THE INFLUENCE OF SAMPLE CELLS FOR DIFFERENTIAL THERMAL ANALYSIS IN CONTROLLED ATMOSPHERES

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ABSTRACT

DTA curves for the thermal decomposition of uranyl oxalate trihydrate and ammonium vanadyl oxalate dihydrate, using different DTA instruments, are compared. It is shown that widely differing and misleading results can be obtained by an incorrect choice of sample cell. The anomalous effects are discussed in terms of the geometry of the sample holders and the consequent ease of removal of product gases and accessibility of the reactant gas.

It is recommended that uranyl oxalate trihydrate could be used to assess the conditions of flow-rate, sample size, etc., necessary to achieve correct atmosphere control with a given DTA cell.

INTRODUCTION

In a recent publication[1] we presented DTA results for the thermal decomposition of $UO_2 \cdot C_2O_4 \cdot 3H_2O$ and showed that widely different results could be obtained for the dehydration of the trihydrate to the monohydrate using different DTA equipment. The differences were attributed to differing cell designs, leading to varying efficiency of product water removal. We have since then re-examined DTA curves for dehydration reactions of other salts and conclude that inflexions on the main dehydration peaks for many of these could well be due to similar effects. Although the present discussion is concerned primarily with dehydration reactions as an illustration, the inferences apply equally well to atmosphere control during other reactions where evolved gases can either react with the residue or provide a stagnant 'blanket' which prevents free access of reactant gas, e.g., oxidative decomposition of metal oxysalts.

To investigate the effect of different cell designs on the dehydration of $UO_2 \cdot C_2O_4 \cdot 3H_2O$, a single sample of this material was investigated using several

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commercial instruments with different cells. Additionally, a 'custom-built' cell[2] was used to investigate the effect of sample size on the dehydration peak. Uranyl oxalate trihydrate seems particularly susceptible to giving anomalous results if product water vapour is not efficiently removed. It is for this reason that the material was chosen, on the basis that splitting of the main dehydration endotherm can readily be detected in those cases where correct atmosphere control (i.e., removal of product water in this case) is not achieved.

EXPERIMENTAL

Materials

The preparation of uranyl oxalate trihydrate, $UO_2 \cdot C_2O_4 \cdot 3H_2O$, has been given previously[1].

Ammonium vanadyl oxalate dihydrate, $(NH_4)_2 \cdot VO(C_2O_4)_2 \cdot 2H_2O$ was prepared by the method described by Palmer[3].
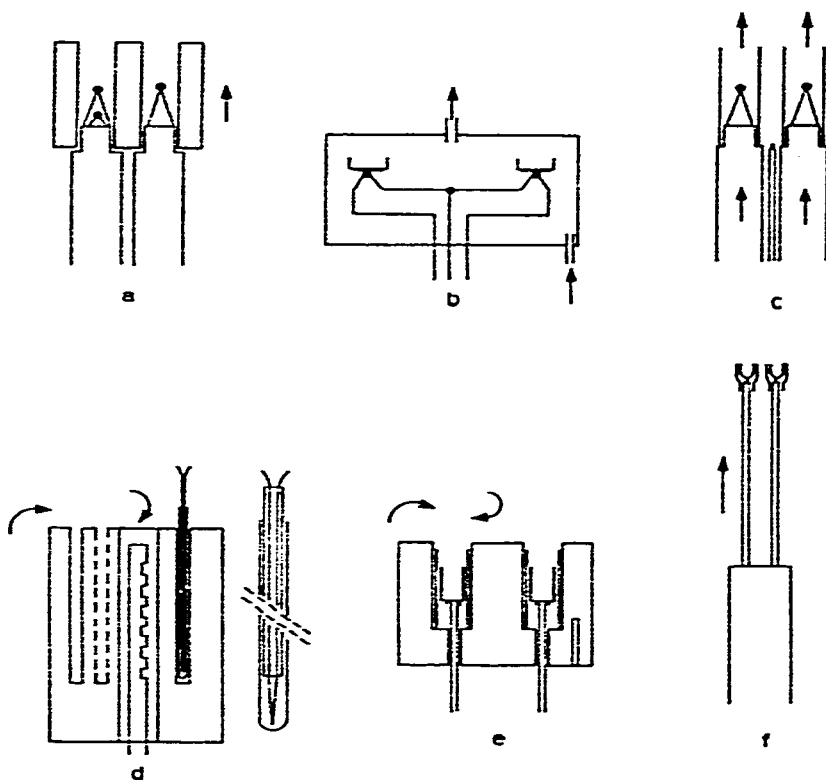

