Thermal behaviour and Kinetics of manganese myristate and stearate by thermogravimetric analysis

DR. CHANDRAWATI
Associate Professor,
Head, Department of chemistry
D.P.D.S. P.G. College Anoopshahr, Bulandshahr (U.P.) India

Abstract:
TGA technique have been used to applied for manganese myristate and stearate soaps to determine their thermal analysis kinetics and evaluation of energy of activation by using the various equation Freeman Carroll's, Coat-Redfern's and horowitz-Metzer's equations. Thermogravimetric analysis of these soaps carried out by 780 series Stanton redford UK in the static air medium at constant 180 degree per minute and maintaining similar conditions throughout the investigation the result revels that the decomposition reaction for manganese myristate and stearate soaps are found to be kinetically zero order and the value for the energy of activation of metal soaps lies in the range 13.81-25.48K.cal/mole and activation energy increases with increasing the chain length.

Keywords: *TGA, isothermally, transition metal, decomposition, Kinetic, activation energy, chain length, manganese, myristone, stearone*

1. Introduction

The metal soaps are generally insoluble in water but possesses high solubility in non-polar solvents and have comparatively high metal content which land them unique properties and make them useful in various industries and are finding application in many diversify field. The utility of metal soaps mainly depends on their physical state, stability, chemical reactivity and solubility in various non polar solvent or solvent mixture. The physico chemical characteristics and structure of metal soaps can be maintained up to an extent by the method and condition of their preparation. The heavy metal soaps have valuable application in technological field and academic and other important role in many diversify field like as dryers, thickeners, Paints, catalysts, lubricants, wetting agent, plastic, cosmetics, ink, stabilizers etc. by several workers.TGA measure the amount of weight change of material of manganese myristate and stearate either as a function of increasing temperature isothermally or as a function of time by maintaining similar conditions throughout the investigation.

2. Method and materials

All the chemicals used were of AR grade. The purity of chemical checked by elemental analysis. Potassium myristate and stearate soaps were prepared by refluxing equivalent amount of corresponding fatty acids (myristate and stearate) and aquous solution of potassium Hydroxide for 6 to 8 hours. Manganese soaps were prepared by direct metathesis of corresponding potassium soaps (myristate and stearate) with slight excess of manganese chloride. The precipitated soaps washed many times with Acetone and distilled water. The prepared soaps dried in an air oven at 50 degree to 60 degree. The final drying of precipitated soaps was carried out under reduced pressure, finally the soaps were purified by crystallization with Benzene Methanol mixture the purity of soaps was confirmed by their melting point and absence of Hydroxide group in the soaps were confirmed by studying their infrared absorption spectrum. Thermogravimetric analysis of manganese and stearate soaps were carried out by 780 series Stanton UK in static air medium at constant heating rate 10 degree per minute in nitrogen atmosphere and maintaining similar condition throughout the investigations.

Result and discussion

The values of decomposition process of heavy metal soaps reveals that initially decreases slowly because of removal or loss of water and carbon dioxide molecule and then fast due to the removal of ketone (carbonyl)and finally it is constant due to formation of oxide of manganese as mention in table 1-2.The weight of final Residue metal oxides are in agreement with theoretically calculated weight of manganese oxide from the molecular formula of the corresponding soaps .Thermal decomposition may be expressed as.

$(RCOO)_2MRCOR$ + MO or M_2O_3 + CO_2
Ketone   Metal oxide   Carbon Dioxide
$\longrightarrow$

where R is $–C_{13}H_{27}$, and $–C_{17}H_{35}$ for myristate and stearate, respectively and M is manganese metal and treatment data mention in table 1.2

The result of thermal decomposition of manganese so have been explained in terms of various equation, Freeman Carroll’s rate equation for thermal decomposition for various metal soaps may be expressed as.

