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Simultaneous differential scanning calorimetry and reflected light intensity (DSC–RLI) in the study of inorganic materials

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Abstract

This paper re-examines work on inorganic materials and oxalates, but combines differential scanning calorimetry (DSC) measurements with simultaneous observation and recording of the reflected light intensity to obtain more detailed information about the physical and chemical changes occurring. The method indicates the nature of the changes recorded by the DSC, both physical and chemical and gives additional confirmation of the nature of complex and overlapping DSC peaks for ammonium salts, copper carbonate and the potassium oxalato-complexes of aluminium, copper, iron and chromium. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In September 1964, at a Symposium on Thermal Analysis held at Battersea College of Technology, Dr. David Dollimore gave a lecture entitled "The use of TGA in studying the Thermal Decomposition of Oxalates" [1]. The methods and investigations described at this symposium encouraged many workers to try to apply them in other fields of chemistry and materials science. Both the instrumentation and the applications of thermal analysis have multiplied in the intervening years, but the fascination of experimenting with thermal methods on an industrial or laboratory sample remains.

The changes in colour and texture which may occur in inorganic substances when heated have been investigated by many workers, and an especially important paper by Harmelin and Duval [2] published in 1962 describes the results for 32 inorganic substances heated between 35°C and 450°C and showed that allotropic changes, dehydration and decomposition can all cause colour changes. They stress that the nature of the sample, the rate of heating and the surrounding atmosphere may affect the temperature at which these changes occur and hence caution should be used if they are to be employed as temperature indicators. They also note the value of thermogravimetry in clarifying certain of the observed changes. Their paper was in honour of the 70th birthday of Prof. Fritz Feigl, which gives an added relevance here.

Dollimore and his co-workers have made vital contributions to the subsequent work using thermoanalytical and other techniques on a very wide range of materials through their papers on oxalates [3–8], formates [9], sintering and surface studies [10,11] and a wide range of other topics. At the conclusion of his Battersea paper [1] he comments that "to derive the

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maximum information from thermal decomposition studies, all possible methods must be used''. This is still as true today, but frequently some methods such as thermomicroscopy remain under-used.

It has been shown that by combining DSC with observations using a microscope and recording the light intensity reflected from the sample reflected light intensity (RLI), significantly more information may be obtained [12]. Other instruments study DSC and the light transmitted through a transparent sample [13] to give similar observations. The advantage of using reflected light becomes apparent when the sample is opaque. The DSC–RLI method has been used to study phase changes of both organic and inorganic materials, the decomposition of copper sulphate pentahydrate and manganese formate dihydrate [12], tin formate [14] as well as polymers [15], foods [16] and fire-retarded materials.

While the full and formal investigation of decompositions requires a large amount of time, sophisticated equipment and the study of many relevant earlier studies, a simple quantitative investigation of some thermal decompositions may be a valuable educational exercise [17]. The direct observation of mass loss and of colour change will give both quantitative and qualitative analytical information on the structure and decomposition mechanism of inorganic compounds. Although direct observations of optical changes have often been noted, there are advantages to recording the optical and energetic events simultaneously.

2. Experimental

The apparatus used in these investigations has already been described [12]. It comprises a Perkin-Elmer DSC 1-B fitted with a Beck stereo microscope. A light–tight cover replaced the normal DSC cell cover. The RLI detector was a CdS photoconductive cell, and the amplified RLI signal was recorded on the same chart recorder as the DSC temperature and heat-flow signals. The DSC was calibrated in accordance with the manufacturers instructions with high-purity metals. Confirmatory TG runs were performed under similar conditions using a Perkin-Elmer TGA 7 system.

Samples as originally received were fine powders and in each case about 15 mg was placed in open aluminium sample pans. The heating rate was generally 16 K/min and the atmosphere static air. Since the maximum temperature which could be reached on this instrument was 500°C, some changes did not occur to completion, but direct observation indicated the probable course of reaction. The primary objective of this work did not include the quantitative determination of the enthalpies of the various changes observed. The sensitivity of the DSC corresponded to a full-scale deflection of around 100 mW.

