

Thermal decomposition of furans with oxygenated substituents: A combined experimental and quantum chemical study

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Abstract

Furans are an important class of compounds that can be thermochemical or enzymatically produced from biomass. Despite of their importance little is known about the thermal decomposition of furans with oxygenated substituents. In this work, the influence of the -CH₃, -CH₂OH and -CHO functional groups on the molecular and radical decomposition chemistry is studied with a combined quantum chemical and experimental approach using 2-furfuryl alcohol and 5-methyl furfural as model components.

The quantum chemistry calculations show that both reactants can decompose by a ring-opening isomerization reaction and through carbene intermediates. The latter are formed by the shift of a hydrogen atom or a -CHO functional group within the furan ring structure. The -CHO functional group on the furan ring structure accelerates the molecular ring-opening isomerization reaction, while it suppresses carbene formation channels compared to other functional groups.

The weaker C-H and C-O bonds in 2-furfuryl alcohol and 5-methyl furfural compared to furan and furfural respectively result in a higher importance of radical chemistry that cannot be neglected. This is confirmed experimentally by analyzing the product spectrum with molecular beam synchrotron VUV photoionization mass spectrometry at a pressure of 0.04 bar and for temperatures between 923 K to 1223 K for 2-furfuryl alcohol and 973 K to 1273 K for 5-methyl furfural. For both reactants several radical intermediates are observed starting from 923 K for 2-furfuryl alcohol and from 973 K for 5-methyl furfural. Examples of measured radicals are those initial formed from the reactant by a C-H homolytic bond scission and methyl, allyl, propargyl, 1,2-butadiene-4-yl, 2-furanyl-methyl, 2,5-dihydrofuran-2-yl and 1-hydroxyl-2-furanyl-methyl radicals.

Keywords

Substituted furans, pyrolysis, SVUV-PIMS, radical detection, carbene chemistry

1. Introduction

The pyrolysis of lignocellulose biomass, at elevated temperatures and in the absence of molecular oxygen, produces a complex mixture of liquid organic material called bio-oil. The majority of the lignocellulose biomass is composed of carbohydrates, which produce the largest fraction of the bio-oil with furans as an important class of compounds [1, 2]. Furan, 2-methyl furan, furfural, 2-furfuryl alcohol, 3-furfuryl alcohol and 5-methyl furfural are all important products of fast pyrolysis [3-5]. Many studies have focused on the catalytic upgrading of these furans for the production of fuels and chemicals, but only few have studied their thermal decomposition. The aim of this work is to study the difference in reactivity of various furans caused by the substituents on the furan ring structure. Such knowledge is useful in the development of models for the fast pyrolysis of lignocellulose biomass aiming at improved properties of the produced bio-oil.

For furan [6-9] and furans with alkyl substituents, such as 2-methyl furan [9-13] and 2,5-dimethyl furan [9, 14-17] the thermal decomposition has been studied thoroughly. Some have investigated the thermal decomposition of furfural [18-21]. Studies on other furans with oxygenated substituents, on the other hand, are scarce [22]. Furan is known to react through carbene chemistry. The carbene intermediates are formed after a shift of a hydrogen atom on the furan ring structure. Subsequently, the ring structure reacts to open-chain intermediates that react further to CO, propyne, acetylene and ketene as major products. Furfural was found to react by a ring-opening isomerization reaction to an open-chain intermediate. This intermediate can form 2-pyrone by a concerted cyclization reaction or it can react to furan and CO. At higher temperatures, furan and furfural can also react by radical chemistry. The weak C-H bond in the -CH₃ substituents on 2-methyl furan and 2,5-dimethyl furan cause radical chemistry to dominate the thermal decomposition of these furans.

This work focuses on the thermal decomposition of 2-furfuryl alcohol and 5-methyl furfural and the difference in reactivity, caused by the substituents on the furan ring structure. The molecular decomposition chemistry is studied by performing quantum chemical calculations and by comparing

barrier heights for different furans. To study the importance of radical chemistry, experiments are performed in a tubular reactor with molecular beam sampling and photoionization of the products by synchrotron radiation followed by mass spectrometry. At sufficiently low pressures this technique enables the detection of reactive intermediates, such as radicals. The increased radical stabilization caused by the furan ring structure makes 2-furfuryl alcohol and 5-methyl furfural ideal candidates to gain an understanding of the radical chemistry in this experimental unit. Note that furan and 2-methyl furan pyrolysis have been studied with this technique before [7, 10]. The detection of radicals in these experiments was limited to methyl, propargyl and benzyl radicals, and the radicals directly formed from furan or 2-methyl furan were not reported.

