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Experimental and computational study of the initial decomposition of gamma-valerolactone

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Abstract

The thermal decomposition of gamma-valerolactone (GVL) diluted 1:10 mol/mol in nitrogen was studied experimentally in a tubular flow reactor. Variation of the temperature from 873 K to 1073 K for a residence time of approximately 400 ms at 0.17 MPa covered the complete GVL conversion range from 1% to 98%. Comprehensive 2D MS analysis of the effluent revealed that the main products observed at temperatures below 1000 K are CO, CO_2, C4-olefins and 4-pentenoic acid. Initially, GVL is consumed predominantly through isomerization to 4-pentenoic acid, although minor contributions of bimolecular decomposition channels cannot be ruled out. CBS-QB3 level characterization of the $C_5H_8O_2$ potential energy surface reveals the existence of a low energy barrier for ring-opening to 4-pentenoic acid. The weak C—C bond between C_2 and C_3 in 4-pentenoic acid allows formation of radicals that further convert gamma-valerolactone or 4-pentenoic acid. The 4-pentenoic acid yield increases steadily with rising temperature before a sharp decrease around 1010 K. The latter can be explained by radical chemistry taking over at high temperatures.

Keywords: Gamma-valerolactone; Pyrolysis; Comprehensive 2D GC, 4-Pentenoic acid; Molecular decomposition

1. Introduction

The use of biofuels, that is fuels derived from biomass, has been a major focus of scientific research of the last decades. Recently, the potential of γ-valerolactone (GVL), a cyclic ester, as a platform chemical and biofuel has been highlighted [1,2]. Proposed production routes include (i) the acid catalyzed transformation of sugars into levulinic acid followed by reduction to GVL on noble-metal catalysts using H_2 [3], and (ii) sequential hydrogenation and hydrolysis of furfural from hemicellulose [4] catalyzed by zeolites with Brønsted and Lewis acid sites [5]. In contrast to some other biofuels such as ethanol, GVL does not form an azeotrope with water. Purification of GVL streams formed by the aforementioned production routes can thus proceed through simple distillation, which is less energy demanding and cheaper.

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While some fuel properties of GVL (chemical formula $C_5H_8O_2$) such as its high oxygen content, which is known to decrease soot emissions [6], as well as its high density and high boiling point, are well established, its pyrolysis chemistry is not yet documented and no experimental data regarding its thermal decomposition is currently available to the best of our knowledge. Such data could provide insight in the stability of the molecule, help to identify important intermediate species and evaluate its soot or deposit formation tendency [7,8]. Therefore, the aim of this work is to provide a first set of GVL pyrolysis data using a continuous flow tubular reactor setup with dedicated online analysis section for product identification and quantification. A qualitative interpretation of the observations is presented, supported by CBS-QB3 calculations of bond dissociation energies of GVL and important intermediates as well as selected aspects of the $C_5H_8O_2$ potential energy surface.

2. Experimental methods

The experimental apparatus has been described extensively by Djokic and Harper [7,9]. A detailed description of the setup is provided as Supplemental material. The main features of the experimental and analytical methods used are summarized below.

Gamma-valerolactone (Sigma Aldrich, stated purity +99%) is fed to an evaporator kept at 573 K using a peristaltic pump. Nitrogen (Air Liquide, purity +99.999%) is used as a diluent and its flow rate is controlled using a Coriolis mass flow controller. N_2 is heated to the same temperature as the gaseous GVL feed. Both gasses are mixed prior to entering the reactor.

The reactor is 1.475 m long and has an internal diameter of 6 mm. Eight equally spaced thermocouples allow for continuous temperature measurements. Furthermore, two manometers are present, positioned at the inlet and the outlet of the reactor, respectively. The measured pressure drop across the reactor was found to be negligible.

Products and unconverted feed are identified and quantified online, downstream of the reactor, using several dedicated gas chromatographs, see also the Supplemental material. A refinery gas analyzer (RGA) permits detection of all permanent gasses, using a thermal conductivity detector (TCD), as well as the C4-hydrocarbon fraction of the effluent, using a flame ionization detector (FID). Furthermore, a light oxygenates analyzer (LOA), equipped with a TCD, allows quantification of water. Finally, a two dimensional chromatograph (GC×GC) permits identification of the complete reactor effluent ranging from methane to pyrene [10,11] with a TOF-MS, as well as quantification of these products using a FID. The calibration factors for H_2, CO, CO_2 and C_4-hydrocarbons were determined using a gaseous calibration mixture (Air Liquide, Belgium). The response factors of all other species were calculated using the effective carbon number method [12]. N_2 is used as internal standard. The obtained results had good repeatability and the error for the major species is estimated to be 5%, mainly caused by uncertainties in flow rate and calibration factors. Elemental balances typically closed within 3%. Data treatment is discussed more elaborately in Supplemental material.

3. Computational methods

To support the interpretation of the experimental data, electronic structure calculations were performed at the CBS-QB3 level of theory [13] as implemented in the Gaussian 09 suite of programs [14]. Since this method is well-known and established, only deviations will be discussed here. The most important one is that those low frequency vibrations that resemble torsions around single bonds are approximated as 1-dimensional hindered internal rotations. All single bonds, including those in the reactive moiety of the transition state, have been treated in this way. For the reactions considered, rather little coupling between internal rotors was observed. Rotors with hindrance potentials exceeding 50 kJ/mol were excluded and treated as harmonic oscillators. Hindrance potentials of these rotations are calculated at the B3LYP/6-31G(d) level of theory via relaxed surface scans obtained with a step size of 10°, in which all coordinates except for the dihedral angle of the rotation were re-optimized at each scan angle. The data are then fitted to truncated Fourier series expansions. Reduced moments of inertia for asymmetric internal rotors are calculated at the $I^{(2,3)}$ level as defined by East and Radom [15] based on the equilibrium geometry of the most stable conformer of the species. For each internal rotor, the 1-D Schrödinger equation is solved using the eigenfunctions of the 1-D free rotor basis functions and the energy eigenvalues are used to calculate its contributions to the thermodynamic functions. Inspections of the hindered rotor potentials also help ensure that the optimized geometry of a molecule corresponds to the lowest energy minimum. Transition states are identified by having one imaginary frequency, which is animated to verify that it corresponds to the desired reaction coordinate. In ambiguous cases, intrinsic reaction coordinate analyses ensured that specified transition states were connected to specific reactants and products.