanism. Note however that these reactions have to be written for consuming the compounds formed by the primary mechanisms: e.g. unsaturated esters, alcohols or ethers and hydroperoxides, cyclic ethers, ketones and aldehydes bearing an additional ester, alcohol or ether function. They are considered in details by EXGAS.

The only reaction class specific to the primary mechanism of oxygenated molecules is molecular reactions, such dehydrations in the case of alcohols, or alcohols eliminations in the case of ethers. For several others types of reactions (unimolecular initiations, bimolecular initiations and H-abstractions, decompositions of radicals by β -scission, intramolecular isomerizations), only changes in the kinetic parameters have to be taken into account. For the remaining types of reactions, no change was needed.

VI.1. Molecular reactions

Figure 4 presents typical molecular pericyclic reactions in the case of ethers, alcohols and esters. In the case of ethers, a molecular reaction involving the transfer of a H-atom bound to an atom of carbon in β position of the atom of oxygen to give an alcohol molecule and an alkyl radical via a favored four centered cyclic transition state (see first reaction in figure 4) should be taken into account as proposed by Choo et al. [131]. The activation energies of the rate constants used in EXGAS for this reaction class are 52 kcal/mol for ethyl tert-butyl ether and 59 kcal/mol for methyl tert-butyl ether [123].

Intramolecular dehydration leading to the formation of water and an alkene molecule via a favored four centered cyclic transition state (see figure 4) is an important reaction class for alcohols. Note that if we consider isomers of butanol, there is one possible intramolecular dehydration reaction for 1-butanol (see second reaction in figure 4), iso-butanol and tert-butanol, and two for 2-butanol. Few kinetic parameters have been published concerning these reactions (e.g. [132][133], with activation energy from 62 to 69 kcal/mol) and disagreements can be observed between the proposed rate constants, which have been shown to be sensitive parameters in detailed kinetic modeling [27]. Molecular dehydrogenations of alcohols leading to aldehydes have been recently proposed [65] but are not yet considered in EXGAS.

In the case of esters, El-Nahas et al. [129] have theoretically investigated several types of molecular reactions, but no easy decomposition appeared in the case of methyl esters. The only one having an impact on detailed kinetic modeling is the formation of ethylene and acid from ethyl esters via a favored six-centered cyclic transition state (see third reaction in figure 4). The activation energy of the rate constant used in EXGAS for this reaction class is 47.3 kcal/mol [80].

IV.2. Unimolecular initiations

The rate constants for unimolecular initiations (decompositions) given by EXGAS are obtained from the data on the reverse reactions, *i.e.* combinations, using thermochemical data calculated with THERGAS software [125]. Activation energies for every combination are taken to be zero. The pre-exponential factor for the combination of two free radicals is estimated from modified collision theory [134].

In the case of ethers and alcohols, the activation energies of unimolecular initiations were also calculated using THERGAS [125]. In the case of esters, the activation energies of unimolecular initiations, which involve the breaking of the C-C bonds located in α - and β -positions from the ester function, have been updated from the BDEs (see figure 3) recently calculated by El-Nahas et al. [129]. For the other unimolecular initiations, the bond energies used in THERGAS [125] were in agreement to about ± 1 kcal.mol⁻¹ with those proposed by El-Nahas et al. [129] and were not modified.

IV.3. Bimolecular initiations and H-abstractions

Bimolecular initiations and H-abstractions are usually the most important for the fuel consumption. In the case of hydrocarbons, the rate constants of these reactions depend only of the type of alkyl H-atoms which can be abstracted: primary -CH₃, secondary -CH₂ or tertiary -CH. The abstraction of a primary H-atom is the most difficult, that of a tertiary one is the easiest. In oxygenated reactants, more types of H-atoms have to be considered. As shown in figure 3, in all oxygenated compounds, there are C-H bonds close to the oxygen atom which are more easily breakable. This involves easiest bimolecular initiations and H-abstractions.

In the case of ethers, the activation energy used by EXGAS for the bimolecular initiations involving the abstraction of an H-atom from a carbon atom in the α -position of the oxygen atom has been reduced by a factor about 4 kcal/mol compared to the case of alkanes [122] and no change was considered for H-abstractions.

In the case of alcohols, bimolecular initiations and H-abstractions can involve the abstraction of alkylic or alcoholic (-OH) H-atoms. In EXGAS, the rate constants for bimolecular initiations were estimated using the correlation proposed by Ingham et al. [135] for hydrocarbons (the activation energy is taken equal to the reaction enthalpy) and the rate constants for the abstractions were generally those used for the alkanes [122]. However the rate constants for the abstraction of a H-atom from a carbon atom located in the α -position of the alcohol function, the fastest of the H-atom abstraction reactions, have been evaluated using an Evans–Polanyi type correlation from Dean and Bozzelli [136], developed for the abstraction of H-atoms from hydrocarbons:

$$k = n_H A T^n \exp(-\{E_0 - f(\Delta H_0 - \Delta H)\} / RT)$$

where n_H is the number of abstractable H-atoms; A, n, and E_0 are the rate parameters for the case of a metathesis by the considered radical from ethane; ΔH_0 is the enthalpy of the metathesis by the considered radical from ethane; ΔH is the enthalpy of the metathesis by the considered radical from the reacting molecule; f is a correlation factor, the values of which are given by Dean and Bozzelli [136] for each considered radical; and R is the gas constant. While, according to Luo [128], the BDE of the O-H bond for the alcohol function is between 102 and 106 kcal.mol⁻¹, a value equal to that of a C-H bond in the case of an alkylic primary H-atom, the kinetic parameters for an H-atom abstraction from an alcohol function used by EXGAS are equal to those for the abstraction of a tertiary alkylic H-atom. That has been shown to be closer to experimental values for H-atom abstractions.

The BDE of the C-H bonds carried by the carbon atom just neighboring an ester function (94.3 kcal/mol [129]) is close to that of a tertiary atom of carbon (e.g., 95.7 kcal/mol in isobutene [128]). Thus, for the abstraction of this type of H-atoms, the correlations were taken by EXGAS the same as those used for the abstraction of tertiary H-atoms from alkanes, except in the case of the abstractions by $\bullet O\bullet$ and $\bullet H$ atoms and by $\bullet OH$, $\bullet HO_2$ and $\bullet CH_3$ radicals. For these last atoms and radicals, the rate parameters have been evaluated using the Evans–Polanyi type correlation proposed by Dean and Bozzelli [136] previously described.

IV.4. Decompositions of radicals by β -scission

Table 4 shows a summary of the activation energies which are used in EXGAS for the decompositions by β -scission involving the breaking of a C-C or a C-O bond in radicals deriving from saturated oxygenated molecules. At temperature above 800 K, decompositions by β -scission are the major way of consumption of radicals obtained from the fuel molecules by H-abstractions. While the data related to ethers, which have been proposed in 2000 [109], were based on rough estimations, the data related to esters, proposed in 2010 [84], have been obtained from quantum calculations. These quantum calculations were performed for model reactions at the CBS-QB3 level of theory using Gaussian03 [137]. Intrinsic Reaction Coordinate (IRC) calculations have been systematically performed at the B3LYP/6-31G(d) level of theory on transition states, to ensure that they are correctly connected to the desired reactants and products.

If we considered that the activation energy of the breaking of a C-C bond in saturated hydrocarbons is usually between 26 and 31 kcal/mol [122], table 4 illustrates well that the

presence of oxygen atoms in the involved radicals can have a significant impact on the values of the activation energies of the this reaction class.

IV.5. Intramolecular isomerizations

Intramolecular isomerizations involving the transfer of a H-atom through a cyclic transition state are important reactions of alkyl ($R\bullet$) and peroxyalkyl ($RO_2\bullet$) radicals during the oxidation of hydrocarbons. The rate constants of the isomerizations of peroxyalkyl radicals have been shown to be particularly sensitive parameters during the low-temperature oxidation of alkanes [122]. These reactions need also to be considered in the case of oxygenated reactants. In EXGAS, the activation energy for an isomerization is set equal to the sum of two contributions: the activation energy for H-abstraction from the molecule by analogous radicals and the strain energy involved in the cyclic transition state [122]. For modeling the low-temperature oxidation of ethyl tert-butyl ether and methyl tert-butyl ether [123], the same values for these contributions have been taken as for alkanes. EXGAS has never been used to generate mechanism for the low-temperature oxidation of alcohols.

