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Standard Enthalpies, Entropies, and Gibbs Functions of Sublimation of Four Alkyl-Substituted Malonic Acids

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The Knudsen mass-loss effusion technique was used to measure the vapor pressures at different temperatures of the following crystalline dicarboxylic acids: methylmalonic acid, between 341.13 K and 354.74 K, dimethylmalonic acid, between 347.18 K and 363.26 K, ethylmalonic acid, between 347.52 K and 362.34 K and butylmalonic acid, between 348.20 K and 362.18 K. From the temperature dependence of the vapor pressure, the standard molar enthalpies of sublimation were derived by the Clausius−Clapeyron equation and the molar entropies of sublimation at equilibrium pressures were calculated. Using estimated values for the heat capacity differences between the gas and the crystal phases of the studied compounds the standard (pressure $p^0 = 10^5$ Pa) molar enthalpies, entropies and Gibbs functions of sublimation at $T = 298.15$ K, were derived.

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1. Introduction

In a recent work,[1] we reported experimental results for the vapor pressures, and the enthalpies and entropies of sublimation of straight-chain dicarboxylic acids $(CH_2)_n(COOH)_2$ for $n = 1$, 3, 5, 7 and 9. For malonic acid ($n = 1$) we obtained the values $\Delta_{cr}^{g}H_m^\circ$ ($T = 298.15$ K)/kJ·mol^{-1} = 111.4 ± 0.7 and $\Delta_{cr}^{g}S_m^\circ$ ($T = 298.15$ K)/J·K^{-1}·mol^{-1} = 216 ± 3 using the estimated value $\Delta_{cr}^{g}C_{p,m}^\circ = -50$ J·K^{-1}·mol^{-1} for the heat capacity difference between the gas and the crystal.

In the present work, we present the thermodynamic values of the sublimation equilibrium of four alkyl-substituted malonic acids. The vapor pressures as a function of temperature of the four crystalline compounds were measured using the Knudsen mass-loss effusion technique. From the temperature dependence of the vapor pressure, the molar enthalpies and entropies of sublimation at the mean temperature $\langle T\rangle$ of the experimental temperature range were derived. These values were corrected to the standard state at the temperature 298.15 K using a different method for estimating the heat capacity differences between the gas and the crystal. For comparison reasons the previously reported standard values for the enthalpy and entropy of sublimation of malonic acid were recalculated using the same estimation method.

2. Experimental Section

All the studied compounds were commercially obtained from Aldrich Chemical Co. with the following assessed purities: methylmalonic acid, $HOOCCH(CH_3)COOH$, 99 mass %; dimethylmalonic acid, $HOOCC(CH_3)_2COOH$, 98 mass %; ethylmalonic acid, $HOOCCH(C_2H_5)COOH$, 97 mass %; butylmalonic acid, $HOOCCH(C_4H_9)COOH$, 99 mass %. All the compounds were purified by repeated vacuum sublimation and the melting temperatures of the purified samples were measured using a Stuart Scientific SMP2 calibrated apparatus. Results were as follows: methylmalonic acid $T_{fus} = 407.5$ K (literature:[2] $T_{fus} = 408$ K); dimethylmalonic acid $T_{fus} = 464.6$ K (dec) (literature:[3] $T_{fus} = 465$ K); ethylmalonic acid $T_{fus} = 385.8$ K (literature:[2] $T_{fus} = 387$ K); butylmalonic acid $T_{fus} = 377.2$ K (literature:[2] $T_{fus} = 377$ K − 378 K). Final purities of the samples were quantitatively determined using a differential scanning calorimeter (Setaram DSC 141). The samples of dimethylmalonic acid were hermetically sealed in stainless steel crucibles due to its high vapor pressure at the melting temperature. The samples of the other compounds were sealed in aluminum crucibles. The recorded thermograms (using a heating rate of 3.33×10^{-2} K·s^{-1}) did not show any phase transition between $T = 298$ K and the melting temperature of the samples. The purity of the samples was computed from the DSC thermograms using the fractional fusion technique.[4] For dimethylmalonic acid, decomposition during the melting was observed and no reliable quantification of its purity could be calculated. Results (mean of at least three independent runs) were as follows: methylmalonic acid 99.93 mass %; ethylmalonic acid 99.78 mass %; butylmalonic acid 99.50 mass %.

No influence of impurities could be detected from the results of the subsequent measured vapor pressures.

