

Kinetic Studies of the Non-Isothermal Decomposition of Strontium Nitrate

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The thermal decomposition kinetics of strontium nitrate, $\text{Sr}(\text{NO}_3)_2$ was studied by thermogravimetry using non-isothermal experiments. For the kinetic analysis, the TG/DTG data obtained in the temperature range 30-850 °C at different heating rates (5, 10, 15 and 20 K/min) in the nitrogen atmosphere were processed by model fitting and model free methods. The thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ occurred in a single stage without the formation of intermediate nitrite. The average apparent activation energies of thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ as determined by Straink, Flynn-Wall-Ozawa, KAS and Friedman methods are 344.37, 341.39, 344.05 and 362.62 kJ/mol, respectively. The value of the invariant activation energy (344.83 kJ/mol) obtained by Invariant kinetic parameter method is in a good agreement with integral isoconversional methods. The appropriate conversion model of the process selected by means of the master plot method is "Diffusion model (D4)".

Key Words: Kinetics, Non-isothermal decomposition, Strontium nitrate.

INTRODUCTION

Strontium nitrate in the anhydrous form is a colourless crystalline powder. The principal uses of strontium nitrate are in the manufacture of pyrotechnics, rescue signaling devices, red tracer bullets for the military *etc.*, as it imparts a characteristic brilliant crimson colour to a flame. The oxidizing properties of this salt are advantageous in such applications¹.

The thermal decomposition of common metal nitrates is an important class of reaction in the chemical industry with applications in the preparation of high surface area materials for catalysts, molecular sieves and adsorbents as well as they have interest for ecological and environmental reasons². L'vov and Novichikhin³ have suggested a gasification process whereby the decomposition of metal nitrates proceeds through the gaseous metal oxide as an intermediate product:



followed by



Duval⁴ reported that $\text{Sr}(\text{NO}_3)_2$ is stable upto 280 °C and yields a perfectly horizontal level which starts at room temperature. Decomposition then sets in and proceeds very slowly but becomes explosive above 600 °C. This disintegration appears to be completed over 820 °C. The succeeding horizontal is due to the formation of strontium oxide. Nair *et al.*⁵ studied the effect of γ -irradiation on the thermal decomposition of

$\text{Sr}(\text{NO}_3)_2$ under non-isothermal conditions with a single heating rate plot (4 K/min) and analyzed the data by model fitting methods. They reported that the decomposition of $\text{Sr}(\text{NO}_3)_2$ sets in after melting and the overall decomposition of the salt occurs as:



Historically, model-fitting methods were widely used because of their ability to directly determine the kinetic triplet involving activation energy (E) and frequency factor (A) and conversion function, $f(\alpha)$. But it is well established that force-fitting non-isothermal data to different reaction models results in a widely varying Arrhenius parameters⁶. The only possible way to obtain trustworthy kinetic parameters is to evaluate them in a way that is independent of reaction model. Isoconversional methods are known to allow for model-independent estimation of the activation energy, E, selected to different extents of conversion. So the main goal of this work is to study the thermal decomposition kinetics of $\text{Sr}(\text{NO}_3)_2$ from non-isothermal multi-heating TG data by a new approach that combines the power of isoconversional methods with model-fitting methods.

EXPERIMENTAL

AR grade $\text{Sr}(\text{NO}_3)_2$ was used without further purification. TG/DTG experiments were performed with a SDT Q 600 simultaneous DSC/TGA instrument, in the temperature range of 30-950 °C, under a dynamic atmosphere of nitrogen at a

flow rate of 50 mL/min. Samples with the mass in the range of 9-12 mg were put into platinum crucibles, at a heating rate, β , of 5, 10, 15 and 20 K/min. The recorded total % mass-loss in all cases was 51.33 ± 0.05 confirming the complete conversion of $\text{Sr}(\text{NO}_3)_2$ to SrO. The mass of material left behind after thermal decomposition agreed with the stoichiometry of the reaction (3) and also with the instrument reading.

