

# Kinetic Parameters from Thermogravimetric Curves of Magnesium Soaps

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Thermogravimetric equations have been applied to evaluate Kinetic parameters of magnesium soaps ( $C_8$ ,  $C_{10}$  and  $C_{12}$ ). Coats and Redfern derived equation for the thermal decomposition—shows first order kinetics. The activation energies have been determined from Horowitz-Metzger and Coats-Redfern equations. The data obtained from linear regression are in close agreement and are in the range (2 to 6 K Cal  $\text{mol}^{-1}$ ). The parameters are found to be independent of the chain length of the anion of n-alkanoates.

## INTRODUCTION

Magnesium soaps have been put to a number of uses in industry, technology and allied fields<sup>1-10</sup>. The exact information as to the nature and structure of the soaps plays a vital role for its applications in various fields. With the advent of modern thermoanalytical techniques, it is sinequa-non to collect kinetic data pertaining to solid state reactions and to gain insight of the structural phenomena occurring at high temperatures<sup>11</sup>. Kinetics of the non-isothermal decomposition of magnesium soaps were recently reported by Sawhney et al.<sup>12,13</sup> from DTG curves.

The present work is the study of solid state kinetics, involving the validity of important kinetic equations and to gather systematic account of the thermal stability of magnesium soaps (viz. caprylate, taprate and laurate) by isothermal decomposition using thermogravimetric analysis. Kinetic parameters also throw light in respect of chain length compatibility of the soap anion.

## EXPRIMENTAL

The soaps were prepared and purified by the method described earlier<sup>14</sup>. The thermogravimetric analysis of soaps was carried out at a constant rate of heating  $5^\circ \text{ minute}^{-1}$  on a TGA instrument made by Perkin-Elmer.

## RESULTS AND DISCUSSION

Of-course there has been renaissance of interest in thermal decomposition studies of large number of inorganic compounds. However, it is difficult to correlate thermal stability with all the properties of the compound. One property, nevertheless, namely the order and the energy of

activation of the decomposition reaction of a compound, can definitely be correlated with its thermal decomposition. A perusal of the time versus weight loss curves (Fig. 1) for magnesium soaps ( $C_8$ ,  $C_{10}$  and  $C_{12}$ ) shows that soap decomposes slowly in the beginning followed by rapid

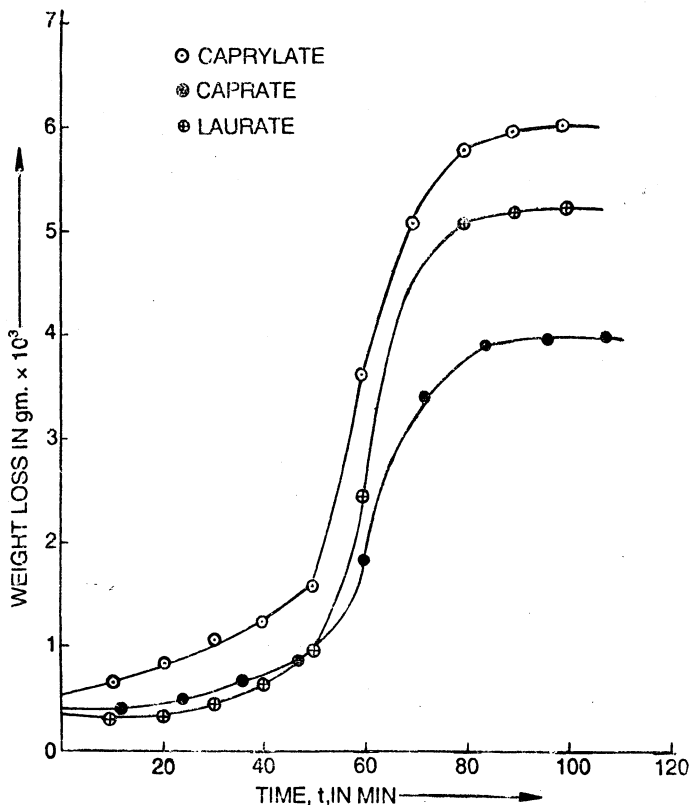


Fig. 1. Thermogravimetric Analysis of Magnesium Soaps.

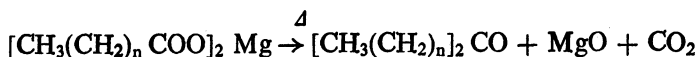
loss and ultimately decomposition ceases. The results of thermogravimetric analysis of magnesium soaps are given in Table 1. The data show that decomposition becomes fast above  $210^{\circ}\text{C}$  and attains steady value at about  $460^{\circ}\text{C}$ .

