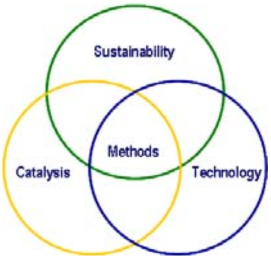

THERMOCHEMICAL INSIGHT INTO "GREEN CHEMISTRY" PROCESSES: EXPERIMENT AND AB INITIO CALCULATIONS

A
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LIST OF PAPERS

This thesis is a summary of the following papers:

1. Toktonov, A. V.; Mognonov, D. M.; Mazurevskaya, Zh. P.; Botoeva, S. O. Synthesis of Polyamidines based on Aromatic Bis(imidoyl) Chlorides in Solution, *Polymer Science, Ser. A* **2006**, *48*(1), 1–10.

2. Verevkin, S.P.; Toktonov, A.V.; Chernyak, Y.; Schäffner, B.; Börner, A. Vapour pressure and enthalpy of vaporization of cyclic alkylene carbonates, *Fluid Phase Equilibria* **2008**, *268*, 1-6.

3. Verevkin, S.P.; Emel'yanenko, V.N.; Toktonov, A.V.; Chernyak, Y.; Schäffner, B.; Börner, A. Cyclic alkylene carbonates. Experiment and first principle calculations for prediction of thermochemical properties, *J. of Chemical Thermodynamics* **2008**, *40*(9), 1428-1432.

4. Emel'yanenko, V.N.; Toktonov, A.V.; Kozlova, S.A.; Verevkin, S.P.; Andrushko, V.; Andrushko, N.; A. Börner. Structure-Energy Relationships in Unsaturated Esters of Carboxylic Acids. Thermochemical Measurements and ab Initio Calculations, *J. Physical Chemistry A* **2008**, *112*(17), 4036–4045.

5. Verevkin, S.P.; Emel'yanenko, V.N.; Toktonov; A.V.; Duwensee, J.; Kragl, U.; Schick, C. Thermodynamics of Sebacic Acid and Butandiol-1,4 and their Biocatalytic Polymerisation, *Industrial&Engineering Chemistry Research*, **2008***, in press.*

6. Verevkin, S.P.; Toktonov; A.V.; Emel'yanenko, V.N.; Goodrich, P.; Hardacre, C. Thermochemistry of Ionic Liquid-Catalysed Reactions. Theoretical and Experimental Study of the Beckmann Rearrangement- Kinetic or Thermodynamic Control? *Industrial&Engineering Chemistry Research* **2009***, submitted.*

7. Verevkin, S.P.; Emel'yanenko, V.N.; Toktonov; A.V.; Börner, A.; Heller, D. Asymmetric Hydrogenation of Non Functionalized Olefins in Propylene Carbonate – Kinetic or Thermodynamic Control? *Industrial&Engineering Chemistry Research* **2009***, submitted.*

8. Verevkin, S.P.; Emel'yanenko, V.N.; Toktonov; A.V.; Leol'ko, A.; Duwensee, J.; Kragl, U.; Sarge, S. Thermochemical and Ab Initio Studies of Biodiesel Fuel Surrogates: 1,2,3-Propanetriol Triacetate, 1,2-Ethanediol Diacetate, and 1,2-Ethanediol Monoacetate. *Industrial&Engineering Chemistry Research* **2009***, accepted.*

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APPENDICES

A. Experimental Procedures, Equipment, and Materials.

1. PREFACE

This work is addressed to the extensive experimental investigation, analysis, and predicting of *energetic* (or *enthalpic*) effects of *chemical reactions*, which are aimed for generating a broad and reliable database of enthalpies of formation ($\Delta_f H_m^\circ$). Such database is required in order to get insight into quantitative structure-energy relationships in organic compounds in terms of *group-additivity values*.

The group-additivity methods serve as a valuable tool to study of quantitative structure-energy relationships. The use of this procedure is straightforward and easy. Any molecule of interest could be collected from additive contributions and some specific non-additive corrections (strains). Strain enthalpy reflects a non-additive contribution to the enthalpy of a molecule. The nature of such deviations from additivity appears unique for each molecule. Following, only a systematic investigation of strain enthalpies allows the detection and prediction of most important interactions. Another advantage of using group-additivity is the convenience of predicting thermodynamic properties for the complex, high molecular weight species, which are usually reaction intermediates of industrially important processes. The residual differences between observation and calculation are small when all the important interactions are taken into account.

In this thesis dealing with the measurements of thermodynamic properties of different compounds in the gaseous, liquid and solid state, an effort is made to relate them to structure of the molecules under study. Thermodynamic properties of compounds, e.g. the enthalpy of vaporization ($\Delta_l^g H_m$)/sublimation ($\Delta_{cr}^g H_m$), the enthalpy of combustion and the enthalpy of formation ($\Delta_f H_m^\circ$) in the liquid/solid phase were derived from experimental methods (vapour pressure measurements and combustion calorimetry). In addition, enthalpies of formation in the gaseous phase were calculated using *ab initio* calculations. The general interrelations of thermodynamic properties are expressed by the following equations:

$$\Delta_f H_m^\circ(g.) = \Delta_f H_m^\circ(liq.) + \Delta_l^g H_m \qquad (1.0),$$

$$\Delta_f H_m^\circ(g.) = \Delta_f H_m^\circ(cr.) + \Delta_{cr}^g H_m \qquad (1.1),$$

$$\Delta_{cr}^g H_m = \Delta_l^g H_m + \Delta_{cr}^l H_m \qquad (1.2).$$

Over the past two decades chemical and engineering research has shown dramatic increase in activity in the area of *green chemistry*, original and innovative approach to environmental protection. Rather than focusing on the control or cleanup of waste and hazardous materials, this approach emphasizes redesigning industrial products and processes to reduce or eliminate the hazards at their source, reducing the amount and toxicity of chemical reactants, hazards of by-products, quantities of waste, and energy consumed, often at reduced costs. To support this strategy, by the year 2020 the chemical industry has established goals of reducing feedstock losses to waste and by-products by 90%, energy intensity by 30%, and emission and effluents by 30%. In surveying the area of green chemistry, there was employed a list of special methods [1]. They are the following:

1. Use of alternative feedstocks that are both renewable and less toxic to human health and to the environment.

2. Use of innocuous reagents that are inherently less hazardous and are catalytic.
3. Employment of natural processes—biosynthesis, biocatalysis, and biotech-based chemical transformations for both efficiency and selectivity.
4. Use of alternative solvents that reduce potential harm to the environment and serve as alternatives to currently used volatile organic solvents, chlorinated solvents, and other hazardous chemicals.
5. Safer chemical design—with principles of toxicology to minimize intrinsic hazards while maintaining needed functionality.
6. Development of alternative reaction conditions that increase selectivity and enable easier separations.
7. Minimization of energy consumption.

In general, chemical processes obey thermodynamic or kinetic control. If we know enthalpies, and equations of state of the chemical species involved, we can predict with accuracy the chemical composition of this final equilibrium state. However, thermodynamics is unable to say anything about the time required to attain equilibrium, or about the behavior, or about the composition of the system during the period of change. These latter problems are the field of chemical kinetics, which is directly concerned with the description of chemical systems the properties of which are varying with time.
In the frame of this thesis we have studied thermodynamic properties of some perspective "*green solvents*", such as alkylene carbonates (Chap. 2 and 3) and ionic liquids (Chap. 4). The subject under study was restricted to several examples of their application in green chemical processes, where the main common rules of thermodynamics and kinetics have been used as important tool for optimization of sustainable chemical processes (including *polycondensation* in Chap. 5 and 6 and *bio-fuels* as renewable energy resource in Chap. 7 and 8). Summaries of seven chapters of the thesis are given below for a short introduction of general ideas:

Chapter 2 *Cyclic Carbonates: Thermochemical Experiment and Ab initio Calculation for Prediction of Thermochemical Properties* contains detailed description of thermodynamic properties of cyclic alkyl carbonates. Enthalpies of vaporization and enthalpies of sublimation of neoteric "green solvents" *ethylene carbonate, propylene carbonate, butylene carbonate, and glycerine carbonate* were obtained from the temperature dependence of the vapour pressure measured by the transpiration technique. Experimental vapour pressure data available in the literature were treated together with the new own experimental data and approximating equations were suggested for all alkylene carbonates under study. The standard molar enthalpies of formation of *ethylene carbonate, propylene carbonate, butylene carbonate* were measured using combustion calorimetry. Ab initio calculations of molar enthalpies of formation of alkylene carbonates were performed using the G3MP2 method. The calculated values were in good agreement with available experimental data. Ring strain corrections were quantified for the refinement of the group-contribution method for prediction of enthalpies of formation and enthalpies of vaporization of alkylene carbonates.

Chapter 3 *Reactions in Cyclic Carbonates: Asymmetric Hydrogenation in Propylene Carbonate.* Propylene carbonate has been revealed as a perfect solvent in the rhodium-catalyzed *asymmetric hydrogenation* and *hydroformylation* of olefins. In this work thermodynamics of the iridium-catalyzed asymmetric hydrogenation of *1-methylene-1,2,3,4-tetrahydronaphthalene* and (*4-methyl-1,2-dihydronaphthalene*) have been performed. In contrast to methylene chloride, high *enantioselectivity* related to *(S)*-enantiomer in propylene carbonate has been observed. Computation studies of Gibb's energy and equilibrium constants in the gaseous and in the liquid state revealed that the asymmetric hydrogenation was kinetically controlled.

Chapter 4 *Thermochemistry of Ionic Liquid-Catalysed Reactions: Experimental and Theoretical Study of Beckmann Rearrangement of 2-Butanone- and Cyclohexanone Oximes*. This work has been undertaken in order to perform thermodynamic analysis of experimental condition of the Beckmann rearrangement of oximes into amides. The question has been addressed whether the reactions obey thermodynamic or kinetic control. To answer this question, thermodynamic properties of the typical Beckmann rearrangement reactions in the ideal gaseous state: *cyclohexanone oxime → caprolactam* and *2-butanone oxime → N-methylpropanamide* were studied by using the quantum mechanical method. Gibbs energies and equilibrium constants of the Beckmann rearrangement have been assessed in the gaseous and the liquid phases. Results of the thermodynamic analysis have shown that Beckmann rearrangements are kinetically controlled. Thus, a search for possible active ionic liquid based catalysts for the mild conditions has been performed.

Chapter 5 *Thermochemical Study of Enzymatic Polymerization based on 1,4-Butanediol and Sebacic Acid*. This investigation was undertaken to establish a consistent set of vapour pressures, sublimation, vaporization, formation and fusion enthalpies of *1,4-butanediol*, *sebacic acid* (*decanedioic acid*), and *dodecanedioic acid*. This data were used for evaluation of the enthalpy of biocatalytic polycondensation of sebacic acid with 1,4-butanediol. The standard molar enthalpies of formation of 1,4-butanediol, sebacic acid, dodecanedioic acid, and polyester based on 1,4-butanediol and sebacic acid were measured using combustion calorimetry. Molar enthalpies of vaporization and sublimation of compounds under study (except for polymer) were obtained from the temperature dependence of the vapour pressure measured by transpiration method. Fusion enthalpies of sebacic acid and dodecandioic acid were measured using DSC. Ab initio calculations of molar enthalpies of formation of 1,4-butanediol, sebacic acid, and dodecanedioic acid have been performed using G3MP2 and DFT methods and results are in good agreement with the experimental data. Enthalpies of polymerization, ΔH_{pol} = -85,5 and -125,3 $\mathrm{kJ \cdot mol^{-1}}$ have been calculated from experimental enthalpies of formation of monomers and polymers and referred to the polycondensation of solid (undissolved) and liquid (dissolved) sebacic acid. Large value of equilibrium constant, $K_{pol} = 6{,}2 \cdot 10^{17}$ has proved that equilibrium shifted towards polymer formation. Following, the polycondensation of 1,4-butanediol with *sebacic acid* is favoured thermodynamically and high yield of the polymer can be achieved under kinetic control with help of an any suitable active catalyst (e.g. lipase from *Candida antarctica B.*).

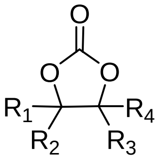
Chapter 6 *Synthesis and Thermochemical Study of Aromatic Polyamidines* contains a detailed description of synthesis and properties of new aromatic polyamidines with two nitrogen atoms in the polymer chain ~NH-CPh=N~. Polyamidines were synthesized *via* reaction of aromatic *diamines* with aromatic *bis-imidoyl chlorides* in solution catalyzed by tertiary amines and pyridine-N-oxide. New model compounds based on the reaction of new aromatic imidoyl chlorides with amines were prepared, isolated and then characterized. The standard molar enthalpy of formation of typical polyamidine was measured using combustion calorimetry. The standard molar enthalpies of formation of the monomers were calculated with help of group additivity procedure. Analysis of the polycondensation process has revealed that polycondensation not especially favored by thermodynamics. Possible reasons for formation of the low-molecular weight polymers are discussed.

Chapter 7 *Unsaturated Esters: Experiment and Ab Initio Calculation for Prediction of Thermochemical Properties.* Standard molar enthalpies of formation in the gaseous state of a series of *alkyl 3-methylbut-2-enoates* have been obtained from combustion calorimetry and results from the temperature dependence of the vapour pressure measured by transpiration method. In order to verify the experimental data, ab initio calculations of all compounds have been performed. Enthalpies of formation derived from G3MP2 method are in good agreement with the experimental results. Quantitative analysis of strain effects in alkyl 3-methylbut-2-enoates was discussed in terms of deviation of $\Delta_f H_m^\circ\ (g.)$ from the group additivity rules. *Energetics* of the *cis-trans isomerization* of carboxylic acids derivatives was studied using G3MP2 and DFT methods. Values of strain and cis-trans corrections derived in this work provide a further improvement on the group-contribution methodology for prediction of the thermodynamic properties of compounds related to biodiesel.

Chapter 8 *"Designer" Biodiesel: Experiment and Ab Initio Calculation for Prediction of Thermochemical Properties.* This work has been undertaken in order to obtain new thermochemical data for *1,2-entandiol* and *propanetriol* (*glycerol*) acetates and to improve the group-contribution methodology for prediction of the thermodynamic properties of compounds related to biodiesel. Standard molar enthalpies of formation in the gaseous state of a series of *1,2-ethandiol monoacetate, 1,2-ethandiol diacetate,* and *1,2,3-propandiol triacetate* have been obtained from combustion calorimetry and results from the temperature dependence of the vapour pressure measured by transpiration method. In order to verify the experimental data, ab initio calculations of all compounds have been performed. Enthalpies of formation derived from G3MP2 method are in good agreement with the experimental results. Strength of the hydrogen bond in 1,2-ethandiol monoacetate and in 1,2-ethandiol have been obtained using ab initio and group-contribution methods.

2. CYCLIC CARBONATES: EXPERIMENT AND AB INITIO CALCULATIONS FOR THE PREDICTION OF THEIR THERMOCHEMICAL PROPERTIES

2.1. INTRODUCTION


(1)

Five-membered alkylene carbonates (*1,3-dioxolan-2-ones*) of the general structure (1) have been the subject of considerable interest. In particular, ethylene carbonate (EC, $R_{1\text{-}4}$=H), propylene carbonate (PC, $R_1=R_2=R_3$=H, $R_4=CH_3$), butylene carbonate (BC, $R_1=R_2=R_3$=H, $R_4 = CH_2CH_3$) and glycerin carbonate (GC, $R_1=R_2=R_3$=H, $R_4 = CH_2OH$) have been available commercially for over 40 years (*Huntsman Co.*) [2]. EC, PC and BC have found numerous applications as both reactive intermediates and inert solvents. They are used in many industrial applications such as cleaning, degreasing, paint stripping, gas treating, textile dyeing, etc. A short survey of their physical properties given in the Table 2.1 proves that alkylene carbonates are attractive candidates to be green solvents.

Table 2.1. Properties of *Ethylene Carbonate*, *Propylene Carbonate*, *Butylene Carbonate* and *Glycerin Carbonate* [3].

Property	EC	PC	BC	GC
Boiling point (°C)	248	242	251	110[c]
Freezing/melting point (°C)	36,4	-49	-45	-69
Flash point (°C)	160	135	135	>190
Viscosity (*cP*, 25 °C)	2,56[a]	2,50	3,16	85,4
% VOC[b] (110°C)	34	28	-	-

[a] supercooled liquid (e.g. water 0,89 *cP*).
[b] volatile organic content.
[c] at 0,1 mm. Hg.

The alkylene carbonates have been increasingly attractive not only for their unique physico-chemical properties but also for their low toxicity and biodegradability [4,5]. Also their relative simplicity of the manufacturing underlines partly such commercial success and academic interest related to sustainable chemistry [6,7]. One of the promising reactions involving CO_2 is a chemical fixation of carbon dioxide as cyclic carbonates with further synthesis of polycarbonates. In addition, EC, PC and BC are widely used utility as electrolytes in the production of lithium ion batteries [8]. Recent studies have revealed specific features of PC towards asymmetric hydrogenation with self-assembling catalysts [9] and for palladium-catalyzed substitution reactions [10]. There is a great interest in the computation of heat balances, equilibrium yields and feasibilities of processes, using the thermodynamic properties of organic compounds. Unfortunately, thermodynamic information is rather limited in the literature [11-14]. Knowledge of vapour pressures and vaporization enthalpies of pure alkylene carbonates is crucial for modeling of phase equilibrium and separation processes. The data for alkylene carbonates reported in the literature are measured at high temperatures up to the normal boiling temperature [15]. In the present chapter the transpiration method makes it possible to obtain vapour pressure data in the range possibly closer to ambient temperatures, which are particularly of interest to environmental chemistry.

Thermodynamic properties of alkylene carbonates such as enthalpies of vaporization ($\Delta_l^g H_m$), sublimation ($\Delta_{cr}^g H_m$), and fusion ($\Delta_{cr}^l H_m$), as well as standard enthalpy of formation ($\Delta_f H_m^\circ$) in the gaseous and condensed states were obtained from experimental studies (vapour pressures measurements and combustion calorimetry). Additionally *ab initio* methods for the calculation of $\Delta_f H_m^\circ$ (g.) were applied for validation of experimental results. Group additivity methods were developed in this work for prediction $\Delta_l^g H_m$ and $\Delta_f H_m^\circ$ (g.) of organic carbonates under study.

2.2. VAPOUR PRESSURES, ENTHALPIES OF SUBLIMATION AND VAPORIZATION

Detailed description of the experimental technique is given in Appendix A. In short, saturated vapour pressure of the organic liquid or solid substance (p_i^{sat}) at the temperature of measurement (T_i) was determined from the mass of sample (m_i) transported by an inert gas and collected in a cold trap within a definite period of time. The (m_i) has been measured by GC-analysis. Assuming that the vapour phase behaves ideally and obeys the *Dalton's law* the values of p_i^{sat} were calculated from the equation:

$$p_i^{sat} = {m_i R T_i}/{V M_i}; \qquad V = V_{N_2} + V_i; \qquad (V_{N_2} \gg V_i) \qquad (2.1),$$

where R = 8,314472 J·K^{-1}·mol^{-1}; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas and T_i is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equations:

$$R \cdot p_i^{sat} = a + \frac{b}{T_i} + \Delta_l^g C_p \cdot \ln\left(\frac{T_i}{298{,}15\ (\mathrm{K})}\right) \qquad (2.2),$$

$$R \cdot p_i^{sat} = a + \frac{b}{T_i} + \Delta_{cr}^g C_p \cdot \ln\left(\frac{T_i}{298{,}15\ (\mathrm{K})}\right) \qquad (2.3),$$

where a and b are constants of the observed linear dependence; $\Delta_l^g C_p$ is difference between molar heat capacity of the substance in the gaseous and liquid phase at 298,15 K; $\Delta_{cr}^g C_p$ is difference between molar heat capacity of the substance in the gaseous and solid phase (298,15 K):

Hence, the expressions for the vaporization $\Delta_l^g H_m$ and sublimation $\Delta_{cr}^g H_m$ enthalpies referred to 298,15 K can be written as follows:

$$\Delta_l^g H_m(298{,}15\ \mathrm{K}) = -b + \Delta_l^g C_p \cdot 298{,}15\ (\mathrm{K}) \qquad (2.4),$$

$$\Delta_{cr}^g H_m(298{,}15\ \mathrm{K}) = -b + \Delta_{cr}^g C_p \cdot 298{,}15\ (\mathrm{K}) \qquad (2.5)$$

Values of $\Delta_l^g C_p$ and $\Delta_{cr}^g C_p$ were derived using the procedure of *Chickos* and *Acree* [19]. Experimental data on vaporization and sublimation enthalpies are given in Table 2.3.

2.2.1. *Ethylene Carbonate*. Vapour pressure data reported in the literature for EC are represented in Fig. 2.1. New results obtained in this work are in good agreement with the earlier measurements obtained by ebulliometry.

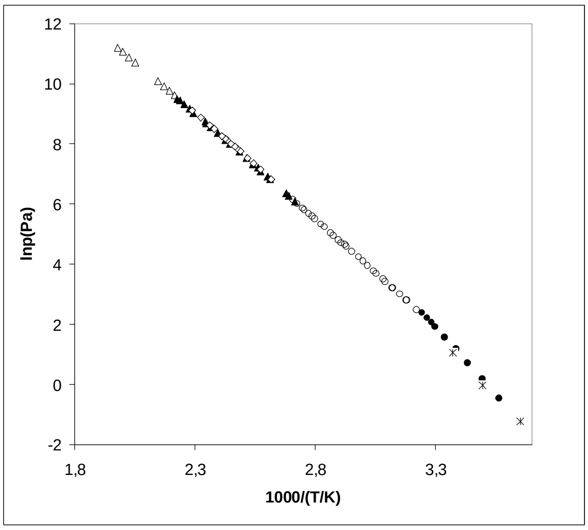


Fig. 2.1. Vapour pressure over the solid and liquid EC measured by different methods: (o)- this work, liquid phase; (•)- this work, solid phase; (Δ)- [15]; (▲)- [16]; ( )- [17]; (ж)- [18].

At the reference temperature (298,15 K) this compound is a solid. The T_{fus} of EC is 309,5 K. There were only three experimental points measured over solid sample using Knudsen method [18]. These data were found to be in a close agreement with the results obtained in our measurements as it shown in the Fig.2-1. Values of vaporization enthalpy, $\Delta_l^g H_m$(298,15 K) = (60,8 ± 0,1) kJ·mol^{-1} and sublimation enthalpy, $\Delta_{cr}^g H_m$(298,15 K) = (74,1 ± 0,6) kJ·mol^{-1} for EC were determined by eqs. (2.4) and (2.5) in the temperature range (at 280,6 K to 302,4 K over solid sample) and in the temperature range (at 310,3 K to 369,5 K over liquid sample) respectively (Table 2.3).

The consistency of our measurements can be verified by comparison of experimental enthalpy of fusion obtained from eq. 2.6:

$$\Delta_{cr}^l H_m(298{,}15\,\text{K}) = \Delta_{cr}^g H_m - \Delta_l^g H_m = 74{,}1 - 60{,}8 = (13{,}3 \pm 0{,}7)\ \text{kJ·mol}^{-1} \quad (2.6)$$

At 298,15 K with the literature value $\Delta_{cr}^l H_m(T_{fus})$ determined by DSC in [19] and then adjusted to the reference temperature 298,15 K. According to [19] the experimental enthalpy of fusion is $\Delta_{cr}^l H_m$ (at T_{fus} 309,49 K) = 13,3 kJ·mol^{-1}. The following equation was applied to adjust the experimental $\Delta_{cr}^l H_m(T_{fus})$ to the reference temperature (298,15 K) [20]:

$$\Delta_{cr}^l H_m(298{,}15\text{K})\}/(\text{J·mol}^{-1}) = \Delta_{cr}^l H_m(T_{fus}/\text{K}) + \{(0{,}75 + 0{,}15\, C_p^{cr})[(T_{fus}/\text{K}) - 298{,}15]\}$$
$$- \{(10{,}58 + 0{,}26\, C_p^l)[(T_{fus}/\text{K}) - 298{,}15]\} \quad (2.7),$$

where the values of experimental isobaric molar heat capacity of EC in the liquid and solid phase are known [21] and they are C_p^l= 136,2 J·mol^{-1}·K^{-1} and C_p^{cr} = 117,4 J·mol^{-1}·K^{-1} respectively. The resulting standard enthalpy of fusion, $\Delta_{cr}^l H_m$ (298,15 K) calculated by eq. (2.7) is 13,0 kJ·mol^{-1}. This value of $\Delta_{cr}^l H_m$ (298,15 K) was in close agreement with our experimental value (13,3±0,7)kJ·mol^{-1}

obtained by eq. (2.6), which confirms the consistency of our vapour pressure measurements. It should be mentioned that the enthalpy of fusion, $\Delta_{cr}^{l}H_m(T_{fus})$ reported by *Vasil'ev* and *Korkhov* and selected for comparison was found to be in good agreement with another values available from the literature [22,23].

2.2.2. *Propylene Carbonate.* Vapour pressures of PC were measured earlier by ebulliometry, static method, and Knudsen effusion method. Results obtained in the literature agree well with those obtained in the present work, except for several data points measured by Knudsen effusion [18] and static [26] methods at low temperatures, as is presented in the Fig. C1 (see Appendix C). Enthalpies of vaporization of PC (see Table 2.3) determined from each sets of vapour pressure data [15-18,25,27] are in close agreement to our new result.

2.2.3. *Butylene Carbonate.* Figure C2 (Appendix C) illustrates the temperature dependence of vapour pressures for BC measured previously and in this work using the transpiration method. Our data evaluated are consistent with those obtained by ebulliometry [15]. Enthalpies of vaporization derived from both data sets are in an acceptable agreement (see Table 2.3).

2.2.4. *Glycerin Carbonate.* The data from vapour pressure measurements of glycerin carbonate is presented in the Fig. C3 (Appendix C) and is found to be also consistent with data determined by ebulliometry [15]. Enthalpies of vaporization (see Table 2.3) derived from both data sets were in a reasonable agreement considering the possible extrapolation errors of high-temperature data to ambient temperatures [15]. There were some complications with GC-analysis of glycerin carbonate. To insure accurate determination of the amount of transported compound (m_i) in eq. (2.1), an alternative analytical procedure was used in addition to the standard GC-technique. Glycerin carbonate was collected in a special cold trap followed by direct weighting of the condensed product using an analytical balance with the accuracy of (±0,0001 g). Vapour pressure data determined by both analytical procedures was found practically indistinguishable as shown in the Fig. C3.

2.3. CORRELATION OF VAPOUR PRESSURES

Having established good agreement between present vapour pressure data and those reported previously, available experimental data of cyclic alkylene carbonates were treated together to get correlations accurately describing the vapour pressure over a temperature range from ambient to the normal boiling point. In Table 2.2 the coefficients of the vapour pressure correlation according to eq. (2.2) as well as the recommended molar enthalpies of vaporization values according to eq. (2.4) at 298,15 K have been summarized.

Table 2.2. Vapor Pressure Coefficients in eq. (2.2) and Recommended Enthalpies of Vaporization ($\Delta_l^g H_m$) at 298,15 K in kJ·mol^{-1} for Cyclic Alkylene Carbonates.

Compound	T-range, K	*a*	*b*	$-\Delta_l^g C_p$ (J·mol^{-1}·K^{-1})	$\Delta_l^g H_m$ (298,15 K)
EC	310,3-505,5	270,02	-76971,19	47,5	62,8±0,1
PC	298,2-513,2	273,41	-76362,22	54,1	60,2±0,1
BC	288,6-522,7	286,38	-81761,66	61,6	63,4±0,2
GC	330,2-455,6	316,35	-105625,97	66,3	85,9±0,2

The primary data on vapour pressures (p_i^{sat}) and vaporization enthalpies ($\Delta_l^g H_m$) of cyclic alkylene carbonates measured in this work are collected in Table B1 (see Appendix B). The summary of available data on enthalpies of vaporization is given in Table 2.3.

Table 2.3. Summary of Vaporization Enthalpies ($\Delta_l^g H_m$) in kJ·mol^{-1} available for Ethylene Carbonate, Propylene Carbonate, Butylene Carbonate and Glycerin Carbonate.

Compound	Method[a]	T-range, K	$\Delta_l^g H_m$ (T)	$\Delta_l^g H_m$ (298,15K)[b]	Ref.
EC (cr.)	K	273,9-296,6	68,7±1,9[c]	68,5±1,9[c]	18
	T	280,6-302,4	74,2±0,6[c]	**74,1±0,6**[c]	this work
EC (liq.)	E	423	56,5	62,4	6
	E	382,1-436,8	58,1±0,3	63,4±0,3	17
	E	451,6-505,5	55,5±0,1	64,0±0,1	15
	E	368,4-449,9	58,4±0,2	63,5±0,2	16
	T	310,3-369,5	58,9±0,1	**60,8±0,1**	this work
PC (liq.)	K	328,2-369,6	33,8±2,3	36,6±2,3	18
	S+E	363,2-508,2	55,5±0,5	62,6±0,5	24
	E	412,8-466,2	53,6±0,1	61,3±0,1	17
	E	459,9-513,2	51,1±0,1	61,3±0,1	15
	E	368,6-462,1	55,7±0.2	61,8±0,2	16
	L	668,6-762,6	48,7±0,6	71,2±0,6	25
	S	298,2-473,2	58,8±0,8	62,9±0,8	26
	S	318,2-473.2	55,8±0,2	60,6±0,2[d]	26
	T	298,4-344,9	60,2±0,3	**61,5±0,3**	this work
BC (liq.)	E	397,3-522.7	54,2±0,1	63,8±0,1	15
	T	288,6-343.8	62,2±0,3	**63,2±0,3**	this work
GC (liq.)	E	429,9-455,6	78,1±0,4	87,8±0.4	15
	T	330,2-398,5	81,2±0,4	**85,4±0,4**	this work

[a] applied methods: E- ebulliometry; S- static manometer; T- transpiration; L- low residence time flow method; K- Knudsen effusion.

[b] literature vapour pressure data were treated with eqs. 2.1-2.5 (Chap. 2) to determine the enthalpy of vaporization at 298,15 K consistent with values presented in Table B1 (Appendix B).

[c] enthalpy of sublimation, $\Delta_{cr}^g H_m$.

[d] first four experimental points from the original work were omitted due to their inconsistency.

2.4. Enthalpies of Formation of Cyclic Alkylene Carbonates

The results of combustion experiments for cyclic alkylene carbonates are given in Tables B9 in Appendix B (see also description to Combustion Experiment in Appendix A). To derive ($\Delta_f H_m^\circ$) in the liquid or solid phase from ($\Delta_c H_m^\circ$) molar enthalpies of formation of H_2O (liq.): (-285,830±0,042) kJ·mol^{-1} and CO_2 (g.): (-393,51±0,13) kJ·mol^{-1} were taken as assigned by *CODATA* [28]. The standard molar enthalpies of combustion and standard molar enthalpies of formation of cyclic alkylene carbonates are listed in the Table 2.4 (first and second columns). The total uncertainties were calculated according to the guidelines recommended by *Olofsson* [29]. They included the absolute standard deviation from combustion of materials, uncertainties from calibration, combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

Table 2.4. Thermochemical Data at 298,15 K and 0,1 MPa for Cyclic Alkylene Carbonates, kJ·mol^{-1}

Compound	$\Delta_c H_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (g.)
EC (cr.)	-1167,4±0,4	-584,8±0,6	74,1±0,6[a] 62,8±0,1	-510,7±0,9
PC (liq.)	-1817,4±0,6	-614,1±0,8	60,2±0,1	-553,9±0,8
BC (liq.)	-2470,8±1,0	-640,1±1,2	63,4±0,2	-576,7±1,2
GC (liq.)	-	-	85,9±0,2	-

[a] enthalpy of sublimation, $\Delta_{cr}^g H_m$.

Enthalpy of combustion of BC was measured for the first time. Earlier calorimetric determinations of $\Delta_f H_m^\circ$ (cr.) for EC had been reported by *Silvestro et al.* [12]: (-580,9±1,3) kJ·mol^{-1}; *Vasil´eva et al.* [13]: (-581,6±0,4) kJ·mol^{-1} and *Calhoun* [14]: (-586,3±3,8) kJ·mol^{-1}. These values are in the agreement with value obtained in this work, but in disagreement with (-584,8±0,6) kJ·mol^{-1},(-682,8±2,1) kJ·mol^{-1} [18], and (-590,9) kJ·mol^{-1} [11].

There are only two values of $\Delta_f H_m^\circ$ (liq.) for PC obtained previously from combustion calorimetry: (-631,8±2,1) kJ·mol^{-1} [18] and (-613,4±1,3) kJ·mol^{-1} [13]. Our value of $\Delta_f H_m^\circ$ (liq.) determined in this work by combustion experiment (-614,1±0,8) kJ·mol^{-1} was found to agree well with value reported by *Vasil´eva et al* [13]. Thus, our new result helps to resolve the uncertainty on standard molar enthalpy for PC available in the literature.

The results obtained from our transpiration and combustion experiments were used for further calculation of standard enthalpies of formation, $\Delta_f H_m^\circ$ (g.) at 298,15 K using eqs. (1.0) and (1.1) (see Preface). The resulting values of $\Delta_f H_m^\circ$ (g.) for cyclic alkylene carbonates are given in the last column of Table 2.4.

2.5. AB INITIO CALCULATIONS OF CYCLIC ALKYLENE CARBONATES

We used G3MP2 to calculate total energies at 0 K and enthalpies at 298,15 K of the molecules studied in this work (see in Table 2.5).

Table 2.5. G3MP2 total energies at 0 K and enthalpies at 298,15 K (in Hartree) for Ethylene Carbonate, Propylene Carbonate, Butylene Carbonate and Glycerin Carbonate.

Compound	E_0	H_{298}
EC	-341,955390	-341,949504
PC	-381,198374	-381,191084
BC	-420,432786	-420,424070
GC	-456,337492	-456,329067

Enthalpies of formation for EC, PC, BC and GC have been calculated using atomization [30] and bond separation reactions [31]. For the latter method the following reactions were applied:

EC: 1) $C_3H_4O_3 \ + \ 8CH_4 \ \leftrightarrows \ 3CH_3OH \ + 4C_2H_6$ (2.10),

2) $C_3H_4O_3 \ + \ 11CH_4 \ \leftrightarrows \ 3H_2O \ + 7C_2H_6$ (2.11),

PC: 1) $C_4H_6O_3 \ + \ 9CH_4 \ \leftrightarrows \ 3CH_3OH \ + 5C_2H_6$ (2.12),

2) $C_4H_6O_3 \ + \ 12CH_4 \ \leftrightarrows \ 3H_2O \ + 8C_2H_6$ (2.13),

BC: 1) $C_5H_8O_3 \ + \ 10CH_4 \ \leftrightarrows \ 3CH_3OH \ + 6C_2H_6$ (2.14),

2) $C_5H_8O_3 \ + \ 13CH_4 \ \leftrightarrows \ 3H_2O \ + 9C_2H_6$ (2.15),

GC: 1) $C_4H_6O_4 \ + \ 10CH_4 \ \leftrightarrows \ 4CH_3OH \ + 5C_2H_6$ (2.16),

2) $C_4H_6O_4 \ + \ 14CH_4 \ \leftrightarrows \ 4H_2O \ + 9C_2H_6$ (2.17).

Enthalpies of these reactions calculated by G3MP2 method and experimental enthalpies of formation $\Delta_f H_m^\circ$ (g), of methane, methanol, water and ethane from *Pedley et al.* [31], were used to determine enthalpies of formation of alkylene carbonates. For example, bond separation energy of reaction in the gaseous phase according to eq. (2.10) was obtained according to the Hess's law. Both procedures applied in calculation enthalpies of formation for cyclic alkylene carbonates (atomization procedure and bond separation reactions) are practically indistinguishable (Table 2.6). The average calculated from both procedures is in close agreement with the experimental results given in the last column.

Table 2.6. Calculated and Experimental Standard Enthalpies of Formation $\Delta_f H_m^\circ$ (g.) for the Different Alkylene Carbonates at 298,15 K in kJ·mol^{-1}.

	$\Delta_f H_m^\circ$ atomization	$\Delta_f H_m^\circ$ eq. (2.10)	$\Delta_f H_m^\circ$ eq. (2.11)	$\Delta_f H_m^\circ$ G3MP2[a]	$\Delta_f H_m^\circ$ exp.
EC	-508,4	-509,5	-508,5	-508,8	-510,7±0,9
PC	-552,3	-552,9	-551,9	-552,4	-553,9±0,8
BC	-573,7	-573,8	-572,8	-573,4	-576,7±1,2
GC	-699,0	-	-699,5	-699,3	-
DMC[b]	-569,5	-571,3	-570,4	-570,4	-571,0±0,4[30]
DEC[c]	-638,4	-639,2	-638,3	-638,6	-637,9±0,8[30]
MCC[d]	-662,9	-661,5	660,5	-661,6	-657,6±4,2[30]

[a] average value from columns 2,3, and 4.

[b] DMC= *dimethyl carbonate.*

[c] DEC= *diethyl carbonate.*

[d] MCC= *methyl-cyclohexyl carbonate.*

2.6. STRUCTURE-ENERGY RELATIONSHIPS. STRAIN ENTHALPIES (H_S) OF CYCLIC ALKYLENE CARBONATES

Conventional strain-enthalpy (H_S) of a molecule is defined as the difference between its experimental enthalpy of formation $\Delta_f H_m^\circ$ (g.) and its estimated sum of the *Benson-type* increments [34,35]. The system of group additive increments based on the standard enthalpies of formation $\Delta_f H_m^\circ$ (g.) and molar enthalpies of vaporization ($\Delta_l^g H_m$) was established recently [33]. The group additivity values

(GAV) are listed in Table 2.7. The new experimental values for $\Delta_f H_m^\circ$ (g.) and $\Delta_l^g H_m$ of the cyclic alkyl carbonates (*see* the Table 2.4) and increments from Table 2.7 were used to determine a strain enthalpy H_S = ($\Delta_f H_m^\circ$ (g.) – $\sum$ increments) for each structure of carbonates under study. The estimated values of H_S as a result of this procedure are presented in Table 2.8. Cyclic alkyl carbonates listed in this table are a typical example of similarly shaped molecules which made up of five-membered rings, where an alkyl substituent R (methyl- or ethyl-group) is attached to the ring. Hence the strain, H_S, of a molecule is expected to provide insight into the energetic interactions of an alkyl substituent R with the ring.

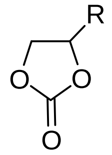


Table 2.7. Group-additivity Values for the Calculation of Enthalpies of Formation ($\Delta_f H_m^\circ$) and Enthalpies of Vaporization ($\Delta_l^g H_m$) of Cyclic Alkylene Carbonates at 298,15 K (in kJ·mol^{-1}).

Increment	$\Delta_f H_m^\circ$ (g.)	$\Delta_l^g H_m$	Increment	$\Delta_f H_m^\circ$ (g.)	$\Delta_l^g H_m$
C-(C)(H)$_3$	-41,32	5,69	C(O)(H$_3$)	-41,32	5,69
C-(C)$_2$(H)$_2$	-22,90	4,88	C(O)(H$_2$)(C)	-32,50	2,64
C-(C)$_3$(H)	-11,12	2,61	C(O)(H)(C$_2$)	-31,85	-1,28
C-(C)$_4$	-3,89	-0,47	C(O)(C$_3$)	-21,75	-6,30
(C-C)$_{1-4}$	2,34	0,10	Ph(O)	95,00	27,71
CO(O$_2$)	-487,64	27,04	5-membered ring	39,5	25,3

The strain enthalpies for all alkyl carbonates derived in this work are approximately 40 kJ·mol^{-1} and this value may be considered as equal within the uncertainties of the experiment as it was expected for similarly shaped 5-membered ring derivatives. H_S value reflects the intrinsic strain that is typical for the cyclic molecules where non-bonded sterical interactions of the carbon and oxygen atoms can be presented. No additional interactions of an alkyl substituent R with the ring could be detected. These strains in cyclic alkylene carbonates are also comparable to the strain H_S = 38,1 kJ·mol^{-1} of the *cyclopentane* (*see* the Table 2.8). Such a similarity of the strains occurred in carbonates enables to make the analogies in the interpretation of the experimental data. For this reason, an additional correction term which takes into account the strain of the five-membered ring should be introduced for the prediction of $\Delta_f H_m^\circ$(g.).

Table 2.8. Corrections to Enthalpies of Formation ($\Delta_f H_m^\circ$ *exp.*) and Enthalpies of Vaporization ($\Delta_l^g H_m$ *exp.*) of Cyclic Alkylene Carbonates at 298,15 K (in kJ·mol^{-1}).

Compound	$\Delta_f H_m^\circ$ (g.) exp.	Σ_{incr}[a]	H_S[b]	$\Delta_l^g H_m$ exp.	Σ_{incr}[c]	GAV[d]
EC	-510,7±0,9	-552,6	41,9	62,8±0,1	32,3	30,5
PC	-553,9±0,8	-593,6	39,7	60,2±0,1	34,1	26,1
BC	-576,7±1,2	-616,2	39,5	63,4±0,2	39,0	24,4
Cyclopentane	-76,4±0,8[e]	-114,5	38,1	28,7±0,1[e]	24,4	4,3

[a] sum of the increments from Table 2.7, column 2.

[b] H_S = ($\Delta_f H_m^\circ$ (g) – $\sum$ increments)= difference between column 2 and 3 of this table.

[c] sum of the increments from Table 2.7, column 3.

[d] the difference between column 5 and 6 of this table.

[e] from work [31].

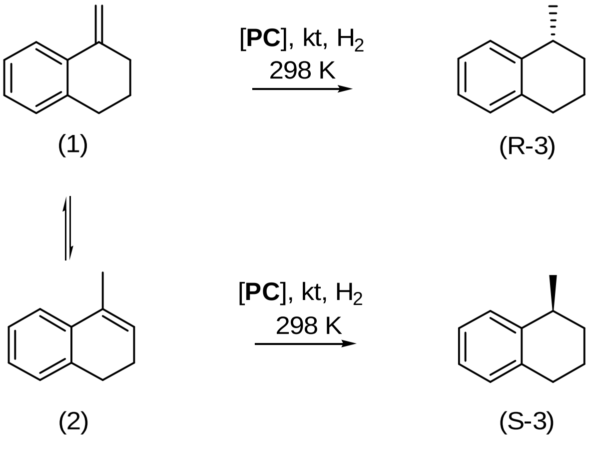
The similar analysis was performed on enthalpies of vaporization, $\Delta_l^g H_m$. According to Table 2.8, the corrections for a five-membered ring for PC (26,1 kJ·mol^{-1}) and BC (24,4 kJ·mol^{-1}) are nearly the same, but are significantly different from the unsubstituted five-membered ring correction of EC (30,5 kJ·mol^{-1}). This discrepancy demonstrates that the interactions of alkyl substituent R with the ring are not negligible for this thermodynamic property. Thus, an additional correction term for the alkyl substituted five-membered ring should be accounted for the prediction of $\Delta_l^g H_m$. Surprisingly, the five-membered ring corrections for the unsubstituted five-membered ring of for EC (30,5 kJ·mol^{-1}) and its alkyl derivatives are substantially larger then those of cyclopentane (4,3 kJ·mol^{-1}).

3. REACTIONS IN CYCLIC CARBONATES: ASYMMETRIC HYDROGENATION IN PROPYLENE CARBONATE

3.1. INTRODUCTION

There is no doubt that one of the most important catalytic methods in synthetic organic chemistry both for laboratory and production scale is hydrogenation. Hydrogen is the attractive and the cleanest reducing agent. In recent years, many organic syntheses have been improved to the points of being environmentally-friendly and hydrogenation itself is not exception. Sometimes the desirable success depends on solvation effect. It was well established that, alkylene carbonates (e.g. propylene carbonate or dimethyl carbonate) are outstanding *aprotic* solvents. Their excellent solvency properties combined with the high flash points, high boiling temperatures, low evaporation rates and low toxicity make them particularly attractive in many processes-in-media today. Alkyl carbonates are anhydrous, non-corrosive, non-toxic, inert to metals and biodegradable. They can be used as the "safe" and environmentally friendly solvents replacing such common and unsafe solvents in chemical industry/laboratory like methylene chloride, acetone, xylenes, and other highly volatile or hazardous solvents.

As stated earlier, propylene carbonate (PC) is an appropriate solvent in the asymmetric *Rh-catalyzed* hydrogenations of functionalized olefins like methyl *N-acetamidoacrylate* or *methyl α-(Z)-N-acetamidocinnamate* [9]. In the recent work some advantages were demonstrated in palladium-catalyzed substitution reactions as well as in asymmetric hydrogenation, where PC was applied in the presence of *phosphane ligands* [10,36]. The reaction kinetics of hydroformylation of *trans-4-octene* in the multiphase systems and acceleration effect of PC has been studied by *Behr et al* [37,38]. Some thermodynamic aspects of chemical reactions in organic carbonates are in the focus of the present work.



(Scheme 1)

Reactions of assymetric hydrogenation in PC discussed here are given in the Scheme 1. We are going to study two aspects. First, is the investigation of thermodynamics of the iridium-catalyzed asymmetric hydrogenation of (1) in PC with transition-metal complex, *[Ir(cod)oxazolidinone phosphite]*$B(C_6H_3(CF_3)_2)_4$, where we want to understand whether this process is thermodynamically or kinetically favoured. For both isomers, *1-methylene-1,2,3,4-tetrahydronaphthalene* (1) and *4-methyl-1,2-dihydronaphthalene* (2) the experimental and computational studies have been performed. Second, is collection of recent experimental data on the hydrogen solubility in the different solvents because systematic investigations of hydrogenation processes are of great interest [39]. Such information helps to select an appropriate solvent for hydrogenation processes. The last IUPAC update of hydrogen solubility data is the "*Solubility Data Series*" published in 1981 [40]. It covers all data presented in the literature until 1979. Unfortunately, the extended and fundamental studies by *Brunner* published in 1978 were not included in this issue. Another literature survey on solubility of hydrogen in the liquid solvents was published by *Valderrama et al.* in 1992 [41]. However, the available information was presented in that work only in two text pages but the figures, tables, and 353 references are deposited as a microfiche which is not readily accessible. Experimental data on hydrogen solubility collected in the present work covers 30 years since 1978 till October, 2008 (see Table B7 in Appendix B).

3.2. ASYMMETRIC HYDROGENATION OF 1-METHYLENE-1,2,3,4-TETRAHYDRONAPHTHALENE, (1)

Asymmetric hydrogenation of non-functionalized olefins in PC according to Scheme 1 was studied using different iridium complexes by *Börner et al.* [10]. The reactions were performed at normal and high pressures and the results were compared with those obtained in methylene chloride (CH_2Cl_2). It was shown that hydrogenation of (1) at normal pressure in CH_2Cl_2 or PC led to a mixture of products (2) and (3) with high conversion (74 to 100%) and enantiomeric excess, (*ee*) for compound (3) included between 3,5 and 73,2%. Under these conditions, the use of CH_2Cl_2 rather than PC as solvent allows to obtain a better ratio (2)/(3) in favour of (3). In order to increase the proportion of (3), an increase of pressure from 1 to 50 bars in CH_2Cl_2 or from 1 to 100 bars in PC was necessary. Thus, good to excellent ratio (2)/(3) was obtained (7/93 to 3/97 in PC and 0/100 in CH_2Cl_2) according to results given in Table 3.1. Good enantioselectivities were obtained with in PC (*ee* up to 82,4%). In this latter case, the use of PC as solvent is clearly advantageous to obtain high enantioselectivities for compound (3). As clearly to be seen, at 50 bar, enantiomeric excess obtained in PC was superior to those obtained in CH_2Cl_2 (81,3 and 16,9% respectively). An increase of pressure from 50 to 85 then 100 bars allowed improving *ee*-values in PC (81,3; 82,1 and 82,4% respectively).

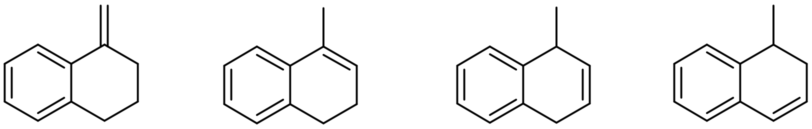
Table 3.1. Results of the *Ir*-catalyzed Asymmetric Hydrogenation of *1-Methylene-1,2,3,4-tetrahydronaphthalene* (1) in PC with the Ligand[a], *[Ir(cod)oxazolidinone phosphite]$B(C_6H_3(CF_3)_2)_4$*.

Solvent	H_2, *bar*	Time, *h*	Conversion, %	2 / 3	*EE*, %
PC	1	20	74	63 / 37	73,2 (*R*)
	50	4	100	13 / 87	81,3 (*R*)
	50	8	100	4 / 96	82,1 (*R*)
	85	4	100	5 / 95	82,1 (*R*)
	100	4	100	3 / 97	82,4 (*R*)

CH_2Cl_2	1	3	100	71 / 29	46,3 (*R*)
	50	3	100	0 / 100	16,9 (*R*)

[a] structure of the ligand is given in [10].

What could be an explanation for this difference of enantioselectivity obtained in PC and in methylene chloride? Is the process of the asymmetric hydrogenation thermodynamically or kinetically controlled? At first, we have carried out some hydrogenations of compound (2) in PC and in CH_2Cl_2 with Ir-complex at 50 bars to check the absolute configuration of the obtained product (3). After three hours, full conversion was obtained in methylene chloride with an enantiomeric excess of 59,5% in favour of (*S*)-enantiomer. Surprisingly, in PC only 24% conversion was obtained after four hours, enantioselectivity being 35,4% (*S*) in this case. Under these conditions, reduction of internal double bond of compound (2) is slower and more difficult in PC than in CH_2Cl_2. On the other hand, in the absence of hydrogen, compound (1) was completely transformed within 10 min to compound (2) in CH_2Cl_2, whereas in PC, only 39% of (2) was obtained. Following, the isomerisation reaction itself was clearly faster in methylene chloride than in PC. This result has provided first evidence, that the asymmetric hydrogenation is likely kinetically controlled, provided that thermodynamic stability of 1-methylene-1,2,3,4-tetrahydronaphthalene (1) is less than those of 4-methyl-1,2-dihydronaphthalene (2).



