

THERMAL DECOMPOSITION OF COMPLEXES OF ANTIMONY(III) BROMIDE WITH HYDROBROMIDES OF SOME AROMATIC AMINES

BOGDAN PTASZYŃSKI

Institute of General Chemistry, Polytechnical University, 90924 Łódź (Poland)

(Received 12 June 1979)

ABSTRACT

Thermal studies have been carried out on crystalline complexes formed between antimony(III) bromide and hydrobromides of some aromatic amines in concentrated hydrobromic acid solutions. Thermal analysis curves of the compounds under study are presented. Kinetic parameters of the thermal decomposition reactions were calculated from the TG curves using the Horowitz—Metzger method. A comparison of the thermal stabilities of the complexes was made.

INTRODUCTION

In our earlier paper [1], the thermal decomposition of some halogenide complexes of antimony(III) and alkali metals was studied and the effect of outer sphere cations on the thermal stability of these compounds discussed. The subject of the present work is the study of the thermal stability and the evaluation of kinetic parameters of some bromoantimonate(III) complexes with aromatic amines differing in basicity as counter ions. The synthesis of the compounds of the type $R_xSb_yBr_z$ where R represents either an aliphatic or aromatic amine has been known since Rosenheim and Stellmann [2] reported the preparation of $(C_5H_5NH)_2SbBr_5$. By using different aliphatic and three aromatic amines Whealy and Yeakley [3] succeeded in synthesizing yellow $R_xSb_yBr_z$ salts having R : Sb : Br ratios of 2 : 1 : 5, 3 : 1 : 6 and 3 : 2 : 7. Expanding considerably the choice of aromatic amines, Stewart et al. [4] obtained a variety of colored salts ranging from deep yellow to orange and red, having R : Sb : Br ratios of 1 : 1 : 4, 2 : 1 : 5 and 3 : 2 : 9. The thermal decomposition of these complexes in dynamic conditions has not been studied so far.

EXPERIMENTAL

Apparatus

Thermal analysis of the compounds under study was carried out using a derivatograph MOM Budapest type OD-102/1500°C. The measurements

were made in air over a temperature range 20–1000°C at a heating rate (10°C min⁻¹). The sensitivity of the galvanometer for DTA curve was 1/10 and for the DTG curve 1/20. TG sensitivity was 100 mg. α -Al₂O₃ was used as a reference material and the mass of the sample was 100 mg.

Preparation, chemical and X-ray analyses

The bromoantimonates(III) under study were prepared by slight variations of the method described in the literature [3,4]. The antimony(III) bromide solution was prepared by dissolving reagent grade antimony trioxide in an excess of hot concentrated 40% hydrobromic acid and the amine hydrobromides by adding an excess of concentrated hydrobromic acid to the amine. The following aromatic amines were used: pyridine, 2-methylpyridine, 3-methylpyridine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, 2-bromopyridine, 2-aminopyridine, 4-aminopyridine and piperidine. After cooling, solutions of amine hydrobromide were added dropwise, with stirring, to the SbBr₃—HBr solutions. Approximately 10 mole of the amine hydrobromide was added for each mole of antimony(III) bromide. The complexes usually formed immediately and in all cases precipitation was complete in a short time. The resulting crystals were left in the mother liquor for 2–3 h before being separated by vacuum filtration through a Buchner funnel. They were rinsed first with isopropanol, then with diethyl ether and dried for 3 days in a vacuum drier at room temperature. The compounds are all fine yellow crystals of varying shade except for the complex with 2-bromopyridine which is red. The bromoantimonate(III) of 2-methylpyridine and 2,6-dimethylpyridine were recrystallized from concentrated hydrobromic acid. Well-formed long needles separated on cooling to ambient temperature.

Antimony and bromide were determined by standard chemical methods.

