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Experimental study of the oxidation of methyl oleate in a jet-stirred reactor

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Abstract

The experimental study of the oxidation of a blend containing n-decane and a large unsaturated ester, methyl oleate, was performed in a jet-stirred reactor over a wide range of temperature covering both low and high temperature regions (550–1100 K), at a residence time of 1.5 s, at quasi atmospheric pressure with high dilution in helium (n-decane and methyl oleate inlet mole fractions of 1.48×10^{-3} and 5.2×10^{-4}) and under stoichiometric conditions.

The formation of numerous reaction products was observed. At low and intermediate temperatures, the oxidation of the blend led to the formation of species containing oxygen atoms like cyclic ethers, aldehydes and ketones deriving from n-decane and methyl oleate. At higher temperature, these species were not formed anymore and the presence of unsaturated species was observed. Because of the presence of the double bond in the middle of the alkyl chain of methyl oleate, the formation of some specific products was observed. These species are dienes and esters with two double bonds produced from the decomposition paths of methyl oleate and some species obtained from the addition of H-atoms, OH and HO₂ radicals to the double bond.

Experimental results were compared with former results of the oxidation of a blend of n-decane and methyl palmitate performed under similar conditions. This comparison allowed highlighting the similarities and the differences in the reactivity and in the distribution of the reaction products for the oxidation of large saturated and unsaturated esters.

Keywords: Oxidation; Combustion; Biodiesel; Methyl esters; Methyl oleate; Methyl palmitate; Jet-stirred reactor; Engine; Kinetics

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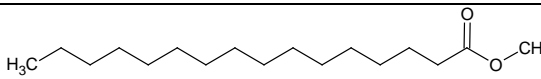
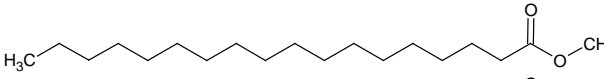
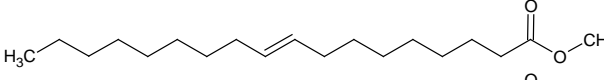
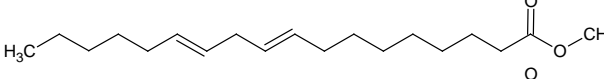
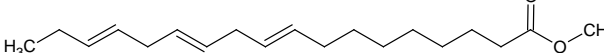
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1. Introduction

The interest in the oxidation of biodiesel fuels is increasing because of their use along with conventional diesel fuels in internal combustion engines [1], [2], [3] and [4]. Biodiesel fuels are alternative renewable fuels which are obtained from vegetable oils and animal fats and are converted into fatty acid esters by trans-esterification with an alcohol (e.g. methanol). When biodiesel fuels are obtained from soybean and rapeseed, they contain five main esters with very similar structures (Table 1). These esters are made of a long alkyl chain attached to an ester group and the main differences are the length of the chain (16 or 18 carbon atoms) and the number of double bonds in the chain (no double bond, one, two, or three double bonds). Methyl oleate ($C_{19}H_{36}O_2$), which is the subject of this study, is the main component found in rapeseed biodiesel fuel: it represents about 60% of its mass content and appears to be a good surrogate for rapeseed biodiesel fuel. This ester has an alkyl chain of 18 carbon atoms with one double bond in the middle.

Table 1. Structures of methyl esters and average composition in rapeseed and soybean biodiesel fuels [5].

Esters	Structure	Average composition (mass %)	
		rapeseed	soybean
methyl palmitate ($C_{17}H_{34}O_2$)		4	6-10
methyl stearate ($C_{19}H_{38}O_2$)		2	2-5
methyl oleate ($C_{19}H_{36}O_2$)		60	20-30
methyl linoleate ($C_{19}H_{34}O_2$)		21	50-60
methyl linolenate ($C_{19}H_{32}O_2$)		13	5-11

Note: Double bond(s) in natural molecules are in the cis conformation.

The oxidation of esters has been the subject of several experimental studies. The most studied ester is methyl butanoate [6], [7], [8] and [9] because it can be handled relatively easily to perform gas phase kinetic studies. These studies allowed making progress in the understanding of the chemistry of the oxidation of methyl esters but they also showed that methyl butanoate is too small compared to esters in real biodiesel fuels to be used as a surrogate. There are fewer studies about larger esters [10], [11], [12], [13], [14], [15], [16], [17], [18], [19] and [20] and very little data about esters with double bonds [9], [11] and [12]. Dagaut et al. [11] studied the oxidation of rapeseed biodiesel fuel in a jet-stirred reactor at temperatures from 800 to 1400 K (corresponding to the region right after the negative coefficient temperature zone), at pressures between 1 and 10 atm, at high dilution in helium and at two equivalence ratios (0.5 and 1). Reaction products were analyzed by gas

chromatography and the formation of carbon oxides, hydrogen, methane, ethylene and olefins from propene to 1-hexene was reported. The formation of unsaturated esters was not mentioned in this work but other studies showed that these species could be formed during the combustion of esters [13], [14], [19] and [20].

Gaïl et al. [9] studied the oxidation of methyl crotonate ($C_5H_8O_2$), an ester with one double bond conjugated with the carbonyl group, in different apparatuses. These experiments were compared to methyl butanoate results obtained under identical conditions. Experiments were performed in a jet-stirred reactor at atmospheric pressure, at high dilution, at temperatures ranging from 850 to 1400 K, at two equivalence ratios ($\Phi = 0.375$ and 0.7) and at a residence time of 0.07 s. Experiments were also performed in an opposed flow diffusion flame at atmospheric pressure (the oxidizer stream was composed of 42% O_2 and 58% N_2 and was sent through the top burner port; the fuel stream was composed of 4.7% fuel and 95.3% N_2 and was sent through the bottom). Mole fraction profiles were plotted for the reactants and for numerous reaction products (small hydrocarbons and oxygenated compounds with no more than four carbon atoms). The comparison between methyl crotonate and methyl butanoate studies showed that these esters had very close reactivities and that the formation of unsaturated species (e.g. acetylene, allene, propyne, 1,3-butadiene) was enhanced in the case of methyl crotonate.

Zhang et al. performed the study of the ignition of C_9 fatty acid esters (ethyl nonanoate, methyl nonanoate, methyl-2-nonenoate, and methyl-3-nonenoate) in a motored CFR engine [12]. Their study showed that these species exhibit different ignition behavior in the low temperature regime and that unsaturated esters were less reactive than the saturated ones according to the differences observed in the magnitude of low temperature heat release.

The purpose of this paper is to present new experimental results about the oxidation of an unsaturated ester larger than methyl crotonate. Methyl oleate was chosen because it is one of the main components found in rapeseed and soybean biodiesel fuels. The oxidation of a blend of n-decane and methyl oleate (74 mol%/26 mol%) was studied in a jet-stirred reactor under the same conditions than those used for a former study of the oxidation of a blend of n-decane and methyl palmitate [20] in order to draw comparisons between the two esters. Note that, it was necessary to dissolve methyl palmitate in n-decane in the previous study because this saturated ester is a solid at ambient temperature. n-Decane was retained because it is also a common surrogate for n-alkanes in diesel fuels.

