

**Thermal and Kinetic Studies of
Octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine
(HMX)**



**A Thesis Submitted to the Department of Chemical Engineering, School of
Chemical and Materials Engineering(SCME),NUST, Islamabad, in the
partial fulfillment of the requirements for the degree of**

Masters of Science (MS)

In

Energetic Materials Engineering

Submitted by

Amir Mukhtar

Supervisor Dr. Abdul Qadeer Malik

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

H-12 Campus Islamabad

2012

Declaration

I Amir Mukhtar, hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of the HEC.

Date: _____

Signature of the student

(Amir Mukhtar)

(2010-NUST-MS PhD-EM-E-16)

Certificate

It is certified that Amir Mukhtar has carried out all the work related to this thesis under my supervision at the School of Chemical and Materials Engineering (SCME) National University of Sciences and Technology (NUST).

Supervisor

Prof. Dr. Abdul Qadeer Malik

SCME (NUST)

IN THE NAME OF ALLAH

THE MOST MERCIFUL

THE MOST BENEFICIENT

Our Lord!

**Grant us good in this world and good in
the life to come and keep us safe from the torment of
fire.**

(2:201)

DEDICATED TO MY

***Dearest Parents and Pakistan
Army***

ABSTRACT

HMX is a very powerful secondary high explosive used in specific military munitions due to its exceptional high velocity of detonation and stability at high temperatures. It is produced as a white crystalline solid and commonly used as polymer bonded explosives filler. Research on thermal decomposition of Octogen has been under progress for quite many years. Since it's a very powerful explosive used in shaped charges mainly and other important military applications. We carried out thermal and kinetic characterization of this explosive to study its thermal decomposition behavior as well as its kinetic parameters. We studied two different samples, a pure fresh one and a 15 years old HMX sample by using Diamond TGA/DTA thermal analyzer and FTIR. Thermal decomposition behavior and the kinetics of both the samples were studied and compared which was also found in line with the values of pure sample given in literature. This work is of exceptional nature since we could not find any such work done where two different sample of HMX were characterized by thermal analysis. The upshot of the present work is that, the HMX explosive is safe and reliable in high temperature climate storage conditions for long duration. The military munitions be used reliably which have been in storage for long.

ACKNOWLEDGMENTS

All Commendations to Almighty Allah, The Most beneficent, The Most Merciful, Who blessed me with intellect, resoluteness and determination to accomplish this research project. All the respects to His Holy Prophet Hazrat Muhammad (Peace be upon him), who enabled us to recognize our creator.

I owe my deepest and sincere gratitude to my gracious and able supervisor Dr. Abdul Qadeer Malik who extended every possible guidance and supervision for completion of this work. I can never forget his guidance, illustrative advice and keen interest without which I would not have been able to complete my work.

My special thanks to Pakistan Army for training me and making me good enough to undergo MS leading to PhD from SCME (NUST). I am also grateful to Sqn Ldr Zaheer-u- din Babar for helping me in my research work and providing me with the curve fitting software. I shall also thank Mr. Noor ul Afsar lab assistant of chemical analysis lab for helping me in every possible manner.

I also applaud the nice company of my class fellows, Major Faisal Naseem Sadiqi, Lieutenant Commander Ijaz, Zubair Malik, Imran, Umair, Raja Asif and Hizba Waheed Awan. I always cherish the happy moments spent with them.

I pay my homage and sweet sensation of love and respect to my family including my father, my mother and my sweet siblings who helped me in every possible manner and prayed for me all the time. It would not have been easy without their cooperation and prayers to attain this target.