The vapor pressures of each of the four acids were measured at several temperatures, using a mass-loss Knudsen-effusion apparatus. A detailed description of the apparatus, procedure, and technique, and the results obtained with two test substances (benzoic acid and ferrocene) have been previously reported.[5] This apparatus enables the simultaneous operation of three Knudsen cells, with three different effusion holes. The agreement of the measured vapor pressures, obtained from effusion through those three holes ensures that an equilibrium pressure was measured. Usually the measurements are extended through a chosen ∼15 K temperature interval and the corresponding measured vapor pressures are in the range 0.1 Pa to 1.0 Pa.

In a typical effusion experiment the crystalline sample is placed at the base of each of the three cylindrical effusion cells which have a hole coaxially located at the top, through

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which the vapor effuses into a space evacuated to a pressure of 10^{-4} Pa. The loss of mass Δm of the samples during a convenient effusion time period t is determined by weighing the effusion cells to ±0.01 mg before and after the effusion period. The samples are assumed to be in thermal equilibrium with a thermostatically controlled to ±0.001 K silicone oil bath where the effusion cells are immersed. At the temperature T of the experiment, the vapor pressure p is calculated by eq 1:

$$p = (\Delta m/A_0 w_0 t)(2\pi RT/M)^{1/2} \qquad (1)$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_0 is the area of the effusion hole, and w_0 is the respective Clausing factor calculated by eq 2 where l is the thickness of the effusion hole and r its radius:

$$w_0 = \{1 + (3l/8r)\}^{-1} \qquad (2)$$

For all the studied compounds the thickness of the used effusion holes was 0.049 mm and their areas and Clausing factors were: hole 1, $A_0/\text{mm}^2 = 0.596$, $w_0 = 0.959$; hole 2, $A_0/\text{mm}^2 = 0.754$, $w_0 = 0.964$; hole 3, $A_0/\text{mm}^2 = 0.862$, $w_0 = 0.966$.

3. Results and Discussion

The integrated form of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$, where a is a constant and $b = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T\rangle)/R$, was used to derive the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range. The entropies of sublimation at equilibrium conditions were calculated as $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}\{\langle T\rangle, p(T = \langle T\rangle)\} = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T\rangle)/\langle T\rangle$. The experimental results obtained from each effusion cell, for each compound, together with the residuals of the Clausius−Clapeyron equation, derived from least squares adjustment, are given in Table 1. For each substance, the calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental error.

Table 2 presents for each hole used and for the global treatment of all the (p,T) points obtained for each studied compound, the detailed parameters of the Clausius−Clapeyron equation together with the calculated standard deviations and the standard molar enthalpy of sublimation at the mean temperature of the experiments $T = \langle T\rangle$. The equilibrium pressure at this temperature $p(T = \langle T\rangle)$ and the entropies of sublimation at equilibrium conditions are also presented. The plots of $\ln p = f(1/T)$ for the global results for methyl and dimethyl malonic acids are presented in Figure 1. Table 3 lists the (p,T) values calculated from the (p,T) equations within the experimental range of pressures used: 0.1 Pa to 1 Pa.

Sublimation enthalpies at the temperature 298.15 K were derived from the sublimation enthalpies calculated at the mean temperature $\langle T\rangle$ of the experiments, by the equation

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15\ \text{K}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T\rangle) + \Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\circ}(298.15\ \text{K} - \langle T\rangle) \qquad (3)$$

Since there are no experimental values of $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\circ}$ for the studied compounds, we used eq 4 derived by Chickos et al.[6] to estimate those values:

$$\Delta_{\text{cr}}^{\text{g}}c_{p,\text{m}}^{\circ} = -\{0.75 + 0.15C_{p,\text{m}}^{\circ}(\text{cr})\} \qquad (4)$$

Table 1. Knudsen-Effusion Results for the Studied Compounds[a]

