SIMULTANEOUS TG, DTG, DTA AND EGA THERMOANALYSIS OF HYDRAZINIUM SULFATE

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ABSTRACT

Simultaneous TG, DTG, DTA and EGA studies of hydrazinium sulfate, $N_2H_6SO_4$ (I), have been carried out under air (oxidising) and argon (neutral) dynamic atmospheres. X-ray diffractometry, IR spectrometry and elemental analysis have been used to identify the precursor (I) and intermediates. The thermal decomposition behavior of (I) is different in air and in argon. The compound is more stable in air (up to 201°C) than in argon (up to 164°C). The DTA curves reveal the presence of two small endotherms for crystalline phase change and melting of (I) followed by relatively large exotherms having enthalpy changes of -235 and -177.7 J g^{-1} in air and argon, respectively. These exotherms represent the degradation and dissociation of (I). In air the sharp exo-peak is followed by a broad one at 297–340°C, which has no counterpart on the DTA curves measured in argon. Large endotherms follow with enthalpy changes of 352.1 (air) and 227.0 J g^{-1} (argon). Each enthalpy system infers the volatilisation and decomposition of the by-product residues. The actual total loss in weight of the samples amounts to 100%.

INTRODUCTION

Hydrazine is a liquid which forms two series [1] of crystalline hydrazinium salts: $N_2H_5^+$ and $N_2H_6^{2+}$. There are four hydrazinium sulfates [2,3], namely hydrazinium(hydrazonium)sulfate $N_2H_6SO_4$ (I), dihydrazinium sulfate, $(N_2H_4)_2 \cdot H_2SO_4$, hydrazinium disulfate, $N_2H_4 \cdot 2H_2SO_4$ and hydrazinium bisulfate, $N_2H_5 \cdot HSO_4$. Hydrazine and its inorganic and alkylated derivatives are powerful reducing and complexing agents [1] and find applications in analytical chemistry [4]. They are well known potential rocket propellants [5,6]. As the corresponding literature does not include information on the relevant test parameters of (I) such as thermoanalytical curves, thermal analyses, sample weights, crucibles, heating rates, atmospheres, sensitivity ranges, and so on, we thought it was worthwhile to conduct thermoanalysis of the most frequently used hydrazinium sulfate (commercially named as hydrazinium sulfate and given the formula $N_2H_4 \cdot H_2SO_4$), and take it as a model hydrazinium salt for the study of thermal stability, crystalline phase change, melting point, volatility, enthalpy of transformation and intermediates in air and argon atmospheres.

EXPERIMENTAL

Materials

Hydrazinium sulfate and α-Al_2O_3 (99.99%) (Fluka AG Buchs) were used as sample and reference materials, respectively, each manually ground using agate mortar and pestle for 15 min. Ultrapure argon and purified air were used as gaseous atmospheres. X-ray diffraction and IR [7,8] confirmed the presence of (I) only in sample materials.

Apparatus

Thermal analysis curves were recorded simultaneously with a Netzsch STA 429 thermal analyzer (Table 1). Two runs were taken for each sample to confirm the values of temperature, thermal stability, weight loss and enthalpy change, EGA curves (not shown for brevity) were recorded and employed for qualitative and quantitative analysis of gaseous products.

RESULTS AND DISCUSSION

The IR spectrum of (I) shows the principal νN–N stretching vibration at 1028 cm^{-1}; whereas its XRD patterns [8] are found to be

