Part II
Thermoanalytical studies

Chapter 3

Nimmy Kuriakose “Physicochemical, thermoanalytical, electrochemical and antitumour studies of transition metal complexes of schiff bases derived from heterocyclic carbonyl compounds” Thesis. Department of Chemistry, St. Thomas College, University of Calicut, 2015

CHAPTER 3

THERMAL DECOMPOSITION KINETICS OF Cr(III) COMPLEXES OF T2YMABA, PHMT2YBA, CTHMT2YBA AND CTHMF2YBA

Cr(III) complexes of four novel potential Schiff bases, (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-phenylhydrazono)methyl] thiophen-2-yl)benzoic acid (PHMT2YBA), (E)-4-(5-[(2-carbamothioylhydrazono) methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) and (E)-4-(5-[(2-carbamothioyl hydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) were synthesized and characterized by different analytical techniques. The details are well explained in Part 1. The thermal behavior of these Cr(III) complexes were studied using thermogravimetry and differential thermal analysis. Using Coats-Redfern method and nine mechanistic equations, the thermodynamic and kinetic parameters like activation energy, change in entropy and Arrhenius frequency factor were calculated. Non-isothermal methods were employed for the evaluation of reaction mechanism using the nine mechanistic equations given by Sestak and Berggren and Satava. The thermal behaviors of all these complexes are described in detail here.

Figures 2.1 to 2.4 represent the structures and instrumental TGA/DTA curves of Cr(III) complexes with four different ligands. The thermal decomposition data of these compounds are given in Tables 2.2 and 2.3.

Thermogravimetric curves of $[CrL^1Ac_2(H_2O)]_2$ (where L^1=T2YMABA) gave a four stage decomposition pattern, in which the second stage comprises of two substages. The first stage of the curve represents the loss of two water molecules from the sample moiety in the temperature range of 60-140^{0}C. This confirmed the presence of coordinated

water molecules in the complex[45]. The loss of two non-bridged acetate groups and two CO_2 molecules from the ligands are exhibited in second stage, i.e. IIa and IIb respectively. The third stage represents the loss of the rest of both the ligands and the removal of two bridged acetate groups is depicted in the fourth stage of decomposition. The overall mass loss according to the TG curve is 81.53% and the theoretical mass loss for the conversion of the complex into Cr_2O_3 is 81.82%. The mass loss according to the pyrolytic data was also found to be in agreement with these results (81.10%).

The complex $[CrL^2Ac_3(H_2O)_2]$ (where L^2=PHMT2YBA) has three stages of decomposition reaction. The first one is due to the removal of two coordinated water molecules from the complex[46-48]. The second stage decomposition corresponds to the loss of one acetate group at around 290^0C and the in the last stage, the ligand and two acetate groups are removed from the complex molecule at 700^0C. The overall mass loss according to the TG curve is 87.37% and the theoretical mass loss for the conversion of the complex into metal oxide is 87.05%. The mass loss according to the pyrolytic data was found to be 86.54%.

The decomposition of Cr(III) complex of CTHMT2YBA, $[CrL^3Ac_2(H_2O)]_2$ also resulted with a definite three stage pattern. The first stage (60-150^0C) is assigned to the loss of two water molecules. Two non-bridged acetate groups and two CO_2 molecules from the ligand are removed in the second stage. The third stage of decomposition corresponds to the loss of rest of both the ligands and two bridged acetates. The percentage mass loss according to the TG curve is 84.82% which is in good agreement with the theoretical value (84.35%). The mass loss from the pyrolysis is found to be 83.94%.

Cr(III) complex of the ligand CTHMF2YBA, $[CrL^4Ac_2(H_2O)]_2$ underwent a four stage decomposition pattern. Loss of two water molecules are observed in the temperature interval 62-137^{0}C in the initial stage. The second stage consists of three substages in the temperature range 137-288^{0}C. Two amino groups, two CO_2 molecules and two acetate groups are lost subsequently in each of these substages. Then in the third stage, two bridged acetate groups are removed and in fourth stage, the rest of both the ligands are lost. Overall mass loss of 83.70% is observed from the thermogravimetric curves. The theoretical and pyrolytic mass loss percentages are 84.03% and 82.95% respectively, which also confirms the probable assignments suggested for the decomposition stages.