Fig. 1. Various cell types. (a) Netzsch standard cell (nickel block, wells approx. 8 mm diameter). (b) Stanton–Redcroft cell (aluminium pans, approx. 6 mm diameter). (c) Netzsch catalytic cell (ceramic sleeves, approx. 8 mm diameter). (d) Du Pont intermediate temperature cell (sample tube approx. 1 mm diameter). (e) Wilburn cell (nickel block, wells approx. 9 mm diameter). (f) Du Pont high temperature cell with platinum liners in place (sample holder approx. 5 mm diameter). Arrows indicate normal direction of gas flow.

Apparatus

A total of six different DTA cells was used to investigate the dehydration of uranyl oxalate trihydrate to uranyl oxalate monohydrate. A sketch of the salient features of each cell type is shown in Fig. 1.

RESULTS AND DISCUSSION

Results for uranyl oxalate trihydrate dehydration are shown in Figs. 2 and 3. Results for ammonium vanadyl oxalate dihydrate are shown in Fig. 4. The DTA curves are *tracings* from the original charts wherever possible, these are indicated in the figure legends. Calcined alumina (α-Al_2O_3) was used as the reference material in each case.

Dehydration of uranyl oxalate trihydrate

Fig. 2 shows the DTA curves for the dehydration reaction:

$$UO_2 \cdot C_2O_4 \cdot 3H_2O \rightarrow UO_2 \cdot C_2O_4 \cdot H_2O + 2H_2O$$

In the earlier publication[1] we proposed that the cause of the splitting effect (Fig. 2) is the accumulation of product water vapour evolved during the dehydration.
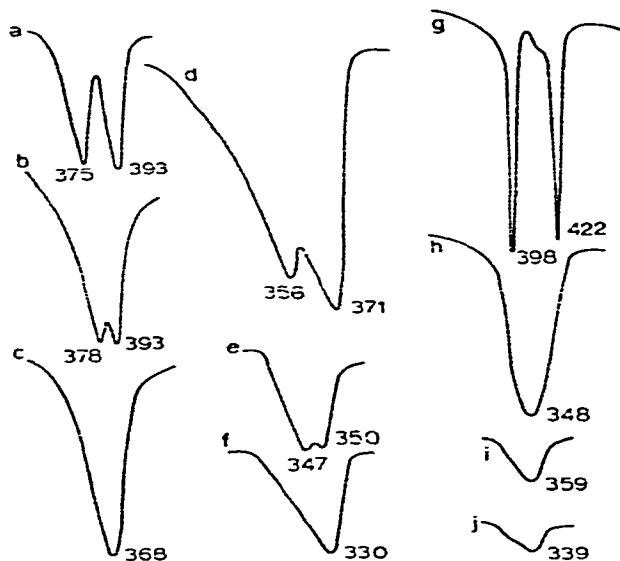

