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SIMULTANEOUS THERMAL ANALYSIS OF ZIRCONIUM(IV) ACETYLACETONATE IN A HELIUM ATMOSPHERE

F. Jasim

DEPARTMENT OF CHEMISTRY, COLLEGE OF SCIENCE, UNIVERSITY OF BAGHDAD, JADRIYA, BAGHDAD, IRAQ

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TG, DTG, DTA, DDTA and ΔH analyses of zirconium(IV) acetylacetonate, $Zr(C_6H_7O_2)_4$ (=I), were performed in a helium atmosphere with a Netzsch Thermal Analyser STA 429. The enthalpies of the main steps of transformation were computed to be $+42.182\ J \cdot g^{-1}$ and $-21.113\ J \cdot g^{-1}$. Pure I is thermally stable up to about 199°C in He gas, and melting too occurs at about 199°C. Four well-defined decomposition steps were observed over the range between ambient and 600 °C, accompanied by a weight loss of 61.59%. The final product contained pure ZrO. The unique shapes of the TG and DTA curves could be used for the identification of I.

More than 60 metal acetylacetonates have been prepared including those of transition, rare earth, alkaline earth and Group III metals [1-4]. The thermal behaviour of acetylacetonates of di- and trivalent metals such as Ca, VO, V, Al, Cr, Fe, Mn, Co, Ni and Cu, alone and in the presence of oxidizing salts, has been studied and reviewed [1].

It was considered worthwhile to make enthalpic and thermogravimetric investigation in He gas, taking I as a model for the group IV-A quartet (Ti, Zr, Hf and Th, which are essentially quadrivalent metals, with a view to obtaining data concerning thermal stability, melting point, enthalpies of decomposition steps, types of final products, and clarification of the reaction mechanism of I.

Experimental

White crystalline zirconium(IV) acetylacetonate obtained from Fluka AG Buchs was manually ground for 15 min with an agate mortar and pestle.

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The TG, DTG, DTA and DDTA curves were recorded with a Netzsch STA 429 thermal analyser under the optimized instrumental conditions (Table 1). The air in the furnace was first evacuated by using the turbo-vacuum pump of the instrument, and He was then allowed to flow in. Volatile pyrolysates were collected and analysed by gas chromatography; solid products were investigated by X-ray diffractometry.

Table 1 Parameters of test and temperature program

Parameters	Settings
Sample	$Zr(C_6H_7O_2)_4$
Reference material	Alumina
Atmosphere	He (dynamic)
Crucibles	Alumina
Samples weight	40.00 mg
Reference weight	40.00 mg
He flow rate	10 ml·min^{-1}
Heating rate	10 deg·min^{-1}
Heating program	Ambient –1250°
Sampling time	3 s
Sensitisities:	
TG	25.00 mg
DTG	2.5 mg·min^{-1}
DTA	50.00 μV
DDTA	50.00 μV·min^{-1}

Results and discussion

Figure 1 depicts the simultaneous TG, DTG and DTA curves of I from ambient to the ceiling temperature of the heating program at 1250° under a He atmosphere. The TG and DTG traces exhibit first a slow degradation step, whose onset temperature is 116.9°. There is next a sudden collapse due to simultaneous melting, volatilization and degradation of I (step 1 in the DTG curve, with T_{max} = 230°). A corresponding very sharp endotherm in the DTA curve is the melting endotherm (T_{min} = 199°) of I (literature value of *m.p.* = 194-196°). The enthalpy of this endotherm between 175.3 and 214.3° was computerized and found to be +42.182 J.g^{-1}, with a peak area of 65481 μV.s and a noise of 0.39 μV/mW (Fig. 2).

The weight loss of 2.4 wt.% just after the onset temperature (116.9°) is due to the escape of moisture and volatile impurities. Figure 1 shows that the melting of I begins immediately before volatilization and subsequent

degradation (first large step in the TG curve). The next three smaller steps (DTG curve), with ΔT_{min} at 320°, 425° and 535°, depict the rather slow degradation of intermediates. The total weight loss of I from ambient to 600° is 61.59 wt.%; thereafter, the TG or DTG curve shows a stable horizontal plateau up to the end of the heating program, where a residue of 37.92 wt.% of the sample weight was obtained.

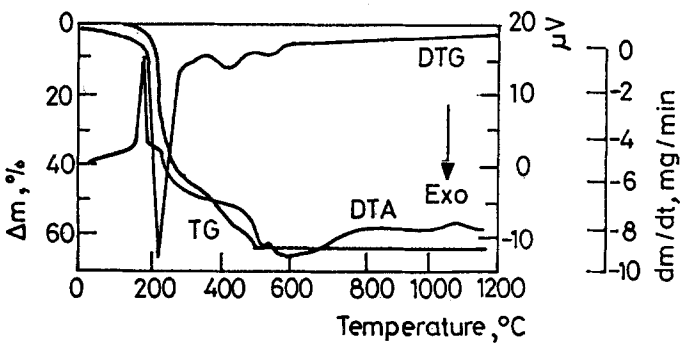

Fig. 1 Simultaneous thermoanalytical curves of zirconium(IV) acetyl acetonate under helium atmosphere

