

Chapter 4

Specificities Related to Detailed Kinetic Models for the Combustion of Oxygenated Fuels Components

Frédérique Battin-Leclerc, Henry Curran, Tiziana Faravelli
and Pierre A. Glaude

Abstract This article presents the specific classes of reactions considered for modeling the oxidation of the two types of oxygenated molecules which are the most usually considered in biofuels: alcohols and esters. Using models for hydrocarbon oxidation as a reference, this paper also reports the major changes to be considered for the kinetic data of the main reaction classes which are the same as those taken into account for non-oxygenated reactants. Details are given in the case of hydrogen atom abstractions, radical decompositions by β -scission, RO_2 -radical chemistry, with especially intramolecular isomerizations, and reactions leading to unsaturated products and HO_2 radicals.

4.1 Introduction

Several reviews (Kohse-Höinghaus et al. 2010; Komninos and Rakopoulos 2012; Lai et al. 2011; Tran et al. 2012) have previously given an overview of the chemistry and the kinetic models related to the combustion of oxygenated

F. Battin-Leclerc (✉) · P. A. Glaude
Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine,
ENSIC, 1 rue grandville, 54000 Nancy, France
e-mail: frederique.battin-leclerc@univ-lorraine.fr

P. A. Glaude
e-mail: pierre-alexandre.glaude@univ-lorraine.fr

H. Curran
Combustion Chemistry Centre, National University of Ireland, Galway,
University Road, Galway, Ireland
e-mail: henry.curran@nuigalway.ie

T. Faravelli
Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano,
Piazza L. da Vinci, 32 20133 Milan, Italy
e-mail: tiziano.faravelli@polimi.it

molecules, which are considered as potential additives of fuels. This chapter does not present a comprehensive list of all of the studies performed on these compounds, but provides only a sample of the kinetic models of interest. As described in [Chap. 1](#) of this book, two main families of oxygenated reactant are considered as fuel additives: alcohols in gasoline and methyl esters in diesel fuels.

The family of molecules for which the largest number of models has been proposed is alcohols (see for example: Marinov [1999](#); Saxena and Williams [2007](#); Frassoldati et al. [2010](#); Cancino et al. [2010](#); Leplat et al. [2011](#); Togbé et al. [2011](#); Lee et al. [2012](#); Yeung and Thomson [2013](#)). Amongst these, many recent studies concern the high temperature reaction of isomers of butanol (e.g., Moss et al. [2008](#); Dagaut et al. [2009](#); Black et al. [2010](#); Grana et al. [2010](#); Harper et al. [2011](#); Karwat et al. [2011](#); Frassoldati et al. [2012](#); Sarathy et al. [2012](#); Yasunaga et al. [2012](#); Cai et al. [2012](#)). In the case of ethanol, the role of the peroxy chemistry can be neglected, as shown by the complete lack of a negative temperature coefficient behavior observed in a rapid compression machine even at the highest investigated pressures of 85 bar (Lee et al. [2012](#)). There have only been a few studies concerning the low temperature (the temperature zone corresponding to cool flame occurrence, see [Chap. 2](#)) oxidation of larger alcohols (e.g., Vranckx et al. [2011](#) for *n*-butanol, Sarathy et al. [2012](#) for isomers of butanol, Heufer et al. [2012](#) for *I*-pentanol, Tsujimura et al. [2012](#) for *iso*-pentanol, Togbé et al. [2010](#) for *I*-hexanol, Heufer et al. [2013](#) for *I*-pentanol and *I*-hexanol), with the papers of Sarathy et al. ([2012](#)) and Tsujimura et al. ([2012](#)) being very detailed about the reaction classes and the kinetic data specific to alcohols. Note also that experimental studies on the low-temperature reactions (550–700 K) of the hydroxyalkyl radicals derived from some C₂–C₅ alcohols have been performed using multiplexed time-resolved tunable synchrotron photoionization mass spectrometry after pulsed laser photolysis (Zádor et al. [2009](#); Welz et al. [2012](#), [2013a](#)).

