Thermochimica Acta, 104 (1986) 387–388
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

DTG AND KINETICS OF NON-ISOTHERMAL DECOMPOSITION OF TRIS(*p*-NITROBENZALDEHYDETHIOSEMICARBAZONATO) M(III) (M = Fe, Al, Cr)

S.S. SAWHNEY, R.M. SATI and K. URMILA SALUJA

Chemistry Department DAV (P.G.) College, Dehra Dun-248 001 (India)

(Received 21 December 1985)

The Dave and Chopra equations [5] yield reliable data from DTG curves derived from TG curves pyrolysed on a manually operated assembly equipped with a Toshniwal balance introducing inconsistencies in variables, viz. temperature, heating rate and crucible geometry etc., known to influence the pyrolysis curves and hence the kinetic data. Sawhney et al. [1–4] showed the applicability and amenability of these equations to the kinetic study of non-isothermal decomposition of metal complexes from DTG curves striking a parallelism to the following type of reaction: A(s) = B(s) + C(g) recommended by Freeman and Carroll [6] for kinetic studies. This report is concerned with the dissociation of tris(*p*-nitrobenzaldehydethiosemicarbazonato) M(III) (M = Fe, Al, Cr).

EXPERIMENTAL

All the chemicals used were of analytical grade. The synthesis of *p*-nitrobenzaldehydethiosemicarbazone was given in an earlier report [7]. Isolation of its metal complexes too, has been detailed there.

RESULTS AND DISCUSSION

The species $Al \cdot L_3$ and $Fe \cdot L_3$, where $L = C_8H_7N_4SO_2$ began to decompose after 60°C, and losses of 2/23 and 5/19 molecules of L up to 160 and 240°C were observed, after which the plateau extended to 200 and 260°C, respectively, corresponding to the stoichiometries of intermediate complexes: Al · 67/23L and Fe · 52/19L which underwent further decomposition resulting in the formation of Al_2O_3 and Fe_2O_3, respectively. Pyrolysis of CrL_3 showed loss of 1/3L (60–180°C), 7/3L (200–300°C) and 1/3L (400–540°C). A plateau after 540°C corresponding to Cr_2O_3 was observed.

0040-6031/86/$03.50

Each sigmoid was analysed kinetically. The kinetic data given in parentheses below the reaction, showed that the accompanying reactions follow first order kinetics (where E is measured in kcal mol^{-1}).

$Al \cdot L_3 \rightarrow Al \cdot 67/23L + 2/23L$

($n = 1$, $E = 7.19$ and $Z = 0.44$)

$Al \cdot 67/23L \rightarrow Al_2O_3 + dp$

($n = 1$, $E = 13.50$ and $Z = 0.16$; $n = 0.67$ and $E = 16.20$ (see eqn. 2)

$Cr \cdot L_3 \rightarrow Cr \cdot 8/3L + 1/3L$

($n = 1$, $E = 5.95$ and $Z = 0.27$)

$Cr \cdot 8/3L \rightarrow Cr \cdot 1/3L + dp$

($n = 1$, $E = 21.90$ and $Z = 1.99$)

$Cr \cdot 1/3L \rightarrow Cr_2O_3 + dp$

($n = 1$, $E = 13.73$ and $Z = 0.35$)

$Fe \cdot L_3 \rightarrow Fe \cdot 52/19L + 5/19L$

($n = 1$, $E = 5.72$ and $Z = 0.70$; $n = 0.70$ and $E = 9.15$ (see eqn. 2)

$Fe \cdot 52/19L \rightarrow Fe_2O_3 + dp$

($n = 1$, $E = 9.95$, $Z = 0.70$; $n = 0.45$, $E = 21.35$ (see eqn. 2)

Abnormally low values of Z indicated the decomposition reactions to be slow processes. Dave and Chopra equations are as follows

$$k = \frac{dx/dt}{A - a} \tag{1}$$

$$\frac{-E/2.303\, R\, T^{-1}}{\log(A - a)} = -n + \frac{\log(dx/dt)}{\log(A - a)} \tag{2}$$

REFERENCES

1 S.S. Sawhney and R.M. Sati, Thermochim. Acta, 70 (1983) 373.
2 S.S. Sawhney and A.K. Bansal, Thermochim. Acta, 66 (1983) 147.
3 S.S. Sawhney and N. Chandra, Thermochim. Acta, 61 (1983) 457.
4 S.S. Sawhney and A.K. Bansal, Thermochim. Acta, 59 (1982) 243.
5 N.G. Dave and S.K. Chopra, Z. Phys. Chem., Neue Folge, 48 (1966) 257.
6 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
7 S.S. Sawhney and R.M. Sati, Thermochim. Acta, 66 (1983) 351.