In the case of esters, some values had to be changed to take into account the influence of the ester group. The activation energy for the internal H-abstraction in α -position from the ester function has been taken equal to that for the abstraction of a tertiary H-atom in the case of alkanes (i.e., 9 kcal.mol⁻¹ for a tertiary H-atom in an alkyl radical and 14 kcal.mol⁻¹ for a tertiary H-atom in peroxy-alkyl radicals [122]). The ring strain energy involved in the transition state of some reactions of isomerization, transferring a H-atom above the ester function, had also to be re-estimated. These isomerizations concern ester alkyl radicals and ester alkyl-peroxy radicals. The ring strain energies of the transition states involved in the reactions of isomerization of ester alkyl radicals were deduced from the enthalpy of formation of the corresponding lactones measured by Wiberg and Waldron [140]. Ring strain energies are (in kcal.mol⁻¹) equal to 9, 11, 11.2, and 12.5 (in kcal.mol⁻¹) for 5, 6, 7, and 8 membered ring lactones, respectively. These values can be compared to the lower ones used for alkyl radicals: 6.3, 1, 6.4, and 9.9 for 5, 6, 7, and 8 membered rings, respectively.

Some isomerizations of peroxyalkyl radicals, shifting a H-atom above the ester function, involve cyclic transition states which contain three oxygen atoms. This kind of isomerizations occurs through seven and eight membered rings as shown in Figure 5. Two configurations are possible according to the position of the peroxy group: either the peroxy group is on the alkyl chain and the shifted H-atom is on the methyl group of the ester function, or the peroxy group is on the methyl part of the ester function and the shifted H-atom is on a carbon atom from the alkyl chain. The strain energies have been considered as equal to the enthalpies of reaction of the isodesmic reactions yielding the cyclic structure from a linear unstrained one (i.e. reactants and products can be decomposed using the same groups according to the group additivity method of Benson [126]) in the case of seven membered ring species [124]. These enthalpies of reaction have been calculated by quantum methods at the CBS-QB3 level of theory using Gaussian03 [137]. Note that the presence of the third oxygen atom in the ring together with the carbonyl group significantly increases the ring strain energy: the calculated strain energies in figure 5 range from 7.7 to 13.6 kcal/mol, while the strain energy for two oxygen cyclic transition states are taken as equal 5 kcal/mol for 7 membered rings and to 4 kcal/mol for 8 membered ring. That involves that the isomerizations of peroxyalkyl radicals is more difficult in the case of esters than for alkanes.

V. SPECIFIC REACTIVITY OF OXYGENATED CYCLIC COMPONENTS OF BIOFUELS

Compared to acyclic oxygenated compounds, the kinetic study of the oxidation of cyclic oxygenated compounds is really at its starting point.

V.1. Saturated cyclic ethers

Reaction classes for the development of detailed chemical kinetic models of saturated cyclic ethers, such as tetrahydrofuran derivatives, are similar to those of cyclic alkanes. If reaction classes are identical, rate parameters can be dramatically different because of the presence of oxygen atom in the molecular structure. Recent years have seen the emergence of a large number of detailed chemical kinetic models for the oxidation of cyclic alkanes [141][144]. It was shown that these compounds are characterized by specific reaction classes. Kinetic models for saturated cyclic ethers can be developed using the same reaction rules. These specific reaction classes of cyclic saturated molecular systems can be considered:

- Unimolecular initiations of cyclic structures lead to biradical species that further isomerize by internal H-transfer to form an unsaturated compound. In the case of cyclic alkanes, with or without a lateral alkyl chain, the initiation step that opens the ring always leads to the formation of the corresponding 1-alkene. Based on electronic structure calculations, it was shown that activation energies for these processes can be estimated by subtracting the ring strain energy of the cyclic structure to the C-C bond dissociation energy of a corresponding linear alkane [145]. The presence of oxygen in the ring increases the complexity of cyclic ether unimolecular initiations. Two types of biradicals can be obtained as the ring opens: a carbon-carbon biradical ($\text{CH}_2\cdot\text{-(CH}_2\text{)}_n\text{-O-(CH}_2\text{)}_n\text{-CH}_2\cdot$) or a carbon-oxygen biradical ($\text{O}\cdot\text{-(CH}_2\text{)}_n\text{-CH}_2\cdot$), where n is characteristic of the size of the chain and each H atom could be replaced with an alkyl group in the case of cyclic ethers with a lateral alkyl chain. According to differences in bond dissociation energies for acyclic ethers (figure 3), one can assume that C-O bond fission will be the most favored initiation pathway compared to the CC bond ring opening. In that case, two molecules could be obtained by an internal hydrogen atom transfer from the biradical ($\text{O}\cdot\text{-(CH}_2\text{)}_n\text{-CH}_2\cdot$): an alkene-alcohol and an aldehyde or a ketone. A proposed biradical initiation mechanism for 2-methyltetrahydrofuran is presented in figure 6. Rate coefficients and branching ratios of the products remain unknown in the literature for these processes.
- The role of a lateral alkyl group becomes critical when the β -scission reaction class of cyclic ether radicals is considered. In the case of cyclic alkyl radicals, it was shown that the presence of a lateral alkyl group allows two types of ring opening reactions: “*exo*” and “*endo*” ring openings [146]. If the cyclic structure is free of any lateral alkyl group, then any radical created from the parent compound can only undergo *endo* ring openings, i.e. the nascent double bond is created inside the cyclic transition state. However, a lateral alkyl group leads to the formation of radicals where the unpaired electron is located on the alkyl group itself, allowing the double bond to be formed outside the cyclic part of the transition state, in an *exo* ring opening reaction. Figure 6 illustrates an *endo* and *exo* ring opening in the case of 2-methyltetrahydrofuran. The impact of the location of the nascent π bond in the transition state (inside or outside the cyclic part of the transition state) on the rate parameters is considerable. In the case of *exo* ring openings of cyclic alkyl radicals, it was shown that rate parameters can be estimated using an Evans-Polanyi correlation that also describes the C-C bond β -scission of acyclic alkyl radicals. However, *endo* ring opening reactions exhibited a considerably different behavior

characterized by higher activation energies. These activation barriers can be so high that C-H bond β -scissions can be competitive. This was observed, for example, in the case of cyclopentyl radical thermal decomposition. Almost, no information on β -scissions of cyclic ether radicals is available in the literature and although these radicals are expected to behave like cyclic alkyl radicals, the associated rate parameters are largely uncertain.

- Isomerization of peroxy radicals formed by the addition of a cyclic radical to O_2 is of course not a reaction class specific to cyclic compounds but it leads to specific elementary reactions that involves bicyclic transition states (figure 6). If *ab initio* calculations are available in the literature for the rate constants of cyclic alkylperoxy radicals [147], rate constants for these processes remain unknown in the case of saturated cyclic ethers.

