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A TG–DSC INVESTIGATION OF THE THERMAL DISSOCIATION OF SELECTED GUANIDINIUM SALTS

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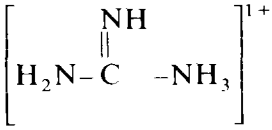
ABSTRACT

The TG and DSC curves of guanidinium acetate, carbonate, chloride, chromate, nitrate, sulfate and thiocyanate are reported for the temperature range 25–500°C. Except for guanidinium carbonate, the TG curves were characterized by a single-step mass-loss reaction, involving thermal dissociation and/or vaporization processes. The DSC curves, with the exception of guanidinium chromate, consisted of two or more endothermic peaks, the lowest temperature peak of which corresponded to the fusion of the compound. Exothermic peaks were found only in the DSC curve of guanidinium chromate.

INTRODUCTION

Guanidinium salts, which contain the cation,



$$\left[H_2N{-}\overset{\overset{\displaystyle NH}{\|}}{C}{-}NH_3 \right]^{1+},$$

and various anions, are widely used in explosives and rocket propellant formulations. Because of these applications, the compounds have been investigated by the thermal analysis techniques of thermogravimetry (TG), differential thermal analysis (DTA), light emission (LE), mass spectrometry (MS), and others. Fauth [1] was one of the first investigators to systematically determine the TG and DTA curves of guanidinium, hydrazinium, and alkyl guanidinium salts. Most of the anions present were very good oxidizing agents, for example nitrate, picrate and styphnate. Using TG, the initial mass-loss temperatures as well as the thermal behavior at the highest temperature studied, were tabulated for these compounds. The DTA curves, using the existing instrumentation of that time, were all poorly characterized and devoid of well-defined endothermic and exothermic peaks. Indeed, most of the curves had no peaks at all but consisted of a continuous smooth curve caused by a constantly changing baseline. More recently, the DTA curves of

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guanidinium acetate [2] and guanidinium nitrate [3] have been reported. Both salts exhibited well defined DTA endothermic and exothermic peaks caused by their thermal dissociation processes. Because of the presence of vigorous oxidizing anions, some of the guanidinium salts exhibited light emission phenomena during their dissociation reactions [4]. Mass spectral data [3] of the dissociation products of guanidinium nitrate showed the absence of a peak for the parent compound but indicated that the salt dissociated by a proton transfer mechanism.

As a result of the need for new thermal analysis data on guanidinium compounds, we wish to report here new TG and DSC data for these salts.

EXPERIMENTAL

The TG curves were obtained using a Perkin–Elmer TGS-2 thermobalance. Sample sizes ranged in mass from 5 to 8 mg and were studied at a furnace heating rate of 10°C min^{-1} in a dynamic N_2 atmosphere.

The DSC curves were obtained using a DuPont Model 990 system equipped with a DSC module. Sample sizes ranged in mass from 10 to 20 mg and were studied at a furnace heating rate of 10°C min^{-1} in a dynamic N_2 atmosphere.

The guanidinium salts were commercially available compounds obtained from the Eastman Kodak Chemical Co. They were all used without further purification.

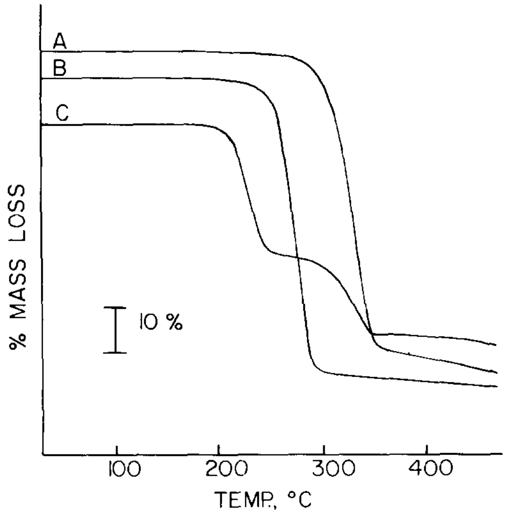

Fig. 1. TG curves of guanidinium salts. (A) Guanidinium thiocyanate; (B) guanidinium acetate; and (C) guanidinium carbonate.

