Thermal and Kinetic Studies of Trinitrotoluene (TNT) and Amatol Vis-a-Vis Oxygen Balance

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ABSTRACT-----Trinitrotoluene (TNT) an extensively used explosive in military has major drawback of incomplete oxidation on detonation due to negative oxygen balance which effects its performance. This anomaly has been addressed by mixing TNT with the ammonium nitrate in the ratio of 20% TNT and ammonium nitrate 80% known as 80/20 amatol explosive. This paper focuses on the thermal and kinetic study of TNT and 80/20 amatol vis-à-vis oxygen balance. Thermal and kinetic parameters along with the oxygen balance of both TNT and 80/20 amatol have been determined using simultaneous thermal analysis. The experiments show that 80/20 amatol beside undergoing almost complete oxidation has more blast effects and is safer in handling in comparison with the TNT due to the higher activation energy and higher decomposition temperature.
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INDEX TERMS----activation energy, 80/20 amatol,heating rates, isomers,kinetic parameters,positive oxygen balance,TG/DTA

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1. INTRODUCTION

Trotyl, tolit, triton, tritol, trilite, and 1-methyl-2,4,6 trinitrobenzene are the different names with which trinitrotoluene is represented. Trinitrotoluene is considered as one of most effective explosive and has been in use after the second world war. It has several advantages which are its good thermal stability, power, safe handling, chemical stability, low toxicity, good properties for melt casting (low melting point), good physical properties and compatibility with the other explosives. TNT isomers are basically six in numbers among which alpha isomer is the one which carries great significance as far as effective explosive is concerned. This is primarily called as TNT and used as a military explosive. Other five isomers are given the name from Greek letters starting from beta till eta with an exception of zeta which is not included in isomers. Trinitrotoluene is basically a crystalline compound which is yellow in color with molecular weight of 227, melting point ranging from 80 degrees centigrade to 81 degrees centigrade. It boils at 345 degrees centigrade at atmospheric pressure. Trinitrotoluene (TNT) has drawback of negative oxygen balance which is about negative 74% which forms the unburnt carbon in the form of soot due to which maximum potential of the explosive cannot be explored. To address this problem 80/20 amatol [12] has been used which has positive oxygen balance which comes out to be positive 1.2%. Due to this positive oxygen balance, it has more blast effects than the TNT due to the high volume of gasses released after the detonation. In the study oxygen balance vis-a-vis thermal and kinetic parameters of the TNT and amatol has been analyzed. This study also highlights the effects of increasing heating rates on the temperature changes of the TNT and amatol. For thermal study of TNT and 80/20 amatol, DTA/TGA techniques have been used in the form of simultaneous thermal method.

2. EXPERIMENTATION

For the experimentation trinitrotoluene (TNT) and highly purified ammonium nitrate (99% pure) were used for the analysis. Experiments were performed by using the TNT and 80/20 amatol (80% ammonium nitrate and 20% TNT). Thermal analysis was carried out of the ammonium nitrate and 80/20 amatol by using the Diamond TG/DTA by Perkins Elmer. The effects due to the thermal changes were studied by varying the heating rates from 5^0C to 25 ^{0}C. The thermal data obtained from the experiments was used to calculate the kinetic parameters such as activation energy, order of reaction, entropy and enthalpy. Firstly, thermal analysis was carried out of the TNT by varying the heating rate from 5^0C to 25 ^{0}C. After that this thermal data was used to calculate the kinetic parameters by using the Horowitz and Metzger Method with the help of curve fitting program. Same procedure was repeated for the thermal and kinetic parameters determination of 80/20 amatol. Oxygen balance of both the TNT and 80/20 amatol was calculated by using the formula Ω= [d - (2a) - (b/2)] x 1600/M for which general formula $C_aH_bN_cO_d$ was used. Weights of samples were kept from 5mg to 7mg with the nitrogen gas environment with flow of 20ml/min for all the experiments. Temperature range was set from the room temperature to the decomposition temperature of about 400 ^{0}C. Experimental conditions were kept similar for all the experiments to compare the results of TNT and 80/20 amatol under similar conditions.

