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The thermal decomposition of complex salts of bismuth(III) bromide with hydrobromides of aromatic amines

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Abstract

The thermal decomposition of sparingly soluble crystalline complex salts formed in the solution of bismuth(III) bromide and hydrobromides of pyridine, 3-methylpyridine, 2,6-methylpyridine, 2-aminopyridine, 4-aminopyridine and piperidine in 40% hydrobromic acid has been studied. Thermal analysis curves (DTA, TG, DTG) are presented. In the course of decomposition, the corresponding amine or its decomposition products, HBr and $BiBr_3$ are liberated. The effect of the basicity of the amide on the melting temperature and thermal stability of the compounds was determined. A comparison with analogous complexes of antimony(III) and arsenic(III) is made.

INTRODUCTION

This work is a continuation of our studies on the thermal decomposition of crystalline halogenide complexes of arsenic(III), antimony(III) and bismuth(III). Bismuth(III) bromide, like $SbBr_3$, forms a number of complex salts with hydrobromides of aromatic and aliphatic amines. Hauser and Vanino [1] reported the preparation of $2BiBr_3 \cdot 3C_5H_5N$, HBr. Robertson et al. [2] determined the crystal structure of the complex of $BiBr_3$ with 3-methylpyridine and McPherson and Meyers [3] reported the structure of $(C_5NH_{11})_2[BiBr_5]$. In both compounds the anions form a distorted octahedron of Br atoms around the bismuth atom with two Br bridges linking neighbouring Bi atoms. Whealy and Osborne [4] prepared 25 compounds by the reactions between bismuth bromide and amine hydrobromides in HBr solution. The compounds were of four different types: $(HL)BiBr_4$, $(HL)_2BiBr_5$, $(HL)_3BiBr_6$ and $(HL)_3Bi_2Br_9$ (where HL represents an amine cation). In our earlier works [5–7], the thermal decomposition of several crystalline complex salts formed between arsenic(III) and antimony(III) bromide with hydrobromides of some aromatic amines in concentrated hydrobromic acid solutions was studied. We found that antimony complexes exhibit higher thermal stability than

TABLE 1

Approximate decomposition data

Amine	Basicity of amine pK_a [a]	Empirical formula of the complex salt	T_m [b] in °C	T_d [c] in °C	Temperature range of total mass loss in °C
Pyridine	5.17	$(C_5NH_6)_3[BiBr_6]$	–	190	190–500
3-Methylpyridine	5.68	$(C_6NH_8)_3[BiBr_6]$	115	200	200–530
2,6-Dimethylpyridine	6.75	$(C_7NH_{10})_3[Bi_2Br_9]$	168	210	210–550
2-Aminopyridine	6.86	$(C_5N_2H_7)_3[Bi_2Br_9]$	188	235	235–570
4-Aminopyridine	9.29	$(C_5N_2H_7)_3[Bi_2Br_9]$	260	270	270–580
Piperidine	11.12	$(C_5NH_{11})_2[BiBr_5]$	–	290	290–620

[a] pK_a, ionization constant of the conjugated acid. [b] T_m, melting temperature determined from the DTA curve. [c] T_d, initial decomposition temperature.