RESULTS AND DISCUSSION

Non-isothermal decomposition: Fig. 1 shows the TG/DTG curves at different heating rates of 5, 10, 15 and 20 °C/min. The decomposition of $\text{Sr}(\text{NO}_3)_2$ occurs totally in one-step process as can be concluded by the presence of only one peak in DTG. The main observations like temperature of inception (T_i), the temperature of completion (T_f) and peak temperature of decomposition (T_p) obtained from thermal curves at different heating rates are summarized in Table-1. In the present investigation $\text{Sr}(\text{NO}_3)_2$ melted at 570 °C which is in good agreement with the melting behaviour reported^{5,7}. The general shift of T_i , T_f and T_p to higher temperature occurs when the heating rate is increased. This is typical for all non-isothermal experiments as described in the literature by different researchers^{8,9}.

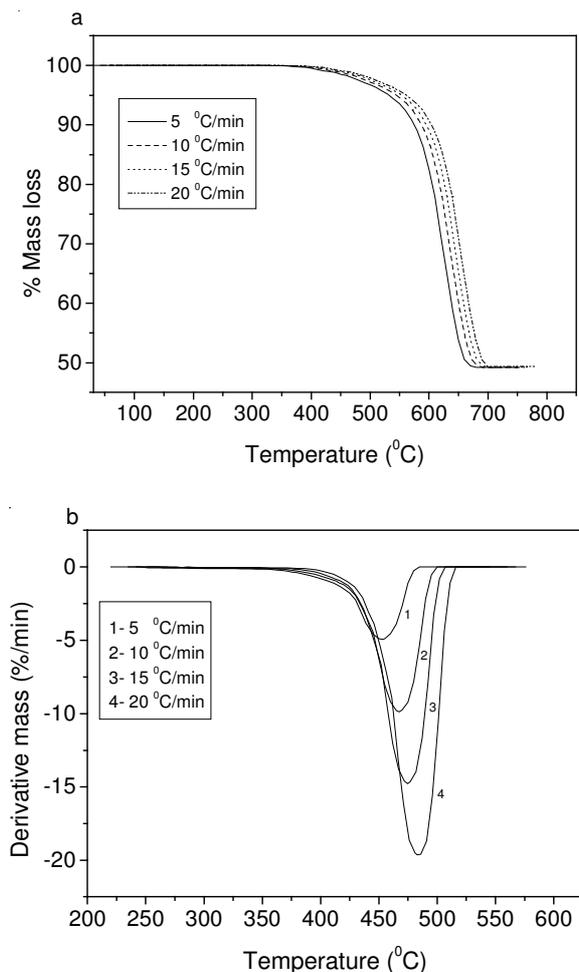


Fig. 1. Experimentally obtained (a) thermogravimetric (TG) and (b) differential thermogravimetric (DTG) curves at the different heating rates ($\beta = 5, 10, 15$ and 20 k/min), for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$

TABLE-1
PHENOMENOLOGICAL DATA FOR THE
THERMAL DECOMPOSITION OF $\text{Sr}(\text{NO}_3)_2$
AT DIFFERENT HEATING RATES

β (°C/min)	Temperature (°C)		
	T_i	T_f	T_p
5	380	679	622
10	392	693	635
15	401	702	644
20	409	708	649

Evaluation of activation energy by using isoconversional methods: In order to apply different kinetic methods on the thermal decomposition process of $\text{Sr}(\text{NO}_3)_2$, the dependence of α versus T at different heating rates for all the samples are plotted (Fig. 2). The sigmoid-shaped curves are shifted to higher temperatures with an increase of heating rates as reported earlier^{8,9}. Initially, the activation energy for the decomposition of $\text{Sr}(\text{NO}_3)_2$ was estimated by using FWO^{10,11}, KAS¹², FR¹³ and straink^{14,15} methods. The details of these methods have already been described^{16,17}.

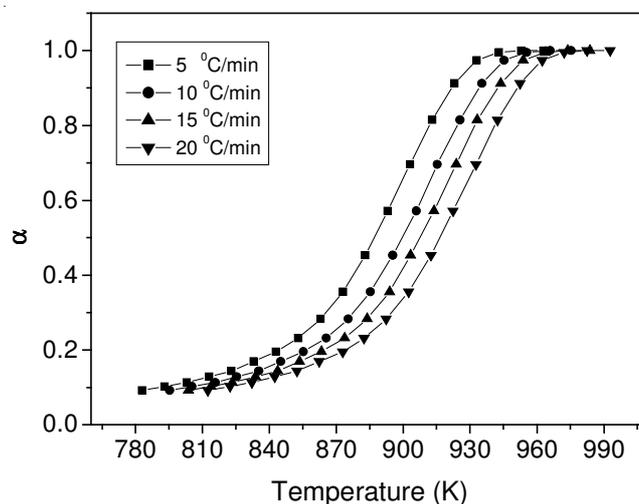


Fig. 2. α -T curves for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ as a function of temperature at different heating rates