Freeman–Carroll[223] rate expression for the thermal decomposition of various soaps may be expressed as:

$$\frac{\Delta[\log(d\omega\omega/dt)]}{\Delta\log\omega_r}=-\frac{E}{2.303R}\times\frac{\Delta[1/T]}{\Delta(\log\omega_r)}+n$$

Where,
T = Temperature on absolute scale;
n = order of decomposition reaction
E = Energy of activation;
ω_r = Difference between the total loss in weight and the loss in weight at time, t i.e. $\omega_0–\omega_t$; and $(d\omega/dt)$ = Value of rate of weight loss obtained from the loss in weight vs time curves at appropriate time. Treatment data of TGA according to above equation given in table 3 and 4

Table-1: **Thermogravimetric Analysis of Manganese Myristate**

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, w × 10^3 (g)	dw/dt.10^6	$w_r.10^3$
1.	5.0	321	0.000	--	0.8874
2.	7.8	359	0.110	1.4102	0.8764
3.	9.8	364	0.0220	2.2449	0.8654
4.	11.7	390	0.0352	3.0085	0.8522
5.	13.2	415	0.0502	3.8030	0.8372
6.	15.4	427	0.0609	3.9545	0.8265
7.	17.6	450	0.0681	3.9261	0.8183
8.	21.4	480	0.0753	3.5189	0.8121
9.	25.2	525	0.0852	3.3809	0.8022
10.	27.2	540	0.1002	3.6838	0.7872
11.	28.9	555	0.1560	5.3979	0.7314
12.	29.5	568	0.2007	6.8034	0.6867
13.	30.2	575	0.2715	8.9900	0.6159

14.	30.9	582	0.3510	11.3592	0.5364
15.	31.6	589	0.4462	14.1202	0.4412
16.	32.3	596	0.5547	17.1734	0.3327
17.	33.4	605	0.6848	20.5029	0.2026
18.	34.8	620	0.7720	22.1839	0.1154
19.	39.3	650	0.8235	20.9542	0.0639
20.	42.9	710	0.8590	20.0233	0.0284
21.	45.1	735	0.8659	19.1995	0.0215
22.	48.4	760	0.8874	18.3347	0.0000

Table 2: **Thermogravimetric Analysis of Manganese Stearate**

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, w × 10^3 (g)	dw/dt.10^6	$w_r.10^3$
1.	14.0	313	0.00	--	0.5580
2.	18.0	453	0.0237	1.3166	0.5343
3.	21.5	489	0.0320	1.4883	0.5260
4.	23.9	508	0.0418	1.7489	2.5162
5.	26.0	533	0.0523	2.0115	0.5057
6.	27.4	547	0.0680	2.4817	0.4900
7.	28.0	554	0.0825	2.9464	0.4755
8.	28.5	558	0.1048	2.6772	0.4532
9.	28.8	561	0.1274	4.4236	0.4306
10.	29.1	565	0.1502	5.0572	0.4078
11.	29.5	568	0.1670	5.6610	0.3910
12.	29.9	572	0.1950	6.5218	0.3630
13.	30.2	575	0.2241	7.4205	0.3339
14.	30.6	579	0.2580	8.4314	0.3000
15.	30.9	582	0.3072	9.9417	0.2508
16.	31.3	586	0.3282	10.4222	0.2318
17.	31.6	589	0.3685	11.6614	0.1895
18.	32.0	593	0.3945	12.3281	0.1635
19.	32.8	597	0.4270	13.0183	0.1310
20.	33.7	605	0.4510	13.3828	0.1070
21.	34.5	618	0.4710	13.6522	0.0870
22.	35.6	627	0.4755	13.3567	0.0825
23.	38.0	653	0.4838	12.7316	0.0742
24.	39.0	663	0.4980	12.7692	0.0600
25.	41.2	678	0.5150	12.5000	0.0430
26.	42.5	695	0.5166	12.1553	0.0414
27.	44.9	713	0.5290	11.7817	0.0290
28.	46.0	743	0.5436	11.8174	0.0144

Table 3: **Freeman – Carroll's Treatment of Thermogravimetric Data of Manganese Stearate**

