

Kinetics on Thermal Decomposition of Iron(III) Complexes of 1,2-Bis(Imino-4'-Antipyrinyl)Ethane with Varying Counter Anions

Fikre Elemo*, Tesfay Gebretsadik*, Mamo Gebrezgiabher*, Yosef Bayeh*, Madhu Thomas#

Department of Industrial Chemistry, Addis Ababa Science and Technology University, Addis Ababa, Ethiopia

Email: #madhu.thomas@aastu.edu.et

How to cite this paper: Elemo, F., Gebretsadik, T., Gebrezgiabher, M., Bayeh, Y. and Thomas, M. (2019) Kinetics on Thermal Decomposition of Iron(III) Complexes of 1,2-Bis(Imino-4'-Antipyrinyl)Ethane with Varying Counter Anions. *Advances in Chemical Engineering and Science*, 9, 1-10. <https://doi.org/10.4236/aces.2019.91001>

Received: October 5, 2018

Accepted: December 2, 2018

Published: December 5, 2018

Copyright © 2019 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

A comparative thermal decomposition kinetic investigation on Fe(III) complexes of a antipyrine Schiff base ligand, 1,2-Bis(imino-4'-antipyrinyl)ethane (GA)), with varying counter anions viz. ClO_4^- , NO_3^- , SCN^- , Cl^- , and Br^- , has been done by thermogravimetric analysis by using Coats-Redfern equation. The kinetic parameters like activation energy (E), pre-exponential factor (A) and entropy of activation (ΔS) were quantified. On comparing the various kinetic parameters, lower activation energy was observed in second stage as compared to first thermal decomposition stage. The same trend has been observed for pre-exponential factor (A) and entropy of activation (ΔS). The present results show that the starting materials having higher activation energy (E), are more stable than the intermediate products, however; the intermediate products possess well-ordered chemical structure due to their highly negative entropy of activation (ΔS) values. The present investigation proves that the counter anions play an important role on the thermal decomposition kinetics of the complexes.

Keywords

Iron(III) Complexes, 1,2-Bis(Imino-4'-Antipyrinyl)Ethane, Thermal Decomposition, Kinetics

1. Introduction

Solid state thermal decomposition of metal complexes and its kinetic evaluation [1] [2] has drawn much attention of many investigators, as it can be a photo type

*The authors wish in to be known that, in their opinion, the first four authors should be regarded as joint first authors.

for investigating the fuel efficiency of solid propellants. Thermal decomposition kinetics analysis of solid propellants can be correlated to combustion characteristics of the fuels [3]. It is crucial to study the thermolytic characteristics on solid propellants so that one can get information on the potential hazard in their handling, storage and processing [4] [5]. Kinetic studies are also useful in modelling and predicting the combustion characteristics of solid rocket propellants [6]. In the present investigation, we have thermally characterised five Fe(III) coordination complexes, which has been synthesised and characterised by the reported procedure [7], and their thermal decomposition kinetics, based on various kinetic parameters like activation energy (E), entropy activation (ΔS), pre-exponential factor (A), are evaluated by Coats-Redfern equation. This kinetic evaluation can be used as photo type for energetic characteristics of solid propellants.

2. Experimental

GA and its Fe(III) complexes were prepared and characterised as reported earlier [7]. The ligand was prepared by simple condensation reaction between glyoxal and 4-aminoantipyrine in ethanolic medium. (Figure 1) [7]. A TGA-7 thermal analyser was used to record the thermograms. The analysis was done under N_2 atmosphere using around 10 mg of samples for each measurement. The kinetic evaluation of the thermal decomposition studies was done using a computer programme in Q-basic.

3. Results and Discussion

Based on the various analytical, physicochemical and spectral studies [7], the complexes in the present studies can be formulated as $[Fe(GA)(ClO_4)](ClO_4)_2$ and $[Fe(GA)X_2]X$ (where $X = NO_3^-$, SCN^- , Cl^- or Br^-). A tetradentate coordination has been observed for through both carbonyl oxygen atoms and azomethine nitrogens in all complexes. One of the perchlorates, two of the nitrates are coordinated in a bidentate and monodentate fashion respectively in the corresponding complexes as evident from the infrared and molar conductance studies. In the thiocyanate complex, two of the thiocyanate ions are coordinated monodentately through nitrogen atoms. In the chloride and bromide complexes, both the halides are coordinated to the metal atom in the respective complexes. From the electronic spectra and the magnetic moment data, a spin free octahedral geometry is assigned to all the synthesized complexes (Figure 2). The TG and DTG curves of all five complexes are shown in the Figures 3-7.

