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Determination of vapor pressures, enthalpies of sublimation, and enthalpies of fusion of benzenetriols

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Abstract

Molar enthalpies of sublimation of 1,2,4-, 1,2,3-, and 1,3,5-tri-hydroxy-benzene, were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. The molar enthalpies of fusion and molar heat capacities of these compounds were measured by DSC. The measured data sets of vaporization, sublimation and fusion enthalpies were checked for internal consistency. Strength of the inter- and intra-molecular hydrogen bonding in di- and tri-hydroxy-benzenes have been assessed.

Keywords: Benzene derivatives; Vapor pressure; Enthalpy of sublimation; Enthalpy of fusion; Hydrogen bonding

1. Introduction

Phenols and poly-phenols may be used as molecular models to investigate the nature of the interaction of more complex biological structures having these moieties (catecholamines, tannins, etc.) with other systems such NAD^+, nucleic-acid bases, proteins, etc. The phenolic aromatic ring and, in particular, the presence of hydroxy groups capable of forming intra-molecular hydrogen bonds appear to be a structural necessity for pharmacological activity. There are surprisingly very little thermochemical data on di- [1–5] and especially on tri-hydroxy-substituted benzenes [6–8]. In this work molar enthalpies of sublimation 1,2,4-, 1,2,3-, and 1,3,5-tri-hydroxy-benzene has been obtained from vapor pressure measurements. The molar enthalpies of fusion of these compounds were measured by DSC.

2. Experimental

2.1. Materials

Samples of substituted benzenes were of commercial origin (Aldrich, Fluka) and were additionally purified by repeated fractional sublimation in vacuum. The degree of purity was controlled using a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett Packard 3390A integrator. The carrier gas (nitrogen) flow was $12.1\ \mathrm{cm^3\,s^{-1}}$. A capillary column HP-5 (stationary phase crosslinked 5% PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was $T = 353\ \mathrm{K}$ for 60 s followed by a heating rate of $0.167\ \mathrm{K\,s^{-1}}$ to $T = 523\ \mathrm{K}$. No impurities (greater than mass fraction 10^{-3}) could be detected in the samples used for the vapor pressure and DSC measurements.

2.2. Measurements of vapor pressure and enthalpies of sublimation using the transpiration method

Vapor pressures and enthalpies of sublimation of the benzenetriols (see Table 1) were determined using the method of transference in a saturated N_2-stream. The method has been described before [9,10] and has proved to give results being in excellent agreement with other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was

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Table 1
Results for the vapor pressure p and $\Delta_{cr}^{g}H_m^\circ$ by the transpiration method