S. No.	$\frac{1}{T}\times10^5$	$-\Delta(\log\omega_r)$	$-\Delta(\log\frac{d\omega}{dt})$	$\frac{-\Delta(1/T)}{-(\log\omega_r)}\times10^4$	$\frac{-\Delta(\log d\omega/dt)}{-\Delta(\log\omega_r)}$
1.	319	3.2534	--	9.8051	--
2.	220	3.2722	5.8807	6.7233	1.7971
3.	216	3.2790	5.8274	6.5873	1.7772
4.	197	3.2871	5.7574	5.9931	1.7515
5.	187	3.2961	5.6966	5.6733	1.7283
6.	183	3.3098	5.6054	5.5290	1.6935
7.	180	3.3228	5.5308	5.4170	1.6645
8.	179	3.3437	5.4345	5.3533	1.6253
9.	178	3.3659	5.3542	5.2883	1.5907
10.	177	3.3895	5.2961	5.2220	1.5625
11.	176	3.4078	5.2471	5.1646	1.5381
12.	175	3.4401	5.1857	5.0871	1.5074
13.	174	3.4764	5.1296	5.0051	1.4755
14.	173	3.5228	5.5229	4.8108	1.5677
15.	172	3.6008	5.6007	4.7767	1.5554
16.	170	3.6349	5.6349	4.6768	1.5502
17.	169	3.7223	5.7224	4.4632	1.5373
18.	168	3.7865	5.7865	4.4368	1.5282
19.	167	3.8827	5.8827	4.3011	1.5151
20.	165	3.9706	5.9706	4.1555	1.5037
21.	162	4.0605	6.0605	3.9896	1.4925
22.	159	4.0835	6.0835	3.8937	1.4922
23.	153	4.1295	6.1296	3.7050	1.4843
24.	157	4.2218	6.2218	3.5766	1.4737
25.	147	4.3665	6.3665	3.3665	1.4580
26.	144	4.3829	6.3830	3.2854	1.4563

Table 4: **Freeman – Carroll's Treatment of Thermogravimetric Data Of Manganese Myristate**

S. No.	$\frac{1}{T}\times10^5$	$-\Delta(\log\omega_r)$	$-\Delta(\log\frac{d\omega}{dt})$	$\frac{1/T}{-\Delta(\log\omega_r)}\times10^4$	$\frac{-\Delta(\log d\omega/dt)}{-\Delta(\log\omega_r)}$
1.	309	3.2822	--	9.4144	--
2.	277	3.2935	5.6925	8.4105	1.7284
3.	243	3.3009	5.6262	7.3616	1.7044
4.	222	3.3118	5.5427	6.7033	1.6736
5.	204	3.3217	5.5043	6.1414	1.6571
6.	182	3.426	5.0684	5.3123	1.4793
7.	175	3.6232	4.8477	4.8299	1.3380
8.	164	3.7770	4.8077	4.3421	1.2729
9.	154	4.1785	4.7528	3.6855	1.1374
10.	145	4.3089	4.7723	3.3651	1.1075
11.	137	4.3706	4.8049	3.1345	1.0993

12.	130	4.5214	4.8369	2.8752	1.0698
13.	123	4.7670	4.8433	2.5835	1.0160
14.	118	4.8508	4.8825	2.4325	1.0065
15.	112	4.8827	4.9092	2.2938	1.0054
16.	108	4.995	4.9342	2.1622	0.9869
17.	103	5.3372	4.9545	1.9298	0.9283
18.	99	5.3872	4.9785	1.8376	0.9241
19.	95	5.5086	5.0075	1.7245	0.9090
20.	92	5.6778	5.0212	1.6221	0.8853
21.	88	--	5.0419	--	--

Table 5: Coats - Redfern's Treatment Of Thermogravimetric Data Of Manganese Myristate

