

Studies on Dynamic Thermogravimetry of Barium salts of α -Amino Substituted Fatty Acids

R.P. VARMA*, HARMENDRA GOEL and V.K. MALHOTRA†

Department of Chemistry,
D.A.V. College, Muzaffarnagar-251 001, India

The thermal decompositions of barium salts of α -amino substituted fatty acids (n-butyric acid, *n*-caproic acid and *iso*-caproic acid) was studied by thermogravimetry (TG) under dynamic conditions. Energies of activation have been evaluated by mechanistic models and Coats and Redfern equation. The order of reaction is found to be zero. The values of frequency factor Z, entropy ΔS and free energy ΔG of activation have been evaluated and a probable mechanism of decomposition has been proposed.

INTRODUCTION

Thermogravimetry is a method in which the weight of the sample is continuously recorded during heating or cooling. It gives informations of the sample composition, thermal stability, thermal decomposition and products formed on heating. Several workers^{1,2} studied the thermal decomposition of barium soaps which yields corresponding ketones on heating. Thermal decomposition of barium soaps was studied^{3,4}, both as a function of temperature and time. The whole range of isothermal decomposition of barium soaps was most adequately expressed by Prout-Tompkins equations using two different rate constants. Thermal decomposition of alkaline earth metal soap was also reported by Lorant⁵. In order to explore the thermal stabilities of barium salts of α -amino substituted fatty acids the non-isothermal decomposition of the salts was examined. Activation energies and other kinetic parameters were calculated to enable the probable mechanism of decomposition to be suggested.

EXPERIMENTAL

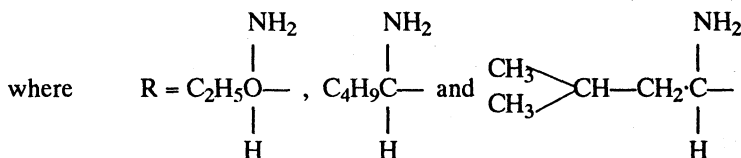
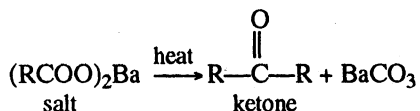
Amino acids were obtained from Sigma Chem. Co., U.S.A. and A.R. barium carbonate from B.D.H. Barium salts of α -amino fatty acids (n-butyric, caproic and *iso*-caproic acids) were prepared by the method described earlier⁶. TGA curve was obtained by derivatograph MOM, Budepest (Hungary), model Paulik Erdy. The samples were powdered and then heated in air at the rate of $10 \pm 1^\circ\text{C min}^{-1}$.

†Department of Chemistry, S.D. College, Panipat (Haryana), India.

RESULTS AND DISCUSSION

Thermogravimetric curves show that the salts decompose insignificantly upto 200–260°C, rapidly and finally no change occurs with further increase in temperature above 400°, 520° and 320°C, respectively for α -amino barium butyrate, α -amino barium caproate and α -amino *iso*-caproate. The results of thermogravimetric analysis show that final residue is barium carbonate.

The weights of the residue of these salts are almost equal to theoretically calculated barium carbonate from the molecular formula of salts. Thus barium salts decompose into barium carbonate and the ketone which goes off from the sample.



In this dynamic TG study the fractional decomposition values, α , were used to study the kinetics of the overall decomposition process by method described elsewhere^{7,8}. The fractional decomposition, α , and the rate of solid state decomposition reaction are related by the general equation $\frac{d\alpha}{dt} = kf(\alpha)$ where $f(\alpha)$ is a function of α which is governed by rate controlling process and $k = Ze^{-E/RT}$. Here Z and E are the frequency factor and energy of activation respectively. The integral $\sum_0^\infty \frac{d\alpha}{f(\alpha)} = g(\alpha)$ can have the following different values:⁷

$$\alpha^2, -\ln(1-\alpha), 1-(1-\alpha)^{1/3}, [-\ln(1-\alpha)]^{1/2}, [-\ln(1-\alpha)]^{1/3}, [1-(1-\alpha)^{1/3}]^2$$

The graphs of $g(\alpha)$ vs. T^{-1} for different possible mechanisms are linear only for those $\log g(\alpha)$ vs. $T^{1/2}$ graphs which illustrate the probable rate controlling process. Here the plots are linear for α^2 , $-\ln(1-\alpha)$ and $[-\ln(1-\alpha)]^{1/2}$. The activation energies have been calculated from these linear plots and are given in Table 1. The energies of activation of the decomposition of these salts have been calculated by Coats and Redfern equation⁸. The plots of $\log \frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}$ vs. T^{-1} for $n=0$ and $\log \frac{-\ln(1-\alpha)}{T^2}$ vs. T^{-1} for $n=1$ results in straight lines. On comparison it is found that energy of activation (Table 1) calculated from the

mechanistic models corresponds only to the zero order. The frequency factor Z , entropy ΔS and free energy ΔG have been calculated from the Coats-Redfern, Eyring and Gibb's equations and are given in Table 2 at 498 K. The values of Z , ΔS and ΔG are found to be same for the soaps of α -amino-*n*-caproic acid and α -amino *iso*-caproic acid but differ much in case of α -amino-*n*-butyric acid.

TABLE 1
ACTIVATION ENERGIES, E (kJ mol^{-1}) OBTAINED FROM DIFFERENT
EQUATIONS FOR BARIUM SALTS

Equations	α -Amino- <i>n</i> -butyrate	α -Amino- <i>n</i> -caproate	α -Amino- <i>iso</i> -caproate
Mechanistic			
α^2	55.2	56.23	-81.23
$-\ln(1 - \alpha)$	49.02	46.23	91.85
$-\ln(1 - \alpha)^{1/2}$	23.28	46.42	75.32
Coats and Redfern			
1	48.95	47.25	-92.30
0	56.25	50.30	-85.25

TABLE 2
FREQUENCY FACTOR, Z , ENTROPIES, ΔS AND FREE ENERGIES,
 ΔG OF ACTIVATION FOR BARIUM SALTS AT 498 K

Parameter	α -Amino- <i>n</i> -butyrate	α -Amino- <i>n</i> -caproate	α -Amino- <i>iso</i> -caproate
Z (s^{-1})	1.528×10^{-5}	2.30×10^{-4}	1.095×10^{-5}
ΔS ($\text{JK}^{-1} \text{mol}^{-1}$)	-328	-308	330
ΔG (kJ mol^{-1})	98.02	89.85	97.85

It is suggested that the surface of the soap molecules remains fully covered all the time by the molecules of the gaseous product. Since the decomposition is fast, the rate of the reaction for such a system can be written as below:

$$\frac{dx}{dt} = \frac{k_1 p}{k_2 p + 1}$$

where k_1 and k_2 are constants and p stands for the pressure of the gaseous product.

When the surface of the soap molecules is fully covered by the product, the rate of decomposition becomes constant and the process is kinetically of zero order. Similar results have been obtained for nickel ammonia complex⁹, zinc stearate¹⁰ and rubidium soaps.

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