

Synthesis and Thermo analytical studies of 5-(4-fluoro-3-phenoxyphenyl)-4, 5-dihydro-3-(3, 4-dimethoxyphenyl) -1-(2, 4-dinitrophenyl)-1H-pyrazole in nitrogen atmosphere - Non-isothermal condition

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ABSTRACT

In the present study, a pyrazoline compound 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN) has been synthesized by refluxing respective chalcone with 2,4-dinitrophenylhydrazine in acidic medium and characterized by physical constant and spectroscopic techniques (FT-IR), NMR (^1H and ^{13}C) and Mass spectra. The thermal decomposition of DMPDN was studied by thermogravimetry under nitrogen atmosphere at different heating rates of 10, 15 and 20 K min⁻¹. The decomposition process of DMPDN is occurred in single step as evidenced from thermogram. The kinetic parameters were calculated using model free methods (Friedman, Kissinger-Akahira-Sucrose (KAS) and Flynn-wall-Ozawa (FWO)) and model-fitting method [Coats Redfern (CR)]. The calculated invariant kinetic parameters of DMPDN are consistent with the average values obtained by Friedmann and KAS isoconversional method of decomposition is followed different kinetic models. The kinetic thermal decomposition of DMPDN was described by a A3 model.

Keywords – Pyrazoline, TG/DTG, non-isothermal, invariant kinetic parameters.

1. Introduction

The most common solid-state reactions are polymorphic transformations and degradations. Solid-state chemistry has recently gained much importance in pharmaceutical sciences, which renders the topic of solid-state kinetics more interesting. The reactions that involve weight or enthalpy changes are greatly studied as their kinetics can be followed by thermo analytical methods¹. For pharmaceutical solids, the solid-state kinetic studies are either desolvation reactions or polymorphic transformations². The stability of solvates is a concern to pharmaceutical scientists since they may convert to an amorphous form upon desolvation while others may become chemically labile³. Another classic example is chloramphenicol palmitate which was reported to exist in more than two crystalline forms and one form was found to be as much as seven times therapeutically more potent than the other forms⁴. Chemical kinetic concepts were originally based on generalization from empirical studies of homogeneous reactions, first in the gas phase. Solid-state kinetics did not develop separately. However, application of these concepts was justified in the solid-state because of similarities to some homogeneous reactions⁵. The thermal decomposition of alkoxides and amides of magnesium by vacuum TGA were studied under both isothermal and non-isothermal conditions⁶. The influence of different conditions on thermal decomposition of triazine herbicides was studied by Drozdowska *et al.*⁷ Non-isothermal and isothermal kinetic studies on the decomposition processes of some

penicillin and commercial drugs were reported by Rodante *et al.*⁸. The kinetic parameters were obtained using model-fitting and model-free methods. Rotaru *et al.*⁹ investigated the decomposition of 4-[(4-chlorophenyl)-oxy]-4'-nitroazobenzene under non-isothermal. The kinetic analyses were performed by means of different multi-heating rates method. A comparative kinetic analysis on the thermal decomposition of tartaric acid and potassium tartrate under the non-isothermal condition was carried out by Vlase *et al.*¹⁰. The thermal stability of diaminofurazan (DAF) and diaminoglyoxime (DAG) were examined by differential scanning calorimetry and simultaneous thermogravimetry-differential thermal analysis techniques¹¹. Yi *et al.*¹² prepared a new high nitrogen compound of hydrazine, 3-nitro-1,2,4-triazol-5-one complex (HNTO) and characterized by non-isothermal reaction kinetics and thermodynamic properties. The thermal vaporization kinetics of Schiff's base was studied by thermogravimetry and differential thermal analysis techniques under non-isothermal conditions.¹³ The kinetic parameters were calculated using model-free and model-fitting methods. The results of the Friedman's isoconversional analysis of the TG data suggest that the investigated vaporization process follows a single-step reaction. The most probable kinetic model for vaporization of the compound is P2 (Power Law). Georgieva *et al.*¹⁴ investigated the non-isothermal kinetics of thermal degradation of chitin in air atmosphere. Venkatesh *et*