T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (Pa)[d]	$p_{exp} - p_{calc}$ (Pa)	$\Delta_{cr}^{g}H_m^\circ$ (kJ mol^{-1})
1,2,3-Benzenetriol (cr) $\Delta_{cr}^{g}H_m^\circ$ (298.15 K) = 103.95 ± 0.35 kJ mol^{-1}[e]					
326.1[f]	0.464	71.30	0.126	0.00	103.27
328.1[f]	0.587	73.19	0.155	0.00	103.22
333.2[f]	0.449	32.11	0.271	−0.01	103.09
338.2[f]	1.997	81.14	0.477	−0.01	102.97
343.0[f]	0.446	11.36	0.760	−0.05	102.85
346.0[f]	0.477	8.89	1.038	−0.06	102.78
347.9[f]	0.409	5.80	1.365	0.02	102.73
351.8[f]	0.550	5.35	1.991	0.00	102.63
352.1[f]	0.602	5.80	2.009	−0.04	102.63
354.1[f]	1.353	10.29	2.546	0.05	102.58
357.9[f]	0.599	3.13	3.710	0.11	102.49
359.2[f]	0.701	3.38	4.018	−0.06	102.45
360.9[f]	0.489	1.98	4.791	0.00	102.41
362.0[f]	0.615	2.26	5.256	−0.09	102.38
364.9[f]	0.630	1.77	6.891	−0.12	102.31
367.9[f]	0.802	1.65	9.426	0.21	102.24
370.9[f]	0.716	1.15	12.024	−0.06	102.16
374.0[f]	0.704	0.86	15.757	−0.06	102.09
326.1[g]	0.778	126.88	0.123	0.00	103.27
330.2[g]	0.812	81.68	0.197	0.00	103.17
332.0[g]	0.706	55.28	0.252	0.01	103.12
333.2[g]	0.828	59.12	0.276	0.00	103.09
334.2[g]	1.065	64.39	0.326	0.01	103.07
337.4[g]	0.560	25.85	0.423	−0.02	102.99
338.0[g]	0.868	36.73	0.464	−0.01	102.97
343.3[g]	1.112	25.64	0.849	0.02	102.84
344.2[g]	1.270	26.02	0.955	0.04	102.82
346.3[g]	1.025	17.79	1.127	−0.01	102.77
348.4[g]	0.852	11.85	1.402	0.00	102.72
349.3[g]	1.262	15.26	1.616	0.08	102.70
352.3[g]	1.404	13.20	2.078	0.00	102.62
356.1[g]	1.222	7.42	3.216	0.19	102.53
358.4[g]	1.325	6.58	3.932	0.15	102.47
361.4[g]	1.049	4.13	4.954	−0.07	102.40
363.2[g]	0.868	2.95	5.736	−0.21	102.36
364.3[g]	1.333	3.92	6.632	0.04	102.33
367.4[g]	1.380	3.08	8.749	−0.02	102.25
370.5[g]	1.080	1.86	11.362	−0.24	102.18
1,2,4-Benzenetriol (cr) $\Delta_{cr}^{g}H_m^\circ$ (298.15 K) = 124.20 ± 0.55 kJ mol^{-1}[h]					
341.1	0.129	111.5	0.024	0.00	123.18
344.1	0.209	121.3	0.035	0.00	123.11
347.3	0.213	86.71	0.050	0.00	123.03
348.1	0.211	76.67	0.056	0.00	123.01
349.1	0.248	77.72	0.065	0.00	122.99
352.1	0.326	73.51	0.091	0.00	122.92
354.3	0.434	71.69	0.124	0.00	122.86
358.3	0.365	36.98	0.202	0.01	122.77
361.3	0.194	15.19	0.261	−0.01	122.70
364.3	0.174	9.92	0.359	−0.02	122.63
365.4	0.336	15.96	0.431	0.00	122.60
367.4	0.332	12.15	0.560	0.03	122.55
368.4	0.340	11.34	0.614	0.02	122.53
370.5	0.289	8.14	0.727	−0.02	122.48
371.2	0.336	8.10	0.849	0.05	122.46
371.2	0.307	8.02	0.783	−0.02	122.46
372.0	0.395	9.11	0.887	0.01	122.44
374.2	0.375	6.93	1.109	0.01	122.39
375.2	0.262	4.46	1.204	−0.02	122.37
376.3	0.307	4.74	1.325	−0.05	122.34
377.3	0.235	3.16	1.520	0.00	122.32
378.3	0.336	4.09	1.682	−0.01	122.29

Table 1 (*Continued*)

T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (Pa)[d]	$p_{exp} - p_{calc}$ (Pa)	$\Delta_{cr}^{g} H_m^\circ$ (kJ mol^{-1})
380.3	0.375	3.73	2.061	−0.01	122.24
382.4	0.492	3.97	2.539	−0.02	122.19
1,3,5-Benzenetriol (cr) $\Delta_{cr}^{g} H_m^\circ$ (298.15 K) $= 135.5 \pm 1.3$ kJ mol^{-1}[i]					
355.2	0.0142	648.7	0.00043	0.0000	134.08
357.1	0.0183	675.5	0.00053	0.0000	134.03
359.1	0.0187	512.4	0.00072	0.0000	133.99
361.2	0.0194	435.0	0.00087	0.0000	133.94
364.7	0.0239	323.9	0.00144	0.0000	133.85
366.6	0.0240	252.0	0.00187	0.0001	133.80
367.4	0.0194	190.2	0.00200	0.0001	133.79
369.3	0.0241	187.9	0.00251	0.0001	133.74
370.4	0.0216	151.9	0.00279	0.0000	133.71
371.8	0.0112	66.64	0.00329	0.0000	133.68
372.2	0.0195	115.4	0.00331	−0.0001	133.67
373.1	0.0189	103.2	0.00360	−0.0002	133.65
373.7	0.0128	60.73	0.00413	0.0001	133.63
375.2	0.0135	51.20	0.00515	0.0003	133.60
376.2	0.0334	126.8	0.00516	−0.0002	133.57
377.2	0.0250	84.70	0.00578	−0.0003	133.55
380.2	0.0205	49.22	0.00817	−0.0003	133.48
381.3	0.0159	31.76	0.00980	0.0002	133.45
382.4	0.0255	45.57	0.01097	0.0002	133.42

