

## Note

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

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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).

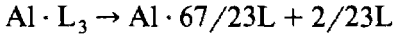
## EXPERIMENTAL

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.

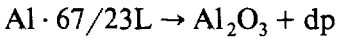
## RESULTS AND DISCUSSION

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:  $Al \cdot 67/23L$  and  $Fe \cdot 52/19L$  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.

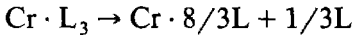
Each sigmoid was analysed kinetically. The kinetic data given in parentheses below the reaction, showed that the accompanying reactions follow first order kinetics (where  $E$  is measured in kcal mol<sup>-1</sup>).



$$(n = 1, E = 7.19 \text{ and } Z = 0.44)$$



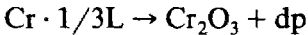
$$(n = 1, E = 13.50 \text{ and } Z = 0.16; n = 0.67 \text{ and } E = 16.20 \text{ (see eqn. 2)})$$



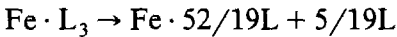
$$(n = 1, E = 5.95 \text{ and } Z = 0.27)$$



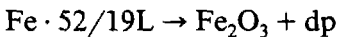
$$(n = 1, E = 21.90 \text{ and } Z = 1.99)$$



$$(n = 1, E = 13.73 \text{ and } Z = 0.35)$$



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



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

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

$$k = \frac{dx/dt}{A - a} \quad (1)$$

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

## REFERENCES

- 1 S.S. Sawhney and R.M. Sati, *Thermochim. Acta*, 70 (1983) 373.
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- 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.