THERMAL PROPERTIES OF MOLTEN SULPHUR-OXYANIONIC SALTS

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Lithium, sodium, potassium and ammonium bisulphate have been shown by detailed TG/DTA studies to have limited application as molten solvents. By contrast, the eutectic bisulphate systems, ammonium-potassium bisulphate and sodium-potassium bisulphate, appear to be excellent molten solvents in view of their low melting points, long liquid ranges and prolonged thermal stability at 200°C. In contrast to previous studies, potassium pyrosulphate has been found to be an excellent molten solvent, provided rigorous preliminary drying procedures have been applied.

A thorough knowledge of the thermal stability of a salt melt is an essential prerequisite if the melt is to be used as a reactive solvent for inorganic solutes. The relatively low melting points of alkali metal and ammonium bisulphates, and also alkali metal pyrosulphates suggest that these compounds may be useful reactive molten solvents. The present work involves various one- and two-component salt systems with a view to investigating the usefulness of these salts as molten solvents. The thermal properties of several of these systems have been reported previously [1-9], however, the wide variation in results due to differences in preliminary sample preparation, operating conditions, and precision of thermoanalytical equipment, made a thorough re-examination of these systems necessary. Isothermal thermogravimetric studies on most of the systems have not been previously reported. The salts investigated in the present programs are sodium bisulphate, potassium bisulphate, lithium bisulphate, ammonium bisulphate, eutectic sodium-potassium bisulphate, eutectic potassium-ammonium bisulphate, and potassium pyrosulphate.

Experimental

Materials

Potassium bisulphate (E. Merck, analytical reagent grade), sodium bisulphate (BDH, Analar), and ammonium bisulphate (Unilab, AR grade), were all ground and dried in a vacuum oven at ~100°C prior to use. This drying procedure for bisulphates has been suggested previously [10]. Lithium bisulphate was prepared by a procedure described in the literature [11], and was dried over P₂O₅. Potassium...
pyrosulphate (E. Merck, analytical reagent grade) was dried by melting at 450° followed by careful evacuation over several hours until water evolution ceased. Potassium bisulphate—sodium bisulphate (53.5% NaHSO₄) and potassium bisulphate—ammonium bisulphate (83% NH₄HSO₄) eutectics were prepared by fusing weighed quantities of the salts together and then filtering the resultant melt in an oven at 160° through sintered disc filter. The water-white melt obtained was then solidified and stored in a dry-box.

Instrumentation

Thermogravimetric analysis was carried out on a Rigaku—Denki (Thermoflex) modular thermal analysis system capable of simultaneous measurement of thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG). The samples, ~20 mg, were heated at 10° per minute in tall open silica crucibles (6 mm x 5 mm) under a constant nitrogen stream (0.1 N per minute) using dry aluminium oxide as the reference material. The finely powdered samples were weighed into the crucibles using a Sartorius Digital Microbalance 2405. It was found necessary to apply rigorous calibration procedures to allow for apparent mass changes which occurred under constant nitrogen flow with temperature increase, and also mass changes which occurred under isothermal heating in a nitrogen stream. The mass range used, 10 mg, was very carefully calibrated with standard masses prior to use and finally checked using the thermal decomposition of calcium oxalate monohydrate as calibrant.

Infrared spectra were measured on a Perkin—Elmer 457 grating spectrophotometer, mass spectra were measured on a Jeol JMS D100 mass spectrometer and Raman spectra were measured on a Spex Ramalog 5 laser Raman spectrometer.

Results

The DTA of potassium bisulphate (Fig. 1) showed that the solid underwent a solid-solid phase change just prior to melting. The melting was accompanied by a very large endothermic peak in the DTA profile at 207°. The TG profile showed that the melt was stable to ~240° under the experimental conditions and then began to show a gradual mass loss which was essentially constant to ~500°. At this latter temperature a step appeared in the TG profile and with further temperature increase, the sample showed steady mass decline to the ceiling temperature of 1000° (Fig. 1).

Corrected mass losses showed that the observed behaviour was consistent with constitutional water loss being almost complete at 500° (> 95%), although it was difficult to assign an exact figure since the TG profile was not horizontal at 500° but changed gradient at this temperature. A rapid mass loss was observed from 500 to 650° (cf. K₂S₂O₇), and from 650 to 800°, a "knee" was evident in the TG profile. This region of the DTA profile showed endothermic drift and also a weak