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Sublimation Enthalpies Study for Barbituric, Tiobarbituric, and Selenobarbituric Acids from Their Vapor Pressure Measurements

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The vapor pressures for solid barbituric acid and tiobarbituric acid were measured by the torsion method; for selenobarbituric acid the vapor pressures were measured in both the solid and liquid phases. The results were fit to the following linear equations: barbituric acid (solid), $\log(p/\mathrm{kPa}) = (11.18 \pm 0.20) - (5920 \pm 200)(\mathrm{K}/T)$ (from 392 to 493 K); tiobarbituric acid (solid), $\log(p/\mathrm{kPa}) = (10.78 \pm 0.20) - (5770 \pm 200)(\mathrm{K}/T)$ (from 400 to 461 K); selenobarbituric acid (solid), $\log(p/\mathrm{kPa}) = (12.00 \pm 0.20) - (7393 \pm 200)(\mathrm{K}/T)$ (from 449 to 486 K); selenobarbituric acid (liquid), $\log(p/\mathrm{kPa}) = (8.33 \pm 0.20) - (5532 \pm 200)(\mathrm{K}/T)$ (from 490 to 557 K). Knudsen measurements of the molecular weight of the vapor show that barbituric and tiobarbituric acids vaporize predominantly in the monomeric form, while the vapor above selenobarbituric acid is prevalently a dimer. The sublimation enthalpies at the middle temperatures [$\Delta_{\mathrm{sub}}H°(442\ \mathrm{K}) = (113 \pm 4)\ \mathrm{kJ{\cdot}mol^{-1}}$, $\Delta_{\mathrm{sub}}H°(430\ \mathrm{K}) = (110 \pm 4)\ \mathrm{kJ{\cdot}mol^{-1}}$, and $\Delta_{\mathrm{sub}}H°(466\ \mathrm{K}) = (141 \pm 4)\ \mathrm{kJ{\cdot}mol^{-1}}$] for solid barbituric, tiobarbituric and selenobarbituric acids respectively were derived. The enthalpy of vaporization [$\Delta_{\mathrm{vap}}H°(523\ \mathrm{K}) = (106 \pm 4)\ \mathrm{kJ{\cdot}mol^{-1}}$] and the enthalpy of fusion [$\Delta_{\mathrm{fus}}H°(486\ \mathrm{K}) = 18\ \mathrm{kJ{\cdot}mol^{-1}}$] for selenobarbituric acid were also derived.

Introduction

The replacement of oxygen by sulfur and selenium in barbituric acid gives two interesting compounds, tiobarbituric and selenobarbituric acids. Apparently no thermodynamic properties associated with the vaporization process of these compounds and of barbituric acid are reported in the literature so that, as part of our ongoing program on the vaporization study of organic substances, the sublimation enthalpies of these acids were determined from their vapor pressures measured by the torsion method.

Experimental and Results

Barbituric acid, 99.9% pure, was supplied by Alfa, and tiobarbituric acid, 98% pure, was supplied by Aldrich, both purities as certified by the suppliers. Selenobarbituric acid was prepared by the condensation of selenourea (supplied by Aldrich, 99.9% pure) with diethyl malonate in the presence of sodium ethoxide following the procedure suggested by Mautner and Clayton (1959). The sample of selenobarbituric acid had a melting point at (486 ± 2) K, as measured by a Leitz 350 heating plate microscope. Apparently the only melting point in the literature is the range (468−483 K), reported by Mautner and Clayton (1959). We are not able to evaluate the purity of the sample, but the reproducibility both of the melting temperature and of the vapor pressure data let us believe that the impurities present in the samples were minor and in any case should not influence the pressure measurements. At each experimental temperature the vapor pressure was determined by the torsion method, measuring the torsion angle of a thin tungsten wire, to which the cell was suspended, due to the effusion of the vapor from the cell in the vacuum (Volmer, 1931; Nesmeyanov, 1963). At some temperature, simultaneously with the torsion pressure measurement, the molecular weight of the vapor was also determined from the mass loss rate of the sample by the Knudsen equation (Knudsen, 1909).

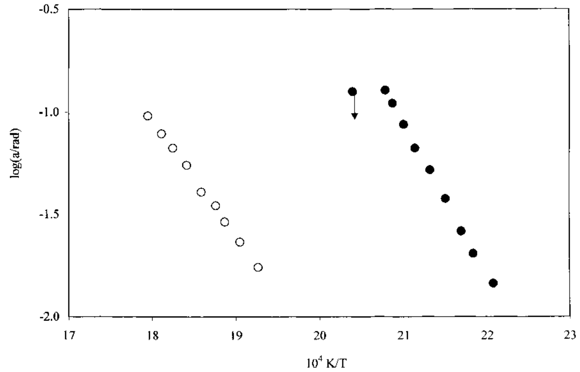

Figure 1. Typical vaporization behavior of selenobarbituric acid by using the cell b: (○) cell b1; (●) cell b2 (see text).

