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Olivier Herbinet, Sarah Bax, Pierre Alexandre Glaude, Vincent Carré, Frédérique Battin-Leclerc. Mass spectra of cyclic ethers formed in the low-temperature oxidation of a series of n-alkanes. *Fuel*, 2011, 90 (2), pp.528-535. 10.1016/j.fuel.2010.09.047 . hal-00724937

HAL Id: hal-00724937

<https://hal.science/hal-00724937>

Submitted on 23 Aug 2012

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Mass spectra of cyclic ethers formed in the low-temperature oxidation of a series of n-alkanes

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Abstract

Cyclic ethers are important intermediate species formed during the low-temperature oxidation of hydrocarbons. Along with ketones and aldehydes, they could consequently represent a significant part of the heavy oxygenated pollutants observed in the exhaust gas of engines. Apart a few of them such as ethylene oxide and tetrahydrofuran, cyclic ethers have not been much studied and very few of them are available for calibration and identification.

Electron impact mass spectra are available for very few of them, making their detection in the exhaust emissions of combustion processes very difficult. The main goal of this study was to complete the existing set of mass spectra for this class of molecules. Thus cyclic ethers have been analyzed in the exhaust gases of a jet-stirred reactor in which the low-temperature oxidation of a series of n-alkanes was taking place. Analyzes were performed by gas chromatography coupled to mass spectrometry and to MS/MS. The second goal of this study was to derive some rules for the fragmentation of cyclic ethers in electron impact mass spectrometry and allow the identification of these species when no mass spectrum is available.

Keywords: Cyclic ether; Engine exhaust gases; Combustion; n-Alkanes; Mass spectrum

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1. Introduction

Cyclic ethers are well known as important species formed in the low temperature gas phase oxidation of different types of fuels [1], [2] and [3]. However while the emissions of carbonyl compounds and alcohols have been quantified in the exhaust gases of internal combustion engines [4] and [5], those of cyclic ethers have been very little investigated [6]. This is mostly due to the fact that these compounds are not easily available for calibration and few data are available about their mass spectra in electron impact mass spectrometry.

In order to illustrate the potential importance of cyclic ethers in the exhaust gases of engines, simulations were run under the conditions observed in HCCI (Homogeneous Charge Compression Ignition) engines [7]. Simulations have been run using the SENKIN code [8] and a detailed kinetic mechanism proposed by Buda et al. [9] to compute the evolution of a 75% n-heptane/25% iso-octane mixture in air (C_7H_{16} : 0.413 mol%; C_8H_{18} : 0.1377%; O_2 : 20.9%; N_2 : 78.55%, equivalence ratio of 0.3) in a variable volume, zero dimensional adiabatic single zone engine. The detailed kinetic model used for the simulations has been successfully validated against experimental ignition delay time data obtained in shock tubes and in a rapid compression machine [9]. Fig. 1 presents the time evolution of the mole fractions of the fuel (the n-heptane/iso-octane mixture) and of tetrahydrofurans (five membered ring cyclic ethers), the main cyclic ethers formed during the low temperature reaction before ignition. It is clear that, when assuming a perfectly homogeneous mixture as in the present simulation, organic compounds are completely consumed during auto-ignition (corresponding to the strong rise of the temperature profile shown in Fig. 1) and should not be present in exhaust gases. However experimental measurements in engines have demonstrated the presence of organic species in the exhaust gases. The persistence of these species would be due to the existence of cold zones in the combustion chamber (e.g. near the walls or in crevices) [10], in which the ignition does not reach its final stage. Fig. 1 shows that the evolution of the mole fraction of the fuel presents a "plateau" during the pre-ignition zone, i.e. for residence times around 18×10^{-3} s. At the same time, the mole fraction of tetrahydrofurans can be as high as 100 ppm, only about 50 times lower than that of fuel. Consequently the fuel, which is emitted in exhaust gases of engines as a result of an incomplete combustion, is likely accompanied by noticeable amounts of cyclic ethers.

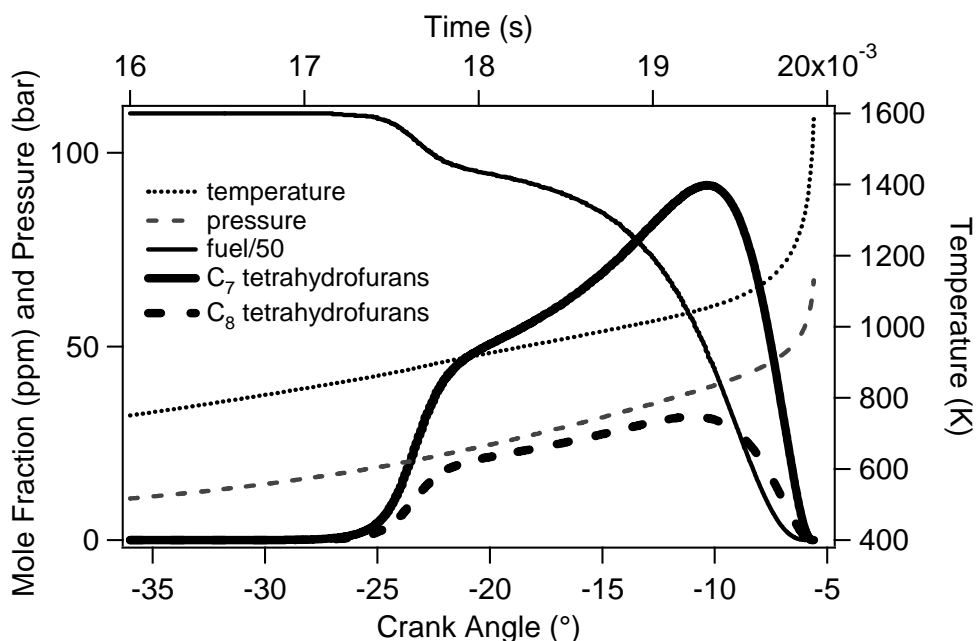


Fig. 1. Simulation of the evolution of the mole fractions of fuel, five membered ring cyclic ethers, pressure and temperature during a part of the compression period of an HCCI engine.

