

The Thermal Transformations in Solid Thallous Nitrate

BY R. N. BROWN AND A. C. McLAREN*

Central Research Laboratories, Imperial Chemical Industries of Australia and New Zealand Limited,
Ascot Vale, Victoria, Australia

(Received 26 December 1961)

The thermal transformations in solid thallous nitrate have been studied by differential thermal analysis, optical microscopy, X-ray diffraction, and measurements of electrical conductance.

It has been found that forms I and II are structurally related and it is suggested that the $II \rightleftharpoons I$ transformations are of the order-disorder type. Form III is structurally unrelated to forms II and I, and the transformations $III \rightleftharpoons II$ do not appear to involve any disordering process.

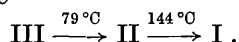
Introduction

As a continuation of a programme of research on the solid state transformations in the nitrates of univalent cations, the transformations in thallous nitrate have been studied by differential thermal analysis (DTA), optical microscopy, X-ray diffraction and measurements of electrical conductance.

Experimental and results

Differential thermal analysis

DTA was carried out in the apparatus previously described by Brown & McLaren (1962*a*). It was confirmed that thallous nitrate has three stable forms between room temperature and the melting point (205 °C.). On heating, transformation temperatures were found to be



On cooling, the $I \rightarrow II$ transformation was observed at 143 °C. No sharp transformation was observed on further cooling to 0 °C., although there was some evidence of a very slow transformation over the range 80 to 20 °C. That a transformation did take place is confirmed by the fact that the $III \rightarrow II$ transformation was again observed at 79 °C. on immediate re-heating.

Optical microscopy

Single crystals of form III grown from aqueous solution were examined under the polarizing microscope. The crystals were anisotropic. At the $III \rightarrow II$ transformation the crystals retained their external shape and, as far as could be judged, their single-crystal character. Form II was also anisotropic. At the $II \rightarrow I$ transformation the crystals became isotropic. The $I \rightarrow II$ transformation was observed at

a slightly lower temperature on cooling. The crystals retained their external shape and often their optical orientation after being through as many as four $II \rightarrow I \rightarrow II$ cycles.

It was found that form II could be cooled to room temperature, but a transformation usually took place within about 12 hr. This transformation was actually observed in one crystal; once started, the rate was many times lower than the rate of the $III \rightarrow II$ transformation. After the $II \rightarrow III$ transformation, the crystals retained their external shape but exhibited no extinction position, indicating that they were in fact polycrystalline.

X-ray diffraction

Single-crystal photographs of form III showed that it is orthorhombic with

$$a = 6.31, b = 12.30, c = 8.01 \text{ \AA}$$

and 8 molecules in the unit cell. This agrees well with the data of Hinde & Kellett (1957). Attempts to take photographs of form II were unsuccessful as the single crystals always broke up into a number of fragments of varying orientations at the $III \rightarrow II$ transformation. On cooling, further fragmentation took place at the $II \rightarrow III$ transformation. Powder patterns were, therefore, obtained for forms III, II and I.

Form I was found to be cubic with $a = 4.326 \text{ \AA}$ at 170 °C.; $d_c = 5.46 \text{ g.cm.}^{-3}$ for $Z = 1$, in agreement with Finbak & Hassel (1937).

Since no information on form II has been published, the pattern obtained by us is given in Table 1.

It was found that although the patterns for III and II are quite distinct, those for II and I show remarkable similarities. The five lines in the pattern of I in the range $15^\circ < 2\theta < 50^\circ$ are identical with the five strongest lines in the pattern of II apart from a shift to smaller Bragg angles in I due to thermal expansion. This suggested that perhaps the crystallographic

* Present address: Physics Department, Monash University, P. O. Box 92 Clayton, Victoria, Australia.