2. Methodology

Quantum chemical calculations

Electronic structure calculations are performed on the high-performance supercomputer at Ghent University at the CBS-QB3 level of theory [23] as implemented in Gaussian 16 [24].

The CBS-QB3 results are used to calculate the heat capacities at different temperatures, the standard entropy and the standard enthalpy of formation. Internal modes are treated as harmonic oscillators except for modes that resemble rotations around single bonds. The latter are approximated by 1-dimensional hindered internal rotations (1D-HIR). All single bonds and bonds in the reactive moiety of the transition state are treated this way as long as the hindrance potential does not exceed 40 kJ mol⁻¹. The hindrance potentials are calculated at the B3LYP/6-31G(d) level of theory with relaxed surface scans. The Fourier series expression of the hindrance potential together with reduced moment of inertia calculated at the I^(2,3) level, as defined by East and Radom [25], are used to construct the Schrödinger equation for 1-dimensional internal rotation. The eigenvalues of the solution are used to determine the partition function as a function of temperature. The thermodynamic data is calculated from the total partition function after correction for the symmetry and the number of optical isomers. The atomization method is applied for the calculation of the enthalpy of formation. The systematic errors of the enthalpy

of formation calculated at the CBS-QB3 level of theory are corrected by applying spin-orbit corrections (SOC) [26] and empirically by applying bond additive corrections (BAC). The BAC used in this work are added to the Supporting Information. Note that the enthalpy values of reactants, products and transition states, used for the construction of potential energy surfaces and to calculate rate coefficients are not SOC and BAC corrected because only relative enthalpies are needed. Moreover, BAC corrections are not defined for transition state bonds. Rate coefficients are determined according to the conventional transition state theory. The regression of modified Arrhenius parameters is done over a temperature range 300–2500 K with 50 K increment. Tunneling is accounted for using the Eckart potential [27].

An overview of the thermodynamic data for stable molecules and transition states and kinetics for these reactions are provided in the Supporting Information. Moreover, ionization energies are calculated for stable species as the negative of the energy of the highest occupied molecular orbital (HOMO). These are used for the identification of isomers and provided as part of the Supporting Information. The effect of Franck Condon interactions is investigated on some main product species at the CBS-QB3 level of theory. The highest observed difference in energy between a vertical and non-vertical excitation is 0.47 eV for 2-furfuryl alcohol. A comparison between the energies is provided in the Supporting Information. It should be noted that, when the experimental ionization energies of radicals are compared to those calculated, no good agreement is achieved. For this reason, ionization energies of radical intermediates are not added to the Supporting Information. For the thermodynamic properties of stable molecules, a comparison is done to experimental data and thermodynamic properties acquired by a theoretical isodesmic approach reported by Simmie et al. [22] Note that the reported thermodynamic values for carbene intermediates and for transition states for reactions that involve these carbene intermediates should be used with caution. For more accurate thermodynamic properties, multiple electronic configurations that might be present in these species and transition states should be accounted for. This can be achieved by performing computationally expensive multi-reference calculations or coupled cluster calculations including triple or even quadruple excitations.

For the calculation of reaction barriers or kinetic parameters, uncertainties associated with thermodynamic data are often canceled out. The accuracy of the CBS-QB3 level of theory on the calculation of kinetic parameters was previously evaluated by Carstensen and Dean for the CO elimination reaction of phenoxy radicals [28]. The influence of the usage of different composite methods on the reaction barriers of furfural decomposition reactions was studied in previous work [21].