The experimental curves from the 3-pen recorder were scanned into a computer and digitised into a spreadsheet. Since open pans needed to be used for sample observation and measurement, the baseline of the DSC trace tended to be curved. While this was certainly due to reaction in some cases, it was possible to correct for the curvature of a ''no-sample'' baseline using a simple computer program on the digitised DSC data. The offset between the DSC and RLI traces was also corrected.

3. Results and discussion

3.1. Ammonium nitrate NH_4NO_3

The sample was a laboratory-grade material. In a previous paper, the DSC–RLI results for potassium nitrate were reported [12] and for that sample the small alteration in the intensity which occurs at the transition at 128°C was enhanced when a pre-melted sample was run. A sample of ammonium nitrate recrystallised in the pan from just above the melting point gave very clear changes in RLI exactly corresponding to the endothermic DSC peaks as shown in Fig. 1.

The first transition, at around 41°C with a small increase in RLI corresponds to the IV → III phase change. The second transition at 83°C is the III → II phase change and shows a small decrease in RLI. The third change gives a very large DSC peak at 129°C, but on the RLI trace it is indicated by a change of slope. This is the II → I change and is followed by the major event of the melting of phase I at 170°C. Factors affecting these transitions have been discussed by Dellien [18]. The possible causes for alterations in reflectance have been considered [12] and the change in the molar refraction, R_L, is one of the reasons. This

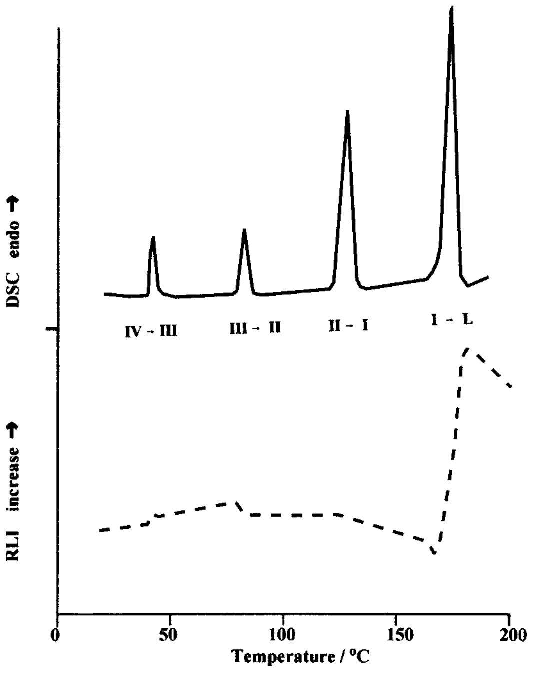

Fig. 1. DSC–RLI of recrystallised ammonium nitrate.

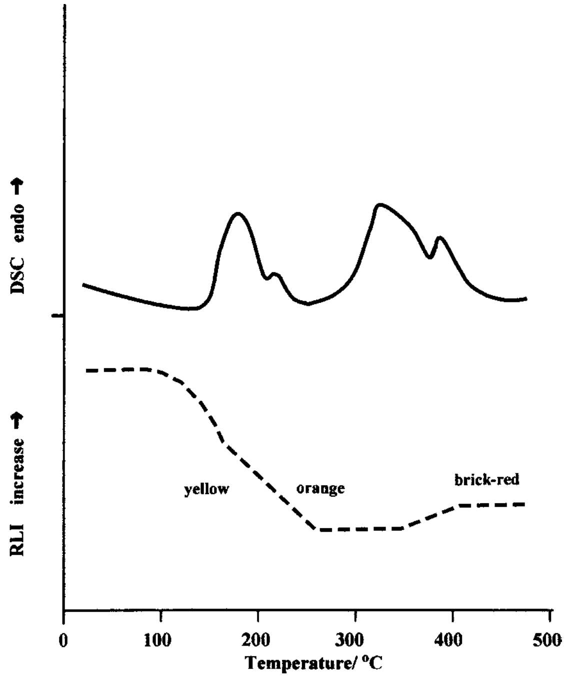

Fig. 2. DSC–RLI of ammonium metavanadate.

