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Thermodynamic properties of 1,3,5-trithiane derived from solid phase heat capacity measurements by adiabatic calorimetry and DSC measurements in the melting range

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Abstract

The thermal properties of 1,3,5-trithiane were measured with adiabatic calorimetry and DSC between 15 and 500 K. It was necessary to purify the compound even as the stated purity of the commercial product was >99%. The impurity present triggers a reaction at the melting point. The absolute entropy at 298.15 K was measured to be (156.2 ± 0.8) J K^{-1} mol^{-1}, the enthalpy increment from 0 to 298.15 K is (22936 ± 100) J mol^{-1}. The enthalpy of melting was found to be (32.2 ± 0.3) kJ mol^{-1}, the fusion temperature 488.4 K. The molar heat capacity of the solid between 100 and 380 K can be described by a polynomial function $C_p = \{24.17 + 0.4004T - 9.9605.10^{-5}T^2\}$ J K^{-1} mol^{-1}, the standard deviation of this fit is 0.24 J K^{-1} mol^{-1}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1,3,5-Trithiane; Calorimetry; DSC; Heat capacity

1. Introduction

Ring systems with different kind of atoms form an interesting group in organic chemistry. Oxygen- and sulfur- containing molecules like 1,3,5-trioxane and 1,3,5-trithiane have been the subjects of several physical chemistry studies. In 1995 Dorofeeva and Gurvich published a survey of the work done on sulfur heterocyclic compounds [1]. Our group presented experimental molar heat capacity measurements of 1,3,5-triazine and 1,3,5-trioxane [2]. Vapour pressures and the derived enthalpy of vaporisation of 1,3,5-trithiane were published in 1983 [3]. Heat capacity measurements made by DSC on 1,3,5-trithiane were published in the temperature range between 300 and 450 K [4]. This work reports on the thermal properties of 1,3,5-trithiane between 15 K and the melt. The aim of this work is to extend the knowledge of thermodynamic properties of the heterogeneous ring compounds.

2. Experimental

1,3,5-Trithiane was obtained from Fluka. The assay of this product was indicated as >99%. As other authors reported that at higher temperatures this compound showed solid-state polymerisation [5], and that the speed and amount of polymerisation probably depended on the impurities in the sample [6], the

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product was subjected to vacuum sublimation. The DSC measurements were performed using a Mettler Toledo DSC821^e. The samples (approximately 6 mg) were encapsulated in aluminium crucibles. In all cases the heating and cooling rates were 5 K min^{-1}. The adiabatic measurements were made with a sample of 0.65 g. A new calorimeter, laboratory design "CAL8" was used [7]. This calorimeter is a scaled down version of CALV, the construction of which has been published in 1987 [8]; improvements in construction and data handling were presented in 1998 [9]. The same electronics are used for both calorimeters. The main difference is the use of a small sample vessel of about 1 cm^3, this vessel fits closely into a sample holder, which is equipped with a heater and a 27 Ω rhodium/iron thermometer. Oxford instruments calibrated the thermometer according to the ITS-90 scale [10]. The thermal contact between the vessel and the holder is very important. A small amount (about 1–2 mg) of Apiezon *N* grease is used to improve the contact between the vessel and the holder. Corrections for the grease are made. However, as it is not always possible to remove the grease used in an earlier experiment completely from the holder, some inaccuracy is introduced. From several experiments with synthetic sapphire [11] and *n*-heptane [12], an inaccuracy in the specific heat measurement of 0.2% was found above 50 K. Below this temperature deviations up to 3% were found. The measured enthalpy of fusion of *n*-heptane (four experiments; all within 0.1%) deviated less than 0.1% from the literature value [12]. We estimate the overall inaccuracy of the heat capacity data and the derived properties to be 0.5%.

