

Thermal Decomposition Analysis on Carboxylates of Vanadium in Solid State

Abstract

The thermal decomposition analysis were made on carboxylates of vanadium (Palmitate, and Stearate) in solid state with a view to determine the Rate of reaction, Order of reaction and Energy of activation. The result show that the order of reaction for the decomposition of carboxylates of vanadium is zero order and the Energy of activation lie between 7.4 - 9.9 k cal mol⁻¹. These results were discussed in term of some well known equation and the results were in agreement with properties.

Keywords: Carboxylates, Order of Reaction, Energy of Activation.

Introduction

The carboxylates of transition metals are being widely used in industry, technology and allied sciences. The uses of metal carboxylates largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents. These metal carboxylates has been a subject intense investigation in the recent past on account of its role in such diversified field as medicine, cosmetic emulsifier, lubricant, germicides and anti oxidant. The methods of preparation of potassium soaps and metal carboxylates were described by several workers (1-6). The IR spectra and x-ray diffraction pattern of manganese and zinc soaps were studied by Upadhyaya et al.(7). The thermal decomposition kinetics of nickel and manganese soaps were studied by Mehrotra et al.(8). The physicochemical studies on Erbium soaps of saturated higher fatty acids in solid state studied by Rajesh et al.(9). The viscometric and spectral studies of copper soap in benzene and methanol mixture were studied by Rawat(10). The ultrasonic behavior on carboxylates of vanadium in mixed organic solvent was studied by Khirwar (11). The studies of ultrasonic velocity and allied properties of manganese, cobalt and copper soaps in non aqueous medium Rawat (12). In the present work attempts have been made to determine the various physical properties (rate of reaction, order of reaction and energy of activation) of carboxylates of Vanadium by thermogravimetric analysis.

Aim of the Study

The results of the survey of literature reveals that the thermogravimetric analysis on carboxylates of Vanadium have not been systematically investigated while they have many uses in industries and academic field. The aim of this research work is to study the thermogravimetric analysis on carboxylates of Vanadium in solid state.

Experimental

The carboxylates of vanadium (Palmitate and Stearate) were synthesized by direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of vanadium nitrate at 50-55°C under vigorous stirring. The precipitated soaps were washed several times with distilled water and acetone to remove the fatty acid and metal nitrate. The soaps were purified by recrystallisation, dried in an air oven at 50-60°C and the finally drying of the soaps were carried out under reduced pressure. The purity of the carboxylates of vanadium were checked by IR spectra and determination of their melting points. The thermogravimetric analysis on carboxylates of vanadium were carried out by a Perkin-Elmer thermogravimetric analyser TGS2 at constant heating rate (10° per minute) in nitrogen atmosphere.

Review of Literature

Present research work reviews the literature relevant with the aim of study. the thermogravimetric analysis on carboxylates of transition metals have been studied by several workers. Some of them are listed below.



M.S.Khirwar

Assistant Professor,
Deptt. of Chemistry,
R.B.S. College,
Agra, U.P.

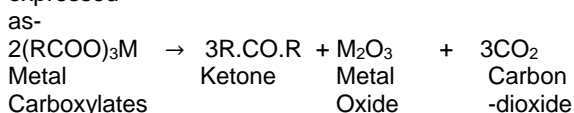
M.S.Khirwar (2016) was studied the thermogravimetric analysis of yttrium soaps in solid.

Rajesh Dwivedi (2014) was studied the Physicochemical Studies on Erbium Soaps of Saturated Higher Fatty Acids in Solid State.

K . N. Mehrotra (1997) was studied the thermal decomposition kinetics of nickel and manganese soaps.

Result and Discussion

The results of thermal decomposition analysis on carboxylates of vanadium (Palmitate and Stearate) and the treatment of the data recorded in (table: 1-3). The final residue on thermal decomposition of vanadium soap is vanadium oxide. This conclusion is in harmony with the fact that the weight of residue is in agreement with theoretically calculated weight of vanadium oxide from the molecular formula of the corresponding soap. It may be pointed out that some white crystalline powder is found condensed at the cold part of the sample tube surrounding the soap and it is identified by the determination of M.P., Plamitone (84.8°C) and stearone (89.6°C) for vanadium carboxylates of Palmitate and Stearate, respectively. The thermal decomposition on carboxylates of vanadium can be expressed



Where, M is vanadium metal, R is C₁₅H₃₁ and C₁₇H₃₅ for Palmitate and Stearate, respectively.