A significant number of models have also been published describing the combustion of methyl esters, with many studies reporting on methyl butanoate (e.g., Fisher et al. [2000](#); Gail et al. [2008](#); Dooley et al. [2008](#); Walton et al. [2009](#); Hakka et al. [2010](#); Grana et al. [2012a](#); Farooq et al. [2012](#)), even if its small size prevents it from having a chemistry representative of the large molecules present in biodiesel. A fair number of models have also been written for methyl esters of intermediate size, from C₇ to C₁₀ (e.g., Dayma et al. [2009](#); Herbinet et al. [2008](#); Glaude et al. [2010](#); Herbinet et al. [2011a](#); Grana et al. [2012b](#); Diévert et al. [2012](#)). However, molecules produced from vegetable oils are methyl esters with a long carbon chain such as methyl palmitate (C₁₇H₃₄O₂) and methyl stearate (C₁₉H₃₈O₂) and models concerning these large compounds are still scarce (Herbinet et al. [2011b](#); Westbrook et al. [2011](#); Naik et al. [2011](#); Saggese et al. [2013](#)) with a lack of experimental data to validate them (Tran et al. [2012](#)). While mono-unsaturated and di-unsaturated esters, such as methyl oleate (C₁₉H₃₆O₂) and methyl linoleate (C₁₉H₃₆O₂), are the most abundant esters in biodiesel, very few studies are interested in their oxidation (Herbinet et al. [2010](#); Bennadji et al. [2011](#); Westbrook et al. [2011](#); Saggese et al. [2013](#); Yang et al. [2013](#)).

Note that the development of numerous models for oxygenated fuels (e.g., those for the butanol isomers by Sarathy et al. ([2012](#)), that for *iso*-pentanol by Tsujimura

et al. (2012) or that for methyl decanoate by Herbinet et al. (2008)) is based on the reaction classes proposed by Curran et al. (1998) for alkanes (see Chap. 2). In addition several models for alcohols (e.g., those proposed by Moss et al. 2008 and Harper et al. 2011) and methyl esters (e.g., those proposed by Glaude et al. 2010; Herbinet et al. 2011a, b; Grana et al. 2012b) have been written using the automatic generation software described in Chap. 3.

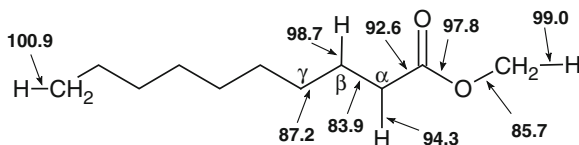
While they will not be the subject of this chapter, it should be mentioned that a large number of models have also been published concerning the combustion of acyclic saturated ethers, such as dimethyl ether (e.g., Curran et al. 2000; Zhao et al. 2008) and methyl-*tert*-butyl ether (e.g., Goldaniga et al. 1998; Glaude et al. 2000; Yasunaga et al. 2011). These models use kinetic data closely derived from those proposed for alkanes. Due to their possible use as biofuels (Román-Leshkov et al. 2007), a recent interest has arisen in modeling the oxidation of cyclic unsaturated ethers, such as furan (Tian et al. 2011), 2-methylfuran (Somers et al. 2013) and 2,5-dimethyl furan (Sirjean et al. 2013). The reactions of these unsaturated ethers are very specific to this type of molecule and cannot be described in a generic way.

The specificities due to the presence of a double bond in unsaturated esters are more related to the chemistry of alkenes (see e.g., Bounaceur et al. 2009 or Mehl et al. 2008) than to the chemistry of oxygenated molecules and will therefore not be described here. The aim of this chapter is to present the specific classes of reactions and kinetic parameters which are considered in the primary mechanism (as defined in Chap. 2) of the oxidation of saturated alcohols and methyl esters. These specificities will be mainly described in light of the knowledge gained in the modeling of reactions of the isomers of butanol and methyl decanoate, respectively.

The presence of the oxygen atoms in an alcohol or ester molecule involves a difference in the bond dissociation energies (BDEs) compared to those observed in hydrocarbon molecules. In the case of esters, the BDEs of the C–H, C–O, and C–C bonds close to the ester functional group were calculated by El-Nahas et al. (2007) for C₃–C₄ esters. Figure 4.1 presents the BDEs of methyl decanoate calculated using THERGAS (Muller et al. 1995) taking into account these newly published values (El-Nahas et al. 2007). Figure 4.1 shows that the C–C and C–H bonds which are the easiest to break are those connected to the C-atom in the α -position, i.e., the bonds closest to the ester functional group.

Only two specific reaction classes can be found in the primary mechanism of alcohols: molecular dehydrations and dehydrogenation reactions. Note that in the secondary mechanism of alcohols, the enol-keto isomerization reactions assisted by radicals and formic acid was found to be a new reaction class important in

Fig. 4.1 Bond dissociation energies (in kcal mol⁻¹) in methyl decanoate. Letters correspond to site identification



converting enols to aldehydes or ketones (Sarathy et al. 2012), but is not described here. For methyl esters, all of the reaction classes are the same as those used to model alkanes. However, while most of the reaction classes used to model oxygenated fuels can be directly derived from the models written for alkanes (H-atom abstractions, fuel radical β -scission decompositions, fuel radical reactions with O_2 , intra-molecular isomerization reactions, etc.), some changes in the kinetic parameters have to be taken into account and are discussed below. The changes in the rates constants of unimolecular initiation reactions mainly reflect changes in BDEs and are not detailed here.

