Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Kinetics and mechanism of thermolysis of hexammine metal perchlorates

Gurdip Singh[a]; Durgesh Kumar Pandey[a]
[a] Chemistry Department, D.D.U. Gorakhpur University, Gorakhpur, India

To cite this Article Singh, Gurdip and Pandey, Durgesh Kumar(2002) 'Kinetics and mechanism of thermolysis of hexammine metal perchlorates', Journal of Energetic Materials, 20: 2, 135 — 152
To link to this Article: DOI: 10.1080/07370650208244817
URL: http://dx.doi.org/10.1080/07370650208244817

KINETICS AND MECHANISM OF THERMOLYSIS OF HEXAMMINE METAL PERCHLORATES

Gurdip Singh* and Durgesh Kumar Pandey
Chemistry Department
D.D.U. Gorakhpur University
Gorakhpur-273 009, India.

ABSTRACT

The thermal decomposition studies on four transition metal hexammine perchlorates, viz. $[Cu(NH_3)_6](ClO_4)_2$, $[Co(NH_3)_6](ClO_4)_2$, $[Ni(NH_3)_6](ClO_4)_2$ and $[Zn(NH_3)_6](ClO_4)_2$, have been carried out using Thermogravimetry (TG), derivative thermogravimetry (DTG) and explosion delay (D_E) measurements. Although, the kinetics of thermolysis of these complexes were evaluated by fitting isothermal TG data in nine mechanism-based kinetic models but the contracting area (n=2) and contracting cube (n=3) give the best fits. It has been observed that deammination takes place at lower temperatures and ammine metal perchlorates and/or metal perchlorates are formed as intermediates which decompose to metal oxides at higher temperatures. The decomposition pathways for hexammine metal perchlorates have also been suggested.

Journal of Energetic Materials Vol. 20, 135-152 (2002)
Published in 2002 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

As a part of our ongoing research programme to understand the mechanism of thermolysis of energetic materials,[1-11] we have reported the preparation and characterisation of hexammine metal perchlorates (HAMPs) in our earlier paper.[12] Studies on thermolysis of these complexes are quite meagre.[13-15] The kinetic data are of practical interest for a number of technologically important processes.[16-18] Thermoanalytical techniques can provide the measurement of overall (global) kinetic parameter of thermally stimulated reactions which permit a deeper insight into the mechanism of decomposition of highly energetic compounds. Thus, it was planned to carry out the thermolysis of HAMP complexes using TG, DTG and explosion delay measurements. The kinetic parameters have been evaluated and plausible pathways for their decomposition have also been proposed in this communication.

EXPERIMENTAL

The preparation of four HAMP complexes, namely $[Cu(NH_3)_6](ClO_4)_2$, $[Co(NH_3)_6](ClO_4)_2$, $[Ni(NH_3)_6](ClO_4)_2$ and $[Zn(NH_3)_6](ClO_4)_2$ have already been reported.[12] The detailed thermolysis of these complexes has been investigated as follows:

Non-isothermal TG

TG studies on these HAMP complexes (wt.20mg, 100-200 mesh) were undertaken in static air at a heating rate of 2°C/min using indigenously fabricated TG Apparatus[19] fitted with temperature indicator-cum-controller (Model CT 808T, Century). Bucket type platinum crucible (h=1cm & d=1cm) was used as sample holder. The plots of percent decomposition (α) vs temperature (°C) are given in Figure 1.

Simultaneous TG-DTG

Simultaneous TG-DTG thermograms on HAMP complexes were obtained on a Mettler Toledo Star system in nitrogen atmosphere (flow rate 50 cm^3/min) at a heating rate of 10°C/min and thermograms are given in Figure 2. TG and DTG data profiles are summerised in Table 1.