3. CALCULATION OF KINETICPARAMETERS

In order to perform the kinetic calculations to study 80/20 amatol, the results obtained from the simultaneous thermal analysis have been used in which TG/DTA curves have been recorded. For that purpose, Horowitz and Metzger Method has been used to determine the activation energy, order of reaction, and enthalpy which has been further used to determine other kinetic parameters.

In order to use the Horowitz and Metzger Method we use the thermal profile obtained by thermal analysis. For that we find the temperature at maximum rate of decomposition which is denoted as Ts and is calculated by using the formula as:

Ts = Wt / Wo =1/e
Where
e = Exponential
Wo = Initial sample weight
Wt = Sample weight at T temperature
Ts = Reference temperature

In the second step curve fitting program, has been used to find activation energy, order of reaction and enthalpy.

RESULTS ANDDISCUSSION

4. Comparison of DTA curves of TNT at Different Heating rates

The experiments were conducted on the TNT with the varying rates of heating which were 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min, 20 ^{0}C/min and 25 ^{0}C/min respectively. Profiles of DTA of all the heating rates in the figure below is shown

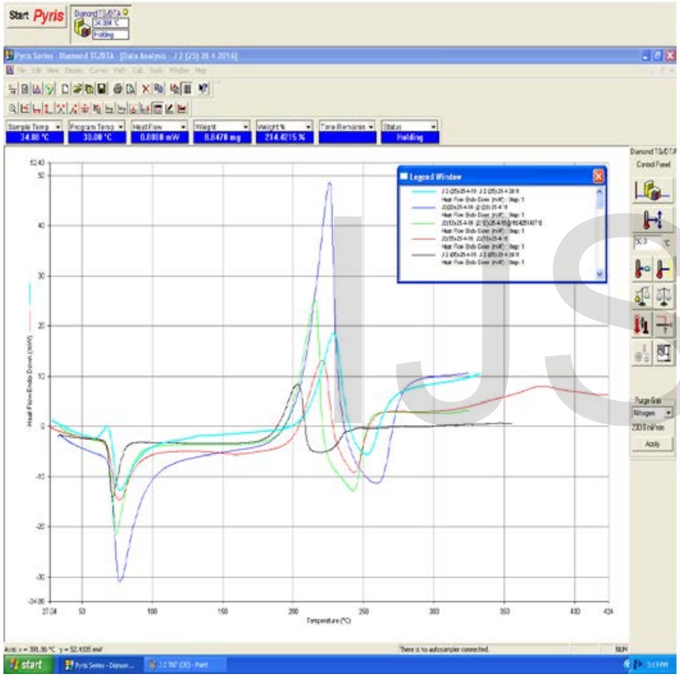

Fig:1 DTA curve of TNT with different Heating Rates

From the graph, it is found that with the increase in the heating rate all the three peaks are showing the variations for which a table has been shown below to evaluate the differences taking place due to the increase in the heating rate. When compare the first endothermic peak representing the solid phase transformation with the different heating rates it is found that with the increase in the heating rate peak temperature for all the consecutive curves increases. Now when compare the second exothermic peaks with the increasing heating rates it is found that temperature also increases for the peak temperature for all the consecutive curves. When compare the third endothermic peaks which are decomposition peaks it is found that for the heating rates of 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min and 20 ^{0}C/min there is increase in the temperature of peaks with the increasing rate but when reach to the heating rate of 25 ^{0}C/min then it is found that there is decrease in the peak temperature.