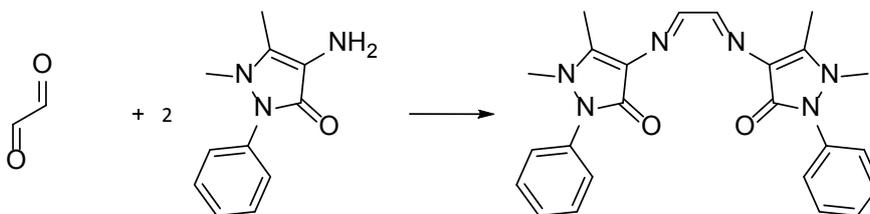


Figure 1. Scheme for the synthesis of 1,2-Bis(imino-4'-antipyrinyl)ethane (GA).

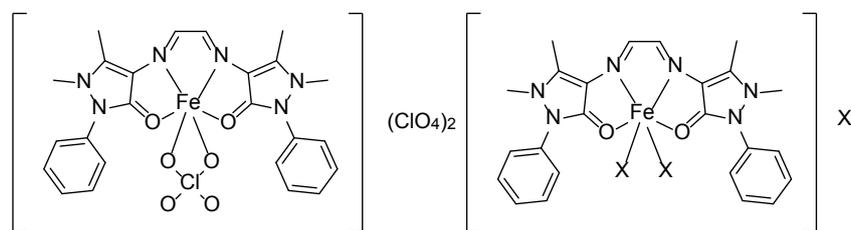


Figure 2. Tentative structures of the Fe(III) perchlorate complex (left), and nitrate, thiocyanate, chloride and bromide complexes ($X = \text{NO}_3^-$, SCN^- , Cl^- or Br^-) (right).

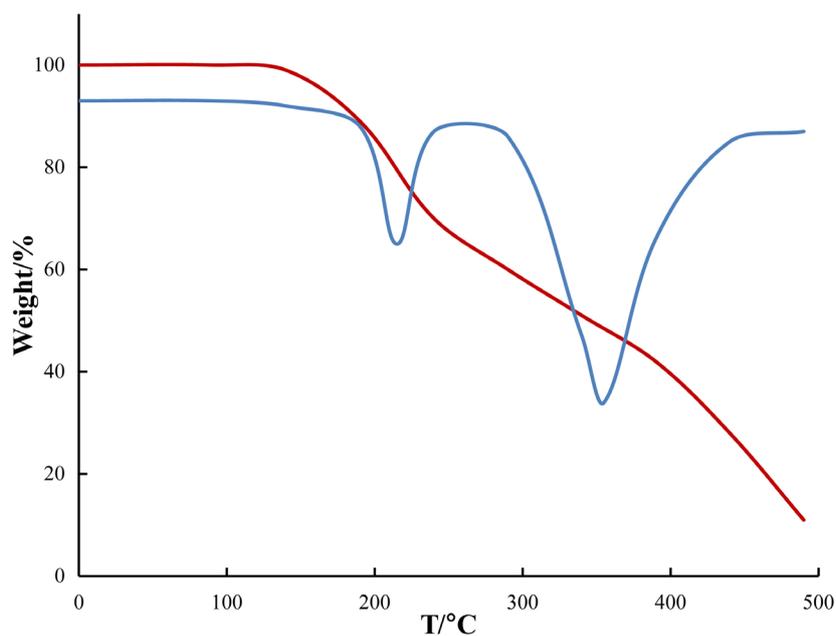


Figure 3. TG (red line) and DTG (blue line) of $[\text{Fe}(\text{GA})(\text{ClO}_4)](\text{ClO}_4)_2$.