*al.*¹⁵ investigated the decomposition kinetics of imidazole, 2-nitroimidazole and 4-nitroimidazole using TG-DTA technique under nitrogen atmosphere. Isoconversional methods were used for the evaluation of kinetic parameters from the kinetic data at different heating temperatures. Two chalcones were synthesized and characterized by spectral analysis.¹⁶ The thermal decomposition of these compounds were studied by TGA and DTA under dynamic nitrogen atmosphere at different heating rates of 10, 15 and 20 K min⁻¹. Recently Rathi *et.al.*,¹⁷ has synthesized a novel pyrazoline and studied TG and DTG under dynamic nitrogen atmosphere at different heating rates of 10, 15 and 20 K min⁻¹. Literature survey reveals that no work has been reported on thermal decomposition of pyrazoline under non-isothermal decomposition in the presence of dynamic nitrogen atmosphere. This prompted us to carry out the synthesis, spectral characterization and thermal studies of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

2. Materials and methods

2.1. Materials

All the chemical namely 3,4-dimethoxyacetophenone, 2,4-dinitrophenylhydrazine

Preparation of Pyrazoline compound

A mixture of an appropriate equimolar quantities of using (E)-3-(3-fluoro-4-phenoxyphenyl)-1-(3,4-dimethoxyphenyl)prop-2-en-1-one (Chalcone) (0.20mmol), 2,4 dinitrophenylhydrazine (0.20 mmol) and anhydrous sodium acetate (0.5 g) was refluxed in (15 mL) ethanol for 6-7h (Scheme 1). The completion of the reaction was monitored by TLC. The reaction

and 4-fluoro-3-phenoxybenzaldehyde were purchased from Sigma aldrich. Other relevant chemicals and solvents procured from sd-fine chemicals in Analar grade used without purification.

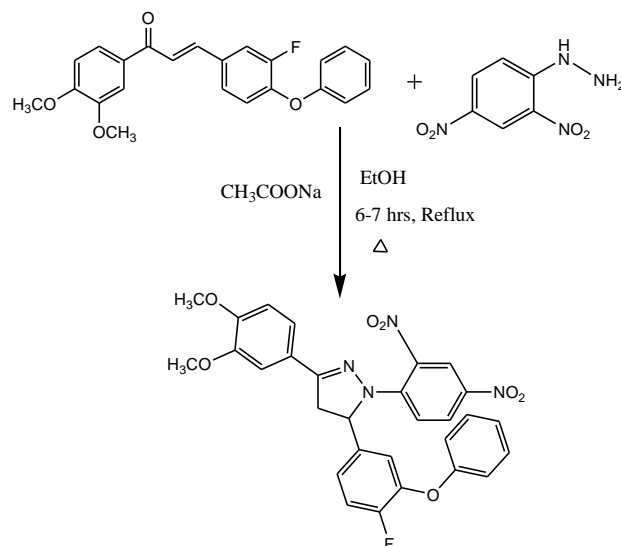
2.2. Instruments

For thin layer chromatography (TLC), pre-coated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness was used. Mettler FP51 apparatus was used for recording Melting point of the synthesized compound in °C without correction. FT-IR measurement was done on KBr pellets for solids using SHIMADZU-2010 Fourier transform Infra-Red (FT-IR) spectrophotometer (4000–400 cm⁻¹). The ¹H and ¹³C NMR spectra were recorded in CDCl₃ using TMS as internal standard with Bruker 400MHz and 100 MHz high resolution NMR spectrometer.