V.2. Unsaturated cyclic ethers

Reaction classes of unsaturated cyclic ethers such as furan derivatives involve specific processes that are different from saturated cyclic ethers. The presence of a lateral alkyl group on the furan ring has also a considerable impact on the reactivity of these compounds. Simmie and Curran [148] recently pointed out that C-X (with X = H or C) bonds of alkylfurans are among the highest bond dissociation energy known. In alkylfurans, the bond dissociation energy of C-H bonds involving carbon atoms belonging to the ring is as high as $119.6 \text{ kcal.mol}^{-1}$ (to be compared with the values presented in Figure 1 for acyclic species). Such high energies tend to favor unusual pathways for unimolecular initiations involving the formation of carbenes. Similarly, rate parameters for H-abstractions are expected to be affected and decomposition pathways by bond β -scission may be more difficult because of such bond strengths. Indeed, the lowest energy decomposition pathways of furyl derivatives radicals involve hydrogen transfer through strained cyclic transition states and/or successive cyclization-isomerization-ring opening sequences. In more details, the following reaction class specificities can be noted:

- Most favored unimolecular initiation mechanisms occur through the formation of carbene intermediates rather than biradical ring opening. Sendt et al. [149] showed that the singlet biradical formed from the ring opening of furan was lying $88.8 \text{ kcal.mol}^{-1}$ above furan (at 0 K) while the energy barrier for hydrogen transfer through a 3 membered ring transition state leading to a carbene was calculated to be $68.9 \text{ kcal.mol}^{-1}$ at several levels of theory (CASPT2, G2MP2). Recent CBS-QB3 calculations from Tian et al. [117] confirmed this 1-2 H-transfer pathway to be favored with a computed barrier of $70.4 \text{ kcal.mol}^{-1}$. As shown in figure 7, the carbene intermediate easily rearranges to formylallene, which in turn decomposes to give CO and propyne through a concerted mechanism involving a hydrogen shift and a C-C bond breaking. It appears that this decomposition pathway is favored because of the ability of the molecule formed from the carbene (formylallene) to easily transfer the aldehydic hydrogen atom. Consequently, this kind of pathway will be largely hindered if a ketone is formed from the carbene intermediate, i.e. a methyl group is bounded to the CO group instead of a H-atom. The presence of a methyl group on the furan ring will therefore have a critical impact on the unimolecular initiation mechanism. Moreover, if a methyl group is bounded to the furan ring one might wonder if a 1-2 CH_3 group transfer, leading to a carbene intermediate, can be competitive with the 1-2 H-atom transfer pathway. Calculations performed at the CBS-QB3 level of theory predict a barrier of $81.1 \text{ kcal.mol}^{-1}$ for 1-2 CH_3 -group transfer in 2,5-dimethylfuran (2,5-DMF). This pathway lies 12 kcal.mol^{-1} above the energy barrier for the competitive 1-2 H-transfer in 2,5-DMF determined at the same level of theory (see figure 7). It also

can be seen that, as already mentioned above, even if 1-2 H-atom transfer is the most favored pathway here, the ketone formed from the carbene intermediate is not able to easily decompose via a concerted reaction because of the methyl group linked to the CO group. Rate parameters for furan unimolecular initiations were proposed by Sendt et al. [149], but no kinetic data is available for methyl- or dimethyl-furan and the presence of methyl groups prevents straightforward analogies with furan kinetic data.

- C-O bond β -scissions of furyl radicals were studied by Tian et al. [117] at the CBS-QB3 level of theory. They showed that relatively high energy barriers (above 33 kcal.mol⁻¹) are involved to decompose furyl radicals by β -scissions. Again, the presence of one or two methyl groups on the furan ring is expected to considerably influence the thermal decomposition pathways of methylfuryl radicals. By analogy with saturated cyclic compounds, one could expect that the presence of a lateral methyl group on the furan ring leads to radicals that can undergo *exo* ring opening with a lower activation energy than that of the *endo* ring opening of furyl radicals. However a calculation at the CBS-QB3 level of theory predicts the energy barrier to be 8.4 kcal.mol⁻¹ higher than the corresponding *endo* ring opening (figure 7). Rate constants for these processes remain unknown and the *ab initio* calculations of Tian et al. [117] on furyl radicals are the only kinetic data available in the literature.
- As furan and furan derivatives are unsaturated compounds, the description of addition reactions of small radicals (notably H atoms and OH radicals) to the double bonds is critical to accurately predict the branching ratios of pyrolysis and/or combustion products. It should be emphasized that almost no information is available in the literature for these types of reaction. Tian et al. [117] studied at the CBS-QB3 level of theory the addition of H atom on furan and the decomposition channels of the adduct formed. These data constitute the only kinetic parameters available in the literature. As emphasized above, analogies with results from furan cannot be applied straightforwardly for methyl- and dimethyl-furans and the fate of the adducts formed by H additions remains unknown.
- Low temperature oxidation mechanism of furan and its derivatives is yet unknown.

VI. CONCLUSION

With the increasing interest to shift from petroleum-based fuels to bio-fuels, many types of oxygenated molecules which could be used as additive to gasoline or diesel fuel have been proposed: alcohols, such as methanol, ethanol, propanols, or butanols, fatty acid methyl esters, acyclic ethers and cyclic ethers of the family of furans. After a first part summarizing the detailed kinetic models existing for the combustion of these molecules, this paper describes the reactions and rates constants which are specific to oxygenated fuels. While a fair number of detailed kinetic models have already been proposed for the combustion and the oxidation of alcohols, methyl esters and acyclic ethers, there are only a very few ones concerning furans and its derivatives. This paper summarizes also the main specificities taken into account in elementary steps and in their kinetic parameters in the case of oxygenated reactants. While the mechanism of the oxidation of saturated cyclic ethers can certainly be close to that of cyclic alkanes, the reactions of unsaturated cyclic ethers have been shown to be very complex and are still very uncertain.

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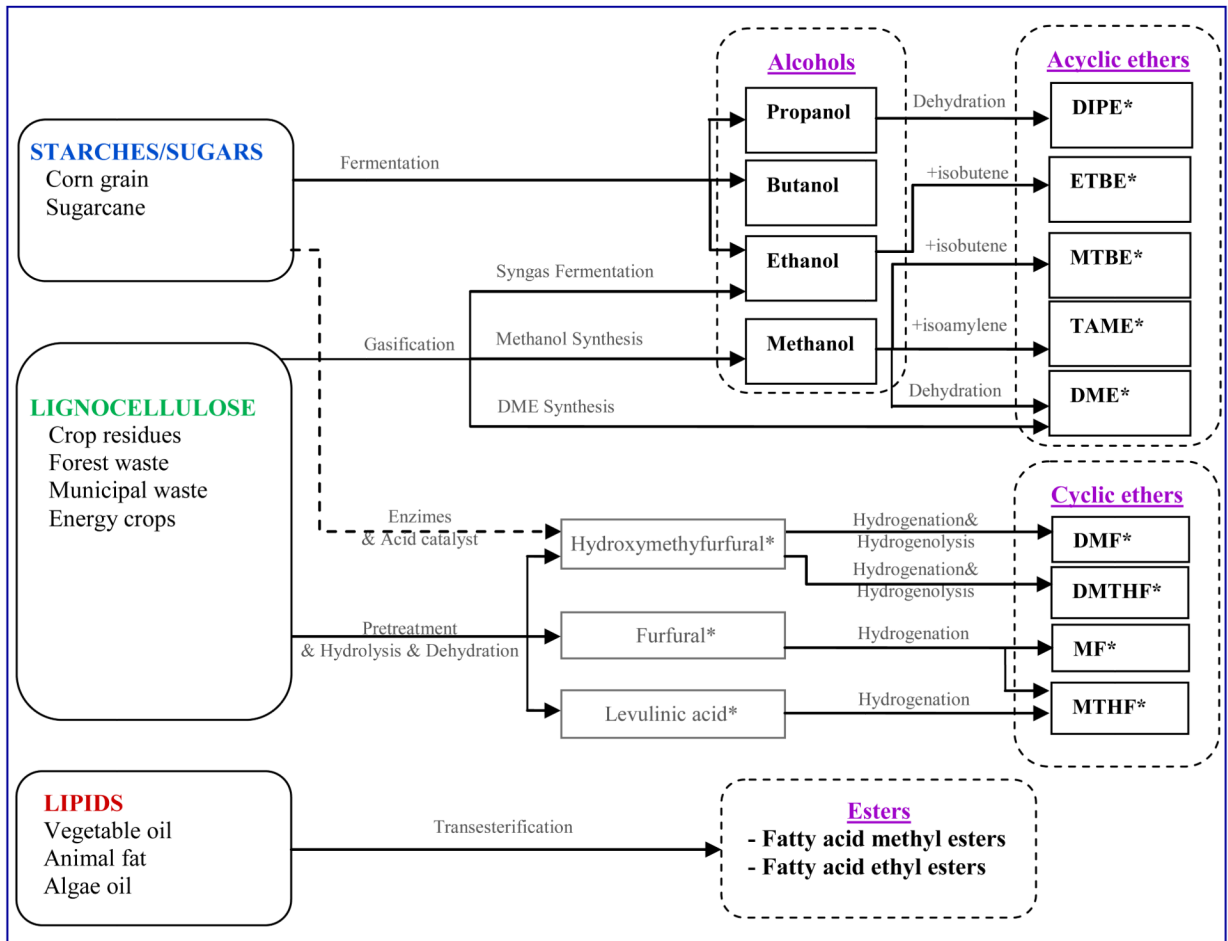


Figure 1. Ways to obtain components of fuels derived from biomass.
*See full names and formulae in table 1.

