UCRL-LR-143960
Thesis

Kinetics of β→δSolid-Solid Phase Transition of HMX

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Master of Science in Chemistry

September 1, 2000

U.S. Department of Energy

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KINETICS OF β→δ SOLID-SOLID PHASE TRANSITION OF HMX

A University Thesis Presented to the Faculty
of
California State University, Hayward

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

By
Randall K. Weese
September, 2000

KINETICS OF β→δ SOLID-SOLID PHASE TRANSITION OF HMX

By

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Approved: Date:

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ACKNOWLEDGMENTS

My sincere thanks to Dr. Charles Perrino for the valuable discussions of kinetics and for serving as my thesis advisor on this project. I would like to thank Dr. Jon Maienschein who allowed me the use of all the facilities with in the Thermal Analysis Laboratory at Lawrence Livermore National Laboratory, LLNL, and made this work possible.

Special thanks to Dr. Randall Simpson and George Overturf, who gave me the opportunity and support to pursue this scientific endeavor. Also, I would like to thank John Weeks of Wavemetrics, Inc., Lake Oswego, Oregon, for his valuable input and software program. Last, but not least, I would like to thank all the personnel within the High Explosives Application Facility, H.E.A.F., at LLNL who educated me in the handling, history and safety of HMX.

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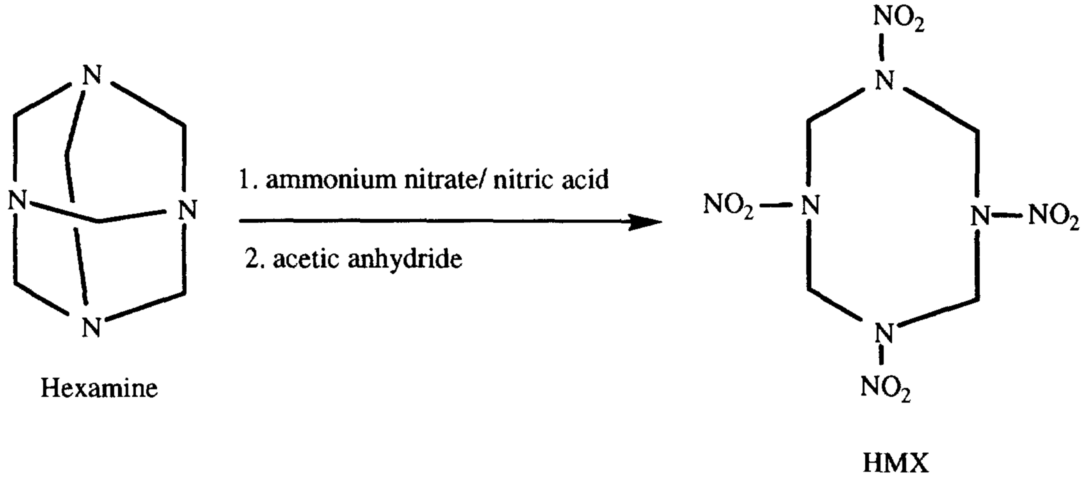
Chapter I INTRODUCTION

Background Discussion

The chemical compound HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is an important nitramine explosive[1]. Initially HMX was discovered as a by-product from the synthesis of RDX (1,3,5,-trinitro-1,3,5-triazacyclohexane) by the Bachmann process[2]. Bauchmann [3-5] and co-workers showed that the nitrolysis of hexamine with ammonium nitrate, nitric acid and acetic anhydride produced mixtures of powerful explosive [6] HMX and RDX. Mechanisms postulated {3-5, 7, 8] for these reactions include the selective cleavage of hexamine, or the total cleavage to simple molecules followed by nitration and recombination. Figure 1 outlines the Bachmann synthesis of HMX.

