



A Comparative Thermal Decomposition Kinetics on 1, 2-Bis (Imino-4'-Antipyrinyl) Ethane and 4-N-(4'-Antipyrilmethylidene) Aminoantipyrine Cu(ii) Complexes with Varying Counter Anions

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Abstract

A comparative thermal decomposition kinetic studies of Cu(II) complexes of 1,2-bis(imino-4'-antipyrinyl)ethane (GA) and 4-N-(4'-antipyrilmethylidene)aminoantipyrine (AA) with a variety of counter anions viz. ClO₄⁻, NO₃⁻, Cl⁻ and Br⁻ has been evaluated by TG analysis. The kinetic parameters ; activation energy (E), pre-exponential factor (A) and entropy of activation (ΔS) were calculated by using Coats–Redfern equation. This study shows that the thermal decomposition kinetics has been controlled by the ligand field as well as the counter anions.



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Introduction

Because of their wide applications, and various coordinating possibilities, Schiff bases derived from antipyrines have been used by many investigators.¹⁻⁵ They exhibit a variety of physiological activities,⁶⁻⁹ and also used as potentiometric sensors for the detection of specific metal ions.¹⁰ There are some reports on antipyrine Schiff base metal complexes,³ while there are only a few on their thermal decomposition

kinetics.¹¹ In our earlier reports, we have proved that the counter anions have played a marked role on thermal decomposition kinetics of the complexes.^{5,6,12-16} Here in the present study, both ligand field and counter anionic effects were taken in to consideration on the comparative investigation of the thermal decomposition kinetics. Thus, a comparative investigation has been done on kinetics of thermal decomposition on 1,2-bis(imino-4'-

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antipyrinyl)ethane and 4-N-(4'-antipyrilmethylidene) aminoantipyrine Cu(II) complexes (Fig. 1 & 2) with various of counter anions like ClO_4^- , NO_3^- , Cl^- and Br^- .

Experimental

Both the Schiff bases and the copper(II) complexes of the present study, were synthesized as reported elsewhere.³ The Schiff bases GA and AA were prepared by a simple condensation reaction between 4-aminoantipyrine and the respective aldehydes, glyoxal and 4-antipyrine-carboxyaldehyde (Fig.1&2)³. Thermogravimetric analysis has been done in a nitrogen atmosphere with exactly 10 mg of sample with the heating rate of 10 °C/min on a Delta Series TGA 7 instrument and thermal decomposition kinetics were evaluated by a computer program in QBasic.

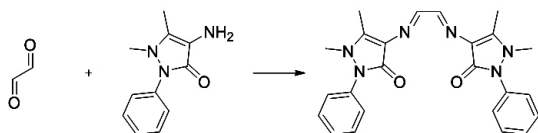


Fig. 1: Scheme for the synthesis of GA

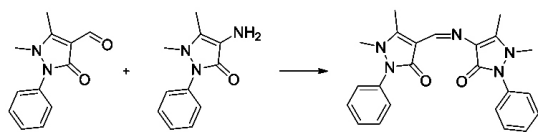


Fig. 2: Scheme for the synthesis of AA

Results and Discussion

Based on the elemental analysis, molar conductance in non-aqueous solvents, molar magnetic moments, infrared, electronic and EPR spectral studies³ of all the complexes described in the present case can be represented as; $[\text{Cu}(\text{GA})](\text{ClO}_4)_2$, $[\text{Cu}(\text{GA})](\text{NO}_3)_2$, $[\text{Cu}(\text{GA})\text{Cl}_2]$ and $[\text{Cu}(\text{GA})\text{Br}_2]$ and $[\text{Cu}(\text{AA})_2](\text{ClO}_4)_2$, $[\text{Cu}(\text{AA})_2](\text{NO}_3)_2$, $[\text{Cu}(\text{AA})_2]\text{Cl}_2$ $[\text{Cu}(\text{AA})\text{Br}] \text{Br}$ for the ligands GA and AA respectively. Both the carbonyl oxygen and imine nitrogen atoms are coordinated in GA complexes and both the counter anions remain non-coordinated in the perchlorate and nitrate species while both the halides are coordinated in the rest of the GA complexes generating a square planar geometry for the perchlorate and nitrate