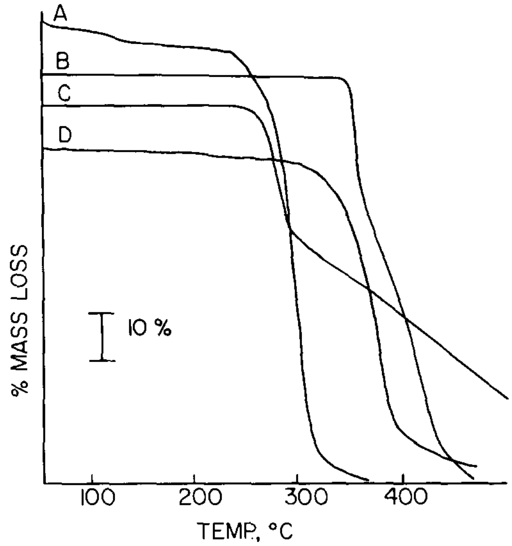

Fig. 2. TG curves of guanidinium salts. (A) Guanidinium nitrate; (B) guanidinium sulfate; (C) guanidinium chromate; and (D) guanidinium chloride.

RESULTS AND DISCUSSION

TG studies

The TG curves of the guanidinium salts are given in Figs. 1 and 2.

Except for guanidinium carbonate, the TG curves are characterized by a single-step mass-loss reaction, involving thermal dissociation and/or vaporization processes. The procedural initial mass-loss temperature ranged from 190°C for guanidinium carbonate to 330°C for guanidinium sulfate. A gradual mass-loss was exhibited by guanidinium nitrate starting at about 50°C but the main thermal dissociation reaction apparently begins at about 215°C. Although the procedural initial mass-loss temperatures are poor

TABLE 1
Procedural initial mass-loss temperatures for guanidinium salts

Compound	This work (°C)	Fauth [1] (°C)
Guanidinium acetate	200	
Guanidinium carbonate	190	
Guanidinium chloride	185	
Guanidinium chromate	230	
Guanidinium nitrate	215 [a]	100; lost 72% up to 250
Guanidinium sulfate	330	270; lost 2% up to 295
Guanidinium thiocyanate	250	

[a] Gradual mass-loss starting at 50°C.

indicators for the thermal stability of these compounds, they are tabulated in Table 1.

DSC studies

The DSC curves of the guanidinium salts are shown in Figs. 3 and 4.

Except for guanidinium chromate, all of the DSC curves consisted of two or more endothermic peaks, the peak at the lowest temperature corresponded to the fusion of the compound (so indicated on the curves). This was followed by additional endothermic peaks caused by dissociation and/or vaporization reactions. The curves were not similar to those obtained by Fauth [1]. Udupa [3] reported the DTA curve of guanidinium nitrate, which consisted of an endothermic fusion peak at 210°C followed by an unsymmetrical exothermic peak at 305°C. The latter was stated to be attributed to the oxidative decomposition of the compound. Such an exothermic peak was not observed in this investigation due perhaps to the sample size, geometry of the sample container (open cup vs. other designs), heating rate, etc. The DTA curve for guanidinium acetate, previously observed by Wendlandt [2] and obtained on a different apparatus, was similar to the DSC curve given here.