The results show that the final residue is magnesium oxide and the weight of the residue is almost equal to the theoretically calculated weight of magnesium oxide from the molecular formula of the soap.

It is found that some white crystalline powder is condensed at the cold part of the tube surrounding the sample and has been identified as caprylone, caprone and laurone corresponding to caprylate, caprate and laurate respectively. The thermal decomposition of the metal soaps can be expressed as

TABLE 1  
THERMOGRAVIMETRIC ANALYSIS OF MAGESIUM SOAPS

Time in Minutes	Temperature °K	Weight loss gm $\times 10^3$	Weight of residue gm $\times 10^3$
<i>Caprylate</i>			
10	383	0.7481	6.0533
20	433	0.8025	5.9989
30	483	0.9385	5.8629
40	533	1.7003	5.1011
50	583	3.1286	3.6728
60	633	5.1962	1.6052
70	683	5.5771	1.2243
80	733	5.7131	1.0883
90	783	5.9172	0.8842
100	833	6.1416	0.6598
<i>Caprate</i>			
12	383	0.3988	4.0334
24	443	0.4300	4.0022
36	503	0.4610	3.9712
48	563	0.9848	3.4474
60	623	2.5542	1.8780
72	683	3.5103	0.9219
84	743	3.7851	0.6471
96	803	3.9092	0.5230
108	863	4.0333	0.3989
<i>Laurate</i>			
10	383	0.7170	5.2567
20	433	0.7568	5.2169
30	483	0.8422	5.1315
40	533	1.3040	4.6697
50	583	2.9450	3.0287
60	633	4.9641	1.0096
70	683	5.3010	0.6727
80	733	5.5107	0.4630
90	783	5.5950	0.3787
100	833	5.6337	0.3400



where  $n$  stands for 6, 8, 10 corresponding to caprylate, caprate and laurate respectively.

Of the various methods of kinetic analysis Coats and Redfern<sup>15</sup> has been found to be the most appropriate in calculating the energy of activation. This method follows the rate law mentioned as under:

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \quad (1)$$

A temperature dependent Arrhenius equation of the type holds valid is:

$$K = Z e^{-E/RT} \quad (2)$$

where ' $\alpha$ ' stands for the fraction of soap transformed, ' $n$ ' for the reaction order, ' $K$ ' for the rate constant, ' $E$ ' for the energy of activation of the reaction, ' $R$ ' the gas constant = 1.987 cal mole<sup>-1</sup> (K)<sup>-1</sup> and ' $Z$ ' for the pre-exponential or frequency factor and is usually assigned to be independent of temperature ' $T$ '.

Integrating a combination of equations (1) and (2) and using approximate expression for inexact integral, Coats and Redfern derived the equation<sup>16</sup>

$$\log \frac{F(\alpha)}{T^2} = \log \frac{Z \cdot R}{\beta E} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.303RT} \quad (3)$$

where ' $\beta$ ' is the linear heating rate and is 5°C minute<sup>-1</sup> for the present investigation—

$$F(\alpha) = -\log(1 - \alpha) \quad \text{for } n = 1$$

Hence equation can be written as:

$$\log \left( \frac{-\log(1 - \alpha)}{T^2} \right) = \log \frac{ZR}{\beta E} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.303RT} \quad (4)$$

The value of activation energies calculated from the slope of plots of  $\log \left( \frac{-\log(1 - \alpha)}{T^2} \right)$  versus  $\frac{1}{T}$  (Fig. 2) are recorded in Table 2. It is clear from the data (Table 2) that the energy of activation increases with the increase in the chain length of the soap anion. This may be attributed to the fact that pyrolytic inhibition becomes more pronounced as the number of carbon atoms increases in the magnesium alkanolate.

To confirm the overall order of the reaction activation energy has again been calculated by Horowitz-Metzger method<sup>17</sup>. The Horowitz and Metzger equation can be written as

$$\log. \ln(1-\alpha)^{-1} = \frac{E}{RT_2^2\theta} \tag{5}$$

Where  $\alpha$  is the fraction of the soap decomposed at time  $t$ ,  $T_2$  is the temperature at which the rate of the decomposition is maximum and  $\theta$  is equal to  $(T-T_2)$ . The plots of  $\log. \ln(1-\alpha)^{-1}$  against  $\theta$  are shown in Fig. 3 and the values of the energy of activation calculated from the slopes of these plots are given in Table 2. The values of activation energies obtained from this equation are in fairly close agreement with the values obtained from Coats-Redfern's method.