The assembly used for the pressure measurements was a simultaneous torsion−Knudsen apparatus described in a previous work (Adami et al., 1987). The mass loss rate of the sample was determined by a vacuum balance (Chan 1000) to which is suspended the torsion apparatus (Hollahan, 1962). Two stainless steel torsion cells were used in this study, a conventional one, cell a, having the effusion holes of both lodgings of equal area (1 mm in diameter), and cell b, having the lodgings with very different areas of their effusion holes (0.3 and 2 mm in diameter, respectively). By filling both lodgings of this cell with the sample, the measured torsion data are referred to the effusion of the vapor from both lodgings (cell b1). Because the sample in the lodging with the larger effusion hole vaporized more rapidly than the other one, when this lodging became empty, the torsion angles rapidly decreased and the new data are referred to the effusion of the vapor from the lodging with the smaller effusion hole (cell b2). In this way the vapor pressures of a compound can be measured in two different temperature ranges in the same experimental

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Table 1. Vapor Pressure of Barbituric Acid by Torsion Measurements

cell a								cell b1		cell b2	
run 1		run 2		run 3		run 4		run 1		run 1	
T/K	− log(p/kPa)	T/K	− log(p/kPa)	T/K	− log(p/kPa)	T/K	− log(p/kPa)	T/K	− log(p/kPa)	T/K	− log(p/kPa)
397	3.66	393	3.96	392	3.96	400	3.66	393	3.96	462	1.68
405	3.36	396	3.66	405	3.36	406	3.48	401	3.48	469	1.53
410	3.18	400	3.66	409	3.26	410	3.36	410	3.26	472	1.40
410	3.26	405	3.48	415	3.12	415	3.18	414	3.12	477	1.27
418	2.96	409	3.26	420	2.96	426	2.81	419	2.96	481	1.16
419	2.92	413	3.12	425	2.76	430	2.64	424	2.76	485	1.09
423	2.81	420	2.88	432	2.51	435	2.48	429	2.60	490	0.95
431	2.53	424	2.78	438	2.32	440	2.33	434	2.43	493	0.89
432	2.48	430	2.55	444	2.14			440	2.27		
436	2.34	436	2.39	449	1.99			445	2.12		
443	2.13	441	2.22					454	1.85		
453	1.84	447	2.04								
462	1.67	452	1.99								
		457	1.74								

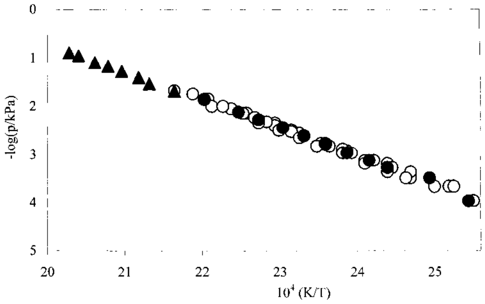

Figure 2. Torsion vapor pressures for barbituric acid: (●) cell a; (○) cell b1; (▲) cell b2.

condition. In Figure 1 is reported a typical vaporization run carried out by using this cell. The instrument constants necessary to convert both the torsion angles in the pressure data and the mass loss rates of the sample in the molecular weight of the vapor were obtained by vaporizing a standard element (cadmium) having well-known vapor pressures (Hultgreen et al.,1973). The temperature of the heated zone in the vacuum system was measured by a calibrated Pt−Pt/Rh 13% Rh thermocouple inserted in a second cell similar to the effusion cell and placed below it. To measure the correct temperature of the sample, a procedure described in a previous work (Piacente et al., 1994) was used. The reliability of the temperature values was also checked by measuring the melting point of cadmium from the intersection of the log p vs $1/T$ lines determined above the solid and molten element during the calibration experiments. Even though the uncertainty associated with the melting point obtained in this way is large (not less than about 5 K), the obtained value was decidedly in good agreement with that selected in the literature (Hultgreen et al., 1973) so that we believe that the error in the temperature measurements could be less than about 2 K. The uncertainties connected to the torsion angle measurements and the torsion constant of the assembly produced a displacement in the log p values of about ±0.05.

The vapor pressures of barbituric acid measured by both torsion cells are reported in Table 1 and Figure 2. For each vaporization run the linear regression of the logarithm of the pressures as a function of the reciprocal temperature was calculated by a least-squares method.

