



Renewable platform chemicals: Evaluation of thermochemical data of alkyl lactates with complementary experimental and computational methods



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ABSTRACT

The standard molar enthalpies of vaporisation of alkyl lactates were derived from the vapour pressure temperature dependences measured by the transpiration method. Thermodynamic data on vaporisation processes available in the literature were collected, evaluated, and combined with own experimental results. Combustion experiments were performed on the highly pure ethyl lactate. We have evaluated and recommended the set of vaporisation and formation enthalpies of alkyl lactates at 298.15 K as the reliable benchmark properties for further thermochemical calculations. Gas phase molar enthalpies of formation of alkyl lactates calculated by the high-level quantum-chemical method G4 were in an excellent agreement with the recommended experimental data. The esterification of lactic acid with alcohols was considered as the model reaction for an industrial processing of biomass conversion to fuels and useful platform chemicals. The high-level quantum chemical calculations have been successfully applied for estimation of reaction enthalpies and the true thermodynamic equilibrium constants in the gas and in the liquid phase. Results of this study could help to reduce the experimental efforts for the assessment of feasibility of the chemical processes of utilization of renewable feedstocks.

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1. Introduction

Lactic acid esters and polymers of lactic acid are known to be environmentally friendly, because of their biodegradability into harmless products. Last decade, the production of lactic acid derivatives from renewable biomass has acquired importance [1]. In order to minimize the cost of lactic acid purification, a reactive distillation process with alcohols, followed by the hydrolysis of alkyl-lactates has been shown to be effective [2]. The reactive distillation optimization requires knowledge of vapour pressures of reaction participants, as well as the reliable energetics of chemical reactions.

Alkyl lactates are considered as the biomass-derived solvents. They can be easily produced from alcohols and lactic acid, which are usually obtained by the fermentation of biomass. Alkyl lactates have excellent solvent properties as well as low toxicity, relatively

low volatility, low viscosity, good biodegradability, and recyclability. Consequently, they have attracted much attention in recent years as a promising candidate to replace toxic organic solvents and volatile organic compounds [2]. This work continues our systematic studies on the lactic acid and its derivatives [3–6]. The objectives of this study is to evaluate the thermochemical data available for alkyl lactates (see Fig. 1) with the complementary experimental and computational methods in order to recommend benchmark thermochemical properties for these compounds, required for the development of new technologies of manufacturing of platform chemicals from renewable sources.

2. Materials and methods

2.1. Materials

The commercially available samples of alkyl lactates (see Table 1) have been used in this work. Samples were additionally purified by the fractional distillation in a vacuum. No impurities (greater than 0.0002 mass fraction) could be detected in samples

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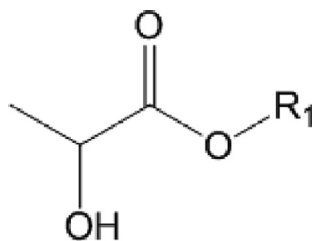


Fig. 1. Alkyl lactates studied in this work with $R = C_2-C_5$.

used for the thermochemical measurements. The degree of purity was determined using a GC equipped with a FID. A capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm . Water mass fraction in the samples was determined using a Mettler Toledo DL38 Karl Fischer titrator using the HYDRANAL™ as the reagent. A not significant mass fraction of water (except for D-ethyl lactate, see Table 1) at the level of 15–20 ppm was measured by the Karl Fisher titration.

2.2. Transpiration method: vapour pressure measurements

Vapour pressures of alkyl lactates were measured using the transpiration method [7–9]. About 0.5 g of the sample was mixed with small glass beads and placed in the thermostatted U-shaped saturator. A nitrogen stream with well-defined flow rate was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using the *n*-alkane as an external standard. The absolute vapour pressure p at each temperature T_i was calculated from the amount of the material, collected in the cold trap within a definite time:

$$p = m_i \cdot R \cdot T_a / V \cdot M_i; V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a, \quad (1)$$

where V is the volume of the gas phase consisting of the n_{N_2} moles of the carrier gas and n_i mole of gaseous compound under study at the atmospheric pressure P_a and the ambient temperature T_a . The amount of the carrier gas n_{N_2} was determined from the flow rate and the time measurement. The amount of the compound under study n_i in the carrier gas was estimated applying the ideal gas law at each temperature.

