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Heat Capacity and Standard Thermodynamic Functions of Triphenylantimony Dimethacrylate over the Temperature Range from (0 to 400) K

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ABSTRACT: Heat capacities of triphenylantimony dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$ were measured by precision adiabatic vacuum calorimetry over the temperature range from T = (6 to 335) K and by differential scanning calorimetry over the temperature range from T = (300 to 470) K. The melting of the sample was observed within the above temperature range. The melting was accompanied by a compound decomposition. On the obtained data, the standard thermodynamic functions of molar heat capacity $C^{\circ}_{p,\mathrm{m}}$, enthalpy $H^{\circ}(T) - H^{\circ}(0)$, entropy $S^{\circ}(T)$, and Gibbs energy $G^{\circ}(T) - H^{\circ}(0)$ of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ were calculated over the range from T = (0 to 400) K. The low-temperature (T < 50 K) heat capacity dependence was analyzed on the basis of Debye's heat capacity theory of solids and its multifractal model, so the characteristic temperatures and the fractal dimension were determined, and some conclusions about the structure topology were made. The standard entropy of formation at T = 298.15 K of $Ph_3Sb(O_2CCMe{=}CH_2)_2$(cr) was calculated.

INTRODUCTION

At the present time, the chemistry of organoantimony(V) complexes attracts considerable interest for research because of the striking structure possibilities ranging from discrete monomeric structures to supramolecular assemblies. These compounds show the coordination number of the central atom equal to 6, 7,[1,2] and 9.[3] Also, the chemistry of polymers with a metal atom, particularly antimony, in the main chains is widely developing.[4] In addition, organoantimony derivatives exhibit significant antimicrobial properties as well as antitumor activities.[5]

Some unsaturated antimony compounds (acrylates, vinylbenzoates) are used now for the synthesis of organic polymers with an antimony atom as a substituent. These polymers display fungicidal and biocidal activities.

Thus, the synthesis and investigation of structures and physicochemical properties of organometallic compounds, particularly highly coordinated antimony compounds, are an actual task.

The purpose of the present study is to measure the low-temperature heat capacity by adiabatic calorimetry over the temperature range from T = (6 to 335) K and by differential scanning calorimetry from T = (300 to 470) K of the crystalline triphenylantimony dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$, to detect possible phase transitions and to estimate their characteristics, to calculate the standard (p° = 0.1 MPa) thermodynamic functions $C^{\circ}_{p,\mathrm{m}}$, $H^{\circ}(T) - H^{\circ}(0)$, $S^{\circ}(T)$, and $G^{\circ}(T) - H^{\circ}(0)$ in the range from T = (0 to 400) K, to determine the characteristic temperatures and fractal dimension D and to establish the structure topology, and to calculate the standard entropy of formation at T = 298.15 K of $Ph_3Sb(O_2CCMe{=}CH_2)_2$(cr).

EXPERIMENTAL SECTION

Synthesis and Characterization of Triphenylantimony Dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$. The sample of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ was synthesized according to the method described in ref 6. It was significant to note that $Ph_3Sb(O_2CCMe{=}CH_2)_2$ was obtained by the oxidative addition of hydrogen peroxide to triphenylantimony in the presence of methacrylic acid:

$$Ph_3Sb + 2CH_2{=}CMeCO_2H + H_2O_2 \rightarrow Ph_3Sb(O_2CCMe{=}CH_2)_2 + H_2O$$

The sample was being cleaned by the recrystallization until constant fusion temperature. The compound was identified by elemental analysis: calculated (for formula $C_{26}H_{25}SbO_4$): C 59.68 %; H 4.82 %; Sb 23.27 %, found: C 59.95 %; H 4.95 %; Sb 23.20 %.

The structure was defined by NMR spectroscopy, IR spectroscopy, and X-ray analysis.

By X-ray analysis[6] of the single crystal of the sample, the antimony atom is in the trigonal-bipyramidal coordination. The methacrylic groups are in axial positions, and the phenylic groups are in equatorial positions. The X-ray experiment was performed at room temperature. The crystals of triphenylantimony dimethacrylate with benzene, $C_{29}H_{28}O_4Sb$, are triclinic, at 298 K: a = 9.3700(19), b = 9.4100(19), c = 15.050(3) Å; α = 77.04(3)°, β = 89.38(3)°, γ = 88.53(3)°; V = 1292.7(5) $Å^3$; d_{calc} = 1.445 $g \cdot cm^{-3}$.