2.3. TG/ DTG analysis

The simultaneous TG/DTG curves were obtained with the thermal analysis system model Perkin Elmer STA 6000, TEQP-II at IIT-Madras, India., India using Perkin Elmer Pyris TGA 6000 (0–200 mL min⁻¹) in an 180 °L ceramic pan with a sample at the heating rates of 10, 15 and 25 K min⁻¹ from 35 to 900 °C.

mixture was cooled, and poured into ice cold water. The precipitate was filtered, dried and subjected to column chromatography n-hexane and ethyl acetate (3:1) as eluent. Finally the product was recrystallized using ethanol. This is characterized by its physical constants and spectral data.



Scheme -1 synthetic route of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

Physical and Spectral data

IR cm^{-1} : 1559.05; ^1H NMR δ (ppm): 3.486(H_a , 1H-*dd*)ppm, 3.829(H_b , 1H-*dd*)ppm, 5.211ppm(H_c , 1H-*d*), 6.787 -7.334(*m*, Aromatic protons)ppm, 3.868 ppm ($-\text{OCH}_3$, 6H-*s*) ; ^{13}C NMR δ (ppm): 156.979(C=N)ppm, 40.802(C_α)ppm, 65.572(C_β)ppm,

55.885, 55.895 ($\text{C}-\text{OCH}_3$)ppm; Mass m/z : 558[M+], 514, 454, 426, 364, 239, 210, 136, 106; m.p. 87°C; Colour : Pale yellow glittering solid; Yield : 74% ; Molecular Formula: $\text{C}_{30}\text{H}_{24}\text{FN}_3\text{O}_3$; M.W: 558

3.1 Non-isothermal TGA

The TG and DTG curves of DMDPN was obtained at three different heating rates (10, 15 and 20 K min^{-1}) and shown in **Fig -1**. The weight loss observed in TG curves on heating DMDPN from room temperature to 973 K corresponds to the peak of the curves. The weight loss is due to partial decomposition of DMDPN and the

curves are asymmetric figures and are seen to move to high temperature with increase in heating rates (**Fig -1**). TG curves show that DMDPN is stable up to 433 K. The decomposition process for DMDPN starts at 430 ends at 480 K min^{-1} .

3.2 Non-isothermal model-free analysis

The non-isothermal decomposition kinetics of DMDPN was first analyzed by model-free methods (Friedman¹⁹, Flynn-Wall-Ozawa²⁰ and Kissinger-Akahira-Sunose²¹ methods). The data in **Table - 1**, show the variation of apparent activation energy E_a as a function of extent of conversion α , for the decomposition of DMDPN. E_a value increases slightly in the conversion range of $0.05 \leq \alpha \leq 0.95$ (**Table - 1**; **Fig - 2**).

obtained by FWO ($E_a = 50.29 \pm 5.70 \text{ kJ mol}^{-1}$) and Friedman methods ($E_a = 41.37 \pm 7.02 \text{ kJ mol}^{-1}$) for single stage²² decomposition of DMDPN.

In order to understand, the processes involved in the thermal decomposition of DMDPN, the E_a values are calculated from TG data over the α range 0.05 - 0.90 with an increment of 0.05 at the heating rates of 10, 15 and 20 K min^{-1} by the isoconversional methods, and the results are shown in **Table - 1**. From **Fig -2** it can be observed that the activation energy took on one plateaus over α range from 0.05 - 0.90, which indicates that the whole process decomposed in one step²³ and each of them may obey one reaction mechanism.

The applied isoconversional method does not suggest a direct way for evaluating either the pre-exponential factor (A) or the analytical form of the reaction model $f(\alpha)$, for the decomposition process of DMDPN. From **Fig - 2**, it is evident that the values of activation energies obtained by the KAS method ($E_a = 42.61 \pm 5.39 \text{ kJ mol}^{-1}$) are slightly greater than

free analyses indicate that activation energy approximately constant, were then fitted into each of the 15 models are listed in **Table - 2** for the applied method.²⁴ Arrhenius parameters ($E_a, \ln A$) exhibit strong dependence on the reaction model chosen.