Isothermal TG

The isothermal TG on these complexes (wt. 20mg, 100-200 mesh) were carried out in static air using the same apparatus as mentioned above at appropriate temperatures. The percent decomposition (α) vs time (min) plots are given in Figure 3. The kinetics of thermal decomposition have been evaluated from isothermal TG data which were fitted in nine mechanism-based kinetic models.[20,21] Contracting area and contracting cube equations (Equations 1 & 2) have been found to give best fits (Figures 4 & 5).

$$1-(1-\alpha)^{1/2} = kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$1-(1-\alpha)^{1/3} = kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The Arrhenius plots are given in Figures. 6 & 7. The correlation coefficient values (r) were also evaluated using the relation:

$$\text{Correlation coefficient (r)} = \frac{\Sigma xy}{\sqrt{(\Sigma x^2)(\Sigma y^2)}} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where x and y are values at abscissa and ordinates, respectively. The calculated values for rate constants (k), E_a and r are reported in Table 2.

Explosion Delay (D_E) and Explosion Temperature (ET) Measurements

These studies were undertaken using tube furnace (TF) technique[22] as reported earlier[11]. The sample (wt. 20 mg, 100-200 mesh) was taken in an ignition tube (l=5 cm &

d=0.4 cm) and time interval between the insertion of the ignition tube into the TF and the moment of an audible explosion, noted with the help of a stop watch, gave the value of explosion delay (D_E) in seconds (s). The time taken for insertion of the ignition tube was also kept constant throughout the measurements. The accuracy of temperature measurement of TF was ±1°C. Each run was repeated three times and mean D_E values are reported in Table 3. The explosion temperatures (ET) were taken of D_E at 30 s to have a comparison between the relative thermal stability of the four complexes and data are reported in Table 3. D_E data were found to fit in the following equation[23-25]

$$1/D_E = Ae^{E^*/RT} \qquad \text{..... (4)}$$

where E* is the activation energy for explosion and T is the absolute temperature.

Typical plots of log D_E vs 1/T are given in Figure 8.

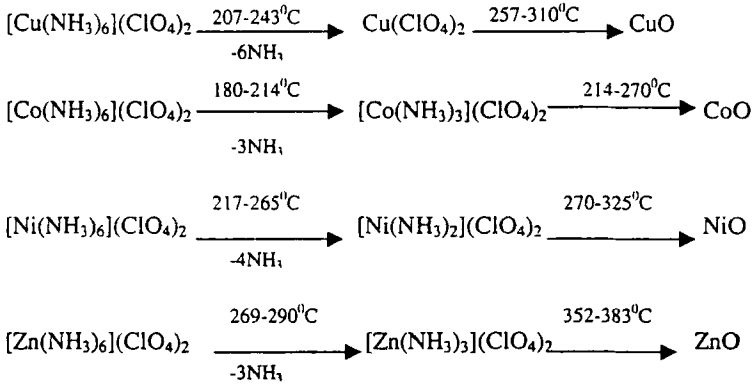
RESULTS AND DISCUSSION

It is evident from TG sigmoidal curves presented in Figure 1 that all these complexes show mass loss (α) up to 75-80%. TG-DTG data (Table 1, Figure 2) show that these complexes undergo decomposition in two stages. Partial deammination takes place at lower temperatures prior to exothermic decomposition of ammine metal perchlorates (formed as intermediates) to their respective metal oxides. However, complete deammination was observed in the case of copper complex. The overall decomposition temperature range has been found in order:

$[Zn(NH_3)_6](ClO_4)_2 > [Ni(NH_3)_6](ClO_4)_2 > [Cu(NH_3)_6](ClO_4)_2 > [Co(NH_3)_6](ClO_4)_2$

Thus, it is clear that cobalt complex is very sensitive towards heat and zinc complex is stable at considerable higher temperatures. Dynamic TG plots reported in Figure 1 are

consistent with this trend. The decomposition pathways for these complexes can be proposed as follows which are based on TG and DTG results reported in Table 1:



The kinetics of thermal decomposition of these HAMPs were evaluated using nine mechanism-based kinetic models out of which contracting area (CA) and contracting cube (CC) equations were found to fit in TG data. Estimated kinetic parameters and correlation coefficients (r) are reported in Table 2. The values of E_a obtained from both CA and CC equations for all the complexes are almost the same. However, copper and cobalt complexes gave the same E_a values which is lower as compared to those of nickel and zinc complexes. However, E_a of these complexes was found in the order:

$[Cu(NH_3)_6](ClO_4)_2 \approx [Co(NH_3)_6](ClO_4)_2 < [Ni(NH_3)_6](ClO_4)_2 < [Zn(NH_3)_6](ClO_4)_2$

These complexes are stable at room temperature and explode when subjected to a sudden high temperatures. Thus, it was deemed to be of interest to undertake explosion delay measurements (Table 3). Copper and cobalt complexes gave the lower value of D_E whereas zinc complex did not explode at furnace temperatures up to and exceeding 400°C. ET and E* for copper and cobalt complexes are found to be similar in both the

cases and are quite low as compared to zinc complex. These values also support the TG data reported in Table 2.