As elemental analysis and IR spectroscopy showed, the content of the main compound in the sample under study was 0.990 molar fraction.

According to the thermogravimetric analysis carried out by us, it was established that the sample was thermally stable up to 400 K.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range of 6 ≤ (T/K) ≤ 335. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[7,8] All of the measurements were performed with a

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computer-controlled measuring system comprising of an analog-to-digital converter, a digital-to-analog converter, and a switch. The calorimetric cell is a thin-walled cylindrical vessel made from titanium with a volume of $1.5 \cdot 10^{-6}$ m^3. Its mass is (1.626 ± 0.005) g. A miniature iron−rhodium resistance thermometer (with the nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on ITS-90 (International Temperature Scale of 1990) by the Russian Metrology Research Institute, Moscow region, Russia. The difference in temperature between the ampule and an adiabatic shield was controlled by a four-junction copper−iron−chromel thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3}$ K, of the analog-to-digital converter 0.1 μV. The energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded and processed online by a computer. The speed of the computer-controlled measuring system was 10 measurements per second.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard materials (K-2 benzoic acid and α-Al_2O_3)[9,10] prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation were measured over the temperature range $6 \leq (T/\text{K}) \leq 335$. The sample masses were (0.768 and 1.500) g, respectively. It was established that the apparatus and measurement technique enabled the determination of the heat capacity of substances with an error not exceeding ± 2 % within the temperature range T = (6 to 15) K, ± 0.5 % between T = (15 and 40) K, and ± 0.2 % within the temperature range of $40 \leq (T/\text{K}) \leq 335$. The phase transition temperatures were measured within about ± 0.01 K and the enthalpies of transformations with the error of ± 0.2 %.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were controlled at $0.01\ \text{K} \cdot \text{s}^{-1}$ and (0.5 to 2) K. The heating duration was about 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within $0.01\ \text{K} \cdot \text{s}^{-1}$ during the acquisition of all heat capacity results. Liquid helium and nitrogen were used as coolants. The ampule with the substance was filled with dry helium as a heat exchange gas to the pressure of 4 kPa at room temperature. The sample mass used for calorimetric measurement was 0.6325 g, which was equivalent to 0.001209 mol in terms of its molar mass, M = 523.2321 $\text{g} \cdot \text{mol}^{-1}$. The molar mass of the object under study was calculated from the International Union of Pure and Applied Chemistry (IUPAC) table of atomic weights.[11] The experimental values of $C^{\circ}_{p,\text{m}}$ (141 points) were obtained in two series reflecting the sequence of experiments. The first series of measurements was completed over the temperature range $6 \leq (T/\text{K}) \leq 90$. The second series of $C^{\circ}_{p,\text{m}}$ measurements was carried out between T = (84 to 335) K. The heat capacity of the sample was between (40 and 70) % of the overall heat capacity of the calorimetric ampule with the substance under temperature change from T = (6 to 335) K.

Differential Scanning Calorimetry and Thermogravimetric Analysis. To measure the heat capacity of the sample under study over the range from T = (300 to 470) K, the differential scanning calorimeter (model: DSC204F1, Netzsch, Germany) was used. The calorimeter was calibrated and tested against melting of n-heptane, mercury, tin, lead, bismuth, and zinc, with an error of ± 0.5 K in temperature and ± 1 % in the enthalpy of transition. The heat capacity was determined by the "ratio

Table 1. Experimental Molar Heat Capacities of Crystalline Triphenylantimony Dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$ (M = 523.2321 $\text{g} \cdot \text{mol}^{-1}$)

