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THERMAL AND RELATED STUDIES OF SOME BASIC ZIRCONIUM SALTS

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Studies of basic zirconium carbonate, oxalate, nitrate and sulphate using TG, DTA and DTG methods, combined with isothermal gaseous product analyses, IR spectroscopy and X-ray diffraction techniques, have shown that the ease of ligand removal from such salts follows the sequence: 'loosely bound' $H_2O > CO_3^{2-} \approx C_2O_4^{2-} > NO_3^- > OH^-$ (or 'tightly bound' $H_2O) > SO_4^{2-}$.

With the exception of the basic sulphate where the high temperature necessary for complete removal of the sulphato groups resulted in direct formation of crystalline monoclinic zirconia, such ligand removal generally led to generation of the cubic crystalline variety.

Although extensive thermal studies of some zirconium compounds, notably the hydrous gels [1], have been made, little work seems to have been devoted to the corresponding basic salts. Recently, it has been advanced that some of these salts (particularly the carbonate) may have useful industrial applications [2, 3]. Like their hydrous oxide counterparts the basic zirconium salts may have some potential as catalyst supports, and for this reason we have looked more closely at their properties.

We report here our investigations of the influence of temperature on the behaviour of basic zirconium carbonate, nitrate, oxalate and sulphate. Structural studies [4] have shown that the zirconium atoms in some of these salts are linked by hydroxo bridges with the corresponding anion being associated with the coordination sphere of the metal atom. This suggests that the thermal behaviour of these compounds could be similar, being governed by the ease with which uni- and bi-dentate ligands are removed from their structures.

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Experimental

Materials

The reagents used in this study were either BDH AnalaR solids or AnalaR Volumetric Standards. Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) was of the "spec-pure" variety supplied by Johnson Matthey Chemicals Ltd. BDH Carbosorb soda asbestos (6–12 mesh) was employed in the gravimetric estimation of carbon dioxide, while Devarda's alloy used for the estimation of nitrate was a BDH analytical reagent. Nitrogen gas (research grade; 99.9% purity) was supplied by the British Oxygen Company. Freshly prepared distilled water was used throughout for all preparative and analytical work.

The basic salts studied in this work were prepared using methods reported previously [4–7]. The zirconium and water contents of all the salts thus prepared were estimated by gravimetric methods; the sulphur content of the basic sulphate was determined as sulphur trioxide following the observations of Chukhlantsev and Galkin [8]; the carbonate and oxalate content of the corresponding salts by isothermal gaseous product analysis (IGPA) and by titration of a solution in sulphuric acid with standard $KMnO_4$ solution [9]; and the nitrate content of the basic nitrate through the use of Devarda's method as described by Vogel [10].

With the exception of the basic carbonate, empirical formulae have already been advanced for all the salts, and analyses of the prepared materials agreed closely with these. The exact stoichiometry of the carbonate has not been reported previously, but our analysis indicates that its empirical formula is similar to that of the oxalate, i.e. both materials contain two molecules of water per zirconium atom*.

Thermal studies

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) was conducted using a Stanton Redcroft STA 780 instrument, which is also capable of providing derivative thermogravimetry (DTG) data. The following experimental conditions were employed throughout: heating rate, 10 deg min^{-1}; sample weight, 20–50 mg; flow gas, N_2; gas flow rate, 100 cm^3 min^{-1}; reference solid, α-Al_2O_3. The monitored temperature was provided by means of a platinum/13% rhodium flat plate thermocouple which formed part of the sample container locator.