The purpose of this paper is to present experimental results about the different cyclic ethers which can be formed during the low-temperature oxidation of a series of linear alkanes. A special care was taken for interpreting the electron impact mass spectra obtained for these compounds so that characteristic fragments can be identified.

2. Formation routes of cyclic ethers during the low-temperature oxidation of alkanes

Cyclic ethers are formed in the low-temperature oxidation of hydrocarbons through a complex but well established mechanism [9]. The formation route of a five membered ring cyclic ether from 1-pentyl radical, formed in the low-temperature oxidation of n-pentane, is displayed in Fig. 2. The first step involved in the formation of cyclic ethers is the addition of an alkyl radical (deriving from the reactant) to a molecule of oxygen to give a peroxy radical ROO• (step 1 in Fig. 2). Then the peroxy radical reacts by isomerization through a five, six, seven or eight membered ring cyclic transition state to yield a hydroperoxy alkyl radical •QOOH (step 2 in Fig. 2). •QOOH radicals can then react by several types of reaction: isomerization, β -scission decomposition, second addition to a molecule of oxygen or decomposition to cyclic ethers. For this last reaction, three, four, five or six membered ring cyclic ethers can be obtained according to the relative positions of the unpaired electron and of the hydroperoxy group (step 3 in Fig. 2).

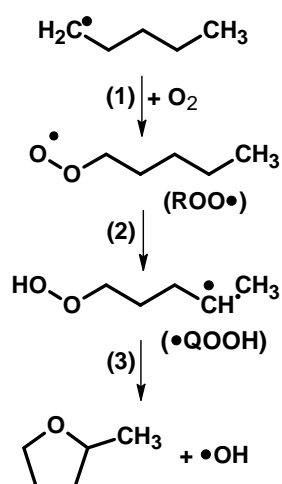
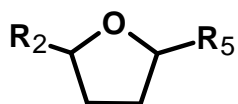


Fig. 2. Route of formation of a five membered ring cyclic ether in the low-temperature oxidation of n-pentane.

Among cyclic ethers, the most abundant are those having a single five membered ring (also called tetrahydrofurans or oxolanes) [2] and [3]. This can be explained by the low ring strain energy involved in the seven membered ring cyclic transition state during the isomerization (step 2 in Fig. 2) in comparison to that of the other cyclic transition states [9]. The formation of four and six membered ring cyclic ethers is usually observed but these species are present in much smaller amounts than five membered ring ones. Three membered ring cyclic ethers are rarely detected during the oxidation of alkanes because the reaction of isomerization through a very strained transition state is very difficult [9] and [11].

The structures of five membered ring cyclic ethers, which can be obtained in the low-temperature oxidation of the different n-alkanes, differ in the nature of the two groups which are linked to the carbon atoms in positions 2 and 5:



R_2 and R_5 can be hydrogen atoms or alkyl groups. It is worth noting that two cis and trans isomers are obtained if both R_2 and R_5 are alkyl groups. As a result, for a n-alkane of formula C_nH_{2n+2} , the number of expected isomers (cis and trans isomers included) for five membered ring cyclic ethers is equal to $n-3$ if n is even, and to $n-4$ if n is odd.

Similarly, for four membered ring cyclic ethers (oxetanes), the number of isomers is $n-3$ if n is even, and $n-2$ if n is odd. For six membered ring cyclic ethers (also called oxanes or tetrahydropyrans), the

number of isomers is $n-5$ if n is even, and $n-4$ if n is odd. For three membered ring cyclic ethers (oxiranes), the number of isomers is $n-1$ if n is even, and $n-2$ if n is odd. From this, it can be understood that the low-temperature oxidation of large n -alkanes leads to the formation of numerous isomers of cyclic ethers which are difficult to separate during chromatographic analyses.

