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Thermal decomposition kinetics of antimony oxychloride in air①

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[Abstract] The DTA and XRD techniques were employed to study thermal decomposition mechanism of antimony oxychloride SbOCl in the air. The thermal decomposition reaction occurs in four steps, and the former three steps as: $SbOCl(s) \rightarrow Sb_4O_5Cl_2(s) + SbCl_3(g) \rightarrow Sb_8O_{11}Cl_2(s) + SbCl_3(g) \rightarrow Sb_2O_3(s) + SbCl_3(g)$. The forth step is the oxidation of Sb_2O_3 by air, $Sb_2O_3(s) + O_2 \rightarrow Sb_2O_4(s)$. The activation energy and the order of the thermal decomposition reaction of antimony oxychloride in three steps presented in DTA curves were calculated according to Kinssinger methods from DTA curves. The values of activation energy and the order are respectively 91.97 kJ/mol, 0.73 in the first step, 131.14 kJ/mol, 0.63 in the second step and 146.94 kJ/mol, 1.58 in the third step.

[Key words] antimony oxychloride; thermal decomposition; kinetics
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1 INTRODUCTION

Antimony oxychloride SbOCl has good flame retardant properties. It can not only be used as a flame retardant alone, but also can give good synergistic effects when used conjunction with a halogenated organic compound. It is especially fit well for soft PVC as flame synergistic retardant[1~3]. The formation of SbOCl in Sb/Cl synergistic systems had been suggested as a solid important flame retardant intermediate substance[4]. In order to reveal the further mechanism of Sb/Cl synergistic effect, it is important to study the kinetics of thermal decomposition of antimony oxychloride SbOCl in different atmosphere.

Still confusion opinions consist in the SbOCl thermal decomposition process[4~6]. There are no studies reported on the kinetics parameters of SbOCl thermal decomposition process so far. Here the kinetics studies on SbOCl thermal decomposition by XRD and DTA methods is described. The kinetics parameters, such as activation energy and reaction orders are obtained.

2 EXPERIMENTAL

SbOCl used in this work is self-prepared in the laboratory[7]. Its mean particle size is 8.10 μm and with purity of 99.65%. The structure had been confirmed by XRD. All DTA curves were obtained with 15~ 30 mg samples on a Japanese Thermal Analyzer and the heating rate used was 2, 5, 10, 20 ℃/min from ambient temperature to 750 ℃. The flow rates were 60 mL/min in air. The DTA cures are shown in Fig. 1. In order to make certain of the thermal decomposition products of each steps, the tail temperatures of DTA peaks (290 ℃, 490 ℃, 600 ℃) were selected as the treating temperature. SbOCl samples were treated for 30 min at the selecting temperature and cooled quickly. The residues were analyzed by XRD (Fig. 2). The pyrogenation proceeded in horizontal electric cooker with the air flow rates of 80 mL/min.