4.2 Molecular Dehydrations and Dehydrogenations of Alcohols

Intra-molecular dehydration, leading to the formation of water and an alkene molecule via a kinetically favored four-centered cyclic transition state ring, is an important reaction class for alcohols. Note that if we consider isomers of butanol, there is one possible intra-molecular dehydration reaction for *1*-butanol, *iso*-butanol and *tert*-butanol, and two for 2-butanol (see Fig. 4.2).

Few kinetic parameters have been published concerning these reactions (e.g., Bui et al. 2002; Tsang 2004; Rosado-Reyes and Tsang 2012a (*1*-butanol); Rosado-Reyes and Tsang 2012b (2-butanol)), with activation energies in the range 62–69 kcal mol^{-1} . Disagreements can be observed between the proposed rate constants, which have been shown to be sensitive parameters in modeling shock tube ignitions delay times (Moss et al. 2008). Grana et al. (2010) have proposed a general rule for estimating the high-pressure limit rate constant for this class of reaction, using as a

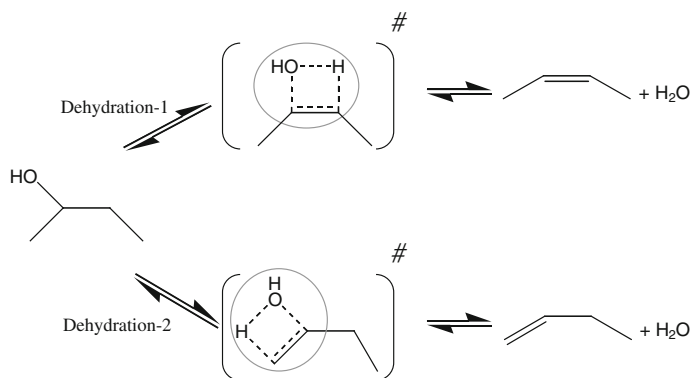


Fig. 4.2 Intramolecular dehydration reactions for 2-butanol

reference reaction the dehydration involving a primary OH group¹ and a single reference primary H-atom² with a rate constant of $k_{\text{Dehydration-ref}} = 5.0 \times 10^{13} \exp(-34,500/T) \text{ s}^{-1}$. The rate constants for the other reactions of the same class are obtained by taking the number of H-atoms which can be transferred for the A-factor into account and also considering a correction in the activation energy reflecting the type of H-atom and OH group involved in the transition state: a reduction of 1 and 3 kcal mol⁻¹ is considered for a secondary and tertiary H-atoms, respectively, and a reduction of 1.5 and 3.5 kcal mol⁻¹ is taken into account for secondary and tertiary OH group, respectively. Using this rule, $k_{\text{Dehydration-1}} = 1.0 \times 10^{14} \exp(-33,300/T) \text{ s}^{-1}$ and $k_{\text{Dehydration-2}} = 1.0 \times 10^{14} \exp(-33,800/T) \text{ s}^{-1}$. Note also that as for unimolecular initiations, Yasunaga et al. (2012) have proposed pressure-dependent rate constants fitted using the Troe formalism.

Grana et al. (2010) also considered dehydrogenation as another class of four-centered elimination reaction. Through this class of reaction, *I*-butanol yields *I*-butanal, 2-butanol produces methylethylketone, and *iso*-butanol gives *iso*-butanal. In the case of 2-butanol, $k_{\text{Dehydrogenation}} = 5.0 \times 10^{13} \exp(-35,000/T) \text{ s}^{-1}$ according to Grana et al. (2010).

Note that in the case of esters, theoretical studies of several types of molecular reactions have been performed (El-Nahas et al. 2007), 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 favorable six-centered cyclic transition state.

4.3 Hydrogen Atom Abstractions

The hydrogen atom abstractions (H-abstractions) by atoms (i.e., ·H, ·O·) and small radicals (i.e., ·OH, ·CH₃, ·HO₂) are usually the most important channels for the fuel consumption. H-abstractions by O₂ are also possible. In the case of hydrocarbons, the rate constants of these reactions depend of the type of alkyl H-atoms which can be abstracted: primary, secondary, or tertiary. The abstraction of a primary H-atom is the most difficult, and that of a tertiary one is the easiest. In oxygenated reactants, more types of H-atoms have to be considered.