complexes while an octahedral geometry for the others (Fig.3). For the Cu(II) complexes of AA, the ligand coordinates via one of the carbonyl oxygens and imine nitrogen in perchlorate, nitrate and chloride complexes while through both the carbonyl oxygens and imine nitrogen in the bromide complex. Both the counter anions remain non-coordinated in perchlorate, nitrate and chloride complexes and one of the bromide is coordinated in the corresponding complex, generating a square planar geometry in all the complexes (Fig. 4). But, AA coordinates in a tridentate mode in bromide complex, via both carbonyl oxygens and the azomethine nitrogen, and also coordinated through one of the bromide anions, thus, generating a square planar geometry (Fig.4). The thermograms of the eight complexes is shown in the Figures 5-12.

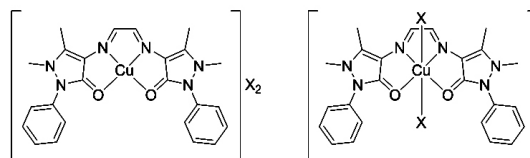


Fig. 3: Tentative structures of the Cu(II) complexes of GA (Left: $\text{X} = \text{ClO}_4^-$ or NO_3^- ; Right: $\text{X} = \text{Cl}^-$ or Br^-)

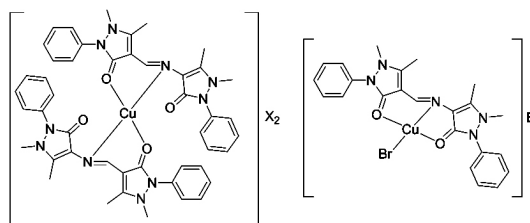


Fig. 4: Tentative structures of the Cu(II) complexes of AA ($\text{X} = \text{ClO}_4^-$, NO_3^- , Cl^-)

Principle

The thermal stability of solid state materials can be investigated by non-isothermal thermogravimetric analysis. In this method, the kinetic parameters can be arrived continuously over an entire range of temperature. The following concept has been used to derive kinetic equation from thermal decomposition reactions.¹⁷

$$\frac{d\alpha}{dT} = K.f(\alpha) \quad \dots(1)$$

where K = specific rate constant, α = amount of sample undergoing reaction, $f(\alpha)$ = conversion function.

For a linear heating rate ϕ , $T = T_0 + \phi t$
Where, T_0 - temperature of initiation

$$\frac{dT}{dt} = \phi \quad \dots(2)$$

Substituting (2) in (1)

$$\frac{d\alpha}{dT} = \frac{K.f(\alpha)}{\phi} \quad \dots(3)$$

The specific rate constant K, which is temperature dependent can be expressed by the Arrhenius equation

$$K = A e^{-E/RT} \quad \dots(4)$$

where A = pre-exponential factor, E = energy of activation, R = gas constant and T = temperature in Kelvin scale.

Substituting (4) in (3)

$$\frac{d\alpha}{dT} = \frac{A e^{-E/RT}}{\phi} . f(\alpha) \quad \dots(5)$$

On integration, taking initial temperature as zero, this assumption is correct as no reaction occurs between $T = 0$ and $T = T_i$.

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_0^T e^{-E/RT} . dT \quad \dots(6)$$

$$g(\alpha) = \frac{A}{\phi} \int_0^T e^{-E/RT} . dT \quad \dots(7)$$

where $g(\alpha)$ is the conversion integral.

The temperature integral can be evaluated by Coats and Redfern equation¹⁸ with Rainville function.¹⁹ The temperature integral t is

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \frac{AR}{\phi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad \dots(8)$$

On plotting L.H.S. of the equation against $1/T$, will be a straight line, from the slope and intercept, we can calculate the energy of activation (E) and the pre-exponential factor (A).

The entropy of activation (ΔS) can be calculated by the following equation.

$$A = \frac{kTs}{h} e^{\Delta S/R} \quad \dots(9)$$

where k = Boltzmann's constant
 h = Planck's constant
 ΔS = Entropy of activation.

