Thermodynamic properties of pyruvic acid and its methyl ester

Vladimir N. Emel'yanenko[a,b,*], Vladimir V. Turovtsev[c,d], Yulia A. Fedina[d,e]

[a] Department of Physical Chemistry, University of Rostock, Dr.-Lorenz-Weg 2, 18059, Rostock, Germany
[b] Department of Physical Chemistry, Kazan Federal University, Kremlevskaya Str. 18, 420008, Kazan, Russian Federation
[c] Department of Physics, Mathematics and Medical Informatics, Tver State Medical University, Sovetskaya 4, 170100 Tver, Russian Federation
[d] Department of General Physics, Physics and Technical Faculty, Tver State University, Zhelyabova 33, 170100 Tver, Russian Federation
[e] EAHS DCSD 1701 Mountain Industrial Blvd, Stone Mountain, GA 30083, USA

ARTICLE INFO

ABSTRACT

In present work, a complete study of thermodynamic properties of pyruvic acid and methyl pyruvate in the condensed and gaseous phases was carried out using experimental and theoretical approaches. Enthalpies of combustion and formation of compounds were evaluated using combustion calorimetry. The transpiration method was used to determine the temperature dependence of the vapor pressures of acid and its methyl ester for the vaporization enthalpy calculation. With *ab initio* calculation it has been determined, that in gas phase pyruvic acid exists predominantly in monomeric form. The values of the enthalpy characteristics of the substances obtained using the composite method G4 were checked for reliability. A good agreement between the calculated and experimental values of the enthalpies of formation of the acid and its methyl ester in the gaseous phase is observed. The methods of quantum chemistry and statistical physics were used to calculate thermodynamic functions of compounds in the ideal gas state in temperature range 298.15–1500 K.

1. Introduction

The pyruvic acid (2-oxopropanoic acid) belongs to the class of ketoacids. The acid being a product of the glycolysis – the breakdown process of glucose in the living organism, its esters and salts contribute to the chemical activity in the cells [1]. The pyruvic acid derived from carbohydrates, fatty acids from lipids, and aminoacids from proteins is eventually converted into the compound acetyl coenzyme A in the matrix of the mitochondrion. This compound, in turn, undergoes a series of chemical reactions to generate energy through the oxidation of acetyl coenzyme A (acetyl-CoA) called the citric acid cycle, or Krebs cycle [2].

In this work enthalpies of formation in the condensed phase and enthalpies of vaporization for pyruvic acid and methyl pyruvate were determined using combustion calorimetry and transpiration technique. Results from combustion calorimetry together with the vaporization enthalpies have been used for calculation of the gas-phase standard enthalpy of formation of acid and ester at 298.15 K. In addition, we use the G4 method to calculate the molar enthalpies of compounds in the gas phase. Thermodynamic functions of the compounds in the gaseous state were computed in the range of T = 298.15–1500 K.

2. Materials and methods

2.1. Materials

Commercial samples of pyruvic acid (Acros, extra pure, 98.0%, CAS 127-17-3) and methyl ester of pyruvic acid (Alfa Aesar, 98%, CAS 600-22-6) were additionally purified by fractional vacuum distillation. No impurities (greater than 0.001 mass fractions) were detected in samples used for the thermochemical measurements (see Table S1). The degree of purity was determined using a GC equipped with an HP-1 capillary column (length of 10 m, an inside diameter of 0.53 mm, and a film thickness of 2.65 μm). The standard temperature program of the GC was T = 363 K for 120 s followed by a heating rate of 0.167 K·s^{-1} to T = 443 K. Water mass fraction in the samples was determined using a Mettler Toledo DL38 Karl Fischer titrator using the HYDRANAL™ as the reagent. A mass fraction of water in purified samples was measured by the Karl Fisher titration (352.0 and 730.7 ppm for acid and ester correspondingly) and the appropriate corrections were applied for combustion experiments.