Summerising these results it can be concluded that thermal decomposition of HAMP complexes involve deammination prior to decomposition yielding corresponding metal oxides as final decomposition product. Copper and cobalt complexes are less thermally stable than those with nickel and zinc.

ACKNOWLEDGEMENTS

Thanks are due to ISRO, Bangalore for financial assistance and Head, Chemistry Department, DDU Gorakhpur University, Gorakhpur for laboratory facility.

REFERENCES

1. G. Singh and I.P.S. Kapoor, J. Phys. Chem., 96, 1215 (1992).
2. G. Singh and I.P.S. Kapoor, Combust. Flame, 92, 283 (1993).
3. G. Singh, I.P.S. Kapoor, S. Mudi Mannan and J. P. Agrawal, Combust. Flame, 97, 355 (1994).
4. G. Singh, R.R. Singh, A.P. Rai and I.P.S. Kapoor, J. Therm. Anal., 36, 253 (1990).
5. G. Singh, I.P.S. Kapoor and S. Mudi Mannan,Thermochim. Acta,262, 117 (1995).
6. G. Singh, I.P.S. Kapoor and S. Mudi Mannan, J. Energ. Mater., 13, 141 (1995).
7. G. Singh, I.P.S. Kapoor and S. K. Tiwari, Indian J. Chem. Tech., 7, 236 (2000).
8. G. Singh, I.P.S. Kapoor, S.K. Tiwari and S.P. Felix, Indian J. Engg. Mater. Sc., 7, 167 (2000).
9. G. Singh, I.P.S. Kapoor and S. Jacob, Indian J. Engg. and Mater. Sc. 5, 140 (1998).
10. G. Singh, I.P.S. Kapoor and S. Mudi Mannan, J. Energ. Mater., 12, 123 (1994).
11. G. Singh, I.P.S. Kapoor, S. Mudi Mannan and S.K. Tiwari, J. Energ. Mater., 16, 101 (1998).
12. G. Singh, I.P.S. Kapoor and D.K. Pandey, J. Energ. Mater., (2001) (communicated).
13. K.C. Patil and E.A. Secco, Can. J. Chem., 49, 3831 (1971).
14. K.C. Patil and V.R. Pai Verneker, Thermochim. Acta, 15, 257 (1976).
15. J. E. House, K.A. Kemper and H.M. Fogel, Thermochim. Acta, 129, 263 (1988).
16. T.B. Brill and K.J. James, Chem. Rev., 93, 2667 (1993).
17. J.H. Peperzho, in "Thermal Analysis in Metallurgy", ed. R.D. Schull, A. Joshi, (P.A. Warrendale), 121 (1992).
18. D. Dollimore, Anal Chem., 68, 63R (1996).

