Experimental and theoretical thermodynamic properties of RS-(±)- and S-(+)-mandelic acids

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ABSTRACT

The enthalpies of formation of RS-(±)- and S-(+)-mandelic acids were measured using high-precision combustion calorimetry. Vapor pressures of the acids were measured using the transpiration method. The enthalpies of sublimation of these compounds at 298.15 K were derived from vapor pressure temperature dependencies. Molar enthalpies of the solid state phase transitions were measured by the DSC. Thermodynamic data on mandelic acids available from the published sources were collected and combined with our experimental results. Thermochemical properties of studied compounds were evaluated and tested for internal and external consistency with different approaches. 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 K–1500 K.

1. Introduction

Mandelic acid (MA) and its derivatives are widely used in the industrial and pharmaceutical sectors. This compound exists as two optical enantiomers and racemic form, which affect its pharmacological properties [1]. The acid has been known for its anti-aging effects on the skin along with antibacterial action in treating acne and preventing bacterial infections [1–3]. MA has a structure similar to that of widely known antibiotics but having no toxic effects, which makes it useful as urinary antiseptic [4–6]. The acid can serve as a raw material in manufacturing of many useful products due to its special structure [7]. It is an intermediate substance that is used in the production of synthetic rubber and polymers. Environmental and occupational exposures to toxic solvents in making paints, dyes, paint thinners, rubber, adhesives, pharmaceutical products and plastic materials cause harmful and adverse effect on the people [8–10]. Due to the growing concern regarding exposure to these toxic substances in surroundings, biological and environmental monitoring to assess potential health hazards is crucial. The chemicals are metabolized to MA and excreted in urine enabling the acid to serve as a biomarker for the biological monitoring and preventive measures [11,12].

The properties of MA have not been fully studied. The published values for the heat of combustion of RS-(±)-MA and S-(+)-MA have been measured in 1894 [13] and 1963 [14] correspondingly but exhibit inconsistency. There are references for the measured temperature and enthalpy of fusion obtained via differential scanning calorimetry method [15–17], but no consistency is observed among these values.

In this study, enthalpies of formation in the condensed phase and enthalpies of phase transitions (fusion, sublimation) for RS-(±)-MA and S-(+)-MA were determined using combustion calorimetry, differential scanning calorimetry and transpiration techniques. This is the original research measuring enthalpies of sublimation of compounds. Thermodynamic functions of the mandelic acid in the ideal gaseous state were computed in the range of $T = 298.15–1500$ K using the molecular and spectral data.

2. Materials and methods

2.1. Materials

Commercial samples of acids – RS-(±)-MA (Alfa Aesar, 99%) and S-(+)-MA (Alfa Aesar, 99 + %) - were additionally purified by fractional vacuum sublimation (see Table S1). A confirmation of the absence of changes in acid structures along with the final degree of their purity has

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been carried out 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) and equals to 99.9 mol %. 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 $T = 473$ K. Water mass fraction in the samples was determined using a Schott Titroline KF titrator. A mass fraction of water in purified samples was measured by the Karl Fisher titration (74.0 and 52.0 ppm for RS-(±) and S-(+)-mandelic acid correspondingly) and the appropriate corrections were applied for combustion experiments.

2.2. Enthalpy of formation of crystal acid via combustion calorimetry

An isoperibolic calorimeter with a static bomb and a stirred water bath has been used to measure standard molar enthalpies of combustion of acids. The detailed procedure has been described previously [18]. After pressing solid samples into pellets with mass ≈ 1.00 g, they were burned in presence of oxygen with addition of 1.00 g of water to the bomb. The acids were burned in absence of auxiliary compound (see Table S2). The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{calor} = 14{,}816.0 \pm 0.7$ J·K^{-1} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Uncertainty of the energy equivalent is the standard uncertainty (0.68 level of confidence). For the reduction of the data to standard conditions, conventional procedures [19] were used. Purge of the calorimetric bomb with oxygen was not performed. Correction for nitric acid formation was based on titration with 0.1 mol·dm^{-3} NaOH (aq). Overall, nine and seven calorimetric experiments were conducted for RS-(±)-MA and S-(+)-MA, respectively (see Table S3 and S4). Typical combustion experiments are given in Table 1.

2.3. Vapor pressure measurements via the transpiration method

The transpiration method was applied to measure vapour pressures of acids [20,21]. About 0.5 g of a solid sample was dissolved in acetonitrile and mixed with small glass beads in a glass beaker. Under vigorous stirring with a spatula and gentle heating, the solvent was removed from beaker producing glass beads covered uniformly with the sample. These covered glass beads were placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (± 0.1 K), while the transported material was collected in a cold trap. The amount of condensed sample was determined by weighing with microbalances of 0.0001 g resolution.

