Journal of Thermal Analysis, Vol. 13 (1978) 321–326

THERMOANALYTICAL INVESTIGATIONS OF THALLOUS NITRATE

R. P. CLARK and F. W. REINHARDT

Sandia Laboratories, Albuquerque, New Mexico, 87185, U.S.A

(Received July 22, 1977)

Thallous nitrate was investigated using TG, DTA, and DSC in conjunction with gas chromatography and X-ray diffraction analysis. TG showed a weight loss beginning at ~ 380° with a 50 percent loss by 520°. This weight loss was demonstrated to be caused by boiling rather than thermal decomposition. The DTA extrapolated onset temperature for the boiling was 467°. Two solid-solid transition points and the melting point were determined by DTA to be 77, 145, and 207°, respectively. Heat of transition values determined by DSC were 0.15 kcal/mole at 77°, 0.87 kcal/mole at 145°, and 2.18 kcal/mole for the melting at 207°.

In the course of an investigation of the surface tension of thallous nitrate conducted in this laboratory by Nissen [1] it became apparent that numerous inconsistencies exist in the literature with regard to the thermal analysis of $TlNO_3$. Of particular concern in this study was the question of weight loss, its cause and temperature. Wendlandt [2] reported decomposition and loss of oxides of nitrogen in the range 265 to 370°. Thomas [3] noted slow decomposition at 300° with a rapid reaction at 450° to form O_2, N_2, nitrogen oxides and Tl_2O_3. Duval [4] reported no weight change up to 410° with decomposition above that temperature. Decomposition at 487° was observed by Protsenko and Protsenko [5]. A boiling point of 430° is listed for $TlNO_3$ by both Mellor [6] and Weast [7]. Rossini *et al.* [8] state that $TlNO_3$ boils at 433°.

Numerous measurements of the melting point of $TlNO_3$ are in general agreement. Brown [9], Retgers [10] and Crooks [11] all reported 205°; Glass [12], Jaeger [13], and Briscoe [14] reported 206°; Bergman [15] stated 207° and Rolla [16], 210°. However, there is not the same agreement concerning the heat of fusion. Kelley [17] calculated heat of fusion values from phase diagram data and obtained six values ranging from 2.01 to 2.40 kcal/mole with a mean of 2.29 kcal/mole. Rolla [16] determined the heat of fusion of $TlNO_3$ by drop calorimetry and obtained 2.109 ± 0.085 kcal/mole. Lumsden [18] used freezing point depression data reported by Rolla [16] and calculated a heat of fusion of 1.96 kcal/mole for $TlNO_3$. Lumsden claimed this discrepancy cast considerable doubt on the accuracy of Rolla's drop calorimetry value.

It has been well established that $TlNO_3$ undergoes two crystal transformations when heated to about 60 to 80°. The orthorhombic crystals (S_{III}) transform into a rhombohedral form (S_{II}), which in turn changes to cubic (S_I) between 125 and 151°. Temperatures reported for these transitions vary considerably. Briscoe [14] reported 61.0 and 143.5°; Jossner [19], 80 and 125; Van Eyk [21], 72.8 and 142.5; Bergman [15], 78.5 and 142.5; and Brown [9], 79 and 143. The only literature values for heats of transition are those of Bridgman [20] who reported 0.24 kcal/mole for $S_{III} \rightarrow S_{II}$ and 0.76 kcal/mole for $S_{II} \rightarrow S_I$.

Experimental

Thallous nitrate (99.5% pure) was obtained from Research Organic/Inorganic Chemical Corporation and further purified by recrystallization from water. The recrystallized material was dried under vacuum 24 hours at 25° followed by 24 hours at 120°.

Thermogravimetry curves were obtained using a Cahn electrobalance system previously described [22]. Samples weighing approximately 20 mg were run in both air and argon atmospheres with a constant heating rate of 6°/min, and a maximum temperature of 750°.

Differential thermal analysis curves were obtained with a Stone differential thermal analysis system using a technique described earlier [23]. DTA samples were also run both in air and argon with a heating rate of 6°/min and a maximum temperature of 750°.

Differential scanning calorimetry, using the Perkin-Elmer Model DSC-2, was employed to determine heat of transition values. Samples weighing a few milligrams were heated in aluminium pans at 5°/min up to 250°.

A $TlNO_3$ sample weighing approximately 1.5 g was sealed in an evacuated Pyrex tube, maintained at 500° for one hour and cooled to room temperature. The residual solid material was analyzed by X-ray diffraction, and its melting point was also determined. Gas chromatographic analysis was used to determine the total amount and composition of gaseous products in the sealed tube.

Results

In all cases the results obtained in an argon atmosphere were identical to those in air. The TG curve for $TlNO_3$ is shown in Fig. 1. $TlNO_3$ begins to lose weight at ~ 380° and has lost 50 per/cent of its original weight at ~ 520°. The rate of weight loss accelerates until only 13 per/cent of the original weight remains at 540°. This curve differs considerably from that reported by Wendlandt [2]. As noted above, the literature is unclear as to whether the $TlNO_3$ weight loss is due to boiling or decomposition.

