THERMO- ANALYTICAL STUDIES OF HMX

M. A. SADEK*, M. H. MOEEN**, M. A. RADWAN**, AND H. H. AMEEN***

ABSTRACT

Thermal decomposition of pure cyclotetramethylene tetranitramine (HMX) shows a small endothermic peak at 191.4°C attributed to β to δ phase transition, an endothermic peak at 281°C assigned to melting of HMX followed by exothermic decomposition leading to a considerable peak at 284.3°C, and a sharp derivative thermogravimetry (DTG) peak at 282°C with 100% mass loss. The activation energy of decomposition is determined using two different techniques, thermogravimetric TG/DTG and differential scanning calorimetry DSC and three different methods of calculation Ozawa [1-3], Kissinger [2,4] and 1st order rate equation [4].

INTRODUCTION

Future composite solid rocket propellants are practically required to be of higher density, low smoke level, high performance level, and of low vulnerability. HMX incorporated inside the matrix of this propellant is considered as an energetic component. Determination of kinetic parameters of thermal decomposition reactions of HMX especially the value of activation energy "E" is very important to judge the stability and the compatibility of HMX with the other components. In this paper the results of DSC and TG/DTG   studies   of HMX , also the calculations of the activation energy based on the kinetic data from the thermodynamic measurements are presented .

EXPERIMENTAL

Fine pure HMX powder with an average particle diameter of 350μm was used (product of Rof .UK). NETZSCH model DSC-200 differential scanning calorimeter and NETZSCH model TGA-209 thermogravemetric analyzer is used. DSC-200 is calibrated using indium and zinc standards. The DSC data for HMX is obtained using samples of 1-2 mg weight. Heating rates of 2,5,7,10 and15°C/min and nitrogen gas at a rate 20ml/min are used. TGA is recorded for samples of 2-3 mg weight using nitrogen gas at a rate of 20ml/min. Isothermal runs in TGA experiments are carried out by heating the samples to the required temperature by a heating rate of 40°C/min, then the temperature is kept constant for different periods of time.

*Professor, **Associate Professor, ***Ph.D. student, Chemical Engineering Branch, Military Technical College [M.T.C.], Cairo, Egypt.

RESULTS AND DISCUSSIONS

DSC thermogram illustrated in fig. (1) shows a small endothermic peak at 191.4°C corresponding to β to δ phase transition [5]. A sharp endothermic peak is obtained at 281°C assigned to melting of HMX [6], followed by a considerable exothermic peak at 284.3°C indicating complete decomposition of the sample. While in fig. (2) TG/DTG thermogram we observed that, a sharp DTG peak at 282°C with100% mass loss. The two results confirm together that, complete decomposition occur at this temperature.

Results of G-Hussain [7] showed that melting takes place at 285°C while complete decomposition was obtained at 325°C by DTG and 290°C by DSC, which is a large difference.

Activation energy of HMX thermal decomposition is determined using three different methods. In Ozawa method the relationship among the heating rate, temperature, and activation energy is given by equation (1).

$$\text{Log } \beta = -0.457 \, E/R \, (1/T) + \text{constant} \tag{1}$$

Thus plotting log β against 1/T gives a straight line of slope = - 0.457 E/R, hence the activation energy could be determined.

In Kissinger method the same relation is given by equation (2).

$$\text{Ln } (\beta / T^2) = -E/R \, (1/T) \tag{2}$$

So plotting of Ln (β /T²) against 1/T will also give a straight line of slope -E/R, hence the activation energy could be evaluated.

In equation 1 and 2 "β" is the heating rate (°C /min), "T" is the temperature, "E" is the activation energy and "R" is universal gas constant (1.98 cal/mole K). Values of these parameters are given in table (1) and represented graphically in fig. [3,4].