Experimental methods

Experiments are performed to study the radical chemistry during pyrolysis of 2-furfuryl alcohol and 5-methyl furfural. The experimental unit consists of a tubular reactor, followed by molecular beam sampling and synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). The detection of radicals with this experimental unit is possible for radicals with a longer life-time, for example due to resonance stabilization. The basic features of the unit and details specific to these experiments are listed below. For a more thorough explanation, the reader is referred to work by Qi et al. [29-31]

The fuel is heated in an electrically heated cylinder filled with quartz beads, mixed with a gaseous flow and fed to the reactor through an electrically heated feed transfer line. The α -Al₂O₃ tubular reactor is heated electrically in the pyrolysis chamber and has an internal diameter of 0.7 cm and a length of 22.0 cm. During previous studies on 2,5-dimethyl furan pyrolysis no catalytic wall effects were found for α -Al₂O₃, as opposed to γ -Al₂O₃ [32]. The total inlet flow rate to the reactor is fixed to 1.0 standard liter per minute (SLM). A movable B-type thermocouple is used to measure the temperature profile at the center of the reactor posterior to experiments in a pure argon environment. The temperature profiles are measured for a set temperature of 773, 1073 and 1373 K. The resulting temperature profiles are provided in the Supporting Information. Temperature profiles for intermediate set temperatures can be determined by interpolation. The reactor and furnace are placed in pyrolysis chamber where the pressure is maintained at 0.04 bar and the temperature at the reactor set temperature. Products are

sampled 10 mm downstream of the reactor outlet to avoid expansion of the nozzle at high temperatures. To account for the additional chemistry between the reactor exit and the sampling point, the temperature profiles are measured from the reactor inlet to the tip of the quartz nozzle. After sampling with the quartz nozzle, the molecules form a molecular beam and are passed into the photoionization chamber. The molecular beam is crossed by the SVUV radiation, the ionized products are separated by their m/z ratio and detected by the TOF-MS [33].

The photoionization cross section (PICS) is measured experimentally for both reactants. For these measurements, the reactor inlet composition equals 0.5 mol% fuel, 97.5 mol% He, used as a diluent, and 2.0 mol% NO, used as a reference for quantification of the PICS [34]. The temperature in the reactor is set to 673 K for 2-furfuryl alcohol and to 773 K for 5-methyl furfural. Both temperatures are below the initial pyrolysis temperature.

The experimental data for the pyrolysis of 2-furfuryl alcohol is measured at 0.04 bar, in a temperature range between 923-1223 K and for a total inlet flow rate of 1.0 SLM with a composition of 1.0 mol% 2-furfuryl alcohol, 98.0 mol% He and 1.0 mol% Kr. The data for the pyrolysis of 5-methyl furfural is measured at 0.04 bar, in a temperature range between 973-1273 K and for a total inlet flow rate of 1.0 SLM with a composition of 1.0 mol% 5-methyl furfural, 98.0 mol% He and 1.0 mol% Kr. The residence time, calculated with the volumetric flow rate and the set temperature and pressure in the reactor, varies between 7.3 ms and 4.8 ms. The temperature is varied in steps of 25 K and the temperature range for both fuels is selected to cover the complete conversion range. The photon energies used for ionization are scanned over a set of pre-defined energies. These energies are carefully selected to distinguish isomers.

Ion intensities measured by the TOF-MS are subsequently used to calculate mole fractions for the main products. The correlation between the ion signal and the species mole fractions as proposed by Cool et al. [35] and extended by Li et al. [36] was used. The relative uncertainty on the mole fractions calculated by this method is 10% for the major products, 25% for the minor products and a factor 2

for species with an unknown PICS. Note that the uncertainty becomes larger in case isomers of the fuel overlap with the fuel signal.

3. Results

Quantum chemical calculations

A first indication for the relative importance of molecular and radical chemistry during the thermal decomposition is given by the bond dissociation energy of the weakest bonds in furans. Once there is sufficient energy to break one of the bonds, radical chemistry will be dominant as the barriers for hydrogen abstraction reactions and radical addition reactions are typically much lower compared to molecular channels. The bond dissociation energy calculated at the CBS-QB3 level of theory for the weakest C-C, C-O or C-H bonds in furan, 2-methyl furan, furfural, 2-furfuryl alcohol and 5-methyl furfural are provided in Figure 1.