quantity is a composite of the molar volume and the refractive index:

$$R_L = V_m\{n^2-1\}/\{n^2+2\}.$$

Szabo et al. [19] report that there is an expansion at the first transition and assuming that the refractive index n of the phases is similar, this would correspond to an increase in the molar volume, V_m and hence an increase in R_L. The contraction at the second transition reverses this. More complex behaviour occurs at the third transition, while the melting produces a clear fluid and allows a very large increase in reflection from the base of the aluminium pan. It is evident that quite small changes in morphology may be observed and complement the measurement of heat changes by the DSC even if no change in the "colour" of the sample accompanies the transition.

3.2. Ammonium metavanadate NH_4VO_3

This sample was an "AnalaR" grade white powder. The DSC trace shows two broad endothermic peaks at around 217°C and 377°C with indications of possible overlapping reactions. The RLI starts to decrease at a much lower temperature of about 100°C turning gradually through light lemon-yellow to orange. From 180°C to 280°C, the powder darkened first to deep orange, and then to dark brown. During the second endotherm, the colour lightened to a strong brick-red by 450°C. This is shown in Fig. 2.

Although it has been suggested that the initial yellowing is due to the presence of potassium vanadate impurity [19] analysis failed to detect any potassium in this sample. The two-stage endotherm around 230°C has been attributed to the production of HVO_3 [2] with a 14.5% loss or $[(NH_4)_2O(V_2O_5)_2]$ (11.1% loss) and then $[(NH_4)_2O(V_2O_5)_3]$ (14.8% loss) [20] or several other possible intermediates. Since the mass losses by TG in the early part of the first stage total 11% and the loss in the complete stage is 14.8%, the ammonium oxyvanadates seem more likely and this is confirmed by analysis [19,21]. The colour changes also suggest this since the oxyvanadates are described as being "golden yellow, ruby red and garnet red" [22]. The second stage is the decomposition to vanadium pentoxide, V_2O_5, a brick red powder. The total loss amounts to 22.3% although it has been suggested that some reduction by ammonia to V_2O_4 may occur [23]. It is of interest that a very definite colour change at low temperatures is detected by RLI before any loss on TG or endotherm on DSC. This suggests that there is minimal bulk reaction and that the colour is confined to the surface of the powder. Recent work investigating ammonium metavanadate supported on alumina has confirmed this behaviour [24]. The many possible intermediates [22] have very similar colours and mass losses, so that distinguishing between them is complicated.

3.3. Basic copper carbonate $CuCO_3{\cdot}Cu(OH)_2$

Dollimore and Taylor [25] have published a comparative thermal analysis study of the decomposition of copper carbonate. In an investigation of various copper carbonates, the combined DSC–RLI technique has given useful additional information. The green mineral, malachite has the formula $CuCO_3{\cdot}Cu(OH)_2$ while azurite is $2CuCO_3{\cdot}Cu(OH)_2$ and deep blue. Other basic carbonates of copper have also been reported. The sample used here was prepared by mixing solutions of copper (II) sulphate and sodium bicarbonate, filtering, washing and drying the precipitate which was dark green in colour. It was shown by X-ray powder diffraction to have the malachite structure, although the broadened diffraction peaks suggested lower crystallinity than the mineral sample. The DSC and RLI curves are shown in Fig. 3. There is a small, broad DSC endotherm below 100°C, which corresponds to a mass loss of 2–3%. The RLI started to decrease at low temperature and continued to do so at an increasing rate as the temperature rose. The major endothermic decomposition occurred around 270°C after which the sample was dark brown or black. Above 330°C the RLI increased sharply and observations indicated that this was due to contraction of the sample, exposing the reflective base of the sample pan.