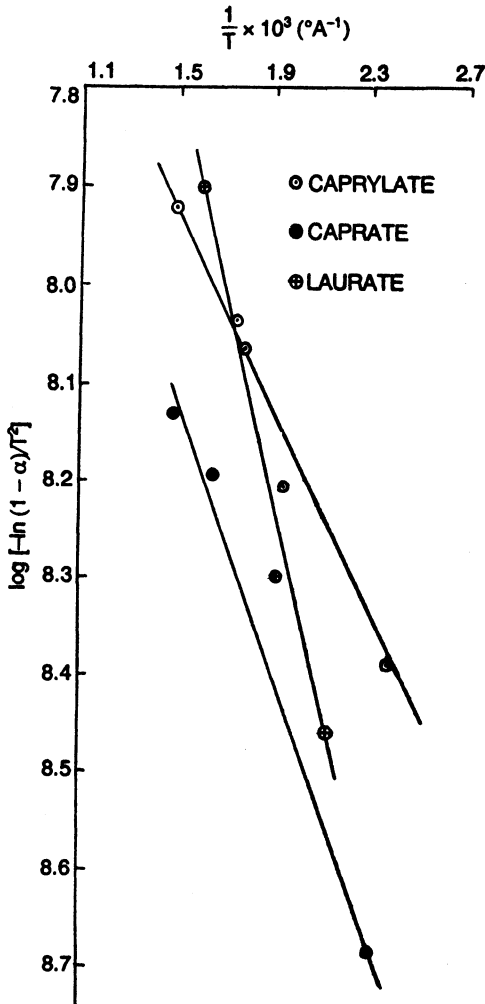


Fig. 2 Coats and Redfern's plots for magnesium soaps

Mention may also be made of the fact that although decomposition of magnesium soap is continuous with respect to time and temperature, but Freeman and Carroll method is not applicable as the plots of

TABLE 2  
ENERGY OF ACTIVATION (IH K Cal. mole<sup>-1</sup>)  
FOR THE DECOMPOSITION REACTION OF  
MAGNESIUM SOAPS FROM DIFFERENT  
EQUATION

Name of the Soap	Coats and Redfern's equation	Horowitz and Metzger's equation
Caprylate	2.8280	3.1110
Caprate	3.2032	3.1569
Laurate	5.2297	5.5515

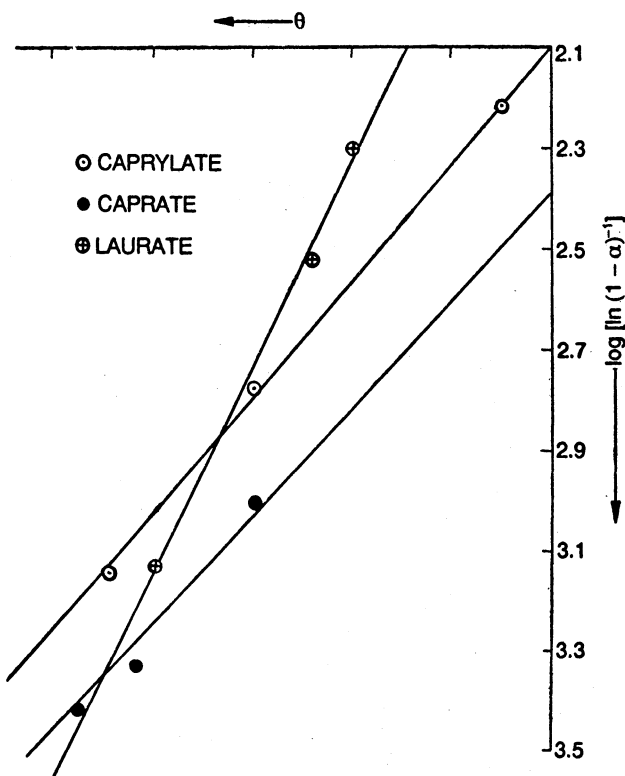


Fig. 3 Horowitz and Metzger's plots for magnesium soaps

$\left[ \frac{\Delta \log \left( \frac{dw}{dt} \right)}{\Delta \log W_r} \right]$  versus  $\Delta \left( \frac{1}{T} \right)$  do not pass through the origin confirming that the order of reaction is not zero.

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