| d (Å) | 3.53 | 3.25 | 4.13 |
| I/I_0 | 100 | 90 | 60 |

TABLE 1

Parameters of test

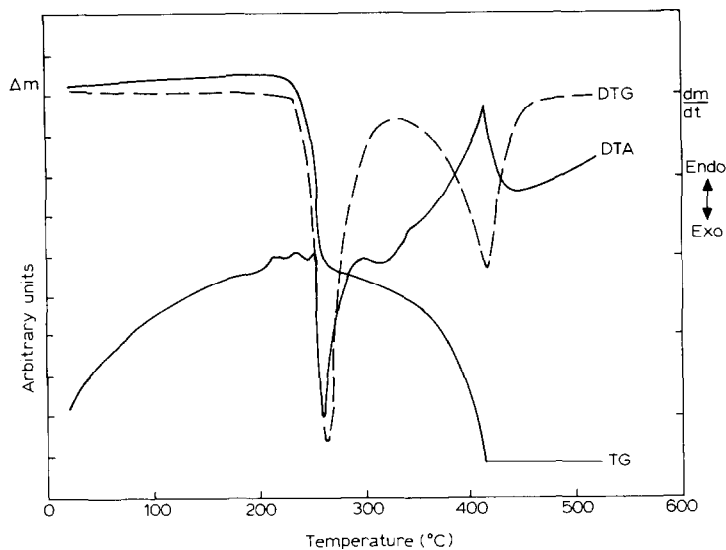| Parameters	Settings
Sample weight	11.6–12.2 mg
Reference weight	10.0–11.6 mg
Crucibles	Alumina No. 445172
Atmospheres	Air, 100 cm^3 min^{-1}
	Argon, 100 cm^3 min^{-1}
Heating rate	10 K min^{-1}
Heating program	20–700 °C
Sensitivity control	X_p 5, Tn 6, Tv 2
Chart speed	240 mm h^{-1}
Ranges	
DTA	100 μV
DTG	200 μV
TG	50 mg
EGA	50%, 100 mA
Measuring system (TC)	Pt–Rh 10/Pt

Fig. 1. TG, DTG and DTA curves of $N_2H_6SO_4$ under air dynamic atmosphere.

Figures 1 and 2 signify that the general profile of the simultaneous thermo-analytical curves of (**I**) in air and argon are not identical (Tables 1–3). For instance, there is a little shift towards higher T_i, T_f, T_{max} and T_{min} values for the decomposition steps in air compared with those in argon. This shift is brought about by the oxidising role of air oxygen. The actual total loss in
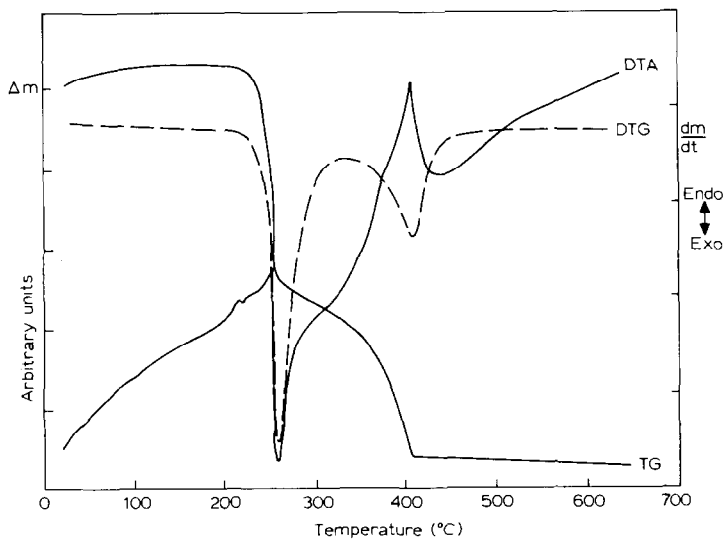

Fig. 2. TG, DTG and DTA curves of $N_2H_6SO_4$ under argon dynamic atmosphere.

TABLE 2

Temperature ranges, weight losses and enthalpies of $N_2H_6SO_4$ in air

Steps	T_i-T_f (°C)	Wt. loss (mg)	(%)	Ratio (%)	Ext. onset (°C)	Range (°C)	T_{max} (°C)	T_{min} (°C)	ΔH (J g⁻¹)	Limit (°C)	µV.S
TG: 1	201–263	5.562	47.95	1	234.9	209–243	–	–	–	–	–
2	269–510	5.655	48.75	1	–	–	–	–	–	–	–
Total	–	11.22	96.7	2	–	–	–	–	–	–	–
DTG: 1	–	–	–	–	–	–	–	262.8	–	–	–
2	–	–	–	–	–	–	–	416.7	–	–	–
DTA: 1	–	–	–	–	–	–	–	260.6	–	–	–
2	–	–	–	–	–	–	415.3	260.6	–	–	–
ΔH: 1	–	–	–	–	–	–	–	–	–234.8	251–300	–942
2	–	–	–	–	–	–	–	–	352.1	340–457	1307

