Thermochimica Acta, 92 (1985) 543-546
Elsevier Science Publishers B.V., Amsterdam

THE THERMAL ANALYSIS OF STRONTIUM OXALATE

David Dollimore, The University of Toledo
Toledo, Ohio, USA
G. R. Heal and N. P. Passalis, Department of Chemistry and Applied Chemistry
The University of Salford, Salford, UK

ABSTRACT

The preparation of single crystals of $SrC_2O_4.2H_2O$ and $SrC_2O_4.H_2O$ is described. The dehydration processes are studied using TG and DTA.

The decomposition of anhydrous strontium oxalate is reported. Experimental methods utilised in this part of the study included TG, both in isothermal and rising temperature modes, DTA, infrared spectroscopy, using KBr discs, and evolved gas pressure measurements. The anhydrous SrC_2O_4 was in a polycrystalline form and the decomposition proceeded to the carbonate. The decomposition was complicated by the disproportionation of the CO product.

The studies on the hydrated salts showed a correlation between their crystal structure and the dehydration. Thus the dehydration of the triclinic single crystal of $SrC_2O_4.H_2O$ proceeded in a single step but the dehydration of strontium oxalate polyhydrate took place in stages depending on the crystal symmetry.

INTRODUCTION

Strontium oxalate exists as the monohydrate, $SrC_2O_4H_2O$ and as a polyhydrate, $SrC_2O_4.2\frac{1}{2}H_2O$. The preparation of the salts in these hydrated forms have been described (1-4). The dehydration of strontium oxalate monohydrate has also been reported (3,5,6). Gerard and Watelle Marion (6) have published the most comprehensive account. The dehydration process showed a Smith-Topley effect (7,8). The dehydration of various polyhydrates is also reported (3,6). The extent of hydration depended on the environment of the preparation and some of the water of crystallization was reported to be zeolitic. In dehydration experiments intermediate stages $SrC_2O_4.2H_2O$ and $SrC_2O_4.1\frac{1}{2}H_2O$ and $SrC_2O_4.H_2O$ are reported to be formed under different conditions. The original water content of samples varied from 2.32 to 2.43 and the formula should be written $SrC_2O_4.(2+x)H_2O$ where $0 < x < 0.5$ (6).

EXPERIMENTAL

Preparation of Samples. A diffusion technique (4) was used in which oxalic acid solution was added slowly to strontium nitrate solution in nitric

---

Proceedings of ICTA 85, Bratislava

acid under dilute conditions. After three weeks well developed crystals had formed (size 3mm) of the hydrate $SrC_2O_4.2.5H_2O$. The monohydrate was prepared by a similar method but without the excess nitric acid. The samples were identified by X-ray diffraction methods and infrared spectroscopy. The $SrC_2O_4.2.5H_2O$ was stored in contact with the mother liquor, the monohydrate in a stoppered bottle after drying over $CaCl_2$.

Thermal Analysis. A Stanton Redcroft thermobalance TG750 was used. The DTA work was carried out on a Dupont 900 unit.

RESULTS AND DISCUSSION

The Dehydration of $SrC_2O_4.H_2O$. Samples of $SrC_2O_4.H_2O$ were dehydrated using the TG unit under one atmosphere of nitrogen (flow rate 60 ml min^{-1}) at heating rates of 3°C min^{-1} except for the first run at 5°C min^{-1}.

There was an initial gain in mass at slow heating rates, enhanced for larger samples but not apparent at a high heating rate. Further the last traces of water are removed at higher temperatures after the main reaction especially in the case of the sample consisting of many small crystals

The DTA in nitrogen (flow rate 0.2 $ml.min^{-1}$) on the Dupont unit with a heating rate of 10°C min^{-1} using a sample mass of 40mg packed as many small crystals, showed one major endothermic peak at 190°C with a small endothermic peak at 170°C. An exothermic peak around 315°C was also seen. X-ray diffraction results for the sample heated to 260°C showed it to be poorly crystalline but after heating to beyond 340°C the crystals were well developed confirming the observation of Negase (et al 9) that this is a recrystallization phenomena. The initial small endotherm is due to the dehydration taking place in a partially closed container. The increasing pressure of water vapor builds up around the sample and dehydration temporarily stops until the equilibrium pressure of water vapor exceeds the pressure of water vapor already in existence around the sample. The 'high temperature' unit of the Dupont DTA system allowed product gases to be disappated more easily and runs at a heating rate of 10°C min^{-1} in nitrogen with 15 mg of sample and a packing of many small crystals showed an endothermic peak at 175°C, which could be altered to 188°C if a static atmosphere of water vapor, raising the endothermic peak observed at 165°C for one crystal to 175°C for three crystals. There is a tendancy for the exothermic peak due to recrystallization to disappear for very small samples. It is suggested that the production of an amorphous anhydrous product (which subsequently goes through a recrystallization) is more pronounced under conditions far removed from equilibrium. Small samples combined with a low heating rate produce dehydration near to equilibrium and so recrystallization of the product can take place at the same time as the chemical change or indeed a crystalline product is the result anyway, and so a net endothermic change is only observed.