3.3 Model-fitting analysis

After model-free analysis is performed, model-fitting can be done in the conversion region where apparent activation energy is approximately constant where a single model may fit. The non-isothermal kinetic data of DMDPN at $0.05 \leq \alpha \leq 0.90$ where model-

a_β and b_β from the slope and intercept, respectively. From the plot of a_β versus b_β , we determined (**Table-3**) invariant kinetic parameters $E_{inv} = 48.97 \pm 1.63 \text{ kJ mol}^{-1}$ and $\ln A_{inv} = 6.29 \pm 0.34 \text{ A min}^{-1}$ (**Table - 4**) with good linear plot $r = 1.000$. For these groups, the invariant activation energy is almost equal to $48.97 \pm 1.63 \text{ kJ mol}^{-1}$ in comparison with FWO, Friedman and KAS methods ($50.29 \pm 5.70 \text{ kJ mol}^{-1}$, FWO; $41.37 \pm 7.02 \text{ kJ mol}^{-1}$, Friedman; $42.61 \pm 5.39 \text{ kJ mol}^{-1}$, KAS).

3.4 Invariant kinetic parameter (IKP) analysis

The apparent kinetic parameters for the thermal decomposition in dynamic nitrogen atmosphere for DMDPN are represented in $\ln A$ versus E_a (**Fig - 3**). The evaluation of the invariant kinetic parameters is performed using the super correlation eqn.(1). The plot of a_β versus b_β , E_{inv} and $\ln A_{inv}$ values were obtained from the slope and intercept of the straight line.

$$a_\beta = \ln A_{inv} - b_\beta E_{inv} \dots\dots\dots (1)$$

For DMDPN, AKM-{D1}, the plots of $\ln A$ versus E_a have highest correlation coefficient gives

$g(\alpha) = [-\ln(1-\alpha)]^{1/3}$, the following equation²⁶ (2) is obtained.

3.5 Kinetic model determination

The most suitable kinetic model for decomposition process of DMDPN is A3²⁵ (Avrami-Erofe'ev). By introducing the derived reaction model

$$[-\ln(1-\alpha)]^{1/3} = \frac{AE_a}{R\beta} p(x) \quad \text{-----}$$

---- (2)

The plot of $[-\ln(1-\alpha)]^{1/3}$ against $E_a p(x)/R\beta$ at the different heating rates is shown in Fig-4 and the most suitable model for the decomposition

3.6 Thermodynamic parameters

From the DTG curves, the peak temperature for DMPDN is 595, 603 and 607 K at different heating rates at 10, 15 and 20 K min⁻¹. These peak temperatures were used to determine single point kinetic parameters.²⁷ The obtained E_a values were 160.1 kJ mol⁻¹.

The thermodynamic parameters, ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger were determined at the peak temperature T_p in the DTG curves for the corresponding stage.²⁸ Since the

4. Conclusion

In the present study, TG/DTG thermal stabilities of decomposition kinetics into a single stage of DMPDN with the absorption of heat were investigated. A3 is the kinetic model for the decomposition mechanism. DMPDN has a lower thermal stability and lower activation energy. The presence of positive free energy suggests that the

process is second order model A3. The activation energy E_a and the frequency factor A were found to be $E_a = 76.6 \pm 0.14$ kJ mol⁻¹ and $A = 4.82 \times 10^{10}$ min⁻¹ ($\ln A = 37.5$). The obtained value of $\ln A$ coincide with the average value of Friedman isoconversional intercept $\ln [A f(\alpha)] = 36.3$.

temperature characterizes the higher rate of decomposition and therefore, it is an important parameter. As can be seen from Table-5, the value of ΔS^\ddagger for the compound is positive. It means that the corresponding activated complex were with lower degree of arrangement than the initial state.²⁹ The positive values of ΔH^\ddagger and ΔG^\ddagger show that they are connected with absorption of heat and are attributed to non-spontaneous process.^{28,30}

decomposition is non - spontaneous process. Because the activation energy values varied slightly depending on the conversion level, the decomposition model was interpreted using the average activation energy values. Entropy is positive in these processes, indicating that the activated compound is less ordered than the reactant.