[a] Temperature of saturation. N_2 gas flow 1.0–1.5 $cm^3\,s^{-1}$.
[b] Mass of transferred sample condensed at $T = 273$ K.
[c] Volume of nitrogen used to transfer mass m of sample.
[d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 273$ K.
[e] $\ln p = (326.121/R) - (111\,285.031/R(T)) - (24.59/R \ln(T/298.15))$.
[f] N_2 gas flow 0.75 $cm^3\,s^{-1}$.
[g] N_2 gas flow 1.38 $cm^3\,s^{-1}$.
[h] $\ln p = (357.179/R) - ((131310.076/R)(T)) - (23.84/R \ln(T/298.15))$.
[i] $\ln p = (341.541/R) - (1\,42\,679.00/R(T)) - (24.21/R \ln(T/298.15))$.

determined by GC analysis using an external standard (saturated hydrocarbon). Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream is valid, values of the vapor pressure p were calculated according to

$$p = \frac{mRT_a}{V(N_2)M} \tag{1}$$

where $R = 8.31451\,J\,K^{-1}\,mol^{-1}$; m the mass of transported compound; $V(N_2)$ the volume of transporting gas; M the molar mass of the compound; and T_a is the temperature of the soap bubble meter. The volume of the gas $V(N_2)$ transferred through the tube was determined from the flow rate and time measurements. The vapor pressure p at each saturation temperature was calculated from the mass of sample collected within a definite time period according to Eq. (1). The equation

$$R \ln(p) = a + \frac{b}{T} + \Delta_{cr}^{g} C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

was fitted to the experimental p–T data using a and b as adjustable parameters. The following equation gives the value of the sublimation enthalpy at temperature T:

$$\Delta_{cr}^{g} H_m^\circ(T) = -b + \Delta_{cr}^{g} C_p\, T \tag{3}$$

T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (here chosen as 298.15 K). The results for benzenetriols together with their corresponding parameters a and b are listed in Table 1. Values of $\Delta_{cr}^{g} C_p$ have been derived from the experimental isobaric molar heat capacities of solid, C_p(cr), benzenetriols with help of the additive procedure suggested by Chickos et al. [11]. The results from vapor pressure measurement on benzenetriols together with the corresponding parameters a and b are listed in the Table 1.

2.3. DSC measurements

The thermal behavior of substituted benzenes including melting temperatures and enthalpies of fusion were determined with a computer controlled Perkin-Elmer DSC-2. For all measurements an empty pan run was subtracted and specific heat capacity was calculated. The fusion temperatures and enthalpies were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_0 = 429.8$ K and $\Delta H_{ref} = 28.5\,J\,g^{-1}$). The thermal behavior of each specimen was investigated during first and second heating after cooling the sample from the melt at a cooling rate of 10 K min^{-1}. The uncertainty for temperature is ±0.5 K and for enthalpy of fusion $\pm 1\,\mathrm{J\,g^{-1}}$. The DSC measurements on each sample of substituted benzenes were repeated twice and values agreed within the experimental uncertainties $\pm 0.2\,\mathrm{kJ\,mol^{-1}}$ for the enthalpy of fusion and $\pm 0.5\,\mathrm{K}$ for the melting temperature.

Values of $C_p(\mathrm{cr})$ at 298.15 K were measured by DSC, $158.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,2,3-tri-hydroxy-benzene; $153.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,2,4-tri-hydroxy-benzene; and $156.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,3,5-tri-hydroxy-benzene. Values of $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_p$, required for the correction of the sublimation enthalpies, were calculated from these experimental $C_p(\mathrm{cr})$ values with help of the additive procedure suggested by Chickos et al. [11]. They are as follows: $24.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,2,3-tri-hydroxy-benzene; $23.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,2,4-tri-hydroxy-benzene; and $24.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 1,3,5-tri-hydroxy-benzene.

3. Results and discussion

Many hydroxy-substituted benzenes undergo phase transitions in the crystalline state. For example, 1,3-di-hydroxy-benzene exhibit α–β phase transition at 369 K [12]. Information about the possible phase transitions in the sample under study is indispensable for the sublimation enthalpy measurements using the transpiration method. Such knowledge helps by choice of the temperature range for investigation and allows to measure vapor pressures within the range where compound of interest exists in only the certain crystalline modification. That is why prior to the transpiration experiments, the samples of tri-hydroxy-benzenes were carefully studied by DSC. No phase transitions except of melting in all compounds of interest have been detected.