Freeman and Carroll's [13] expression for the thermal decomposition of Vanadium carboxylates where the soap disappears continuously with time and temperature and one product is gaseous can be expressed as-

$$\log \left(\frac{dw/dt}{\Delta(\log W_r)} \right) = \frac{-E}{2.303RT} \cdot \frac{\Delta t(1/T)}{\Delta(\log W_r)} + n$$

where E, n, T, W_r and dw/dt are Energy of activation, Order of reaction, Temperature on absolute scale, Difference between the total loss in weight and the loss in weight at time t, and Rate of weight loss

obtained from the loss in weight vs time curves at appropriate times, respectively.

The plots of the loss in weight of the soap, W against time t, and values of (dw/dt) are obtained from the curves by drawing tangents at appropriate times. The values of W_r have been calculated from the total loss in weight of the soap and the loss at predetermined time (table: 1) and the plots of Δ(log(dw/dt))/Δ(log W_r) against Δ(1/T)/Δ(log W_r) are obtained. The treatment of the thermogravimetric data according to Freeman-Carroll's equation is given in (table: 2).

The results indicate that the order of reaction for decomposition of Vanadium carboxylates is zero order and the values of energy of activation lie between 7.4-9.9 k cal mol⁻¹ (table: 4).

It is suggested that the surface of the metal carboxylates molecules remains completely covered all the time by the molecules of the gaseous product as the decomposition is fast so that rate of the decomposition becomes constant and process is kinetically of zero order.

The values of the energy of activation for the thermal decomposition of Vanadium carboxylates have also been calculated by using coats and Redfern's [14] equation which 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, T, R, A, a, E and n are Fraction of the soap decomposed, Temperature on absolute scales, Gas constant, Frequency factor, Rate of heating in °C per minute, Energy of activation, and Order of the reaction, respectively.

The equation for zero order reaction can be written as-

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

The plot of log (α/T²) against (1/T) should be a straight line with its slope equal to [-E/2.303R]. The values of the energy of activation obtained from the plots lie between 7.4-9.9 k cal mol⁻¹ and are in agreement with values obtained from Freeman-Carroll's equation (table: 4).

Table 1 : Thermal decomposition data of Vanadium Carboxylates.

Sr. No.	Time, (Minutes)	Temperature T ⁰	Weight of soap decomposed W x 10 ³ (gms)	$\frac{dw}{dt} \times 10^6$	W _r x 10 ³
Vanadium Palmitate					
1.	6.1	330	83.24	-	72.37
2.	7.4	348	81.23	7.75	70.36
3.	9.3	364	78.80	8.89	67.93
4.	12.3	401	78.21	7.20	66.34
5.	14.3	416	77.61	6.58	66.74
6.	16.0	433	77.40	6.00	66.53
Vanadium Stearate					
1.	6.1	330	114.04	-	82.42
2.	8.4	351	112.43	1.952	80.26
3.	10.1	373	110.88	3.062	79.66
4.	23.4	501	109.28	2.051	77.71
5.	25.1	523	105.33	3.441	73.30
6.	27.2	543	102.92	4.048	71.74

Table 2 : Freeman Carroll's Treatment of Thermogravimetric Data of Vanadium Carboxylates

Sr. No.	$\frac{1}{T} \times 10^5$	$-\Delta(\log w_r)$	$-\Delta\{\log(dw/dt)\}$	$\frac{-\Delta\log(1/T)}{\log W_r \times 10^4}$	$\frac{-\Delta\log(dw/dt)}{\Delta\log W_r}$
Vanadium Palmitate					
1.	303.03	2.140	-	1.416	-
2.	287.35	2.152	4.110	1.335	1.909
3.	274.72	2.171	4.051	1.267	1.869
4.	249.37	2.175	4.142	1.114	1.904
5.	240.38	2.176	1.181	1.105	1.922
6.	230.94	2.179	4.221	1.061	1.939
Vanadium Streatate					
1.	303.03	2.083	-	1.454	-
2.	284.90	2.092	4.709	1.632	2.250
3.	268.09	2.100	4.513	1.276	2.149
4.	199.60	2.109	4.688	0.946	2.222
5.	191.20	2.132	4.463	0.896	2.093
6.	184.16	2.146	4.392	0.858	2.046