T	$C^{\circ}_{p,\text{m}}$	T	$C^{\circ}_{p,\text{m}}$	T	$C^{\circ}_{p,\text{m}}$
K	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	K	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	K	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
		Series 1			
5.69	2.90	17.59	33.15	52.35	138.3
6.38	4.02	18.52	36.15	56.62	149.3
7.10	5.41	19.07	37.69	57.11	150.1
7.71	6.68	19.58	39.20	59.23	155.6
8.27	7.96	21.68	45.73	61.69	161.4
8.80	9.25	24.61	55.52	64.15	167.4
9.02	9.78	26.89	62.82	66.61	173.5
9.38	10.7	28.78	68.55	68.65	178.9
9.91	12.0	31.21	75.90	70.80	183.9
10.45	13.4	33.66	83.66	73.27	189.7
10.84	14.3	31.81	78.04	75.28	193.9
11.30	15.5	33.76	84.46	77.44	199.0
11.73	16.5	36.21	92.11	79.90	204.6
12.10	17.4	38.67	99.54	82.19	210.0
13.05	19.9	41.14	106.6	84.03	214.2
13.67	21.6	43.60	113.8	86.03	217.9
14.66	24.5	46.06	120.5	88.12	222.6
15.64	27.40	48.52	127.2	90.24	227.1
16.62	30.16	50.62	133.3		
		Series 2			
84.36	214.5	95.37	236.4	107.22	258.4
86.44	219.2	97.74	240.6	109.45	262.8
88.53	223.9	100.11	245.2	111.82	266.7
90.62	227.4	102.48	250.0	114.30	271.1
92.99	232.0	104.85	254.0	116.58	275.1
118.96	279.0	175.85	369.5	265.91	505.5
121.34	283.0	178.25	372.5	270.50	511.7
123.72	286.8	180.65	376.2	275.08	518.7
126.10	290.5	183.05	379.6	277.79	522.4
128.48	294.9	184.24	380.9	281.19	527.2
130.59	298.4	187.35	385.8	284.56	532.8
132.70	302.2	190.90	391.1	287.93	538.8
135.08	306.4	194.06	395.5	291.28	544.0
139.60	313.7	197.17	400.2	294.60	550.2
141.30	316.8	200.73	406.0	297.91	555.7
143.40	321.0	204.87	412.6	301.20	561.8
145.22	324.6	209.58	420.0	304.48	566.7
147.60	328.9	214.29	427.0	307.74	572.1
149.99	333.6	218.98	434.2	310.99	577.4
152.36	347.2	223.67	442.1	314.22	583.3
154.75	352.6	228.35	449.1	317.43	588.2
157.14	362.4	232.58	456.1	320.63	592.8
159.53	372.2	236.01	461.0	323.81	597.8
161.92	369.5	240.06	466.4	327.25	602.8
164.34	355.3	244.71	473.3	330.43	607.0
166.76	356.4	249.36	480.0	332.90	611.4
169.15	360.0	252.66	484.9	334.78	614.7
171.60	363.4	256.66	491.7		
173.90	366.7	261.29	497.9		

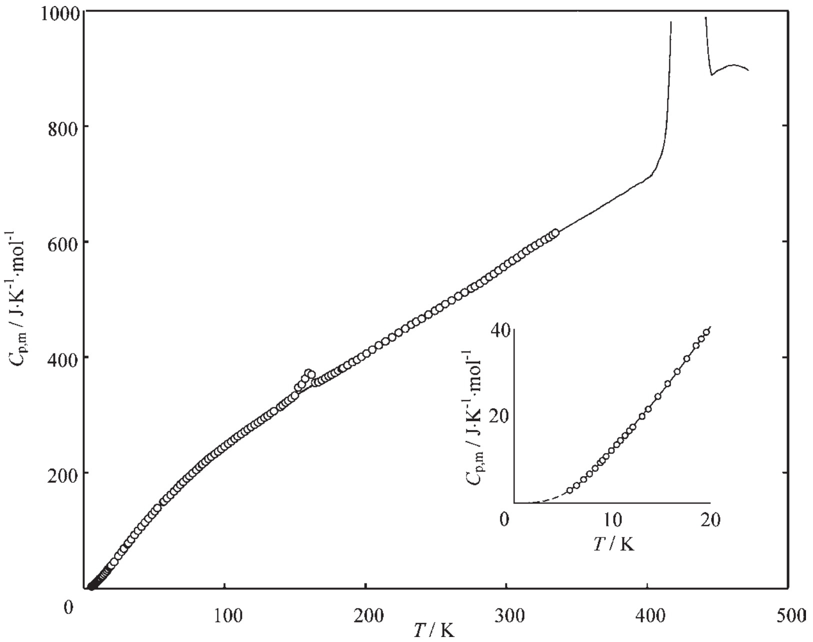

Figure 1. Curve of experimental molar heat capacities of triphenylantimony dimethacrylate vs temperature (T).