Kinetics of decomposition

The mechanism of decomposition reaction of a chelate can be assigned by selecting the appropriate mechanistic equation which has a high degree of correlation coefficient[49-51]. The corresponding function g(α) is chosen from which the kinetic parameters E, A and ΔS were calculated which are in good agreement with those obtained by the integral method.

From the kinetic parameters derived, it is assigned that the first stage decomposition, the first substage of second decomposition step and the third decomposition stage of the chelate $[CrL^1Ac_2(H_2O)]_2$ follows first order kinetics. Since the parameters E, A and ΔS values obtained from the Coats-Redfern method with n=1 are in close agreement with those obtained from the Mampel equation, it can be inferred that the rate controlling process of the reaction is random nucleation with the formation of one nucleus in each particle and is independent of thermal techniques used. For the substage

IIb and fourth stage of decomposition of Cr(III) complex, R_3 mechanism with order of the reaction 2/3 can be assigned which is evident from the comparison of kinetic parameters from mechanistic and non mechanistic Coats-Redfern equation. The R_3 mechanism is based on phase boundary reaction, spherical symmetry and gives the maximum correlation for these decomposition stages.

For the Cr(III) complex of (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl) benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), all the different stages of decomposition process are assigned first order kinetics since the kinetic parameters calculated from the Coats-Redfern equation with n=1 are in good agreement with those obtained for the F_1 mechanism based on Mampel equation. This indicates that the rate controlling process is random nucleation.

In the case of first stage decomposition of the Cr(III) complex of (E)-4-(5-((2-carbamothioylhydrazono)methyl)furan-2-yl)benzoic acid (CTHMF2YBA), the kinetic parameters derived using the non mechanistic equation with n=1/3 are in good agreement with those values obtained from the equation VIII of mechanistic equations. It is therefore concluded that the decomposition process where two coordinated water molecules are removed from the complex, follows R_2 mechanism based on phase boundary reaction with cylindrical symmetry. For all other stages of decomposition, first order kinetics is assigned. The rate controlling process is random nucleation which follows F_1 mechanism based on Mampel equation.

The kinetic parameters such as energy of activation E, pre-exponential factor A and entropy of activation ΔS calculated for the various stages of decomposition of the

complexes using mechanistic and non mechanistic kinetic equations are summarized in Tables 2.4 to 2.8. The mechanisms of decomposition of various stages as well as the order of decomposition of all the various stages of the complexes are given in Tables 2.9 to 2.11. It can be noted that the larger the activation energy for the decomposition, greater the thermal stability of the compound. The relative thermal stabilities of these chelates can be given as $[CrL^3Ac_2(H_2O)]_2$<$[CrL^4Ac_2(H_2O)]_2$<$[CrL^1Ac_2(H_2O)]_2$< $[CrL^2Ac_3(H_2O)_2]$. From the thermal studies it is quite evident that the monomeric structure is more stable to heat than the dimeric structure.