Figure 1: Bachmann Synthesis of HMX



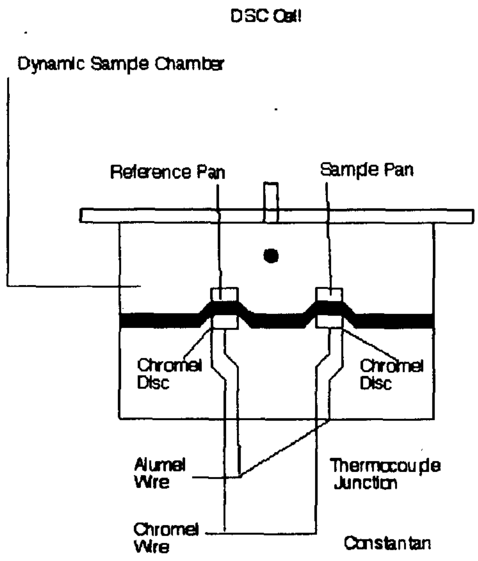
HMX exists in four solid phase polymorphs, labeled α, β, γ, δ-HMX [9], each of which can be prepared by a specific cooling rate of the reaction solution [10]. The phase conversion of the β phase (monoclinic lattice structure) to the δ phase (hexagonal lattice structure) involves a major disruption of the crystal lattice and a ring conformation change from β (chair) to δ (chair-chair). The electrostatic forces created within the HMX lattice produces a potential energy barrier to overcome in the transformation from the β →δ phase [9]. The transformation is a measurable quantity of the activation energy of the crystal lattice. The volume expansion associated with the β →δ phase transition (the density is 1.90g/cm^3 for β and 1.78 g/cm^3 for δ) may produce profound perturbations to the mechanical and combustion characteristics of HMX [9]. The higher density material shows a higher rate of detonation and maintains greater stability towards shock. Sensitivity to impact studies [11] have been investigated for safety of handling and long term storage. β HMX has a recorded height of sensitivity to impact of 31-32 centimeters while δ HMX has a recorded height of sensitivity to impact of 6-12 centimeters.

It is therefore understandable that the kinetic information associated with this β → δ solid phase transition be of interest to manufacturers and handlers of these types of materials. The lack of data on the kinetic relationship of the β → δ solid-solid phase transition is largely due to the difficulty of measuring solid transitions[12]. The work in this research will be to investigate the kinetics of the β phase HMX transition to δ phase HMX and to determine the Arrhenius parameters by Differential Scanning Calorimetry, DSC.

Thermodynamics

The method used to study the β →δ phase transition is Differential Scanning Calorimetry (DSC) [13]. DSC measures the difference in the heat flow between a sample and an inert reference measured as a function of time and temperature. Both the sample and reference are subjected to a controlled environment of time, temperature, and pressure. The instrument design used for making DSC measurements in this work is the heat flux design shown in Figure 2. In this design, a metallic alloy disk, made of constantan, is the primary means of heat transfer to and from the sample and reference [14].

Figure 2: TA Instrument DSC Cell Model 2920



The sample is contained in a metal pan, and it and the reference (an empty metal pan of the same composition as the sample pan) both sit on raised platforms formed in the constantan disc. As heat is transferred through the disc, the differential heat flow between the sample and reference is measured by area thermocouples formed by the junction of the constantan disc and chromel wafers which cover the underside of the platforms. Chromel and alumel wires attach to the chromel wafers and form thermocouples, which directly measures the voltage difference between the sample and reference and converts to temperature.

The dynamic sample chamber (furnace) composition is a silver alloy used to insure good temperature uniformity. Purge gas (nitrogen, helium, oxygen, etc.) is admitted to the sample chamber through an orifice in the heating block before entering the sample chamber. The result is a uniform, stable thermal environment, which assures better baseline flatness and sensitivity (signal-to-noise). Air-cooling is used for fast return to room temperature to improve sample turn around times.

Changes in heat flow between a sample and the inert reference as a function of a linear change of temperature versus time is the premise of the DSC. Equation 1 is used to determine the heat flux proportionality to the heat flow that allows the quantitative measure of events that occur in DSC analysis.