2. Experimental method

The experimental study of the oxidation of methyl oleate blended with n-decane was performed using an apparatus which has already been used in our laboratory for studies of the oxidation of several organic compounds such as iso-butene, n-heptane, iso-octane, toluene, n-decane, n-hexadecane and methyl palmitate [20], [21], [22], [23] and [24]. This apparatus has already been described in former papers [20], [21], [22], [23] and [24] and only its main features are presented here.

2.1. Experimental apparatus specifications

The reactor used to perform this study is a fused silica jet-stirred reactor operated at constant temperature and pressure. This type of reactor has been proven to be well adapted to gas phase kinetic studies and it has been designed to be well stirred for residence times between 0.5 and 5 s [25] and [26]. It is composed of a sphere with an injection cross located at its center. The mixing of the gas-phase inside the reactor is achieved through turbulent jets issued from the four nozzles of the cross. In order to avoid the formation of temperature gradients in the gas phase, the reactor is preceded by an annular preheater in which the temperature of the gas mixture is increased progressively to the reaction temperature. Uncertainties on the temperature of reaction and the residence time of the gas inside the reactor are ± 2 K and $\pm 5\%$, respectively.

The oxidation of the n-decane/methyl oleate blend (74 mol%/26 mol%) was studied in the above described reactor over the temperature range 550–1000 K, at a pressure of 106 kPa (800 Torr), at a residence time of 1.5 s, at stoichiometric conditions, and at high dilution in helium. The inlet fuel mole fraction was set to 0.002.

2.2. Products analyses

Reaction products were analyzed by gas chromatography. The analytical procedure has already been described in details in a previous paper [20]. Analyzed species were hydrocarbons and oxygenated species with more than five heavy atoms (carbon and oxygen atoms are considered as heavy atoms) which were condensed in a trap maintained at liquid nitrogen temperature, light species such as oxygen, carbon monoxide, carbon dioxide, C₁–C₄ hydrocarbons and small oxygenated compounds (online analysis). Water was not quantified. The limit of detection was about 100 ppb for the heaviest species (flame ionization detector, FID) and about 10 ppm for carbon oxides and oxygen (thermal conductivity detector, TCD). Uncertainty estimates are about $\pm 5\%$ for species which are analyzed online and $\pm 10\%$ for species condensed in the trap.

2.3. Identification and calibration of the products

The identification of heavy hydrocarbons and oxygenated compounds was performed by comparison of retention times when injecting available pure substances. The identification was also realized using a gas chromatograph coupled with a mass spectrometer (GC-MS) operating under the same conditions as the gas chromatograph used for the quantification, enabling the direct comparison of both chromatograms. Spectra of some species were not in the GC-MS database (NBS75K) and the deciphering of these spectra was carried out.

The quantification was performed by comparing peak areas with that of n-octane (internal standard). The calibration was performed by injecting known amounts of the pure substances when available, otherwise the method of the effective carbon atoms was used (species having the same number of carbon atoms and the same functional groups were assumed to have the same response in the FID).

The identification and the calibration of light species (e.g. carbon oxides, C₁–C₄ hydrocarbons) were performed by injecting gaseous samples provided by Messer and Air Liquide.

3. Nature of the reaction products

As for the oxidation of the n-decane/methyl palmitate blend [20], the oxidation of the n-decane/methyl oleate blend led to the formation of numerous reaction products. Among light products, the formation of species such as carbon oxides, methanol, acetaldehyde, methane, acetylene, ethylene, ethane, propyne, allene, propene, propane, 1,3-butadiene, 1-butene and n-butane was observed. The formation of formaldehyde likely occurs but this species was not quantified since flame ionization detector does not permit its detection and its concentration was below the sensitivity of thermal conductivity detector in gas chromatography. The reaction also led to the formation of heavier species such 1-alkenes (1-hexene, 1-heptene, 1-octene, 1-nonene, some isomers of decene due to the presence of n-decane as a co-reactant and 1-undecene) and methyl esters with one double bond (methyl acrylate, 3-butene methyl ester, 4-pentene methyl ester, 5-hexene methyl ester, 6-heptene methyl ester, 9-decene methyl ester and 10-undecene methyl ester). The formation of heavier dienes and esters with two double bonds, likely deriving from methyl oleate, was observed. Among dienes, species such as 1,3-undecadiene, 1,3-dodecadiene, 1,7-hexadecadiene were present (Table 2). Esters with two double bonds were 8,10-undecadiene methyl ester, 9,11-dodecadiene methyl ester, 9,12-tridecadiene methyl ester, 9,13-tetradecadiene methyl ester, 9,14-pentadecadiene methyl ester, 9,15-hexadecadiene methyl ester, and 9,16-heptadecadiene methyl ester (Table 2). The mass spectra of these last species were easily recognizable because of the presence of the peak at $m/z = 74$. This peak corresponds to a $\bullet\text{CH}_2\text{-C}^+(\text{-OH})\text{-O-CH}_3$ fragment which is obtained from the decomposition of the molecular ion through a

rearrangement of McLafferty [20]. The formation of low temperature oxygenated products was also observed. These products were mainly C₁₀ cyclic ethers and C₁₀ ketones deriving from n-decane. The presence of species likely deriving from methyl oleate (2-decenal, 2-undecenal, 9-oxo,methyl nonanoate, cis and trans 2-octyl,3-(methyl octanoate)-oxirane and 10-oxo,methyl octadecanoate was also observed (Table 3).

Table 2. Structure of the dienes and of the unsaturated esters observed during the study.

Species	Structure	Molecular weight (g.mol ⁻¹)
1,3-undecadiene (C ₁₁ H ₂₀)		152
1,3-dodecadiene (C ₁₂ H ₂₂)		166
1,7-hexadecadiene (C ₁₆ H ₃₀)		192
methyl acrylate (C ₄ H ₆ O ₂)		86
3-butene methyl ester (C ₅ H ₈ O ₂)		100
4-pentene methyl ester (C ₆ H ₁₀ O ₂)		114
5-hexene methyl ester (C ₇ H ₁₂ O ₂)		128
6-heptene methyl ester (C ₈ H ₁₄ O ₂)		142
9-decene methyl ester (C ₁₁ H ₂₀ O ₂)		184
10-undecene methyl ester (C ₁₂ H ₂₂ O ₂)		198
8,10-undecadiene methyl ester (C ₁₂ H ₂₀ O ₂)		196
9,11-dodecadiene methyl ester (C ₁₃ H ₂₂ O ₂)		210
9,12-tridecadiene methyl ester (C ₁₄ H ₂₄ O ₂)		224
9,13-tetradecadiene methyl ester (C ₁₅ H ₂₆ O ₂)		238
9,14-pentadecadiene methyl ester (C ₁₆ H ₂₈ O ₂)		252
9,15-hexadecadiene methyl ester (C ₁₇ H ₃₀ O ₂)		266
9,16-heptadecadiene methyl ester (C ₁₈ H ₃₂ O ₂)		280

Table 3. Structure of the main oxygenated compounds observed in the low temperature region.