2.1. DSC experiments

In Fig. 1a a H DSC curve obtained with trithiane "as received" is given. The figure shows three measuring curves. Curve A is the heating curve from 330 to 530 K, curve B the cooling curve and curve C the second heating curve. In the first measurement (curve A) an exothermic effect occurred immediately after the melt. This effect was followed by an endothermic effect around 515 K. Close to the melt a small endothermic effect took place. This curve has the same highlights as the curve given by Nadkarni and Schultz [5]. The exothermic effect however was not discussed in this article. The cooling curve B does show several thermal events, indicating that the solid does show two or three polymorphic forms. The second heating curve of the same sample (curve C) made under the same conditions with this sample showed hardly any exothermic effect. The melting peak shifted to lower temperature and the endothermic effect after the melt persisted. A purity analysis indicated a shift in purity from 99.5 in the first run to 98.5% in the second run.

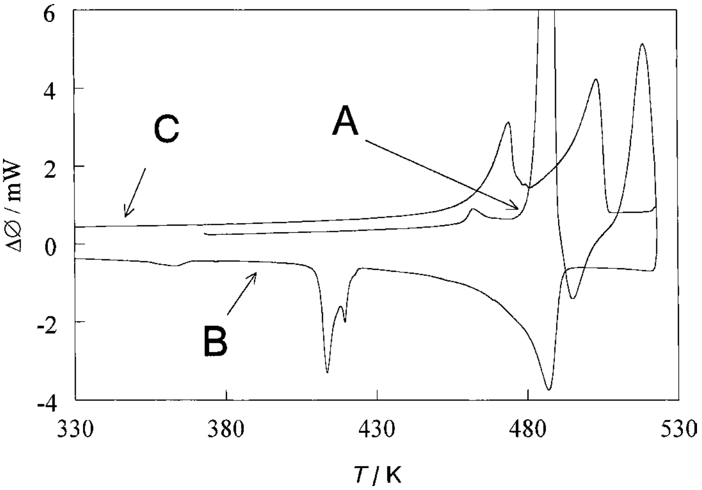

Fig. 1. DSC curve of 4.83 mg of 1,3,5-trithiane "as received". (A) First heating curve; (B) cooling curve; (C) second heating curve. All measurements were made with a rate of 5 K min^{-1}.

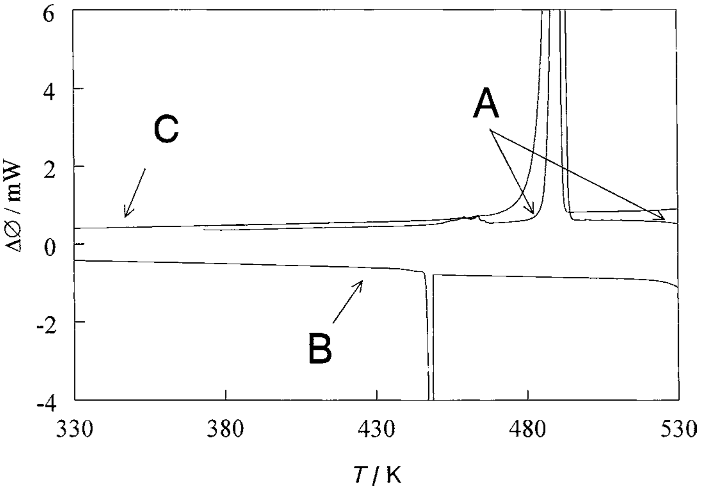

Fig. 2. DSC curve of 6.18 mg of vacuum sublimated 1,3,5-trithiane. (A) First heating curve, note the exothermic tendency of the curve after the melt; (B) cooling curve with a sharp crystallization effect; (C) second heating curve. All measurements were made with a rate of 5 K min^{-1}.

