Understanding the reactivity of unsaturated alcohols: Experimental and kinetic modeling study of the pyrolysis and oxidation of 3-methyl-2-butenol and 3-methyl-3-butenol

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ABSTRACT

The reactivity of unsaturated alcohols with a C=C double bond in the β- and γ-positions to the hydroxyl group is not well established. The pyrolysis and oxidation of two such unsaturated alcohols have been studied, i.e. 3-methyl-2-butenol (prenol) and 3-methyl-3-butenol (isoprenol). Experiments at three equivalence ratios, i.e. $\varphi = 0.5$, $\varphi = 1.0$ and $\varphi = \infty$ (pyrolysis), were performed using an isothermal jet-stirred quartz reactor at temperatures ranging from 500 to 1100 K, a pressure of 0.107 MPa and a residence time of 2 s. The reactant and product concentrations were quantified using gas chromatography. A kinetic model has been developed using the automatic network generation tool "Genesys". Several important rate coefficients are obtained from new quantum chemical calculations. Overall, there is a good agreement between model calculated mole fraction profiles and experimental data. Reaction path analysis reveals that isoprenol consumption is dominated by a unimolecular reaction to formaldehyde and isobutene. At the applied operating conditions, the equivalence ratio has no effect on the isoprenol conversion profile. Pyrolysis and oxidation of prenol is dominated by radical chemistry, with hydrogen abstractions from prenol forming resonantly stabilized radicals as dominating conversion path. Oxidation and decomposition of the resulting radicals are predicted to form 3-methyl-2-butenal and 2-methyl-1,3-butadiene, which have been detected as important products in the reactor effluent.

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1. Introduction

Alcohols are attractive alternative fuels as they can be produced from renewable feedstocks and as their combustion leads to reduced levels of NO_x and soot in the exhaust compared to traditional fossil fuels [1]. Ethanol is a first generation bio-derived fuel and the current biofuel market leader. Disadvantages of ethanol, including high hygroscopicity and low energy density, and novel alcohol-production routes from cellulosic biomass have triggered fundamental research towards understanding the combustion chemistry of larger alcohols, i.e. alcohols having 4 or more carbon atoms. Longer chain alcohols have improved physical properties compared to ethanol. Recent experimental and detailed kinetic modeling studies have highlighted that combustion of such alcohols results in a wide range of products, including ketones, aldehydes and unsaturated alcohols [1–8]. Unsaturated alcohols

are important intermediates and understanding their reactivity is of interest to improve kinetic models for alcohol combustion [1]. Besides being intermediates unsaturated alcohols themselves can be considered next-generation bio-derived fuels for spark-ignition combustion engines. Recently, several groups proposed metabolic engineering of Escherichia coli for the highly selective production of prenol and isoprenol from glucose [9,10].

Unsaturated alcohols have both a hydroxyl group and a C=C double bond incorporated in their molecular structure. The individual effect of either type of functional group has been investigated previously. The presence and position of a hydroxyl group has an impact on the reactivity of the molecule. Ignition delay times are typically higher for alcohols compared to the analogous alkanes at low temperatures (<750 K) while they are lower at high temperatures (<1000 K) [11]. The difference in ignition delay times diminishes as the length of the alkyl chain increases [5,11]. The hydroxyl group in alcohols changes the bond dissociation energies (BDE) of nearby C–C and C–H bonds compared to the analogous alkanes [12, 13]. Those BDE changes have an impact on, e.g. the rate coefficients of hydrogen abstraction reactions, the main consumption channels

a

b
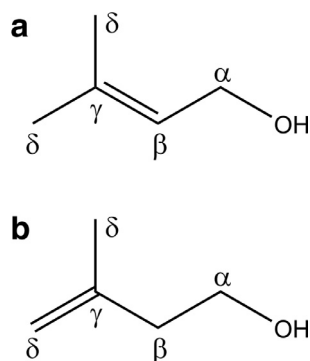
Fig. 1. Molecular representation of prenol (a) and isoprenol (b). Greek letters are atom labels which will be used throughout this work.

of fuels in combustion and pyrolysis. In alcohols, hydrogen abstraction reactions from the α-carbon are favored and the resulting radicals react at oxidizing conditions mainly with molecular oxygen forming an aldehyde and a hydroperoxy radical [14–16], which is rather unreactive at low temperature.

The presence and position of a C=C double bond in hydrocarbons and its effect on combustion characteristics has been investigated previously [17–19]. The C–H bond of the carbon atom in the α-position to the C=C bond and the C–C bond between the carbon atoms in α and β-positions are weak as scission leads to resonantly stabilized radicals [17]. The resonance stabilization in these radicals is lost upon addition of molecular oxygen, important for autoignition and chain branching at low temperatures, and redissociation of the adduct to the initial reactants is therefore a major reaction channel [20]. The low-temperature reactivity of alkenes is reduced compared to alkanes [19].