method", with corundum used as a standard reference sample. The technique for determining $C^{o}_{p,\mathrm{m}}$ according to the data of DSC measurements is described in detail in refs 12 and 13 and the Netzsch Software Proteus. The heat capacity error did not exceed ± 2 %. The heating rate and cooling rate were 5 K·min^{-1}, and the measurement was carried out in argon atmosphere. It put 0.026 g of the compound under study to the crucible.

The thermogravimetric (TG) analysis of $\mathrm{Ph_3Sb(O_2CCMe{=}CH_2)_2}$ was done using a thermal microbalance (model: TG209F1, Netzsch, Germany). TG analysis was carried out in the range from (310 to 500) K in the argon atmosphere. The thermal microbalance TG209F1 allows fixing the mass change in ± 0.1 μg. The mean heating rate was 5 K·min^{-1}. The measuring technique of the TG analysis was standard, according to Netzsch Software Proteus.

RESULTS AND DISCUSSION

Heat Capacity and Phase Transitions. All experimental results of the molar heat capacity of $\mathrm{Ph_3Sb(O_2CCMe{=}CH_2)_2}$ over the range from T = (6 to 335) K (adiabatic vacuum calorimetry, Table 1) and from T = (300 to 470) K (differential scanning calorimetry) are plotted in Figure 1. The tested substance under conditions of our apparatus was cooled from room temperature to the temperature of the measurement onset (~6 K) at a rate of 0.01 K·s^{-1}. The heat capacity of triphenylantimony dimethacrylate rises with temperature increasing.

The experimental points of $C^{o}_{p,\mathrm{m}}$ in the temperature range between T = (12 and 150) K and from T = (167 to 335) K were fitted by means of the least-squares method and the polynomial equations of the $C^{o}_{p,\mathrm{m}}$ versus temperature were the following: for the range from T = (12 to 90) K,

$$C^{o}_{p,\mathrm{m}} = A + B\ln(T/30) + C(\ln(T/30))^2 + D(\ln(T/30))^3 + E(\ln(T/30))^4 + F(\ln(T/30))^5 + G(\ln(T/30))^6 + H(\ln(T/30))^7 + I(\ln(T/30))^8 + J(\ln(T/30))^9 \quad (1)$$

for the ranges from T = (85 to 148) K and T = (167 to 400) K,

$$C^{o}_{p,\mathrm{m}} = A + B(T/30) + C(T/30)^2 + D(T/30)^3 + E(T/30)^4 + F(T/30)^5 + G(T/30)^6 + H(T/30)^7 \quad (2)$$

The corresponding coefficients (A, B, C, etc.) for eqs 1 and 2 are given in Table 2.

Their standard deviations from the smoothed $C^{o}_{p,\mathrm{m}} = f(T)$ curve were listed in Figure 2.

Over the range from T = (6 to 15) K, the smoothing was done according to the Debye law in the low-temperature limit.

Over the ranges from T = (150 to 167) K and from T = (400 to 450) K, phase transitions are seen. The first one is a λ-transition[14] that expresses itself as a positive deviation of the experimental $C^{o}_{p,\mathrm{m}}$ values from a normal trend of $C^{o}_{p,\mathrm{m}} = f(T)$ (the dotted line in Figure 1). This transition was reproduced every time on cooling (0.01 K·s^{-1}) and heating the substance. This anomaly can be interpreted as an order-to-disorder λ-transition. We estimated thermodynamic characteristics of the transition, namely, the temperature interval T = (150 to 167) K, the enthalpy $\Delta_{\mathrm{tr}}H^\circ$ = 216.5 ± 0.4 J·mol^{-1}, and the entropy $\Delta_{\mathrm{tr}}S^\circ$ = 1.370 ± 0.003 J·mol^{-1}·K^{-1}. $\Delta_{\mathrm{tr}}H^\circ$ and $\Delta_{\mathrm{tr}}S^\circ$ were calculated from the area between anomalous and normal trends of the curves $C^{o}_{p,\mathrm{m}} = f(T)$ and $C^{o}_{p,\mathrm{m}} = f(\ln T)$ respectively. This observed anomaly in the trend of the heat capacity curve can probably be explained by the hypothesis that highly blocked internal rotation round the bond "antimony−dimethacrylate group" leads to this transition over the mentioned temperature range from the state with one molecular conformation to the state with two or more molecular conformations. However, only calorimetric data are not enough for the explanation of the transition character, and another experimental investigation is necessary.