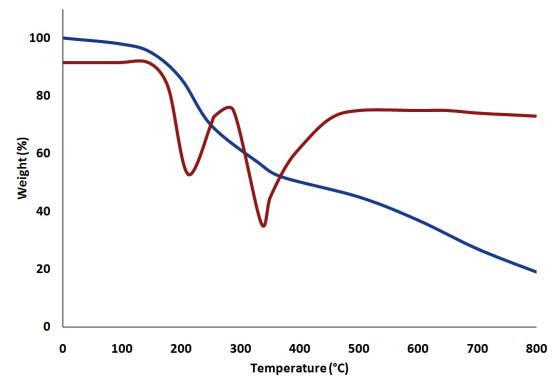


Fig. 5: TG (blue) and DTG (red) of $[Cu(GA)](ClO_4)_2$

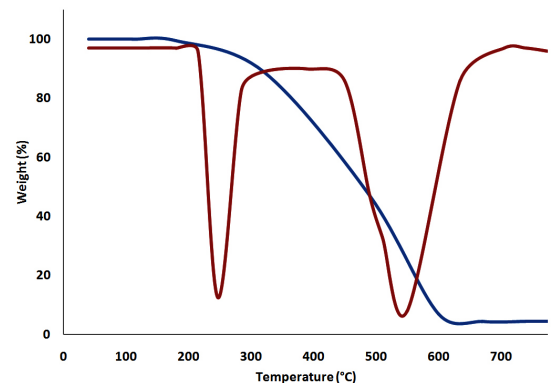


Fig. 6: TG (blue) and DTG (red) of $[Cu(GA)](NO_3)_2$

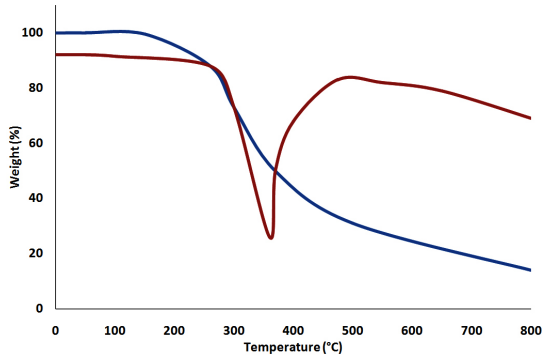


Fig. 7: TG (blue) and DTG (red) of [Cu(GA)Cl₂]

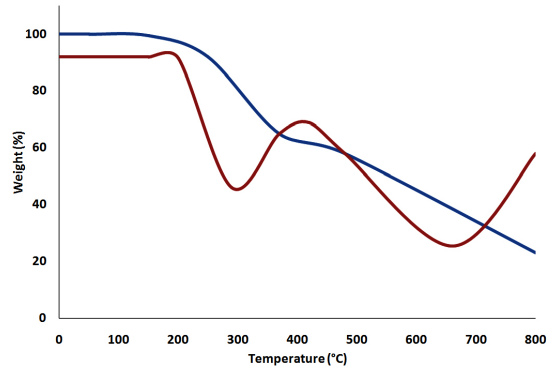


Fig. 8: TG (blue) and DTG (red) of [Cu(GA)Br₂]

