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ENZYME-CATALYSED HYDROLYSIS OF *L*-AMINO ACID ESTERS IN A LOW WATER ORGANIC SOLVENT STUDIED BY ISOTHERMAL CALORIMETRY

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Isothermal calorimetry and UV-visible spectrophotometry have been used to study the thermochemistry of the enzyme-catalyzed hydrolysis of hydrophobic L-amino acid esters in organic solvents with low water content at 298 K. The *p*-nitrophenyl esters of *Z*-*L*-tyrosine and *Z*-*L*-phenylalanine were used as model hydrophobic substrates. Acetonitrile was used as a model organic solvent. A special preparation protocol of the reactants in the calorimetric vessel was applied in order to determine the heat effects accompanying the enzyme-catalyzed hydrolysis reaction in organic mixtures with low water content and the Tris buffer ionization enthalpies over the whole range of water content in acetonitrile.

It was found that the molar enthalpy of the hydrolysis of *p*-nitrophenyl esters and buffer ionization enthalpy depend significantly and similarly on the water content in acetonitrile. However, the reaction enthalpy corrected for the buffer ionization enthalpy does not depend on the water content in organic solvent mixtures. An explanation of the effect of the selected organic solvent on the thermochemical parameters was provided on the basis of the IR spectroscopic data for the hydrogen bond network of water in acetonitrile. The results obtained show that the state of water in organic solvents is an important factor that determines the reaction enthalpy as well as buffer ionization enthalpy.

Keywords: *acetonitrile, biocatalysis in organic solvents, bovine pancreatic α-chymotrypsin, buffer ionization enthalpy, ester hydrolysis, isoperibolic batch calorimetry, reaction enthalpy*

$(\Delta H)_0$Introduction

The use of the enzyme-catalyzed reactions in non-aqueous media including organic solvents and ionic liquids is highly promising for modern biotechnology. There are many advantages in employing organic solvents for biocatalytic processes. Enzymes in organic media exhibit new remarkable properties including increased solubility of hydrophobic substrates, catalysis of synthetic reactions impossible in water and increased thermostability, prevention of autolysis [1–3]. Enzymes in organic solvents display high regio- and enantioselectivity, which makes these catalysts especially attractive for pharmaceutics and agrochemistry. Hence, the knowledge of the thermodynamic and kinetic parameters of biocatalytic reactions in organic liquids appears important for the understanding of various enzyme activities.

Since an enthalpy change is observable in all biocatalytic reactions, the corresponding heat effects accompanying the enzyme-catalyzed reactions might be a very information-full property of the intermolecular processes influencing the activity of enzymes in low water organic solvents. Calorimetry is therefore an interesting and reliable method to determine quantitatively the thermodynamic properties of a reaction and to obtain information about the reaction rate [4–9]. The use of a calorimeter as a prototype of a research reactor provided with thermochemical detection is helpful for the development of biochemical processes. In such equipments it is possible to carry out processes under various conditions: low and high temperatures, electrolyte solutions, water – organic mixtures, low and high humidities [10–15]. Due to these advantages, isothermal calorimetry has a great potential for the investigation of the state and properties of proteins in organic solvents. For example, the enthalpy changes and structural rearrangements accompanying the interaction of bovine pancreatic α-chymotrypsin with pure organic solvents including hydrocarbons, alcohols and hydrogen bond accepting solvents were recently studied by isothermal calorimetry and FTIR spectroscopy [16, 17]. It was observed that the enthalpy changes depend cooperatively on the solvent hydrophilicity. The hydrophilicity was characterized by the Gibbs energy of dissolved water in the organic solvent. Considerable structural rearrangements were observed in hydrophilic solvents. The interaction enthalpies of α-chymotrypsin with hydrophilic liquids like methanol, ethanol and DMSO were strongly exothermic reactions. The enthalpy and

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structural changes of α-chymotrypsin in hydrophobic and medium hydrophilic liquids were close to zero.