Heating Rate	1st Endo Peak	2nd Exo Peak	3rd Decomposition Peak
5 $^{0/}$min	72.02 ^{0}C	202.95 ^{0}C	219.27 ^{0}C
10 $^{0/}$min	73.90 ^{0}C	215.01 ^{0}C	242.89 ^{0}C
15 $^{0/}$min	76.04 ^{0}C	220.70 ^{0}C	243.04 ^{0}C
20 $^{0/}$min	76.45 ^{0}C	225.67 ^{0}C	260.62 ^{0}C
25 $^{0/}$min	76.68 ^{0}C	228.70 ^{0}C	252.38 ^{0}C

Table:1 Comparison of temperature of DTA curve of TNT with different Heating Rates

5. Comparison of TG curves of TNT at Different Heating rates

The experiments were conducted on the TNT with the varying rates of heating which were 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min, 20 ^{0}C/min and 25 ^{0}C/min respectively. Profiles of TGA of all the heating rates in the figure below are shown

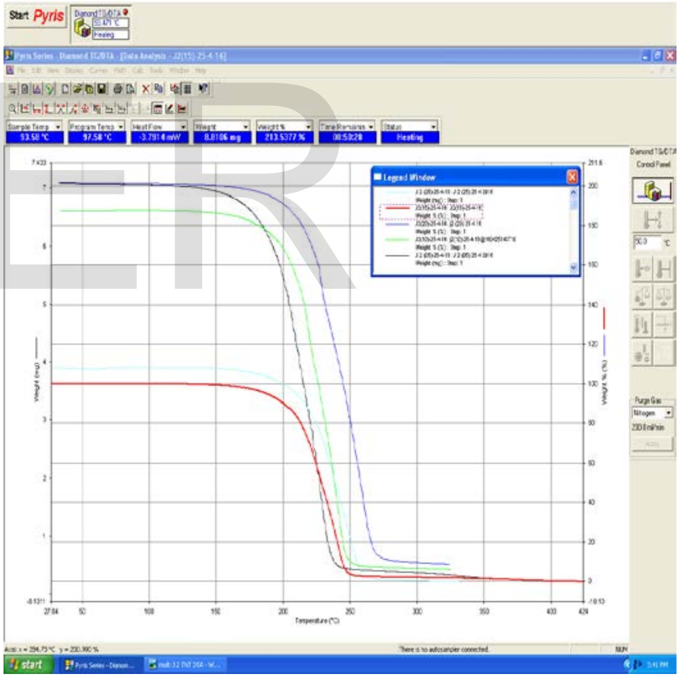

Fig:2 TGA curve of TNT with different Heating Rates

From the comparative profile, it is found that with the variation in the heating rate there is change in the temperature at which sample is completely decomposed. The table shown below shows the decomposition temperature at increasing heating rate. It is found that with the increasing heating rate from 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min and 20 ^{0}C/min there is increase in the decomposition temperature but when the experiment is done at 25 ^{0}C the decrease in the temperature occurs at which decomposition takes place.

Comparison of TG curves of TNT at Different Heating

rates

Heading Rate	Decomposition Temperature
5 ^{0}/min	240
10 ^{0}/min	255
15 ^{0}/min	257
20 ^{0}/min	275
25 ^{0}/min	265

6. Comparison of Activation Energy of TNT at Different Heating Rate

From the table shown below it is evident that with the increase in the heating rate there is increase in the activation energy when TNT kinetic parameters are observed. It is found from the kinetic parameters i.e. activation energy that for the heating rate from 5$^{0/}$min to 20$^{0/}$min, activation energy increases but for the heating rate of 25$^{0/}$min activation energy shows decrease in the value. This behavior can be resembled with the DDT phenomenon where in the start heat produced is less which increases with the confinement leading to the detonation. Likewise, in case of TNT, as the heating rate is increased to 25 ^{0}C/min heating rate is increased to the level after which activation energy starts reducing. It shows that as the heating rate is increased then energy produced is so much more than the energy dissipated and it also overcomes the thermal lag due to which activation energy starts reducing at higher heating rate in TNT.