3.1. 1,2,3-Tri-hydroxy-benzene

The spread of the sublimation enthalpies of 1,2,3-tri-hydroxy-benzene available from the literature is confusing. Hirschbrunner [13] reported value of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(387.5\,\mathrm{K}) = 89.1\,\mathrm{kJ\,mol^{-1}}$ from calorimetric measurements in the temperature range 377–398 K. Adjusting of his value to the reference temperature with help of $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_p$ and procedure from this work provides $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(298.15\,\mathrm{K}) = 91.3\,\mathrm{kJ\,mol^{-1}}$. This value corresponds well with the result by Smirnov et al. [8] derived from transpiration method $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(325.5\,\mathrm{K}) = 92.3 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$, which we slightly corrected with our $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_p$ value to the reference temperature: $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(298.15\,\mathrm{K}) = 93.0 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$. Surprisingly, a substantial higher value of the standard enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(298.15\,\mathrm{K}) = 116.9 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$ has been reported by Ribeiro da Silva et al. [7] from the drop-microcalorimetric method. However, as a mater of fact, the measurements in this work were performed “at a suitable temperature between 397 and 493 K” and the observed sublimation enthalpy (which is not reported) was corrected to 298.15 K contribution estimated by group-additivity method with values of Stull et al. [14].

The value $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(298.15\,\mathrm{K}) = 103.9 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ of 1,2,3-tri-hydroxy-benzene was measured in this work (see Table 1) and this value meet the average result of sublimation enthalpies available from the literature [7,8]. It is worse mentioning, that we performed vapor pressure measurements on 1,2,3-tri-hydroxy-benzene twice (with interval of about 6 months), using two different saturation cells, different gas-flows (see Table 1) and different external standards (hydrocarbons tridecane and tetradecane) for calibration of GC. Results from both sets of measurements were indistinguishable and we treated them together to obtain the value of enthalpy of sublimation of 1,2,3-tri-hydroxy-benzene (Table 1). Very important additional information to this striking situation could provide results from ebulliometric vapor pressure measurements on liquid 1,2,3-tri-hydroxy-benzene reported by von Terres et al. [15] in the temperature range 450.4–582.0 K. Using their experimental p–T results and Eqs. (2) and (3), the value of vaporization enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ\,(298.15\,\mathrm{K}) = 87.5\,\mathrm{kJ\,mol^{-1}}$, has been calculated with help of $\Delta_{\mathrm{l}}^{\mathrm{g}} C_p = 69.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$ (assessed by additive procedure [11]). A valuable test of the consistency of the experimental data on vaporization enthalpy [15] and sublimation enthalpy (this work) is to obtain the enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ$, of 1,2,3-tri-hydroxy-benzene. Indeed, the enthalpy of fusion can be calculated as the difference $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ\,(298.15\,\mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ - \Delta_{\mathrm{l}}^{\mathrm{g}} H_m^\circ = 103.9 - 87.5 = 16.4\,\mathrm{kJ\,mol^{-1}}$ (both enthalpies referred to $T = 298.15\,\mathrm{K}$) and can be compared with the experimental value measured by DSC. However, the experimental enthalpy of fusion, measured in this work, $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ(T_{\mathrm{fus}}) = 25.9\,\mathrm{kJ\,mol^{-1}}$, is at the melting temperature 405.6 K. Because of the deviation from $T = 298.15$ this observed value of the enthalpy of fusion of 1,2,3-tri-hydroxy-benzene had to be corrected to this reference temperature. The correction was calculated from the equation [11]:

$$\{\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ(T_{\mathrm{fus}}\,\mathrm{K}) - \Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ\,(298.15\,\mathrm{K})\}\,(\mathrm{kJ\,mol^{-1}}) = \Delta_{\mathrm{cr}}^{\mathrm{l}} C_p\{(T_{\mathrm{fus}}\,\mathrm{K}) - 298.15\} \qquad (4)$$