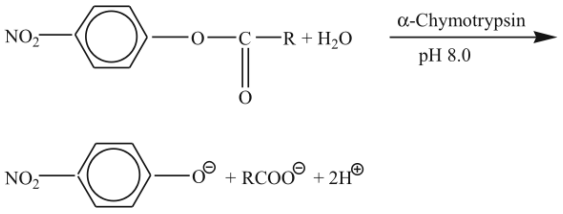
In general, the enzyme activity and structure in organic solvents is a complex function of the water content in the organic media and of the hydration 'history' of an enzyme [18–20]. Several characteristic dependencies of enzymatic activity on the water content in organic solvents are given in [21–24]. These curves can be divided into three different parts:

- The first concentration range corresponds to the mixtures with high water content. Hydrolytic activity with high selectivity can be observed in this range. However, many industrially important reactions including peptide synthesis and esterification are suppressed in aqueous solutions due to the unfavorable shift of reaction equilibria.
- A sharp decrease in enzyme activity was observed after a certain threshold concentration of the organic solvent had been reached. The position of this minimum depends on the physico-chemical properties of the solvent [22]. Organic solvents may perturb the enzyme structure by weakening the hydrophobic interactions, by changing the electrostatic interactions of the polar protein groups, or by direct interaction with biocatalysts.
- The third concentration range corresponds to the mixtures with low water content. Due to the reduced conformational flexibility in organic solvents with low water content, the enzymes remain in the active conformation. This active conformation is not the thermodynamically most stable conformation in water-organic mixtures. The enzymes are in a kinetically 'frozen' state in this range [2, 20].

The enthalpy changes for enzyme-catalyzed reactions in water at different pH values and buffer systems were published previously [9, 25–30]. A limited number of reports is known for calorimetric studies of reactions catalysed by enzymes in the presence of small concentrations of organic solvents (3% (vol.) [28] and 3–7% (vol.) [27] ethanol, 1.6–10% (vol.) acetonitrile [9]). However, no measurements are known for the determination of the enthalpy change of the enzyme-catalyzed reactions in organic solvents with small water content using direct calorimetric measurements.

The aim of the present paper was to determine the enthalpy change for the enzyme-catalyzed reactions of *p*-nitrophenyl ester hydrolysis in organic solvents with low water content by isothermal calorimetry. These results were compared with corresponding values [9, 27, 28] for the enzyme-catalyzed reactions in systems with high water content.

Hydrolysis of the hydrophobic *p*-nitrophenyl esters catalyzed by bovine pancreatic α-chymotrypsin in the presence of Tris buffer used as a model



Scheme 1 Hydrolysis of *p*-nitrophenyl esters catalyzed by α-chymotrypsin [9]

reaction. The investigated reaction is characterised by Scheme 1:

The used Tris buffer provided a constant pH value and caused an increase in the measurable heat exchange by the buffer ionization enthalpy. The buffer ionization reaction occurs concurrently to the ester hydrolysis: $R–NH_2+H^+ \rightarrow R–NH_3^+$.

The non-specific nature of the calorimetric measurements makes it often difficult to interpret the results from complex reaction systems. Therefore, the progress of the hydrolysis reaction was controlled in our investigations by UV-visible spectrophotometry.

Experimental

Reagents

Bovine pancreatic α-chymotrypsin (C-4129, essentially salt free; EC 3.4.21.1, specific activity of 52 units mg^{-1} of solid) purchased from Sigma. *Z-L*-tyrosine *p*-nitrophenyl ester, *Z-L*-phenylalanine *p*-nitrophenyl ester (Scheme 2), acetonitrile (HPLC grade, water <0.02%), tris[hydroxymethyl]aminomethane (Tris), tris[hydroxymethyl]amino-methane hydrochloride (Tris*HCl), *p*-nitrophenol were obtained from Sigma and Fluka. Doubly distilled water was used.

Preparation of reactants

Solutions of different composition (Table 1) consisting of the water-acetonitrile mixtures with Tris*HCl and *p*-nitrophenyl esters were prepared directly in the calorimetric vessel. The water content in acetonitrile was 30% (*v*/*v*). This water content corresponds to the low water range [21–24]. The volume of the calorimetric vessel was 67 mL. The pH value of the solution before the start of the reaction was 4.5. The stability of *p*-nitrophenyl esters with regard to hydrolysis was controlled by UV-visible spectrophotometry at 400 nm. No noticeable variation in absorbance was observed for at least 24 h.

