Decomposition and isomerization of 1-pentanol radicals and the pyrolysis of 1-pentanol

Ruben Van de Vijver [a],[1], Kevin M. Van Geem [a], Guy B. Marin [a], Judit Zádor [b],*

[a] *Laboratory for Chemical Technology, Ghent University, Ghent, Belgium*
[b] *Combustion Chemistry Department, Sandia National Laboratories, Livermore, CA, USA*

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ABSTRACT

Stable species and saddle points on the $C_5H_{11}O$ potential energy surface relevant for 1-pentanol pyrolysis and combustion have been determined starting from the terminal adduct of the $OH + 1$-pentene reaction. A large number of stationary points were explored automatically with the KinBot software at the M06-2X/6-311++G(d,p) level. The kinetically relevant stationary points have been further characterized using UCCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G(d,p) quantum chemistry calculations. The entrance channel consists of a barrierless outer transition state leading into a van der Waals well followed by a submerged saddle point, overall described with an effective two-transition-state model. The master equation has been solved to obtain pressure- and temperature-dependent rate coefficients for all reactions on the potential energy surface in the 300–2500 K temperature range and 0.01–100 atm pressure range. The newly obtained rate coefficients have been implemented in a kinetic model for the thermal decomposition of 1-pentanol diluted in a nitrogen stream. We measured the conversion of major species using gas chromatography with a flame ionization detector, and two-dimensional gas chromatography with time-of-flight mass spectrometric and flame ionization detectors in the effluent of a flow reactor at 0.17 MPa between 913 and 1023 K. Comparison of the simulated versus the experimental data acquired in this work shows that the reactions found by KinBot, for which earlier only poor estimates existed, are of significant importance to correctly describe conversion and product selectivities. It proves to be possible to generate adequate chemical models automatically provided that the underlying high-level ab initio data is computationally affordable.

1. Introduction

The demand for alternative fuel and base chemical resources are driven by the increasing worldwide energy needs and the efforts to reduce greenhouse gas emission. Many studies have reported industrial, experimental, and theoretical results on feedstocks derived from non-fossil processes, among which urban waste and biological feedstocks are the most promising [1,2]. Primary alcohols have already been considered for decades as sustainable fuels; ethanol, a first generation biofuel, is a widespread substitute for conventional diesel [3]. Other alcohols, such as propanol and *n*- and *iso*-butanol, gained significant interest in the past for their higher energy density, higher cetane numbers and lower hygroscopicity [4–9] compared to ethanol. To increase the energy content even more, the second-generation biofuel

1-pentanol is now extensively studied: its performance in engines has been studied to minimize the CO, hydrocarbon, NOx, smoke [10,11], and particulate emissions [12], to understand its mixing characteristics [13], and to optimize the cetane number [14] of a pentanol/diesel blend. Experimental and modeling work on the combustion properties of 1-pentanol such as laminar flame speeds [15,16] and ignition characteristics [17] have been also reported.

Optimizing a chemical process, such as combustion or pyrolysis requires the quantitative characterization of the details of the underlying chemistry. Alternative feedstocks have fundamentally different chemical composition and properties compared to fossil resources, and the growing experimental database characterizing the fundamental chemical and combustion properties of these feedstocks is the first step towards optimal chemical processes. However, experimental investigations are expensive, time-consuming, and have several constraints on operating conditions and reactor configurations. Therefore, engineering approximations and computer simulations developed by chemists and chemical engineers complementing the experimental probes are crucial in allowing di-

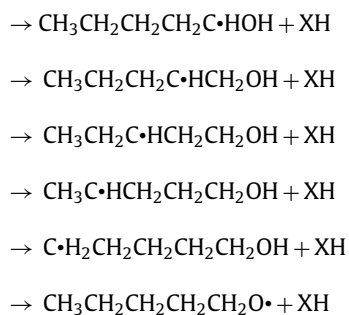rected experimental design and in lowering the cost and time of the process development.

A fundamental part of the computer simulation-aided optimization of chemical processes is the chemical kinetic model consisting of a set of rate expressions of the reactions involved. Kinetic models for thermal decomposition, steam cracking, and combustion processes can contain thousands of reactions, for which most of the rate coefficients have never been measured experimentally. Estimation methods are the main fallback in the case of data shortage, but the accuracy of these procedures beyond the training set they were developed on is poor or at least not well known. At the same time, with the growing computational power and availability of high-performance computing solutions, many rate coefficients can be now calculated using *ab initio* methods accurately enough to be used in these chemical models. However, characterizing all species and their reactions through high level quantum chemistry calculations is also time consuming with current technologies, because (1) many manual interventions are necessary, (2) even for small molecules, finding all the reaction pathways is tedious and pathways can easily be overlooked, (3) locating transition states sometimes needs to be done on a trial-and-error basis, and (4) systematic conformational searches by hand become practically impossible for molecules with several torsional modes. To circumvent a large part of these time-consuming tasks and ensure a full exploration of the potential energy surface (PES) for the purposes of kinetics calculations, automated approaches are being developed (e.g., Refs. [18–22]). One of them is the computer code called KinBot [23], which has been successfully used for several systems already [22,24–26].