TABLE 3

Temperature ranges, weight losses and enthalpy changes of $N_2H_6SO_4$ in argon

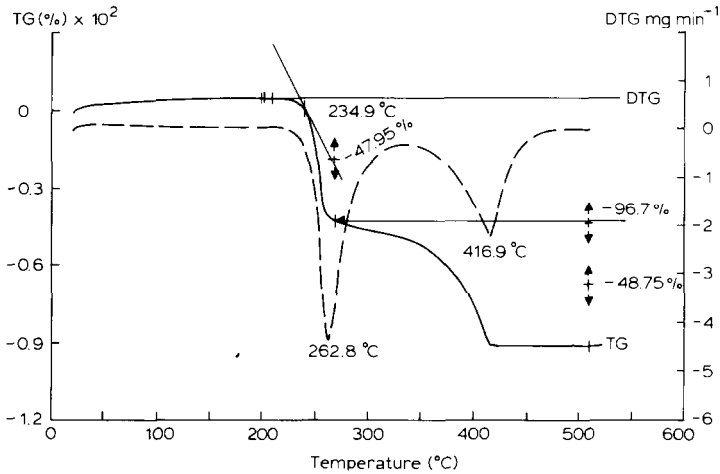| Steps	T_i-T_f (°C)	Wt. loss (mg)	(%)	Ratio (%)	Ext. onset (°C)	Range (°C)	T_{max} (°C)	T_{min} (°C)	ΔH (J g⁻¹)	Limit (°C)	μV.S
TG: 1	164.1–269.1	6.763	55.43	1.2	239	189–247	–	–	–	–	–
2	267.1–638.1	5.550	45.49	1.0	–	–	–	–	–	–	–
Total	–	12.28	100.6	2.2	–	–	–	–	–	–	–
DTG: 1	–	–	–	–	–	–	–	260.3	–	–	–
2	–	–	–	–	–	–	–	407.9	–	–	–
DTA: 1	–	–	–	–	–	–	–	257.9	–	–	–
2	–	–	–	–	–	–	406.3	–	–	–	–
3	–	–	–	–	–	–	211.3	–	–	–	–
4	–	–	–	–	–	–	249.4	–	–	–	–
ΔH: 1	–	–	–	–	–	–	–	–	–177.7	250–299.9	–748
2	–	–	–	–	–	–	–	–	227.0	358–438.1	885

Fig. 3. TG and DTG curves illustrating the percentage decomposition of $N_2H_6SO_4$ under air dynamic atmosphere.

weight under both atmospheres amounts to 100% although the apparent total weight loss is 100.6% and 96.7% in argon and air, respectively (Figs. 3 and 4). This rather negligible difference is found to be due mainly to buoyancy and could be eliminated by registering separately the buoyancy correction curves. The differences in steepness and height of the TG steps and the areas under the DTG and DTA peaks are real, however.
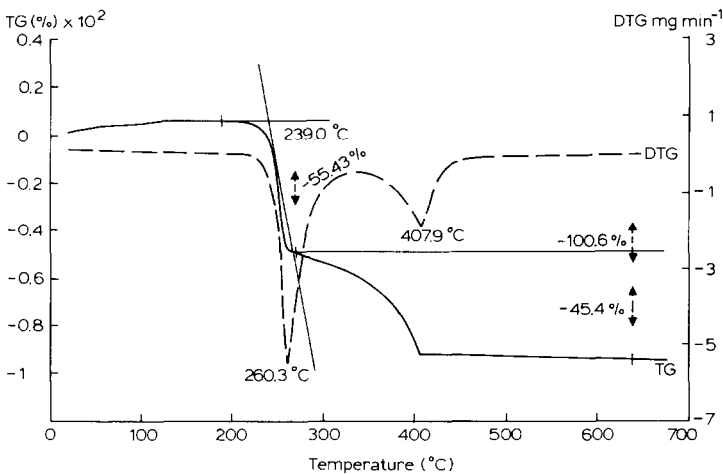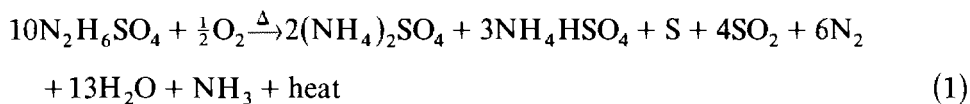

Fig. 4. TG and DTG curves illustrating the percentage decomposition of $N_2H_6SO_4$ under argon dynamic atmosphere.