The DSC curve obtained from a measurement using a vacuum sublimated sample is given in Fig. 2. The indications A, B and C in the figure have the same meaning as in Fig. 1. Obviously there is only a very small exothermic effect after the melt. The endothermic effect before the melt (around 463 K) decreased significantly. The cooling curve B shows only one very sharp thermal effect. The second heating curve does indicate a slight increase in impurity, the onset temperature of the melt changed from 488.4 in the first run to 485.9 K in the second. In Table 1 the main aspects of the curves and the measured temperatures and enthalpies are collected. The enthalpy of fusion could only be calculated reliably from the experiments with the vacuum sublimated sample. In the measurement of the sample "as received" the exothermic effect makes it impossible to draw a base line. Repeating the measurement with the vacuum sublimated sample showed that after storing the product for about a week already a lower melting point and a lower enthalpy of fusion were measured. One sample cup with a vacuum sublimated sample was, after measuring it twice, stored for 4 months. Repeating the measurement showed no difference with the earlier second run. Measurement of a sample of the same vacuum sublimated batch, stored in a glass vessel for the same period of 4 months showed a marked increment of the endothermic effect at 463 K and a lower onset temperature. This is a strong indication that light is the cause of the formation of the impurity.

Table 1
Summary of DSC experiments

Sample treatment and storage time	Amount (mg)	Transition temperature (K)	Fusion onset temperature (K)	$\Delta H_{\mathrm{trans}}$ (J mol^{-1})	ΔH_{fus} (J mol^{-1})	Remarks
As received	5.66	463	481.9	760		Exothermic effect after melt
As received	4.83	462	483			Exothermic effect followed by endothermic effect
Freshly sublimated	6.18	464	488.4	487	32200	Very small exothermic effect between 513 and 523 K
Second measurement	6.18	463	485.9		30100	No exothermic effect
Sublimated, stored for 3 days	11.21	462	487.3	335	31775	Used for C_p measurement

Table 2
Experimental molar heat capacities of 1,3,5-trithiane in chronological order

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
Series 1		232.75	111.95	34.54	22.60	361.13	155.66
115.18	68.63	234.72	112.82	Series 5		365.23	156.92
117.14	69.42	236.68	113.48	36.79	24.36	369.36	158.37
119.91	70.51	238.64	113.86	39.11	27.35	373.50	159.69
122.63	72.00	240.59	114.35	41.10	28.34	377.67	161.16
125.31	72.95	242.52	115.01	43.37	30.43	Series 7	
127.97	73.62	244.44	116.26	45.71	32.21	300.57	135.61
130.59	75.26	246.36	116.89	48.09	33.20	304.55	137.19
133.19	75.83	248.27	117.46	50.49	36.15	308.51	138.64
135.75	76.62	250.18	118.06	52.92	37.44	312.48	139.61
138.29	77.52	252.08	118.65	55.39	39.39	316.45	140.99
140.80	78.89	253.98	119.42	57.92	41.21	320.43	142.31
143.30	79.37	255.89	119.71	60.47	42.81	324.41	143.68
145.79	79.74	257.79	120.64	63.05	43.85	328.40	145.11
148.23	81.89	259.68	121.40	65.67	45.76	332.39	146.39
150.66	82.74	261.56	122.01	68.31	46.72	336.40	147.62
153.06	83.53	263.44	122.79	70.97	48.64	340.41	149.01
155.45	84.21	265.32	123.68	73.65	50.18	344.43	150.41
157.82	84.97	267.19	124.23	76.36	51.34	348.47	151.57
160.18	85.73	269.06	124.67	79.08	52.64	352.51	152.86
162.52	86.68	270.93	125.55	81.82	54.11	356.56	153.85
164.84	87.49	272.79	126.08	84.58	55.43	360.63	155.55
167.15	88.38	Series 2		87.35	56.66	364.71	156.88
169.44	89.25	10.97	0.42	90.13	58.29	368.81	158.15
171.72	90.06	12.90	1.09	92.92	59.42	372.92	159.57
173.98	90.91	14.75	2.48	95.72	60.85	377.05	161.08
176.22	91.80	16.80	4.07	98.53	61.99	381.20	162.47
178.46	92.65	19.03	6.34	101.35	63.04	385.37	163.69
180.68	93.46	21.38	8.95	104.18	64.72	Series 8	
182.89	94.54	23.85	11.60	107.02	65.93	247.05	116.66
185.09	95.30	26.46	14.23	109.87	66.80	250.98	117.96
187.27	95.96	29.19	16.74	112.72	68.19	254.90	119.39
189.44	96.39	Series 3		115.58	69.19	258.82	120.91
191.60	96.83	11.38	0.52	118.45	70.40	262.74	122.35
193.75	97.68	13.29	1.45	121.32	71.59	266.66	123.82
195.89	98.54	15.24	2.99	Series 6		270.60	125.07
198.02	99.49	17.45	4.74	293.29	133.39	274.53	126.62
200.13	100.09	19.77	7.05	297.31	134.54	278.47	128.18
202.24	100.92	22.21	9.74	301.27	136.13	282.41	129.56
204.34	101.78	24.73	12.67	305.21	137.58	286.36	131.08
206.42	102.47	27.39	15.07	309.14	138.64	290.32	132.26
208.50	103.21	30.18	17.48	313.07	139.90	294.28	133.41
210.57	103.95	33.09	21.09	317.00	141.37	298.25	135.46
212.62	104.37	Series 4		320.95	142.58	302.22	135.97
214.67	105.39	11.63	0.69	324.91	143.90	306.20	137.52
216.72	106.12	13.17	1.61	328.87	145.15	310.19	138.74
218.75	106.77	15.35	2.93	332.85	146.44	314.19	140.11
220.77	107.69	17.73	5.19	336.84	147.75	318.20	141.08
222.79	108.15	20.14	7.79	340.85	149.14	322.22	142.95
224.80	108.81	22.71	10.63	344.88	150.25	326.25	144.31
226.80	109.97	25.45	13.65	348.91	151.66	330.28	145.68
228.79	110.55	28.33	16.33	352.96	153.10		
230.78	111.16	31.36	19.82	357.04	154.02		