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Table -1 Temperatures corresponding to the same degree of conversion at different heating rates for 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

α	Heating Rates			FWO method			KAS method			Friedman method	
	10 (K min ⁻¹)	15 (K min ⁻¹)	20 (K min ⁻¹)	<i>E_a</i> (KJ mol ⁻¹)	ln <i>A</i> (A min ⁻¹)	<i>r</i>	<i>E_a</i> (KJ mol ⁻¹)	ln <i>A</i> (A min ⁻¹)	<i>r</i>	<i>E_a</i> (KJ mol ⁻¹)	<i>r</i>
0.05	433.05	454.67	454.84	39.51	7.64	-0.913	34.18	7.98	-0.879	37.87	-0.898
0.1	468.85	486.75	497.43	44.26	7.92	-0.998	38.54	8.32	-0.997	42.55	-0.998
0.15	491.95	510.07	524.15	43.91	7.29	-1.000	37.74	7.56	-1.000	36.42	-0.948
0.2	512.74	529.7	547.91	43.76	6.82	-0.995	37.21	6.98	-0.992	36.73	-0.954
0.25	534.69	563.39	567.96	44.08	6.41	-0.954	37.21	6.51	-0.931	38.17	-0.792
0.3	554.33	577.71	592.75	46.56	6.56	-0.999	39.45	6.69	-0.999	42.50	-0.974
0.35	570.5	578.26	600.81	56.21	8.31	-0.935	49.38	8.81	-0.911	43.84	-0.373
0.4	582.05	602.12	614.63	59.72	8.66	-0.999	52.88	9.25	-0.998	63.06	-0.988
0.45	592.44	613.83	628.22	56.77	7.86	-1.000	49.58	8.29	-0.999	36.06	-0.709
0.5	602.84	630.61	639.53	54.15	7.13	-0.980	46.65	7.42	-0.970	47.64	-0.764
0.55	615.54	631.56	653.01	58.13	7.70	-0.986	50.59	8.10	-0.980	52.81	-0.794
0.6	635.18	652.18	677.69	54.43	6.67	-0.981	46.33	6.85	-0.971	38.87	-0.564
0.65	652.5	669.61	698.81	52.34	6.03	-0.974	43.81	6.05	-0.959	36.83	-0.900
0.7	671.99	690.47	722.67	50.85	5.49	-0.973	41.88	5.37	-0.956	37.05	-0.917
0.75	687.16	707.65	741.19	50.34	5.19	-0.977	41.07	4.99	-0.962	37.32	-0.963
0.8	703.33	726.06	760.84	50.00	4.91	-0.981	40.41	4.65	-0.967	37.73	-0.986
0.85	720.65	746.56	782.12	49.68	4.64	-0.986	39.76	4.30	-0.976	37.32	-0.996
0.9	739.13	765.01	802.34	50.66	4.57	-0.984	40.47	4.22	-0.972	41.91	-0.983
				50.30 ± 5.70						41.37 ± 7.02	

Table - 2 Arrhenius parameters for non-isothermal decomposition of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