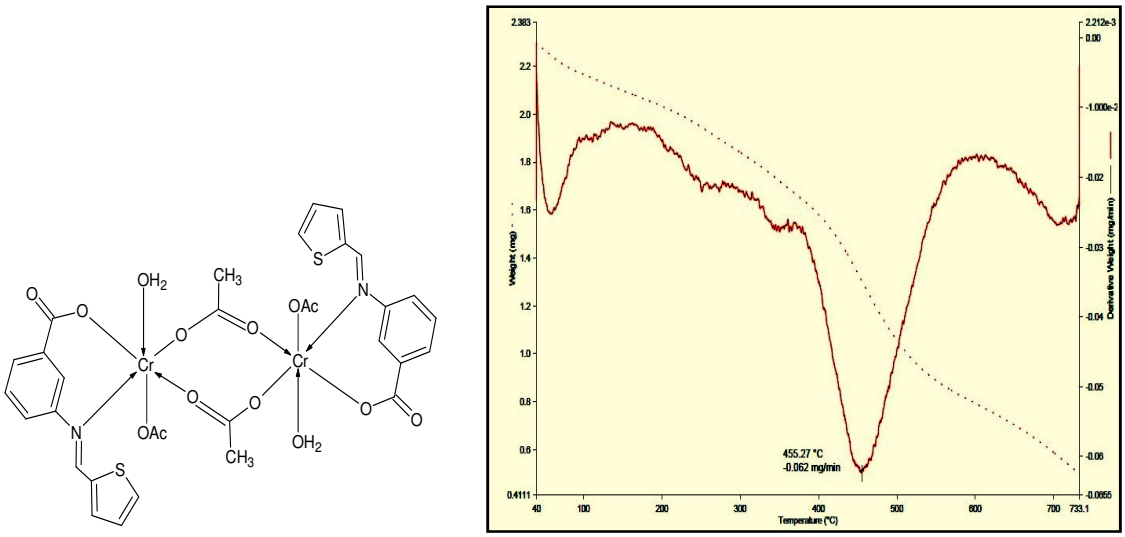

Fig. 2.1 Structure, TGA and DTA curves of $[CrL^1Ac_2(H_2O)]_2$

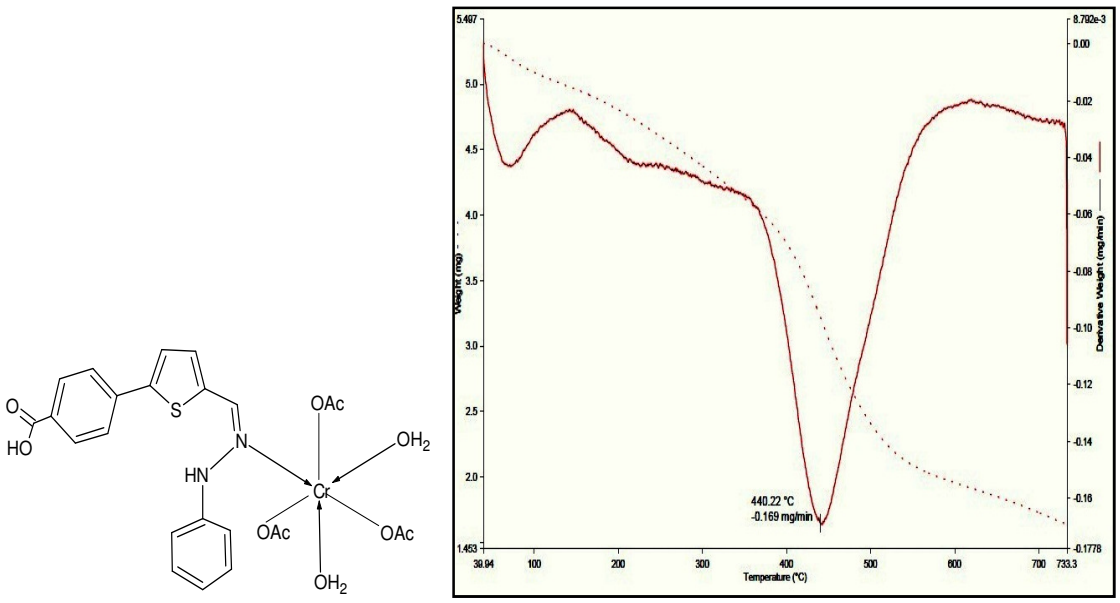

Fig. 2.2 Structure, TGA and DTA curves of $[CrL^2Ac_3(H_2O)_2]$

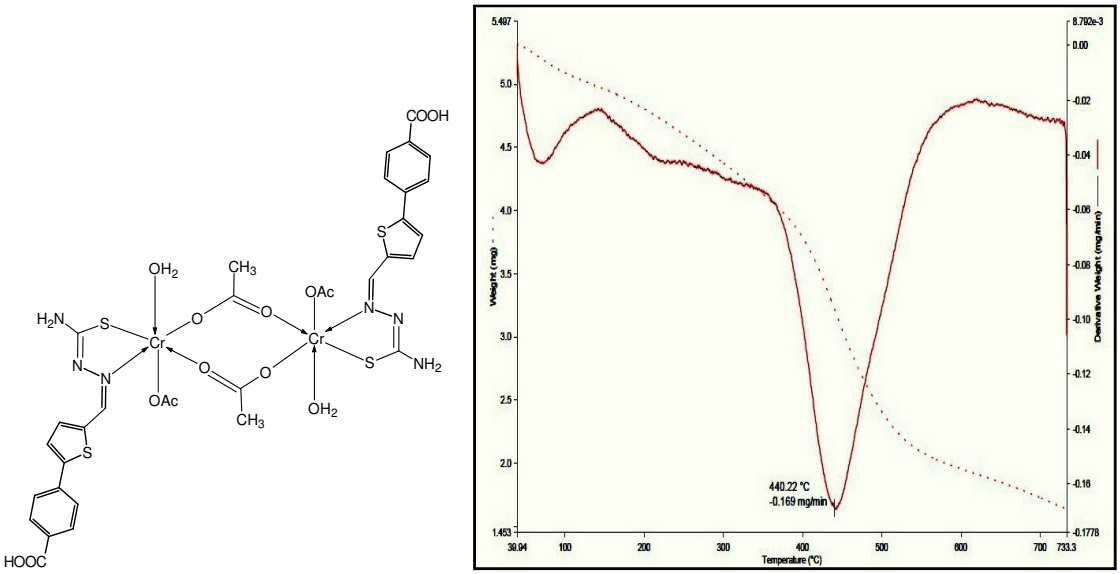