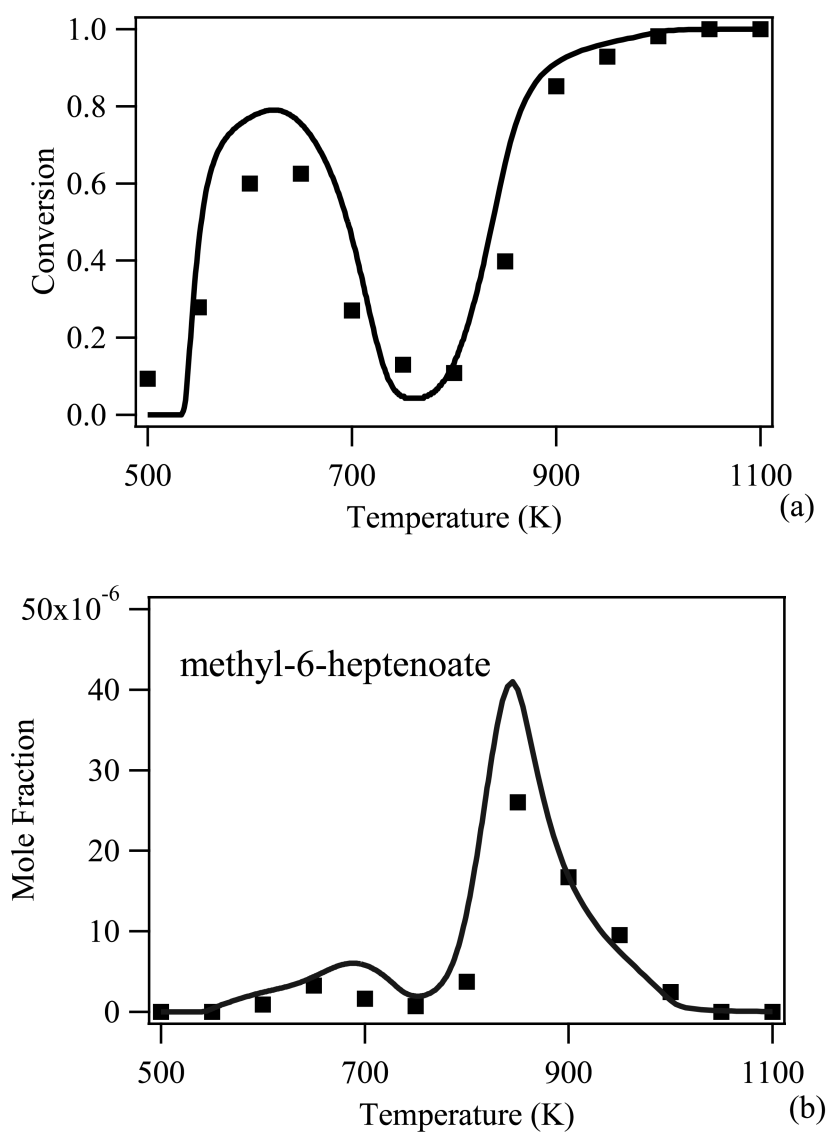


Figure 2. Simulated (lines) and experimental (points) evolution with temperature of the mole fractions of (a) reactant and (b) methyl-6-heptenoate. Model generated using EXGAS software; experimental mole fraction measured by on-line gas chromatography during the oxidation in a jet-stirred reactor of a stoichiometric mixture of methyl decanoate/O₂ diluted in helium at atmospheric pressure [84].

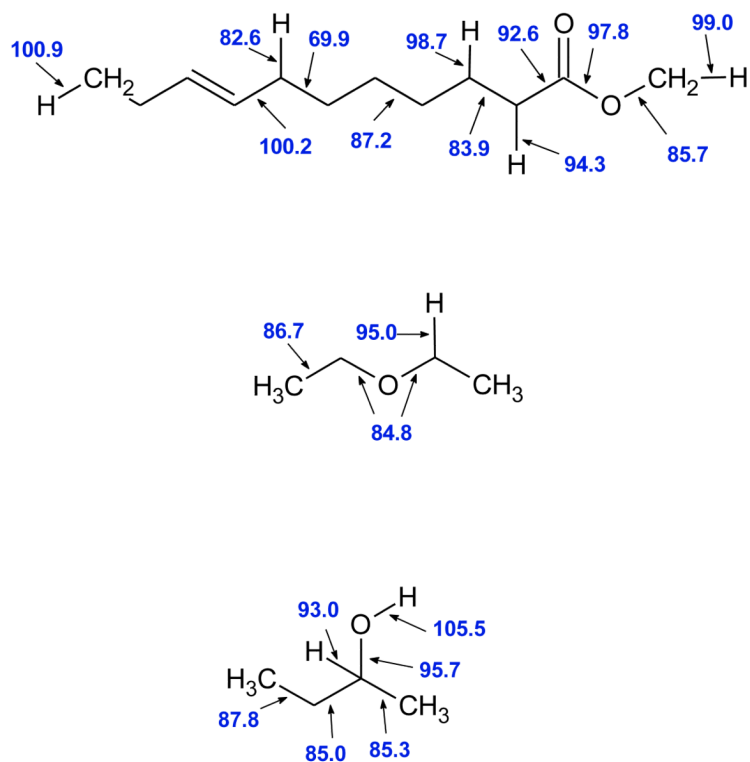


Figure 3. Examples of bond dissociation energies (in kcal/mol) in ester, ether, and alcohol molecules. R is an alkyl group larger than a methyl one.

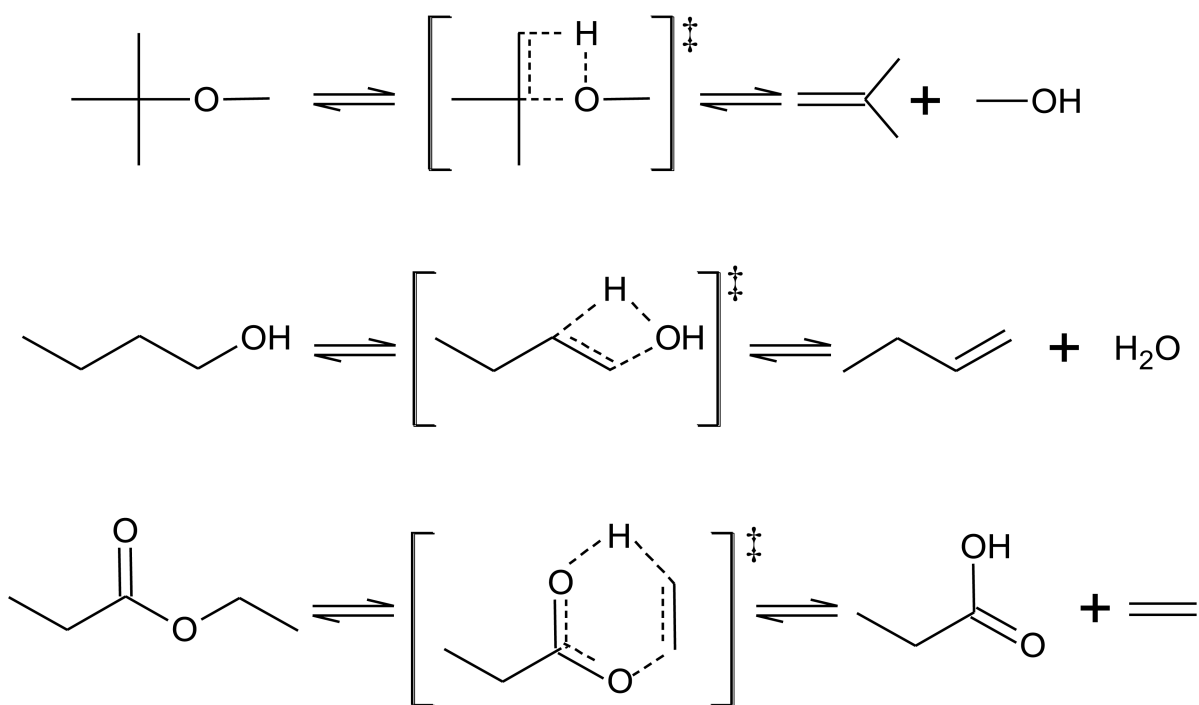


Figure 4.
Examples of molecular reactions which can be observed in ethers, alcohols and ethyl esters.

