WORLD JOURNAL OF PHARMACY AND PHARMACEUTICAL SCIENCES
SJIF Impact Factor 5.210
Volume 4, Issue 09, 1163-1170 Research Article ISSN 2278 – 4357

THERMAL STUDIES OF SOME TRANSITION METAL COMPLEXES OF NITRO DERIVATIVE OF PHENYLAZO-ETHYLACETOACETATE

Dr. Harmeet Kaur Kohli*

Department of Chemistry, Guru Nanak Khalsa College, Matunga, Mumbai-400019, India.

Article Received on
09 July 2015,

Revised on 31 July 2015,
Accepted on 24 Aug 2015

***Correspondence for Author**
Dr. Harmeet Kaur Kohli
Department of Chemistry, Guru Nanak Khalsa College, Matunga, Mumbai-400019, India.

ABSTRACT

This paper is a continuation of the research work on nitrophenylazoethylacetoacetate complexes and particularly emphasizes the structural characterization of the complexes by thermal analysis (TG and DTA). Thermal analysis shows not only the structural changes of the complexes during thermal treatment, but also the mode of coordination as well as geometry of the coordination sphere of complexes, the structure of which had not been determined by X-ray analysis. Nitrophenylazoethylacetoacetate complexes of the type M(NO_2-PAEA)n, where M is ZrO(IV), Th(IV), Zn(II) and Cd(II), n is the valency of the metal, and NO_2-HPAEA is nitrophenylazoethylacetoacetate, have been studied thermally. The object of the study is to investigate water of hydration, coordinated water and thermal stability of the complexes by Thermogravimetry (TG) and Differential thermal analysis (DTA). Also parameters like activation energy of decomposition reaction and order of reaction are calculated by use of Freeman Carroll's equation.

KEYWORDS: Thermogravimetric analysis (TGA), Entropy change, Order of the reaction, Freeman-Carroll method.

INTRODUCTION

There has been a growing interest in the study of hydrazones because of their physiological activity, coordinative ability and applications in analytical chemistry.[1,2] The coordination chemistry of nitro-oxygen donor ligands is an interesting area of research. A great deal of attention in these areas has been focused on the complexes formed by transition metal ions with hydrazones. Hydrazones themselves are useful chelating agents and are of biological importance. Further coordination compounds containing hydrazone ligands have been

reported to act as inhibitors of enzymes and antifungal/antibacterial agents. Also they have remarkable applications in diverse areas such as non-linear optics, magnetochemistry, molecular sensors and wide range of biological applications.[3-5] The thermal degradation studies of complexes have become a subject of recent interest. It is an important property of the complexes, which decides the thermal stability of the complexes. The study of thermal behaviour of complexes in air at different temperatures provides important information about its practical applicability. Yaul, Dhande et al studied the thermal decomposition of the complexes of aroyl hydrazones[6] and found that the thermal decomposition of the complexes follow first order kinetics. The thermal decomposition of these complexes were studied kinetically using both Coats-Redfern and Horowitz-Metzer methods. We have earlier reported synthesis and spectroscopic studies of ZrO(IV), Th(IV), Zn(II) and Cd(II)complexes of nitrophenylazoethylacetoacetate. In this paper the above complexes were subjected to thermal analysis and various kinetic parameters were calculated using Freeman-Carroll method.

MATERIALS AND METHODS

All reagents and chemical were used as AR grade.

Preparation of Ligand and the metal complexes

The ligand nitrophenylazoethylacetoacetate NO_2-HPAEA (Structure 1) was prepared by standard method as described in the earlier paper. The ZrO(IV), Th(IV), Zn(II) and Cd(II) complexes of NO_2-HPAEA were prepared by standard methods.0.01molar solution of the metal salt was prepared in 80:20 alcohol water medium. To this 0.02 molar solution of the reagent NO_2-HPAEA in the same medium was added by constant stirring so that the reaction mixture contained metal to ligand molar ratio as 1:2. The 1:2 molar ratio of metal to ligand was confirmed by conductance measurements & by Job's method. The pH of the reaction mixture was slowly raised by adding very dilute liquor NH_3 solution. Complex was separated. It was dried in oven at 70 ^oC.[7]