Fig. 2.3 Structure, TGA and DTA curves of $[CrL^3Ac_2(H_2O)]_2$

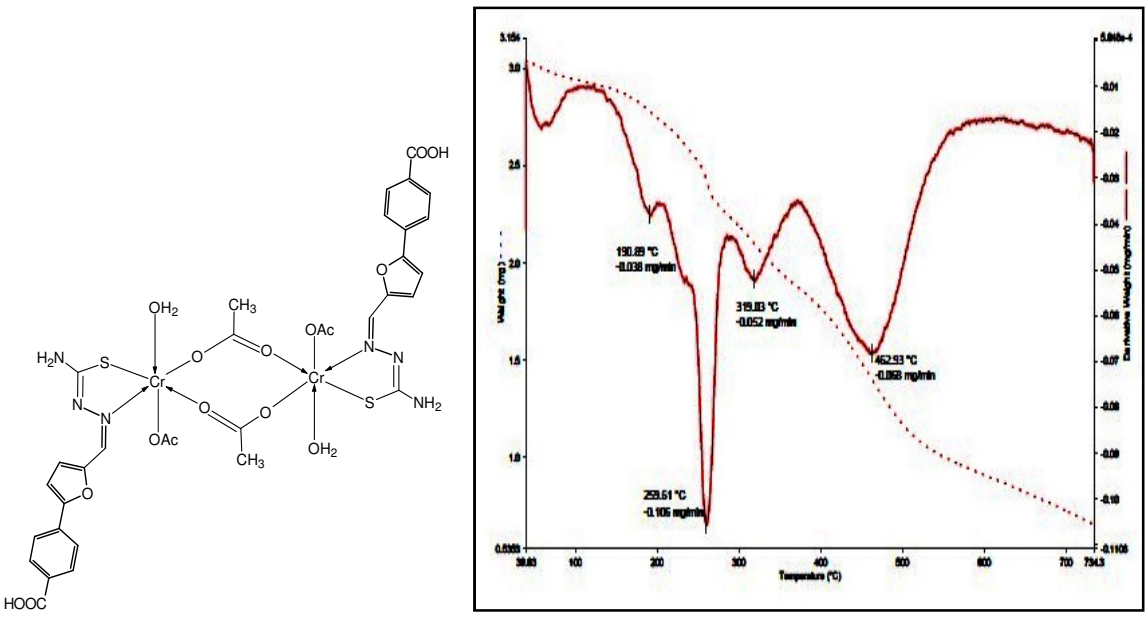

Fig. 2.4 Structure, TGA and DTA curves of $[CrL^4Ac_2(H_2O)]_2$

Table 2.2 Thermal decomposition data of Cr(III) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA)

