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Full Length Article

Thermal study of Butanamide 3-oxo-N-phenyl-2-(4-methyl phenyl hydrazono) complexes of Cd(II), MoO_2(VI), Th(IV) and ZrO(IV)

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ABSTRACT

Cd(II), MoO_2(VI), Th(IV) and ZrO(IV) complexes of Butanamide 3-oxo-N-phenyl-2-(4-methyl phenyl hydrazono) have been synthesized in pure solid state and analysed. All these complexes have been subjected to thermal studies using thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) and experimental data obtained from the TGA has been utilized to confirm the composition of complexes and to establish their relative thermal stabilities. The activation energy (Ea) of the decomposition reactions of the complexes have been evaluated graphically by Coats-Redfern equation. The kinetic parameters such as enthalpy of activation (ΔH), entropy of activation (ΔS), and free energy change (ΔG) for the first stage of decomposition were evaluated by Coats-Redfern equation. The complexes exhibited considerable antibacterial activity against gram positive *S.Aureus*, gram negative *E.coli*.

Key words Cd(II), MoO_2(VI), Th(IV) and ZrO(IV) hydrazone complexes, thermal studies.

INTRODUCTION

β-diketones and anilides are found to be very good complexing agents especially for transition and inner transition metal ions (Shetary*etal*, 1988). Their complexing ability is enhanced by introduction of active groups like hydrazones. The complexes are found to exhibit striking structural features and applications in diverse areas (Yagi and Yoshiharu, 1963. Hydrazone compounds exhibit biological activities as anti-fungal, anti-bacterial, anti-convulsant, anti-inflammatory, anti-malarial, analgesic, anti-tuberculosis, anti-viral, anti-tumor diseases and as anti-diabetic. The lone pair on trigonally hybridized nitrogen atom of the azomethine group is responsible for the chemical and biological activity (Korolkovas and Burckhalter, 1976). The object of our study is to investigate water of hydration and thermal stability of complexes by thermo-gravimetric and differential thermal analysis. The result can be used in thermal decomposition optimization (Harikumaran Nair ML and Thankamani D., 2010; Ibrahim KM *et al*., 2011; Deshmukh PS *et al*., 2010.)

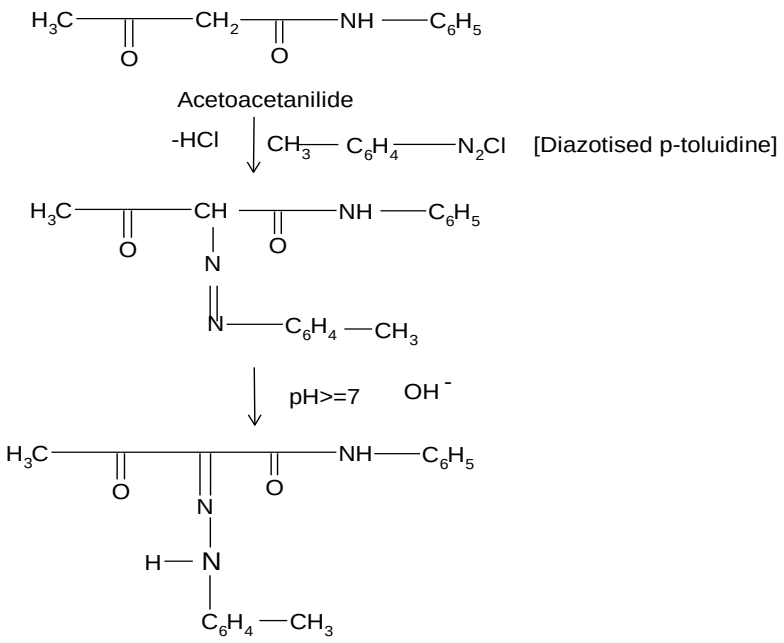
MATERIALS AND METHODS

All pH measurements, concerned with isolation of complexes and their related analysis were carried out on *Equiptronics EQ-614A*. Thermograms of metal complexes were recorded on DTG-60H simultaneous DTA-TG apparatus, *Shimadzu* at a heating rate of 10^{o}C/min.The antibacterial study of a compound was assessed by diffusion in solid media.It was conducted using MH agar media. The bacterial strains selected for the present work were (1) *Escherichia Coli (Gram– ve)*(2) S*taphylococcusaureus (Gram – +).*It depends on assessing by some means the extent of inhibition of growth.

