Thermochimica Acta, 146 (1989) 95–99
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF MOLYBDENUM(V) THIOGLYCOLATE 2-HYDRATE

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(Received 27 September 1988; in revised form 30 November 1988)

ABSTRACT

The thermal decomposition of molybdenum(V) thioglycolate, having the composition $[Mo_2(L)_5(H_2O)_2]$ ($H_2L = CH_2SHCOOH$, thioglycolic acid), has been studied in argon, air and oxygen atmospheres in the 300–900 K region by TG and DTA methods. The results indicate a simultaneous gradual dissociation of ligand along with the removal of water molecules, without exhibiting any distinct steps in the TG curve. It is interesting to find that the compound decomposes in argon atmosphere to amorphous Mo metal as an end product at about 700 K, which was identified from its X-ray photoelectron and EPR spectra (conduction electrons), and XRD. The end product obtained in air or oxygen atmospheres appears to be a non-stoichiometric molybdenum oxide. A scheme for the thermal dissociation of the compound in argon atmosphere is discussed by combining the TG and DTA data.

INTRODUCTION

Thermal decomposition studies of many transition metal carboxylates have been carried out in order to understand the mechanism of their decomposition and the nature of the decomposed products [1–4]. However, very little is known about the corresponding mercapto acid compounds such as the thioglycolates [5]. Due to the presence of two different types of coordinating atoms (sulphur and oxygen) in the mercapto acid group compared to only the oxygen atoms in the carboxylic acids, a variety of interesting thermal decomposition products, depending on the atmospheric environment, are expected. This paper reports the thermal decomposition of molybdenum(V) thioglycolate 2-hydrate in air, oxygen and argon atmospheres.

EXPERIMENTAL

The paramagnetic binuclear $[Mo_2(L)_5(H_2O)_2]$ was prepared by the reaction between hydrated molybdenum(VI) oxide $MoO_3 \cdot H_2O$ and thioglycolic

0040-6031/89/$03.50

acid (1 : 3 ratio respectively) in an argon atmosphere. After about four hours of continuous stirring and occasional warming, a clear dark reddish-brown solution was obtained which was filtered and evaporated to dryness in vacuum over P_2O_5. The dark brown solid obtained was thoroughly washed with acetone and dried. The composition was ascertained from elemental analysis [6].

TG was carried out in air, oxygen and argon atmospheres on a Shimatzu DT-30 micro TG instrument. The initial sample taken was in the 10 mg range. A locally assembled DTA instrument was used for the studies.

X-ray photo electron spectra (XPS) were recorded on vacuum generators ESCA-3, Mark II with Mg $K\alpha$ and Al $K\alpha$ sources. The sample in powder form was mounted on conducting scotch tape. The binding energy values were determined by comparing with the standard C-1*s* peak. The EPR spectra were recorded on a Varian V-4502 spectrometer operating on X-band frequencies. DPPH was used as a *g*-marker and the magnetic field was measured using a NMR gauss-meter. X-ray diffraction data was taken on a Philips goniometer using Cu $K\alpha$ radiation with a Ni filter.

RESULTS AND DISCUSSION

The TG results of the compound studied in an argon atmosphere are shown in Fig. 1. The weight loss up to 175 ° C corresponds to around 6%, beyond this and up to 500 ° C, there is a gradual mass loss of about 68% of the initial sample. Further mass loss was found to be very small on increasing temperature. The expected weight loss due to complete dissociation of all the thioglycolate ligand molecules along with the water molecules is 71.7%. Microanalysis of the end product obtained beyond 500 ° C indicated the absence of carbon, hydrogen, oxygen and sulphur.

The XPS results obtained for the molybdenum $3d_{5/2}$ core electrons are shown in Fig. 2. The B.E. value of 227.3 eV, the intensity ratio of the $3d_{5/2}$ and $3d_{3/2}$ peaks and their half widths are very close to those reported for molybdenum metal [7]. The X-ray diffraction pattern showed two very broad peaks with estimated *d*-values characteristic of Mo metal. Based on these observations, the end product was identified as molybdenum metal.

An intense EPR signal obtained for the end product has been observed to have very little temperature dependance between room temperature and 77 K, with respect to its line position (g-factor), line shape, width and intensity. The EPR signal asymmetry (line shape) (Fig. 3) closely resembles the reported conduction electron spin resonance spectra of metal cluster atoms [8]. The observance of an EPR signal for the molybdenum residue suggests the presence of fine particles confirming the XRD pattern.