19. G. Singh and R.R. Singh, Res. Ind. 23, 92 (1978).

20. V. Satava, Thermochim. Acta, 2, 423 (1971).

21. C.M. Wyandt and D.R. Flanagan, Thermochim. Acta, 196, 379 (1992).

22. G. Singh, I.P.S. Kapoor and S.K. Vasudeva, Indian J. Tech., 29, 589(1991).

23. N. Semenov, "Chemical Kinetics and Chain Reactions", Clerendon Press, Oxford (1935).

24. E.S. Freeman and S. Gordon, J. Phys. Chem., 60, 867 (1956).

25. J. Zinn and R.N. Rogers, J. Phys. Chem., 66, 2646 (1962).

TABLE 1

TG-DTG Data Profile on Hexammine Metal Perchlorates

S. No.	Decomposition mode	DTG Peak Temperature(^{0}C)			% Mass loss	
		Onset	Ts	Endset	Obs.	Cal.
1.	$[Cu(NH_3)_6](ClO_4)_2$					
	Loss of $6NH_3$	207	213	243	25.8	27.9
	Decomposition of $Cu(ClO_4)_2$	257	298	310	54.2	50.3
2.	$[Co(NH_3)_6](ClO_4)_2$					
	Loss of 3 NH_3	180	200	214	13.5	14.2
	Decomposition of $[Co(NH_3)_3](ClO_4)_2$	214	236	270	63.9	65.0
3.	$[Ni(NH_3)_6](ClO_4)_2$					
	Loss of 4 NH_3	217	244	265	17.6	18.8
	Decomposition of $[Ni(NH_3)_2](ClO_4)_2$	270	288	325	59.5	60.4
4.	$[Zn(NH_3)_6](ClO_4)_2$					
	Loss of 3 NH_3	269	278	290	12.5	13.9
	Decomposition of $[Zn(NH_3)_3](ClO_4)_2$	352	370	383	64.5	64.1

TABLE 2

Kinetic Parameters and Correlation Coefficients (r) for Isothermal Decomposition of HAMP Complexes

Comp. No.	Contracting area (n=2)							Contracting cube (n=3)						
	Rate Constants ($k.10^{-3}$/min.) at (T/K)					r	Ea/kJmole^{-1}	Rate Constants ($k.10^{-3}$/min) at (T/K)					r	Ea/kJmole^{-1}
1.	5.1	6.6	12.2	24.0	55.1	0.9987	63.8	6.5	9.1	12.0	23.5	55.0	0.9896	63.5
	(553)	(573)	(583)	(593)	(613)			(553)	(573)	(583)	(593)	(613)		
2.	7.3	6.5	8.9	16.5	32.2	0.9965	64.5	5.6	6.9	10.0	22.4	30.3	0.9923	64.8
	(533)	(553)	(563)	(573)	(593)			(533)	(553)	(563)	(573)	(593)		
3.	6.3	8.5	12	35	38.1	0.9833	71.6	7.2	7.8	12.9	28.0	35.4	0.9922	71.2
	(633)	(653)	(663)	(693)	(713)			(633)	(653)	(663)	(693)	(713)		
4.	4.1	5.7	9.0	15.8	25.9	0.9975	80.6	5.0	4.8	12.9	20.1	32.5	0.9891	79.8
	(633)	(643)	(653)	(673)	(693)			(633)	(643)	(653)	(673)	(693)		

TABLE 3

Explosion Delay (D_E), Explosion Temperature (ET) and Activation Energy (Ea) of HAMP Complexes

Comp. No.	D_E (s) at various temperatures(°C)										ET(°C) for D_E of 30s	E* (kJmole^{-1})
	250	275	300	325	350	375	400	425	450	475		
1.	180±3	143±0	69.2±1	60.8±3	51.0±2	44.0±2	41.0±3	35.0±1	32.1±1	29.0±2	399	34.9
2.	150.0±2	120.0±1	90.0±1	75.0±3	65.1±2	40.3±1	38.0±2	34.1±1	29.3±3	28.5±1	402	35.3
3.	240.5±1	175.0±0	115.2±2	105.0±2	50.4±1	48.5±3	45.3±2	42.0±1	36.0±0	31.1±1	446	36.6
4.	DNE	DNE	DNE	DNE	DNE	DNE	DNE	235.1±1	145.5±1	125.0±2	537	45.4