The highest enthalpy of fusion measured was 233 J g^{-1}, corresponding to 32.22 kJ mol^{-1} (molar mass = 138.28 g mol^{-1}). The onset temperature of the fusion in this measurement was 488.4 K. The enthalpy of fusion is much higher than the value reported in [5], which is 148 J g^{-1}. Heat capacities were measured with samples of about 12 mg between 305 and 525 K. The measurements were performed by making three measuring runs, one with the empty sample cups; one with a sample of 22 mg sapphire in one of the cups and a third with the sample. The values obtained are given in Table 4. The measurements with the sample were made in two series. Results of the first series, from 300 to 390 K, correspond completely with the adiabatic calorimetry results. The second series, from 390 to 500 K, was started after a period of about 2 h at 390 K. The results do suggest that a slight exothermic effect is taken place, resulting in a lowering of the observed heat capacity.

Table 4
Molar heat capacities of 1,3,5-trithiane measured by DSC

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
303.15	135.1	395	160.7
308.15	137.1	400	161.2
313.15	139.2	405	161.9
318.15	141.0	410	162.7
323.15	142.6	415	163.4
328.15	144.7	420	164.5
333.15	146.3	425	166.0
338.15	148.1	430	167.5
343.15	149.9	435	170.3
348.15	152.1	440	174.3
353.15	153.9	445	180.4
358.15	155.7	450	189.3
363.15	157.3	455	198.6
368.15	158.7	460	210.5
373.15	160.2	465	193.8
378.15	161.9	470	194.5
383.15	162.9	475	212.1
388.15	164.5	480	267.1
393.15	166.3	485	837
		490	6867
		495	247.1
		500	237.6