Complex	Stage	Temp range in TG (^{0}C)	Peak temp in TG (^{0}C)	Peak temp in DTA (^{0}C)	Loss of mass %			Probable assignment
					From TG	Cald.	From Pyrolysis	
$[CrL^1Ac_2(H_2O)]_2$	I	60-140	80	84	4.87	4.31	-	Loss of $2H_2O$
	IIa	140-305	255	258	13.98	14.11	-	Loss of two acetate groups
	IIb	305-375	341	344	10.22	10.53	-	Loss of two CO_2 molecules from ligands
	III	375-600	454	456	38.92	38.76	-	Loss of rest of both ligands
	IV	600-748	712	715	13.54	14.11	-	Loss of two bridged acetate groups
					81.53	81.82	81.10	
$[CrL^2Ac_3(H_2O)_2]$	I	60-145	82	85	5.98	6.13	-	Loss of $2H_2O$
	II	145-298	222	224	10.28	10.05	-	Loss of one acetate
	III	298-742	438	441	71.11	70.87	-	Loss of ligand and two acetate groups
					87.37	87.05	86.54	

L^1= T2YMABA, L^2 = PHMT2YBA

Table 2.3 Thermal decomposition data of Cr(III) complexes of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid(CTHMF2YBA)

Complex	Stage	Temp range in TG (^{0}C)	Peak temp in TG (^{0}C)	Peak temp in DTA (^{0}C)	Loss of mass %			Probable assignment
					From TG	Cald.	From Pyrolysis	
$[CrL^3Ac_2(H_2O)]_2$	I	60-152	65	66	4.02	3.66	-	Loss of $2H_2O$
	II	152-346	236	239	21.52	21.14	-	Loss of two acetate groups and two CO_2 molecules
	III	346-741	451	452	59.28	59.56	-	Loss of rest of both ligands and two bridged acetate groups
					84.82	84.35	83.94	
$[CrL^4Ac_2(H_2O)]_2$	I	62-137	78	82	3.89	3.78	-	Loss of $2H_2O$
	IIa	137-199	188	191	3.52	3.36	-	Loss of 2 NH_2 groups
	IIb	199-242	232	234	9.08	9.24	-	Loss of two CO_2 molecules
	IIc	242-288	257	260	12.14	12.39	-	Loss of two acetate groups
	III	288-373	318	319	13.06	12.39	-	Loss of two bridged acetate groups
	IV	373-734	461	463	42.01	42.87	-	Loss of rest of both ligands
					83.70	84.03	82.95	

L^3 = CTHMT2YBA, L^4 = CTHMF2YBA

Table 2.4 Kinetic parameters of the decomposition of Cr(III) complex of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[CrL^1Ac_2(H_2O)]_2$	E	85.95	96.46	111.21	101.23	61.008	27.489	16.319	48.956	52.594
	A	6.22×10^9	1.5×10^{11}	7.16×10^{12}	1.89×10^{11}	4.1×10^6	32.424	0.4997	23×10^4	6.06×10^3
Stage I	ΔS	-58.82	-32.38	-0.226	-30.425	-119.69	-217.38	-252.08	-162.71	-154.76
	r	0.8400	0.8701	0.904	0.8824	0.9230	0.9071	0.8863	0.8770	0.8942
	E	165.48	181.25	202.5	188.16	109.47	51.06	31.59	92.3425	97.58
Stage IIa	A	7.93×10^{16}	4.02×10^{18}	4.31×10^{20}	6.67×10^{18}	5.28×10^{10}	4.18×10^3	14.33	1.69×10^8	5.31×10^8
	ΔS	73.85	106.49	145.36	110.70	-44.38	-180.33	-227.53	-92.16	-82.63
	r	0.8693	0.8921	0.9174	0.9012	0.9331	0.9240	0.9130	0.8993	0.9117
	E	295.77	324.91	364.40	337.73	199.31	94.60	59.69	167.41	177.15
Stage IIb	A	5.13×10^{22}	1.13×10^{25}	9.16×10^2	3.6×10^{25}	7.56×10^{14}	4.99×10^5	351.59	4.64×10^{11}	2.41×10^{12}
	ΔS	183.84	228.67	284.38	238.33	33.92	-141.83	-202.17	-27.58	-73.89
	r	0.8927	0.9135	0.9359	0.9217	0.9499	0.9448	0.9389	0.9219	0.9325
	E	237.75	257.73	284.72	266.48	151.64	69.93	42.69	129.81	136.47
Stage III	A	2.55×10^{14}	5.07×10^{15}	1.58×10^{17}	5.61×10^{15}	3.76×10^8	255.58	1.776	3.21×10^6	7.45×10^6
	ΔS	23.48	48.33	76.90143	49.17	-88.17	-206.23	-247.54	-127.74	-120.76
	r	0.9144	0.9315	0.9500	0.9382	0.9607	0.9539	0.9454	0.9366	0.9458