Species	Structure	Molecular weight (g.mol ⁻¹)
2-decenal (C ₁₀ H ₁₈ O)		154
2-undecenal (C ₁₁ H ₂₀ O)		168
9-oxo,methyl nonanoate (C ₁₀ H ₁₈ O ₃)		186
2-octyl,3-(methyl octanoate)-oxirane ^a (C ₁₉ H ₃₆ O ₃)		312
10-oxo,methyl octadecanoate (C ₁₉ H ₃₆ O ₃)		312

^a Two isomers (cis and trans) were observed for this species.

4. Results and discussion

Experimental conversions and product mole fractions obtained in this study are displayed in [Fig. 1], [Fig. 2], [Fig. 3] and [Fig. 4]. These experimental data were compared with results obtained in a previous study about the oxidation of a blend containing methyl palmitate and n-decane [20].

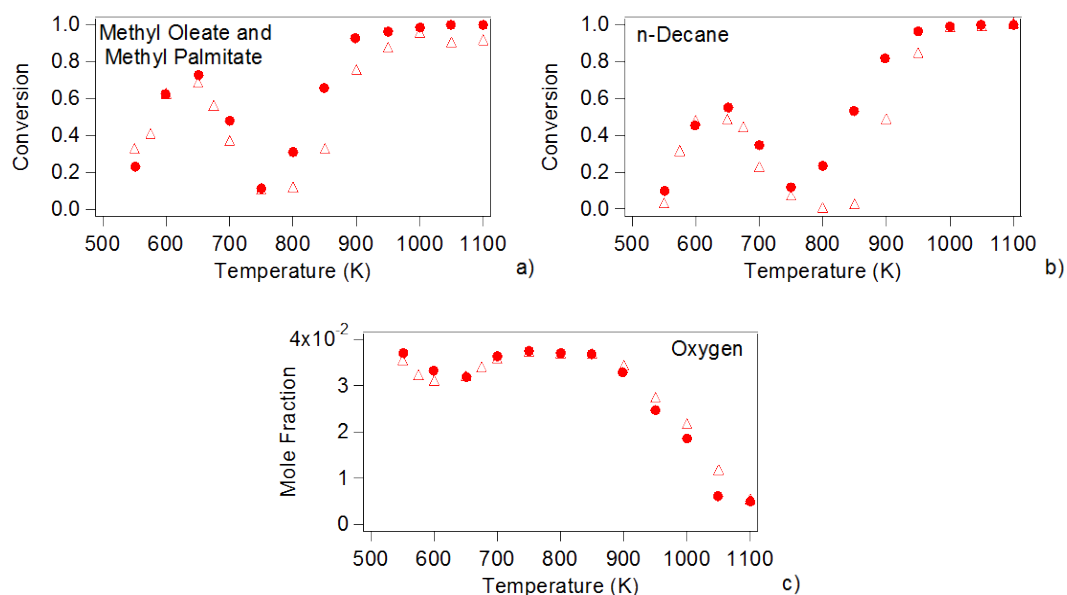


Fig. 1. Conversion of methyl oleate, methyl palmitate and n-decane and mole fraction of oxygen as a function of the temperature (● – methyl oleate/n-decane; Δ – methyl palmitate/n-decane [20]).

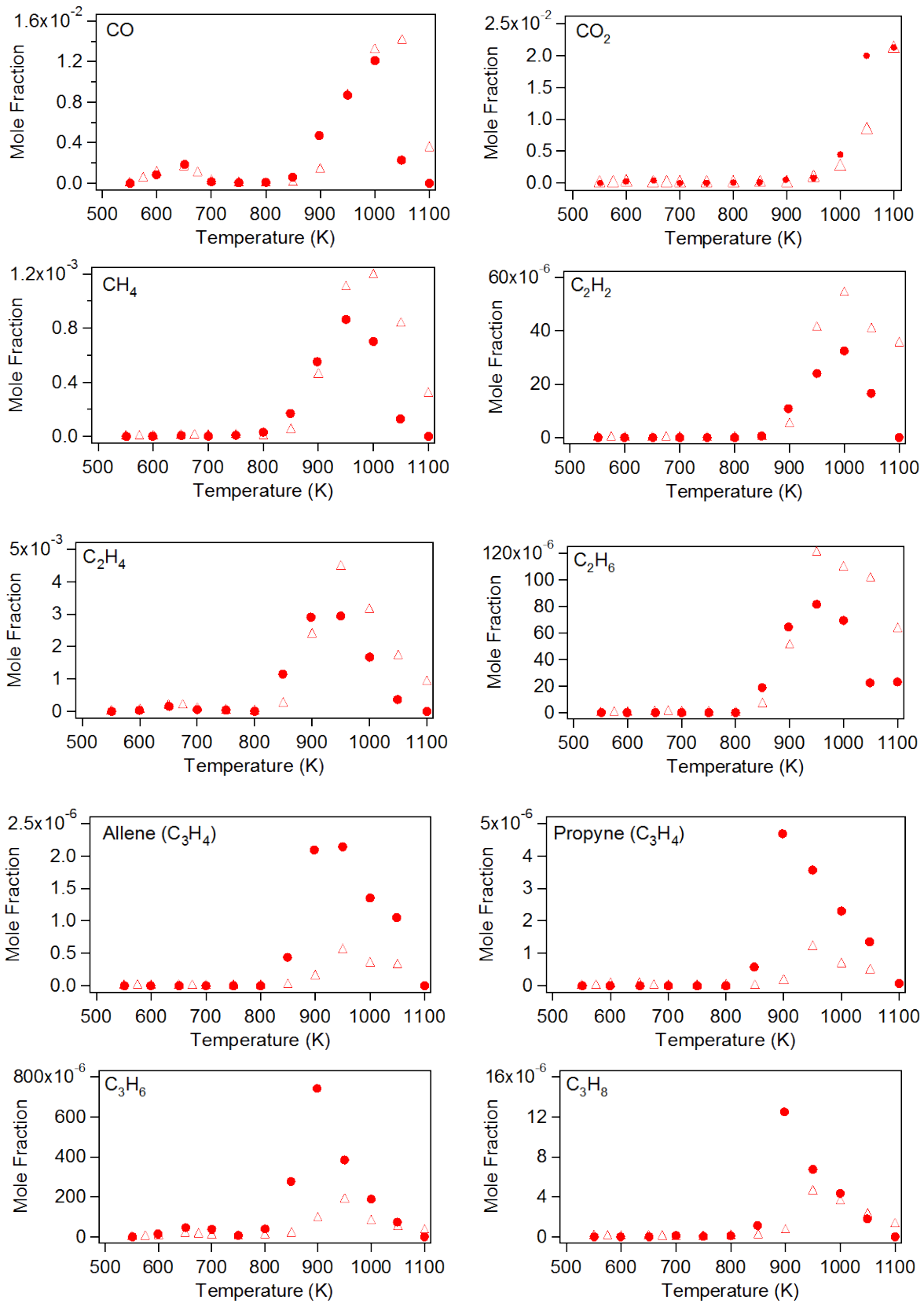


Fig. 2. Evolution of the mole fractions of reaction products (from CO to propane) with the temperature (● – methyl oleate/n-decane; Δ – methyl palmitate/n-decane [20]).