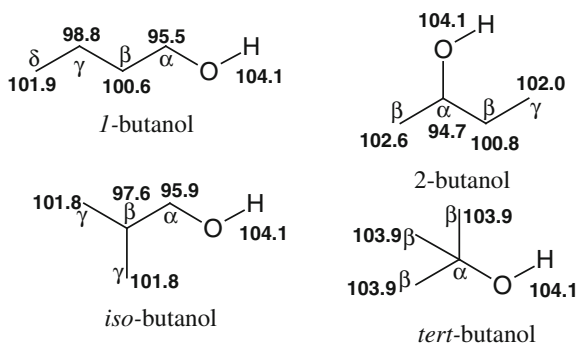
Figure 4.3 displays the C–H BDEs for the four isomers of butanol and shows that different values are obtained depending on the position of the C-atom in the molecule, with the lowest value being obtained for the αC–H bond.

These differences in BDEs result in differences in rate constants and consequently in differences in the selectivity of the primary radicals obtained by H-abstractions. To illustrate this, Fig. 4.4 presents the selectivity of C₄H₉O radicals obtained from *I*-butanol by H-abstraction with ·OH radicals as calculated by

¹ Primary OH group: –CH₂–OH, secondary: –CH–OH, tertiary: –C–OH.

² Primary H-atom: –CH₂–H, secondary: –CH–H, tertiary: –C–H.

Fig. 4.3 C–H bond dissociation energies (in kcal mol⁻¹) for the four isomers of butanol (the values are taken from Sarathy et al. 2012). Letters correspond to site identification



Frassoldati et al. (2012). The abstraction from the α C-atom is clearly the most favored. A similar result has been found for the abstraction by \cdot H atoms (Frassoldati et al. 2012).

Note that the BDE of the C–H bonds associated with the carbon atom in the α -position in an alcohol (from 94.7 to 95.9 kcal mol⁻¹ as shown in Fig. 4.3) or just neighboring an ester functional group (94.3 kcal mol⁻¹ (Fig. 4.1)) is close to that of a tertiary carbon atom (e.g., 95.7 kcal mol⁻¹) in isobutene (Luo 2003). Also, as shown in Fig. 4.3, the BDE of the O–H bond in alcohols is close to the BDE of the C–H bond in a primary carbon atom. This similarity has been used as a first approximation to derive rate constants for H-abstractions in oxygenated fuels by comparison to those used in alkanes (e.g., Grana et al. 2010 and Moss et al. 2008 for alcohols, Herbinet et al. 2008 for esters). In a second approximation, the changes induced in rate constants by the difference in C–H BDEs can be estimated using an Evans–Polanyi type correlation, such as that developed for the abstraction of H-atoms from hydrocarbons by Dean and Bozzelli (2000). This method has been implemented in automatic generation software such as EXGAS (Moss et al. 2008 for alcohols, Glaude et al. 2010 for esters) or used by Tsujimura et al. (2012) in their model of *iso*-pentanol. More details about automatic generation software

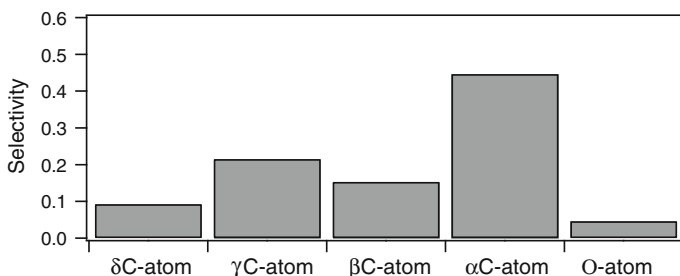


Fig. 4.4 Selectivity at 1000 K of the C₄H₉O radicals obtained from *1*-butanol by H-abstraction with \cdot OH radicals as calculated by Frassoldati et al. (2012)

are given in [Chap. 3](#). In the method of Dean and Bozzelli (2000), the rate constant for the H-abstraction is estimated as:

$$k = n_{\text{H}} A T^n \exp(-\{E_0 - f(\Delta H_0 - \Delta H)\}/RT) \quad (4.1)$$

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 (2000) for each radical considered; and R is the gas constant.