(Amir Mukhtar)

Table of Contents

CHAPTER 1	1
ENERGETIC MATERIALS	1
1.1 WHAT ARE ENERGETIC MATERIALS	1
1.2 WHAT IS AN EXPLOSION?	2
1.2.1 PHYSICAL	3
1.2.2 CHEMICAL	3
1.2.3 NUCLEAR	4
1.3 TYPES OF REACTIONS IN AN EXPLOSIVE	4
1.3.1 COMBUSTION	4
1.3.2 DEFLAGRATION	5
1.3.3 DETONATION	5
1.4 CLASSIFICATION OF EXPLOSIVES	6
1.4.1 LOW EXPLOSIVES	6
1.4.2 HIGH EXPLOSIVES	7
1.4.2.1 PRIMARY EXPLOSIVES	7
1.4.2.2 SECONDARY EXPLOSIVES	8
1.5 PROPERTIES AND CHARACTERISTICS OF EXPLOSIVES	8
1.5.1 STABILITY	9
1.5.2 DENSITY	9
1.5.3 VELOCITY OF DETONATION	10
1.5.4 BRISANCE	10
1.5.5 SENSITIVITY	10
1.5.6 WATER RESISTANCE	11
1.5.7 OXYGEN BALANCE	11
1.6 EFFECTS OF EXPLOSION	11
1.6.1 BLAST PRESSURE WAVE	12
1.6.2 BLAST PRESSURE SECONDARY EFFECTS	12
1.6.3 SECONDARY BLAST PRESSURE EFFECTS: EARTH AND WATER SHOCK	13
1.6.4 FRAGMENTATION EFFECT	13

1.6.5 THERMAL INCENDIARY EFFECTS	14
1.7 MILITARY APPLICATIONS OF HIGH EXPLOSIVES	14
1.8 HIGH MELTING EXPLOSIVE	15
1.8.1 DEVELOPMENT AND PRODUCTION OF HMX	15
1.8.2 CHEMICAL PROPERTIES OF HMX	15
1.8.3 APPLICATIONS OF HMX	16
1.9 AIM OF PRESENT STUDY	17
REFERENCES	19
CHAPTER 2	20
2.1 LITERATURE REVIEW	20
2.2 HMX THERMAL DECOMPOSITION: CHEMICAL AND MORPHOLOGICAL CHANGES INDUCED AT SLOW DECOMPOSITION RATES	20
2.3 THERMAL DECOMPOSITION BEHAVIOR OF HMX	21
2.4 HEATING RATE EFFECT IN THE HMX THERMAL DECOMPOSITION	22
2.5 HMX MIXED WITH CONTAMINANTS	23
2.6 KINETICS OF HMX $\beta \rightarrow \delta$ SOLID-SOLID PHASE TRANSITION	24
2.7 THERMOLYSIS OF HMX AND ITS PBXS CONTAINING ESTANE	24
2.8 THERMAL DECOMPOSITION KINETICS OF HMX	25
REFERENCES	27
CHAPTER 3	28
THERMAL ANALYTICAL TECHNIQUES	28
3.1 THERMAL ANALYSIS	28
3.2 THERMO-ANALYTICAL TECHNIQUES CLASSIFICATION	29
3.3 THERMOGRAVIMETRIC ANALYSIS (TGA)	29
3.3.1 TGA MEASUREMENT PRINCIPLE	30
3.3.2 FACTORS EFFECTING TG CURVE	31
3.3.3 APPLICATIONS OF THERMOGRAVIMETRIC ANALYSIS	32
3.4 DIFFERENTIAL THERMAL ANALYSIS (DTA)	32
3.4.1 REFERENCE MATERIAL	33
3.4.2 (DTA) MEASUREMENT PRINCIPLE	33
3.4.3 FACTORS AFFECTING DTA CURVE	34

