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Renewable platform-chemicals and materials: Thermochemical study of levulinic acid

Sergey P. Verevkin [a,b,*], Vladimir N. Emel'yanenko [b]

[a] Faculty of Interdisciplinary Research, Department "Science and Technology of Life, Light and Matter", University of Rostock, Rostock, Germany
[b] Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg 1, D-18059 Rostock, Germany

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ABSTRACT

The standard molar enthalpy of formation in the gaseous state (-613.5 ± 2.2) $\text{kJ} \cdot \text{mol}^{-1}$ of levulinic acid has been obtained from combustion calorimetry and results from the temperature dependence of the vapour pressure measured by the transpiration method. In order to verify the experimental data, *first-principles* calculations have been performed. Enthalpies of formation derived from G4 and G3MP2 methods are in an excellent agreement with the experimental results. Thermodynamic analysis of the hydrolysis of 5-hydroxymethylfurfural to the levulinic and formic acids has revealed very high feasibility of these reactions with equilibrium constants completely shifted to the desired reaction products even at $T = 298.15$ K.

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1. Introduction

A sustainable future for the chemical industry requires feed stocks based on renewable rather than steadily depleting sources. Glucose and fructose, two abundant six-carbon sugar molecules, are potential feed stocks for this purpose, and recent efforts have focused on converting them to 5-hydroxymethylfurfural (HMF), a versatile intermediate between biomass-based carbohydrate chemistry and petroleum-based industrial organic chemistry [1]. One of new promising options seems to be a development of effective ways to produce hydrogen from biomass. An interesting catalytic reaction system for production of hydrogen in very high selectivity from glucose or cellulose in very mild conditions has been reported recently [2]. This catalytic reaction system is based on the Ru-complex catalyst dissolved and stabilized in an ionic liquid medium [2]. In this process, the next to last reaction in the sequence leading to the H_2 is the reaction of HMF hydrolysis with formation of levulinic and formic acid (see figure 1). Formic acid is further converted to H_2. Levulinic acid has been identified as one of the promising biomass-derived chemicals by the US Department of Energy. It can be also produced from cellulose-containing biomass in high yields using the "Biofine" process [3]. Levulinic acid can be converted to methyl-tetrahydrofuran, a fuel extender or it is an attractive starting material in producing many useful five-carbon compounds such as γ-valerolactone, esters, and other derivatives [4]. This work extends our previous thermodynamic studies on the conversion of HMF into bulk intermediates [5] with measurements and first-principles calculations of levulinic acid thermochemical properties.

2. Experimental

2.1. Materials

The solid samples of levulinic acid or 4-oxo-n-pentanoic acid [CAS 123-76-2] were obtained from Merck and further purified by fractional sublimation in vacuum. The degree of purity was determined by GC. No impurities (greater than mass fraction $5 \cdot 10^{-4}$) could be detected in samples for thermochemical study. The products were analysed with a Hewlett Packard gas chromatograph 5890 Series II with a flame ionisation detector and Hewlett Packard 3390A integrator. The capillary column HP-5 with stationary phase cross linked 5% PH ME silicone and the column length, inside diameter, and film thickness were 25 m, 0.32 mm and 0.25 μm, respectively. The starting point for the GC temperature program was 323 K with a heating rate of $0.167 \text{ K} \cdot \text{s}^{-1}$ up to $T = 523$ K.

2.2. Vapour pressure measurements of levulinic acid

Vapour pressures of levulinic acid were determined using the method of transpiration [6,7] in a saturated nitrogen stream. About

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[*] Corresponding author at: Faculty of Interdisciplinary Research, Department "Science and Technology of Life, Light and Matter", University of Rostock, Rostock, Germany. Tel.: +49 381 498 6508; fax: +49 381 498 6524.

E-mail address: sergey.verevkin@uni-rostock.de (S.P. Verevkin).

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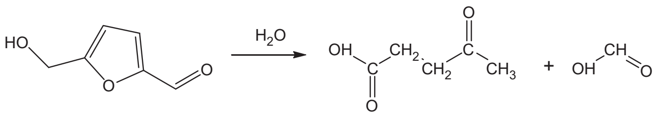

FIGURE 1. Formation of levulinic acid from HMF.