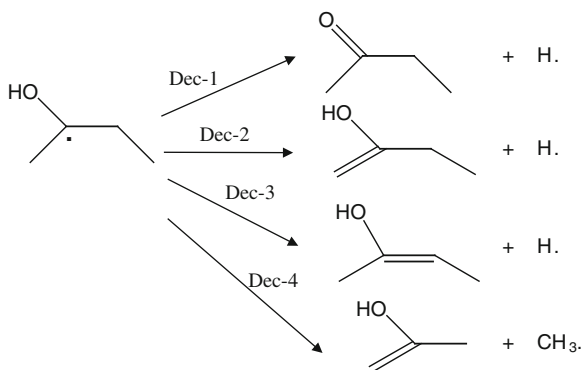
As discussed by Sarathy et al. (2012), in the case of the abstractions by $\cdot\text{OH}$ radicals, which in most cases is the dominant abstracting radical, more accurate rate constants can be derived from recent experimental measurements (e.g., Vasu et al. 2010 for *I*-butanol, Pang et al. 2012 for 2-butanol) and theoretical calculation (e.g., Zhou et al. 2011 for *I*-butanol). Zhou et al. (2011) have found that, in considering abstraction by oxygenated radicals such as $\cdot\text{OH}$ and $\text{HO}_2\cdot$ from oxygenated molecules, it is not accurate to assume similarity with abstraction from alkanes, as hydrogen bonding between the radical and the molecule in the transition state generally lowers the activation energy for abstraction but also ties up a rotor in the molecule. Thus rate constants for abstraction from alcohols by hydroxyl (Zhou et al. 2011) and hydroperoxyl radicals (Zhou et al. 2012) have been shown to be generally faster at lower temperature (due to the decrease in activation energy for abstraction) but slower at higher temperature (due to the decrease in entropy change) compared to alkanes.

4.4 Radical Decompositions by β -Scission

At temperature above 800 K, decomposition via β -scission reactions are the major consumption pathways for radicals produced from fuel molecules via H-atom abstraction. The presence of oxygen atoms in the radicals produced from alcohols and esters can have a significant impact on the values of the activation energies of this reaction class.

In the case of alcohols, radicals produced by H-atom abstractions are alkoxy and hydroxyalkyl radicals. The rate constants for the decompositions of alkoxy radicals have been studied by Rauk et al. (2003). The reactions of hydroxyalkyl radicals are not fully specific to alcohols as these radicals can also be formed from alkenes by the addition of $\cdot\text{OH}$ radicals to the double bond, with subsequent isomerizations allowing for the production of a number of possible isomers in large alkenes (Touchard et al. 2005). Figure 4.5 presents the possible decompositions via β -scission of the hydroxybutyl radical obtained from 2-butanol produced by H-abstraction from the carbon atom at the α -position. Figure 4.5 shows that decompositions by β -scission can be a source of enols, products first reported

Fig. 4.5 Decompositions by β -scission from the hydroxybutyl radical obtained from 2-butanol by H-abstraction from the carbon atom in α -position



by Taatjes et al. (2005) and most recently experimentally observed in a laminar premixed flame (Sarathy et al. 2012).

In the mechanism of Yasunaga et al. (2012), the rate constants for decompositions by β -scission are given for the reverse reactions: the value for the addition of a \cdot H atom to acetaldehyde is used for $k_{\text{Dec-1}}$, one close to that for the addition of a \cdot H atom to propene is assumed for $k_{\text{Dec-2}}$ and $k_{\text{Dec-3}}$, and that for the addition of a methyl radical to propene is considered for $k_{\text{Dec-4}}$. In the case of the hydroxybutyl radicals obtained by H-abstraction from a carbon atom in the β -position, breaking of C–O bonds is also possible with rate constants for the reverse reactions derived from those of the addition of an \cdot OH radical to butenes according to Yasunaga et al. (2012). This last channel is the main pathway for the formation of butenes at their peak locations in low-pressure laminar premixed flames of the four butanol isomers according to Sarathy et al. (2012). In the EXGAS software (Moss et al. 2008), the activation energies for these reactions were evaluated using Evans-Polanyi correlations not detailed here.

Decompositions by β -scission are also considered in the case of methyl esters and the breaking of C–C bonds is a source of unsaturated esters, products experimentally observed in a jet-stirred reactor (Herbinet et al. 2011a). Table 4.1 shows a summary of the activation energies, which are used in the EXGAS software for the decompositions by β -scission involving the breaking of a C–C, a C–O, or a C–H bond in radicals deriving from methyl esters.

4.5 RO₂· Radical Chemistry: Intramolecular Isomerizations

At temperature below 800 K, the radicals obtained from the fuel molecules by H-abstractions react mostly by addition to oxygen molecules to form peroxy radicals (RO₂·). The rate constants of these additions for alcohols and methyl esters are mostly derived from those used for alkyl radicals.