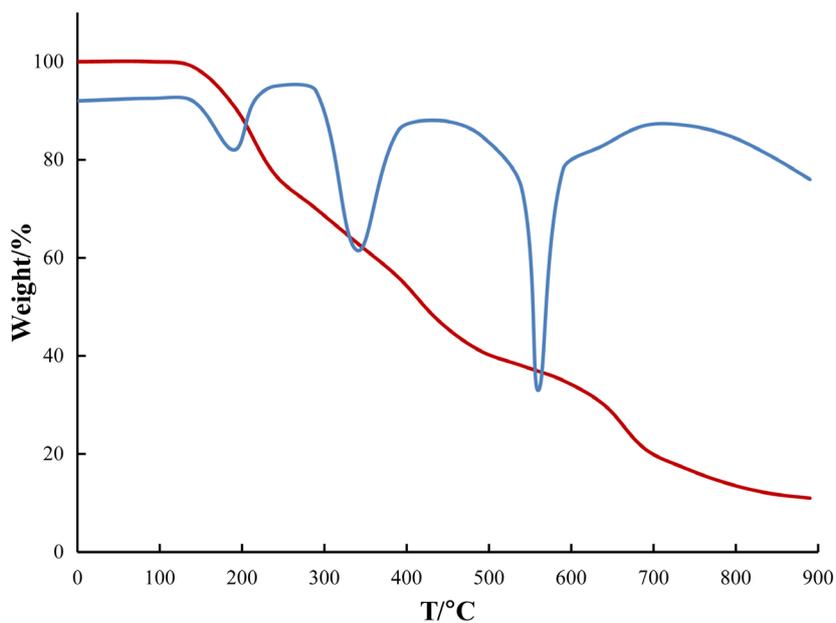


Figure 4. TG (red line) and DTG (blue line) of $[\text{Fe}(\text{GA})(\text{NO}_3)_2]\text{NO}_3$.

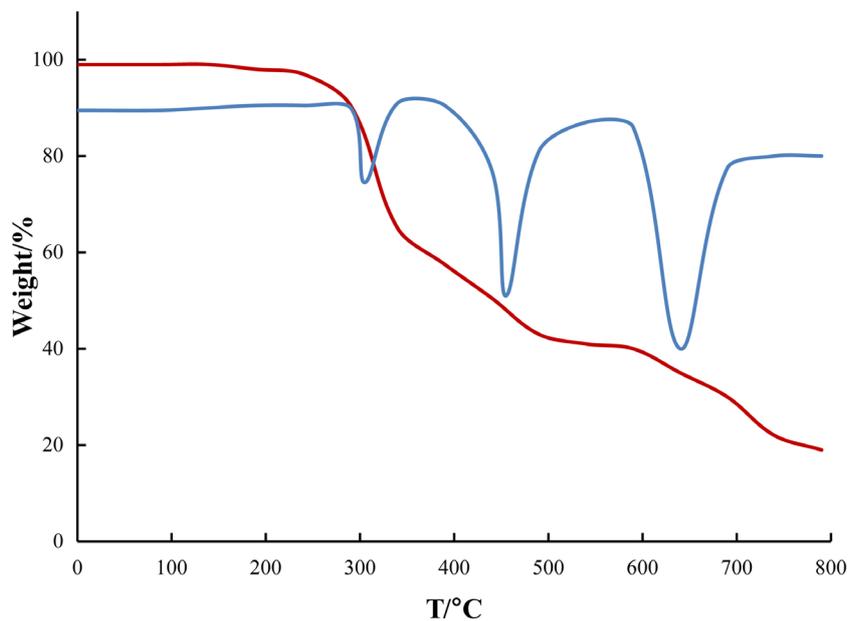


Figure 5. TG (red line) and DTG (blue line) of $[\text{Fe}(\text{GA})(\text{SCN})_2]\text{SCN}$.

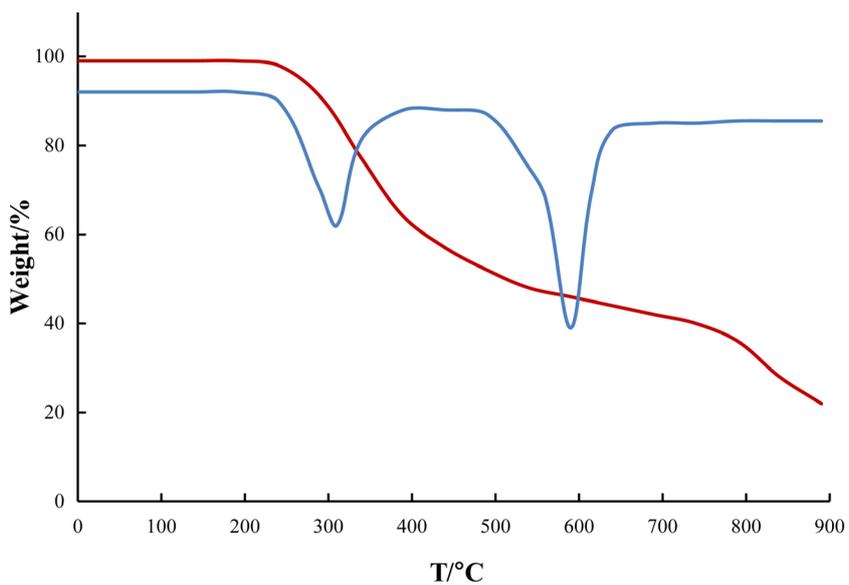


Figure 6. TG (red line) and DTG (blue line) of $[\text{Fe}(\text{GA})\text{Cl}_2]\text{Cl}$.