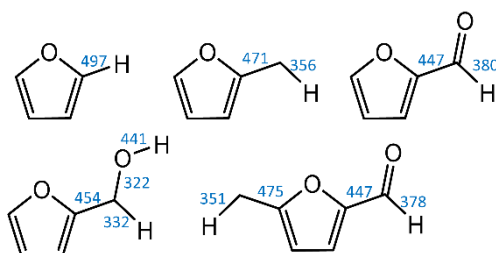


Figure 1. Bond dissociation energies of the weakest bonds in furan, 2-methyl furan, furfural, 2-furfuryl alcohol and 5-methyl furfural calculated at the CBS-QB3 level of theory. Values are indicated in blue and the units are kJ mol⁻¹.

The weakest bond in 2-furfuryl alcohol is the C-O alkoxy bond with a bond dissociation energy equal to 322 kJ mol⁻¹. The weakest C-H bond in 2-furfuryl alcohol, has a bond strength equal to 332 kJ mol⁻¹. For 5-methyl furfural, the bond strength of the C-H bond in the methyl group equals 351 kJ mol⁻¹, very similar to the C-H bond in the methyl group in 2-methyl furan. The C-H bond strength in the aldehyde substituent is equal to 378 kJ mol⁻¹ and similar to the weakest bond in furfural.

It should be noted that both 2-furfuryl alcohol and 5-methyl furfural have weaker bonds compared to furan and furfural. Hence, it is expected that radical chemistry will kick in at lower temperatures. The

relative importance of radical and molecular chemistry also depends on the barriers for initial molecular decomposition channels.

From previous studies on the pyrolysis of furans, it is known that unimolecular decomposition can occur through a ring-opening isomerization reaction or through carbene intermediates. The former channel was found to be the most important for furfural pyrolysis, while carbene intermediates dominate the furan decomposition and contribute to the decomposition of 2-methyl furan. Similar pathways are calculated for the thermal decomposition of 2-furfuryl alcohol and 5-methyl furfural. A selected part of the potential energy surface with channels that have the lowest energy barriers is given in Figure 2 for 2-furfuryl alcohol (left) and 5-methyl furfural (right). It should be noted that in some cases cis/trans isomers can appear in the transition state or can be formed as products. In that case, for simplicity of the figure, only the energy of the trans isomer is presented.

The barrier for the ring-opening isomerization of 2-furfuryl alcohol is 324 kJ mol^{-1} . The formed open-chain isomer, **(1)** in Figure 2, can subsequently undergo (i) a dehydration reaction, (ii) a dehydrogenation reaction, (iii) a keto-enol tautomerization and (iv) a concerted cyclization reaction. The dehydrogenation reaction has the highest barrier (359 kJ mol^{-1}), followed by the dehydration reaction (332 kJ mol^{-1}) and the keto-enol tautomerization (240 kJ mol^{-1}). The concerted cyclization, clearly has the lowest barrier (72 kJ mol^{-1}) and leads to the formation of 2-pyranol.

Three different carbenes can be formed from 2-furfuryl alcohol, indicated by the numbers **(2)** to **(4)** in Figure 2. The initial carbene formation channels have barriers equal to 277, 295 and 289 kJ mol^{-1} . The formed carbenes can react further to open-chain intermediates. Subsequent decarbonylation, dehydration and dehydrogenation reactions all have barriers higher than the reverse cyclization to the carbene intermediate and are therefore omitted in Figure 2.