Table 4.1 Activation energies used for the decompositions by β -scission of oxygenated radicals involved in the oxidation of methyl esters (/ stands for a simple bond and // for a double bond)

Types of reaction	E_a (kcal mol ⁻¹)
$R/C(//O)/O^\bullet \rightarrow R^\bullet + CO_2^a$	5.1
$R/C(//O)/O/CH_2^\bullet \rightarrow R/C^\bullet//O + CH_2//O^a$	31.9
$R/CH^\bullet/C(//O)/O/CH_3 \rightarrow R/CH//C//O + CH_3O^\bullet{}^b$	49.0
$R/CH^\bullet/CH_2/C(//O)/O/CH_3 \rightarrow R/CH//CH_2 + CH_3O/C^\bullet//O^b$	30.7
$R/CH_2/C^\bullet//O \rightarrow R^\bullet + CH_2//C//O^c$	39.9
$R/CH^\bullet/CH_2/C(//O)/O/CH_3 \rightarrow H^\bullet + R/CH//CH/C(//O)/O/CH_3^b$	34.9

These values were calculated using quantum calculations performed at the CBS-QB3 level of theory (Glaude et al. 2010)

^a The calculation has been performed for $R^\bullet = CH_3^\bullet$

^b The calculation has been performed for $R^\bullet = H^\bullet$

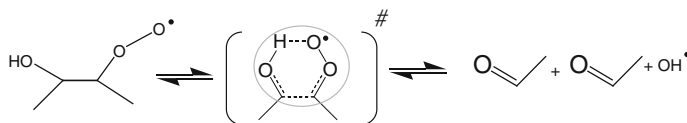
^c The calculation has been performed for $R^\bullet = C_2H_5^\bullet$

Intra-molecular isomerizations involving the transfer of a H-atom through a cyclic transition state are important reactions of alkyl and peroxy-alkyl radicals in the oxidation of hydrocarbons. The rate constants of the isomerizations of peroxy-alkyl radicals have been shown to be particularly sensitive parameters during the low-temperature oxidation of alkanes (Buda et al. 2005). These reactions also need to be considered in the case of oxygenated reactants.

As already reported in the case of alkenes (Stark and Waddington 1995) and as experimentally proven in the case of alcohols (e.g., Welz et al. 2013a), the isomerizations of hydroxyl-alkylperoxy radicals deriving from hydroxyl-alkyl radicals obtained by H-abstraction from a carbon atom in the β -position of an alcohol functional group can occur through the mechanism shown in Fig. 4.6 for 2-butanol.

This reaction, via the so-called “Waddington mechanism,” leads to the formation of aldehydes or ketones and $\cdot OH$ radicals, as shown in Fig. 4.6 for a peroxy radical obtained from 2-butanol. Note that Sarathy et al. (2012) considered that the formation of *I*-hydroperoxyacetone and a methyl radical can be a minor channel of the reaction via the Waddington mechanism for 2-butanol.

The rates constants of the isomerizations of radicals obtained from butanols involving a transition state with five or six members have been calculated by Zheng and Truhlar (2010) using quantum chemistry methods. These values were used by Sarathy et al. (2012) in their models written to describe the oxidation of the butanol isomers.

**Fig. 4.6** Isomerization of 2-hydroxy-3-butylperoxy radicals according to the mechanism of Waddington (Stark and Waddington 1995)

For heavier reactants for which theoretical calculations are difficult to perform, the activation energy for an isomerization can be estimated as the sum of two contributions as proposed by Benson (1976): (i) the activation energy for H-atom abstraction from the molecule by analogous radicals and (ii) the strain energy involved in the cyclic transition state.

The rate constants of the peroxy radicals deriving from alcohols are mostly directly derived from those used for alkanes (e.g., Curran et al. 1998), with just a correction in the activation energy when the abstracted H-atom is carried by the carbon atom in the α -position: e.g., the same value is used as that for a reaction involving a tertiary H-atom (Sarathy et al. 2012) or $-3.3 \text{ kcal mol}^{-1}$ (Tsujimura et al. 2012). The rate constants used by Sarathy et al. (2012) for the reaction via the Waddington mechanism are mainly derived from a study by Sun et al. (2007).

As shown by Glaude et al. (2010), 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 the α -position from the ester functional 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 (Buda et al. 2005)).

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 isomerization of ester alkyl radicals were deduced from the enthalpy of formation of the corresponding lactones measured by Wiberg and Waldron (1991). Ring strain energies are 9, 11, 11.2, and $12.5 \text{ kcal mol}^{-1}$ for five-, six-, seven-, and eight-membered ring lactones, respectively. These values can be compared to those used for alkyl radicals deriving from alkanes, i.e., 6.3, 1.0, 6.4, and $9.9 \text{ kcal mol}^{-1}$ for five-, six-, seven-, and eight-membered rings, respectively (Buda et al. 2005). The ring strain energies of the transition states involved in the isomerization of alkyl radicals obtained from esters are significantly higher than those obtained in the case of alkanes making the related isomerizations more difficult.