Thermal behavior of (I) under air (oxidising) atmosphere

Figures 1 and 3 depict the thermoanalysis curves of $N_2H_6SO_4$ in flowing air. Temperature ranges, weight losses and enthalpy changes of thermal analysis steps are given in Table 2. The first TG stage of (I) is observed in the range 201–269°C and is accompanied by weight loss of 47.95% (Fig. 3). The gaseous products evolved have been shown to contain water vapor, sulfur dioxide, ammonia and nitrogen. The decomposition reaction is

$$10N_2H_6SO_4 + \tfrac{1}{2}O_2 \xrightarrow{\Delta} 2(NH_4)_2SO_4 + 3NH_4HSO_4 + S + 4SO_2 + 6N_2$$

$$+ 13H_2O + NH_3 + heat \tag{1}$$

The XRD patterns of the solidified melts isolated at 269°C indicate the presence of $(NH_4)_2SO_4$ [9]

d (Å)	4.33	4.39	3.06
I/I_0	100	60	40

and NH_4HSO_4 [10]

d (Å)	4.79	3.72	3.92
I/I_0	100	100	40

and a trace of S_6 [11]

d (Å)	3.93	2.74	3.09
I/I_0	100	15	15

The identification of traces of ammonium pyrosulfate [12]

d (Å)	4.97	3.39	3.19
I/I_0	100	100	25

suggests that the latter is a precursor of ammonium sulfate and ammonium hydrogen sulfate. The next decomposition step (endothermic) occurs beyond 269°C and corresponds to

$$(NH_4)_2SO_4 \xrightarrow{\Delta} NH_4HSO_4 + NH_3 \tag{2}$$

$$NH_4HSO_4 \xrightarrow{\Delta} NH_3 + H_2O + SO_3 \tag{3}$$

The percent ratios of the two endo- and exothermic peaks (Tables 2 and 3) correspond with the percent weight loss of each TG step. Doubling the DTG and DTA sensitivities resulted in the formation of twin peaks (not shown for brevity) within the original endotherm, inferring the volatilisation and decomposition of ammonium sulfate and ammonium hydrogen sulfate consecutively. In argon the twin peaks do not show up because of different decomposition mechanisms. The sharp exotherm at T_{max} 260.6°C (enthalpy change = -235 J g^{-1}) (Fig. 1 and Table 2) is partly ascribed to the breaking
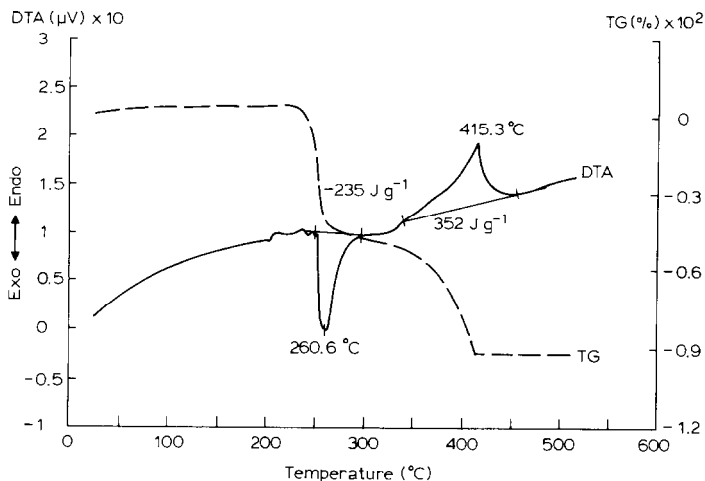
Fig. 5. Enthalpy change for the decomposition stages of $N_2H_6SO_4$ under air dynamic atmosphere.