Equation 1: $dQ/dt = Cp\beta + f(T,t)$ [14]

Where dQ/dt = total heat flow

Cp = heat capacity

β = heating rate

$f(T,t)$ = heat flow from kinetic processes

The $Cp\beta$ component is a function of the sample's heat capacity and rate of temperature change, while $f(T,t)$ is a function of absolute temperature and time.

Acquisition of thermal information in DSC can be conducted with linear heating or cooling rates as fast as 100°C per minute, or to very slow rates that approach 0°C per minute (isothermal).

Observable thermal events that take place during DSC analysis can be quantified to yield thermodynamic information such as phase transitions and decomposition. Endothermic reactions (reactions in which energy is absorbed) and exothermic reactions (reactions in which energy is given off) can be measured by the DSC.

DSC is usually run at constant pressure (atmospheric) and the heat flux measured as a function of temperature and time.

Equation 2: $H = U + pV$

Where U is the internal energy of the system

p is the pressure of the system

V is the volume of the system

The change in enthalpy is equal to the heat supplied at constant pressure to a system as long as the system does no additional work, Equation 2.

Equation 2: $H = U + pV$

$w = - pdV$

$\Delta H = \Delta U + \Delta(pV)$

$\Delta H = \Delta U + pdV + Vdp$

$\Delta H = q + w + pdV + Vdp$

$\Delta H = q - pdV + pdV + Vdp$

w is work done by the system

Since system is open and pressure is constant $Vdp = 0$

$\Delta H_p = \Delta q$ where q is heat.

Kinetic Treatment

In the section, Data Analysis of the β→δ Phase Transition of HMX , equation 3 defines the rate constant, k. The energy of activation, E_a, can be extracted by plotting ln (natural logrithum) of the rate constant k versus the inverse of the peak temperature (1/T) of the β→δ phase transformation at different heating rates [1]. The information will then be used to calculate the Arrhenius parameters k, and E_a.

Equation 3: $k = A\,e^{-Ea/RT}$

Where k is the rate constant

A is the pre exponential factor

E_a is the energy of activation

$R = 8.314\ J \bullet K^{-1} \bullet mol^{-1}$

T is the temperature in Kelvin

The derivation of the kinetic parameters measured during this experiment was done by assuming that the extent of reaction is equal to the change in the enthalpy ΔH as a function of time. Several assumptions are made for the calculations [14]. First, the reaction is assumed to have Arrhenius type temperature dependence. Second, it is assumed that only one reaction is taking place at a time. Third, other factors such as lattice fracture during transformation, nucleation, phase boundary reaction and diffusion are ignored.

Objective of this Experiment

The need to understand the kinetics related to the $\beta \rightarrow \delta$ transformation of HMX is largely due to the safety and storage of this material with respect to time and temperature. In Table 1, properties of HMX polymorphs with respect to density and sensitivity to impact are listed.

Table 1:

Properties of RDX and the HMX Polymorphs

Property	**α-HMX**	**β-HMX**	**γ-HMX**	**δ-HMX**
Stability Range,°C	146-156	to 146	>156	Metastable all temps.
Density, g/ml.	1.82	1.90	1.76	1.78
Sensitivity to Impact, Cm.	5-50	31-32	6-25	6-12

