On the high-temperature unimolecular decomposition of ethyl levulinate

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Abstract

The pyrolysis of ethyl levulinate (EL) was studied behind reflected shock waves over the temperature range of 1015–1325 K and pressures of 750–1650 Torr. The reaction progress was followed by measuring ethylene mole fraction using CO_2 gas laser absorption near 10.532 μm. The rate coefficients for the unimolecular dissociation of EL were extracted from the initial slope method and further ascertained by using a complete kinetic model. Our data exhibited no discernible pressure dependence under the current experimental conditions. To rationalize our results further, high-level quantum chemical and master equation calculations were employed to calculate the pressure- and temperature-dependence of the reaction. Our calculations revealed that unimolecular dissociation of EL involves simultaneous 1,5-hydrogen shift of the β-hydrogen to the carbonyl group, rupture of the O–C ester bond and formation of the π-bond (C_α–C_β). Our results present evidences that the C_2H_4 elimination from EL occurs in a concerted manner. To our knowledge, this work represents the first experimental and theoretical study of the thermal unimolecular dissociation of ethyl levulinate.
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1. Introduction

Diminishing petroleum reserves, fluctuating energy prices, increasing energy demand, and environmental considerations are driving the need to develop alternative fuels. Methods are continuously being developed to convert biomass to fuels and useful chemicals with a focus on cost, yield and the potential for use in the current infrastructure [1]. Fuels made from lignocellulosic biomass, categorized as second-generation biofuels, have attracted considerable attention because lignocellulose is likely not a human food [2]. Among various molecules that can be produced from lignocellulose, levulinic acid (LA, $CH_3C(O)CH_2CH_2COOH$) appears quite promising and has been selected as one of the top 12 building block candidates by the

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National Renewable Energy Laboratory (NREL) in USA [3].

Levulinic acid (LA) can be converted to alkyl levulinates via esterification process. Alkyl levulinates have been proposed as gasoline and diesel fuel additives [4], and have the unique property of containing two functional groups – a carbonyl and an ester group. Ethyl levulinate (EL, $CH_3C(O)CH_2CH_2COOC_2H_5$) is expected to have a very high octane number (RON $\sim$ 120) and can, therefore, be added to gasoline as octane enhancer. EL has also been used as a diesel additive due to the relatively high boiling point (206 °C) and good lubricating properties [5]. Christensen et al. [5] showed that the addition of EL resulted in decreased soot formation in a diesel engine. However, relatively low cetane number (DCN $\sim$ 5) and poor solubility in diesel at low temperatures prohibited blending in large proportions. In another diesel engine study, Janssen et al. [6] studied ignition of mixtures of butyl levulinate and *n*-tetradecane. They observed marked decrease in soot emissions compared to pure diesel fuel but the unburnt-HC and CO emissions were higher. These engine studies highlighted the potential of using alkyl levulinates as potential biofuels or as additives to the conventional fuels. However, fundamental studies targeted at understanding the chemical kinetic behavior and the role of functional groups are needed to further the efforts of introducing these fuels in the market.

Recently, Thion et al. [7] carried out a theoretical kinetic study to study the oxidation of methyl levulinate (ML) over 500–1300 K. Absolute rate constants for H-abstraction by OH and CH_3 radicals were calculated using the G3//MP2/aug-cc-pVDZ level of theory coupled with transition state theory (TST). This interesting work showed that the sites between the two functional groups are most favorable for H-abstraction reactions. Additionally, unimolecular decomposition of ML radicals was studied by computing rate constants for β-scission and H atom transfer reactions.

Unimolecular decomposition reactions of alkyl esters involve six center transition states leading to the formation of carboxylic acids and olefins [8]. Low values of the activation energies observed in these reactions are consistent with the nature of the proposed transition state. The kinetics for the pyrolysis of these alkyl esters have indicated that the acid group forming the ester has little influence on the dissociation rates of these esters [9]. However, systematic substituent effects were observed for the six-center elimination. The current work is aimed at understanding the effect of the additional carbonyl group on the high-temperature pyrolytic reactions of alkyl esters. Here, we have carried out experimental and theoretical study to investigate the pyrolysis of ethyl levulinate at temperatures ranging 1015–1325 K and pressures

of 750–1650 Torr. Infrared laser absorption was used to measure ethylene time-histories during the shock-heated thermal decomposition of EL and absolute rate constants were determined from the experimental data. In addition, EL decomposition was studied using high-level abinitio and master equation calculations.

2. Experimental details

2.1. Shock tube facility

Unimolecular decomposition of ethyl levulinate (EL) was studied in a heated low-pressure shock tube (LPST) facility at KAUST. Details of the shock tube facility can be found elsewhere [10]; only a brief description is provided here. The shock tube is constructed from stainless steel with an inner diameter of 14.2 cm. The driven section is 9 m long and the driver section has a modular design to vary its length to a maximum of 9 m. The mixture-filled driven section was separated from the helium-filled driver section by a polycarbonate diaphragm. Incident shock speed was measured by a series of five PCB 113B26 piezoelectric pressure transducers (PZTs) placed in the last 1.3 m of the driven section. Shock jump relations [11] and known thermodynamic parameters were used to calculate the post-reflected shock conditions (P_5 and T_5) with a maximum uncertainty of 1%. Ethylene laser diagnostic and a Kistler PZT were located at a sidewall location 2 cm from the shock tube endwall. Since EL has relatively low saturation vapor pressure of $\sim$0.2 Torr at room temperature, the shock tube driven section was heated to 323 K.

Ethyl levulinate/argon mixtures were prepared in a magnetically-stirred mixing tank. After evacuating the mixing tank to pressures less than 1×10^{-3} Torr, liquid ethyl levulinate was injected directly in the heated (373 K) mixing tank. The vapor pressure of ethyl levulinate was found to be $\sim$22 Torr at 373 K. The injection was made through a septa rubber valve that has high sealing properties. Following the fuel evaporation and pressure stabilization, the vapor pressure was measured using MKS pressure gauge (0–20 Torr range). Argon was added slowly to inhibit the condensation of EL which can lead to inaccuracy in the test mixture composition. Gaseous mixtures were left in the mixing vessel for at least one hour prior to shock tube experiments. When filling the shock tube driven section with EL/Ar mixtures (0.4–2.0% in argon), a passivation technique was used to minimize the potential of adsorption of EL on the shock tube walls. High-purity EL ($\geq$99%) was purchased from Sigma Aldrich and research-grade argon was obtained from AH Gas Company.