The second transition is caused by the sample under study melting. The heat capacity curve was not reproduced on subsequent

Table 2. Coefficients of Equations 1 and 2

		T/K					
		12 to 22	20 to 90	85 to 147	167 to 266	250 to 335	300 to 400
coefficients/($J \cdot K^{-1} \cdot mol^{-1}$)	A	$-2.2371344 \cdot 10^{-2}$	4.28181	$-8.2619595 \cdot 10^{3}$	$2.0997533 \cdot 10^{2}$	$4.2362692 \cdot 10^{5}$	$-1.01596 \cdot 10^{4}$
	B	$-5.5259302 \cdot 10^{1}$	1.29317	$1.3225371 \cdot 10^{4}$	$-3.4493429 \cdot 10^{3}$	$-2.2947603 \cdot 10^{5}$	$3.48718 \cdot 10^{3}$
	C	$-3.1705874 \cdot 10^{2}$	$-9.12607 \cdot 10^{-2}$	$-8.6242756 \cdot 10^{3}$	$2.8643145 \cdot 10^{3}$	$4.5602234 \cdot 10^{4}$	$-4.30892 \cdot 10^{2}$
	D	$-9.8904 \cdot 10^{2}$	$8.24303 \cdot 10^{-2}$	$2.988413 \cdot 10^{3}$	$-9.767262 \cdot 10^{2}$	$-3.1832834 \cdot 10^{3}$	$2.38839 \cdot 10^{1}$
	E	$-1.89461782 \cdot 10^{3}$	-2.56792	$-5.7733638 \cdot 10^{2}$	$1.760754 \cdot 10^{2}$	$-1.7813121 \cdot 10^{2}$	$-4.94791 \cdot 10^{-1}$
	F	$-2.310394 \cdot 10^{3}$	3.46291	$5.8907939 \cdot 10^{1}$	$-1.7674823 \cdot 10^{1}$	$4.3752497 \cdot 10^{1}$	
	G	$-1.7956894 \cdot 10^{3}$	5.73167	-2.478598	$9.3646983 \cdot 10^{-1}$	-2.667983	
	H	$-8.6057264 \cdot 10^{2}$	$-1.69623 \cdot 10^{1}$		$-2.0459729 \cdot 10^{-2}$	$5.6879789 \cdot 10^{-2}$	
	I	$-2.315311 \cdot 10^{2}$	$1.41481 \cdot 10^{1}$				
	J	$-2.6741152 \cdot 10^{1}$	-4.03922				

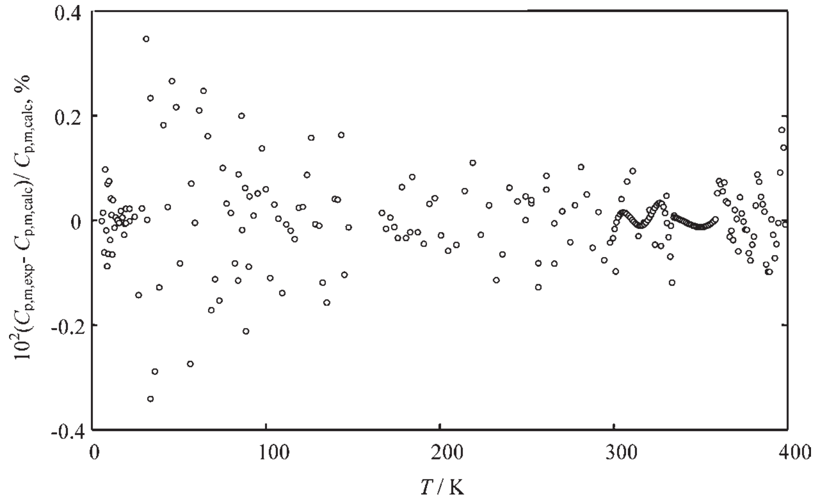

Figure 2. Deviations of experimental heat capacities from values calculated from eqs 2 and 3.