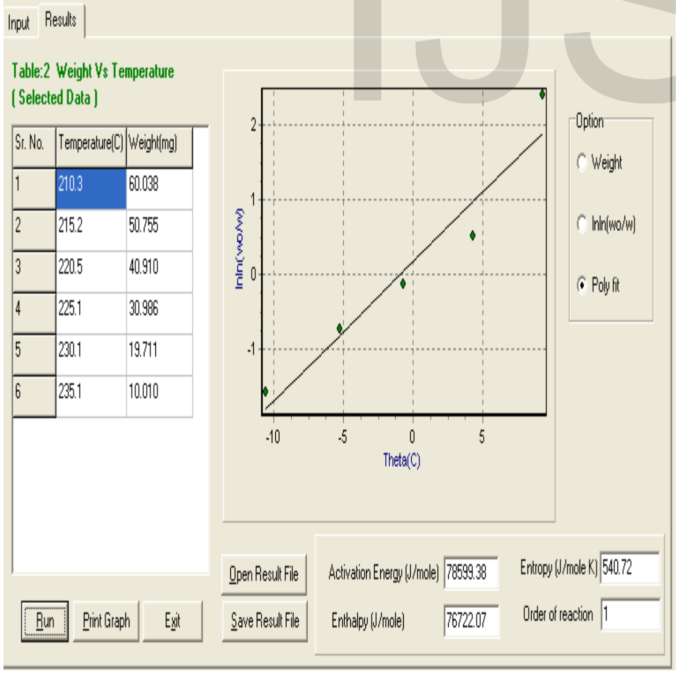

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	210.3	60.038
2	215.2	50.755
3	220.5	40.910
4	225.1	30.986
5	230.1	19.711
6	235.1	10.010

Activation Energy (J/mole) 78599.38
Entropy (J/mole K) 540.72
Enthalpy (J/mole) 76722.07
Order of reaction 1

7.THERMAL STUDIES OF AMATOL

Thermal analysis of 80/20 amatol has been carried out byusing the Diamond TG/DTA by Perkins Elmer. Simultaneous study method of TG/DTA have been utilized for our study. We have used 80/20 amatol sample with varying rate of heating i.e. 5 ^{0} C ,10 ^{0} C, 15 ^{0} C, 20 ^{0} C and 25 ^{0} C. Experiments were conducted in nitrogen atmosphere by maintaining flow of 20 ml/min with the temperature range from ambient temperature to 400 ^{0} C.

8.Comparison of Peak of DTA Temperature of Amatol at Different Heating Rate

The experiments were conducted on the 80/20 amatol with the varying rates of heating which were 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min, 20 ^{0}C/min and 25 ^{0}C/min respectively. Profiles of DTA of all the heating rates have been shown in the figure below.