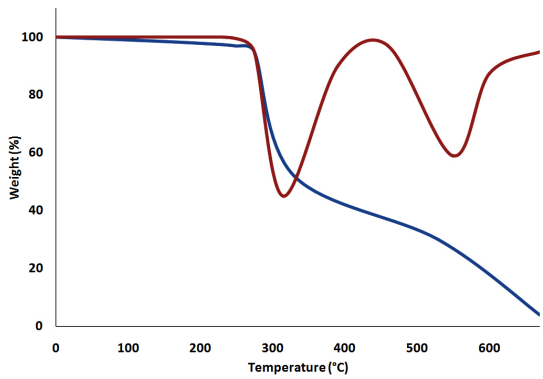


Fig. 9: TG (blue) and DTG (red) of [Cu(AA)₂](ClO₄)₂

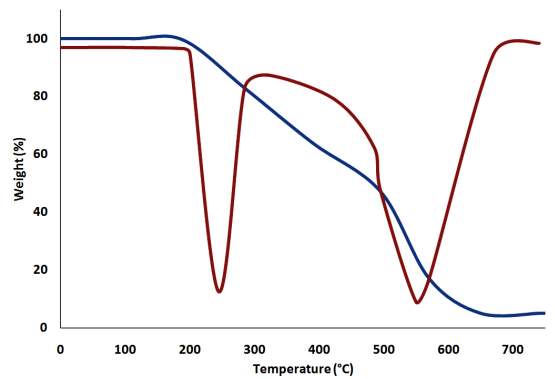


Fig. 10: TG (blue) and DTG (red) of [Cu(AA)₂](NO₃)₂

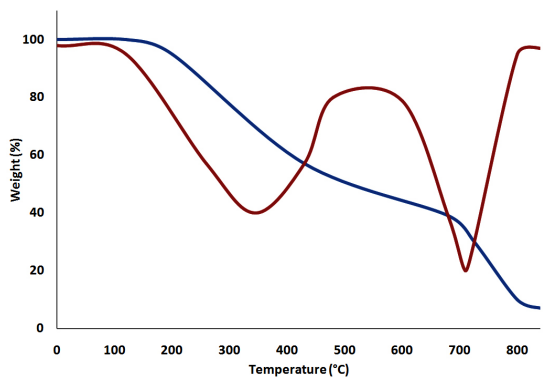


Fig. 11: TG (blue) and DTG (red) of [Cu(AA)₂Cl₂]

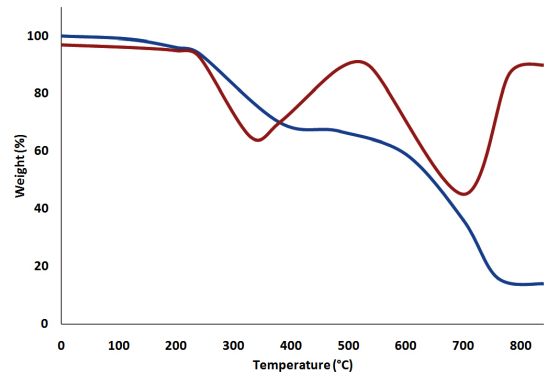


Fig. 12: TG (blue) and DTG (red) of [Cu(AA)Br]Br

Phenomenological Aspects

The phenomenological aspects of the complexes under study are given in tables 1 and 2.

Complexes of GA

The perchlorate complex decomposes in three stages. The first stage which starts at 137°C and ends at 266°C having a DTG peak at 220°C, corresponds to the mass loss of 30.90 % due to the decomposition of half of the GA molecule.¹⁴ This observation has been confirmed by IR spectra of the intermediate residue. The thermal decomposition stage between (266-513°C) with mass loss of 18.75 % with DTG peak at 350°C is due to the decomposition of the two perchlorates in to chlorides. The third stage, which starts at 513°C is a continuous one, can be due to the removal of the remaining half of the ligand molecule together with the volatilization of anhydrous copper chloride above this temperature.²⁰

The nitrate complex $[\text{Cu}(\text{GA})](\text{NO}_3)_2$ decomposes in two stage between 228-611°C. The first stage corresponds to a mass loss of 43.57 % between 228-464°C with a DTG peak at 245°C is due to the removal of half of the ligand molecule and one nitrate ion. The second stage which starts at 464°C and ends at 611°C, with a mass loss of 44.28 % was owing to the decomposition of the residual half of GA and nitrate ion. The corresponding DTG-peak is observed at 561°C for this stage. The decomposition gets completed at 611°C yielding anhydrous copper oxide as the final product as confirmed, qualitatively.

The chloride complex, $[\text{Cu}(\text{GA})\text{Cl}_2]$ decomposes in two stages. The first decomposition stage between 178-427°C with a DTG-peak was at 348°C. Removal of half of the molecule of GA occurs at this stage with a mass loss of 38.08 %. The above observation is confirmed by the IR spectrum of the intermediate residue at 427°C. The thermal decomposition, which is happening above 427°C is a contentious one, which can be due to the decomposition of the residual ligand molecule along with the volatilization of anhydrous cupric chloride formed at this stage.