FWO method is an integral method which is based on the measurement of the adequate temperature to certain values of the conversion α , for experiments effectuated to different rates of heating. The equation corresponding to this method is

$$\ln \beta = \ln \left[\frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (4)$$

where $g(\alpha)$ is integral reaction model, α is extent of conversion, E is activation energy, A is pre-exponential factor, T is temperature and R the gas constant. For selected α values from 20-90 %, the plots of $\ln \beta$ versus $1/T$ give a group of straight lines (Fig. 3). The values of activation energy E were calculated from the slopes of the regression lines and are given in Table-2.

KAS method is one of the best isoconversional methods and is based on the equation

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left[\frac{AR}{Eg(\alpha)} \right] - \frac{E}{RT} \quad (5)$$

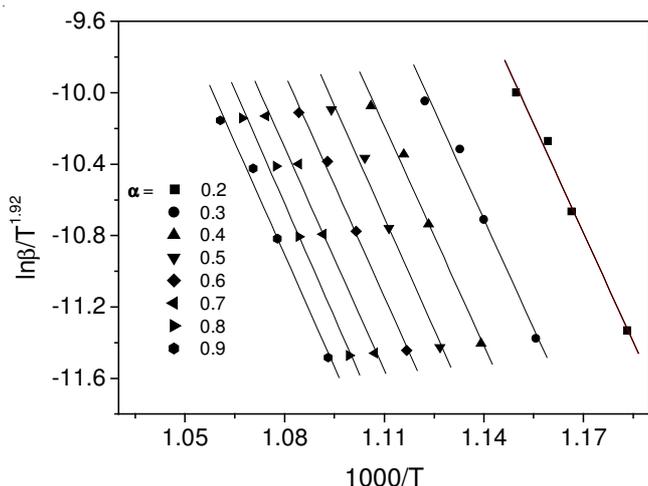


Fig. 3. Straink plots for the determination of activation energy at different α for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$

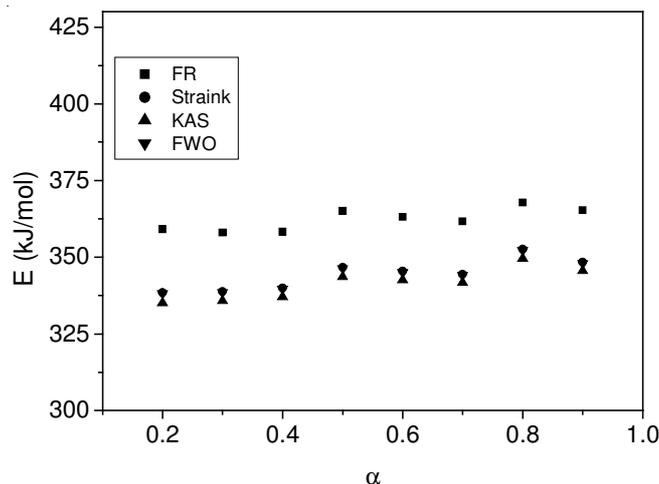


Fig. 4. Dependence of the activation energy (E) on the degree of conversion (α) determined using the FR, Straink, KAS and FWO methods for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$

TABLE-2
ACTIVATION ENERGIES AT DIFFERENT EXTENT OF CONVERSIONS (α) OBTAINED FROM TG DATA BY DIFFERENT ISOCONVERSIONAL METHODS FOR THE THERMAL DECOMPOSITION OF $\text{Sr}(\text{NO}_3)_2$

Conversion (α)	Activation energy, E (kJ/mol)			
	FR	Straink	FWO	KAS
0.2	359.15	338.47	335.12	338.18
0.3	358.02	338.86	335.80	338.54
0.4	358.34	340.02	337.10	339.7
0.5	365.06	346.69	343.61	346.37
0.6	363.16	345.47	342.57	345.14
0.7	361.70	344.48	341.75	344.15
0.8	367.78	352.61	349.57	352.28
0.9	365.33	348.37	345.62	348.03
Average	362.32	344.37	341.39	344.05

Another more accurate temperature integral relation has been suggested by Straink and is given as

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = -1.0008\left(\frac{E}{RT}\right) + \text{const.} \quad (6)$$

The Friedman method is a differential isoconversional method and the equation corresponding to this method is

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dt}\right) = \ln[af(\alpha)] - \frac{E}{RT} \quad (7)$$

The results of analysis of the present data using KAS, Straink and FR methods as described earlier^{16,17} are also presented in Table-2.