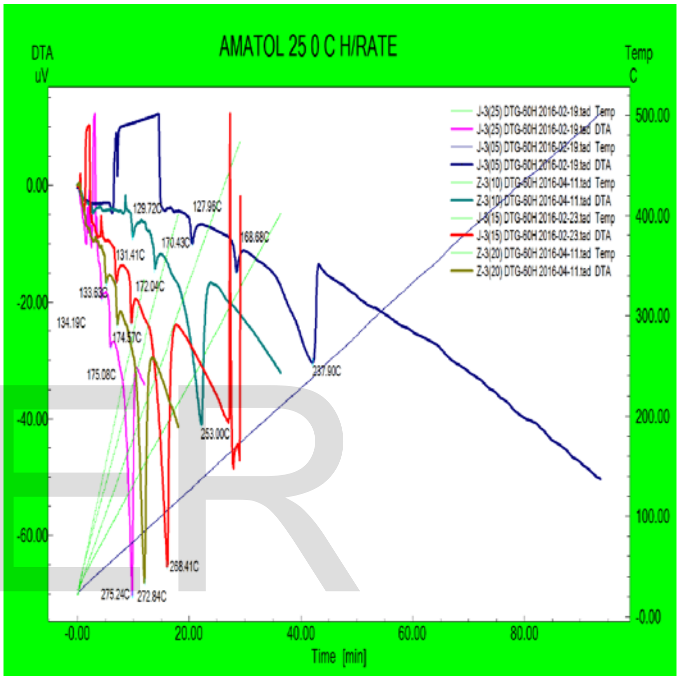

Fig:3 DTA curve of amatol at different heating rates

From the above graph, we find that with the increase in the heating rate there is increase in the peak temperatures. In the table below we have shown the temperatures at the peaks at increasing heating rates. When compare the first endothermic at increasing heating rate it is found that all the peak temperatures increase for the solid phase transformation peak. When compare the second peak which represents the melting point it is found that with the increase in the heating rate the temperatures at all the peaks increase. When compare the third peak which represents the decomposition peak it is found that with the increase in the heating rates there is increase in the peak temperature

Heating Rate	Activation Energy
5 $^{0/}$min	78.6 KJ/mole
10 $^{0/}$min	84.9 KJ/mole
15 $^{0/}$min	86.5 KJ/mole
20 $^{0/}$min	127.7 KJ/mole
25 $^{0/}$min	125.6 KJ/mole

Comparison of Peak Temperature at Different Heating Rate

Heating Rate	**1st Endo Peak**	**2nd Endo Peak**	**3rd Decomposition Peak**
5	127.96		237.90
10	129.72	170.43	253.00
15	131.59	172.04	268.41
20	133.07	173.85	272.29
25	134.67	175.25	275.64

9.Comparison of Amatol Decomposition Temperature of TG at Different Heating Rate

The experiments were conducted on the 80/20 amatol with the varying rates of heating which were 5 ^{0}C/min,10 ^{0}C/min,15 ^{0}C/min, 20 ^{0}C/min and 25 ^{0}C/min respectively. Profiles of TGA of all the heating rates have been shown in the figure below.

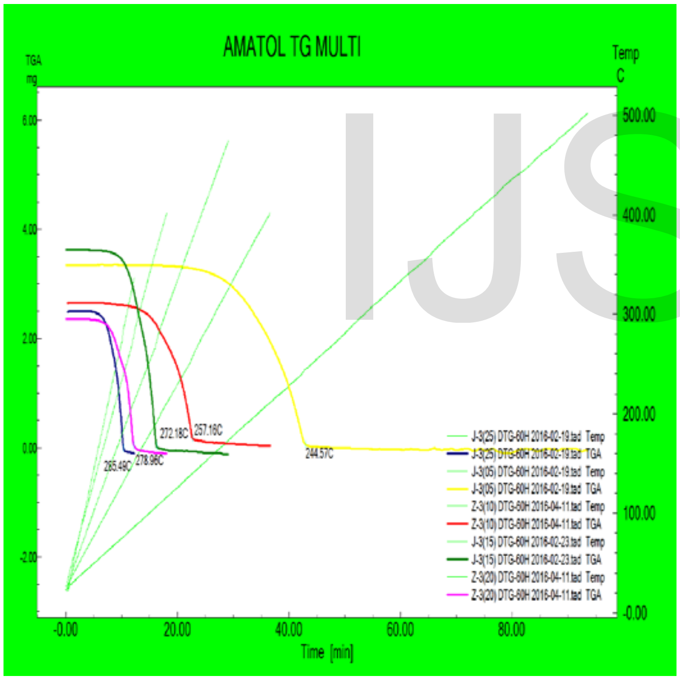

Fig:4 TGA curve of amatol at different heating rates

From the graph, it is found that with the increase in the heating rate there is increase in the decomposition temperature which has been shown below in the table. This trend clearly states that increase in the heating rate has great influence on the decomposition temperature.