3.1. Principle

The non-isothermal thermogravimetric analysis is generally used to investigate the thermal stability of solid state materials. In this method, the various kinetic parameters are calculated over an entire range of temperature in a continuous manner. The rate of a solid state reaction can be generally expressed by [8].

$$\frac{d\alpha}{dt} = K \cdot f(\alpha) \quad (1)$$

(K = specific rate constant, α = the sample undergoing reaction and $f(\alpha)$ = conversion function).

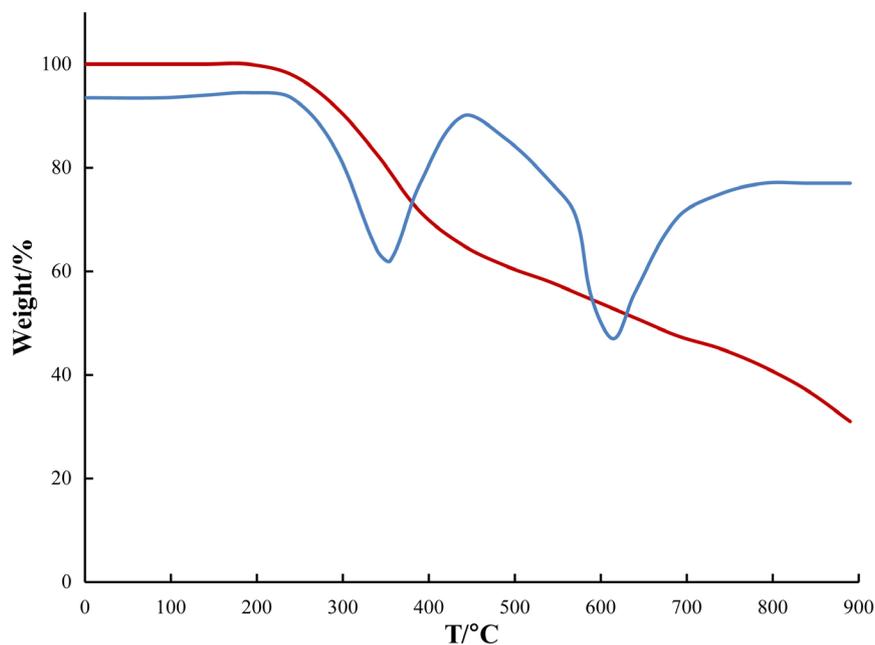


Figure 7. TG (red line) and DTG (blue line) of $[\text{Fe}(\text{GA})\text{Br}_2]\text{Br}$.

In linear heating rate ϕ , $T = T_0 + \phi t$ (T_0 —temperature of initiation)

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

Substituting (2) in (1)

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

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

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

(A —Pre-exponential factor, E —energy of activation, R —gas constant and T —temperature in Kelvin).

Substituting (4) in (3)

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

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

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

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

($g(\alpha)$ —conversion integral).

The temperature integral can be evaluated by Coats and Redfern equation [9] with Rainville function [10]. The temperature integral t is

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

where, T —temperature, A —pre-exponential factor, R —gas constant, ϕ —heating rate and E —activation energy.

On plotting L.H.S. of the equation, which includes $g(\alpha)$ versus $1/T$, will be a straight line, from the slope and intercept are used to calculate the activation energy (E) and the pre-exponential factor (A).

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

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

(k —Boltzmann constant, h —Planck's constant and ΔS —Entropy of activation).