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.5 Kinetic parameters of the decomposition of Cr(III) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[CrL^1Ac_2(H_2O)]_2$ Stage IV	E	369.34	401.84	284.72	266.49	238.83	111.66	69.27	204.12	214.78
	A	$3. x10^{17}$	$1.7 x10^{19}$	$1.5 x10^{17}$	$5.61 x10^{15}$	$5.79 x10^{10}$	3066.01	9.2039	$2.31 x10^{8}$	$6.83 x10^{8}$
	ΔS	81.98	113.48	76.90	49.17	-48.81	-188.09	-236.39	-94.72	-85.72
	r	0.8930	0.9123	0.9329	0.9198	0.9449	0.9375	0.9287	0.9184	0.9283
$[CrL^2Ac_3(H_2O)_2]$ Stage I	E	83.157	94.397	110.79	99.65	61.910	27.944	16.621	48.336	52.38
	A	$2.76 x10^{9}$	$8.8 x10^{10}$	$7.72 x10^{12}$	$1.34 x10^{11}$	$6.46 x10^{6}$	41.009	0.5887	20660.05	62811.57
	ΔS	-65.59	-36.79	0.4056	-33.305	-115.93	-215.44	-250.72	-163.71	-154.46
	r	0.8349	0.8674	0.9059	0.8814	0.9289	0.9143	0.8949	0.8769	0.8961
Stage II	E	110.31	118.58	128.12	121.74	65.05	28.55	16.38	57.73	60.08
	A	$9.04x10^{8}$	$4.52x10^{9}$	$1.41x10^{10}$	$2.41x10^{9}$	$2.67x10^{4}$	$1.99x10^{3}$	$6.3x10^{3}$	$1.66x10^{3}$	$2.2x10^{3}$
	ΔS	-78.8	-65.50	-56.05	-70.71	-165.58	-244.61	-273.29	-188.70	-186.47
	r	0.9797	0.9848	0.9894	0.9865	0.9916	0.9888	0.9845	0.9854	0.9878
Stage III	E	121.49	129.79	140.74	133.36	72.50	32.29	18.88	63.70	66.41
	A	$8.8 x10^{9}$	$4.5 x10^{10}$	$2.1 x10^{11}$	$2.7 x10^{10}$	$1.5 x10^{5}$	5.082	0.1255	6138.59	8882.89
	ΔS	-58.75	-45.14	-32.28	-49.38	-149.95	-235.61	-266.38	-176.61	-173.53
	r	0.9449	0.9558	0.9665	0.9599	0.9700	0.9623	0.9513	0.9569	0.9624

