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Thermodynamics of a model biological reaction: A comprehensive combined experimental and theoretical study

Vladimir N. Emel'yanenko [a], Andrei V. Yermalayeu [a], Matthias Voges [c], Christoph Held [c, *], Gabriele Sadowski [c], Sergey P. Verevkin [a, b, **]

[a] Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg 1, D-18059 Rostock, Germany
[b] Department "Science and Technology of Life, Light and Matter, University of Rostock, Dr-Lorenz-Weg 1, D-18059 Rostock, Germany
[c] Department BCI, Laboratory of Thermodynamics, Technische Universität Dortmund, Emil-Figge-Str 70, D-44227 Dortmund, Germany

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ABSTRACT

In this work we applied experimental and theoretical thermodynamics to methyl ferulate hydrolysis, a model biological reaction, in order to calculate the equilibrium constant and reaction enthalpy. In the first step, reaction data was collected. Temperature-dependent equilibrium concentrations of methyl ferulate hydrolysis have been measured. These were combined with activity coefficients predicted with electrolyte PC-SAFT in order to derive thermodynamic equilibriums constants K_a as a function of temperature.

In a second step, thermochemical properties of the highly pure reaction participants methyl ferulate and ferulic acid were measured by complementary thermochemical methods including combustion and differential scanning calorimetry. Vapor pressures and sublimation enthalpies of these compounds were measured by transpiration and TGA methods over a broad temperature range. Thermodynamic data on methyl ferulate and ferulic acid available in the literature were evaluated and combined with our own experimental results. Further, the standard molar enthalpy of methyl ferulate hydrolysis reaction calculated according to the Hess's Law applied to the reaction participants was found to be in agreement with the experimental reaction enthalpy from the equilibrium study.

In a final step, the gas-phase equilibrium constant of methyl ferulate hydrolysis at 298.15 K was calculated with the G3MP2 method. This value was adjusted to the liquid phase using the experimental vapor pressures of the reaction participants. As a result, the liquid phase K_a value calculated by quantum chemistry with additional data on the pure reaction participants was in good agreement with the experimental K_a reported in the literature for the aqueous phase. The thermodynamic procedure based on the quantum-chemical calculations is found to be a valuable option for assessment of thermodynamic properties of biologically relevant chemical reactions.

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1. Introduction

Thermodynamics plays an important role in biochemical reactions. Key reaction properties such as Gibbs energies of reactions or reaction enthalpies are accessible by thermodynamic tools. Such tools can be experimental considerations, theoretical approaches at different levels of molecular size or time-scale, or combined approaches making use of experiments and theory. This work presents a comprehensive thermodynamic study of a biological model reaction, aiming at application of combined experimental and theoretical state-of-the-art methods to the methyl ferulate hydrolysis as an archetype of a biological reaction. The hydrolysis of methyl ferulate presents an appropriate model reaction for the breakdown of hemicellulose from plants and thus for investigations on the enzyme-catalyzed ester hydrolysis of hemicellulose [1], which is an important step in the production route of biofuel from biomass. In this work the methyl ferulate hydrolysis in the presence of the feruloyl esterase is investigated. Methyl ferulate hydrolysis is presented by the following overall biochemical reaction (1a) and the reference chemical reaction (1b):

* Corresponding author.
** Corresponding author. Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg 1, D-18059 Rostock, Germany.
E-mail addresses: christoph.held@bci.tu-dortmund.de (C. Held), sergey.verevkin@uni-rostock.de (S.P. Verevkin).

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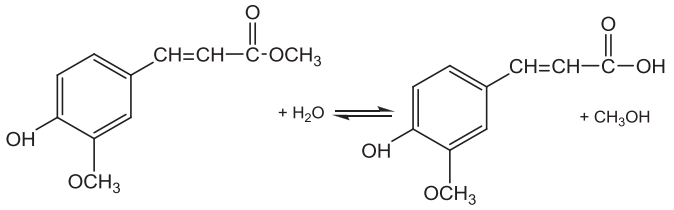

methyl ferulate + *water* ⇋ *ferulic acid* + *methanol* (1a)

methyl ferulate (*aq*) + *water*(*liq*) ⇋ *ferulic acid*$^-$(*aq*) + H^+(*aq*) + *methanol*(*aq*) (1b)

In addition, methyl ferulate hydrolysis is a meaningful model reaction from thermodynamic point-of-view, since the hydrolysis of methyl ferulate is limited by thermodynamic equilibrium. Such limitations can be overcome by manipulating the reaction conditions (e.g. *T*, *pH*, reactant concentration, initial reactant ratio) in a way that allows shifting the equilibrium position towards the side of products. From a thermodynamic point, it is most reasonable to change reaction temperature, as this does not influence the composition of the reaction medium (which would be necessary for changing pH, reactant concentration or reactant ratios, respectively). Thus, it is convenient in reaction engineering to optimize reaction temperature as a first step in order to shift the equilibrium position towards the product side for increasing yield. Varying reaction temperature requires that the enzyme is still active in the temperature window under consideration. Note, that temperature-dependent enzyme activity was not of particular interest of the current work.

