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Thermal evaluation of bioactive *p*-hydroxy-*m*-nitro acetophenone and it's metal complexes

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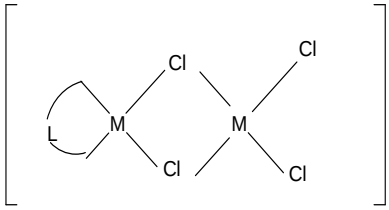
ABSTRACT

Studies on thermal properties of substances have a great importance from both scientific and practical point of view. In industries stability of row materials/ intermediates /final product have become essential criteria. In pharmaceutical industries, as per the requirement of the drug for the receptor site of the body drug stability counts a lot, thus thermal properties play a very significant role in day to day life. Thermal properties of synthesized para - Hydroxy - meta - nitro acetophenone compound 1, and its three novel complexes 4-hydroxy-3-Nitro-acetopnenone Cu (II) di µ - Chloro dichloro copper (II) compound 2, 4-hydroxy-3-Nitro-acetopnenone Ni (II) di µ - Chloro Nickel (II) chloride trihydrate compound 3 and Aqua-Chloro-4-hydroxy-3-Nitro-acetopnenone Co (III) di µ Chloro aqua tri Chloro Cobalt (III) compound 4 were assessed. The thermal kinetic parameters such as order of reaction η' and energy of activation 'Ea' were established from computer programme of rising temperature expression of Coats and Redfern. This study signifies that metal complexes are less stable than ligand. This kinetic study has been performed for the first time.

Key words: Thermal kinetic parameters, order of reaction, activation energy, *p*-hydroxy-*m*- nitro acetophenone.

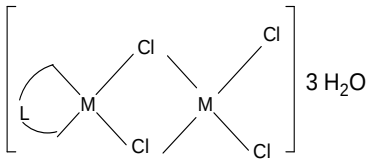
INTRODUCTION

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups[1-3] and it is multiplied many fold when the ligands have biological importance[4,5]. The coordination chemistry along with structure and bonding of metal ions in their active sites can be evaluated by applying new analytical approaches[6].Metal ions bind to ligands that are strong and selective. Some stereo selective and stereo specific complexes are of importance. The ligands impart their own functionality and can tune properties of the overall complexes that are unique from those of the individual ligand or metal. Metal ions change their oxidation states which are investigated by cyclic voltametry (CV). The thermodynamic and kinetic properties of metal-ligand interactions influence ligand exchange reactions[7].With this rationale the present work on the metal complexes of the synthesized bio- active ligand has been proposed. Structures have been determined by the appraisal of UV, IR, LC-MS, AAS, magnetic susceptibility and CV. The study of thermal properties such as order of reaction, energy of activation and kinetics is furnished with the help of thermo gravimetric analysis for the first time.



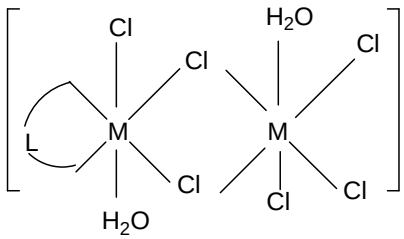
Compound 2

4- Cu(II)di µ-Chloro dichloro copper (II) hydroxy-3-Nitro-acetopnenone



Compound 3

4-hydroxy-3-Nitro-acetopnenone Ni (II) di µ-Chloro Nickel (II) chloride trihydrate



Compound 4

Aqua-Chloro-4-hydroxy-3-Nitro-acetopnenone Co (III) di µ-Chloro aqua tri Chloro Cobalt (III)

MATERIALS AND METHODS

Reagents and solvents used were of commercially available analytical grade. **Compound 1** was synthesized by nitration of *para* hydroxy acetophenone. This reaction mixture was refluxed on oil bath at 50 ^{0}C for five minutes. Yellow solid with gummy mass poured into boiling water. Fine yellow product was obtained. The product was recystallized from ethyl acetate: hexane. Sharp melting nature indicated purity. Formation of product was confirmed by reported values. Structure was confirmed by modern analytical spectral techniques. The ethanolic solution of **compound 1** (0.001 mol) was added slowly with constant stirring to the ethanolic solution of Copper (II) chloride dihydrate,Nickel (II) chloride hexahydrate and cobalt (II) chloride hexahydrate (0.002 mol) separately. The colour of the resulting solution changes from bottle green to light green, fluroscent green and blue respectively for Cu (II), Ni (II) and Co (II) complexes. The resulting mixture was refluxed for one and half hour. The solvent was removed under reduced pressure. The residue was triturated with chloroform. Chloroform soluble part was separated. Residue after washing with diethyl ether, ethanol yielded compounds **2, 3** and **4** respectively.