2.2. Combustion calorimetry

The combustion energy of compounds was measured in a modified

B-08MA calorimeter with an isothermal cover. The procedure of calorimetric experiments has previously been described [3]. The thermal value of the calorimeter was determined using standard reference sample of benzoic acid (National Institute of Standards and Technology, Standard Reference Material *39 j*) and it was equal to (14,799.7 ± 0.9) $J \cdot K^{-1}$. Uncertainty of the energy equivalent is the standard uncertainty (0.68 level of confidence). Purge of the calorimetric bomb with oxygen was not performed. The amount of produced nitric acid was determined by the titration of water collected from the bomb using standard 0.1 $mol \cdot dm^{-3}$ solution of NaOH. The calculation of the standard enthalpy of combustion and formation was conducted according to the standard methodology [4]. The deviations of the combustion energy of the studied compound and secondary substances (cotton thread and polyethylene) as well as calibration errors [4] were considered while calculating the uncertainty of the enthalpy of combustion. Atomic weights were taken from the IUPAC Technical Report [5] as the average values of the stated intervals. Values of standard enthalpies of formation of water and CO_2 required for calculations were taken from [6]. Auxiliary values for combustion calorimetry are collected in Table S2.

2.3. Transpiration method

Vapor pressures (*p*) and the enthalpy of vaporization ($\Delta_l^g H_m$) of compounds were obtained by transpiration method, that is described in details earlier [7]. The amount of condensed sample was determined by weighing with microbalances of 0.0001 g resolution and by GC using an internal standard (n-alkanes). The difference in the heat capacities of acid and ester in the gaseous and liquid states $\Delta_l^g C^p$ were obtained according to the group additivity methodology reported in [8].
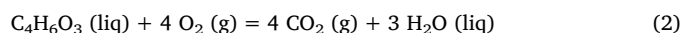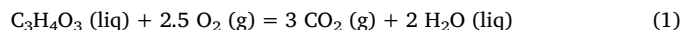
2.4. Computations

Quantum chemical calculations were performed with the Gaussian 09 series software [9]. An initial search for the stable conformers was performed with the force field MMFF94 method [10]. In addition, the methods B3LYP, MP2 and mPW2PLYP with 6-311 + +G(3df, 3pd) 6d 10f basis set have been used to investigate the internal rotation around all bonds in pyruvic acid and to identify the positions of energy minimum and transition states on the potential energy curves (PES) including transition barriers between conformers. The parameters of internal rotation and its contribution to the properties of methyl pyruvate were found using B3LYP/aug-cc-pVTZ 6d 10f. Energy of the conformers of molecules involved in this study was calculated using the G4 method [11]. The enthalpies of formation in gaseous state of acid and ester were computed with the procedures „from atomization reaction " and "from isomerization reaction" [12]. The procedure of calculating the thermodynamic properties considering the mole fraction of the conformers in the ideal gas state in the wide temperature range has previously been described [13,14].

3. Results and discussion

3.1. Enthalpies of formation of the liquid phase

The enthalpy of formation of studied compounds was found using the Hess's law [4] along with the combustion reactions of pyruvic acid and its methyl ester, respectively:

$$C_3H_4O_3 \text{ (liq)} + 2.5 \text{ } O_2 \text{ (g)} = 3 \text{ } CO_2 \text{ (g)} + 2 \text{ } H_2O \text{ (liq)} \qquad (1)$$

$$C_4H_6O_3 \text{ (liq)} + 4 \text{ } O_2 \text{ (g)} = 4 \text{ } CO_2 \text{ (g)} + 3 \text{ } H_2O \text{ (liq)} \qquad (2)$$

The values of $\Delta_f H_m^\circ$ (liq) of compounds were calculated using standard molar enthalpies of formation of H_2O (*l*) and CO_2 (g) assigned by CODATA [6]. Uncertainties related to the combustion experiments were estimated according to the procedure recommended by Olofsson [4]: the uncertainty of the molar enthalpy of combustion and of the molar enthalpy of formation is twice the overall standard deviation; the uncertainty of the molar enthalpy of combustion includes the uncertainties from calibration, from the combustion energies of the auxiliary materials (the ratio between the mass of compound and the mass of the auxiliary material was taken into account for each combustion experiment [4]); the uncertainties of the enthalpies of formation include uncertainties the reaction products H_2O and CO_2 [6].