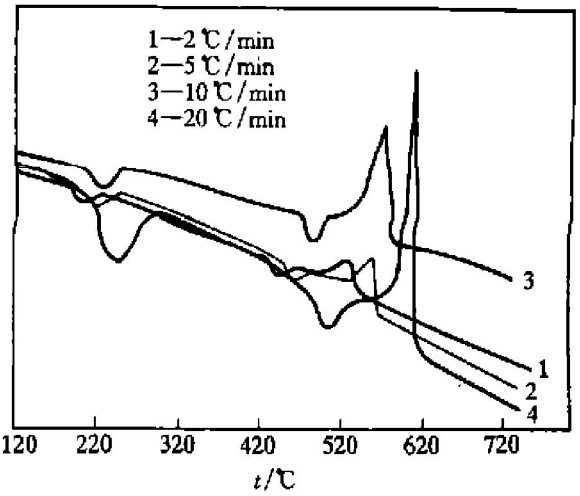

Fig. 1 DTA curves of SbOCl at different heating rates

3 RESULTS AND DISCUSSION

3.1 DTA curve analysis

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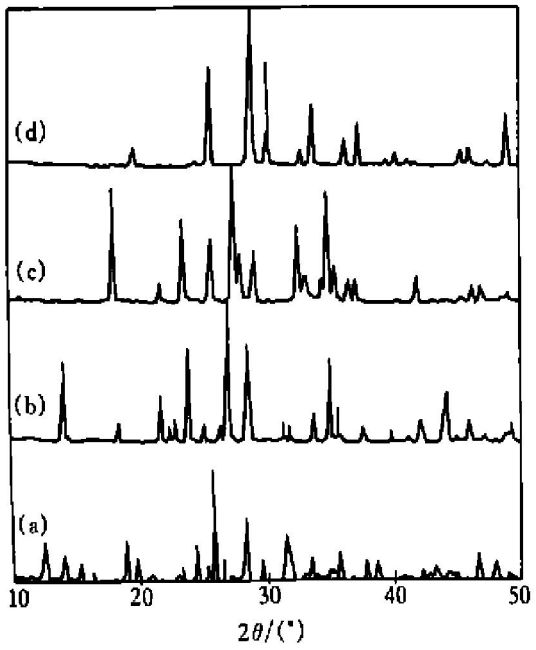

Fig. 2 XRD spectra of SbOCl residues in each step
(a) —SbOCl at 20 ℃; (b) —Heated to 290 ℃; (c) —Heated to 490 ℃; (d) —Heated to 600 ℃

As shown in Fig. 1, three peaks appear in the DTA curves of SbOCl thermal decomposing in air. The first two peaks are endothermic peaks and the peak shapes extend slowly, which indicate that the thermal effects of the reaction are weak and the decomposition rate is slow. The third peak is exothermic peak. The peak shape is steep and sharp, which indicates its strong exothermic effects and the coarse crystal of the residue. Though the decomposition temperatures are different at different heating rates, the peak shapes are quite similar. Higher the heating rates, higher the decomposition temperatures in each stage. According to the four DTA cures, the range of SbOCl thermal decomposition temperature of the first peak is 192~ 296 ℃, the second is 425~ 521 ℃, and the third 496~ 608 ℃, which differs in some degree to the reported results[4~6,8]. Especially, the lowest beginning decomposition temperature of the first stage is about 192 ℃ (2 ℃/min of the heating rate), that is similar to Ref. [6], but differs to Ref. [5] (which was 245 ℃) and Ref. [8] (which was 170 ℃). These differences result from the differences of the purity, granularity, preparing methods of SbOCl and the heating rates that the distinct researchers adopted in the experiments. Even the sample holder used in DTA analysis can change the decomposition temperature and process[4]. In this work, the heating rates are slow, the reaction activity of SbOCl prepared according to Ref. [7] is higher, and the corundum sample holder may catalyze the decomposition reactions. So the beginning decomposition temperature in this work is on the low side. The terminal decomposition temperature is about 608 ℃.

3.2 Thermal decomposition mechanism in air

The thermal decomposition products of SbOCl in air are distinct according to different researchers, especially in the second decomposition residue. Using SbOCl self-prepared in the laboratory to be decomposed, the XRD spectra of the residues of each step are shown in Fig. 2. When comparing to the standard data, it can be confirmed that the first step residue is $Sb_4O_5Cl_2$, the second is $Sb_8O_{11}C_{l2}$, which consistent to Belluomini[6], but differs to Pitts[5]. The third step residue is Sb_2O_4.