Table 3 : Coats-Redfern's Treatment of Thermogravimetric Data of Vanadium carboxylates

Sr. No.	Temperature T	$\frac{1}{T} \times 10^5$	α	$\alpha/10^7$	$-\log(\alpha/T^2)$
Vanadium Palmitate					
1.	330	303.03	0.133	12.21	5.913
2.	345	287.35	0.146	12.26	5.911
3.	364	274.72	0.158	11.92	5.923
4.	401	249.37	0.171	10.63	5.973
5.	416	240.38	0.210	12.13	5.915
6.	433	230.94	0.235	12.53	5.901
Vanadium Streatate					
1.	330	303.03	0.214	19.65	5.706
2.	351	284.90	0.224	18.18	5.740
3.	373	268.09	0.240	17.25	5.763
4.	501	199.60	0.255	10.15	5.993
5.	523	191.20	0.265	9.68	6.013
6.	543	184.16	0.280	9.49	6.022

Table:4 Energy of activation(k cal mol⁻¹) for the Decomposition of Vanadium Carboxylates by Various Equations

Sr No.	Name of Metal Carboxylates	Freeman-Carroll's equation	Coats-Redfern's equation
1.	Vanadium Palmitate	9.6	9.9
2.	Vanadium stearate	8.4	7.9

Conclusion

It is therefore, concluded that the rate of decomposition of Vanadium carboxylates is kinetically zero order and the energy of activation for the process lies in the range of 7.4-9.9 k cal mol⁻¹ through thermogravimetric analysis.

Reference

1. Matsumote, Norichika, *Jpn, Kolai, Tollyo Koha Jp*, 38. 198 (2002) (Cl. C11 D 13/02) 6 Feb-(2002) April 2000/222. 603, 24 July (2000).
2. Matsumote, Norichika, *Jpn, Kolai, Tollyo Koha Jp*, 317. 199 (2002); (Cl. C11 D 13/00) 31 Oct-(2002) April 2001/122. 673, 2pp 20 April 2001 (Japan).
3. Zein, E., Shoeb, M., Sayed Hammad, A.A., Yousef Grases Aceites (Sevilla). (Eng.) 50(6), 426-434 (1999).
4. Baillie, M.J., Brown, D.H., Moss, K.C. and Sharp, D.W.A. *J.Chem. Soc. (A)*, 3110 (1968).
5. Chowdowska, J., Palicka and Nilsson, M., *Acta Chem. Scand.*, 25, 3353 (1970).
6. Malik, W.U. and Ahmad, S.L., *Kolloid, Z.Z., Polym*, 234(1), 1045-48 (1989).
7. Upadhyaya, S.K. and Prem, S., *Asian J. Chem.*, 9(3), 388-394 (1997).
8. Mehrotra, K.N., Rajwanshi, P., Mishra, S. and Rawat, M.K., *J. Indian Chem. Soc.*, 74(5), 399-401 (1997).
9. Dwivedi, R., Gangwar, B., and Sharma, M., *Int. J. Curr. Microbid. App. Sci.* 3(9), 501-504(2014).
10. Rawat, M.K., *J. Indian Council Chem.*, 16(2), 29-35 (1999).
11. Khirwar, M.S., *Remarking An Analisation*, Vol. 3, Issue-7, 01-04 (2018).
12. Rawat, M.K. and Sharma, Geeta, *J. Ind. Chem. Soc.*, 84, 46-49 (2007).
13. Freeman, E.S. and Caroll, B., *J. Phys, Chem.*, 62, 394 (1958).
14. Coats, A.W. and Redfern, J.P., *Nature*, 68 201 (1964).