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Phenomenological and Kinetic Aspects of The Thermal Decomposition of Fe(III) Buformin Complex

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Fe(III) complex of butyl biguanide (buformin) having an octahedral structure has been subjected to thermal analysis. The phenomenological and kinetic aspects of the decomposition have been studied. The Coats-Redfern equation was used for the kinetic studies.

Key Words: Buformin, Deprotonation, Octahedral, Coats-Redfern.

INTRODUCTION

Biguanides and their derivatives are highly versatile ligands and are very important from the chemotherapeutic point of view[1]. The iron(III) complex of buformin have been prepared and found to have an octahedral structure[2]. The complex is neutral and complexation takes place after deprotonation. The hydrogen atom is lost from the nitrogen coming in between the carbon atoms. The structure of buformin and the complex is given in Figs. 1 and 2, respectively. In the present study the non isothermal thermogravimetric study of Fe(III) complex of buformin is undertaken[3]. The phenomenological and kinetic aspects of the decomposition of the complex are followed employing the techniques of thermogravimetry and derivative thermogravimetry. There are different methods for obtaining suitable kinetic equations[4]. Among them integral methods[5-8] are considered to be the most accurate method available for the determination of kinetic parameters from TG data[9,10]. Coats-Redfern method[11] is the important and largely used integral method and in the present study, the decomposition behaviour of the complex is analyzed using Coats-Redfern plots.

EXPERIMENTAL

TG and DTG were recorded on a Mettler Toledo SR System thermal analyzer in nitrogen atmosphere. The heating rate was 100/min and the flow rate was 5mL/min. The sample was heated to a maximum of 800 ºC.

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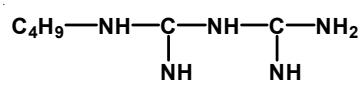

Fig. 1.

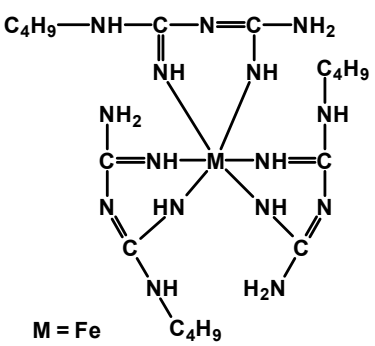

Fig. 2.

RESULTS AND DISCUSSION

The complex shows a three stage decomposition pattern. The temperature range and peak for all the three stages are given in Table-1. The TG data shows that the complex is stable upto 190 ºC as there is a horizontal layout upto 190 ºC. This shows the absence of any hydrated or coordinated water. This has also been proved in the structural studies. Peak temperature for the first stage of decomposition is 234 ºC. For the second and third stages it is 318 and 578 ºC, respectively. The first stage of decomposition starts at 190 ºC and ends at 250 ºC and shows a loss of 13.9 % of mass. The second stage of decomposition starts at 280 ºC and ends at 380 ºC and shows a loss of 55.8 % of mass. For the third stage of decomposition the starting temperature is 500 ºC and the final temperature is 660 ºC which shows a mass loss of 9.2 %.

TABLE-1
PHENOMENOLOGICAL DATA OF DECOMPOSITION

	Temperature	Wt. (mg)	Wt. loss in mg (w_α)	Wt. loss (%)
		Stage-I		
T_i	190	3.46	0.48	13.9
T_f	250	2.98		
T_p	234			
		Stage-II		
T_i	280	2.89	1.93	55.8
T_f	380	0.96		
T_p	318			
		Stage-III		
T_i	500	0.78	0.32	9.2
T_f	660	0.46		
T_p	578			

The computational details of the thermal decomposition in the three stages are given in Table-2. All the three stages have an order parameter n = 2. The Coats-Redfern plots of the three stages were made. The kinetic parameters such as activation energy, pre-exponential factor and entropy were calculated based on the plot and are listed in Table-3.

TABLE-2
COMPUTATIONAL DETAILS FOR THERMAL DECOMPOSITION

Temp.	Weight (W)	C	g(α)	log[g(α)/T^2]	1/T × 10^3
State-I					
w_α = 0.48 mg, n = 2, r = 1, slope = -1.5476, intercept = 2.7481					
200	0.14	0.71	0.4084	-4.99	5.00
210	0.23	0.52	0.9230	-4.67	4.76
220	0.29	0.40	1.5000	-4.57	4.54
230	0.37	0.23	3.3400	-4.19	4.35
240	0.44	0.08	11.5000	-3.69	4.16
State-II					
w_α = 1.93 mg, n = 2, r = 0.9998, slope = -3.72, intercept = 6.87					
290	0.17	0.91	0.098	-5.93	3.45
300	0.40	0.79	0.265	-5.53	3.33
310	0.67	0.65	0.530	-5.25	3.22
320	0.97	0.49	1.040	-4.99	3.13
330	1.27	0.34	1.940	-4.75	3.03
340	1.53	0.21	3.760	-4.48	2.94
350	1.75	0.09	10.100	-4.08	2.85
360	1.89	0.02	49.000	-3.42	2.77
State-III					
w_α = 0.32 mg, n = 2, r = 0.9999, slope = -7.2, intercept = 7.37					
530	0.06	0.81	0.23	-6.08	1.88
540	0.11	0.66	0.51	-5.75	1.85
550	0.14	0.56	0.78	-5.58	1.81
560	0.18	0.43	1.33	-5.37	1.78
570	0.22	0.31	2.23	-5.16	1.75
580	0.26	0.18	4.55	-4.86	1.72
590	0.28	0.13	6.69	-4.72	1.69

The activation energy for the three stages of decomposition are comparatively small and entropy of activation is found to have a negative value. This normally happens when the products of decomposition are gases[12]. Thus from the kinetic parameters, it has to be inferred that in all the three stages of decomposition, gaseous products are formed leaving behind the

TABLE-3
KINETIC PARAMETERS FOR THE THREE STAGES OF DECOMPOSITION

Stage	Peak temperature	Activation energy (J/mol)	Pre exponential term, A (s^{-1})	Entropy of activation (J/K/mol)
I	234	29.68	1.9987×10^{4}	-160.588
II	318	71.23	6.2900×10^{8}	-77.010
III	578	137.09	3.8000×10^{9}	-67.030

solid residue in the final stage. A negative value of entropy shows that the activator complex is more ordered. Since the decomposition involves volatilization, there is a possibility that the collision between the molecules are reduced, especially in the first stage.

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