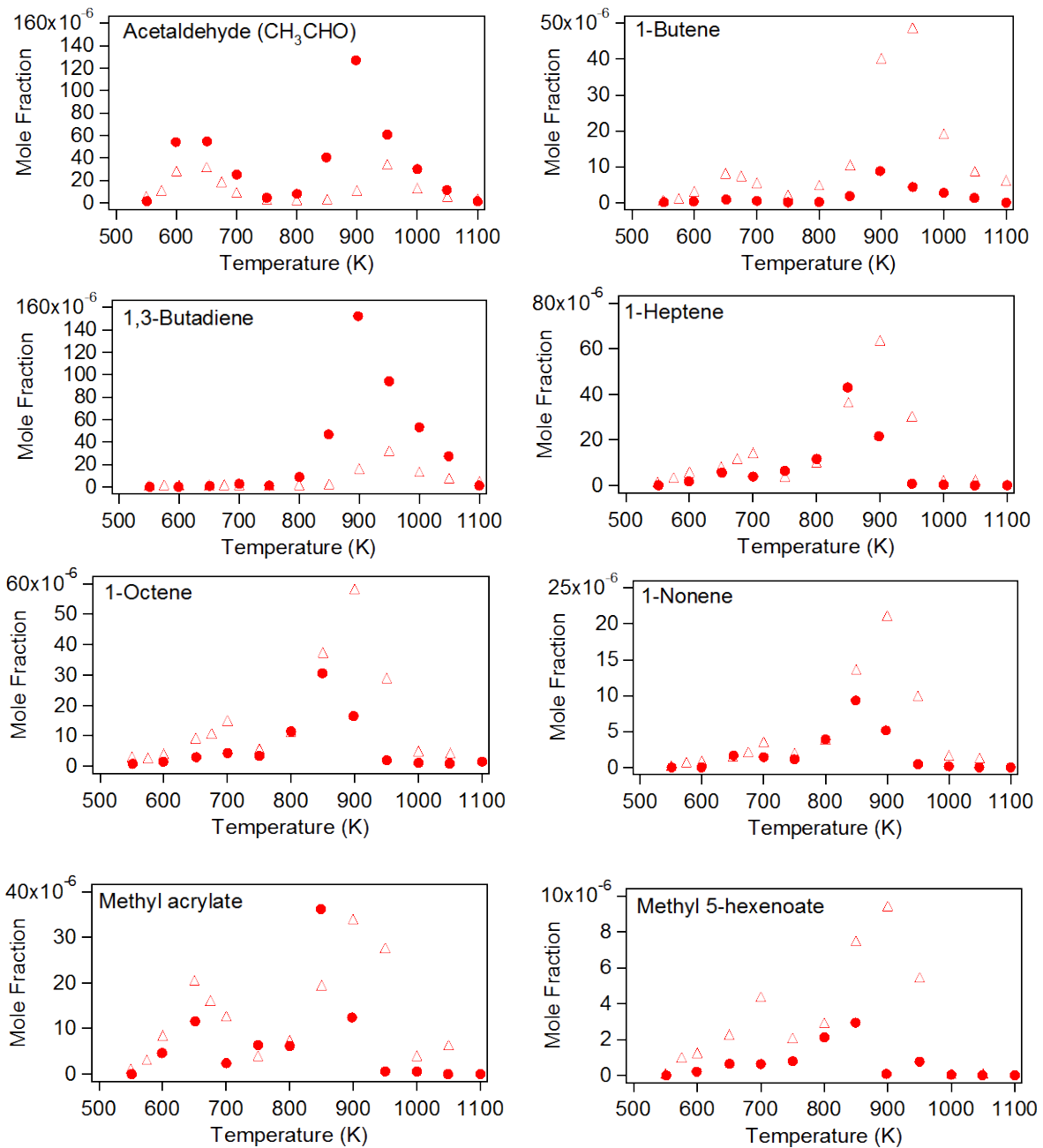


Fig. 3. Evolution of the mole fractions of reaction products with the temperature (● – methyl oleate/n-decane; Δ – methyl palmitate/n-decane [20]).

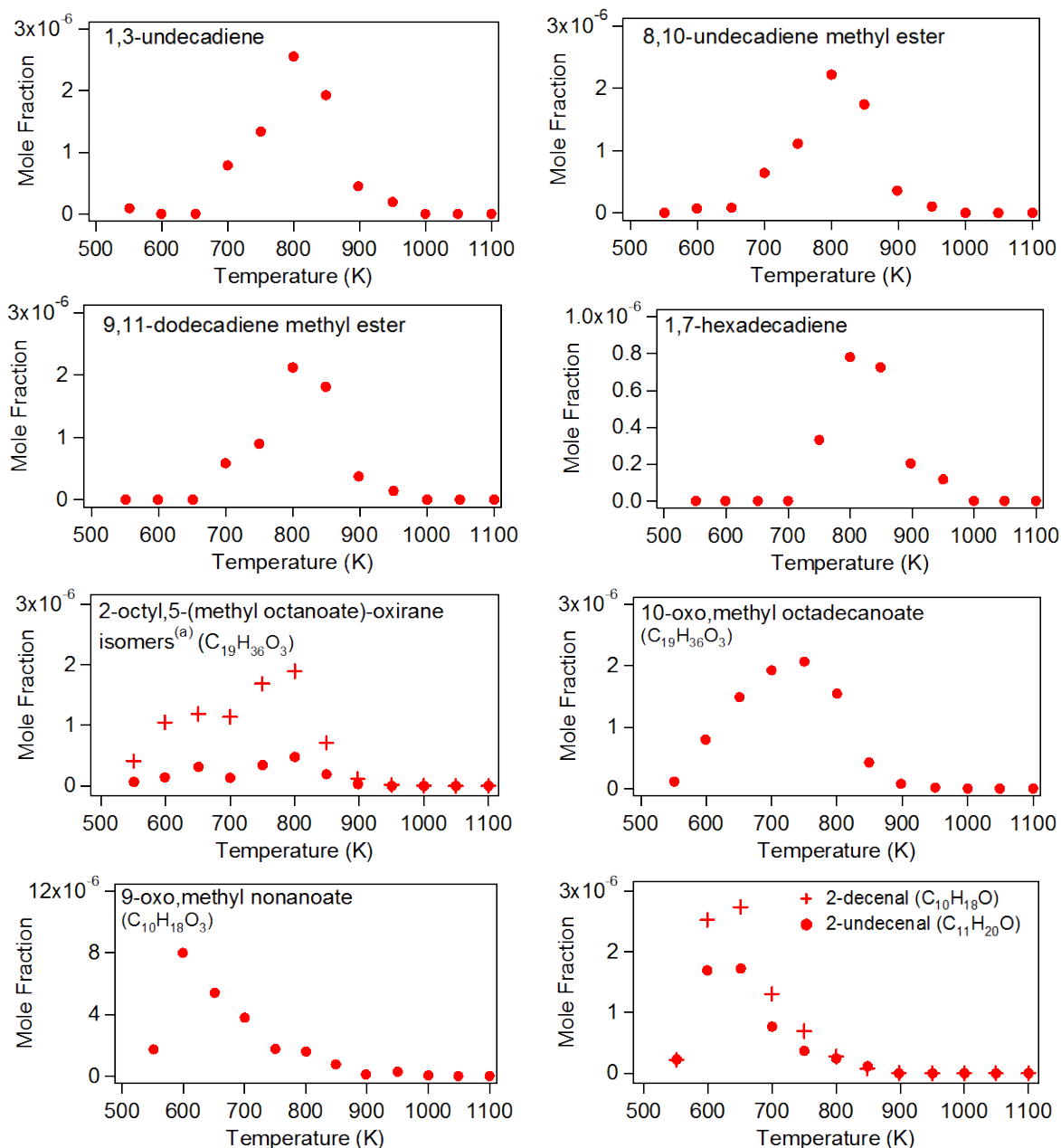


Fig. 4. Evolution of the mole fractions of products specific to methyl oleate. (a) Cis and trans isomers were well separated but we were not able to distinguish between the two isomers.