$[\text{Cu}(\text{GA})\text{Br}_2]$, the bromide complex decomposes in two stage in the temperature ranges 197-492°C and 492-893°C respectively. In the first stage a mass loss of 32.74% occurs, owing to the removal of the half of the GA molecule and this observation is confirmed by the IR spectral analysis of the intermediate residue. The corresponding DTG peak is observed at 297°C. In the second stage also the same observation like that of the first stage is repeating i.e. the removal of the remaining half of the ligand molecule. The DTG peak for this stage occurs at 684°C. The decomposition completed at 893°C leaving final residue of cupric bromide.

Complexes of AA

The complex, $[\text{Cu}(\text{AA})_2](\text{ClO}_4)_2$, decomposes in two stage, between 190-615°C. The first decomposition stage of occurred between 190-328°C with a DTG peak at 314°C, owing to the mass loss of 43.47% was due to the decomposition of one ligand molecule

Table 1: Phenomenological data of Cu(II) complexes of GA.

Complex	stage of decomposition	TG plateau (°C)	DTG peak (°C)	mass loss (%)
$[\text{Cu}(\text{GA})](\text{ClO}_4)_2$	I	137-266	220	30.90
	II	266-513	350	18.75
	III	513-	-	continuous
$[\text{Cu}(\text{GA})](\text{NO}_3)_2$	I	228-464	245	43.57
	II	464-611	561	44.28
$[\text{Cu}(\text{GA})\text{Cl}_2]$	I	178-427	348	38.08
	II	427-	-	continuous
$[\text{Cu}(\text{GA})\text{Br}_2]$	I	197-492	297	33.33
	II	492-893	684	32.74

together with the conversion of a perchlorate into chloride. For the second stage having a DTG peak at 564°C, the same observation like that of the first stage occurred, i.e. the removal of the remaining AA molecule along with the decomposition of the remaining perchlorate into chloride. The decomposition gets completed at 615°C leaving anhydrous cupric chloride as final residue confirmed qualitatively.²⁰

For the nitrate complex, a two stage decomposition in the temperature ranges 203-464°C and 464-615°C has been observed. In the first stage, a mass loss of 46.37% occurred due to the expulsion of a ligand molecule together with a nitrate ion. For the second stage, the same observation has been observed leaving anhydrous cupric oxide as the final residue. The rate of maximum mass loss occurred at 245 and 561°C for the first and second stage respectively as indicated by the DTG peak.

The chloride complex having the formula, $[\text{Cu}(\text{AA})_2]\text{Cl}_2$, decomposes in two stages between 181°C and 807°C. The first stage between 181-489°C and having a DTG peak at 347°C, with a mass loss of 41.10 % was owing to the removal of a molecule of AA. The second stage with a mass loss of 41.01 % between 489°C and 807°C having a DTG-peak at 718°C was due to the decomposition of the residual AA molecule. Anhydrous cupric chloride was left behind as the final residue as confirmed by qualitatively.

The bromide complex $[\text{Cu}(\text{AA})\text{Br}]\text{Br}$, is decomposed in a two stage process in the temperature range 186-719°C. The first stage, corresponding to a mass loss

of 32.78%, in the temperature range 186-549°C was owing to the removal of half a molecule of AA. The second decomposition between 549 -719°C with a mass loss of 32.17 % showing a DTG peak at 698°C, can be attributed to the removal of the remaining half of the ligand molecule. The decomposition is completing at 719°C, with a residue of anhydrous cupric bromide as confirmed by qualitative analysis.

Kinetic Aspects

Kinetic parameters like activation energy (E), pre-exponential factor (A) and entropy of activation (ΔS) for the thermal decomposition of copper(II) complexes of both GA and AA are given in Table 3.

Complexes of GA

The activation energy (E) for all well-defined stages, varies from 33.98 to 63.08 kJ mol^{-1} for first stage, while for second stage the activation energy varies from 40.86 to 140.72 kJ mol^{-1} . In all cases higher second stage activation energy has been observed, except for the perchlorate complex. On comparing the first stage activation energies, the perchlorate complex is most, while the bromide complex is least stable among the series yielding the order of stability Perchlorate > Nitrate > Chloride > Bromide. For the second stage, the respective trend is, Nitrate > Perchlorate > Bromide. The same trend cannot be observed in the case of other kinetic parameters like pre-exponential factor (A) or entropy activation (ΔS).