Table 2 gives the slopes and intercepts of the equations so calculated for barbituric acid and for the other studied acids, together with the experimental temperature ranges. The associated errors are standard deviations.

Weighting slope and intercept of each equation proportionally to the experimental points, the following equation, representative of the vapor pressure of barbituric acid in the temperature range (392−493 K), was selected:

$$\log(p/\mathrm{kPa}) = (11.18 \pm 0.20) - (5920 \pm 200)/T \quad (1)$$

where the associated errors were estimated.

The vapor pressures of solid tiobarbituric acid, measured by cell a, are reported in Table 3 and in Figure 3. When about 80% of the original mass of the sample was sublimed, the vapor pressure values slowly decreased. At the end of each experiment a final brown residue of about 5% of the original mass was observed. The vapor pressure of this residue was not measurable up to about 650 K. We are not able to evaluate if this small amount of residue is an original impurity or a substance derived from a partial decomposition of the tiobarbituric acid during its heating. On this basis only the well-reproducible vapor pressure values obtained with ascending and descending temperature in the first step of the vaporization experiments were considered reliable and used in the calculation of the linear regressions reported in Table 2. Following the same procedure of barbituric acid, the best line of the temperature dependence of the vapor pressure of this acid, in the temperature range 400−461 K, is

$$\log(p/\mathrm{kPa}) = (10.78 \pm 0.20) - (5770 \pm 200)(\mathrm{K}/T) \quad (2)$$

where the associated errors were estimated.

The vapor pressure values of selenbarbituric acid, measured by both cells, are reported in Table 4 and in Figure 4. Employing cell a, the vapor pressures were measured above solid and molten compound so that in each experimental run two log p vs $1/T$ linear regressions above both phases were calculated and reported in Table 2. When cell b was used filling both lodgings (cell b1), the only vapor pressures measured above the solid phase (below 486 K) were used in the evaluation of the linear regressions. At higher temperatures, when the effusion cell was used as cell b2 (i.e. when the sample in the lodging with the large effusion hole was completely vaporized and the sample is present only in the lodging with small effusion hole), only pressure data measured over the molten compound were taken in account. The linear regressions calculated for each run are in Table 2. Considering the small covered temperature ranges and the limited number of points determined in each run above both phases for selenobarbituric acid, the standard deviations were not considered significant.

The following equations, representative of the temperature dependence of the vapor pressures for solid and molten selenobarbituric acid, were selected from those

Table 2. Temperature Dependence of the Vapor Pressure for Barbituric, Tiobarbituric, and Selenobarbituric Acids

compd	run (cell)	no. of points	ΔT/K	sample	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$ A	 B
barbituric acid	1(a)	13	397−462	solid	10.89 ± 0.21	5780 ± 90
	2(a)	14	393−457	solid	11.24 ± 0.29	5943 ± 124
	3(a)	10	392−449	solid	11.29 ± 0.30	5966 ± 127
	4(a)	8	400−440	solid	11.27 ± 0.29	5986 ± 120
	1(b1)	11	393−454	solid	11.35 ± 0.31	5987 ± 130
	1(b2)	8	462−493	solid	11.09 ± 0.32	5900 ± 151
tiobarbituric acid	1(a)	10	407−455	solid	10.77 ± 0.34	5782 ± 145
	2(a)	9	400−451	solid	10.94 ± 0.14	5809 ± 60
	3(a)	11	408−461	solid	10.43 ± 0.23	5623 ± 98
	4(a)	11	401−456	solid	11.00 ± 0.20	5874 ± 84
selenobarbituric acid	1(a)	8	459−486	solid	12.09	7356
	1(a)	4	496−511	liquid	8.47	5605
	2(a)	6	453−484	solid	12.12	7393
	2(a)	6	490−511	liquid	8.14	5448
	3(a)	7	449−480	solid	11.72	7235
	1(b1)	9	453−481	solid	12.30	7456
	1(b2)	6	499−531	liquid	8.15	5427
	2(b1)	7	466−485	solid	12.21	7422
	2(b2)	9	519−557	liquid	8.60	5674
	3(b1)	7	461−483	solid	12.34	7485
	3(b2)	8	525−557	liquid	8.24	5477

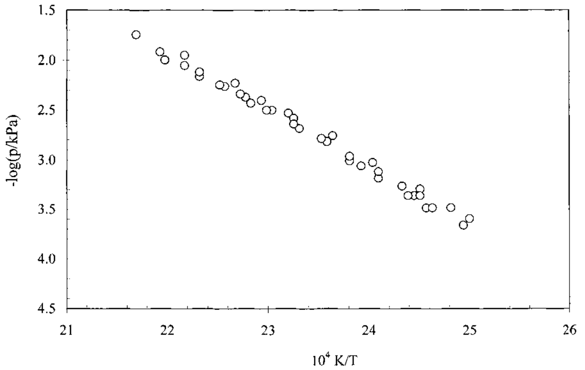

Figure 3. Torsion vapor pressures for tiobarbituric acid by using cell a.