In the third method, the decomposition reaction is considered to be a first order reaction [1] obeying the following rate equation

$$-K \, t = \text{Ln } (C_A/ C_{A°}) \tag{3}$$

where k is the reaction rate constant, $C_{A°}$ is the initial mass of the sample in milligram and C_A is the mass of the sample at any time (t).

Plotting Ln (C_A /$C_{A°}$) against t, results in the determination of the rate constant -k. Different k values are estimated at different temperatures. Using Arrhenius equation, the activation energy is obtained by plotting Ln k against 1/T, this will give a straight line with slope [- E/R].

Data and results of the third method are illustrated in table (2) and fig. (5) and (6) . The values of activation energy determined by the three methods are given in table (3). Values of "E" determined by different workers are illustrated in table (4) for comparison.

CONCLUSION

The thermal decomposition of HMX was investigated by DSC and TGA techniques. The DSC traces show that there were two endothermic peaks and an exothermic one. The endothermic peak at 191.4°C attributed to phase transition from β to δ and at 281°C could be attributed to melting of HMX. Exothermic peak at 284.3°C was attributed to the complete decomposition. Also, TGA traces show sharp DTG peak at 282°C with 100% mass losses.

The activation energy of thermal decomposition of HMX was found to be 102.6 and 105.7 kcal/mole from the DSC data (temperature range 270-285°C) and 65.76 kcal/mole from TGA data (temperature range 230-255°C). The difference between these values of activation energy could be attributed to the adopted techniques, as in DSC analysis the "E" value was relevant to the ignition temperature of HMX, while in TG analysis the "E" value was relevant to the slow decomposition of HMX. Therefore, to construct a burning rate model for HMX, the activation energy of decomposition to ignition of HMX could be 104.15kcal/mole, while for establishing a chemical stability relationship (relation between storage time, temperature and mass loss) the activation energy value of 65.67 kcal/mole could be considered.

REFERENCES

[1] E.Cohen. Nir and H. Sannier " A contribution to Study of Decomposition and Combustion of HMX, Influence of Some Additives ", Propellant, Explosives, Pyrotechnics 10: 163-169 (1985).

[2] K.N. Ninan , K. Krishnan , R. Rajeev, and G. Viswanathan " Thrmoanalytical Investigations on the Effect of Atmospheric Oxygen on HTPB Resin", Propellant, Explosives ,Pyrotechnics 21: 199-202 (1996).

[3] T.Ozawa, Bull " A New Method of Analyzing Thermogravimetreic Data " Chem.Soc. Japan 38,1881(1965).

[4] M.A. BenMahamed "Determination of Reaction Kinetics Data From Thermodynamic Measurements Catalyzed Composite.Propellants", 29th international Annual Conference of ICT June 30- July3, 1998.

[5 D.I.,Autera,J.R.,Velicky,R.W." Deuterium Kinetic Isotope Effect in The Thermal Decomposition of RDX and HMX" J.Phys.Chem.90,4121,1986.

[6] S.A.Shackelford, M.B.Coolidge, B.B.Goshgarian, B.A.Loving "Deuterium Isotope Effects in Condensed – Phase Thermochemical Decomposition reaction of HMX" J.Phys.Chem.89, 3118,1985.

[7] G. Hussain and G.J.Rees "Thermal Decomposition of HMX and Mixtures ", Propellant, Explosives, Pyrotechnics 20: 74-78 (1995).

[8] J.Kimura and N.Kubota" Thermal Decomposition Process of HMX", Propellant and Explosives 5: 1-8 (1980).

[9] K. Kishore , Kubota, " Fundamentals of Solid- Propellant Combustion", V.90, pp.140, The American Institute of Aeronautics and Astronautics, Inc.NewYork,1984.

[10] T.B.Brlll and R.J. Karpowlcz " Solid Phase Transition Kinetics. The Role of Intermolecular Force in the Condensed – Phase decomposition of HMX ", J.Phys.Chem.86,4260-4265,1982.

