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Note

KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF MAGNESIUM SOAPS FROM DTG CURVES

S.S. SAWHNEY, D.N. DANGWAL, S.K. CHANDEL, S.R.S. ARYA and S.K. BHARDWAJ

Chemistry Department, D.A.V. (P.G.) College, Dehra Dun-248001 (India)

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The industrial and technological importance of metallic soaps, especially those of magnesium, as water-repelling agents, catalysts, stabilisers and lubricants [1,2], has led to increased investigation of these soaps. Marwedel [3], Easterfield and Taylor [4], Ludlam [5], Friedel [6], Williamson [7] and Melhrotra and Varma [8] have enriched the subject through their contributions. The literature reveals that the kinetics of transformation of metallic soaps have not been probed thermally; this note concerns the kinetics of the pyrolytic decomposition of magnesium soaps using Dave–Chopra [9] expressions, eqns. (1–3), which have previously been employed by Sawhney et al., for the kinetics of non-isothermal decomposition of metal complexes [10–16]. The Dave–Chopra method is chosen in preference to slope-dependent methods [17–19]. Varma and Kumar [20] described thermogravimetrically some magnesium soaps concluding the decomposition of soaps to be

$$[CH_3(CH_2)_{n'}COO]_2\,Mg \rightarrow CH_3(CH_2)_{n'}COCH_3(CH_2)_{n'} + CO_2 + MgO$$

where $n' = 3$ for valerate, $n' = 4$ for caproate, $n' = 6$ for caprylate, $n' = 8$ for caprate and $n' = 10$ for laurate.

$$k = \frac{(A/m_0)^{n-1}(\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

When $n = 1$, eqn. (1) reduces to

$$k = \frac{\mathrm{d}x/\mathrm{d}t}{A-a} \tag{2}$$

$$-\frac{(\mathrm{E}/2.303R)(1/T)}{\log(A-a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{3}$$

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EXPERIMENTAL

The derivative curve was obtained by manual differentiation of the TG curve which was recorded by Varma and Kumar [20] on a Stanton automatic recording balance at a heating rate of 250° h^{-1} under an air atmosphere.

RESULTS AND DISCUSSION

Thermogravimetric curves of magnesium soaps displayed only a sigmoid which was analysed, using the Dave–Chopra expressions, to give the kinetic data of non-isothermal decomposition, corresponding to different temperatures.

The values of A, a and dx/dt were calculated from the derivative thermogravimetric (DTG) curves. Assuming that the non-isothermal decomposition of the magnesium soaps follows first order kinetics, a plot of $\log k$ vs. $1/T$ [eqn. (1)] was drawn; first order kinetics was confirmed by the straight line relationship. The slope, $-E/2.303\,R$, and intercept, $\log Z$, were used for evaluating E and Z (collision number), respectively. Equation (3) was used to substantiate the kinetic data. A graph of $(1/T)/\log(A-a)$ was plotted against $\log(dx/dt)/\log(A-a)$; the intercept of the straight line so obtained gave the value of n (order of the reaction), and the value of E was obtained from the slope. Table 1 contains the kinetic data. Values of $\log Z$ are very low which led the authors to believe that the decomposition of the soaps is a slow process. The kinetic data derived from eqns. (2) and (3) tallied.

The Dave–Chopra procedure is preferred to other slope-dependent methods which exercise significant influences on kinetic data if the parameters, viz. heating rate, temperature variation, crucible geometry, etc., are not kept constant; in the Dave–Chopra procedure, slight fluctuations in these parameters do not affect the kinetic data.

TABLE 1

Kinetic data of the non-isothermal decomposition of magnesium soaps by the reaction $[CH_3(CH_2)_{n'}\cdot COO]_2Mg \rightarrow CH_3(CH_2)_{n'}\cdot COCH_3(CH_2)_{n'} + CO_2 + MgO$

n'	Temp. range (°C)	Eqn. (1)			Eqn. (2)	
		n	Z	E (kcal $mole^{-1}$)	n	E (kcal $mole^{-1}$)
3	162–657	1	0.40	9.15	1.075	5.95
4	118–620	1	0.17	8.97	1.100	6.61
6	129–662	1	0.05	5.72	1.080	4.12
8	106–518	1	0.22	7.63	1.050	5.95
10	150–485	1	0.07	6.41	1.010	5.95

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