Table 3. Vapor Pressure for Tiobarbituric Acid by Torsion Measurements with Cell a

run 1 T/K	 − log (p/kPa)	run 2 T/K	 − log (p/kPa)	run 3 T/K	 − log (p/kPa)	run 4 T/K	 − log (p/kPa)
407	3.48	400	3.59	408	3.36	401	3.66
409	3.36	403	3.48	411	3.26	406	3.48
415	3.18	408	3.29	415	3.12	410	3.36
420	3.01	416	3.02	420	2.96	415	3.12
424	2.81	423	2.76	430	2.58	418	3.06
429	2.68	431	2.53	434	2.50	425	2.78
435	2.50	436	2.40	439	2.37	430	2.64
438	2.43	441	2.23	444	2.25	435	2.50
443	2.26	451	1.95	448	2.16	440	2.34
455	2.00			451	2.05	448	2.12
				461	1.74	456	1.92

Table 4. Vapor Pressures for Selenobarbituric Acid by Torsion Measurements

run 1 T/K	 − log(p/kPa)	run 2 T/K	 − log(p/kPa)	run 3 T/K	 − log(p/kPa)
Cell a (Above Solid and Liquid Phase)					
459	3.94	453	4.24	449	4.39
468	3.64	460	3.94	456	4.16
471	3.54	467	3.69	460	4.03
475	3.39	473	3.50	465	3.86
478	3.26	478	3.34	469	3.69
479	3.24	484	3.20	475	3.51
484	3.09			480	3.37
486	3.09	490	3.00		
		493	2.90		
496	2.84	497	2.81		
502	2.69	502	2.72		
506	2.60	505	2.63		
511	2.51	511	2.53		
Cell b1 (Above Solid Phase)					
453	4.14	466	3.74	461	3.88
458	3.99	469	3.60	466	3.76
461	3.88	473	3.49	470	3.58
465	3.72	475	3.38	474	3.42
469	3.58	479	3.30	476	3.35
473	3.48	482	3.19	479	3.28
476	3.36	485	3.09	483	3.18
479	3.26				
481	3.19				
Cell b2 (Above Liquid Phase)					
499	2.75	519	4.34	525	2.21
502	2.66	525	4.22	531	2.07
508	2.50	530	4.12	536	1.96
515	2.39	533	4.04	540	1.90
525	2.19	538	3.97	544	1.83
531	2.08	543	3.84	548	1.75
		548	3.76	552	1.68
		552	3.69	557	1.60
		557	3.60		
Cell a (Sample Constituted by Recondensed Vapor, See Text)					
T/K	− log(p/kPa)	T/K	− log(p/kPa)	T/K	− log(p/kPa)
442	4.75	461	4.05	449	4.45
447	4.53	464	3.95	459	4.12
451	4.38	473	3.67	468	3.81
455	4.23	437	4.93		

reported in Table 2, weighting the constants proportionally to the number of points:

$$\text{solid } \log(p/\mathrm{kPa}) = (12.00 \pm 0.20) - (7393 \pm 200)(\mathrm{K}/T) \quad (449{-}486\ \mathrm{K}) \quad (3)$$

$$\text{liquid } \log(p/\mathrm{kPa}) = (8.33 \pm 0.20) - (5532 \pm 200)(\mathrm{K}/T) \quad (490{-}557\ \mathrm{K}) \quad (4)$$

where the associated errors were considered equal to those estimated for the other acids.

Discussion and Conclusion

During the pressure measurements, the molecular weight of the vapor of the studied compound was determined by the Knudsen method, measuring the weight loss rate of the sample. The molecular weights so determined show that while the vapor above barbituric and tiobarbituric acids is prevalently constituted by the monomer form,

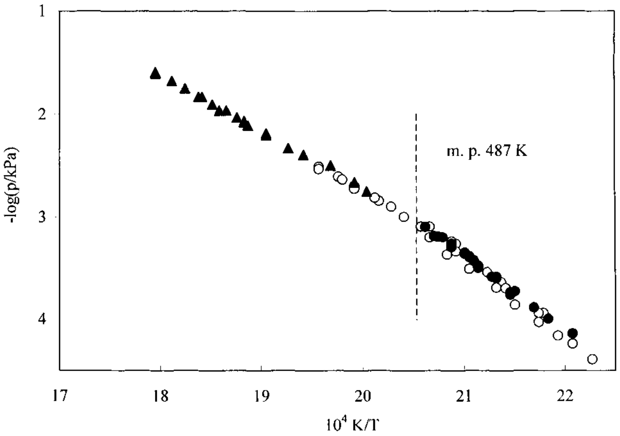

Figure 4. Torsion vapor pressures for selenobarbituric acid: (●) cell a; (○) cell b1; (▲) cell b2.