where value of $\Delta_{\mathrm{cr}}^{\mathrm{l}} C_p = 65.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$ has been derived from the isobaric molar heat capacities of liquid, C_p^{l} (assessed by additive procedure [11]), and solid, $C_p(\mathrm{cr})$, measured in this work. With this correction (the uncertainty of the correlation was not taken into account), value of the standard enthalpy of fusion at $T = 298.15\,\mathrm{K}$, $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ\,(298.15\,\mathrm{K}) = 18.9\,\mathrm{kJ\,mol^{-1}}$ was calculated. Thus, the enthalpy of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_m^\circ$ measured by calorimetry (and adjusted to $T = 298.15\,\mathrm{K}$) is in acceptable agreement with the value calculated from difference $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ - \Delta_{\mathrm{l}}^{\mathrm{g}} H_m^\circ = 22.8\,\mathrm{kJ\,mol^{-1}}$ (even taking into account a long way of extrapolation of the vaporization enthalpy). Thus, values of vaporization and sublimation enthalpies taken for comparison posses internal consistency, in other words, combination of the result for vaporization enthalpy from von Terres et al. [15] with the experimental fusion enthalpy supports the value of sublimation enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 103.0 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$ of 1,2,3-tri-hydroxy-benzene derived in this work using transpiration method. It should be mentioned that enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ(T_{\mathrm{fus}})$, measured in this work in disagreement with another value available from the literature [16]: $18.55\,\mathrm{kJ\,mol^{-1}}$ at 407 K, measured by using a Dupont-9900 thermal analysis DSC. Surprisingly, they purified the sample of 1,2,3-tri-hydroxy-benzene by repeated distillation under reduced pressure and stored it in the dark flask. From our experience due to the relatively high melting temperature of this compound, certain decomposition could happen during distillation, as well as, fresh sublimed white crystals of 1,2,3-tri-hydroxy-benzene become pink even after several days of storage in the dark flask. Taking into account the disagreement with the literature we repeated DSC measurements on 1,2,3-tri-hydroxy-benzene (with interval of about 6 months), using another fresh sublimed sample and the fusion enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ(T_{\mathrm{fus}}) = 25.9\,\mathrm{kJ\,mol^{-1}}$ was very close to the first mesurement.

3.2. 1,2,4-Tri-hydroxy-benzene

The standard enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 124.2 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$ of 1,2,4-tri-hydroxy-benzene was measured in this work by transpiration method within the temperature range 341–382 K (see Table 1) and this value is in disagreement with the result $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(325.5\,\mathrm{K}) = 93.8 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ derived by Smirnov et al. [8] using also the transpiration method within the temperature range 298–353 K. Correction of their result (with our value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_p = 23.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$) to the reference temperature gives somewhat larger value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 94.5 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$, but disagreement is still obviously. Searching for reason we analysed the technique applied by Smirnov et al. [8] and reveal, that they used spectroscopic method for the determination of masses of the transported material. Tri-oxybenzene are known as very sensitive to the light and from our experiences such analytic could suffer from uncontrolled decomposition of the compound in presence of the light and solvent solvent. Opposite to their technique, we used GC method and any possible decomposition of the analyt could be detected. Ribeiro da Silva et al. [7] reported $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 119.8 \pm 1.2\,\mathrm{kJ\,mol^{-1}}$ from the drop-microcalorimetric method and their value is in fair agreement with our result (see Table 1).

3.3. 1,3,5-Tri-hydroxy-benzene

The standard enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 135.5 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$ of 1,3,5-tri-hydroxy-benzene was measured in this work by transpiration method within (see Table 1) and this value is in a close agreement with the result $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 131.7 \pm 1.0\,\mathrm{kJ\,mol^{-1}}$ reported by Ribeiro da Silva et al. [7] from the drop-microcalorimetric method. Vapor pressures of the 1,3,5-tri-hydroxy-benzene were measured with a simultaneous torsion and mass loss effusion technique [6]. The value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(394.99\,\mathrm{K}) = 127.0\,\mathrm{kJ\,mol^{-1}}$ was derived in this work as a mean from two methods. Correction of this result (with our value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_p = 24.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$) to the reference temperature gives the value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(298.15\,\mathrm{K}) = 129.2\,\mathrm{kJ\,mol^{-1}}$, which is still in acceptable agreement with two aforementioned results. However, the result $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ(343\,\mathrm{K}) = 155.1 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ derived by Smirnov et al. [7] from the transpiration method within the temperature range 323–363 K is again in a crucial disagreement with another available data, confirming our doubt on analytical procedure used in their work.

