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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°. 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° 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 P_2O_5. 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% $NaHSO_4$) and potassium bisulphate–ammonium bisulphate (83% NH_4HSO_4) 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 × 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. $K_2S_2O_7$), 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 broad endothermic peak at ~650°. The mass loss to 650° corresponded to a total loss of 24%. At 1000° the mass loss was ~34% which was consistent with almost complete production of potassium sulphate (theoretical ≃36%).

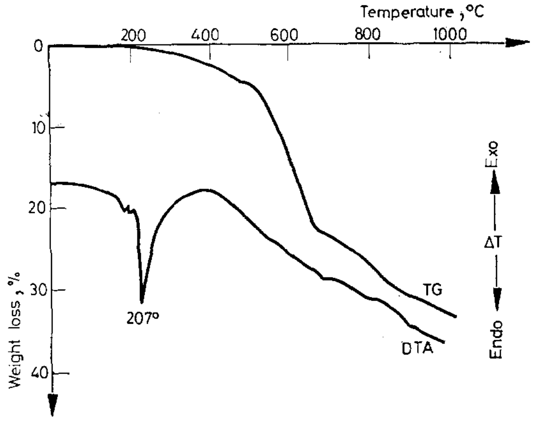

Fig. 1. TG and DTA curves of $KHSO_4$ in N_2 atmosphere

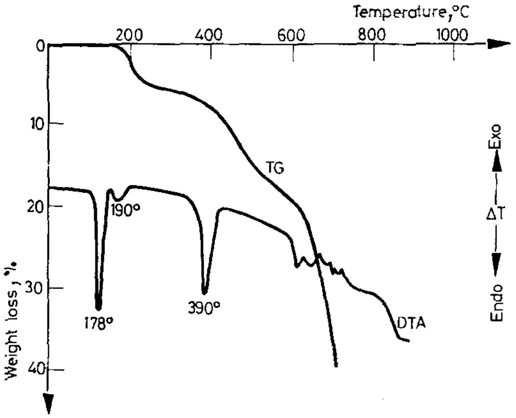

Fig. 2. TG and DTA curves of $NaHSO_4$ in N_2 atmosphere

The DTA of sodium bisulphate showed a most pronounced endotherm at ~178° (melting point) and a smaller endothermic peak at ~190° accompanied by a small step in the TG profile corresponding to 5.7% loss in mass (Fig. 2). A further endotherm was observed at ~390° and corresponded with a change in direction of the TG profile. The mass loss to this point was ~7.4%; theoretical loss for complete pyrosulphate production was 7.5%. The DTA profile at temperatures >600° showed considerable "noise" probably due to gases escaping from the decomposing pyrosulphate mass. In one analysis, a large solid bubble

~1 cm in diameter was formed on the lip of the sample pan on heating $NaHSO_4$ to 1000°. The total weight loss to 900° corresponded to almost complete production of sodium sulphate (i.e. found 43%, theoretical ~41%).

