



Renewable platform chemicals: Thermochemical study of levulinic acid esters



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ABSTRACT

Equilibrium of the levulinic acid esterification with methanol, ethanol, and 1-butanol was studied in a broad temperature range (323 K–473 K) for reactions catalyzed by the enzyme Novozym 435 as well as for uncatalysed reaction systems. Thermodynamic equilibrium constants were derived with help of activity coefficients of reaction participants, which were predicted with the equation of state PC-SAFT. The liquid phase standard molar enthalpies of formation of methyl-, ethyl-, and n-butyl-esters of levulinic acid were measured by using the high-precision combustion calorimetry. Vapor pressures of these esters were measured by using the transpiration method. The standard molar enthalpies of vaporization of alkyl levulinates at 298.15 K were derived from vapor pressure temperature dependencies. Thermochemical data of alkyl levulinates were collected, evaluated, and tested for internal consistency. The high-level G4 quantum-chemical method was used for mutual validation of the experimental and theoretical gas phase enthalpies of formation of studied esters. Thermodynamic analysis of the levulinic acid esterification has been performed. Using the levulinic acid esterification with alcohols as the model reaction for an industrial processing of biomass conversion to fuels and useful platform chemicals, we have shown that qualitatively correct agreement between results from equilibrium study, from thermochemical data (combustion and transpiration), and from G4 calculations was observed. Reasonable combination of the quantum-chemical methods and of PC-SAFT modelling with empirical methods could serve to reduce experimental efforts for assessment of feasibility of the chemical processes of utilization of renewable feedstocks.

1. Introduction

Levulinic acid (LA) can be produced on the large scale by high temperature acid hydrolysis of carbohydrates, such as glucose, galactose, sucrose, fructose, chitose and also from biomeric material such as wood, starch and agricultural wastes [1]. Levulinic acid contains a ketone group and a carboxylic acid group, which make LA a potentially versatile building block for the synthesis of various platform chemicals such as levulinate esters, acrylic acid, 1,4-pentanediol, γ -valerolactone, 2-methyl tetrahydrofuran, δ -amino levulinic acid, etc. [2–4]. Esterification of levulinic acid with alkanols to alkyl levulinates is a valuable process for utilization LA [4,5]. Alkyl levulinates are broadly used in industry as plasticizers, solvents and odorous [5]. Alkyl levulinates are promising renewable chemicals in the field of transportation fuels [6]. Surprisingly, the available in the literature results for the kinetics and thermodynamics of the LA esterification reactions are scarce and

contradicting [4,5]. For example, the esterification of the LA with 1-butanol was claimed to be an endothermic reaction in contradiction with the common knowledge on the esterification of the acetic acid, where esterification reactions with ethanol or 1-butanol were shown to be exothermic [7,8] in accord with the thermochemical calculations by using the Hess's Law (with help of standard molar enthalpies of formation of reaction participants [9]).

The thermodynamic properties of the levulinic acid and its derivatives are required for optimization of reaction conditions for production of useful platform chemicals from the renewable sources. In our previous work [10], thermochemical properties of the pure levulinic acid have been measured. In this work, we studied the chemical equilibrium of the LA esterification with alkanols (see Fig. 1), as well as a set of thermochemical data on alkyl levulinates were measured and tested for an internal consistency.

An extended thermochemical studies of the alkyl levulinates

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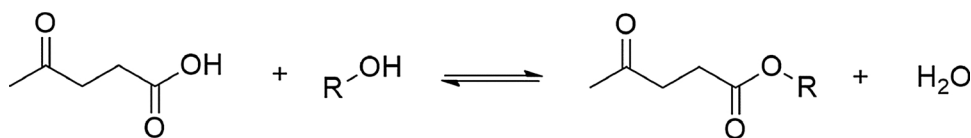


Fig. 1. Reaction (1): esterification of levulinic acid (LA) with alcohols (R = methyl-, ethyl- or n-butyl-).

including the high-precision combustion calorimetry and vapor pressure measurements have been performed leading to the standard molar thermodynamic properties of these compounds in the liquid as well as in the gas phase. The high-level quantum-chemical method G4 has been applied aiming to the prediction of the theoretical thermodynamic equilibrium constant of the LA esterification reaction and comparison with the experimental value, as well as for validation of the experimental results from thermochemical studies. This work extends our systematic study [11–18] of application of quantum-chemical methods for prediction of thermodynamic equilibrium constants in the liquid state, where the most of industrially relevant chemical reactions are usually occur.