The average values of activation energy worked out through KAS, Straink and FWO methods vary slightly, so the results are credible. The values of activation energy obtained from the Friedman method are higher than the values obtained from the other three isoconversional methods. As it can be seen in Fig. 4, the activation energies slightly varied with the degree of conversion, indicating that there exists high probability for the presence of a single step reaction¹⁸. Since the average values of activation energy worked out by the KAS, Straink and FWO method are very close, we chose the mean values of these three as the value of activation energy used in the master plot method.

Determination of reaction model by using master plot method: Integral master plot method¹⁹ was used for the determination of the reaction model for the decomposition of $\text{Sr}(\text{NO}_3)_2$. Essentially the master plot method is based on the comparison of theoretical master plot, which are obtained for a wide range of ideal kinetic models, with the experimental master plot.

The integral function of conversion in the solid state non-isothermal decomposition reactions is expressed as

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \left(\frac{AE}{\beta R}\right) p(u) \quad (8)$$

where $u = E/RT$. The temperature integral, $p(u) =$

$$\int_{\infty}^u -\left(\frac{e^{-u}}{u^2}\right) du \text{ has no analytical solution and can be expressed}$$

by an approximation. The rational approximation of Doyle²⁰ gives sufficiently accurate results

$$p(u) = 0.00484 \cdot \exp(-1.0516u) \quad (9)$$

Using a reference at point $\alpha = 0.5$ and according to eqn. 8, one gets

$$g(0.5) = \left(\frac{AE}{\beta R}\right) p(u_{0.5}) \quad (10)$$

where $u_{0.5} = E/RT_{0.5}$.

When eqn. 8 is divided by eqn. 10, the following equation obtained

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(u)}{p(u_{0.5})} \quad (11)$$

Plotting $g(\alpha)/g(0.5)$ against α corresponds to the theoretical master plots of various kinetic functions. Using the predetermined value of E , along with the temperature measured as a function of α , $p(u)$ can be calculated according to the eqn. 9. Then the experimental master plots of $p(u)/p(u_{0.5})$ against α under various heating rates from experimental data can be drawn. Both of the experimental master plots and theoretical

master plots of various kinetic functions (Table-3) are shown in Fig. 5. The experimental master plots at different heating rates are practically identical, indicating that the kinetic decomposition process of $\text{Sr}(\text{NO}_3)_2$ should be described by a single kinetic model. As can be seen, the experimental curve of $\text{Sr}(\text{NO}_3)_2$ overlaps the master-curves $g(\text{D4})/g(0.5)$ indicating that thermal decomposition belongs to D4 reaction mechanism.

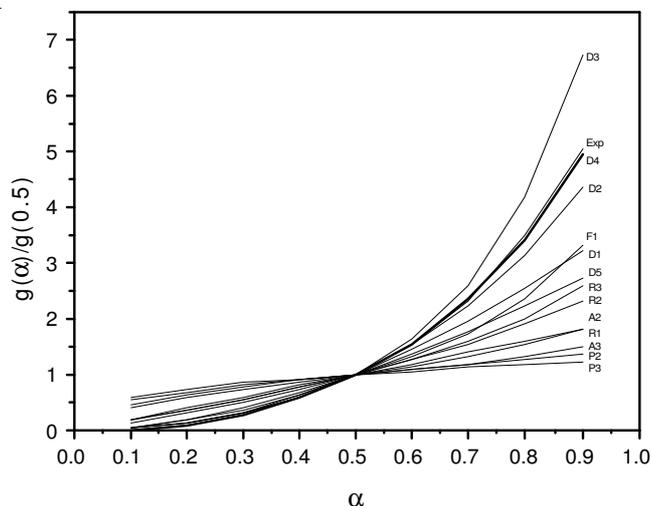


Fig. 5. Master plots of theoretical $g(\alpha)/g(0.5)$ against α for various reaction models and experimental data for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$