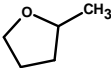
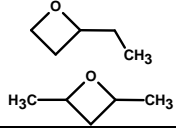
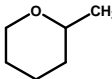
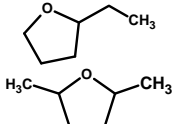
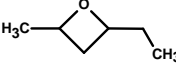
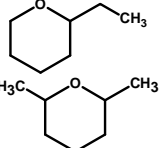
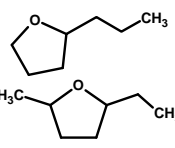
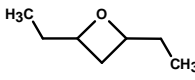
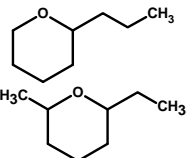
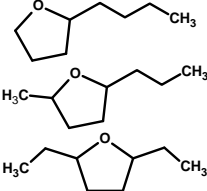
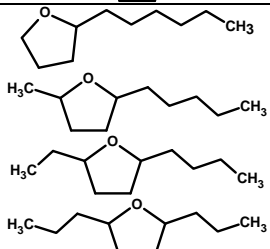
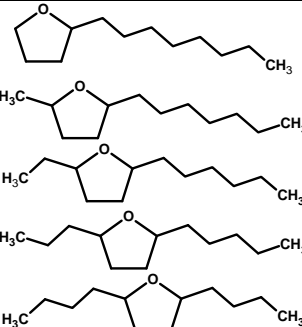
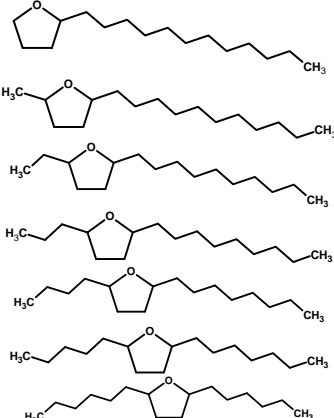
Very few cyclic ethers are available for identification and calibration. Mass spectra are unknown for most of them and there is a lack of data in the different mass spectra bases. As far as five membered ring cyclic ethers are concerned, the NIST 08 Mass Spectral Library [12] provides mass spectra for 2-methyl-tetrahydrofuran ($C_5H_{10}O$), 2,5-dimethyl-tetrahydrofuran ($C_6H_{12}O$), 2-propyl-tetrahydrofuran and 2,5-methyl,ethyl-tetrahydrofuran ($C_7H_{14}O$), 2,5-diethyl-tetrahydrofuran and 2-butyl-tetrahydrofuran ($C_8H_{16}O$), 2-hexyl-tetrahydrofuran, 2,5-methyl,pentyl-tetrahydrofuran, 2,5-ethyl,butyl-tetrahydrofuran and 2,5-dipropyl-tetrahydrofuran ($C_{10}H_{20}O$). Note that n -heptane and n -decane are the only n -alkanes for which the mass spectra of all the five membered ring cyclic ethers which can be potentially detected in the exhaust gas of an engine fueled with these reactants are included in the NIST 08 Mass Spectral Library. Experimental mass spectra obtained in this study were compared with the mass spectra of the NIST 08 Mass Spectral Library for confirmation. The NIST 08 Mass Spectral Library also contains mass spectra of two tetrahydropyrans: 2-methyl-tetrahydropyran ($C_6H_{12}O$) and 2-propyl-tetrahydropyran ($C_8H_{16}O$). No mass spectrum was found for oxetanes.

3. Experimental procedure and results

The low-temperature oxidation of several n -alkanes was performed in a jet-stirred reactor at a temperature of 650 K (temperature at which the mole fraction of cyclic ethers is maximum [2]), for a residence time of about 1 s, and under atmospheric pressure. This type of reactor was used for numerous gas phase kinetic studies [2], [13] and [14] and was described in detail in [13]. The gas mixture entering the reactor was composed of fuel, carrier gas (helium) and oxygen. The liquid fuel was evaporated using gas (helium and oxygen) bubbling at ambient temperature. The helium and oxygen flow rates were the same for all n -alkanes. Oxygen was introduced in large excess in order to maximize the low-temperature oxidation of the different fuels and to enhance the formation of oxygenated species such as cyclic ethers. Species leaving the reactor were condensed in a trap maintained at liquid nitrogen temperature and were then injected in a gas chromatograph (Agilent 6850) coupled with a mass spectrometer (Agilent 5973) with electron impact at 70 eV. The column used for the separation was an HP-5 capillary column (constant flow rate of 1 mL/min helium). The oven temperature profile was: 40 °C during 30 min; ramp of 5 °C/min up to 200 °C and a final isotherm during 28 min.

Experiments were performed with seven linear alkanes from C5 to C16: n -pentane, n -hexane, n -heptane, n -octane, n -decane, n -dodecane and n -hexadecane. Table 1 presents the list of all the detected cyclic ethers.

Table 1. List of the cyclic ethers identified during the low-temperature oxidation of linear n-alkanes from C₅ to C₁₆.

Initial reactant	6 membered ring cyclic ethers	5 membered ring cyclic ethers	4 membered ring cyclic ethers
n-pentane			
n-hexane			
n-heptane			
n-octane			
n-decane			
n-dodecane			
n-hexadecane			

Tetrahydrofurans were the most abundant oxygenated products and all expected isomers were detected (cis and trans isomers were well separated but we were not able to distinguish between them as they have very close mass spectra). The formation of small amounts of four and six membered ring cyclic ethers was observed for small n-alkanes only (up to n-octane). This can be explained by the fact that for large n-alkanes numerous isomers are formed with lower individual amounts. These species are formed in small amounts and their peaks are not well separated from others. No three membered ring cyclic ether was detected.

4. Interpretation of the mass spectra of cyclic ethers

The Figures presented hereafter ([Fig. 3], [Fig. 4], [Fig. 5], [Fig. 6] and [Fig. 7]) display a selection of mass spectra useful for the discussion. The complete set of mass spectra is available as supplemental material on the web site of this journal. Note that cis and trans isomers have very close mass spectra and only one of them is presented in the figure displayed in the paper and in the supplemental material.