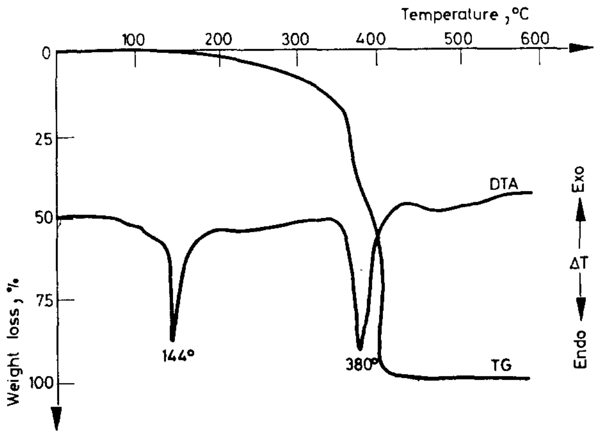

Fig. 3. TG and DTA curves of NH_4HSO_4 in N_2 atmosphere

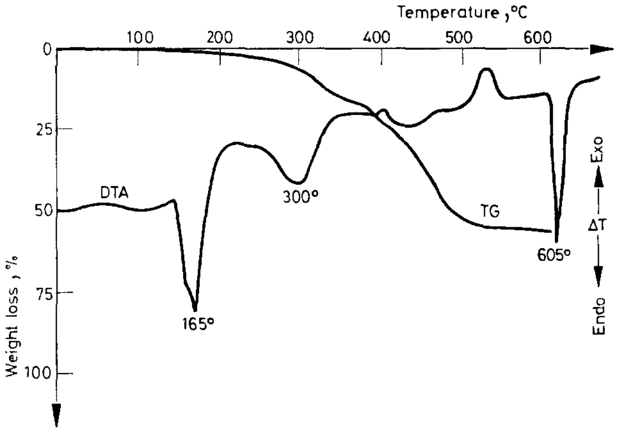

Fig. 4. TG and DTA curves of $LiHSO_4$ in N_2 atmosphere

The DTA profile of ammonium bisulphate showed a strong endotherm at the melting point (144°) and another large endotherm at ~380° (Fig. 3). The TG profile showed that NH_4HSO_4 lost mass slowly beginning at ~160° and the rate of mass loss increased steadily to ~300° where a dramatic change took place, the rate of mass loss being maximal at ~380°. The shape of the TG profile in this region indicated that the decomposition was probably not a simple one-step process. The mass loss at ~430° corresponded to ~97% of the NH_4HSO_4 added and the TG profile at this temperature was essentially horizontal.

The DTA profile of lithium bisulphate showed a large endotherm at ~165° and a shallow broad endotherm at ~300° (Fig. 4). The DTA profile was quite complex in the 400 – 500° region, where a large mass loss took place. The mass loss to ~550° was ~49% (theoretical for production of Li_2SO_4, 47.1%) and both the TG and DTA profiles were essentially steady at this temperature. The appearance of a strong endotherm at 605° is consistent with a solid state phase change in lithium sulphate [12].

The DTA profile of eutectic potassium–ammonium bisulphate showed a large endotherm at ~110° (melting) and another endotherm at 400° (Fig. 5). The TG profile showed a plateau to ~250° where a slight mass loss began. A steep descent was observed from ~300 to 400°. The mass loss to 400° was ~77%, although

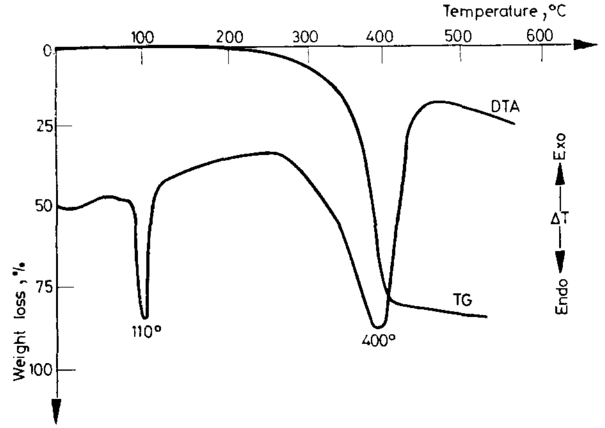

Fig. 5. TG and DTA curves of $NaHSO_4$: $KHSO_4$ eutectic in N_2 atmosphere

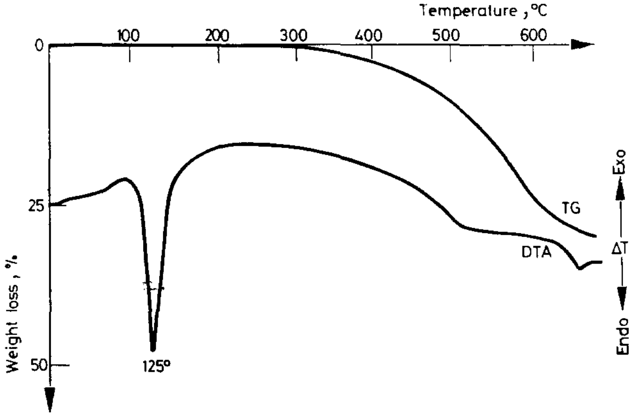

Fig. 6. TG and DTA curves of NH_4HSO_4 : $KHSO_4$ eutectic in N_2 atmosphere

the TG profile indicated that extra mass loss was occurring slowly after this temperature (theoretical mass loss for loss of NH_4HSO_4, 83%). An isothermal study showed that on holding the melt at 200° for an extended period, only a very slight mass loss took place (Fig. 8.)

The DTA profile of sodium-potassium bisulphate eutectic showed a single sharp endotherm at 125° (melting) (Fig. 6).

