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THERMAL ANALYSIS OF OXIDATION PROCESS OF ANTIMONY AND GALLIUM SULFIDES

Part I. Kinetics and mechanism of Sb_2S_5 oxidation process

N. Štrbac[1], Ž. Živković[1], D. Živković[1], D. Grujičić[1] and B . Boyanov[2]

[1]Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Yugoslavia
[2]Plovdiv University "Paisiy Hilendarski",
Department of Inorganic Chemical Technology,
24 Tsar Assen St., 4000 Plovdiv, Bulgaria

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Abstract

The results of experimental investigations of Sb_2S_5 oxidation process in an air atmosphere are presented in this paper. DTA-TG-DTG, DSC and X-ray analysis, used as the investigation methods, enabled the determination of heat effects, kinetic parameters and mechanism of the investigated process.

Keywords: oxidation process, Sb_2S_5, DTA-TG-DTG, DSC, kinetics

1. Introduction

Antimony and sulfur form Sb_2S_3 and Sb_2S_5 sulfides [1]. Antimony trisulfide or stibnite, Sb_2S_3, could be found in literature [2-6], as well as recent results on characteristics of its oxidation process [7]. But, there are insufficient data on the other antimony sulfide - Sb_2S_5. It is known that this sulfide is an amorphous powder of yellow-orange color, and that its density is 4.12 g/cm^3 [1]. Also, there are data about Sb_2S_5 chemistry, synthesis and application - usually used as a pigment, in making matches and in pyrotechnics [1].

Due to a lack of literature data for Sb_2S_5 behavior during oxidation, results of DTA-TG-DTG, DSC and X-ray analysis for its oxidation process are presented in this paper in order to determine the mechanism and kinetic parameters.

2. Experimental

Sb_2S_5 sample was synthesized and prepared at Department of Inorganic Chemistry, University "Paisiy Hilendarski", Plovdiv, Bulgaria.

Non-isothermal investigations were performed using simultaneous DTA-TG-DTG and DSC analysis, on Derivatograph 1500 (MOM Budapest) and DSC-404 (NETZSCH, Germany). Roentgen Siemens, with Cu-antikatode and Ni-filters, current intensity of 18mA and voltage 40kV, was used for characterization of initial sample and oxidation products.

3. Results and discussion

X-ray analysis of the initial sample, given in Fig1, confirms amorphous nature of Sb_2S_5, as was given in literature [1].

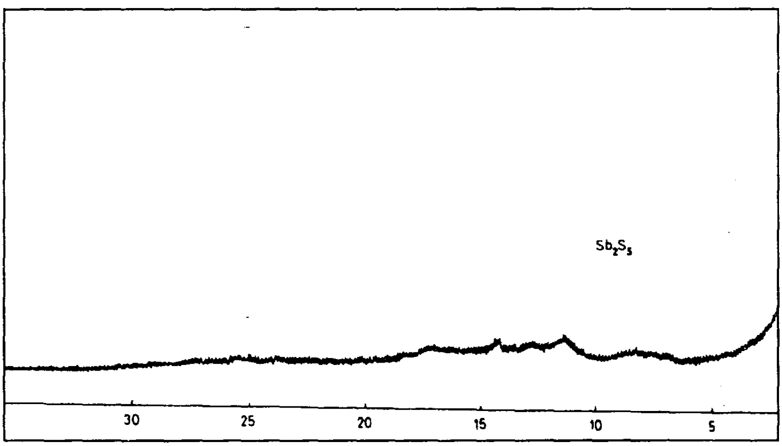

Fig.1. Results of X-ray analysis for the initial sample

Plots of DTA-TG-DTG curves vs. temperature for the process of oxidation process of Sb_2S_5, obtained for the heating rate of 2.5°C min^{-1}, are presented in Fig.2.

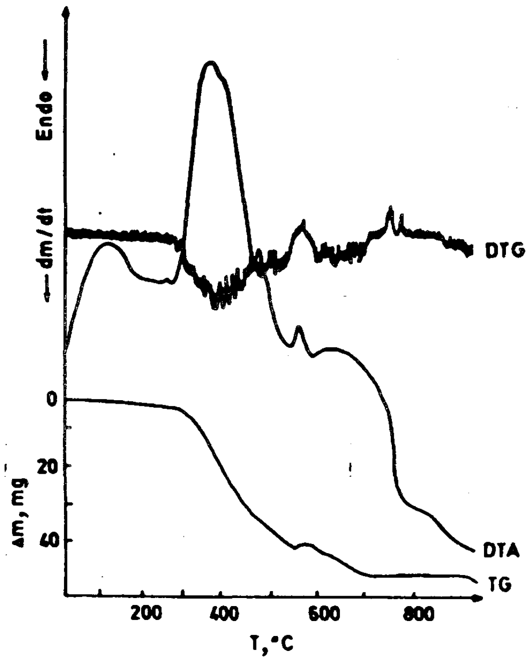

Fig.2. Results of DTA-TG-DTG analysis

There are three exothermal peaks on diagram in Fig.3 (temperature intervals 478-554K, 554-804K and 804-878K). As seen on TG curve, there is a significant decrease of sample mass for the first two exothermal peaks, while mass increases for the third exothermal peak interval. Further increase of temperature, from 878K up to 981K, could be considered as the fourth endothermic peak, which is not so well presented on thermograme, but confirmed by further DSC analysis.