The reaction in the calorimetric vessel was initiated by breaking a glass ampoule. A mixture of solid Tris and chymotrypsin powders was contained in the glass ampoule. The chymotrypsin and Tris

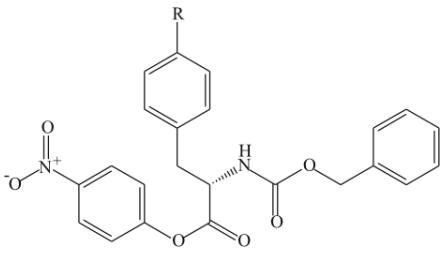
Table 1 Preparation protocol of reactants

Type of experiment	Ampoule	Calorimetric vessel
Blank	Solid Tris	Solution of Tris*HCl in water-acetonitrile mixtures
Reaction	Solid Tris and α-chymotrypsin powders	Solution of *p*-nitrophenyl ester and Tris*HCl in water-organic mixtures. Water content in acetonitrile is 30% (*v*/*v*). $C_{substrate}$ is $3.0 \cdot 10^{-3}$ mol L^{-1}
Buffer ionization	Solid Tris	a) Solution of 0.1 mol L^{-1} HCl in water or water-acetonitrile mixtures; b) Solution of 0.1 mol L^{-1} NaOH in water or water-acetonitrile mixtures

buffer concentrations in the calorimetric vessel were after mixing $1.8 \cdot 10^{-5}$ and 0.033 mol L^{-1}, respectively. The resulting pH value of the reacting solution was 8.0. This special preparation protocol was necessary because of the instability of the ester in solutions near pH 8.0. The enthalpy change for the dissolution of Tris was determined in a blank experiment (Table 1) as 17.3±0.5 kJ mol^{-1}. This value is in good agreement with the enthalpy change measured for the dissolution of Tris in 0.05 mol L^{-1} NaOH at 298 K [34]. The enthalpy change in the blank experiment was taken into account in the calculation of the reaction enthalpy.

Calorimetric measurements

Calorimetric measurements were performed at 298 K using a modified isoperibolic LKB 8700 calorimeter [31]. The calorimeter was calibrated using the Joule effect and tested with dissolution of potassium chloride in water according to the recommendations [32, 33].



Scheme 2 Structure of *Z*-*L*-amino acid *p*-nitrophenyl esters (*R*=OH for *Z*-*L*-tyrosine *p*-nitrophenyl ester, *R*=H for *Z*-*L*-phenylalanine *p*-nitrophenyl ester)

Spectrophotometric measurements

The reaction mixtures were prepared similarly as described for the calorimetric experiments. An aliquot of 0.2 mL of reaction solution was diluted to 3 mL with an acetonitrile-Tris buffer mixture (the resulting pH value of the mixture was 7.0) and the optical density was determined in a Unicam 8625 UV-visible spectrophotometer. The results of our spectrophotometric experiments are in good agreement with the published data [9].

The release of *p*-nitrophenol as a function of time was measured at 400 nm. The absorbance at 400 nm in the reaction solution was normalized with respect to the absorbance of the *p*-nitrophenol solution under similar conditions. The values of the relative absorbance at 400 nm correspond to the progress of the hydrolysis of *p*-nitrophenyl ester. From the calorimetric and spectrophotometric experiments it was observed that the non-enzymatic hydrolysis brings a minor contribution to the calorimetric and spectrophotometric curves.

Buffer ionization enthalpy

Buffer ionization enthalpies in water-organic mixtures were calculated using Eq. (1):

$$\Delta_r H_{ion} = \Delta_{diss} H_{HCl} - \Delta_{diss} H_{NaOH} \quad (1)$$

$\Delta_{diss} H_{HCl}$ is the enthalpy of dissolution of solid Tris in water or water-organic mixtures containing 0.1 mol L^{-1} HCl (Table 1). The molar ratio of HCl/Tris was 10. The resulting pH value of mixtures was about 1.0. At this pH value Tris is in the completely protonated form.

$\Delta_{diss} H_{NaOH}$ is the enthalpy of dissolution of solid Tris in water or water-organic mixtures containing 0.1 mol L^{-1} NaOH. The molar ratio of NaOH/Tris was 10. The resulting pH value of mixtures was about 13.0. At this pH value Tris is in the completely deprotonated form.

