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Thermodynamic Parameters of Sublimation of Acrylic Acid Phenyl- and Furyl-containing Derivatives

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Abstract—Temperature dependence of saturated vapor pressure has been determined for five phenyl and furyl derivatives of acrylic acid. Processing of the experimental data has given standard enthalpy, entropy, and the Gibbs free energy of sublimation of the studied compounds. Additivity of the sublimation enthalpies has been confirmed, and enthalpies of sublimation of the constituting fragments have been calculated.

Keywords: acrylic acid, enthalpy, entropy, the Gibbs free energy, sublimation

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Acrylic acid derivatives are widely used in production of construction mixtures, industrial glues, pastes, sealers, liquid holders, superabsorbents, fertilizers, paint-and-lacquer materials, polyacrylonitrile fibers, and acrylate rubbers [1]. Acrylic acid derivatives containing cyclic fragments are used as drugs and biologically active materials in medicine [2] as well as components of polymer, lightproof, and phosphor materials [3]. Optimization of preparation, purification, and application of these compounds often faces certain complications due to scarce information on thermodynamic parameters of their phase transitions. In particular, many technological tasks require knowledge of dependence of saturated vapor pressure on temperature, whereas sublimation enthalpy is a crucial parameter to determine thermal characteristics of the substance at its critical point. The sublimation enthalpy, entropy, and the Gibbs energy bear information on intermolecular interactions on the crystal surface.

In this work we studied the phenyl-containing derivatives of acrylic acid **I**–**III** and mixed derivatives containing both phenyl and furyl substituents **IV** and **V**: 3-phenylacrylic acid (**I**), 3-(4-dimethylaminophenyl)acrylic acid (**II**), 3-(4-methoxyphenyl)acrylic acid (**III**), 3-(5-phenylfur-2-yl)acrylic acid (**IV**), and 3-[5-(4-methoxyphenyl)fur-2-yl]acrylic acid (**V**).

Due to low fugacity of the studied compounds, temperature dependence of their saturated vapor pressure was determined by the Knudsen integral effusion method. Although this measurement procedure is less rapid than the differential method, it is free of the major drawbacks of the latter: the condensation of the vapor at the suspension filament and high error of determination of temperature of the effusion chamber and the membrane [4].

In our experiments, mass of the effused substance was at least 0.0013 g, and effusion took no shorter than 1800 s; thus, those parameters were determined with significant accuracy (the relative error was below 1%). For each of the studied compounds, 7–8 measurements were performed, over the temperature range of at least 25 K. The correlation coefficient of fitting temperature dependence of the saturated vapor pressure was 0.9960–0.9998, and relative error of determination of sublimation standard enthalpy and entropy was below 5%.

Complications of calculation of sublimation enthalpy are described in detail in [4, 5]. In particular, Lebedev and Miroshnichenko [4] noted that the available experimental data were not sufficient for application of the additivity method to calculate the sublimation enthalpy, hence, an indirect scheme was suggested: determination of enthalpies of formation of the compound in solid and gaseous states by the additive method, and elucidation of the sublimation enthalpy as the difference of the formation enthalpies. In [6], the sublimation enthalpy of benzene- and carborane-

Table 1. Primary data of effusion experiment run to determine enthalpy of sublimation of benzoic acid

T, K	τ, s	$\Delta m \times 10^3$, g	P_{ch}, Pa	P, Pa
312.0	3070	1.400	0.6603	0.7528
314.0	3214	1.600	0.7231	0.8244
315.0	3248	1.700	0.7615	0.8681
315.8	3130	1.700	0.7902	0.9008
319.2	1916	1.500	1.1466	1.3071
334.6	2676	10.050	5.6320	6.4205
335.7	2752	10.200	5.5668	6.3462
339.1	1845	11.840	9.6872	11.0434
340.9	1842	12.090	9.9341	11.3249
342.2	1841	13.655	11.2475	12.8222

containing compounds was determined using the additive method, similarly to calculation of evaporation enthalpy [4].