Comparison of Amatol Decomposition Temperature at Different Heating Rate

Heating	**Decomposition**
5 $^{0/}$min	244.57 ^{0}C
10 $^{0/}$min	257.16 ^{0}C
15 $^{0/}$min	272.18 ^{0}C
20 $^{0/}$min	278.96 ^{0}C
25 $^{0/}$min	285.49 ^{0}C

10. Comparison of Activation Energy of Amatol at Different Heating Rate

Calculation of the activation energy for the 80/20 amatol at different heating rates has been done which are shown in the table below. From the table, we find that with the increase in the heating rate there is decrease in the activation energy. This brings us to the conclusion that activation energy is inversely proportional to the heating rate i.e. it is effected inversely with the increase in the heating rate.

Heating Rate	**Activation Energy**
5 $^{0/}$min	168.3 KJ/mole
10 $^{0/}$min	165.8 KJ/mole
15 $^{0/}$min	136.05 KJ/mole
20 $^{0/}$min	106.6 KJ/mole
25 $^{0/}$min	96.34 KJ/mole

11. Comparison of TG Decomposition curves of TNT and Amatol at Different Heating rates

Heating Rate	**Decomposition Temperature TNT**	**Decomposition Temperature Amatol**
5 $^{0/}$min	240	244.57 ^{0}C
10 $^{0/}$min	255	257.16 ^{0}C
15 $^{0/}$min	257	272.18 ^{0}C
20 $^{0/}$min	275	278.96 ^{0}C
25 $^{0/}$min	265	285.49 ^{0}C

12. Comparison of Activation Energy of TNT and Amatol at Different Heating Rates

Heating Rate	**Activation Energy TNT**	**Activation Energy Amatol**
5 ^{0}C/min	78.6 KJ/mole	168.3
10 ^{0}C/min	84.9 KJ/mole	165.8
15 ^{0}C/min	86.5 KJ/mole	136.05 KJ/mole
20 ^{0}C/min	127.7 KJ/mole	106.6
25 ^{0}C/min	125.7 KJ/mole	96.34

12. DISCUSSION

In the table shown above comparison of the results of the thermal studies along with the kinetic parameters has been carried out. In the first table comparison of the results of DTA curve of decomposition peak of the TNT and Amatol has been done. It is found that with the increase in the heating rate there is increase in the decomposition temperature of amatol but in case of TNT it is noted that there is increase in the decomposition temperature till the heating rate of 20 ^{0}C/min but at the heating rate of 25^{0}C/min there is a decrease in the temperature i.e. temperature reduces. In the second table comparison of the TG curve of amatol and TNT has been carried out. It is seen that same trend of increase in the temperature has been found out in the amatol with the increase of the heating rate. In case of TNT it has been noted that there is increase in the temperature of decomposition till the heating rate of 20 ^{0}C/min and then after that at the heating rate of 25 ^{0}C/min there is decrease in the decomposition temperature. From the TG curve, it is also evident that amatol is safer in handling than the amatol as it has higher decomposition temperature making it more stable in use. In the third table comparison of the activation energy of the TNT and Amatol has been carried out at different heating rates. It is seen from the results in case of TNT there is increase in the activation energy with the increase in the heating rate till the heating rate of 20 ^{0}C/min but at the heating rate of 25 ^{0}C/min there is decrease in the activation energy. This behavior somewhat resembles with the DDT phenomenon where in the start heat produced is less which increases with the confinement leading to the detonation. Likewise, in case of TNT, as the heating rate is increased to 25 ^{0}C/min heating rate is increased to the level after which activation energy starts decreasing. It shows that as the heating rate is increased then energy produced is so much more than the energy dissipated and it also overcomes the thermal lag due to which activation energy starts reducing at higher heating rate in TNT. In case of amatol it is seen from the results that there is inverse trend of the values of activation energy i.e. with the increase of the heating rate there is decrease in the value of the activation energy. Some of the reasons of such trends in the thermal analysis are as under:

a. **Thermal lag phenomenon**

It occurs due to the non-uniform heating of the sample caused by the thermal lag. The sample is exposed for less time for the specific heating rate at higher heating rate [1]. Similar effects have been observed by other researches as well [2].