RESULTS AND DISCUSSION

The TG of compound **1 (Fig 1)** demonstrates the mass loss as a function of temperature which is seen in one step. The decomposition of the molecule starts at nearly at 1000C and completed at 5110C with removal of total organic molecule to get nearly 100% weight loss. Kinetic parameters are presented (**Table 1).**Kinetic parameters are calculated by Coats-Redfern method where correlation coefficient 'r' may be positive or negative which meets to 0.999. The kinetic data such as order of reaction and activation energy for the molecule have been reported (**Table 2)**. Kinetic plots are depicted **(Fig 2).**

Compound 2

The TG of **compound 2 (Fig 3)** demonstrates the mass loss as a function of temperature which is seen in two steps. In the first step the decomposition of the molecule up to temperature 110 ^{0}C occurs with % weight loss 23.83 (observed) and 23.65(calculated) with removal of three chlorine atoms. The second step of decomposition shows % weight loss 64.80(observed) and 64.80(calculated) in the temperature range 110-650^{0}C corresponding to the removal of one chlorine atom and the organic ligand $C_8H_6NO_2$.Residue at 650^{0}C is 35.85% (observed) and 35.43 %(calculated) as 2CuO gives composition of metal complex M_2LCl_4 was observed. The complete decomposition of the complex is confirmed by constant platue after 650^{0}C.The kinetic data for step I & step II given in **(Table 3** & **4)** and their kinetic plots are presented in **(Fig 4** & **5)**.The kinetic parameters are reported in **(Table 5).**

Compound 3

TG of **compound 3** displays in **(Fig 6)** the mass loss as a function of temperature which is seen in two steps. In the first step the decomposition of the molecule up to temperature 217 ^{0}C occurs with % weight loss 39.7 (observed) & 39.69(calculated) with removal of four chlorine atoms and loss of three water molecules. The second step of decomposition confirms % weight loss 72.75 (observed) and 72.96(calculated) in the temperature range 217-530^{0}C corresponding to the loss of one organic ligand $C_8H_6NO_2$.Residue at 530^{0}C is 30.41% (observed) and 30.28 %(calculated) as 2NiO gives composition of metal complex [M_2LCl_4] 3 H_2O was observed that complete decomposition of the complex is confirmed by constant platue after 530^{0}C. The kinetic data for step I & step II given in **(Table 6** & **7)** and their kinetic plots are presented in **(Fig 7** & **8)** respectively. The kinetic parameters are reported in **(Table 8).**

Compound 4

TG of **compound 4**, show in **(Fig 9)** exhibits the mass loss as a function of temperature which is seen in three steps. In the first step the decomposition of the molecule up to temperature 100 ^{0}C occurs with % weight loss 19.2 (observed) & 19.45(calculated) with removal of three chlorine atoms. The second step of decomposition confirms % weight loss 36.13 (observed) and 35.72 (calculated) in the temperature range 100-205^{0}C corresponding to the loss of two chlorine atoms and one water molecule. The third step of decomposition confirms % weight loss 73.07 (observed) and 72.58 (calculated) in the temperature range 205-525^{0}C corresponding to the loss of one chlorine atom, one water molecule and a part of organic ligand as $C_8H_6NO_2$. Residue after 530^{0}C is 26.91% (observed) and 27.59 % (calculated) as $2C_oO$ gives composition of metal complex [$M_2LCl_6 2H_2O$]. The kinetic data for step I ,II & III are given in **(Table 9,10** & **11)** and their kinetic plots of steps I ,II & III are presented in **(Fig 10,11** & **12)**.The kinetic parameters are reported in **(Table 12)**

Table 1 Data from Dynamic TGA for compound 1 (Air atmosphere)