S. No.	Temperature, T (A)	$1/T \times 10^5$	α	$-[\log(\alpha/T^2)]$
1.	321	311	0	--
2.	359	278	0.010	7.1101
3.	364	275	0.020	6.6211
4.	390	256	0.033	6.6636
5.	415	241	0.048	6.5548
6.	427	234	0.058	6.4974
7.	450	222	0.066	6.4868
8.	480	208	0.072	6.5051
9.	525	190	0.081	6.5318
10.	540	185	0.095	6.4871
11.	555	180	0.148	6.3183
12.	568	176	0.191	6.2276
13.	575	174	0.258	6.1077
14.	582	172	0.334	6.0061
15.	589	170	0.425	5.9118
16.	596	168	0.528	5.8278
17.	605	165	0.652	5.7492
18.	620	161	0.735	5.7184
19.	650	154	0.784	5.7315
20.	710	141	0.818	5.7897

Table 6: Coats - Redfern's Treatment of Thermogravimetric Data of Manganese Stearate

S. No.	Temperature, T (A)	$1/T \times 10^5$	α	$-[\log(\alpha/T^2)]$
1.	313	319	--	--
2.	453	220	0.037	6.7439
3.	489	216	0.051	6.6710
4.	508	197	0.065	6.5988
5.	533	187	0.083	6.5343
6.	547	183	0.107	6.4466
7.	554	180	0.130	6.3730
8.	558	179	0.166	6.2731
9.	561	178	0.201	6.1947
10.	565	177	0.237	6.1293
11.	568	176	0.264	6.0871
12.	572	175	0.308	6.0262
13.	575	174	0.354	5.9703
14.	579	173	0.408	5.9146
15.	582	172	0.486	5.8432
16.	586	170	0.516	5.8231
17.	589	169	0.583	5.7745
18.	593	168	0.624	5.7509
19.	597	167	0.675	5.7226
20.	605	165	0.713	5.7104
21.	618	162	0.745	5.7098
22.	627	159	0.752	5.7183
23.	653	153	0.765	5.7461
24.	663	151	0.788	5.7465
25.	678	147	0.815	5.7513
26.	695	144	0.817	5.7717

As a result from Freeman Carroll's equation indicate that the thermal decomposition of these soaps shows kinetically of zero order and the value of activation for the decomposition of manganese soaps obtained from the plot lie in the range14.06 – 15.17 K. calorie / mole.

Coats and Redfern's[224] equation (Table 5and 6) also provides a method for the evaluation of energy of activation for the thermal decomposition of metal soaps Coats and Redfern's equation for the thermal decomposition of a compound can be expressed as :

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

Where,
α = Fraction of the soap decomposed;
T = Temperature on absolute scale;
R = Gas constant;
A = Frequency factor;
a = Rate of heating in ^{O}C per minute;
E = Energy of activation; and

n = Order of reaction

The equation for zero order reaction can be written as:

$$\log\frac{\alpha}{T^2}=\log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

It may be pointed out that the plots of log(a/T) against (1/T) should be a straight line with its slope equal to (-E/2.303R). The values of the energy of activation for manganese soaps lie in the range 13.81 to 17.84 k.cal per mole.

The value of energy of energy of activation for the thermal decomposition of manganese soaps of different fatty acids have also been calculated by using Horowitz and Metzger's equation and expressed as

$$\ln\left[\ln(1-\alpha)^{-1}\right]=\frac{E}{RT_S^2}.\theta$$

Where,

α = Fraction of the soap decomposed at time, t

E = Energy of activation

T_S = Temperature on absolute scale at which the rate of decomposition is maximum, and

$\theta = T - T_s$

The plots of ln [ln (1 - α)$^{-1}$] against θ for manganese myristate, manganese stearate shows the value of energy of activation obtained from the slope of the curve lies in the range of 24.33 to 25.48K. cal. Mol^{-1} and treatment data mention in table 7and 8.