Some isomerizations of peroxy-alkyl radicals, shifting a H-atom above the ester function, involve cyclic transition states, which contain three oxygen atoms. This kind of isomerizations occurs via seven- and eight-membered rings as shown in Fig. 4.7. Two configurations are possible according to the position of the peroxy group: either the peroxy group is on the alkyl chain with the shifted H-atom on the methyl group of the ester function, or the peroxy group is on the methyl part of the ester function with the shifted H-atom on a carbon atom from the alkyl chain. Note that according to theoretical calculations (Glaude et al. 2010), the presence of the third oxygen atom in the ring together with the carbonyl group significantly increases the ring strain energy of the transition state involved: the calculated strain energies in Fig. 4.7 range from 7.7 to $13.6 \text{ kcal mol}^{-1}$, while the strain energy for two oxygen cyclic transition states are taken to be 5 kcal mol^{-1} for seven-membered rings and 4 kcal mol^{-1} for eight-membered rings. This dictates

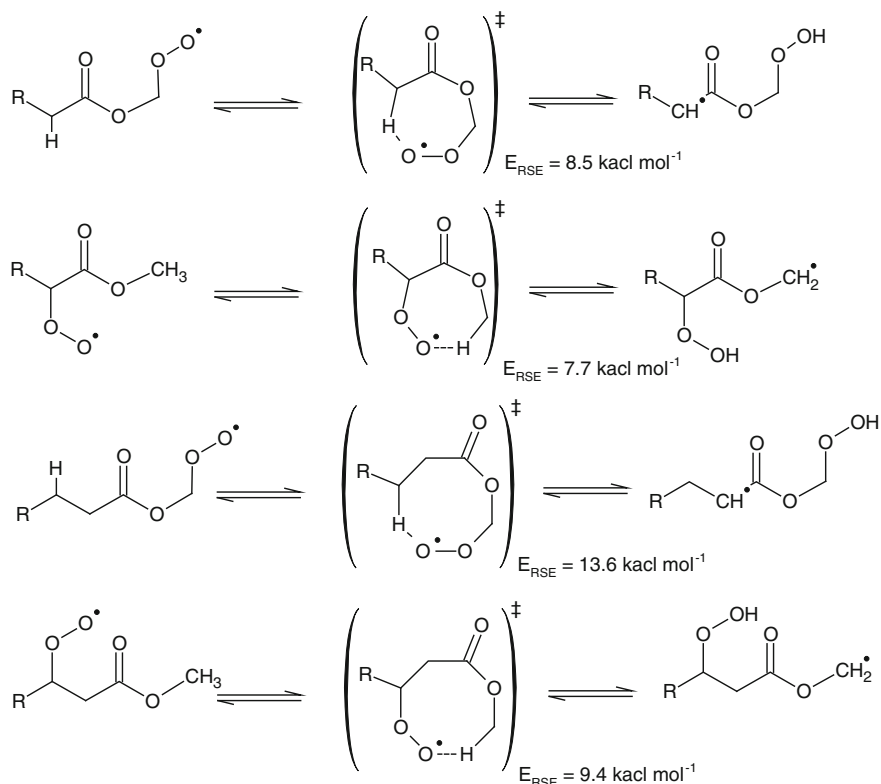
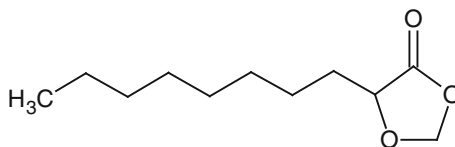


Fig. 4.7 Intramolecular isomerization involving transition states including seven and eight membered rings which contain three oxygen atoms, and related ring strain energies (E_{rse}) of the involved transition states (adapted from Glaude et al. (2010)). These values were calculated using quantum calculations performed at the CBS-QB3 level of theory (Glaude et al. 2010)

that isomerizations of peroxyalkyl radicals in esters are more difficult compared to those for alkanes.

In the oxidation mechanism of alkanes, the hydroperoxy-alkyl radicals (QOOH \cdot) obtained by intra-molecular isomerization from RO $_2\cdot$ radicals react mainly via a second addition to molecular oxygen or by decomposition reactions yielding cyclic ethers and \cdot OH radicals. While in the cases of alcohols, only the model of Tsujimura et al. (2012) for *iso*-pentanol considers the formation of an hydroxy cyclic ether, cyclic ethers with an ester function are common products in the oxidation of long-chained methyl esters. For instance, seven different C $_{11}$ H $_{20}$ O $_3$ methyl esters including a furan ring have been observed during the oxidation of methyl decanoate in a jet-stirred reactor (Glaude et al. 2010), amongst them a compound with the ester function included in the ring as shown in Fig. 4.8. The rate constant used for the formation of cyclic ethers from alcohols and ethers are directly derived from those used in the case of alkanes. This is also mostly the

Fig. 4.8 Cyclic ether with the ester function included in the ring (3-octyl,1,4-dioxola-2-one) as analyzed during the methyl decanoate oxidation in a jet-stirred reactor (Glaude et al. 2010)



case for the kinetic parameters used for the addition of QOOH· radicals to molecular oxygen.