The Dehydration of Strontium Oxalate Polyhydrate. The dehydration process for the strontium oxalate polyhydrate was studied using a combination of TG,DTA and X-ray diffraction methods and shown to be complicated. Thus in the case of a single crystal possessing the symmetry of a prism or a bipyramid four TG plateaux and three peaks in the DTA appeared. When a tetragonal spheroid single crystal was used three TG plateaux were traced. The TG pattern and the DTA curves were only reproducible within certain limits due to the different structural imperfections of individual crystals arising from the preparation conditions or the formation of product nuclei present before commencement of the heat treatment. It also depends as already explained on the build up of water vapor around the sample. The X-ray diffraction data also indicated the formation of $SrC_2O_4.H_2O$ as an intermediate. It is concluded that kinetic factors and not the formation of definite pure lower hydrates are responsible for the TG plateaux and the DTA peaks. It is also thought that initially structural factors are responsible for the course of the reaction but later the presence of the reaction product becomes important (10,11).

Thermal Decomposition of Anhydrous Strontium Oxalate, SrC_2O_4. The polycrystalline anhydrous strontium oxalate decomposes into strontium carbonate and CO,

$$SrC_2O_4 = SrCO_3 + CO$$

and this was shown by TG,DTA and infrared spectroscopic data. There is a gaseous secondary reaction,

$$2CO \rightleftarrows C + CO_2$$

but in an oxidising atmosphere the CO and the C can be oxidised to CO_2. These side reactions are exothermic and could alter the kinetics of the main reaction causing temperature gradients inside the sample. This can be supported from a comparison of DTA and TG curves in air and an inert atmosphere. The infrared spectroscopy data showed the main decomposition reaction proceeding at lower temperatures than shown by TG or DTA data. The removal of the last traces of water overlap into the region where decomposition occurs and the kinetics of the decomposition reaction could be influenced by water retained in the lattice in the spectroscopic studies. DTA and TG date both in air and nitrogen showed that the decomposition of the SrC_2O_2 derived from the dehydration of $SrC_2O_4.H_2O$ to take place at higher temperatures than those for SrC_2O_4 derived from the polyhydrate salt. This was due to the different dehydration proceses arising from the individual crystalline structures and the water content of the starting hydrated oxalates.

Kinetics. The kinetics of the decomposition of the anhydrous salt was studied using a simple high vacuum unit to measure the pressure of evolved gas from a single crystal (12) and also by TG experiments operated isothermally and in the rising temperature mode. The calculated values of A and E in typical isothermal experiments in nitrogen (I atmosphere) for α values up to 0.20 are $E = 317 \pm 3$ $kJmol^{-1}$ and $A=10^{16.55}$ sec^{-1} where a first order decay law describes the kinetics. In the further region of α up to 0.60,$E=305 \pm 3$ $kJmol^{-1}$ and $A=10^{15.75}$ sec^{-1} on the basis of an Avrami-Erofeev equation. The initial behavior would then be consistent with a single nucleus being able to initiate decomposition of a single crystallite. These values must be compared with a value quoted by Freeberg et al (13) for E of 272.09-284.65 $kJmol^{-1}$ and by Bol dyrev et al (14) of 167.44-175.81 $kJmol^{-1}$. The value of E calculated from rising temperature studies were different except in the low value region of α. The magnitude of the values found in this study would suggest that the postulates of Freeberg et al and Boldyrev et al are appropriate, namely that the rate controlling step is the rupture of C-C bonds in oxalate ions. This would, however, only be true for the initial region of α as the reaction beyond 0.20 particularly in the case of the rising temperature experiments is complicated by the secondary reactions already noted.

REFERENCES

1. G. Bertrand, M. Lallemant and G. Watelle, Materials Research Bull. 12 (1977) 1155
2. G. Brunhns, Z. anorg. allg. Chemie, 95 (1916) 210
3. L. Walter-Levy and J. Lanpiepce, C. R. Acad. Sci. Paris, 260 (1965) 3617
4. N. A. Klasens, W. G. Perdok and P. Terpstra, Z. Kristallog. A96 (1937) 227
5. D. Dollimore and D. L. Griffiths, J. Thermal Analysis, 2 (1970) 229
6. N. Gerard and G. Watelle-Marion, Bull. Soc. Chim. Fr. (1969) 58
7. E. Joly and N. Gerard, C. R. Acad Paris, 277C (1973) 595
8. E. Joly, A. Borbet and N. Gerard, C. R. Acad. Paris, 278C (1974) 935
9. K. Negase, K. Sato and N. Tanaka, Bull Chem. Soc. Japan, 48 (1975) 439
10. V. V. Boldyrev, Russ Chem Revews, 42 (1973) 515
11. V. V. Boldyrev, J. Therm. Analysis, 7 (1975) 685
12. A. K. Galwey, J. Chem. Educ. 37 (1960), 1968
13. F. E. Freebert, K. O. Hartman, I. C. Hisatsune, and J. M. Schempf, J. Phys. Chem.; 71 (1967) 397.
14. V. V. Boldyrev, V. I. Eroshkin, V. T. Pismenko, I. A. Ryzhak, A. A. Medvinsy I. V. Schmidt, and L. M. Kefeli, Kinetica i Kataliz, 9 (1968) 260