DNE = Did not explode

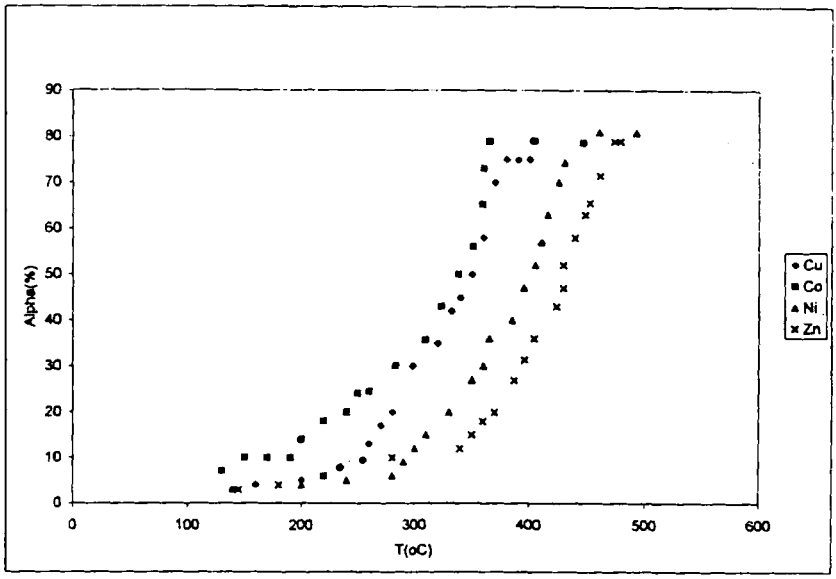


FIGURE 1
Nonisothermal TG Thermograms of HAMP Complexes

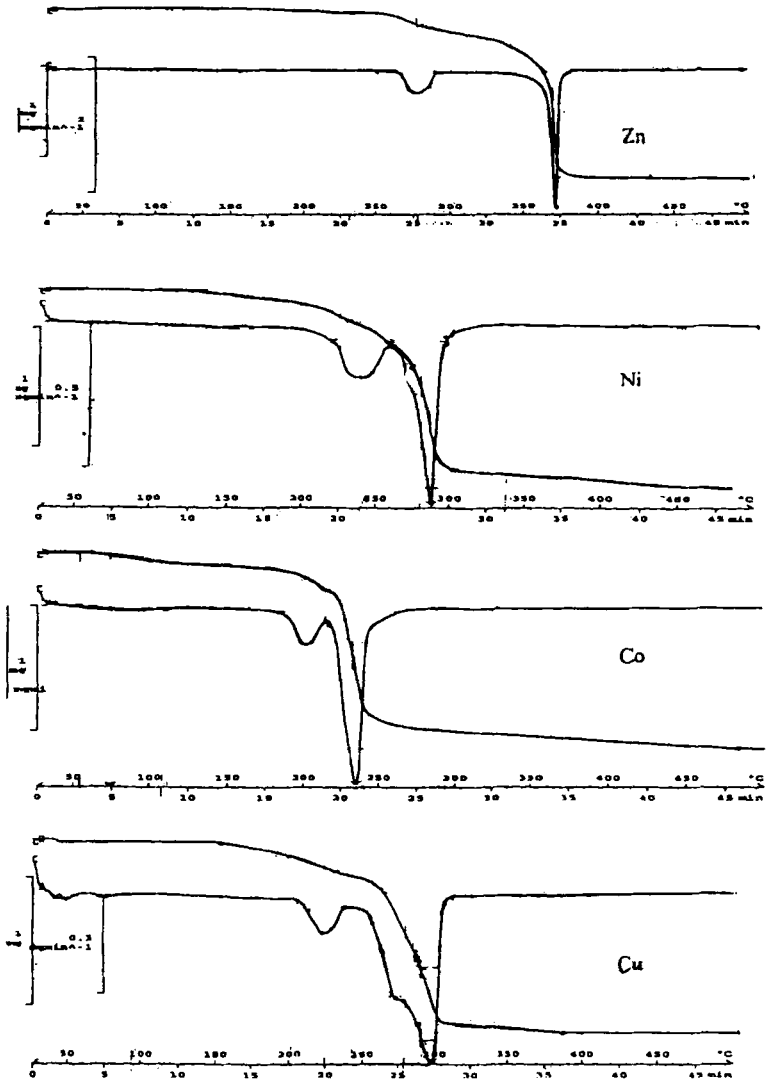


FIGURE 2
TG-DTG Thermograms of HAMP Complexes