Step	Temp. range (^{0}C)	% wt. Loss Observed	% Wt. Loss calculated	Loss of probable moiety	Order of reaction (n)	Ea (KJ/mol)
I	100-511	100	100	C_8H_7 N O_4	2.8	64.06

Table 2 Kinetic data from TG of compound 1 in air atmosphere

Initial % Wt loss = 0		Final % Wt loss = 100	
T (Kelvin)	Wt	1/T	F (α)
312	9.44	0.00225	-14.40
350	15.42	0.00219	-13.93
390	22.25	0.00214	-13.59
412	29.09	0.00211	-13.30
460	35.92	0.00209	-13.08
484	41.89	0.00207	-12.91
530	49.56	0.00204	-12.72

Table 3 Kinetic data from TG of compound 2 in air atmosphere (Step I)

Initial % Wt loss = 0		Final % Wt loss = 23.83	
T (Kelvin)	Wt	1/T	F (α)
313	4.69	0.0032	-12.99
323	7.34	0.0030	-12.60
334	9.98	0.0029	-12.31
356	16.60	0.0028	-11.74
368	19.25	0.0027	-11.55
379	20.57	0.0026	-11.47
380	23.20	0.0025	-11.13

Table 4 Kinetic data from TG of compound 2 in air atmosphere (Step II)

Initial % Wt loss = 23.83		Final % Wt loss = 64.80	
T (Kelvin)	Wt	1/T	F (α)
389	2.04	0.0025	-14.85
522	4.69	0.0019	-14.50
562	6.01	0.0017	-14.34
662	8.66	0.0015	-14.19
761	11.31	0.0013	-14.07
864	13.96	0.0011	-13.97
920	15.28	0.0010	-13.91

Table 5 Data from Dynamic TGA for compound 2 (Air atmosphere)

Step	Temp. range (^{0}C)	% wt. Loss Observed	% Wt. Loss Calculated	Loss of probable moiety	Order of reaction (n)	Ea (KJ/mol)
I	40-110	23.83	23.65	3 Cl	0.7	21.73
II	110-650	64.80	64.58	1Cl+ $C_8H_6NO_2$	2.9	5.30

Table 6 Kinetic data from TG of compound 3 in air atmosphere (Step I)

Initial % Wt loss = 0		Final % Wt loss = 39.70	
T (Kelvin)	Wt	1/T	F (α)
320	4.81	0.0030	-13.62
345	7.45	0.0029	-13.23
362	11.42	0.0028	-12.81
390	18.03	0.0026	-12.34
442	21.99	0.0024	-12.13
465	29.93	0.0022	-11.64
489	33.90	0.0022	-11.31

Table 7 Kinetic data from TG of compound 3 in air atmosphere (Step II)

Initial % Wt loss = 39.70		Final % Wt loss = 72.75	
T (Kelvin)	Wt	1/T	F (α)
490	1.60	0.0019	-15.51
566	2.70	0.0018	-15.06
588	4.20	0.0017	-14.62
612	6.60	0.0016	-14.13
655	9.90	0.0015	-13.66
742	15.50	0.0014	-12.94
789	19.50	0.0013	-12.43

Table 8 Data from Dynamic TGA for compound 3 (Air atmosphere)

Step	Temp. range (^{0}C)	% wt. Loss Observed	% Wt. Loss Calculated	Loss of probable moiety	Order of reaction (n)	Ea (KJ/mol)
I	45 - 217	39.70	39.69	4 Cl + 3 H_2O	1.3	20.92
II	217 - 530	72.75	72.96	$C_8H_6NO_2$	2.8	48.78

Table 9 Kinetic data from TG of compound 4 in air atmosphere (Step I)

Initial % Wt loss = 0.0		Final % Wt loss = 19.20	
T (Kelvin)	Wt	1/T	F (α)
320	1.48	0.0031	-14.05
334	3.72	0.0030	-13.08
345	5.96	0.0029	-12.54
351	7.64	0.0028	-12.22
356	9.88	0.0028	-11.81
362	11.56	0.0028	-11.53

Table 10 Kinetic data from TG of compound 4 in air atmosphere (Step II)