RESULTS AND DISCUSSION

THERMAL ANALYSIS

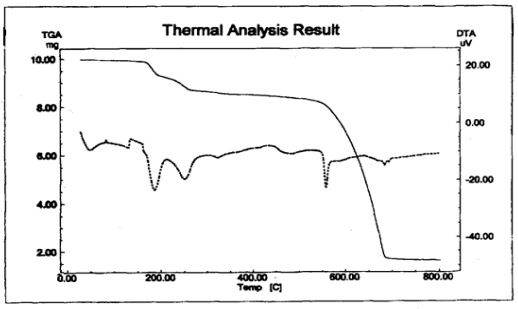
The thermal analysis of the complexes was studied by TG (thermogravimetry) and DTA (differential thermal analysis) by heating them in air at a rate of 10^oC/min.

Thermogravimetic studies of the complex $Cd(NO_2\text{-}PAEA)_2$ showed that the complex decomposes in three stages.[8,9] The first stage of decomposition was observed from 170^oC, corresponding to 8% amounting to the loss of two C_2H_5 groups, second stage of decomposition was observed at 227 ^oC corresponding to 5% amounting to the loss of two CH_3 groups and the third stage of decomposition is observed at 553 ^oC corresponding to 67 % amounting to loss of two groups of $C_6H_5N_2$, two groups of CO_2, two groups of CO and two groups of NO_2. The residue obtained is CdO.[10-12]

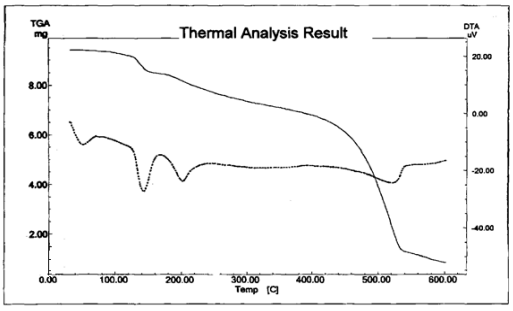
Thermogravimetic studies of the complex $Zn(NO_2\text{-}PAEA)_2.2H_2O$ showed that the complex decomposes in three stages. The first stage of decomposition was observed at 125-150 ^oC, corresponding to 5.55 %, decomposition amounting to the loss of two lattice H_2O groups. The second stage of decomposition is observed from 165 ^oC corresponding to 8.42%, decomposition amounting to the loss of two groups of C_2H_5 and the third stage of decomposition is observed at 470 ^oC corresponding to loss of two $C_6H_5N_2$, two groups of CH_3, two groups of CO_2 (5.19 %), and two groups of CO and two groups of NO_2 (total weight loss of 72.63%). The residue of ZnO is obtained.[11-13]

Thermogravimetic studies of the complex $Th(NO_2\text{-}PAEA)_2.2H_2O$ showed that the complex decomposes in three stages. The first stage of decomposition was observed at 160-260^oC, corresponding to 4.36%, decomposition amounting to the loss of two coordinated H_2O molecules. The second stage of decomposition is observed from 282 ^oC corresponding to loss of two groups of $C_6H_5N_2$ and two groups of C_2H_5 (weight loss of 31.72 %). The third stage of decomposition is observed at 548 ^oC corresponding to loss of two groups of CH_3, two groups of CO_2, two groups of NO_2 and two groups of CO (total weight loss of 32.75%). The residue remaining is ThO_2.[14-16]

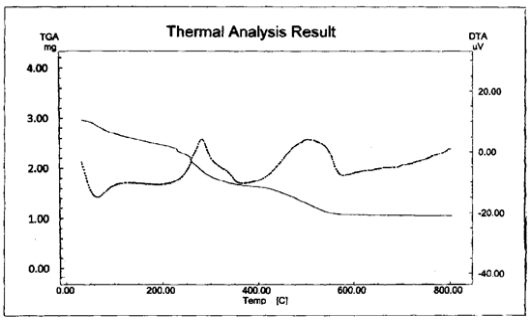
Thermogravimetic studies of the complex $[Zr(NO_2\text{-}PAEA)_2].4H_2O$ showed that the complex decomposes in three stages. The first stage of decomposition was observed at 82-150^oC, corresponding to 10%, decomposition amounting to the loss of four lattice H_2O molecules.[17,18] The second stage of decomposition is observed at 260 ^oC corresponding to loss of two groups of $C_6H_5N_2$ and loss of two groups of C_2H_5 (loss of 35.55%). The third stage of decomposition is observed at 515 ^oC corresponding to loss of two groups of CH_3, two groups of NO_2, two groups of CO_2 and two groups of CO (loss of 35.55 %). Residue remaining is ZrO_2.[14-16]