The transpiration apparatus identical to those in Rostock has been constructed in Samara, and results of parallel measurements on alkyl lactates in Samara and in Rostock have been considered as a validation of the transpiration procedure transferred to the new lab. All parts of the equipment in Samara have been identical to those in Rostock except for the GC analysis of the transported mass. A chromatograph equipped with a 100 m \times 0.25 mm capillary column covered with a non-polar DB-1 phase was used for determination of masses of alkyl lactates collected

in the cold trap. Results measured by the transpiration (T) in Rostock are labelled in this work as TR, and results measured in Samara are labelled as TS.

2.3. Combustion calorimetry: enthalpy of formation of ethyl lactate

The standard molar energies of combustion of D-ethyl lactate were measured with a self-made high-precision isoperibolic calorimeter with a static bomb and a stirred water bath. The liquid sample was transferred (in the glove box) into the polyethylene bulb (Fa. NeoLab, Heidelberg, Germany) with a syringe. The neck of the bulb was compressed with special tweezers and was sealed by heating the neck in a close proximity to a glowing wire. The bulb with the liquid sample was placed in the crucible and it was burned in oxygen at a pressure of 3.04 MPa. Test experiments with and without purging with O_2 showed results consistent within the experimental uncertainty. The detailed procedure has been described previously [10,11]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\epsilon_{\text{calor}} = (14816.0 \pm 0.7) \text{ J} \cdot \text{K}^{-1}$, was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid formation was based on titration with 0.1 mol·dm⁻³ NaOH (aq). For the reduction of the data to standard conditions, conventional procedures [12] were used. Auxiliary data required for the reduction of the experimental results to the standard conditions are collected in Table S1.

3. Results and discussion

3.1. Vapour pressures of alkyl lactates from the transpiration method

Alkyl lactates vapour pressures temperature dependencies were measured in this work by the transpiration method and they are given in Table 2. The temperature dependences of vapour pressure p were fitted with the following equation [7]:

$$R \ln p = a + \frac{b}{T} + \Delta_1^g C_{p,m}^g \ln \left(\frac{T}{T_0} \right) \quad (2)$$

where a and b are adjustable parameters and $\Delta_1^g C_{p,m}^g$ is the difference of the molar heat capacities of the gas and the liquid phases respectively. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be $T_0 = 298.15$ K) and R is the molar gas constant.

3.2. Comparison of available vapour pressures

A detailed discussion of vapour pressures of methyl-lactates have been performed just recently [6]. It has been noticed that vapour pressures of the enantiopure material has slightly lower vapour pressure in comparison to the racemate. In this work, we

Table 1
Provenance, purity, methods of purification, and analysis of chemicals used in this work.

Compound	Molar mass/g·mol ⁻¹	CAS	Source	Initial purity	Final purity ^a
D-ethyl lactate ^b	118.131	7699-00-5	TCI	0.97	0.999
DL-ethyl lactate	118.131	97-64-3	Sigma	0.99	0.999
DL- <i>n</i> -propyl lactate	132.158	616-09-1	TCI	0.95	0.998
DL- <i>n</i> -butyl lactate	146.184	138-22-7	TCI	0.98	0.999
DL- <i>n</i> -pentyl lactate	160.211	6382-06-5	Sigma	0.99	0.999
L- <i>iso</i> -propyl lactate	132.158	63697-00-7	Acros	0.99	0.999
D- <i>tert</i> -butyl lactate	146.184	68166-83-6	Aldrich	0.99	0.999

^a Purification was performed by the fractional distillation in vacuum. Mass fraction impurity determined by the gas chromatography. Not significant mass fraction of water at the level of $(15-20) \times 10^6$ was measured by the Karl Fisher titration. The final purities are given on the water-free basis.

^b Residual amount of water was measured to be 105.3×10^6 and the appropriate corrections were applied for combustion experiments.

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