The final stages of the decomposition were not complete until about 350°C. These results generally agree with other work [25–27]. The small peak at low temperature is probably due to retained moisture. Since the development of the brown colour starts at low temperature also, this seems to form a part of the total structure. The single peak for DSC and for the complementary TG run, suggests that the loss of CO_2 and H_2O occurs at the same time which agrees with the findings of Henmi et al. [26,27]. The final shrinkage appears to be due to sintering of the very fine particles.

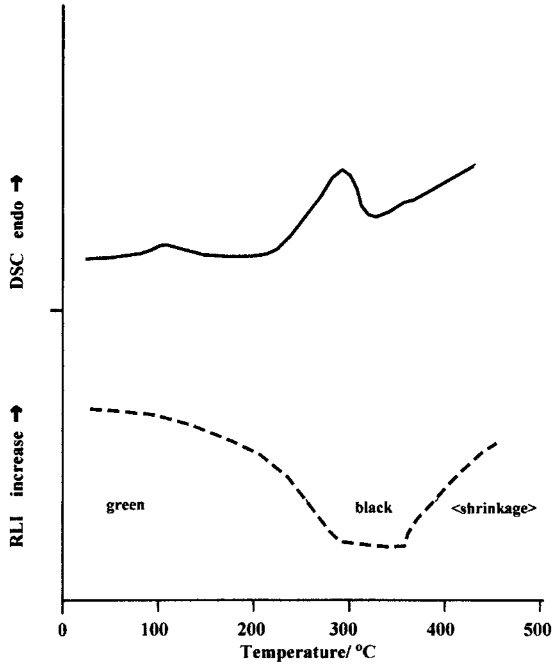

Fig. 3. DSC–RLI of basic copper carbonate.

3.4. Complex oxalates

The study of the thermal behaviour of simple and complex oxalates using thermal analysis and complementary methods has been greatly enhanced by the many papers of Dollimore and his co-workers. The effects of catalysis, atomic number, bond length and thermodynamic parameters and the multiplicity of techniques are all excellent examples of the power of thermal analysis [6]. The complex oxalates used here were prepared by methods reported in the literature [17,28,31].

3.4.1. Potassium trioxalato aluminate (III) trihydrate $K_3Al(C_2O_4)_3{\cdot}3H_2O$

The thermal analysis of this sample presents a more complicated situation than might be expected. Firstly, the water content can be variable and even "dry" samples are reported as having 3 [17] or 2.8 [28] moles of water. Secondly, hydroxo-oxalato aluminates may be present as a contaminant [28]. The thermal analysis

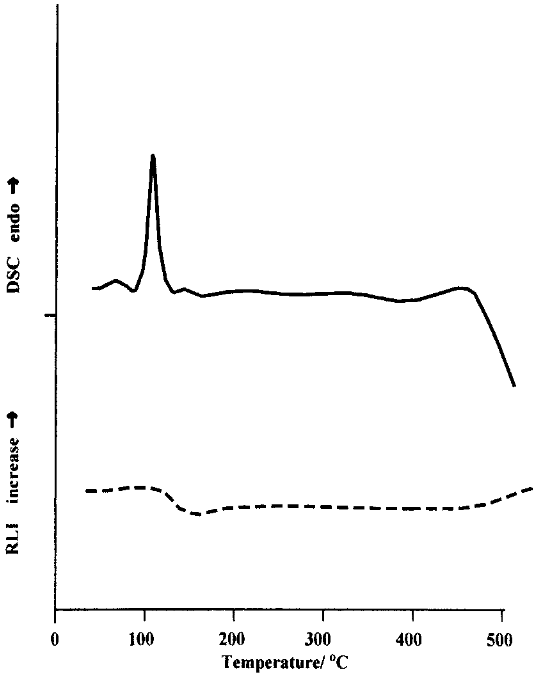

Fig. 4. DSC–RLI of potassium trioxalato aluminate (III) trihydrate.