The decomposition process of SbOCl in the air is a course of liberating the gaseous $SbCl_3$ gradually, and $SbCl_3$ is the exact flame retardant substance in Sb/Cl flame retardant systems. The reactions corresponding to the three steps of DTA curve are as

$$SbOCl(s) \longrightarrow Sb_4O_5Cl_2(s) + SbCl_3(g) - Q \quad (1)$$

$$Sb_4O_5Cl_2(s) \longrightarrow Sb_8O_{11}Cl_2(s) + SbCl_3(g) - Q \quad (2)$$

$$Sb_8O_{11}Cl_2(s) + O_2 \longrightarrow Sb_2O_4(s) + SbCl_3(g) + Q \quad (3)$$

The reaction (3) corresponding to the third DTA peak is a mixture of the two reactions as

$$Sb_8O_{11}Cl_2(s) \longrightarrow Sb_2O_3(s) + SbCl_3(g) - Q \quad (4)$$

$$Sb_2O_3(s) + O_2 \longrightarrow Sb_2O_4(s) + Q \quad (5)$$

The Sb_2O_3 oxidizes to Sb_2O_4 by the oxygen in high temperature when the thermal decomposition proceeded in the air. That releases a great quality of heat. But it is found that, when analyzed the residues of Sb/Cl synergetic flame retardant systems, Sb_2O_3 and Sb_2O_4 do not exist in the flame residues. Element Sb exists as antimony oxychlorides, such as $Sb_8O_{11}Cl_2$, $Sb_4O_5Cl_2$ and the like. It indicates that even if SbOCl had been formed and decomposed to Sb_2O_3 in Sb/Cl synergetic flame retardant systems under the process of combustion, Sb_2O_3 would be rapidly chlorinated to antimony oxychlorides $Sb_8O_{11}Cl_2$, $Sb_4O_5Cl_2$ and so on. Reaction (5) would not occur under real combustion process.

3.3 Calculation of kinetics parameters by Kinssinger method

3.3.1 Formula of Kinssinger method

Kinssinger method was named as well as the maximal rate method or changing heating rate method. It is a data processing technique brought forward for DTA wholly to study the kinetics. The virtue of this method is not to consider the concrete kinetics equations, and it can be adapted to deal with the complicated DTA peak shapes[10]. In this method several heating rates are used to plot figures, so the data are reliable and repeatable. The equation is as

$$d[\ln(\varphi/T_m^2)] = (-E/R) \cdot d(1/T_m)$$

The integral equation is

$$\ln(\varphi/T_m^2) = (-E/R)\cdot(1/T_m) + C$$

where φ is the linear heating rate, E is the apparent activation energy, R is the gas constant and T_m is the maximum absolute temperature of DTA peak. It is evident that $\ln(\varphi/T_m^2)$ vs $1/T_m$ is in linear relation. The apparent activation energy E can be obtained from the slope of the line $(-E/R)$. In addition, Kinssinger pointed out that the reaction order n could be calculated from the shape index I for peak of DTA curve, $n = 1.26I^{1/2}$, and $I = a/b$. The calculation method of a, b is shown in Fig. 3.

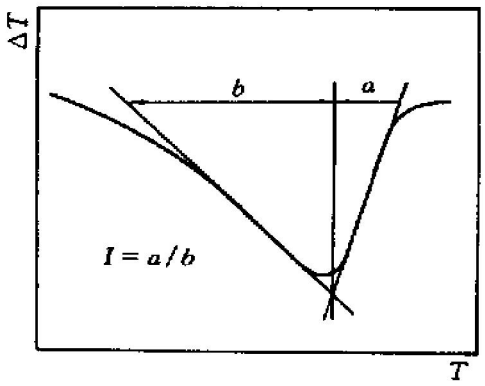

Fig. 3 Shape index for peak of DTA curves using Kinssinger method

3.3.2 Calculation of apparent activation energy and reaction order by Kinssinger method

The kinetics data calculated from DTA curves of SbOCl thermal decomposition using Kinssinger method are listed in Table 1.

The T_m^{-1} vs $\ln(\varphi/T_m^2)$ correlation curves plotted from the data in Table 1 are shown in Fig. 4. All the three are in line relation. The three apparent activation energies E calculated from the slopes and the three reaction orders calculated from the shape indexes I list in Table 2.