The products eliminated during high temperature treatment of the various solids were studied separately through IGPA methods using a specially designed silica cell

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* Analysis of basic zirconium carbonate, $(ZrO)_2(OH)_2CO_3 \cdot 4H_2O$: Calculated (%): ZrO_2, 66.84; CO_2, 11.57; H_2O, 21.59. Found (%): ZrO_2, 66.83; CO_2, 11.46; H_2O, 21.71.

to contain individual samples, similar to that described by Cventanovic and Amenomiya [11]. This cell was flushed continuously by a stream of dry nitrogen gas maintained at a constant flow rate. The cell temperature was monitored by means of a platinum/13% rhodium thermocouple located directly above the heated solid, and was raised in 100° steps using an external high precision furnace (Stanton Redcroft VK) in conjunction with a Stanton Redcroft linear temperature programmer (model Mark II LVP). This arrangement gave an isothermal control accuracy of ± 1° at each temperature studied. The evolved gases were swept by the nitrogen flow into wash bottles and estimated as follows: SO_3—absorption in freshly prepared distilled water followed by titration with standard NaOH solution; various nitrogen oxides—absorption in NaOH solution followed by estimation using Devarda's method [10]; CO_2—absorption in Carbosorb followed by analysis using the method described by Vogel [12].

Infrared spectra have been measured using a Pye–Unicam SP3–100 instrument with the solid samples pressed into KBr discs. X-ray powder diffraction data for all samples before and after thermal treatment were obtained using a Philips 1008 X-ray unit, employing radiation corresponding to the CuK_α line supplemented by measurements at a shorter wavelength (MoK_α) when confirmation of the amorphous nature of a given sample was necessary.

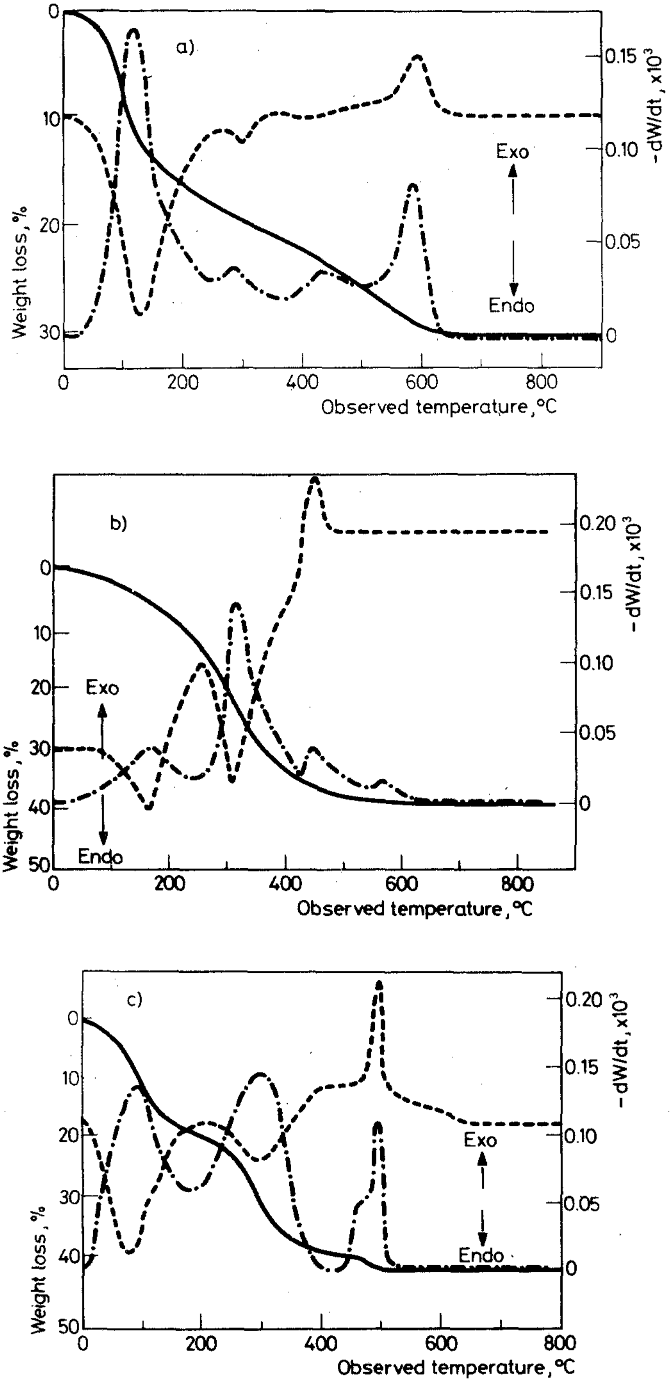
Results and discussion

Basic zirconium carbonate

The thermal curve for the basic carbonate [Fig. 1(a)] shows that the greatest weight loss occurred over the temperature range 50–300°, similar to that observed for hydrated zirconia gel [1], and was due mainly to removal of absorbed and coordinated water accompanied by loss of carbon dioxide.