Fig. 2. DTA curves for $UO_2 \cdot C_2O_4 \cdot 3H_2O \rightarrow UO_2 \cdot C_2O_4 \cdot H_2O + 2H_2O$ using various DTA cells (all results traced). (a) Netzsch standard cell, diluted sample, 300 ml min^{-1} nitrogen over sample. (b) Netzsch catalytic cell, diluted sample, 500 ml min^{-1} air over sample. (c) Netzsch catalytic cell, diluted sample, 5 ml min^{-1} air through sample. (d) Stanton–Redcroft cell, undiluted sample, 25 ml min^{-1} air over sample. (e) Stanton–Redcroft cell, diluted sample, static air. (f) Stanton–Redcroft cell, diluted sample, 10 ml min^{-1} nitrogen. (g) Du Pont intermediate temperature cell, undiluted sample, 400 ml min^{-1} nitrogen over sample. (h) Du Pont intermediate temperature cell, undiluted sample, in vacuo (1.9 kN m^{-2}). (i) Du Pont high temperature cell, with liner, diluted sample, 500 ml min^{-1} air over sample. (j) Du Pont high temperature cell, without liner, diluted sample, 500 ml min^{-1} air over sample. Diluted samples: 20% w/w with α-Al_2O_3, peak temperatures in K.

On this basis it is clear that the magnitude of the splitting effect is a direct measure of the efficiency of the removal of product water vapour.

Netzsch Model 404. Fig. 2a shows that, using the Netzsch standard cell under the specified conditions, complete removal of product water vapour is not achieved. Using the catalytic cell (Fig. 2b) with air flow *over* the sample as in Fig. 2a, the splitting effect is less pronounced. However, using the catalytic cell the splitting effect can be *completely* eliminated by a flow of gas *through* the bulk sample (Fig. 2c), illustrating the highly efficient removal of product water vapour in this case.

Stanton–Redcroft DTA 671. Fig. 2d shows the curve obtained using the DTA 671 instrument with an undiluted sample. Again peak splitting is apparent. Fig. 2e shows that, using a diluted sample, the splitting is considerably reduced even though no gas flow was used. Use of a flowing gas atmosphere produced complete elimination of the splitting effect (Fig. 2f).

Du Pont 900. Using the Du Pont 900 with the intermediate temperature cell, undiluted samples gave complete separation of the two components of the main peak. Almost identical results were obtained earlier using diluted samples[1]. Flow-rates as high as 2 l min^{-1}, using an external flowmeter, produced similar results. Clearly, the construction of the cell substantially impedes removal of product gases[1]. However, using this cell, product water vapour can be efficiently removed by continuous evacuation. Fig. 2h shows the curve obtained for an undiluted sample in vacuo and illustrates the elimination of the splitting effect by this means. Again, similar results were obtained using diluted samples[1].

Use of the high temperature cell with the liner in place (Fig. 2i) produced complete elimination of the splitting effect. Since it is possible that indirect contact of the thermocouple, via the liner, could produce thermal lag and an 'evening-out' effect, the material was also examined in absence of the liner (Fig. 2j). As can be seen, an inflexion is apparent on the initial downward slope of the peak although this represents a relatively small thermal lag when the liner is in place.

Wilburn cell. Figure 3 shows the results obtained using the Wilburn cell to investigate the effect of sample size on peak separation. A reduction of sample size, under otherwise constant conditions, leads to enhanced efficiency of product water removal and consequently less pronounced splitting of the main peak. Sample weights below 40 mg were not investigated although, clearly, smaller weights would eventually produce a single endotherm.

Decomposition of ammonium vanadyl oxalate dihydrate

Dehydration. Figure 4 shows the various DTA curves obtained for the dehydration (ca. 390 K) and decarboxylation (ca. 520–620 K) of ammonium vanadyl oxalate dihydrate. The dehydration peaks (Figs. 4a–d) show inflexions both on the downward and upward portions of the main dehydration peak. In common with most other hydrated salts, splitting of the main dehydration peak is not so pronounced as with uranyl oxalate trihydrate. The shoulders seen in Figs. 4c and d were variable in size, duplicate determinations sometimes produced a larger shoulder on the down-

ward portion of the main peak. The curve obtained using the Du Pont intermediate temperature cell in vacuo (Fig. 4e) again shows a single endotherm when product water is efficiently removed by this means. Using the Du Pont high temperature cell a single endotherm was obtained, again showing efficient product water removal (Figs. 4f and g).