Studies regarding the combined effect of both a hydroxyl group and a C=C double bond on the reactivity of a molecule have focused on enols [21]. Enols are unsaturated alcohols of the general structure RC=C(R)OH, where a hydroxyl group is attached to a vinylic carbon atom. In the pyrolysis and oxidation of saturated alcohols, they are produced by hydrogen abstraction from the carbon atom in alpha position of the hydroxyl group followed by subsequent β-scission [1]. They are also formed in the oxidation of hydrocarbons [21,22], for example $C_2H_4 + \cdot OH \rightleftharpoons \cdot CH_2CH_2OH \rightleftharpoons CH_2=CHOH + \cdot H$ [23] and $C_3H_6 + \cdot OH \rightleftharpoons CH_3 \cdot CHCH_2OH \rightleftharpoons CH_3CH=CHOH + \cdot H$ [24,25]. Enols may isomerize to their corresponding aldehydes by keto-enol tautomerization, which is catalyzed by hydrogen atoms, hydroperoxy radicals [26] and carboxylic acids [27] in the gas phase.

In the past, the reactivity of unsaturated alcohols, in which the hydroxyl group is separated from the C=C double bond by one or more carbon atoms, has not received much attention except for studies that focused at atmospheric or low-pressure conditions [28]. Recently, Welz et al. investigated the oxidation of 3-methyl-2-buten-1-ol (prenol) and 3-methyl-3-buten-1-ol (isoprenol), see Fig. 1, at 550 K and low pressure (8 Torr) [29]. In their experiments, chlorine atoms, which were generated from Cl_2 by pulsed laser photolysis, abstract hydrogen from prenol and isoprenol. The radicals reacted with oxygen and the product spectrum was analyzed using multiplexed synchrotron photoionization mass spectrometry. The main products during prenol and isoprenol oxidation were the corresponding aldehydes, 3-methyl-2-butenal and 3-methyl-3-butenal respectively. The formation of these aldehydes was supported mechanistically with quantum chemical calculations. The reactions $C=C(C)CC\cdot OH + O_2 \rightleftharpoons C=C(C)CC(OO\cdot)OH \rightleftharpoons C=C(C)CC=O + HO_2\cdot$ and $CC(C)=CC\cdot OH + O_2 \rightleftharpoons CC(C)=CC(OO\cdot)OH \rightleftharpoons CC(C)=CC=O + HO_2\cdot$ are the only energetically accessible reaction paths starting from the prenol and isoprenol radicals with O_2.

Welz et al. concluded that unsaturated alcohols have reduced low-temperature reactivity compared to saturated alcohols, similar to unsaturated and saturated methyl esters [30].

This work aims at providing a better understanding of the reactivity of unsaturated alcohols in which the double bond is separated from the hydroxyl group by one and two carbon atoms. An extensive experimental dataset was obtained for the oxidation and pyrolysis of prenol and isoprenol in a dedicated jet-stirred reactor. Furthermore, a kinetic model was developed with the automated network generation code Genesys [31]. Several high level theoretical calculations were conducted to describe special reactions that could not be treated automatically. The model calculated mole fraction profiles were compared with the newly obtained experimental data and important reactions were identified. The developed kinetic model should be helpful to improve existing kinetic models for the oxidation and pyrolysis of saturated alcohols.

2. Experimental setup and procedure

The applied experimental setup has been extensively described by Herbinet and coworkers [32–34] and only the main features are summarized below. The interested reader is referred to the aforementioned literature for additional information. The setup consists of three parts: feed section, reactor section and analysis section.

The feed section ensures a stable, continuous stream of helium, oxygen and prenol or isoprenol to the reactor. Helium and oxygen were provided by Messer (purities of 99.99% and 99.999%, respectively). Their flow rates to the reactor were controlled using two gas-mass-flow controllers. Prenol and isoprenol were provided by Sigma Aldrich (purity of 98%). The flow rate to the reactor was controlled using a liquid-Coriolis-flow-controller. The liquid flow was mixed with helium and passed through an evaporator. The fuel/helium blend was subsequently mixed with oxygen. Prior to entering the reactor, the gaseous mixture is heated to the reactor temperature in an annular pre-heating zone. Heating is provided by Thermocoax resistance wires. The residence time in this zone is short compared to the residence time in the reactor.

The reactor is a spherical jet-stirred reactor made out of quartz. The reactive mixture enters the reactor through four nozzles, positioned in the center of the reactor. The nozzles were designed to ensure thermal homogeneity and avoid concentration gradients inside the reactor. Heating of the reactor is again provided by Thermocoax resistance wires. The reaction temperature is measured by a type K thermocouple positioned in a glass finger in the center of the reactor. The uncertainty on the temperature reading is approximately 5 K. The pressure in the reactor is controlled using a needle valve positioned downstream of the reactor.

The reactor effluent was analyzed using three dedicated gas chromatographs. The first gas chromatograph is equipped with a thermal conductivity detector and a Carbosphere packed column. It was used to quantify O_2, CO and CO_2. The second gas chromatograph is equipped with a flame-ionization detector and a PlotQ capillary column. The flame-ionization detector was preceded by a methanizer to detect CO, CO_2 and formaldehyde with improved sensitivity. This gas chromatograph was used to quantify molecules containing up to five carbon atoms. The third gas chromatograph is equipped with a flame-ionization detector and a HP-5MS capillary column for quantifying molecules containing at least five carbon atoms. Response factors for O_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, CH_2O, prenol, isoprenol, benzene and toluene were determined by injecting calibration mixtures. Response factors for other species were determined using the effective carbon number method.

The exit of the reactor is connected with the aforementioned gas chromatographs through heated transfer lines kept at 473 K to avoid condensation. Online sampling allowed to obtain