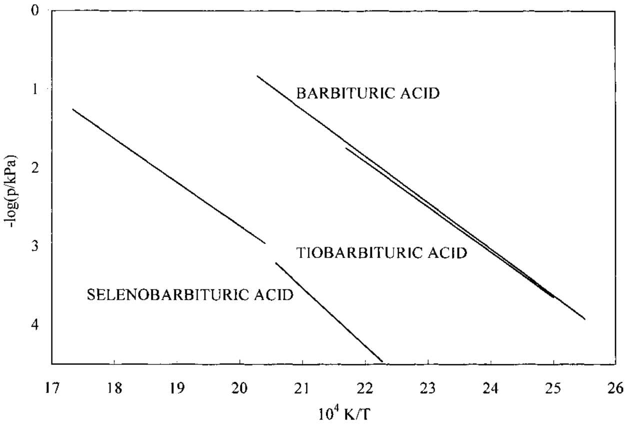

Figure 5. Comparison of the pressure−temperature equations for barbituric, tiobarbituric, and selenobarbituric acids.

above selenobarbituric acid the dimer form is the principal gaseous species present. On this basis the sublimation of the acids occurs prevalently according to the following reactions:

$$C_4H_4N_2O_3(s) \rightarrow C_4H_4N_2O_3(g) \qquad (5)$$

$$C_4H_4N_2O_2S(s) \rightarrow C_4H_4N_2O_2S\ (g) \qquad (6)$$

$$2C_4H_4N_2O_2Se(s,l) \rightarrow (C_4H_4N_2O_2Se)_2(g) \qquad (7)$$

The selected linear regression lines of vapor pressures for barbituric, tiobarbituric, and selenobarbituric acids are plotted for comparison in Figure 5. From the slopes of these lines, the enthalpies of these sublimation reactions at the middle temperature of the experimental range, $\Delta_{sub}H°(442\ K) = (113 \pm 4)\ kJ\cdot mol^{-1}$, $\Delta_{sub}H°(430\ K) = (110 \pm 4)\ kJ\cdot mol^{-1}$, and $\Delta_{sub}H°(466\ K) = (141 \pm 4)\ kJ\cdot mol^{-1}$ for reactions 5−7, respectively, and the vaporization enthalpy for molten selenobarbituric acid, $\Delta_{vap}H°(523\ K) = (106 \pm 4)\ kJ\cdot mol^{-1}$, were calculated. While barbituric and tiobarbituric acids present a similar vaporization behavior, both the lower vapor pressures and the higher sublimation enthalpy for selenobarbituric acid show that this compound could be considered more stable than the other ones. This different vaporization behavior can probably be due to more polarization of the selenobarbituric molecule.

In a previous study (Piacente and Gigli, 1992), during the vaporization of selenurea, a partial decomposition of this compound in selenium and cyanamid was observed. To check if a partial decomposition also occurs during the vaporization of selenobarbituric acid, a sample of this compound was sublimed under vacuum in a separate experiment and its vapor appropriately condensed. Both the melting point of this condensate (488 ± 2) K and the temperature dependence equation of its vapor pressures measured by using the cell a, $\log(p/kPa) = 11.66 \pm 0.23 - (7240 \pm 106)(K/T)$ (the experimental data are in Table 4), were decidedly in agreement with those measured employing the original sample. This led to the conclusion that insignificant decomposition occurs during the heating and the sublimation of selenobarbituric acid.

A very rough melting point of this acid, 506 K with a large error, not less than about 10 K, was derived from the intersection of the log p vs $1/T$ lines selected for solid and molten compound (eqs 3 and 4). This value is comparable enough with that experimentally observed (486 ± 2) K, and this is very important because it shows that the temperature values and the pressure data determined by using different torsion cells can be considered reliable. A rough enthalpy of fusion of selenobarbituric acid can be also derived, $\Delta_{fus}H° = 18\ kJ\cdot mol^{-1}$, as the difference between the sublimation and vaporization enthalpies of this compound.

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