2.2. Adiabatic measurements

0.6518 g of vacuum sublimated 1,3,5-trithiane was loaded in a glove box in CAL8. The vessel was evacuated and about 1000 Pa of helium was admitted as heat exchange gas before closing. As we feared thermal decomposition at higher temperatures, measurements were started at low temperature. In Table 3 the temperature range, the heating and stabilisation periods and the mean heating rate for the different series are given. In the measuring range there was no indication of a phase transition. Temperature drifts in the stabilisation periods were within the normal range, indicating that no measurable reaction took place. The mean molar heat capacities and the mean temperature of the interval over which the measurement was made are given in Table 2. In Table 5 the heat capacity, the entropy and enthalpy increments from 0 K are given at rounded temperatures. For the calculation of the entropy and enthalpy it was assumed that below 15 K the low temperature Debye relation, $C_p = \alpha T^3$, could be applied. The table is extended to the liquid phase by using the DSC results. For this calculation it was assumed that the heat capacity as measured by adiabatic calorimetry between 300 and 380 K could be extrapolated linearly to the melting point. The function used is

Table 3
Adiabatic heat capacity measurement series in chronological order[a]

Temperature range (K)	Stabilisation time (s)	Input time (s)	Mean heating rate (K h^{-1})
113–273	500	560	6.8
11–29	100	100	45
11–33	100	100	48
11–34	150	100	42
36–121	400	400	12
290–377	500	500	14
297–385	350	500	17
244–330	350	500	17

[a] The temperature range, the stabilisation and input times and the mean heating rate are given.

$$C_p = \{38.08 + 0.3255T\}\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The heat capacity data are plotted in Fig. 3. In Fig. 4 the data for $T > 300$ K is given, together with the heat capacity values calculated from the DSC experiments. The drawn line in Fig. 4 represents the data we published in 1983 [4]. Between 100 and 380 K the molar heat capacity data can be represented within the

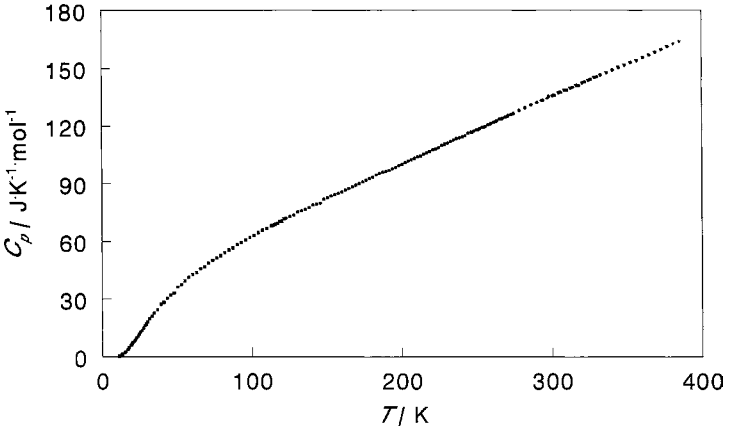

Fig. 3. Experimental molar heat capacities of 1,3,5-trithiane as measured by adiabatic calorimetry.

Table 5
Thermodynamic properties at selected temperatures for 1,3,5-trithiane[a]

T (K)	$C^0_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	S^0_m (J K^{-1} mol^{-1})	$H^0_\mathrm{m}(T) - H^0_\mathrm{m}(0)$ (J mol^{-1})
15	2.746	0.9150	10.3
20	7.534	2.349	35.7
25	13.04	4.575	86.3
30	17.31	7.269	160.4
35	23.00	10.65	270.5
40	27.81	13.80	388.5
45	31.70	17.31	537.8
50	35.67	20.80	703.7
55	39.09	24.35	889.9
60	42.54	27.90	1094
65	45.31	31.31	1307
70	47.96	34.75	1539
75	50.76	38.16	1786
80	53.13	41.50	2045
85	55.63	44.80	2317
90	58.23	48.04	2601
95	60.51	51.24	2897
100	62.53	54.40	3205
105	65.10	57.50	3523
110	66.85	60.57	3853
120	70.56	66.57	4543
130	75.09	72.39	5270
140	78.15	78.02	6030
150	82.75	83.59	6837
160	85.65	88.99	7675
170	89.40	94.25	8542
180	93.19	99.54	9468
190	96.86	104.59	10402
200	100.04	109.70	11398
210	103.75	114.67	12417
220	107.35	119.58	13472
230	110.92	124.42	14562
240	114.19	129.22	15690
250	118.03	133.96	16852
260	121.51	138.66	18048
270	124.91	143.30	19278
280	128.72	147.90	20543
290	132.16	152.47	21847
298.15	135.31	156.18	22936
300	135.52	157.02	23187
310	138.71	161.51	24558
320	142.08	165.98	25965
330	145.57	170.39	27400
340	148.87	174.80	28877
350	151.96	179.16	30381
360	155.31	183.49	31918
370	158.60	187.79	33486
450	*184.6*	*221.3*	*47209*
488.4[b]	*197.1*	*236.9*	*54536*
488.4[c]	*240.0*	*303.4*	*87036*
500	*240.0*	*309.1*	*89820*