Preparation of Ligand

The Ligand CH_3HPAAC was prepared knowing that β-dicarbonyl compounds like acetoacetanilide undergo diazo coupling at the reactive methylene group Diazotization was carried with p-toluidine

(at 0-5^{o}C).The elemental analysis is agreeing well with the expected value. M.P of ligand=126^{o}C



Preparation of Cd(II), MoO_2(VI), Th(IV) and ZrO(IV) complexes of CH_3HPAAC

(0.005 moles) solutions of Cd(II), MoO_2(VI), Th(IV), ZrO(IV) with appropriate A.R. quality salts were prepared by dissolving in very minimum quantity of distilled water and equal amount of alcohol was added. To this, (0.01 moles) of ligand CH_3HPAAC dissolved in required quantity of alcohol was added by constant stirring so that reaction mixture contained metal to ligand molar ratio of 1:2and suitable pH was adjusted. Yellow colour complexes were separated. Each of the complexes were filtered, washed with alcohol and dried. It was found to be almost insoluble in water and most of the common organic solvents. The thoroughly dried complex was analysed.

Table 1.Analytical and physicochemical parameters of Cd(II), MoO_2(VI), Th(IV), ZrO(IV) complex of CH_3HPAAC

Formula of the Complex	Molecular weight	Colour	pH	Carbon Hydrogen Nitrogen Metal%			
				Obs(Cal)	Obs(Cal)	Obs(Cal)	Obs(Cal)
MeHPAAC	295	Yellow		69.23 (69.15)	5.80 (5.76)	14.21 (14.23)	---------
$Cd(MePAAC)_2.2H_2O$	736.4	Yellow	7.4	55.32 (55.40)	4.67 (4.88)	11.88 (11.40)	15.87 (15.26)
$MoO_2(MePAAC)_2$	715.9	Light Yellow	6.4	57.33 (56.99)	4.24 (4.46)	11.87 (11.73)	13.77 (13.40)
$Th(MePAAC)_2.2H_2O$	856	Yellow	3.43	47.17 (47.67)	4.45 (4.20)	10.20 (9.81)	27.15 (27.10)
$ZrO(MePAAC)_2.1H_2O$	713	Yellow	3.85	57.38 (57.22)	4.95 (4.77)	11.56 (11.78)	12.88 (12.76)

RESULTS AND DISCUSSION

The elemental analysis of the complexes showed metal to ligand ratios of 1:2. The complexes were found to be stable in air and non hygroscopic. Thermo-gravimetric analysis of the complex is used to get the 1) information on the water of hydration (lattice or coordinated water) if present outside or inside the coordination sphere of the central metal ion. 2) Scheme of thermal decomposition of the complexes.

3) To find thermal stability of the complexes. Apart from thermal stability, this study also provided adequate support for the formulation of complexes.

It was found that all the complexes decompose at temperature much above 100°C. On heating in inert (N_2) atmosphere, they start losing weight due to loss of ligand groups stepwise and finally forming a metal oxide. Coordinated water molecules are eliminated at higher temperatures 100-250^{o}C with an endothermic peak in DTA. All the complexes lose organic ligand in large exothermic or endothermic process in the range of 300-800^{o}C (Hegazy and Motawaa, 2011, Calinescu *et al.,* 2011 and Deshmukh *et al.,* 2010). The temperature ranges and percentage mass losses of the decomposition reactions are given in Table 2 together with evolved moiety and the theoretical percentage mass losses.

Table 2: Thermal decomposition data of complexes of CH_3HPAAC

Complex	Temp range(^{o}C)	Groups decomposed	Percent wt loss Observed	Theoretical	DTA peak (^{o}C)	Enthalpy change (ΔH)KJ/mole
Cd(CH_3PAAC)$_2$.2H_2O	150-160	2H_2O	4.80	4.888	150.31	63.426
	220-280	2$CH_3C_6H_4N_2$, 2C_6H_5, 2CONH	69.55	69.79	268	190.374
	280-500	2CH_3, 2CO	82.14	81.475	-	-
	Above500	Residue left CdO	17.842	17.436		
MoO_2 (CH_3PAAC)$_2$	210-290	2 $CH_3C_6H_4N_2$	33.99	33.244	285.32	86.54
	280-450	2CH_3, 2CO	45.67	45.53	327.01 424.25	103.884 -243.706
	500-620	2C_6H_5, 2CONH	80.00	78.779	-	-
	650	Residue left MoO_3	19.99	20.10		
Th(CH_3PAAC)$_2$.2H_2O	170-180	2H_2O	4.195	4.205	160.26	6.822
	200-275	2$CH_3C_6H_4N_2$, 2CONH, 2CO, 2CH_3	51.86	52.085	306.86	-29.583
	275-500	2C_6H_5,	69.12	70.082	-	-
	Above500	Residue left ThO_2	30.866	30.841		
ZrO(CH_3PAAC)$_2$.1H_2O	160-200	1H_2O	2.491	2.524	164.18	29.48
	240-300	2$CH_3C_6H_4N_2$, 2C_6H_5, 2CONH,	70.37	69.56	303	201.183
	300-500	2CH_3, 2CO	82.77	81.624	-	-
	Above500	Residue left ZrO_2	17.213	17.25	-	-