Invariant kinetic parameter (IKP) method: The application of the IKP method is based on the study of the compensation effect and the details of this method have already been described¹⁷⁻¹⁹. The sets of $\ln A$ and E can be calculated at different heating rates for various kinetic functions (Table-3) by using the Coats and Redfern (CR) method²¹

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (12)$$

The obtained values of $\ln A$ and E are given in Table-4. The plot of $\ln A$ versus E gives the straight lines (Fig. 6) for each heating rate, according to

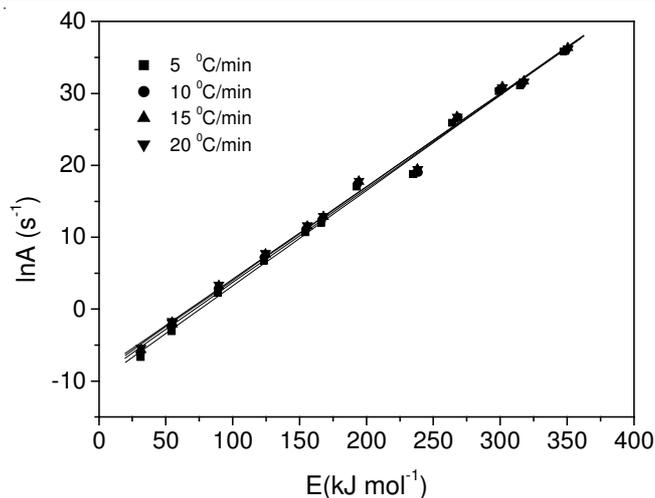


Fig. 6. IKP plots obtained from the Coats-Redfern method at different heating rates ($\beta = 5, 10, 15$ and 20 k/min), for the non-isothermal decomposition of $\text{Sr}(\text{NO}_3)_2$

$$\ln A = \alpha^* + \beta^* E \quad (13)$$

The slopes and intercepts of the plot give the compensation parameters α^* and β^* and the values are presented in Table-5. The significance of α^* and β^* being characteristics of the experimental conditions has been demonstrated²²⁻²⁴. The lines of the plot (Fig. 6) are found to intercept at a point that corresponds to the 'true' values of E and $\ln A$ for the 'true' kinetic model, which were called by Lesnikovich and Levichik the invariant kinetic parameters, E_{inv} and A_{inv} ²³. Due to the fact that certain variations of the experimental conditions determine regions of intersections, the intersection is only approximate. Therefore in order to eliminate the influence of experimental conditions on the determinations of E_{inv} and A_{inv} , they were determined from the slope and intercept of the so called supercorrelation relation

$$\alpha^* = \ln A_{\text{inv}} - \beta^* E_{\text{inv}} \quad (14)$$

Results appearing in Fig. 7 show good straight line proving the existence of a super correlation relation. Obtained value of E_{inv} (344.83 kJ/mol) was in very good agreement with the corresponding ones estimated by integral isoconversional methods.

TABLE-3
EXPRESSIONS FOR $f(\alpha)$ AND $g(\alpha)$ FOR THE MOST FREQUENTLY USED REACTION MODELS
TO DESCRIBE THE REACTION KINETICS IN HETEROGENEOUS SOLID STATE SYSTEMS

Reaction models	Symbols	$f(\alpha)$	$g(\alpha)$
Contracting linear	R1	1	α
Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
One-dimensional diffusion	D1	$1/2 \alpha$	α^2
Two-dimensional diffusion	D2	$[\ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)[\ln(1-\alpha)]$
Diffusion 3D	D3	$3(1-\alpha)^{2/3}/[2(1-(1-\alpha)^{1/3})]$	$[1-(1-\alpha)^{1/3}]^2$
Diffusion 3D	D4	$3/2((1-\alpha)^{-1/3}-1)$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
Diffusion 3D	D5	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$
Avrami-Erofeev	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami-Erofeev	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
First-order	F1	$1-\alpha$	$-\ln(1-\alpha)$
Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$

TABLE-4
VALUES OF ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF $\text{Sr}(\text{NO}_3)_2$ OBTAINED FROM VARIOUS KINETIC MODELS BY USING COATS-REDFERN METHOD AT DIFFERENT HEATING RATES