(1) (2) (4) (5)

0,0 -17,1 +4,8 -7,2

(Scheme 2. Possible isomeric structures of *naphthalene derivatives* and their relative (to isomer 1) energies at B3LYP/6-311G(d,p) level).

3.3. Computational and Thermochemical Study of Isomers, 1-Methylene-1,2,3,4-tetrahydronaphthalene, (1) and 4-Methyl-1,2-dihydronaphthalene, (2)

The thermodynamic stability of all possible isomers of compound (1) with their relative energies were assessed by preliminary DFT-calculations (B3LYP/6-311G(d,p) level) at 298,15 K as shown in the Scheme 2. The isomeric structure (2) is the most stable; the isomers (5) and (1) are less one, whereas the isomer (4) is the least stable. An experimental existing of isomers (1) and (2) were additionally studied using G3MP2 method. Results from *ab initio* calculations are presented in Table 3.2.

Table 3.2. Enthalpies and Gibbs Energies of the Isomerisation Reaction (1) ⇔ (2) at the Different Temperatures (in kJ·mol^{-1}).

Temperature, K	G3MP2		B3LYP/6-311G(d,p)	
	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$
298,15	-15,2	-15,9	-17,8	-18,5
373,15	-14,4	-15,4	-17,6	-18,7

Thermodynamic functions of isomers (1) and (2) derived from ab initio calculations enable us to predict the *thermodynamic equilibrium constant*, K_p, of isomerization reaction (1)⇔(2) and hence to predict the equilibrium composition of the reaction mixture in the gaseous phase according to the general equation:

$$\Delta_r G = -RT \times \ln K_p \qquad (3.1).$$

Using $\Delta_r G$ = -15,9 kJ·mol^{-1} from G3MP2 method (see Table 3.2) the value for K_p = 612 have been calculated. This result suggested that in the gas phase during isomerization (1)⇔(2) an equilibrium is completely shifted to the side product (2). Because in the present study catalytic reactions occur in the liquid phase, the value of the equilibrium constant in the liquid phase, K_a, is required:

$$K_a = K_p \cdot (p_1 / p_2) \qquad (3.2),$$

where p_1 and p_2 are an appropriate saturation vapor pressures of isomers (1) and (2). The latter vapor pressures have been measured using the transpiration method in the temperature range 293-359 K (see Table B2 in Appendix B). From this results the vapor pressures p_1 = 13,6 Pa and p_2 = 12,2 Pa at 298,15 K have been obtained and used for calculation of K_a = 682 in the liquid phase. It is now apparent that equilibrium of the reaction (1)⇔(2) in the liquid phase is also completely shifted to the product (2), however, the impact of the temperature on to the equilibrium should be explored. For this purpose ab initio calculations of the reaction (1)⇔(2) have been performed at 373 K (see Table 3.2). Together with the results for vapor pressures p_1 = 1442 Pa and p_2 = 1201 Pa at 373,15 K (obtained using data from Table 3.2) the values for K_p =143 in the gaseous phase and K_a = 160 in the liquid phase have been calculated. The same trend has been obtained from calculations with the B3LYP/6-311G(d,p) method. As can be seen from this calculation, the isomerization (1)⇔(2) demonstrate strong temperature dependence, thus elevated temperatures could be also recommended in order to avoid formation of the side product (2) in the liquid phase.

According to the experimental and computational studies we are able now to conclude that the asymmetric hydrogenation of (1) is definitely kinetically controlled. It is now apparent, that the isomerisation of the external olefin of compound (1) to the most stable internal isomer (2), which occurs during the hydrogenation reaction, is faster in CH_2Cl_2 than in PC. Hydrogenation of these two prochiral isomeric olefins (1) and (2) gives corresponding products with opposite absolute configuration, (1) giving (*R*)-enantiomer whereas (2) give (*S*)-enantiomer (Scheme 1).

3.4. Hydrogen Solubility in Various Solvents

For comparison of the catalytic activity in various solvents under equal conditions (e.g. at 298,15 K and total pressure 0,101325 MPa) the reliable experimental data on hydrogen solubility are required [39]. In this chapter we restricted the variety of solvents to that one, which could be potentially useful for chemical hydrogenation processes. Taking into account that a large amount of primary results was already given in the extended compilation of experimental data in "*Solubility Data Series*" we collected in the Table B7 (Appendix B) only new data except for methyl halogenated compounds [40]. In the recent literature the gas solubility is evaluated of mole fraction, x or Henry`s constant, k_H. Most of the solubility measurements presented in the literature (see *ibid.*) were performed at several constant temperatures and pressures (about 1 to 10 MPa).

According to evaluation procedure suggested in the "*Solubility Data Series*", mole fraction solubility values have been calculated at the hydrogen partial pressure of 0,101325 MPa assuming the gas to be ideal, Henry`s law to be obeyed. Such assumption probably introduce errors, however, they are, as a rule, less than the experimental uncertainties of the solubility measurement.

A large number of the primary experimental results on pressure dependences of mole fraction solubility, x have been collected from the literature. They have been treated uniformly in order to derive x and k_H at a constant temperature and total pressure 0,101325 MPa [42]. In the case where solubility was studied at several temperatures the data were treated by following linear regression [40]:

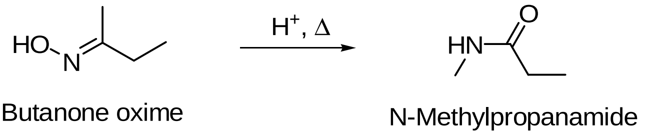
$$\ln x = a + b/(T/100K) \qquad (3.3),$$

where a and b are adjustable parameters which also given in Table B2. Data compiled in this table could give valuable information for selection of solvent and kinetic data treatment of hydrogenation reactions.

4. THERMOCHEMISTRY OF IONIC LIQUID-CATALYZED REACTIONS: EXPERIMENTAL AND THEORETICAL STUDY OF BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME AND 2-BUTANONE OXIME

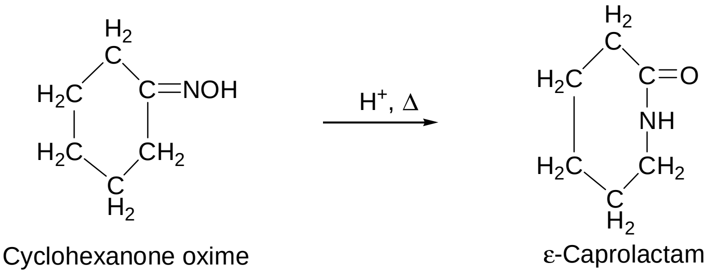
4.1. INTRODUCTION

Beckmann revealed that *ketoximes*, RRC(=NOH), can be easily transformed into *substituted amides*, RCONHR. In his classical experiments *benzophenone oxime* readily formed *benzanilide* in the presence of PCl_5 [43]. Later there was found that the esters, O-ethers of ketoximes and N-ethers of aldoximes were also able to form the corresponding amides. Then, aliphatic, aromatic and heterocyclic ketoximes prepared from the corresponding ketones were found to undergo the Beckmann rearrangement upon the treatment of acidic reagents (concentrated H_2SO_4, formic acid, $SbCl_5$, liquid SO_2, $SOCl_2$, $POCl_3$, HCl-HOAc-Ac_2O, silica gel, polyphosphoric acid and *Beckmann solution*- Ac_2O in glacial AcOH saturated with HCl) in the presence of different media at comparatively low temperature or at high temperature upon *phase-transfer catalysis* on silica gel. The Scheme 1 illustrates one of these transformations.



(Scheme 1)

The heating of ketoximes in the presence of $Me_x(SO_4)_y$, oxides and hydroxides causes the partial destruction of ketoximes with ammonia liberation. Therefore they are used seldom with the exception of Al, B, Si, Cr(III), Ta(V) oxides in the presence of Lewis's acids (e.g. $AlCl_3$, $FeCl_3$ and $ZnCl_2$). Experimental and mechanistic details of the homogeneous catalyzed Beckmann rearrangement have been described in the work [44]. The modern mechanistic principals of Beckmann rearrangement in the presence of different heterogeneous catalysts (e.g. at the zeolite surface) are presented in work [45].



(Scheme 2)

As it was first revealed by *Wallach* [46], alicyclic oximes, such as *cyclopentanone, cyclooctanone*, *cyclododecanone oximes* and especially *cyclohexanone oxime* are able to form *lactams* (e.g. ε-caprolactam, in the Scheme 2). This isomerization in the presence of large amount of oleum and temperature approximately 130°C was the milestone in chemical industry. Today, cyclohexanone oxime is one of the most important precursors for the polycaprolactam (*polyamide-6* or *Nylon-6*) production.

Application of “green” homogeneous and heterogeneous catalysts for the Beckmann rearrangement is a new trend in the chemistry of alicyclic ketoximes for the last 10 years. Some attempts have been made to develop new synthetic pathways in isomerization process of cyclohexanone oxime in the gaseous phase or in the media of ionic liquids [47,48]. However, taking into account the essential role of the main principles of sustainable chemistry in the modern chemical processes the usage of ionic liquids as an environmentally benign media for the catalytic reactions of ketoximes is a challenging problem [49,50]. Industrial catalytic transformations of ketoximes into corresponding amides include the application of large amounts of concentrated sulfuric acid. As a result, large amounts of ammonium sulfate are precipitated as a by-product. In order to overcome this difficulty, many efforts have been put into development of the ammonium sulfate-free processes. The Beckmann rearrangement was found to be efficiently progressed using (ILs) [51-53]. In this context we decided to explore applicability of some ionic liquids for possible improvement of production of caprolactam, especially on the stage of conversion of cyclohexanone oxime to caprolactam. Thermodynamic properties of caprolactam [54] and cyclohexanone oxime [55] in the condensed and in the gaseous state have been investigated recently. However one of the decisive questions for the latter rearrangement – in which way is this process controlled kinetically or thermodynamically? To answer this question, the thermodynamic properties of the typical Beckmann rearrangement reactions in the ideal gaseous state according to Schemes 1 and 2 were calculated by using the quantum mechanical method. Gibbs energy and equilibrium constants of the Beckmann rearrangement have been assessed in the gaseous and the liquid phases. Results of the thermodynamic analysis have shown that Beckmann rearrangements are kinetically controlled. Thus, search for possible active catalysts for the mild reaction conditions has been performed.

4.2. VAPOUR PRESSURES, ENTHALPIES OF VAPORIZATION

4.2.1. N-Methylpropanamide. A summary of vapor pressures measured in this work is presented in Table B3 (Appendix B). Comparison of the vapor pressures for N-methylpropanamide with the literature data is given in Fig. 4-1. As can be seen, our new results are in good agreement with those from *ebulliometry* [56,57] (however, the proper comparison is difficult, because the literature data were measured at the elevated temperatures close to the boiling point). In contrast, the data from *static manometry* [58] are in substantial disagreement with the vapor pressure measured in the present work. The apparent disagreement with the vapor pressures measured by static method has been observed, but we do not have any reasonable explanation for it.

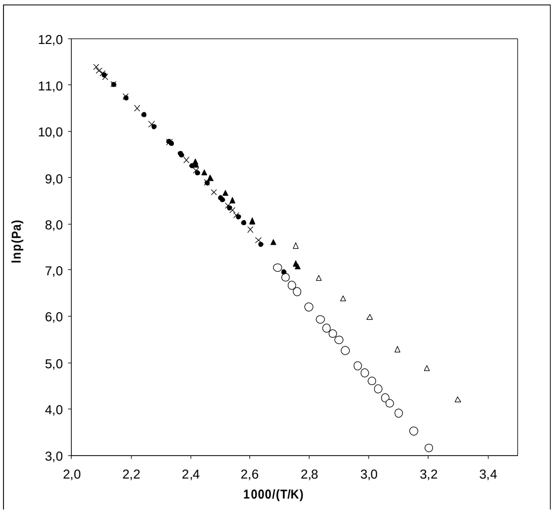


Fig. 4.1. Experimental data of the vapor pressures of the *N-methylpropanamide* (○)- this work; (●)- [56]; (Δ)- [59]; (×)- [57]; (▲)- [58].

Available data [58,59] on vaporization enthalpies of N-methylpropanamide are given in Table 4.1. The vaporization enthalpies reported in the literature were not adjusted to the reference temperature 298,15 K. That is why we treated the primary experimental results [56-60] using eqs. 2.2 and 2.4 (Chapter 2), and calculated $\Delta_l^g H_m$ (298,15 K) for the sake of comparison with our results (see Table 4.1). Vaporization enthalpy $\Delta_l^g H_m$ (298,15 K) for N-methylpropanamide measured in this work is again in agreement with those from ebulliometry and in disagreement with results from static method, following the same pattern as for the vapor pressure. Only two earlier experimental data points for vapor pressure of 2-butanone oxime were measured using *isoteniscope* [61]. Vaporization enthalpy calculated from this data is in a good agreement with our new results (Table 4.1).

Table 4.1. Summary of Vaporization Enthalpies ($\Delta_l^g H_m$) in kJ·mol^{-1} Available for N-Methylpropanamide and 2-Butanone Oxime.

Compound	Method [a]	T-range, K	$\Delta_l^g H_m$ (T), kJ·mol^{-1}	$-\Delta C_p$ [b] J·mol^{-1}·K^{-1}	$\Delta_l^g H_m$ (298,15 K), [c] kJ·mol^{-1}	Ref.
N-Methyl-propanamide	S	303-363	49,0±1,7	57,1	50,9±1,7	59
	E	380,4-479,9	56,6±0,2	(179,0)[51]	63,9±0,2	57
	C	298,15			64,9±0,3	60
	S	362,2-414,1	53,9±0,2		59,0±0,2	58
	E	368,1-473,5	57,9±0,4		64,7±0,4	56
	T	307,2-371,2	64,0±0,2		**66,56±0,19**	this work
2-Butanone oxime	S	313-333	57,2	64,2	57,7	61
	T	283,4-329,3	58,55±0,2	(206,3)	**59,05±0,20**	this work

[a] applied methods: E = ebulliometry; C- calorimetry; T = transpiration; S = static method.

[b] values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid, C_p^l or solid C_p^{cr} compounds (they are in brackets) according to the procedure developed by *Chickos* and *Acree* [19].

[c] vapor pressure available in the literature were treated using eqs. 2.1-2-5 (Chap.2) in order to evaluate enthalpy of vaporization at 298,15 K in the same way as our own results presented in the Table B3 (Appendix B).

4.3. Enthalpies of Formation (Combustion Calorimetry)

Results of combustion experiments for *2-butanone oxime* are summarized in Table B9 (Appendix B). The mean of the standard specific energy of combustion $\Delta_c u^\circ$ = (-31189,9±2,4) J·g^{-1} was derived from two experiments performed with the homemade calorimeter and four experiments with the *Parr-6100*. To derive $\Delta_f H_m^\circ$ (liq.) = (-139,9±0,9) kJ·mol^{-1} from the measured molar enthalpy of combustion $\Delta_c H_m^\circ$ = (-2720,4±0,7) kJ·mol^{-1}, molar enthalpies of formation of H_2O and CO_2 have been used [28].

Only one previously measured value of enthalpy of formation for 2-butanone oxime was determined by *Landrieu* [62] using combustion calorimetry. This value is in disagreement (10 kJ·mol^{-1}) with the result obtained in the present work. Surprisingly their value $\Delta_f H_m^\circ$ (cr.) = -151 kJ·mol^{-1} was referred to the solid state, however the melting temperature for 2-butanone oxime reported in the work [63] as T_{fus} = 243,65 K. We do not have any reasonable explanation for such a disagreement, but we intend to validate our value using ab initio calculations in the next paragraph. Enthalpy of formation of N-methylpropanamide, $\Delta_f H_m^\circ$ (liq.) = (-320,1±0,8) kJ·mol^{-1} was measured using combustion calorimetry by *Vasil'eva* and *Zhil'tsova* [64] and was used in the present work.

Values of vaporization enthalpies of 2-butanone oxime and N-methylpropanamide, derived in this work (Table 4.1) have been used together with the results from combustion experiments (Table 4.2) for further calculation of the gaseous standard enthalpies of formation, $\Delta_f H_m^\circ$ (g.) at 298,15 K according to eq. (1.0) and (1.1). The resulting values of $\Delta_f H_m^\circ$ (g.) are given in the last column in Table 4.2.

Table 4.2. Thermochemical Data at 298,15 K and 0,1 MPa for Compounds (in kJ·mol^{-1}).

Compound	$\Delta_f H_m^\circ$ (cr.)	$\Delta_f H_m^\circ$ (liq.)	$\Delta_{cr}^{g} H_m$	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (g.)
2-Butanone oxime	-	-139,9±0,9	-	59,1±0,2	-80,8±1,1
N-Methylpropanamide	-	-320,1±0,8[64]	-	66,6±0,2	-253,5±0,8
Cyclohexanone oxime	-153,2±2,5[65]	-143,5±2,5 [a]	78,8±0,1[55]	69,1±0,1 [b]	-74,4±2,5[55]
ε-Caprolactam	-329,4±1,7[66]	-316,5±1,7 [a]	87,5±0,6[54]	74,6±0,6 [b]	-241,9±1,8[54]

[a] derived as explained in Table B10 (Appendix B).

[b] calculated by eq. $\Delta_l^g H_m = \Delta_{cr}^g H_m - \Delta_{cr}^l H_m$, where the values $\Delta_{cr}^l H_m$ (298,15 K) were taken from Table B10 (Appendix B).

4.4. Ab Initio Calculations

In the recent work [67] it was established a remarkable ability of the G3MP2 *ab initio* method to predict accurately equilibrium constants and reaction enthalpies of different types of chemical reactions such as isomerization or transalkylation. It was well established, that those chemical reactions are thermodynamically controlled. Thus, desired yields of goal products could be possibly predicted with help of *ab initio* calculations. In the current work we have applied the ab initio procedure in order to understand whether the Beckmann rearrangement governed by kinetic or thermodynamic control?

4.4.1. Thermodynamic Analysis of Beckmann Rearrangement: Kinetic or Thermodynamic Control?

In general, knowledge of the Gibbs energy $\Delta_r G$ of any chemical reaction allows an assessment of the thermodynamic equilibrium constant K_p (see eq. 3.1 in the previous chapter). In the case that equilibrium constant $K_p \geq 1$ estimated according to this equation the desired yields of goal products could be apparently higher than 50%. In this work, thermodynamic functions of reactions in the Schemes 1 and 2: Gibbs energy, $\Delta_r G_m^\circ$, reaction enthalpy, $\Delta_r H_m^\circ$, reaction entropy, $\Delta_r S_m^\circ$, have been calculated using B3LYP and G3MP2 method. Calculated values are given in Table 4.3 and Table B11 in Appendix B.

Table 4.3. *Ab Initio* Calculated Enthalpies of Reaction ($\Delta_r H_m^\circ$), Entropies of Reactions ($\Delta_r S_m^\circ$), and Gibbs Energies of reaction ($\Delta_r G_m^\circ$) in the Gaseous Phase at 298,15 K.

Reaction in the Scheme	G3MP2			B3LYP/6-311G(d,p)		
	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
1	-175,9	-170,4	18,6	-187,2	-179,7	25,1
2	-164,3	-164,5	-0,6	-172,1	-172,4	-1,0

However, before calculation of the equilibrium constant K_p of the Beckmann rearrangement, we have to establish validity of the *ab initio* methods towards compounds involved in the chemical reactions presented in the Schemes 1 and 2. Such test provides comparison of the reaction enthalpies obtained from experimental enthalpies of formation ($\Delta_f H_m^\circ$) and from *ab initio* calculations. Generally, the enthalpy of chemical reaction ($\Delta_f H_m^\circ$) is defined as stoichiometric difference between the enthalpies of the products and initial reagents in the pure states. Enthalpies of reactions calculated directly from enthalpies of reaction participants using B3LYP and G3MP2 are given in Table 4.4. The values calculated using G3MP2 method, $\Delta_r H_m^\circ(g.)_{G3MP2}$, are in a good agreement with the experimental values (*columns* 3 and 4 in the Table 4.3). The values calculated using DFT method, $\Delta_r H_m^\circ\ (g)_{DFT}$, are slightly overestimated (*columns* 1 and 4 in that Table).
Values of $\Delta_r H_m^\circ$ (g.) related to the standard reaction enthalpies, $\Delta_r H_m^\circ$ (liq.), in the liquid state can be estimated by the following equation:

$$\Delta_r H_m^\circ(liq.) = \Delta_r H_m^\circ(g.) - \sum_i v_i \cdot \Delta_l^g H_{m_i} \qquad (4.1),$$

where $\Delta_l^g H_{m_i}$ are the molar enthalpies of vaporization of the pure compounds i at the reference temperature 298,15 K. The latter values for compounds involved in the Beckmann rearrangement (Scheme 1 and 2) are available in the literature [54,55] or measured in this work (*see* Table 4.2) Enthalpies of these transformations, $\Delta_r H_m^\circ$ (liq.)$_{DFT}$ and $\Delta_r H_m^\circ$ (liq.)$_{G3MP2}$ calculated according to eq. 4.1 are listed for comparison with experimental values in Table 4.4. The calculated values of $\Delta_r H_m^\circ$ (liq)$_{DFT}$ are found to be slightly more negative, but values of $\Delta_r H_m^\circ$ (liq)$_{G3MP2}$ are found to be in the good agreement (within the boundaries of experimental uncertainties) with those derived from the experimental enthalpies of formation (*columns* 5,6,7 of the Table 4.4). It should be stressed, that we have calculated values of the $\Delta_r H_m^\circ$ (liq.)$_{DFT}$ and $\Delta_r H_m^\circ$ (liq.)$_{G3MP2}$ for reactions in Schemes 1 and 2 using enthalpies H_{298} (see Table B12 in Appendix B) of the reaction participants directly available from the *ab initio* protocol. In this case we are able to avoid any ambiguity due to calculations associated with the enthalpies of formation, $\Delta_f H_m^\circ$ (g.) as described below. Such a straightforward procedure allows calculating a required enthalpy of reaction by ab initio method more reliable.

Table 4.4. Compilation of Data from Ab Initio Calculations of Enthalpies of Beckmann Rearrangement ($\Delta_r H_m^\circ$) in the Gaseous and in the Liquid Phases at 298,15 K (in kJ·mol^{-1}).

Reaction in the Scheme	$\Delta_r H_m^\circ$ (g.) (DFT)[a]	$\Delta_r H_m^\circ$ (g.) (G3MP2)	$\Delta_r H_m^\circ$ (g.) (exp.)	$\Delta_r H_m^\circ$ (liq.) (DFT)[a]	$\Delta_r H_m^\circ$ (liq.) (G3MP2)	$\Delta_r H_m^\circ$ (liq.) (exp.)
1	-179,7	-170,4	**-172,7**±1,4	-187,2	-177,9	**-180,2**±1,4
2	-172,4	-169,4	**-167,5**±3,1	-177,9	-174,9	**-173,0**±3,0

[a] B3LYP/6-311G(d,p).

Having established the ability of *ab initio* methods for prediction thermodynamic properties of oximes and amides properly, we have calculated (using eq. 3.1) the thermodynamic equilibrium constants in the gaseous phase, K_p, of the Beckmann rearrangements under study at 298,15 K (*see* Table 4.5). As can bee seen, the very high values of K_p for both reactions provide an evidence, that at 298,15 K the equilibrium of the Beckmann rearrangements is completely shifted to the desired direction of the amide formation. Taking into account, that the ε-caprolactam synthesis in industrial conditions is performed at elevated temperatures, we have repeated calculations of the K_p at 373,15 K (*see* Table B11 in Appendix B). As can bee seen from this table, the values of K_p of the Beckmann rearrangements are substantially dependent on the temperature, but even at 373,15 K, the position of equilibrium remains completely shifted to the amide side. Thus, our calculations of K_p of the Beckmann rearrangements in the gaseous phase have ensured the thermodynamic feasible conditions. However, the industrial synthesis of ε-caprolactam proceeds in the liquid phase at 373-403 K. How to transfer results of *ab initio* calculations to the liquid state? Thermodynamic equilibrium constant, K_p, for the gas phase reaction of oximes and thermodynamic constant, K_a, of the transformation in the liquid phase are related by eq. 3.2. In this case p_1 and p_2 are the saturation vapour pressures of oxime and its product of transformation (amide) respectively. The latter vapour pressures have been measured in the present work using the transpiration method (*see* Table 4.1) or for N-methylpropanamide and 2-butanone oxime they can be taken from the literature [54,55]. Using the values K_p for the gaseous reactions (Scheme 1 and 2) calculated on the basis of B3LYP and G3MP2-methods and presented in the Table 4.4, the thermodynamic equilibrium constants K_a in the liquid phase were successfully estimated. It is now apparent from the value of $K_a = 9{,}6 \cdot 10^{29}$ that equilibrium of the reaction of the Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam in the liquid phase is also completely shifted to ε-caprolactam. Thus, according to our computational studies, it is possible to conclude that the Beckmann rearrangement is definitely kinetically controlled process, because according to thermodynamics, the equilibrium of the reaction is always shifted to the products. As can be seen from our computations, the Beckmann rearrangement demonstrates strong temperature dependence. The lower temperatures are more thermodynamically favourable. So, elevated temperatures are not necessarily required for obtaining high yields, provided that the active catalytic system is applied.

Table 4.4. Thermodynamic Function $\Delta_r G_m^\circ$ (in kJ·mol^{-1}) and Equilibrium Constants K_p and K_a of the Beckmann Rearrangement at 298,15 K.

Reaction on the Scheme	$\Delta_r G_m^\circ$ (G3MP2)	$\Delta_r G_m^\circ$ (DFT)^a	K_p (G3MP2)	K_p (DFT)^a	K_a^{b} (G3MP2)	K_a^{b} (DFT)^a
1	-175,9	-187,2	$6{,}7\cdot 10^{30}$	$6{,}3\cdot 10^{32}$	$(1{,}6\cdot 10^{32})^c$	$(1{,}5\cdot 10^{34})^c$
2	-164,3	-172,2	$6{,}2\cdot 10^{28}$	$1{,}5\cdot 10^{30}$	$(9{,}6\cdot 10^{29})^d$	$(2{,}2\cdot 10^{31})^d$

[a] B3LYP/6-311G(d,p).

[b] calculated according to eq. 4.4.

[c] ratio of saturation vapour pressures of reaction participants p_1/p_2 = 23.6 (*see* the text).

[d] ratio of saturation vapour pressures of reaction participants p_1/p_2 = 15.5 (*see* the text).

4.4.2. G3MP2-Enthalpies of Formation of Amides and Oximes

From the series of recent works there was demonstrated good ability of G3MP2-method to predict enthalpies of formation of different compounds [33,68-72]. In the present work the standard atomization reactions as well as the bond separation/isodesmic reaction have been applied for calculating of the enthalpies of formation in the gaseous phase, $\Delta_f H_m^\circ$ (g.), of 2-butanone oxime and N-methyl-propanamide (eqs. 4.2-4.4), cyclohexanone oxime and ε-caprolactam (eqs. 4.5-4.7) have been estimated using the following reactions:

$$C_4H_9NO \ + \ 8CH_4 \ \rightarrow \ NH_3 + H_2O + 6C_2H_6 \qquad (4.2)$$

$$C_4H_9NO \ + \ 2CH_4 \ \rightarrow \ C_2H_5NO + 2C_2H_6 \qquad (4.3)$$

$$C_4H_9NO \ + \ 6CH_4 \ \rightarrow \ NH_2OH + 5C_2H_6 \qquad (4.4)$$

$$C_6H_{11}NO \ + \ 12CH_4 \ \rightarrow \ NH_3 + H_2O + 9C_2H_6 \qquad (4.5)$$

$$C_6H_{11}NO \ + \ 6CH_4 \ \rightarrow \ C_2H_5NO + 5C_2H_6 \qquad (4.6)$$

$$C_6H_{11}NO \ + \ 10CH_4 \ \rightarrow \ NH_2OH + 8C_2H_6 \qquad (4.7)$$

Enthalpies of formation, $\Delta_f H_m^\circ$ (g.), of 2-butanone oxime and N-methyl-propanamide are given in Tables B13 and B14 (Appendix B). Results estimated from atomization procedure, isodesmic and bond separation reactions are found to be in the close agreement (*see* Tables B13 and B14). The average value of $\Delta_f H_m^\circ$ (g.) taken from these calculations is in the good agreement with the experimental results (see Table 4.2).

4.5. Experimental Study of Beckmann Rearrangement in the Liquid Phase

Having established that the Beckmann rearrangement proceeds under kinetic control, it is of interest to find such a catalytic system which could be able to carry out the reaction in the mild condition. It is known from the literature that the strong Lewis acids, such as $AlCl_3$, gave high yields of ε-caprolactam at low temperatures, in the presence of solvent or in the bulk [73]. It is also well known that *chloroaluminate ionic liquids* possess a wide range of Lewis acidity depending on their molar ratio to reactants [74]. Following, use of chloroaluminate imidazolium-containing ionic liquids as a catalyst could be promising candidates to proceed reaction under milder conditions. In the present work an attempt has been made to investigate the Beckmann rearrangement of cyclohexanone oxime in the presence of different chloroaluminate imidazolium catalysts in methylbenzenes as a solvent (see Table 4.5). Unfortunately, it turned out that the reaction under experimental conditions applied (at 378/413 K, closed vials with constant magnet stirring) led to formation of *cyclohexanone* instead desired ε-caprolactam. One of the possible reasons is that we used small quantities of heterogeneous catalyst, chloroaluminate (about 10% wt.) with the small surface area, which were not sufficient to obtain good yields.

Table 4.5. The Beckmann Rearrangement of Cyclohexanone Oxime into ε-Caprolactam: Experimentally Determined Composition of Mixtures in the Liquid Phase, (T is the temperature of investigation; x_i is the mole fraction measured GC-equipment).

Catalyst	T^a, K	Time, *h.*	$x_{cyclohexanone}$	$x_{cyclohexanone\ oxime}$	$x_{caprolactam}$
[EMIM][HSO_4]	413	0,5	0,2014	0,7755	0,0231
	413	1,0	0,2598	0,7162	0,0240
	413	2,0	0,3066	0,6717	0,0217
[BMIM][HSO_4]	413	0,5	0,2651	0,7294	0,0055
	413	1,0	0,3121	0,6839	0,0040
	413	2,0	0,3592	0,6378	0,0030
[BMIM][$AlCl_3$]$_{1.1}$	413	0,5	0,6095	0,3799	0,0106
	413	1,0	0,7057	0,2808	0,0135
	413	2,0	0,8051	0,1801	0,0148
[HMIM][$AlCl_3$]$_{1.1}$	413	0,5	0,3649	0,6055	0,0296
	413	1,0	0,4499	0,5136	0,0365
	413	2,0	0,5395	0,4153	0,0452
[BMIM][$AlCl_3$]$_2$	378	0,5	0,0100	0,9900	0,0000
	378	2,0	0,0419	0,9461	0,0104
	378	1,2	0,9125	0,0771	0,0104
[BMIM][$AlCl_3$]$_2$	413	0,5	0,1478	0,8349	0,0173
	413	1,0	0,5624	0,4236	0,0140
	413	2,0	0,7086	0,2761	0,0153

[a] studies at 378 K were performed in toluene and at 413 K in mesitylene.

Different kinds of acidic catalysts are traditionally used in the Beckmann rearrangement [47]. In the present work the catalytic activity of some Bronsted acidic ionic liquids was investigated. They are:

- of imidazolium, based [EMIM][HSO_4] and [BMIM][HSO_4],
- of tetra-alkyl-ammonium, based [N_{8881}][HSO_4],
- of tetra-alkyl-phosphonium, based [P_{8888}][HSO_4].

Similar to the chloroaluminate ionic liquids, the Beckmann rearrangement of cyclohexanone oxime in the presence of these Bronsted catalysts cyclohexanone was found as the main product (see Table 4.5).

The new acidic ionic liquids with *alkanesulfonic* group in *pyridinium* cation presented in Scheme 3 have been reported recently [75].

N-Propane sulfone pyridinium (**PPyr**) N-Butane sulfone pyridinium (**BPyr**)

(Scheme 3)

Classified as *task-specific ionic liquids* these catalysts are found to possess a good catalytic activity in *esterification* reactions. In this work they were applied as catalyst in Beckmann rearrangement of cyclohexanone oxime. Results are presented in Table 4.6. In both cases catalyst was not dissolved in toluene (or mesitylene) and biphasic reaction mixture was observed in all experiments. Better results were achieved using [PPyr][HSO_4] when a complete conversion of cyclohexanone oxime was observed after 1 h. at 413 K. In spite of side reaction leading to the by-product (cyclohexanone), this catalyst has the promising features for further improvement and optimising of the reaction conditions.

Table 4.6. Experimentally Determined Composition of Reaction Mixtures in the Liquid Phase, (x_i is the mole fraction measured GC-equipment).

Catalyst	T^a, K	Time, *h*.	$x_{cyclohexanone}$	$x_{cyclohexanonoxime}$	$x_{caprolactam}$
[PPyr][HSO_4]	378	0,5	0,8102	0,1288	0,0610
	378	1,0	0,8659	0,0653	0,0687
	378	15	0,8737	0,0011	0,1252
[PPyr][HSO_4]	413	0,3	0,3288	0,2251	0,4461
	413	0,5	0,1084	0,1153	0,7763
	413	1,0	0,1437	0,0097	0,8466
[BPyr][HSO_4]	413	0,3	0,2249	0,5222	0,2529
	413	0,5	0,3597	0,2985	0,3418
	413	1,0	0,4699	0,1525	0,3775
	413	2,0	0,5104	0,1127	0,3769

^{a} studied at 378 K in *toluene* and at 413 K in *mesitylene*.

From the literature review other promising catalytic systems have been found and selected to illustrate the general possibility of mild condition of Beckmann rearrangements (*see* Table 4.7). In accord with our investigation, very high yields (94-100%) of ε-caprolactam were already achieved even at room temperatures using *2,4,6-trichloro-triazine* [75], Lewis acidic ionic liquids [77], and 2-halogene-pyridinium salts [78]. However, a further search for the active and technologically suitable catalysts for the mild condition of Beckmann rearrangements remains a challenging task.

Table 4.7. The Beckmann Rearrangement of Cyclohexanone Oxime.

Catalyst	Solvent	°C/*h*.	Yield, %	Ref.
$Cl_3C\text{-}CH(OH)_2$	-	90/7,5	67	[79]
2,4,6-trichloro-triazine	diMe-formamide	25/3	100	[76]
2,4,6-trichloro-triazine/$ZnCl_2$	acetonitrile	90/2	30	[80]
H_2NSO_3H	acetonitrile	90/6	40	[81]
$ClSO_3H$	toluene	90/0,5	71	[54]
$(HBO_2)_n$	-	140/42	62	[55]
$[1\text{-Me-3-}(CH_2)_3\text{-}SO_2ClIm]^+[CF_3SO_3]^-$	-	25/0,25	99	[77]
$[1\text{-Et-3-}(CH_2)_3\text{-}SO_2ClIm]^+[PF_6]^-$	-	80/2	98	[84]
$[1\text{-Et-2-F-3-MePyr}]^+[FSO_3]^-$	dimethoxyethane	25/6	94	[78]
P_2O_5/ CF_3SO_3H	diMe-formamide	120/0,5	63	[85]
$[1\text{-Bu-3-MeIm}]^+PF_6^-/P_2O_5$	-	75/16	99	[51]
$[1\text{-Bu-3-MeIm}]^+CF_3COO^-$/ PCl_5	-	80/2	99	[52]
$([1\text{-Bu-3-MeIm}]^+PF_6^-/(HBO_2)_n$	-	90/3	97	[53]

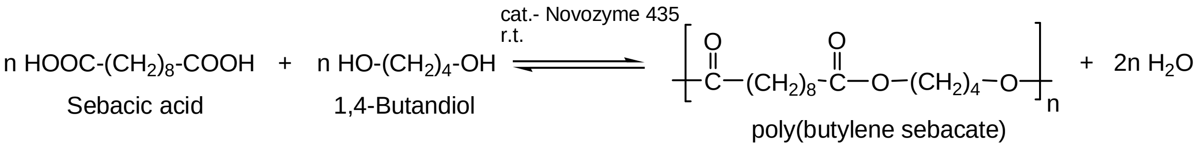
5. THERMOCHEMICAL STUDY OF ENZYMATIC POLYMERIZATION BASED ON REACTION OF 1,4-BUTANEDIOL WITH SEBACIC ACID

5.1. INTRODUCTION

Aliphatic dicarboxilic acids and diols are commonly used for the polyester manufacture. These polymers (also *poly(lactide)s* obtained *via* ring opening polymerization of lactones) have some outstanding properties what have been shown to differ them favourably from the other polycondensation polymers (high elasticity and susceptibility to enzymatic degradation) [86-88]. Polyesters and their copolymers (for example, *poly(ester amide)*) have a broad application in biomedical field, such as surgical sutures [89,90], matrices for drug delivery, and scaffolds in tissue engineering. They also play a very significant role as biomaterials [91-95].

The *lipase-catalyzed* synthesis of polyesters is also of interest, because the *enzymatic polymerisation* itself using lipase as one of the new methods provides biodegradable polymer syntheses without toxic catalysts [96]. Furthermore, *via* enzymatic polymerisation and other *biocatalytic* chemical processes there is a possibility to utilize non-petrochemical renewable resources as monomers for polymerisation what is particularly essential for the global sustainable use of natural resources and environment protection [97,98]. It is also known that lipase has been widely used not only in the enantioselective synthesis of pharmaceutical precursors and temperature-labile fine chemicals biocatalysts, but also in the synthesis of biodegradable and biocompatible polymers enzymes [99-101]. It is, however, much more difficult to obtain high molecular weight polymers by the enzymatic polymerization than by the metal-catalyzed polymerization. Comprehensive investigations of thermodynamic properties (vapour pressures, sublimation, vaporization, and formation and fusion enthalpies) of the monomers and polymers are rare.

The present part of this work is focused on, first, the thermodynamic studies of the properties of monomers, dicarboxilic acids (and especially *sebacic acid*) and *1,4-butanediol*, second, on the thermodynamic study of their polyesterification reaction which had been proceeded in the mild conditions according the following Scheme 1:



(Scheme 1)

The lipase-catalyzed polycondensation of sebacic acid and 1,4-butanediol has been carried out in a biphasic reaction system at room temperature by working group of Prof. *U. Kragl*. Previously, the common polyesterification in nonaqueous media required high enzyme concentration and long time periods to achieve even low molecular weights. To increase the polyester yield different approaches have been attempted to solve the problem of the shifting the equilibrium in forward direction. In the biphasic system the polyester is continuously extracted by an organic solvent and therefore higher yields can be achieved. In the presence of enzyme molecular weights of polyester are much lower than in monophasic systems (the average of the molecular weights < 4000 g·mol^{-1}) but the molecular weight distribution of the product is reduced to *1,4*. Also good yield can be obtained with product removal. In the previous study of this reaction in solution at 70°C the water evolved in reaction was removed *in situ* and molecular weight of the obtained poly(butylene sebacate) was about 42000 g·mol^{-1} after 3 days in diphenyl ether [102]. *Poly(butylene sebacate)* with higher molecular weight 56000 g·mol^{-1} and 130000 g·mol^{-1} were synthesised in the bulk polycondensation by *Linko et al.* [103].

In this work poly(butylene sebacate) obtained by lipase-catalyzed poly-condensation of 1,4-butanediol with decandioic acid in the working group by Prof. *U. Kragl* was thermodynamically investigated.

5.2. VAPOUR PRESSURES, ENTHALPIES OF SUBLIMATION AND VAPORIZATION OF MONOMERS

Experimental data on vapour pressures of the monomers (*1,4-butanediol and dicarboxilic acids*) measured using transpiration are given in Table B4 (*see* Appendix B).

5.2.1. Butanediol-1,4. Vapor pressure data for 1,4-butanediol available in the literature was measured by using all possible techniques in the temperature range from 329 K to 723 K and the experimental results are remarkably consistent except for the work [104] as shown in Fig. C5 (*see* Appendix C). Vapor pressure of 1,4-butanediol at ambient temperatures and at the reference temperature 298,15 K was studied for the first time. The standard enthalpy of vaporization of 1,4-butanediol $\Delta_l^g H_m$ (298,15 K) = 79,0±0,2 kJ·mol^{-1} obtained indirect from temperature dependence of the vapor pressure in this work (see Table 5.1) agrees within ±1,5 kJ·mol^{-1} with the most of available results presented in this table, and is also in very good agreement with two calorimetric results measured directly at the reference temperature [105, 106].

5.2.2. Decanedioic acid (Sebacic acid). Only two experimental studies on vapour pressure measurements of *decane*- und *dodecanedioic acids* are available in the literature [107,108]. In the first work authors carried out extended vapour pressure measurements of the acids over the solid samples by Knudsen effusion technique. In the second work authors measured the vapour pressures of the liquid decandioic acid. The standard enthalpies of vaporization of dicarboxylic acids from C_4 to C_{16} have been measured recently by correlation gas chromatography [109]. The vapour pressure data for decandioic acid is in very close agreement with those obtained by effusion technique (Fig. C6, Appendix C). Our vapor pressures over the liquid decandioic acid are distinctly lower in comparison to those available from ebulliometric method reported by *Stull* [108]. This disagreement is apparently because of the possibility of anhydride formation and/or decomposition at high temperatures as discussed recently by *Roux et al* [109]. However, adjusted to T = 298,15 K using eqs. 2.1-2.5 (Chap. 2), our results for sublimation enthalpy and also for vaporization enthalpy are in good agreement with values reported by *Roux et al.* [109], *Davies* and *Thomas* [107] and by *Stull* [108] (see Table 5.1).

5.2.3. Dodecanedioic acid. The vapour pressures obtained for the dodecanedioic acid in this work are in disagreement with results obtained by effusion technique

[108] as shown in Fig. C7 (Appendix C). But the value of standard enthalpy of sublimation is still in close agreement with experimental value reported previously [107] (Table 5.1). However, our new result for the enthalpy of vaporization differs from result obtained by GC-correlation measurements [109] (see Table 5.1).

Table 5.1. Compilation of Data on Enthalpies of Sublimation, $\Delta_{cr}^{g}H_m$, and Enthalpies of Vaporization, $\Delta_{l}^{g}H_m$.

Compound	Method[a]	T- range, K	$\Delta_{l}^{g}H_m$ (T), J·mol⁻¹·K⁻¹	$-\Delta C_p$[b], J·mol⁻¹·K⁻¹	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ (at 298,15 K)[c,e], kJ·mol⁻¹	Ref.
1,4-Butanediol (liq.)	E	419-490	62,3±0,8	71,4	(76,6±1,7)[d]	110
				(233,8)[19]	73,5±1,7	
	LRTF	522,0-723,8	52,5±0,3		75,5±0,3	111
	E	416,2-502,8	65,6±0,4		76,9±0,4	112
	E	416,3-501,5	66,2±0,4		77,5±0,5	20
	n/a	380-510	68,4		78,4	19
	E	380,3-481,2	69,3		78,5	104
	C	298,15			78,3±0,3	105
	C	298,15			79,3±0,5	106
	T	329,2-363,2	76,0±0,9		79,0±0,9	27
	T	298,4-349,3	77,2±0,2		**79,0±0,2**	this work
Decanedioic acid (cr.)	K	375-403	160,7	42,4[b]	165,2±2,9	107
	GC			(277,4)	165,2±5,9	109
	T	390,2-403,2	158,6		**162,7±2,5**	this work
Decanedioic acid (liq.)	E	456,0-625,4		122,4[b]	120,4	108
	GC			(430,0)[b]	124,8±2,2	109
	T	406,7-443,9	107,2		**122,7±0,7**	this work
Dodecanedioic acid (cr.)	K	375-396	153,1	52,6[b]	158,1±3,3	108
	GC			(345,5)	171,3±3,8	109
	T	391,9-400,8	157,0		**162,2±2,1**	this work
Dodecanedioic acid (liq.)	GC			139,0[b]	129,9±2,3	109
	T	404,2-438,8	103,9	(493,8)[b]	**120,8±0,4**	this work

[a] applied methods: E = ebulliometry; LRTF = Low Residence Time Flow Method; T = transpiration; K = mass-loss effusion Knudsen method; GC = gas-chromatographic correlation; C- calorimetry.

[b] values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid, C_p^l or solid C_p^{cr} compounds (they are in brackets) according to the procedure developed by *Chickos* and *Acree* [19].

[c] literature data on vapour pressures were treated by eqs. 2.1-2-5 in Chap. 2 in order to estimate the enthalpy of vaporization at 298,15 K in the same way as our own results in Table B4 (Appendix B).

[d] value cited as they reported in the original literature.

[e] values in bold used for the thermochemical calculations.

5.3. ENTHALPIES OF FUSION OF ALKANEDIOIC ACIDS

The melting temperatures and enthalpies of fusion of the alkanedioic acid measured in the present work and those available from the literature are compiled in Table 5.2. No phase transitions other than melting of decanedioic and dodecanedioic acids have been detected in contrast to results reported by *Roux et al* [109]. Our new result for decanedioic acid is in close agreement with the most recent available data [113]. New result for dodecanedioic acid is noticeable higher in comparison to the available data (see this table, firth column), apparently due to the careful purification of our sample for the thermochemical measurements.

Table 5.2. Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_{cr}^{l}H_m$, of Alkanedioic Acids.

Compound	T_{onset}, K	T_{peak}, K	T_{end}, K	$\Delta_{cr}^{l}H_m(T_{\mathrm{fus}})$, kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$ ^{a} (298,15K), kJ·mol^{-1}
Decandioic acid	404,0			40,8 [114]	
	-			43,1[111]	
	-			36,2[112]	
	403,9±0,4			46,6±5,0[109]	
	405,6±0,1			45,3±0,7[113]	
	406,2±0,2	412,6	417,0	47,1±0,2 [this work]	38,5±0,2[this work]
Dodecandioic acid	402,5			50,6[114]	
	400,3±0,6			49,8±1,1[109]	
	400,2±0,5	402,1	406,7	52,4±0,5 [this work]	43,6±0,5[this work]

[a] the experimental enthalpies of fusion $\Delta_{cr}^{l}H_m$ measured at T_{fus} and adjusted to 298,15 K (*see* the text).

5.4. CONSISTENCY TEST OF ENTHALPIES OF VAPORIZATION, SUBLIMATION AND FUSION

Since a significant discrepancy between available experimental enthalpies of vaporization of dodecanedioic acid have been found, additional arguments to support the reliability of our new measurements are required. A valuable test providing the examination of consistency of the experimental data on enthalpies of sublimation and vaporization (*dodecanedioic acid*) consists in their comparison with the experimental values of enthalpy of fusion, $\Delta_{cr}^{l}H_m$ = (52,4±0,5) kJ·mol^{-1} obtained by DSC (see Table 5.2). As a matter of fact, in this work vapour pressures of dodecanedioic acid were measured in wide temperature range over the solid and liquid sample (T_{fus} = 405,6 K). The comparison of the enthalpy of fusion $\Delta_{cr}^{l}H_m$= (41,4±2,1) kJ·mol^{-1} calculated as the difference between $\Delta_{cr}^{g}H_m$ and $\Delta_{l}^{g}H_m$ (both values are referred to T = 298,15 K) from Table 5.1 and the enthalpy of fusion calculated according to eq. 2.7 (Chapter 2). The isobaric molar heat capacities, C_p^{cr} and C_p^{l}, of the solid and liquid alkanedioic acids were calculated according to procedure in the work [19]. Thus, $\Delta_{cr}^{l}H_m$ = (43,6±0,5) kJ·mol^{-1} (adjusted to T = 298,15 K) were found to be in perfect agreement in the margins of experimental error. We had applied the same procedure to compare the data obtained for decanedioic acid and the value of enthalpy of formation in liquid state for this compound {$\Delta_{cr}^{l}H_m = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ = (40,0±2,6) kJ·mol^{-1}} was also in good agreement with the value measured by DSC {$\Delta_{cr}^{l}H_m$ = (38,5±0,2) kJ·mol^{-1}}. So the experimental dataset on enthalpies of vaporization and sublimation of alkanedioic acids in the Table 5.1 possesses the internal consistency.

5.5. ENTHALPIES OF FORMATION OF MONOMERS

Results of combustion experiments for 1,4-butanediol, decanedioic and dodecanedioic acids are summarized in Table 5.3 and in Table B9 (see Appendix B). The values of the standard specific energy of combustion, $\Delta_c u^{\circ}$, the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$ and the standard molar enthalpy of formation in the crystalline state $\Delta_f H_m^\circ$ (cr.) were based on the reactions:

$$C_4H_{10}O_2 + 5{,}5O_2 \rightarrow 4CO_2 + 5H_2O \qquad (5.1),$$

$$C_{10}H_{18}O_4 + 12{,}5O_2 \rightarrow 10CO_2 + 9H_2O \qquad (5.2),$$

$$C_{12}H_{22}O_4 + 15{,}5O_2 \rightarrow 12CO_2 + 11H_2O \qquad (5.3).$$

The values of the molar enthalpies of formation, $\Delta_f H_m^\circ$ (liq. or cr.) for all compounds under study have been obtained from the *enthalpic balance* according to the chemical eqs. (5.1-5.3) and Hess's law using the molar enthalpies of formation of H_2O (liq.) and CO_2 (g.) as assigned by *CODATA* [28].