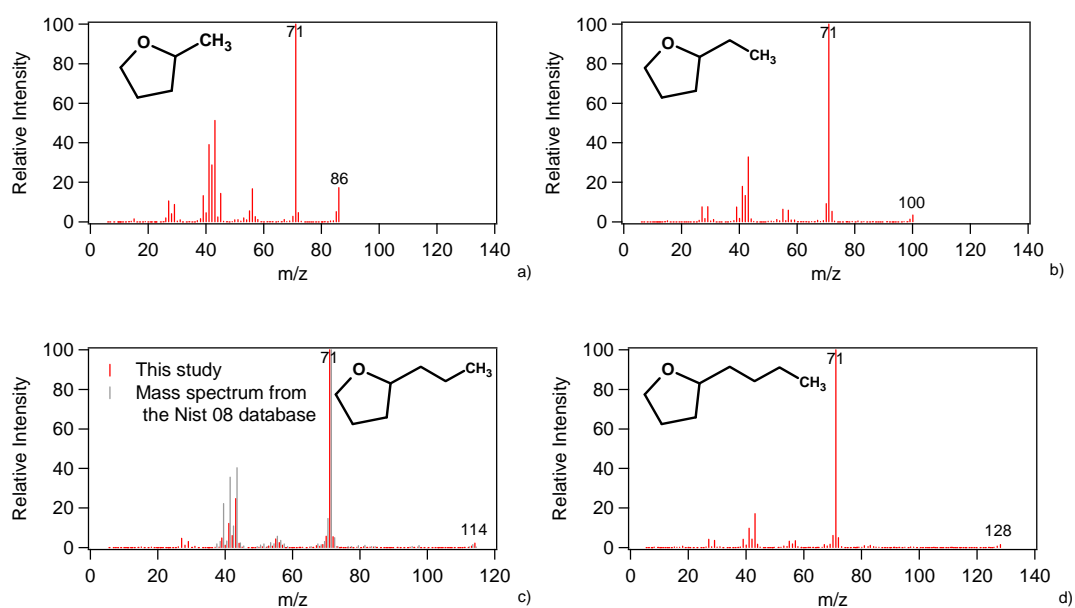


Fig. 3. Mass spectra of 2-alkyl-tetrahydrofurans. (a) 2-Methyl-tetrahydrofuran, (b) 2-ethyl-tetrahydrofuran, (c) 2-propyl-tetrahydrofuran and 2-propyl-tetrahydrofuran from the NIST 08 Mass Spectral Library [12], and (d) 2-butyl-tetrahydrofuran.

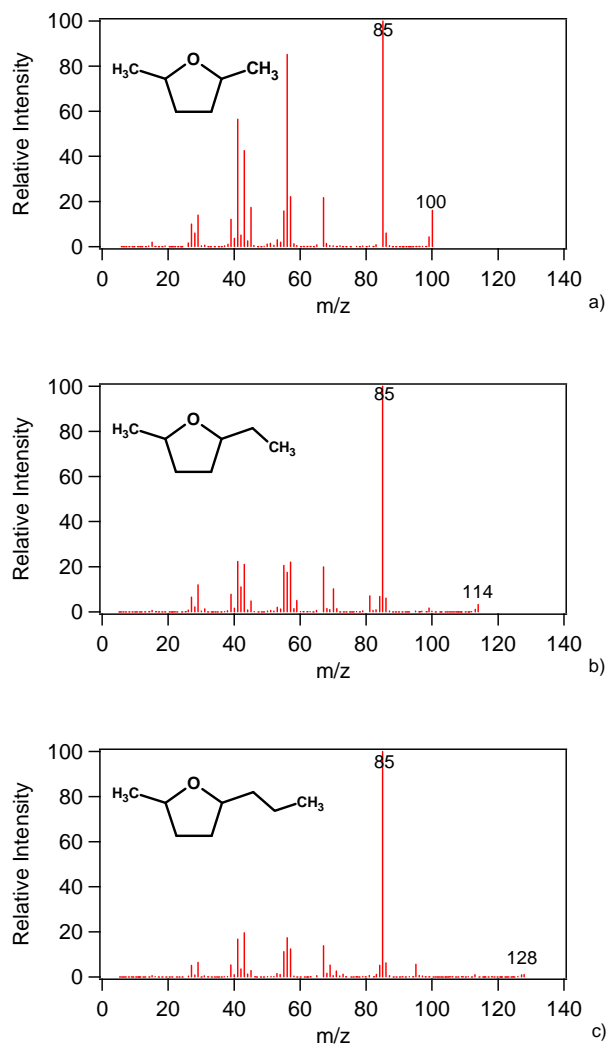


Fig. 4. Mass spectra of (a) 2,5-dimethyl-tetrahydrofuran, (b) 2,5-methyl,ethyl-tetrahydrofuran, and (c) 2,5-methyl,propyl-tetrahydrofuran.

