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Note

Differential thermal analysis of hydrazinium derivatives

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Hydrazinium salts are usually prepared by neutralizing aqueous hydrazine with hydrogen acids[1, 2]. Thermal properties of hydrazinium nitrate[3–5], perchlorate[6–8] and halides[9, 10] have been investigated. Recently, we reported[11] the preparation of a number of hydrazinium derivatives by the reaction of solid ammonium salts with hydrazine hydrate. During the course of our investigations of the thermal properties of these hydrazinium derivatives, we found certain differences in our data and those already reported. It is the purpose of this communication to bring out these discrepancies as well as to report the thermal characteristics of some hydrazinium derivatives not studied earlier.

EXPERIMENTAL

Hydrazinium derivatives were prepared by reacting stoichiometric amounts of appropriate ammonium salts with calculated amounts of hydrazine hydrate (99–100%). Ammonium salts dissolved in hydrazine hydrate with the evolution of ammonia. The crystalline products were obtained from the solutions by removing water over P_2O_5 in a vacuum desiccator. Details of the preparation and characterization have been described elsewhere[11]. The reaction of ammonium sulfite, $(NH_4)_2SO_3$, with hydrazine hydrate gave $N_2H_3SO_2N_2H_5$ (% N_2H_4: obs. 50.00; theor. 50.00). Ammonium oxalate hydrate, $(NH_4)_2C_2O_4 \cdot H_2O$, when treated with hydrazine hydrate yielded $(N_2H_5)_2C_2O_4 \cdot N_2H_4$ (% N_2H_4; obs. 52.70; theor. 51.61). Evaporation of ammonium iodide solution in hydrazine hydrate on water bath gave $(N_2H_5I)_2 \cdot N_2H_4$ (% N_2H_4; obs. 27.00; theor. 27.28). Hydrazine content was determined by titration with 0.05 M potassium iodate under Andrews condition as described elsewhere[11]. Differential thermal analysis (DTA) curves were recorded using a Universal DTA-02 instrument manufactured by Franz Wagner Industrille Elektronika of the German Democratic Republic. All experiments were carried out in air using platinum cups as sample holders. The heating rate employed was 7 °C min^{-1} and 40–50 mg of the samples were used for the experiments.

RESULTS AND DISCUSSION

The results of the DTA studies have been summarized in Table 1. The DTA curves of some compounds not reported earlier are shown in Fig. 1. All the hydrazinium salts show an endotherm corresponding to melting. The reported melting points[1, 2] of the known compounds are in agreement with ours. All the hydrazinium derivatives except hydrazinium azide decompose exothermally. Hydrazinium azide, $N_2H_5N_3$, melts at 82°C and volatilizes at ~170°C. No explosion occurred during the DTA experiments although $N_2H_5N_3$ has been reported to be explosive[1]. This property of $N_2H_5N_3$ is comparable with ammonium azide, NH_4N_3, which volatilizes without explosion. However, both $N_2H_5N_3$ and NH_4N_3 explode when properly initiated.

The hydrazinium derivative of hydrazido sulfite, $N_2H_3SO_2N_2H_5$, melts at 100°C and decomposes exothermically at ~230°C. The final endotherm at 372°C is due to the volatilization of sulfur formed during the decomposition.

Hydrazinium oxalate hydrazinate, $(N_2H_5)_2C_2O_4 \cdot N_2H_4$, looses a hydrazine molecule at ~90°C and melts at ~150°C. It decomposes exothermally in two steps.

Hydrazinium perchlorate hemihydrate decomposes in two stages. The first endothermic peak is broad and may be attributed to dehydration and melting. The anhydrous compound decomposes violently. Hydrazinium sulfate melts and decomposes exothermally.

Hydrazinium nitrate, $N_2H_5NO_3$, melts at ~60°C and decomposes in two steps. The intermediate after the first exotherm (~180°C) was identified as ammonium nitrate by qualitative analysis of the residue just after the first exotherm. The peak temperature of the second exotherm (240°C) also agrees with the decomposition of ammonium nitrate[12].