Cd(CH_3HPAAC)$_2$.2H_2O

First stage of decomposition of Cd (MePAAC)$_2$.2H_2O complex was found to be in temperature range 150-160^{o}C with 4.80% loss corresponding to two H_2O groups. Second stage decomposition of Cd (MePAAC)$_2$.2H_2O was observed between 220-280^{o}C. It corresponds to 69.55% weight loss due to two $CH_3C_6H_4N_2$, two C_6H_5, two CONH group. Third stage decomposition of Cd (MePAAC)$_2$.2H_2O was observed between 280-500^{o}C corresponding to 82.14%. This loss was due to two CH_3 and two CO groups. DTA of Cd(MePAAC)$_2$.2H_2O showed two peaks at 150.31^{o}C and at 268.0^{o}C and both the peaks were endothermic in nature.

MoO_2 (CH_3HPAAC)$_2$

First stage of decompositions of MoO_2 (MePAAC)$_2$ complex was found in the temperature range 210-290^{o}C with 33.99% loss corresponding to two $CH_3C_6H_4N_2$ groups. Higher decomposition temperature of MoO_2 (PAAC)$_2$ showed it to be thermally more stable. Second stage decomposition of MoO_2 (MePAAC)$_2$ was observed in the temperature range 280-450^{o}C. It corresponds to 45.67% weight loss due to two CH_3, two CO groups. Third stage decomposition of MoO_2 (PAAC)$_2$ was observed between 500-620^{o}C corresponding to 80.00%. This loss was due to two C_6H_5, two CONH groups. The sample showed another weight loss in the region 680-790^o C.

The weight of the sample at 780°C was less than that may be expected if MoO_3 was formed. This may be due to volatilization of MoO_3 above 770°C (Deshmukh *et al.,* 2010, Harikumaran and Thankamani, 2009). DTA of MoO_2 $(MePAAC)_2$ showed three peaks at 285.32°C and 327.01°C which were endothermic and at 424.25°C which was exothermic in nature.

$Th(CH_3HPAAC)_2.2H_2O$

First stage of decompositions of $Th(MePAAC)_2.2H_2O$ complex was found in the temperature range 170-180°C with 4.195% loss corresponding to two H_2O. Second stage decomposition of $Th(MePAAC)_2.2H_2O$ was observed in the temperature range 200-275°C. It corresponds to 51.86% weight loss due to two $CH_3C_6H_4N_2$, two CONH, two CO, $2CH_3$ group. Third stage decomposition of $Th(MePAAC)_2.2H_2O$ was observed between 275-500°C corresponding to 69.12%. This loss was due to two C_6H_5 groups. DTA of $Th(MePAAC)_2.2H_2O$ showed two peaks at 160.26°C which was endothermic and at 306.86°C which was exothermic in nature.

$ZrO(CH_3HPAAC)_2.1H_2O$

First stage of decompositions of $ZrO(MePAAC)_2.1H_2O$ complex was found in the temperature range 160-200°C with 2.491% loss corresponding to one H_2O molecule. Second stage decomposition of $ZrO(MePAAC)_2.1H_2O$ was observed in the temperature range 240-300°C. It corresponds to 70.37% weight loss due to two $CH_3C_6H_4N_2$, two C_6H_5, two CONH group. Third stage decomposition of $ZrO(MePAAC)_2.1H_2O$ was observed between 300-500°C corresponding to 82.77%. This loss was due to two CH_3, two CO groups. DTA of $ZrO(MePAAC)_2.1H_2O$ showed two peaks at 164.18°C and at 303°C which were endothermic in nature.

The theoretical weight losses were in good agreement with that observed in the T.G. analysis, also weight of residue was found to be in agreement with molecular formula of the complex on basis of which molecular weight and formula of the complex were confirmed.

Relative thermal Stability on basis of first decomposition temperatures

The initial decomposition temperature is often used to define the relative thermal stability of the complex. However, the degree of decomposition is neglected when the initial decomposition temperature is used to define the stability parameter. First decomposition temperature is higher indicates higher thermal stability (Sahebalzamani *et al.*, 2010).