The initial sample examined was subjected to oxidation in an air atmosphere at different heating rates from 2.5 to 20°C min^{-1} under the same conditions, and the results obtained for the maximum dependence on the heating rate in the DTA curve are shown in Fig.3.

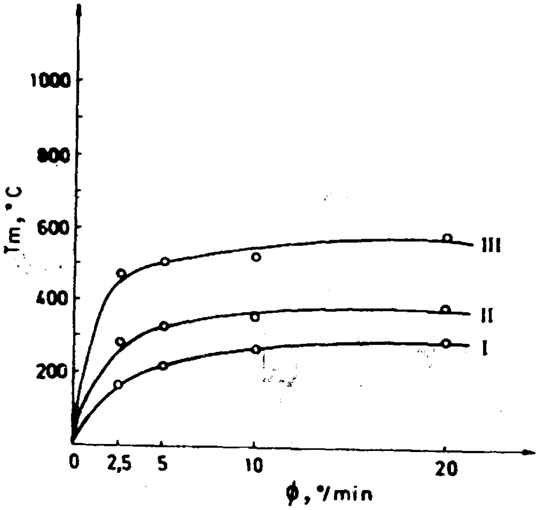

Fig.3. Dependence of T_m on heating rate for DTA results

DSC curves for heating of Sb_2S_5 up to 1273K, given in Fig.4, generally agree with DTA results. Certain deviation could be explained by much smaller sample mass used for DSC analysis, and because of different heating rates.

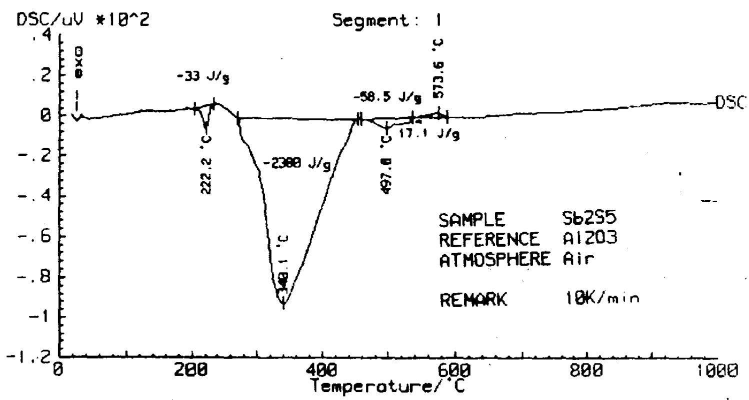

Fig.4. DSC curves and heat effects of characteristic peaks for Sb_2S_5 oxidation process in an air atmosphere

As can be seen, three exothermal peaks and one endothermic peak occur according to DSC analysis. Considering exothermic peaks, the first peak is characteristic for the interval 477-505K

with enthalpy of -33J/g, second peak occurs in the temperature interval 543-725K with enthalpy of -2300J/g, and the third one occurs in the interval 733-810K with enthalpy value of -58.5J/g. The fourth endothermic peak is characteristic for the temperature interval 810-860K with enthalpy of 17.1J/g.

According to DTA and DSC results, mechanism of the Sb_2S_5 oxidation process is defined, as follows:

- *first peak (exo):* $Sb_2S_5 + 0.5O_{2\,(g)} = Sb_2S_{4.5} + 0.5SO_{2\,(g)}$ .... (1)
- *second peak (exo):* $Sb_2S_{4.5} + 6O_{2\,(g)} = Sb_2O_3 + 4.5SO_2$ .... (2)
- *third peak (exo):* $Sb_2O_3 + O_{2\,(g)} = Sb_2O_5$ .... (3)
- *fourth peak (endo):* $Sb_2O_5 = Sb_2O_4 + 0.5O_{2\,(g)}$ .... (4)

In order to prove the suggested mechanism of Sb_2S_5 oxidation process, values of Gibbs free energy change for the proposed reactions (1-4) vs. temperature were calculated, which is presented in Fig.5.

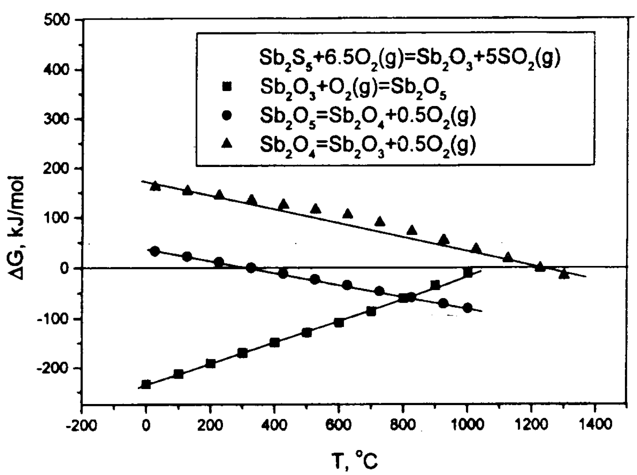

Fig.5. Graphic presentation of $\Delta G^o = f(T)$ for the reactions (1-4)

Also, X-Ray analysis of the products of Sb_2S_5 oxidation was done as a confirmation of the suggested mechanism. The results are given in Fig.6.