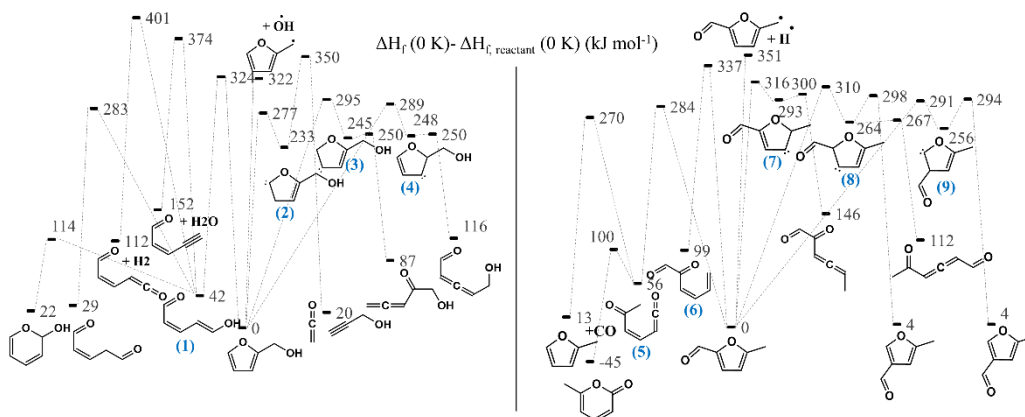


Figure 2. Potential energy surface of 2-furfuryl alcohol (left) and 5-methyl furfural (right). Values are $\Delta H_f(0K)$ relative to the $\Delta H_f(0K)$ of the reactant calculated at the CBS-QB3 level of theory in kJ mol^{-1} .

Two ring-opening isomerization channels are possible for 5-methyl furfural, shown in Figure 2 (right). The first one involves a hydrogen shift from the $-\text{CH}_3$ substituent. The barrier for this channel is 337 kJ mol^{-1} and the resulting product is indicated by number (6) in Figure 2. Another ring-opening isomerization with a hydrogen shift from the $-\text{CHO}$ substituent results in the intermediate indicated by number (5) in Figure 2. The barrier for this second channel is much lower and equal to 284 kJ mol^{-1} . Intermediate (5) can react further through a concerted cyclization reaction to 6-methyl-2-pyrone. This cyclic product, is 45 kJ mol^{-1} more stable compared to 5-methyl furfural. Alternatively, decarbonylation and cyclization of intermediate (5) results in the formation of CO and 2-methyl furan. Two carbene intermediates, numbers (7) and (8) in Figure 2, can be formed by a hydrogen shift reaction in 5-methyl furfural. Additionally, a $-\text{CHO}$ group shift leads to the formation of a third carbene, number (9) in Figure 2. The barrier for the formation of the carbene intermediates are 316, 310 and 291 kJ mol^{-1} respectively. A shift of a $-\text{CHO}$ function group from carbene intermediates (8) and (9) in Figure 2 results in the formation of 5-methyl-3-furaldehyde, which is only 4 kJ mol^{-1} less stable compared to 5-methyl furfural.

Experimental SVUV-PIMS results

The thermal decomposition of 2-furfuryl alcohol and 5-methyl furfural is studied experimentally at 0.04 bar. Low pressures are used to aim at the detection of radicals, but also mole fractions of stable

products are calculated. The mole fractions of major products as a function of temperature can be found in the Supporting Information. For the calculation of the species mole fractions, the PICS of the reactants are determined experimentally and product PICS are determined from an online database [37].

It should be noted that, although the SVUV-PIMS technique is known for its superior isomer detection compared to other ionization techniques, this might not hold for isomers of the reactant. For both molecules studied in this work, especially for 5-methyl furfural, isomers of the reactant are expected as part of the product spectrum. For proper quantification of all isomers (1) the mole fractions of the isomers need to be of a similar order of magnitude and (2) the ionization energies of the isomers need to be substantially different. For 5-methyl furfural, 6-methyl-2-pyrone and 2-methyl-4-furaldehyde, the ionization energies are 8.86, 8.93 and 9.00 eV respectively. These small differences in ionization energy do not allow the individual detection of isomers. The product mole fractions are calculated relative to the reactant mole fraction, whose signal cannot be separated from the isomer signals, hence these can influence the results for all products.

At 1023 K and 0.04 bar, the onset of pyrolysis is observed experimentally with 5% 2-furfuryl alcohol conversion. The product formed with the highest mole fraction is CO, with an increasing trend as a function of temperature. Other major products include acetylene, water, but-1-yn-3-ene with the highest mole fractions, ethylene, propyne, 1-butyne as other major hydrocarbons and formaldehyde, furan, furfural as other major oxygenates. Minor products include methane, propadiene, diacetylene, cyclopentadiene, benzene, ketene, methyl ketene, vinyl ketene and cyclopentadienone. As the PICS of vinyl ketene is unknown, similarities to the PICS of ketene and methyl ketene are used for the determination of the product mole fraction.