The DTG and DTA curves in Fig. 1(a) [and the IGPA plots in Fig. 2(a)] support this view and indicate that a number of steps were involved, the most important at ca. 125° corresponding to endothermic removal of absorbed water. The IGPA plots show that even at this relatively low temperature some carbon dioxide was also lost. However, the greatest loss of carbon dioxide occurred at ca. 200°, suggesting that this was mainly associated with the elimination of physically entrapped gas. Further carbon dioxide loss at higher temperatures is more likely linked to the breakdown of bidentate carbonato ligands contained within the structure of the salt, a process requiring considerable thermal energy.

The IR spectra in Fig. 3(a) support this view. Thus the absorption bands in the spectra at ca. 1350, 1050 and 840 cm^{-1}, respectively, attributed to various


a)
Weight loss, %
0
10
20
30
-dW/dt, x10³
0.15
0.10
0.05
0
Exo
Endo
0
200
400
600
800
Observed temperature, °C
b)
Weight loss, %
0
10
20
30
40
50
-dW/dt, x10³
0.20
0.15
0.10
0.05
0
Exo
Endo
0
200
400
600
800
Observed temperature, °C
c)
Weight loss, %
0
10
20
30
40
50
-dW/dt, x10³
0.20
0.15
0.10
0.05
0
Exo
Endo
0
200
400
600
800
Observed temperature, °C

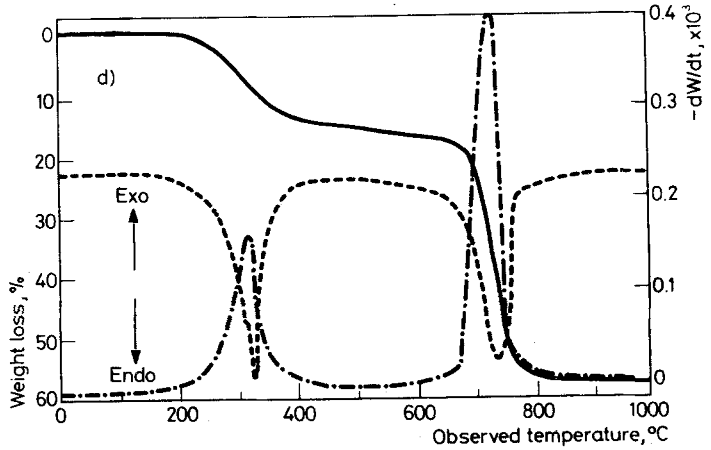


Fig. 1 TG, DTG and DTA curves (depicted as —, – · – · – and – – –, respectively) for the various basic zirconium salts studied. (a) Carbonate; (b) oxalate; (c) nitrate; and (d) sulphate

deformation and stretching modes associated with the CO bond in the carbonate group, persist even on heating the sample to 400° and only disappear after its exposure to 550°.

Removal of the last traces of water (probably derived from bidentate hydroxo groups) was also not achieved until the samples were heated above 500°. This is demonstrated by the sharp peak in the DTG curve over the temperature range 500–650°, and by the persistence of the broad and intense absorption band at 2800–3600 cm^{-1} (corresponding to the stretching vibrations of hydroxide groups associated with water molecules) in the IR spectra up to an outgassing temperature of 550°. The absorption peak at ca. 1600 cm^{-1} (attributed to the deformation vibrations of the hydroxide group) was also present in the spectra up to the same temperature, thus providing clear evidence of the strength of attachment between hydroxo ligands and zirconium atoms.