TABLE 1

Results of calculating kinetic paramters

Amine	Basicity of amine pK _a *	Empirical formula of the complex	T _s (°C)	E _a (kcal mole ⁻¹)	Z (min ⁻¹)
2-Bromopyridine	0.90	(C ₅ NH ₅ Br) ₂ [SbBr ₅]	281	22.42	2.8 × 10 ⁸
Pyridine	5.71	(C ₅ NH ₆) ₂ [SbBr ₅]	333	19.92	4.5 × 10 ⁶
3-Methylpyridine	5.68	(C ₆ NH ₈) ₂ [SbBr ₅]	342	26.29	6.8 × 10 ⁸
2-Methylpyridine	5.97	(C ₆ NH ₈) ₂ [SbBr ₅]	333	24.65	2.8 × 10 ⁸
2,6-Dimethylpyridine	6.75	(C ₇ NH ₁₀) ₃ [Sb ₂ Br ₉]	340	28.42	5.7 × 10 ⁹
2-Aminopyridine	6.86	(C ₅ N ₂ H ₇) ₃ [Sb ₂ Br ₉]	370	28.82	2.4 × 10 ⁹
2,4,6-Trimethylpyridine	7.60	(C ₈ NH ₁₂) ₃ [Sb ₂ Br ₉]	341	25.68	5.1 × 10 ⁸
4-Aminopyridine	9.29	(C ₅ N ₂ H ₇) ₂ [SbBr ₅]	437	27.95	1.2 × 10 ⁸
Piperidine	11.22	(C ₅ NH ₁₁) ₂ [SbBr ₅]	354	45.46	4.7 × 10 ¹⁵

* pK_a = ionisation constant of the conjugated acid.

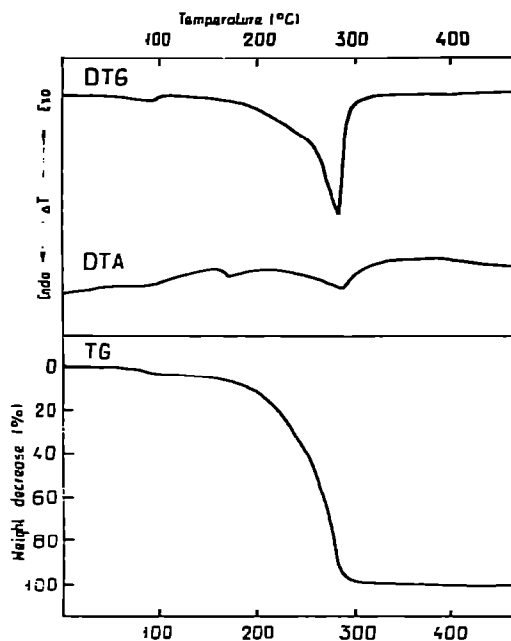


Fig. 1. Thermal analysis curves of the complex of SbBr_3 with 2-bromopyridine.

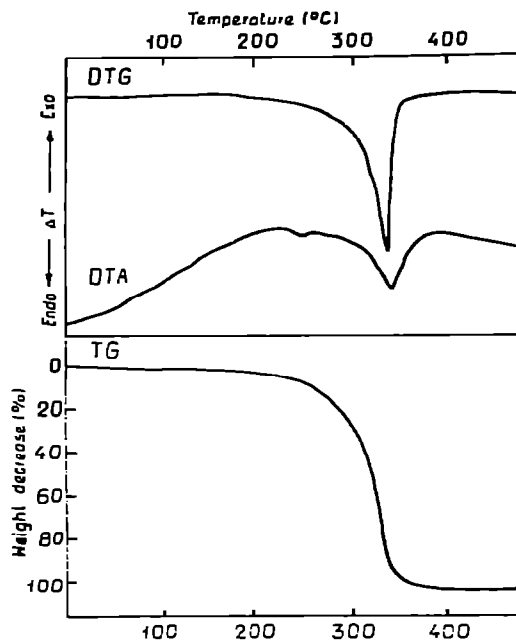


Fig. 2. Thermal analysis curves of the complex of SbBr_3 with pyridine.

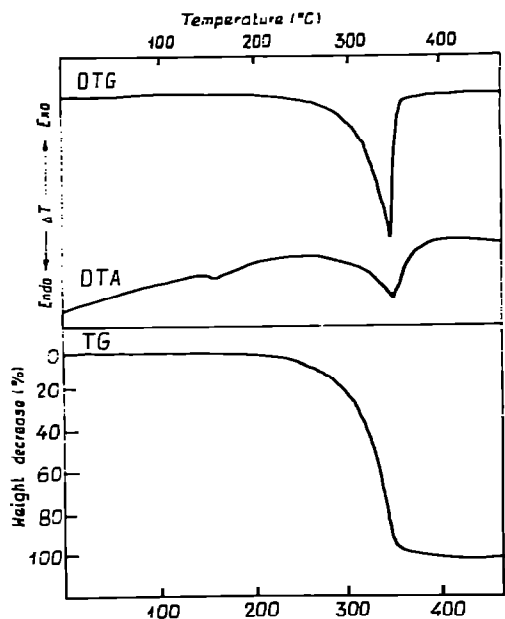


Fig. 3. Thermal analysis curves of the complex of SbBr_3 with 3-methylpyridine.