4.1. Reactivity of methyl oleate and methyl palmitate

Fig. 1 displays the evolution of the conversion of methyl oleate (Fig. 1a) and n-decane (Fig. 1b) with temperature. For both species a decrease of reactivity corresponding to the negative temperature coefficient (NTC) zone takes place in the temperature range 650–750 K. The conversions of methyl oleate and methyl palmitate are compared in Fig. 1a. They are very similar in the low temperature region (below 750 K), whereas methyl oleate is slightly more reactive than methyl palmitate in the zone following the NTC region. The similarities in the conversions of both esters at low temperature

show that the presence of the double bond in methyl oleate does not affect the reactivity of this fuel. This can be explained by the fact that the double bond is located between two large alkyl chains making low temperature chain branching possible. Note that Zhang et al. [12], in their engine study, observed that C₉ unsaturated esters are less reactive than saturated ones in the low temperature regime. This could be due to the shortest length of the alkyl chains which disfavored the low temperature reactions leading to chain branching (mainly isomerizations of peroxy radicals) as demonstrated in the case of linear isomers of hexene [27].

For n-decane (Fig. 1b), there is no measurable difference at low temperature. In the zone following the NTC region, the conversion of n-decane is slightly higher in the case of the n-decane/methyl oleate blend than in the case of the n-decane/methyl palmitate blend. The higher conversion of n-decane at these higher temperatures is likely induced by the higher reactivity of methyl oleate. For oxygen (Fig. 1c), mole fractions are slightly higher at the lowest temperatures and slightly lower at the highest temperatures in the case of the n-decane/methyl oleate blend.

4.2. Comparison of the mole fractions of the reaction products

Mole fraction profiles of products from the oxidation of n-decane/methyl oleate (this work) and n-decane/methyl palmitate [20] observed in both studies were compared ([Fig. 2] and [Fig. 3]). Products common to both studies are small oxygenated species like carbon oxides (Fig. 2) and acetaldehyde (Fig. 3), hydrocarbons like methane, acetylene, ethylene, ethane, allene, propyne, propene, propane (Fig. 2), 1,3-butadiene, 1-butene, 1-heptene, 1-octene and 1-nonene (Fig. 3) and unsaturated esters like methyl acrylate and methyl 5-hexenoate (Fig. 3).

Mole fraction profiles of carbon oxides obtained in both studies are very similar except at temperatures greater than 1000 K. In this temperature region the mole fraction of CO decreases earlier in the methyl oleate study whereas the opposite trend is visible for carbon dioxide (Fig. 2). As far as other products are concerned, it can be seen in [Fig. 2] and [Fig. 3] that the maximum mole fraction in the high temperature region is reached at a lower temperature (1000 K) in the methyl oleate study than in the methyl palmitate study (maximum mole fraction at about 950 K). These observations are consistent with the reactivity of methyl oleate in the temperature region following the NTC (Fig. 1). Mole fractions of methane and of the three C₂ hydrocarbons are slightly lower in the methyl oleate study whereas mole fractions of unsaturated C₃ species, 1,3-butadiene, acetaldehyde and methyl-5-hexenoate are larger.

4.3. Specific products of the reactions of methyl oleate: chemistry of unsaturated species

The formation of specific species, which were not present in the n-decane/methyl palmitate study, was observed because of the presence of the double bond in the middle of the alkyl chain of methyl oleate. Their formation can be explained by the specific reactions involved in the oxidation of unsaturated species. These pathways were recently reviewed in [27], [28], [29] and [30]. The specific species observed in this study were dienes, esters with two double bonds, aldehydes conjugated with one double bond, C₁₉ cyclic ethers with a three member ring and a C₁₉ oxo ester. Mole fraction profiles of these species are displayed in Fig. 4. The presence of small amounts of numerous C₁₉H₃₆O₃ isomers was observed at low temperature. Because of the proximity of the peaks, we were not able to identify these species accurately. They are likely five member ring cyclic ethers and ketones deriving from methyl oleate.

The formation of dienes and esters with two double bonds was observed for temperatures greater than 650 K. Mole fraction profile for 1,3-dodecadiene is not presented in Fig. 4 because the corresponding peak was interfering with other peaks. 2-decenal, 2-undecanal, 9-oxo,methyl nonanoate and 10-oxo,methyl octadecanoate had very similar mole fraction profiles: these species were mainly formed at low temperature and were not observed at temperatures greater than 900 K. The mole fraction profiles of the two isomers of 2-octyl,3-(methyl octanoate)-oxirane exhibit a very similar behavior with a decrease of the reactivity in the NTC region and two maxima at 650 K and 800 K. Because of the proximity of their mass spectra, we were not able to distinguish between the cis and the trans forms. It is worth noting that the two isomers are present in different amounts.

The formation of 1,7-hexadecadiene can be explained by the reaction of β -scission of the radical with the radical center in the position four of the chain (Fig. 5). Because of the vicinity of the ester function, the energy of the bond between the carbon atoms in the positions two and three (84.3 kcal mol⁻¹ [31]) is lower than the energy of the other C-C bond which can be broken (89.1 kcal mol⁻¹ [31]). Thus the decomposition to 1,7-hexadecadiene is favored as it was the case for 1-tetradecene in the oxidation of methyl palmitate [20].

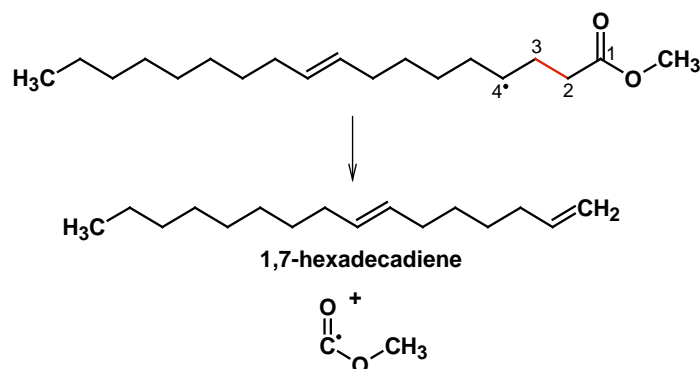


Fig. 5. Reactions of decomposition by β -scission of the radical obtained from methyl oleate which leads to the formation of 1,7-hexadecadiene.

In the following three paragraphs, the routes of formation of specific products obtained from the resonance stabilized radicals formed through H-atom abstractions from methyl oleate are discussed.