Initial % Wt loss = 19.20		Final % Wt loss = 36.13	
T (Kelvin)	Wt	1/T	F (α)
390	21.07	0.002564	-13.9582
401	22.19	0.002494	-13.4255
412	24.99	0.002427	-12.4654
423	26.67	0.002364	-11.9982
440	28.91	0.002273	-11.363
445	30.03	0.002247	-10.9868
468	32.27	0.002137	-10.0679

Table 11 Kinetic data from TG of compound 4 in air atmosphere (Step III)

Initial % Wt loss = 36.13		Final % Wt loss = 73.07	
T (Kelvin)	Wt	1/T	F (α)
485	37.32	0.002062	-15.756
540	38.44	0.001852	-15.2611
589	40.12	0.001698	-14.8152
622	41.24	0.001608	-14.6257
679	42.92	0.001473	-14.4361
742	45.16	0.001385	-14.1578
770	46.84	0.001316	-13.9956

Table 12 Data from Dynamic TGA for compound 4 (Air atmosphere)

Step	Temp. range (^{0}C)	% wt. Loss Observed	% Wt. Loss Calculated	Loss of probable moiety	Order of reaction (n)	Ea (KJ/mol)
I	45 - 100	19.20	19.45	3 Cl	1.7	62.37
II	110 - 205	36.13	35.72	2 Cl + H_2O	3.0	75.76
III	205 - 525	73.07	72.58	Cl + H_2O+ $C_8H_6NO_2$	2.9	19.32

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Fig 1 Dynamic TGA in Air atmosphere compound 1