recooling and reheating because of the substance under study melts with a partial decomposition. This result was also confirmed with the thermogravimetric analysis data. It was established that the mass loss after the first set of measurements was ≈2 % to the finishing temperature of fusion (T = 440 K). Thus, it is impossible to calculate the enthalpy and the entropy of the melting for the substance under study. The similar thermal behavior was established by us earlier for pentaphenylantimony Ph_5Sb,[15] tetraphenylantimony benzophenoneoximate $Ph_4SbONCPh_2$,[16] and tetraphenylantimony acetophenoneoximate $Ph_4SbONCPhMe$.[17] The melting temperature of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ was estimated as the temperature of the transition beginning according to Netzsch Software Proteus, $T^{\circ}_{fus} = 418.7 \pm 0.5$ K.

Low-temperature heat capacity data were used to calculate a value of a fractal dimension D.[18] The fractal dimension is an exponent at temperature in the basic equation in the fractal version of Debye's theory of heat capacity of solids. The value of D gives a possibility to draw a conclusion about a character of a topology structure of a compound. D can be obtained from a $\ln C_v - \ln T$ plot for a compound.[18] It follows from eq 3:

$$C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/\Theta_{max})^D \quad (3)$$

Here N is the number of atoms in a molecular unit, k is the Boltzmann constant, $\gamma(D + 1)$ is the γ-function, $\xi(D + 1)$ is the Riemann ξ-function, and Θ_{max} is the characteristic temperature. For a particular solid $3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(1/\Theta_{max})^D = A$ is a constant value, and eq 3 can be written as eq 4:

$$\ln C_v = \ln A + D \ln T \quad (4)$$

At $T < 50$ K, the experimental values of $C^{\circ}_{p,m}$ are equal to C_v. Thus, using experimental heat capacity data in the range from (20 to 50) K and eq 4 the value of the fractal dimension can be obtained. D for $Ph_3Sb(O_2CCMe{=}CH_2)_2$ is equal to 1.5, the characteristic temperature $\Theta_{max} = 227.6$ K. At calculated values of D and Θ_{max}, eq 3 reproduces the $C^{\circ}_{p,m}$ values over this temperature range with an error in ± 0.6 %.

According to the multifractal version of the theory of heat capacity of solids,[19] $D = 1$ corresponds to the solids with a chain structure, $D = 2$ corresponds to ones with a layered structure, and $D = 3$ corresponds to ones with a spatial structure. The obtained value of D points out the chain-layer topology structure of $Ph_3Sb(O_2CCMe{=}CH_2)_2$. This conclusion corresponds to an X-ray diffraction study.[6]

Standard Thermodynamic Functions of $Ph_3Sb(O_2CCMe{=}CH_2)_2$. To calculate the standard thermodynamic functions (Table 3) of $Ph_3Sb(O_2CCMe{=}CH_2)_2$, their smoothed molar heat capacities $C^{\circ}_{p,m}$ were extrapolated from the

Table 3. Smoothed Molar Heat Capacities and Thermodynamic Functions of Crystalline Triphenylantimony Dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$ (M = 523.2321 g·mol^{-1}, p^o = 0.1 MPa)