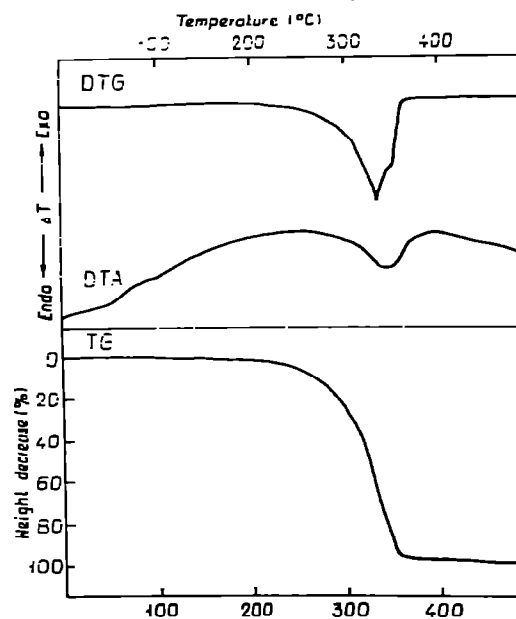


Fig. 4. Thermal analysis curves of the complex of SbBr_3 with 2-methylpyridine.

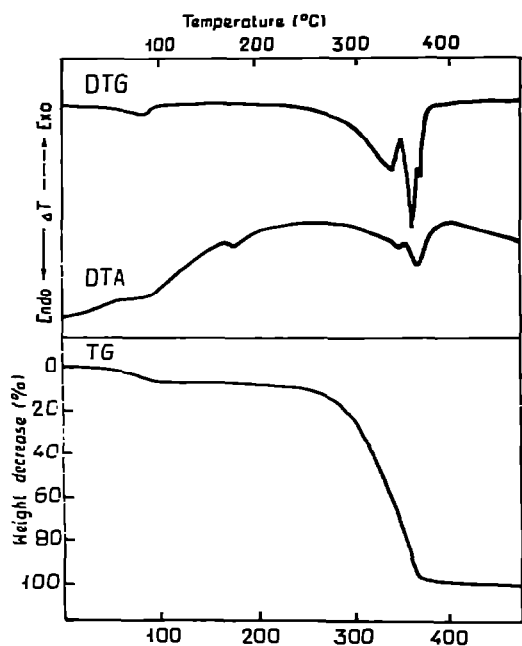


Fig. 5. Thermal analysis curves of the complex of SbBr_3 with 2,6-dimethylpyridine.

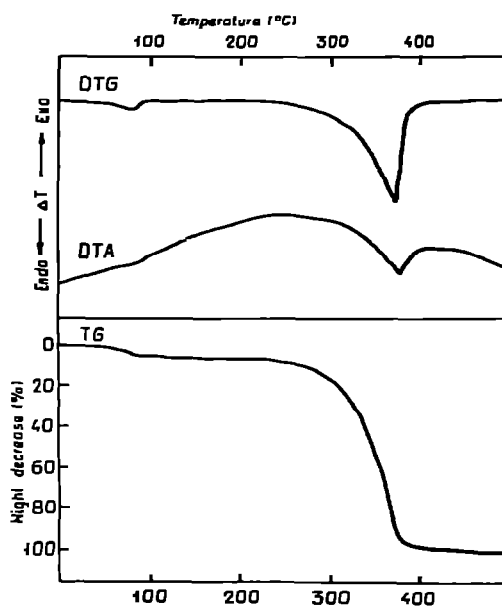


Fig. 6. Thermal analysis curves of the complex of SbBr_3 with 2-aminopyridine.