At 0.04 bar and 1023 K or 5% 2-furfuryl alcohol conversion, the partial mass spectrum measured at 7.9 eV is used to detect radicals. The mass spectrum is given in Figure 3 (left). For 2-furfuryl alcohol, six radicals are observed at $m/z = 39, 41, 53, 69, 81$ and 97 . The most probable radicals for the respective m/z ratios are indicated on the figure. Only for a few radicals, experimentally measured

PICS are available from the online database [37]. Because of the unknown cross sections for most of the radicals detected in this work, their mole fractions are not calculated. The profiles of the ion signal relative to the gas expansion factor as a function of temperature are given in Figure 3 (right). All radicals are initially formed between 923-973 K. The radical profiles as a function of temperature have a peak around 1048 K. The ion signals have the same shape and order of magnitude for all six radicals initially formed, except for propargyl radical which has an increasing trend at higher temperatures. The highest ion signal intensities are measured for allyl and 2-furanyl-methyl radicals, followed by 1,2-butadiene-4-yl and 2,5-dihydrofuran-2-yl radicals. Slightly lower ion signal intensities are measured for propargyl and 1-hydroxyl-2-furanyl-methyl radicals.

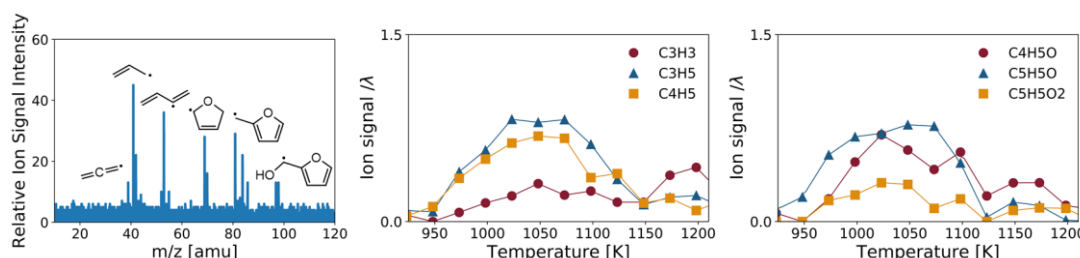


Figure 3. Left: Mass spectrum measured during the pyrolysis of 2-furfuryl alcohol at 7.9 eV and 1023 K (5% 2-furfuryl alcohol conversion) Right: Ratio of ion signals of radicals to the gas expansion factor as a function of temperature.

At 1073 K and 0.04 bar, 6% 5-methyl furfural conversion is observed experimentally. CO is the main product formed during pyrolysis, while 1-butyne has the second highest product mole fraction, followed by 2-methyl furan. It should be noted that two of the major products, CO and 2-methyl furan, were expected as major products from the quantum chemical calculations. Other major products are methane, acetylene, propyne, but-1-yn-3-ene and ketene. Minor hydrocarbon products include ethylene, propadiene, diacetylene, 1-butyne, cyclopentadiene, benzene and minor oxygenated products are CO₂, formaldehyde, methyl ketene, vinyl ketene, furan, furfural and 2,5-dimethylfuran.

The partial mass spectrum measured at 1073 K, 6% 5-methyl furfural conversion, 0.04 bar and 7.9 eV is used to study the radicals formed. The partial mass spectrum and the most probable radicals associated with the m/z ratio are presented in Figure 4 (left). The ratio of the relative ion signals to the

gas expansion factor of the radicals are plotted as a function of temperature in Figure 4 (right). Methyl radicals are detected but not present in the partial mass spectrum at 7.9 eV as they have a higher ionization energy of 9.84 eV. The measurements at 10.35 eV are used for the determination of the relative ion signal of this radical. The highest ion signals are measured for the radical directly formed from the 5-methyl furfural and 1,2-butadiene-4-yl radicals. The highest radical intensities are measured at 1023 K, after this temperature, the radical ion signals decrease. The same profile is observed for 2-furanyl-methyl radicals, but the signal intensity is slightly lower. Other radicals that have a relative ion signal one order of magnitude lower are methyl, propargyl, vinyloxy and furfuraoyl radicals.