The X-ray diffraction data listed in Table 1 indicate that the small but unsymmetrical exothermic peak in the DTA curve at 500–620° is associated with conversion of the amorphous material to cubic crystalline zirconia. The unsymmetrical shape of this exotherm arises from simultaneous endothermic evolution of water over the same temperature range. An increase in the outgassing temperature to 650° led to transformation of the cubic into the monoclinic variety, which then persisted in all samples heated up to 1000°.

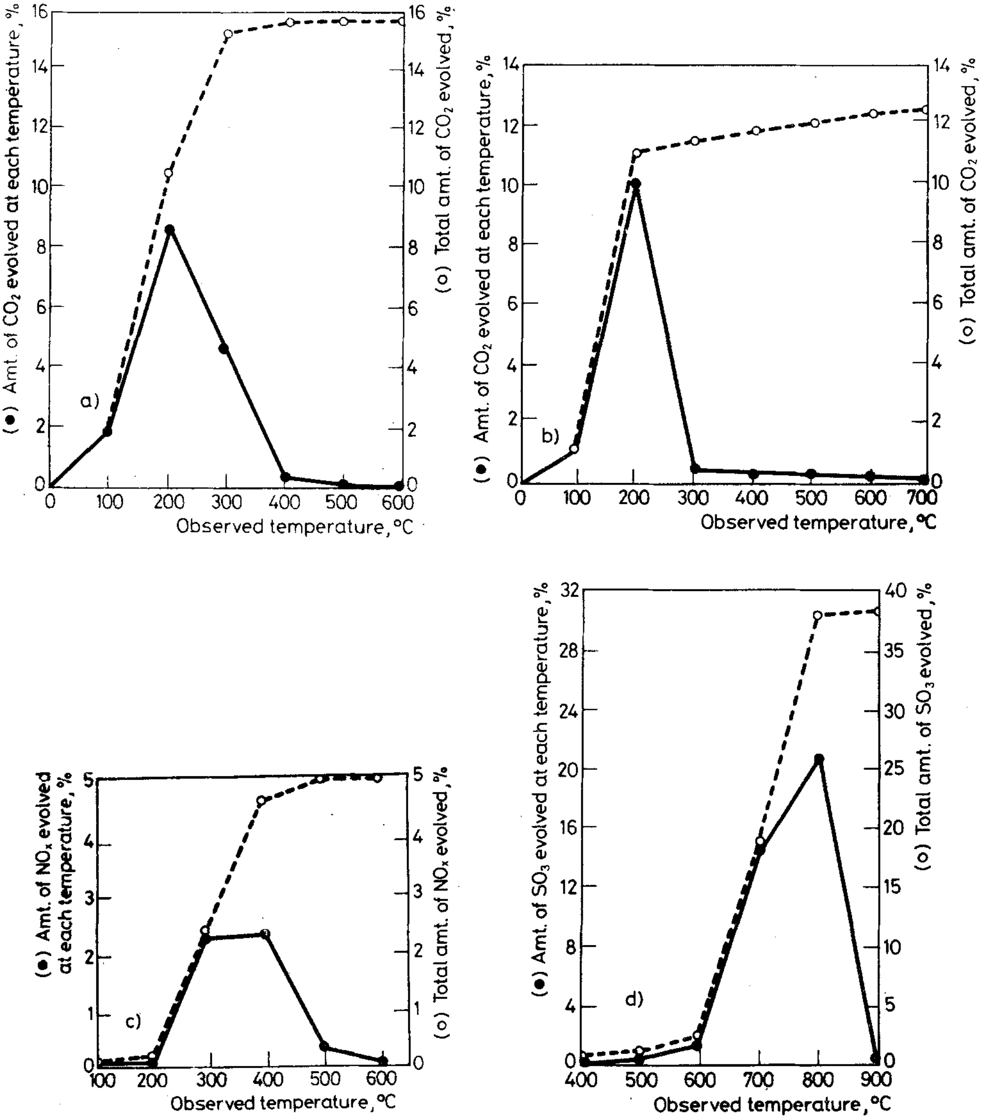


Fig. 2 IGPA plots for the various basic zirconium salts studied. (a) Carbonate; (b) oxalate; (c) nitrate; and (d) sulphate

Basic zirconium oxalate

Despite containing ligands capable of generating carbon dioxide when disrupted, the TG, DTG and DTA results of Fig. 1(b) [and the IGPA plot of Fig. 2(b)] indicate that the thermal behaviour of the basic oxalate is substantially different from that of the carbonate.