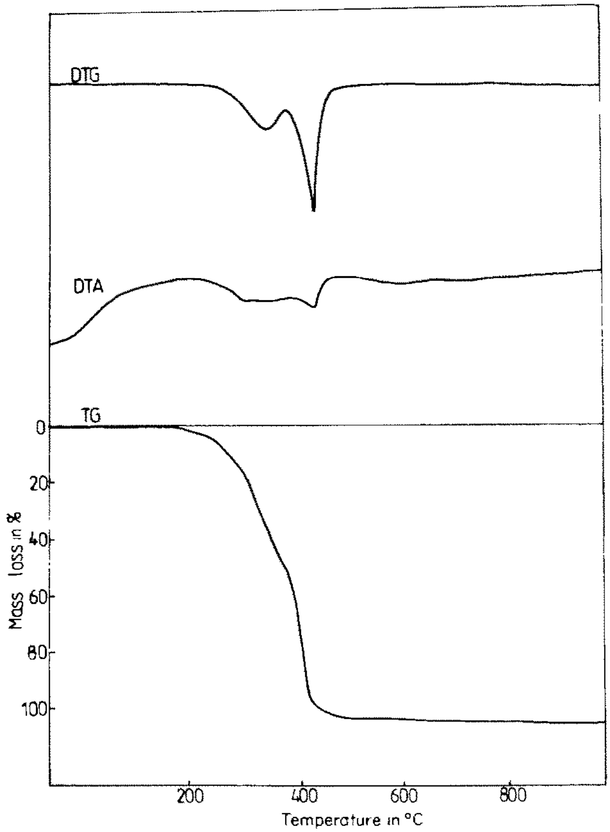

Fig. 1. DTA, TG and DTG curves of $(pyridine)_3[BiBr_6]$.

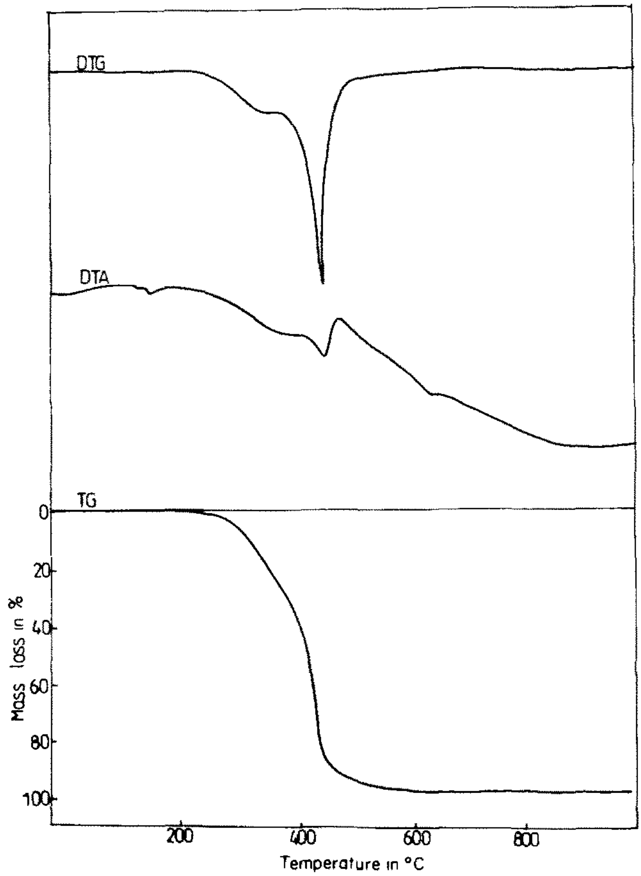

Fig. 2. DTA, TG and DTG curves of (3-methylpyridine)$_3$[BiBr$_6$].

the analogous arsenic compounds with the same outer-sphere amine. In the antimony(III) salts, the initial decomposition temperatures as well as the corresponding DTA peak temperatures increase with increasing basicity of amine. The effect of the basicity of the amine on the thermal stability of arsenic(III) complexes is not clear.

The object of the present work was to study the thermal decomposition of some bismuth(III) bromide complexes with aromatic amines of different basicity as counter ions.

EXPERIMENTAL

Apparatus

DTA, TG and DTG measurements on the compounds under study were carried out in air, using a MOM Budapest OD102/1500°C thermal analyser over the temperature range from 20 to 1000°C at a heating rate of