curves shown in Fig. 4 present a rather incomplete picture of the decomposition. The sample used in this investigation was analysed by ICP and found to contain 25.8% K (theory: 25.3%) and 5.5% Al (theory: 5.8%). It also appeared to pick up atmospheric moisture easily and contained slightly more than $3H_2O$. The DSC shows several dehydration endotherms between room temperature and 300°C, of which the largest occurs around 100°C. This is confirmed by TG and is similar to the reported behaviour [28–30] of the loss of adherent water followed by a series of poorly-resolved dehydration steps at increasing temperature. The RLI changes little until the later part of the dehydration when it decreases, indicating that the largest structural change occurs with the elimination of the final H_2O. The sharp, exothermic phase change reported by Verdonk [28] around 250°C was not observed on the DSC, although a broad change in slope was noted and very slight changes in the RLI did occur around this temperature. The decomposition of the oxalatoaluminate structure starts around 400°C and overlaps the oxalate decomposition which continues until above 500°C, that is, above the range of this instrument. However, the commencement of these changes was signalled by a broad, shallow exotherm peaking around 400°C and followed by a strong exothermic deflection above 450°C. The RLI shows a small increase, as would be expected if the highly-reflective alumina is formed.

The changes observed and projected are as identified by Dollimore and co-workers [30].

$$K_3Al(C_2O_4)_3 \cdot nH_2O = K_3Al(C_2O_4)_3 + nH_2O$$

$$2K_3Al(C_2O_4)_3 = 3K_2C_2O_4 + Al_2O_3 + 3CO + 3CO_2$$

$$K_2C_2O_4 = K_2CO_3 + CO$$

These steps may be followed at higher temperatures by reaction to form the aluminate:

$$K_2CO_3 + Al_2O_3 = K_2Al_2O_4 + CO_2$$

and also the formation of K_2O. This accounts for the further mass losses up to 1300°C

3.4.2. Potassium trioxalato chromate (III) trihydrate $K_3Cr(C_2O_4)_3 \cdot 3H_2O$

Wendlandt et al. [31] performed TG and DTA runs on this dark green compound and found that it lost water around 100°C and decomposed in several stages between 300°C and 450°C and that the final residue at around 600°C in air was the yellow potassium chromate K_2CrO_4. House and Blumthal [32] detected five steps in the decomposition of this compound, Horvath and Kristof [33] report a rather simpler behaviour. The DSC–RLI curves for the potassium oxalato chromate (III) trihydrate and shown in Fig. 5. The endothermic dehydration gives several shallow peaks up to about 200°C and is accompanied by a decrease in RLI . The original greeny-blue crystals become less crystalline and darker. Between 150°C and 300°C, the RLI continues to decrease and a small exothermic peak at about 300°C, also reported in [33], coincides with a lessening of the rate of decrease. A strong exothermic trend commences around 350°C and continues to the upper temperature limit of 500°C and the RLI decreases until 450°C and then gradually increases. In order to achieve the highest conversion, the sample was held isothermally at 500°C for about 30 min, when the final colour was bright yellow and the product was fully soluble in water. Classical wet-analysis tests confirmed the presence of carbonate and chromate.