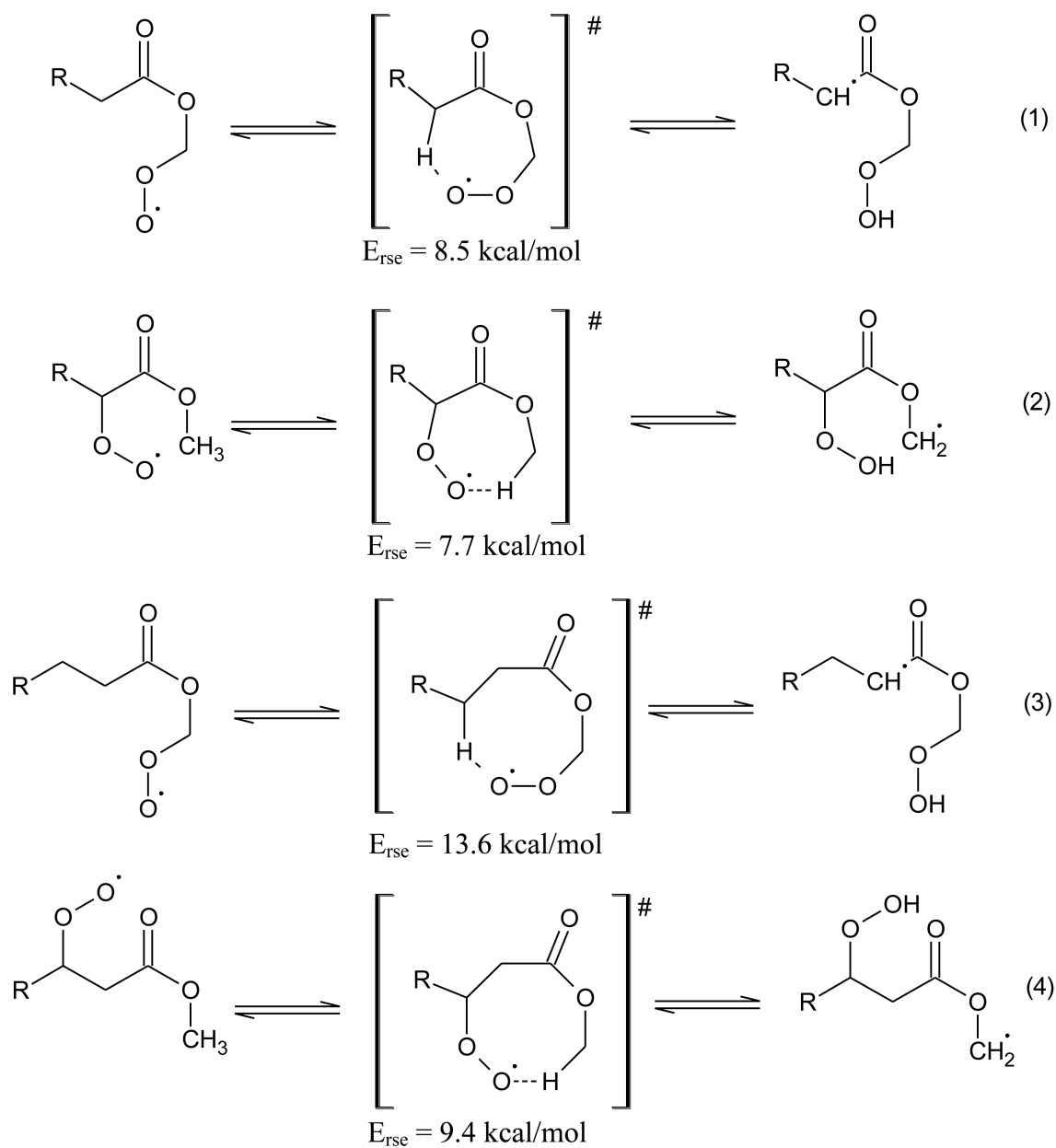


Figure 5. Reactions of intramolecular isomerization involving transition states including seven and eight membered rings, which contain three oxygen atoms and related to ring strain energies (E_{rse}) in kcal/mol.

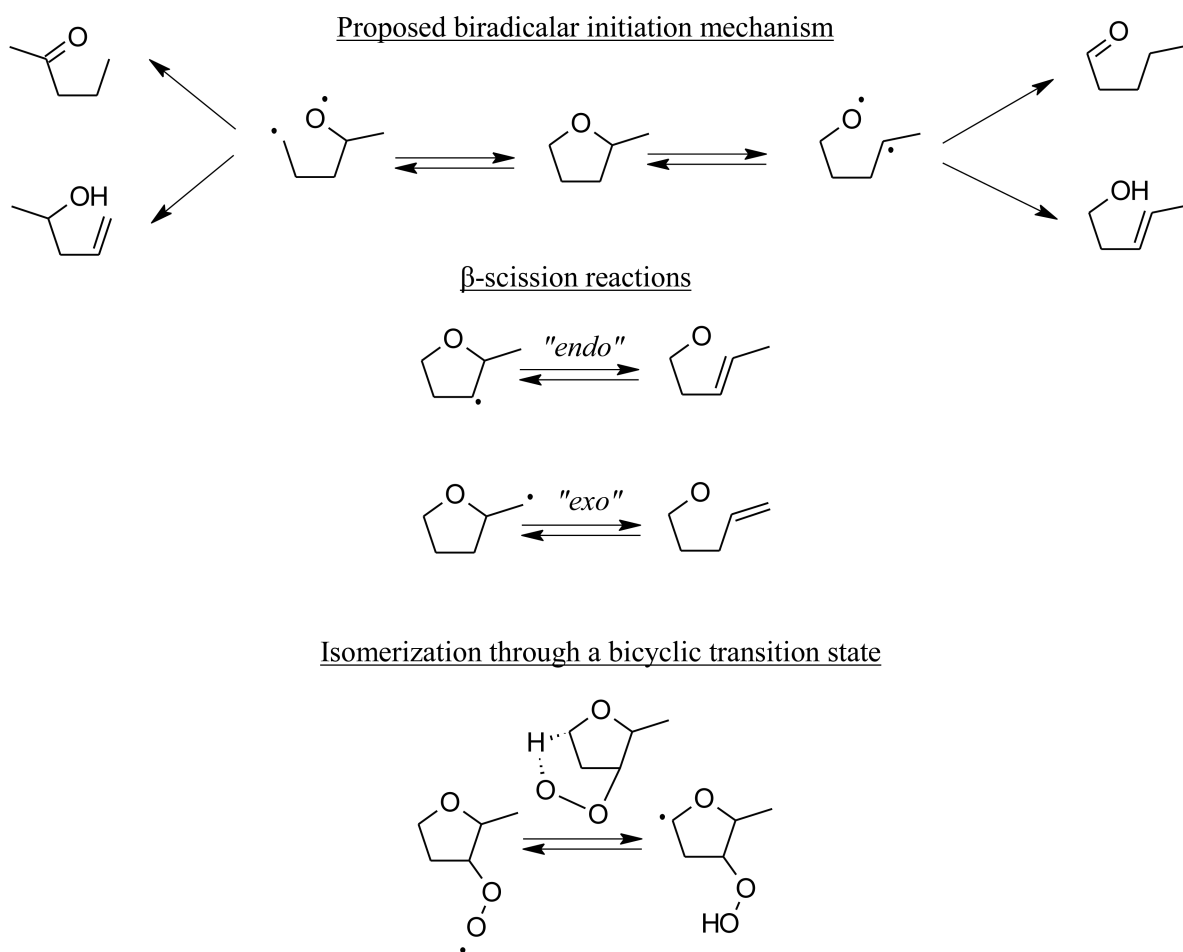
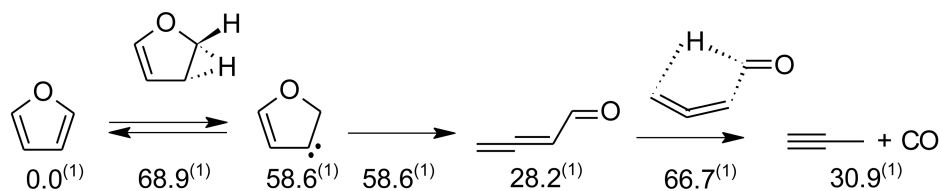
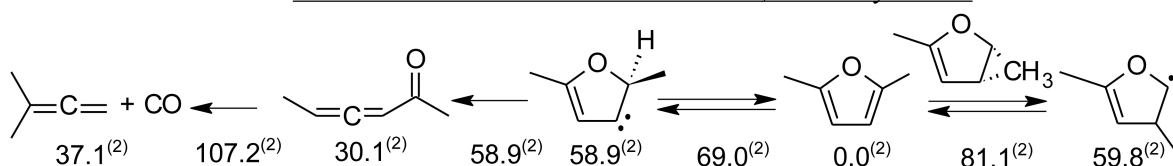