3.2. Phenomenological Aspects

Table 1, describes the phenomenological aspects on the thermal decomposition of the present complexes under study. The perchlorate complex having the formula $[\text{Fe}(\text{GA})(\text{ClO}_4)](\text{ClO}_4)_2$, undergoes a thermal decomposition in two stages in the temperature range $146^\circ\text{C} - 482^\circ\text{C}$. The decomposition stage between $146^\circ\text{C} - 220^\circ\text{C}$, with a DTG peak at 197°C , having a mass loss of (24.52%) corresponds to the first stage. The corresponding mass loss happened due to the decomposition of three perchlorates into chlorides, which has been confirmed the chemical analysis and the infrared spectrum, by the intermediate compound analysis. The second stage having a mass loss of (54.72%), corresponds to the removal of a GA molecule occurs in the temperature range $220^\circ\text{C} - 482^\circ\text{C}$. The corresponding mass loss is attributed to the removal of the ligand molecule GA. The corresponding DTG peak occurs at 369°C . The final residue is anhydrous ferric chloride as confirmed by qualitative analysis.

Table 1. Phenomenological data for the thermal decomposition of Fe(III) complexes of GA.

Complex	Stage of decomposition	TG plateau ($^\circ\text{C}$)	DTG peak ($^\circ\text{C}$)	Mass loss (%)
$[\text{Fe}(\text{GA})(\text{ClO}_4)](\text{ClO}_4)_2$	I	146 - 220	197	24.52
	II	220 - 482	369	54.72
$[\text{Fe}(\text{GA})(\text{NO}_3)_2]\text{NO}_3$	I	142 - 264	192	27.00
	II	264 - 497	325	31.00
	III	497 - 910	583	31.50
$[\text{Fe}(\text{GA})(\text{SCN})_2]\text{SCN}$	I	190 - 313	303	31.00
	II	313 - 515	453	25.87
	III	515 - 801	636	32.02
$[\text{Fe}(\text{GA})\text{Cl}_2]\text{Cl}$	I	211 - 400	307	36.01
	II	400 - 874	637	36.17
$[\text{Fe}(\text{GA})\text{Br}_2]\text{Br}$	I	240 - 408	350	29.10
	II	408 - 856	620	29.00

$[\text{Fe}(\text{GA})(\text{NO}_3)_2]\text{NO}_3$, the nitrate complex, decomposes in three stages. The thermal decomposition stage between 142°C - 264°C with a mass loss of 27% corresponds to the first stage. The mass loss happens at this stage corresponds to the decomposition of three nitrate ions. This observation was confirmed by the infrared spectral analysis of the intermediate residue at 264°C . The second decomposition stage between 264°C - 497°C with a mass loss (31%) occurs, corresponding to the decomposition of half a molecule of ligand [2]. The partial removal of the ligand at this stage is confirmed by the infrared spectrum of the residue after this stage the third stage, which happens between 497°C - 910°C . A mass loss of (31.50%), occurring at this stage, is due to the removal of the remaining part of GA. The corresponding DTG peaks were observed at 192, 325 and 583°C for the first, second and third stages of the decomposition, respectively. The decomposition gets completed at 910°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The thiocyanate complex, $[\text{Fe}(\text{GA})(\text{SCN})_2]\text{SCN}$, decomposes in three stages between the temperature range 190°C - 801°C . The thermal decomposition between 190°C - 313°C , the DTG peak at 303°C having a mass loss of (31%) is owing to the removal of half a molecule of GA [2], corresponds to the first stage. This observation is confirmed by the infrared spectrum of the residue after this stage. The second stage having a mass loss of 25.87%, is due to decomposition of three thiocyanate ions occurs between 313°C - 515°C , having a DTG peak at 453°C . Absence of thiocyanate ions above 515°C , is confirmed by infrared spectral analysis of the intermediate residue at this stage. The decomposition stage between 515°C - 801°C with the DTG peak at 636°C , corresponds to the third stage. The mass loss (32.02%) occurs at this stage is owing to the removal of the remaining ligand molecule. The decomposition gets completed at 801°C , leaving behind anhydrous metal oxide as final residue as proved qualitatively.

$[\text{Fe}(\text{GA})\text{Cl}_2]\text{Cl}$, the chloride complex decomposes in two stages. The thermal decomposition occurs between 211°C - 400°C corresponds to the first stage. The mass loss (36.01%), occurring at this stage is owing to the decomposition of half a molecule GA [2], and this observation was also confirmed by the infrared spectral analysis of the intermediate residue. The DTG peak of this stage occurs at 307°C . The decomposition stage between 400°C to 874°C with the DTG peak at 637°C corresponds to the second stage. The mass loss (36.17%) occurring at this stage is attributed to the decomposition of the remaining GA molecule, leaving behind anhydrous ferric chloride as confirmed by qualitative analysis.