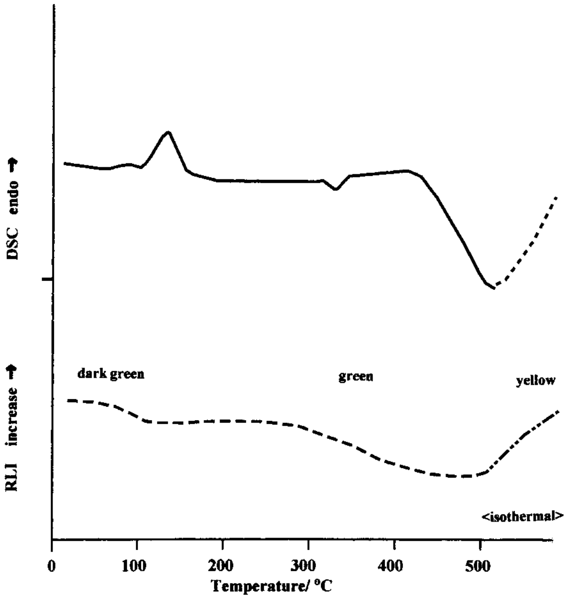

Fig. 5. DSC–RLI of potassium trioxalato chromate (III) trihydrate.

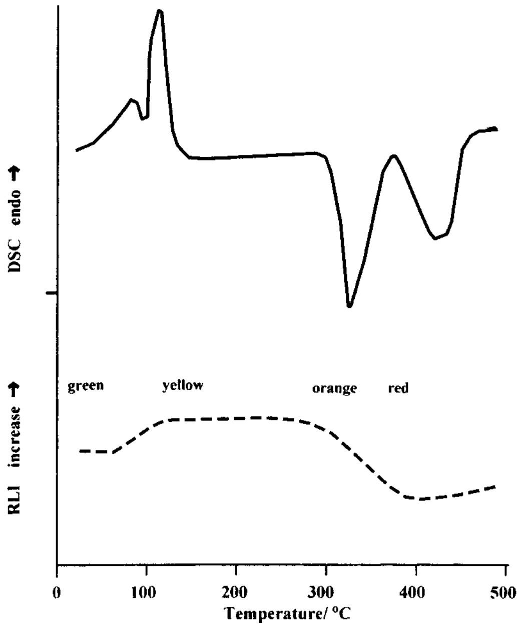

Fig. 6. DSC–RLI of potassium trioxalato ferrate (III) trihydrate.

The dehydration occurs over a fairly wide temperature range and involves at least two overlapping steps. The major RLI change coincides with the first stage. The anhydrous complex oxalate starts to decompose, possibly accompanied by a phase change, around 300°C, and the decompositions of the oxalates occur over the range 300–500°C and are followed in the later stages and at higher temperatures by the reaction in air to form the chromate:

$$K_3Cr(C_2O_4)_3 \cdot 3H_2O = K_3Cr(C_2O_4)_3 + 3H_2O$$

$$\begin{aligned} K_3Cr(C_2O_4)_3 &= 3/2K_2CO_3 + 1/2Cr_2O_3 \\ &\quad + 3CO + 3/2CO_2 \end{aligned}$$

$$K_2CO_3 + 1/2Cr_2O_3 + 3/4O_2 = K_2CrO_4 + CO_2$$

3.4.3. Potassium trioxalato ferrate (III) trihydrate $K_3Cr(C_2O_4)_3{\cdot}3H_2O$

This pale-green complex is light sensitive and was stored in a blackened container , but no colour change was observed when a sample was illuminated in the apparatus for 15 min at room temperature (Fig. 6). On heating, dehydration occurred almost immediately to produce light yellow crystals which became opaque at just above 100°C. These reactions corresponded to two strong endothermic peaks on the DSC trace. The anhydrous material started to decompose around 280°C and changed through orange to dark red by 360°C. This matched the large exothermic peak with a maximum at 350°C. The exotherm peaking at 400°C corresponded to a very small increase in the RLI the sample appearing to be more matt. The change to a dark red during the first exotherm suggests that this is corresponds to the decomposition of the complexed iron to its oxide, whereas the higher temperature exotherm would be due to the potassium oxalate decomposition. This agrees exactly with the findings of Dollimore and co-workers [4,5] and complements their findings with simultaneous observation and recording of the colour changes. The small exotherm at 260°C noted by Horvath and Kristof [33] was not observed with this sample.