Figure 6. Examples of reaction classes (unimolecular initiation, *endo* and *exo* β -scissions, and isomerization of a peroxy radical) specific to saturated cyclic ethers.

Unimolecular initiation mechanism of furan (carbene intermediate) :



Unimolecular initiation mechanism of 2,5-dimethylfuran :



endo and exo β-scission of furan and 2,5-dimethylfuran :

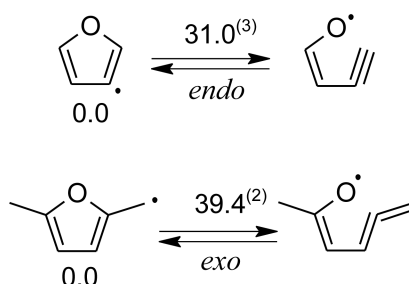
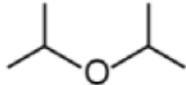

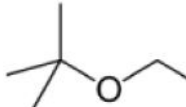
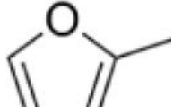
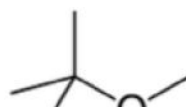
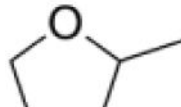
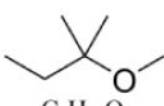
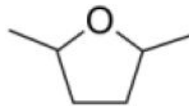
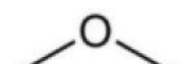



Figure 7. Specific reactions of unsaturated cyclic ethers: unimolecular initiation mechanisms of furan and dimethyl furan and comparison between *endo* and *exo* β-scissions for furan and dimethyl furan. ⁽¹⁾ Energies at 0 K from ab initio calculations of Sendt et al. [149]. ⁽²⁾ Enthalpies at 298 K computed at the CBS-QB3 level of theory (present work). ⁽³⁾ Enthalpies at 298 K from ab initio calculations of Tian et al. [117].

Table 1

Full names and formulae of species shown in figure 1 and in tables 2 and 3.

Acyclic ethers		Cyclic ethers	
Species	Formula	Species	Formula
Diisopropyl ether (DIPE)	 $C_6H_{14}O$	2,5- Dimethylfuran (DMF)	 C_6H_8O
Ethyl <i>tert</i> -butyl ether (ETBE)	 $C_6H_{14}O$	2-Methylfuran (MF)	 C_5H_6O
Methyl <i>tert</i> -butyl ether (MTBE)	 $C_5H_{12}O$	2-Methyltetrahydrofuran (MTHF)	 $C_5H_{10}O$
Tertiary amyl methyl ether (TAME)	 $C_6H_{14}O$	2,5-Dimethyltetrahydrofuran (DMTHF)	 $C_6H_{12}O$
Dimethyl ether (DME)	 C_2H_6O	Tetrahydrofuran (THF)	 C_4H_8O

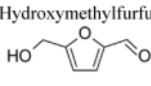
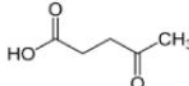
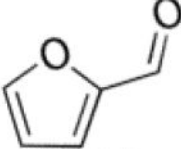
Other species		
<p>5-Hydroxymethylfurfural</p>  <p>$C_6H_6O_3$</p>	<p>Levulinic acid</p>  <p>$C_5H_8O_3$</p>	<p>Furfural</p>  <p>$C_5H_4O_2$</p>

Table 2

Properties of several oxygenated fuels and conventional fuels.

	Chemical Formula	MW ^b (g/mol)	Density (kg/l)	Boiling Point (K)	LHV ^b (MJ/kg)	AIT ^b (K)	RON/MON ^b	CN ^b
Alcohols								
Methanol	CH ₃ OH	32.04	0.796 [22]	337.9 [22]	20.0 [22]	783 [23]	126/96 [22]	0-3 [22]
Ethanol	C ₂ H ₅ OH	46.07	0.794 [22]	351.6 [22]	26.8 [22]	763 [23]	120/99 [22]	5-8 [24]
<i>n</i> -Propanol	C ₃ H ₇ OH	60.10	0.804 [25]	355.4 [26]	30.9 [25]	753 [23]	112/-- [26]	--
<i>n</i> -Butanol	C ₄ H ₉ OH	74.12	0.810 [25]	355.9 [26]	33.1 [27]	703 [23]	96/78 [27]	--
<i>n</i> -Pentanol	C ₅ H ₁₁ OH	88.15	0.811 [25]	393.0 [28]	34.8 [25]	573 [29]	--	--
Acyclic ethers								
DME ^d	CH ₃ OCH ₃	46.07	0.66 ^a [11]	248.3 [11]	28.6 [11]	623 [30]	--	>55 [30]
MTBE ^d	C ₄ H ₉ OCH ₃	88.15	0.74 [22]	328.5 [22]	35.2 [22]	733 [31]	118/101 [22]	<0 [22]
ETBE ^d	C ₄ H ₉ OC ₂ H ₅	102.17	0.75 [22]	346.0 [22]	35.9 [22]	--	117/101 [22]	<0 [22]
TAME ^d	C ₆ H ₁₄ O	102.17	0.75 [22]	359.5 [22]	36.5 [22]	703 [32]	114/100 [22]	<0 [22]
DMM ^b	CH ₃ OCH ₂ OCH ₃	76.09	0.86 [24]	315.2 [24]	22.4 [24]	510 [24]	--	25-30 [24]
DEE ^b	C ₂ H ₅ OC ₂ H ₅	74.12	0.71 [30]	307.6 [30]	33.9 [30]	433 [30]	--	>125 [30]
Methyl esters								
DMC ^b	C ₃ H ₆ O ₃	90.08	1.07 [33]	363.2 [34]	15.8 [33]	--	--	35.5 [33]
Biodiesel ^c	C ₁₂ -C ₂₂ FAME ^b	≈300	0.88 [35]	455-611 [35]	37.2 [35]	589 [24]	--	48-65 [35]
Cyclic ethers								
THF ^{d, e}	C ₄ H ₈ O	72.11	0.89 [36]	339.2 [36]	--	594 [36]	--	--
MTHF ^d	C ₅ H ₁₀ O	86.13	0.85 [37]	353.4 [37]	32.0 [38]	--	86/72 [39]	--
DMTHF ^d	C ₆ H ₁₂ O	100.16	0.83 [40]	364.1 [19]	--	--	82 /-- [19]	--
Furan	C ₄ H ₄ O	68.07	0.94 [31]	305.2 [31]	--	663 [31]	--	--
DMF ^d	C ₆ H ₈ O	96.13	0.89 [41]	366.5 [28]	33.7 [19]	559 [42]	119 /-- [19]	--
MF ^d	C ₅ H ₆ O	82.10	0.91 [31]	62.9 [19]	--	--	131 /-- [19]	--
Conventional fuels								
Gasoline ^c	C ₄ -C ₁₄ HC	≈102	0.74 [22]	303-473 [22]	42.7 [22]	≈723 [23]	95/85 [22]	--
Diesel ^c	C ₈ -C ₂₅ HC	≈200	0.84 [22]	443-633 [22]	43.0 [22]	≈533 [23]	--	40-55 [22]

^aNotes: Density at 1 atm and 298 K.^bLHV-Lower Heating Value (LCV- Lower Calorific Value); RON-Research Octane Number; MON-Motor Octane Number; CN-Cetane Number; AIT-Autoignition Temperature; MW- Molecular Weight; C₁₂-C₂₂ FAME - Methyl Esters of C₁₂ to C₂₂ Fatty Acids; DEE-Diethyl Ether; DMC-Dimethyl Carbonate; DMM-Dimethoxy Methane.^cFuel standard.^dSee full names and formulae in Table 1.^eNot directly considered as a biofuel, but from the same family as potential biofuels.