T	$C^o_{p,m}$	$H^o(T) - H^o(0)$	$S^o(T)$	$-[G^o(T) - H^o(0)]$
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
5	2.01	0.00250	0.671	0.000840
10	12.3	0.0352	4.78	0.0126
15	25.4	0.128	12.1	0.0541
20	40.48	0.2928	21.52	0.1375
25	56.85	0.5354	32.28	0.2715
30	72.23	0.8585	44.02	0.4620
35	88.24	1.259	56.34	0.7125
40	103.4	1.739	69.14	1.026
45	117.5	2.292	82.14	1.404
50	131.7	2.915	95.25	1.848
60	157.4	4.363	121.6	2.932
70	181.9	6.059	147.7	4.279
80	204.8	7.994	173.5	5.885
90	226.3	10.15	198.9	7.747
100	245.1	12.51	223.7	9.861
110	263.4	15.05	247.9	12.22
120	280.8	17.78	271.6	14.82
130	297.4	20.67	294.8	17.65
140	314.6	23.73	317.4	20.71
150	333.6	26.96	339.7	24.00
160	372.6	30.51	362.6	27.51
170	361.2	34.13	384.6	31.25
180	375.2	37.81	405.6	35.20
190	389.6	41.64	426.3	39.36
200	404.7	45.61	446.6	43.72
210	420.5	49.73	466.8	48.29
220	436.3	54.02	486.7	53.06
230	451.7	58.46	506.4	58.02
240	466.6	63.05	526.0	63.18
250	481.2	67.79	545.3	68.54
260	496.3	72.67	564.5	74.09
270	511.1	77.71	583.5	79.83
280	525.9	82.89	602.3	85.76
290	541.9	88.23	621.1	91.88
298.15	555.9	92.71	636.3	97.00
300	559.1	93.74	639.7	98.18
310	576.3	99.42	658.3	104.7
320	592.0	105.3	676.9	111.3
330	607	111	695	118
340	621	117	714	125
350	635	124	732	132
360	649	130	750	140
370	664	137	768	147
380	679	143	786	155
390	694	150	804	163
400	709	157	821	171

temperature of the measurement beginning at approximately T = 6 K to $T \rightarrow 0$ K with the Debye law in the low-temperature limit:[20]

$$C^o_{p,m} = n\mathbf{D}(\Theta_D/T) \tag{5}$$

where n = 6 is the number of degrees of freedom, **D** is the Debye function, and Θ_D = 62.2 K refers to the Debye characteristic temperature. Using the above parameters,[20] eq 5 describes the $C^o_{p,m}$ values of the compound over the range $6 \leq (T/K) \leq 15$ with the uncertainties of ± 1.3 %. In calculating the functions, it was assumed that eq 5 reproduced the $C^o_{p,m}$ values of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ at $T \leq 6$ K with the same error.

The calculations of $[H^o(T) - H^o(0)]$ and $S^o(T)$ were made by numerical integration of the curves with respect to T and ln T, respectively. The Gibbs energy $[G^o(T) - H^o(0)]$ was calculated from $[H^o(T) - H^o(0)]$ and $S^o(T)$ values at corresponding temperatures. The zero entropy of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ was assumed to be zero. The calculation procedure was described in detail in ref 21. The errors determined for the function values are ± 2 % at T < 15 K, ± 0.6 % from T = (15 to 40) K, ± 0.3 % from T = (40 to 335) K, and ± 2.0 % from T = (300 to 400) K.

Using the value of the absolute entropy of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ in Table 3 and the elemental substances, namely, carbon,[22] hydrogen,[23] oxygen,[23] and antimony,[24] the standard entropy of formation at T = 298.15 K was estimated. $\Delta_f S^o_m$(298.15, $Ph_3Sb(O_2CCMe{=}CH_2)_2$,cr) = −1599 ± 16 J·K^{-1}·mol^{-1}.

The obtained value fits the equation

$$26C(gr) + 25/2H_2(g) + 2O_2(g) + Sb(cr) \rightarrow Ph_3Sb(O_2CCMe{=}CH_2)_2(cr)$$

where gr, cr, and g are graphite, crystal and gas, respectively.

CONCLUSIONS

This work reports heat capacities measured by adiabatic vacuum and differential scanning calorimetry of the crystalline triphenylantimony dimethacrylate $Ph_3Sb(O_2CCMe{=}CH_2)_2$. The standard thermodynamic functions of $Ph_3Sb(O_2CCMe{=}CH_2)_2$ (cr) over the range from T = (0 to 400) K and the standard entropy of formation at T = 298.15 K $\Delta_f S^o_m$(298.15, $Ph_3Sb(O_2CCMe{=}CH_2)_2$, cr) = −1599 ± 16 J· K^{-1} ·mol^{-1} were derived from these experimental results.

The low-temperature ($T \leq 50$ K) dependence of the heat capacity was analyzed on the basis of the heat capacity theory of solids of Debye and the multifractal variant, and as a result, a chain-layer structure topology was established.

It has been revealed that triphenylantimony dimethacrylate melts with a partial decomposition.

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