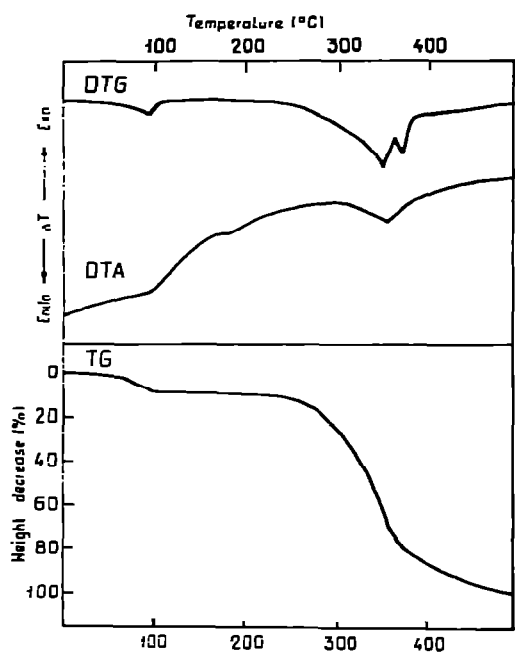


Fig. 7. Thermal analysis curves of the complex of SbBr_3 with 2,4,6-trimethylpyridine.

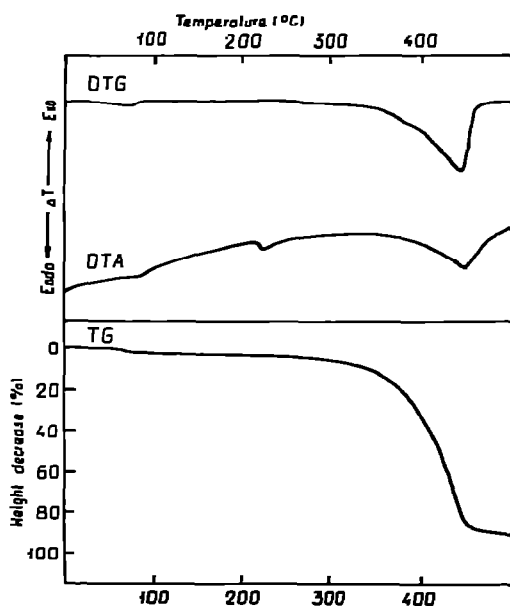


Fig. 8. Thermal analysis curves of the complex of SbBr_3 with 4-aminopyridine.

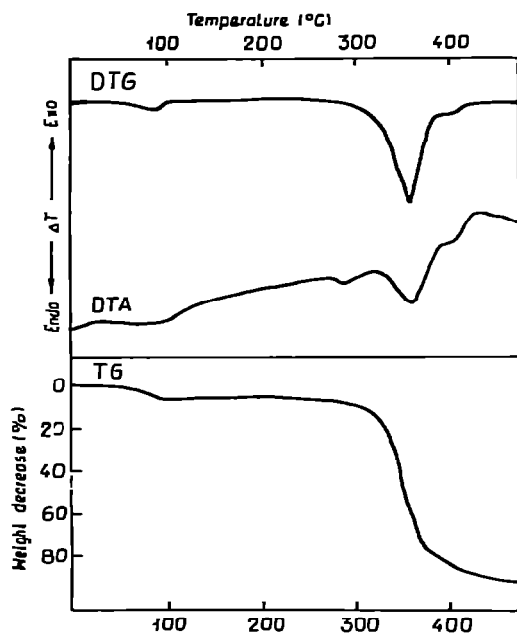


Fig. 9. Thermal analysis curves of the complex of SbBr_3 with piperidine.

Proposed empirical formulae of the complexes under study are collected in the Table 1.

Thermal analysis

Thermal analysis curves of compounds under study are shown in Figs. 1–9. At temperatures below 100°C there are low peaks on the DTA and DTG curves and appropriate loss of mass on the TG curves connected with loss of hygroscopic water. The DTA curves of complexes of SbBr_3 with pyridine, 3-methylpyridine, 2-bromopyridine, 2-aminopyridine, 4-aminopyridine and piperidine exhibit two endothermic peaks (followed, in the case of the complex with piperidine, by a diffuse exothermic peak). The small peaks, occurring at lower temperatures correspond to melting of the samples. The next endothermic peaks, sharp and relatively strong, are connected with the decomposition of the compounds. The exothermic peaks probably correspond to the oxidation of carbon left in the crucible by the decomposition of piperidine. There is only one sharp and strong peak on each DTG curve showing single-staged decomposition reaction. Thermal analysis curves of the other compounds differ slightly from those described above. Peaks on DTA curves of complexes with 2,6-dimethylpyridine and 2,4,6-trimethylpyridine corresponding to 175 and 182°C , respectively, are connected with the melting of samples. The analogous peak for the complex with 2-methylpyridine is not distinctly marked on the DTA curve connected with the decomposition of compounds split. For the compound of SbBr_3 with 2-methylpyridine, the split is hardly visible; adjacent peaks overlap. In the case of the complex with 2,6-dimethylpyridine, the peaks are separated