In order to recalculate the primary effusion data taking into account the experimental setup, we first measured vapor pressure of benzoic acid under the same conditions. The data (total effusion time τ, mass of the effused substance Δm, vapor pressure in the chamber P_{ch}, and the saturated vapor pressure P at temperature T) are given in Table 1.

The measured data was processed applying the least-squares method to the following fitting equation:

$$\ln P\,[\text{Pa}] = A + B/T,$$

where A = $\Delta_s S^0$, B = $-\Delta_s H^0/R$. In the case of benzoic acid, $A = 33.24 \pm 0.84$ and $B = 10510 \pm 270$ K with the correlation coefficient of 0.9987 (the errors were estimated assuming the Student distribution at confidence probability of 0.95). Standard sublimation enthalpy of benzoic acid at 312–342 K was 87.4 ± 2.2 kJ/mol. The sublimation enthalpy was reduced to 298.15 K using Eq. (1) [7].

$$\Delta_s H^0_{298.15} = \Delta_s H^0_T + [C_p(s) - C_p(g)](T - 298.15)$$
$$= \Delta_s H^0_T + [0.75 + 0.15 C^0_{p,298.15}(s)](T - 298.15). \quad (1)$$

In Eq. (1), $\Delta_s H^0_T$ is the standard sublimation enthalpy averaged over the studied temperature range; the difference of heat capacities of the substance in solid and in gaseous states [$C_p(s) - C_p(g)$] was expressed via the substance standard heat capacity in the solid state $C^0_{p,298.15}(s)$ following [8]. The $C^0_{p,298.15}(s)$ value in the case of benzoic acid was taken equal to 149.1 J mol^{-1} K^{-1} [9]. The so calculated sublimation enthalpy ($\Delta_s H^0_{298.15}$ 88.1 ± 2.2 kJ/mol) coincided well with the reference data (89.7 ± 1.0 kJ/mol) [9].

Table 2. Primary data of effusion experiments with the studied acrylic acid derivatives

Comp. no.	T, K	τ, s	$\Delta m \times 10^3$, g	P_{ch}, Pa	P, Pa
I	379.6	3360	38.870	17.20	19.61
	383.7	2963	48.375	23.80	27.13
	385.7	2310	49.625	31.40	35.79
	387.6	1801	46.500	37.85	43.15
	390.4	1800	68.875	56.26	64.14
	393.7	1802	70.255	57.63	65.69
	399.9	1800	124.115	102.61	116.98
	404.3	1630	162.480	149.15	170.03
II	396.7	25260	1.725	0.0890	0.1015
	401.9	28140	2.865	0.1337	0.1524
	403.1	15960	1.980	0.1632	0.1860
	408.3	7660	1.515	0.2618	0.2984
	415.1	7202	2.840	0.5144	0.5864
	422.6	3601	2.455	1.1554	1.3172
	425.9	3610	4.215	1.5233	1.7365
III	394.3	6042	9.445	2.107	2.401
	398.7	3720	8.520	3.103	3.538
	403.2	2402	9.795	5.556	6.334
	407.4	1800	11.675	8.884	10.128
	411.9	1811	20.575	14.427	16.446
	417.0	1759	36.590	22.814	26.008
	421.8	1796	43.980	40.176	45.800
IV	389.3	12405	1.725	0.1698	0.1936
	389.3	12121	1.450	0.1453	0.1656
	399.1	4870	1.620	0.4113	0.4689
	404.7	3600	2.350	0.8128	0.9266
	407.1	1829	1.830	1.2489	1.4237
	412.8	1808	3.705	2.5771	2.9379
	417.6	1803	4.330	3.4341	3.9149
	421.2	1800	7.045	4.9732	5.6695
V	395.3	7020	1.325	0.2175	0.2480
	398.4	5655	1.350	0.2762	0.3149
	403.7	3840	2.055	0.6241	0.7115
	407.3	5282	3.630	0.8040	0.9166
	412.0	3608	3.945	1.4216	1.6207
	418.1	3601	9.220	2.7255	3.1071
	423.6	3613	11.860	3.91580	5.4822
	425.2	3604	17.475	5.7960	6.6075