Enthalpy of formation of 1,4-butanediol was measured in the work [110] using combustion calorimetry, where $\Delta_f H_m^\circ$ (liq.) = (-503,3±2,0) kJ·mol^{-1}. This value was in good agreement (within the boundaries of their experimental uncertainties) with the value reported in [115], where $\Delta_f H_m^\circ$ (liq.) = (-505,3±5,7) kJ·mol^{-1}. However, the large uncertainty of the available results has prompted our experimental efforts. The result for 1,4-butanediol, $\Delta_f H_m^\circ$ (liq.) = (-505,2±1,5) kJ·mol^{-1} from this work (Table 5.3) is in good agreement with earlier values. But our value is more accurate.

The standard molar enthalpies of formation $\Delta_f H_m^\circ$ (cr.) of decanedioic and dodecanedioic acids were measured using combustion calorimetry [116]. Their results were of 22 kJ·mol^{-1} and 29 kJ·mol^{-1} less negative than our values given in the Table 5.3. The reasonable explanation for such disagreement is assumed to be due to insufficient purities of the samples. For example, if a small amount of water (about 0,4 %) is suggested in their samples, a reasonable agreement with our new combustion results could be achieved.

Table 5.3. Compilation of Thermochemical Data of Dicarboxylic Acids $HOOC(CH_2)_nCOOH$ at 298,15 K (in kJ·mol^{-1}).

Dicarboxilic acid, *n*	$\Delta_{cr}^{g} H_m$	$\Delta_f H_m^\circ$ (cr.)	$\Delta_{cr}^{l} H_m$[109]	$\Delta_f H_m^\circ$ (liq.)[a]	$\Delta_f H_m^\circ$ (g.)
2	119,6±1,7[109]	**-940,9±0,5**[117] -940,1±0,5[116]	26,5±2,3	-914,4±2,4 -913,6[116]	-821,3±1,8
3	121,0±1,7[109]	**-960,5±1,2**[117] -959,3±0,5 [116]	17,6±1,1	-942,9±1,6 -941,7[116]	-839,5±2,1
4	132,1±0,9[109]	**-994,3±0,8**[118] (-987,8±1,4) [116]	26,9±2,1	-967,4±2,2 (-960,9)[116]	-862,2±1,2
5	139,1±1,2[109]	(-1009,4±1,0)[116]	20,9±1,8	(-988,5±2,1)[116]	-(870,3±1,6)
6	148,9±1,9[109]	(-1038,0±1,3)[116]	34,4±2,3	(-1003,6±2,6)[116]	(-889,1±2,3)
7	159,5±1,9[109]	(-1054,3±1,9)[116]	24,5±1,8	(-1029,8±2,6)[116]	(-894,8±2,7)
8	162,7±2,5[b]	(-1082,6±2,1)[116] **-1104,8±2,9**[117]	**38,5±0,2**[c]	(-1044,1±2,1)[116] -1066,3±2,9	-942,1±3,8
9	162,7±2,3[109]	(-1099,4±2,5)[116]	36,4±2,5	(-1063,0±3,5)[116]	(-936,7±3,4)
10	162,2±2,1[b]	(-1130,0±2,8)[116] **-1159,0±3,2**[c]	43,6±0,5[c]	(-1086,4±2,8)[116] -1115,4±3,2	-996,8±3,8
11	-	(-1148,3±3,3)[116]	41,8±2,3	(-1106,5±4,0)	-

experimental data, which are in the brackets, were considered as not reliable.

[a] enthalpy of formation was resulted from eq.: $\Delta_f H_m^\circ$ (l.) = $\Delta_f H_m^\circ$ (cr.) + $\Delta_{cr}^{l} H_m$.

[b] data from DSC measurements.

[c] data from this work.

5.6. ENTHALPIES OF FORMATION OF ALKANEDIOIC ACIDS IN THE LIQUID STATE

The standard enthalpies of formation of decanedioic and dodecanedioic acids, $\Delta_f H_m^\circ$ (cr.), derived from the combustion experiments are referred to the crystalline state. For lipase-catalyzed polyester synthesis between sebacic acid and 1,4-butanediol we need the standard molar enthalpies of sebacic acid in the liquid phase, $\Delta_f H_m^\circ$ (liq.), which is defined as

$$\Delta_f H_m^\circ \text{ (liq.)} = \Delta_f H_m^\circ \text{ (cr.)} + \Delta_{cr}^{l} H_m \qquad (5.4),$$

where $\Delta_{cr}^{l} H_m$ the enthalpy of fusion of *decanedioic acid* is already known from Table 5.3. As a rule, all three thermodynamic quantities in the chemical eqs. 5.1-5.3 should be referred to the same temperature, often to the reference temperature 298,15 K. However, experimental enthalpies of fusion of alkanedioic acids measured by DSC are obtained at the melting temperature T_{fus}. The difference between experimental enthalpy of fusion and enthalpy of fusion relative to the reference temperature was calculated using eq. 2.7. Omitting the uncertainty of the correlation, which was not taken into account, the molar enthalpies of fusion, $\Delta_{cr}^{l} H_m$ (298,15 K), were calculated with this adjustment (Table 5.3). Using these values in eq. (5.4), standard molar enthalpies of formation of decandioic acid and dodecanedioic acid in the *undercooled metastable liquid phase,* $\Delta_f H_m^\circ$ (liq.), have been derived and listed in Table 5.3. Combining the values of vaporization and sublimation enthalpies of compounds under study with the results from our combustion experiments, the gas standard enthalpies of formation $\Delta_f H_m^\circ$ (g.) at 298,15 K were calculated according to eqs. 2.8 and 2.9. The resulting values of $\Delta_f H_m^\circ$ (g.) are given in the last column of Table 5.3.

5.7. VALIDATION OF THE LIQUID PHASE AND THE GAS PHASE ENTHALPIES OF FORMATION (ALKANEDIOIC ACIDS)

Another way to check the internal consistency of the experimental results is the correlation of enthalpies of formation (or enthalpies of vaporization) with the number of C-atoms in the series of homologues. Enthalpies of formation in the liquid or in the gaseous phase are expected to be a linear function of the number of carbon atoms [119,120]. Enthalpies of formation in the liquid phase were derived according to eq. (5.5) and given in Table 5.3. In Fig. 5-1 the plot of $\Delta_f H_m^\circ$ (liq.) referred to 298,15 K against the number of C-atoms in the aliphatic dicarboxylic acids (HOOC-$(CH_2)_n$-COOH, where n varies from 2 to 10) represents the linear dependence which can be expressed as follows:

$$\Delta_f H_m^\circ \text{ (liq.) at 298,15 K / kJ·mol}^{-1} = -866{,}1 - 25{,}1 \cdot n \quad (r = 0{,}9996) \qquad (5.5)$$

Now using this equation, the standard enthalpy of formation $\Delta_f H_m^\circ$ (liq.) of any other representatives of this series with $n > 10$ can be easily calculated. Now, it is also possible to check the experimental data obtained by *Verkade et al* [116] for dicarboxylic acids with $n = 2$ to 11 using eq. 5.5. As can be seen in Fig. 5.1, the values of $\Delta_f H_m^\circ$ (liq.) at 298 K for diacids with $n = 2,3,4$ and 5 are consistent with the results selected from the literature (see Table 5.3). However, the deviation observed for diacids with $n = 6$ to 11 from the straight line according to eq. 5.5 seems to be systematic and these data apparently need to be revised in the nearest future.

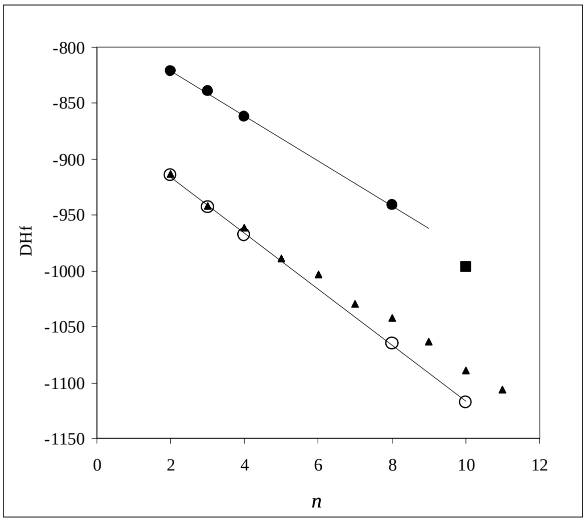
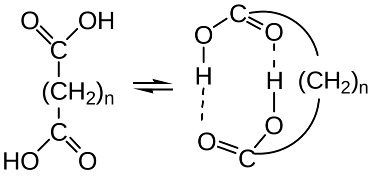


Fig. 5.1. Correlation of the standard enthalpies of formation (data from Table 5.3) with the number of methylene groups *n* in the *aliphatic dicarboxylic acids* HOOC-$(CH_2)_n$-COOH: ○- $\Delta_f H_m^\circ$ (liq.); ▲- $\Delta_f H_m^\circ$ (liq.) of compounds measured in [116]; ●- $\Delta_f H_m^\circ$ (g.); ■ - $\Delta_f H_m^\circ$ (g.) of *dodecanedioic acid*.

The standard enthalpies $\Delta_f H_m^\circ$ (g.) in the gaseous phase listed in the last column of Table 5.3 are also plotted as a function of the number of methylene groups in the aliphatic dicarboxylic acids $HOOC(CH_2)_nCOOH$ with n = 2 to 8 and given in Fig. 5.1. As found for other homologous series [119], a good linear correlation is observed for the smaller members of the series. A linear regression of $\Delta_f H_m^\circ$ (g.) for C_2, C_3, C_4, and C_8-homologues can be expressed as:

$$\Delta_f H_m^\circ \text{ (g.) at 298,15 K / kJ·mol}^{-1} = -780{,}6 - 20{,}1\cdot n \qquad (r = 0{,}9996) \qquad (5.6)$$

However, once the number of methylene groups exceeds *8*, a definite departure from linearity is observed. The similar slope behaviour has been reported for the $\Delta_l^g H_m$ (298,15 K) plotted as a function of *n* [109]. This departure from linearity has been interpreted [107,109] as a result of an equilibrium established between a linear and cyclic form of the diacid in the gas phase as depicted in the Scheme 2. It has been suggested [107,109] that as the number of methylene groups in the diacid increases, the ring becomes large enough to accommodate the type of hydrogen bonding observed in the gas phase dimerization of smaller mono-carboxylic acids at ambient temperatures. For this reason, eq. 5.6 could be used only for interpolation of enthalpies of formation $\Delta_f H_m^\circ$ (g) at 298,15 K of other representatives of this series within *n* = *2* to *8*. The larger diacids exist in equilibrium with a cyclic and acyclic form; the degree of such association in the gas phase has not been firmly established [109]. Therefore the experimental vaporization, sublimation, and formation enthalpies for diacids with *n* > *8* should not be used in any thermochemical interpretation without appropriate adjustments for the equilibrium observed in the gas phase as reported previously for the mono-carboxylic acids [121].



(Scheme 2)

5.8. AB INITIO CALCULATIONS OF MONOMERS

High-level *ab initio* calculations have been successfully applied for the validation of experimental enthalpies of formations of organic carbonates [33,72], ethers [122], esters [123], aromatic amines [70], benzoic acids [69], and nitro-phenols [71]. In this work we have used the ab initio calculations to verify the experimental enthalpies of formations, $\Delta_f H_m^\circ$ (g.), of 1,4-butanediol, decanedioic and dodecanedioic acids.

5.8.1. CONFORMATIONAL EQUILIBRIUM AND RELATIVE ENERGIES OF 1,4-BUTANEDIOL CONFORMERS

1,4-Butanediol is very flexible molecule since it has five possible rotameric dihedral angles leading to many possible local minima. Study of conformational equilibrium of 1,4-butanediol is important for correct calculation of its $\Delta_f H_m^\circ$ (g). The computational procedures in determination of the low-energy conformations using a systematic search method are very expansive. Hence, we were able to use at first the force-field calculations (MM3) to perform the preliminary conformational analysis and to select the most stable conformers. According to results obtained by DFT *11 most stable conformers* were selected [124,125]. These conformers have been fully optimized by the G3MP2 method and their energy differences related to the appropriate most stable conformer (St) given in the Table B15 (Appendix B). The low-energy conformers were weighed by their Boltzman populations and then used to calculate the weighed mean enthalpy of 1,4-butanediol, $\Delta_f H_m^\circ$ (g.)$_{\mathrm{G3MP2}}$, in the gaseous state. The thermal population p_i of the conformers at T = 298,15 K is expressed by the following equation:

$$p_i = \frac{e^{-\frac{\Delta G_i}{RT}}}{1+\sum_{i=1}^{n} e^{-\frac{\Delta G_i}{RT}}} \qquad (5.7),$$

where $\Delta G_i = G_i - G_{st}$. Results on p_i were used for calculation of the energies and enthalpies of the equilibrium mixture of conformers (Tables B15 and B16 in Appendix B). It has turned out that the four most stable conformers of 1,4-butanediol are stabilized in the gaseous phase by an intramolecular hydrogen bond between the hydroxyl groups. Also in the liquid phase the band assigned to the intramolecular bonding was observed by *IR spectroscopy* in dilute solution of CCl_4 [124].

5.8.2. VALIDATION OF EXPERIMENTAL ENTHALPY OF FORMATION (1,4-BUTANEDIOL)

In this work we need the enthalpy of formation $\Delta_f H_m^\circ$ (liq.) of 1,4-butanediol obtained from experiments are used for calculation of enthalpy of polymerization. Extended conformational analysis performed in this work for 1,4-butanediol and energies of its conformers calculated by G3MP2 level of theory have allowed deriving the standard molar enthalpies of formation $\Delta_f H_m^\circ$ for 1,4-butanediol in the gaseous phase.

In present part of the work atomization and *isodesmic* or *homodesmic* reactions methods were applied. Standard enthalpy of formation $\Delta_f H_m^\circ$ (g.) of 1,4-butanediol was calculated on the basis of the atomization reaction,

$$C_4H_{10}O_2 \rightarrow 4C + 10H + 2O \qquad (5.8)$$

as well as on the basis of the selected isodesmic reactions:

$$C_4H_{10}O_2 + 4CH_4 \rightarrow 2CH_3OH + 3C_2H_6 \quad (5.9),$$

$$C_4H_{10}O_2 + 6CH_4 \rightarrow 2H_2O + 5C_2H_6 \quad (5.10),$$

$$C_4H_{10}O_2 + 5C_2H_6 \rightarrow 2CH_3OH + 4C_3H_8 \quad (5.11),$$

$$C_4H_{10}O_2 + 7C_2H_6 \rightarrow 2H_2O + 6C_3H_8 \quad (5.12).$$

Results of calculations are given in Table B16. The populations of all conformers obtained by eq. 5.7 have been taken into consideration for calculation of $\Delta_f H_m^\circ$ (g.) at 298,15 K. Results calculated from atomization procedure by chemical eq. 5.8 and four isodesmic chemical eq. 5.9-5.12 were found to be very close (Table B16). The average of theoretical enthalpies of formation obtained for 1,4-butanediol $\Delta_f H_m^\circ$ (g.)$_{\text{G3MP2}}$ = (-430,4±1,7) kJ·mol^{-1} was calculated using enthalpies of reactions obtained by G3MP2 from eq. 5.9-5.12.

Now, having established consistent theoretical values, $\Delta_f H_m^\circ$ (g.)$_{\text{G3MP2}}$, for 1,4-butanediol using G3MP2 procedure the enthalpy of formation of the liquid 1,4-butanediol could be estimated by the following equation:

$$\Delta_f H_m^\circ \text{ (liq.)} = \Delta_f H_m^\circ \text{ (g)}_{\text{G3MP2}} - \Delta_l^g H_m \quad (5.13)$$

Enthalpy of vaporization of 1,4-butanediol $\Delta_l^g H_m$ required for this equation was deliberately measured in this work (see Table 5.1). Thus, using eq. 5.13 and standard enthalpy of formation of 1,4-butanediol in the gaseous phase, $\Delta_f H_m^\circ$ (g.)$_{\text{G3MP2}}$ = (-430,4±1,7) kJ·mol^{-1}, the enthalpy of formation of 1,4-butanediol in the liquid state, $\Delta_f H_m^\circ$ (liq.) = (-507,6±1,9) kJ·mol^{-1} was estimated using G3MP2 result. This value is in good agreement with our new result $\Delta_f H_m^\circ$ (liq.) = (-505,2±1,5) kJ·mol^{-1} measured by combustion calorimetry in the present part of the work. Thus, the results of *ab initio* calculations have helped to establish thermodynamic consistency of the experimental results obtained from the transpiration and from the combustion calorimetry.

5.8.3. VALIDATION OF THE LIQUID PHASE AND THE GAS PHASE ENTHALPIES OF FORMATION (ALKANEDIOIC ACIDS)

The experimental standard enthalpies of formation $\Delta_f H_m^\circ$ (cr.) of decanedioic and dodecanedioic acids were found to be in disagreement with earlier results (*see* Table 5.3). It is hoped that *ab initio* calculations will be helpful to prove new experimental results, similar as it has been just done for 1,4-butanediol. However, decanedioic acid and dodecanedioic acid are very large molecules for the G3MP2 method and calculation of these species is close to the limit of our computational capacity. For this reason, an additional less timeconsuming DFT B3LYP/6-311+(d,p) calculations have been performed for dodecanedioic and dodecanedioic acid.

a) Decanedioic acid. The standard enthalpy of formation $\Delta_f H_m^\circ$ (g.) of decanedioic acid has been calculated using six selected isodesmic reactions (Table B17, Appendix B). Theoretical standard enthalpies of formation of decanedioic acid $\Delta_f H_m^\circ$ (g.) have been calculated by G3MP2 and DFT B3LYP/6-311+(d,p) with help of available standard enthalpies of formation of other reaction participants [32]. Results were calculated by G3MP2 method from *isodesmic* and *homodesmic* reactions. The average value from all 6 reactions $\Delta_f H_m^\circ$(g.)$_{\text{G3MP2}}$ = (-944,1±2,8) kJ·mol-1 is close to the experimental one $\Delta_f H_m^\circ$ (g.)$_{\text{exp}}$ = (-942,1±3,8) kJ·mol^{-1} (see Table 5.3). Having established this theoretical value, the standard enthalpy of formation of the solid decanedioic acid could be calculated by the following equation:

$$\Delta_f H_m^\circ \text{ (cr.)} = \Delta_f H_m^\circ \text{ (g.)}_{\text{G3MP2}} - \Delta_{cr}^{g} H_m \qquad (5.14)$$

Using the sublimation enthalpy for this compound, $\Delta_{cr}^{g} H_m$, given in the second column of Table 5.3, the standard enthalpy of formation of decanedioic acid $\Delta_f H_m^\circ$ (cr.) = (-1106,8±3,8) kJ·mol^{-1} is obtained. Calculated result is in good agreement with the experimental result obtained from calorimetric experiment $\Delta_f H_m^\circ$ (cr.) = (-1104,8±2,9) kJ·mol^{-1} (see Table 5.3). Such good agreement between experimental and theoretical (G3MP2) values is valuable check of their mutual consistency.

b) Dodecanedioic acid. The standard enthalpy of formation $\Delta_f H_m^\circ$ (g.) of dodecanedioic acid has been calculated using G3MP2 and DFT B3LYP/6-311+(d,p) using also six selected *isodesmic* reactions presented in Table B17 (Appendix B). Results calculated using G3MP2 from isodesmic and homodesmic reactions (Table B17 in Appendix B), $\Delta_f H_m^\circ$ (g.)$_{\text{G3MP2}}$ = (-1014,4±3,2) kJ·mol-1 is in disagreement with the experimental value $\Delta_f H_m^\circ$(g.)$_{\text{exp}}$ = (-996,4±3,8) kJ·mol^{-1} (see Table 5.3). Such a discrepancy is apparently due to the intramolecular hydrogen bonding in this molecule in the gaseous phase. It should be noticed, that in calculations presented in Table B17 only the most stable cyclic conformer of dodecandioic acid was taken into account. However, as it has been mentioned above, the equilibrium mixture of the linear and cyclic species could be expected in the gaseous state for this compound. But according to our DFT B3LYP/6-311+(d,p) calculations the mixture consists from 16% of the linear and 84% of the cyclic conformer. According to our G3MP2 calculations the mixture consists from 1% of the linear and 99 % of the cyclic conformer. In contrast to the success of the composite ab initio method G3MP2, our calculations of $\Delta_f H_m^\circ$ (g.) using the DFT method B3LYP/6-31G(d,p) and have shown the inacceptable spread of values over 80 kJ·mol^{-1} (see Table B17). Similar scatter we observed recently even for less sophisticated molecule such as *tert-butylbenezene* using B3LYP/6-31G(d) calculations [67]. These results confirm a recommendation from the recent studies, which DFT methods have to be applied with caution, because of systematic errors, which could be traced back to the neglect of dispersion interactions in DFT [67,126].

5.9. KINETICS AND THERMODYNAMICS OF ENZYMATIC POLYCONDENSATION

The polycondensation of decanedioic acid with 1,4-butanediol was catalysed by a lipase from *Candida antarctica B*. Although the lipase catalyses the esterification as well as the hydrolysis, the condensation can be effectively carried out by integrated product removal [127,128]. Especially the usage of biphasic systems offers new possibilities for lipase-catalyzed polycondensation. Because polycondensation reactions are stepwise processes, monomers can react either with other monomers as well as with dimer and other oligomers. The application of lipase as biocatalyst offers the possibility to control this mechanism and therewith chain length and *polydispersity* of the product can be adjusted. To estimate the driving force of the equilibrium reaction the equilibrium constant has been calculated as described below.

Addition of a monomer molecule to the growing species in polycondensation is a reversible reaction. The equilibrium constant of this reaction, K_{pol}, is a function of the Gibbs free energy change, ΔG_{pol}, which in turn is governed by the changes of enthalpy, ΔH_{pol}, and entropy, ΔS_{pol}, during reaction:

$$\Delta G_{pol} = \Delta H_{pol} - T\Delta S_{pol} = -RT \cdot lnK_{pol} \qquad (5.15)$$

Polycondensation (polymerization) is thermodynamically possible if the ΔG_{pol}-value for the transformation of monomer molecules into polymer unit is negative. For the majority of polymerisation systems both enthalpy and entropy of polymerisation have been found negative [129].

Values of ΔH_{pol} reflect the difference in bonding energies in monomer and polymer. Polymerisation enthalpies are usually measured or calculated from the results of combustion calorimetry. Because the polymerisation is an association reaction, the entropy of polymerisation is as a rule negative and the overall entropy change is a sum of contributions involving changes of transitional, rotational, and vibrational entropies. *Daiton* and *Ivin* stated that the loss of external rotational entropy nearly balances the gain in vibrational and internal rotational entropy during the polymerisation step [129]. Consequently, ΔS_{pol} reflects mainly the lost of translational entropy, and thus is fairly independent of the structure of the monomer. Analysis of ΔS_{pol} values for different types of polymerizations indeed indicates that the entropy changes are generally within (80-120 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) [129-131].

The position of equilibrium in a polymerisation is governed by both enthalpy and entropy factors. Because the entropy factor (T–ΔS_{pol}), even for relatively high polymerisation entropy values, contributes usually no more than 35 $\mathrm{kJ \cdot mol^{-1}}$ (at ambient temperatures) to the ΔG_{pol}-value, the position of equilibrium depends mainly on the ΔH_{pol}-value. If the polymerisation enthalpy is strongly negative, the equilibrium constant K_{pol} is high and the equilibrium position is shifted to the right-hand side. From the thermodynamic constant of polymerisation-depolymerisation equilibrium, K_{pol}, the equilibrium concentrations of monomer, $[\mathrm{M}]_e$, and polymer, $[\mathrm{P}]_e$, in a reaction mixture at any temperature could be calculated:

$$[M]_e = \exp\left(\Delta G_{pol}/RT\right) \qquad (5.16),$$

with taking into account $[M]_e = 1/K_{pol}$:

$$[P]_e = 1 - \exp\left(\Delta G_{pol}/RT\right) \qquad (5.17)$$

Knowledge about amounts of monomers which remain in equilibrium with the polymer helps to optimize reaction conditions.

Reaction of diol with alkanedioic acid provides a convenient model system for studying of the polymer thermodynamics. Only a few works on thermodynamics of the polycondensation were found in the literature [132,133]. In this part of work polycondensation of 1,4-butanediol with decanedioic acid (Scheme 1) have been studied. Enthalpies of formation of monomers and polymer have been measured by combustion calorimetry (see Table B9 in Appendix B). Enthalpy of polymerisation ΔH_{pol} = -85,5 $\mathrm{kJ \cdot mol^{-1}}$ has been calculated from these results and refers to the following process:

$$\mathrm{nHO\text{-}(CH_2)_4\text{-}OH\ (liq.) + nHOOC\text{-}(CH_2)_8\text{-}COOH\ (cr.) = Polymer\ (cr.) + 2n\ H_2O\ (liq.)} \qquad (5.18)$$

for the case, when of 1,4-butanediol is in the liquid phase, but decanedioic acid and the polymer are in crystalline phase. If the polycondensation reaction performed in the liquid phase, the enthalpy of polymerisation ΔH_{pol} = -125,3 kJ·mol^{-1} has been calculated. It referred to the following process:

$$nHO\text{-}(CH_2)_4\text{-}OH\ (liq.) + nHOOC\text{-}(CH_2)_8\text{-}COOH\ (liq.) = Polymer\ (cr.) + 2n\ H_2O\ (liq.) \quad (5.19)$$

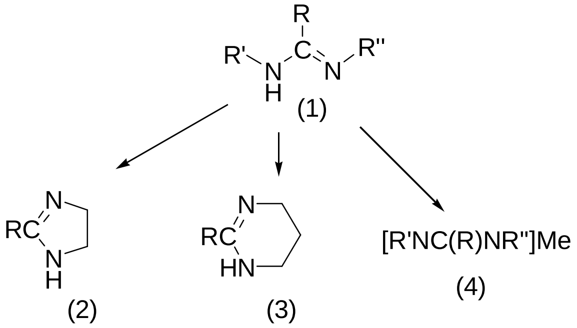
for the case, when of 1,4-butanediol and decanedioic acid are in the liquid phase and the polymer is in crystalline phase. Both results for polymerisation enthalpy have fulfilled our expectations- they are strong negative. For comparison, reaction enthalpy of 1,4-butanediol with *1,4-diisocyanatobutane,* ΔH_{pol} = -152 kJ·mol^{-1} was obtained [132] for the polycondensation process with liquid monomers and crystalline polymer (similar to eq. 5.18).

We are able to assess the Gibbs function, ΔG_{pol}, of polycondensation under assumption of typical value ΔS_{pol} = -80 J·mol^{-1}·K^{-1} [129]. For the polycondensation process according to eq. 5.19 the values of ΔG_{pol} = -101,5 kJ·mol^{-1} and K_{pol} = 6,2·10^{17} were calculated using eq. 5.15. The large negative value of Gibbs function, ΔG_{pol}, and very large equilibrium constant indicate that the equilibrium of the polymer reaction is completely shifted towards polymer formation. Following, polycondensation of 1,4-butanediol with decanedioic acid is thermodynamically favoured and high yield of polymer could be achieved under kinetic control in the presence of effective catalyst, like i.e. lipase of *Candida antarctica B*.

6. SYNTHESIS AND THERMOCHEMICAL STUDY OF POLYAMIDINES

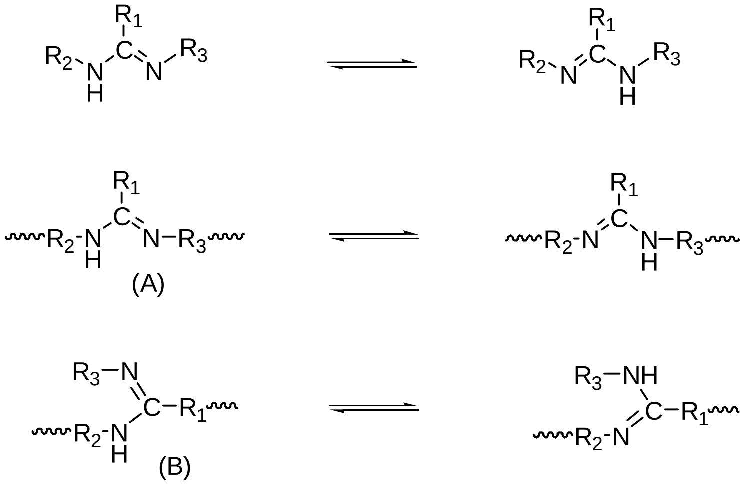
6.1. INTRODUCTION

Presented in the Scheme 1 *amidines* (1) (where R, R´, R´´=H, Alk or Ar) are known in preparative organic chemistry as precursors for the synthesis of cyclic analogues, *imidazolines* (2), *tetrahydropyrimidines* (3) [134] and *metal amidinate complexes* (4), where Me = Li, Al, Ti [135-138]. Alkyl and aromatic substituted derivatives of amidines, alkyl *formamidines* (1, where R´=H) as well as diamidines $[H_2N\text{-}C(=NH)\text{-}R\text{-}]_2R$ (where R=Alk), and organic *bis-formamidinium salts* are used in medicine. They are used as antiprotozoal and antituberculous drugs, inhibitors for enzymes, synthetic analogues of natural hormones, and also preparation of biologically active imidazolines and *imidazoles* [139-143]. Last two decades it has been found an increasing interest to aromatic amidines [144-147].



(Scheme 1)

Monosubstituted amidines, formamidines, and polymers containing amidine groups are strong bases ($pK_a \geq 10$ in aq. solution) and exhibit *tautomerism* illustrated in the Scheme 2. Due to this fact the hydrolysis of amidines produces a mixture of amides and amines.

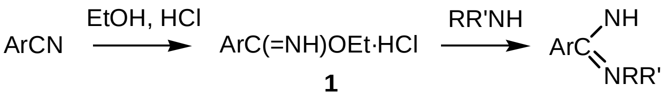


(Scheme 2)

Polymers containing amidine groups (*polyamidines*) have not found a broad application yet. They were used as UV plastic stabilizers and polymeric adhesives [148-153]. Aliphatic polyamidines were first mentioned in 1959 [154], and the general structure A given in Scheme 2 was assigned for these new polymers.

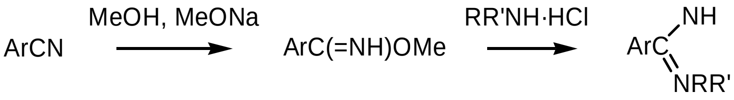
Later, the term “polyamidine” was extended to other structure like (B), presented also in Scheme 2.

Synthesis of aromatic/aliphatic amidines and polyamidines is usually based on the reaction of amines with: 1) nitriles in the presence of some condensation agents (for example, $AlCl_3$); 2) carboxylic acids, amides, N-substituted amides (*via* formation *imidoyl chlorides*) at high temperature in the presence or absence condensation agents; 3) *ketenimines*. Results of typical experiments for synthesis of amidines and polyamidines via reactions of amines are summarized in the Table B18 (Appendix B). As a rule amines undergo considerable conversion upon treatment with nitriles in the presence of HCl in anhydrous alcoholic solution (*Pinner's method*) [155-157]. General, reaction proceeds *via* formation of imidic ester hydrochlorides (**1**, Scheme 3):



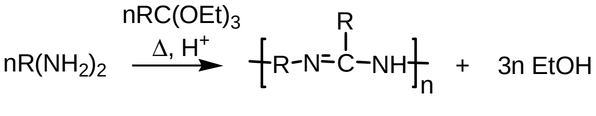
(Scheme 3)

In 1978 *Piskov* and *Kasperovich* reported modification of Pinner's method [158] (Scheme 4). According to this scheme amidines are readily formed in reaction of benzonitriles with the strong electron-withdrawing groups connected to the aromatic ring in presence of hydrochlorides of amines:



(Scheme 4)

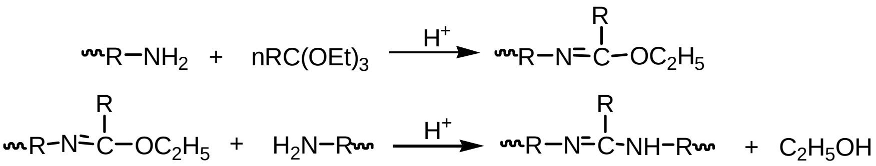
For the preparation of wide variety of amidines in preparative organic chemistry, both methods are still the most useful methods reported in the literature. Following, it could be of importance to extend Pinner's method to the preparation of aromatic and aliphatic polyamidines [150]. Aromatic substituted polyamidines (polyformamidines) can be formed with the high yield from ortho-esters and diamines in presence of H^+ in alcoholic solution [144-145]. Such polycondensation (Scheme 5, where R= Alk, Ar) has been carried out in melt (or bulk) at low pressure with catalytic amounts of acid (benzoic or acetic) and it provided low molecular weight polyamidines:



$$nR(NH_2)_2 \xrightarrow[\Delta,\ H^+]{nRC(OEt)_3} \left[R-N=\overset{R}{\overset{|}{C}}-NH \right]_n + 3n\ EtOH$$

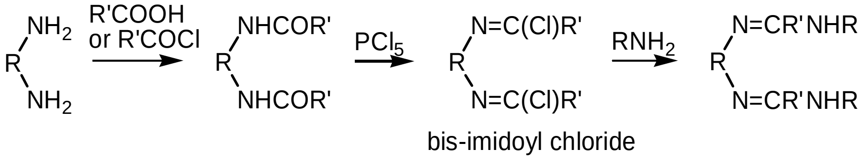
(Scheme 5)

Apparently in the first step of this reaction, an imidoester-group is formed as intermediate (see Scheme 6) which further reacts with the second amino-group of diamine in the final step giving the amidine-group:



(Scheme 6)

In this work we have been interested to develop the synthesis of polyamidines containing two nitrogen atoms in the polymer chain (structure (A) in Scheme 2), using not only well established Pinner's method, but also *via* new reaction of aromatic bis-imidoyl chlorides with diamines. Already in 1858 *Gerhardt* reported preparation of 1,2-diphenylbenzamidine by addition of N-phenylbenzimidoyl chloride to amine [159]. Later, *Wallach*, *Bamberger*, *Lorenzen* and *von Pechmann* [160-163] developed this reaction as a general method for preparation of aromatic amidines. Results related to aminolisis of bis-imidoyl chlorides were first mentioned by *Rao* and *Wheeler* [164] and elaborated by *Hill* and *Johnston* [165]. Aromatic amidines with the structure ~N(R)-C(=NR′)~ were synthesized by addition of ammonia or ammonium salt (or an amine) to nitriles [166]. The different new diamidines were prepared according to the Scheme 7 (where R=R'=Alk, Ar):



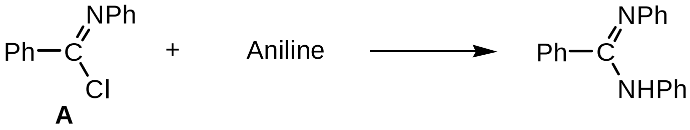
(Scheme 7)

In this work synthesis of polyamidines containing both nitrogen atoms in the polymer chain using aromatic bis-imidoyl chlorides and amines were developed as the alternative method of polymerization in different solvents. Aromatic bis-imidoyl chlorides were prepared according to Scheme 7. Since R could be easily varied by the choice of the diamine, different polyamidines were possible to synthesize and to investigate their properties.

6.2. Synthesis of Model Compounds

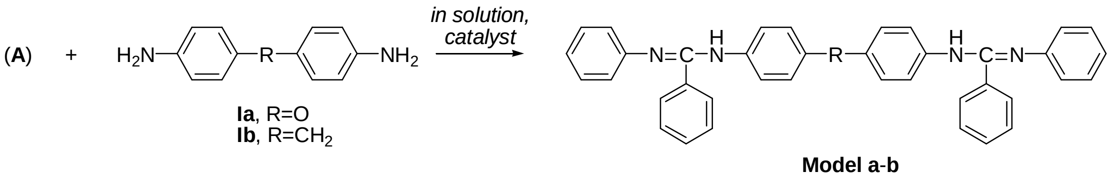
It is reasonable to begin the development of any synthetic method using model reactions. In this work we have used reactions presented in Scheme 8-10 to prepare the model compounds containing amidine group. Reaction presented in the Scheme 8 is similar to reaction of benzoyl chloride with aniline studied previously [167].

It is known that the non-catalytic reactions of aniline with benzoyl chloride at 25°C in benzene proceeds almost in 15 times slower than that in polar solvent like nitrobenzene [167]. It is also known that aniline reacts with N-phenylbenzimidoyl chloride in the presence of catalytic amounts of tertiary amines in benzene in 7000 times faster than in the case of non-catalytic reaction [168]. *Pyridine-N-oxide* was found to be able to accelerate reactions of carboxylic acid chloranhydrides with amines in benzene, but this compound did not affect the final composition [169]. Reaction of imidoyl chlorides with amines was as a rule carried out in the presence of pyridine in dimethylformamide as acceptor of by-product, HCl [170]. In this work the use of pyridine-N-oxide as a catalyst and reaction of N-phenylbenzimidoyl chloride (**A**) with aniline was completed in 1 hour in N-methylpyrrolidone-2 (MP) with good yield of final product- 1,2-diphenylbenzamidine (Scheme 8):



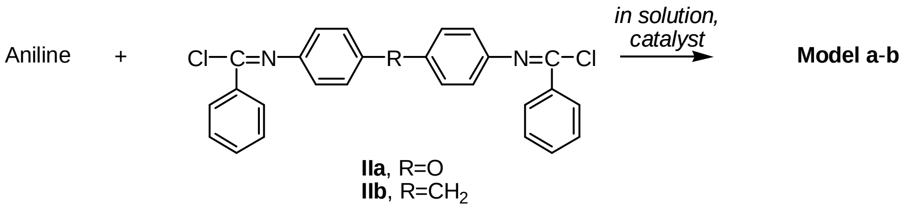
(Scheme 8)

This reaction was utilized for the preparation of novel bis-amidines as model compounds from (**A**) and diamines such as 4,4'-diaminodiphenyl oxide (DAPO) or 4,4'-diaminodiphenylmethane (DADPM) in MP in the presence of Et_3N and pyridine-N-oxide (Scheme 9):



(Scheme 9)

Alternatively, these model compounds were also synthesized via reaction of 4,4'-bis(N-phenylenebenzimidoyl chloride)oxide or 4,4'-bis(N-phenylenebenzimidoyl chloride) methane with aniline in polar solvent and in the presence of Et_3N (Scheme 10):

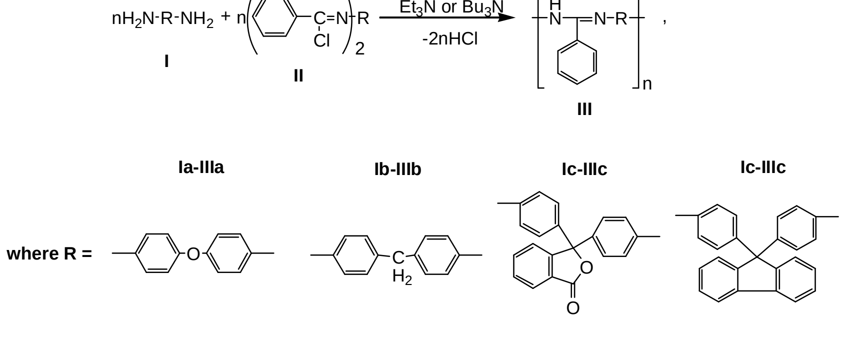


(Scheme 10)

Summary of experiments according to Schemes 8-10 is given in Table 6.1.

6.3. SYNTHESIS OF POLYMERS

Synthesis of polyamidines based on aromatic bis(imidoyl) chlorides is given on Scheme 11. According to this scheme, polycondensation of 4,4'-bis(N-phenylene-benzimidoyl chloride) oxide (IIa) with diamine Ia was performed in MP using Et_3N as a catalyst (Scheme 11):



(Scheme 11)

The effect of the loading order of reagents on polymer viscosity has been determined in the series of experiments for the reaction of Ia with IIa. Results are listed in Table B19 in Appendix B. The effect of the other reaction condition (concentration of the reagents, temperature, and duration of the synthesis) on molecular weight of polymer IIIa is illustrated on the Figures 6.1-6.4.

Table 6.1. Preparative Conditions for Model Compounds according to Scheme 8-10 in N-methylpyrrolidone-2.

Starting reagent/ catalyst	Reagent [a]/Catalyst (molar ratio)	Reagent [a] concentration, $mol\cdot l^{-1}$	Duration, hour	T_{fus}, °C	Yield, %
A + Ia/Et_3N	0,11	2,02	3	94	49
A + Ia/Pyridine-N-oxide	46,4	4,64	1.5	183	82
A + Ib/Et_3N	0,10	2,0	3	150	70
Aniline + IIa/Et_3N	0,12	2,23	3	190-193	54
Aniline + IIb/Et_3N	0,38	6,77	3	110	70
Aniline + A/Pyridine-N-oxide	1,0	7,4	1	144-145	82

[a] concerning only *bis*- or *monoimidoyl chloride.*

In order to understand how the molecular weight of polymer can be affected by the varying of loading catalyst order and its concentration, the synthesis of polyamidines was performed at 90°C and total monomer concentration of 0,6 M, and a reaction time of 2,5 hours (the conditions of model compounds synthesis) in the presence of the Et_3N. It has been previously investigated that the similar reaction of m-phenylenediamine with isophthaloyl chloride in a polar solvent proceeds to give the best results upon varying monomer concentrations in the range of 0,5 to 0,8 M and the solid acid dichloride loading to a solution of diamine [171].

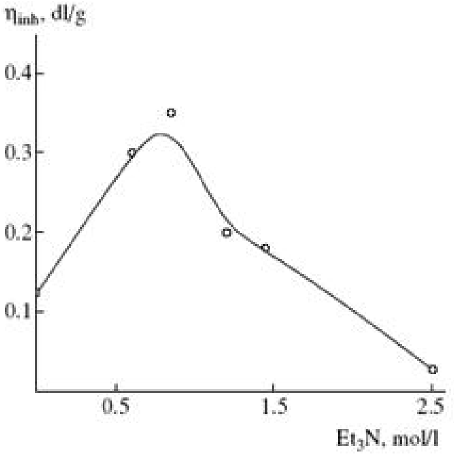


Fig. 6.1. The plot of η_{inh} for the solution of polyamidine IIIa prepared by the interaction of IIa with Ia vs. the concentration of catalyst Et_3N at 90°C and reaction duration of 2,5 hours.

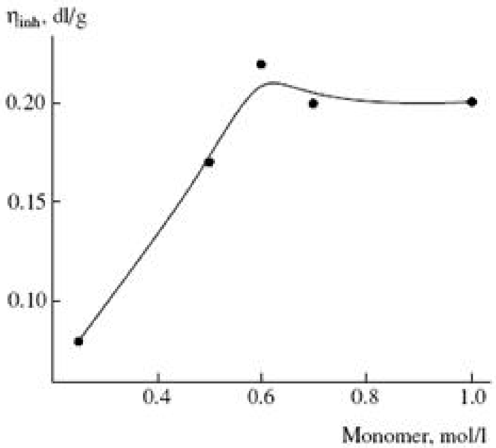


Fig. 6.2. The plot of η_{inh} for the solution of polyamidine IIIa vs. the total concentration of monomers at 110°C and reaction duration of 5 hours.

Fig. 6.1 shows that increasing of catalyst concentration leads to decreasing of molecular weight of polymer (a solid bis(imidoyl) chloride was added to the diamine solution in MP). The viscosity of polymer solution (η_{inh}) is getting low. It was found that the catalyst concentration was 0,5 to 1,0 M as the optimal and corresponded to catalyst-monomer ratios of 1:1 and 3:1. When the amount of the catalyst was larger than the 5-fold molar excess refer to monomer, the yield of the polymer and its η_{inh} were minimal. Synthesis of IIIa in MP was also carried out without any catalyst and produced polymers with η_{inh} 0,12 ($dl\cdot g^{-1}$). Dependence of η_{inh} of resulting polymers versus molar concentration of monomers in reaction is presented in Fig. 6.2. It was found that concentration of the monomers varying within 0,5-0,7 M was optimal. Increase of concentration to 1 M had no significant effect on the molecular weight of polymer (η_{inh}). The temperature dependence of η_{inh} of 2,5 and 5 hours synthesis of polyamidine is shown in Fig. 6.3. The higher value of η_{inh} was achieved at 80-90°C in the presence of Et$_3$N. In these conditions η_{inh} decreases with increase of the temperature. The time dependence of η_{inh} of polyamidine at optimal conditions is presented in Fig. 6.4. It can be seen that at these conditions the reaction was completed in 2-2,5 hours.

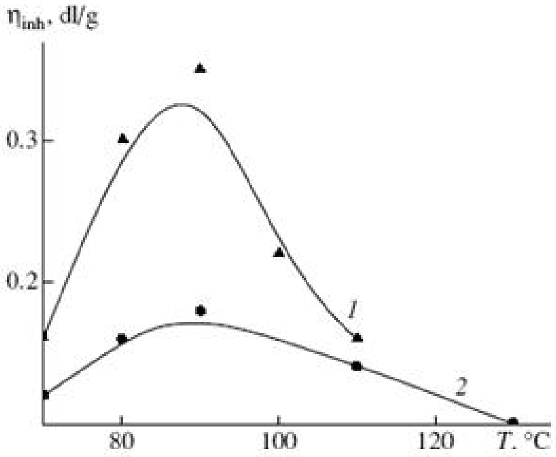


Fig.6.3. The temperature dependence of η_{inh} for the solution of polyamidine IIIa. The monomer concentrations are (1) 0,6 and (2) 0,5 M; the reaction durations are (1) 2,5 and (2) 5 hour.

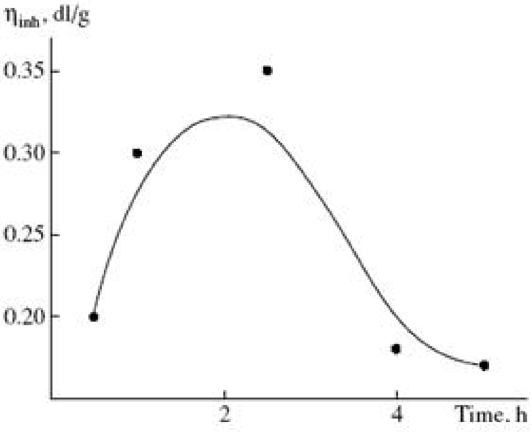


Fig. 6.4. The plot of η_{inh} for the solution of polyamidine IIIa vs. the reaction duration at 90°C. The concentration of monomers is 0,6 M, and the concentration of catalyst Et$_3$N is 0,83 M.

Inspection of Table B19 reveals a considerable influence of order of the monomers loading on the polymer viscosity of resulting polyamidines. It turned out that the value of polymer viscosity of IIIa depends on whether bis(imidoyl) chloride is added to diamine solution in the solid state or as a solution. Sufficient decreasing of molecular weight of polymer was observed when the solution of IIa was added to solution of Ia in MP (η_{inh} = 0,06 $dl\cdot g^{-1}$). In contrast, the loading of monomer IIa to solution of Ia caused the significant increase of the molecular weight of resulting polymer (η_{inh} = 0,35 $dl\cdot g^{-1}$). It was found that after first minutes of reaction without catalyst the resulting polymer was already precipitated from solution. In our opinion this fact could be interpreted by formation of insoluble *polyamidine hydrochloride*, which took place due to the side reaction between resulting polymer and evolving by-product, HCl. It worth mentioning that precipitated polymer was then dissolving after 1 hour again.

It was also interesting to study whether the molecular weight of polymer depends on order of catalyst (pyridine-N-oxide) loading. There was no effect on the molecular weight of resulted polymers from the order of catalyst loading (after the beginning of the synthesis or after 3-5 hours).

The effect of catalyst concentration on molecular weight of polymer (η_{inh}) has also been determined for the same reaction of 4,4'-bis(N-phenylenebenzimidoyl chloride) oxide with Ia in MP under optimal conditions. When IIa was added to the solution containing the catalyst and diamine Ia in molar ratio of 1:3, polyamidines with highest η_{inh} 0,17-0,22 (dl·g^{-1}) were yielded. Increasing of pyridine-N-oxide content up to 1,0 M in molar ratio to the monomer 3:1 leads to the negligible increasing of the polymer viscosity, η_{inh} 0,17 (dl·g^{-1}). The influence of nature of polar solvents on polymer viscosity is listed in Table 6.2.

Table 6.2. Results (h_{inh}^{a}/yield) for Polyamidines (IIIa) obtained according to Scheme 11 in Various Polar Solvents in the Presence of Catalysts[b].

Solvent	Catalyst [c]	
	Et_3N, dl·g^{-1}/%	Bu_3N, dl·g^{-1}/%
Dimethylformamide	0,34/97	0,1/94
Dimethylacetamide	0,35/97	0,22/99
Tetramethylurea	0,10/72	-
Dimethylpropylenurea	0,18/95	-
1,3-Dimethyl-2-imidazolidinone	0,08/86	-
Nitrobenzene	0,22/82	-
Hexamethylphosphorous triamide	-	0,13/96
Dimethylsulfoxide	traces	-

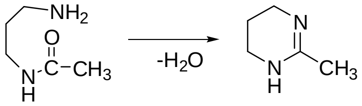
[a] η_{inh} is inherent viscosity of a polymer. This value is a measure of molecular weight of polymer. The ratio of the natural logarithm of the *relative viscosity*, η_r, to the mass concentration of the polymer, *c*, i.e. η_{inh} (dl·g^{-1}) ≡ η_{ln} = (ln η_r)/*c*.

[b] synthesis proceeded under following conditions: T = 90°C, the monomer concentration is 0,6 mol·l^{-1} and duration 2,5 hours.

[c] concentration of catalysts varied from 0,7 to 0,8 M.