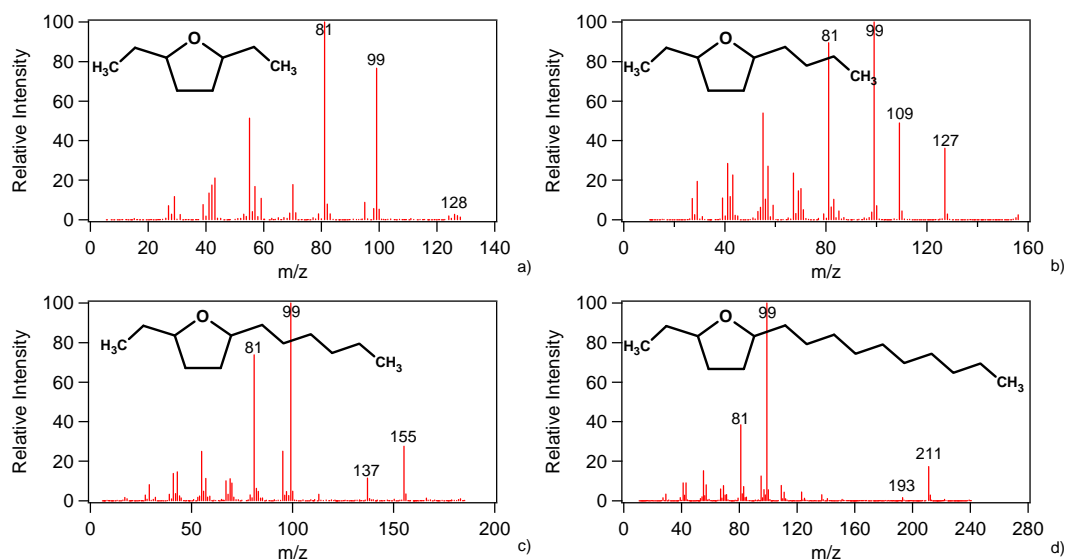


Fig. 5. Mass spectra of (a) 2,5-diethyl-tetrahydrofuran, (b) 2,5-ethyl, butyl-tetrahydrofuran, (c) 2,5-ethyl, hexyl-tetrahydrofuran, and (d) 2,5-ethyl, decyl-tetrahydrofuran.

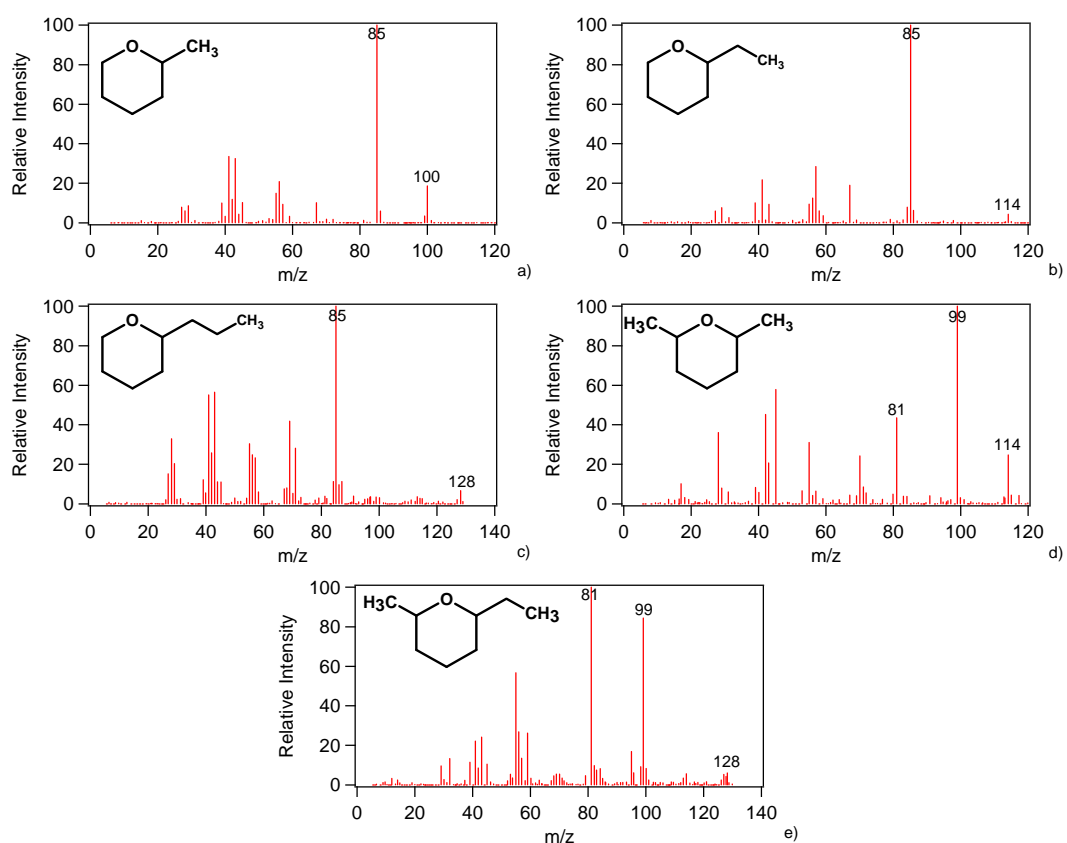


Fig. 6. Mass spectra of (a) 2-methyl-tetrahydropyran, (b) 2-ethyl-tetrahydropyran, (c) 2-propyl-tetrahydropyran, (d) 2,6-dimethyl-tetrahydropyran, and (e) 2,6-methyl, ethyl-tetrahydropyran.