Table (1), The DSC data for HMX

heating rate (β) (°C/min.)	DSC peak temp. T[K]	$(1/T).10^3$	$Ln\ (\beta/T^2)$	$Log\ (\beta)$
2	546.4	1.8301	-11.9135	0.301
5	551.0	1.8148	-11.0140	0.698
7	552.9	1.8086	-10.6844	0.845
10	555.7	1.7995	-10.3378	1
15	557.3	1.7943	-9.9381	1.176

Table (2), The TGA data for HMX

Initial mass(mg) "$C_{A°}$"	T (K)	$(1/T).10^3$	total mass loss %	-k (slope)	$k.10^3$	Ln k
2.223	503	1.98	36	-0.0039	3.9	1.3609
2.536	513	1.94	69	-0.0239	23.9	3.1738
2.656	518	1.93	95	-0.0523	52.3	3.9569
2.394	523	1.91	91	-0.0503	50.3	3.9180
2.404	528	1.89	88	-0.0779	77.9	4.3554

Table (3), Activation energy values calculated from DSC and TGA data.

techniques	Method	Temperature rang [°C]	E (Kcal /mol)
Dynamic DSC	Ozawa	270-285	102.6
Dynamic DSC	Kissinger	270-285	105.7
Isothermal-TGA	1ˢᵗ order rate equation	230-255	65.76

Table (4), Activation energy for HMX according to different studies.

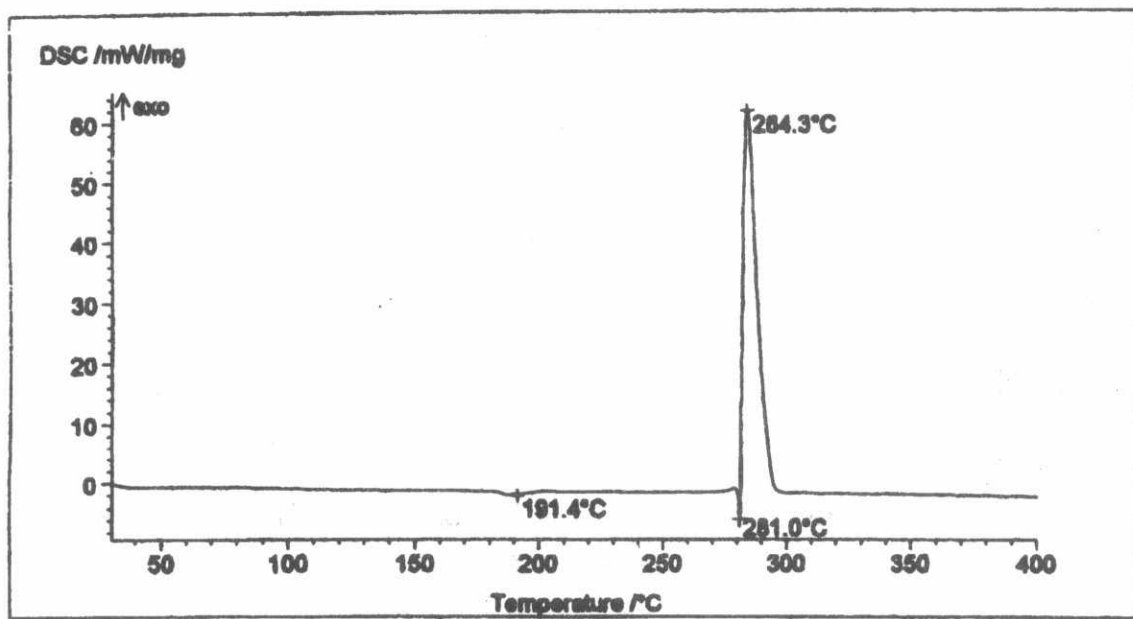| Temperature range [°C]	E[Kcal/mo]	techniques	Ref.
230-271	47.0	Dynamic-DSC	1
250-265	62	Isothermal TGA	8
276-295	65	Dynamic-DTA	,,
233-241	63.23	Dynamic-DTA	,,
232-	65.79	Isothermal –DTA	,,
270-285	51.3	Isothermal –DSC	
273-285	52.9	Isothermal –DSC	9
267-278	180-210	Dynamic-DSC	,,
<255	66.4	TG-DTG	,,
253-264	22.9	TG-DTG	,,
264-276	61.8	TG-DTG	
229-269	35.1	Isothermal TGA	,,
271-285	51.1	Isothermal –DSC	10