Table 3

Major models for the combustion of potential oxygenated components of fuel.

Components		References of chemical kinetic models	Conditions of validation
Alcohols	Ethanol	Natarajan and Bhaskaran 1981 [21]	- Shock tube (T=1300-1700 K, P=101-203 kPa, $\Phi=0.5-2.0$) [21].
		Dunphy et al. 1991 [43]	- Shock tube (T=1080-1660 K, P=182-466 kPa, $\Phi=0.25-2.0$) [44].
		Norton and Dryer 1992 [45]	- Flow reactor (T=1100 K, P=101kPa, $\Phi=0.61-1.24$) [45].
		Marinov et al. 1999 [46]	- Shock tube [21] [*] , [44] [*] ; Flow reactor [45] [*] . - Laminar burning velocities in constant volume bomb (P=100-800 kPa, $\Phi=0.7-1.4$) [47] and in counterflow twin-flame (P=101 kPa, $\Phi=0.55-1.8$) [48]. - Jet-stirred reactor (T=1000-1200 K, P=101 kPa, $\Phi=0.2-2.0$) [49].
		Saxena and Williams 2007 [50]	- Shock tube [21] [*] , [44] [*] ; Counterflow twin-flame [48] [*] . - Counterflow diffusion and partially premixed flames (P=101 kPa) [50]. - Extinction in counterflow diffusion flames (P=101 kPa) [51].
		Li et al, 2007 [52]	- Shock tube [21] [*] , [44] [*] ; Laminar burning velocities [47] [*] , [48] [*] ; Counterflow flames [50] [*] . - Flow Reactor (T=800-950 K, P=304-1216 kPa, $\Phi=0.3-1.4$) [52].
		Cancino et al, 2010 [53]	- Shock tube [44] [*] and (P=1000-5000 kPa, T=750-1220K, $\Phi=0.3-1.0$) [53].
		Leplat et al. 2011 [54]	- Shock tube [21] [*] , [44] [*] ; Counterflow flames [50] [*] . - Jet stirred reactor (P=101 kPa, T=890-1250 K, $\Phi=0.25-2.0$) [54]. - Premixed laminar flat flame (P=5 kPa, $\Phi=0.75-1.25$) [54]. - Laminar burning velocities in constant volume bomb (P=100-1000 kPa, $\Phi=0.7-1.4$) [55][56].
	n-and iso-Propanol	Johnson et al. 2009 [57]	- Shock Tube (T=1350-2000 K, P=101 kPa, $\Phi=0.5-2.0$) [57].
		Frassoldati et al. 2010 [58]	- Shock tubes [57] [*] . - Counterflow diffusion flame (P= 101 kPa) [58]. - Flow reactors (P=101 kPa, T=1020-1120 K, $\Phi=0.61-1.18$) [59]. - Premixed laminar flat flame (P=3.3-4.7 kPa, $\Phi=1.0-1.94$) [60].
	Butanol	Moss et al. 2008 [27] (<i>4 isomers of butanol</i>)	- Shock tube (T=1200-1800K, P=100-400 kPa, $\Phi=0.25-1.0$) [27].
		Dagaut et al. 2009 [61][62] (<i>n-butanol</i>)	- Jet stirred reactor (P=101-1010 kPa, T=800-1250 K, $\Phi=0.25-2.0$) [61][62]. - Counterflow diffusion flame (P=101 kPa) [61][62]. - Laminar burning velocities in constant volume bomb (P=90 kPa, $\Phi=0.8-1.2$) [62][63].
		Black et al. 2010 [64] (<i>n-butanol</i>)	- Jet stirred reactor [61] [*] . - Shock Tube (T=1100-1800 K, P=101-811 kPa, $\Phi=0.5-2$) [64].
		Grana et al.2010 [65] (<i>4 isomers of butanol</i>)	- Shock tube [27] [*] , [64] [*] ; Flow reactors [59] [*] ; Jet stirred reactor [61] [*] , [62] [*] . - Counterflow diffusion flame [62] [*] and (P=101 kPa) [65]. - Shock tube <i>pyrolysis</i> (P=71-101 kPa, T=1200-1600 K) [66].
		Harper et al. 2011 [67] (<i>n-butanol</i>)	- Shock tube [27] [*] , [64] [*] ; Jet-stirred reactor [61] [*] , [62] [*] ; Counterflow diffusion flame [62] [*] . - Shock tube (butanol:T=1200-1600 K, P=142-167 kPa, $\Phi=1.0-2.0$) [68]. - Butanol-doped methane diffusion flame (P=101 kPa) [69]. - Pyrolysis experiments in flow reactor (T _{ini} =673-749 K, T _{max} = 923-1080 K, P=172 kPa) [67].
	n-Pentanol	Togbé et al. 2011 [70]	- Jet-stirred reactor (P=1013 kPa, T=770-1220 K, $\Phi=0.35-4.0$) [70].