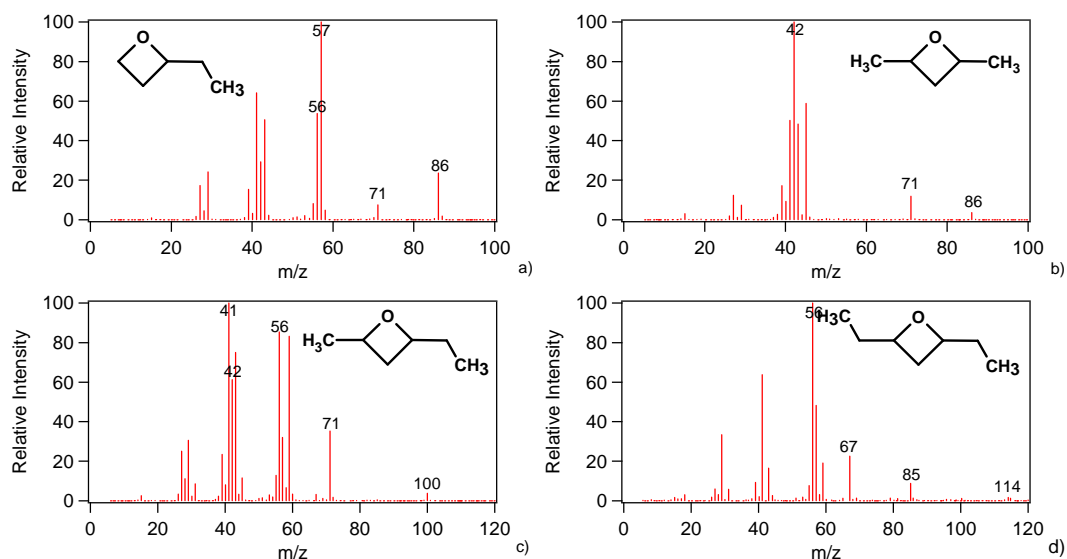


Fig. 7. Mass spectra of (a) 2-ethyl-oxetane, (b) 2,4-dimethyl-oxetane, (c) 2,4-methyl,ethyl-oxetane, and (d) 2,4-diethyl-oxetane.

4.1. Five membered ring cyclic ethers

The mass spectra given in Fig. 3 correspond to 2-alkyl-tetrahydrofurans (cyclic ether with only one alkyl chain in the position 2) from 2-methyl-tetrahydrofuran ($C_5H_{10}O$, Fig. 3a) to 2-butyl-tetrahydrofuran ($C_9H_{18}O$, Fig. 3d). It can be seen that all the mass spectra exhibit a main peak at m/z 71 corresponding to a $C_4H_7O^+$ fragment. For 2-methyl-tetrahydrofuran (86 u), the difference $86-71$ is equal to 15 which corresponds to the loss of a methyl radical. In the case of 2-ethyl-tetrahydrofuran (100 u), the difference $100-71$ is 29 which is the mass of an ethyl radical. Similar observations were made for cyclic ethers with larger alkyl chains meaning that the main peak is likely obtained from the loss of the side alkyl chain during the fragmentation.

The mass spectrum of 2-propyl-tetrahydrofuran from the NIST 08 Mass Spectral Library [12] is also displayed in Fig. 3c. This mass spectrum compares well with the one that we obtained for this species except that there are slight differences in the relative abundance of the lowest masses in the range 39–43. Mass spectra obtained in this study were compared with those of the NIST 08 Mass Spectral Library when available. The comparison is given as supplementary data. It shows that there is a very good agreement between our data and those of the literature. As for 2-propyl-tetrahydrofuran, slight differences in the relative abundance of peaks are visible for 2,5-dimethyl-tetrahydrofuran and 2,5-ethyl, butyl-tetrahydrofuran. These differences are likely due to the difficulty in separating all the isomers during the chromatographic analysis.

Fig. 4 displays the mass spectra for 2,5-methyl,alkyl-tetrahydrofurans from C₆ to C₈. For these species a large peak at m/z 85 (corresponding to a CH₃C₄H₆O⁺ fragment) can be observed. For 2,5-dimethyl-tetrahydrofuran (C₆H₁₂O, 100 u) in Fig. 4a, the difference 100–85 is 15 which corresponds to the loss of a methyl radical. For 2,5-methyl,ethyl-tetrahydrofuran (C₇H₁₄O, 114 u) in Fig. 4b, the difference 114–85 is the mass of the ethyl group. It is interesting to note that there is no peak at m/z 99 (loss of a methyl radical). This is also the case for 2,5-methyl,propyl-tetrahydrofuran (C₈H₁₆O, 128 u) in Fig. 4c: there is a peak at m/z 85 but no peak at m/z 113. This can be explained by the easier C-C bond breaking during the fragmentation when the alkyl chain includes at least two carbon atoms (this is discussed further in this paper). This is also in agreement with the relative importance of the peaks in the mass spectrum of 2,5-dimethyl-tetrahydrofuran (Fig. 4a): the peak at m/z 85 is the largest but the ratio with the molecular ion is smaller than in the case of the 2,5-methyl,ethyl-tetrahydrofuran and 2,5-methyl,propyl-tetrahydrofuran. It can then be deduced that the fragmentation is more difficult when the alkyl group is a methyl radical.

The mass spectra obtained for cyclic ethers with two alkyl groups containing each at least two carbon atoms confirm this assumption. Fig. 5 displays the mass spectra for a series of 2,5-ethyl,alkyl-tetrahydrofurans from C₈ to C₁₆. All these mass spectra exhibit a large peak at m/z 99 which corresponds to a C₂H₅C₄H₆O⁺ fragment obtained through the loss of the alkyl chain. For cyclic ethers other than 2,5-diethyl-tetrahydrofuran, which is symmetric, a peak at M–29 due to the loss of the ethyl group is observed, e.g. the peak at m/z 127 in the case of 2,5-ethyl,butyl-tetrahydrofuran (Fig. 5b).

The presence of other large peaks can be observed in the mass spectra corresponding to 2,5-ethyl,alkyl-tetrahydrofurans. In the case of 2,5-diethyl-tetrahydrofuran (Fig. 5a), this peak is at m/z 81. It is worth noting that it corresponds to the mass of the fragment obtained through the loss of an ethyl group minus 18. This could be due to the elimination of a molecule of water from this fragment. Similar observations can be made for larger 2,5-ethyl,alkyl-tetrahydrofurans. For example, in the case of 2,5-ethyl,butyl-tetrahydrofuran (Fig. 5b), there are a peak at m/z 81 (corresponding to the elimination of a molecule of water from the fragment with m/z 99) and a peak at 109 (which is 127–18). A small peak (at m/z = 67) corresponding to the possible loss of water is also observed in the mass spectra of 2,5-methyl,alkyl-tetrahydrofurans (Fig. 3). These last observations mean that:

- an elimination of water likely occurs from the main fragments obtained from the molecular ion,
- this elimination takes place only if there is a remaining alkyl group attached to the tetrahydrofuran ring, and this is why it does not occur for 2-alkyl-tetrahydrofurans (Fig. 2),
- this elimination is much easier when the remaining alkyl group contains at least two carbon atoms.