Results and discussion

A typical calorimetric curve is given in Fig. 1 (curve 1). The $\Delta T(t)$ curves were corrected for the heat–flow using a cooling constant determined in special calibration experiments. The temperature rise is proportional to the heat power in the calorimetric vessel.

The determination of reaction development of the hydrolysis of *p*-nitrophenyl esters was the next step of our investigation. The advance of the reaction was characterized quantitatively by the release of *p*-nitrophenol, one of the products of the *p*-nitrophenyl ester hydrolysis. A typical progress curve of the *p*-nitrophenol release is given in Fig. 1 (curve 2). As it

can be concluded from Fig. 1, there is a good agreement between calorimetric and spectrophotometric data. This observation indicates the reliability of our thermochemical experiments.

The plateau value of the $\Delta T(t)$ curve (ΔT_{max}) depends linearly on the concentration of the substrate (Fig. 2). We have calculated the molar reaction enthalpies (ester hydrolysis and buffer ionization) from the slope of the linear dependence between ΔT_{max} and the substrate concentration (C) using Eq. (2):

$$\Delta_r H = \frac{(d\Delta T_{max}/dC)C_{cal}}{\alpha V} 100\% \quad (2)$$

where C_{cal} is the heat capacity of calorimeter (J K^{-1}); V is the volume of calorimetric vessel (67 cm^3); α is the yield of reaction (%). The parameters of Eq. (2) are given in Table 2.

The presented molar reaction enthalpy includes two contributions: enthalpy of ester hydrolysis and buffer ionization enthalpy (Eq. (3)):

$$\Delta_r H = \Delta_e H + \sum_i \Delta n_i \Delta_r H_{ion} \quad (3)$$

where $\Delta_r H$ is the molar reaction enthalpy (kJ mol^{-1}); $\Delta_e H$ is the enthalpy of ester hydrolysis (kJ mol^{-1}); $\Delta_r H_{ion}$ is the buffer ionization enthalpy (kJ mol^{-1}); Δn is the number of protons released or absorbed by the buffer.

The hydrolysis of *p*-nitrophenyl esters releases two protons (Scheme 1). Correspondingly, the number of protons absorbed by the Tris buffer is two. Therefore, Eq. (3) can be transformed into Eq. (4):

$$\Delta_r H = \Delta_e H + 2\Delta_r H_{ion} \quad (4)$$

Tris ionization enthalpies are given in Table 3. As it can be concluded from Table 3, there is a good agreement between our data and published [35] data measured in water. Figure 3 shows the molar reaction enthalpy and buffer ionization enthalpy plotted *vs*. the water concentration in organic solvent. This work is the first example where the Tris ionization enthalpies were determined over the whole range of the water content in organic solvent. As it can be concluded from Table 3 and Fig. 3, reaction enthalpies and buffer ionization enthalpies depend markedly and similarly on the water content in the organic solvent.

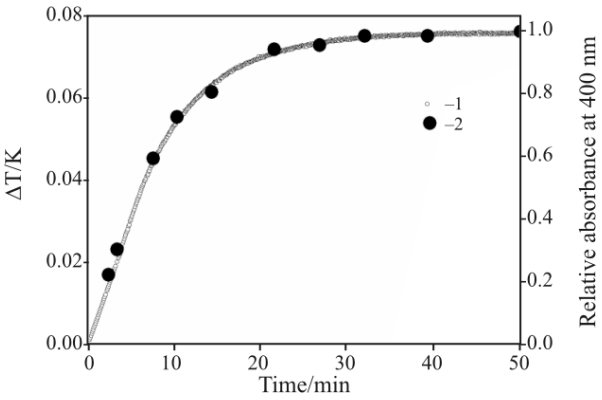


Fig. 1 1 – Typical $\Delta T(t)$ curve for the α-chymotypsin-catalyzed hydrolysis of *Z*-*L*-phenylalanine *p*-nitrophenyl ester in acetonitrile. 2 – Progress curve of the *p*-nitrophenol release for the α-chymotypsin-catalyzed hydrolysis of *Z*-*L*-phenylalanine *p*-nitrophenyl ester in acetonitrile