Decarboxylation. As is usually observed with metal oxalates, ammonium vanadyl oxalate decarboxylates exothermally in an oxidising atmosphere (Fig. 4a
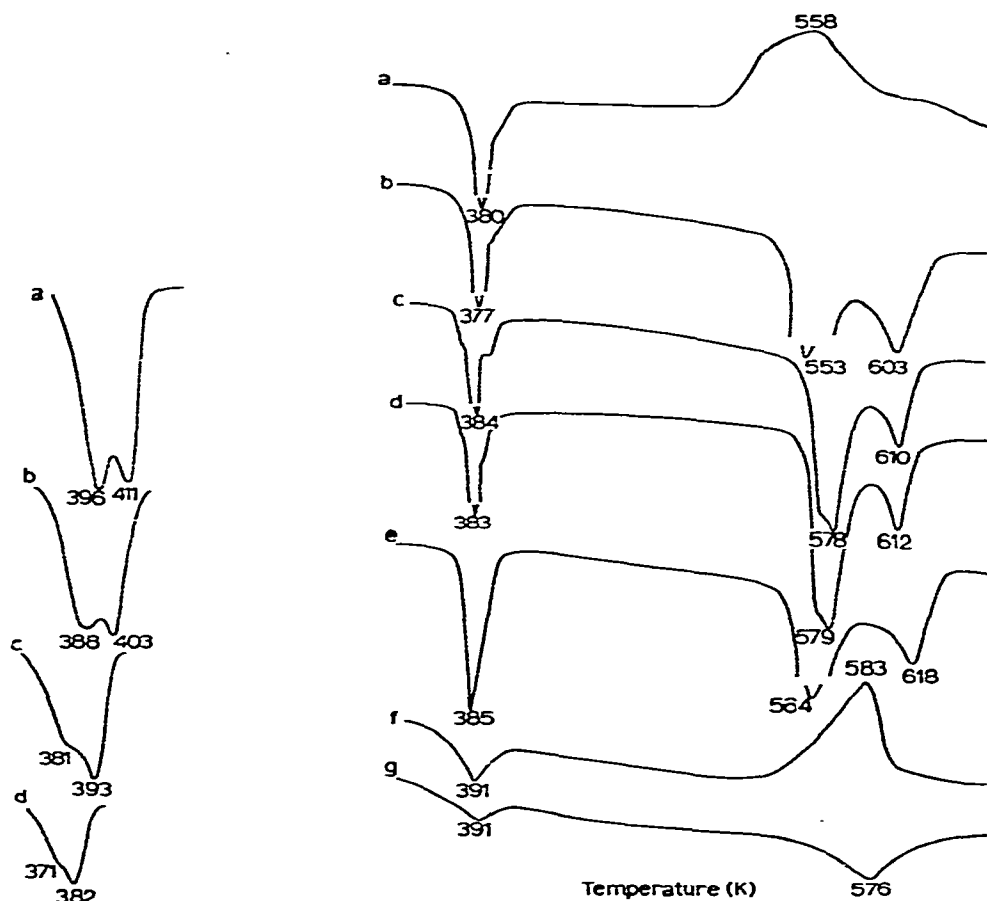

Fig. 3. Effect of sample size on peak splitting during the reaction $UO_2 \cdot C_2O_4 \cdot 3H_2O \rightarrow UO_2 \cdot C_2O_4 \cdot H_2O$. Wilburn cell, 20% w/w sample in α-Al$_2$O$_3$, 10 K min^{-1}, 300 ml min^{-1} nitrogen, results replotted, peak temperatures in K. Total weight of diluted sample: (a) = 160 mg, (b) = 120 mg, (c) = 80 mg, (d) = 40 mg.