up of the active energy-rich N–N bond in $(H_3N–NH_3)^{2+}SO_4^{2-}$ to the $(:N\equiv N:)^0$ molecule and partly due to the air oxidation of some decomposition products such as SO_2 to SO_3 (secondary process). The flat exotherm appearing at 297–340 °C (Fig. 5), although not indicated on the relevant TG and DTG curves (Figs. 1 and 5), has been shown to be due to very slow combustion of small amounts of sulfur [11]. This exotherm has not shown up under argon, however.
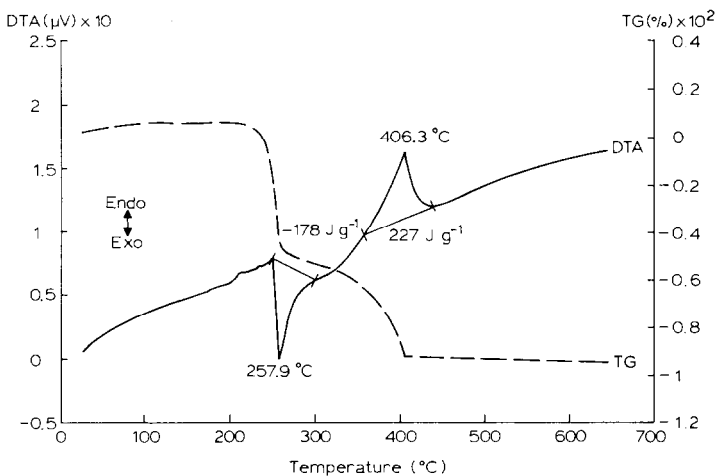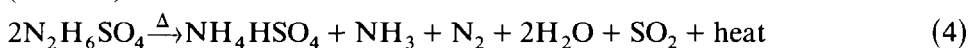

Fig. 6. Enthalpy change for the two decomposition stages of $N_2H_6SO_4$ under argon dynamic atmosphere.

TABLE 4

Thermal behavior of (I) in air and argon

Parameter	Air	Argon
Thermal stability	Ambient–201°C	Ambient–164°C
Crystalline phase change	T_{max} 214°C	T_{max} 212°C
Melting endotherm	T_{max} 250°C	T_{max} 256°C
TG steps	Less steep	Steeper and sharper
1st step	Smaller	Bigger
Enthalpy change	Larger	Smaller
Mechanism of decomposition	Different	Different
Percent wt. loss ratio		
1st. step	1	1.2
2nd. step	1	1
Total	2	2.2

Thermal behavior of (I) under argon (neutral) atmosphere

Table 4 shows some features of clear-cut differences in thermal behavior of (I) in argon and air. For example, the first TG decomposition step in argon is bigger (55.43%) than the one measured in air (47.95%). This is because of the difference in decomposition mechanisms, as is self-explained by eqns. (1)–(3), in the two atmospheres. Experiments have shown that the following scheme could be proposed for the thermal behavior of (I) in argon (Table 3)

$$2N_2H_6SO_4 \xrightarrow{\Delta} NH_4HSO_4 + NH_3 + N_2 + 2H_2O + SO_2 + \text{heat} \tag{4}$$

$$NH_4HSO_4 \xrightarrow{\Delta} NH_3 + H_2O + SO_2 \tag{5}$$

The percent ratio (theoretical) calculated from eqns. (4) and (5) matches that determined experimentally (Table 3), that is 1.2.

Experiments did not disclose the formation of ammonium sulfate or free sulfur under argon atmosphere. The enthalpy change (-177.7 J g^{-1}) of the exotherm is less than that measured in air (-234.8 J g^{-1}). The net difference between them represents the enthalpy transition of the secondary oxidation process. Therefore the value -177.7 J g^{-1} is equivalent to the energy released from rupture of the N–N bond.

Table 4 discloses that (I) is thermally more stable in air than in argon. It is probable that the rate of collisions of monoatomic argon with molten hydrazinium sulfate is faster than that of air; therefore rupture of the N–N bond is expected to occur at comparatively lower temperature.

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