Thermochimica Acta, 29 (1979) 301–304

A STUDY OF THE DECOMPOSITION OF SALTS OF PROPAN-2-ONE-1,3-DISULPHONIC ACID

F.G. BUTTLER and S.R. MORGAN

Teesside Polytechnic, Middlesbrough, Cleveland, England

ABSTRACT

The thermal decomposition of the magnesium, cobalt, nickel and zinc salts of propan-2-one-1,3-disulphonic acid using thermogravimetry and mass spectrometry are described. The results show that after the water of crystallisation had been lost there was a rapid decomposition of the salts with a complete breakdown of the disulphonate ion. The products of these decomposition were often complex mixtures, the composition of which depended on the atmosphere used.

INTRODUCTION

Little work has been reported previously on the decomposition of salts of sulphonic acids of ketones other than that for the breakdown of disodium propan-2-one-1,3-disulphonate (ref. 1). In that case it was found that mixtures of sodium sulphate and sodium carbonate were formed, the proportions depending on the conditions of the experiment. In this study four salts of propan-2-one-1,3-disulphonic acid with divalent metal ions have been used in order to ascertain the products formed during their decomposition in atmospheres of both oxygen and nitrogen.

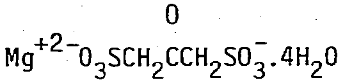
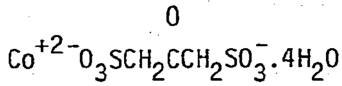
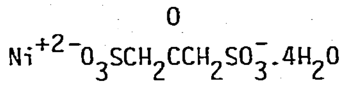
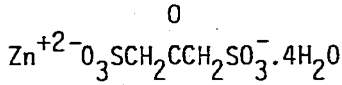
EXPERIMENTAL

Equipment

The decomposition reactions were studied in dynamic atmospheres of both nitrogen and oxygen using a Stanton Redcroft Massflow vacuum and gas atmosphere thermobalance, the samples being contained in conical fused alumina crucibles of 2 cm^3 capacity. The X-ray powder diffraction of solid products from various stages of the decompositions was carried out using a Siemens Kristalloflex 4 generator and a Siemens Diffractometer (Type F). The volatile fragments of the decompositions were examined using a Hitachi RMU 6D mass spectrometer with an electron impact source which was coupled to the oven of an F11 Perkin-Elmer gas-liquid chromatograph. The mass spectra were recorded for each 50^oC interval of temperature rise up to 400^oC, and helium was used as the carrier gas.

Preparation of materials

Propan-2-one-1,3-disulphonic acid was prepared by the method described by Grot (ref. 2). The salts used in this study were made by adding the carbonate of each metal to an aqueous solution of the disulphonic acid until an excess carbonate was present which was then removed by filtration. The disulphonates were precipitated from the filtrate by the addition of ethanol, the precipitates removed by filtration, washed with small portions of ethanol, sucked dry in air and finally dried over anhydrous calcium chloride in a vacuum desicator. Each of the salts was analysed for the metal ion present and the following results were obtained. The calculated figures are based on the formulae of the tetrahydrates.

	% metal ion found	% metal ion calculated
 $\mathrm{Mg^{+2}\,{}^{-}O_3SCH_2\overset{O}{C}CH_2SO_3^{-}.4H_2O}$	7.75	7.78
 $\mathrm{Co^{+2}\,{}^{-}O_3SCH_2\overset{O}{C}CH_2SO_3^{-}.4H_2O}$	17.02	16.97
 $\mathrm{Ni^{+2}\,{}^{-}O_3SCH_2\overset{O}{C}CH_2SO_3^{-}.4H_2O}$	16.86	16.92
 $\mathrm{Zn^{+2}\,{}^{-}O_3SCH_2\overset{O}{C}CH_2SO_3^{-}.4H_2O}$	18.45	18.49

RESULTS AND DISCUSSION

Decomposition of the magnesium salt.

In atmospheres of either oxygen or nitrogen the water of crystallisation was lost in two equal stages, at 100 and 180°C respectively. These stages were then followed by the rapid decomposition of the disulphonate ion over the temperature range 300-330°C. In oxygen magnesium sulphate was the only solid product present at the end of this stage, and there was no further loss in mass until magnesium oxide was formed at temperatures in excess of 1000°C.