Table 1. Powder diffractometer pattern of $TlNO_3-II$ at 130 °C.
(Cu $K\alpha$ radiation)

d (Å)	I/I_0	Index	d (Å)	I/I_0	Index
5.76	3	101	2.387	5	311
4.28	80	111	2.175	5	401
3.45	4	210	2.146	6	222
3.11	3	211	1.921	28	303
3.04	77	112	1.917	40	411
3.03	100	300	1.824	3	223
2.883	5	202	1.758	26	501
2.525	5	212	1.753	48	412
2.474	87	221			

relationship between I and II is analogous to that existing between III and IV of rubidium nitrate (see Brown & McLaren, 1962b).

A hexagonal unit cell for II was proposed on this assumption and it fitted the observed powder pattern. The cell dimensions were refined by least squares to give

$$a = 10.47, c = 7.527 \text{ \AA}; \text{ at } 130 \text{ }^\circ\text{C}.; \\ d_c = 5.57 \text{ g.cm.}^{-3} \text{ for } Z = 9.$$

Electrical conductance

Measurements of the electrical conductance were made under vacuum with the apparatus described previously by Brown & McLaren (1962a).

It was found that at the III \rightarrow II transformation a sharp decrease in conductance was observed. In the first experiment, the conductance decreased by a factor of 200. On cooling, the conductance decreased normally with temperature down to ca. 40 °C. when violent instability was observed. On recycling, similar results were obtained, but the decrease in conductance at the III \rightarrow II transformation was reduced. After several such cycles, this decrease in conductance was reduced to a factor of 1.3 only. The conductance of a second sample, which had been maintained under vacuum with a liquid-nitrogen trap for over a week, decreased only by a factor of 14 on being heated through the III \rightarrow II transformation for the first time. These results suggest that the fall in conductance at this transformation is probably associated with the removal of moisture, and that in a perfectly dry sample little or no change would be observed. In support of this, Komatsu (1951) claims that he could not observe any change in electrical conductance at the III \rightleftharpoons II transformations.

At the II \rightarrow I transformation the conductance increased by a factor of 100. The I \rightarrow II transformation

took place at a slightly lower temperature with a corresponding decrease in conductance.

Discussion

The results described suggest that the transformations between III and II, and between II and I are not of the same type. Although the III \rightarrow II transformation takes place readily, the II \rightarrow III transformation is difficult to initiate and the rate of growth is comparatively slow. The III \rightleftharpoons II transformations involve fairly drastic structure changes, but the conductance changes are (in dry samples) small. Conversely, the II \rightleftharpoons I transformations take place at approximately the same temperature, the two structures are simply related and the changes in electrical conductance are large.

Rowland & Bromberg (1958) have shown by thallium magnetic resonance that the Tl^+ ion mobility in form I near the melting point is as high as in the melt. Therefore, it is suggested that the 100-fold increase in conductance at the II \rightarrow I transformation is due to the onset of positional disorder of the Tl^+ ions. Thallium magnetic-resonance line-width measurements around the transformation temperature could, in principle, confirm this (compare Brown & McLaren, 1962a).

Finbak & Hassel (1937) suggest that the NO_3^- ions are freely rotating in form I. Although this rotation has not been conclusively demonstrated, some degree of orientational disorder of the NO_3^- ions seems likely to be associated with the probable positional disorder of the Tl^+ ions.

The II \rightleftharpoons I transformations are, therefore, probably of the order-disorder type. Conversely, the electrical measurements suggest that both forms III and II are ordered structures.

References

- BROWN, R. N. & MCLAREN, A. C. (1962a). *Proc. Roy. Soc.* **A 266**, 329.
 BROWN, R. N. & MCLAREN, A. C. (1962b). *Acta Cryst.* **15**, 974.
 FINBAK, C. & HASSEL, O. (1937). *Z. phys. Chem.* **35**, 25.
 HINDE, R. M. & KELLETT, E. A. (1957). *Acta Cryst.* **10**, 383.
 KOMATSU, H. (1951). *Reports Institute of Science and Technology, Univ. Tokyo*, **5**, 15.
 ROWLAND, T. J. & BROMBERG, J. P. (1958). *J. Chem. Phys.* **29**, 626.