6.4. PROPERTIES OF POLYMERS

Thermal and *reological* properties of polymers prepared in this work are collected in Table 6.3. As can be seen, the higher polymer viscosity values were typical for the polymers synthesized in dimethylformamide, dimethylacetamide, and MP using Et_3N as the catalyst. It worth mentioning that the minor increase of η_{inh} and T_g occurs after heating of polymer IIIa in vacuum at 200–250°C for 6 hours. This fact could be due to the subsequent polycondensation of end groups of the polymer, such as NH_2-groups from diamine and a PhC(O)–NH-groups from the second monomer resulted from hydrolysis of his PhC(Cl)=N groups, when the polymer was separated in the water after reaction. Similar pattern occurs during cyclisation of low-molecular-weight amides forming cyclic amidines (Scheme 12) [172]:



(Scheme 12)

IR spectra of polyamidine IIIa before and after heating are presented in Figure 6.5. As can be seen, absorption bands (3400 cm^{-1}) that correspond to the stretching vibrations of NH-bond of amidine group are broader and they are shifted to the low-frequency region. In contrast, the stretching vibrations of NH-bonds of 1,2-diphenylbenzamidine were observed at 3300 cm^{-1}. It can be referred to intermolecular hydrogen bonds of a secondary group NH with a nitrogen atom of the C=N bond of amidine fragments (so-called “amino-imine” hydrogen bonding).

Table 6.3. Properties of Polyamidines (IIIa-d) obtained according to Scheme 11 in N-Methylpyrrolidone-2.

Polyamidine	IIIa				IIIb	IIIc	IIId
	Catalyst						
	-	Pyridine-N -oxide	Et_3N	Bu_3N	Et_3N		
h_{inh} (dl·g^{-1})/yield (%)	0,12/97	0,17-0,22/80-95[a]	0,30[b]-0,35/81-94	0,18/98	0,21/95	0,07/93	0,09/90 0,08/92[c]
P_n[d]	-	6-11	6-7	-	21[144]	-	-
T_g,°C[f]	-	170[e]	155	-	165 158[144]	140	225
TGA:10% weight loss	-	-	435	-	441 461[144]	350	420

[a] concentration of catalyst varied from 0,1 to 1,0 M.

[b] in the presence of LiCl. Molar ratio Et_3N : LiCl varied from 1:6 to 1:18.

[c] in the presence of the pyridine-N-oxide (equimolar ratio).

[d] degree of polymerization was determined by potentiometric titration of polyamidines’ end-groups.

[e] the sample with h_{inh} = 0,15 dl·g^{-1} was heated in vacuum at 250 °C (before heating h_{inh} = 0,13 dl·g^{-1}).

[f] glass transition temperature.

Upon heating of the samples, this interaction becomes more intense due to formation of a large amount of associates with both intermolecular and intramolecular hydrogen bonds. This is also evident from increase in the T_g of the samples after heating. As it could be expected, the intensity of stretching and bending vibrations of C=N and NH-bonds somewhat decreases. Indeed, it was observed from the GPC study of the molecular-weight characteristics of polyamidine IIIa that the polymers prepared in the presence of pyridine-N-oxide contain a smaller amount of low-molecular-weight fractions than the polymers synthesized in the presence of Et_3N. The highest T_g values were observed for products containing fluorene unities (polymer IIId). Especially, these polymers demonstrate good solubility in amide solvents, DMSO, glacial acetic acid, and concentrated sulfuric and phosphoric acids (under heating) but are insoluble in xylene, toluene, and CCl_4. According to our experimental observations we are able to conclude that the polycondensation of aromatic diamines with bis(imidoyl) chlorides in the presence of tertiary amines and pyridine-N-oxide in solution yields amidine-containing polymers with relatively low molecular weight. A possible reason for formation of polymers with low molecular weight could be due to cyclisation of macromolecules in the initial phase of polycondensation.

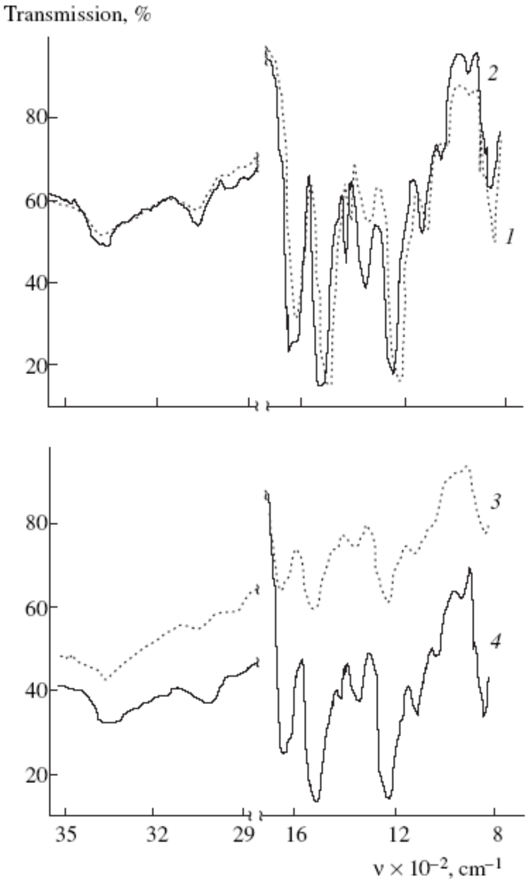


Fig. 6.5. IR spectra of polyamidine IIIa synthesized in the presence of (***1***) *Et_3N* and (***2***) *pyridine-N-oxide*, as well as of heated polymer samples with (***3***) η_{inh} = 0,15 dl·g^{-1} (before heating η_{inh} = 0,13 dl·g^{-1}) at 250°C for 6 hours and (***4***) η_{inh} = 0,28 dl·g^{-1} (before heating η_{inh} = 0,22 dl·g^{-1}) at 200°C for 4 hours.

6.5. THERMOCHEMICAL PROPERTIES OF MONOMERS AND POLYMERS

The Gibbs free energy of a system at temperature T id defined as $G = H - T \cdot S$, where H is the enthalpy and S the entropy of the system. The free energy change for any polymerization will be, therefore,

$$\Delta G_{pol} = G_{polymer} - G_{monomer} = H_{polymer} - H_{monomer} - T\left(S_{polymer} - S_{monomer}\right) =$$
$$= \Delta H_{pol} - T \cdot \Delta S_{pol}$$

When the polymer has a lower free energy than the initial monomer, a polymerization can occur spontaneously, and the sign of ΔG_{pol} is negative. A positive sign for ΔG_{pol} signifies, therefore, that the polymerization is not spontaneous.

There is a lack of thermochemical information on polyamidines. Thus, in this work we have performed experimental study of two typical polyamidines (IIIa). Additionally we have performed calculations of enthalpies of formation of the starting monomers in order to assess the appropriate ΔH_{pol} using group additivity method. Results on combustion calorimetry of polyamidines IIIa (Scheme 11) are presented in Table B9 (Appendix B).

It was interesting to consider our new thermochemical result for polyamidines in context of available data for polymers of different structures. Empirical correlation between enthalpy of combustion and number of oxygen molecules required for combustion of 11 commercial and developmental nitrogen containing polymers is illustrated in the Fig. 6.6. Enthalpies of combustion of polymers presented in this figure were measured by standard experimental procedure for determining *gross* and *net calorific value* using adiabatic oxygen bomb calorimetry [173]. Polymers studied in those work were thermally stable, thermoplastics and *thermoset resins* containing a significant degree of *aromaticity* and heteroatoms including nitrogen and oxygen in chains and heterocyclic unities. It was observed that the enthalpy release is proportional to amount of oxygen consumed in combustion reaction [174]. These values (specified as gross calorific values of combustion or *higher heating value* (see Chap. 8) per 1 mol of polymer, Q_c. W_H is the weight fraction of hydrogen in the repeated unit of polymer; h_c is so called net calorific value of combustion (or *low heating value;* see Chap. 8). Comparison of enthalpies of combustion estimated according to the Hess's law and using molecular weight of the polymer unit with the values experimental gross heats of combustion is given in Table 6.4. These values are in very close agreement with experimental values. The average relative deviation of the experimental and calculated enthalpies of combustion from so called oxygen consumption thermochemistry (Q_c) does not exceed 5 %.

Table 6.4. Combustion Data for Polymeric Materials[a].

№	Polymer/Trade name	Repeat unit/ M_w	W_H, wt	Q_c (exp.), kJ·mol^{-1}	h_c[b], kJ·mol^{-1}	Q_c[c] (calc.), kJ·mol^{-1}
1	Poly(hexamethyleneadipamide)/ Nylon 66	$C_{12}H_{22}N_2O_2$/226,32	0,098	6996,9	6508,9	7797,9
2	Poly(p-phenylene terephthalamide)/KEVLAR™	$C_{14}H_{10}N_2O_2$/238,24	0,042	6416,0	6194,2	6869,9
3	Polyamideimide/TORLON 4203L	$C_{15}H_8N_2O_3$/264,24	0,031	6601,1	6423,7	6977,6
4	Bisphenol-E Cyanate Ester/ AroCy L-10	$C_{16}H_{12}N_2O_2$/264,28	0,046	7766,5	7500,3	7942,8
5	Bisphenol-A Cyanate Ester/ AroCy B-10	$C_{17}H_{14}N_2O_2$/278,31	0,051	8328,6	8018,1	8622,1
6	Polybenzimidazole/CELAZOLE™	$C_{20}H_{12}N_4$/308,34	0,039	9760,0	9493,8	9448,4
7	Polyimide/CAS 26023-21-2	$C_{22}H_{10}N_2O_5$/382,33	0,026	9952,1	9730,3	10018,0
8	Novolac Cyanate Ester/Primaset PT-30	$C_{23}H_{15}N_3O_3$/381,38	0,040	10923,6	10590,9	11091,9
9	Bisphenol-M Cyanate Ester/ AroCy XU-366	$C_{26}H_{24}N_2O_2$/396,48	0,061	13639,9	13107,6	13592,8
10	Polybenzoxaine of bisphenol-A and aniline	$C_{31}H_{30}N_2O_2$/462,58	0,066	16143,3	15477,9	16417,9
11	Polyetherimide/CAS 61128-46-9	$C_{37}H_{24}N_2O_6$/592,60	0,041	17539,9	17007,6	17921,5
12	Polyamidine (IIIa)[d]	$C_{19}H_{14}N_2O$/286,33	0,049	6777,1	6469,0	9409,1

[a] selected data for polymers were taken from the work [173].

[b] net calorific value of combustion (or low heating value) was estimated by eq. $h_c = Q_c$ (exp.) – 21,96 · $M_w \cdot W_H$ [174].

[c] estimated according to the Hess's law from chemical equation of combustion $C_nH_pN_yO_z$ (s.) + xO_2 (g.) = nCO_2 (g.) + $0,5pH_2O$ (liq.) + yNO_2 (g.).

[d] synthesized acc. Scheme 11.

Thermochemical calculation of the gross calorific value of combustion from enthalpy of formation of products and reactants for our aromatic polyamidine IIIa with repeated unit $C_{19}H_{14}N_2O$ listed in Table 6.4. This value differs not significantly from correlation for high molecular polymers presented in Fig. 6.6.

The coefficients in combustion reaction for polyamidine IIIa and estimated Q_c ($kJ \cdot mol^{-1}$) were as follows:

$$C_{19}H_{14}N_2O \text{ (cr.)} + 24O_2 \text{ (g.)} = 19CO_2 \text{ (g.)} + 7H_2O \text{ (liq.)} + 2NO_2 \text{ (g.)} + 9409{,}1$$

This value (with the opposite sign) is found to be in agreement with the value estimated by equation from linear dependence in Fig. 6.6 (where x = 24, number of O_2 in combustion chemical equation):

$$Q_c = 441{,}558 \cdot 24 - 1221{,}096 \approx -9376{,}3 \text{ } (kJ \cdot mol^{-1})$$

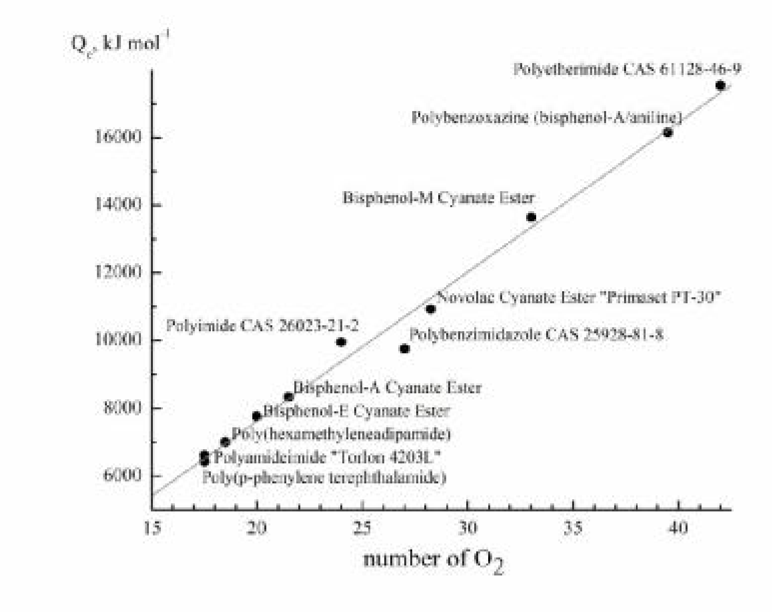


Fig. 6.6. Correlation plot of the experimental gross heats of combustion for *11 polymers* versus number of *molecular oxygen* consumed in reaction of combustion (line is $y = 441{,}558 \cdot x - 1221{,}096$; $r = 0{,}995$).

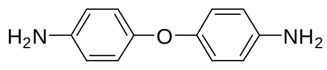
In order to assess enthalpy of polymerization for polyamidines synthesized in this work, enthalpies of formation of monomers and polymer are required. We used Benson group additivity method [34] to predict $\Delta_f H_m^\circ$ (liq.) of monomers. This approach suggests that the thermodynamic properties of a molecule could be divided into different contributions from the individual groups. Such contributions or group additivity values for alkanes and aromatics (in $kJ \cdot mol^{-1}$) required in this work are well established [175]:

$$C\text{-}(C)_2(H)_2 = -27{,}23 \text{ } kJ \cdot mol^{-1}; \quad C\text{-}(C)(H)_3 = -48{,}5 \text{ } kJ \cdot mol^{-1};$$

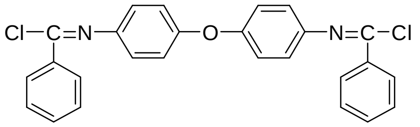
$$Cb\text{-}(Cb)_2(H) = 8{,}17 \text{ } kJ \cdot mol^{-1} \text{ and } Cb\text{-}(Cb)_2(C) = 19{,}11 \text{ } kJ \cdot mol^{-1},$$

where Cb is C-atom of benzene ring

Enthalpies of formation, $\Delta_f H_m^\circ$ (liq.), of monomers participating in the reaction of polyamidine formation according to Scheme 11: 4,4’-diaminodiphenyl oxide (Ia) and 4,4'-bis(N-phenylenebenzimidoyl) chloride oxide, (IIa), were calculated using group additivity values developed in this work. Both monomers under study



Monomer (Ia)



Monomer (IIa)

have the common fragment Cb-O-Cb. We have estimated this contribution from the value $\Delta_f H_m^\circ$ (liq.) = -14,9±1,5 kJ·mol^{-1} of *diphenyl oxide* [32] as follows:

(Cb-O-Cb) = $\Delta_f H_m^\circ$ (liq.)$_{diphenyl\ oxide}$ – 10×Cb-(Cb)$_2$(H) = -14,9 – 81,7 = -96,6 kJ·mol^{-1}

To calculate contribution for the (NH$_2$-Cb)-group, the value $\Delta_f H_m^\circ$ (liq.) = 31,3±1,0 kJ·mol^{-1} *aniline* [32]) was used:

(NH$_2$-Cb) = $\Delta_f H_m^\circ$ (liq.)$_{aniline}$ – 5×Cb-(Cb)$_2$(H) = 31,3 – 40,85 = -9,6 kJ·mol^{-1}

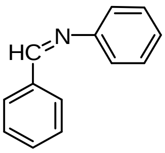
Having developed these two new increments, $\Delta_f H_m^\circ$ (liq.) of the first monomer, 4,4'-diaminodiphenyl oxide (Ia), was calculated as follows:

$\Delta_f H_m^\circ$ (liq.)$_{monomer\ Ia}$ = 8×8,17 – 96,6 – 9,6 = -50,4 kJ·mol^{-1}

For the second monomer, 4,4'-bis(N-phenylenebenzimidoyl) chloride oxide (IIa), two new groups were developed: (Cl-C) and (Cb-C=N-Cb). The (Cl-C) group was calculated using $\Delta_f H_m^\circ$ (liq.) of = -102,4±1,5 kJ·mol^{-1} CH_3Cl [176] as follows:

(Cl-C) = $\Delta_f H_m^\circ$ (liq.)$_{CH_3Cl}$ – C-(C)(H)$_3$ = -102,4 – (-48,5) = -53,9 kJ·mol^{-1}

To calculate the increment (Cb-C=N-Cb) we used the enthalpy of formation of *N-phenylbenzylideneimine* (NPb)



$\Delta_f H_m^\circ$ (liq.) = 200,5±1,5 (kJ·mol^{-1} [177]):

(Cb-C=N-Cb) = $\Delta_f H_m^\circ$ (liq.)$_{NPb}$ – 10×Cb-(Cb)$_2$(H) = 200,5 – 10×8,17 = 118,8 kJ·mol^{-1}

The following procedure for the estimation of $\Delta_f H_m^\circ$ (liq.) of 4,4'-bis(N-phenylene-benzimidoyl) chloride oxide (IIa) was applied:

$\Delta_f H_m^\circ$ (liq.)$_{monomer\ IIa}$ = 18× Cb-(Cb)$_2$(H) + (Cb-O-Cb) + 2×(Cl-C) + 2×(Cb-C=N-Cb) =
= 18×8,17 + (-96,6) + 2×(-53,9) + 2×118,8 = 180,3 kJ·mol^{-1}.

Thermochemical data obtained for monomers and polymers is summarized in Table 6.4.

Table 6.4. Thermochemical Data at 298,15 K and 0,1 MPa for Compounds (reaction participants according to Scheme 11) (in kJ·mol^{-1}).

Compound	$\Delta_c H_m^\circ$	$\Delta_f H_m^\circ$
Monomer Ia	-	-50,4(liq.)
Monomer IIa	-	180,3(liq.)
Polyamidine IIIa	-6777,07 [a]	375,2

[a] the average of $\Delta_c H_m^\circ$ obtained for two samples of the polymer with h_{inh} = 0,13 and 0,15 dl·g^{-1}.

According to the chemical reaction presented in Scheme 11, where two monomers (Ia) and (IIa) are in the liquid state and the resulting polymer (IIIa) is in the solid state, the enthalpy of polycondensation was estimated from enthalpies of formation of the monomers derived using group additivity values and enthalpies of formation of the polymers measured using combustion calorimetry:

$$\Delta H_{pol}\ (298{,}15\ \mathrm{K}) = \Delta_f H_m^{\circ}\ (\mathrm{cr.})_{polymer} + 2\times\Delta_f H_m^{\circ}(\mathrm{sol.})_{\mathrm{HCl}} - \Delta_f H_m^{\circ}\ (\mathrm{liq.})_{\mathrm{Ia}} - \Delta_f H_m^{\circ}\ (\mathrm{liq.})_{\mathrm{IIa}}$$

$$\Delta H_{pol}\ (298{,}15\ \mathrm{K}) = 375{,}2 + 2\times(-153{,}2) - (-50{,}4) - 180{,}3 = -61{,}1\ \mathrm{kJ\cdot mol^{-1}}.$$

We used the value of $\Delta_f H_m^{\circ}$ (HCl) = $\Delta_f H_m^{\circ}$ (sol.) = 153,2±1,0 $\mathrm{kJ\cdot mol^{-1}}$ for aqueous HCl [179]. According to our thermochemical study, the polycondensation of (Ia) with (IIa) in the liquid state is not especially favoured to polymer formation. Typical values of polymerization enthalpies are on the level (-100÷-120 $\mathrm{kJ\cdot mol^{-1}}$). Thus, the value of polymerization enthalpy in formation of polyamidines (IIIa) (-61 $\mathrm{kJ\cdot mol^{-1}}$) is rather small. Due to this reason, formation of low molecular weight polymers seems to be thermodynamically preferred. However, additional thermochemical studies of the model compounds are still required in order to optimize synthesis of this rare class of amidine containing polymers.

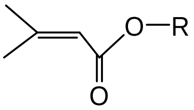
7. UNSATURATED ESTERS: EXPERIMENT AND AB INITIO CALCULATION FOR PRIDICTION OF THEIR THERMOCHEMICAL PROPERTIES

7.1. INTRODUCTION

Alkyl esters of long chain fatty acids contained in biodiesel are obtained from vegetable oils or animal fats by *transesterification* with alcohols. The resulting monoalkyl esters (biodiesel) possess physical properties that are comparable with petrodiesel. The advantages of biodiesel compared to petrodiesel are: biodegradability, higher flash point, reduction of exhaust emissions, miscibility in all ratios with petrodiesel, and acceptable heat of combustion. Technical problems with biodiesel include oxidative stability, cold flow, and increased NO_x exhaust emissions. These problems could be solved by using of *additives* or modifying the fatty acids compositions.

The most common fatty esters contained in biodiesel are *palmitic* (*hexadecanoic*) acid, *stearic* (*octadecanoic*) acid, *oleic* (*9(Z)-octadecanoic*) acid, *linoleic* (*9(Z),12(Z)-octadecanoic*) acid, and *linolenic* (*9(Z),12(Z),15(Z)-octadecatrienoic*) acid. More than 30% (wt.) are unsaturated esters [180]. This has prompted interest in the thermochemical properties of unsaturated and saturated aliphatic esters [181-188].

Direct studies of typical biodiesels, are currently difficult because the laboratory experiments would have to be carried out on complex, largely in volatile mixtures and also because the modeling and simulation is not sufficiently developed to be able to tackle such large molecules [189]. In the present chapter the model compounds, *alkyl 3-methylbut-2-enoates* (Scheme 1) have been studied using experimental and theoretical thermochemical methods. In addition, these compounds could be considered as the possible additives to biodiesel.



where R= Me, Et, Pr, iPr, Bu, iBu, Pe

(Scheme 1)

There is surprisingly little known about $\Delta_l^g H_m$ and $\Delta_f H_m^\circ$(liq.) of esters of aliphatic unsaturated carboxylic acids in the literature. Practically all available experimental results on measurements of enthalpies of combustion were reported by *Schjanberg* in the 1930s [190]. Only several recent publications [191-194] have somewhat extended database. In this context a systematic investigation of the homologues series of alkyl 3-methylbut-2-enoates seems to be highly desirable.

7.2. VAPOUR PRESSURES AND ENTHALPIES OF VAPORIZATION

A summary of vapour pressures and vaporization enthalpies of alkyl 3-methylbut-2-enoates measured in this work is presented in Table B5 (in Appendix B). The only comparison is possible with the data measured using the static apparatus with a membrane zero-manometer [193]. As can be seen in the Fig. 7.1 the values of $\Delta_l^g H_m$(298,15 K) for methyl-, propyl-, and butyl-3-methylbut-2-enoates obtained from *Van-Chin-Syan et al.* [193] are systematically lower of 6 to 7 kJ·mol^{-1} in comparison to our results. At the same time the vaporization enthalpy $\Delta_l^g H_m$(298,15 K) of pentyl-3-methylbut-2-enoate is in close agreement with our result. The reason for such a disagreement is not quite clear now. Thus, it is required to check consistency of the experimental data set on $\Delta_l^g H_m$ (298,15 K) of alkyl 3-methylbut-2-enoates with help of any correlation procedure.

7.3. CONSISTENCY TEST OF ENTHALPIES OF VAPORIZATION

a) ***C-Number***. The correlation of enthalpies of vaporization with the number of C-atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. Vaporization enthalpies $\Delta_l^g H_m$ appear to be a linear function of the number of carbon atoms of the aliphatic esters [185] and aliphatic nitriles [195]. The plot of $\Delta_l^g H_m$ (298,15 K) against the number of C-atoms in the alkyl 3-methylbut-2-enoates (alkyl = Me, Et, Pr, Bu, and Pe) is presented in Fig. 7.1.

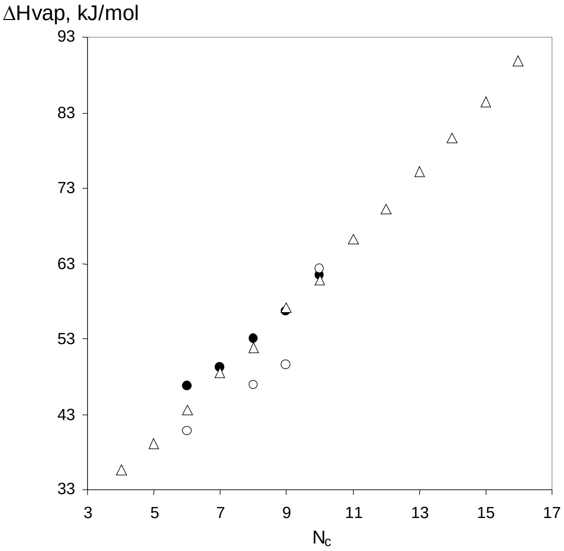


Fig. 7.1. Correlation of $\Delta_l^g H_m$ of *alkyl 3-methyl-but-2-enoates*: (o)-ref. [193], (•)- this work) and *n-alkyl acetates*: (Δ)- ref. [185] with the number of C-atoms in esters.

As can be seen in Fig. 7.1, the first representative- methyl-3-methylbut-2-enoate is slightly out of the linear correlation. Such an anomaly has been also observed for the first representatives of aliphatic esters [185] and aliphatic nitriles [195], and this fact might be caused by the high dipole moment of these species. The dependence of vaporization enthalpy for the linear alkyl 3-methylbut-2-enoates on the total number of C-atoms in a molecule $n \geq 6$ is expressed by the following equation:

$$\Delta_l^g H_m \text{ (298,15 K) / kJ·mol}^{-1} = 20{,}9 + 4{,}02 \cdot n \qquad (r = 0{,}9957) \qquad (7.1).$$

Enthalpy of vaporization $\Delta_l^g H_m$ (298,15 K) for other linear homologues with $n >$ 10 can be calculated.

It is well established [196] that introduction of the double C=C bond in a linear molecule instead of the single C-C bond does not impact vaporization enthalpies very much. For example the differences between vaporization enthalpies of hexane and hexene (or decane and decene) are only on the level of 1 kJ·mol^{-1}. In order to check validity of this observation for the esters, we have presented in the Fig. 7.1 the comparison of our data on $\Delta_l^g H_m$ for unsaturated esters with those for linear aliphatic alkyl acetates. As can be seen, our data for alkyl 3-methylbut-2-enoates are in line with those for alkyl acetates within 1 kJ·mol^{-1}. At the same time the values of $\Delta_l^g H_m$ (298,15 K) for alkyl 3-methylbut-2-enoates obtained from *Van-Chin-Syan et al.* [193] are definitely out of correlation (except for pentyl-3-methylbut-2-enoate).

b) ***Kovat`s indices***. The correlation of the enthalpies of vaporization with the *Kovat`s indices* of the organic compounds is another valuable method to study the systematic behavior in homologous series. Kovat`s index is the retention characteristics acknowledged among analytic chemists for the identification of the individual compounds in diverse mixtures. In the Kovat`s index n-alkanes serve as the standards and logarithmic interpolation is utilized defined by following equation:

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \cdot 100 + 100 \cdot N \qquad (7.2),$$

where x refers to the adjusted retention time, N is the number of carbon atoms of the n-alkane eluting before, and $(N + 1)$ is the number of carbon atoms of the n-alkane eluting after the peak of interest. According to the established GC procedure, all retention times are corrected for the “dead” retention time adjusted from the retention times of the homologues n-hydrocarbons [197].

The vaporization enthalpy $\Delta_l^g H_m$ appears to be a linear function of the Kovat`s indices in homologous series of alkanes, alcohols, and aliphatic esters [185]. We have used Kovat`s indices available from the literature [198] for three stationary phases SE-30 and OV-225, and DC-230 in order to test how the results fit into a linear dependence on the Kovat`s indices. It can be seen from the Fig. 7.2 that the data for $\Delta_l^g H_m$ (298,15 K) fit very well in the linear correlation, again except for methyl 3-methylbut-2-enoate. The following empirical equation for the enthalpy of vaporization of the linear and also branched alkyl 3-methylbut-2-enoates (except for methyl-3-methylbut-2-enoate) is suggested:

$$\Delta_l^g H_m \text{ (298,15 K)} / (\text{kJ}\cdot\text{mol}^{-1}) = 7{,}9 + 0{,}045 \cdot J_x \quad (r = 0{,}9851) \quad \text{for SE-30} \quad (7.3),$$

$$\Delta_l^g H_m \text{ (298,15 K)} / (\text{kJ}\cdot\text{mol}^{-1}) = -0{,}7 + 0{,}043 \cdot J_x \quad (r = 0{,}9914) \quad \text{for OV-225} \quad (7.4),$$

$$\Delta_l^g H_m \text{ (298,15 K)} / (\text{kJ}\cdot\text{mol}^{-1}) = 11{,}4 + 0{,}041 \cdot J_x \quad (r = 0{,}9855) \quad \text{for OV-225} \quad (7.5),$$

where J_x is the Kovat`s index of an ester. This linear relationship can be used as evidence of the internal consistency of our experimental results for vaporization enthalpies.

Thus, values of vaporization enthalpies of alkyl 3-methylbut-2-enoate derived in this work show internal consistency and they can be used with high reliability for further calculation of the standard enthalpies of formation, $\Delta_f H_m^\circ$ (g.) at 298,15 K.

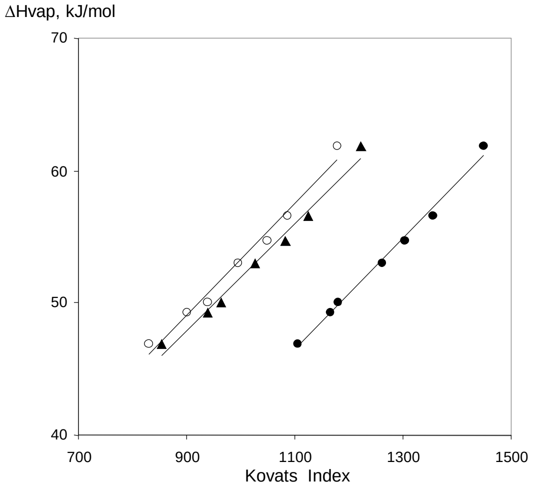


Fig. 7.2. Correlation of $\Delta_l^g H_m$ of *alkyl 3-methyl-but-2-enoates* with *Kovat`s indices* at 423 K: (○)- SE-30; (▲)- DC-230; (●)- OV-225 (stationary phases) [198].

7.4. ENTHALPIES OF FORMATION (COMBUSTION CALORIMETRY)

Results of typical combustion experiments for esters are summarized in Table B9 (Appendix B). The means of individual values of the standard massic energies of combustion, $\Delta_c u^\circ$, were derived as a rule from 5 to 8 independent experiments. Table 7.1 lists the derived standard molar enthalpies of combustion, and standard molar enthalpy of formation of the esters derived in this work.

Table 7.1. Thermochemical Data at 298,15 K and 0,1 MPa for *Alkyl 3-methyl-but-2-enoates* (kJ·mol^{-1}).

Compound	$\Delta_c H_m^\circ$ (liq.)	$\Delta_f H_m^\circ$ (liq.)	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (g.) (exp.)	$\Delta_f H_m^\circ$ (g.) (calc.)^a	Hs^b
Methyl ester	-3372,8±1,3	-417,5±1,5	46,9±0,2	-370,6±1,5	-387,9	17,3
Ethyl ester	-4014,5±2,1	-455,0±2,3	49,3±0,2	-405,7±2,3	-421,6	16,0
Propyl ester	-4669,6±2,6	-479,4±2,8	53,0±0,2	-426,4±2,8	-443,1	16,7
Butyl ester	-5319,0±2,6	-509,3±2,9	56,6±0,3	-452,6±2,9	-464,6	12,0
iso-Propyl ester	-4657,5±3,2	-491,4±3,4	50,0±0,2	-441,4±3,4	-441,4	19,8

[a] calculated as the sum of strain-free increments (*see* text).

[b] strain enthalpy $Hs = \Delta_f H_m^\circ$ (g.) (exp.) – $\Delta_f H_m^\circ$ (g.) (calc.).

Some previous experimental values of $\Delta_f H_m^\circ$ (liq.) for methyl-, propyl-, butyl-, and pentyl-3-methylbut-2-enoates have been determined by *Van-Chin-Syan et al.* [193] using combustion calorimeter with the static bomb. Their values are systematically in disagreement (about 20 kJ·mol^{-1}) with those obtained in this work (see Fig. 7.3). It was apparently something wrong with the data treatment of the combustion results published in the work [193], because some years later the same authors presented revision of their data [ibid.] and the re-calculated data became closer to the result obtained in this work (Fig. 7.3). But, the agreement between two data sets remains still very poor. One of the possible reasons for the disagreement of combustion results could be traces of water, which (in contrast to our work) were not determined and taken into account in the references [193,194].

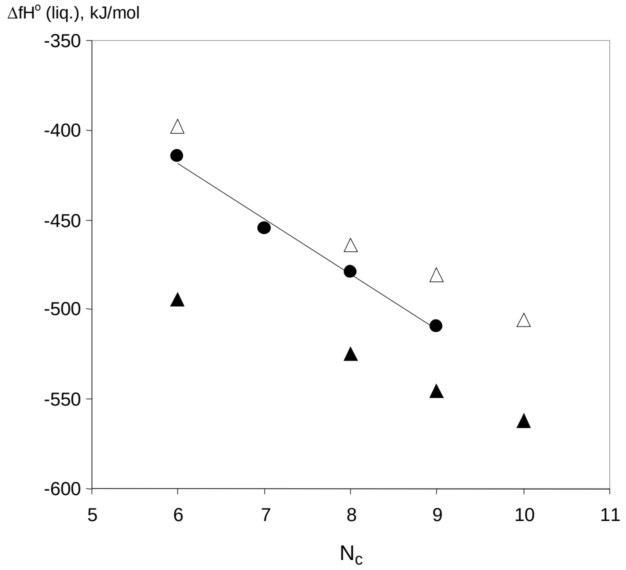


Fig. 7.3. Correlation of $\Delta_f H_m^\circ$ (liq.) of *alkyl 3-methylbut-2-enoates* (alkyl = Me, Et, Pr, Bu) with the number of C-atoms in esters: (△)- ref. [194]; (▲)- ref. [193]; (●)- this work.

7.5. CONSISTENCY TEST OF ENTHALPIES OF FORMATION

***a) Liquid Phase*: *Correlation of $\Delta_f H_m^\circ$ (liq.) of alkyl 3-methylbut-2-enoates with those $\Delta_f H_m^\circ$ (liq.) of analogous n-alkyl-acetates*.** Taking into account the reactivity and thermal lability of the unsaturated esters, which could aggravate purification and thermochemical measurements, evidence of the reliability of the results derived in this work seems to be desirable. Values of $\Delta_f H_m^\circ$ (liq.) of alkyl 3-methylbut-2-enoate derived in this work could be checked for internal consistency using enthalpies of formation of n-alkyl acetates where reliable experimental data is available from the literature [32]. Such a procedure has been applied for the benzyl derivatives successfully [199]. Indeed, considering the general structures of alkyl esters of the carboxylic acids (R_1-CO_2-R_2) it is obvious, that the alkyl 3-methylbut-2-enoate under study in this work, are parent to the structures of the n-alkyl acetates because of the common alkyl R_2. Thus, the correlation of the enthalpies of formation of alkyl 3-methylbut-2-enoate with those for n-alkyl-acetates should give a linear correlation if the data used for the correlation are consistent. It can be seen from the Fig. 7.4 that data involved in comparison fit very well in to the linear correlation with correlation coefficient *r* =0,9990. This near to perfect relationship can subsequently be used at least as an indication of the internal consistency of our experimental results.

Thus, values of enthalpies of formation of alkyl 3-methylbut-2-enoate derived in this work show internal consistency and they have been used for calculation of the standard enthalpies of formation, $\Delta_f H_m^\circ$ (g.) at 298,15 K.

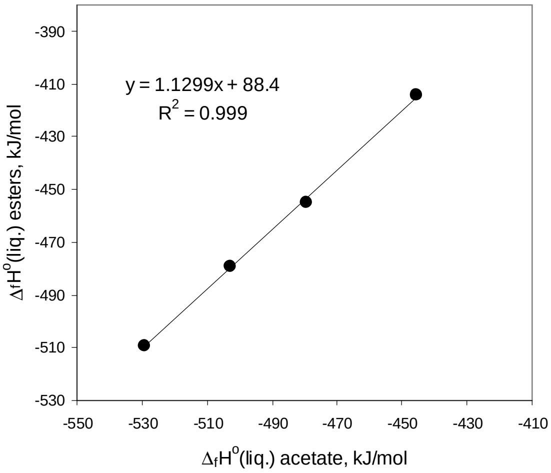


Fig. 7.4. Correlation of $\Delta_f H_m^\circ$ (liq.) of *alkyl 3-methylbut-2-enoates* with those $\Delta_f H_m^\circ$ (liq.) of analogous *n-alkyl acetates* (alkyl = Me, Et, Pr, Bu) [32].

***b) Gaseous Phase*: *Correlation of $\Delta_f H_m^\circ$ (g.) of alkyl 3-methylbut-2-enoates with those $\Delta_f H_m^\circ$ (g.) of analogous n-alkyl-acetates*.** Gaseous enthalpies of formation, $\Delta_f H_m^\circ$ (g.) of alkyl 3-methylbut-2-enoates were derived in this work as the sum of the own experimental results of $\Delta_f H_m^\circ$ (liq.) and of enthalpies of vaporization listed in the Table 7.1. The set of the $\Delta_f H_m^\circ$ (g.) of alkyl 3-methylbut-2-enoates derived in this work could be further checked for internal consistency using gaseous enthalpies of formation of n-alkyl acetates in the same way as it has just been performed for the enthalpies of formation in the liquid state. As can be seen from the Fig. 7.5, methyl, ethyl, propyl, and butyl esters involved in comparison fit well in to the linear correlation with correlation coefficient r^2 = 0,9994. At the same time, the point for the R_2 = *iso*-propyl is slightly out of correlation. However, as it will be discussed below, a possible explanation for such a deviation could be sterical repulsions of the methyl-groups in *iso*-propyl-3-methylbut-2-enoate, which are expected to be substantial large as those in *iso*-propyl acetate.

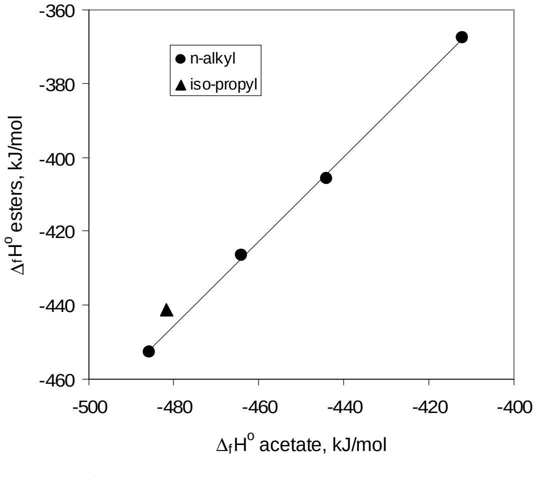


Fig. 7.5. Correlation of $\Delta_f H_m^\circ$ (g.) of *alkyl 3-methylbut-2-enoates* with those $\Delta_f H_m^\circ$ (g.) of analogous *n-alkyl acetates* (alkyl = Me, Et, Pr, Bu, and *i*Pr) [32].

7.6. STRUCTURE-ENERGY RELATIONSHIPS (NON-BONDED INTERACTIONS AND STRAIN ENTHALPIES)

Conventional strain-enthalpy, H_S, of a molecule is defined as the difference between its experimental enthalpy of formation $\Delta_f H_m^\circ$ (g.) and the calculated sum of the Benson type increments [34,35] for this molecule. Indeed, alkyl 3-methylbut-2-enoates listed in Table 7.1 present a typical example of similarly shaped molecules (R_1-CO_2-R_2), where an alkyl substituent R_2 is attached to the carboxyl group. Hence the strain, H_S, of a molecule is expected to provide insight into the energetic interactions of an alkyl substituent R_2 with the (R_1-CO_2-) moiety.

The system of strain-free increments [200] is based on the standard enthalpies of formation $\Delta_f H_m^\circ$ (g.) of simple homologous („strainless") molecules. Strain-free group additivity increments for hydrocarbons [200] are well defined. Their advantage with respect to the classic Benson increments [34] is the possibility to determine strain enthalpies directly. All the increments necessary in this work are as follows [35,200]: CH_3[C] = -42,05 kJ·mol^{-1}; CH_2[2C] = -21,46 kJ·mol^{-1}; CH[3C] = -9,04 kJ·mol^{-1}; $C_dH_2[C_d]$ = 26,4 kJ·mol^{-1};$C_dH[C, C_d]$ = 36,0 kJ·mol^{-1}; C_d [2C, C_d] = 42,7 kJ·mol^{-1} (C_d represents the double bonded C atoms). Strain-free group additivity increments for ester [188]: CO_2[2C] = -327,05 kJ·mol^{-1}; $CH_3[CO_2]$ = -42,05 kJ·mol^{-1}; $CH_2[CO_2, C]$ = -17,4 kJ·mol^{-1}; CH[CO_2, 2C] = -7,4 kJ·mol^{-1}; CH_2[O] = -42,05 kJ·mol^{-1}; CH_2[O, C] = -33,8 kJ·mol^{-1}; CH[O, C] = -31,3 kJ·mol^{-1}; $C_dH[CO_2, C_d]$ = 22,7 kJ·mol^{-1} (derived from n-butylacrylate [191]). Using these group-additivity parameters given and the values of $\Delta_f H_m^\circ$ (g.) of compounds (Table 7.1) derived in this research, the values of strain enthalpies H_S = ($\Delta_f H_m^\circ$ (g.) – Δ increments) of alkyl 3-methylbut-2-enoates have been estimated. These resulting strain interactions are listed in the last column of Table 7.1.

All studied alkyl 3-methylbut-2-enoates are noticeable strained of about 15 kJ·mol^{-1} refer to Table 7.1. These strains are equal (within the boundaries of their experimental uncertainties) as expected for linear alkyl derivatives. Indeed, according to the Fig. 7.6, the origin of strain in alkyl 3-methylbut-2-enoates is mainly due to the non-bonded repulsions of oxygen lone pairs (and also possibly of the π-electrons of the double bond) with the methyl substituent in the *3^d^* position. At the same time, the linear substituent R_2 is out of interactions due to free rotation and it is hardly able to contribute to the strain.

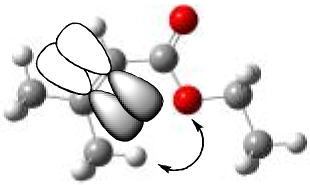


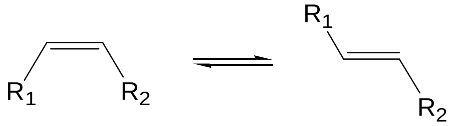
Fig. 7.6. Steric repulsions in *ethyl 3-methylbut-2-enoate*.

Such a similarity of strains in n-alkyl derivatives again proves the consistency of the procedure and the experimental data involved in the interpretation. It makes oneself conspicuous, that the strain of the ester with the branched R_2, namely *iso*-propyl-3-methylbut-2-enoate, H_S = 19,8 kJ·mol^{-1}, is somewhat large then for ester with the linear R_2. This strain reflects the intrinsic strain, typical for the branched molecules, due to non-bonded sterical interactions of methyl groups and attached to the secondary carbon atom [184,201]. Thus, this additional strain is apparently the reason for outlying of the appropriate point for *iso*-propyl derivative on the Fig. 7.6 as discussed above.

7.7. Structure-Energy Relationships (Relative Stability of *Cis*- and *Trans*-Isomers)

Due to the fact, that biodiesel from vegetable oils is composed of a blend of unsaturated and saturated fatty acid esters position of the double bond in the molecule is not fixed and could occur at any part of the alkyl chain, close or distant from the carboxyl group. Following, a diverse *cis*- and *trans*-isomers are naturally presented in the biodiesel. In order to predict "energetic" of unsaturated esters as well as of biodiesel, the knowledge of the appropriate corrections for *cis*-*trans*-interactions is required.

One of the basic rules of organic chemistry is that *trans*-isomers of alkenes are more stable than the *cis*-forms. This orientation is readily explained by the short CH_3....CH_3 distance in *cis*-but-2-ene. Allowing for the bond distortions, the non-bonded repulsions between the methyl groups stabilize the *trans*-form of about 4-5 kJ·mol^{-1} (*see* Table 7.2 below). However it is well known [202] that attachment of halogens to the 1 and 2 positions of the ethane stabilizes the *cis*-form. Unfortunately, experimental evidences of *cis*-*trans* preferences in the unsaturated carboxylic acid derivatives are limited or of a questionable quality. For this reason we decided to use *ab initio* methods for study of the following reaction (Scheme 2) of *cis*-*trans*-isomerization:



where R_1 = Me or Et; R_2 = Me, Et, COOH, $COOCH_3$

(Scheme 2)

Taking into account the similarity of the molecules under calculations, the relative energies calculated using the composite G3MP2 and DFT methods are expected to predict the more stable structure correctly. A systematic quantum mechanical study of the possible conformations and their relative stabilities has been conducted. The molecules were considered as a two rotor system having internal rotation about C-C and C-O bonds with the possibility of hindered rotation of the alkyl group. The most stable conformers of *cis*- and trans-configuration of each species involved in the reaction isomerization were taken into account for the calculation of *cis*-trans conversion presented in the Table 7.2. As can be seen in this table, for alkenes, unsaturated carboxylic acids and unsaturated esters the trans isomer is of 5-7 kJ·mol^{-1} more stable than *cis*-isomer according to the *ab initio* calculations. The results from both G3MP2 and DFT methods are generally indistinguishable and they are also acceptable close to the experimental data available only for alkenes (*see* Table 7.2).

Table 7.2. Enthalpy of Isomerization of Unsaturated Compounds, $\Delta_r H_{cis®trans}$.

Compound	Theor. $\Delta_r H_{cis®trans}$(kJ·mol^{-1})		Exp. $\Delta_r H_{cis®trans}$ (kJ·mol^{-1})
	G3MP2	DFT^a	
CH_3-CH=CH-CH_3	-5,1	-6,1	-4,3 [203]
CH_3-CH=CH-CH_2-CH_3	-5,2	-6,6	-4,9 [203]
CH_3-CH_2-CH=CH-CH_2-CH_3	-5,3	-7,2	-4,0 [204]

HOOC-CH=CH-CH_3	-7,4	-7,4	-
HOOC-CH=CH-CH_2-CH_3	-7,3	-7,0	-
HC_3OOC-CH=CH-CH_3	-7,3	-7,3	-
HC_3OOC-CH=CH- CH_2-CH_3	-7,2	-7,9	-

[a] B3LYP/6-31G(d)

Our calculations performed for but-2-ene, 2-butenoic acid, and methyl-2-butenoate provide the effect of *cis–trans*-interactions of Me, -COOH, or -COOMe with the terminal CH_3-group, which are representative for relatively short molecules. Because unsaturated esters in biodiesel are usually long chained molecules, it is of interest to study whether extension of the alkyl chains to the left and to the right side from the double bond (formally- exchange methyl with methylene group) impacts the *cis*-trans interactions or not? From the general point of view the CH_2-group possesses somewhat less spatial requirements in comparison to CH_3-group, thus it is reasonable to expect that *cis-trans* interactions in such molecules as pentene-2 or hexene-3, 2-penetenoic acid, or methyl-2-pentenoate should be less intensive (*see* Table 7.2). However, according to the result from our ab initio calculations listed in this table, the *trans*-isomer of the latter compound are in the same way of 5-7 kJ·mol^{-1} more stable than *cis*-isomer. Following, the individual corrections for the strain of *cis*-isomer in the Table 7.2 could be simply applied for the longer molecules which parent to the structures studied in this work.

Although, the strain corrections determined in this work are moderate, these values are useful for a further improvement on the group-contribution methodology for estimation of the thermodynamic properties of unsaturated esters of carboxylic acids. The derived values of increments and H_S can be applied for the prediction of the energy content of biofuels and for modeling and simulation of the thermochemistry and kinetics of decomposition reactions of biofuels [189]. For instance, gaseous enthalpy of formation of for (*Z*)-9-hexadecenoic acid, methyl ester $CH_3(CH_2)_5CH=CH(CH_2)_7COOCH_3$ (one of the unsaturated esters detected in the *Babassu biodiesel* [180]) could be calculated with help of the aforementioned group contributions:

$$\Delta_f H_m^\circ \text{ (g.)} = CH_3[C] + 11\times CH_2[2C] + CH_2[CO_2, C] + CH_3[O] + CO_2[2C] +$$
$$+ 2\times C_dH[C, C_d] + cis\text{-correction (alkenes)} \qquad (7.6)$$

7.8. AB INITIO CALCULATIONS

Combination of quantum methods with thermochemical experiments have been applied quite often [205-207]. It has been shown, that *ab initio* calculations are suitable to predict formation enthalpies of norbornane [68] or substituted benzenes [69,70]. For this reason, experimental enthalpies of formation $\Delta_f H_m^\circ$ (g.) of alkyl 3-methylbut-2-enoates have been compared with those obtained from the high level ab initio methods. In this chapter we have applied a G3MP2 method for predicting gaseous enthalpies of formation of esters. G3MP2 theory uses geometries from second-order perturbation theory and scaled zero-point energies from *Hartree-Fock* theory followed by a series of single-point energy calculations at the MP2(Full)/6-31G(d), QCISD(T)/6-31G(d) and MP2/GTMP2Large levels of theory (for details *see* ref. 208). The enthalpy values of the studied compounds at T = 298 K, were evaluated according to the standard thermodynamic procedures [209].