In the present studies, it can be concluded that the relative thermal stabilities of metal complexes of CH_3HPAAC follows the following order on basis of first decomposition temperatures obtained from TG and DTA. (**Table 2**)

MoO_2(VI)>ZrO(IV)>Th(IV)>Cd(II)

Decomposition kinetics

Various methods to calculate kinetics are Differential method of Freeman and Carroll, Integral method of Coats and Redfern, Horowitz Metzger, Flynn-Wall Ozawa method. The activation energy, (E_a) and the order of reaction (n) for the volatilization reaction are calculated by Integral method of Coats and Redfern.

Coats- Redfern equation

The kinetic analysis parameters such as activation energy (E_a), enthalpy of activation (ΔH), entropy of activation (ΔS), free energy change (ΔG) of decomposition were evaluated graphically by employing Coats-Redfern relation (1) (Harikumaran and Thankamani, 2009; Seleem, 2011; Yaul *et al.,* 2010; Seleem and Mousa, 2011; Harikumaran and Thankamani, 2010; Ibrahim *et al.,* 2011)

$$\mathbf{Log[-log(1-\alpha)/T^2]=[logAR/\theta E_a][1-2RT/E_a]-E_a/2.303RT} \quad (1)$$

Where α is the mass loss up to the temperature T, R is the gas constant, E_a is the activation energy in $Jmol^{-1}$, θ is the linear heating rate and $(1-2RT/E_a)=1$. A plot of left hand side of Eq(1) against 1/T gives a slope from which E_a was calculated and A (Arrhenius constant) was determined from the intercept. From relevant data, linearization plots have been drawn which confirms first order kinetics. **Figure 1**

α is the fraction reacted.

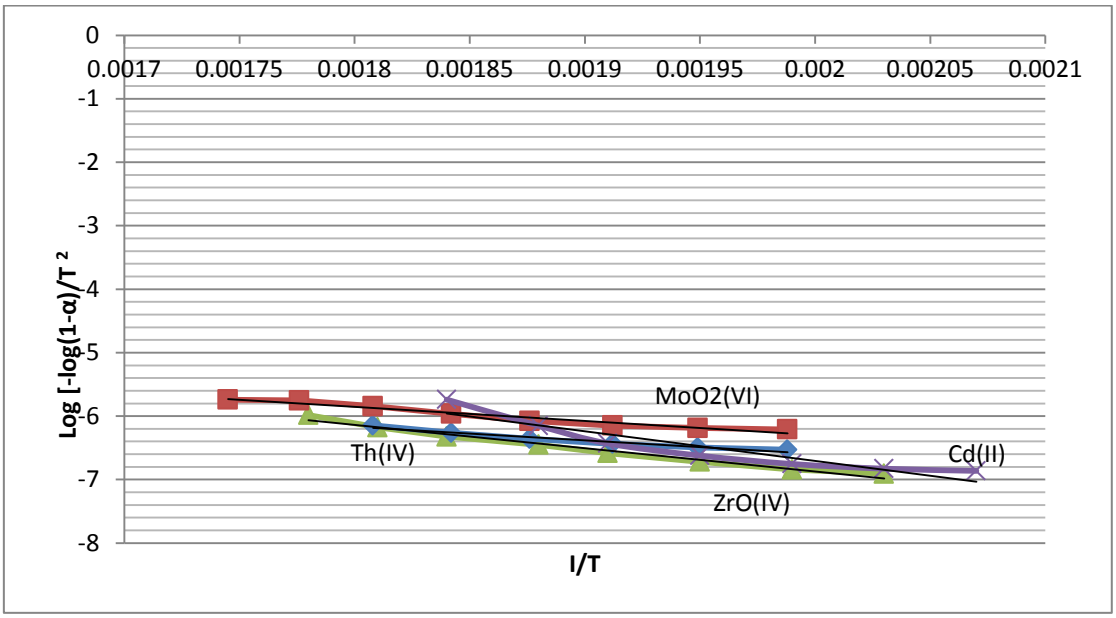
$\alpha=W_0-W_t/W_0-W_f$ where W_0 is the initial mass of the sample, W_t is the mass of the sample at temperature t, and W_f is the final mass at a temperature at which the mass loss is approximately unchanged.