Table 1 X-ray diffraction data for basic zirconium salts studied

Basic salt	Treatment	Maximum temperature attained, °C	X-ray diffraction identity	*d*, Å	Comments
Carbonate	Non-trated	25	Amorphous		No lines
	DTA product	300	Amorphous		No lines
	N_2 adsorption	550	Cubic	2.95	Very weak lines
	product*	590	Cubic	3.00, 2.57, 1.84, 1.56	
	DTA product	620	Cubic		Sharp lines (just after exothermic peak)
	N_2 adsorption product	650	Monoclinic	3.16, 2.85	Weak lines
	DTA product	1000	Monoclinic	3.16, 2.85, 2.62	Very sharp lines
Oxalate	Non-treated	25	Amorphous		No lines
	DTA product	300	Amorphous		No lines
	N_2 adsorption product	500	Cubic	3.00, 1.84, 1.55	Sharp lines
	DTA product	520	Cubic		Sharp lines
	DTA product	600	Cubic		Sharp lines
	DTA product	800	Cubic		Sharp lines
	DTA product	1000	Monoclinic	3.16, 2.85, 2.62, 1.82	Very sharp lines
Nitrate	Non-treated	25	Amorphous		No lines
	N_2 adsorption product	400	Amorphous		No lines
	DTA product	447	Amorphous		Just before exothermic peak; no lines
	N_2 adsorption product	500	Cubic	3.00, 1.84, 1.56	Weak lines
	DTA product	521	Cubic		Just after exothermic peak; sharp lines
	DTA product	1000	Monoclinic	3.16, 2.85, 2.63, 1.82	Very sharp lines

Table 1 continued

Basic salt	Treatment	Maximum temperature attained, °C	X-ray diffraction identity	*d*, Å	Comments
Sulphate	Non-treated	25	Monoclinic	7.54, 5.60, 4.75, 3.80	Very sharp lines
	DTA product	400	?		Very weak lines
	DTA product	600	Amorphous		No lines
	N_2 adsorption product	800	Monoclinic	3.15, 2.85	Weak lines
	DTA product	1000	Monoclinic	3.70, 3.16, 2.85, 2.63	Sharp lines

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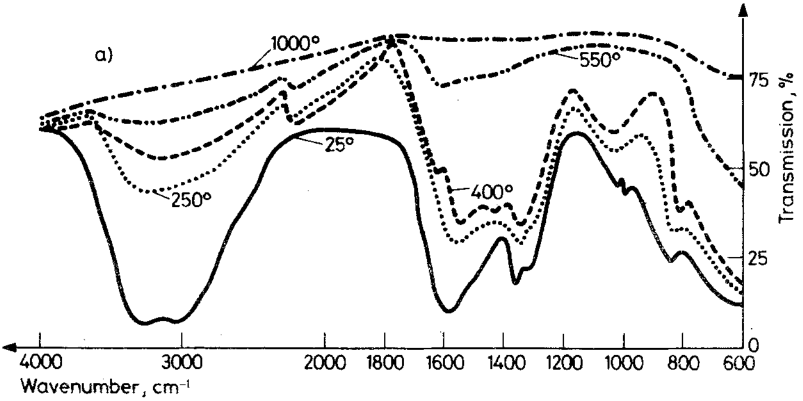
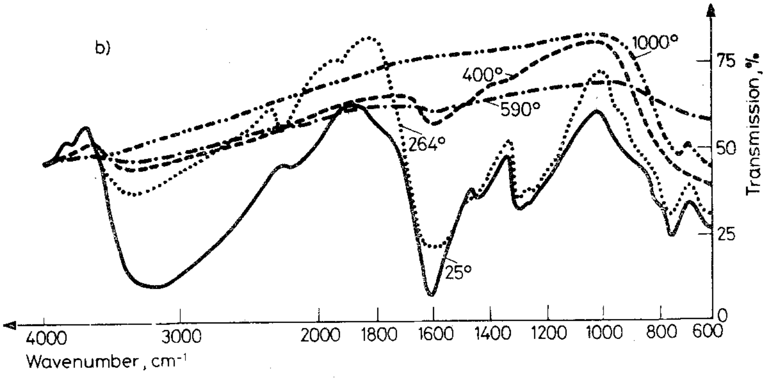
* Nitrogen adsorption studies associated with these products will be described elsewhere.