Enthalpies of formation of alkyl 3-methylbut-2-enoates have been estimated by atomization procedure [210] and by the following bond separation reactions (for example, $C_6H_{10}O_2$ is methyl-3-methylbut-2-enoate):

$$C_6H_{10}O_2 + 12CH_4 \rightarrow 2H_2O + 9C_2H_6 \qquad (7.7),$$

$$C_6H_{10}O_2 + 3CH_4 \rightarrow H_2C{=}CH{-}COOH + 3C_2H_6 \qquad (7.8),$$

$$C_6H_{10}O_2 + 8CH_4 \rightarrow H_3CC(CH_3){=}O + 2H_2O + 3C_2H_6 \qquad (7.9).$$

Based on enthalpies of these reactions (eqs. 7.7-7.9) calculated by G3MP2 method and well-known enthalpies of formation, $\Delta_f H_m^\circ$(g.) of other participants taken from *Pedley et al.* [32], the enthalpies of formation of alkyl 3-methylbut-2-enoates have been estimated (*see* Table 7.3). Literature value of enthalpy of formation $\Delta_f H_m^\circ$ (g.) for acrylic acid was not found to determine correctly [211]. In the present chapter the value of $\Delta_f H_m^\circ$(g.) = -323,3±1,8 kJ·mol^{-1} of acrylic acid was determined (*see* Appendix B, p. 131) and was used in the bond separation reaction (7.8).

Enthalpies of formation of alkyl 3-methylbut-2-enoates calculated by G3MP2 method using the bond separation reactions and atomization procedure are found to be indistinguishable within 1-2 kJ·mol^{-1}. The averaged values of $\Delta_f H_m^\circ$(g.)$_{\mathrm{G3MP2}}$ are presented in the Table 7.3 and they are in good agreement with the experimental data obtained from experiment (*see* Table 7.1).

Table 7.3. Data from G3MP2 Calculation of $\Delta_f H_m^\circ$ (g.) at 298,15 K for the *Alkyl 3-methyl-but-2-enoates* (kJ·mol^{-1}).

Compounds	G3MP2				$\Delta_f H_m^\circ$G3MP2[a]	$\Delta_f H_m^\circ$(exp.)
	atomization	bond separation				
		1	2	3		
Methyl ester	-373,4	-371,1	-372,4	-371,9	-372,2±1,0	-370,6±1,5
Ethyl ester	-407,0	-404,2	-405,6	-405,0	-405,5±1,2	-405,7±2,3
Propyl ester	-427,4	-424,2	-425,5	-424,9	-425,5±1,4	-426,4±2,8
Butyl ester	-448,4	-444,6	-445,9	-445,4	-446,1±0,8	-452,6±2,9
iso-Propyl ester	-445,3	-442,0	-443,4	-442,8	-443,4±1,4	-441,4±3,4
iso-Butyl ester	-457,7	-453,9	-455,3	-454,8	-455,4±1,6	-

[a] calculated as the average from atomization and bond separation procedures (*see* text).

8. “DESIGNER” BIODISEL: EXPERIMENT AND AB INITIO CALCULATION FOR PREDICTION OF THERMOCHEMICAL PROPERTIES

8.1. INTRODUCTION

Biodiesel is defined as a fuel, made from natural, renewable sources, such as new vegetable oils and animal fats [212]. Biodiesel is produced by *transesterification* of vegetable oils to the mixture of mono-alkyl esters of long chain fatty acids. Glycerol is a main byproduct of this reaction. In industrial process 100 kg of glycerol are produced for every 1 tone of biodiesel.

The thermochemical properties of fuels are commonly discussed in terms of their *specific* characteristics, the enthalpy of combustion (calorific or heating value) per mass (or specified quantity) unit of material (Table 8.1.).

Table 8.1. Thermochemical Properties of Some Common Fuels.

Fuel	Combustion equation	$\Delta_cH°$ [a], kJ·mol^{-1}	Heating Value [b], MJ·kg^{-1}		*WI* [c], kJ·m^{-3}		Enthalpy density, kJ·dm^{-3}
			HHV	*LHV*	Upper *WI*	Lower *WI*	
H_2	H_2 (g.)+0,5O_2 (g.) → H_2O (liq.)	-285,8	141,8	120,1	48,2	40,6	13
CH_4	CH_4 (g.)+2O_2 (g) → →CO_2 (g.)+ 2H_2O (liq.)	-890,0	55,5	50,1	53,3	47,9	40
C_3H_8	C_3H_8 (g.)+5O_2 (g.) → →3CO_2 (g.)+ 4H_2O (liq.)	-2220,0	50,3	45,8	81,1	74,5	99
C_8H_{18}	C_8H_{18} (liq.)+12,5O_2 (g.) → →8CO_2 (g.)+ 9H_2O (liq.)	-5471,0	47,9	-	-	-	$3{,}4\cdot10^4$
CH_3OH	CH_3OH (liq.)+1,5O_2 (g.) → →CO_2 (g.)+ 2H_2O (liq.)	-726,0	22,7	-	-	-	$1{,}8\cdot10^4$
C(graphite)	C (s.)+ O_2 (g.) → CO_2 (g.)	-393,5	34,1	33,3	-	-	$7{,}4\cdot10^4$
Petrodiesel	-	-	43,9	-	-	-	$3{,}9\cdot10^4$ [d]
Biodiesel	-	-	39,9	-	-	-	$3{,}5\cdot10^4$ [d]
Tristearin (beef fat)	$C_{51}H_{110}O_6$ (liq.)+ 75,5O_2 (g.) → →51CO_2 (g.)+ 55H_2O (liq.)	35830,6	39,8	-	-	-	$3{,}7\cdot10^4$ [e]

[a] data from NIST *ChemWebBook* or are available in [213].

[b] heating value is commonly determined by use of a bomb calorimeter and can be expressed also in kcal·kg^{-1}, J·mol^{-1}, Btu·m^{-3}; Higher heating value (HHV) and Lower heating value (LHV).

[c] *Wobb index* (WI) is heat-value factor that indicates the quality of a fuel gas, measured from the heat produced by burning through a defined orifice in standard temperature and pressure conditions. Quantitatively defined as the ratio of HHV (in MJ·m^{-3} or Btu's per cubic foot) to the square root of the specific gravity of the gas (defined as the ratio of gas fuel density to the density of water).

[d] density 0,88 g·cm^{-3} (298,15 K).

[e] density 0,94 g·cm^{-3} (338,15 K).

The precise determination of the heating value is of great importance for trading fuel because the heating value is the most important parameter for determining the price of the fuel. The *higher heating value* (HHV, also known as *gross calorific value* or *gross energy*) of a fuel is defined as the amount of heat released by a specified quantity (initially at 298,15 K) once it is burned and the products have returned to a reference temperature (298,15 K). In contrast, when the *lower* *heating value* (LHV, also known as *net calorific value*) is determined, the cooling is stopped at 423,15 K and the reaction heat is only partially recovered. Thereby the quantity known as LHV is determined by subtracting the heat of vaporization of the water produced by combustion from the HHV. The difference between the two heating values depends on the chemical composition of the fuel. For hydrocarbons the difference depends on the hydrogen content. It is quite clear that the more water is formed the more the difference is occurred. For diesel and natural gas the HHV exceeds the LHV by about 7% and 11% respectively. Some examples of calculations of fuel energetics are given in Appendix A.

The aim of this work was an experimental and computational study to gain thermochemical properties of compounds parent to biodiesel components. Direct studies of typical biodiesels, are currently difficult because the laboratory experiments would have to be carried out on complex mixtures and also because the modeling and simulation is not sufficiently developed to be able to tackle such large molecules [189]. Hence, we have chosen to work on model compounds, 1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, and 1,2,3-propanetriol tri-acetate which are in shape relevant to the main and side products of biodiesel synthesis and therefore are useful to provide insight into the thermochemistry of the synthetic processes. It has also been found recently, that 1,2-ethanediol monoacetate is a very promising candidate as a oxygenating additive to diesel fuels [214].

In this work the thermochemistry of 1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, and 1,2,3-propanetriol triacetate including the vaporization enthalpies, $\Delta_l^g H_m$, and the standard enthalpies of formation in the liquid state, $\Delta_f H_m^\circ$(liq.), using experimental methods (combustion calorimetry and vapor pressure measurements) have been studied. For a validation of the experimental data on these compounds, high-level ab initio calculations of $\Delta_f H_m^\circ$(g.) of these molecules have been performed using the GAUSSIAN-03 program package. Using the new experimental results a group-contribution methodologies for the prediction of thermodynamic properties of compounds relevant to biodiesel have been developed.

8.2. VAPOUR PRESSURES AND ENTHALPIES OF VAPORIZATION

There is surprisingly little known about $\Delta_l^g H_m$ and $\Delta_f H_m^\circ$(liq.) of *ethanediol* (ethylene glycol) and *propanetriol* (glycerol) derivatives. Only enthalpies of combustion for the several liquid *glycerol acetates* were measured in 1956 [215]. In this context a systematic study of thermochemistry of ethanediol and propanetriol acetyl derivatives seems to be desirable.

Compilation of $\Delta_l^g H_m$ (298,15 K) is given in Table 8.2. $\Delta_l^g H_m$ of 1,2-ethanediol diacetate and glycerol triacetate is found to be in close agreement with that from the literature. The result obtained for 1,2-ethanediol monoacetate, $\Delta_l^g H_m$(298,15 K) = 63,9±0,3 kJ·mol^{-1} is higher than that obtained by *Schmid et al.* from ebulliometric measurements [216]. In our opinion the presence of a small content of water (96,8 ppm) in the sample for ebulliometry study could cause such disagreement.

Table 8.2. Thermochemical Data of Vaporization ($\Delta_l^g H_m$).

Compound	Method[a]	T-range, K	$\Delta_l^g H_m$ (*T*), kJ·mol^{-1}	$-\Delta C_p$[b], J·mol^{-1}·K^{-1}	$\Delta_l^g H_m$ (at 298,15 K), kJ·mol^{-1}	Ref.
1,2-Ethanediol monoacetate	E	363,2-448,8	55,0	63,4	61,7±0,3	216
	T	301,3-346,3	62,3	(203,0)[223]	63,9±0,3	this work
1,2-Ethanediol diacetate	E	373-463	53,4		62,8±0,8	217
	C	298,15		80,6	61,0±0,1	218
	C	298,15		(269,2)[219]	61,4±0,2	219
	T	291,2-334,2	60,3		61,4±0,2	this work
1,2,3-Propanetriol triacetate	S	284,2-318,2	82,0	111,7	82,3±0,2	220
	C	298,15		(389,0) [219]	83,4±1,0	221
	C	298,15			85,7±0,3	219
	E	439,5-590,2	59,7		83,8±0,9	222
	T	320,1-360,9	76,9		81,9±0,3	this work

[a] applied methods: E = ebulliometry; T = transpiration; S = static method (piston manometer); C- calorimetry.

[b] values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid, C_p^l (it is in the brackets) according to the procedure developed by *Chickos* and *Acree* [19].

[c] literature data on vapour pressures were treated by eqs. 2.1-2.5 (Chap. 2) in order to estimate the enthalpy of vaporization at 298,15 K in the same way as our own results in Table B6 (Appendix B).

Data on vapour pressures and vaporization enthalpies of acetates derivatives ($\Delta_l^g H_m$) is presented in Table B6 (Appendix B). The comparison of linear dependences on vapour pressures versus 1/T with those known from the literature is illustrated in Fig. C8-C10 (Appendix C).

8.3. CONSISTENCY TEST OF ENTHALPIES OF VAPORIZATION

The correlation of $\Delta_l^g H_m$ (298,15 K) with the number of C-atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. As it already known, $\Delta_l^g H_m$ can be plotted as linear function of the number of carbon atoms of the aliphatic esters, diesters of carboxylic acids and nitriles [185,195,224]. The plot of $\Delta_l^g H_m$ (298,15 K) against the number of C-atoms in the linear aliphatic chains of 1,2-ethanediol alkanoates: R-CO_2-CH_2-CH_2-CO_2-R with R = (Me, Et, and Pr) is presented in Fig. 8.1. The dependence of vaporization enthalpy on the number of C-atoms, N_C, is expressed by the following equation:

$$\Delta_l^g H_m \text{ (298,15 K)/ kJ·mol}^{-1} = 5{,}9 \cdot N_C + 55{,}6 \qquad (8.1),$$

from which enthalpy of vaporization $\Delta_l^g H_m$ (298,15 K) other representatives of this series can be easily calculated.

8.4. ENTHALPIES OF FORMATION (COMBUSTION CALORIMETRY)

Summary of thermochemical data for compounds under study is given in Table 8.3.

Table 8.3. Thermochemical Data at 298,15 K and 0,1 MPa (in kJ·mol^{-1}).

Compound	State	$\Delta_c H_m^\circ$,	$\Delta_f H_m^\circ$ (liq.)	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (g.)
1,2-Ethanediol monoacetate	liq.	-2060,7±2,2	-656,7±2,3	63,9±0,3	-592,8±2,3
1,2-Ethanediol diacetate	liq.	-2931,6±1,3	-858,7±1,6	61,4±0,2	-797,3±1,6
1,2,3-Propanetriol triacetate	liq.	-4278,2±1,6	-1264,2±2,0	81,9±0,3	-1182.3±2,0

Results of typical combustion experiments for esters are summarized in Table B9 (Appendix B). The means of individual values of the standard specific energies of combustion, $\Delta_c u^\circ$, were derived as a rule from 4 to 6 independent experiments.

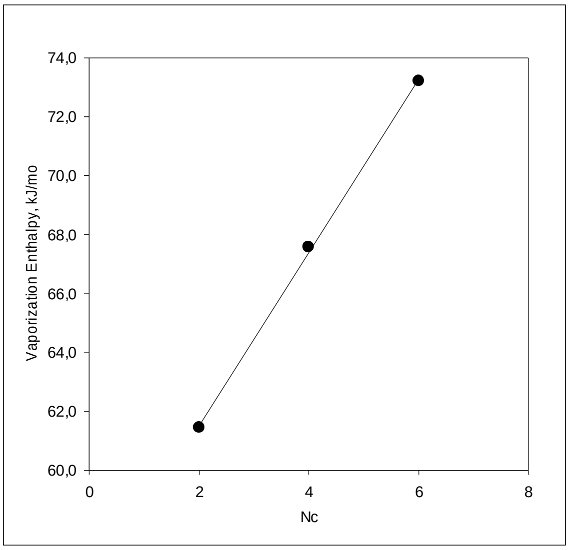


Fig. 8.1. Enthalpy of vaporization, $\Delta_l^g H_m$ (298,15 K), against the number of C-atoms in the linear aliphatic chains measured for *1,2-ethanediol alkanoates*: *R*-CO_2-CH_2-CH_2-CO_2-*R* with *R* = (Me, Et, and Pr). Experimental data are given in the Table B20 (Appendix B).

Only one previous experimental value of $\Delta_f H_m^\circ$ (liq.) for triacetin has been determined by *Tavernier* and co-wokers using combustion calorimetry [215]. Their value $\Delta_f H_m^\circ$ (liq.) = -1330,8±4,2 kJ·mol^{-1} is in disagreement by 67 kJ·mol^{-1} with the result obtained in this work. We do not have any reasonable explanation for such a disagreement, but we intend to validate our value using ab initio calculations in the next paragraph.

Schmid et al. published the results on esterification of 1,2-ethanediol with acetic acid *via* 1,2-ethanediol monoacetate to 1,2-ethanediol diacetate catalyzed by *Amberlist-36* [216]. Enthalpy of the following reaction:

1,2-ethanediol monoacetate + CH_3COOH = 1,2-ethanediol diacetate + H_2O,

($\Delta_r H_m^\circ$ = -3,2 kJ·mol^{-1}) was taken from this work to estimate the enthalpy of formation of 1,2-ethanediol monoacetate, $\Delta_f H_m^\circ$ (liq.) = -657,8 kJ·mol^{-1} according to *Hess´s* Law using enthalpies of formation of acetic acid [32], 1,2-ethanediol diacetate (from Table 8.3.) and the water [28]. The calculated value is found to be in good agreement with results obtained from direct calorimetric measurements (Table 8.3.).

The values of $\Delta_l^g H_m$ of ethanediol and propanetriol acetates (Table 8.3.) have been used together with the results from our combustion experiments for further calculation of the gaseous standard enthalpies of formation, $\Delta_f H_m^\circ$(g.) at 298,15 K. The resulting values of $\Delta_f H_m^\circ$(g.) are given in the last column in Table 8.3.

8.5. Ab Initio Calculations

Results of *ab initio* molecular orbital methods for calculation of the enthalpy of formation of ethanediol and propanetriol acetates have not been yet reported in the literature. We have calculated the gaseous enthalpies of formation with help of the standard atomization reactions as well as using the bond separation reactions [210,225]. Using enthalpies of these reactions calculated by G3MP2 method and enthalpies of formation $\Delta_f H_m^\circ$(g.), for simple molecules as recommended by *Pedley et al.* [32], enthalpies of formation of ethanediol and propanetriol acetates have been calculated (see Tables B21-B23 in Appendix B).

8.5.1. Ethanediol Monoacetate

Study of conformational equilibrium of 1,2-ethanediol monoacetate is important for the estimation of its enthalpy of formation, $\Delta_f H_m^\circ$(g.). According to conformational analysis using the G3MP2 method, there were found four possible arrangements in the molecule of 1,2-ethanediol monoacetate towards double bond of the carbonyl group. Calculations have revealed a possibility of the intra-molecular hydrogen bonding formation in conformers M2 and M3 (see Fig. 8.2). The distance between hydrogen of the OH-group and the oxygen in the chain equals to 2,33 Å in the conformer M2. Also the distance between the hydrogen of OH-group and the oxygen of the carbonyl group is 1,93 Å in M3. For the comparison, in 1,2-ethanediol, where the *intramolecular* hydrogen bond is well established, the very similar distance, 2,24 Å, between the hydrogen of the OH- and the oxygen of second OH-group was calculated using the same G3MP2 method. The energy differences of the 4 conformers of 1,2-ethanediol monoacetate related to the appropriate most stable conformer M3.

Conformer M1, (8,5)/(6,9)

Conformer M2, (0,1)/(0,0)

Conformer M3, (0,0)/2,2

Conformer M4, (8,4)/(7,4)

Fig. 8.2. Stable conformations of 1,2-ethanediol monoacetate, (relative free energie, G3MP2, kJ·mol^{-1})/(relative free energie, G3MP2, kJ·mol^{-1}).

The thermal population p_i of the conformers at T = 298,15 K is given by equation (5.10 in Chapter 5). Results on p_i were used for the calculation of energies and enthalpies of the conformers' equilibrium mixture and finally applied for calculation $\Delta_f H_m^\circ$(g.) and enthalpies of formation of the gaseous 1,2-ethanediol monoacetate. The gaseous enthalpy of formation of 1,2-ethanediol monoacetate ($C_4H_8O_3$) can be calculated by the standard atomization reaction as well as the following isodesmic (8.2) and bond separation (8.3 and 8.4) reactions:

$$C_4H_8O_3 + H_2O \rightarrow CH_3COOH + HOCH_2CH_2OH \quad (8.2),$$

$$C_4H_8O_3 + 7CH_4 \rightarrow 3CH_3OH + 4C_2H_6 \quad (8.3),$$

$$C_4H_8O_3 + 2CH_4 \rightarrow CH_3COOCH_3 + CH_3OH + C_2H_6 \quad (8.4).$$

Estimated enthalpy of formation of 1,2-ethanediol monoacetate from atomization procedure and from reactions (8.2-8.4) are very similar (Table B21 in Appendix B). The average value calculated from atomization, bond separation and isodesmic reactions are also in agreement with the experimental result presented in Table 8.3.

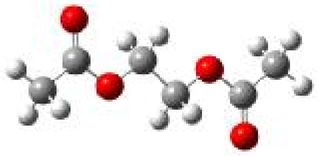


Fig. 8.3. The most stable conformation of *1,2-ethanediol diacetate*.

8.5.2. ETHANEDIOL DIACETATE

The most stable conformation of 1,2-ethanediol diacetate ($C_6H_{10}O_4$) is presented in the Fig. 8.3. The energy differences of other less stable conformers related to the appropriate most stable conformer exceeded 10 kJ·mol^{-1} and they were not taken into account. Enthalpy of formation of 1,2-ethanediol diacetate derived with help of the atomization procedure and the reactions (8.5) to (8.10) are in close agreement (see Table B22 in Appendix B). Their average is found to be also in agreement with our experimental results presented in Table 8.3.

$$C_6H_{10}O_4 + 2H_2O \rightarrow 2CH_3COOH + HOCH_2CH_2OH \quad (8.5),$$

$$C_6H_{10}O_4 + 12CH_4 \rightarrow 4CH_3OH + 7C_2H_6 \quad (8.6),$$

$$3C_6H_{10}O_4 + 16CH_4 \rightarrow 4CH_3COOCH_3 + 4CH_3OH + 9C_2H_6 \quad (8.7),$$

$$C_6H_{10}O_4 \leftrightarrow HOOC(CH_2)_4COOH \quad (8.8),$$

$$C_6H_{10}O_4 \leftrightarrow H_5C_2OOC - COOC_2H_5 \quad (\textit{di-Ethyl ester ethanedioic acid}) \quad (8.9),$$

$$C_6H_{10}O_4 \leftrightarrow (H_3C)O = COCH(CH_3)OC = O(CH_3) \quad (\textit{1,1-Diacetoxyethane}) \quad (8.10).$$

8.5.3. PROPANETRIOL TRIACETATE

Ab initio calculations using *HF method* revealed 109 *rotamers* within 12 kJ·mol^{-1} from the global minimum of the 1,2,3-propanetriol triacetate ($C_9H_{14}O_6$) [226]. The three most stable conformers are presented in the Fig. 8.4. The thermal population p_i of these conformers at T = 298,15 K according to eq. 5.10 in the Chapter 5 was taken into account by calculating $\Delta_f H^\circ_m$(g.) according to following chemical reactions:

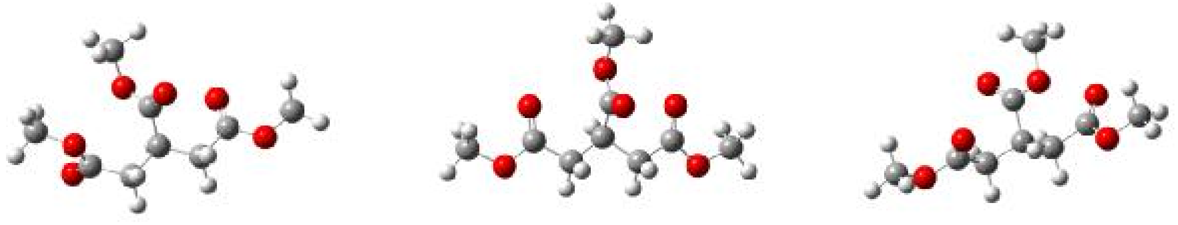
$$C_9H_{14}O_6 + 3H_2O \rightarrow 3CH_3COOH + HOCH_2CH(OH)CH_2OH \quad (8.11),$$

$$C_9H_{14}O_6 + 9CH_4 \rightarrow 2CH_3COOCH_3 + 2CH_3OH + 5C_2H_6 \qquad (8.12),$$

$$C_9H_{14}O_6 + 6C_2H_6 \rightarrow 3CH_3COOCH_3 + 4C_3H_8 \qquad (8.13),$$

$$C_9H_{14}O_6 + 33C_2H_6 \rightarrow 6H_2O + 25C_3H_8 \qquad (8.14).$$

In contrast to ethanediol acetates, enthalpy of formation of 1,2,3-propanetriol triacetate obtained from atomization procedure as well as the reactions (8.11) to (8.14) have shown a large spread of values (*see* Table B23 in Appendix B). Most probably one of the reasons of this fact may be a large size of the molecules. However, the average result on $\Delta_f H_m^\circ$ (g.) calculated theoretically is still in an acceptable agreement with the experimental result presented in Table 8.3.



(0,30) (6,30) (0,00)

Fig. 8.4. The most stable conformations of 1,2,3-propanetriol triacetate (relative energie, G3MP2, kJ·mol^{-1}).

8.6. ADDITIVE CALCULATIONS OF THERMODYNAMIC PROPERTIES OF MODEL COMPOUNDS RELATED TO BIOFUELS

Enthalpies of formation of the model compounds such as ethanediol and propanetriol actetates could be successfully predicted using high-level ab initio method. However, it should be mentioned, that the composite G3MP2 method used in this work is the quite time consuming method. For small molecules such as ethanediol monoacetate a required computational measurements takes 4 hours only for the longest step 4 with QCISD(T)/6-31G(d). For middle size molecules such as ethanediol diacetate a required time for the calculation is about 36 hours (the calculations were performed at University of Rostock, in computational centre with help of *Dual Core AMD Opteron 2220 SE* operated by 2 processors and 2500 Mb RAM). But already for 1,2,3-propanetriol triacetate it was possible to complete our calculations within 120 hours. Following, an alternative group-additivity procedure is required for predicting thermochemical properties of large molecules related to glycerin derivatives and other model compounds for biofuels.

The group-additivity methods [34,35,200,227] serve as valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes. *Benson`s group additivity method* [35] seems to have the most widespread acceptance at present, and the overall best record for reliability of estimation techniques. A group is defined by Benson [34] as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands". In this work we follow the Benson’s methodology.

8.6.1. ENTHALPIES OF FORMATION OF ALIPHATIC ESTERS IN THE LIQUID AND IN THE GASEOUS STATE

Our approach for evaluation of the *Group Additivity Values* (GAVs) was similar to that of others [35,175] in that we began by deriving GAVs for alkyl groups using as a data base the set of thermodynamic properties for 68 compounds such as developed by *Cohen* [35]. The method of polyfunctional least squares was used to evaluate the additivity parameters. The group-contributions values, which are specific for alkanes: C-(C)(H_3), C-(C_2)(H_2), C-(C_3)(H), C-(C_4), and correction for 1-4 C-C interactions $(C\text{-}C)_{1\text{-}4}$ are well established [175] (*see* Table B24 in Appendix B). With these values fixed, we then turned to esters to derive GAVs necessary for those compounds: carboxyl group (CO_2)-$(C)_2$, and alkyl chain attached to the carbonyl side C-(C)$(H)_2$(CO_2), C-$(C)_2$(H)(CO_2), C-$(C)_3$(CO) and for the alkyl chain attached to the oxygen of the carboxyl group: C-(C)$(H)_2$(O), C-$(C)_2$(H)(O), C-$(C)_3$(O). Similar to alkanes, a correction for interaction between C- atom of alkane chain with the double bonded oxygen of carbonyl group $(C\text{-}CO)_{1\text{-}4}$ and a correction for interaction between C-atom of alkane chain with the oxygen on the other side of the carbonyl group $(C\text{-}O_e)_{1\text{-}4}$ was introduced. For example, for the prediction of the enthalpy of formation of butyl acetate ($CH_3COOCH_2CH_2CH_2CH_3$) the following contributions should be accounted:

$$(CO_2)\text{-}(C)_2\times1 + C\text{-}(C)(H)_2(O)\times1 + C\text{-}(C)(H_3)\times2 + C\text{-}(C)_2(H)_2\times2 + (C\text{-}C)_{1\text{-}4}\times1 + (C\text{-}Oe)_{1\text{-}4}\times1$$

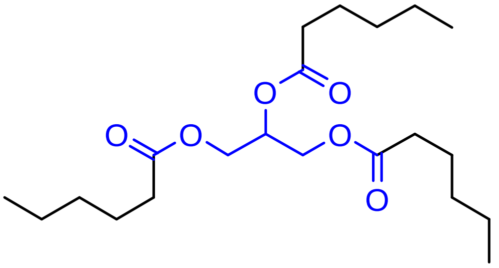
For deriving GAVs for the aliphatic esters we have collected a series of compounds with the secondary, tertiary and quaternary branching of the alkyl substituents. These compounds have constituted a matrix (see Table B25 in Appendix B), which has been solved using the method of polyfunctional least squares and the group-additivity parameters have been evaluated (Table B24).

8.6.2. ENTHALPIES OF VAPORIZATION OF ALIPHATIC ESTERS

Original works by *Benson* [34] and updating compilation [35] do not provide group-additivity values for calculation of vaporization enthalpies, $\Delta_l^g H_m$, at 298,15 K. There is not the fault of the empirical and half-empirical methods for estimation of the enthalpies of vaporization of organic compounds [175,228,229]. However, it seems to be logical to follow the Benson`s methodology for this thermodynamic property as well. In this part of our work the same definition of groups and the same evaluation procedure have been applied to predict the enthalpies of vaporization of aliphatic esters as well as their enthalpies of formation. The GAVs's estimation procedure in prediction of enthalpy of vaporization, $\Delta_l^g H_m$, is based on experimental data (see Table B26 in Appendix B). Group-additivity parameters can be estimated *via* the method of the least squares. These parameters are presented in the Table B24. Results presented in the Table B26 (Appendix B) show that the average standard deviations of the selected data are found to be in the perfect boundaries of 1-2 $kJ\cdot mol^{-1}$.

8.6.3. ENTHALPIES OF FORMATION AND VAPORIZATION OF COMPOUNDS RELATED TO BIOFUELS

Main parts of biofuels are glycerol derivatives with long alkyl chains. Having established experimental enthalpies of formation and enthalpies of vaporization of 1,2-ethanediol and 1,2,3-propantriol acetates it is reasonable to perform a general group-additivity procedure for prediction of thermochemical properties of the similar compounds with long alkyl chains. Previously the incremental scheme for *alkylurea* derivatives which consists of the determination of increments for substitution of H atoms by CH_3 groups in the standard series starting with urea has been applied [230]. This procedure showed the consistent results. In the present chapter a similar procedure is suggested, where ester functional group with alcohol moiety of 1,2-ethanediol monoacetate (EDM), 1,2-ethanediol diacetate (EDD) and 1,2,3-propanetriol triacetate (PTT) is taken as the invariable part of the molecule. Thus, subtracting an appropriate number of CH_3-increments from EDM, EDD, and PTT leads to the invariable part of these molecules mentioned above (C_{EDM}, C_{EDD}, and C_{PTT} respectively). For example, for the prediction of the enthalpy of formation or the vaporization enthalpy of *1,2,3-propanetriol trihexanoate* the following calculations should be performed:



C_{PTT} +

$3\times C\text{-}(C)(H_2)(CO_2) + 9\times C(C)_2(H)_2 +$

$+\ 3\times C\text{-}(C)(H)_3 + 9\times(C\text{-}C)_{1\text{-}4} +$

$+\ 3\times(C\text{-}CO)_{1\text{-}4}$,

where C_{PTT} fragment (blue colour) consists of the following increments:

$$C_{PTT} = 3\times(CO_2)\text{-}(C)_2 + 2\times C\text{-}(C)(H)_2(O) + 1\times C\text{-}(C)_2(H)(O) + 2\times(C\text{-}O_e)_{1\text{-}4},$$

however this fragment has been considered as the special unity, C_{PTT}, and its value was derived from the experimental property of 1,2,3-propanetriol triacetate (see Table B24). For the hydrocarbon chains attached to C_{PTT} the further additional contributions: $3\times C\text{-}(C)(H_2)(CO_2) + 9\times C(C)_2(H)_2 + 3\times C\text{-}(C)(H)_3 + 9\times (C\text{-}C)_{1\text{-}4} + 3\times(C\text{-}CO)_{1\text{-}4}$ have been taken into account. Group-contributions values, which are specific for alkanes and alkanols are well established [175]. The group-additive parameters specific for aliphatic esters have been just derived in the previous section. Now, using the new GAVs: C_{EDM}, C_{EDD}, and C_{PTT}, the gaseous or liquid enthalpy of formation of any arbitrarily large ester or triglyceride could be predicted.

8.7. VALIDATION OF EXPERIMENTAL RESULTS ON BIOFUELS' COMPONENTS

A large number of experimental enthalpies of combustion of compounds parent to bioufuels- fatty esters and tryglycerides were measured in the 1989 by *Freeman* and *Bagby* [231]. Vapour pressures and vaporization enthalpies for a large number of triglycerides with saturated and unsaturated alkyl chains were measured using the *pendulum-tensimeter method* [232]. *Goodrum* and co-workers measured vapour pressure of large fatty esters and triglycerides by TGA and DSC [233-236]. Compilation of the available experimental data on these compounds is listed in the Tables 8.4. (*see below*) and Table B27 (Appendix B). Thus, one needs a criterion to assess the reliability of the experimental results available for biofuel components in the literature. One of the best flags to possible experimental errors is a large discrepancy between experimental and calculated values – especially if other, closely related compounds show no such discrepancy. In this context it was interesting to check archival data available for the triglycerides [230-236]. Calculations of the $\Delta_l^g H_m$ for triglycerides (Table 9 in Appendix B) with help of parameters listed in Table 8 have provided values which are mostly 10 to 90 kJ·mol^{-1} deviate from our predictions (except for the calorimetric measurements by *Nilsson* and *Wadsö* [219]). Calculations of the $\Delta_f H_m^\circ$ (liq.) for triglycerides (Table 8.4) have shown values which are 60 to 800 kJ·mol^{-1} deviate from our predictions. In our opinion the thermochemistry for triglycerides required the further extended additional experimental measurements.

8.8. STRENGTH OF INTRAMOLECULAR HYDROGEN BOND IN THE MOLECULE OF ETHANEDIOL MONOACETATE

According to computational analysis of conformers presented in the section 8.5.2, there are two conformers of 1,2-ethanediol monoacetate with *intramolecular* H-bonding interactions. The spectroscopic observation of such hydrogen bond in this compound has been performed in [237]. In the case of experimentally approaches there were scarcely proven to determine the hydrogen bond strength quantitatively [70,71]. One of the possible approaches to do it is still *ab initio* method. The hydrogen bond strength in 1,2-ethanediol monoacetate could be defined as the energetic difference between H-bonded conformers and an appropriate conformers obtained by rotation of OH-group by 180° around the C-O single bond with subsequent geometry optimization procedure. But unfortunately, by means of spectroscopic investigations it is possible to provide the qualitative description of intra-molecular hydrogen bonding. Our G3MP2 calculations of H-bond strength of both conformers M2 and M3 performed on this way provided values 7,1 and 7,0 kJ·mol^{-1}. Another simple way to assess H-bond strength is to consider the enthalpy differences between H-bonded and non-H-bonded conformers M1 and M2 or M4 and M3, which are also about 8,5 kJ·mol^{-1}. Thus, the H-bond strength on the level of 7 to 8 kJ·mol^{-1} could be predicted using two procedures based on ab initio calculations.

Table 8.4. Triglycerides: Standard Enthalpies of Formation, $\Delta_f H_m^{\circ}$ (298,15 K) (in kJ·mol^{-1}).

Compound	T_{fus}, K	$\Delta_{cr}^{l}H_m$ [a]	$\Delta_f H_m^{\circ}$ (cr.)	$\Delta_f H_m^{\circ}$ (liq.) [b]	additive [c]	Δ
Triacetin, C1 (liq)	-	-	-	-1330,8	-1264,2	-66,2
Tributyrin, C4 (liq.)	-	-	-	-1496,0	-1407,1	-88,9
Tricaproin, C6 (liq.)	-	-	-	-	-1558,4	-
Tricaprylin, C8 (liq.)	-	-	-	-2501,3	-1709,7	-791,6
Tricaprin, C10 (cr.)	304,8	3,0	-1971,8	-1968,8	-1861,1	-107,7
Trilaurin, C12 (cr.)	318,9	10,8	-2175,1	-2164,3	-2012,4	-151,9
Trimyristin, C14 (cr.)	330,3	19,0	-2336,5	-2317,5	-2163,7	-153,8
Tripalmitin, C16 (cr.)	339,1	27,2	-2447,6	-2420,4	-2315,0	-105,4
Tristearin, C18 (cr.)	345,7	35,1	-2320,1	-2285,0	-2466,3	181,3
Triarachidin, C20 (cr.)	351,0	42,9	-2732,7	-2689,8	-2617,7	-72,1
Tribehenin, C22 (cr.)	354,9	50,3	-3065,7	-3015,4	-2769,0	-246,4

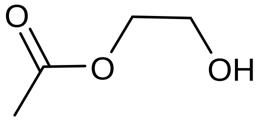
[a] enthalpy of fusion at 298,15 K calculated from the experimental values measured at the fusion temperature, T_{fus} [238] according to the procedure by *Chickos* and *Acree* [178].

[b] enthalpy of formation was resulted from eq.: $\Delta_f H_m^{\circ}$ (liq.) = $\Delta_f H_m^{\circ}$ (cr.) + $\Delta_{cr}^{l}H_m$.

[c] estimated using GAVs from the Table B24 (in Appendix B).

We have shown recently, that thermochemistry is also able to contribute to the quantification of HB strength [110]. Group additivity procedure is conventionally applied for this purpose. According to this method, special effects (e.g H-bond strength) of a compound could be obtained as the difference between the observed enthalpy of formation in the gaseous state, $\Delta_f H_m^{\circ}$ (g.), and a value calculated with

GAVs. In such a manner we have discussed substituent effects of benzene derivatives recently [69-71,110]. In this work for quantitative analysis of H-bond strength we have used the group-additivity parameters developed in the present work. Indeed, we can collect the molecule of 1,2-ethanediol monoacetate (EDM) from the following increments:



$\Delta_f H^\circ_m$ (g.)$_{\text{add.}}$ = C-(C)(H)$_3$ + 1×(CO$_2$)(C)$_2$ + 1×C-(C)(H)$_2$(O) + 1×C-(C)(H)$_2$(OH) + +1×O-(C)(H) = -590,3 kJ·mol^{-1},

and the difference between the experimental and the additive value could be a measure of the hydrogen bonding strength (HB):

$$(\text{HB})_{\text{EDM}} = \Delta_f H^\circ_m \text{ (g.)}_{\text{exp.}} - \Delta_f H^\circ_m \text{ (g.)}_{\text{add.}} = -592{,}8 + 590{,}3 = (-2{,}5 \pm 2{,}3) \text{ kJ·mol}^{-1}$$

As can be seen, this value is in accord (within the boundaries of experimental uncertainties) with that strength (-8,5±4,9) kJ·mol^{-1} obtained above from the ab initio calculations (see Fig. 8.2).

To assess consistency of this result, it is interesting to calculate the hydrogen bonding strength of the 1,2-ethanediol (ED) using its enthalpy of formation, $\Delta_f H^\circ_m$ (g.) = -388,0±2,0 kJ·mol^{-1} [110] and the same group additivity method:

$$\Delta_f H^\circ_m \text{ (g.)}_{\text{add.}} = 2\times\text{O-(C)(H)} + 2\times\text{C-(C)(H)}_2\text{(OH)} = (-375{,}3 \pm 2{,}0) \text{ kJ·mol}^{-1}$$

and the difference between the experimental and the additive value could be a measure of the hydrogen bonding strength (HB) in the 1,2-ethanediol (ED):

$$(\text{HB})_{\text{ED}} = \Delta_f H^\circ_m \text{ (g.)}_{\text{exp.}} - \Delta_f H^\circ_m \text{ (g.)}_{\text{add.}} = -388{,}0 + 375{,}3 = (-12{,}7 \pm 2{,}0) \text{ kJ·mol}^{-1}$$

and as expected the strength of the H-bond in 1,2-ethanediol monoacetate is somewhat lower than those in 1,2-ethanediol. Such a similarity of hydrogen bond strength in ethanediol derivatives proves the consistency of the procedure and the experimental data involved in the interpretation.

The purpose of this work was to establish a consistent set of experimental thermochemical quantities for aliphatic esters of carboxylic acids, 1,2-ethanediol and 1,2,3-propanetriol acetates, which are parent compounds to the main components of biofuels. Values of group additive values derived in this work provide a further improvement on the group-contribution methodology for prediction of the thermodynamic properties of a broad range of compounds relevant to biodiesel. The derived values of increments can be applied for the prediction of the energy content of biofuels, for modeling and simulation of the thermochemistry and kinetics of decomposition reactions of biofuels.

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APPENDIX A

EXPERIMENTAL PROCEDURES, EQUIPMENT AND MATERIALS

1. COMBUSTION CALORIMETRY

High-precision combustion calorimetry has been applied for the measurement of molar enthalpies of organic substances in the liquid and solid state (incl. polymers) mentioned in this work. *Isoperibol* calorimeters were used for this purpose (type *V-08MA* and *Parr 6200*, USA). The reaction is started by electrically burning the calibrated ignition platinum wire and carried out in a steel bomb, filled with oxygen (up to 30 bar) and a sample (tablet-shaped or in the sealed PE ampoule) placed into the platinum pan (see Fig. A1).

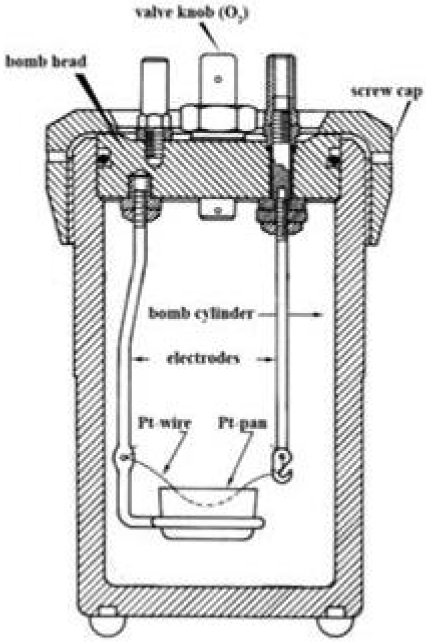


Fig. A1. Parts of Oxigen Bomb.

The heat evolved during the combustion of the sample is then dissipated in the known amount of water that surrounds the bomb, contained in the calorimeter pail. From the rise in temperature and the known *water value* (or *energy equivalent* of the calorimeter, ε_{calor}) of the whole setup, the heat of reaction can be determined by equation: $\Delta H = \varepsilon_{calor} \cdot \Delta T$, where ΔH is the heat of reaction and ΔT, the measured increase in temperature.

A careful insulation of the substance sample into calorimeter bomb is required due to its hygroscopic nature. For the liquid substances were used PE ampoules as sample containers (value 1 cm^3 commercially available at *NeoLab*, Germany). The sample was transferred from the stock bottle into PE ampoule with a syringe and sealed immediately according to the procedure described in [239]. The solid substances were pressed into tablets of mass ≈400 mg and were burned in oxygen at p = 3,04 MPa. The detailed procedure has been previously described [27,240]. The completeness of the combustion of the crystalline samples was ensured by the addition of about 50 mg of oil to the tablet. 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 was determined with a standard reference sample of benzoic acid (sample *SRM 39i*, NIST). Correction for nitric acid formation was based on the titration with 0.1 M aq. solution of NaOH. The atomic weights used were recommended by the IUPAC Commission [241]. The sample masses were reduced to vacuum taking into consideration the density values. The densities of the commercially available liquid compounds were taken from the *Aldrich* catalogue. Densities of the solid substances have been determined by submergence their tablets in a calibrated 10 cm^3 pycnometer filled with water. The molar heat capacities of the solid samples have been measured by DSC. For converting the energy of the actual combustion process to that of the isothermal process and reducing to standard states the conventional procedure was applied [242]. All calorimetric data obtained in this work and data presented in the literature are tabulated and represented in Appendix B. To derive $(\Delta_f H_m^\circ)$ in the liquid or solid phase from $(\Delta_c H_m^\circ)$ molar enthalpies of formation of H_2O (liq.): (-285,830±0,042) $kJ \cdot mol^{-1}$ and CO_2 (g.): (-393,51±0,13) $kJ \cdot mol^{-1}$ were taken as assigned by *CODATA* [28]. The total uncertainties were calculated according to the guidelines recommended by *Olofsson* [29]. They included the absolute standard deviation from combustion of materials, uncertainties from calibration, combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

2. ENERGY CALCULATION FOR THE FUELS (BIODIESEL)

1) If we consider the combustion reaction H_2 (g.) + $0.5O_2$ (g.) → H_2O (liq.) in the bomb calorimeter we can write that the specific energy content of H_2 is equal to enthalpy of combustion, $\Delta_c H^\circ$, that is equal to HHV and $\Delta_f H^\circ$ (298 K) of H_2O (liq.) -285,8 $kJ \cdot mol^{-1}$. Hence, the HHV is obtained when, after the combustion, the water is in the condensed (liquid) form.

For the LHV, the water is considered to be completely in the vapour phase (steam) because the reaction H_2 (g.) + $0.5O_2$ (g.) → H_2O (g.) is stopped at elevated temperature (423 K) and the standard enthalpy in this case is -243,8 $kJ \cdot mol^{-1}$. For estimation of value of standard enthalpy at 423,15 K the following values of the molar heat capacities, $C^\circ_{p,m}$, at constant pressure: H_2O (g.) 33,58 $J \cdot K^{-1} \cdot mol^{-1}$; H_2 (g.) 28,84 $J \cdot K^{-1} \cdot mol^{-1}$; O_2 (g.) 29,37 $J \cdot K^{-1} \cdot mol^{-1}$ were taken into account. Assuming that the heat capacities are independent of the temperature, we can calculate:

$$\Delta_r H^\circ \text{ (423 K)} = \Delta_r H^\circ \text{ (298 K)} + (423 - 298) \times \Delta_r C^\circ_p \qquad (1.1),$$

where $\Delta_r C^\circ_p = \Sigma\ \nu C^\circ_{p,m}$ (products) – $\Sigma\ \nu C^\circ_{p,m}$ (reactants), and ν are the stoichiometric coefficients in the chemical equation:

$$\Delta_r C^\circ_p = C^\circ_{p,m}\ H_2O\text{ (g.)} - \{C^\circ_{p,m}\ H_2\text{(g.)} + 0{,}5\ C^\circ_{p,m}\ O_2\text{(g.)}\} = -9{,}94\ J \cdot K^{-1} \cdot mol^{-1},$$

and then, according to equation (1.1)

$$\Delta_r H^\circ \text{ (423 K)} = -241{,}8 + 125 \text{ (K)} \times (-9{,}94) = -243{,}0\ kJ \cdot mol^{-1}$$

The HHV is larger then LHV because it includes the enthalpy of vaporization of water. The difference between the HHV and LHV can be significant. If the fuel contains traces of water it is possible to reveal by measurement of LHV.

Now we can combine calculated value from equation (1.1) with the enthalpy of formation of H_2O (liq.) to determine the value of water phase transition takes place in the temperature range from 423 K to 298 K and compare with the known in literature. The enthalpy of transition H_2O (g.→liq.) defined as enthalpy of vaporization with inverse sign, $\Delta_{trs}H°$, is calculated as follows:

$$\Delta_{\text{trs}}H° = \Delta_r H° \text{ (298 K)} - \Delta_r H° \text{ (423 K)} = -285{,}8 + 243{,}0 = -45{,}8 \text{ kJ·mol}^{-1}$$

This estimate is in good agreement with experimental value of enthalpy of vaporization of water at 298 K, $\Delta_{vap}H° = 44{,}02$ kJ·mol^{-1}.
The same procedure is applied to other fuels containing carbon atoms:

2) $C(s.) + O_2 (g.) \rightarrow CO_2 (g.)$, $\Delta_f H° CO_2$ (g.) at 298 K = HHV = $\Delta_c H° = -393{,}5$ kJ·mol^{-1};

$$C°_{p,m}\ CO_2 \text{(g.) } 37{,}11 \text{ kJ·mol}^{-1};\ C°_{p,m} \text{ C(graphite) } 8{,}53 \text{ kJ·mol}^{-1}.$$

$$\Delta_r C°_p = C°_{p,m}\ CO_2\text{(g)} - \{C°_{p,m} \text{ C(graphite)} + C°_{p,m}\ O_2 \text{(g.)}\} = -0{,}78 \text{ J·K}^{-1}\text{·mol}^{-1}, \text{ then}$$

$$\Delta_r H° \text{ (423 K)} = -393{,}5 + 125 \text{ (K)} \times (-0{,}78) = -393{,}6 \text{ kJ·mol}^{-1}.$$

In this case the obtained LHV slightly varies from the HHV into the heat capacities' difference at the observed temperature range. The difference is large when the carbon as a fuel contains water, sulfur, and nitrogen contaminants.

3) $CH_4 (g.) + 2O_2 (g.) \rightarrow CO_2 (g.) + 2H_2O (g.)$, HHV = $\Delta_c H° = -802{,}3$ kJ·mol^{-1};

$$C°_{p,m}\ CH_4 \text{(g.) } 37{,}11 \text{ kJ·mol}^{-1};$$

$$\Delta_r C°_p = \{C°_{p,m}\ CO_2 \text{(g.)} + 2C°_{p,m}\ H_2O \text{ (g.)}\} - \{2C°_{p,m}\ O_2 \text{(g.)} + C°_{p,m}\ CH_4 \text{(g.)}\} = 10{,}24 \text{ J·K}^{-1}\text{·mol}^{-1}, \text{ then}$$

$$\Delta_r H° \text{ (423 K)} = -802{,}3 + 125 \text{ (K)} \times 10{,}24 = -801{,}0 \text{ kJ·mol}^{-1}$$

$$\Delta_{\text{trs}}H° \ (2H_2O) = \Delta_r H° \text{ (298 K)} - \Delta_r H° \text{ (423 K)} = -890{,}0 + 801{,}0 = -89{,}0 \text{ kJ·mol}^{-1}$$

$$\Delta_{\text{trs}}H° = -89{,}0 : 2 \text{ (mol)} = -44{,}5 \text{ kJ·mol}^{-1}$$

Calculated result is also in good agreement with the experimental value of enthalpy of vaporization at 298 K, $\Delta_{vap}H° = 44{,}02$ kJ·mol^{-1}.