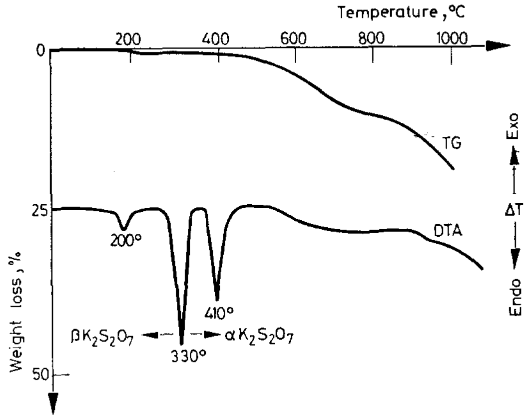

Fig. 7. TG and DTA curves of $K_2S_2O_7$ in N_2 atmosphere

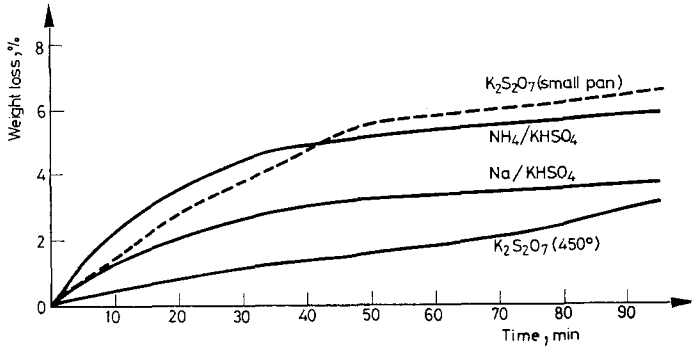

Fig. 8. Fully corrected isothermal mass change at 200° for bisulphates in N_2 stream and at 450° for potassium pyrosulphate

The TG profile was essentially horizontal to ~230° where a very slow change began. The rate of mass loss was slow and constant to ~450° where the rate of change accelerated. Isothermal studies at 200° under nitrogen showed that only minor changes were occurring in the melt. No signs of sulphur oxides were evident in the mass spectrum of the vapour above the melt even after several hours at 200°.

DTA of potassium pyrosulphate showed a weak endotherm at 200° and large endothermic peaks at 330 and 410° (Fig. 7). The DTA showed no sign of water evolution which meant the success of the drying procedure. Raman and infrared spectra of the solid pyrosulphate were identical with those reported in the literature [13] and the solid yielded >99.4% of the expected acid content (acidimetric determination). These results indicated clearly that the drying procedure was not in any way detrimental to the pyrosulphate.

The TG profile was horizontal to ~200° where a small mass change took place. The profile was essentially horizontal to 470° where a mass loss was evident, the rate being maximal at ~510°. The rate of descent slowed considerably at 610° and was constant to 700° where the rate of mass loss increased and was still increasing at the ceiling temperature of 960°.

Isothermal studies at 450° showed only minor change when the melt was held for an extended period.

Discussion

The thermal analyses reported in this paper have all been carried out under nitrogen atmosphere (dynamic), employing rigorous calibration procedures and involved very careful preliminary drying procedures. This differs from previous reports on some of these compounds where analysis was carried out in air and no buoyancy corrections were applied [8]. The absence of adhering moisture in the compounds, as evidenced in the DTA and TG profiles, verified the success of the drying procedures used.

Potassium bisulphate and sodium bisulphate were both found to behave in a manner similar to that reported by De Vries and Gellings [8]. The results showed quite clearly that constitutional water loss in these compounds began soon after melting and was complete when the pyrosulphates formed began to decompose. In the case of sodium bisulphate, the bisulphate is much less stable forming pyrosulphate rapidly. This conclusion is substantiated by the appearance of an endotherm at 390° in the DTA profile due to the melting of $Na_2S_2O_7$ (melting point ~400°). The interrupted nature of the TG profile in both of these compounds suggested that bisulphate decomposition, to ultimately yield sulphate, is not a simple two-step process but involves the formation of a complex series of intermediate compounds. The degree of complexity of the thermal decomposition mechanism would appear to be greater for sodium bisulphate than for potassium bisulphate. Both of these compounds have very narrow melt ranges, although potassium bisulphate showed some promise as a molten solvent provided the temperature was not permitted to exceed 250°.

Lithium bisulphate was found to be most unstable and was showing mass loss prior to the melting point at 165°. DTA and TG data indicated that lithium bisulphate was converted almost completely to lithium sulphate at ~500°. The extreme hygroscopic nature of this salt (as evidenced in moisture uptake despite extreme precautions) together with inherent thermal instability of the melt, made this material unsuitable as a possible molten solvent.

Ammonium bisulphate was found to be a reasonably stable melt at temperatures slightly above the melting point. The melt appeared to lose constitutional water beginning at 200° and pyrosulphate formation was effectively complete at 300° after which a rapid decomposition was observed which ultimately resulted in complete volatilization of the decomposition product. This observation was not surprising since the likely product, $(NH_4)_2SO_4$, is unstable at these temperatures.