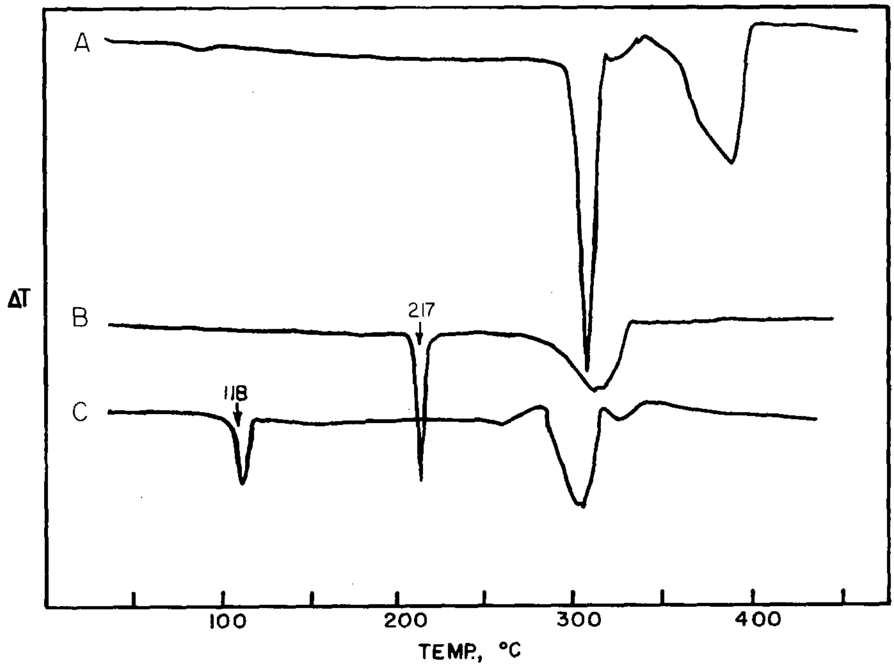

Fig. 3. DSC curves of guanidinium salts. (A) Guanidinium sulfate; (B) guanidinium nitrate; and (C) guanidinium thiocyanate. Fusion temperatures noted.

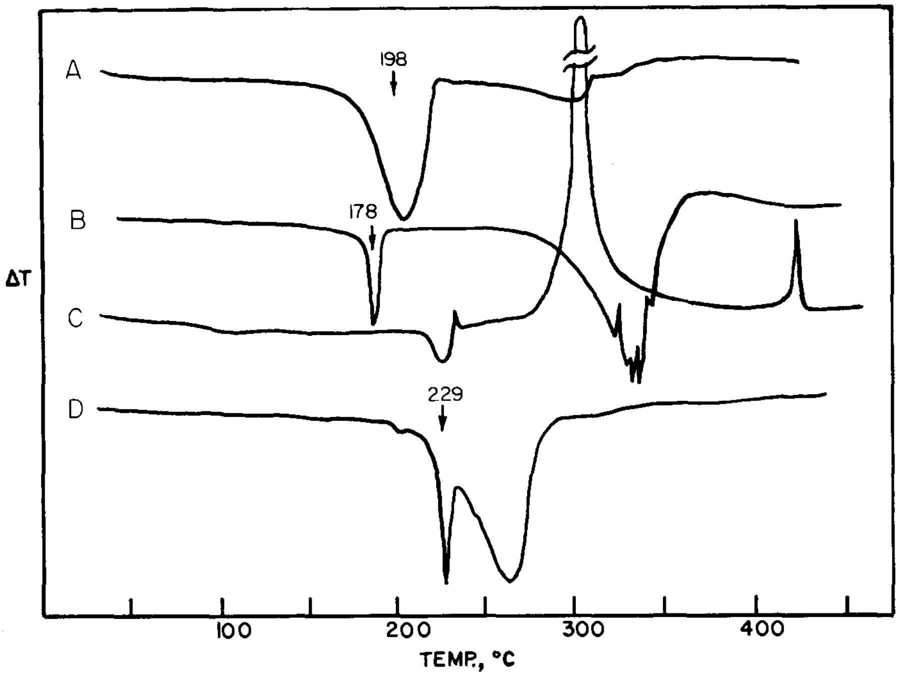

Fig. 4. DSC curves of guanidinium salts. (A) Guanidinium carbonate; (B) guanidinium chloride; (C) guanidinium chromate; and (D) guanidinium acetate. Fusion temperatures noted.

For guanidinium chromate (Fig. 4A), a small endothermic peak was observed with a ΔT_{min} of 250°C, followed by a small exothermic peak at a ΔT_{max} of 265°C, and then a very large exothermic peak with a ΔT_{max} of 305°C. At still higher temperatures, another exothermic peak was observed with a ΔT_{max} of 423°C. Because of the presence of vigorous reducing (guanidinium ion) and oxidizing (chromate ion) groups present in the salt, this behavior is not unexpected. The violent exothermic reaction results also in light emission from the compound, as reported by Wendlandt [4]. Light emission was also observed for the thiocyanate, carbonate and chloride salts but for reasons other than those given above.

The composition of the thermal dissociation products of the guanidinium salts, with the exception of the nitrate [3], remains unknown. For guanidinium nitrate, thermal dissociation is thought to proceed by a proton transfer mechanism. The compound undergoes dissociation into neutral molecules which are then vaporized and ionized. Three major pathways of fragmentation are possible: (a) the guanidinium cation and its disintegration products; (b) the nitrate anion; and (c) the oxidation products of the organic moiety by the nitrate ion.

ACKNOWLEDGMENT

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