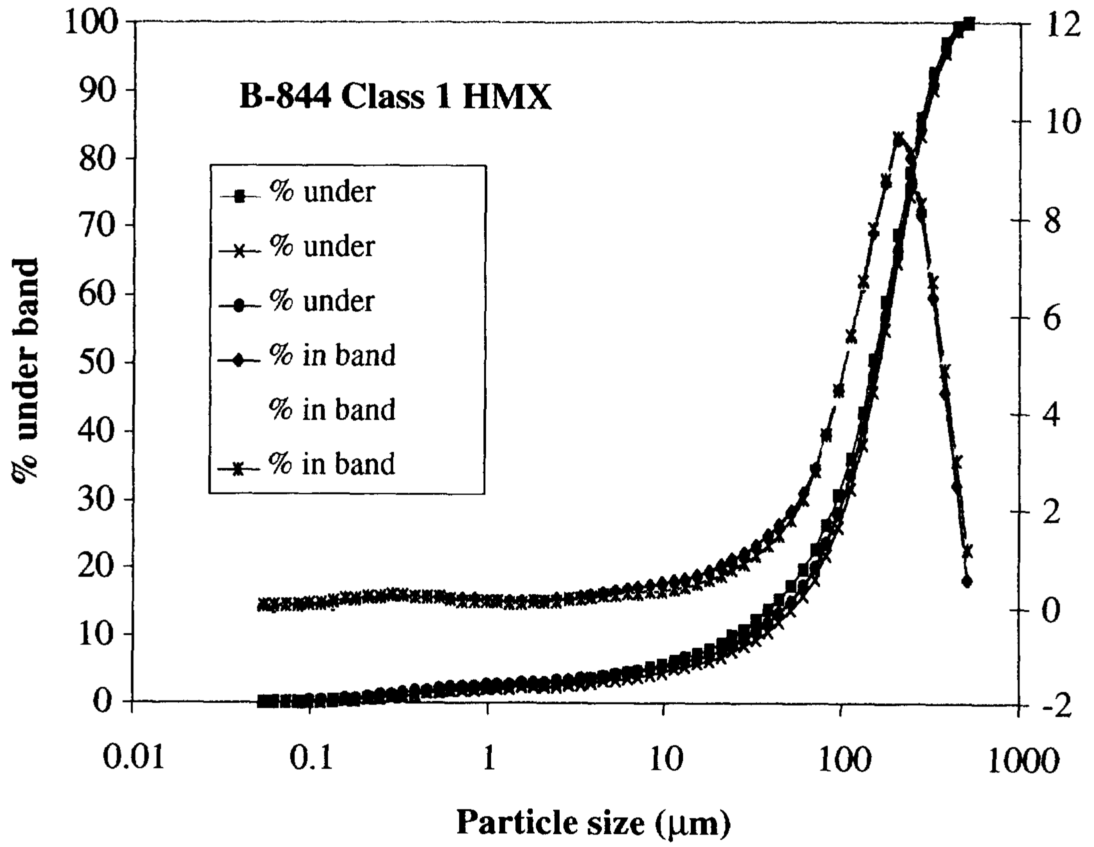
Values are approximate for a 5-kilogram weight and are dependent upon the crystal size and shape to some degree [14].

Differential Scanning Calorimetry, DSC, makes it possible to determine the kinetic parameters of the β→δ solid-solid phase transition of HMX. The change in enthalpy, ΔH, is a function of time and temperature during this reaction. The assumption that ΔH is proportional to the extent of reaction is required. Other experimenters [15] using different analytical methods that require labor intensive methods have determined the energy of activation. These previous works have laid a clear path for the use of Differential Scanning Calorimetry (DSC), an instrument, which is very affordable, and commonly used in characterization laboratories. It is the objective of this work to determine the energy of activation and the Arrhenius parameters of the β→δ transformation of HMX by Differential Scanning Calorimetry,

Chapter II INSTRUMENTATION and PROCEDURE

The materials used for this research: Differential Scanning Calorimeter, TA Instrument Model 2920. Aluminum sample pans, average total mass of 24.500 mg, supplied by Perkin-Elmer Corporation, Kit Number 0219-0062. Calibration standards of: Indium, Tin, Lead, and Zinc. Supplied by TA Instruments. The HMX (β phase), was of high purity > 99.90%, supplied by Dr. Mark Hoffman, prepared by the Bachmann process, manufactured by Lawrence Livermore National Laboratory, and analyzed by HPLC for RDX contamination was used. Particle size determinations are shown in figure 3 as provided by Dr. Mark Hoffman.