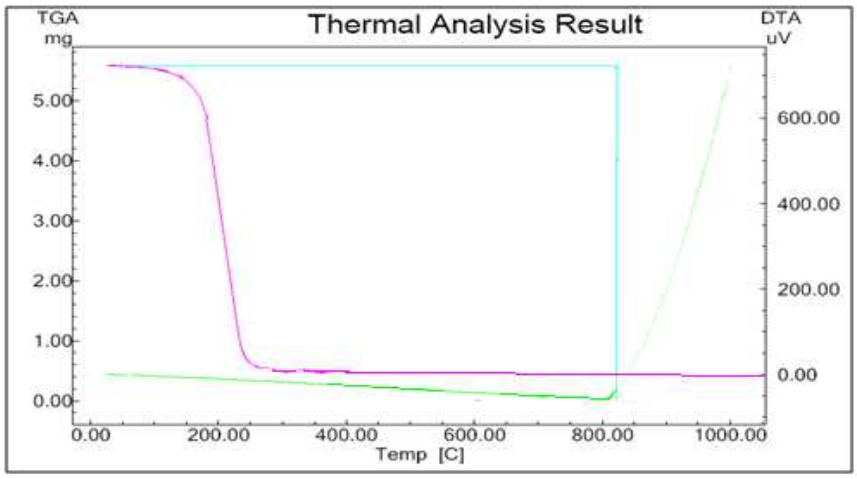


Fig 2 Kinetic plot of 1/T Vs f (*α*) from TG of compound 1

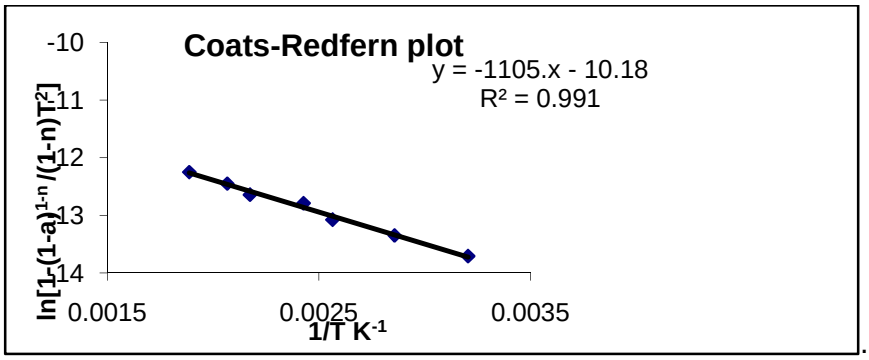


Fig 3 Dynamic TGA in Air atmosphere compound 2

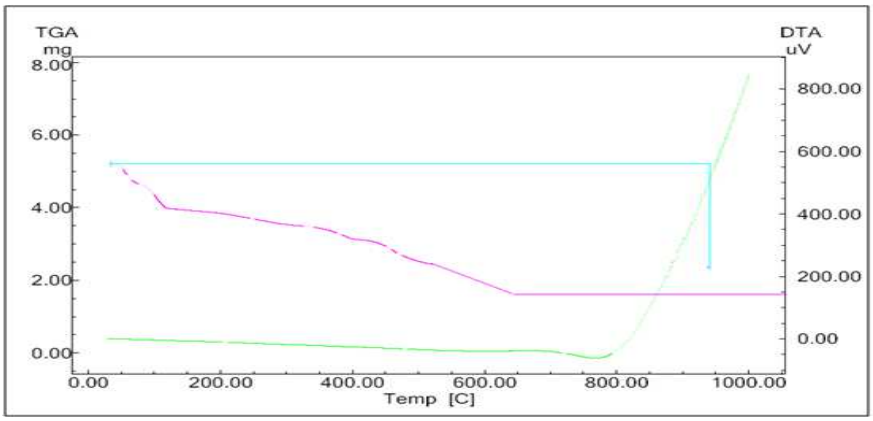


Fig 4 Kinetic plot of 1/T Vs f (*α*) from TG of compound 2 (Step I)

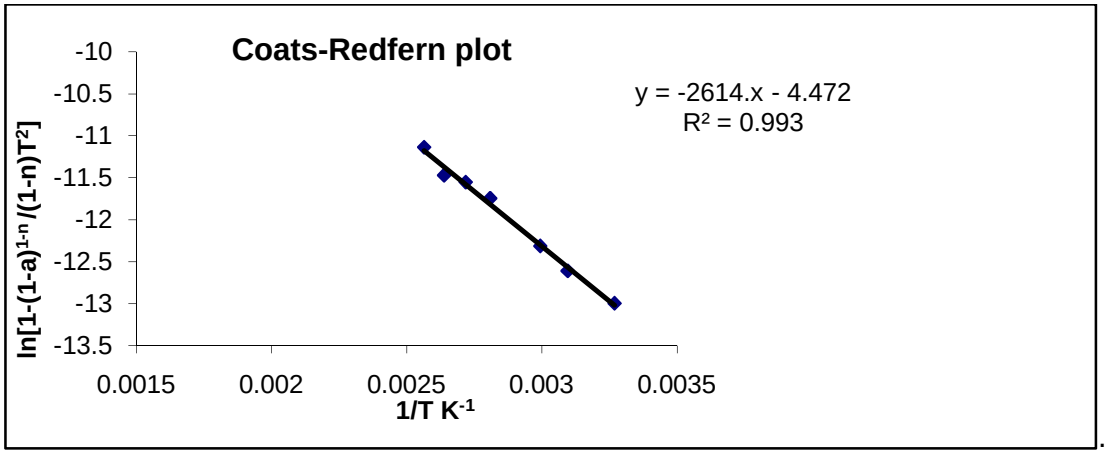


Fig 5 Kinetic plot of 1/T Vs f (α) from TG of compound 2 (Step II)

