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Note

THE LIGHT EMISSION OF THERMALLY STIMULATED PROCESSES. SOME HYDRAZINIUM AND AMMONIUM SALTS

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The measurement of the light emitted by thermally stimulated processes has been of interest in this laboratory for a number of years. Two principle types of light emission have been studied: (a) oxyluminescence; and (b) light emission of compounds containing vigorous oxidizing and reducing groups. In oxyluminescence, a surface reaction of the compound with molecular oxygen is probably responsible for the light emitting process [1]. Numerous polymers, both natural and synthetic, exhibit this phenomena when heated to moderate temperatures (150–300°C) in the presence of air or oxygen atmospheres. In the second type of compounds, an internal redox reaction involving the oxidizing and reducing groups is responsible for the light emission processes. This phenomena has been noted in coordination compounds involving both oxidizing and reducing ligands [2–4].

In a continuation of the investigations of the light emission (LE) of the second type of compounds [4], we wish to report the LE of some hydrazinium, ammonium and hydroxylammonium salts.

EXPERIMENTAL

The LE apparatus used has been previously described [3]. A furnace heating rate of 12°C min^{-1} was employed on samples whose mass ranged from 5 to 20 mg. All measurements were made using a dynamic O_2 atmosphere with a flow rate of about 40 ml min^{-1}. The voltage output from the photometer and the temperature of the sample-holder, as detected by a Chromel–Alumel thermocouple, were recorded on a Bascom–Turner Model 8110-4 data center recorder [5]. The LE curves were not corrected for background emission [6].

The compounds used were all commercially available samples obtained from various manufacturers.

RESULTS AND DISCUSSION

The LE curves of the various compounds are given in Figs. 1 and 2.

The thermally stimulated processes of these compounds results in narrow

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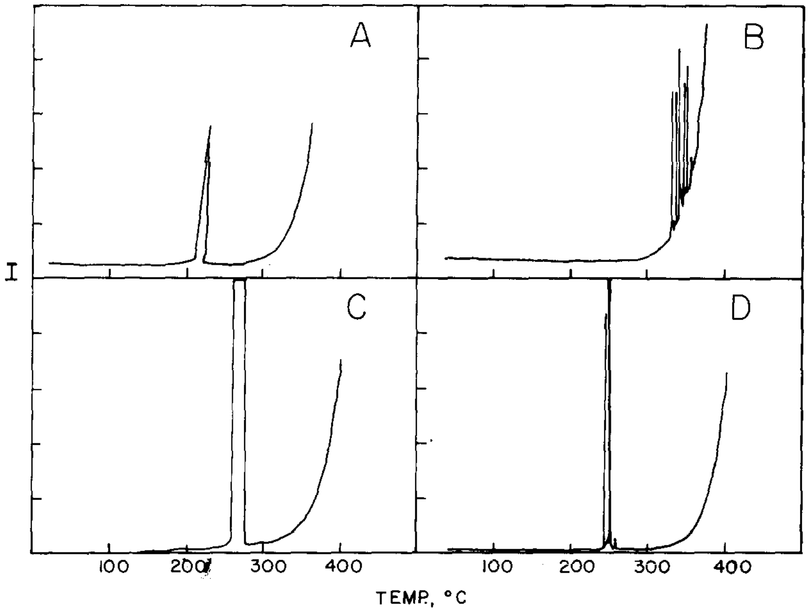

Fig. 1. LE curves of various compounds. (A) Hydroxylammonium sulfate (I/2); (B) ammonium sulfate (I/2); (C) hydrazinium sulfate; and (D) ammonium dichromate.

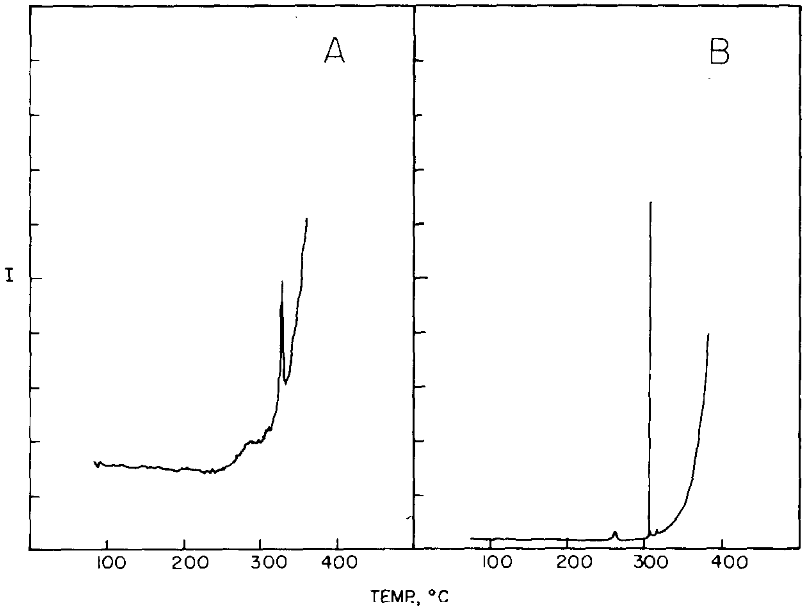

Fig. 2. LE curves of various compounds. (A) Hydrazinium chloride (I/10); and (B) sulfamic acid.

LE peaks which extend over a 10–20° temperature interval in the 200–350°C temperature range. This behavior is similar to that observed for various coordination compounds previously reported [2,3]. The LE process is a result of the highly exothermic dissociation reaction involving various redox reactions. This is evident in the LE curve of hydroxylammonium sulfate shown in Fig. 1A. This curve peak, which has a slope leaning towards the higher temperature side of the x-axis, is a result of the increase in sample-holder temperature caused by the exothermic thermal dissociation reaction.

The two ammonium salts investigated, ammonium sulfate and ammonium dichromate, Fig. 1B and D, exhibited numerous narrow LE peaks. These narrow peaks, in the former compound, were almost masked because of the background emission of the furnace and sample-holder. In both compounds, the NH_4^+ ion acted as the reducing agent while the sulfate and dichromate ions were the oxidizing agents, respectively. The LE curve of ammonium dichromate was similar to that previously obtained by Collins and Wendlandt [7] who used a different experimental apparatus. In both investigations, the main LE reaction occurred between 200 and 300°C.

The two hydrazinium salts, hydrazinium sulfate and hydrazinium chloride, Fig. 1C and Fig. 2A, respectively, also exhibited narrow LE peaks. The curve for the latter compound is similar to that observed for ammonium sulfate. The former compound, however, exhibited a prominent LE peak in the 200–300°C temperature range.

The last compound investigated, sulfamic acid, gave a small LE peak at about 260°C and a much larger peak, which was very narrow, at 310°C.

For all of the compounds reported here, the LE curves were similar to those observed for coordination compounds and guanidinium salts [4]. They all involved internal redox reactions activated by thermally stimulated processes.

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