Vapor pressures p_i measured at different temperatures were fitted using the equation [20]:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_{cr}^{g} C_p \cdot \ln\left(\frac{T}{T_0}\right) \tag{1}$$

where a and b are adjustable parameters and $\Delta_{cr}^{g} C_{p,m}$ is the difference of the molar heat capacities of the gaseous and the crystalline phases, respectively. T_0 appearing in Eq. (1) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from Eq. (1) the expression for the sublimation enthalpy at temperature $T = 298.15$ K was derived:

$$\Delta_{cr}^{g} H_m(T) = -b + \Delta_{cr}^{g} C_p \cdot T \tag{2}$$

Experimental values are shown in Table 2.

2.4. Enthalpy of fusion via DSC

The thermal behavior of acids in solid state was studied with a Metller Toledo 822. The instrument was standardized using indium metal with a mass fraction of 0.9999. The samples were hermetically sealed in 40 mm^{-3} pans supplied by Thepro. The thermal behavior of the specimen was investigated during heating the sample with a rate of 50 K·min^{-1}. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties u $(\Delta_{cr}^{l} H^m) = 0.2$ kJ·mol^{-1} for the enthalpy of fusion and $u(T) = 0.5$ K for the melting temperature.

2.5. Computations

Quantum chemical calculations of mandelic acids were performed with the Gaussian 09 series software [22]. Energies of molecules were calculated using the composite G4 method [23]. General computational details within this approach were reported elsewhere [24]. Enthalpies, H_{298}, of each compound were calculated according to standard thermodynamic procedures [25]. The procedure of calculation of the thermodynamic properties in the ideal gas state in the wide temperature range has previously been described [26,27].

3. Results and discussion

3.1. Enthalpies of formations in the condensed state

The standard specific energies of combustion $\Delta_c u°(cr)$ of MA have been used to derive the standard molar enthalpies of combustion

Table 1
Results for typical combustion experiments at $T = 298.15$ K ($p° = 0.1$ MPa) for mandelic acids.[a]

	RS-(±)-MA			S-(+)-MA		
m (substance) /g	1.015193	1.060403	1.010329	0.992896	1.021188	1.045039
m'(cotton) /g	0.000980	0.001087	0.000847	0.001164	0.001127	0.001142
ΔT_c /K	1.67405	1.74899	1.66615	1.63859	1.68445	1.72396
$(\varepsilon_{calor})·(-\Delta T_c)$ /J	−24802.7	−25913.0	−24685.7	−24277.4	−24956.8	−25542.3
$(\varepsilon_{cont})·(-\Delta T_c)$ /J	−26.76	−28.16	−26.61	−26.08	−26.98	−27.67
ΔU_{decomp} HNO$_3$ /J	46.59	47.78	43.30	45.69	39.72	45.99
ΔU_{corr} /J	19.13	20.11	19.05	18.66	19.32	19.79
-$m'·\Delta_c u'$ /J	16.61	18.42	14.35	19.72	19.10	19.35
$\Delta_c u°$ (cr) /(J·g^{-1})	−24376.8	−24382.1	−24383.7	−24392.7	−24388.9	−24386.5
$-\Delta_c u°$ (cr) /(J·g^{-1})	24,387.3			24,392.0		
$u(\Delta_c u°)$ / J·g^{-1}	3.9[b]			5.6[b]		

[a] The definition of the symbols assigned according [19] are as follow: m(substance) and m'(cotton) are the mass of compound burnt and the mass of cotton thread used in each experiment, respectively, masses were corrected for buoyancy and water content; V(bomb) = 0.32 dm^3 is the internal volume of the calorimetric bomb; p^i(gas) = 3.04 MPa is the initial oxygen pressure in the bomb; m^i(H$_2$O) = 1.00 g is the mass of water added to the bomb for dissolution of combustion gases; $\Delta T^c = T^f - T^i + \Delta T_{corr}$ 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 $(\varepsilon_{cont})·(-\Delta T_c) = (\varepsilon_{cont}^i)·(T^i - 298.15) + (\varepsilon_{cont}^f)·(298.15 - T^f + \Delta T_{corr.})$. ΔU_{decomp} HNO$_3$ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.
[b] Uncertainties in this table are expressed as the standard deviation of the mean.