3.5 SIMULTANEOUS THERMAL ANALYSIS.....	35
3.6 CALCULATION OF KINETIC PARAMETERS	36
3.6.1 CALCULATION OF ACTIVATION ENERGY	36
REFERENCES.....	39
CHAPTER 4	40
EXPERIMENTAL SET UP	40
4.1 DIAMOND TG/DTA ANALYZER	40
4.1.1 BASIC MODULES	41
4.1.2 TG/DTA INSTRUMENT CONFIGURATION	42
4.2 DIAMOND TGA MEASUREMENT PRINCIPLE.....	43
4.3 DIAMOND DTA MEASUREMENT PRINCIPLE.....	43
4.4 SPECIFICATIONS OF THE SYSTEM	44
4.5 AIM OF THE PRESENT STUDY	44
4.6 ANALYSIS METHOD	45
4.7 MATERIAL USED FOR INVESTIGATION	45
4.8 EXPERIMENTAL CONDITIONS.....	46
4.9 EXPERIMENTAL PROCEDURE	46
CHAPTER 5	48
RESULTS AND DISCUSSION	48
5.1 CHARACTERIZATION OF HMX BY FTIR.....	48
5.2 THERMAL STUDIES OF HMX.....	50
5.3 THERMAL STUDIES STANDARD HMX SAMPLE	51
5.3.1 THERMAL ANALYSIS RESULTS.....	51
5.3.2 DTA ANALYSIS	51
5.3.3 STANDARD HMX DTA CURVE	51
5.3.4 TG CURVE OF STANSARD HMX SAMPLE	53
5.3.5 KINETIC PARAMETERS OF STANDARD HMX.....	55
5.3.6 DISCUSSION.....	57
5.4 THERMAL STUDIES OF OLD HMX SAMPLE.....	57
5.4.1 RESULTS	58
5.4.2 DTA CURVE.....	58

5.4.3 TGA CURVE.....	60
5.4.4 KINETIC PARAMETERS.....	61
5.4.5 DISCUSSION.....	63
5.5 COMPARISON OF SAMPLE INVESTIGATION BY DTA	63
5.6 COMPARISON OF TGA CURVES.....	64
CONCLUSION.....	67

List of Figures

Figure 3-1: Block Diagram showing main components of TGA equipment.....	31
Figure 3-2: Block Diagram showing main components of DTA equipment.....	34
Figure 3-3: Typical TG/DTA Curve.....	36
Figure 4-1: Diamond TG/DTA instrument by Perkin Elmer.....	40
Figure 4-2: TG/DTA instrument base and measurement units.....	41
Figure 4-3: Configuration of TG/DTA module set up.....	42
Figure 4-4: Diamond TGA Measurement principle.....	43
Figure 5-1: FT_IR Spectra of Standard/ fresh HMX sample.....	49
Figure 5-2: FT_IR Spectra of Old HMX sample	49
Figure 5-3: DTA curve of Standard/ fresh HMX sample 1	52
Figure 5-4: DTA curve of Standard/ fresh HMX sample	52
Figure 5-5: TGA curve of Standard/ fresh HMX sample 1	54
Figure 5-6: TGA curve of Standard/ fresh HMX sample 2	54
Figure 5-7: Graph for kinetic Parameters of HMX Sample 1.....	56
Figure 5-8: Graph for kinetic Parameters of HMX Sample 2.....	56
Figure 5-9: DTA curve of Old HMX sample 1.....	58
Figure 5-10: DTA curve of Old HMX sample 2.....	59
Figure 5-11: TGA curve of Old HMX sample 1.....	60
Figure 5-12: TGA curve of Old HMX sample.....	61
Figure 5-13: Graph for Calculation of Kinetic Parameters of Old HMX Sample 1	62
Figure 5-14: Graph for Calculation of Kinetic Parameters of Old HMX Sample 2	62
Figure 5-15: DTA curves of HMX Samples.....	64
Figure 5-16: TGA curves of HMX Samples.....	65

List of Tables

<u>Table 1-1: Properties of HMX</u>	16
<u>Table 4-1: Specifications of TGA/DTA Instrument</u>	44
<u>Table 4-2: Experimental Conditions</u>	46
<u>Table 5-1: FT-IR Absorption Frequencies</u>	50

ABBREVIATIONS

HMX	High Melting Explosive (Cyclotetramethylenetetranitramine)
TGA	Thermo gravimetric Analysis
DTA	Differential Thermal Analysis
PBX	Plastic Bonded Explosives
RDX	Royal Development Explosive (Cyclotrimethylenetrinitramine)
Ea	Activation Energy
STA	Simultaneous Thermal Analysis
NVR	Non-Volatile Residue
ICTA	International Confederation of Thermal Analysis
FT-IR	Fourier Transform Infrared Transmission Spectroscopy