The saturated vapor pressure of the studied compounds was determined similarly. The primary effusion data are collected in Table 2. The $A = \Delta_s S$ and

Table 3. Standard enthalpy and entropy of sublimation of the studied acrylic acid derivatives, as determined from linear fitting of temperature dependence of the saturated vapor pressure

Comp. no.	Temperature range T, K	A	$-B \times 10^{-2}$, K	r	$\Delta_s H^0_T$, kJ/mol	$\Delta_s S^0_T$, J mol^{-1} K^{-1}
I	379.6–404.3	38.1±1.9	133.2±7.6	0.9960	110.7±6.3	221±16
II	396.7–425.9	40.0±1.9	168.0±8.0	0.9977	139.7±6.7	237±16
III	394.3–421.8	46.7±1.6	180.7±6.6	0.9987	150.2±5.5	298±13
IV	389.3–421.1	44.2±2.2	178.9±9.2	0.9968	148.7±7.6	272±19
V	395.3–425.2	45.6±2.0	186.0±8.1	0.9977	154.6±6.7	283±16

Table 4. Standard enthalpy, entropy, and the Gibbs free energy of sublimation of the studied acrylic acid derivatives at 298.15 K

Comp. no.	$\Delta_s H^0_{298.15}$, kJ/mol	$\Delta_s S^0_{298.15}$, J mol^{-1} K^{-1}	$\Delta_s G^0_{298.15}$, kJ/mol
I	113.8±6.3	230±16	45.2±7.9
II	144.5±6.7	251±16	69.7±8.2
III	154.6±5.5	310±13	62.2±6.7
IV	152.6±7.6	283±19	68.2±9.5
V	160.0±6.7	298±16	71.2±8.2

$B = -\Delta_s H^0/R$ coefficients of the ln P [Pa] = $A + B/T$ fitting equation, the corresponding correlation coefficients r, and the calculated enthalpy $\Delta_s H^0{}_T$ and entropy $\Delta_s S^0{}_T$ of sublimation (averaged over the studied temperature range) are collected in Table 3.

The standard entropy of sublimation was reduced to 298.15 K using Eq. (2).

$$\begin{aligned}\Delta_s S^0_{298.15} &= \Delta_s S^0{}_T + [C_p(s) - C_p(g)]\ln (T/298.15)\\ &= \Delta_s S^0{}_T + [0.75 + 0.15C^0_{p,298.15}(s)]\ln (T/298.15). \qquad (2)\end{aligned}$$

The standard heat capacity of the studied compounds in the solid state was calculated using the increments of the additive group method [7].

The so calculated standard enthalpy, entropy, and the Gibbs free energy of sublimation of the studied compounds at 298.15 K are given in Table 4.

The following enthalpies of sublimation corresponding to certain structural fragments were determined from the data on sublimation enthalpy of alkanes, alcohols, and aliphatic carboxylic acids [4]: CH_3 (10.3 kJ/mol), CH_2 (8.5 kJ/mol), COOH (44.8 kJ/mol); the corresponding value for benzene ring fragment C_6H_5 and C_6H_4 was 38 kJ/mol. The application of the similar method to enthalpies of sublimation of compounds **I**–**V**, using the previously calculated group contributions led to the overdetermined set of five linear equations with two unknown quantities; its solution gave sublimation enthalpies corresponding to CH= group (33 ± 5 kJ/mol) and furan cycle C_4H_4O 30±5 kJ/mol).

Enthalpies of sublimation of the studied compounds followed the additivity rules; therefore, the determined group contributions can be further used to estimate sublimation enthalpy of compounds containing the same structural fragments.