$[\text{Fe}(\text{GA})\text{Br}_2]\text{Br}$, the bromide complex, undergoes two-stage decomposition. The first stage starts at 240°C and ends at 408°C , with a mass loss (29.10%) is due to the decomposition of half a molecule of GA [2]. The partial removal of GA at this stage is confirmed by the infrared spectral analysis of the residue at this stage. The corresponding DTG peak of this stage is observed at 350°C . The decomposition, which starts at 408°C and ends at 856°C , corresponds to the second stage (DTG peak at 620°C). A mass loss (29%) occurs at this stage is due

to the removal of the remaining half of the ligand molecule. Anhydrous ferric bromide, left behind as final residue, which has been confirmed by qualitative analysis.

3.3. Kinetic Aspects

Activation energy (E), pre-exponential factor (A) and entropy of activation (ΔS) for the thermal decomposition of Fe(III) complexes are given in **Table 2**. On comparing the various kinetic parameters, lower activation energy was observed in second stage as compared to first thermal decomposition stage. The same trend has been observed for pre-exponential factor (A) and entropy of activation (ΔS). The present results show that the starting materials having higher Activation energy (E), are more stable than the intermediate products however; the intermediate products possess well-ordered chemical structure due to their highly negative entropy of activation (ΔS) values.

3.4. Comparison of the Kinetic Parameters with Structure and Thermal Stability

The activation energies (E) of iron(III) complexes vary in the range 31.75 to 82.23 $\text{kJ}\cdot\text{mol}^{-1}$. The corresponding values of pre-exponential factor (A) of these complexes come in the range 1.56×10^{-2} to 66.20 S^{-1} while the respective values of entropy of activation (ΔS) of these complexes fall in the range -288.61 to $-213.83 \text{ J}\cdot\text{mol}^{-1}$. As the decomposition proceeds, it has been observed that there is a decrease in the value of all the kinetic parameters as we move from first stage to the second stage may be due to the more ordered structure of intermediate compound attained after the first decomposition stage.

Based on the activation energies obtained from first and second stages of

Table 2. Kinetic parameters for the thermal decomposition of Fe(III) complexes containing different counter anions

Complex	Stage	$E(\text{kJ}\cdot\text{mol}^{-1})$	$A (\text{S}^{-1})$	$\Delta S (\text{J}\cdot\text{mol}^{-1})$
[Fe(GA)(ClO ₄)](ClO ₄) ₂	I	82.23	66.20	-213.83
	II	35.36	5.11×10^{-2}	-275.99
[Fe(GA)(NO ₃) ₂]NO ₃	I	55.42	2.14	-242.24
	II	42.77	7.94×10^{-2}	-271.75
	III	81.09	0.28	-264.20
[Fe(GA)(SCN) ₂]SCN	I	76.18	33.11	-220.22
	II	32.06	2.01×10^{-2}	-261.78
	III	61.94	1.87	-231.11
[Fe(GA)Cl ₂]Cl	I	55.42	0.71	-253.28
	II	31.75	1.87×10^{-2}	-287.26
[Fe(GA)Br ₂]Br	I	57.04	0.74	-253.43
	II	32.89	1.56×10^{-2}	-288.61

thermal decomposition of these complexes; perchlorate and nitrate complexes were found to be highly stable respectively, while chloride complex was found to be least stable in both stages. The negative value of the entropy of activation also indicates that the activated complexes are more ordered than reactants [6] [7] [8] [9] [10]. Even though there is a common GA molecule is present in all the complexes, there is a variation in the different kinetic parameters. This variation could be due to the effect of counter anions on the thermal decomposition of the complexes. Hence, herein we report that the counter anions play an important role on the thermal decomposition kinetic parameters of the complexes and this result was found in line with our previous reports [2] [11] [12] [13].