In this work, we have studied the pyrolysis of pentanol, with special emphasis on some of the initial steps. During the pyrolysis of pentanol the first radicals appear when the C–C, C–O, C–H, or O–H bonds break, and while these initial homolytic unimolecular dissociation reactions of the fuel molecule continue to be important as long as the fuel is still present in significant concentration, after a short induction period the chemistry is largely driven by abstraction reactions mostly by $X = H$, CH_3, OH under practically relevant conditions. These abstraction reactions yield six different 1-pentanol radicals:

$$CH_3CH_2CH_2CH_2CH_2OH + X$$

$$\rightarrow CH_3CH_2CH_2CH_2C\bullet HOH + XH$$

$$\rightarrow CH_3CH_2CH_2C\bullet HCH_2OH + XH$$

$$\rightarrow CH_3CH_2C\bullet HCH_2CH_2OH + XH$$

$$\rightarrow CH_3C\bullet HCH_2CH_2CH_2OH + XH$$

$$\rightarrow C\bullet H_2CH_2CH_2CH_2CH_2OH + XH$$

$$\rightarrow CH_3CH_2CH_2CH_2CH_2O\bullet + XH$$

which are the main subjects of this work. Note that we will not mark the radical site of the structures in the rest of the paper, and will denote the formed radicals in order as α-R, β-R, γ-R, δ-R, ε-R, and o-R, alluding to the location of the radical site.

While directly determined parameters for the unimolecular reactions of smaller alcoholic radicals are available in the literature, the information on the decomposition reactions of the radicals from 1-pentanol only consist of estimates or values derived from indirect or relative experiments. The unimolecular decomposition of β-R is known to primarily lead to OH + 1-pentene, but only the reverse reaction has been investigated directly. Nip and Paraskevopoulos [27], Biermann et al. [28], and McGillen et al.

[29] measured the absolute rate coefficient of the OH + 1-pentene reaction around room temperature, and the study of McGillen et al. also determined the temperature dependence of the rate coefficient in the 262–312 K range. These values are only of limited use in combustion simulations, for three reasons. First, the addition of OH to 1-pentene leads to a mixture of β-R and 2-hydroxy-1-propyl (addition to the second carbon) adducts, while for 1-pentanol pyrolysis only the terminal adduct, β-R, is relevant. Second, some fraction (according to Biermann et al. [28] it is ∼13%) of the reaction proceeds via abstraction even at room temperature. And finally, the temperature range at which these experiments were carried out is outside the range of interest for pyrolysis studies. Nevertheless, some comparison can be made with these experiments. There are two studies that determined the unimolecular dissociation and isomerization rate coefficients for ε-R: the indirect determination of Heimann et al. [30], and the direct one of Hein et al. [31]; however, they were only able to put a lower limit on the isomerization rate coefficient. No direct experimental information on the kinetics of the other radicals is available in the literature.

The Ab Initio Transition State Theory Master Equation (AITSTME) approach has been successfully used in the past to study the decomposition and isomerization reactions of smaller alcohol radicals up to C_4 [25,32–36]. Here we want to extend the same methodology to the 1-petanol radicals and calculate AITSTME-based pressure- and temperature-dependent rate coefficients for 1-pentanol radical decomposition and isomerization at the UCCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G(d,p) level of theory. To aid the exploration of the potential energy surface and the calculation of the large number of molecular parameters, we employ KinBot to explore and characterize the relevant stationary points. We also summarize trends for radical decompositions in this class of reactions, and compare our calculations to state-of-the-art rate rule estimates of the automatic kinetic model generator Genesys [37]. Finally, we use our calculated rate coefficients to update a Genesys-generated chemical mechanism for 1-pentanol pyrolysis and compare it against our own flow reactor experimental results.

2. Methods

2.1. Theoretical kinetics

A large number of the known reaction types for hydrocarbon and oxygenate species have been translated into automatic procedures in the KinBot code [22,23]. KinBot builds on the idea that most reactions can be classified into broad and generic reaction types. Each reaction type in KinBot is characterized by a 3-D template that determines the structure of the "reaction center." The premise of the approach in KinBot is that there are relatively few templates [22], and that they are largely independent of the molecular structures outside the reaction centers. For instance, a 5-member H-atom transfer reaction's reactive center in KinBot consists of the four heavy atoms and the transferred H atom, which form a particular non-planar pentagon. The approximate geometry of this pentagon is largely independent of the nature and order of the heavy atoms (C and O atoms currently), and their possible side-chains. The templates are used in KinBot to translate the structure of the reactant into the geometrical structure of the transition state guess. These template-driven guesses are then optimized to the true saddle points using the robust saddle-point finding algorithm of Gaussian, such as the Berny algorithm [38,39]. KinBot has a number of templates built from available chemical knowledge on possible reactions for hydrocarbons and oxygenate molecules, based on which KinBot can automatically explore a plethora of reaction pathways efficiently and automatically. The proposed pathways are then filtered based on their