Kinetic model	$\beta=10 \text{ Kmin}^{-1}$			$\beta=15 \text{ Kmin}^{-1}$			$\beta=20 \text{ Kmin}^{-1}$		
	$E_a(\text{KJ mol}^{-1})$	$\ln A$ ($A \text{ min}^{-1}$)	r	$E_a(\text{KJ mol}^{-1})$	$\ln A$ ($A \text{ min}^{-1}$)	r	$E_a(\text{KJ mol}^{-1})$	$\ln A$ ($A \text{ min}^{-1}$)	r
P2	2.88	-4.51	-0.761	3.26	-3.99	-0.751	2.42	-4.25	-0.952
P3	-1.23	-3.43	0.547	-1.10	-2.97	0.455	-1.75	-2.76	0.930
P4	-3.27	-1.56	0.899	-3.27	-0.98	0.876	-3.82	0.86	0.902
F1	22.79	1.52	-0.998	24.48	2.11	-0.995	22.73	1.78	-0.996
F2	33.10	4.46	-0.986	35.56	5.13	-0.988	33.33	4.66	-0.989
F3	45.73	7.91	-0.961	49.15	8.68	-0.965	46.33	8.02	-0.965
D1	49.00	13.96	-0.989	52.05	14.68	-0.986	49.72	14.16	-0.987
D2	44.03	4.73	-0.991	46.99	5.41	-0.986	44.28	4.79	-0.987
D3	49.33	4.68	-0.997	52.67	5.40	-0.994	49.71	4.69	-0.994
D4	45.78	3.71	-0.993	48.86	4.41	-0.989	46.07	3.75	-0.990
A2	6.68	-2.71	-0.989	7.34	-2.19	-0.980	6.33	-2.35	-0.978
A3	1.30	-5.34	-0.835	1.62	-4.74	-0.811	0.85	-5.31	-0.596
A4	-1.37	-3.24	0.860	-1.23	-2.78	0.764	-1.87	-2.18	0.871
R2	18.65	-0.41	-0.989	20.04	0.14	-0.983	18.48	-0.13	-0.982
R3	17.47	-0.50	-0.983	18.77	0.05	-0.976	17.27	-0.21	-0.975

Table -3 The compensation effect parameters for several combinations of kinetics models for 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-pyrazole dinitrophenyl)-1H-(DMPDN)

β (K min ⁻¹)	AKM			AKM - {D1}		
	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r
10	-5.1100	0.2638	0.897	-4.5739	0.2219	0.951
15	-4.6487	0.2519	0.899	-4.1137	0.2126	0.953
20	-4.7262	0.2557	0.893	-4.1954	0.2140	0.946
β (K min ⁻¹)	AKM - {D1; D3}			AKM - {D1;D3; D4}		
	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r
10	-4.7769	0.2375	0.959	-5.0701	0.2636	0.981
15	-4.3173	0.2272	0.961	-4.6103	0.2514	0.983
20	-4.3957	0.2298	0.955	-4.6781	0.2557	0.979
β (K min ⁻¹)	AKM - {D1; D3; D4; D2}			AKM - {D1; D4; D3;D2;A2}		
	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r	a_{β} (Amin ⁻¹)	b_{β} (mol J ⁻¹)	r
10	-5.3605	0.2914	0.996	-5.5917	0.2978	0.999
15	-4.8967	0.2768	0.997	-5.1175	0.2825	0.999

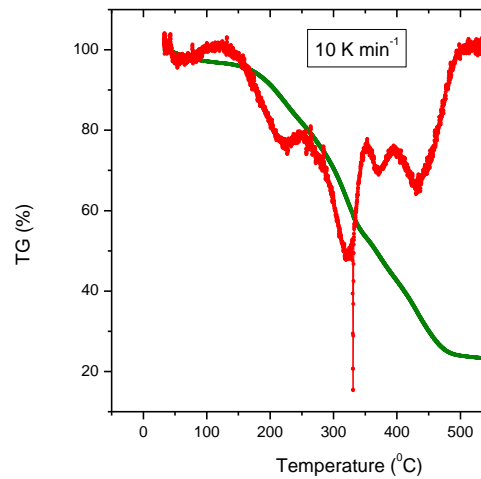
20	-4.9565	0.2833	0.995	-5.2178	0.2905	0.998
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Table – 4 IKP for several combinations of kinetics model for 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