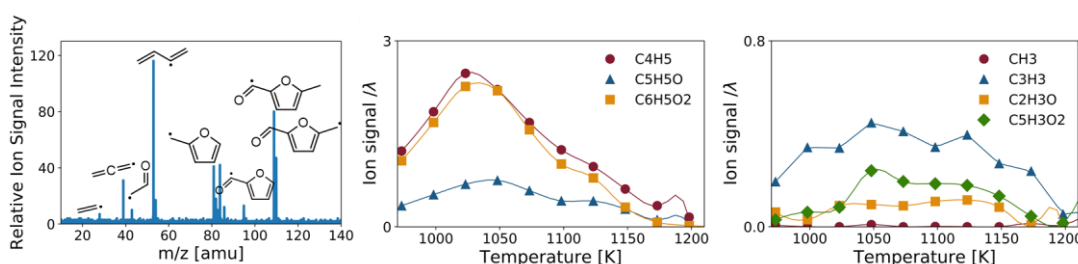


Figure 4. Left: Mass spectrum measured during the pyrolysis of 5-methyl furfural at 7.9 eV and 1073 K (6% 5-methyl furfural conversion) Right: Ratio of ion signals of radicals to the gas expansion factor as a function of temperature.

4. Discussion

The chemistry for the decomposition of furans is strongly dependent on the functional groups on the furan ring. The dominating chemistry can be either through carbene intermediates (e.g. furan), be of radical nature (e.g. 2,5-dimethyl furan) or even molecular (e.g. furfural). For the thermal decomposition of 2-furfuryl alcohol and 5-methyl furfural our quantum chemical calculations show the importance of the ring-opening isomerization and pathways through carbene intermediates, while the experimental results show the formation of radicals already at temperatures of 923 K for 2-furfuryl alcohol and 973 K for 5-methyl furfural.

Unimolecular (non-radical) chemistry

During the ring-opening isomerization reaction, the furan ring structure opens while a hydrogen atom is transferred from a $-CH_3$, $-CH_2OH$ and $-CHO$ functional group to the furan ring structure. For 2-furfuryl alcohol the barrier height is 324 kJ mol^{-1} . During this reaction, intermediate (1) in Figure 2 is formed. The barrier is similar to the bond dissociation energy of the weakest bond in 2-furfuryl alcohol of 322 kJ mol^{-1} . Within 5-methyl furfural, the barrier heights for both ring-opening isomerization reactions are below the bond dissociation energy of the weakest bond (351 kJ mol^{-1}). The lowest barrier (284 kJ mol^{-1}) is for the ring-opening isomerization involving a hydrogen shift from the $-CHO$ group which forms intermediate (5) in Figure 2. The barrier for this channel is close to the one for the similar reaction in furfural decomposition (291 kJ mol^{-1}). The open-chain product of the ring-opening isomerization reaction can react to 6-methyl-2-pyrone, 2-methyl furan and CO. The latter two were experimentally observed as major products, an indication of the importance of this channel during the decomposition of 5-methyl furfural. Unfortunately, SVUV-PIMS does not allow the detection of 6-methyl-2-pyrone, as it is an isomer of the reactant with similar ionization energy. The difference in ionization energy of both species is calculated to be 0.07 eV , which is too low to distinguish isomers. The second ring-opening isomerization involves a hydrogen shift from the methyl substituent. The barrier for this reaction is 337 kJ mol^{-1} and the reaction leads to the formation of intermediate (6) in Figure 2.

The formation of carbene intermediates from 2-furfuryl alcohol occurs by a hydrogen shift reaction within the furan ring structure. The formed carbenes are indicated by numbers (2) to (4) in Figure 2. The barriers for these reactions are similar to those found for carbene formation in furan (280 kJ mol^{-1} and 295 kJ mol^{-1}), but lower compared to the ring-opening isomerization and compared to the lowest bond dissociation energy in 2-furfuryl alcohol. Carbene formation in the case of 5-methyl furfural can proceed through a hydrogen shift or a shift of the $-CHO$ functional group leading to intermediates (7) to (9) in Figure 2. Compared to furan and 2-furfuryl alcohol the barrier heights for the formation of carbene intermediates are $10\text{-}20 \text{ kJ mol}^{-1}$ higher. A similar observation was made for carbene formation

starting from furfural. Nevertheless, because the carbenes (8) and (9) in Figure 2, can react further to 5-methyl-3-furaldehyde, it is expected that this channel will have a non-negligible contribution to the overall thermal decomposition of 5-methyl furfural. Unfortunately, the 5-methyl-3-furaldehyde signal could not be distinguished from the 5-methyl furfural signal detected with SVUV-PIMS as it is an isomer of the reactant with a similar ionization energy.