In nitrogen the solid products remaining after the decomposition of the disulphonate ion was a mixture of magnesium sulphate and carbon. The amount of sulphur dioxide liberated during this stage indicated that some other sulphur compounds were also formed. The mass spectral results showed that carbon disulphide and carbon oxysulphide were present in the volatile fragments, together with sulphur dioxide, carbon dioxide, water and a peak with m/e = 43 almost certainly due to CH_3CO. On further heating in nitrogen the carbon present reduced most of the magnesium sulphate present to give magnesium oxide over the temperature range 500-700°C.

This stage was then followed by the decomposition of the magnesium sulphate remaining, to give magnesium oxide as the final product of the decomposition.

Decomposition of the cobalt and nickel salts.

In many respects the decomposition of these salts was similar to that observed for the corresponding magnesium salt. The main differences were

1. The loss of the water of crystallisation was not as clearly defined, but was complete by 200°C. The decomposition of the disulphonate ion again occurred over the temperature range 300-330°C.
2. In oxygen cobalt(II) sulphate was the only solid product present at the end of the stage involving the decomposition of the disulphonate ion. On the other hand, at a corresponding point, the nickel salt gave a mixture of nickel(II) sulphate and nickel(II) oxide. The formation of nickel oxide could well have arisen by the rapid combustion of the carbon deposited during the decomposition, with a corresponding rapid rise in the temperature of the sample. This was illustrated by the rapid rate of loss of mass during the later parts of this step.
3. In atmospheres of nitrogen a mixture of cobalt(II) sulphate and tricobalt tetroxide was present after the disulphonate ion had decomposed, and no carbon was detected. On the other hand the nickel salt gave a mixture of nickel sulphate, nickel oxide and carbon, the latter phase then being removed over the temperature range 500-700°C according to $NiSO_4 + C \rightarrow NiO + CO + SO_2$. At high temperatures the $CoSO_4$ and excess $NiSO_4$ decomposed to give Co_3O_4 and NiO as the final solid products of the decomposition reactions.
4. As in the case of the magnesium salt the amount of sulphur dioxide liberated during the decomposition of the disulphonate ion indicated that some other sulphur containing compounds were also formed. In these cases however, no evidence for CS_2 and COS was observed by mass spectrometry of the volatile fragments.

Decomposition of the zinc salt.

In both oxygen and nitrogen the water of crystallisation was lost as a single step which was completed by 140°C. In oxygen this step was followed by the decomposition of the disulphonate ion at 300°C to give a mixture of zinc sulphate and zinc oxide, and there was then no further reaction until the zinc sulphate decomposed to give zinc oxide as the final product.

In nitrogen a mixture of zinc sulphate, zinc oxide and carbon were the solid products remaining after the decomposition of the disulphonate ion. A much greater proportion of carbon was present in this case than with the other salts and was always greater than 2.5 mol. C/mol. starting material. On further heating the zinc sulphate was reduced by the carbon present to give a mixture of zinc oxide and zinc sulphide, and these reactions were completed by 650°C.

At the end of this stage some carbon remained in the system. In the temperature range 800-900°C a further large percentage loss in mass was observed with no evolution of sulphur dioxide. This was due to the volatilisation of elemental zinc formed by the reduction of the zinc oxide present, and most of the zinc originally present in the samples was removed in this way. The final solid product of the reaction in nitrogen was a mixture of zinc sulphide and zinc oxide still containing a trace of carbon. On adding oxygen at high temperatures there was a rapid evolution of sulphur dioxide as the zinc sulphide was converted to oxide, and at the same time the last traces of carbon were removed.

The mass spectral results obtained during the decomposition of the disulphonate ion were similar to those from the cobalt and nickel salts.

CONCLUSIONS

The four salts studied show that the propan-2-one-1,3-disulphonate ion decomposes rapidly at 300°C, but that the composition of the solid phases present after the decomposition and the volatile compounds liberated were different in each case. No evidence was found for the formation of metal carbonates, which contrasts with the decomposition of the disodium salt, and no organic compounds detected in the volatile products other than the CH_3CO. group.

REFERENCES

1 F.G. Buttler, A. Giles, F. Harrison and S.R. Morgan, Journal of Thermal Analysis, 10(1976)13-20.
2 W.G. Grot, J. Org. Chem., 30(1965)515.