Results of the gas chromatographic analysis showed that a 1.5667 g sample of $TlNO_3$ heated under vacuum to 500° for 1 hour and cooled to room temperature left a residual gas content of 272 Torr · cc. At 760 Torr this corresponds to

0.358 cc or 0.016 × 10^{-3} mole. The gas was mainly O_2 (83.5 %) with lesser amounts of N_2, N_2O, H_2O, and CO_2. The total weight of the gas would be ~ 0.53 mg, representing a weight loss of ~ 0.03 per/cent for the $TlNO_3$. These data indicate that the $TlNO_3$ weight loss observed using TG is caused by boiling rather than thermal decomposition. This conclusion is further supported by the X-ray diffraction analysis of the residual solid material which was identified as $TlNO_3$. A slight shift in the observed diffraction pattern indicates that the $TlNO_3$ stoichiometry could be slightly off. However, no more than ~ 2 per/cent impurity could be present [24]. The melting point of the residual solid was 206°, thus supporting the X-ray and gas chromatography results.

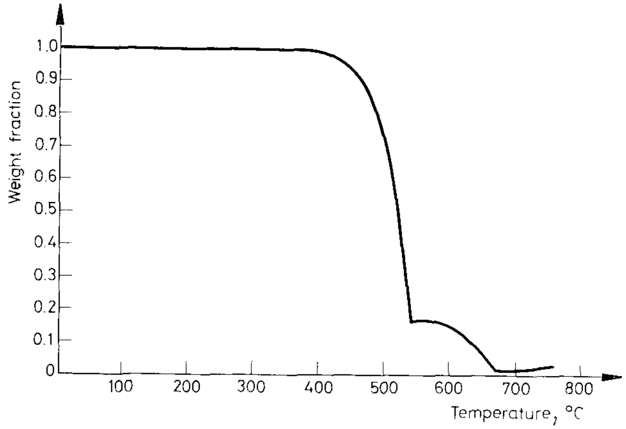

Fig. 1. TG curve for $TlNO_3$. Heating rate: 6°/min. Atmosphere: air or argon

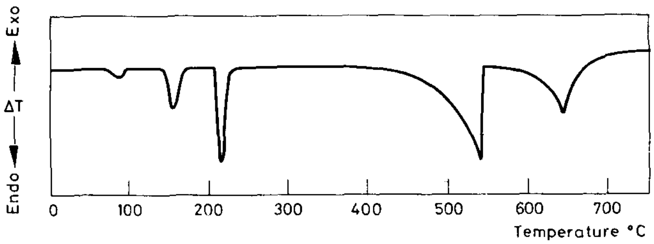

Fig. 2. DTA curve for $TlNO_3$. Heating rate: 6°/min. Atmosphere: air or argon

The DTA data are shown in Fig. 2. The extrapolated onset temperature for boiling is 467°. In addition to the endotherms between 400 and 700° which correspond to the events observed in the TG curve, three additional endotherms were observed at temperatures below 250°. The first two events occur at, 77 and 145°, respectively, and are the transformations

$$S_{III} \xrightarrow{77^\circ} S_{II} \xrightarrow{145^\circ} S_I$$

previously mentioned. The third event is the fusion of $TlNO_3$ (S_I) at 207°. These temperatures agree well with the previously reported values.

The heats involved in the two solid-solid transformations and in the fusion process were determined by DSC. The results are given in Table 1.

Table 1

Heats of transition values for $TlNO_3$ measured by DSC

Transition	Temperature, °C	ΔH, kcal/mole	Std. dev., kcal/mole
$S_{III} \rightarrow S_{II}$	77	0.15	0.01
$S_{II} \rightarrow S_I$	145	0.87	0.01
$S_I \rightarrow L$	207	2.18	0.03

The heat of transition values (0.15 and 0.87 kcal/mole) disagree significantly with those reported by Bridgman [20] (0.24 and 0.76 kcal/mole). Bridgman measured volume changes as a function of pressure and temperature and calculated ΔH values using the Clapeyron equation. He readily admitted experiencing significant experimental difficulties in measuring ΔH values for $TlNO_3$ and expressed doubts concerning the accuracy of his determinations. In an earlier paper [25], Bridgman noted major differences between his ΔH numbers and values previously published in the literature. In some cases Bridgman used the literature values to apply correction factors to his data. Considering these facts, it is not disturbing that our numbers differ from those of Bridgman, and it is believed that the heat of transition values reported in the present work are more accurate.

The heat of fusion value from Table 1 (2.18 kcal/mole) is intermediate between that determined by Rolla [16] (2.109 ± 0.085 kcal/mole) and that reported by Kelley [17] (2.29 kcal/mole).

Conclusions

TG has shown that $TlNO_3$ loses weight beginning at ~ 380° at a heating rate of 6°/min with a 50% weight loss at 520°. This loss has been shown to be the result of volatilization of the $TlNO_3$ with very little thermal decomposition. The DTA extrapolated onset temperature for the volatilization is 467°.

DTA has been used to confirm previously reported temperatures for two solid-solid transformations and for the melting of $TlNO_3$. These values are 77, 145, and 207°, respectively.