TABLE 1

DTA DATA OF HYDRAZINIUM DERIVATIVES

Compound	*Peak temperatures*[a] *(°C)*
$N_2H_5N_3$	82(m), 173(−)
$N_2H_3SO_2 \cdot N_2H_5$	100(m), 230(+), 372(−)
$(N_2H_5)_2C_2O_4 \cdot N_2H_4$	89(−), 153(m), 234(+), 270(+)
$N_2H_5ClO_4 \cdot 0.5H_2O$	86(−), 224(+)
$(N_2H_5)_2SO_4$	84(m), 245(+)
$N_2H_5NO_3$	70(m), 178(+), 240(+)
N_2H_5Cl	89(m), 241(+), 308(−)
N_2H_5Br	80(m), 225(+), 350(−)
N_2H_5I	125(m), 170(+), 330(−)
$(N_2H_5I)_2 \cdot N_2H_4$	90(m), 165(+), 340(−)

[a] m = melting; (−) = endo; (+) = exo.

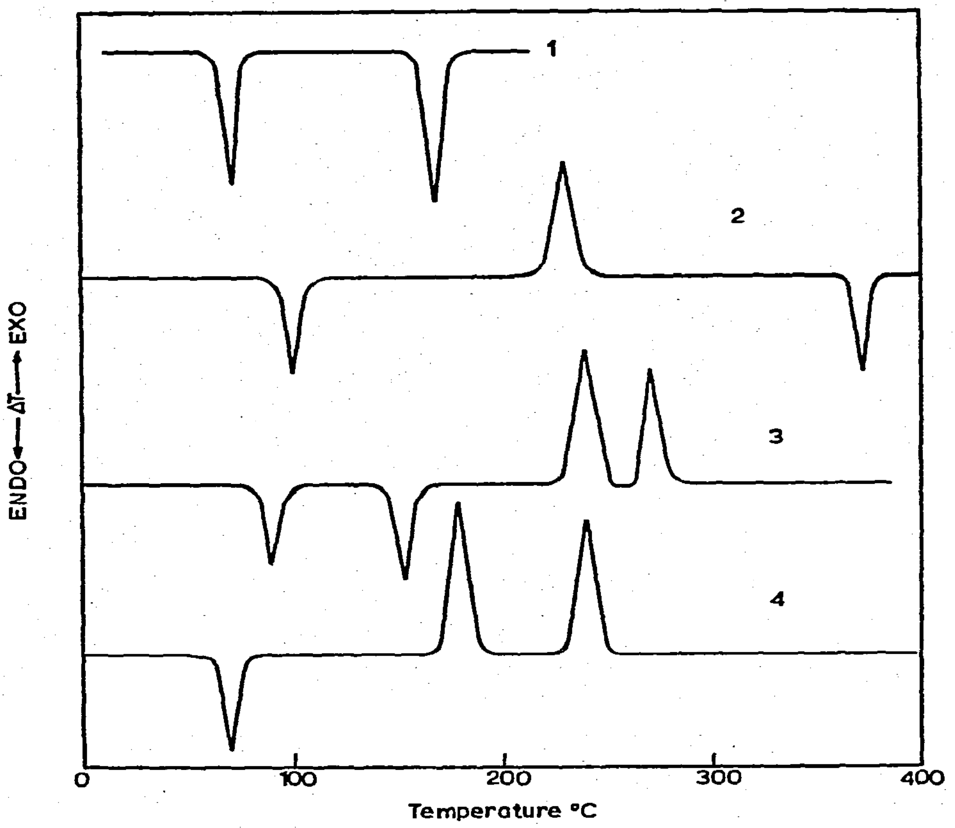

Fig. 1. DTA traces of 1, $N_2H_5N_3$; 2, $N_2H_3SO_2N_2H_5$; 3, $(N_2H_5)_2C_2O_4 \cdot N_2H_4$; 4, $N_2H_5NO_3$.

Hydrazinium halides (Cl, Br and I) melt and decompose exothermally to the respective ammonium halides. The ammonium halides formed sublime at higher temperatures. Decomposition of $(N_2H_5I)_2 \cdot N_2H_4$ is similar to that of N_2H_5I except that its melting point is lower. Our results are in agreement with those of Milojevic and Slivnik[9].

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