4. Conclusion and Summary

A comparative thermal decomposition kinetic investigation on Fe(III) complexes of 1,2-Bis(imino-4'-antipyrynyl)ethane (GA)), with varying counter anions (ClO_4^- , NO_3^- , SCN^- , Cl^- , and Br^-), by using Coats-Redfern equation has been done by thermogravimetric traces. The kinetic parameters (activation energy (E), pre-exponential factor (A) and entropy of activation (ΔS) were quantified and compared. The present study proves that the counter anions play an important role on the thermal decomposition kinetic parameters of the complexes. The studies also give an insight into the energetic characteristics of solid propellants.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Vinodkumar, C.R., Nair, M.K. and Radhakrishnan, P.K. (2000) Thermal Studies on Lanthanide Nitrate Complexes of 4-*N*-(2'-Furfurylidene)Aminoantipyryne. *Journal of Thermal Analysis and Calorimetry*, **61**, 143-149. <https://doi.org/10.1023/A:1010120909987>
- [2] Madhu, N.T., Esther, T.K., Tesfay, G.A., Bekele, G.M., Sirak, T.B. and Linert, W. (2017) Ligand Field and Counter Anion Effects on the Thermal Stability of Copper(II) Complexes of 1,2-Di(imino-4-Antipyrynyl)Ethane and 4-*N*-(4'-Antipyrylmethylidene)Aminoantipyryne. *Journal of Chemistry and Applied Chemical Engineering*, **1**, 1-8. <https://doi.org/10.4172/2576-3954.1000110>
- [3] Yan, Q.-L., Zhao, F.-Q., Kuo, K.K., Zhang, X.-H., Zeman, S. and DeLuca, L.T. (2016) Catalytic Effects of Nano Additives on Decomposition and Combustion of RDX-, HMX-, and AP-Based Energetic Compositions. *Progress in Energy and Combustion Science*, **57**, 75-136. <https://doi.org/10.1016/j.pecs.2016.08.002>
- [4] Vargeese, A.A., Muralidharan, K. and Krishnamurthy, V. (2015) Kinetics of Nano Titanium Dioxide Catalyzed Thermal Decomposition of Ammonium Nitrate and Ammonium Nitrate-Based Composite Solid Propellant. *Propellants, Explosives, Pyrotechnics*, **40**, 260-266. <https://doi.org/10.1002/prep.201400131>
- [5] Trache, D. and Khimeche, K. (2013) Study on the Influence of Ageing on Thermal Decomposition of Double-Base Propellants and Prediction of Their In-Use Time. *Fire and Materials*, **37**, 328-336. <https://doi.org/10.1002/fam.2138>

- [6] Rocco, J., Lima, J., Frutuoso, A., Iha, K., Ionashiro, M., Matos, J., *et al.* (2004) TG Studies of a Composite Solid Rocket Propellant Based on HTPB-Binder. *Journal of Thermal Analysis and Calorimetry*, **77**, 803-813. <https://doi.org/10.1023/B:JTAN.0000041659.97749.fe>
- [7] Madhu, N.T. and Radhakrishnan, P.K. (2001) Iron(III) Complexes of 1,2-Di(Imino-4'-Antipyrinyl)Ethane. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **31**, 1663-1673. <https://doi.org/10.1081/SIM-100107711>
- [8] Wenlandt, W.W. (1985) *Thermal Analysis*. 3rd Edition, John Wiley and Sons, New York.
- [9] Coats, A.W. and Redfern, J.P. (1964) Kinetic Parameters from Thermogravimetric Data. *Nature*, **201**, 68-69. <https://doi.org/10.1038/201068a0>
- [10] Rainville, D. (1960) *Special Functions*. MacMillan, New York.
- [11] Madhu, N.T., Radhakrishnan, P.K., Grunert, M., Weinberger, P. and Linert, W. (2003) A Thermal Decomposition Study on Cobalt(II) Complexes of 1,2-Di(Imino-4'-Antipyrinyl)Ethane. *Thermochim Acta*, **400**, 29-36. [https://doi.org/10.1016/S0040-6031\(02\)00475-6](https://doi.org/10.1016/S0040-6031(02)00475-6)
- [12] Madhu, N.T., Radhakrishnan, P.K., Grunert, M., Weinberger, P. and Linert, W. (2003) Synthesis and Thermal Studies on Iron(III) Complexes of 4-N-(4' Antipyrilmethylidene)-Aminoantipyrine with Varying Counter Ions. *Thermochim Acta*, **407**, 73-84. [https://doi.org/10.1016/S0040-6031\(03\)00309-5](https://doi.org/10.1016/S0040-6031(03)00309-5)
- [13] Madhu, N.T., Radhakrishnan, P.K. and Linert, W. (2007) Thermolytic Investigations on Nickel(II) Complexes of 4-N-(4'-Antipyrilmethylidene)Aminoantipyrine with Various Counterions. *International Journal of Chemical Kinetics*, **39**, 53-58. <https://doi.org/10.1002/kin.20216>