	p/Pa			$10^2\Delta\ln(p/\text{Pa})$		
T/K	hole 1	hole 2	hole 3	hole 1	hole 2	hole 3
			Methylmalonic Acid			
341.132	0.2165	0.2150	0.2139	0.01	−0.95	−1.19
342.157	0.2461	0.2455	0.2418	−0.40	−2.02	−1.22
343.137	0.2793	0.2692	0.2651	−1.26	0.35	1.20
345.164	0.3416	0.3332	0.3312	2.78	2.77	2.77
347.136	0.4417	0.4305	0.4354	0.34	0.02	−1.67
349.167	0.5566	0.5361	0.5314	0.89	1.35	1.73
351.105	0.7241	0.6831	0.6872	−3.08	−0.93	−1.97
352.910	0.8650	0.8395	0.8283	−0.28	−1.32	−0.36
354.745	1.0462	1.0166	1.0079	1.40	−0.11	0.42
			Dimethylmalonic Acid			
347.180	0.1836	0.1805	0.1803	−1.24	−2.90	−3.09
349.200	0.2190	0.2126	0.2112	3.20	2.90	3.17
351.714	0.2938		0.2841	0.93		0.63
353.658	0.3783	0.3508	0.3513	−3.65	0.85	0.10
357.141	0.5301	0.5185	0.5139	−0.87	−1.54	−1.41
359.192	0.6384	0.6195	0.6193	1.71	1.94	1.12
361.150	0.7948	0.7891	0.7674	−0.21	−2.18	−0.33
363.256	0.9777	0.9523	0.9502	0.34	0.38	−0.43
			Ethylmalonic Acid			
347.517	0.1923	0.1873	0.1821	−2.34	−3.34	−0.17
348.935	0.2155	0.2065	0.2126	1.78	2.55	0.08
351.317	0.2824	0.2697	0.2700	0.53	1.85	2.31
353.209	0.3540	0.3440	0.3501	−1.84	−2.08	−3.16
355.211	0.4246	0.4174	0.4139	1.15	−0.07	1.57
357.194	0.5040	0.4923		4.75	4.34	
360.143	0.7295	0.7078	0.7058	−1.81	−1.29	0.06
362.345	0.9091	0.8880	0.8854	−1.43	−1.39	0.09
			Buthylmalonic Acid			
348.196	0.1995	0.1886	0.1835	−2.15	−1.38	0.42
350.197	0.2401	0.2305	0.2336	3.30	2.72	0.69
352.192	0.3225	0.3084	0.3101	−2.56	−2.59	−3.58
354.174	0.3941	0.3725	0.3721	0.61	1.92	1.83
356.190	0.4954	0.4744	0.4780	1.09	1.26	0.55
358.362	0.6324	0.6115	0.6098	1.54	0.93	1.51
360.171	0.7994	0.7753	0.7722	−1.40	−2.17	−1.25
362.177	0.9938	0.9452	0.9608	−0.70	0.65	−0.23

[a] The equilibrium vapor pressure is denoted by p, and the deviations of experimental results from those given by the Clausius−Clapeyron equation are denoted by $\Delta\ln(p/\text{Pa})$.

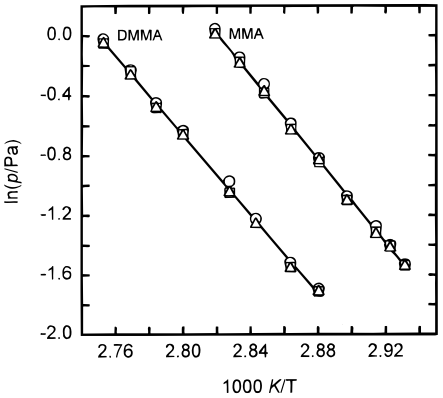

Figure 1. Plots of $\ln(p/\text{Pa})$ against $1/T$ for methylmalonic acid (MMA) and for dimethylmalonic acid (DMMA): ○, hole 1; □, hole 2; △, hole 3.

According to these authors the results obtained by this equation have a standard deviation of 33 $\text{J·K}^{-1}\text{·mol}^{-1}$.

Heat capacities of the crystals were calculated using a group additivity method developed by Chickos et al.[7] The calculated values for the studied compounds and for malonic acid are presented in Table 4, which also includes the standard molar enthalpies of sublimation at $T = 298.15$ K and the standard molar entropies of sublimation at $T =$

Table 2. Experimental Results for the Studied Compounds Where a and b Are from the Clausius−Clapeyron Equation $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$ and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T\rangle)/R$ with $R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

hole number	a	b	$\langle T\rangle$/K	$p(T=\langle T\rangle)$/Pa	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T\rangle)$/kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle, p(T=\langle T\rangle)\}$/J·K^{-1}·mol^{-1}
			Methylmalonic Acid			
1	39.885 ± 0.446	14128 ± 155			117.5 ± 1.3	
2	39.159 ± 0.395	13886 ± 137			115.5 ± 1.1	
3	39.260 ± 0.446	13923 ± 155			115.8 ± 1.3	
global results	39.435 ± 0.325	13979 ± 113	347.93	0.476	116.2 ± 0.9	334 ± 3
			Dimethylmalonic Acid			
1	36.440 ± 0.516	13244 ± 183			110.1 ± 1.5	
2	36.582 ± 0.570	13305 ± 203			110.6 ± 1.7	
3	36.412 ± 0.458	13247 ± 163			110.1 ± 1.4	
global results	36.465 ± 0.347	13260 ± 123	355.22	0.421	110.2 ± 1.0	310 ± 3
			Ethylmalonic Acid			
1	36.513 ± 0.672	13270 ± 238			110.3 ± 2.0	
2	36.799 ± 0.722	13382 ± 256			111.3 ± 2.1	
3	37.004 ± 0.493	13452 ± 175			111.8 ± 1.5	
global results	36.778 ± 0.394	13370 ± 140	354.93	0.410	111.2 ± 1.2	313 ± 3
			Butylmalonic Acid			
1	40.340 ± 0.596	14615 ± 212			121.5 ± 1.8	
2	40.596 ± 0.581	14721 ± 206			122.4 ± 1.7	
3	41.026 ± 0.512	14874 ± 182			123.7 ± 1.5	
global results	40.654 ± 0.456	14737 ± 162	355.19	0.433	122.5 ± 1.4	345 ± 4