Note that a new reaction class for the hydroperoxy-alkyl radicals (QOOH·) deriving from alcohols has recently been proposed by Cord et al. (2012) and experimentally and theoretically confirmed by Welz et al. (2013b). As shown in Fig. 4.9 in the case of a radicals deriving from 2-butanol, this reaction involved a water elimination producing an oxo-aldehyde which further decomposes by β -scission and is a source of ketones or aldehydes.

4.6 Reactions Leading to Unsaturated Products and HO₂· Radicals

The reaction of the fuel radicals with molecular oxygen via H-atom abstractions is also a source of unsaturated species, both in the case of alcohols and methyl esters. In the mechanisms of the low-temperature oxidation of alcohols (Sarathy et al. 2012; Tsujimura et al. 2012) written based on the reactions classes proposed by Curran et al. (1998) for alkanes, the concerted elimination of HO₂ radicals and enol or unsaturated alcohols from hydroxyalkyl-peroxy radicals has been considered as a new reaction class. The rate constant calculated by DeSain et al. (2003) for *n*-propyl radical has been used in the model of Sarathy et al. (2012). In the ester mechanisms written using the same philosophy, this new reaction class is not taken into account, and unsaturated esters are obtained from the QOOH· radicals by a C–C bond scission with the same rate constants used as those for alkanes. In the mechanisms generated by EXGAS, HO₂· radicals and unsaturated alcohols or esters are directly formed from the radicals obtained from the fuel molecules by H-atom abstractions with the same rate constants as those used for alkanes.

As illustrated in the case of 2-butanol in Fig. 4.10, another pathway for the generation of HO₂· radicals is from hydroxyl-alkyl radicals obtained by H-atom abstraction from a carbon atom in the α -position. This reaction leads to the formation of an aldehyde or a ketone of the same size as the reactant.

This reaction class was already considered in the case of the oxidation of large alkenes by Touchard et al. (2005) with rate constants derived from a study by Miyoshi et al. (1990). This reaction class was then automatically considered in the butanol mechanism of Moss et al. (2008). More recently, a theoretical study by Da

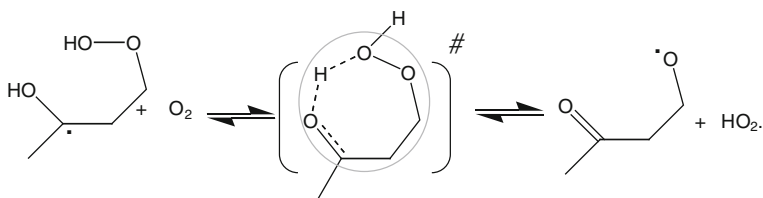


Fig. 4.9 H_2O elimination from a hydroperoxy-alkyl radicals ($\text{QOOH}\cdot$) radical obtained from 2-butanol by H-abstraction from the carbon atom in β -position, addition to oxygen and isomerization

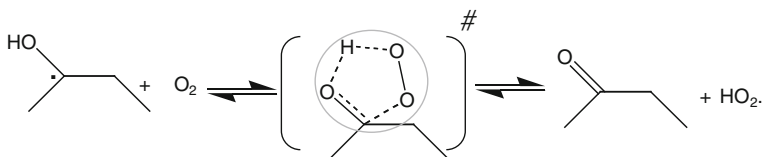


Fig. 4.10 HO_2 radical elimination from the hydroxybutyl radical obtained from 2-butanol by H-abstraction from the carbon atom in α -position

Silva et al. (2009) on ethanol has shown that this reaction proceeds with such a low barrier that the collision stabilization of the hydroxyl-peroxy radicals is unimportant. This would explain why ignition delay times for ethanol are longer than those for ethane as measured in a shock tube (Cooke et al. 1991). This reaction class has been taken into account in recent models for the oxidation of alcohols (Sarathy et al. 2012; Tsujimura et al. 2012) with the rate constant proposed by Da Silva et al. (2009), but still considering the formation of stabilized hydroxyl-peroxy radicals for radicals obtained by H-atom abstraction from a carbon atom in the α -position.

4.7 Conclusion

Two new reaction classes and the specificities in kinetic parameters associated to reaction classes in common with alkanes have been discussed for detailed kinetic oxidation models proposed in the cases of alcohols and methyl esters, two important types of oxygenated reactants considered as promising biofuels. This has been based on the important literature which has recently appeared on the modeling of the oxidation of these oxygenated molecules.

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