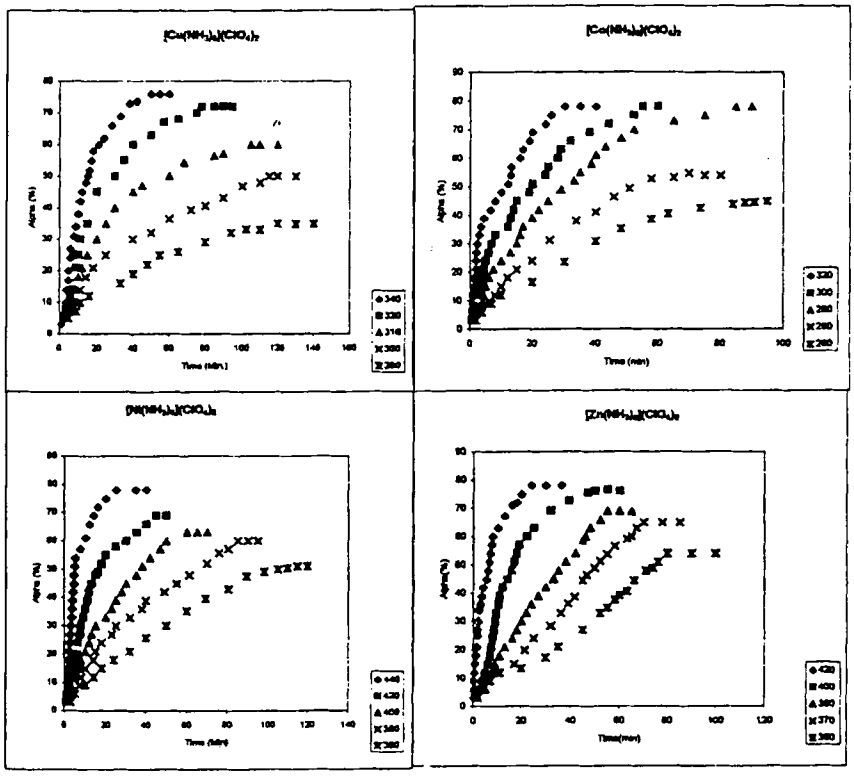


FIGURE 3
Isothermal Decomposition of HAMP Complexes

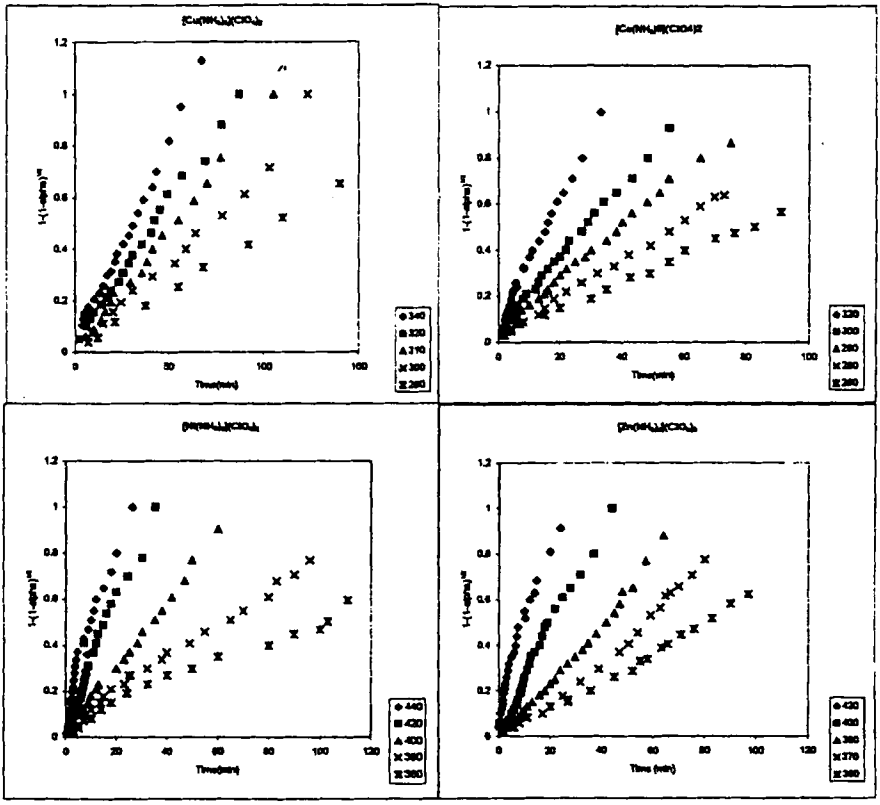


FIGURE 4
Kinetic Analysis of HAMP Complexes by the Contracting area equation (n=2)