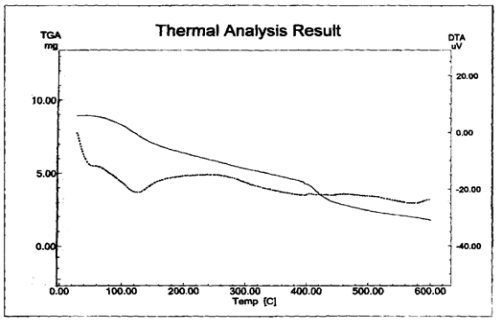
TG-DTA curve of Cd(II) complex of of NO_2-HPAEA



TG-DTA curve of Zn(II) complex of NO_2-HPAEA



TG-DTA curve of Th(IV) complex of NO_2-HPAEA



TG-DTA curve of ZrO(IV) complex of NO_2-HPAEA

EVALUATION OF KINETIC PARAMETERS

For evaluating the kinetic parameters, such as Order of reaction 'n' and Activation Energy 'E_a' method described by Freeman and Carroll has been adopted.

Freeman Carroll method

The straight line equation derived by Freeman and Carroll[19], which is in the form of n

$$\frac{[\Delta \log (dw/dt)]}{\Delta \log Wr} = \frac{(-Ea)}{2.303R} \times \frac{\Delta (1/T)}{\Delta \log Wr} + n$$

Where, dw/dt = rate of change of weight with time.

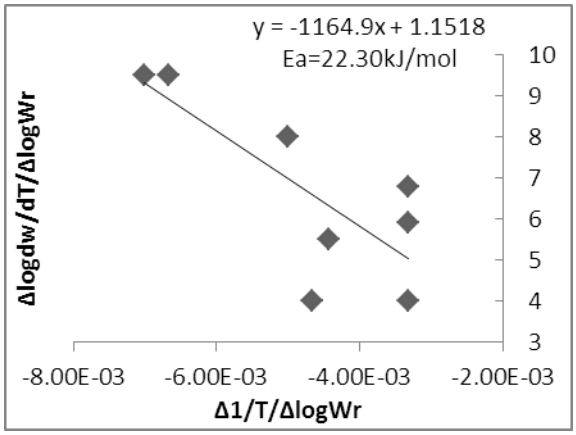
Wr = Wc-W, Wc = weight loss at completion of reaction.

W = fraction of weight loss at time t.

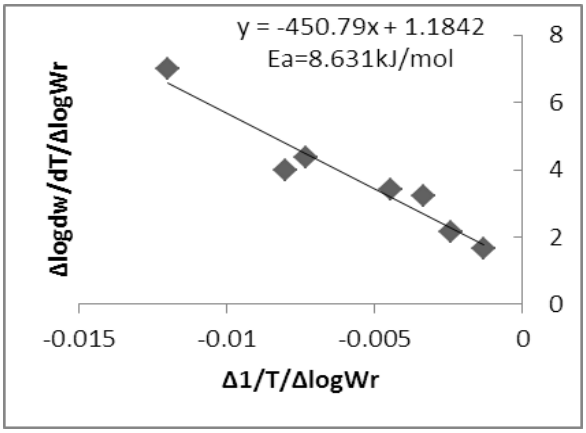
Ea = energy of activation.

n = order of reaction.

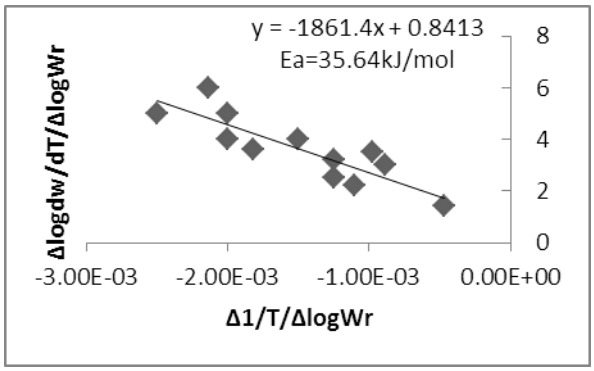
The plot between the terms [Δ log (dw/dT)] / Δ log Wr v/s Δ (1/T) / Δ log Wr gives a straight line from which slope we obtained energy of activation (Ea) and intercept on Y-axis as order of reaction (n).