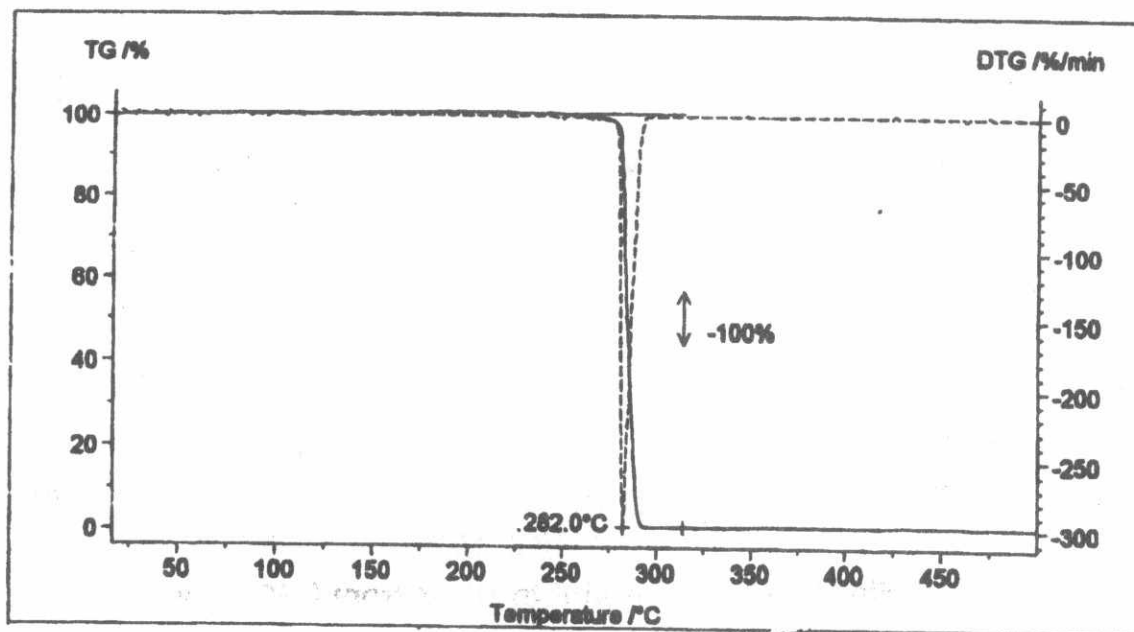Fig. 1 DSC Thermogram of HMX

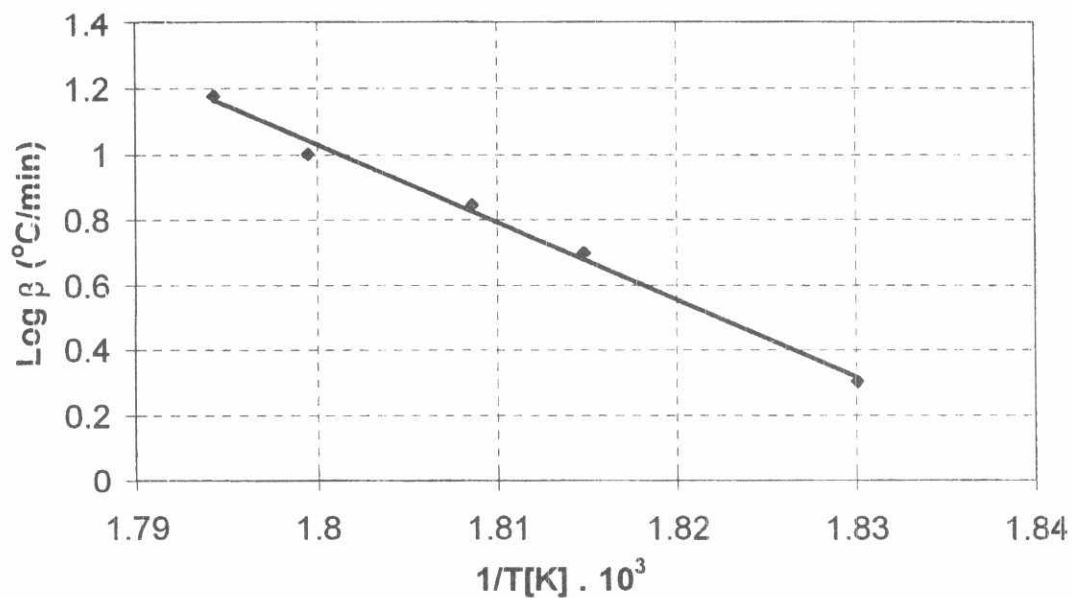Fig. 