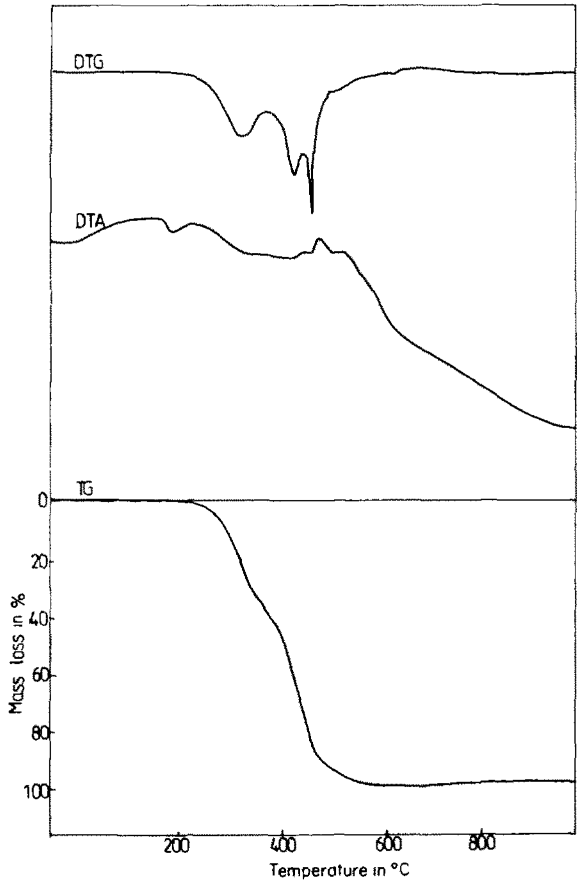

Fig. 3. DTA, TG and DTG curves of (2,6-dimethylpyridine)$_3$[Bi$_2$Br$_9$].

10°C min^{-1}, with sample mass 100 mg, galvanometer sensitivity for DTA and DTG 1/10, TG sensitivity 200 mg, and α-Al$_2$O$_3$ as reference material.

Preparation

The compounds under study were prepared by adding dropwise (with stirring) a solution of amine hydrobromide in 40% hydrobromic acid to a solution of (BiO)$_2$CO$_3$ in concentrated HBr. Approximately 10 moles of amine hydrobromide were added for each mole of bismuth(III) bromide. The following amines were used: pyridine, 3-methylpyridine, 2,6-dimethylpyridine, 2-aminopyridine, 4-aminopyridine and piperidine. The fine, yellow crystalline precipitates separated instantly from the solution. They were left in the mother liquor for 12 h, separated by vacuum filtration through a Buchner funnel, rinsed with diethyl ether and dried at room

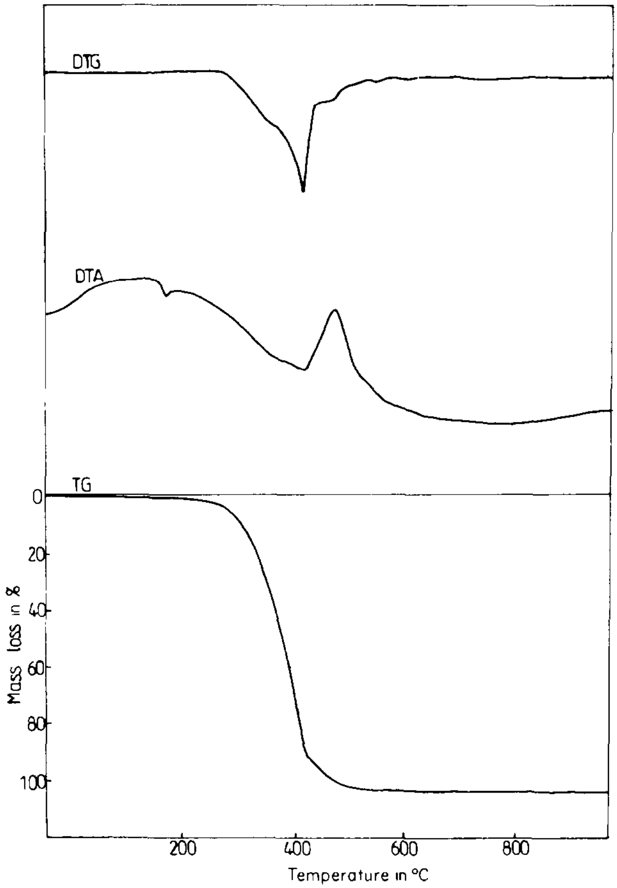

Fig. 4. DTA, TG and DTG curves of (2-aminopyridine)$_3$[Bi_2Br_9].

temperature. Bismuth and bromide were determined by standard chemical methods. The proposed empirical formulae of the obtained complex salts are collected in Table 1.