Components		References of chemical kinetic models	Conditions of validation
			- Laminar burning velocities in constant volume bomb (P=101 kPa, $\Phi=0.7-1.4$) [70].
	<i>n</i> -Hexanol	Togbé et al. 2010 [71]	- Jet-stirred reactor (P=1013 kPa, T=560-1220 K, $\Phi=0.5-3.5$) [71]. - Laminar burning velocities in constant volume bomb (P=100-1000 kPa, $\Phi=0.7-1.5$) [71].
Methyl esters	Dimethyl carbonate	Glaude et al. 2005 [72]	- Counterflow diffusion flame (P=101 kPa) [73].
	Methyl butanoate	Fisher et al. 2000 [74]	- Static reactor (P=40 kPa, T=541-741 K, $\Phi=3.25$) [75].
		Gaïl et al. 2007 [76], 2008 [77]	- Jet-stirred reactor (T= 800-1400 K, P= 101 kPa, $\Phi=0.375-1.13$) [76] [77]. - Flow reactor (T=500-900 K, P= 1266 kPa, $\Phi=0.35-1.5$) [76]. - Counterflow diffusion flame (P= 101 kPa) [76].
		Dooley et al. 2007 [78], 2008 [79].	- Jet-stirred reactor [76] [*] ; Counterflow diffusion flame [76] [*] ; Flow reactor [76] [*] . - Shock Tube (T= 1100-1760 K, P=101-405 kPa, $\Phi=0.25-1.5$) [79], [78]. - Rapid compression machine (T= 640-949 K, P=1013-4053 kPa, $\Phi=0.33-1.0$) [79].
		Hakka et al. 2010 [80]	- Shock Tube [78] [*] and (T=1280-1990K, P=770-922 kPa, $\Phi=0.25-2.0$) [80]. - Rapid compression machine (T= 935–1117 K, P=1000 kPa, $\Phi=0.4$) [81]. - Jet-stirred reactor (T= 800- 850 K, P= 101 kPa, $\Phi=0.5-1.0$) [80].
	Methyl-2-butenoate	Gaïl et al. 2008 [77]	- Jet-stirred reactor [77] - Counterflow diffusion flame (P=101 kPa) [77].
		Bennadji et al. 2011 [82]	- Shock Tube (T=1280-1930K, P=700-965 kPa, $\Phi=0.25-2.0$) [82].
	Methyl hexanoate	Dayma et al. 2008 [83]	- Jet-stirred reactor (T=500-1000 K, P=1013 kPa, $\Phi=0.5-1.5$) [83].
	Methyl heptanoate	Dayma et al.2009 [85]	- Jet-stirred reactor (T=550-1150 K, P=1013 kPa, $\Phi=0.6-2.0$) [85].
		Glaude et al. 2010 [84]	- Jet-stirred reactor [85] [*]
	Methyl Decanoate	Herbinet et al. 2008 [86]	No direct validation.
		Glaude et al. 2010 [84]	- Jet-stirred reactor (T=500-1100 K, P=106 kPa, $\Phi=1.0$) [84].
	Methyl Decenoates	Herbinet et al. 2010 [87]	No direct validation.
	Heavier methyl esters	Naik et al. 2011 [88] (<i>Methyl Stearate, Methyl Oleate</i>)	No direct validation.
Herbinet et al. 2011 [89] (<i>Saturated C₁₃, C₁₅, C₁₇, C₁₉</i>)		- Jet-stirred reactor (P=106 kPa, T=550–1100 K, $\Phi=1.0$) [90] (<i>Methyl Palmitate/n-decane mixture</i>).	
Westbrook et al. 2010 [91][92] (<i>Saturated C₁₇ and C₁₉ methyl esters, methyl oleate, methyl minoleate, methyl linolenate</i>)		- Jet-stirred reactor [90] [*] (<i>Methyl Palmitate/n-decane mixture</i>). - Jet-stirred reactor ((P=106 kPa, T=550–1100 K, $\Phi=1.0$) [92] (<i>Methyl Oleate/n-decane mixture</i>).	
Acyclic ethers	DME**	Dagaut et al. 1996 [93], 1998 [94]	- Shock tube (T=650-1600 K, P=350-4000 kPa, $\Phi=0.5-2.0$) [94]. - Jet-stirred reactor (P=101-1013 kPa, T=550-1275 K, $\Phi=0.2-2.5$) [93] [94].
		Curran et al. 1998 [95], 2000 [96]	- Jet-stirred reactor [93] [*] , [94] [*] . - Shock tube (T=650-1300 K, P=1317-4053 kPa, $\Phi=1.0$) [97]. - Flow reactor (T=550-855 K, P=1216-1824 kPa, $\Phi=0.7-4.2$) [96].

Components		References of chemical kinetic models	Conditions of validation
		Fischer et al. 2000 [98]	- Shock tube [94] [*] ; Jet-stirred reactor [93] [*] . - Flow reactor <i>pyrolysis</i> (T=1060 K, P=253 kPa), <i>near-pyrolysis</i> (T=1118 K, P=101 kPa) and oxidation (T=1080-1086 K, P=101 kPa, $\Phi=0.3-3.4$) [98] - Flow reactor (T=600-1500 K, P=101 kPa, $\Phi=0.5$) [99].
		Zhao et al. 2008 [100]	- Shock tube [94] [*] [97] [*] ; Flow reactor [96] [*] , [98] [*] , [99] [*] ; Jet-stirred reactor [93] [*] , [94] [*] . - Shock tube (T=1241-1538 K, P=182-197 kPa, $\Phi=1.0-2.0$) [100] - Flow reactor <i>pyrolysis</i> (T=980 K, P=1013 kPa) [100]. - Premixed laminar flat flame (P=4 kPa, $\Phi=0.98$) [101] and (P=101 kPa, $\Phi=0.67$) [102]. - Laminar flame speeds in spherical bomb (P=101-1013 kPa, $\Phi=0.6-1.7$) [103][104] and stagnation flame burner (P=101 kPa, $\Phi=0.7-1.4$) [105].
	MTBE ^{**}	Brocard et al. 1983 [106]	- Static reactor (T=573-773 K, P=13 kPa, $\Phi=7.5$) [106].
		Curran et al. 1992 [107]	- Shock tube (T=1100-1900 K, P=355 kPa, $\Phi=0.15-2.4$) [107].
		Goldaniga et al. 1998 [108]	- Shock tube [107] [*] . - Jet-stirred reactor (P=1013 kPa, T=800-1150 K, $\Phi=0.5-2.0$) [108].
		Glaude et al. 2000 [109]	- Flow reactor [45] [*] ; Static reactor [106] [*] . Jet-stirred reactor [108] [*] .
		Yasunaga et al. 2010 [110]	- Shock tube <i>pyrolysis</i> (T=900-1500 K, P=101-274 kPa) [110]. - Shock tubes <i>oxidation</i> (T=1400-1800 K, P=142-263 kPa) [110].
	ETBE ^{**}	Goldaniga et al. 1998 [108]	- Jet-stirred reactor [108] [*] .
		Glaude et al. 2000 [109]	- Jet-stirred reactor [108] [*] .
		Ogura et al. 2007 [111]	- Jet stirred reactor [108] [*] .
		Yahyaoui et al. 2008 [112]	- Shock tube (T=1280-1750 K, P=200-1000 kPa, $\Phi=0.25-1.5$) [112]. - Laminar burning velocity in constant volume bomb (P=101 kPa, $\Phi=0.5-1.5$) [112].
		Yasunaga et al. 2010 [110]	- Shock tube <i>pyrolysis</i> [110] [*] . - Shock tubes <i>oxidation</i> [110] [*] .
	Diethyl ether	Yasunaga et al. 2010 [113]	- Shock tube <i>pyrolysis and oxidation</i> (P=101-405 kPa, T=900-1900 K) [113]
	Dimethoxy methane	Daly et al. 2001 [114]	- Jet-stirred reactor (P=507 kPa, T=800-1200K, $\Phi=0.444-1.778$) [114].
		Dias et al. 2010 [115]	- Premixed laminar flat flame ($\Phi=0.24-1.72$, P=5 kPa) [115].
TAME ^{**}	Goldaniga et al. 1998 [108]	- Jet-stirred reactor [108]	
DIPE ^{**}	Goldaniga et al. 1998 [108]	- Jet-stirred reactor [108]	
Cyclic ethers	THF ^{**} , ***	Dagaut et al. 1998 [116]	- Shock tube (P=203-507 kPa, T=1000-1800 K, $\Phi=0.5-2.0$) [116]. - Jet-stirred reactor (P=101-1013 kPa, T=800-1100 K, $\Phi=0.5-1.0$) [116].
	Furan ^{***}	Tian et al. 2011 [117]	- Premixed laminar flat flame (P=4.7 kPa, $\Phi=1.4-2.2$) [117]. - Shock tube <i>pyrolysis</i> (T=1100-1700 K, P=2017 kPa) [118] (T=1533 K, P=26 kPa) [119].

* Conditions presented above. Φ - equivalence ratio; T- temperature; P- pressure.

** See full names and formulae in Table 1.

*** Not directly considered as a biofuel, but from the same family as potential biofuels.

Table 4Activation energies used for the decompositions by β -scission of oxygenated radicals.

Reaction class	E_a (kcal/mol)
	5.1 ^a
	15.0 ^b
	24.0 ^b
	29.0 ^c
	26.0 ^d
	30.7 ^e
	31.9 ^a
	34.9 ^e
	39.9 ^f
	15.6 ^g
	49.0 ^e

^aNotes: CBS-QB3 [137] calculation performed for $R^\bullet = CH_3^\bullet$.^bEstimated based on the kinetics of the reverse step of the addition of alkyl radical on a ketone, i.e. 10 kcal/mol according to Benson [126].^cfrom Wilk et al. [138].^dEstimated based on the kinetics of the reverse step of the for the addition of an alkoxy radical on an alkene, according to Choo et al. [131], R5 can be an H-atom.^eTheoretical calculation performed for $R^\bullet = H^\bullet$.^fTheoretical calculation performed for $R^\bullet = C_2H_5^\bullet$.^gfrom Mereau et al. [139].