4) $C_3H_8 (liq.) + 5O_2 (g.) \rightarrow 3CO_2 (g.) + 4H_2O (g.)$, HHV = $\Delta_c H° = -2044{,}0$ kJ·mol^{-1};

$$C°_{p,m}\ C_3H_8 \text{(liq.) } 73{,}5 \text{ kJ·mol}^{-1};$$

$$\Delta_r C°_p = \{3C°_{p,m}\ CO_2 \text{(g.)} + 4C°_{p,m}\ H_2O \text{ (g.)}\} - \{5C°_{p,m}\ O_2 \text{(g.)} + C°_{p,m}\ C_3H_8 \text{(liq.)}\} = 25{,}4 \text{ J·K}^{-1}\text{·mol}^{-1}, \text{ then}$$

$$\Delta_r H° \text{ (423 K)} = -2044{,}0 + 125 \text{ (K)} \times 25{,}4 = -2040{,}8 \text{ kJ·mol}^{-1}$$

$$\Delta_{\text{trs}}H° \ (4H_2O) = \Delta_r H°\text{(298 K)} - \Delta_r H°\text{(423 K)} = -2220{,}0 + (-2040{,}8) = -179{,}2 \text{ kJ·mol}^{-1}$$

$$\Delta_{\text{trs}}H° = -179{,}2 : 4 \text{ (mol)} = -44{,}8 \text{ kJ·mol}^{-1}$$

Thus, thermochemical calculations have shown that differences between the HHV and LHV can be significant (about 8 or 9%).

3. Transpiration Method (Vapour Pressure Measurement of Organic Substances)

Vapour pressure measurements has been measured by transpiration method using saturated nitrogen flow (carrier gas) [27,270]. Approximately 0,5-0,8 g of the sample (solid or liquid) has been mixed with glass beads and placed into thermostatically controlled U-shaped saturation tube (length 45 cm and diameter 0,9 cm) of the glass vessel (24,5 cm × 9,5 cm) presented in Fig. A2. Commercially available small glass beads (diameter ≈1 mm) provided a surface large enough to get saturation of carrier gas at the constant temperature (±0,1 K). To mix uniformly the solid substance with the glass beads, it must be dissolved in the light solvent and then dried up under N_2 flow. The flow rate of the carrier gas in the saturation tube should be not very slow to avoid diffusion effect of the substance's transport.

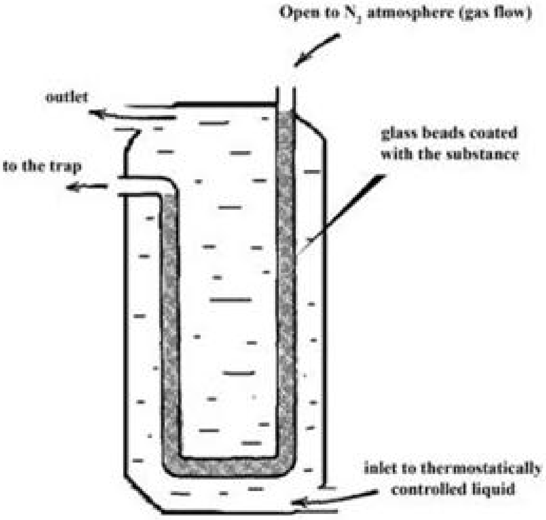


Fig. A2. Thermostatically controlled glass vessel in measurement of vapour pressures by transpiration method.

On the other hand it should be not very fast to achieve the vapour saturation. The transport contribution from diffusion of the substance was negligible at the flow rate up to 0,45 $dm^{-3}\cdot h^{-1}$. The upper limit for our saturator was at the level of equal to 9,0 $dm^{-3}\cdot h^{-1}$. The flow rate of the nitrogen was measured using soap bubble flow meter. The flow rate was kept to be constant using a high precision needle valve (*Hoke*). The accuracy of the volume V_{N_2} measurements from the flow rate was assesed to be ± 0,02-0,03%. A condensed amount of the substance in cold trap was dissolved immediately in methanol (or acetonitrile) and then analysed using GC (*HP-5890 Series II* gas chromatograph with flame ionization detector, auto-sampler and *HP 3390A* integrator) with external standard (aliphatic hydrocarbons C_9-C_{14}). The uncertainties of the mass determination did not exceed 1-3%. The saturated vapour pressure of the sample (p_i^{sat}) at each temperature (T_i) was determined from mass of the substance (m_i) collected in the cold trap within the known period of time. Assuming that the vapour phase behaves ideally and obeys the *Dalton's law* the values of p_i^{sat} were calculated from the *perfect (or ideal) gas equation*:

$$p_i^{sat} = {}^{m_i R T_i}/_{V M_i}$$

$V = V_{N_2} + V_i$, where $V_i \ll V_{N_2}$ is the volume contribution of the sample to the gaseous phase and it assumed to be negligible; V_{N_2} is the volume of the carrier gas determined from the flow rate and time measurements; R = 8,314472 J·K^{-1}·mol^{-1}; M_i is the molar mass of the compound under study.

Data of the saturated vapour pressure p_i^{sat} as a function of temperature were approximated using the following equations:

$$R \cdot p_i^{sat} = a + \frac{b}{T_i} + \Delta_l^g C_p \cdot \ln\left(\frac{T_i}{298{,}15\ (\mathrm{K})}\right),$$

$$R \cdot p_i^{sat} = a + \frac{b}{T_i} + \Delta_{cr}^g C_p \cdot \ln\left(\frac{T_i}{298{,}15\ (\mathrm{K})}\right),$$

where a and b are adjustable parameters, of $\Delta_l^g C_p$ is difference between molar heat capacity of the substance in the gaseous and liquid phase at 298,15 K; $\Delta_{cr}^g C_p$ is difference between molar heat capacity of the substance in the gaseous and solid phase (298,15 K). Then, the expressions for the vaporization $\Delta_l^g H_m$ and sublimation $\Delta_s^g H_m$ enthalpies referred to 298,15 K can be written as follows:

$$\Delta_l^g H_m(298{,}15\ \mathrm{K}) = -b + \Delta_l^g C_p \cdot 298{,}15\ (\mathrm{K}),$$

$$\Delta_{cr}^g H_m(298{,}15\ \mathrm{K}) = -b + \Delta_{cr}^g C_p \cdot 298{,}15\ (\mathrm{K})$$

Values of $\Delta_l^g C_p$ and $\Delta_{cr}^g C_p$ were calculated according to the procedure of *Chickos* et al. [19]. Uncertainties from the calculations of $\Delta_l^g C_p$ and $\Delta_{cr}^g C_p$ values were not taken into account. Detailed error analyses of the vapour pressure measurement using transpiration method were performed in the work [27]. Vapour pressure data were approximated by linear dependence ln(p_i^{sat}) from inverse temperature (1/T) using the least-squares method. Uncertainties from the calculations of enthalpies of vaporization and sublimation were assumed to be equal to the average deviation of experimental ln(p_i^{sat}) values from this linear correlation. The total uncertainty of the data obtained by transpiration technique was established to be up to 3 % including GC experimental errors. Experimental vapour pressure data and parameters a and b in these equations are tabulated and given in the Tables B1-B6 (Appendix B).

4. PHASE TRANSITIONS IN THE SOLID STATE (DSC-MEASUREMENTS)

Measurements of enthalpies of fusion and melting temperatures and phase transitions of the solid samples were required to choose the temperature range for transpiration investigations. This is the reason why we use DSC-measurements prior to the transpiration experiments.

In this work the thermal behavior *alkanedioic acids* has been determined with a computer controlled *Perkin-Elmer Pyris Diamond DSC*. For all measurements an empty pan was used as reference. The heating rate was equal to 10 K·min^{-1}. The temperature and enthalpy of fusion were determined by extrapolation onset of melting to the baseline and peak integration respectively. The temperature and heat flow rate scale of DSC have been calibrated by measuring high-purity *indium*, T_{fus}= 429,8 K and ΔH_{fus}= 28,4 J·g^{-1} (lit.). DSC measurements were repeated twice for each sample and values obtained were found to be within the experimental uncertainties ±0,2 kJ·mol^{-1} for ΔH_{fus} and ±0,5 K for T_{fus}.

5. COMPUTATION PROCEDURES

Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs [243]. Energies were obtained at the G3MP2 and B3LYP/6-311G(d,p) level of theory. 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 [208]. For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. The corresponding harmonic vibration frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to potential energy minima and to evaluate the corresponding zero-point vibration energies, ZPE, and the thermal corrections at 298,15 K. ZPE values were scaled by the empirical factor 0,9135. All the minima found at the HF/6-31G(d) level were again fully reoptimized at the MP2(FULL)/6-31G(d) level. G3MP2 theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartry-Fock theory followed by a series of single-point energy calculations at the MP2(Full), QCISD(T) and MP2/GTMP2Large levels of theory [208]. No corrections for internal rotors have been taken into account. The enthalpy values at T = 298,15 K were evaluated according to standard thermodynamic procedures [209].

6. MATERIALS

Alkylene carbonates (Chapter 2): samples of alkylene carbonates of commercial purity were obtained from *Huntsman Corporation* and were further purified by fractional distillation at reduced pressures. The degree of purity was determined using a *Hewlett Packard* gas chromatograph *5890 Series II* equipped with a flame ionization detector and a *Hewlett Packard 3390A* integrator. A *HP-5* capillary column (stationary phase crosslinked 5% PH ME silicone) was used in all our experiments. The column was 30 m long, 0,32 mm inside diameter, and had a film thickness of 0,25 µm. The flow rate of the carrier gas (nitrogen) was maintained at 7,2 dm^3·h^{-1}. The starting temperature for the GC was T = 323 K for the first 3 minutes followed by heating to T = 523 K at the rate of 10 K·min^{-1}. No impurities greater than 0,02 mass per cent were detected in all samples used in this work.

Naphthalene derivatives (Chapter 3): preparation of 1-methylene-1,2,3,4-tetrahydronaphthalene [CAS 25108-63-8] and 4-methyl-1,2-dihydronaphthalene [CAS 4373-13-1] as well their hydrogenation in propylene carbonate were performed according to experimental procedures given in [244]. The purity analyses were performed using GC with a flame ionization detector as described above. No impurities greater than 0,02 mass per cent were detected in all samples used in this work.

Oximes (Chapter 4): samples of cyclohexanone oxime [CAS 100-64-1] and ε-caprolactam [CAS 105-60-2] N-methylpropanamide [CAS 1187-58-2] were of commercial origin (*Fluka* and *Aldrich*). Having a mass-fraction purity of about 0,99 they were used without further purification. The sample of 2-butanone oxime [CAS 96-29-7] (*Aldrich*) was purified by repeated distillation at reduced pressure. The degree of purity was determined using GC described above. No impurities (≤ 0,01 mass per cent) could be detected by GC in combustion sample of 2-butanone oxime. The exact amount of residual water in the sample of 2-butanone oxime was measured by using *Karl Fisher* titration and the appropriate correction to the mass of sample has been performed. Chloroaluminate ionic liquids were prepared according to a general procedure [74]. Catalyst, anhydrous $AlCl_3$, was slowly added to imidazolium, quaternary ammonium, or phosphonium based ionic liquids. The mixture was stirred at 426 K until the catalyst completely dissolved. Brønsted-acidic ionic liquids were prepared according to a general procedure [75].

Study of Beckmann rearrangement in the liquid phase: glass vials with screwed caps and small magnetic stirrers were filled with initial liquid mixture of solvent with cyclohexanone oxime. Catalyst was added as a solid catalyst. The quantity of catalyst was approximately 10% from the mass of the mixture. Then the reaction mixture in the closed vials was controlled within T_i ±0,1 K under continuous stirring. After definite time intervals the vial was cooled rapidly in ice and opened. In all cases a catalyst was not soluble in reaction mixture and a clear phase boundary was observed. A sample for the GC analysis was taken from the upper liquid phase using a syringe. The thermostatically controlled vial was then preceded at the same temperature. The compositions of the reaction mixtures were determined with a gas chromatograph.

Monomers for polyesterification reaction (Chapter 5): the liquid sample of 1,4-butanediol (purchased from *Fluka*) having a mass-fraction purity of about 0,99 was purified by repeated distillation in vacuum. The solid samples of sebacic acid (decanedioic acid), purchased from *Fluka* and dodecanedioic acid (*Merck*) were purified by repeated sublimation in vacuum. Examination of the samples using GC showed no discernible amounts of impurities. The water concentration in 1,4-butanediol was 588 ppm. It was determined by *Karl Fischer* titration just before starting the experiments and appropriate corrections have been made for combustion results. The samples of dicarboxylic acids did not appear to be hygroscopic but the sublimed samples for combustion experiments were subjected to pellet-drying to remove traces of occluded water and were kept in a dessicator over P_2O_5. The immobilized lipase, trade name *Novozyme*® 435, was obtained from Novozymes (*Bagsvaerd*, Denmark) and consists of *Candida antarctica Lipase type B* (CaLB) adsorbed within a macroporous polymethacylate resin (specific activity 3 $U \cdot mg^{-1}$).

Synthesis and characterization of Polyester based on Sebacic Acid and Butanediol-1,4 were described in [245].

Synthesis and characterization of amidines/polyamidines (Chapter 6): commercially available solvents N-methyl-2-pyrrolidone (*Fluka*), 1,3-dimethyl-3,4,5,6-tetrahydro-2(^{1}H)-pyrimidinone, or dimethylpropyleneurea (*Aldrich*), dimethylformamide, dimethylacetamide, tetramethylurea, 1,3-dimethyl-2-imidazolidinone (Fluka), nitrobenzene, and hexamethylphosphorous triamide were purified according to standard techniques [246,247] and stored over molecular sieves 4 Å. Triethylamine Et_3N, tributylamine Bu_3N, pyridine, benzoyl chloride, benzene, *n*-hexane, petroleum ether, and *n*-octane were also purified as described in [247]. Aromatic diamines 4,4'-diaminodiphenylmethane (Ia), 4,4'-diaminodiphenyl oxide (Ib), 3,3-bis(4'-aminophenyl) phthalide (Ic), and 9,9-bis(4'-aminophenyl) fluorene (Id) were purified according to standard techniques. The T_{fus} values of diamines were 90-91, 190-192, 203-204, and 235-236°C, respectively [248]. Pyridine N-oxide was obtained by oxidating pyridine by hydrogen peroxide in acetic acid according to [249]. ^{13}C NMR spectrum: δ139,87 (α-^{13}C) and 126,7 (β- and γ-^{13}C) ppm. The ratio of integral intensities of signals due to α-^{13}C and to β- and γ-^{13}C was 2/3. The *relative* viscosity of a polymer (0.05 g) solution in DMAA (or HCOOH) (10 ml) was measured at 25˚C. The IR spectra of the polymers were recorded in the 400–3600 cm^{-1} range on a Specord IR-20 spectrometer using KBr prisms. Molecular mass was estimated by GPC with the aid of a Bruker LC21 chromatograph. Measurements were made with the use of CH_2Cl_2 as a solvent (the flow rate was 1 ml/min) and Styragel linear columns. ^{1}H and ^{13}C NMR spectra were recorded at 30°C on a Bruker AMX 400 spectrometer operating at 400,13 and 100,61 MHz, respectively. Tetramethylsilane was used as an internal standard.

1) *Preparation of 1,2-diphenylbenzamidine (acc. Scheme 8, Chap. 6).* In a 25-ml two-necked flask equipped with a stirrer, compound A ($7{,}4 \cdot 10^{-3}$ mol; 1,58 g) was dissolved in MP (6 ml) in a flow of argon at room temperature and an equimolar amount of pyridine-N-oxide was added. When aniline (1 ml, 20% molar excess) was added, the temperature was raised to 80˚C (~7 min) under intense stirring. Approximately 30 min after the attainment of this temperature, a light precipitate was formed. The reaction mixture was aged for another 0,5 h. under continuous stirring, cooled to room temperature, and precipitated into ammonium water. The precipitate was filtered off and repeatedly washed with water. The product was recrystallized from aqueous DMF in the presence of a small amount of $NaHSO_3$ to produce colorless needles that were dried in vacuum at 80˚C. Yield 69%.

2) *Preparation of 4,4'-bis(N-phenylenebenzamidine) oxide.*
a) Synthesis in the presence of Et_3N (*Scheme 9, Model a*). In the two-necked flask equipped with the stirrer, DAPO ($8{,}08 \cdot 10^{-4}$ mol; 0,1618 g) and compound A ($2{,}02 \cdot 10^{-3}$ mol; 0,4359 g) were successively dissolved in MP (3 ml) in a flow of argon at room temperature and Et_3N ($1{,}8 \cdot 10^{-3}$ mol) was then added. The temperature was raised to 80˚C (~7 min), and the reaction mixture was aged for 3 h. under continuous stirring, cooled to room temperature, and precipitated into ammonium water. The precipitate was filtered off and repeatedly washed with water; the product was dried in vacuum at 50˚C. Yield 49%;
b) (*Scheme 10, Model a*). In the 25-ml two-necked flask equipped with the stirrer IIa ($2{,}23 \cdot 10^{-4}$ mol; 0,0993 g) was dissolved in MP (3 ml) in a flow of argon at room temperature and aniline ($3{,}39 \cdot 10^{-3}$ mol; ~0,31 ml) and Et_3N ($1{,}8 \cdot 10^{-3}$ mol) were successively added. The temperature was raised to 90˚C (~10 min), and the reaction mixture was aged for 3 h. under continuous stirring (the precipitate formed). The product was isolated and dried as described above. Yield 54%.
c) Synthesis in the presence of pyridine-N-oxide (*Scheme 10, Model a*). In the 25-ml two-necked flask equipped with the stirrer, compound A ($4{,}64 \cdot 10^{-3}$ mol; 1,0 g) and DAPO ($2{,}08 \cdot 10^{-3}$ mol; 0,4178 g) were successively dissolved in a 0.1M solution of pyridine-N-oxide in MP (3,7 ml). The temperature was raised to 80˚C (~7 min), and the reaction mixture was aged for 1 h. under continuous stirring in a flow of

argon. The product was isolated as described above, reprecipitated from aqueous methanol, and dried under vacuum at 80°C. Yield 82%.

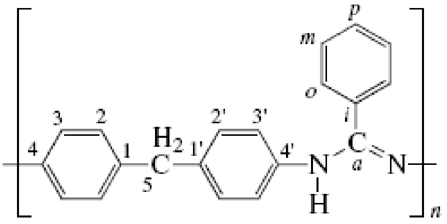
3) *Synthesis of 4,4'-bis(N-phenylenebenzamidine)-methane (Scheme 10, Model b).* In the 25-ml two-necked flask equipped with the stirrer, 4,4'-bis(N-phenylenebenzimidoyl chloride) methane, IIb ($6,77\cdot10^{-4}$ mol; 0,3 g) was dissolved in MP (3 ml) at room temperature and aniline ($1,69\cdot10^{-3}$ mol; ~0,15 ml) and Et_3N ($1,8\cdot10^{-3}$ mol) were successively added. The temperature was raised to 90°C (~10 min), and the reaction mixture was aged for 3 h. under continuous stirring in a flow of argon (the precipitate formed). The product was isolated and dried as described above. Yield 70%.

4) *Synthesis of bis-benzanilides- intermediates in the synthesis of bis-imidoyl chlorides (IIa–IId)*: 4,4'-Bis(N-phenylenebenzanilide) oxide with T_{fus}=262–264°C, 4,4'-bis(N-phenylenebenzanilide)methane with T_{fus}=248–249°C and 368–370°C, 3,3'-bis(4'-N-phenylenebenzanilide)phthalide with T_{fus}=180°C, and 9,9-bis(4'-phenylenebenzanilide)fluorene with T_{fus}=340,5–342°C were prepared according to a procedure used for the synthesis of aromatic polyamides (the yield was up to 95%) [250] and by the *Schotten–Baumann* method (the yield was up to 76%) [251].
For $C_{27}H_{22}N_2O_2$: calc. (%): C, 79,78; H, 5,46; N, 6,89; found (%): C, 79,81; H, 5,29; N, 7,04.
For $C_{34}H_{24}N_2O_4$: calc. (%): C, 77,85; H, 4,61; N, 5,34; found (%): C, 77,66; H, 4,54; N, 5,29.

5) *Synthesis of bis-imidoyl chlorides (IIa–IId)*: A 50-ml three-necked flask equipped with a reflux condenser and a dropping funnel was loaded at room temperature successively with bis-benzanilide (5 g), $SOCl_2$ (5-10 molar excess), and a small amount of DMF (≤0,5 ml) used as a catalyst. The reaction mixture was heated to 80-90°C for 1-3 h. until evolution of gaseous products ceased. The transparent reaction mixture was cooled to room temperature, dried *n*-hexane (or petroleum ether) (50 ml) was added, and the solvent was then vacuum distilled off together with the excess of $SOCl_2$. The product was dried in vacuum at 80-85°C for 10 h.
For $C_{26}H_{18}Cl_2N_2O$ (IIa; 61% yield): calc. (%): C, 72,12; H, 4,07; N, 6,29; found (%): C, 72,16; H, 3,98; N, 6.21.
For $C_{27}H_{20}Cl_2N_2$ (IIb, 60% yield): calc. (%): C, 73,14; H, 4,55; N, 6,32; found (%): C, 73,21; H, 4,43; N, 6,29.
For $C_{34}H_{22}Cl_2N_2O_2$ (IIc, 73% yield): calc. (%): C, 72,73; H, 3,95; N, 4,99; found (%): C, 72,41; H, 3,74; N, 4,91.
For $C_{39}H_{26}Cl_2N_2$ (IId, 68% yield): calc. (%): C, 78,92; H, 4,42; N, 4,72; found (%): C, 78,80; H, 4,38; N, 4.68.
IR (IIa–IId), ν cm^{-1}: 1680 (C=N), 1180 (aromatic C–H), 1445 and 1510 (arom. C–C), 610 and 900 (out-of-plane aromatic C–H), 770 (C–Cl), 1260 (C(Ph)–N), 700 and 830 (arom. =CH and monosubst. C–C). The intense absorption band observed at 1770 cm^{-1} in the spectrum of IIc is related to the stretching vibrations of the C=O bond of a phthalide lactone fragment. The intense absorption band at 1680 cm^{-1} corresponds to the stretching vibrations of the C=N double bond, and the band at 1320 cm^{-1} is due to the stretching vibrations of the C−N bond.
Synthesis of polyamidines (Scheme 11, Chap. 6):
6) *Synthesis in the presence of tertiary amines.* A 25-ml three-necked flask equipped with a stirrer and an inlet for feeding argon was successively loaded

with diamine (0,75-3,0 mmol), a neat solvent (3 ml), and an equimolar amount of bis-imidoyl chloride. After the resulting mixture was dissolved at room temperature, a catalyst (1,0-5,4 mmol) or a benzene-Bu_3N (1:1) mixture (0,8 ml) was added. The reaction mixture was slowly heated (~0,15 h.) in the flow of argon to 80-170˚C under continuous stirring. The duration of synthesis was varied from 1 to 7 h. When the synthesis was completed, the reaction mixture was cooled to room temperature and precipitated into ammonium water. The precipitate was filtered and repeatedly washed with water. The product was dried initially in air at 70˚C and then in vacuum at 90–100˚C for 5-7 h. The yield of the polymer was 80-95%.

7) *Synthesis in the presence of LiCl and Et_3N*: In the three-necked flask equipped with the stirrer and the inlet for feeding argon, reagent-grade LiCl (0,219-0,903 mmol) was dissolved at room temperature in MP (3 ml) and diamine and bis-imidoyl chloride were successively added at an equimolar ratio. Et_3N (1,0-5,4 mmol) was added dropwise to the resulting solution, and the temperature was gradually raised to 80-90˚C. The resulting mixture was aged for 1-3 h. under continuous stirring in the flow of argon. The polymer was isolated and dried as described above.
For the repeating unit of polyamidine IIIa, $C_{19}H_{14}N_2O$: calc. (%): C, 79,70; H, 4,93; N, 9,78; found (%): C, 79,65; H, 4,94; N, 9,77. The IR spectrum of polyamidine IIIa, ν, cm^{-1}: 1640 (C=N), 1335 (C–N), 1220 (C(Ph)–N), 3050 and 3400 (NH), 1410 and 1500 (arom. C–C), 840 (out-of-plane 1,4-disubst. arom. C–H), 710, 765, and 785 (arom. =CH and monosubst. C−C). On the whole, the IR spectra of polyamidines are characterized by an appreciable widening of all absorption bands; the stretching vibrations of C=N bonds are shifted to higher frequencies (to 1650 cm^{-1}), while vibrations of ordinary bonds C–N at 1330 cm^{-1} are less pronounced than those characteristic of low molecular weight analogues. The latter are inherent to compounds containing strong intramolecular hydrogen bonds, such as 1,5-diarylphormazanes, ozazones, hydrazonazomethynes of α-dicarbonyl compounds, and even monohydrazones of dicarbonyl compounds [252]. The ^{13}C NMR spectrum of polyamidine IIIb (see Scheme 1) in $CDCl_3$, ppm: $C_1/C_{1'}$ 134,7; $C_2/C_{2'}$ 128,3; C_3 121,2; $C_{3'}$ 120,37; C_4 147,3; $C_{4'}$ 144,1; C_5 39,9 and 40,1; C_a 154,5; C_i 135,49 and 135,90; and $C_{o,\ m,\ p}$ 128,6; 129,0; and 129,4.



(Scheme 1)

Alkyl 3-methylbut-2-enoate (Chapter 7): commercially available methyl 3-methylbut-2-enoate and of ethyl 3-methylbut-2-enoate have been studied (Aldrich, Alfa). Samples of iso-propyl, propyl-, iso-butyl, butyl, and pentyl 3-methylbut-2-enoates were synthesized and well described in [123]. A small amount of isomeric impurity in sample usually does not impact results of thermochemical studies within the boundaries of experimental uncertainties. Thus, no additional corrections were applied by data treatment. Small amounts of water (about 400 ppm) were not possible to remove from the sample prepared for thermochemical measurements. The exact amount of water in each sample was measured by using Karl Fisher titration and the appropriate corrections to the mass of sample have been performed.

Samples of Biofuels (Chapter 8): samples of 1,2,3-propanetriol triacetate (or triacetin) [CAS 102-76-1] and 1,2-ethanediol diacetate [CAS 111-55-7] were of commercial origin (Fluka and Aldrich), having a mass-fraction purity of about 0,99 was purified by repeated distillation in vacuum. Sample of 1,2-ethanediol monoacetate [CAS 102-76-1] was prepared and purified according to the established procedure [216,253]. The purity analyses were performed using GC with a flame ionization detector as described above. The purities of samples for thermochemical investigations determined by GC were better than 0,999 mole fraction.

APPENDIX B

TABLES

Table B1. Experimental Vapour Pressures, (p) and Molar Enthalpies of Vaporization/Sublimation ($\Delta_{l}^{g}H_m$ / $\Delta_{cr}^{g}H_m$ at 298,15 K) of Alkylene Carbonates Measured by Transpiration Method.

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}-p_{calc})$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	$kJ \cdot mol^{-1}$
Ethylene Carbonate; $\Delta_{cr}^{g}H_m$ (298,15 K) = (**74,08**±0,63) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{278,64}{R} - \frac{79556,09}{R \cdot (T,K)} - \frac{18,4}{R} \ln\left(\frac{T,K}{298,15}\right)$						
280,6	2,51	113,2	9,57	0,62	-0,01	74,41
286,2	2,93	69,1	9,60	1,19	0,01	74,30
291,3	2,74	38,2	9,60	2,00	-0,03	74,21
295,5	3,18	27,4	9,60	3,25	0,10	74,13
299,4	3,44	20,3	9,60	4,72	0,06	74,06
303,2	3,09	12,8	9,57	6,75	-0,02	73,99
304,4	3,38	12,0	9,60	7,85	0,24	73,97
306,4	3,63	11,2	9,57	9,07	-0,13	73,93
308,4	3,70	9,6	9,57	10,77	-0,34	73,89
Ethylene Carbonate; $\Delta_{l}^{g}H_m$ (298,15 K) = (**60,81**±0,12) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{264,13}{R} - \frac{74971,42}{R \cdot (T,K)} - \frac{47,5}{R} \ln\left(\frac{T,K}{298,15}\right)$						
310,3	7,53	17,53	9,56	12,00	0,10	60,23
314,4	7,37	12,75	9,56	16,15	0,02	60,04
314,5	3,11	5,39	7,19	16,14	-0,11	60,04
317,3	3,77	5,27	7,19	20,00	0,11	59,90
320,3	4,82	5,39	7,19	24,99	0,39	59,76
320,4	6,73	7,59	9,30	24,75	-0,03	59,75
324,4	6,47	5,51	7,19	32,81	0,15	59,56
323,5	1,04	0,958	2,87	30,50	-0,21	59,61
327,4	6,77	4,80	7,21	39,39	-0,59	59,42
331,3	7,70	4,20	7,21	51,19	-0,49	59,24
328,6	1,11	0,718	2,87	43,12	-0,17	59,37
335,4	8,84	3,61	7,21	68,48	1,29	59,04
333,6	10,08	4,72	5,67	59,62	-0,31	59,13
342,3	6,07	1,65	3,29	103,13	0,29	58,71
341,4	9,02	2,58	6,18	97,80	0,40	58,76
338,7	10,40	3,50	5,67	83,12	0,56	58,89
345,2	9,39	2,16	6,18	121,26	-1,03	58,58
349,0	13,02	2,36	5,67	153,99	1,31	58,40
343,8	9,25	2,36	5,67	109,42	-3,11	58,64
347,6	6,77	1,37	3,29	137,93	-2,85	58,46
354,0	11,71	1,61	5,67	203,68	0,91	58,16
352,4	7,34	1,10	3,29	186,92	1,56	58,23
357,5	7,28	0,822	3,29	247,33	1,33	57,99
363,2	9,02	0,767	3,29	328,31	-5,60	57,72
364,1	18,87	1,51	5,67	348,61	-1,46	57,68

360,6	9,17	0,877	3,29	292,05	1,18	57,85
358,9	13,40	1,42	5,67	264,20	-1,24	57,93
366,7	11,12	0,767	3,29	404,73	4,07	57,56
369,5	13,82	0,822	3,29	469,45	7,24	57,42

Propylene Carbonate; $\Delta_l^g H_m$ (298,15 K) = (**61,48**±0,31) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{277{,}7}{R} - \frac{77611{,}3}{R\cdot(T,K)} - \frac{54{,}1}{R}\ln\left(\frac{T,K}{298{,}15}\right)$$

298,4	5,26	14,93	9,00	8,50	0,29	61,47
303,3	5,55	10,72	9,00	12,47	0,22	61,21
308,2	5,07	6,75	9,00	18,10	0,11	60,94
311,3	3,89	4,20	9,00	22,30	-0,49	60,77
313,2	6,49	6,18	5,19	25,29	-1,00	60,67
318,2	6,76	4,37	5,19	37,23	-0,64	60,40
321,2	7,28	3,89	5,19	45,03	-1,84	60,24
322,7	3,73	1,73	5,19	51,93	-0,11	60,16
324,2	7,41	3,03	5,19	58,93	1,19	60,07
326,6	7,81	2,77	5,19	67,88	-0,12	59,94
329,6	7,47	2,16	5,19	83,07	-0,04	59,78
332,7	6,23	1,47	5,19	101,9	0,11	59,61
335,7	6,68	1,25	5,19	128,1	4,65	59,45
337,7	7,41	1,30	5,19	137,5	-2,55	59,34
338,8	7,68	1,21	5,19	152,5	2,54	59,28
340,8	8,04	1,12	5,19	172,1	2,44	59,18
341,8	12,21	1,64	5,19	178,7	-1,60	59,12
344,9	10,96	1,21	5,19	217,8	0,38	58,95

Butylene Carbonate; $\Delta_l^g H_m$ (298,15 K) = (**63,19**±0,31) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{285{,}6}{R} - \frac{81554{,}2}{R\cdot(T,K)} - \frac{61{,}6}{R}\ln\left(\frac{T,K}{298{,}15}\right)$$

288,6	2,46	28,17	9,014	1,86	0,03	63,78
293,5	3,96	29,60	9,014	2,84	-0,01	63,48
298,5	3,05	14,27	9,014	4,53	0,13	63,17
303,4	2,57	8,37	4,974	6,49	-0,14	62,87
307,3	2,55	6,22	4,974	8,70	-0,40	62,63
310,3	2,74	4,97	4,974	11,64	0,11	62,44
313,3	4,00	5,88	5,687	14,39	-0,14	62,26
316,3	4,11	4,74	5,687	18,37	0,14	62,07
319,3	4,09	3,79	5,687	22,81	0,07	61,89
322,5	3,85	2,90	4,974	28,05	-0,61	61,69
327,4	4,01	2,07	4,974	40,92	0,52	61,39
330,3	3,98	1,74	4,974	48,39	-0,84	61,21
333,6	6,04	1,99	5,687	64,15	2,79	61,01
338,7	6,17	1,52	5,687	86,00	0,62	60,69
343,8	7,80	1,42	5,687	115,9	-1,6	60,38

Glycerine Carbonate; $\Delta_l^g H_m$ (298,15 K) = (**85,42**±0,37) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{315{,}1}{R} - \frac{105182{,}6}{R\cdot(T,K)} - \frac{66{,}3}{R}\ln\left(\frac{T,K}{298{,}15}\right)$$

330,2	3,13	221,7	9,09	0,29	0,00	83,29
333,2	3,25	174,4	9,37	0,39	0,01	83,09
338,3	3,24	109,8	9,09	0,62	0,01	82,76
343,2	2,25	51,67	9,09	0,91	-0,01	82,43
348,4	2,40	34,62	9,09	1,44	0,03	82,09
351,2	2,25	27,12	9,09	1,73	-0,03	81,90

355,5	3,80	31,71	9,35	2,50	0,02	81,62
360,6	2,56	14,73	9,35	3,62	-0,03	81,28
363,7	2,04	9,81	9,80	4,33	-0,27	81,07
366,4	2,36	9,09	9,09	5,42	-0,20	80,89
369,4	2,37	7,27	9,09	6,81	-0,16	80,69
371,8	3,49	9,32	9,48	7,82	-0,43	80,54
373,2	2,25	5,30	9,09	8,86	-0,23	80,44
377,2	2,13	3,79	9,09	11,71	-0,25	80,18
359,8 [e]	22,3	125,1	10,37	3,68	0,23	81,33
384,5 [e]	7,7	7,93	6,70	20,19	0,77	79,69
387,3 [e]	11,8	10,26	6,41	23,92	0,67	79,51
388,0 [e]	9,0	7,57	5,94	24,71	0,40	79,46
392,7 [e]	12,3	7,66	5,78	33,39	0,76	79,15
398,5 [e]	12,4	5,49	5,78	46,94	0,54	78,77

[a] saturation temperature.

[b] mass of transferred sample condensed at T = 243 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 243 K.

[e] the amount of condensed product was determined by weighing (±0.0001 g).

Table B2. Experimental Vapour Pressures, (p) and Molar Enthalpies of Vaporization, ($\Delta_l^g H_m$ at 298,15 K) of Naphthalene Derivatives (1) and (2) (Scheme 3.1 in Chap. 3) Measured by Transpiration Method.

1-Methylene-1,2,3,4-tetrahydro-naphthalene (1); $\Delta_l^g H_m$ (298,15 K) = (**59,21**±0,70) kJ·mol^{-1}

$$\ln(p/\text{Pa}) = \frac{294,1}{R} - \frac{81152,8}{R\cdot(T/K)} - \frac{73,6}{R}\ln\left(\frac{T/K}{298,15}\right)$$

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ·mol^{-1}
293,0	1,49	2,90	6,96	8,93	-0,23	59,59
293,1	1,87	3,42	7,08	9,54	0,34	59,58
295,0	1,72	2,78	6,91	10,62	-0,16	59,44
296,1	1,42	2,02	7,08	12,23	0,45	59,36
298,1	1,39	1,77	7,08	13,63	-0,28	59,21
298,1	1,23	1,62	6,96	13,17	-0,71	59,21
300,0	1,57	1,73	6,91	15,62	-0,59	59,07
303,1	2,03	1,74	6,96	20,17	-0,36	58,85
305,1	2,35	1,73	6,91	23,24	-0,70	58,70
308,1	2,27	1,22	3,92	32,19	2,10	58,47
308,1	2,95	1,74	6,96	29,32	-0,75	58,48
313,2	1,59	0,643	1,09	42,90	-0,68	58,10
313,2	4,37	1,72	6,79	43,67	0,21	58,10
316,2	1,29	0,436	0,94	50,99	-2,77	57,88
318,2	2,62	0,679	1,09	67,17	5,44	57,73
318,2	6,06	1,70	6,79	61,36	-0,46	57,73
321,2	1,15	0,265	0,94	75,26	-0,50	57,51
323,4	1,57	0,290	1,09	94,12	6,78	57,35
323,4	1,59	0,312	1,14	87,64	0,25	57,35
326,3	1,69	0,273	0,94	107,09	1,62	57,14
328,3	1,99	0,272	1,09	126,85	6,58	56,99
328,3	1,87	0,284	1,14	112,89	-7,15	56,99
330,3	2,56	0,327	0,94	135,26	-1,03	56,84
333,3	2,58	0,272	1,09	164,49	-0,15	56,62
333,4	2,64	0,283	1,13	159,57	-5,78	56,61
334,4	2,70	0,255	1,02	181,48	6,37	56,54
338,4	3,82	0,272	1,09	243,74	20,64	56,25
338,4	3,40	0,260	1,02	223,63	1,06	56,25
338,5	3,52	0,283	1,13	212,34	-11,95	56,24
343,5	5,03	0,278	1,02	308,56	9,34	55,87
343,6	4,75	0,283	1,13	286,46	-14,47	55,87
346,4	4,90	0,234	0,94	359,68	5,53	55,65
347,5	5,11	0,234	0,94	376,23	1,21	55,58
348,5	5,47	0,234	0,94	402,15	5,65	55,50
348,6	6,33	0,283	1,13	381,70	-18,31	55,49
353,6	8,29	0,283	1,13	499,77	-23,83	55,13
358,8	11,06	0,283	1,13	667,52	-16,43	54,75

4-Methyl-1,2-dihydro-naphthalene (2); $\Delta_l^g H_m$ (298,15 K) = (**56,61**±0,46) kJ·mol^{-1}

$$\ln(p/\text{Pa}) = \frac{295,5}{R} - \frac{81941,7}{R\cdot(T/K)} - \frac{74,9}{R}\ln\left(\frac{T/K}{298,15}\right)$$

293,0	2,10	4,45	7,20	8,05	0,19	60,00
295,0	2,17	3,99	7,20	9,39	0,10	59,85
298,5	1,95	2,76	7,20	12,15	-0,23	59,58
303,1	2,41	2,40	7,20	17,32	-0,49	59,24
308,2	2,11	1,42	4,73	25,59	-0,48	58,86
313,2	0,83	0,382	1,09	37,94	0,32	58,49
314,2	2,31	0,972	1,14	40,82	0,45	58,41

318,2	2,24	0,724	1,14	53,16	-0,54	58,11
323,4	2,14	0,495	1,14	74,09	-1,91	57,72
328,2	1,97	0,324	1,14	104,37	0,43	57,36
333,4	2,43	0,286	1,14	146,10	1,72	56,97
338,4	3,29	0,286	1,14	197,75	1,73	56,59
341,5	4,29	0,318	1,14	231,15	-2,94	56,37
343,4	4,47	0,287	1,09	265,52	3,22	56,22
343,5	4,26	0,286	1,14	255,73	-7,62	56,21
358,6	13,93	0,394	1,09	602,76	4,45	55,08

[a] saturation temperature.

[b] mass of transferred sample condensed at T = 243 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 243 K.

Table B3. Experimental Vapour Pressures, (*p*) and Molar Enthalpies of Vaporization, ($\Delta_l^g H_m$ at 298,15 K) of 2-Butanone Oxime and N-Methylpropanamide presented in Scheme 1 (Chap. 4) Measured by Transpiration Method.

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ·mol^{-1}
2-Butanone oxime; $\Delta_l^g H_m$(298,15 K) = (**59,05**±0,20) kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{304{,}28}{R} - \frac{78193{,}23}{R\cdot(T/K)} - \frac{64{,}2}{R}\ln\left(\frac{T/K}{298{,}15}\right)$						
283,4	4,95	3,18	3,47	44,51	-0,2	60,00
285,9	5,49	2,83	3,47	55,38	-0,4	59,84
288,3	5,15	2,08	3,47	70,44	1,7	59,69
290,7	5,05	1,68	3,05	85,23	0,8	59,53
293,4	5,26	1,39	2,25	107,8	1,9	59,36
295,9	5,22	1,16	3,47	127,9	-2,2	59,20
298,3	5,39	0,946	2,27	159,2	1,3	59,05
300,7	5,10	0,762	3,05	189,5	-1,3	58,89
303,3	6,37	0,757	2,27	234,1	0,6	58,72
305,8	5,40	0,553	2,01	277,2	-5,2	58,56
308,4	6,06	0,499	1,76	344,6	1,8	58,40
310,9	5,68	0,395	1,58	406,3	-5,4	58,24
313,4	5,32	0,302	0,91	498,9	6,3	58,08
315,9	4,46	0,224	0,90	563,7	-23,8	57,92
318,3	7,24	0,295	0,89	691,7	-2,0	57,76
318,6	5,66	0,231	0,92	694,3	-13,8	57,74
321,4	6,84	0,231	0,92	855,9	-0,1	57,56
323,5	8,12	0,227	0,91	1012,4	28,1	57,43
325,4	9,10	0,231	0,92	1140,4	25,4	57,31
327,4	8,96	0,199	0,91	1269,5	0,7	57,18
329,3	10,21	0,200	0,92	1444,2	12,0	57,06
N-Methylpropanamide; $\Delta_l^g H_m$ (298,15 K) = (**66,56**±0,19) kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{296{,}10}{R} - \frac{83583{,}26}{R\cdot(T/K)} - \frac{57{,}1}{R}\ln\left(\frac{T/K}{298{,}15}\right)$						
307,2	1,87	3,692	7,64	14,37	-0,2	66,04
309,7	1,78	2,884	7,52	17,74	-0,2	65,90
312,2	2,27	2,851	7,78	23,33	1,3	65,76
317,3	1,91	1,653	6,61	33,57	0,5	65,47
322,3	1,79	1,047	4,19	49,35	0,8	65,18
325,7	1,54	0,713	2,85	61,80	-0,8	64,99
327,2	2,10	0,876	3,50	69,27	-0,6	64,90
329,7	1,86	0,635	2,54	84,06	0,3	64,76
332,2	1,52	0,441	1,76	99,17	-0,8	64,62
334,8	6,87	1,658	1,72	118,98	-0,9	64,47
337,3	1,70	0,357	1,43	137,44	-4,9	64,33
342,2	3,44	0,519	2,40	191,17	-6,4	64,05
344,7	6,78	0,810	3,04	239,08	6,5	63,90
347,2	6,40	0,661	1,89	277,50	4,4	63,76
349,7	6,10	0,561	2,24	311,33	-8,4	63,62
352,2	6,17	0,472	1,89	374,05	0,7	63,48
357,1	6,19	0,360	1,44	492,98	-9,5	63,20
362,3	6,13	0,255	1,02	680,96	-0,6	62,90
364,7	7,03	0,255	1,02	785,95	4,1	62,76
367,3	8,28	0,255	1,02	924,04	19,0	62,61

371,2	10,26	0,255	1,02	1150,75	28,5	62,39

Notes to the **Table B3**:

[a] saturation temperature.

[b] mass of transferred sample condensed at T = 243 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 243 K.

Table B4. Experimental Vapour Pressures, (*p*) and Molar Enthalpies of Vaporization/Sublimation, ($\Delta_l^g H_m$ / $\Delta_{cr}^g H_m$ at 298,15 K) of 1,4-Butanediol, Sebacic Acid (Decanedioic Acid), and Dodecanedioic Acid Measured by Transpiration Method.

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	(p_{exp}-p_{calc})	$\Delta_{cr}^g H_m$ or $\Delta_l^g H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ·mol^{-1}
1,4-Butanediol; $\Delta_l^g H_m$ (298,15 K) = (**79,01**±0,24) kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{333{,}57}{R} - \frac{100293{,}64}{R\cdot(T,K)} - \frac{71{,}4}{R}\ln\left(\frac{T,K}{298{,}15}\right)$						
298,4	1,03	39,05	3,17	0,73	0,00	78,99
303,2	1,35	31,12	3,17	1,19	-0,01	78,65
308,2	0,54	7,55	3,17	1,97	-0,03	78,29
313,2	1,84	15,33	3,17	3,30	0,06	77,93
317,2	1,03	6,00	3,17	4,71	-0,03	77,65
322,3	1,42	5,07	3,17	7,71	0,17	77,28
325,3	1,43	4,02	3,17	9,79	-0,04	77,07
328,3	1,78	3,80	3,17	12,87	0,13	76,86
331,3	1,37	2,32	3,17	16,25	-0,20	76,64
334,4	1,55	2,01	3,17	21,27	0,00	76,42
337,4	1,56	1,59	3,17	27,15	-0,01	76,21
340,4	1,65	1,32	3,17	34,33	-0,16	75,99
343,3	1,66	1,06	3,17	43,27	0,00	75,79
346,3	1,58	0,79	3,17	54,72	0,28	75,57
349,3	1,36	0,55	3,17	67,49	-0,70	75,36
Decanedioic acid, $\Delta_{cr}^g H_m$ (298,15 K) = (**162,7**±2,5) kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{453{,}87}{R} - \frac{175368{,}56}{R\cdot(T,K)} - \frac{42{,}4}{R}\ln\left(\frac{T,K}{298{,}15}\right)$						
390,2	10,4	291,7	10,06	0,43	0,00	158,83
393,1	8,7	172,6	10,06	0,61	-0,01	158,70
395,0	8,9	135,6	10,14	0,79	0,01	158,62
396,0	12,8	173,2	9,35	0,90	0,01	158,58
399,0	9,9	93,0	9,47	1,29	0,02	158,45
400,0	14,3	126,4	10,06	1,37	-0,06	158,41
401,9	9,4	64,1	10,11	1,77	-0,01	158,33
403,2	25,0	143,0	10,14	2,11	0,04	158,28
Decanedioic acid, $\Delta_l^g H_m$ (298,15 K) = (**122,71**±0,69) kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{438{,}23}{R} - \frac{159199{,}02}{R\cdot(T,K)} - \frac{122{,}4}{R}\ln\left(\frac{T,K}{298{,}15}\right)$						
406,7	10,6	45,32	10,34	2,82	-0,05	109,42
406,9	23,4	96,42	10,34	2,94	0,03	109,40
411,7	28,7	82,12	10,34	4,22	-0,04	108,81
415,2	13,2	28,68	10,43	5,58	0,04	108,38
418,5	13,8	23,35	10,34	7,14	0,04	107,98
421,5	15,3	20,68	10,34	8,97	0,12	107,61
423,4	12,7	15,85	10,34	9,67	-0,48	107,38
425,4	14,3	14,48	10,34	11,97	0,26	107,14
426,2	18,2	17,38	10,43	12,58	0,18	107,04
428,3	14,8	12,41	10,34	14,45	0,08	106,78
430,2	18,3	13,65	10,43	16,25	-0,16	106,55
431,2	17,3	11,89	10,34	17,51	-0,07	106,43

432,9	14,3	8,60	10,43	20,14	0,38	106,22
434,2	14,4	7,76	10,34	22,35	0,77	106,06
436,0	13,6	6,78	10,43	24,31	-0,05	105,84
438,1	12,2	5,17	10,34	28,40	0,38	105,58
438,9	15,0	6,08	10,43	29,88	0,34	105,48
440,9	13,9	5,17	10,34	32,36	-1,42	105,23
441,8	16,3	5,56	10,43	35,51	-0,31	105,12
443,9	15,0	4,48	10,34	40,71	-0,30	104,87

Dodecanedioic acid, $\Delta_{cr}^{g}H_m$ (298,15 K) = (**162,2**±2,1) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{459{,}36}{R} - \frac{177853{,}53}{R\cdot(T,K)} - \frac{52{,}6}{R}\ln\left(\frac{T,K}{298{,}15}\right)$$

391,9	8,7	266,8	10,62	0,34	0,00	157,24
392,9	8,0	220,0	10,32	0,39	0,00	157,19
394,9	9,1	191,9	10,62	0,50	0,01	157,08
395,8	11,9	227,1	10,65	0,55	0,00	157,04
395,9	8,8	166,0	10,32	0,56	0,00	157,03
396,8	12,8	214,5	10,62	0,63	0,01	156,98
397,9	9,0	137,3	10,37	0,70	-0,01	156,93
398,6	9,6	133,3	10,75	0,76	-0,02	156,89
399,6	10,5	126,7	10,75	0,87	0,01	156,84
400,8	8,9	93,9	10,43	1,01	0,01	156,77

Dodecanedioic acid, $\Delta_{l}^{g}H_m$ (298,15 K) = (**120,87**±0,37) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{446{,}03}{R} - \frac{162308{,}39}{R\cdot(T,K)} - \frac{139{,}0}{R}\ln\left(\frac{T,K}{298{,}15}\right)$$

404,2	26,9	215,97	5,60	1,32	0,03	106,13
405,2	17,0	129,64	5,60	1,39	-0,01	105,99
405,6	19,1	137,18	10,34	1,48	0,03	105,93
407,0	18,6	122,23	7,74	1,62	0,00	105,74
408,0	13,5	83,02	5,45	1,73	-0,01	105,60
410,2	12,9	68,07	10,34	2,01	-0,04	105,30
414,4	11,2	43,34	10,32	2,74	-0,06	104,71
418,3	12,5	35,59	10,34	3,73	0,01	104,17
421,3	13,1	31,02	10,34	4,48	-0,11	103,75
423,6	13,5	26,38	7,76	5,42	0,02	103,43
424,2	14,1	26,40	10,32	5,67	0,04	103,35
424,7	12,3	22,40	5,43	5,85	0,01	103,28
425,7	12,9	21,84	8,68	6,27	0,03	103,14
428,1	12,4	17,84	10,34	7,38	0,04	102,81
428,6	14,8	20,33	8,56	7,74	0,15	102,74
429,5	13,6	17,92	5,60	8,06	-0,04	102,61
430,6	12,8	15,97	5,43	8,51	-0,18	102,46
431,5	14,1	16,18	8,48	9,27	0,05	102,34
432,9	14,4	14,96	10,32	10,22	0,11	102,14
433,5	10,0	10,13	5,60	10,49	-0,06	102,05
435,8	12,0	10,25	10,34	12,43	0,22	101,74
436,3	11,1	9,40	8,48	12,56	-0,04	101,67
437,8	13,6	10,34	10,34	13,97	0,09	101,46
438,8	11,9	8,68	5,60	14,56	-0,23	101,32

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[a] saturation temperature.