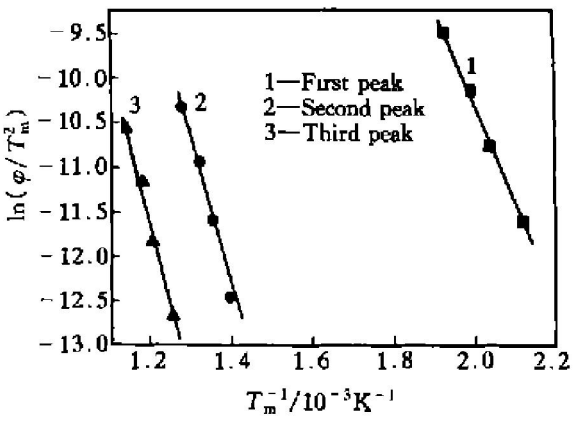

Fig. 4 T_m vs $\ln(\varphi/T_m^2)$ for calculating activation energies using Kinssinger method

4 CONCLUSIONS

1) Three peaks appeared in the DTA curves of SbOCl thermal decomposing in the air. The decomposition temperatures of each stage moves to the higher temperature when the heating rate increased. The beginning decomposition temperature is about 192 ℃, which is higher than that of some thermoplastic polymers, such as PVC. So SbOCl is a suitable flame retardant for such polymers. The ending decomposition temperature of SbOCl is about 608 ℃.

2) The apparent activation energies of the three peaks of TDA curve are respectively 91.97 kJ/mol, 131.14 kJ/mol, 146.94 kJ/mol; and the reaction orders are 0.73, 0.63, 1.58.

3) Corresponding to the three DTA steps, the three decomposition reactions and the ranges of SbOCl decomposition temperatures in the air are as

$$SbOCl(s) \xrightarrow{192\sim 296\ ℃} Sb_4O_5Cl_2(s) + SbCl_3(g) - Q$$

$$Sb_4O_5Cl_2(s) \xrightarrow{425\sim 521\ ℃} Sb_8O_{11}Cl_2(s) + SbCl_3(g) - Q$$

Table 1 Kinetic data calculated from DTA curves of SbOCl using Kinssinger method

Position	φ/(K·min^{-1})	t_m/℃	T_m/K	T_m^{-1}/(10^{-3}K^{-1})	$\ln(\varphi/T_m^2)$
The first peak	20	245.4	518.6	1.928	−9.506
	10	222.4	495.6	2.018	−10.109
	5	218.0	491.2	2.036	−10.784
	2	199.0	472.2	2.118	−11.622
The second peak	20	510.6	783.8	1.276	−10.333
	10	480.9	754.1	1.326	−10.948
	5	464.8	739.0	1.353	−11.598
	2	442.6	715.8	1.399	−12.454
The third peak	20	606.1	879.3	1.137	−10.563
	10	568.4	841.6	1.188	−11.168
	5	559.0	832.2	1.202	−11.839
	2	525.1	798.3	1.253	−12.672

Table 2 Activation energies and reaction orders of three peaks

Position	Slope / 10^{-3}	Activation energy / ($kJ \cdot mol^{-1}$)	Reaction order
The first peak	− 11.062	91.97	0.73
The second peak	− 15.773	131.14	0.63
The third peak	− 17.674	146.94	1.58

$$Sb_8O_{11}Cl_2(s) + O_2 \xrightarrow{496\sim 608\ ℃} Sb_2O_4(s) + SbCl_3(g) + Q$$

In fact, the third reaction above which corresponding to the third DTA peak is a mixture of the following two reactions,

$$Sb_8O_{11}Cl_2(s) \xrightarrow{496\sim 608\ ℃} Sb_2O_3(s) + SbCl_3(g) - Q$$

$$Sb_2O_3(s) + O_2 \xrightarrow{496\sim 608\ ℃} Sb_2O_4(s) + Q$$

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