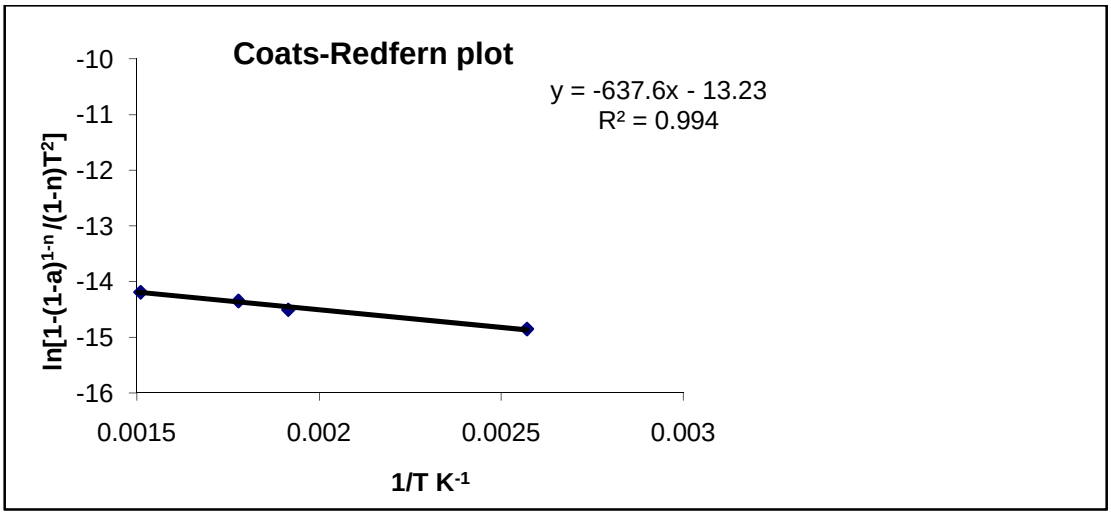


Fig 6 Dynamic TGA in Air atmosphere compound 3

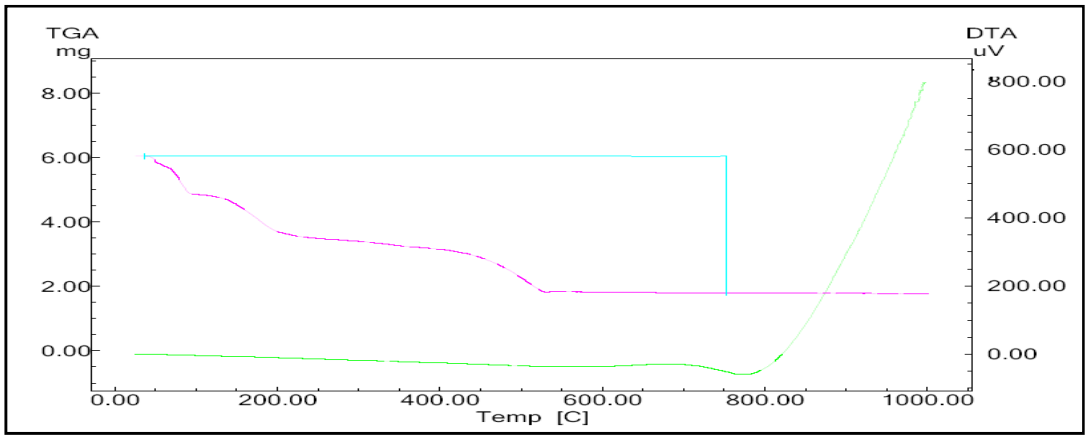


Fig 7 Kinetic plot of 1/T Vs f (α) from TG of compound 3 (Step I)

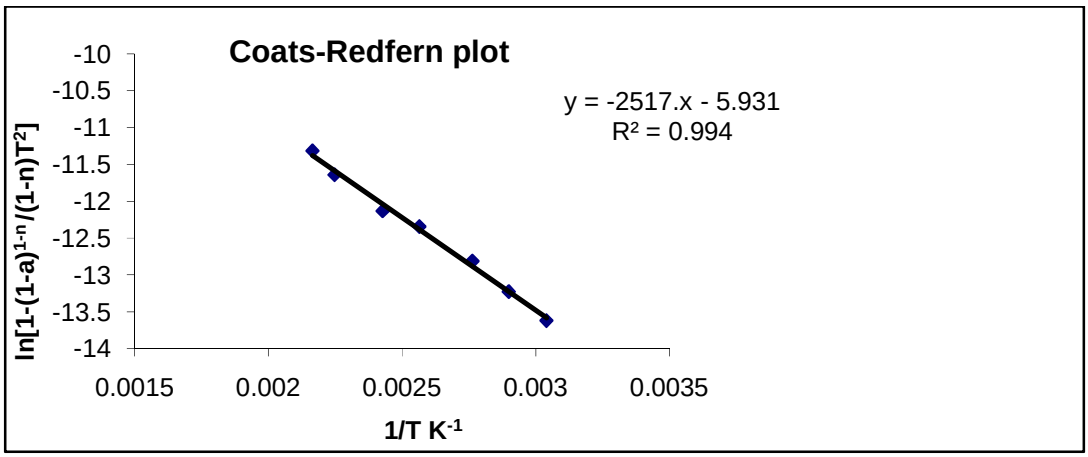


Fig 8 Kinetic plot of 1/T Vs f (α) from TG of compound 3 (Step II)