Table 7: Horowitz – Metzger's Treatment of Thermogravimetric Data of Manganese Myristate

S. No.	Temperature, T (A)	$\theta = (T - T_S)$	$1 - \alpha$	$\frac{1}{(1-\alpha)}$	$-l_n\left[-l_n(1-\alpha)^{-1}\right]$
1.	321	299	--	--	--
2.	359	261	0.990	1.0101	4.6001
3.	364	256	0.980	1.0204	3.9019
4.	390	230	0.967	1.0341	3.3945
5.	415	205	0.952	1.0504	3.0120
6.	427	193	0.942	1.0615	2.8175
7.	450	170	0.934	1.0706	2.6841
8.	480	140	0.928	1.0775	2.5939
9.	525	95	0.919	1.0881	2.4713
10.	540	80	0.905	1.1049	2.3043
11.	555	65	0.852	1.1737	1.8315
12.	568	52	0.809	1.2361	1.5513
13.	575	45	0.742	1.3477	1.2093
14.	582	38	0.666	1.5015	0.9002
15.	589	31	0.575	1.7391	0.5917
16.	596	24	0.472	2.1186	0.2866

17.	605	15	0.348	2.8735	0.0540
18.	620	0	0.265	3.7735	+0.2836
19.	650	-30	0.216	4.6296	+0.4268
20.	710	-90	0.182	5.4945	+0.5328
21.	735	-115	0.176	5.6818	+0.5523
22.	760	-140	0.155	6.4516	+0.6229

Table 8: Horowitz – Metzger's Treatment of Thermogravimetric Data of Manganese Stearate

S. No.	Temperature, T (A)	θ = (T – T_S)	1 - α	$\frac{1}{(1-\alpha)}$	$-l_n\left[-l_n(1-\alpha)^{-1}\right]$
1.	313	305	--	--	--
2.	453	165	0.963	1.0384	3.2780
3.	489	129	0.945	1.0582	2.8722
4.	508	110	0.935	1.0695	2.6999
5.	533	85	0.917	1.0905	2.4459
6.	547	71	0.893	1.1198	2.1788
7.	554	64	0.870	1.1494	1.9713
8.	558	60	0.834	1.1990	1.7063
9.	561	57	0.799	1.2515	1.4943
10.	565	53	0.763	1.3106	1.3075
11.	568	50	0.736	1.3587	1.1824
12.	572	46	0.692	1.4451	0.9992
13.	575	43	0.646	1.5479	0.8279
14.	579	39	0.592	1.6892	0.6458
15.	582	36	0.514	1.9455	0.4072
16.	586	32	0.484	2.0661	0.3206
17.	589	29	0.417	2.3980	0.1339
18.	593	25	0.376	2.6595	0.0220

19.	597	21	0.325	3.0769	+0.1168
20.	603	13	0.287	3.4843	+0.2217
21.	618	0	0.255	3.9215	+0.3122
22.	627	-9	0.248	4.0322	+0.3324
23.	653	-35	0.235	4.2553	+0.3703
24.	663	-45	0.212	4.7169	+0.4390
25.	678	-60	0.185	5.4054	+0.5237
26.	695	-77	0.183	5.4645	+0.5296
27.	713	-95	0.163	6.1349	+0.5955
28.	743	-125	0.140	7.1428	+0.6760
29.	761	-143	0.125	8.0000	+0.7321
30.	798	-180	0.117	8.5470	+0.7632

It is suggested that the surface of the soap molecule remain completely covered all the time by the molecule of gases product as the decomposition is fast and so the rate of decomposition becomes constant and the process a kinetically of zero order and the comparative activation energy of the manganese soaps for the process lies in the range of 13.8 1 – 25.4 8 k. cal. per mole in table 9

Table 9: Energy of activation (k cal. Mol^{-1}) for the decomposition of manganese soaps by using various equations

S. No.	Name of the soap	Freeman and Carroll’s Equation	Coats and Redfern’s Equation	Horowitz and Metzger’s Equation
1.	Manganese myristate	14.08	13.81	24.33
2.	Manganese stearate	15.17	17.84	25.48

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