Fig. 4. Dehydration and decarboxylation of $(NH_4)_2 \cdot VO(C_2O_4)_2 \cdot 2H_2O$. (a) Netzsch standard cell, diluted sample, 500 ml min^{-1} air (replotted). (b) Netzsch standard cell, diluted sample, 500 ml min^{-1} nitrogen (replotted). (c) Du Pont intermediate temperature cell, undiluted sample, 400 ml min^{-1} air (traced). (d) Du Pont intermediate temperature cell, undiluted sample, 400 ml min^{-1} nitrogen (traced). (e) Du Pont intermediate temperature cell, undiluted sample, in vacuo (16 kN m^{-2}) (traced). (f) Du Pont high temperature cell, diluted sample, 500 ml min^{-1} air downwards (traced). (g) Du Pont high temperature cell, diluted sample, 500 ml min^{-1} nitrogen downwards (traced). Heating rate = 10 K min^{-1} throughout. Diluted samples = 20% w/w with α-Al$_2$O$_3$.

and f) and endothermally in an inert atmosphere (Fig. 4b and g). However, examination of Figs. 4c and d shows that the DTA curves for the decarboxylation in air and nitrogen are *identical* using the Du Pont intermediate temperature cell. The expected exothermic reaction in air is not observed with this particular cell because access of reactant oxygen and removal of reaction product gases is severely restricted, to the extent that completely erroneous results are obtained for the material. Confirmation of this effect was obtained by examination of the material after decomposition in the DTA cell. The product was dark green (indicative of lower oxides of vanadium) instead of the characteristic orange-yellow of V_2O_5 invariably obtained when the material is decomposed in an ample supply of air. Similar behaviour using this cell has been observed during decomposition of other oxysalts (e.g., ammonium metavanadate, uranyl oxalate, vanadyl oxalate).

Figs. 4b–e indicate that the decarboxylation under inert atmosphere is a two-stage process. However, Fig. 4g shows a single-stage process. Whether the different behaviour is due in this case to atmosphere control is uncertain. However, no indication of a two-stage process was apparent using rising temperature thermogravimetry (to be published).

CONCLUSIONS

It has been shown that a correct choice of sample cell is essential for certain types of reaction. For reversible reactions (e.g., many dehydration reactions) or reactions where product gases can either react with the residue or form an inert 'blanket' (e.g., decomposition of metal oxysalts where reducing gases are formed during decomposition), it is necessary to establish whether proper atmosphere control is achieved using any particular DTA cell design. Since many investigators have access to only one apparatus, often used as a 'universal' instrument for a variety of studies, it is clear that the required conditions (e.g., flow-rate, sample weight, etc.) necessary to eliminate secondary reactions must be established for the particular instrument and cell available. Since uranyl oxalate trihydrate is particularly susceptible to rehydration by product water vapour, we recommend that this material could be used to assess instrument performance in this manner. It is a relatively simple matter to optimise the conditions required to eliminate, or at least minimise, 'splitting' of the main dehydration endotherm. This does not, of course, *guarantee* that these pre-determined conditions will eliminate such problems with the material to be subsequently investigated but it would, at least, be a guide to the minimum flow-rate, sample size, etc., required. A note of caution must be inserted—a commercial sample of uranyl oxalate was previously investigated[1] and found to be substantially impure. The impurity gave rise to an additional large endotherm at around 373 K, which clearly interferes with the observation of splitting of the dehydration peak for uranyl oxalate trihydrate. However, the laboratory preparations described previously are easy to carry out and give pure materials in each case.

It has been shown in the present study that, in those cases where gas flow is not

directly through the bulk sample, an important factor during decomposition in controlled atmospheres is the *geometry* of the sample holder rather than the sample size, flow-rates, etc., used. Thus small, thinly spread samples lead to efficient product gas removal but small samples contained by narrow, restricted tubes lead to a serious loss in efficiency of product removal.

Finally, it should be borne in mind that many different cell designs are commercially available, each type being particularly suited to different investigations[4]. Thus the Du Pont instrument has been extensively used for the investigation of organic materials although it is also used in the investigation of other materials. Similarly, the 'Wilburn' cell is specifically intended for quantitative work in glass-making reactions. The results presented here do not represent a systematic study of the materials using the various DTA cells but are rather an illustrative collection. The variation of results with any particular cell has not been exhaustively studied but it is shown that with most of the cells it is possible, by selection of appropriate conditions, to eliminate or at least minimise accumulation of product gases.

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