Thermal analysis

DTA, TG and DTG curves of the complexes under study are shown in Figs. 1–6 and concise thermoanalytical data are presented in Table 1. The thermogravimetric curves indicate two overlapping decomposition stages. However, their temperature limits cannot be precisely determined. In the case of the 3-methylpyridine and 2-aminopyridine salts, the two reaction stages are barely visible, and only on the DTG curves. In the first stage of the thermal decomposition, the corresponding amines, or the products of

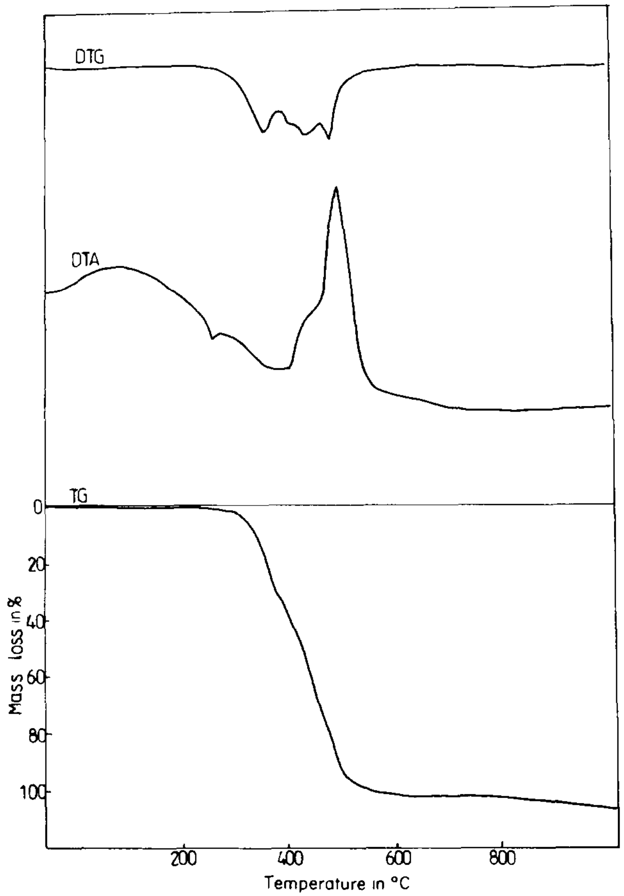

Fig. 5. DTA, TG and DTG curves of (4-aminopyridine)$_3$[Bi_2Br_9].

their decomposition, and hydrogen bromide are liberated. The subsequent loss of mass is connected with the evaporation of bismuth bromide. The total mass loss of all the compounds under study amounts to 100% and takes place within the temperature range of about 310–340°C. The small endothermic peaks on the DTA curves occurring at lower temperatures correspond to the melting of the samples. The complexes of $BiBr_3$ with pyridine, and also probably with piperidine, decompose without prior melting. Before decomposition, (piperidine)$_2$[$BiBr_5$] undergoes complicated phase transformations. At higher temperatures, the DTA curves exhibit diffuse endothermic peaks associated with the decomposition of the compounds, followed by exothermic peaks which probably correspond to the combustion of carbon remaining in the crucible after the decomposition of amine. The exothermic effects generally increase with increasing basicity of the amine. The precise temperatures of these peaks cannot be determined.