3.4. Consistency test of the experimental results

The embarrassing scatter of the experimental results available from the literature and their sometimes drastic disagreement with our own results has prompted careful testing of our results for consistency with those measured by another methods. For this purpose we selected from the

Table 2
Experimental results for hydroxy-benzenes

Compound (1)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ$ [a] at 298.15 K ($\mathrm{kJ\,mol^{-1}}$) (2)	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ$ [b] at T_{fus} ($\mathrm{kJ\,mol^{-1}}$) (3)	T_{fus} [c] (K) (4)	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ$ [d] at 298.15 K ($\mathrm{kJ\,mol^{-1}}$) (5)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m^\circ$ [e] at 298.15 K ($\mathrm{kJ\,mol^{-1}}$) (6)	Δ [f] ($\mathrm{kJ\,mol^{-1}}$) (7)
1,2,3-Tri-hydroxy-benzene	103.9 ± 0.3	25.9	405.6	18.9	85.1	36.0
1,2,4-Tri-hydroxy-benzene	124.2 ± 0.5	28.8	413.2	20.6	103.6	55.7
1,3,5-Tri-hydroxy-benzene	135.5 ± 1.3	34.5	491.8	21.3	114.2	66.7
1,2-Dihydroxy-benzene	87.5 ± 0.3 [2]	22.9 [24]	377.6 [24]	18.6	68.9	25.4
1,3-Dihydroxy-benzene	96.4 ± 1.7 [5][g]	18.9 [24]	382.6 [24]	15.2	81.2	41.5
1,4-Dihydroxy-benzene	105.3 ± 1.0 [4][g]	27.2 [24]	443.7 [24]	18.3	87.0	44.6
Hydroxy-benzene	68.7 ± 0.5 [22]	11.5 [23]	314.1 [23]	11.0	57.7	19.7

[a] From transpiration method (see Table 1).

[b] The enthalpy of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ$ measured by DSC with precision $\pm 0.2\,\mathrm{kJ\,mol^{-1}}$.

[c] Extrapolated peak onset temperature from DSC measurements.

[d] The enthalpy of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ$ measured by DSC and adjusted to 298.15 K (see text).

[e] The enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_m^\circ$, calculated as the difference $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ - \Delta_{\mathrm{cr}}^{\mathrm{l}}H_m^\circ$ (the difference between column 2 and 5).

[f] The difference between vaporization enthalpies in column 6 with those of methyl-benzenes (see text).

[g] The enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ$ measured in the literature [4,5] at elevated temperatures was adjusted to 298.15 K.

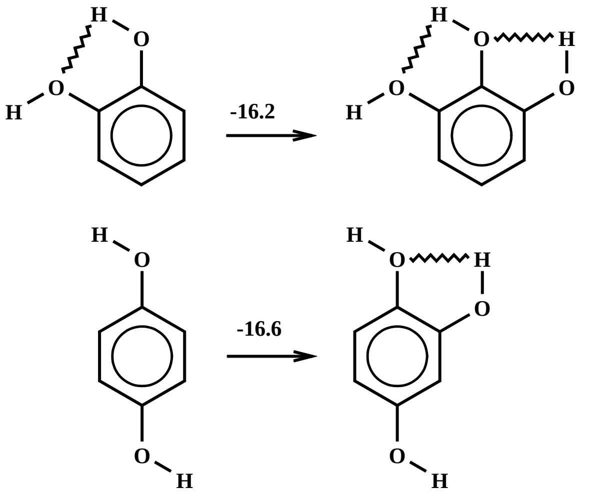

Fig. 1. Presentation of the consistency (see text) of experimental vaporization enthalpies for di- and tri-hydroxy-benzenes (kJ mol^{-1}).

literature the set (Table 2, column 2) of the reliable sublimation enthalpies of 1,2-dihydroxy-benzene (calorimetry [2]), of 1,3-di-hydroxy-benzene (quarzfiber [5]), and of 1,4-di-hydroxy-benzene (simultaneous torsion and mass loss-effusion technique [4]). The validity of the results measured for tri-hydroxy-benzenes by transpiration method in this work can be verified by comparison with these selected results in the way presented in Fig. 1. Indeed, two molecules 1,2-di-hydroxy-benzene and 1,2,3-tri-hydroxy-benzene differ by a hydroxy group, which apparently builds the intra-molecular bridge to the neighboring oxygen atom. The difference of the enthalpies of vaporization (Table 2, column 6) between 1,2-di-hydroxy-benzene and 1,2,3-tri-hydroxy-benzene ($68.9 - 85.1 = -16.2$ kJ mol^{-1}) presents a contribution to the enthalpy of vaporization due to this intra-molecular boned brick. Let us consider another pair of molecules—1,4-di-hydroxy-benzene and 1,2,4-tri-hydroxy-benzene are also differ by a hydroxy group, which similarly builds the intra-molecular bridge to the neighboring oxygen atom in the latter. Following, the difference of the enthalpies of vaporization (Table 2, column 6) between 1,4-di-hydroxy-benzene and 1,2,4-tri-hydroxy-benzene ($87.0 - 103.6 = -16.6$ kJ mol^{-1}) should be again due to this intra-molecular boned brick and it virtually is the same (-16.6 kJ mol^{-1}) for both pairs taken into consideration. It is worth to mention, that for this test the results from three different experimental techniques have been involved. Thus, consistency of the set of the experimental results measured in this work has been proven successfully.