2 TG/DTG Thermogram of HMX

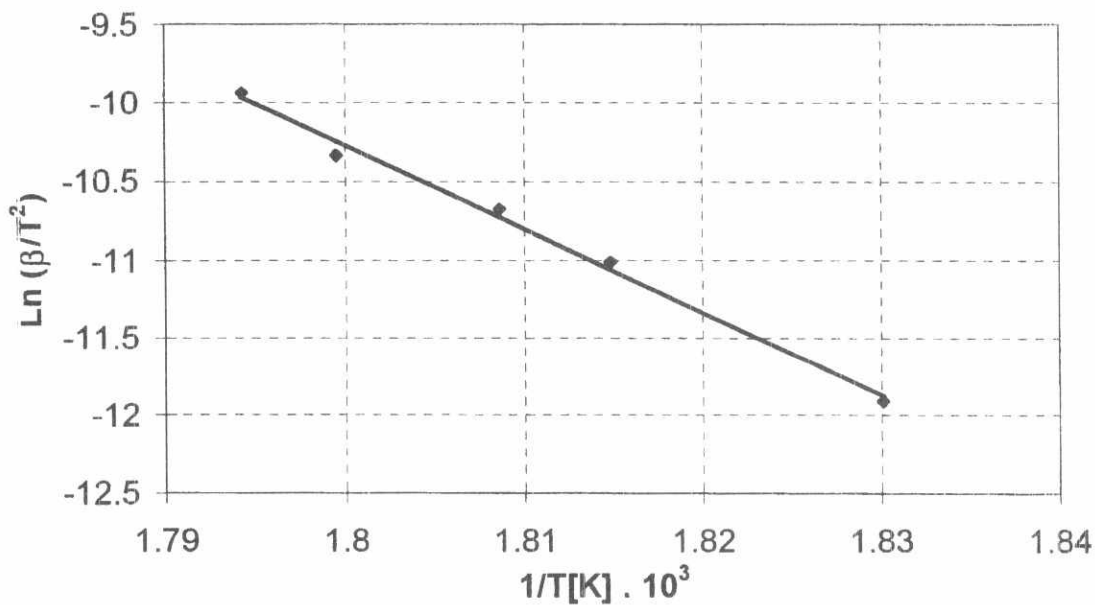**Fig. 3   Ozawa plot for HMX from DSC data**

