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Note

EVALUATION OF THE KINETIC PARAMETERS OF THE NON-ISOTHERMAL DECOMPOSITION OF SOME POLYMERIC METAL COMPLEXES OF TEREPHTHALALDEHYDE BIS-(4-PHENYLTHIOSEMICARBAZONE) FROM DIFFERENTIAL THERMOGRAVIMETRIC CURVES

S.S. SAWHNEY, S.D. MATTA and R.M. SATI

Chemistry Department, D.A.V. (P.G.) College, Dehra Dun (U.P.) (India)

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Thiosemicarbazones form coordination polymers with bivalent metal ions [1—4]. Their derivatives have found applications in medicine [4—8]. Maurya et al. [9] have described the synthesis, general properties, stoichiometry, IR and reflectance spectra, magnetic susceptibility measurements and thermogravimetric analysis of complexes of Co(II), Ni(II), and Cu(II) with terephthalaldehyde bis-(4-phenylthiosemicarbazone) and assigned them the general formula $(ML \cdot 2\,H_2O)_n$, where n is the degree of polymerization, M is the metal ion and L is $C_{22}H_{18}N_6S_2$. The present communication concerns the evaluation of the kinetic parameters for the non-isothermal decomposition of these polymeric metal complexes, which do not find mention in the literature, with the help of the method of Dave and Chopra [10] and DTG curves of the complexes.

EXPERIMENTAL

Differential thermogravimetric curves were obtained utilizing the data from pyrolysis curves [9] obtained using a manually operated assembly with a heating rate of $10°C\ min^{-1}$.

RESULTS AND DISCUSSION

Since the data from TG curves obtained using a manually operated assembly have been utilized for DTG curves (dx/dt vs. temperature or time), the fluctuations in heating rate and temperature variations could not be ruled out. Thus the pyrolytic decomposition of polymeric complexes of Co(II), Cu(II) and Ni(II) with terephthalaldehyde bis-(4-phenylthiosemicarbazone) could not be probed kinetically using the method of Freeman and Carroll [11] in which the fluctuation in heating rate and temperature variation, etc., increasingly influence the kinetic data. Under such conditions, Dave and Chopra [10] recommended the use of the relationship

$$k = \frac{(A/m_0)^{n^*-1}(-dx/dt)}{(A-a)^{n^*}} \qquad (1)$$

where A is the total area under the differential thermogravimetric curve for any reaction, a is the area for the reaction up to time t, dx/dt is the height of the curve at time t, m_0 is the initial mole fraction of the reactant, and n^* is the order of the reaction with respect to the reactant.

When $n^* = 1$

$$k = \frac{(-dx/dt)}{(A-a)} \qquad (2)$$

Desolvation/decomposition of these polymers resembles the reaction

$As \rightarrow Bs + Cg$[11]

Values of ln k, calculated using eqn. (2) for first order reaction and the DTG curves, were plotted against the reciprocal of absolute temperature. A straight line relationship was obtained, thereby supporting the idea that non-isothermal desolvation/decomposition of polymeric complexes of Co(II), Ni(II), Cu(II) with terephthaladehyde bis-(4-phenylthiosemicarbazone) follow first order kinetics. The activation energy (E) and frequency factor (Z) were obtained from the slope ($-E/R$) and the intercept of the straight line (ln Z).

Table 1 gives the values of E and Z for different reactions. Data obtained by the method of Dave and Chopra are quite dependable as it does not

TABLE 1

Kinetic parameters for the pyrolytic decomposition of polymeric metal complexes of terephthalaldehyde bis-(4-phenylthiosemicarbazone)

Reaction	Temperature range (°C)	E (kcal mole^{-1})	n	Z
$(CO \cdot C_{22}H_{18}N_6S_2 \cdot 2\,H_2O)_n \rightarrow$ $(CO \cdot C_{22}H_{18}N_6S_2)_n + (2\,H_2O)_n$	90—200	1.39	1	1.42
$(CO \cdot C_{22}H_{18}N_6S_2)_n \rightarrow$ CO_3O_4 + dissociation product	230—550	7.95	1	1.28
$(Cu \cdot C_{22}H_{18}N_6S_2 \cdot 2\,H_2O)_n \rightarrow$ $(Cu \cdot C_{22}H_{18}N_6S_2)_n + (2\,H_2O)_n$	90—190	14.90	1	2.23
$(Cu \cdot C_{22}H_{18}N_6S_2)_n \rightarrow$ CuO + dissociation product	205—550	8.94	1	2.86
$(Ni \cdot C_{22}H_{18}N_6S_2 \cdot 2\,H_2O)_n \rightarrow$ $(Ni \cdot C_{22}H_{18}N_6S_2)_n + (2\,H_2O)_n$	90—200	11.92	1	1.82
$(Ni \cdot C_{22}H_{18}N_6S_2)_n \rightarrow$ NiO + dissociation product	270—605	14.90	1	17.28

involve the measurement of the slope of TG curves. Moreover, the plots (dx/dt vs. temperature) are joined by a smooth curve and the enclosed areas are used in the calculations; thus the effect of small fluctuations in the original TG tracings is largely minimized.

Looking at the abnormally low values of Z, it is concluded that the decomposition reaction of polymeric complexes of Co(II), Cu(II), Ni(II) with terephthalaldehyde bis-(4-phenylthiosemicarbazone) can be classed as slow reactions; no other possible reason can be given.

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