Table 3. *(p,T)* Values from the Vapor-Pressure Equations

	T/K									
	p/Pa = 0.1	p/Pa = 0.2	p/Pa = 0.3	p/Pa = 0.4	p/Pa = 0.5	p/Pa = 0.6	p/Pa = 0.7	p/Pa = 0.8	p/Pa = 0.9	p/Pa = 1.0
malonic acid[a]	336.54	342.64	346.32	348.97	351.06	352.79	354.26	355.54	356.68	357.71
methylmalonic acid	334.93	340.58	343.98	346.43	348.36	349.95	351.31	352.49	353.54	354.48
dimethylmalonic acid	342.05	348.28	352.03	354.74	356.87	358.63	360.13	361.44	362.60	363.65
ethylmalonic acid	342.13	348.31	352.03	354.71	356.83	358.57	360.06	361.36	362.51	363.55
buthylmalonic acid	343.06	348.69	352.07	354.50	356.42	357.99	359.34	360.51	361.56	362.49

[a] Values from ref 1.

Table 4. Calculated Values of the Heat Capacities of the Crystalline Compounds, of the Heat Capacity Differences between the Gaseous and the Crystalline Phases, and of the Standard (p° = 0.1 MPa) Molar Enthalpies, Entropies, and Gibbs Functions of Sublimation at T = 298.15 K

substance	$C_{\mathrm{p,m}}^{\circ}$ (cr)/J·K^{-1}·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}$/J·K^{-1}·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$/kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}$/J·K^{-1}·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}$/kJ·mol^{-1}
malonic acid[a]	133.1	−21 ± 33	110.0 ± 1.8	212 ± 6	46.8 ± 2.5
methylmalonic acid	151.8	−24 ± 33	117.4 ± 1.9	236 ± 7	47.0 ± 2.8
dimethylmalonic acid	174.4	−27 ± 33	111.7 ± 2.1	212 ± 8	48.5 ± 3.2
ethylmalonic acid	178.7	−28 ± 33	112.8 ± 2.2	215 ± 8	48.7 ± 3.2
buthylmalonic acid	232.5	−36 ± 33	124.6 ± 2.3	248 ± 9	50.6 ± 3.5

[a] Recalculated values from the experimental results presented in ref 1.

298.15 K calculated by eq 5, where $p^{\circ} = 10^5$ Pa, and the standard molar Gibbs functions of sublimation at this temperature.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}(T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle, p(T = \langle T\rangle)\} + \Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}\ln(298.15\ \mathrm{K}/\langle T\rangle) - R\ln\{p^{\mathrm{o}}/p(T = \langle T\rangle)\} \quad (5)$$

The uncertainties assigned to $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}$ (T = 298.15 K) were obtained considering the uncertainties of $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle, p(T=\langle T\rangle)\}$ and of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}$ presented in Tables 2 and 3 and the uncertainties of ln $p(T = \langle T\rangle)$ calculated from the standard deviations of the parameters of the Clausius−Clapeyron equations, for the global results, presented in Table 2.

In our calculations it was assumed that for the experimental pressure range no significant association occurres in the vapor phase of the studied malonic acids similarly with which was found for oxalic acid[8] and succinic acid[9] under the same low-pressure conditions.

Compared to malonic acid, the standard molar entalpies of sublimation of their dimethyl and ethyl substituted compounds are equal within the experimental uncertainties assigned to them; for methylmalonic acid a higher (7.4 kJ·mol^{-1}) value was obtained and a significantly larger one (14.6 kJ·mol^{-1}) is observed for butylmalonic acid. However as the values of the standard molar entropies of sublimation of the methylmalonic and the butylmalonic acids are also higher than the corresponding values for the other compounds, the volatility of all the studied malonic acids are similar as can be seen from the values of the standard molar Gibbs functions of sublimation presented in Table 4.

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