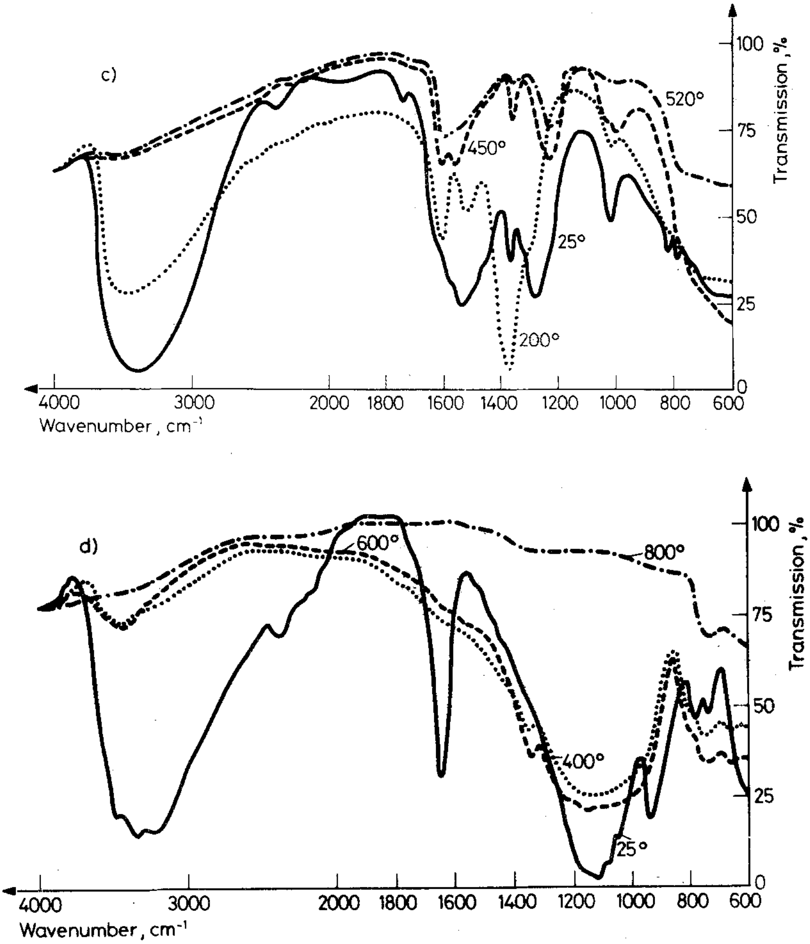


Fig. 3 IR spectra for the various basic zirconium salts studied, obtained after outgassing the latter at the various indicated temperatures. (a) Carbonate; (b) oxalate; (c) nitrate; and (d) sulphate

Whereas the thermogram suggests a weight loss occurring smoothly with increasing temperature over the temperature range 50-ca. 400°, the DTG curve indicates the involvement of four distinct steps. Although the first (with a maximum at 170° and extending to 250°) is connected with loss of absorbed water, it is also associated with removal of carbon dioxide since the IGPA curves in Fig. 2(b) indicate the elimination of substantial amounts of this gas over this temperature range. The IR spectra of Fig. 3(b) support this conclusion, but the persistence of peaks at ca. 1600, 1300, 900 and 800 cm^{-1} in the spectrum of the sample outgassed at 264° shows that some water and oxalato ligands are retained at this temperature.