Kinetic model	E_{inv} (kJmol ⁻¹)	lnA _{inv} (A min ⁻¹)	r
AKM	40.06	5.47	0.986
AKM - { D1}	48.97	6.29	1.000
AKM - { D1; D3}	45.43	6.02	0.997
AKM - { D1; D3;D4}	39.02	5.24	0.977
AKM - { D1; D3; D4; D2}	32.58	4.18	0.943
AKM - { D1; D4; D3; D2;A2}	30.73	3.61	0.941
AKM - { D1; D4; D3; D2; A2; R2}	31.02	3.75	0.954

Table - 5 Values of kinetic and thermodynamic parameters for thermal decomposition of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN) in dynamic nitrogen atmosphere

Parameter	Value
E_a (kJ mol ⁻¹)	160.1
ln A (A min ⁻¹)	31.69
ΔG^\ddagger (kJ mol ⁻¹)	152.46
ΔH^\ddagger (kJ mol ⁻¹)	155.16
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	4.47
r	-0.995



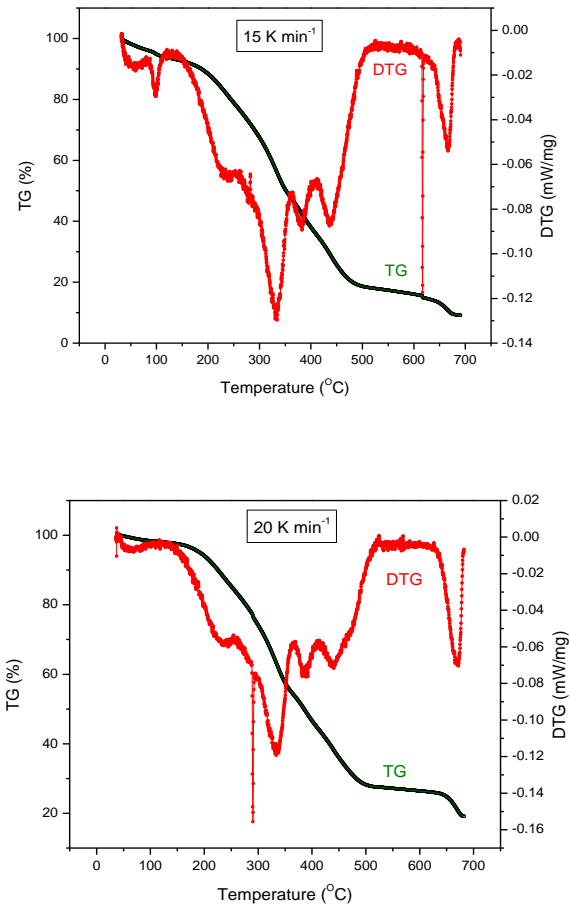


Fig -1 TG – DTG curves of of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN) at 10, 15 and 20 K min⁻¹ heating rates in dynamic nitrogen atmosphere

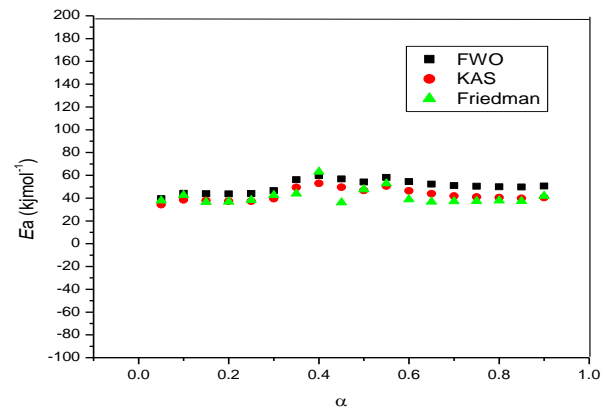


Fig – 2 Plot of E_a verses α for of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