However, the caution should be exercised when referring to the accuracy of calorimetric experiments for pyruvic acid and its methyl ester. As correctly noted by one of the reviewers, if the calorimetric bomb is not purged with oxygen to remove air nitrogen, it is unlikely but possible that not only HNO_3 but also HNO_2 is formed. The thermal effects of these processes are different. Unfortunately, we do not have analytical methods for the qualitative and quantitative determination of HNO_2 in combustion products. Thus, it is impossible to account for the influence of the formation of HNO_2 on the value of the error in determining $\Delta_f H_m^\circ$ (liq) of compounds. However, this fact must be considered in the future when performing thermochemical calculations involving the values $\Delta_f H_m^\circ$ (liq) of the investigated compounds.

The percentage of the heat effect corresponding to HNO_3 formation to the total heat effect (0.2%) was estimated from the heat effect of HNO_3 formation (line 7 in Tables 1 and 2) and the total heat released in

Table 1
Results for combustion experiments at *T* = 298.15 K ($p°$ = 0.1 MPa) for pyruvic acid[a].

m (substance) /g	0.529345	0.398597	0.705292	0.619193	0.584162	0.578474
m'(cotton) /g	0.001091	0.001048	0.001196	0.000994	0.001234	0.001333
m''(polyethylene) /g	0.299083	0.365688	0.293861	0.295954	0.304292	0.303029
ΔT_c /K	1.41338	1.50416	1.55382	1.48320	1.47856	1.46974
$(\varepsilon_{calor}) \cdot (-\Delta T_c)$ /J	−20917.5	−22261.0	−22995.9	−21950.8	−21882.2	−21751.6
$(\varepsilon_{cont}) \cdot (-\Delta T_c)$ /J	−23.02	−24.59	−25.76	−24.25	−24.39	−24.10
ΔU_{decomp} HNO_3 /J	39.72	40.02	41.81	40.02	40.02	39.72
ΔU_{corr} /J	10.65	10.0	13.06	11.86	11.57	11.45
$-m' \cdot \Delta_c u'$ /J	18.49	17.76	20.27	16.84	20.91	22.59
$-m'' \cdot \Delta_c u''$ /J	13864.59	16952.31	13622.60	13719.63	14106.16	14047.61
$\Delta_c u°$ (liq) /($J \cdot g^{-1}$)	−13237.3	−13210.0	−13220.0	−13221.6	−13229.1	−13231.9
$- \Delta_c u°$ (liq) /($J \cdot g^{-1}$)	13,225.0					
$u(\Delta_c u°)$ / $J \cdot g^{-1}$	4.0[b]					

[a] The definition of the symbols assigned according to [4] are as follow: *m*(substance), *m'*(cotton) and *m''*(polyethylene) are, the mass of compound burnt, the mass of cotton thread and auxiliary polyethylene used in each experiment, respectively, masses were corrected for buoyancy and water content (352.0 and 730.7 ppm for acid and ester correspondingly); $\Delta T_c = T^f - T^i + \Delta T_{corr}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f, with the correction ΔT_{corr} for heat exchange during the experiment; ε_{cont} are the energy equivalents of the bomb contents in their initial ε_{cont}^i and final states ε_{cont}^f, the contribution for the bomb content is calculated with $(\varepsilon_{cont}) \cdot (-\Delta T_c) = (\varepsilon_{cont}^i) \cdot (T^i - 298.15) + (\varepsilon_{cont}^f) \cdot (298.15 - T^f + \Delta T_{corr})$. ΔU_{decomp} HNO_3 is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.

[b] The standard deviations of the mean.