Using DSC, accurate values have been established for the heats of transition

(0.15 kcal/mole at 77° and 0.87 kcal/mole at 145°). In addition, a heat of fusion was determined (2.18 kcal/mole) which agreed with previously reported values.

*

The authors thank F. J. Conrad and W. J. Andrzejewski for gas analysis results and G. T. Gay for X-ray diffraction analyses.

This work was supported by the United States Department of Energy.

References

1. D. A. Nissen, J. Chem. Eng. Data, 22 (1977) 389.
2. W. W. Wendlandt, Texas J. Sci., 10 (1958) 392.
3. V. Thomas, Compt. Rend., 138 (1904) 1967.
4. C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, New York, N.Y., 1963, p. 613.
5. P. I. Protsenko and A. V. Protsenko, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol., 8 (1965) 160.
6. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. V, John Wiley and Sons, New York, N.Y., 1961, p. 473.
7. R. C. Weast, ed., Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 1976, p. B-168.
8. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, Nat'l Bur. Std. (U.S.) Circ. 500, 1952, p. 22.
9. R. N. Brown and A. C. McLaren, Acta Cryst., 15 (1962) 977.
10. J. W. Retgers, Z. Phys. Chem., 4 (1889) 593.
11. W. Crookes, J. Chem. Soc., 17 (1864) 112.
12. H. M. Glass, K. Laybourn and W. M. Madgin, J. Chem. Soc., (1932) 2713.
13. F. M. Jaeger, Z. Anorg. Chem., 101 (1917) 111.
14. H. V. A. Briscoe, C. Evans and P. L. Robinson, J. Chem. Soc., (1932) 1100.
15. A. G. Bergman, J. Russ. Phys. Chem. Soc., 54 (1922) 200.
16. M. Rolla, P. Franzosini and R. Riccardi, Discussions Faraday Soc., 32 (1961) 84.
17. K. K. Kelley, U. S. Bur. Mines Bull., 393 (1936) 123.
18. J. Lumsden, Thermodynamics of Molten Salt Mixtures, Academic Press, New York, N.Y., 1966, p. 116.
19. B. Gossner, Z. Kryst., 38 (1903) 110.
20. P. W. Bridgman, Proc. Am. Acad. Arts Sci., 51 (1916) 581.
21. C. Van Eyk, Z. Phys. Chem., 51 (1905) 721.
22. R. P. Clark and F. W. Reinhardt, Thermochim. Acta, 8 (1974) 185.
23. R. P. Clark and F. W. Reinhardt, Thermochim. Acta, 12 (1975) 309.
24. G. T. Gay, Sandia Laboratories, private communication.
25. P. W. Bridgman, Phys. Rev., 3 (1914) 153.

Résumé — On a étudié le nitrate de thallium(I) par TG, ATD et DSC conjointement à la chromatographie en phase gazeuse et à l'analyse par diffraction des rayons X. La TG révèle une perte de masse à partir d'environ 380°, avec une perte de 50 p. c. à 520°. On montre que cette perte de masse est provoquée par l'ébullition plutôt que par la décomposition thermique. La température initiale de l'ébullition, extrapolée à partir des données ATD, est de 467°. Deux points de transition solide-solide ainsi que le point de fusion ont été déterminés par ATD et correspondent aux températures respectives de 77, 145 et 207°. Les valeurs des chaleurs de transition ont été déterminées par DSC: 0.15 kcal. mol^{-1} à 77°, 0.87 kcal. mol^{-1} à 145° et 2.18 kcal. mol^{-1} pour la fusion à 207°.

ZUSAMMENFASSUNG — Thallium(I)nitrat wurde mittels TG, DTA und DSC, mit Gaschromatographie und Röntgendiffraktionsanalyse gekoppelt, untersucht. TG zeigte einen beginnenden Gewichtsverlust ab etwa 380° und einen Verlust von 50% bis 520°. Es wurde gezeigt, daß dieser Gewichtsverlust eher vom Sieden als von der thermischen Zersetzung verursacht wird. Die aus DTA-Daten extrapolierte Anfangs-Siedetemperatur war 467°. Die Fest-festphasen Übergangspunkte und der Schmelzpunkt lagen, wie durch DTA ermittelt, bei 77, 145, bzw. 207°. Die mittels DSC bestimmten Wärmen der Übergangswerte betrugen 0.15 kcal/Mol bei 77°, 0.87 kcal/Mol bei 145° und 2.18 kcal/Mol für das Schmelzen bei 207°.

Резюме — *Нитрат таллия был исследован, используя ТГ, ДТА и ДСК в соединении с* газовой хроматографией и рентгено-диффракционным анализом. ТГ показала потерю веса, начинающуюся при 380° с 50% потерей при 520°. Показано, что потеря веса вызвана скорее кипением, чем термическим разложением. ДТА экстраполированная начальная температура для кипения была 467°. Точки перехода типа твердое тело-твердое тело и точка плавления, определенные с помощью ДТА, соответственно равны 77, 145 и 207°. Значения теплот перехода, определенные с помощью ДСК, соответственно равны 0.15 ккал/моль при 77°, 0,87 ккал/моль при 145° и 2.18 ккал/моль для плавления при 207°.