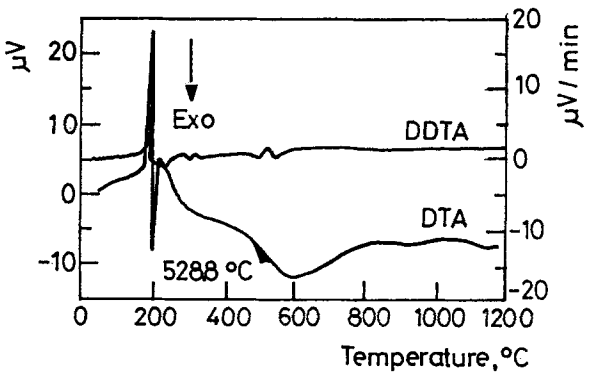

Fig. 2 DTA and DDTA curves of zirconium(IV) acetyl acetonate under helium atmosphere

The degradation of zirconium(IV) acetylacetonate (see Fig. 3 for structural diagram) culminates at about 300° (first step), where about 45 wt.% is eliminated due to the loss of two molecules of CH_3COCH_3 and one molecule of $CH_3COCH_2COCH_3$, resulting in the formation of non-

stoichiometric co-ordinated species of the type $[Zr(OH)CHCOO]^{2+}$, which slowly disproportionates in three consecutive chemical processes between 300° and 535° into ZrO and CH_3COOH; the latter decomposes to form CH_4 and CO_2. The exotherm at 528.9° (Fig. 2, DTA curve) reveals a $solid_1$-$solid_2$ (amorphous-crystalline) transformation, which could be attributed to ZrO formation. This is confirmed by the XRD pattern of the final product. The calculated enthalpy (probably due to exothermic crystalization of ZrO) at ΔT_{max} = 528.8° was found to be –21.113 $J \cdot g^{-1}$. Since the heat of formation of ZrO is +84 $kJ \cdot g\text{-mole}^{-1}$ [5], the formation of free Zr and subsequent oxidation to ZrO are excluded as reaction mechanisms.

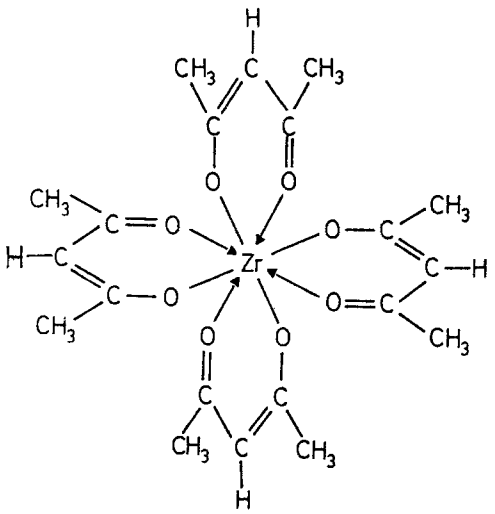

Fig. 3 Schematic structural formula of zirconium(IV) acetyl acetonate

For a DTA curve to be particularly suitable for thermal analysis, a linear program rate and a high degree of baseline stability are required. In the present case, the steps beyond the melting endotherm (DTA curves in Fig. 2) are not clearly shown and the baseline is not stable due to changes in the heat capacities of the intermediates with elevation of the temperature. An aid to the detection and clarification of these and other steps is afforded by the simultaneous use of the First Derivative Computor (FDC-1) along with the standard DTA curve. The trace at the top (Fig. 2) shows the derivative DTA curve (DDTA). The fact that the DDTA curve produces a peak frequently makes the detection of overlapping peaks easier by eliminating

the thermal noise accompanying DTA curves. For example, the DDTA curve clearly exhibits small maxima at 230°, 320° and 528.8°. Further, the large broad trough with ΔT_{min} = 535° (DTA curve) is reduced to a small minimum in the DDTA curve.

The shapes of the DTG and DTA curves of I are unique compared with those of other metal acetylacetonates studied [1] and could therefore be used for identification of the compound.

References

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Zusammenfassung — Mittels eines Netzsch Thermal Analyser STA 429 wurden in einer Heliumatmosphäre TG-, DTG-, DTA-, DDTA- und ΔH- Analysen von Zirkonium(IV)-acetylacetonat der Formel $Zr(C_6H_7O_2)_4$ (=I) durchgeführt. Die Enthalpien für die Hauptumwandlungen wurden mit $+42.182\ J \cdot g^{-1}$ bzw. $-21.113\ J \cdot g^{-1}$ berechnet. Reines (I) ist bis 199°C thermisch stabil und schmilzt auch bei dieser Temperatur. Im Temperaturbereich von Raumtemperatur bis 600°C wurden vier scharf abgesetzte Zersetzungsschritte beobachtet, die von einem Massenverlust von insgesamt 61.5% begleitet wurden. Das Endprodukt enthält reines ZrO. Der Verlauf der TG- und DTA-Kurven konnte zur Identifizierung von (I) benutzt werden.