3.5. Strength of the inter-molecular hydrogen bond in di- and tri-hydroxy-benzenes

Another possibility to test the consistency of the data derived from the transpiration method is the comparison of enthalpies of vaporization of hydroxy-benzene (Table 2, column 6) and those of their homomorph methyl-benzenes. Such test could be performed in the similar way as we suggested recently [10] for the comparison of enthalpies of vaporization of *n*-alkanols and those of alkanes. Indeed, for alkanes only non-associating intermolecular van der Waals' interactions determine the values of their enthalpies of vaporization. Enthalpies of vaporization of alkanes which are obtained by replacing the OH-group by a CH_3-group (R–CH_3) will essentially represent the non-associative contribution of the alcohol (R–OH) to its enthalpy of vaporization. The difference of the enthalpies of vaporization between alkanols, R–OH, and its homomorph, R–CH_3, presents a crude measure for contribution to the enthalpy of vaporization due to self-association of alcohols [10,17]. A remarkable constancy

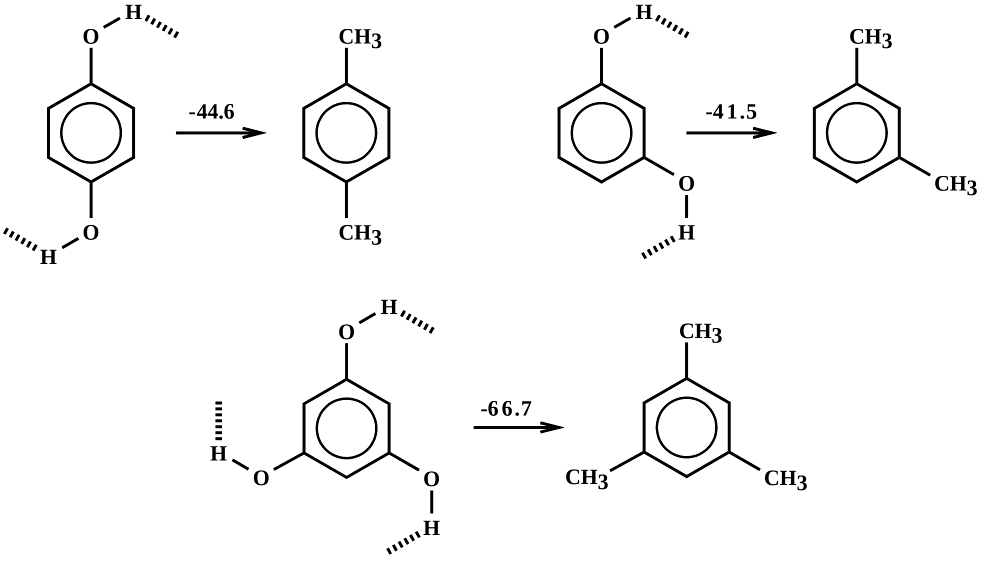

Fig. 2. Interpretation of strength of the inter-molecular hydrogen bond from vaporization enthalpies of di- and tri-hydroxy-benzenes and their homomorphs (kJ mol^{-1}).

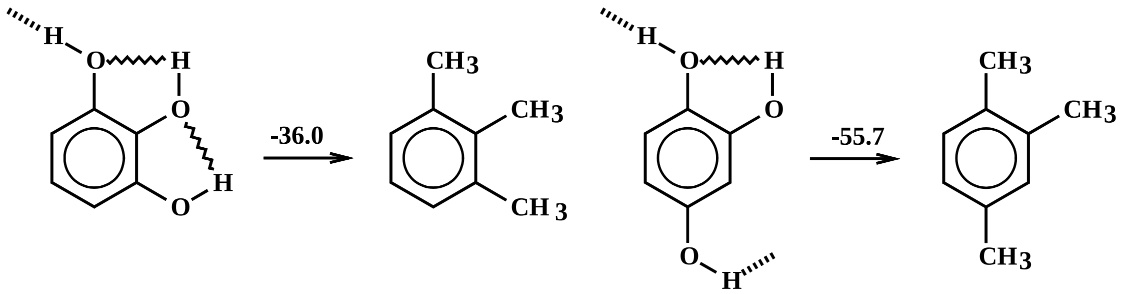

Fig. 3. Interpretation of strength of the intra-molecular hydrogen bond from vaporization enthalpies of tri-hydroxy-benzenes and their homomorphs (kJ mol^{-1}).