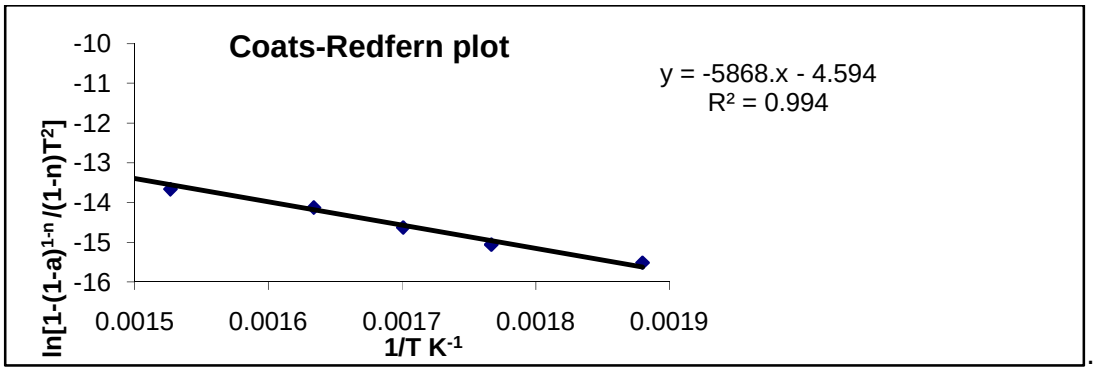


Fig 9 Dynamic TGA in Air atmosphere compound 4

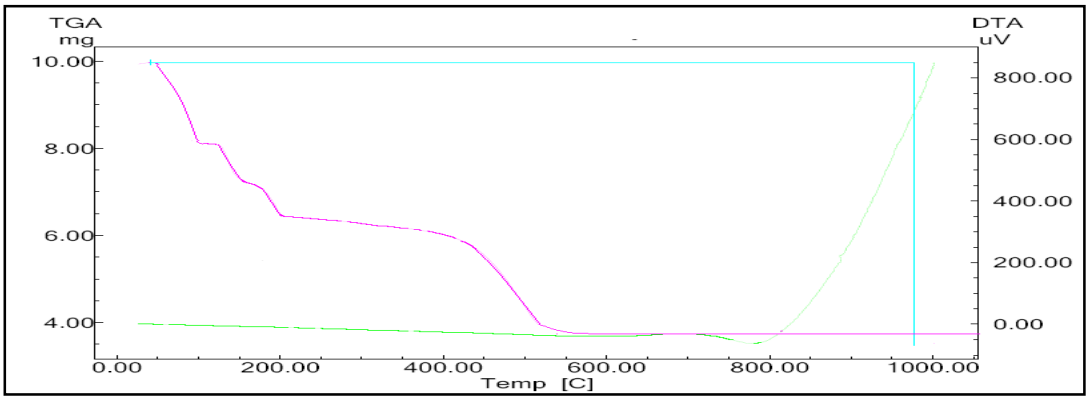


Fig 10 Kinetic plot of 1/T Vs f (α) from TG of compound 4 (Step I)

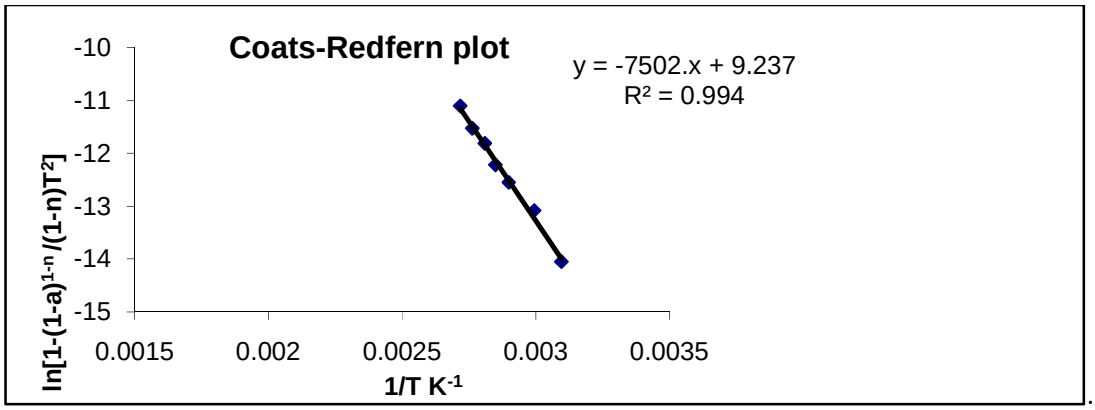


Fig 11 Kinetic plot of 1/T Vs f (α) from TG of compound 4 (Step II)