[b] mass of transferred sample condensed at T = 293 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 293 K.

Table B5. Experimental Vapour Pressures, (*p*) and Molar Enthalpies of Vaporization, ($\Delta_l^g H_m$ at 298,15 K) of Methyl-, Ethyl-, iso-Propyl-, n-Propyl-, n-Butyl-, iso-Butyl-, n-Pentyl-3-methyl-but-2-enoate presented in Scheme 1 (Chap. 7) Measured by Transpiration Method.

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}$-$p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	$kJ \cdot mol^{-1}$

Methyl 3-methyl-but-2-enoate [CAS 924-50-5]; $\Delta_l^g H_m$(298,15 K) = (**46,90**±0,19) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{282{,}395}{R} - \frac{66906{,}7}{R \cdot (T/K)} - \frac{67{,}1}{R} \ln\left(\frac{T/K}{298{,}15}\right)$$

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}$-$p_{calc})$	$\Delta_l^g H_m$
274,2	2,2	0,250	0,79	200,4	2,2	48,51
277,2	2,5	0,224	0,79	251,7	2,3	48,31
277,2	2,4	0,224	0,79	248,0	-1,3	48,31
280,2	2,9	0,204	0,79	322,8	10,9	48,11
280,2	3,2	0,229	0,81	301,5	-10,5	48,11
283,2	3,2	0,185	0,79	387,1	-1,0	47,91
283,2	3,3	0,189	0,76	386,5	-1,6	47,91
283,2	3,6	0,202	0,81	386,2	-1,9	47,91
286,2	3,4	0,158	0,79	473,8	-6,4	47,71
286,2	3,8	0,175	0,81	468,9	-11,2	47,71
289,2	4,8	0,177	0,76	603,1	12,1	47,50
289,2	5,2	0,189	0,81	604,1	13,2	47,50
289,2	5,1	0,189	0,81	593,3	2,4	47,50
292,2	4,8	0,151	0,76	704,2	-19,4	47,30
292,2	5,4	0,162	0,81	733,0	9,5	47,30
292,2	4,9	0,148	0,81	726,8	3,3	47,30
295,2	5,3	0,135	0,81	858,9	-22,7	47,10
295,2	6,6	0,162	0,81	894,8	13,3	47,10
298,2	6,5	0,135	0,81	1062,2	-6,8	46,90
301,2	8,0	0,135	0,81	1298,8	8,7	46,70
304,2	9,7	0,135	0,81	1562,7	12,7	46,50

Ethyl 3-methyl-but-2-enoate [CAS 638-10-8]; $\Delta_l^g H_m$(298,15 K) = (**49,30**±0,19) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{291{,}2}{R} - \frac{71776{,}7}{R \cdot (T/K)} - \frac{75{,}4}{R} \ln\left(\frac{T/K}{298{,}15}\right)$$

T [a]	m [b]	$V_{(N2)}$ [c]	Gas-flow	p [d]	$(p_{exp}$-$p_{calc})$	$\Delta_l^g H_m$
273,9	6,3	1,77	7,09	72,5	1,4	51,13
275,4	7,1	1,77	7,09	82,0	1,3	51,01
276,5	7,7	1,77	7,09	88,4	0,6	50,93
278,2	8,7	1,77	7,09	98,9	-1,7	50,80
279,0	3,9	0,71	2,85	105,2	-1,8	50,74
280,3	10,4	1,77	7,09	117,1	-1,4	50,65
282,1	5,3	0,761	2,85	135,2	-0,9	50,51
283,3	5,4	0,720	2,88	149,0	-0,1	50,42
286,3	7,4	0,785	2,85	181,5	-4,9	50,19
287,2	7,2	0,713	2,85	197,8	-1,4	50,13
288,2	7,7	0,720	2,88	211,3	-3,0	50,05
290,1	3,3	0,256	1,02	247,1	1,4	49,91
292,1	11,6	0,791	2,88	286,9	3,9	49,76
293,2	8,3	0,516	1,11	315,3	9,7	49,67
294,4	4,4	0,256	1,02	334,7	2,7	49,58

295.7	15.7	0.850	3.40	361.0	-1.9	49.48
297.1	5.2	0.256	1.02	392.0	-7.0	49.38
298.2	6.0	0.267	1.07	439.0	9.5	49.30
302.3	7.5	0.256	1.02	563.8	1.8	48.99
303.2	8.2	0.267	1.07	599.9	4.4	48.92
306.2	9.6	0.256	1.02	726.5	6.6	48.69
307.2	10.5	0.267	1.07	761.0	-5.1	48.62
310.2	12.2	0.256	1.02	915.8	-4.9	48.39
312.2	13.8	0.256	1.02	1041.5	3.4	48.24
314.1	14.2	0.229	0.92	1198.1	36.7	48.10
314.2	16.1	0.267	1.07	1165.8	-2.4	48.09
315.0	16.3	0.256	1.02	1230.9	6.8	48.03
316.0	17.3	0.267	1.07	1252.4	-44.9	47.95
317.2	17.9	0.252	0.92	1374.9	-15.0	47.86
318.2	32.8	0.428	0.92	1481.7	10.3	47.79
319.1	21.3	0.267	1.07	1536.5	-11.8	47.72

iso-Propyl 3-methyl-but-2-enoate [CAS 25859-51-2]; $\Delta_l^g H_m$(298,15 K) = (**50,01**±0,17) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{301,2}{R} - \frac{74902,2}{R\cdot(T/K)} - \frac{80,7}{R}\ln\left(\frac{T/K}{298,15}\right)$$

278,5	4,4	0,825	2,20	97,2	1,86	52,43
281,5	4,5	0,678	2,20	123,9	0,45	52,19
284,5	5,5	0,660	2,20	154,6	-2,77	51,95
287,5	5,9	0,550	2,20	195,1	1,03	51,71
290,5	6,4	0,477	2,20	241,0	-1,26	51,46
293,5	7,3	0,440	2,20	300,2	-1,24	51,22
298,4	8,1	0,348	2,20	430,0	-7,29	50,83
303,4	10,4	0,312	2,20	589,2	1,57	50,42
308,4	11,0	0,238	2,20	793,0	2,44	50,02
313,4	9,4	0,147	2,20	1092,0	12,98	49,61

n-Propyl 3-methyl-but-2-enoate [Beilstein Registry 6774200];

$\Delta_l^g H_m$ (298,15 K) = (**53,00**±0,19) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{305,1}{R} - \frac{77056,7}{R\cdot(T/K)} - \frac{82,4}{R}\ln\left(\frac{T/K}{298,15}\right)$$

278.3	4.6	1.37	2.54	62.2	0.1	54.13
281.3	5.3	1.18	2.54	80.1	0.3	53.88
284.3	6.6	1.16	2.54	103.5	1.6	53.63
287.3	6.9	1.03	2.54	128.0	-1.3	53.39
290.3	8.0	0.933	2.54	160.3	-2.8	53.14
293.3	8.9	0.852	2.54	201.3	-3.3	52.89
296.3	10.1	0.761	2.54	257.3	2.0	52.65
299.3	11.1	0.679	2.54	321.0	4.3	52.40
302.3	12.0	0.591	2.54	390.0	-0.8	52.15
305.3	13.3	0.510	2.54	480.0	0.2	51.90
308.3	13.4	0.426	2.54	582.6	-3.6	51.66
311.3	13.4	0.337	2.54	717.6	4.8	51.41

n-Butyl 3-methyl-but-2-enoate [CAS 54056-51-8]; $\Delta_l^g H_m$ (298,15 K) = (**56,62**±0,27) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{314,4}{R} - \frac{84050,0}{R\cdot(T/K)} - \frac{92,0}{R}\ln\left(\frac{T/K}{298,15}\right)$$

278,9	1,5	2,44	5,43	9,9	-0,1	58,40
282,5	1,6	1,81	5,43	14,0	0,3	58,06
285,8	1,5	1,35	1,50	17,7	-0,6	57,76
290,1	1,6	0,933	1,51	26,4	0,3	57,37
294,6	2,2	0,935	1,52	38,0	0,4	56,95
297,5	2,3	0,785	1,57	46,7	-0,4	56,68
299,4	3,0	0,925	1,59	53,4	-1,1	56,51
299,8	2,3	0,666	1,41	56,0	-0,2	56,47
302,6	3,0	0,687	1,59	70,4	1,2	56,22
303,3	1,8	0,378	1,51	74,3	1,4	56,15
306,3	2,9	0,503	1,59	92,4	1,9	55,87
307,2	3,1	0,506	1,52	98,8	2,2	55,79
311,3	5,3	0,662	1,59	128,6	-0,1	55,41
312,2	3,2	0,385	1,54	132,8	-4,1	55,33
315,3	6,0	0,565	1,61	169,8	1,1	55,05
316,2	3,9	0,341	1,46	181,1	2,0	54,96
316,3	6,4	0,580	1,58	176,8	-3,4	54,95
318,3	6,6	0,514	1,62	202,8	-2,7	54,77
318,3	5,4	0,410	1,59	210,4	4,9	54,77
318,3	9,9	0,767	1,59	204,2	-1,3	54,77
319,3	6,5	0,477	1,51	216,9	-2,3	54,68
321,3	5,8	0,375	1,61	245,4	-3,8	54,49
323,3	9,4	0,527	1,76	284,9	2,2	54,31

iso-Butyl 3-methyl-but-2-enoate [CAS 30434-54-9]; $\Delta_l^g H_m$ (298,15 K) = (**54,68**±0,22) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{313,8}{R} - \frac{81600,4}{R\cdot(T/K)} - \frac{90,3}{R}\ln\left(\frac{T/K}{298,15}\right)$$

279,6	2,1	1,22	2,87	27,7	-0,3	56,36
282,5	2,1	0,961	2,88	35,9	0,1	56,10
284,4	2,4	0,931	2,87	41,8	-0,2	55,92
285,6	3,2	1,105	2,88	46,9	0,5	55,82
288,5	2,7	0,721	2,88	59,4	0,6	55,55
291,5	3,5	0,745	2,88	76,1	1,6	55,28
293,5	5,5	1,029	2,87	86,6	-0,4	55,10
293,5	5,9	1,077	2,87	87,8	0,8	55,10
293,6	2,7	0,480	1,15	90,8	3,1	55,09
295,5	2,4	0,382	1,15	100,6	-0,8	54,92
297,4	6,4	0,886	2,87	116,1	-0,8	54,75
298,4	2,6	0,345	1,15	122,7	-3,2	54,66
300,5	2,6	0,288	1,15	144,7	-2,2	54,47
303,3	3,2	0,288	1,15	181,2	1,7	54,22
304,3	2,9	0,230	0,92	196,9	4,2	54,13
306,4	4,0	0,288	1,15	218,8	-4,2	53,94
307,4	4,9	0,335	2,87	232,7	-6,2	53,85
308,3	4,6	0,297	1,15	250,4	-3,7	53,77
309,3	5,3	0,307	0,92	273,4	1,5	53,68

310,4	5,2	0,288	1,15	288,2	-4,6	53,58
313,4	6,3	0,288	1,15	350,1	-6,8	53,30
314,3	5,9	0,253	0,92	369,1	-9,4	53,22
317,3	6,3	0,215	0,92	463,3	4,7	52,95
320,4	5,7	0,161	0,92	563,9	7,2	52,67
323,5	63,7	1,44	2,87	704,3	31,8	52,39

n-Pentyl 3-methyl-but-2-enoate [Beilstein Registry Number 8048681];

$\Delta_l^g H_m$ (298,15 K) = (**61,83**±0,40) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{331{,}0}{R} - \frac{91737{,}6}{R \cdot (T/K)} - \frac{100{,}3}{R} \ln\left(\frac{T/K}{298{,}15}\right)$$

288,6	1,9	3,71	4,95	7,3	0,1	62,80
291,3	2,1	3,30	4,95	9,0	-0,2	62,53
293,5	2,2	2,89	4,96	10,9	-0,2	62,30
296,4	2,4	2,47	4,95	14,2	0,0	62,01
298,5	2,5	2,07	4,96	17,0	0,1	61,80
300,4	2,2	1,61	4,83	19,8	0,0	61,61
303,4	2,1	1,23	2,55	25,0	-0,4	61,31
305,3	2,5	1,21	4,85	30,2	0,8	61,12
308,4	2,4	0,936	2,55	38,1	0,6	60,81
310,3	2,5	0,801	1,92	44,4	1,1	60,62
313,2	8,2	2,252	2,73	52,6	-1,3	60,33
315,4	2,5	0,561	1,92	63,9	0,6	60,11
323,3	6,7	0,865	2,73	110,5	0,1	59,32
323,3	3,8	0,501	2,73	108,3	-2,1	59,32

[a] saturation temperature.

[b] mass of transferred sample condensed at T = 243 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 243 K.

Table B6. Experimental Vapour Pressures, (*p*) and Molar Enthalpies of Vaporization, ($\Delta_l^g H_m$ at 298,15 K) of 1,2-Ethanediol Monoacetate, 1,2-Ethanediol Diacetate and 1,2,3-Propanetriol Triacetate (Chap. 8) Measured by Transpiration Method.

1,2-Ethanediol monoacetate; $\Delta_l^g H_m$ (298,15 K) = (**63,89**±0,32) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{304{,}87}{R} - \frac{82789{,}41}{R\cdot(T/K)} - \frac{63{,}4}{R}\ln\left(\frac{T/K}{298{,}15}\right)$$

T ^{a} K	m ^{b} mg	$V_{(N2)}$ ^{c} dm^3	Gas-flow dm^3/h	p ^{d} Pa	(p_{exp}-p_{calc}) Pa	$\Delta_l^g H_m$ kJ·mol^{-1}
301,3	6,13	4,22	2,22	34,44	0,13	63,69
305,4	5,46	2,67	3,90	48,40	0,17	63,43
308,3	5,20	2,07	2,22	59,14	-1,86	63,25
311,9	4,99	1,47	3,68	79,96	-1,10	63,02
315,4	5,11	1,15	2,22	106,3	0,2	62,80
319,1	5,57	0,921	3,68	142,8	2,8	62,56
322,2	4,46	0,610	2,22	175,9	0,3	62,37
324,2	4,68	0,537	2,15	206,8	4,0	62,24
325,9	4,54	0,462	1,85	233,2	4,5	62,13
329,6	6,03	0,490	1,90	296,2	0,6	61,90
332,7	7,11	0,462	1,85	366,1	1,3	61,70
336,7	9,37	0,474	1,90	475,9	0,7	61,45
340,3	12,53	0,493	1,85	601,5	2,2	61,22
343,6	11,01	0,366	1,13	721,6	-15,8	61,01
346,3	13,09	0,360	1,20	864,0	-6,8	60,84

1,2-Ethanediol diacetate; $\Delta_l^g H_m$ (298,15 K) = (**61,40**±0,15) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{317{,}21}{R} - \frac{85434{,}25}{R\cdot(T/K)} - \frac{80{,}6}{R}\ln\left(\frac{T/K}{298{,}15}\right)$$

T ^{a} K	m ^{b} mg	$V_{(N2)}$ ^{c} dm^3	Gas-flow dm^3/h	p ^{d} Pa	(p_{exp}-p_{calc}) Pa	$\Delta_l^g H_m$ kJ·mol^{-1}
291,2	5,62	4,29	2,74	22,04	0,07	61,97
293,4	5,95	3,74	2,74	27,04	0,43	61,79
295,5	8,16	4,19	2,74	32,77	0,92	61,62
298,2	6,52	2,77	2,13	39,84	-0,12	61,40
300,4	5,08	1,82	2,74	47,38	-0,52	61,23
305,6	5,46	1,31	2,12	70,63	-1,97	60,81
306,2	5,91	1,32	2,74	75,92	-0,16	60,76
310,7	4,26	0,687	2,75	105,4	-2,0	60,40
312,2	5,35	0,777	2,12	118,1	-2,5	60,27
315,8	6,40	0,687	2,75	157,8	1,3	59,98
318,2	6,42	0,585	2,06	185,8	-0,1	59,79
319,2	7,39	0,635	2,12	199,1	-0,4	59,71
320,6	6,55	0,495	1,98	222,2	2,2	59,60
323,3	7,02	0,447	2,06	265,9	0,7	59,38
325,5	6,05	0,331	1,32	308,0	0,1	59,20
326,2	5,64	0,298	1,19	322,5	-0,1	59,15
328,4	8,00	0,363	1,45	373,1	-0,2	58,97
330,8	8,50	0,331	1,32	433,4	-3,1	58,78
333,3	8,91	0,290	1,34	520,7	8,4	58,57
334,2	9,52	0,298	1,19	547,1	4,8	58,50

1,2,3-Propanetriol triacetate [e]; $\Delta_l^g H_m$ (298,15 K) = (**81,88**±0,33) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{374{,}98}{R} - \frac{115182{,}27}{R\cdot(T/K)} - \frac{111{,}7}{R}\ln\left(\frac{T/K}{298{,}15}\right)$$

320,1	23,2	114,7	5,90	2,40	0,03	79,43
322,1	25,4	104,5	5,90	2,87	0,01	79,21
323,9	23,5	79,76	6,14	3,31	-0,05	79,01
325,9	12,5	35,45	5,89	3,89	-0,13	78,78
328,0	11,5	27,01	6,41	4,89	0,04	78,55
330,0	10,8	22,31	6,41	5,56	-0,21	78,33
333,0	9,3	13,66	5,94	7,59	0,13	77,99
335,9	12,8	15,15	5,90	9,57	0,07	77,67
338,0	7,4	7,13	5,94	11,52	0,23	77,43
340,0	13,7	11,80	5,90	13,14	-0,14	77,21
341,9	11,1	8,07	5,90	15,56	0,10	77,00
342,9	33,8	22,00	5,89	16,97	0,25	76,89
345,9	18,6	9,77	5,81	21,25	0,13	76,55
347,9	34,0	15,93	4,14	24,39	-0,22	76,33
349,9	16,5	6,29	5,81	29,26	0,65	76,10
349,9	32,5	12,62	4,14	29,43	0,82	76,10
351,9	30,0	10,41	4,14	33,61	0,42	75,88
352,9	13,	4,06	5,81	34,96	-0,76	75,77
353,9	13,2	3,99	6,14	37,13	-1,29	75,66
354,9	42,0	11,67	4,07	41,10	-0,21	75,55
354,9	14,3	3,79	6,14	42,40	1,09	75,55
355,9	14,0	3,48	5,81	44,77	0,38	75,43
356,9	37,0	8,69	4,07	48,64	0,96	75,32
357,9	11,2	2,32	5,81	52,66	1,48	75,21
358,9	38,4	8,08	4,07	53,22	-1,68	75,10
359,9	12,4	2,42	5,81	57,08	-1,81	74,99
360,9	13,5	2,32	5,81	62,27	-0,84	74,88

[a] saturation temperature.

[b] mass of transferred sample condensed at T = 243 K.

[c] volume of nitrogen used to transfer m of the sample.

[d] vapor pressure at temperature T, calculated from the m and the residual vapor pressure at T = 243 K.

[e] the amount of condensed product was determined by weighing (±0.0001 g).

Table B7. Compilation of Data on Hydrogen Solubility in Various Solvents (Total Pressure 0,1 MPa).

	1	*2*	*3*	*4*	*5*	*6*	*7*
Solvent	T, K	*p*-range,[a] MPa	$x \times 10^4$	k_{H}, MPa	$\ln x = a + b / (T/100K)$[b]		Ref.
					a	*b*	
Methanol	248,4	0,56-2,27	1,08	935	-	-	254
	263,4	0,48-2,04	1,14	885	-	-	254
	278,0	0,45-3,01	1,40	723	-	-	254
	291,2	0,43-2,51	1,56	651	-	-	254
	308,2	0,75-3,43	1,85	547	-	-	254
	298,2	-	1,65[c]	-	2,84	-6,97[d,e]	254
	291	1,1-3,62	1,71	585	-	-	255
	291	1,64-4,85	1,14	878	-	-	257
Ethanol	298	0,3-2,0	1,95	513	-	-	256
	323	0,3-2,0	2,27	441[d]	-	-	Ibid.
	291	1,39-3,12	2,20	455	-	-	255
Propanol-1	298	2,5-9,9	2,22	450,1	-0,9041	0,5684	258
	323	2,4-10,6	2,51	398	-	-	258
	373	2,3-9,8	3,39	295	-	-	258
	291	1,27-3,04	2,44	410	-	-	255
Propanol-2	298	0,75-9,72	2,59	386,5	-0,7987	0,5794	258
	323	0,7-9,24	2,83	353	-	-	
	373	0,94-8,92	3,95	253	-	-	
Butanol-1	298	0,58-9,73	2,56	391	-0,5307	0,4932	258
	323	0,49-9,93	2,90	345	-	-	
	373	0,98-7,8	3,70	270	-	-	
	291	1,52-3,10	2,79	359	-	-	255
Butanol-2	298	2,81-9,86	2,65	377	-0,8896	0,6233	258
	323	3,01-9,86	3,05	328	-	-	
	373	1,98-10,0	4,22	237	-	-	
2-Methylpropanol-1	298	2,65-9,72	2,70	370,1	-0,5587	0,5216	258
	323	3,45-8,25	3,10	323	-	-	
	373	2,65-8,89	4,00	250	-	-	
Pentanol-1	298	2,72-9,8	2,87	349	-0,4724	0,5112	258
	323	2,54-8,84	3,25	308	-	-	
	373	3,34-7,97	4,20	238	-	-	
Hexanol-1	298	3,01-9,87	3,10	322,2	-0,4613	0,5383	258
	323	3,4-10,34	3,65	274	-	-	
	373	3,26-10,24	4,67	214	-	-	
2-Ethylhexanol-1	298	1,97-9,46	3,64	274,6	-0,3109	0,5389	258
	323	5,03-9,78	4,2	238	-	-	
	373	6,26-9,65	5,46	183	-	-	
2-Methoxy-ethanol	298	3,42-10,10	1,42	705,6	-1,7482	0,7068	258
	323	3,36-8,10	1,74	576	-	-	
	373	2,75-8,78	2,42	413,1	-	-	
2-Ethoxy-ethanol	298	2,39-10,82	1,99	502,4	-1,1835	0,6289	258
	323	2,62-10,3	2,35	426	-	-	
	373	5,61-10,2	3,19	313	-	-	
2-Butoxy-ethanol	298	4,41-84,4	2,95	339,3	-0,7058	0,5941	258
	323	3,44-10,27	3,29	304	-	-	
	373	3,62-8,4	4,57	219	-	-	

Continue of Table	*1*	*2*	*3*	*4*	*5*	*6*	*7*
Ethandiol-1,2	298	2,53-8,59	0,38	2616,1	-2,8693	0,6404	258
	323	2,68-8,97	0,45	2219,3			
	373	3,94-8,74	0,62	1616,9			
Propandiol-1,3	298	1,93-10,31	0,63	1584	-2,0278	0,5258	259
	323	1,71-10,32	0,72	1390			
	373	1,88-10,22	0,94	1068			
Butanediol-1,4	298	1,54-9,89	0,86	1163	-1,6979	0,5178	259
	323	2,17-9,6	0,97	1033			
	373	2,53-9,42	1,26	793			
Ethylene glycol dimethyl ether	298	1,16-9,53	3,44	291	-0,7483	0,6668	259
	323	1,71-9,82	4,12	243			
	373	2,13-9,73	5,68	176			
Diethylene glycol	298	1,92-9,99	0,74	1359	-2,2195	0,6437	259
	323	2,74-9,96	0,88	1139			
	373	2,41-9,99	1,20	836			
Diethylene glycol monomethyl ether	298	1,44-10,19	1,66	602	-1,5643	0,698	259
	323	1,49-10,41	2,02	494			
	373	2,11-10,63	2,82	355			
Triethylene glycol monomethyl ether	298	1,76-10,26	1,95	513	-1,4034	0,6971	259
	323	1,66-10,38	2,36	423			
	373	1,81-10,30	3,30	303			
Triethylene glycol	298	2,05-10,06	1,00	996	-2,0989	0,7067	259
	323	1,99-10,41	1,21	826			
	373	2,59-9,97	1,71	585			
Octene-1	298	0,3-2,0	6,41	156	-	-	256
	323	0,3-2,0	7,41	135	-	-	
Acetone	298	0,3-2,0	2,74	365			256
	323	0,3-2,0	3,43	292			
	298	1,47-9,48	2,81	356	-1,243	0,7651	260
	323	1,76-9,96	3,45	290			
	373	3,14-8,44	5,0	200			
Acetonitrile	298	0,3-2,0	1,83	545			256
	323	0,3-2,0	2,10	476			
	298	1,59-10,25	1,71	584	-1,5924	0,7168	260
	323	1,55-10,05	2,08	480			
	373	0,95-10,39	2,94	340			
1-Hexane	298	1,53-9,19	6,76	148	0,3946	0,5088	260
	323	1,38-8,82	7,69	130			
	373	2,05-9,81	9,90	101			
1-Octane	298	2,89-14,77	6,13	163	0,3174	0,5054	260
	323	2,40-14,37	7,14	140			
	373	3,05-15,27	9,01	111			
1-Decane	298	2,37-10,35	6,41	156	0,1338	0,5832	260
	323	2,82-9,42	7,69	130			
	373	2,04-9,4	10,0	100			
Toluene	298	0,87-10,12	3,05	328	0,8138	0,6511	260
	323	1,02-9,88	3,70	270			
	373	0,98-9,79	5,00	200			
N,N-diMethyl formamide	298	3,28-9,77	1,42	704	-1,8673	0,7473	260
	323	2,75-10,06	1,75	570			
	373	2,43-9,73	2,50	400			
Tetrahydrofuran	298	3,71-9,66	2,71	369	-1,2194	0,7461	260
	323	2,95-8,66	3,33	300			
	373	3,38-9,58	4,76	210			

Continue of Table	*1*	*2*	*3*	*4*	*5*	*6*	*7*
1,4-Dioxane	298	1,90-9,46	1,81	552	-1,6554	0,7595	260
	323	2,86-9,94	2,27	440			
	373	2,78-9,12	3,23	310			
1-Me-pyrrolidone	298	2,78-8,34	1,40	714	-1,7548	0,7035	260
	323	2,17-8,72	1,69	590			
	373	1,41-9,74	2,38	420			
Methyl formate	291	1,19-2,71	1,93	517	-	-	255
Ethyl formate	291	1,6-4,1	2,76	362	-	-	
Methyl acetate	291	1,15-3,1	2,50	400	-	-	
Ethyl acetate	291	1,6-4,6	3,37	297	-	-	
1-Propyl acetate	291	1,59-4,09	4,07	246	-	-	
2-Propyl acetate	291	1,31-3,04	4,81	208	-	-	
1-Butyl acetate	291	1,42-3,10	4,42	226	-	-	
Methyl propanoate	291	1,6-4,1	3,61	277	-	-	
Methyl butanoate	291	1,59-3,85	4,48	223	-	-	
Methyl 2-MePropanoate	291	1,59-4,12	4,58	218	-	-	
Aminoethane	298	5,3-8,77	3,10	322,4	-1,5393	0,8923	260
	323	5,3-8,84	3,77	265,5			
	373	5,86-9,85	6,02	166,8			
1,2-diAminoethane	298	5,34-7,37	0,72	1393,5	-3,2792	0,9895	260
	323	2,25-8,52	0,93	1081			
	373	3,03-8,07	1,51	662,6			
1-Aminopropane	298	2,87-8,67	3,33	300,3	-0,9392	0,72	260
	323	2,76-7,51	4,03	248			
	373	1,93-7,37	5,73	174,6			
2-Aminopropane	298	1,01-7,37	3,80	262,9	-1,2015	0,85	260
	323	3,08-7,96	4,67	214,3			
	373	4,07-7,3	7,18	139,2			
1,3-diAminopropane	298	3,89-9,72	0,97	1026,3	-2,8033	0,9344	260
	323	5,0-9,42	1,26	795,5			
	373	5,48-7,69	1,97	507,1			
Pyrrolidine	298	4,53-10,27	2,02	495,3	-1,5412	0,7536	260
	323	3,67-8,85	2,45	407			
	373	4,2-9,34	3,55	281,3			
Piperidine	298	4,02-8,7	2,34	426,5	-1,445	0,7724	260
	323	4,54-9,82	2,88	346,7			
	373	2,81-5,11	4,20	238,3			
1-Me-pyrrolidine	298	3,17-9,8	3,82	262	-0,33	0,5611	260
	323	3,03-9,92	4,43	225,7			
	373	3,26-8,49	5,82	171,7			
1-diMe-amino-propylamine-3	298	4,42-10,51	2,98	336,1	-0,8407	0,6522	260
	323	5,65-8,29	3,62	276,1			
	373	6,73-9,59	4,89	204,7			
1-Me-piperidine	298	2,78-10,3	3,72	268,5	-0,4228	0,5816	260
	323	2,96-9,89	4,27	234,3			
	373	5,06-9,8	5,75	173,9			
Triethylamine	298	3,41-9,38	5,71	175,1	0,206	0,522	260
	323	2,11-8,22	6,84	146,2			
	373	2,69-9,88	8,53	117,2			
1,6-Diamino-hexane	298	9,53-30,2	2,23	449	-0,4822	0,4405	260
	323	4,94-30,2	2,68	372,7			
	373	4,94-30,1	3,15	317,8			

Continue of Table	*1*	*2*	*3*	*4*	*5*	*6*	*7*
Bis-(3-aminopropyl)-amine	298	6,1-9,74	1,47	679,9	-1,9354	0,7855	260
	323	4,74-8,55	1,89	530,3			
	373	4,21-9,95	2,68	373,3			
di-Methylamino cyclohexane	298	5,04-8,3	3,81	262,5	-0,2482	0,534	260
	323	4,16-7,94	4,42	226			
	373	4,89-8,9	5,70	175,3			
di-n-Buthylamine	298	3,99-9,23	5,28	189,5	0,0044	0,5627	260
	323	2,38-7,57	6,37	157,1			
	373	2,07-8,39	8,12	123,1			
N,N-Bis-(3-aminopropyl)-ethylenediamine	298	3,15-9,15	1,72	582,1	-1,8295	0,7994	260
	323	4,48-8,73	2,17	461,8			
	373	4,43-8,39	3,15	317,6			
Tri-nBu-amine	298	4,38-9,06	6,93	144,4	0,5584	0,4672	260
	323	4,4-7,5	8,10	-			
	373	4,41-7,68	9,91	-			
di-Methyl carbonate	298	-	2,42	418	-	-	261
di-Ethyl carbonate	298	-	3,89	260	-	-	
Propylene carbonate	283	0,10-1,01	1,01	1003	-	-	
	298	0,10-1,01	1,13	903	-	-	
	323	0,10-1,01	1,43	704	2,85	-8,08	262
	283	8,07-11,63	0,72	1410	-	-	
	298	7,32-12,25	0,84	1210	-	-	
	323	7,35-13,72	1,01	1008	2,4	-7,74	263
	298	0,25-3,1	1,10	921	-	-	
	323	0,25-3,1	1,15	881	-	-	
	398	0,25-3,1	1,81	560	2,85	-8,08	264
Butylene carbonate	283,3	1,47-9,12	1,19	845	-	-	265
	298,2	2,24-9,18	1,35	753	-	-	
	323,1	1,58-9,27	1,60	635	2,57	-6,79	
CH_2Cl_2	298	0,71-0,82	1,86	538	4,17	-10,58	266
$CHCl_3$	298	0,63-0,72	2,16	463	4,56	-11,32	266
	298		2,20	454			267
CCl_4	298		3,22	311			266

[a] saturation vapour pressure of the solvent [268-270] at T was taken into account.

[b] coefficients of the linear regression $\ln x_2 = a + b/(T/100K)$.

[c] calculated using eq. 3.3 (Chap. 3).

[d] additional data on the high-temperature solubility are given in the work [271,272].

[e] additional data on the high-temperature solubility are given in the work [257].

Table B8. Formula, Density, ρ (293 K), Massic Heat Capacity, C_p (298,15 K), and Expansion Coefficients $(\delta V/\delta T)_p$ of Compounds, studied in this work.

Compound	Formula	ρ [c]	C_p [d]	$(\delta V/\delta T)_p$ [e] $\cdot 10^{-6}$
		$g \cdot cm^{-3}$	$J \cdot K^{-1} \cdot g^{-1}$	$dm^3 \cdot K^{-1}$
Polyethylene[a]	$CH_{1,93}$	0,92	2,53	0,1
Cotton[b]	$CH_{1,774}O_{0,887}$	1,50	1,67	0,1
Ethylene carbonate	$C_3H_4O_3$	1,32	1,33	0,1
Propylene carbonate	$C_4H_6O_3$	1,23 [f]	1,20	1,0
Butylene carbonate	$C_5H_8O_3$	1,14	1,20	1,0
2-Butanone oxime	C_4H_9ON	0,932	2,37	1,0
1,4-Butanediol	$C_4H_{10}O_2$	1,010	1,20	1,0
Decanedioic acid	$C_{10}H_{18}O_4$	1,209 [g]	1,20	0,1
Dodecanedioic acid	$C_{12}H_{22}O_4$	1,190 [g]	1,20	0,1
Polybutylene sebacate	$C_{14}H_{24}O_4$	1,10	1,20 [h]	0,1
1,2-Ethanediol monoacetate	$C_4H_8O_3$	1,110	1,95	1,0
1,2-Ethanediol diacetate	$C_6H_{10}O_4$	1,128	1,84	1,0
1,2,3-Propanetriol triacetate	$C_9H_{14}O_6$	1,160	1,78	1,0
Polyamidine (IIIa)	$C_{13}H_9ON_2$	1,20	1,20 [h]	0,1

[a] $\Delta_c u^\circ = -(46361{,}0 \pm 3{,}1)$ $J \cdot g^{-1}$ based on 13 combustion experiments.

[b] $\Delta_c u^\circ = -(16945{,}2 \pm 4{,}2)$ $J \cdot g^{-1}$ based on 10 combustion experiments.

[c] measured with pycnometer.

[d] C_p (liq. or cr.) / M_w, where C_p (liq. or cr.) was calculated acc. to procedure in [19];

[e] tabulated for solids (0,1 $dm^3 \cdot K^{-1}$) and liquids (1,0 $dm^3 \cdot K^{-1}$).

[f] from the work [273].

[g] from the work [274].

[h] from DSC measurements.

Table B9.[a] Compilation of Typical Data Obtained from Combustion Calorimetry for Compounds at 298,15 K and 0,1 MPa.

	2	3	4	5	6	7	8	9	10	11	12	13
Compound	№	$m_{\text{(comp.)}}$, g [b]	$m'_{\text{(cotton)}}$, g [b]	$m''_{\text{(polyethylene)}}$, g [b]	ΔT_c/K [c]	$(e_{calor})\cdot(-\Delta T_c)$, J	$(e_{cont})\cdot(-\Delta T_c)$, J	ΔU_{decomp} (HNO_3), J	ΔU_{corr} [d], J	$-m'\cdot\Delta_C u'$, J	$-m''\cdot\Delta_C u''$, J	$\Delta_C u^\circ$ (cr.) or (liq.), ($J\cdot g^{-1}$)
Ethylene carbonate	1	1,032182	0,003649	-	0,92930	-13755,6	-15,93	-	15,52	61,83	-	-13267,2
	2	1,068698	0,00356	-	0,96230	-14243,9	-16,62	-	16,14	60,32	-	-13272,3
	3	1,030644	0,004035	-	0,92873	-13747,1	-15,96	-	15,51	68,37	-	-13272,4
	4	1,012889	0,003655	-	0,91161	-13493,6	-15,59	-	15,2	61,93	-	-13261,1
	5	1,017638	0,004068	-	0,91689	-13571,8	-15,69	-	15,29	68,93	-	-13269,2
	6	1,008019	0,003501	-	0,90804	-13440,8	-15,52	-	15,12	59,32	-	-13275,4
	7	1,036652	0,004235	-	0,93439	-13830,8	-16,03	-	15,6	71,76	-	-13273
Propylene carbonate	1	0,497919	0,003551	0,283244	1,49185	-22083,3	-27,5	43,00	9,99	60,17	13131,48	-17806,4
	2	0,491504	0,003376	0,297263	1,52777	-22615	-28,25	44,20	10,13	57,21	13781,41	-17803,1
	3	0,575586	0,003686	0,291872	1,61265	-23871,4	-30,12	45,99	11,21	62,46	13531,48	-17808,5
	4	0,529713	0,003179	0,292214	1,55741	-23053,7	-28,8	44,20	10,56	53,87	13547,33	-17795,6
	5	0,53881	0,003722	0,290877	1,56596	-23180,3	-28,61	44,79	25,36	63,07	13485,35	-17799,0
Butylene carbonate	1	0,393786	0,003535	0,288258	1,47442	-21825,3	-27,01	44,79	8,62	59,9	13363,93	-21268,1
	2	0,603616	0,003363	0,302798	1,82201	-26970,5	-34,62	52,56	11,78	56,99	14038,02	-21281,3
	3	0,441995	0,003386	0,288243	1,5434	-22846,3	-28,43	44,79	9,27	57,38	13363,23	-21267,4
	4	0,367577	0,003395	0,294574	1,45614	-21554,7	-26,57	42,41	8,37	57,53	13656,75	-21264,1
	5	0,30439	0,003536	0,29045	1,35243	-20019,4	-24,46	40,02	7,48	59,92	13465,55	-21258,7
2-Butanone oxime [e]	1	0,313627	0,003436	0,2823	1,55155	-22966,9	-28,52	61,52	6,52	58,22	13087,71	-31188,2
	2	0,312235	0,003682	0,276796	1,53174	-22673,8	-28,15	59,73	6,43	62,39	12832,54	-31197,1
	3	0,310214	0,003604	0,277683	1,53004	-22648,6	-28,08	59,62	6,45	62,41	12873,66	-31186,3
	4	0,328539	0,003214	0,276697	1,56542	-23172,3	-28,82	65,7	6,55	54,46	12827,95	-31187,9
1,4-Butanediol [f]	1	0,429923	0,003311	0,284385	1,69911	-25158,9	-32,16	48,08	7,45	56,1	13184,37	-27668,0
	2	0,478599	0,003038	0,283669	1,7884	-26481	-34,19	50,77	7,91	51,48	13151,18	-27693,1
	3	0,415055	0,003202	0,286182	1,6775	-24838,9	-31,73	48,98	7,32	54,26	13267,68	-27688,9
	4	0,44535	0,003262	0,27958	1,71286	-25362,5	-32,57	48,38	7,53	55,27	12961,61	-27668,8
	5	0,45933	0,003044	0,286494	1,76122	-26078,6	-33,59	51,07	7,74	51,58	13282,15	-27691,8
	6	0,444315	0,003015	0,30304	1,7837	-26411,4	-34	51,36	7,89	51,09	14049,24	-27651,2

Sebacic acid (Decanedioic acid) [f]	1	0,535288	0,003078	0,284317	1,86025	-27544,9	-35,43	49,57	11,8	52,16	13181,22	-26687,7
	2	0,521116	0,003292	0,285018	1,83731	-27205,2	-34,92	50,17	11,57	55,78	13213,72	-26690,6
	3	0,523119	0,002914	0,281731	1,82989	-27095,3	-34,72	50,17	11,54	49,38	13061,33	-26681,5
	4	0,513292	0,003298	0,270997	1,7782	-26330	-33,56	48,98	11,18	55,88	12563,69	-26659
	5	0,504985	0,003533	0,2867	1,81408	-26861,3	-34,31	49,57	11,32	59,87	13291,7	-26700,1
	6	0,546377	0,003213	0,294554	1,9123	-28315,6	-36,46	52,26	12,14	54,44	13655,82	-26680,1
Dodecanedioic acid [f]	1	0,399131	0,001076	0,375895	1,96335	-29071,6	-37,67	51,07	10,82	18,23	17426,87	-29068,8
	2	0,487733	0,001154	0,252601	1,75192	-25940,9	-33,06	47,18	10,04	19,55	11710,83	-29086,3
	3	0,366511	0,001245	0,409833	2,00574	-29708,7	-38,28	51,96	11,19	21,1	19000,27	-29091,7
	4	0,306905	0,001271	0,423914	1,93295	-28630,4	-36,63	51,66	10,43	21,54	19653,08	-29098
	5	0,472464	0,001338	0,370035	2,08941	-30948	-40,54	56,44	11,86	22,67	17155,19	-29086,5
Polybutylene sebacate [g]	1	0,698081	0,001535	0,349821	2,53324	-37532,5	-45,26	60,92	16,48	26,01	16215,78	30452,8
	2	0,450212	0,000958	0,101392	1,24464	-18440,6	-19,54	31,66	7,64	16,23	4699,98	-30440,3
	3	0,618291	0,001063	-	1,26971	-18812	-19,93	39,42	8,63	18,01	-	-30454,1
Methyl 3-methylbut-2-enoate [f]	1	0,379873	0,00113	0,425501	2,09231	-30981	-39,96	58,53	10,94	19,15	19726,65	-29498,5
	2	0,343892	0,001097	0,396752	1,93113	-28594,5	-36,51	53,75	9,92	18,59	18393,82	-29529,4
	3	0,33505	0,001111	0,365043	1,8139	-26858,6	-33,89	50,47	9,23	18,83	16923,76	-29518,4
	4	0,319133	0,000995	0,356817	1,75629	-26005,6	-32,7	49,57	8,87	16,86	16542,39	-29519,5
	5	0,354138	0,000965	0,358857	1,83251	-27134,2	-34,28	50,77	9,4	16,35	16636,97	-29522,4
	6	0,342581	0,001204	0,400988	1,94145	-28747,3	-36,69	54,35	9,97	20,4	18590,2	-29508,6
Ethyl 3-methylbut-2-enoate [f]	1	0,504222	0,002959	0,288531	1,97317	-29216,9	-37,48	54,95	10,39	50,14	13376,59	-31260,7
	2	0,389369	0,002853	0,279383	1,70302	-25216,7	-31,52	48,98	8,55	48,34	12952,48	-31306,8
	3	0,473725	0,002824	0,289855	1,91422	-28344,1	-36,21	54,95	9,93	47,85	13437,97	-31304,2
	4	0,456115	0,003095	0,305124	1,92471	-28499,4	-36,37	52,26	9,98	52,44	14145,85	-31297,5
	5	0,413918	0,003157	0,288676	1,78295	-26400,4	-33,35	49,57	9,09	53,5	13383,31	-31258
	6	0,440839	0,003516	0,297724	1,86872	-27670,4	-35,09	53,75	9,6	59,58	13802,78	-31257,9
	7	0,4336	0,003215	0,28195	1,80439	-26717,8	-33,74	49,57	9,25	54,48	13071,48	-31288,7
	8	0,326432	0,002931	0,29275	1,61157	-23862,6	-29,68	46,89	7,91	49,67	13572,18	-31295
Propyl 3-methylbut-2-enoate [f]	1	0,411326	0,001181	0,290363	1,82339	-26999,2	-34,24	45,39	9,08	20,01	13461,52	-32814,4
	2	0,427197	0,001122	0,28717	1,84823	-27367	-34,7	50,77	9,19	19,01	13313,49	-32793,3
	3	0,426025	0,001156	0,28544	1,84082	-27257,2	-34,54	50,47	9,14	19,59	13233,28	-32813,2
	4	0,441383	0,001182	0,300262	1,9202	-28432,7	-36,32	53,16	9,64	20,03	13920,45	-32773,6
	5	0,376785	0,001161	0,275804	1,70053	-25180	-31,54	45,39	8,31	19,67	12786,55	-32781,5

iso-Propyl 3-methylbut-2-enoate [f]	1	0,420622	0,001203	0,293636	1,85259	-27431,4	-34,77	52,26	9,2	20,38	13613,26	-32739,9
	2	0,366099	0,001291	0,303801	1,76241	-26096,2	-32,78	50,77	8,59	21,88	14084,52	-32677,6
	3	0,343037	0,001265	0,292052	1,67478	-24798,6	-30,92	48,68	8,08	21,44	13539,82	-32683
	4	0,426375	0,001014	0,325973	1,96624	-29114,4	-37,3	55,55	9,85	17,18	15112,43	-32733,3
	5	0,383103	0,001133	0,321762	1,85715	-27499	-34,92	51,36	9,16	19,2	14917,21	-32724,8
	6	0,397856	0,001296	0,335523	1,93265	-28616,9	-36,49	55,55	9,58	21,96	15555,18	-32703,1
Butyl 3-methylbut-2-enoate [f]	1	0,369233	0,001205	0,283264	1,73734	-25725	-32,28	48,68	8,31	20,42	13132,4	-33982,6
	2	0,356069	0,001407	0,290332	1,72999	-25616,1	-32,14	48,98	8,24	23,84	13460,08	-34002,2
	3	0,377629	0,001315	0,275982	1,73389	-25673,9	-32,23	49,57	8,3	22,28	12794,8	-33978,4
	4	0,387514	0,001386	0,28562	1,78746	-26467,1	-33,35	52,56	8,58	23,49	13241,63	-33996,8
	5	0,395691	0,001099	0,289821	1,81983	-26946,5	-34,03	52,56	8,76	18,62	13436,39	-34026,9
	6	0,35939	0,001196	0,285788	1,72347	-25519,7	-31,96	49,87	8,18	20,27	13249,42	-34012,8
1,2-Ethanediol monoacetate [g,h]	1	0,432902	0,000859	0,31932	1,58078	-23408,54	-26,2	40,91	8,84	14,56	14801,92	-19793,2
	2	0,411172	0,000911	0,340708	1,61815	-23961,89	-26,86	41,21	8,95	15,44	15793,35	-19772,3
1,2-Ethanediol diacetate [i]	1	0,391465	0,001254	0,282057	1,41534	-20969,7	-22,84	38,23	8,31	21,25	13074,61	-20053,2
	2	0,490975	0,001282	0,290231	1,57579	-23346,9	-25,98	41,81	9,76	21,72	13453,51	-20054,0
	3	0,493032	0,001147	0,286014	1,56498	-23186,7	-25,83	43,6	11,00	19,44	13258,04	-20040,2
	4	0,535352	0,001105	0,287365	1,62731	-24110,2	-26,95	44,2	10,29	18,72	13320,66	-20067,7
	5	0,604066	0,001015	0,291952	1,73364	-25685,6	-29,05	44,79	11,31	17,20	13533,29	-20044,2
	6	0,488865	0,000978	0,302224	1,60996	-23853,2	-26,53	43	9,91	16,57	14009,44	-20048,1
1,2,3-Propanetriol triacetate [j]	1	0,432706	0,001173	0,282503	1,45909	-21617,9	-23,63	38,82	9,06	19,88	13095,29	-19594,2
	2	0,539617	0,001106	0,273749	1,57351	-23313,1	-25,83	41,51	10,37	18,74	12689,5	-19604,3
	3	0,442128	0,001084	0,285406	1,4806	-21936,6	-24	38,82	9,23	18,37	13229,85	-19596,8
	4	0,59528	0,001124	0,279512	1,66532	-24673,3	-27,7	42,41	11,27	19,05	12956,64	-19607
Polyamidine IIIa [k]	1	0,360767	0,000684	0,234061	1,52281	-22561,2	-23,62	50,77	10,77	11,59	10849,1	-32327,1
	2	0,146811	0,000769	0,276937	1,19038	-17636,1	-18,16	35,84	6,63	13,03	12836,47	-32438,2

[a] for the definition of the symbols in columns 2-13 *see* the work [242]. Calorimeter: T_h = 298,15 K; V(bomb) = 0,2664 dm^3; p^i (gas) = 3,04 MPa; m^i (H_2O) = 1,00 g.

[b] masses obtained from apparent masses.

[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(e_{cont})\cdot(-\Delta T_c) = (e^i_{cont})\cdot(T^i - 298{,}15\text{ K}) + +(e^f_{cont})\cdot(298{,}15\text{ K} - T^f + \Delta T_{corr})$.

[d] ΔU_{corr} -the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in the work [242]; e_{calor} = 14802,0±1,0 $J\cdot K^{-1}$.

[e] water content 1045 ppm.

[f] e_{calor} = 14807,1±0,7 $J\cdot K^{-1}$.

[g] e_{calor} = 14816,0±0,9 $J\cdot K^{-1}$.

[h] water content 1094,5 ppm.

[i] water content 364,76 ppm.

[j] water content 117,43 ppm.

[k] e_{calor} = 14815,5±0,9 $J\cdot K^{-1}$.

Table B10. Compilation of Experimental Data on Enthalpies of Fusion ($\Delta_{cr}^{l}H_m$) of Cyclohexanone oxime[a] and ε-Caprolactam[b].