Complexes of AA

The activation energy (E) for all well-defined first and second decomposition stages ranges from 38.96 to 108.96 kJ mol^{-1} and 40.49 to 179.58 kJ mol^{-1} respectively. On top of this, in all cases higher second

Table 2: Phenomenological data of Cu(II) complexes of AA.

Complex	Stage of decomposition	TG plateau (°C)	DTG peak (°C)	mass loss (%)
$[\text{Cu}(\text{AA})_2](\text{ClO}_4)_2$	I	190-328	314	43.47
	II	328-615	564	43.11
$[\text{Cu}(\text{AA})_2](\text{NO}_3)_2$	I	206-464	245	46.37
	II	464-615	561	46.10
$[\text{Cu}(\text{AA})_2]\text{Cl}_2$	I	181-489	347	41.10
	II	489-807	718	41.01
$[\text{Cu}(\text{AA})\text{Br}]\text{Br}$	I	186-549	330	32.78
	II	549-719	698	32.17

Table 3: Kinetic parameters of Cu(II) complexes of GA and AA for all well-defined stages

Complexes	Stage	E (kJ mol ⁻¹)	A (S ⁻¹)	ΔS (J mol ⁻¹)
[Cu(GA)](ClO ₄) ₂	I	63.08	3.54	-238.56
	II	40.86	7.28 x 10 ⁻²	-272.80
[Cu(GA)](NO ₃) ₂	I	39.57	0.19	-262.78
	II	140.72	175.98	-209.40
[Cu(GA)Cl ₂]	I	38.66	7.63 x 10 ⁻²	-272.40
	I	33.98	4.62 x 10 ⁻²	-275.85
[Cu(GA)Br ₂]	II	52.81	4.15 x 10 ⁻²	-281.04
	I	108.96	9.50 x 10 ⁻²	-270.21
[Cu(AA) ₂](ClO ₄) ₂	II	40.49	4.24	-241.46
	I	100.80	2.22 x 10 ³	-180.17
[Cu(AA) ₂](NO ₃) ₂	II	159.18	1.94 x 10 ²	-209.64
	I	38.96	6.87 x 10 ⁻²	-273.31
[Cu(AA) ₂]Cl ₂	II	128.51	5.68	-240.48
	I	39.32	6.46 x 10 ⁻²	-273.52
[Cu(AA)Br]Br	II	179.58	1.66 x 10 ²	-212.30

stage activation energy was observed except for the perchlorate complex. On comparing the activation energy along the series, the perchlorate complex is the most stable and chloride complex is the least stable, and it is in the order, Perchlorate > Nitrate > Bromide > Chloride for the first decomposition stage while it is, Bromide > Nitrate > Chloride > Perchlorate for the second stage. Here also, the same trend cannot be observed in the case of other kinetic parameters like pre-exponential factor (A) or entropy activation (ΔS).

Comparison of Kinetic parameters

In comparison, the activation energy (E) in both copper(II) complexes of GA and AA, varies from 33.98 to 108.96 kJ mol⁻¹ and 40.49 to 179.58 kJ mol⁻¹ for first and second decomposition stages respectively. In the present case for all except the perchlorate complexes have higher second stage activation energy,²¹ may be due to the less steric strain occurring at this stage.¹⁴ For the first decomposition stage of both GA and AA complexes, the perchlorate is the most stable with respect to

the activation energy. For all the complexes the corresponding values of pre-exponential factor (A) varies from 4.62 x 10⁻² to 2.22 x 10³s⁻¹ for the first stage while for second stage it varies from 4.15 x 10⁻² to 1.94 x 10²s⁻¹. The respective values of the entropy of activation (ΔS) were also fall in the range -275.85 to -180.17 J mol⁻¹ for the first stage, while it is in the range -281.04 to -209.40 J mol⁻¹ for second stage. The negative values for the entropy of activation reveals that the activated complexes are more ordered than the reactants or intermediate and the reaction is slower than normal¹²⁻¹⁶. Generally, copper(II) complexes of AA was found to have higher activation energy as comparing that of complexes of GA. Comparing the various kinetic parameters, copper(II) complexes of AA was found to be more stable than that of GA.

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