2. Materials and methods

2.1. Materials

Provenance and purity of chemicals used in this work is given in Table S1. Commercial samples of alkyl levulinates with the purity 98–99% were additionally purified by fractional distillation in vacuum. No impurities (greater than 0.001 mass fractions) were detected in samples used for the thermochemical measurements. The degree of purity was determined using a GC equipped with an HP-5 capillary column with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm . The standard temperature program of the GC was $T = 333\text{ K}$ for 180 s followed by a heating rate of 0.167 K s^{-1} to $T = 523\text{ K}$. The enzymatic catalyst Novozym 435, based on the lipase B from *Candida antarctica* was used in the equilibration studies as the immobilized form on acrylic resin (5 U mg^{-1} , Sigma-Aldrich GmbH).

2.2. Equilibrium study of the levulinic acid esterification with alcohols

Equilibrium of the esterification of the LA with alcohols (methanol, ethanol and 1-butanol) was studied in the liquid phase at $T = 323.15 \pm 0.03\text{ K}$. The feed reaction mixtures contained slight amounts of water due to improved catalytic activity. The catalyst is not miscible with the reaction mixture and a gentle stirring ensured homogeneous mixing and mass transfer to Novozym 435 without mechanical damage of the immobilized enzyme. In order to establish achievement of the equilibrium, small samples have been withdrawn from the reaction mixture and analyzed. Mole fractions of the alcohols and esters were analyzed by the gas chromatography with Agilent Technology 7890A GC equipped with an Agilent INNOWax column (30 m, 0.32 mm, 0.5 mm) and a flame ionization detector. For GC calibration the following procedure was applied. For the analytical determination of ethyl levulinate and ethanol, n-butyl levulinate was used as an internal standard. For the analytical determination of butyl levulinate and 1-butanol, ethyl levulinate was used as an internal standard. The reacting agents were dissolved in tetrahydrofuran. The retention times for tetrahydrofuran, 1-butanol, ethyl levulinate and n-butyl levulinate were 3.00, 3.76, 4.84, and 5.31, respectively, in minutes. The GC calibration factors for 1-butanol, ethyl levulinate and n-butyl levulinate were found to be 0.712, 0.885, and 1.184, respectively, which were used to determine the weight fractions of each analyte by multiplying the calibration factor with ratio of the peak areas of analyte and internal standard. The mole fraction of water was separately determined using Karl-Fisher titration with a Metrohm 915 KF Ti-Touch (Metrohm, Herisau, Switzerland). All measurements were

performed in triplicate.

2.3. Combustion calorimetry

An isoperibol bomb calorimeter described previously [19] was used for the measurements of energies of combustion of the alkyl esters of levulinic acid. The liquid samples of compounds were weighed with a microbalance of 10^{-6} g resolution. We used commercial polyethylene 1 ml ampoules (Fa. NeoLab, Heidelberg, Germany) for encapsulation of the liquid samples. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39j, NIST). Correction for nitric acid formation was based on the titration with 0.1 mol dm^{-3} NaOH (aq.). The relative atomic masses used for the elements were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011 [20] for each of these elements. Auxiliary values for combustion calorimetry are collected in Table S2. The residual amount of water in samples for combustion calorimetry was determined for each ester (see Table S2) by using the Karl-Fisher titration and the appropriate correction to the combustion energy was applied.

2.4. Transpiration method

Absolute vapor pressures of methyl-, ethyl- and n-butyl levulinates at different temperatures were measured with the transpiration method [21,22]. A nitrogen stream was passed through the thermostatted ($\pm 0.1\text{ K}$) U-shaped saturator filled with small glass beads mixed with the fine powdered sample. At a series of constant temperatures, the transported at equilibrium conditions material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using an external standard n-tridecane. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Absolute values of vapor pressures p_i were calculated with equation:

$$p_i = m_i R T_a / V M_i; V = V_{N_2} + V_i; (V_{N_2} \gg V_i) \quad (2)$$

where R is the universal gas constant; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement.

2.5. Computations

Activity coefficients of the LA esterification reaction participants have been calculated by using PC-SAFT [23,24]. In this procedure, the molecules are regarded as chains of hard spheres, which represent the reference system by accounting for repulsive interactions among chains. This model is based on the perturbation theory of Barker and Henderson [25] and calculates the residual Helmholtz energy of a system. Perturbations of the chain are considered due to the attractive Helmholtz energy contributions in form of dispersive van der Waals attraction and hydrogen bonds. Details have been reported elsewhere [26,27].

Quantum-chemical calculations have been performed with the Gaussian 09 series of programs [28]. Energies of the stable

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