From the quantum chemical calculations, it can be concluded that the -CHO substituent lowers the barrier for the ring-opening isomerization compared to -CH₂OH and -CH₃ substituents, even though the latter two substituents have weaker C-H bond strengths. On the other hand, the presence of the -CHO substituent destabilizes the formation of carbene intermediates compared to furan, while the presence of -CH₂OH and -CH₃ substituents have a negligible influence on barrier heights for carbene formation.

Radical chemistry

The thermal decomposition of furan and furfural is known to proceed mainly through molecular chemistry at lower temperatures. The weakest bonds in these furans have a bond dissociation energy equal to 497 kJ mol⁻¹ and 380 kJ mol⁻¹ respectively. On the contrary, 2-furfuryl alcohol and 5-methyl furfural can form resonantly stabilized radicals after scission of a C-H or C-O bond. The weakest bonds in the reactants have bond dissociation energies of 322 and 351 kJ mol⁻¹ respectively. This is similar to 2-methyl furan, where the weakest C-H bond has a bond dissociation energy of 356 kJ mol⁻¹. 2-Methyl furan is known to decompose mainly by radical chemistry. As demonstrated by the experimental results in this work, radical chemistry is indeed important at the lowest measured temperatures for the studied reactants. For 2-furfuryl alcohol, the radicals formed by homolytic C-H scission or C-O scission of the weakest bonds in the reactant are observed experimentally. For 5-methyl furfural, the radical formed by homolytic C-H scission of the weakest bond in the reactant is detected. From the quantum chemistry calculations, 2-methyl furan is expected to be one of the main initial decomposition products during 5-methyl furfural pyrolysis. Also the radical formed by

homolytic C-H scission of the weakest bond in 2-methyl furan is observed experimentally. Besides the detection of these reactive intermediates, also the presence of water during 2-furfuryl alcohol pyrolysis and methane during 5-methyl furfural pyrolysis are an indication of the importance of radical chemistry. Although water can be formed through dehydration reactions, hydrogen abstraction reactions by hydroxyl radicals are expected to be the main source of water, while hydrogen abstraction reactions by methyl radicals are responsible for methane formation.

5. Conclusions

The non-radical (molecular) and radical decomposition chemistry of 2-furfuryl alcohol and 5-methyl furfural has been studied in a combined quantum chemical and experimental study.

The presence of the –CHO substituent accelerates the ring-opening isomerization reaction compared to –CH₃ and –CH₂OH substituents, despite the higher bond strength of the transferred hydrogen atom. Carbene intermediates are primarily formed by a hydrogen shift reaction or by the shift of a –CHO substituent. Barriers for carbene chemistry compared to furan are hardly influenced by the presence of a –CH₃ or –CH₂OH substituent. The –CHO substituent, on the other hand suppresses the hydrogen shift reaction, resulting in higher barriers for the carbene channels.

The weak C-H or C-O bond dissociation energies in 2-furfuryl alcohol and 5-methyl furfural are a first indication that also the importance of radical chemistry cannot be neglected. This is supported by experimental measurements of radical intermediates with SVUV-PIMS. During the experiments, for 2-furfuryl alcohol, six radicals are detected at a temperature of 1023 K (5% conversion). For the decomposition of 5-methyl furfural, seven radicals are detected at 1073 K (6% conversion). Three of those have a higher ion signal intensity compared to the others.

The alcohol functionality and the weak bond strengths make that radical pathways are favored for the decomposition of 2-furfuryl alcohol. For 5-methyl furfural, both radical and molecular decomposition channels are important.

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Supporting Information

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