4.2. Six membered ring cyclic ethers

According to the analysis of their mass spectra (Fig. 6), the observations made for five membered ring cyclic ethers seems to also apply to six membered ring cyclic ethers. 2-alkyl-tetrahydropyrans (Fig. 6a to c) have a peak at m/z 85 which corresponds to a $C_5H_9O^+$ fragment obtained from the loss of the side alkyl chain from the molecular ion. 2,6-Methyl,alkyl-tetrahydropyrans (Fig. 6d and e) have a large peak at m/z 99 corresponding to a $CH_3C_5H_8O^+$ fragment obtained through the loss of the alkyl chain and another large peak at m/z 81 corresponding to the possible elimination of water from the fragment at m/z 99.

4.3. Four membered ring cyclic ethers

Behaviors analog to five and six membered cyclic ethers are observed again in the case of four membered ring cyclic ethers (Fig. 7) but the characteristic peaks are not the largest ones. This may be explained by the high ring strain energy of the four membered rings compared to that of five and six membered rings. Oxetanes are more fragile and decompose more easily to small fragments. 2-ethyl-oxetane (Fig. 7a) is the only identified 2-alkyl-oxetane. One large peak at m/z 57, corresponding to a $C_3H_5O^+$ fragment (loss of the ethyl group), is visible on the mass spectrum of this species. There is also a small peak at m/z 71 which could correspond to the loss of the terminal methyl group in the alkyl chain. For 2,4-dimethyl-oxetane (Fig. 7b) and 2,4-methyl,ethyl-oxetane (Fig. 7c), a peak at m/z 71 corresponding to a $CH_3C_3H_4O^+$ fragment is observed. It seems that the elimination of water doesn't occur because no peak is observed at m/z 53. At least, for 2,4-diethyl-oxetane (Fig. 7d), a peak at m/z 85 corresponds to the loss of an ethyl group and a peak at m/z 67 to the possible elimination of water from the fragment with m/z 85. For 2,4-dimethyl-oxetane (Fig. 7b) and 2,4-diethyl-oxetane (Fig. 7d) two large peaks can be observed at m/z 42 and at m/z 56, respectively. A route of formation of these fragments is proposed in Section 6 of this paper.

5. Confirmation of the origin of the main fragments using GC-MS/MS

In order to confirm the origin of the main fragments present in the mass spectra of cyclic ethers, a gas chromatograph (Agilent 7890A) coupled to an MS/MS (Agilent 7000A) was used. This apparatus combines two quadrupoles with a collision cell between them allowing the fragmentation of parent ions from the first fragmentation and separated by the first quadrupole. The different analysis modes provide very useful information for the understanding of the fragmentation of ions. For this study, we focused on the fragmentation of 2,5-dimethyl-tetrahydrofuran (mass spectrum in Fig. 4a), a cyclic ether formed in the oxidation of n-hexane. Several analyses were performed with the ion precursor scan mode (a product ion of interest is selected in the second quadrupole whereas a scan is performed

in the first one allowing the identification of all the precursor ions leading to the formation of the product ion of interest). The energy in the collision cell was 0 eV.

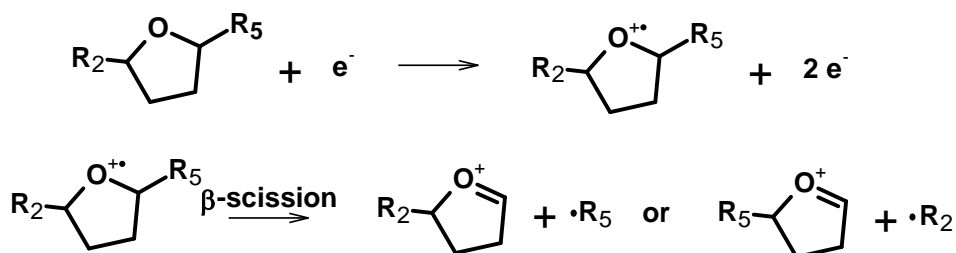
The origin of the product ions of mass 85 and 67 were investigated. The different precursor ions for these product ions are 85 and 100 for mass 85 and 67 and 85 for mass 67. These new data confirm that the fragment of m/z 85 comes from the decomposition of the molecular ion (m/z 100) which likely occurs through the loss of a methyl radical as it is discussed in Section 4. The neutral loss of 18 is also confirmed as the fragment of m/z 67 is formed from the one with m/z 85. This new experimental observation is in good agreement with the probable elimination of water from the main fragments obtained from the molecular ion which was also discussed in Section 4.

6. Rules of fragmentation of cyclic ethers

According to the previous observations, four, five and six membered ring cyclic ethers behave similarly in electron impact mass spectrometry meaning that the fragmentation occurs through similar rules. The only difference is in the relative importance of the peaks in the case of four membered ring cyclic ethers which seem to decompose more easily to smaller fragments.

