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Note

KINETIC PARAMETERS FROM PYROLYSIS CURVES OF MAGNESIUM SOAPS

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Varma and Kumar [1] described the pyrolysis of magnesium soaps and arrived at the proposal that, since no plateau indicating the formation of an intermediate compound, probably magnesium carbonate, was observed, magnesium soaps decompose to magnesium oxide, carbon dioxide and the respective ketone (1)

$$[CH_3(CH_2)_{n'}COO]_2Mg \rightarrow \underset{\text{ketone}}{CH_3(CH_2)_{n'}COCH_3(CH_2)_{n'}} + CO_2 + MgO \quad (1)$$

where $n' = 3$ for valerate, $n' = 4$ for caproate, $n' = 6$ for caprylate, $n' = 8$ for caprate, and $n' = 10$ for laurate. In a previous communication Sawhney et al. [2] listed the kinetics of the non-isothermal decomposition of magnesium soaps using non-slope-dependent Dave and Chopra expressions [3] and their DTG curves. This note centres around the use of the slope-dependent Coats and Redfern [4] expression (2) and the comparison of these two different approaches.

$$-\log_{10}\left(\frac{-\log(1-\alpha)}{T^2}\right) = \log\frac{aE}{AR}\left(1 - \frac{2\,RT}{E}\right) + \frac{E}{2.3\,RT} = X + \frac{E}{2.3\,RT} \quad (2)$$

EXPERIMENTAL

The TG curves of Varma and Kumar [1] for the pyrolysis of magnesium soaps in air, obtained on a Stanton automatic recording balance, which meets all the necessary conditions for applying the slope-dependent expression (Coats and Redfern) for such a study, at a heating rate of 250°C h^{-1}, were used.

RESULT AND DISCUSSION

The kinetic study of the pyrolytic decomposition of magnesium soaps was made to a point after which the TG curves of the soaps under study,

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TABLE 1

Kinetic data for the non-isothermal decomposition of magnesium soaps due to Coats and Redfern (I) and Dave and Chopra (II, III) methods $[CH_3(CH_2)_{n'}COO]Mg \rightarrow CH_3(CH_2)_{n'}COCH_3(CH_2)_{n'} + CO_2 + MgO$

n'	Temp. range (°C)		n	X	E	α	$X + \log A$	$A \times 10^6$
3	I 168–282	I	1	6.90	9.20	0.01–0.10	1.19–1.16	1.90–1.80
	II, III 162–657	II	1		9.15			
		III	1.07		5.95			
4	I 100–230	I	1	5.80	9.11	0.01–0.10	1.20–1.17	25.10–25.00
	II, III 118–620	II	1		8.97			
		III	1.10		6.61			
6	I 120–306	I	1	6.25	4.60	0.01–0.12	0.80–0.68	158–120
	II, III 129–662	II	1		5.72			
		III	1.08		4.12			
8	I 96–228	I	1	6.40	10.25	0.01–0.11	1.26–1.24	7.20–6.90
	II, III 106–518	II	1		7.63			
		III	1.05		5.95			
10	I 156–312	I	1	6.80	6.80	0.01–0.11	1.01–0.97	1.60–1.40
	II, III 150–455	II	1		6.41			
		III	1.01		5.95			

displaying a sigmoid, assumed steepness. The fraction of soap decomposed, determined from the experimental weight data [w_0(initial weight), w(weight at time, t) and w_f(final weight)] was used to evaluate $-\log_{10}[-\log(1-\alpha)/T^2]$ which, when plotted against $1/T$, gave a straight line of slope $E/2.3\,R$ and intercept X; the latter ranged from 5.80 to 6.90. Values of $X+\log A$ (A being a constant) stood at 1.19–1.16, 1.20–1.17, 0.80–0.68, 1.26–1.24 and 1.01–0.97 for magnesium soaps with $n' = 3,4,6,8$ and 10, respectively, clearly upholding Coats and Redfern's concept on the evident constancy of $\log aE/AR(1-2RT/E)$ over the temperature range under study. Abnormally low values of frequency factor for all the reactions suggested that these thermal decomposition reactions are slow processes. Further, the kinetic data determined through slope-dependent and non-slope-dependent method were in good agreement (Table 1).

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