Figure 3: HMX Particle Size Distribution



Ultra high purity nitrogen purge gas at a flow rate of 50 cc/min. was used for all calibration and analyses in this experiment.

Instrumentation and Experimental Procedure

All samples were weighed in a balance (CAHN Model 25 Automatic Electro balance); the average sample mass was 1.15 milligrams. All sample pan total weights were matched accordingly with a reference pan of the same mass or within 100 micrograms to match heat flow due to the mass of aluminum (C_p, heat capacity) of the sample and reference. When the weighing was completed a 5 micrometer perforation was inserted into the sample top (to guarantee constant pressure) and then the pan lid was compression sealed.

HMX $\beta \rightarrow \delta$ Phase Change Experimental Procedure

1) Perforate aluminum pan top.
2) Weigh aluminum pan top and pan bottom
3) Tare aluminum pan bottom, then charge approximately 1.150 mg of pure HMX.
4) Remove weighed material from balance and place in compression die. Place pan top into the proper position and seal pan top to bottom pan by compression.
5) Place sample onto sample stage.
6) Place reference pan onto reference stage.

7) Open Thermal Solutions (TA Instrument software program) and record appropriate mass, sample identification, and thermal analysis parameters.
8) Start analysis and allow collection of data.

Chapter III OBSERVATIONS and DATA

Multiple scans at various linear temperature increases (ramp rates) were used. Four specific heating rates were used and replicated four times each for each data set of this experiment. The rates were 1, 2, 5, and 10°C/ minute. $\beta \rightarrow \delta$ phase transitions for this research were observed between 170°C and 220°C on scans in Appendix 1. Using TA Instruments software program Universal Analysis, the endotherms were evaluated by plotting Heat Flow versus Temperature °C. Due to the high sensitivity of the instrument, observations of the phase transition were well defined and quantitative. Listed in Table 2: Sample identification, sample weight in milligrams (mg), analysis ramp rate, endotherm peak temperature (°C), peak temperature converted from Celsius to Kelvin (K), Kelvin inverse temperature, and observed heat flow in Joules per gram (J/g) for each sample. Refer to Appendix 1 which shows initial data.

Table 2: Sample Identification

Sample ID	Wt (mg)	Rate,°C/min	Peak T°C	T(K)	1/T*1000	ΔH (J/g)
99-896.01	1.1430	1	190.15	463.30	2.158	33.70
99-897.01	0.9610	1	190.30	463.45	2.158	31.82
99-898.01	1.1570	1	188.32	461.47	2.167	33.09
99-899.01	1.004	1	191.21	464.36	2.154	33.59
		Mean	190.00	463.15	2.159	33.05
		SDev	0.84	0.84	0.004	0.86
99-889.01	0.9410	2	194.86	468.01	2.137	33.03
99-890.01	1.3300	2	192.19	465.34	2.149	32.34
99-891.01	1.1940	2	191.14	464.29	2.154	31.88
99-892.01	1.2890	2	191.70	464.85	2.151	33.26
		Mean	192.47	465.62	2.148	32.63
		SDev	1.19	1.19	0.006	0.63
99-877.01	1.2940	5	193.78	466.93	2.142	33.12
99-878.01	1.1640	5	197.56	470.71	2.125	32.92
99-879.01	1.1530	5	197.16	470.31	2.126	30.43
99-880.01	1.1960	5	195.56	468.71	2.134	30.51
		Mean	196.02	469.17	2.132	31.75
		SDev	1.35	1.35	0.006	1.48
99-871.01	0.8080	10	198.49	471.64	2.120	31.46
99-872.01	1.1330	10	197.67	470.82	2.124	32.23
99-873.01	1.1080	10	198.09	471.24	2.122	31.65
99-874.01	1.0730	10	198.84	471.99	2.119	30.29
		Mean	198.08	471.23	2.122	31.41
		SDev	0.28	0.28	0.001	0.81

Chapter IV DATA ANALYSIS OF THE $\beta \rightarrow \delta$ PHASE TRANSITION OF HMX

Data with a linear temperature increase (ramp rate) were reduced in order to obtain the Arrhenius parameters [15].