Fig. 6 displays the possible routes of formation of species with two conjugated double bonds: 1,3-undecadiene, 1,3-dodecadiene, 8,10-undecadiene methyl ester and 9,11-dodecadiene methyl ester. These four species can be formed from the two resonance stabilized radicals which can be obtained from methyl oleate through H-atom abstraction by OH radicals for example. Note that the formation of these resonance stabilized radicals is favored as the H-atoms which are involved in these abstractions are allylic ones with a C–H bond energy lower than the one of secondary alkylic H-atoms ($83.6 \text{ kcal mol}^{-1}$ and $98.7 \text{ kcal mol}^{-1}$, respectively). Because of the resonance, two mesomeric forms can be obtained from these radicals (by shifting the double bond from the initial position in methyl oleate towards the radical center) as shown in Fig. 6 and two reactions of β -scission can be written for each radical. The decomposition of the resonance stabilized radical obtained by the abstraction of the H-atom on the ester function side leads to the formation of 1,3-dodecadiene plus 6-hexenyl methyl ester radical when the broken C–C bond is on the ester function side and to 8,10-undecadiene methyl ester plus 1-heptyl radical when the broken C–C bond is on the alkyl chain side. The decomposition of the second radical (obtained from the abstraction of the H-atom on the chain end side) gives 1,3-undecadiene plus 7-heptyl methyl ester radical when the broken C–C bond is on the ester function side and 9,11-dodecadiene methyl ester plus 1-hexyl radical when the broken C–C bond is on the alkyl chain side.

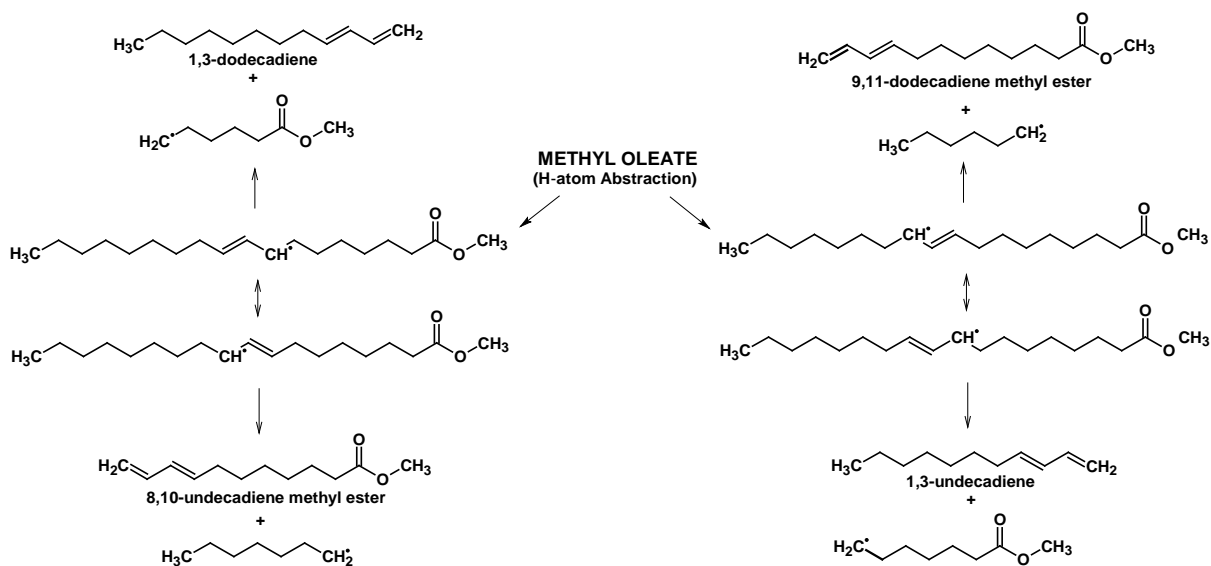


Fig. 6. Reactions of decomposition by β -scission of the two radicals obtained from methyl oleate which are stabilized by resonance with the double bond.

The mole fraction profiles of these species with two double bonds are different from the profiles obtained for olefins (Fig. 3). First, dienes and esters with two double bonds are formed from 650 K whereas the formation of olefins is observed at lower temperatures. This can be explained by the

fact that radicals leading to these resonance stabilized radicals are more stable than alkyl radicals disfavoring the reactions of decomposition. Then it can be seen in Fig. 4 that mole fractions of dienes and esters with two double bonds decrease from 800 K whereas mole fractions of olefins keep increasing up to 850 K. This is likely due to the greater reactivity of unsaturated species in this temperature region and to the reactions of additions of radicals to double bonds which are favored in the case of dienes and esters with two double bonds.

The formation of aldehydes with the carbonyl group conjugated to a C–C double bond (2-decenal and 2-undecenal) can be explained by a more complex mechanism in three steps [28] as shown in Fig. 7. First, the resonance stabilized radicals (shown in Fig. 6) obtained from methyl oleate by H-atom abstraction react with HO₂ radicals (which are very abundant at low temperature) by combination to form an hydroperoxide species. The second step consists of the scission of the fragile O–O bond leading to OH and unsaturated alkoxy radicals. These last radicals are very unstable species which react then by β-scission reactions to form aldehydes and alkyl or alkyl ester radicals. This sequence of steps has an accelerating effect on the kinetics of the reaction because a rather unreactive HO₂ radical is consumed to produce a reactive OH radical. The resonance stabilized radical obtained by the abstraction of the H-atom on the ester function side leads to 2-undecenal when the broken C–C bond is on the ester function side and to 10-oxo,methyl-8-decenoate when the broken C–C bond is on the alkyl chain side. The decomposition of the second resonance stabilized radical (obtained from the abstraction of the H-atom on the chain end side) gives 2-decenal when the broken C–C bond is on the ester function side and 11-oxo,methyl-9-undecenoate when the broken C–C bond is on the alkyl chain side. While the two unsaturated aldehydes were quantified, the two unsaturated oxo esters were not observed in this study.

In the following paragraphs, the routes of formation of specific products likely obtained from the reactions of addition of radicals to the double bond in the chain of methyl oleate are discussed.

The formation of three membered ring cyclic ethers can be explained by the addition of HO₂ radicals to the C–C double bond of methyl oleate (Fig. 8). The two new radicals formed by the addition can then decompose to yield a three member ring cyclic ether and OH radicals. According to Walker et al. [32] the addition of HO₂ radicals does not lead to hydroperoxyalkyl radicals, but directly to the formation of oxiranes and OH radicals. Five membered ring cyclic ethers were not quantified in this study because the numerous different isomers were present in very small amount compared to five membered ring cyclic ethers from methyl palmitate. This is in agreement with the slightly lower reactivity of methyl oleate at low temperature. Five membered ring cyclic ethers are typical products deriving from the low temperature oxidation of radicals (R) formed from the reactant through H-atom abstractions by OH radicals for example. The first step in the sequence of reactions is the addition of the radicals R to oxygen forming peroxy radicals (ROO). Peroxy radicals can lead back to R and oxygen or also isomerize to hydroperoxy radicals (QOOH) by internal transfer of a H-atom. Note that the presence of a double bond in an alkyl chain makes these reactions of isomerization more difficult [27]. QOOH radicals can then decompose to cyclic ether plus OH. Three, four, five and six

membered ring cyclic ethers can be obtained (five membered ring ones being the most abundant) according to the positions of the hydroperoxy function and of the radical center. The decomposition into cyclic ether plus OH is in competition with other reactions: decomposition to unsaturated species plus HO₂ when the radical center is on the carbon atom next to the one which have the hydroperoxy group, and second addition to oxygen forming a peroxy hydroperoxy radical (OOQOOH). This last class of reactions is very important as they lead to chain branching through reactions of isomerization giving OH radicals plus ketohydroperoxides (the decomposition of such a molecule by the scission of the weak O–O bond of the hydroperoxy group generates two radicals, one of them being another reactive OH radical).