Complete removal of water occurs during the second step between 250° and 400°. This is demonstrated by the disappearance of the broad absorption band at 2800–3600 cm^{-1} and the virtual elimination of the peak at ca. 1600 cm^{-1} from the IR spectrum of the sample outgassed at 400°. However, removal of oxalato ligands over the same temperature range was probably more complicated. According to Zaitsev and Bochkarev [7] decomposition of oxalato ligands takes place at higher temperatures, and Dollimore et al. [13] have suggested that such decomposition is accompanied by the evolution of carbon dioxide *and carbon monoxide.* The IGPA plots show that such evolution was substantially reduced at temperatures above ca. 300°, although the persistence in the IR spectra of the weak absorption band assigned to the stretching vibration of the $O—C=O$ groups indicates further decomposition of oxalato ligands up to 590°.

The third and fourth steps at 420–540° and 540–620° are related to evolution of more strongly bound CO/CO_2 and elimination of water derived from adjacent bridging hydroxo ligands. The small exothermic peak in the DTA curve which virtually coincides with the DTG peak at 420–540° may be associated with transition of the amorphous powder to the cubic crystalline variety, as indicated by the X-ray diffraction data recorded in Table 1. The relatively small size of the exotherm is due to compensation from endothermic decomposition of oxalato ligands over this temperature range. In contrast to the situation with the basic carbonate, conversion of cubic zirconia into the monoclinic variety did not occur readily but was delayed until the temperature reached ca. 1000°.

Basic zirconium nitrate

Both the TG and DTG curves [Fig. 1(c)] indicate decomposition of the basic nitrate via three distinct steps at 30–170°, 180–400° and 440–520°, respectively. The sharp endothermic peak in the DTA plot coinciding with the first of these steps corresponds to the removal of absorbed water, which the IGPA plots of Fig. 2(c) show occurred with little or no evolution of nitrogen oxides.

The greatest loss of nitrogen oxides occurred between 200° and 400°, although small amounts were still evolved up to 500°. Such evolution is associated with the second peak in the TG and DTG curves, and with the second endothermic peak in the DTA curve. This latter peak is followed by a sharp exotherm between 450° and 500°, corresponding to conversion of the amorphous material to the cubic crystalline variety (see data listed in Table 1). However, this exotherm probably obscures another endotherm associated with the third peak in the TG and DTG curves. This peak, with a maximum at ca. 475°, corresponds both to the elimination of water between adjacent hydroxo groups in the structure and to the further elimination of nitrogen oxides, although only very small amounts of the latter are evolved over this temperature range [see Fig. 2(c)].

These interpretations are fully supported by the IR spectra for samples of the basic nitrate outgassed at various temperatures illustrated in Fig. 3(c). The continued existence of absorption bands at 1530, 1380, 1030 and 820 cm^{-1} in the IR spectrum of the sample outgassed at 450° indicate that some nitrato ligands were still retained at this temperature, and even treatment at 520° was insufficient to remove them completely.

Basic zirconium sulphate

In contrast to the salts discussed above, thermal decomposition of the basic sulphate occurred in two distinct steps at widely separated temperatures. Thus, the TG and DTG curves depicted in Fig. 1(d) indicate sharp weight losses at 175–450° and 600–800°, respectively, with two large endotherms in the DTA curve over the same temperature ranges. However, unlike the other DTA curves, that for the basic sulphate *possessed no exothermic peak whatsoever.*

The IGPA plots of Fig. 2(d) support the view that the first step corresponds to elimination of water. These plots also show that evolution of sulphur trioxide (the decomposition product of sulphato ligands) commenced above 400° and reached a maximum at ca. 800°. Hence the second step is associated with the breakdown of sulphato ligands over the temperature range 600–900°, a highly endothermic process probably obscuring elimination of water from adjacent hydroxo groups in the structure occurring at the lower temperature end of this step.