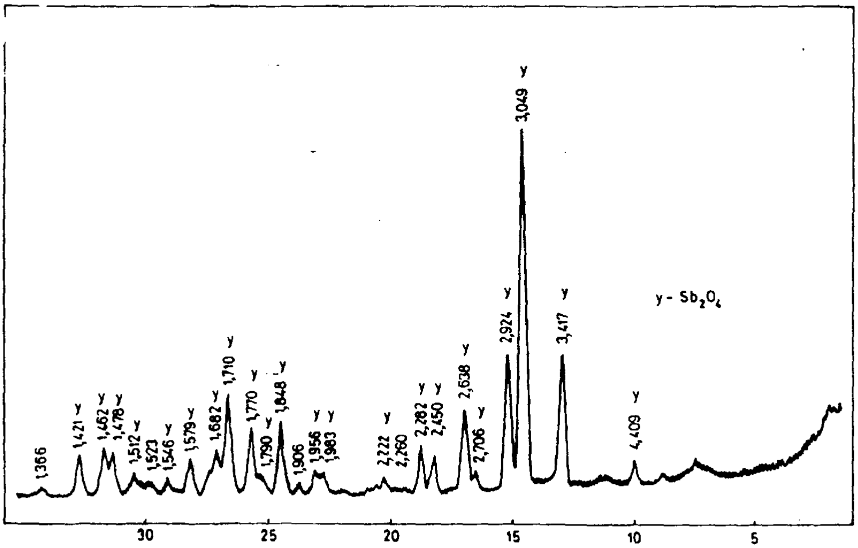

Fig.6. X-ray diagram of the Sb_2S_5 sample, heated at 1273K in an air atmosphere

Results from Fig.6 confirm the suggested mechanism, having in mind that antimony - tetra-oxide decomposes on much higher temperatures [8].

Kinetic analysis of the investigated oxidation process of Sb_2S_5 was done according to methods developed by Kissinger [9] and Ozawa [10]. Fig.7. shows the dependencies $\ln(\phi/T_m^2) = f(1/T_m)$ and $\ln\phi = f(1/T_m)$, where ϕ is the heating rate and T_m is the temperature of the maximum on the DTA curve.

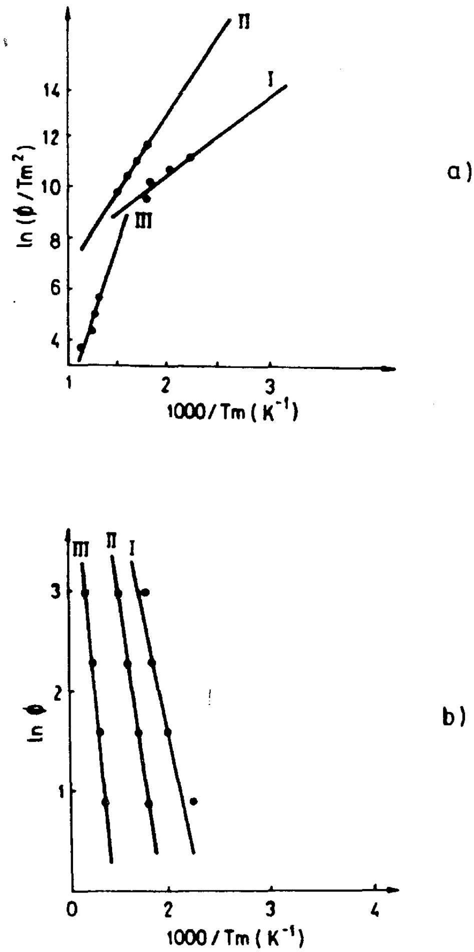

Fig.7. Dependencies ln $(\phi/T_m^2) = f(1/T_m)$ *(a) and* $\ln\phi = f(1/T_m)$ *(b) for the* Sb_2S_5 *oxidation process*

Based on these results, the corresponding values for activation energy E and the integration constants C and C_1 have been calculated for the studied process and presented in Table 1.

Table 1. Calculated values for activation energy and integration constants for the oxidation process of Sb_2S_5

PROCESS	Method			
	Kissinger		*Ozawa*	
	E, kJ/mol	C	E, kJ/mol	C_1
I	28	$2.04\ 10^{-2}$	36	$3.79\ 10^{4}$
II	56	1.34	66	$3.63\ 10^{6}$
III	95	$1.74\ 10^{4}$	102	$3.69\ 10^{7}$

Obtained values indicate that oxidation of Sb_2S_5 takes place in kinetic region, which implies that reaction surface and temperature have the limiting influence on reaction rate.

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