Although the TG curve (Fig. 1) showed only a gradual mass change without any sharp weight loss, the DTA curves in argon atmosphere suggest

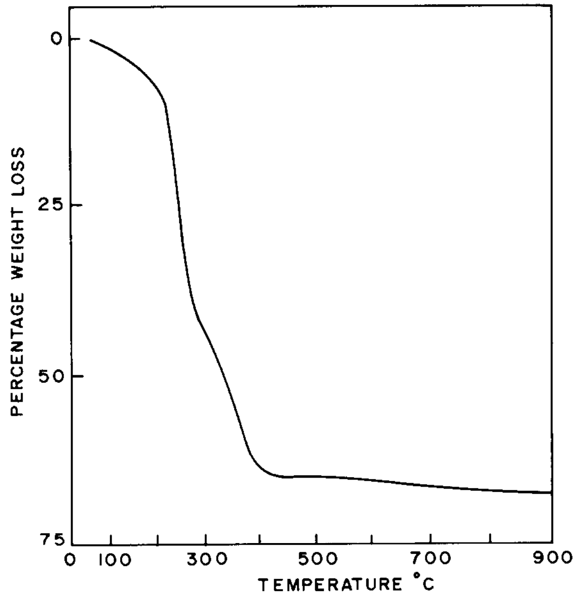

Fig. 1. TG curve in argon atmosphere. Heating rate = 10 °C min^{-1}.

four steps in its decomposition behaviour. The first step presumably corresponds to the loss of water molecules along with the decomposition of the ligand. In the subsequent three stages, it appears that dissociation of all the thioglycolate molecules is complete, yielding the end product of molybdenum metal. Although no isothermal analyses of the reaction products were carried out, hydrogen sulphide and sulphur have been identified qualitatively. Based on the observed TG and DTA data it appears that the likely

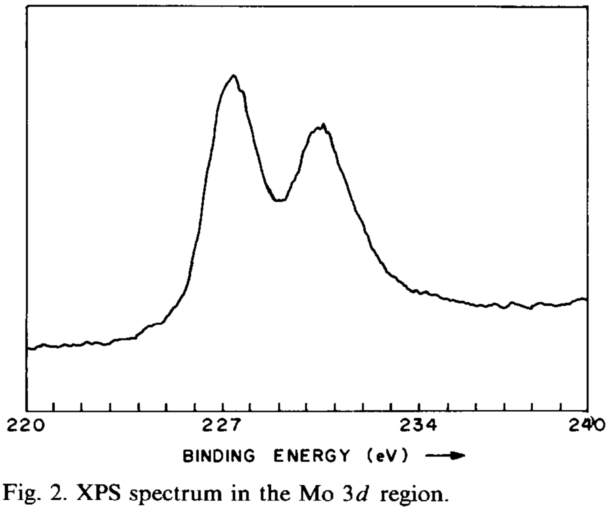

Fig. 2. XPS spectrum in the Mo 3*d* region.

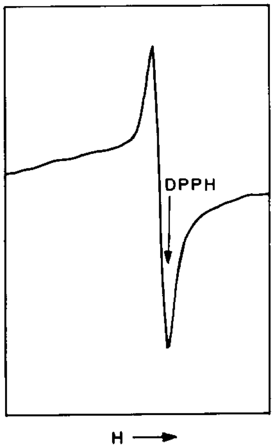

Fig. 3. Conduction electron spin resonance spectrum.

scheme of dissociation of molybdenum thioglycolate involves an intermediate molybdenum disulphide, which, due to the simultaneous evolution of reducing gases carbon monoxide and hydrogen (the likely dissociation products along with H_2S and S), decomposes to give molybdenum metal. A similar type of decomposition mechanism for a molybdenum(V) complex containing sulphur ligand atoms has been reported [9].

Thermal decomposition of the studied compound in air or oxygen leads to the formation of a yellow non-stoichiometric molybdenum oxide, the exact composition of which depends on the rate of heating and the oxygen flow rate.

In conclusion, it should be mentioned that while in air or oxygen, molybdenum(V) thioglycolate decomposes to give an oxide end product as expected, in argon it decomposes to give molybdenum metal.

ACKNOWLEDGEMENTS

We thank Dr. A.B. Phadnis, Water Chemistry Division, BARC for his assistance in recording the TG and DTA spectra.

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