by 20°C and for the complex with 2,4,6-trimethylpyridine by 29°C. Corresponding peaks on the DTA curves overlap.

Determination of kinetic parameters

Apparent activation energies of the decomposition reactions of the compounds under study were calculated from thermogravimetric traces using the Horowitz—Metzger approximate method [5]. The following equation, applicable to any reaction in which all the products are gases, was used.

$$\ln \ln \frac{W_0}{W} = \frac{E_a \theta}{RT_s^2} \quad (1)$$

where E_a is the activation energy, R the gas constant, W_0 the initial weight of the sample and W the weight at the temperature T . $\theta = T - T_s$ where T_s is the temperature at which $W_0/W = 1/e$. Equation (1) corresponds to the characteristic shapes of the thermogravimetric traces, i.e. to the gradual weight loss followed by a sharp drop and then zero slope when decomposition is complete. Plots of $\ln \ln(W_0/W)$ versus θ were drawn and appeared to be linear within the appropriate range of temperature. From the slopes, the apparent activation energies were calculated by the method of least squares. The pre-exponential factors, Z , were calculated using the equation

$$Z = \frac{q}{RT_s^2/E_a} \exp(E/RT_s) \quad (2)$$

where q is the heating rate. Because all the thermal decomposition reactions of the compounds under study give only gaseous products, nothing can be learned about the reaction order. The final results of calculations are presented in Table 1.

DISCUSSION

From solutions of antimony(III) bromide and aromatic amines in concentrated (ca. 40%) hydrobromic acid, compounds of the general formula $R_xSb_yBr_z$ (where R represents the amine) crystallise in high yield. With the exception of the compound with 2-bromopyridine which is red and that with 2-aminopyridine which is pale yellow-tan, all the compounds are pale yellow. Under identical conditions, bismuth(III) forms analogous colored complexes but when arsenic(III) is used, salts of the type $pAs_2O_3 \cdot qAsOBr \cdot rRBr \cdot sHBr$ [6] crystallize in low yield. Complexes of antimony(III) are hygroscopic. The samples contain 2–8% of water which is removed at temperatures below 100°C. Thermal decomposition is preceded by melting of samples. Experimental melting points are 5–10°C lower than those determined from the DTA curves. The thermal decomposition of the compounds under study are, in general, single-stage processes; however, when complexes of $SbBr_3$ with 2,6-dimethylpyridine and 2,4,6-trimethylpyridine decompose, an additional inflection point occurs on the TG curves at higher temperatures. All reactions take place within a temperature range of about 200°C. In the

course of decomposition, gaseous SbBr_3 and the corresponding amine (or decomposition products of the amine) are liberated. A 100% mass loss is observed. The effect of the basicity of the aromatic amines on the thermal stability of the complexes, defined by E_a and the temperatures at which the decomposition reaction starts, is not evident. However, the tendency can be seen that the thermal stability increases with increasing basicity of the amine. The most stable is a complex formed between SbBr_3 and piperidine.

ACKNOWLEDGEMENT

I should like to thank Professor A. Cygański for valuable discussions.

REFERENCES

- 1 B. Ptaszyński, Polish J. Chem., in press.
- 2 A. Rosenheim and W. Stellmann, Ber. Dtsch. Chem. Ges., 34 (1901) 3377.
- 3 R.D. Whealy and R.L. Yeakley, J. Inorg. Nucl. Chem., 25 (1963) 365.
- 4 J.M. Steward, K.L. McLaughlin, J.J. Rossiter, J.R. Hurst, R.G. Haas, V.J. Rose, B.E. Ciric, J.A. Murphy and S.L. Lawton, Inorg. Chem., 13 (1974) 2767.
- 5 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
- 6 M. Olczak-Kobza and B. Ptaszyński, Polish J. Chem., 4 (1980) in press.