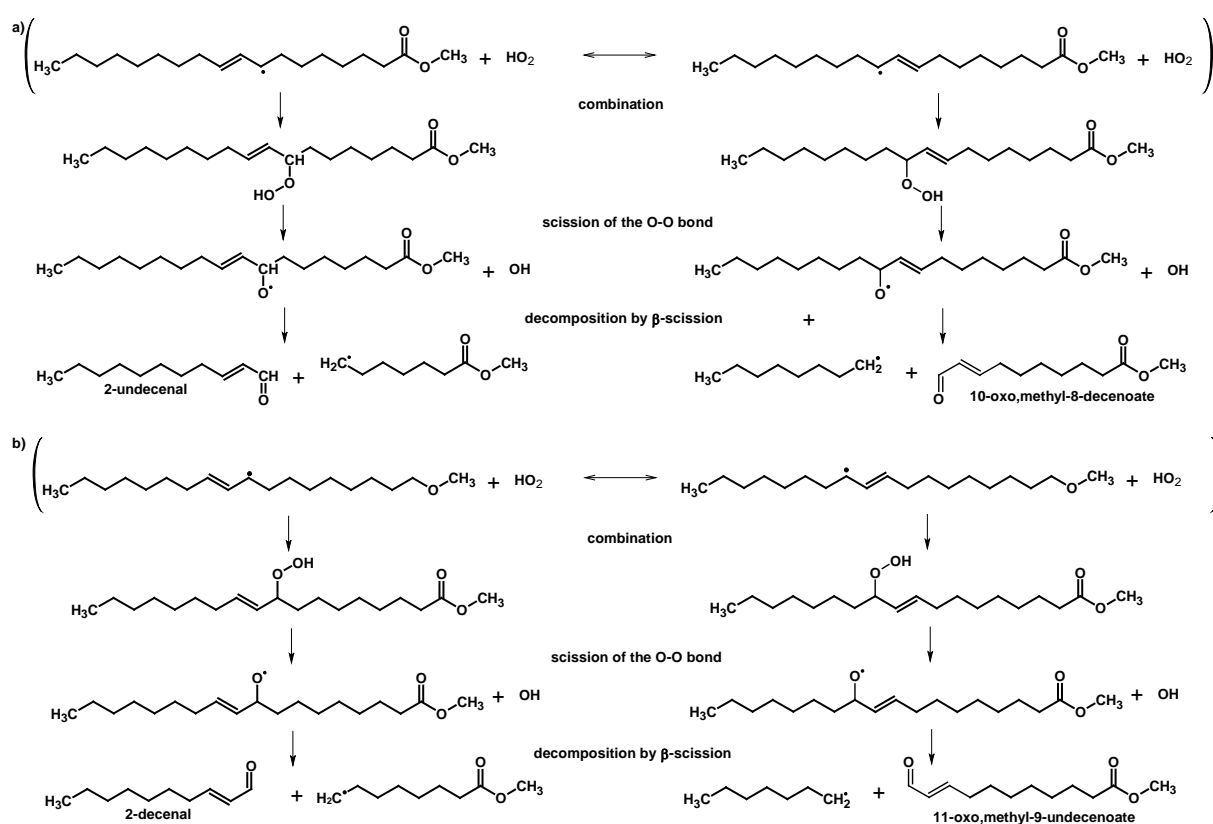


Fig. 7. Possible channels of formation of: (a) 2-undecenal and 10-oxo, methyl-8-decenoate and (b) 2-decenal and 11-oxo, methyl-9-undecenoate.

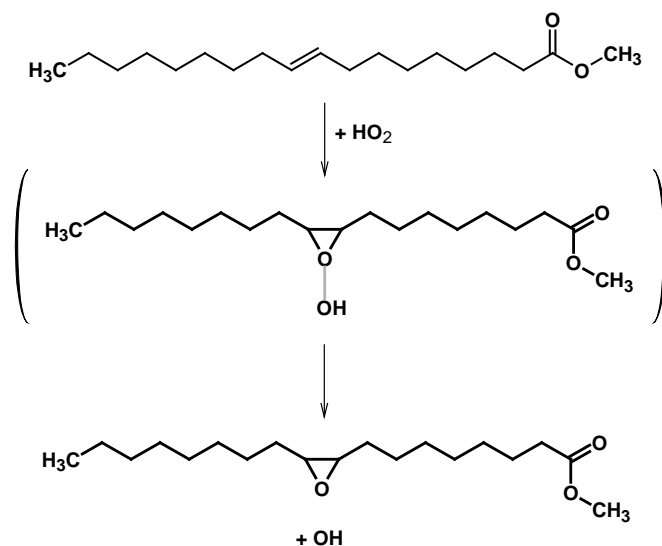


Fig. 8. Possible channels of formation of 2-octyl,3-(methyl octanoate)-oxirane by addition of HO_2 to the double bond of methyl oleate.

The formation of oxo-methyl esters (e.g. 9-oxo,methyl nonanoate in Table 3) can be explained by the mechanism of Waddington for hydroxyalkyl peroxy radicals [33]. These radicals are obtained from the addition of OH radicals to the double bond followed by the addition of the hydroxyalkyl radical to oxygen. A concerted mechanism through a cyclic transition state leads to aldehydes and OH radicals (Fig. 9). Fig. 9a displays the reaction of the 10-hydroxyl,9-peroxy,methyl-stearate radical obtained from the addition of an OH radical to the carbon atom located in the alkyl chain side whereas Fig. 9b displays the reaction of 9-hydroxyl,10-peroxy,methyl-stearate radical obtained when the addition occurs in the ester function side. Note that the same species are obtained from the decomposition of these two radicals.