Some rules of fragmentation were derived from the analysis of the mass spectra obtained for the cyclic ethers identified in this study. Fig. 8 displays the sequence of reactions leading to the formation of the main fragments from the molecular ion (loss of an alkyl group) in the case of a five membered ring cyclic ether. R_2 and R_5 in Fig. 8 are hydrogen atoms or alkyl groups. The first step corresponds to the abstraction of an electron from the oxygen atom embedded in the ring. The radical ion which is obtained decomposes through a reaction of β -scission leading to a smaller ion and an alkyl radical. Note that the reaction of β -scission doesn't occur if R_2 or R_5 is a hydrogen atom and is disfavored when R_2 or R_5 is a methyl group. This is due to the high energies of the C-H and the C-CH₃ bonds (e.g. 95 kcal mol⁻¹ in cyclopentane and 85.6 kcal mol⁻¹ in methyl-cyclopentane respectively [15]) compared to the energy of a C-R bond (84.0 kcal mol⁻¹ in ethyl-cyclopentane [15]) where R is an alkyl group with at least two carbon atoms. The β -scissions leading to the ring opening are disfavored in the case of five and six membered ring cyclic ethers because these reactions are much more difficult than the breaking of a C-C bonds outside the ring [16]. On the contrary in the case of four membered ring cyclic ether, the ring opening is favored by a lower activation energy than that of a β -scission breaking a C-C bond in a linear alkyl chain [16]. Note that fragments with even m/z are obtained for oxetanes. These fragments likely come from the opening of the ring followed by the breaking of the C-O bond (with the transfer of the two electrons on the oxygen atom) forming an aldehyde and an alkyl cation radical (View the MathML source) as displayed in Fig. 8. These fragments correspond to the peaks at m/z 42 ($n = 3$) and 56 ($n = 4$) in the mass spectra in Fig. 6.

Loss of a side alkyl chain (oxetanes, oxolanes and oxanes):



Opening of the ring (oxetanes only):

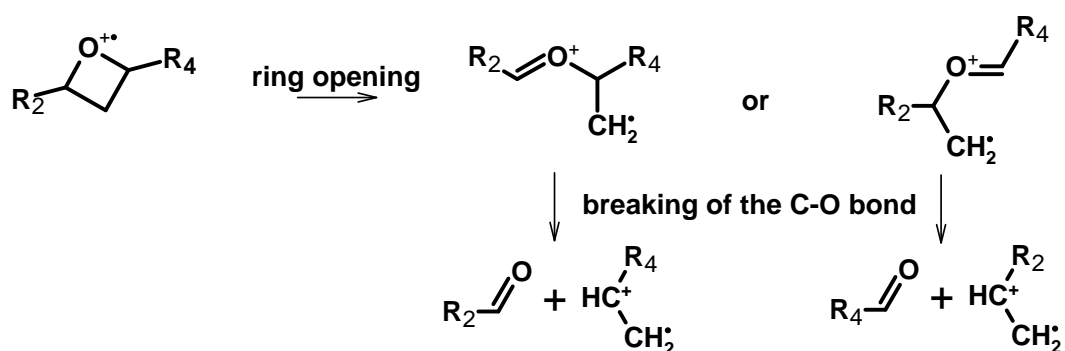


Fig. 8. Rules of fragmentation of cyclic ethers.

According to the analysis of the mass spectra, the possible elimination of water occurs only if there is a remaining alkyl chain on the fragment and the reaction seems to be difficult if the alkyl group is a methyl one. This likely means that hydrogen atoms attached to the first carbon atom of the alkyl chain are involved in the elimination of the water molecule. Indeed the energy of a C–H bond in a methyl group (100.9 kcal mol⁻¹ [15]) is higher than the energy of a C–H bond involving a secondary carbon atom (98.5 kcal mol⁻¹ [15]).

The mechanism accounting for the loss of water is likely more complex than the mechanism which is proposed in the case of alcohols [17]. The first step in this mechanism is probably a reaction leading to the opening of the ring. Then several rearrangements likely occur leading to a structure close the one of an alcohol. The last step could be the loss of water from this alcohol like fragment.

7. Conclusion

A wide range of cyclic ethers have been analyzed during the low temperature (650 K) oxidation of a series of linear alkanes. Tetrahydrofurans (five membered ring cyclic ethers) were the most abundant oxygenated products. The formation of small amounts of four and six membered ring cyclic ethers was also observed. No three membered ring cyclic ether was detected.

The analysis of the mass spectra has been performed and some rules of fragmentation of four, five and six membered ring cyclic ethers from the low-temperature oxidation of n-alkanes were derived from these observations:

- the main fragments derive from the reaction of β -scission of the C–C bonds outside the rings in the case of five and six membered ring cyclic ethers;
- a reaction of elimination of water occurs from the main fragments;
- the reaction of β -scission of the C–C bonds outside the rings and the elimination of water occurs in the case of four membered ring cyclic ethers to a lesser extent. For these species the main fragments likely come from the decomposition of the ring.

Future work will consist in the study of the formation of cyclic ethers from the low-temperature oxidation of other species present in automobile fuels such as iso-alkanes, olefins, esters, alcohol, and alkyl-cyclo-alkanes. There are still very little data about the fate of cyclic ethers emitted in the exhaust gases from engines and this constitutes a new field of investigation (recently Ballesteros et al. studied the tropospheric reaction of tetrahydropyran with chlorine atoms [18]).

Acknowledgments

This work was funded by the European Commission through the “Clean ICE” Advanced Research Grant of the European Research Council. The authors would like to thank Professor R. Minetti of PC2A-Lille for sharing mass spectra of C10 five membered ring cyclic ethers.

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