of differences in enthalpies of vaporization at 298.15 K of 21–25 kJ mol^{-1} was observed indicating that the contribution to $\Delta_l^g H_m^\circ$ of alcohols due to inter-molecular hydrogen bonding is nearly independent on the chain length [10].

Following this pattern, experimental data on the enthalpies of vaporization of hydroxy-benzenes at 298.15 K (Table 2, column 6) were compared with those $\Delta_l^g H_m^\circ$(298.15 K) on their homomorphs (methyl-benzenes), available from the literature [18]: 1,2,3-tri-methyl-benzene 49.1 kJ mol^{-1}, 1,2,4-tri-methyl-benzene 47.9 kJ mol^{-1}, 1,3,5-tri-methyl-benzene 47.5 kJ mol^{-1}, 1,2-di-methyl-benzene 43.5 kJ mol^{-1}; 1,3-di-methyl-benzene 42.7 kJ mol^{-1}, 1,4-di-methyl-benzene 42.4 kJ mol^{-1}, and methyl-benzene 38.1 kJ mol^{-1}. The differences of the enthalpies of vaporization between hydroxy-benzenes and methyl-benzenes are listed in the Table 2, column 7. For the 1,3-di-, 1,4-di-, and 1,3,5-tri-hydroxy-benzenes, these differences could be interpreted as contribution to the enthalpy of vaporization due to self-association for these three hydroxy-benzenes. In other words, these differences are a rough measure for the strength of the inter-molecular hydrogen bonding in these species. According to the Fig. 2, it is obvious, that 1,3-di-hydroxy-benzene and 1,4-di-hydroxy-benzene possess two inter-molecular hydrogen bonds, and 1,3,5-tri-hydroxy-benzene three inter-molecular hydrogen bonds. Thus, enthalpic differences presented in (Table 2, column 7), for these molecules, divided with the number of bonds (for 1,4-di-hydroxy-benzene $-44.6 : 2 = 22.3$ kJ mol^{-1}; for 1,3-di-hydroxy-benzene $-41.5 : 2 = 20.8$ kJ mol^{-1}; for 1,3,5-tri-hydroxy-benzene $-66.7 : 3 = 22.3$ kJ mol^{-1}), provide a very consistent quantity of about 22 kJ mol^{-1} as assessment of the strength of the inter-molecular hydrogen bond in di- and tri-hydroxy-benzenes. This value is consonant with the strength of the inter-molecular hydrogen bond 19.7 kJ mol^{-1} (Table 2, column 7) obtained in the similar way for mono-hydroxy-benzene (phenol).

3.6. Strength of the intra-molecular hydrogen bond in di- and tri-hydroxy-benzenes

According to the Fig. 3, it is apparent, that 1,2,3-tri-hydroxy-benzene exhibit one inter-molecular hydrogen bond and two intra-molecular hydrogen bonds. As well as, 1,2,4-tri-hydroxy-benzene possess two inter-molecular hydrogen bonds and one intra-molecular hydrogen bond. The enthalpic differences of the enthalpies of vaporization between tri-hydroxy-benzenes and tri-methyl-benzenes are listed in the Table 2, column 7. Bearing in mind the value of 22 kJ mol^{-1}, derived above as assessment of the strength of the inter-molecular hydrogen bond in di- and tri-hydroxy-benzenes, the strength of the intra-molecular hydrogen bond in tri-hydroxy-benzenes could be calculated: for 1,2,3-tri-hydroxy-benzene $[-36.0$ to $(-22.0)]\ 2 = -7.0$ kJ mol^{-1}; for 1,2,4-tri-hydroxy-benzene $[-55.7$ to $(-22.0)]\ 2 = -11.7$ kJ mol^{-1}. The average value of 9.3 kJ mol^{-1} presents a crude measure of the strength of the intra-molecular hydrogen bond in hydroxy-benzenes and this value in agreement with the range $(-3.0$ to $9.7)$ kJ mol^{-1} measured by IR [19,20] and NMR [21] spectroscopy for the 1,2-di-hydroxy-benzene (catechol).

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