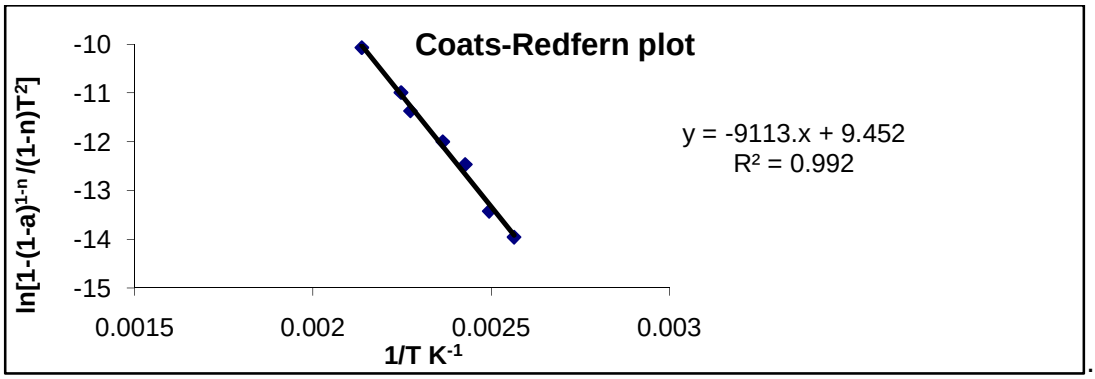
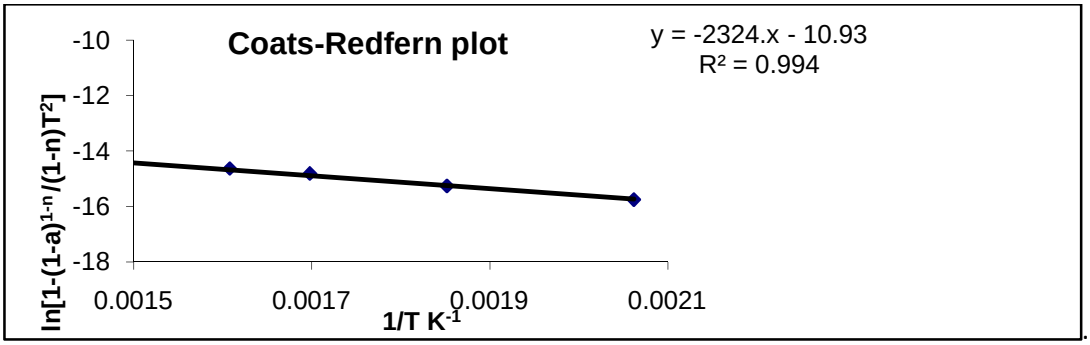


Fig 12 Kinetic plot of 1/T Vs f (α) from TG of compound 4 (Step III)



CONCLUSION

All the observed values for decomposition of each step are in superior conformity with the calculated values. The final decomposition products of all complexes **(compound 2 - 4)** are in accordance with calculated percentage reside. Decomposition of metal complexes starts at approximately 45^0C where as that of ligand starts at 100 ^{0}C.This data suggests that metal complexes are less stable than ligand. Copper complex, **compound 2** have less activation energy than ligand and Nickel and Cobalt complexes. Therefore copper complex is more active than Nickel and Cobalt complex, which is in accordance with the bioactivity results. Presence of water molecules in the sphere or outside the co-ordination sphere has been studied by the activation energy of complexes. Therefore, water molecules in Nickel complex are adsorbed water molecules and they are outside the coordinated sphere while water molecules in cobalt complex **compound 4** are coordinated to cobalt.

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