Compound	C_p^l, J·mol^{-1}·K^{-1}	C_p^{cr}, J·mol^{-1}·K^{-1}	T_{fus}, K	$\Delta_{cr}^{l}H_m$ at T_{fus}, kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$ [c] at 298,15 K, kJ·mol^{-1}	$\Delta_f H_m^{\circ}$ (cr.) at 298,15 K, kJ·mol^{-1}	$\Delta_f H_m^{\circ}$ (liq.) [d] at 298,15 K, kJ·mol^{-1}
Cyclohexanone oxime	234,1	196,3	362,2	12,45	9,7	-153,2±2,5	-143,5±2,5
ε-Caprolactam	333,3	156,8	342,3	16,10	12,9	-329,4±1,7	-316,5±1,7

[a] data are taken from work [55].

[b] data are taken from work [66].

[c] the experimental enthalpy of fusion, $\Delta_{cr}^{l}H_m$ (T_{fus}) of cyclohexanone oxime and ε-caprolactam were measured at melting temperature and due to the deviation of the melting temperature from T = 298,15 the observed values had to be adjusted to the reference temperature of 298,15 K. The adjustment was calculated using the equation [19]:

$\{\Delta_{cr}^{l}H_m\ (T_{\text{fus}}/\text{K}) - \Delta_{cr}^{l}H_m\ (298{,}15\ \text{K})\}/(\text{J}\cdot\text{mol}^{-1}) =$

$\{(0{,}75 + 0{,}15C_p^{cr})[(T_{\text{fus}}/\text{K}) - 298{,}15]\} - \cdot\{(10{,}58 + 0{,}26C_p^{l})\,[(T_{\text{fus}}/\text{K}) - 298{,}15]\}$,

where values of $\Delta_{cr}^{l}C_p$ has been derived from the isobaric molar heat capacities of liquid, C_p^l, and the solid, C_p^{cr}, oxime or amide.

[d] Calculated as the sum of values referred to 298,15 K: $\Delta_f H_m^{\circ}$ (liq.) = $\Delta_f H_m^{\circ}$ (cr.) + $\Delta_{cr}^{l}H_m$.

Table B11. Results of Calculations of Enthalpies ($\Delta_r H_m^\circ$), Entropies ($\Delta_r S_m^\circ$) Gibbs energies of reaction ($\Delta_r G_m^\circ$) and Equilibrium Constants (K_p) in the Gaseous Phase at 298,15 K and at 373,15 K and at 0,1 MPa for the Beckmann Rearrangement of Cyclohexanone oxime into ε-Caprolactam (see Scheme 2 in the text).

	HF/3-21G*				B3LYP/6-311G(d,p)			
T, K	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$	K_p	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$	K_p
298,15	-180,7	-182,6	-6,2	$4{,}6 \cdot 10^{31}$	-172,2	-172,5	-1,0	$1{,}5 \cdot 10^{30}$
373,15	-174,	-176,2	-5,5	$2{,}4 \cdot 10^{24}$	-166,2	-165,9	0,74	$1{,}8 \cdot 10^{23}$

Table B12. G3MP2 Energy and Enthalpy at 298,15 K (in Hartree) of the Most Stable Conformers of Molecules Studied in Chap. 4.

Compound	G3MP2	
	E_0	H_{298}
Cyclohexanone oxime	-364,588537	-364,579701
Caprolactam	-364,651055	-364,642359
2-Butanone oxime	-287,305986	-287,297271
N-Methylpropanamide	-287,371208	-287,362180
Ethanone oxime	-208,830040	-208,824039
Hydroxylamine	-131,551000	-131,546844
NH_3	-56,470142	-56,466333
Methane	-40,422100	-40,418284
Ethane	-79,651199	-79,646714
Water	-76,342404	-76,338629

Table B13. Results of G3MP2 Calculations of Standard Enthalpy of Formation, $\Delta_f H_m^\circ$ (g.) of 2-Butanone oxime and N-Methylpropanamide at 298,15 K (in kJ·mol^{-1}).

Compound	$\Delta_f H_m^\circ$ (g.) calc.				Average	$\Delta_f H_m^\circ$ (g.) exp.
	Atomization	(4.2) [b]	(4.3) [b]	(4.4) [b]		
Butanone oxime	-79,82	-81,89	-83,33	-88,53	-83,4±1,9[a]	-80,8±1,1
N-Me-propanamide	-250,24	-252,30	-253,75	-258,95	-253,8±1,9[a]	-253,5±0,8

[a] calculated as the average from bond separation and isomerization reactions.
[b] see the text on p. 27.

Table B14. Results of G3MP2 Calculations of Standard Enthalpy of Formation, $\Delta_f H_m^\circ$ (g.) of Cyclohexanone oxime and ε-Caprolactam at 298,15 K (in kJ·mol^{-1}).

Compound	$\Delta_f H_m^\circ$ (g.) calc.				Average	$\Delta_f H_m^\circ$ (g.) exp.
	Atomization	(4.5) [b]	(4.6) [b]	(4.7) [b]		
Cyclohexanone oxime	-73,94	-74,18	-75,63	-80,83	-76,2±1,6[a]	-74,4±2,5
ε-Caprolactam	-238,44	-238,69	-240.14	-245,34	-240.7±1,6[a]	-241,9±1,8

[a] calculated as the average from bond separation and isomerization reactions.
[b] see the text on p. 27.

Table B15. Conformational Analysis of 1,4-Butanediol.

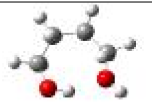
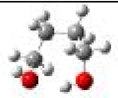
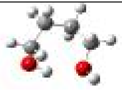
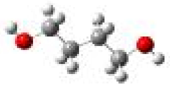
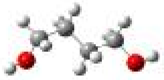
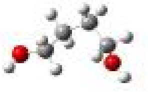
Konformer	E_0, Hartree	H_{298}, Hartree	G_{298}, Hartree	Relative Energy, kJ·mol^{-1}	Relative Free Energy, kJ·mol^{-1}
 **1**	-308,401136	-308,392813	-308,432362	0,00	0,00
 **2**	-308,400944	-308,392668	-308,431999	0,38	0,95
 **3**	-308,401104	-308,392700	-308,432193	0,30	0,44
 **4**	-308,399805	-308,390942	-308,431955	4,91	1,07
 **5**	-308,398662	-308,389598	-308,431004	8,44	3,57
 **6**	-308,398632	-308,389657	-308,430953	8,29	3,70
 **7**	-308,397332	-308,388312	-308,429815	11,82	6,69
 **8**	-308,397590	-308,388684	-308,430053	10,84	6,06

Table B16. Conformational Analysis of 1,4-Butanediol (Summary).

Konformer	ΔG, kJ·mol^{-1}	$exp^{(\Delta G^0/RT)}$	x_i	$\Delta_f H$ AT	$\Delta_f H$ BS1	$\Delta_f H$ BS2	$\Delta_f H$ BS3	$\Delta_f H$ BS4
1	0,00	1,00	0,2643	-431,1	-432,1	-431,5	-434,6	-435,2
2	0,95	0,68	0,1801	-430,7	-431,7	-431,1	-434,2	-434,8
3	0,44	0,84	0,2213	-430,8	-431,8	-431,2	-434,3	-434,9
4	1,07	0,65	0,1716	-426,2	-427,2	-426,5	-429,7	-430,3
5	3,57	0,24	0,0626	-422,6	-423,6	-423	-426,1	-426,7
6	3,70	0,22	0,0594	-422,8	-423,8	-423,2	-426,3	-426,9
7	6,69	0,07	0,0178	-419,3	-420,3	-419,6	-422,7	-423,4
8	6,06	0,09	0,0229	-420,2	-421,2	-420,6	-423,7	-424,3
				-428,6	**-429,6**	**-429,0**	**-432,1**	**-432,7**
					average	**-430,4±1,7**		

Table B17. Results from DFT B3LYP/6-311+G(d,p) and G3MP2 Calculations of $\Delta_f H_m^\circ$ (g.) of Alkanedioic Acids at 298,15 K (in kJ·mol^{-1}).

Reaction	DFT	G3MP2
Decanedioic acid		
$C_{10}H_{18}O_4 + 8\ CH_4 = 2\ CH_3COOH + 7\ C_2H_6$	-895,0	-942,8
$C_{10}H_{18}O_4 + 9\ C_2H_6 = 2\ CH_3COOH + 8\ C_3H_8$	-933,9	-946,1
$C_{10}H_{18}O_4 + 10\ C_3H_8 = 2\ CH_3COOH + 9\ C_4H_9$	-941,8	-946,2
$C_{10}H_{18}O_4 + 20\ CH_4 = 4\ H_2O + 15\ C_2H_6$	-942,3	-937,5
$C_{10}H_{18}O_4 + 25\ C_2H_6 = 4\ H_2O + 20\ C_3H_8$	-1039,7	-945,9
$C_{10}H_{18}O_4 + 30\ C_3H_8 = 4\ H_2O + 25\ C_4H_9$	-1061,3	-946,0
		-944,1±2,8
Dodecanedioic acid		
$C_{12}H_{22}O_4 + 10\ CH_4 = 2\ CH_3COOH + 9\ C_2H_6$	-933,3	-1012,5
$C_{12}H_{22}O_4 + 11\ C_2H_6 = 2\ CH_3COOH + 10\ C_3H_8$	-981,9	-1016,7
$C_{12}H_{22}O_4 + 12\ C_3H_8 = 2\ CH_3COOH + 11\ C_4H_9$	-991,4	-1016,8
$C_{12}H_{22}O_4 + 22\ CH_4 = 4\ H_2O + 17\ C_2H_6$	-980,5	-1007,2
$C_{12}H_{22}O_4 + 27\ C_2H_6 = 4\ H_2O + 22\ C_3H_8$	-1087,6	-1016,5
$C_{12}H_{22}O_4 + 32\ C_3H_8 = 4\ H_2O + 27\ C_4H_9$	-1110,9	-1016,6
		-1014,4±3,2

Table B18. Basic Preparation Methods of Low Molecular Weight Amidines based on the Reactions of Amines with the Different Reagents.

Type of amidines	Via reaction/catalyst	Condition	η_{inh}[a], $dl \cdot g^{-1}$ /yield,%	Ref.
~NR-CR´=N~	*s*-triazine	in mass, 80°C(2 h.)→ 200-210°C (5 h.)	not quoted/ 91-100	[154]
	$RC(OEt)_3$/acetic or benzoic acids	in mass [b], 80-120°C (10-45min) → 200-250°C(1-3 h./0,1-10 mbar)	0,09-0,56/ not quoted	[144-146]
	RCOOH/PPSE [c]	in mass, 160°C(5 h.)	-/65-88	[280]
	Ph or ArC(Cl)=NMe Ph(Cl)C=N-R-N=C(Cl)Ph	in solution, r.t. (2-5 h.) in solution, 100°C (2 h.)	-/54-96 -/not quoted	[158] [280]
	MeC(Cl)=NR $PhCH_2C(Cl)=NHPh$ $PhCH(Ph)CN\text{-}OH/SOCl_2$ [d]	in solution, ≤70°C (2,5 h.) in mass, ≤95°C (5 min) in solution, ≤0°C→ r.t.	-/≤95 -/not quoted -/15-20	[281] [282] [282]
	1,3,5$(EtN=CCl)_3Ar$	in solution, -10°C (1 h.)→ r.t (overnight)	-/56	[283]
	ArC(NHEt)=N-Et [e]	in solution, r.t.(5 days)	-/98	[284]
	RCN/SmI_2	in mass, 55-80°C (1-2 days)	-/18-86	[285]
	$RCONH(CH_2)_2NHCOR/PCl_5$ [f]	in solution, -10°C→95°C (2-24 h.)	-/10-25	[165]
	$\{(Ph)_2C=C=N\}_2R$	in solution, 95°C (1-2 days)	0,06-0,45/ 68-96	[286]
	Diphenyl-*a*-Aryl-*a*-Aminoarylphosphonates [g]	in solution, -30°C	-/45-97	[287]
	$(Me)_2NCH(OEt)_2$ (DMFE) [h]	in solution, r.t.-55°C (3-6 h.)	-/44-99	[288]
	$COCl_2$ in DMF [i]	in solution, r.t. (17 h.)	-/95	[148]
~NR-C(=NR´)~	$\{EtOC(=NH)\text{-}\}_2(CH_2)_4/NH_4Cl$	in mass, 40-80°C (100-760 mm. Hg, 36-66 h.)	0,07-0,14 [j] / 46-54	[150]
	$PhCN/AlCl_3$	in solution, ≤125°C (0,5 h.)	0,17-0,28/≤90	[149]
	Me-, $PhCN/HCl\text{-}AlCl_3$	in solution, r.t (1 month)	-/≤82	[158]
	$MeSO_2ArCN/NH_3$ or ammonium salt	160-180°C (2-15 h.)	-/39-79	[166]
	Ar- or PhCN/Na	in solution, ≤70°C (1-3 days)	-/≤76	[289]
	ArCN/MeONa [e] Ph- or *m*-ClArC(Cl)=NMe [k] *p*-ClArCN/EtMgBr Ph- or *p*-MeArC(=NH)OEt·HCl	in solution, r.t (5-10 days) >>, r.t. (2-5 h.) >>, 40°C (4 h.) >>, r.t. (2-3 days)	-/54-71 -/47-61 -/65 -/34-41	[158] [158] [158] [158]
	N,N´-diethyl-4-vinylbenzamidine	emulsion polymerization	not quoted	[290]
	ArBr, PhONa, RNC [l] /$PdCl_2$ and dppf [m]	in solution, 98°C (11 h.)	-/49-84	[291]
	Ar´CH=N-NHAr´´/$NaNH_2$ or PhLi [n]	in solution, >150°C	-/22-65	[292-293]

Notes to the **Table B18**:

[a] concerning only polymers, e.g. polyamidines: inherent viscosity (as a measure of molecular weight of polymer), η_{inh} (dl·g^{-1})= ($ln\ \eta_r$)/c, where c = mass concentration of polymer (in g/100 ml) and η_r= ratio of flow times of solution and of solvent.

[b] melt condensation.

[c] polyphosphoric acid trimethylsilyl ester (condensation agent).

[d] reaction proceeds via amide formation (Beckmann rearrangement) *in situ*.

[e] reaction proceeds with hydrochloric amine.

[f] reaction proceeds *via* formation of bis(imidoyl chlorides) *in situ*.

[g] reaction proceeds with nitroso benzene.

[h] reaction of N,N´-dimethylformamide diethylacetal (DMFE) with aryl- or alkylimino-dimagnesium, RN(MgBr)$_2$.

[i] reaction with dimethylformamide (DMF).

[j] specific viscosity.

[k] reaction with ammonia (20-25%- water solution).

[l] cyclohexyl or butyl isocyanide (reaction proceeds via formation of imidates).

[m] 1,1´-bis(diphenylphosphino)ferrocene.

[n] *Robev* rearrangement.

Table B19. Effect of Order of the Monomer Loading in the Synthesis of Polyamidine IIIa in MP (T = 363,15 K, Monomer Concentration is 0,6 M, and the Duration of Synthesis is 2,5 hours) in the Presence of Et_3N (Molar Ratio of Et_3N to Monomer is 3:1).

№ of experiment	Monomer/Solvent (molar ratio)		Polymer	
	Ia/MP (3 ml)	IIa/MP (3 ml)	Yield, %	h_{inh} (DMAA, 298,15 K), $dl \cdot g^{-1}$
1	1:35	1:0	98	0,35
2	1:0	1:0	95	0,18
3	1:35	1:0	-	0,13
4	1:17.5	1:17.5	-	0,06
5	1:0	1:35	85	0,13
6	1:0	1:35	95	0,13
7 (without catalyst)	1:0	1:0	85	0,12

Notes to the **Table B19**:

Experiment № **1**: The monomer IIa was introduced to a solution of diamine and the mixture was stirred under nitrogen at room temperature for 5 minutes. Then catalyst was added and the heating proceeded to the desired temperature level.

Experiment № **2**: Two monomers were simultaneously dissolved at room temperature in MP and obtained homogeneous solution was stirred and heated to the reaction temperature. After 5 min a solution then was slowly cooled and the catalyst was loaded at room temperature. The solution was heated again to the desired temperature level.

Experiment № **3**: When the catalyst was added to the solution of diamine at room temperature, compound IIa was loaded.

Experiment № **4**: When the solution of compound IIa was first added to a solution of diamine at room temperature, after 10 minutes of stirring the catalyst was loaded.

Experiment № **5**: When the solution of the catalyst and compound IIa in MP were stirred under nitrogen at 50°C for 5 min and then was slowly cooled to room temperature, the diamine was added and the temperature was raised again to the desired level.

Experiment № **6**: When the diamine was added to the solution of catalyst and compound IIa at room temperature, the heating proceeded to the desired temperature level.

Experiment № **7**: When the monomers were simultaneously dissolved at room temperature, the heating proceeded to the desired temperature level.

Calculation of the gaseous enthalpy of formation, $\Delta_f H_m^{\circ}$ (g.) of acrylic acids

Experimental data on acrylic acid is in disarray according to work [211].
In order to obtain the experimental value of $\Delta_f H_m^{\circ}$ (liq.) for this compound we selected the following data:

$\Delta_f H_m^{\circ}$ (liq.) = -377,8±9,3 kJ·mol^{-1} from the work [275].
and

$\Delta_f H_m^{\circ}$ (liq.) = -379,1±5,0 kJ·mol^{-1} from [276].

The average value $\Delta_f H_m^{\circ}$ (liq.) **= -378,5**±1,4 kJ·mol^{-1}

$\Delta_f H_m^{\circ}$ (298,15 K) = 53,1±4,2 kJ·mol^{-1} from [277].

$\Delta_l^g H_m$ (298,15 K) = 57,3±1,3 kJ·mol^{-1} from [275].

$\Delta_l^g H_m$(298,15 K) = 55,3 kJ·mol^{-1} from data treatment which we made using the vapor pressure measurements (293-343 K) reported in [278] and data on association enthalpy of acrylic acid given in [279].

The average value $\Delta_l^g H_m$(298,15 K) = **55,2**±1,2 kJ·mol^{-1}

The enthalpy of formation in the gaseous state:

$\Delta_f H_m^{\circ}$ (g) = $\Delta_f H_m^{\circ}$ (liq.) + $\Delta_l^g H_m$= -378,5 + 55,05 = -323,3±1,8 kJ·mol^{-1}

the latter value is in excellent agreement with the recommendation -321±38 kJ·mol^{-1} derived from ab initio calculations recently [211].

Table B20. Thermochemical Data of Compounds at 298,15 K and 0,1 MPa (in kJ·mol^{-1}) to the Chap. 8.

Compound	CAS	$\Delta_f H_m^\circ$ (liq.)	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (g.)
Water	[7732-18-5]	-285,8±0,1[28]	44,0±0,1[28]	-241,8±0,1
Methanol	[67-56-1]	-239,1±0,3[32]	37,6±0,1[32]	-201,5±0,3
1,2-Ethanediol	[107-21-1]	-455,6±0,8[110]	67,6±1,8[110]	-388,0±2,0
di-Ethyl ester ethanedioic acid	[95-92-1]	-809,7[294]	57,9±0,5[a]	-751,8
1,1-Diacetoxyethane	[542-10-9]	-826,3±0,5[186]	57,8±0,7[186]	-812,6±1,1
Hexanedioic acid (cr.)	[124-04-9]	-994,3±0,8[118]	132,1±2,5[295]	-862,2±2,6
Ethylene glycol, dipropionate	[123-80-8]	-	67,59±0,50[219]	-
Ethylene glycol, di-n-butanonate	[105-72-6]	-	73,21±0,60[219]	-

[a] to be published, private communication Dr. *S.P. Verevkin*.

Table B21. Results of G3MP2 Calculations of the Standard Enthalpy of Formation, $\Delta_f H_m^\circ$ (g.) for 1,2-Ethanediol Monoacetate at 298,15 K (in kJ·mol^{-1}).

Conformer	$\Delta_f H_m^\circ$					$exp^{(\Delta G^o/RT)}$	x_i	$\Delta_f H_m^\circ$ (g.) [a]
	atom.	(8.2) [b]	(8.3) [b]	(8.4) [b]	average			
M1	-584,1	-591,8	-587,5	-589,1	-588,1	0,06	0,02	
M2	-592,6	-600,3	-595,9	-597,6	-596,6	1,00	0,66	
M3	-592,7	-600,4	-596,0	-597,7	-595,0	0,42	0,28	
M4	-584,3	-592,0	-587,7	-589,3	-588,3	0,05	0,04	-595,7±2,5

[a] calculated according to eq. 5.7 (Chap. 5) as the average from atomisation, bond separation and isodesmic reactions.

[b] see the text on p. 71.

Table B22. Results of G3MP2 Calculations of the Standard Enthalpy of Formation, $\Delta_f H_m^\circ$ (g.) for 1,2-Ethanediol Diacetate at 298,15 K (in kJ·mol^{-1}).

$\Delta_f H_m^\circ$ (g.) atomization	$\Delta_f H_m^\circ$ (g.)						$\Delta_f H_m^\circ$ (g.) exp.
	(8.5) [b]	(8.6) [b]	(8.7) [b]	(8.8) [b]	(8.9) [b]	(8.10) [b]	
-792,1	-802,3	-795,4	-797,6	-794,8	-792,4	-793,6	
						average: **-796,0±3,0**[a]	**-797,3±1,6**

[a] calculated as the average from bond separation and isomerization reactions.

[b] see the text on p. 72.

Table B23. Results of G3MP2 Calculations of the Standard Enthalpy of Formation, $\Delta_f H_m^\circ$ (g.) for 1,2,3-Propanetriol Triacetate at 298,15 K (in kJ·mol^{-1}).

$\Delta_f H_m^\circ$ (g.) atomization	$\Delta_f H_m^\circ$ (g.)				$\Delta_f H_m^\circ$ (g.) exp.
	(8.11) [b]	(8.12) [b]	(8.13) [b]	(8.14) [b]	
-1156,4	-1183,1	-1164,3	-1168,4	-1170,7	
				average: **-1171,6±8,1**[a]	**-1182,3±2,0**

[a] calculated as the average from bond separation and isomerization reactions.

[b] see the text on p. 72.

Table B24. Group-Additivity Values for the Calculation of Enthalpy of Formation, ($\Delta_f H_m^\circ$) and Enthalpy of Vaporization, ($\Delta_l^g H_m$) for Aliphatic Esters at 298,15 K (in kJ·mol^{-1}).

Increment	$\Delta_f H_m^\circ$ (g.)	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$ (liq.)
Hydrocarbons			
C-(C)(H)$_3$	-41,80	6,33	-48,50
C-(C)$_2$(H)$_2$	-23,06	4,52	-27,23
C-(C)$_3$(H)	-10,49	1,24	-10,37
C-(C)$_4$	-3,17	-2,69	1,90
(C-C)$_{1-4}$	2,56	0,26	2,01
C$_d$(C)(H)	36,0	3,8	32,2
C-(C$_d$)(C)(H)$_2$	-18,8	3,8	-23,9
Esters			
(CO$_2$)-(C)$_2$	-327,6	18,82	-346,3
C-(C)(H)$_2$(CO$_2$)	-20,96	4,38	-25,60
C-(C)$_2$(H)(CO$_2$)	-13,46	1,56	-15,36
C-(C)$_3$(CO$_2$)	0,83	-0,53	0,43
C-(C)(H)$_2$(O)	-33,31	3,13	-36,44
C-(C)$_2$(H)(O)	-28,67	-0,51	-27,09
C-(C)$_3$(O)	-21,67	-6,01	-14,19
(C-CO)$_{1-4}$	0,83	-1,57	3,19
(C-Oe)$_{1-4}$	0,16	-0,27	-0,14
Alcohols [a]			
C-(C)(H)$_2$(OH)	-29,03	6,90	-32,25
OH-(C)	-158,6	31,80	-190,4
Biofuels			
C$_{EDM}$	-551,0	57,6	-608,2
C$_{EDD}$	-713,7	48,7	-761,7
C$_{PTT}$	-1056,9	62,9	-1118,7

[a] increments for alcohols were taken from work [175].

Table B25. Results of Calculation of the Standard Enthalpies of Formation, $\Delta_f H_m^\circ$ (g.) and $\Delta_f H_m^\circ$ (liq.), for the Aliphatic Esters in the Gaseous and in the Liquid State at 298,15 K in kJ·mol^{-1} [32].

Compound	$\Delta_f H_m^\circ$ (g.) exp.	$\Delta_f H_m^\circ$ (g.) add.	Δ	$\Delta_f H_m^\circ$ (liq.) exp.	$\Delta_f H_m^\circ$ (liq.) add.	Δ
Methyl-ethanoate	-413,5	-411,2	-2,3	-445,9	-443,3	-2,6
Methyl-pivalate	-490,9	-491,6	0,7	-530,1	-530,3	0,2
Methyl-pentanoate	-470,3	-472,4	2,1	-514,2	-516,1	1,9
Methyl-hexanoate	-514,8	-513,4	-1,4	-567,1	-566,5	-0,6
Ethyl-ethanoate	-444,6	-444,5	-0,1	-480,2	-479,7	-0,5
Ethyl -propionate	-465,0	-465,5	0,5	-504,2	-505,3	1,1
Ethyl -butanoate	-485,2	-485,2	0	-528,4	-527,3	-1,1
Ethyl -pentanoate	-506,5	-505,7	-0,8	-553,6	-552,5	-1,1
Ethyl -isopentanoate	-516,1	-516,1	0	-560,4	-560,4	0
Ethyl -pivalate	-525,6	-524,9	-0,7	-566,9	-566,7	-0,2
Ethyl -heptanoate	-527,5	-526,2	-1,3	-579,2	-577,7	-1,8
iso-Propyl-ethanoate	-481,7	-481,7	0	-518,9	-518,9	0
Butyl-ethanoate	-485,6	-487,9	2,3	-529,2	-532,2	3,0
tert-Butyl-ethanoate	-516,5	-516,5	0	-554,5	-554,5	0

Table B26. Results for Calculation of Enthalpies of Vaporization of Aliphatic Esters at 298,15 K (in kJ·mol^{-1}).

Compound	$\Delta_l^g H_m$ exp.	$\Delta_l^g H_m$ additive	Δ
Methyl ethanoate	32,60 [a]	31,41	1,2
Ethyl ethanoate	35,60 [a]	34,54	1,1
Propyl ethanoate	39,10 [a]	39,32	-0,2
Butyl ethanoate	43,60 [a]	43,54	-0,1
iso-Propyl ethanoate	37,20 [b]	37,20	0
sec-Butyl ethanoate	41,70 [b]	41,19	0,5
tert-Butyl ethanoate	38,00 [b]	38,00	0
Ethyl Propanoate	39,20 [c]	38,93	0,3
Ethyl Butanoate	43,20 [c]	42,13	1,1
Methyl Pentanoate	43,90 [c]	43,79	0,1
Ethyl Pentanoate	47,10 [c]	46,93	0,2
Ethyl sec-pentanoate	44,30 [c]	44,30	0
Methyl hexanoate	48,20 [c]	48,60	-0,4
Ethyl hexanoate	51,60 [c]	51,73	-0,1
Methyl pivalate	39,20 [c]	38,69	0,5
Ethyl pivalate	41,30 [c]	41,81	-0,5
Methyl heptanoate	52,30 [c]	53,40	-1,1
		average:	**±0,5**

[a] taken from the work [185].

[b] from [296].

[c] from [196].

Table B27, Compilations of Data on Enthalpies of Vaporization of Triglycerides.

Compound	CAS	Technique [a]	T- range, K	$\Delta_l^g H_m$, kJ·mol^{-1}			Δ^d	$-\Delta C_p{}^b$	Ref.
				at T-mean	at 298,15 K	additive[c]		J·mol^{-1}·K^{-1}	
Tripropin, C3	[139-45-7]	C	-	-	91,4±0,4	90,3	1,1	126,1	26
Tributyrin, C4	[60-01-5]	C	-	-	**107,1±1,0**	104,7	2,4	159,3	26
		S	325-366	81,4	88,5		-16,2		47
		TGA	464-591	62,4	97,5		-7,2		48
		TGA	323-583	78,4	99,1		-5,6		49
Tricaproin, C6	[621-70-5]	TGA	358-633	92,8	128,6	133,4	-4,7	209,0	49
		TGA	511-641	78,0	**135,5**		2,1		50
		S	356-406	94,8	111,3		-22,1		47
Tricaprylin, C8	[538-23-8]	TGA	398-653	117,2	**170,7**	162,0	8,7	258,8	49
		TGA	552-658	104,0	182,7		20,7		50
		S	396-453	116,4	147,7		-14,3		47
Tricaprin, C10	[621-71-6]	TGA	586-668	146,6	248,1	190,7	57,4	308,6	48
		TGA	438-668	138,6	212,3		21,6		49
		S	437-485	124,7	**173,3**		-17,4		47
Trilaurin, C12	[538-24-9]	TGA	621-675	221,1	346,5	219,4	-	358,3	4
		S	458-520	136,1	202,4		-17,0		8
Trimyristin, C14	[555-45-3]	TGA	629-676	199,0	343,7	248,1	95,6	408,1	51
		S	488-551	147,8	**235,8**		-12,3		47
Tripalmitin, C16	[555-44-2]	TGA	647-672	474,3	640,0	276,8	-	457,9	51
		S	506-572	160,7	**268,5**		-8,3		47
Tristearin, C18	[555-43-1]	TGA	625-778	220,8	400,2	305,4	94,8	507,6	51
		S	521-588	167,4	**294,9**		-10,5		47
Triarachidin, C20	[620-64-4]	-	-	-	-	334,1	-	357,0	-
Tribehenin, C22	[18641-57-1]	-	-	-	-	362,8	-	387,0	-
Tribenzoin	[614-33-5]	S	423-476	123,5	153,1	153,3	-0,2	206,5	47
1-Capryl-2-lauryl-3-myristin	[30283-10-4]	S	464-526	131,9	197,1	209,8	-12,7	341,7	47
1-Lauryl-2-myristyl-3-palmitin	[60138-25-2]	S	491-551	147,8	236,4	248,1	-11,7	408,1	47
1-Myristyl-2-palmityl-3-stearin	[60183-20-7]	S	508-572	158,2	266,4	276,8	-10,4	457,9	47
1-Myristyl-2-capryl-3-stearin	-	S	491-551	148,2	233,1	238,5	-5,4	391,5	47
1-Myristyl-2-lauryl-3-stearin	-	S	493-559	150,7	245,1	257,6	-12,5	424,7	47
1-Palmityl-2-capryl-3-stearin	-	S	506-558	154,9	247,9	248,1	-0,2	408,1	47
1-Palmityl-2-lauryl-3-stearin	-	S	506-566	159,9	262,4	267,2	-4,8	474,4	47
2-Oleyl-1,3-distearin	[2846-04-0]	S	523-593	165,8	294,4	287,4	7,0	505,5	47

Notes to the **Table B27**:

[a] techniques: S- static pendulum-tensimetric method; C-calorimetry.

[b] values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid, C_p^l or solid C_p^{cr} compounds (they are in brackets) according to the procedure developed by *Chickos* and *Acree* [19].

[c] calculated using GAVs from Table B24.

[d] difference between experimental value and those calculated with increments from Table B24.

APPENDIX C

FIGURES

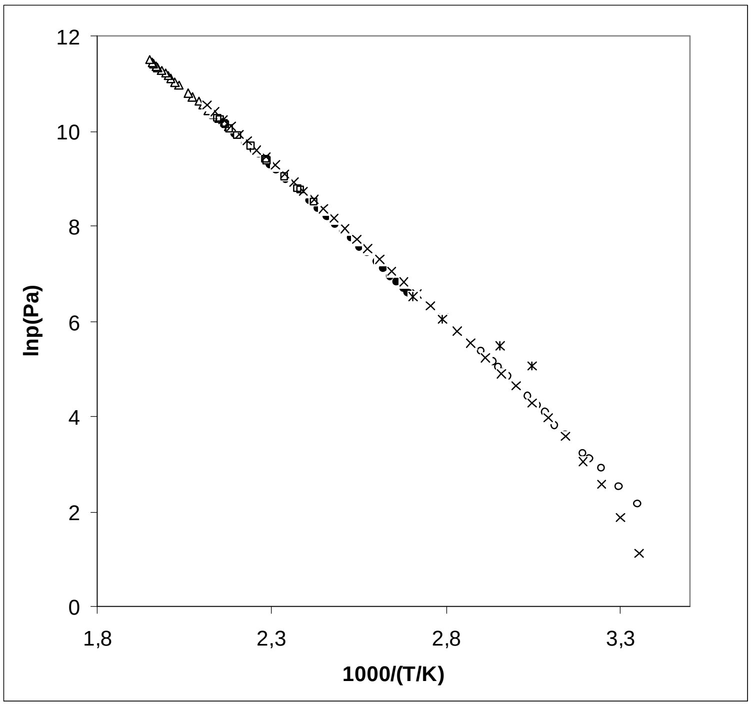


Fig. C1. Experimental vapour pressure of the liquid *propylene carbonate* measured by different methods: (o)- this work, (Δ)- [15]; (ж)- [18]; (+)- [24]; (●)- [16]; ( )- [17]; (x)- [26].

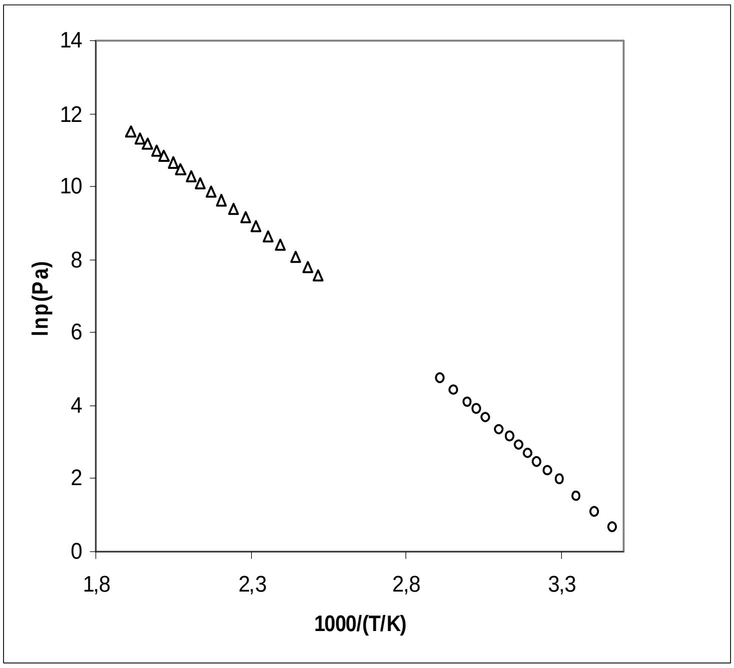


Fig. C2. Experimental vapour pressure of the liquid *butylene carbonate* measured by different methods: (o)- this work; (Δ)- [15].

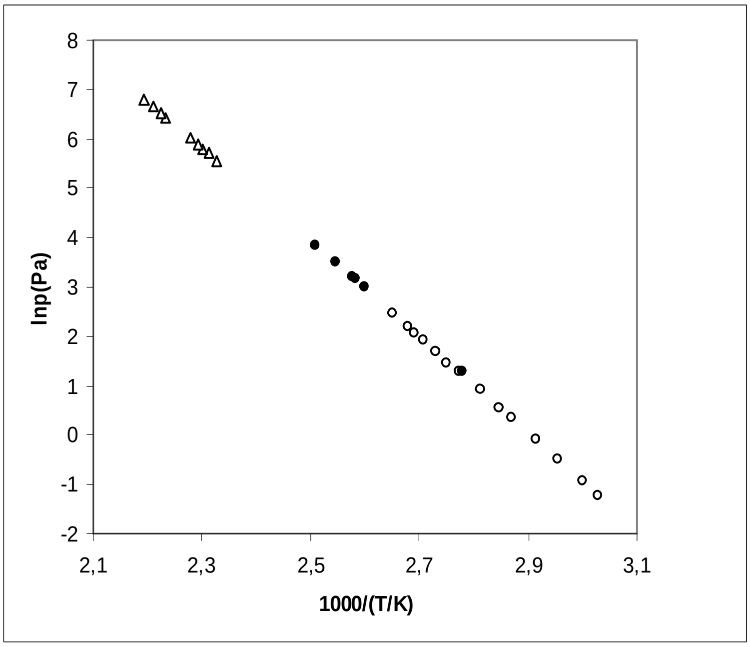
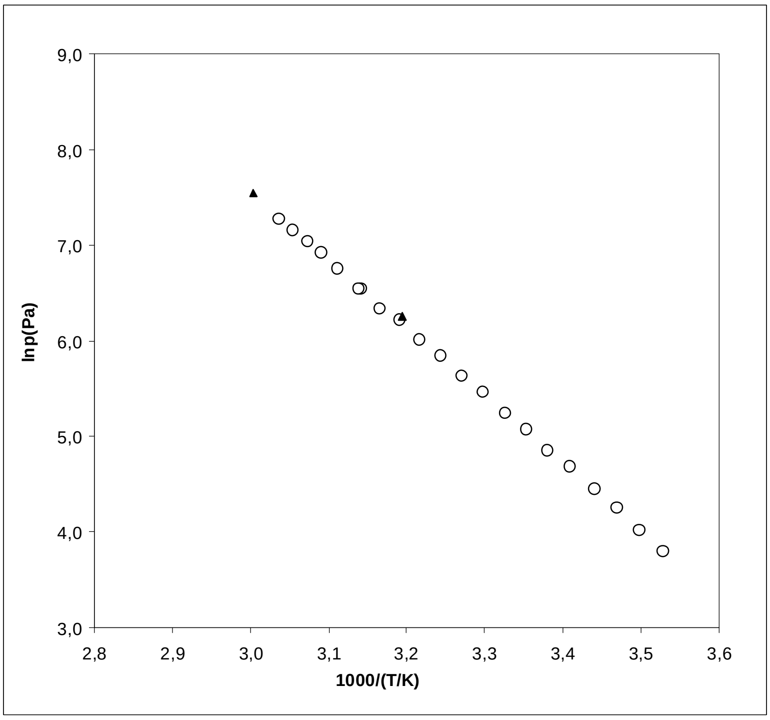


Fig. C3. Experimental vapour pressure of the liquid *glycerine carbonate*: (o)- this work, GC; (●)- this work, by weighing; (Δ)- [15].



Fig, C4, Experimental vapour pressure of the liquid *2-butanone oxime*: (○)- this work; (▲)- [30].

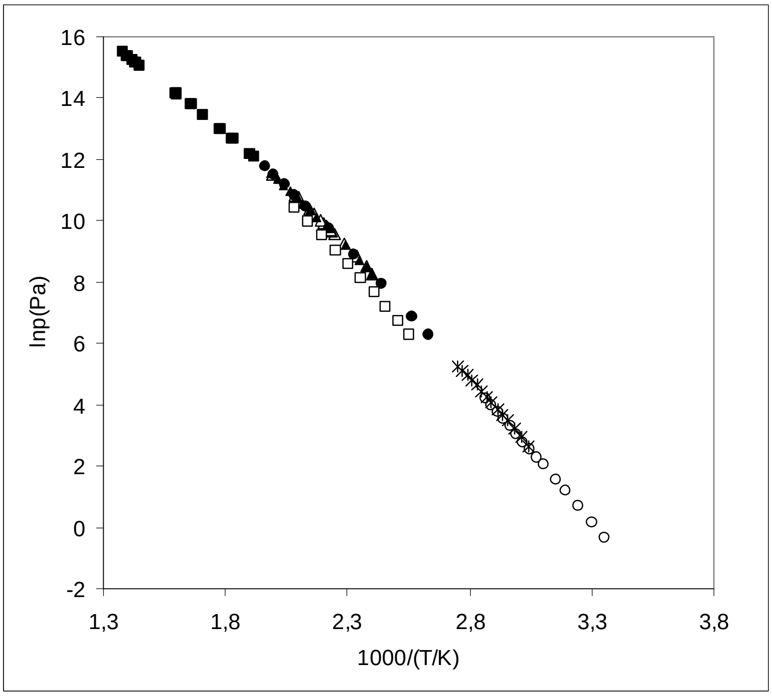


Fig. C5. Experimental data of the vapor pressures of *1,4-butanediol* in the liquid state: (ж)- [297]; (●)- [269]; (□)- [104]; (■)- [25]; (Δ)- [298]; (▲)- [299]; (○)- this work.

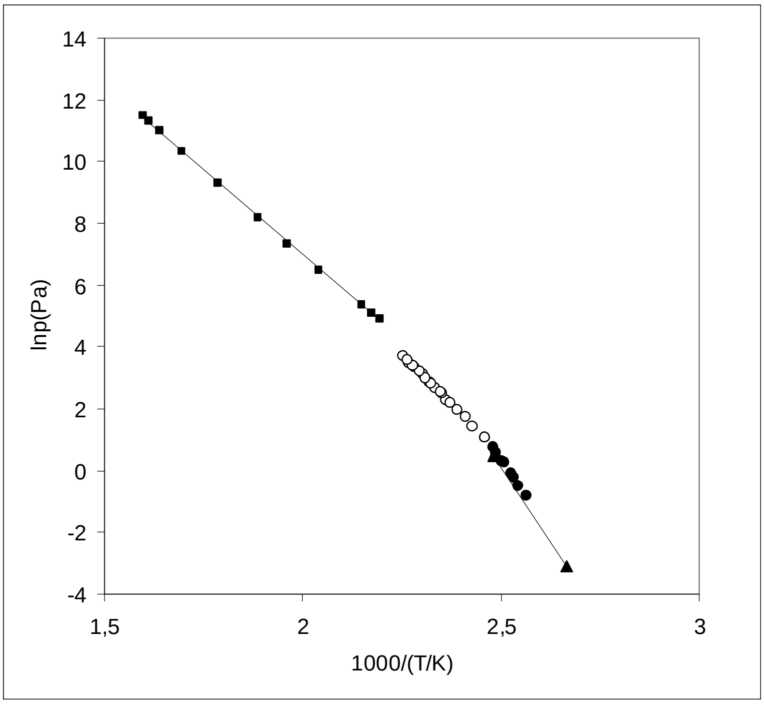


Fig. C6. Experimental data of the vapor pressures of *decandioic (sebacic) acid* (liq. and cr.): (●)- sublimation (this work); (○)- vaporization (this work); (▲)- sublimation [107]; (■)- vaporization [108].

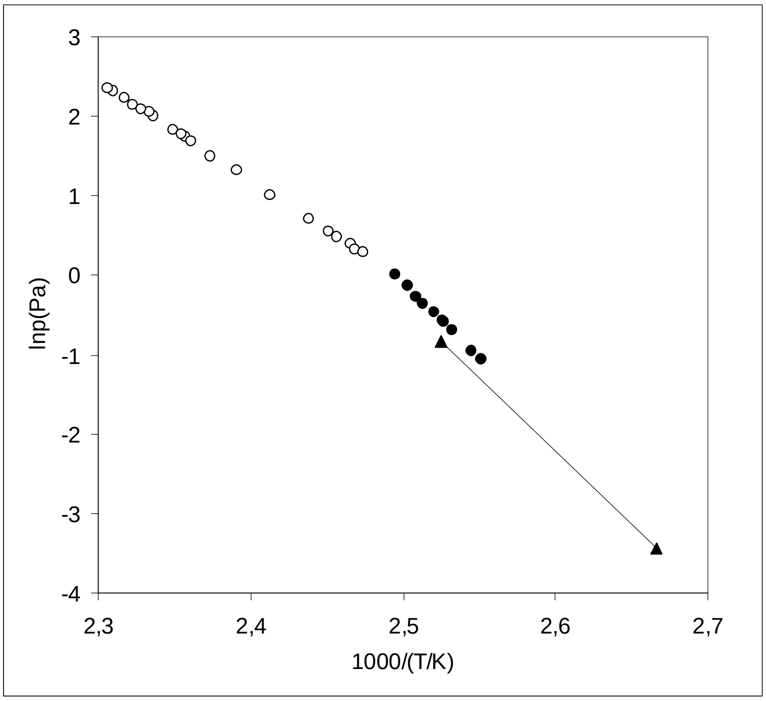


Fig. C7. Experimental data of the vapour pressures of *dodecandioic acid* (liq. and cr.): (●)-sublimation (this work); (○)- vaporization (this work); (▲)- sublimation [107].

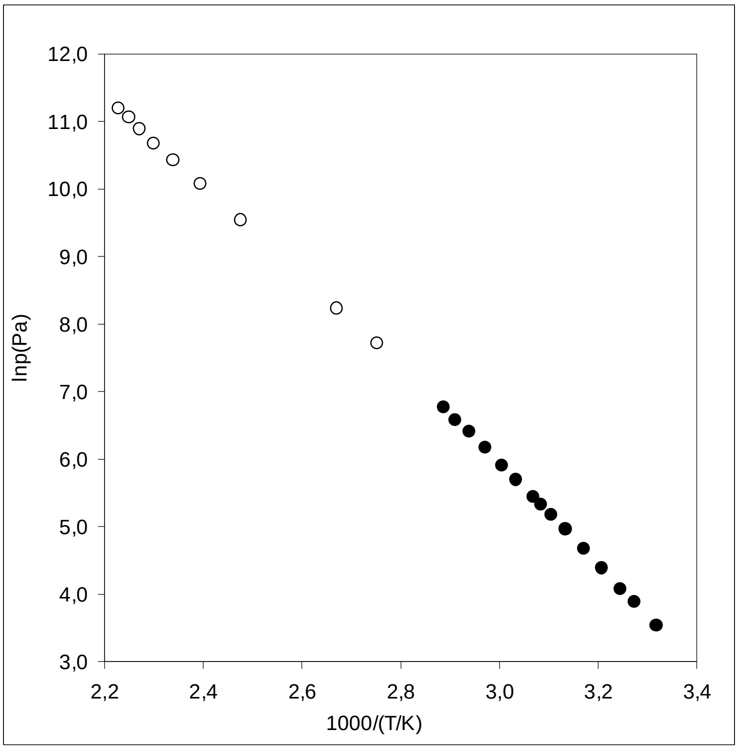


Fig. C8. Experimental data of the vapour pressures of the *1,2-ethanediol monoacetate*: (○)- [253]; (●)- this work.

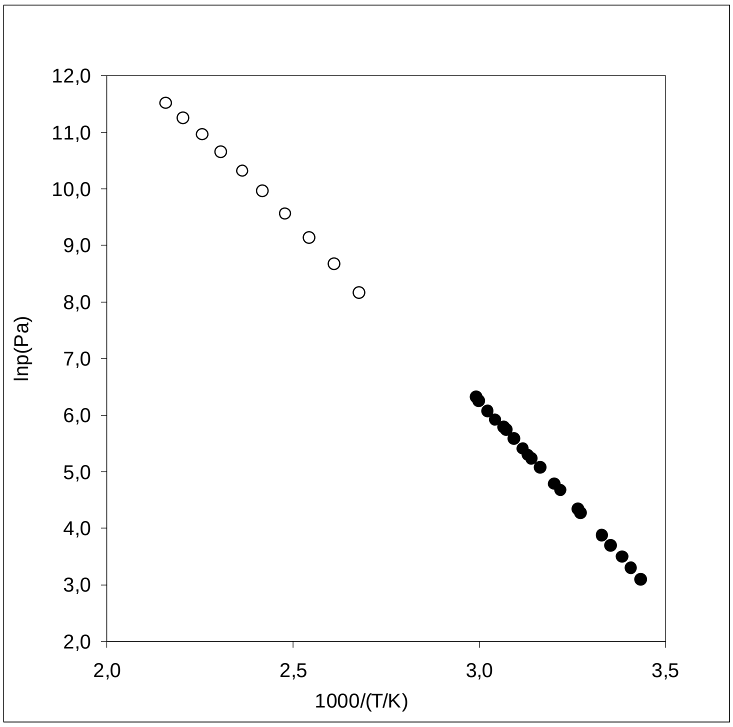


Fig. C9. Experimental data of the vapour pressures of the *1,2-ethanediol diacetate*: (o)- [217]; (●)- this work.

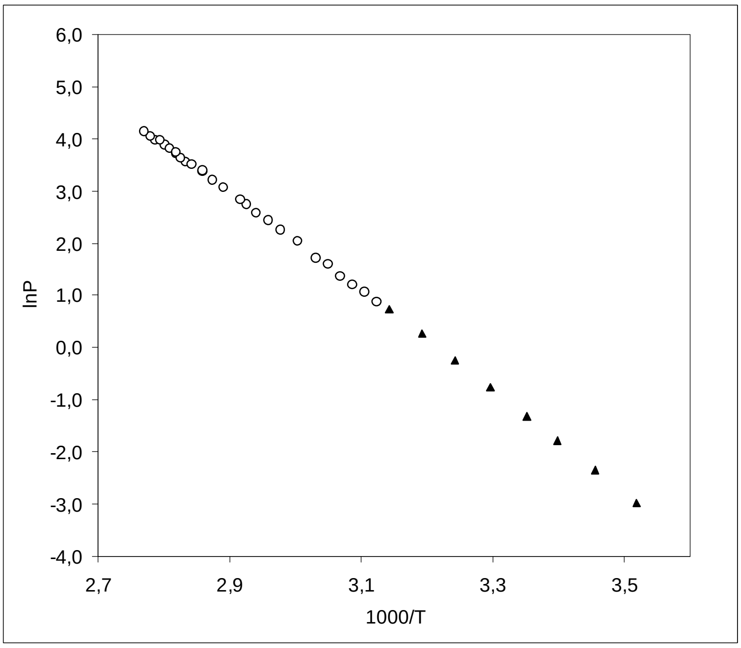


Fig. C10. Experimental data of the vapour pressures of the *1,2,3-propanetriol triacetate*: (▲)- [220]; (o)- this work.

ERKLÄRUNG

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

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Alexey V. Toktonov