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Note

THE LIGHT EMISSION OF SELECTED GUANIDINE SALTS

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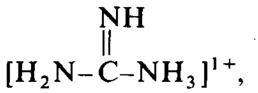
Among numerous other uses, guanidinium salts,  $[\mathrm{H_2N{-}\overset{\overset{NH}{\|}}{C}{-}NH_3}]^{1+}$, are used in explosives, rocket propellant compositions, and fireproofing agents. Thermal analysis techniques, especially DTA and TG, have been widely used to investigate the temperature range within which the reactions occurring are endothermic or exothermic and the rate of maximum reaction [1]. In one early DTA–TG study, Fauth [2] determined the thermal properties of guanidine sulfate, styphnate, picrate, nitrate, and other explosive compounds. Due to the primitive equipment employed, the DTA curves were poorly characterized in terms of exothermic and endothermic reactions although there were some indications in the curves that these reactions were taking place. The initial mass-loss temperatures were also recorded using TG as well as the thermal behavior at the highest temperatures attained. For the guanidine salts, the minimum mass-loss temperatures recorded were: sulfate, 270°C; styphnate, 130°C; picrate, 220°C; and nitrate, 100°C.

Using the thermal analysis technique of thermophotometry, we have found that selected salts exhibit light emission (LE) during their thermal decomposition reactions. This light emission is not due to oxyluminesence, such as has been previously described by Ashby [3] and Schard and Russell [4] for various polymeric materials. Rather, it is more like the light emission behavior of certain coordination compounds, as previously investigated by Wendlandt [5,6].

EXPERIMENTAL

The LE apparatus has been described previously [6,7]. The outputs from the photometer and temperature sensor were recorded on a Bascom-Turner Model 8110-4 data center recorder [8]. This recorder permitted disk storage of the raw data and mathematical manipulation to obtain the corrected LE data [9]. The sample sizes ranged in mass from 3 to 29 mg; a furnace heating rate of 12°C $\min^{-1}$, and an oxygen gas flow rate of 40 ml $\min^{-1}$ were employed.

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The guanidine salts were obtained from Eastman Organic Chemicals, Rochester, NY.

RESULTS AND DISCUSSION

As noted by previous investigators, the guanidine salts generally decompose by a vigorous exothermic reaction, which accounts for their use in explosives and rocket propellant formulations. Rather surprisingly, the tetraborate, phosphate, sulfate, and polyphosphate salts, among others, are used as fireproofing agents [10]. A formulation with ammonium nitrate, triethyl acetylcitrate, cellulose acetate, guanidine nitrate, and others, has been proposed as a rocket propellant mixture [11].

The unusual light emission properties of selected guanidine salts are shown in Figs. 1 and 2.

Three types of LE behavior are noted for these compounds: (a) narrow band light emission similar to that observed for coordination compounds; (b) ignition of the compound; and (c) weak, broad LE spread out over a wide temperature range. Guanidine sulfate and chromate exhibit type (a) LE. Like coordination compounds [5,6] containing reducing (NH_3, ethylenediamine, etc.) and oxidizing (NO_3^-, ClO_4^-, SO_4^{2-} etc.) groups, guanidine sulfate and chromate possess reducing and oxidizing ions. Hence, the LE curves are similar to those observed for coordination compounds. The highly exothermic nature of the decomposition reaction is clearly shown by the LE curve of guanidine chromate in which there is a rapid temperature excursion that distorts the temperature axis of the curve. This behavior has previously been seen on the LE–DTA curves of certain coordination compounds [6].

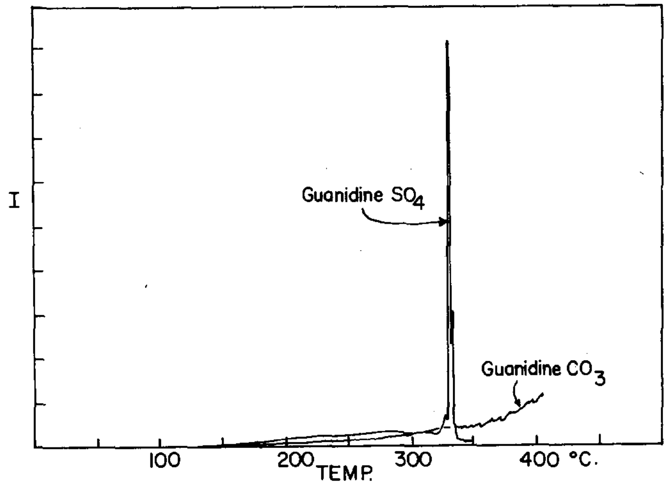

Fig. 1. LE curves of guanidine sulfate and carbonate.

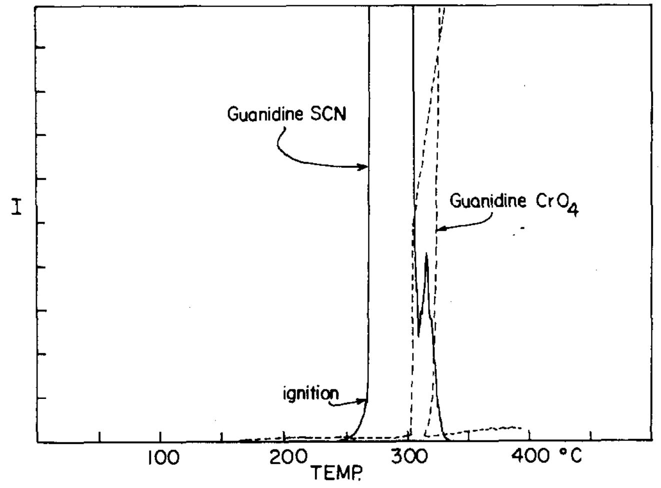

Fig. 2. LE curves of guanidine thiocyanate and chromate.

Guanidine thiocyanate exhibits type (b) LE in which the compound or its decomposition products ignite during the reaction. Since the reaction was carried out in an oxygen atmosphere, this behavior is probably expected.

Type (c) LE behavior is shown by guanidine carbonate and also guanidine chloride (not shown here). The LE observed for the carbonate was probably more a result of background radiation than any thermal process, while the chloride did not exhibit any LE properties. This behavior is understandable in that carbonate and chloride ions are not considered to be oxidizing anions.

CONCLUSIONS

In type (a) LE compounds, the light emission is the result of an internal redox reaction involving oxidizing and reducing groups. It is not a surface oxidation which results in oxyluminescence. Type (b) LE is due to the ignition of the compound or its decomposition products; it would not occur in an oxygen-free atmosphere. This type of LE has been previously investigated for various substances by Collins and Wendlandt [12]. The last type of LE, type (c), results in a very weak LE or else none at all, and is exhibited by guanidine salts containing non-oxidizing anions.

ACKNOWLEDGEMENT

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