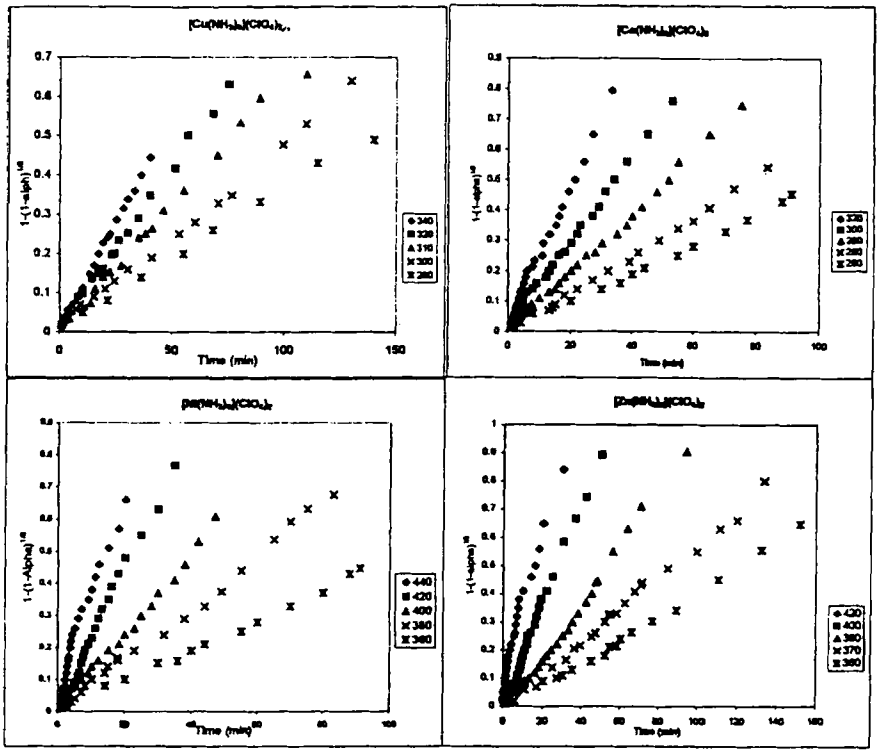


FIGURE 5
Kinetic Analysis of HAMP Complexes by the Contracting cube equation (n=3)

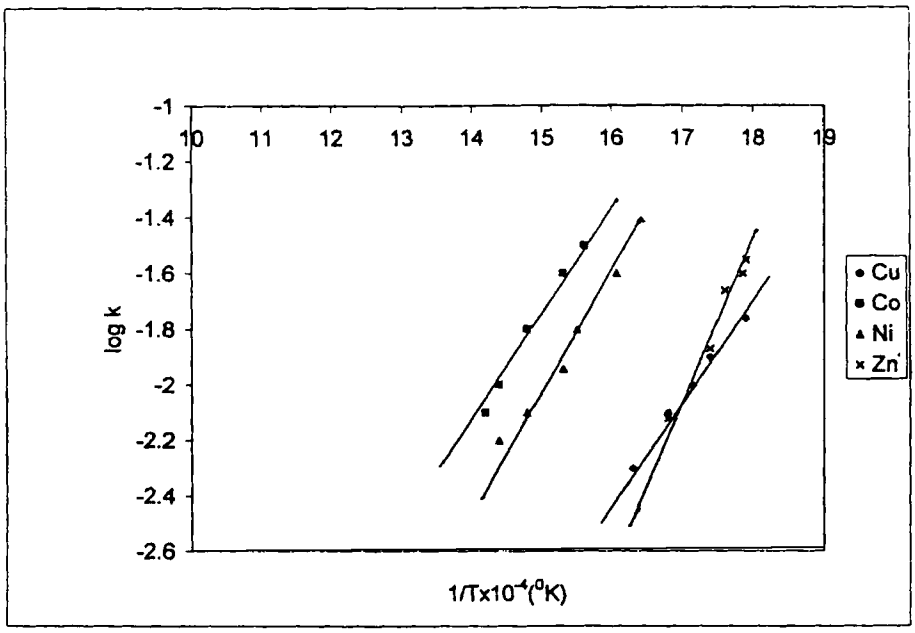


FIGURE 6
Arrhenius Plots of HAMP Complexes for Contracting area equation (n=2)