The entropy of activation (ΔS) and the free change of activation (ΔG) were calculated using Eqs. (2) & (3)

$$\mathbf{\Delta S\ (JK^{-1}mol^{-1}) = 2.303\ R\ [log\ (Ah/kT)]} \quad (2)$$

$$\mathbf{\Delta G(Jmol^{-1})=\Delta H-T\Delta S} \quad (3)$$

Where k and h are the Boltzmann and Planck's constant, respectively. The values of E_a, A, ΔS, ΔH and ΔG for the decomposition steps has been calculated (**Table 3**)



Δ=MoO_2(VI), ×=Cd(II), □= Th(IV), ◇ = ZrO(IV)

Fig 1.Coats-Redfern plots of Cd(II), MoO_2(VI), Th(IV) and ZrO(IV) complexes of Butanamide 3-oxo-N-phenyl-2-(4-methyl phenyl hydrazono)

Table3. Kinetic and Thermodynamic parameters by Coats-Redfern equation

Name	Ea Kj/mol	Z	Decomp T	ΔS J/mol/K	ΔH KJ/mol	ΔG KJ/mol
$Cd(MePAAC)_2.2H_2O$	95.200	3283.08	541	-182.578	90.702	189.48
$MoO_2(MePAAC)_2$	38.850	2.41	558.32	-242.84	34.208	169.79
$Th(MePAAC)_2.2H_2O$	42.507	11.87	579.86	-229.912	37.686	171.00
$Zr(MePAAC)_2.1H_2O$	80.016	44981.7	576	-161.334	75.227	168.16

From the results following remarks can be pointed out.

1) The high values of the energy of activation E_a, of the complexes reveal the high stability of such chelates due to their covalent bond character.

2) The positive sign of ΔG for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound and all the decomposition steps are non-spontaneous processes.

3) The positive values of ΔH mean that the decomposition processes are endothermic.

4). The negative value of ΔS indicates that the activated complex has a more ordered structure than the reactants or intermediates and the reactions are slower than normal.

The kinetic parameters show a somewhat different trend from that of thermal stability. This may be due to the fact that the decisive criteria in kinetics are often quite different from those which decide thermal stability. The values of kinetic parameters are nearly same for each complex. This similarity indicates that the basic steps involved in the thermal degradation of the complexes are the same.

Relative thermal stability on basis of energy of activation E_a

The high values of energy of activation E_a of the complexes reveals the high stability of metal chelates due to their covalent bond character.

The relative kinetic stability (**Table 2)** on basis of E_a found from Coats-Redfern equation for complexes of CH_3HPAAC was found to follow the following order**:-**

Cd(II)>ZrO(IV)>Th(IV)>MoO_2(VI)

Anti-microbial study

Anti-microbial agent is the one that interferes with the growth and metabolism of microbes.

Anti-microbial agents include a number of organic compounds whose biological activity depends on size, shape and structure of molecules. It is observed that certain functional groups (Florey, 1949), especially, electron-rich groups like aromatic or aliphatic carboxy-aldehyde, phenolic-OH, halogens, amino, etc. are responsible for antimicrobial activity exhibited by the compounds. It has been found that majority of the metal complexes possessing biological activities are chelates. The relationship of metal complexes to biological response is reflected in several reviews.

Therefore, the present work is considered worthwhile to examine the antimicrobial activity of ligand CH_3HPAAC and their Cd(II), MoO_2(VI), Th(IV) and ZrO(IV) complexes .The bacterial strains selected for the present work were (1) *Escherichia Coli (Gram– ve)*(2) S*taphylococcusaureus (Gram – +).*Each depends on assessing by some means the extent of inhibition of growth. Fifty micro liters of the 100 ppm solutions of the ligand CH_3HPAAC and complexes in DMSO (negative control) were added in the wells. Positive control used for antibacterial activity was 10 ppm Ciprofloxacin. Zones of inhibition were measured around the wells which indicated antimicrobial activity.

Table 4: Antibacterial and antifungal activities of ligand and its metal complexes

Sr No.	Compound	E coli Diameter of zone of inhibition in mm	S.Aureus Diameter of zone of inhibition in mm
1.	MeHPAAC	8	9
2.	$Cd(MePAAC)_2.2H_2O$	10	12
3.	$MoO_2(MePAAC)_2$	9	-
4.	$Th(MePAAC)_2.2H_2O$	-	10
5.	$ZrO(MePAAC)_2.1H_2O$	9	10

The mechanism of the lethal process may be protein denaturation, enzyme inactivation, and damage to a membrane or blocking of an essential metabolic path. The results reveal that the activity of the ligand was enhanced on complexation with the metal, but less than standard. The enhanced activity of the complexes may be explained by chelation theory, according to which chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the donor groups and possible π- electron delocalization within the whole chelating ring. Thus chelation increases the lipophilic character in the complex. Since the microorganism's cell is surrounded by a lipid membrane which favors the passage of lipid soluble materials, increased lipophilicity allows the penetration of complex into and through the membrane and deactivates the active enzyme sites of the microorganisms (Yaul., 2010).

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