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.6 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[CrL^3Ac_2(H_2O)]_2$	E	83.16	94.39	110.79	99.66	61.91	27.94	16.62	48.34	52.38
	A	2.76×10^9	8.8×10^{10}	7.72×10^{12}	1.34×10^{11}	6.46×10^6	41.01	0.5887	20660.1	62811.6
Stage I	ΔS	-65.22	-36.44	0.7667	-32.94	-115.57	-215.08	-250.35	-163.71	-154.1
	r	0.8349	0.8675	0.9059	0.8814	0.9289	0.9143	0.8949	0.8769	0.8961
	E	124.37	133.33	145.23	137.19	75.24	33.59	19.71	65.65	68.59
	A	1.28×10^{10}	7.64×10^{10}	4.46×10^{11}	4.92×10^{10}	2.49×10^5	6.5667	0.1499	8435.495	12892.4
Stage II	ΔS	-58.81	-43.975	-29.307	-47.64	-148.99	-236.67	-268.1	-177.16	-173.63
	r	0.9374	0.9499	0.9627	0.9547	0.9681	0.9601	0.9488	0.9517	0.9582
	E	221.49	237.67	258.81	244.56	135.46	62.08	37.62	118.54	123.76
	A	5.81×10^{13}	6.53×10^{14}	8.22×10^{15}	5.41×10^{14}	4.92×10^7	90.7×10^{10}	0.8730	914489.5	1688475
Stage III	ΔS	11.19	31.29	52.35	29.73	-105.05	-214.85	-253.45	-138.20	-133.10
	r	0.9316	0.9446	0.9574	0.9493	0.9629	0.9561	0.9473	0.9472	0.9535

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.7 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[CrL^4Ac_2(H_2O)]_2$	E	38.72	54.99	88.58	64.98	65.12	29.39	17.49	24.62	41.13
	A	628.43	1.17×10^5	3.13×10^9	8.73×10^5	1.41×10^7	59.43	0.7432	73.62	1058.32
Stage I	ΔS	-192.69	-149.23	-64.49	-132.52	-109.35	-212.30	-248.73	-210.53	-188.36
	r	0.9954	0.9978	0.9743	0.9935	0.9221	0.9072	0.8877	0.9941	0.9705
	E	197.58	211.98	230.497	217.97	121.84	57.27	35.75	107.01	111.59
	A	4.33×10^{10}	1.41×10^{22}	6.89×10^{23}	1.82×10^{22}	1.393×10^{12}	2.29×10^4	46.98	8.89×10^9	2.29×10^{10}
Stage IIa	ΔS	146.52	175.48	207.82	177.62	-16.05	-165.04	-216.53	-58.07	-50.20
	r	0.9260	0.9396	0.9534	0.9446	0.9609	0.9561	0.9502	0.9438	0.9504
	E	317.09	341.77	373.59	352.17	200.13	95.99	61.24	174.85	182.69
	A	7.9×10^{30}	2.12×10^{33}	1.51×10^{36}	6.61×10^{33}	1.009×10^{19}	7.19×10^7	1.12×10^4	7.78×10^{15}	3.88×10^{16}
Stage IIb	ΔS	342.21	388.68	443.33	398.15	114.51	-98.88	-171.7	54.92	68.29
	r	0.9171	0.9319	0.9473	0.9376	0.9569	0.9534	0.9494	0.9378	0.9451

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.8 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[CrL^4Ac_2(H_2O)]_2$	E	317.26	360.19	419.59	379.51	238.57	114.82	73.574	190.721	205.33
Stage IIc	A	2.82×10^{28}	3.2×10^{32}	7.15×10^{37}	6.37×10^{33}	1.89×10^{21}	9.93×10^{8}	6.54×10^{4}	1.26×10^{16}	2.6×10^{17}
	ΔS	294.95	372.57	474.98	397.45	157.65	-77.461	-157.49	58.50	83.69
	r	0.8887	0.9097	0.9351	0.9187	0.9544	0.9515	0.9483	0.9210	0.9329
Stage III	E	294.48	323.44	363.28	336.34	199.29	94.733	59.88	166.89	176.73
	A	2.31×10^{23}	5.9×10^{25}	6.55×10^{28}	2.06×10^{26}	2.5×10^{15}	9.51×10^{5}	552.29	1.18×10^{12}	6.61×10^{12}
	ΔS	196.68	242.71	301.05	253.15	44.47	-136.15	-198.10	-19.52	-5.17
	r	0.8828	0.9049	0.9297	0.9139	0.9462	0.9409	0.9347	0.9143	0.9261
Stage IV	E	223.27	242.91	269.53	251.53	143.89	66.075	40.14	122.32	128.899
	A	2.59×10^{13}	4.95×10^{14}	1.47×10^{16}	5.39×10^{14}	1.1×10^{18}	134.68	1.134	$9. \times 10^{5}$	2.21×10^{6}
	ΔS	4.385	28.90	57.12	29.61	-98.44	-211.64	-251.36	-137.81	-130.91
	r	0.9114	0.9293	0.9485	0.9363	0.9591	0.9518	0.9424	0.9345	0.9439