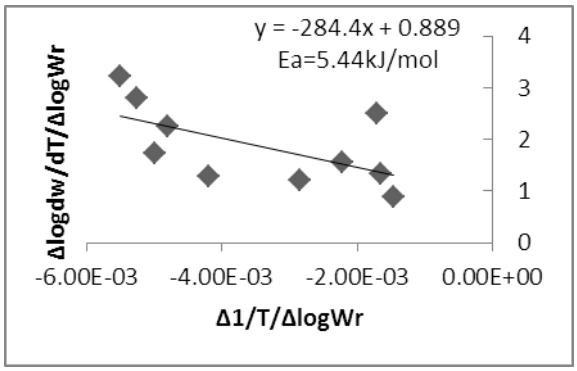
FREEMAN-CARROLL PLOT of Cd(II) complex of NO_2-HPAEA



FREEMAN-CARROLL PLOT of Zn(II) complex of NO_2-HPAEA



FREEMAN-CARROLL PLOT of Th(IV) complex of NO_2-HPAEA



FREEMAN-CARROLL PLOT of ZrO(IV) complex of NO_2-HPAEA

THERMAL DATA OF THE COMPLEXES

Complexes	Freeman Carroll method	
	Ea in kJ/mol	n
$Cd(NO_2\text{-HPAEA})_2$	22.3	1.15
$Zn(NO_2\text{-HPAEA})_2$	8.631	1.18
$Th(NO_2\text{-HPAEA})_2$	35.64	0.84
$ZrO(NO_2\text{-HPAEA})_2$	5.43	0.889

The analysis of data using the Freeman-Carroll equation gives the order of the decomposition reaction near unity for these complexes.

The relative thermal stability of the complexes (on the basis of Ea) is found to be

ZrO(IV) < Zn (II)<Cd(II) <Th(IV)

CONCLUSION

The results of thermal analysis TG-DTA are in good agreement with the theoretical formula and suggested structure of the complexes i.e. square pyramidal structure for ZrO(IV) complex, octahedral structure for Th(IV) complex and tetrahedral structures for the Zn (II)and Cd(II) complexes of this ligand. It also confirms presence or absence of water molecules in the complexes. The initial loss upto150^{o}C in the Zn(II) and ZrO(IV) complexes corresponds to loss of lattice water whereas in the Th(IV) complexes loss between 170-240 ^{o}C corresponds to loss of coordinated water. The loss of organic moieties shows a steep decrease in the TG-DTA curves of all the metal complexes. Final residue in all the complexes is the metal oxide of the corresponding metal complexes.

Freeman Carroll equation was used to calculate 'Energy of Activation' and order of reaction of all the complexes. The analysis of data using the Freeman-Carroll equation gives the order of the decomposition reaction near unity for these complexes.

ACKNOWLEDGEMENTS

The author is thankful to ICT for rendering their help for thermal analysis and the principal of G.N. Khalsa College, Dr. Kiran Mangaonkar and the Head, Department of Chemistry Dr. Chandra B. Maurya for their continuous and extended support.

REFERENCES

1. Naik V.M.; Sambrani M.I.; Mallur M.B., (Synthesis, spectroscopic and thermal studies of bivalent transition metal complexes with the hydrazone derived from 2-benzimidazolyl mercaptoacetobhydraxide and 0-hydroxy aromatic aldehyde), Indian J. Chem, 2008; 47(12)A: 1793-1797.
2. Narang K. K., Singh V.P.,Synth. React. Inorg. Met-Org. Chem, 1997; 27: 721
3. Moreau S., Varache-Lembege M., Larrouture S., Fall D., Neveu A., Deffiux G., Vercauteren J., Nuhric A.,(2-Arylhydrazonomethyl substituted Xanthones as antimycotics: Synthesis and fungistatic activity against Candida species), Eur, J Med Chem., 2003; 37(3): 237-53.
4. Xiao W, Zhang H.Y., et al,(Classification coordination, and properties of Acylhydrazone compounds),online on www.ijprd.com, 2001; 40(1): 39.
5. Abu-El-halawah R., Basem Fares Ali, et al, (synthesis and characterisation of metal-2-pyridine carboxaldehyde-N-methyl-N-2-pyridyl hydrazone complexes and their microbiological activity), J. Cord. Chem, 2004; 57: 13.