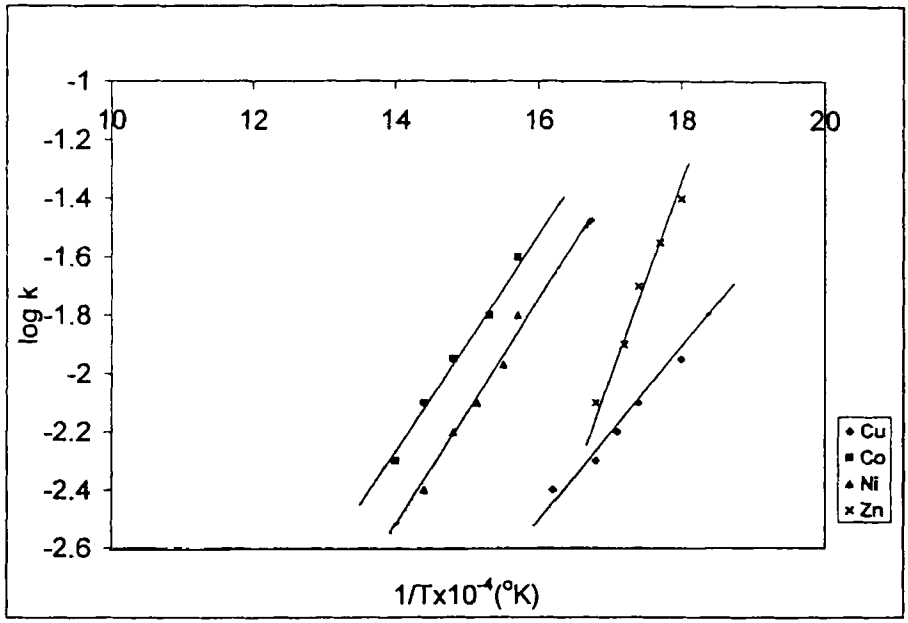


FIGURE 7
Arrhenius Plots of HAMP Complexes for Contracting cube equation (n=3)

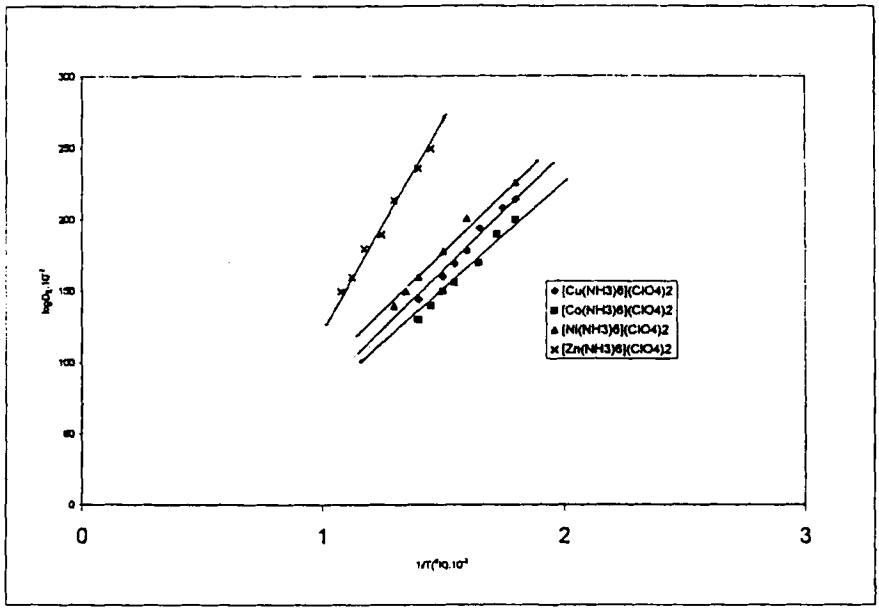


FIGURE 8
Plots of log D_E vs 1/T (^{0}K) for HAMP Complexes