The eutectic bisulphate systems $NH_4HSO_4 : KHSO_4$ and $NaHSO_4 : KHSO_4$ undoubtedly offer the best balance of thermal properties for a molten bisulphate; low melting points, long liquid ranges and satisfactory thermal stability. While they have relatively low melting points, the liquids are very viscous at temperatures just above the melting point and need to be used at temperatures in the 160 – 200° range to facilitate easier manipulation. Isothermal studies showed conclusively that these solvents were fairly stable on extended heating at 200°, however, the lifetime of the melt is limited. Thermal decomposition of the $NaHSO_4 : KHSO_4$ eutectic appeared to proceed via a series of complex intermediates in a manner similar to the constituent bisulphates. This is supported by the appearance of shallow endotherms at ~500° and 650° in the DTA profile.

Potassium pyrosulphate was found to be more stable than is expected on the basis of previous reports [4, 5]. This may have been due to the effective removal of water from the pyrosulphate by the evacuation procedures employed. Spectroscopic, acidimetric and TG/DTA studies all confirmed the success of the drying procedure. The DTA profile showed three endothermic peaks at 200°, 330° and 410°. The cause of the 200° peak is uncertain although it is conceivable that the potassium pyrosulphate could contain a small amount of potassium bisulphate. The melting point at 410° was preceded by a solid-solid crystal structure change from the β form to the α form at 330° [14]. The melt did not appear to show significant decomposition until ~500° after which a slow decomposition was observed. As in the case of potassium bisulphate, the TG profile indicated that the decomposition proceeded via formation of a complex intermediate rather than a simple one-step production of sulphate.

One further observation that may well account for discrepancies in previous reports on pyrosulphates, and possibly bisulphates also, was that the rate of thermal decomposition was markedly affected by the sample pan geometry. In Fig. 8, an isothermal study is shown of potassium pyrosulphate at 450° (under nitrogen) using shallow silica crucibles (2.5 mm × 5 mm). Comparison of this plot with that for the deeper crucibles illustrates clearly that the melt exhibited more stable behaviour in the deeper crucible. This phenomenon is not unusual and in this system is probably a result of an equilibrium established in the container volume above the melt surface in the larger container. Such an equilibrium could not be established in the shallow silica crucibles under a dynamic nitrogen atmosphere. The taller crucibles employed in the current studies were used because it was considered that they allowed a closer approximation to the situation when a molten salt was maintained in a tube furnace at elevated temperatures. The results indicated that this was a valid assumption.

In further isothermal studies under static nitrogen atmosphere, potassium pyrosulphate was found to liberate sulphur dioxide at temperatures >500° as evidenced by a mass spectrum of the evolved gas. This observation supported the conclusion based on isothermal TG/DTA studies that "dry" potassium pyrosulphate melt was essentially stable at 450° and could be used as a satisfactory molten inorganic solvent.

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Résumé — On montre par une étude TG/ATD approfondie que les hydrogénosulfates de lithium, de sodium, de potassium et d'ammonium n'ont qu'une application limitée en tant que solvants fondus. Les systèmes eutectiques des hydrogénosulfates ammonium/potassium et sodium/potassium paraissent, au contraire, être des solvants fondus excellents, en raison de leurs points de fusion bas, de leurs larges intervalles d'existence à l'état liquide et de leur stabilité thermique prolongée à 200°. Contrairement à des études antérieures, on a trouvé que le pyrosulfate de potassium est un solvant fondu excellent, à la condition d'appliquer un mode opératoire rigoureux lors du séchage préliminaire.

Zusammenfassung — An Hand eingehender TG/DTA-Untersuchungen wurde gezeigt, daß die Bisulfate von Lithium, Natrium, Kalium und Ammonium nur eine begrenzte Anwendung als geschmolzene Lösungsmittel finden können. Die eutektischen Bisulfat-Systeme Ammonium/Kalium Bisulfat und Natrium/Kalium Bisulfat scheinen wegen ihrer niedrigen Schmelzpunkte, ihres weiten Flüssigkeitsbereichs und ihrer dauerhaften Thermostabilität bei 200° ausgezeichnete geschmolzene Lösungsmittel zu sein. Im Gegensatz zu früheren Untersuchungen erwies sich Kaliumpyrosulfat als ein ausgezeichnetes geschmolzenes Lösungsmittel, vorausgesetzt daß vorangehend strenge Trocknungsverfahren angewandt wurden.

Резюме — Детальными ТГ/ДТА изучениями показано, что бисульфат лития, натрия, калия и аммония имеют ограниченное применение в качестве расплавленных растворителей. В противоположность этому, такие эвтектические бисульфатные системы как аммоний-калий и натрий-калий бисульфаты являются превосходными расплавленными растворителями с точки зрения их низких температур плавления, широкожидкостных областей и продолжительной термической стабильности при 200°. В противоположность предыдущим исследованиям, было найдено, что пиросульфат калия может быть превосходным расплавленным растворителем при условии, что применены строгие предварительные процессы сушки.