3.4.4. Potassium dioxalato cuprate (II) dihydrate $K_2Cu(C_2O_4)_2{\cdot}2H_2O$

This blue, crystalline compound gives the thermal analysis curves shown in Fig. 7. The dehydration gives a single endotherm peaking at about 120°C and accompanied by a colour change from blue crystals to an opaque light-blue mass, resulting in an increase in RLI. The mass loss for this stage (10.1%) confirms the presence of two molecules of water of crystal-

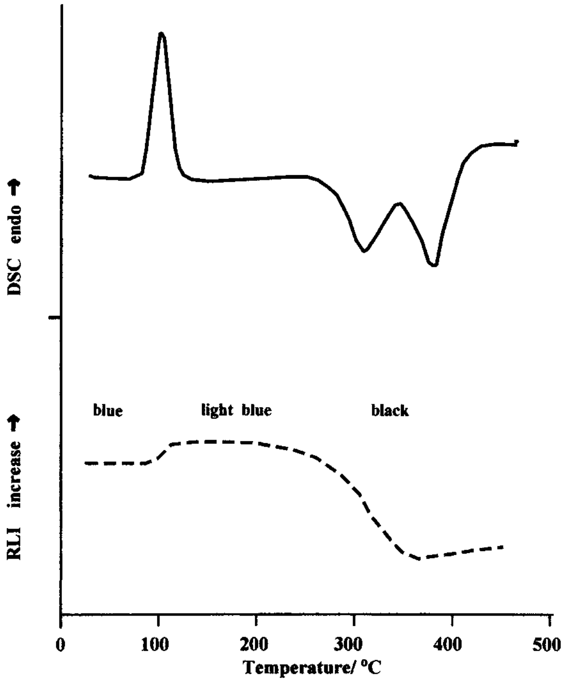

Fig. 7. DSC–RLI of potassium dioxalato cuprate (II) dihydrate.

lisation. The anhydrous complex oxalate is stable up to about 270°C when decomposition occurs in two exothermic stages. During the first stage up to 320°C, the sample turns black with a large decrease in RLI, whereas in the second, from 320°C to around 400°C, little change in the intensity trace occurs. This strongly suggests that the first exotherm is due to the decomposition of the complex to copper (II) oxide, while the second stage corresponds to the loss of CO and the formation of potassium carbonate. The total mass loss of 38.9% agrees with the reactions:

$$K_2Cu(C_2O_4)_2 \cdot 2H_2O = K_2Cu(C_2O_4)_2 + 2H_2O, \quad \text{loss } 10.2\% \text{ (calc.)}$$

$$K_2Cu(C_2O_4)_2 = K_2C_2O_4 + CuO + CO + CO_2, \quad \text{loss } 20.4\% \text{ (calc.)}$$

$$K_2C_2O_4 = K_2CO_3 + CO, \quad \text{loss } 7.9\% \text{ (calc.)}$$

In the presence of air, the CO is oxidised to CO_2 and thus little reduction of the copper oxide occurs. No evidence of metallic copper was found in these experiments. Although Dollimore and co-workers [34] found the decomposition reactions in air to yield a single DTA exotherm, the two stages of the decomposition, of the complex and of the potassium oxalate were well separated on the DSC and the complementary TG runs, provided small samples were used. However, since the decompositions are highly exothermic larger samples cause them to overlap considerably.

4. Conclusion

The advice to employ every technique to separate and identify the changes which occur on heating has been heeded here. Direct observation of the changes, their physical or chemical nature and the alteration of colour provides a useful additional method of confirming thermal events in a range of inorganic compounds.

The study of thermochromic changes has several potential applications. While some changes occur over a sufficiently narrow temperature range to act as temperature sensors or calibration materials, others may be useful as thermal indicators. Work on thermochromic changes in solution [35] and in solids [36–38] has demonstrated some of these applications and coating such temperature-sensitive materials onto fibre–optic probes may offer advantages in temperature control.

Other inorganic materials which have been studied include additives which impart fire-retardancy in polymer systems, organometallic catalysts and antiperspirants.

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