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Kinetic parameters of the thermal decomposition of complexes of arsenic(III) and antimony(III) with some aromatic amines

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Abstract

The activation energy and reaction order of the first step of the thermal decomposition reactions of crystalline complex salts formed between arsenic(III) and antimony(III) with aromatic amines in hydrobromic acid solutions were calculated from TG curves. The effect of the basicity of the amine on the thermal stability and the activation energy was determined.

INTRODUCTION

In our earlier works [1,2], several crystalline complex salts formed between arsenic(III) and antimony(III) with hydrobromides of some aromatic amines in concentrated hydrobromic acid solutions were prepared. On the basis of chemical analysis, empirical formulae were established. Thermal studies in dynamic conditions and X-ray studies were carried out. Some conclusions on the thermal stability were drawn. The subject of the present work is the evaluation of the kinetic parameters of thermal decomposition reactions of these compounds, as well as a comparison of their thermal stabilities and activation energy values with respect to the basicity of the outer-sphere amine.

THERMAL ANALYSIS

Typical thermoanalytical curves of the two compounds under study are presented in Figs. 1 and 2. The thermal decomposition of the antimony(III) complexes is, in general, a single stage process resulting in the liberation of antimony tribromide and the appropriate amine or amine decomposition

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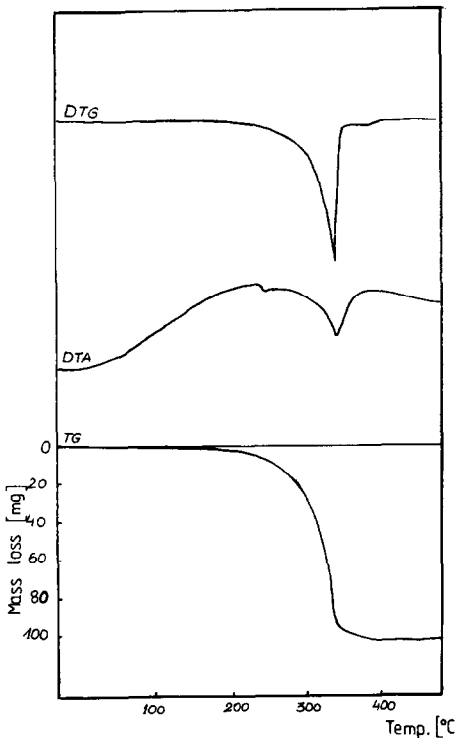

Fig. 1. Thermoanalytical curves of the complex salt of antimony(III) with pyridine.

products. This takes place within a temperature range of about 200°C. It can be observed that the thermal stability increases with increasing basicity of the amine. The thermal decomposition of arsenic(III) complex salts is a more complicated, multi-step process. In the first step of the reaction, which finishes below 300°C, amines or products of their decomposition and hydrogen bromide are liberated. At higher temperatures, decomposition of AsOBr and sublimation of As_2O_3 occur. The initial decomposition temperatures, the temperatures of the DTA peaks corresponding to the first step of the decomposition of the compounds under study and the basicity of the appropriate amine are listed in Tables 1 and 2. The temperatures corresponding to a 2% mass loss on the TG curves were taken as the initial decomposition temperatures.

DETERMINATION OF KINETIC PARAMETERS

Kinetic parameters (activation energy and reaction order) of the thermal decomposition reactions of complexes of antimony(III) bromide with hydrobromides of aromatic amines and of the first stage of decomposition of compounds formed between arsenic(III) and aromatic amines in hydrobromic acid solutions were determined from their thermogravimetric traces

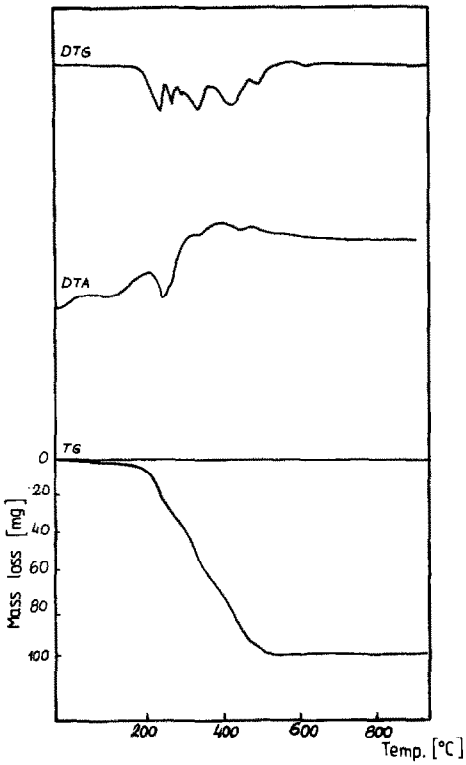

Fig. 2. Thermoanalytical curves of the complex salt of arsenic(III) with pyridine.

TABLE 1

Initial decomposition temperatures (T_d), DTA peak temperatures (T_{DTA}) and kinetic parameters of antimony(III) complexes.