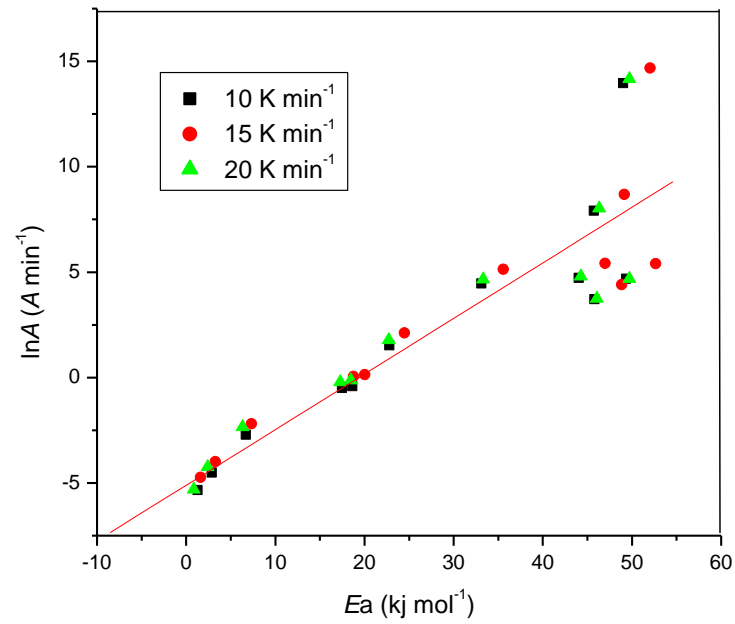


Fig – 3 Dependency of frequency factor on extent of conversion using the Coats – Redfern method for of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN)

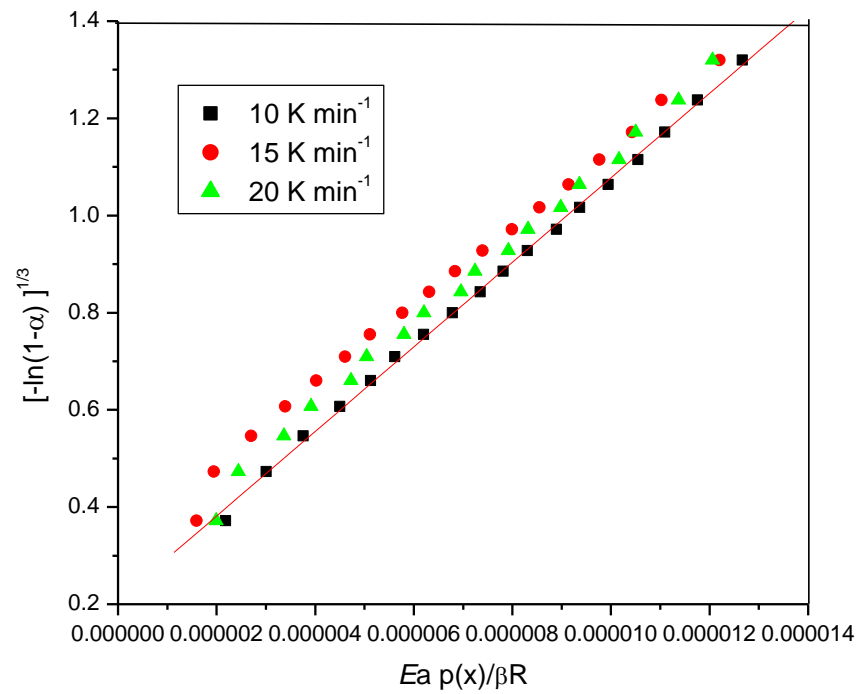


Fig – 4 Determination of A value by plotting $[-\ln(1-\alpha)]^{1/3}$ against $E_a p(x)/R\beta$ for the decomposition process of 5-(4-fluoro-3-phenoxyphenyl)-4,5-dihydro-3-(3,4-dimethoxyphenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole (DMPDN) at different heating rates (β)