EXPERIMENTAL

Under normal conditions all studied compounds were fine crystalline solids. Compound **I** was prepared via reaction of benzaldehyde with acetic anhydride (Perkin reaction). Compounds **II**–**V** were prepared via the Knoevenagel condensation. In particular, compound **II** was prepared via reaction of 4-dimethylaminobenzaldehyde with malonic acid in pyridine and piperidine [10], compound **III** was prepared via a method adopted from [10], whereas compounds **IV** and **V** were prepared via condensation of the corresponding arylfurfurals with malonic acid [11, 12]. The prepared products were purified by recrystallization from ethanol.

Structures of compounds **I**–**V** were confirmed by elemental analysis, IR spectroscopy, NMR spectroscopy, and molecular mass determination (cryoscopy). The compounds purity was determined by HPLC (Milikhrom-1 with UV detector); content of the major component in all the cases was above 99.5 wt %.

Construction of the Knudsen apparatus used in this work was described elsewhere [13]. The chamber and the membrane were manufactured using recommendations given in [14], and the measurement method was modified accordingly. In particular, the effusion chamber was made of stainless steel, a highly heat conductive material, inert towards the studied compounds in solid as well as in gaseous state. The membrane was made of nickel foil (0.05 mm thick) with a hole (0.5903 mm in diameter). The copper spacer of hyperbolic shape allowed avoiding overcooling of the membrane surface upon effusion of vapor into a vacuum. The heat exchanging gas was helium [14]; temperature equilibrium between the specimen, the effusion chamber, and the thermostat was attained within 20 min. Hence, the evaporation proceeded under isothermal conditions, at the temperature close to that of the thermostat.

Constant temperature was maintained within ±0.1 K during the experiment, and the effusion time was measured with an accuracy of ± 0.5 s. Mass of the effused specimen Δm was determined by weighing the effusion chamber before and after the experiment with an accuracy of $\pm 5 \times 10^{-6}$ g. The evacuated setup allowed attaining the residual pressure as low as 0.1 Pa within 62±10 s. Effective time (the calculated effusion time under the stationary conditions corresponding to the effused specimen mass equal to that under non-stationary conditions) was determined separately, by carrying out the similar experiment with benzoic acid. The effective time was 41 s for the setup used in this study. Details of the effusion experiment and the apparatus setup are to be found in [15].

The accuracy and reproducibility of the results were determined in a separate experiment with the reference benzoic acid sample (K-1, 99.995 mol %), the vapor pressure at 312–342 K was measured in ten replicates.

Vapor pressure in the effusion chamber P_{ch} was calculated as follows.

$$P_{\text{ch}} = m/KS\tau\alpha\sqrt{2\pi RT/M}. \qquad (3)$$

where m, the mass of specimen effused from the chamber during time τ through the hole with the area of S; T, absolute temperature; R, gas constant; M, the vapor molecular mass [5].

The condensation coefficient α (reflecting deviation of the measured evaporation rate from that calculated from the equilibrium vapor pressure) is unity for the majority of substances [16, 17]. The studied acrylic acid derivatives containing cyclic fragments formed molecular crystals that underwent sublimation without change of geometry and mass of the molecules; therefore in this work we assumed $\alpha = 1$. The validity of this assumption was indirectly proved by the data reported in [18]; in that work precise measurements of saturated vapor pressure with the torsion, Knudsen, and Langmuir methods revealed that in the case of *trans*-stilbene, benzoic acid, benzophenone, and adamantane $\alpha = 1$.

Klausing coefficient K (accounting for the membrane resistance to the molecular vapor flow) in the case of the hole with the ratio of the length l to the radius r of 0 to 1.5 was determined using the empirical Kennard relation [19].

$$K = 1/(1 + 0.5l/r).$$

The presence of the hole in the chamber prevented attaining equilibration between the substance crystals and vapor, the vapor pressure being dependent on the effusion hole area. In order to elucidate the correction factor and calculate the vapor pressure [4], benzoic acid vapor pressure determined in the chambers with different holes was extrapolated to zero hole area [6]; in the case of 0.5903 mm thick membrane, the correction factor was 1.14. Volatile impurities that could disfigure the results were eliminated at the initial stage of the experiment. That stage was assumed to be completed when the specimen evaporation rate was reproducible within 1% at a given temperature.

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