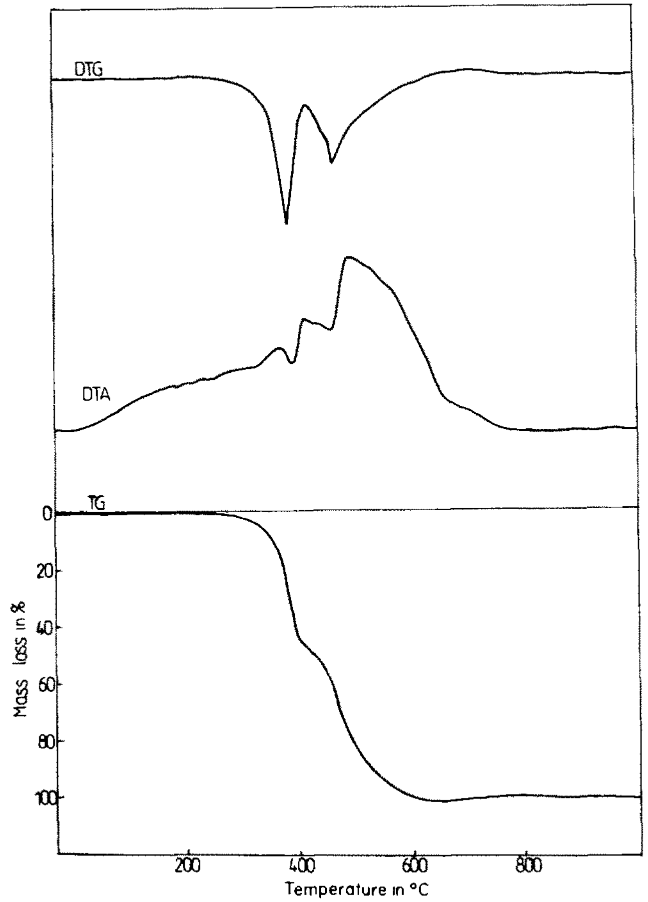

Fig. 6. DTA, TG and DTG curves of $(\text{piperidine})_2[\text{BiBr}_5]$.

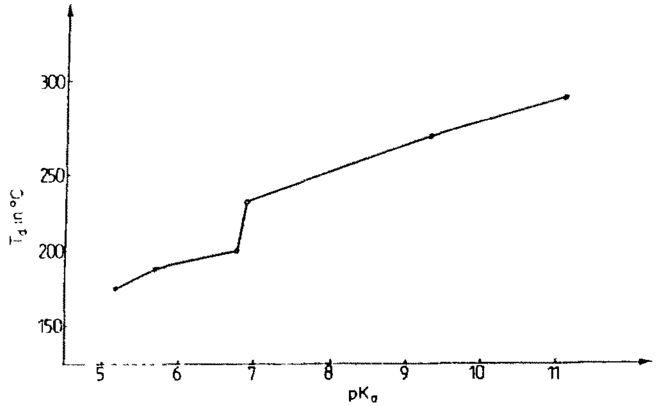

Fig. 7. The effect of the basicity of amine on the initial decomposition temperature T_d.

CONCLUSIONS

From solutions of bismuth(III), bromide, aromatic amines or piperidine in concentrated (approx. 40%) hydrobromic acid at a molar ratio of bismuth to amine of 1:10, sparingly soluble compounds of the type $R_x[Bi_yBr_z]$ (where R represents amine) crystallize in almost 100% yield (Table 1). Under identical conditions, antimony(III) bromide forms analogous complex salts [5] but when arsenic(III) is used, compounds of the type $p\mathrm{As_2O_3} \cdot q\mathrm{AsOBr} \cdot r\mathrm{RBr} \cdot s\mathrm{HBr}$ crystallize with low yield [6]. Complexes of bismuth, in contrast to the antimony salts, are not hydroscopic. The thermal decomposition of the bromobismuthates under study is, with the exception of the pyridine and, probably, the piperidine salts, preceeded by the melting of the sample. The melting temperature T_m as determined from the DTA curves increases with increasing basicity of the amine (Table 1). The decomposition takes place about 300°C. In the course of the reaction, the corresponding amine or its decomposition products, HBr and $BiBr_3$ are liberated. At high temperatures, 100% mass loss is observed. The effect of the basicity of the amine on the thermal stability of the compounds under study, defined by the temperature at which the decomposition starts T_d, is presented in Fig. 7. The thermal stability increases with increasing basicity of the amine. The analogous antimony complexes exhibit slighly higher thermal stabilities [7].

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