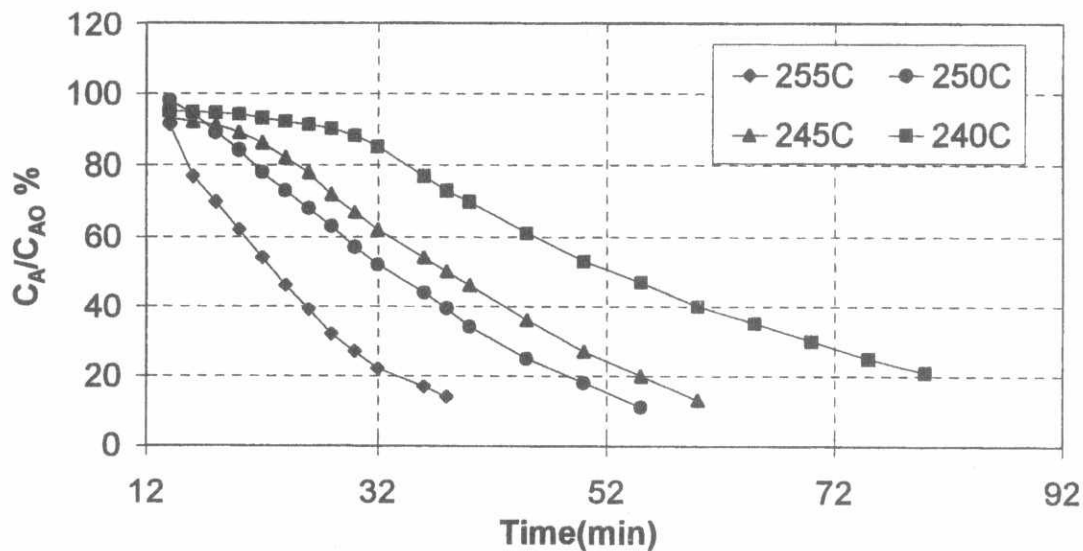**Fig. 4   Kissinger plot for HMX from DSC data**
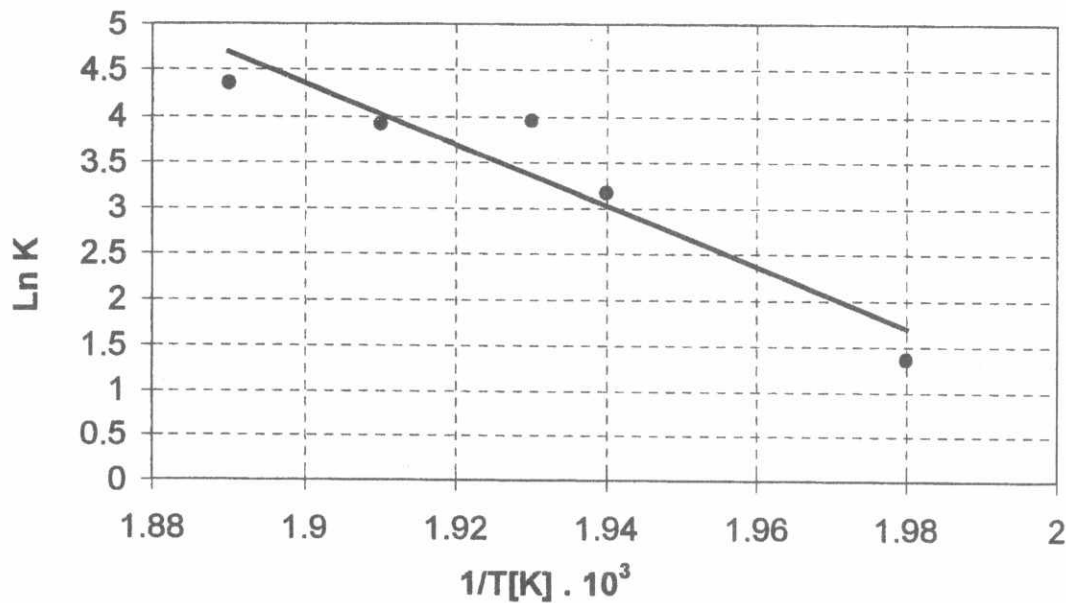
Fig. 5 Mass change versus time for the isothermal run of HMX

Fig. 6 Arrhenius plote for HMX from TGA data