b. **Influence of the Furnace Atmosphere**

The mechanism of many chemical reactions is influenced by the atmosphere and in particular by the gas pressure. With increasing partial pressure reaction moves to the higher temperature. With the higher partial pressure DTA effects are more pronounced [3]. The hot humid gases formed by the decomposition reaction diffuse slower into the furnace atmosphere than new gases are produced.

c. **Influence of the Heating Rate**

As the heating rate is increased, temperature rises quickly, causes less time for the substance transition from one state to the other, thus chemical reactions move to higher temperatures. In addition, there is local change in the furnace atmosphere and on the sample surface in contrast to the bulk of material, as reaction rate is linked with the temperature increase [4]. Higher the heating rate higher will be gases output, lower will be gases diffusion rate in the atmosphere which will increase the partial pressure thus increasing the decomposition temperature.

d. **Higher Heat Dissipation**

It may be explained that at a higher heating rate, heat is dissipated more conveniently so decomposition process starts at the higher temperatures and also has the higher heat of diffusion. [5]

13. CONCLUSION

The efficiency of all the explosives is dependent upon many factors among them oxygen balance factor is considered as of great importance. TNT has been used extensively for the military purpose but it has negative oxygen balance of 74%, which has been addressed by using 80/20 amatol for different shades of operations which gives us the positive oxygen balance of 1.2%. Due to this positive oxygen balance of 80/20 amatol blast effects are increased to generate more practical effects. Explosives are very dangerous material and warrant extreme caution for the safe handling which may be for the practical use or research. When using the explosive for the research purpose we need to use very safe techniques for the analysis for which reason thermal analysis methods are considered most appropriate. For thermal study of TNT and 80/20 amatol, DTA/TGA techniques have been used in the form of simultaneous thermal method. In case of TNT thermal analysis, it is found that with the increase in the heating rate thermal decomposition temperature and activation energy increases till heating rate of 20^{0}C/min after that decomposition temperature and activation energy reduces at heating rate of 25^{0}C/min. This effect is similar to the DDT phenomenon which takes place due to increase in heat rate due to which heat generated is more than the heat liberated which results in the increase of internal temperature and reduction in the activation energy, here as well, as the heating rate is increased beyond 20 ^{0}C/min more heat is generated resulting in the reduction of activation energy of TNT.During the study, several experiments were conducted with the increasing heating rates on the 80/20 amatol and it was found from the data that when we increase the heating rate for the 80/20 amatol thermal analysis, peak temperatures also increase for all the peaks which leads us to the conclusion that peak temperatures are dependent to the increase in the heating rate. This is due to the thermal lag, higher heat dissipation and furnace atmosphere. The data obtained from the thermal analysis of 80/20 amatol was further used to obtain the kinetic parameters i.e. activation energy, order of reaction, enthalpy etc. From the kinetic data, we found that for the 80/20 amatol activation activation energy reduces with some proportion. This phenomenon is due to the several factors effecting the thermal phenomenon which are thermal lag, effects of the furnace temperature, higher heat dissipation and higher heating rate. From the data, we have seen that decomposition temperature of the TNT is 240 ^{0}C while in case of the 80/20 amatol the decomposition temperature comes out to be about 245 ^{0} C making the 80/20 amatol more stable in handling. The upshot of this study is that 80/20 amatol has more blasting capabilities than the TNT due to the positive oxygen balance resulting in the production of higher volume of gases. Also, the decomposition temperature of TNT is lower than the decomposition temperature of the 80/20 amatol due to which 80/20 amatol is considered to be safer in the handling. Thirdly when comparing the activation energy of the TNT with 80/20 amatol it is found that activation energy of the 80/20 amatol (168.3 KJ/mole) at the heating rate of 5 ^{0}C/min is higher than the TNT (78.6 KJ/mole) which makes it safer in the handling.

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energy is effected by the heating rate. From the data, it is concluded that activation energy is inversely dependent upon the heating rate. When we increase the heating rate,

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