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.9 Kinetic parameters of the decomposition of Cr(III) complex of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[CrL^1Ac_2(H_2O)]_2$	Coats-Redfern	61.01	$4.1x10^6$	-119.69	0.9230	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
Stage I	Equation V	61.01	$4.1x10^6$	-119.69	0.9230		
Stage IIa	Coats-Redfern	109.47	$5.3x10^{10}$	-44.38	0.9331	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	109.47	$5.3x10^{10}$	-44.38	0.9331		
Stage IIb	Coats-Redfern	177.1	$7.162x10^{12}$	-4.83	0.9325	2/3	R_3 mechanism. Phase boundary reaction. Spherical symmetry
	Equation IX	177.15	$2.41x10^{12}$	-13.89	0.9325		
Stage III	Coats-Redfern	151.6	$3.76x10^8$	-88.17	0.9607	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	221.165	$3.76x10^8$	-88.17	0.9607		
Stage IV	Coats-Redfern	214.7	$2.04x10^9$	-76.64	0.9283	2/3	R_3 mechanism. Phase boundary reaction. Spherical symmetry
	Equation IX	214.78	$6.83x10^8$	-85.72	0.9283		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.10 Kinetic parameters of the decomposition of Cr(III) complexes of (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[CrL^2Ac_3(H_2O)_2]$	Coats-Redfern	61.91	$6.46x10^6$	-115.9	0.9289	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
Stage I	Equation V	61.91	$6.46x10^6$	-115.9	0.9289		
Stage II	Coats-Redfern	65.05	$2.67x10^4$	-165.58	0.9916	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	65.05	$2.67x10^4$	-165.58	0.9916		
Stage III	Coats-Redfern	72.50	$1.5x10^5$	-37.18	0.9953	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	72.50	$1.5x10^5$	-37.18	0.9953		
$[CrL^3Ac_2(H_2O)]_2$ Stage I	Coats-Redfern	61.910	$6.46x10^6$	-115.57	0.9289	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	61.910	$6.46x10^6$	-115.57	0.9289		
Stage II	Coats-Redfern	75.24	$2.49x10^5$	-148.99	0.9681	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	75.24	$2.49x10^5$	-148.99	0.9681		
Stage III	Coats-Redfern	135.46	$4.92x10^7$	-105.05	0.9629	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	135.46	$4.92x10^7$	-105.05	0.9629		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.11 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[CrL^4Ac_2(H_2O)]_2$ Stage I	Coats-Redfern	25.88	12.13	-225.51	0.9949	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	24.62	73.62	-10.52	0.9941		
Stage IIa	Coats-Redfern	121.84	$1.39x10^{10}$	-16.05	0.9609	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	121.84	$1.39x10^{10}$	-16.05	0.9609		
Stage IIb	Coats-Redfern	200.13	$1.01x10^{10}$	-16.06	0.9569	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	200.13	$1.01x10^{10}$	-16.06	0.9609		
Stage IIc	Coats-Redfern	238.57	$1.89x10^{21}$	-157.65	0.9544	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	238.57	$1.89x10^{21}$	-157.65	0.9544		
Stage III	Coats-Redfern	199.29	$2.59x10^{15}$	-44.47	0.9462	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	199.29	$2.59x10^{15}$	-44.47	0.9462		
Stage IV	Coats-Redfern	143.89	$1.1x10^{8}$	-98.44	0.9591	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	143.89	$1.1x10^{8}$	-98.44	0.9591		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$