Amine	Basicity of amine pK_a [a]	Empirical formula of the complex	T_d (°C)	T_{DTA} (°C)	C–R [b]		Z [c]	
					E [d]	n [e]	E [d]	n [e]
2-Bromopyridine	0.90	$(C_5NH_5Br)_2[SbBr_5]$	160	283	13.9	0.6	14.2	0.6
Pyridine	5.17	$(C_5NH_6)_2[SbBr_5]$	212	335	19.7	0.8	19.9	0.8
3-Methylpyridine	5.68	$(C_6NH_8)_2[SbBr_5]$	220	345	15.6	0.4	16.0	0.4
2-Methylpyridine	5.97	$(C_6NH_8)_2[SbBr_5]$	220	347	17.2	0.7	17.4	0.7
2,6-Dimethylpyridine	6.75	$(C_7NH_{10})_3[Sb_2Br_9]$	240	360	19.0	0.8	19.0	0.8
2-Aminopyridine	6.86	$(C_5N_2H_7)_3[Sb_2Br_9]$	248	375	21.1	0.9	21.5	0.9
2,4,6-Trimethylpyridine	7.60	$(C_8NH_{12})_3[Sb_2Br_9]$	235	360	22.9	2.0	22.4	1.9
4-Aminopyridine	9.29	$(C_5N_2H_7)_2[SbBr_5]$	292	443	25.7	0.5	26.0	0.5

[a] pK_a, ionisation constant of the conjugated acid.
[b] C–R, Coats and Redfern method.
[c] Z, Zsako method.
[d] E, activation energy (kcal mol^{-1})
[e] n, reaction order.

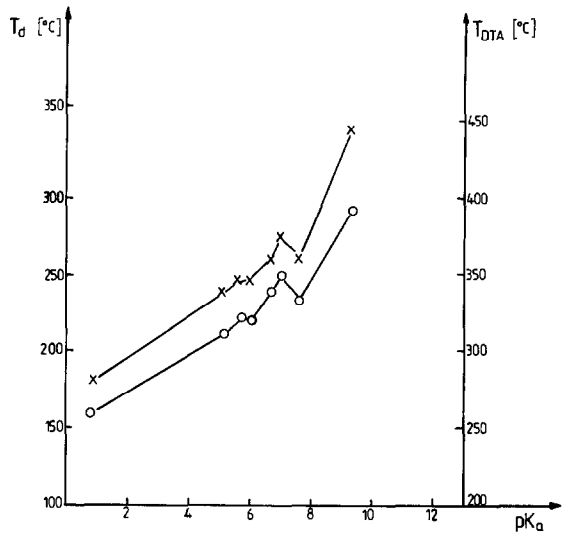

Fig. 3. The effect of the basicity of the amine on the initial decomposition temperature T_d and DTA peak temperature T_{DTA} of the antimony(III) complexes.

using the Coats and Redfern [3] and Zsako [4] methods. Computer programs were based on the mathematical formulae given by the authors. The final results of the calculations are listed in Tables 1 and 2.

CONCLUSIONS

The effect of the basicity of the amine on the thermal stability of the compounds under study, defined by both the initial decomposition temperature and the temperature of the DTA peak corresponding to the first step

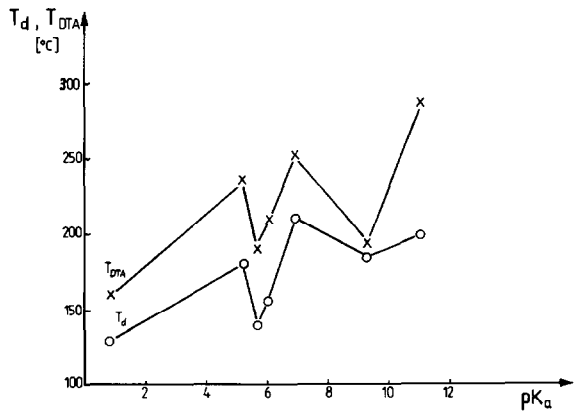

Fig. 4. The effect of the basicity of the amine on the initial decomposition temperature T_d and DTA peak temperature T_{DTA} of the arsenic(III) complexes.

TABLE 2

Initial decomposition temperatures (T_d), DTA peak temperatures (T_{DTA}) and kinetic parameters of arsenic(III) complexes.

Amine	Basicity of amine pK_a	Empirical formula of the complex	T_d (°C)	T_{DTA} (°C)	C–R		Z	
					E	n	E	n
2-Bromopyridine	0.90	$3As_2O_3 \cdot C_5H_4NBr \cdot HBr$	130	160	19.0	1.3	20.0	1.3
Pyridine	5.17	$2As_2O_3 \cdot C_5H_5N \cdot HBr$	180	235	28.0	0.6	28.0	0.6
3-Methylpyridine	5.68	$AsOBr \cdot 2As_2O_3 \cdot C_6H_7N \cdot HBr$	140	190	13.6	0.4	14.9	0.7
2-Methylpyridine	5.97	$AsOBr \cdot 2As_2O_3 \cdot C_6H_7N \cdot Br$	155	210	15.5	0.6	15.9	0.7
2-Aminopyridine	6.86	$5As_2O_3 \cdot 2C_5H_6N_2 \cdot 4HBr$	210	252	18.7	0.6	18.9	0.0
4-Aminopyridine	9.29	$2AsOBr \cdot 0.5As_2O_3 \cdot C_5H_6N_2 \cdot 2HBr$	185	194	12.7	0.9	13.0	0.9
2-Hydroxypyridine	11.0	$2As_2O_3 \cdot C_5H_5NO \cdot 2HBr$	200	286	32.1	1.1	32.0	1.1

See footnotes to Table 1.

of decomposition, is presented in Figs. 3 and 4. From a comparison of the initial decomposition temperatures and of the DTA peak temperatures (Tables 1 and 2), it can be seen that the antimony(III) compounds exhibit higher thermal stability than the analogous arsenic(III) complexes with the same outer-sphere amine. In the antimony(III) complex salts, the initial decomposition temperatures as well as the DTA peak temperatures, generally increase with increasing basicity of the amine (except the complex with 2,4,6-trimethylpyridine). The effect of the basicity of the amine on the thermal stability and the activation energy values of the arsenic(III) complexes is not evident. However, the thermal stability of these compounds also tends to increase with increasing basicity of the amine.

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