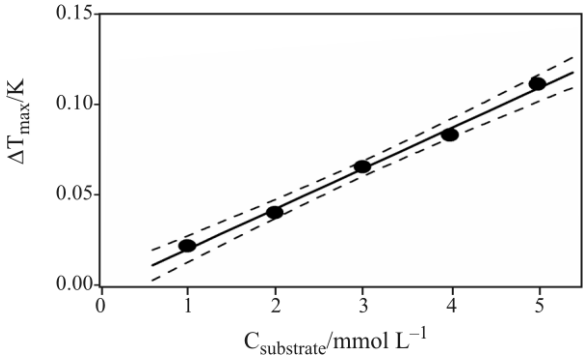


Fig. 2 Correlation between the ΔT_{max} value and the initial substrate concentration. $C_{substrate}$ range is 1.0–5.0·10^{-3} mol L^{-1}. Water content in acetonitrile is 30% (*v*/*v*)

Table 3 Buffer ionization enthalpy in water – acetonitrile mixtures

No.	Water content/%	$\Delta_r H_{ion}$/kJ mol^{-1}	Ref.
1	100	–47.4	[35]
2	100	–47.5±0.2	This work
3	90	–47.4±0.2	This work
4	70	–46.7±0.3	This work
5	30	–40.6±0.3	This work
6	10	–28.7±0.3	This work
7	3	–22.6±0.3	This work

Table 2 Thermochemical parameters of the α-chymotrypsin-catalyzed hydrolysis of *p*-nitrophenyl esters in water – acetonitrile mixtures

Substrate	Water content/%	$\Delta_r H$/kJ mol^{-1}	$d\Delta T_{max}/dC$/K L mol^{-1}	α/%	Ref.
p-nitrophenyl acetate	98.4	–100±8	20±1	87.5	[9]
p-nitrophenyl acetate	96	–106±8	20±1	86	[9]
p-nitrophenyl acetate	90	–102±5	19±1	82.5	[9]
Z-*L*-phenylalanine *p*-nitrophenyl ester	30	–82.3±0.9	23.0±1.0	98.5	This work
Z-*L*-tyrosine *p*-nitrophenyl ester	30	–82.0±1.0	22.8±0.9	97.9	This work

Table 4 Enthalpies of the hydrolysis reaction in compounds with ester bond

No.	Substrate	Water content in organic solvent /vol. %	$\Delta_e H$/kJ mol^{-1}	Ref.
1	*N*-acetyl-*L*-tyrosine ethyl ester	97	–1.1	[28]
2	*N*-acetyl-*L*-tyrosine ethyl ester	97	–1.0	[28]
3	*N*-acetyl-*L*-tyrosine ethyl ester	95	–2.0	[27]
4	*N*-acetyl-*L*-tyrosine ethyl ester	93	–1.1	[27]
5	*p*-nitrophenyl acetate	98.4	–5.2±8	[9]
6	*p*-nitrophenyl acetate	96	–11.2±5	[9]
7	*p*-nitrophenyl acetate	90	–7.2±5	[9]
8	*Z-L*-phenylalanine *p*-nitrophenyl ester	30	–1.5±1.2	This work
9	*Z-L*-tyrosine *p*-nitrophenyl ester	30	–1.8±1.3	This work

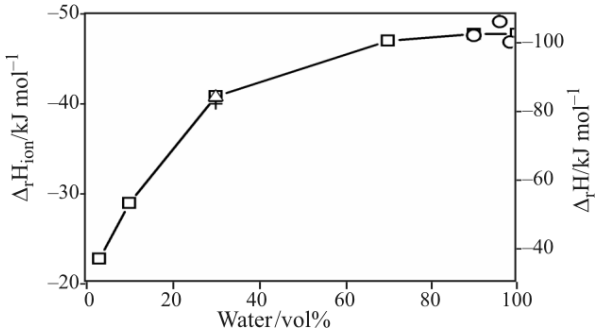


Fig. 3 The enthalpy of the hydrolysis reaction of *p*-nitrophenyl esters and buffer ionization enthalpy plotted *vs*. water content in acetonitrile: O – *p*-Nitrophenyl acetate [9]. + – *Z-L*-tyrosine *p*-nitrophenyl ester. Δ – *Z-L*-phenylalanine *p*-nitrophenyl ester. □ – Tris ionization enthalpies