This view accords with the IR spectra for samples of the basic sulphate outgassed at various temperatures as recorded in Fig. 3(d). Hence the absorption band arising from coordinated water molecules persisted in spectra of solids heated to 600°. Such molecules were gradually released on heating the salt to 800°, when sulphato groups were also lost as indicated by changes in the broad absorption band at 900–1340 cm^{-1}. At 800° the material was converted to crystalline zirconium dioxide.

Complicated structural changes occur in basic zirconium sulphate on heating. The results listed in Table 1 show that the X-ray pattern of solids maintained at room temperature contained very sharp lines corresponding to the monoclinic variety of the basic salt, in agreement with the observations of McWhan and Lundgren [4]. However, heat treatment to 400° led to the development of a spectrum possessing very weak lines, probably as a result of the disruption of the crystalline structure of the solid by elimination of loosely held water molecules. All the diffraction lines disappeared from the X-ray spectra of samples heated to 600°, clearly indicating that they were amorphous. Samples heated to higher temperatures underwent further conversion to monoclinic ZrO_2, the percentage of the latter increasing as the treatment temperature increased within the range 800–1000°.

The absence of an exotherm in the DTA curve for the basic sulphate corresponding to formation of cubic zirconia, and direct conversion of amorphous material into the monoclinic variety above 800°, may be attributed to strong retention of sulphato ligands in the structure hindering normal conversion to the cubic form at ca. 500°.

Conclusions

The reported results confirm and extend appreciably the observations of earlier workers [5–8]. Furthermore, they establish a stability sequence for ligands coordinated to zirconium which was not available previously, either from thermal investigations of appropriate solids or from solution studies of complex species.

The present work has shown that the ease of ligand removal from zirconium with increasing temperature follows the sequence: 'loosely bound' $H_2O > CO_3^{2-} \approx C_2O_4^{2-} > NO_3^- > OH^-$ (or 'tightly bound' H_2O) $> SO_4^{2-}$, which accords with the common observation that unidentate ligands are removed more readily than multidentate ligands from coordination spheres of metal atoms. In general, ligand removal led to the generation of cubic crystalline ZrO_2 which converted to the monoclinic form at ca. 1000°. However, the high temperatures necessary for complete removal of sulphato groups from the basic sulphate gave the monoclinic variety directly in that case.

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Zusammenfassung — Auf Grund von TG-, DTA- und DTG-Untersuchungen, verbunden mit einer isothermen Gasprodukteanalyse, sowie IR-spektsoskopischen und Röntgendiffraktionsuntersuchungen von basischen Zirkoniumkarbonaten, -oxalaten, -nitraten und -sulfaten wurde festgestellt, dass die relative Abspaltbarkeit eines Liganden solcher Salze der folgenden Reihenfolge entspricht: „locker gebundenes“ $H_2O > CO_3^{2-} > C_2O_4^{2-} > NO_3^- > OH^-$ (bzw. „stark gebundenes“ $H_2O) > SO_4^{2-}$. Mit Ausnahme des basischen Sulfates, bei dem zur vollständigen Abspaltung der Sulfatogruppen eioe hohe Temperatur notwendig ist und sich die direkte Bildung von kristallinem, monoklinem Zirkoniumdioxid abspielt, führen solche Ligandenabspaltungen im allgemeinen zu einer kubischen Kristallmodifikation.

Резюме — Исследования основных солей карбоната, оксалата, нитрата и сульфата циркония, проведенные методами ТГ, ДТА и ДТГ, сопряженных с изотермическим газовым анализатором, а также методами ИК спектроскопии и диффракции рентгеновских лучей, показали, что легкость выделения лиганда из таких солей располагается в последовательности: слабосвязанные лиганды $H_2O > CO_3^{2-} \approx C_2O_4^{2-} > NO_3^- > OH^-$ или жесткосвязанные — $H_2O > SO_4^{2-}$. Выделение лигандов приводит к образованию кристаллической двуокиси циркония с кубической структурой, за исключением основной соли сульфата циркония, для которой полное удаление лиганда требует более высокой температуры и приводит к образованию кристаллической двуокиси циркония с моноклинной структурой.