Kinetic models	$\beta = 5$ (K/min)			$\beta = 10$ (K/min)			$\beta = 15$ (K/min)			$\beta = 20$ (K/min)		
	E (kJ/mol)	ln A (s^{-1})	-r	E (kJ mol $^{-1}$)	ln A (s^{-1})	-r	E (kJ/mol)	ln A (s^{-1})	-r	E (kJ/mol)	ln A (s^{-1})	-r
R1	123.5	6.8	0.9992	123.4	7.2	0.9983	124.5	7.6	0.9991	124.5	7.75	0.9987
R2	154.4	10.7	0.9961	155.6	11.1	0.9973	155.7	11.5	0.9962	155.8	11.6	0.9961
R3	166.3	12.1	0.9937	166.7	12.5	0.9956	167.7	12.8	0.9938	167.8	12.9	0.9938
D1	264.2	25.9	0.9992	268.6	26.7	0.9994	268.1	26.7	0.9989	268.1	26.7	0.9989
D2	299.0	30.3	0.9982	299.3	30.4	0.9986	301.8	30.8	0.9980	301.8	30.8	0.9980
D3	314.9	31.1	0.9972	315.4	31.2	0.9980	317.7	31.7	0.9972	317.9	31.6	0.9971
D4	347.3	35.8	0.9942	348.3	35.9	0.9959	350.5	36.3	0.9943	350.8	36.2	0.9943
D5	234.8	18.7	0.9992	238.7	19.0	0.9979	237.8	19.5	0.9990	238.2	19.4	0.9987
A2	89.0	2.3	0.9851	89.2	2.8	0.9887	89.6	3.2	0.9853	89.7	3.4	0.9855
A3	54.4	-2.8	0.9825	54.4	-2.2	0.9868	54.7	-1.8	0.9827	54.7	-1.6	0.9831
F1	192.6	17.1	0.9989	193.2	17.4	0.9903	194.3	17.7	0.9873	194.4	17.8	0.9875
P2	54.4	-3.1	0.9989	54.3	-2.5	0.9977	54.8	-2.1	0.9988	54.7	-1.9	0.9983
P3	31.4	-6.6	0.9986	31.2	-6.0	0.9969	31.5	-5.6	0.9984	31.4	-5.4	0.9977

TABLE-5
VALUES OF α^* AND β^* FOR $\text{Sr}(\text{NO}_3)_2$ VERSUS HEATING RATES

β (K/min)	$-\alpha^*$ (min^{-1})	$-\beta^*$ (mol/kJ)	r
5	0.13241	9.974	0.9979
10	0.13042	9.305	0.998
15	0.1294	8.997	0.9988
20	0.12856	8.6662	0.9978

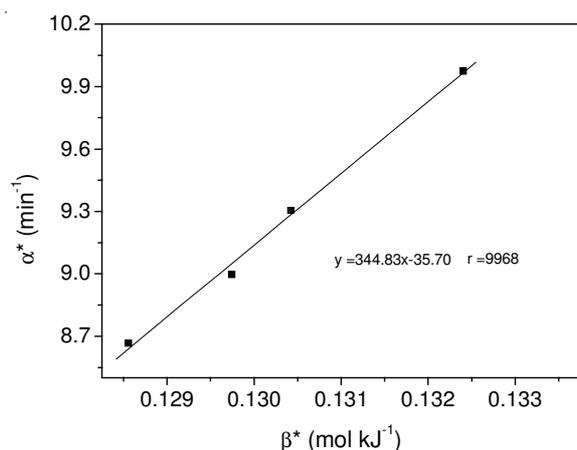


Fig. 7. Supercorrelation relationship for the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$

Conclusion

The kinetic analysis of the thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ in nitrogen atmosphere is presented. Non-isothermal thermogravimetric measurements at various heating rates enable calculation of kinetic parameters characterizing the decomposition process. The different isoconversional methods like Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Straink methods as well as IKP method were used for kinetic analysis of TG curves. The values of activation energy obtained from the Friedman method are higher than the values obtained from the other three isoconversional methods. The activation energy value obtained by the IKP method displays a good agreement with the values obtained by integral isoconversional methods in the conversion range of $0.20 \leq \alpha \leq 0.90$. In this region of α , little dependence of E on α indicated that there

exists a high probability for the presence of a single step reaction. The master plot method revealed that the decomposition of $\text{Sr}(\text{NO}_3)_2$ follows Ginstling-Brounshtein model (D4) equation, $g(\alpha) = (1-2\alpha/3)-(1-\alpha)^{2/3}$.

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