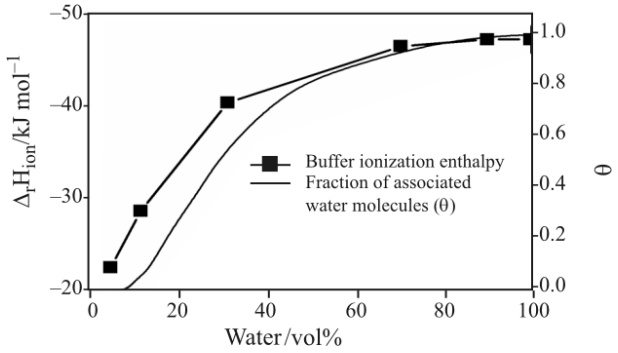


Fig. 4 Buffer ionization enthalpy and fraction of the H-bond associated water molecules (modified data from [36]) plotted *vs*. water content in acetonitrile

We assume that the buffer ionization process strongly depends on the state of water hydrogen bond network in organic liquids. The state of water in acetonitrile was previously studied by IR spectroscopy [36]. It was found that water molecules in acetonitrile exist either as associated (H-bonded) molecules or as single molecules complexed with organic molecules. A sharp decrease in the fraction of associated water molecules was observed in low water organic mixtures (Fig. 4, modified data from [36]). Changes in the buffer ionization enthalpies occur simultaneously with this decrease in the fraction of associated water molecules.

The enthalpy values of ester hydrolysis were estimated using Eq. (5):

$$\Delta_e H = \Delta_r H - \Delta n \Delta_r H_{ion} \quad (5)$$

As it can be concluded from Table 4, there is a good agreement between our and published data for the mixtures with high water content. Table 4 shows that the enthalpy of ester hydrolysis does not depend on the water content in the organic solvent within the limits of experimental errors.

Conclusions

The results of this work can be summarized as follows.

- A special preparation protocol of the reactants in the calorimetric vessel was applied in order to determine the heat effects accompanying the enzyme-catalyzed hydrolysis reaction in organic mixtures with low water content and the Tris buffer ionization enthalpies over the whole range of water content in the organic solvent. The reaction enthalpy of the hydrolysis of *Z-L*-phenylalanine *p*-nitrophenyl ester was determined as (–82.3±0.9) kJ mol^{-1} (0.033 mol L^{-1} Tris buffer, pH 8.0, 298 K, acetonitrile containing 30% (*v*/*v*) of water). The reaction enthalpy of the hydrolysis of *Z-L*-tyrosine *p*-nitrophenyl ester is (–82.0±1.0) kJ mol^{-1} (0.033 mol L^{-1} Tris buffer, pH 8.0, 298 K, acetonitrile containing 30% (*v*/*v*) of water).
- It was shown that the Tris buffer ionization enthalpy and molar enthalpy of the hydrolysis of *p*-nitrophenyl esters depend significantly and similarly on the water content in acetonitrile. It was found that the state of hydrogen bond network of water in acetonitrile is an important factor that

controls the reaction enthalpy as well as the buffer ionization enthalpy.

- The reaction enthalpies were corrected for the buffer ionization enthalpy. The corrected enthalpy of the hydrolysis reaction of *Z*-*L*-phenylalanine *p*-nitrophenyl ester was found to be (–1.5±1.2) kJ mol^{-1} (0.033 mol L^{-1} Tris buffer, pH 8.0, 298 K, acetonitrile containing 30% (*v*/*v*) of water). The enthalpy of the hydrolysis reaction of *Z*-*L*-tyrosine *p*-nitrophenyl ester was found to be (–1.8±1.3) kJ mol^{-1} (0.033 mol L^{-1} Tris buffer, pH 8.0, 298 K, acetonitrile containing 30% (*v*/*v*) of water). The enthalpy values obtained were compared with the published data for the corresponding enthalpy of the hydrolysis reaction in compounds with an ester bond. It was concluded that these enthalpy changes do not depend on the water content in organic solvent mixtures within the limits of experimental errors.

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