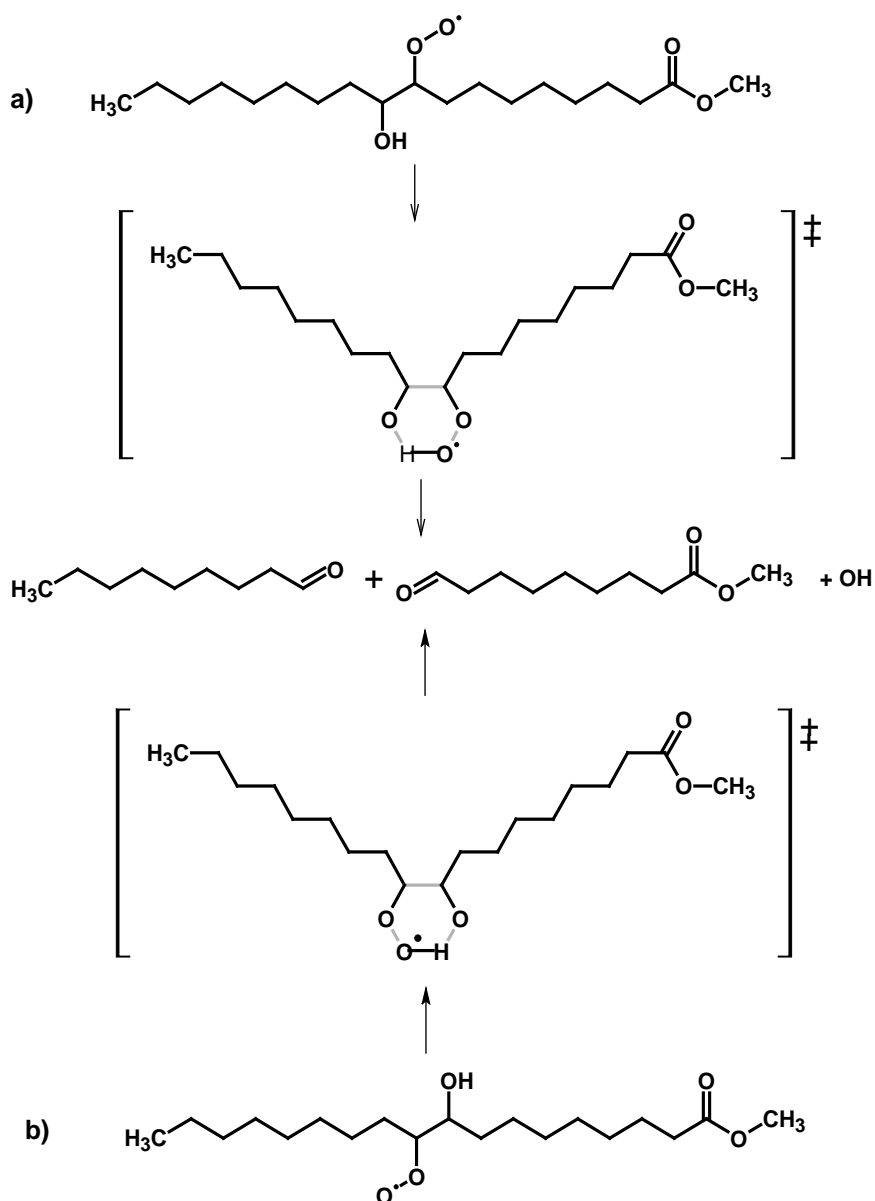


Fig. 9. Isomerization of: (a) 10-hydroxyl,9-peroxy,methyl-stearate and (b) 9-hydroxyl,10-peroxy,methyl-stearate radicals to nonanal and 9-oxo,methyl nonanoate according to the mechanism of Waddington [31].

The channel of formation of 10-oxo,methyl octadecanoate is very uncertain. This species might come from the addition of OH radicals to the double bond of methyl oleate followed by an isomerization and a β -scission (Fig. 10). Note that the activation energy of the isomerization steps is relatively high (more than 30 kcal mol^{-1}) because of three membered ring cyclic transition states, making this possible channel very difficult.

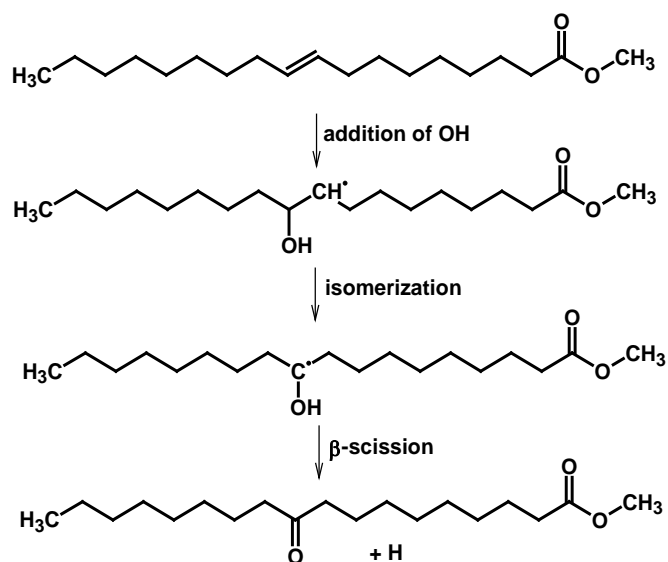


Fig. 10. Some possible channels accounting for the formation of 10-oxo, methyl octadecanoate.

The formation of small amounts of 1-undecene, 9-decene methyl ester and 10-undecene methyl ester was observed above 800 K. These species cannot be obtained from the reactions of decomposition of radicals deriving from methyl oleate because of the presence of the double bond in the middle of the chain. They likely come from the addition of H-atoms to the double bond of methyl oleate followed by reactions of decomposition. No quantification was performed due to low mole fractions and difficulty with separating the peaks in the chromatograms.

5. Conclusion

The experimental study of the oxidation of a blend containing methyl oleate and n-decane (26 mol%/74 mol%) was performed in a jet-stirred reactor over the temperature range 550–1000 K, at a pressure of 106 kPa (800 Torr), at a residence time of 1.5 s and at high dilution in helium (inlet fuel mole fraction set to 0.002). The results obtained in this work were then compared with previous results from the oxidation of a blend of n-decane and methyl palmitate in order to highlight the influence of the double bond in the middle of the chain on the reactivity and the reaction products.

The comparison of reactant mole fractions showed that methyl oleate seems to be slightly less reactive than methyl palmitate in the low temperature region whereas the opposite trend is observed in the zone following the NTC region. The lower reactivity before the NTC region is likely due to the double bond in the middle of the chain. The reactions of isomerization of peroxy radicals to give hydroperoxy radicals are disfavored by the presence of the double bond as it was demonstrated in the case of the isomers of n-hexene.

The formation of specific products due to the presence of the double bond located in the middle of the chain was observed. These species were dienes and esters with two double bonds, aldehydes conjugated with one double bond, C₁₉ three member ring cyclic ethers and a C₁₉ oxo ester. Dienes and esters with two double bonds were obtained from the decomposition of the two allylic radicals from methyl oleate. C₁₉ three member ring cyclic ethers and a C₁₉ oxo ester were likely products from the addition of radicals such as OH and HO₂ on the double bond in methyl oleate. Aldehydes conjugated with one double bond likely came from the reaction of combination of HO₂ radicals with the resonance stabilized radicals from methyl oleate. Products of the addition of H-atoms to the double bond were observed but were not quantified due to low mole fractions and difficulties in separating peaks. Five member ring cyclic ethers were not quantified in this study (whereas they were in the methyl palmitate study) because there were too many isomers (chromatographic peaks were not well separated and the individual amount of each isomer was too low).

Rapeseed and soybean biodiesel fuels contain mainly unsaturated species. They are expected to react in a same way as species such as methyl oleate which seems to be a better surrogate than saturated methyl esters. The modeling of this type of species is a challenge because of the large size of the molecule (19 atoms of carbon) and of the complexity of the reaction pathways due to the presence of the double bond and the ester function. Based on our recent research on the modeling of large saturated methyl esters, a detailed model for methyl oleate generated by EXGAS would contain more than 50,000 reactions and 6000 species making its use very difficult.

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