0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide surface large enough for rapid (vapour liquid) equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimised in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by weighing of the cold trap with the balances of resolution 10^{-4} g. The saturation vapour pressure p_i (see table 1) at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i were calculated with equation:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i), \tag{1}$$

where $R = 8.314472\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is the volume contribution to the gaseous phase. The V_{N_2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement.

2.3. Combustion calorimetry

An isoperibol bomb calorimeter was used for the measurement of the energy of combustion of levulinic acid. Results from combustion experiments are given in table 2. The detailed procedure has been described previously [8]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none of these substances was detected. The energy equivalent of the calorimeter $\varepsilon_{calor} = 14832.2 \pm 1.0\ \mathrm{J \cdot K^{-1}}$) was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on the titration with 0.1 mol · $\mathrm{dm^{-3}}$ NaOH (aq.). The atomic weights used were those recommended by the IUPAC Commission [9]. The sample masses were reduced to vacuum, taking into consideration their density values (see table S1, supporting information). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure [10] was applied. From a practical point of view, careful encapsulation of the sample of levulinic acid is required due to its hygroscopic nature. In the present study, we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 $\mathrm{cm^3}$ volume as the container for the liquid samples. Charge of the sample into the polyethylene bulb with a syringe was easier to perform using the melted levulinic acid. The liquid sample was transferred into the polyethylene bulb with a syringe under nitrogen stream in a glove-box. The fine neck of the container was compressed with a special tweezers and was sealed outside the glove-box by heating of the neck in a close proximity to a glowing wire. Then, the container was placed in the crucible and was burned in oxygen at a pressure 3.04 MPa. The stock of levulinic acid was kept in the special glass device under an inert atmosphere. Small amounts of water could not be removed from the samples prepared for thermochemical measurements. The water concentration in the stock was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. Apparently due to a residual amount of water in the sample (10169.51 ppm) it has remained as undercooled liquid in the bulb during the combustion experiments. To ensure the absence of crystallisation of the sample in the bomb prior combustion, the experiment was stopped shortly before ignition several times but no crystallisation has been observed. Thus, the combustion energy in our experiments has been referred to the liquid state.

2.4. Computations

Standard *ab initio* molecular orbital calculations were performed with the Gaussian 03 Rev. 04 series of programs [11]. Energies were obtained at the G3, G3MP2, and G4 level of theory. The G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on *ab initio* molecular orbital theory. A modification of G3 theory that uses reduced orders of Moller–Plesset perturbation theory is G3MP2 theory [12]. The G4 composite model [13] combines high-level correlation/moderate basis set calculations with lower level correlation/larger basis set calculations to approximate the results of a more expensive calculation. The composite energy

TABLE 1
Results from measurements of the vapour pressure p of levulinic acid using the transpiration method.

T^a/K	m^b/mg	$V_{N2}{}^c/\mathrm{dm^3}$	Gas-flow/$\mathrm{dm^3 \cdot h}$	p^d/Pa	$(p_{exp} - p_{calc})$/Pa	$\Delta_l^g H_m/(\mathrm{kJ \cdot mol^{-1}})$
		$\Delta_l^g H_m(298.15\ \mathrm{K}) = (70.32 \pm 0.68)\mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{302.97}{R} - \frac{91905.67}{R \cdot T/\mathrm{K}} - \frac{72.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$				
328.4	17.5	55.57	3.99	7.05	0.1	68.13
333.4	26.0	54.77	3.99	10.45	0.4	67.77
338.3	10.0	15.42	3.99	14.14	−0.2	67.41
343.3	8.5	8.77	3.99	20.96	0.6	67.05
343.4	3.1	3.32	3.99	20.19	−0.2	67.05
348.3	14.0	11.17	3.99	27.02	−1.4	66.69
353.3	9.2	5.18	3.99	38.10	−1.2	66.33
358.3	12.7	5.15	4.83	52.78	−1.1	65.97
358.4	11.5	4.79	3.99	51.48	−2.7	65.96
363.4	15.1	4.25	3.99	75.87	2.5	65.60
368.4	11.0	2.33	3.99	100.96	2.6	65.24
373.4	10.3	1.63	3.99	134.93	4.1	64.88

[a] Saturation temperature.
[b] Mass of transferred sample condensed at T = 293 K.
[c] Volume of nitrogen used to transfer mass m of sample.
[d] Vapour pressure at temperature T, calculated from m and the residual vapour pressure at the cooling temperature T = 293 K, calculated by an iterative procedure.

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