6. A.R. Yaul, V.V. Dhande, S. G. Bhadange, A.S. Aswar, (Synthesis, Structural studies and biological activity of dioxomolybdenum(VI), dioxotungsten(VI), thorium(IV), and dioxouranium(VI) complexes with 2-Hydroxy-5-methyl and 2-hydroxy -5-chloroaceto phenonebenzoylhydrazone); Russ. J. Inorg. Chem., 2011; 56: 589-594.
7. S .M. Parmeter in Organic Reactions, John Viley London, 1959.
8. M. Arshad, S. Rehman, S. A. Khan, K. Masud, N. Arshad, A. Ghani, A thermal analysis study of 1,2-dipiperidinoethane complexes of cobalt, nickel, copper, zinc and cadmium by TG-DTG-DTA techniques; Thermochimica Acta, 2000; 364: 143-153.
9. L. Mitu, M. Ilis, N. Raman, M. Imran and S. Ravichandran, Transition Metal Complexes of Isonicotinoyl–hydrazone-4-diphenylaminobenzaldehyde: Synthesis, Characterization and Antimicrobial Studies; E-Journal of Chemistry, 2012; 9(1): 365-372.
10. F. A. El-Saeid, M. E. Shakdofa and A. N. Al-Hakimi, Synthesis, Characterization and Antimicrobial Activities of Hydrazone Ligands Derived from 2-(phenylamino)acetohydrazide and Their Metal Complexes; Journal of the Korean Chemical Society, 2011; 55(3): 444-453.
11. E. Canpolat, M.Kay, A. Yazici, Russian J. Coord. Chem, 2004; 30: 87-93.
12. A.A. Saleh, S. M. E. Khalik,M. F. Eid, M.A. El-Ghamry, Synthesis, Spectral and Magnetic Studies of Mononuclear and Binuclear Mn(II), Co(II), Ni(II) and Cu(II) Complexes with Semicarbazone Ligands Derived from Sulfonamide; J. Coord. Chem, 2003; 56: 467-480.
13. I. Babahan, H. Anil, N. Sarikavakli, Synthesis, characterisation and antimicrobial activities of vicdioxime derivatives containing heteroaromatic hydrazone groups and their metal complexes; Turk. J. Chem, 2011; 35: 613-624.
14. M. Joshi, H. D. Juneja and J. P. Kanfade, Synthesis and Characterization of Metallic Gel Complexes Derived from Carboxymethyl Cellulose; International Journal of Knowledge Engineering, 2012; 3(1): 69-71.
15. S.R.Kelode and P.R.Mandlik, Synthesis, Characterization and Microbiological evaluation of Co(II), Cu(II), Zn(II) Cr(III) and Fe(III) complexes of 2,4-dimethylaniline salicylaldimine; Oriental Journal of Chemistry, 2012; 28(1): 531-535.
16. R.K. Mohapatra, and D. C. Dash, Synthesis and Characterization of UO2(VI), Th(IV), ZrO(IV) and VO(IV) Complexes with Schiff-Base Octaazamacrocyclic Ligands; Journal of the Korean Chemical Society, 2010; 54(4): 395-401.

17. S. M. El-Megharbel, A.A. A. Majid, M.S. Refat, Study of the Thermal Behaviour of the Complexation between Norfloxacin Drug with ZrO^{2+} and UO_2^{2+} Ions: TGA and DTG Investigations ; Life Science Journal, 2012; 9(2).
18. F. A. El-Saeid, M. E. Shakdofa and A. N. Al-Hakimi, Synthesis, Characterization and Antimicrobial Activities of Hydrazone Ligands Derived from 2-(phenylamino)acetohydrazide and Their Metal Complexes; Journal of the Korean Chemical Society, 2011; 55(3): 444-453.
19. E.S. Freeman and B. Carroll, The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate; J. Phy. Chem., 1958; 62: 394.