[a] Values in italic represent DSC data.
[b] Represents solid.
[c] Represents liquid.

experimental accuracy by a second order polynomial fit;

$$C_p[100 - 380\,\mathrm{K}] = \{24.17 + 0.4004T - 9.9605.10^{-5}T^2\}\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The standard deviation of this fit is 0.24 J K^{-1} mol^{-1}.

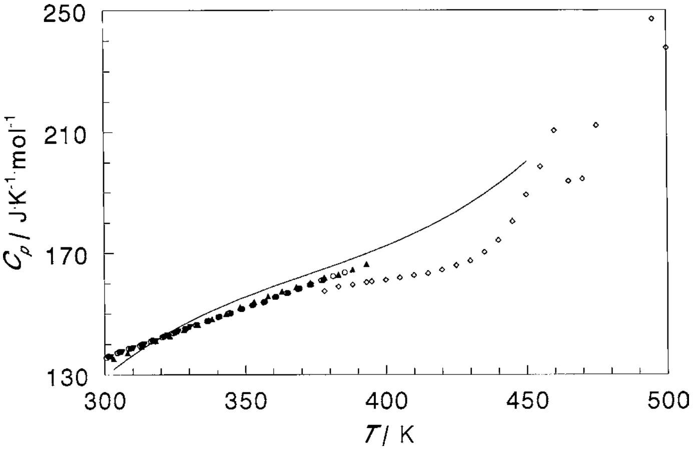

Fig. 4. High temperature molar heat capacity data of 1,3,5-trithiane. (○) and (●) adiabatic measurements; (▲) and (◇) DSC measurement; (—) DSC measurements from 1983 [4].

3. Discussion

Heat capacities of 1,3,5-trithiane were measured between 15 K and the melt. The absolute entropy and the enthalpy increment from zero Kelvin were calculated. No phase transitions were encountered before the melt.

Two subjects need to be discussed. Firstly, Nadkarni and Schultz [5] assumed the thermal effect at 463 K to be caused by a solid–solid phase transition. We think that this effect is caused by the impurity in the sample and that it can be seen as a eutectic transition. The changing value of the effect as a function of purification supports this assumption. In the product “as received” we measured an effect of 5.5 J g^{-1}, with an onset temperature of the melt of 481.9 K. After sublimation this effect reduced to 3.5 J g^{-1} and the onset temperature of the melt increased to 488.4 K. Nadkarni and Schultz [5] reported an effect of 10.8 J g^{-1}, they did not report the onset temperature, but we estimate it to be 473.1 K from the plot given. Extrapolating these effects to a zero heat of transition results in a temperature of fusion of 494.4 K. The *R*-squared value of this fit is 0.97.

Secondly, the compound does show an exothermic effect immediately after the melt. However in the second run this effect has almost disappeared. It is more pronounced in samples that show a larger heat effect at 463 K. We suggest that the impurity in the sample is involved in a reaction at the melting temperature. The impurity is then transformed in a product that does not trigger a reaction when the sample is heated again to that temperature.

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