1.1. Thermodynamic approach used in this study

A general sketch which comprises the experimental and theoretical methods involved in this work is presented in Fig. 1. The detailed explanation of this figure will be given along the text, but the main idea behind this study is a development of a procedure suitable for the reliable prediction of thermodynamic properties, as well as reasonable assessment of equilibrium constants of biochemical reactions. Using the model reaction of methyl ferulate hydrolysis Eq. (1) we intend to perform mutual validation of experimental and theoretical methods presented in Fig. 1 in order to extend this thermodynamic procedure to more complex reactions.

The key property that allows evaluating thermodynamic limitations and reaction yield is the thermodynamic equilibrium constant K_a. From the van't Hoff relation

$$\mathrm{d}\ln K_a/\mathrm{d}T = \Delta_r H^\circ_m \Big/ RT^2 \quad (2)$$

the slope of a plot $R(\ln K_a)$ vs $1/T$ provides the standard molar enthalpy of reaction $\Delta_r H^\circ_m$. The derivation of reaction enthalpy from the temperature-dependence of the equilibrium constant is commonly referred to the *Second Law Method*. This method is well established for chemical reactions in the liquid [2,3] or in the gas phase [4]. However, this method becomes very demanding and time consuming especially for biologically relevant or enzyme catalyzed reactions, which mostly proceed in aqueous medium. In contrast to common chemical reactions, apparent equilibrium constants of the overall chemical reaction (1a) K'_m (where m means that K'_m is molality based) are mostly used instead of the thermodynamic equilibrium constant of a reference chemical reaction K_a (where a means that K_a is activity based). The apparent equilibrium constant K'_m is usually calculated from equilibrium molalities of the reaction participants of the overall biochemical reaction (see Eq. (1a)). The apparent equilibrium constant K'_m provides very useful information for biochemical reactions, but it crucially depends on the composition of the reaction medium. Admittedly, only the calculations based on thermodynamic equilibrium constant K_a can lead to standard thermodynamic properties. Usually, K_m values are determined from measured equilibrium molalities of the reaction participants of the reference chemical reaction (see Eq. (1b)). Knowledge on activity coefficients γ_i or γ_i^* (depending on the reference state of the reaction participant) of all reaction participants allows converting K_m values into the K_a value using $K_a = K_m K_\gamma$,

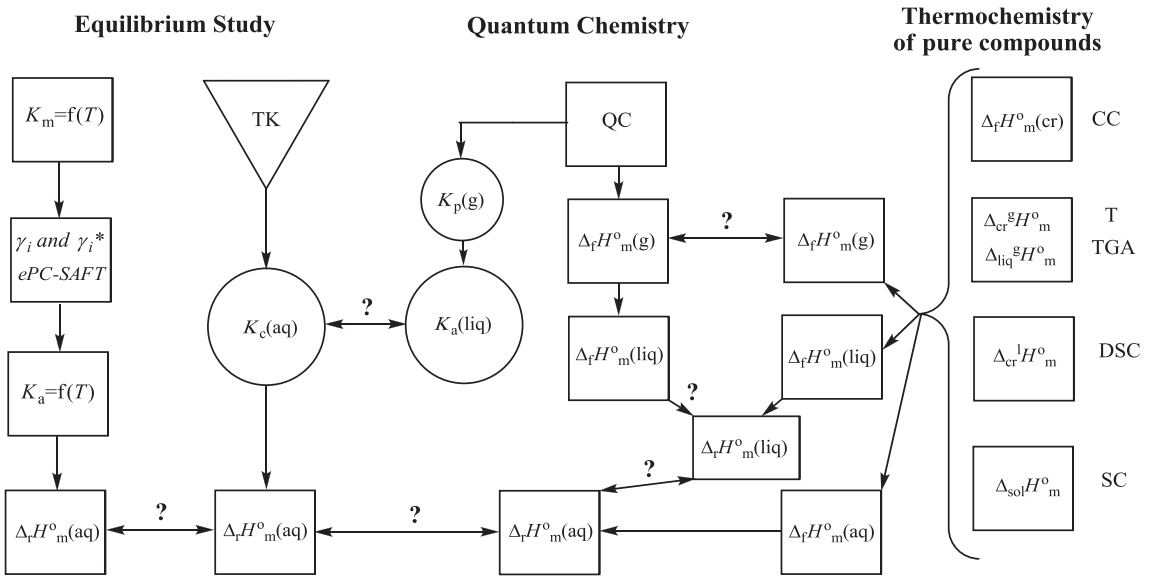

Fig. 1. Sketch of thermodynamic calculations performed in this work. The question sign shows the points of mutual validation of the experimental results. TK – titration calorimetry, QC – quantum-chemistry, CC – combustion calorimetry, T – transpiration method, TGA – thermogravimetry, DSC – differencial scanning calorimetry, SC – solution calorimetry.

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