1) Energy of activation
2) rate constant
3) Arrhenius pre-exponential factor

Heat Flow (W/g) vs time (minutes) data were collected to determine the conversion of the $\beta \rightarrow \delta$ phase transition of HMX, to calculate kinetic parameters:

Where

Equation 4: α = extent of reaction = $\Delta H_t/\Delta H_o$

ΔH_t is the heat evolved at time t

ΔH_o is the total heat of reaction

the reaction rate can thus be expressed as:

Equation 5: $d\alpha/dt = dH/dt*1/\Delta H_o$

$d\alpha/dt = kf(\alpha)$

k = rate constant of the reaction

$f(\alpha)$ = function of the degree of conversion

Equation 3: $k = Ae^{-Ea/RT}$

Equation 6: $f(\alpha) = (1-\alpha)^n$ for single step reactions

$n = 1$ assuming 1st order kinetics

Equation 7: $d\alpha/dt = Ae^{-Ea/RT}(1-\alpha)$

From the observed endothermic phase transition, the total area of the curve, ΔH_o can be determined. The change in H with respect to time yields ΔH_t, which is directly measured by the DSC in Watts per gram (W/g). Taking $\Delta H_t/\Delta H_o = \alpha_t$ gives α as a function of t. The ratio, 20-80% conversion range, $d\alpha/dt$ versus $f(\alpha)$ (refer to equation 5), is equal to the rate constant, k, where temperature is changing with time. Of great importance is that when a least squares fit is applied to the plot of ln k vs 1/T, the slope is equal to $-E_a/R$ and the y-intercept is A. This method allows the determination of the energy of activation and the Arrhenius pre-exponential factor using four independent linear rates of temperature increase (ramp rates).

Therefore: $k = Ae^{-Ea/RT}$

Averaged rate constant data generated at each ramp rate is listed in Table 3. For each ramp rate a rate constant k was calculated from equation 5, the results are shown in Table 4, and reduced in Table 4 for plotting to analyze the Arrhenius parameters. Results are shown in Figure 4 and Table 5. Appendix 2 shows data analysis with respect to Heat Flow vs time (minutes), Integrated Heat Flow vs. time (minutes), α (alpha) vs time (minutes), $1-\alpha$ vs time (minutes), and $d\alpha/dt$. Also, listed in Appendix 2 is plot of k as a function of time that clearly shows that k is not constant.

Table 3: Rate Constant Data

Sample I.D.	Ramp Rate °C/minute	Rate Constant, k(s^{-1})
99-896.01	1	0.19690
99-897.01	1	0.23226
99-898.01	1	0.18832
99-899.01	1	0.21428
	Mean	0.20794
	Sdev	0.0195
99-889.01	2	0.36076
99-890.01	2	0.33589
99-891.01	2	0.39747
99-892.01	2	0.35669
	Mean	0.36270
	Sdev	0.0256
99-877.01	5	0.88491
99-878.01	5	0.90749
99-879.01	5	0.87309
99-880.01	5	0.70646
	Mean	0.84299
	Sdev	0.0921
99-871.01	10	1.57168
99-872.01	10	1.29769
99-873.01	10	1.37086
99-874.01	10	1.39020
	Mean	1.40761
	Sdev	0.1164

Table 4: Kinetic Data, summarizes the determined rate constants, k, at the various heating rates, the natural logarithm of those rate constants, ln k, the β→δ phase transition peak temperature in degrees Kelvin (K), and the inverse temperature, 1/T (K). These values were used to generate Figure 4, the plot of ln k vs 1/T used to calculate the Arrhenius Parameters for the β→δ phase transition of HMX.

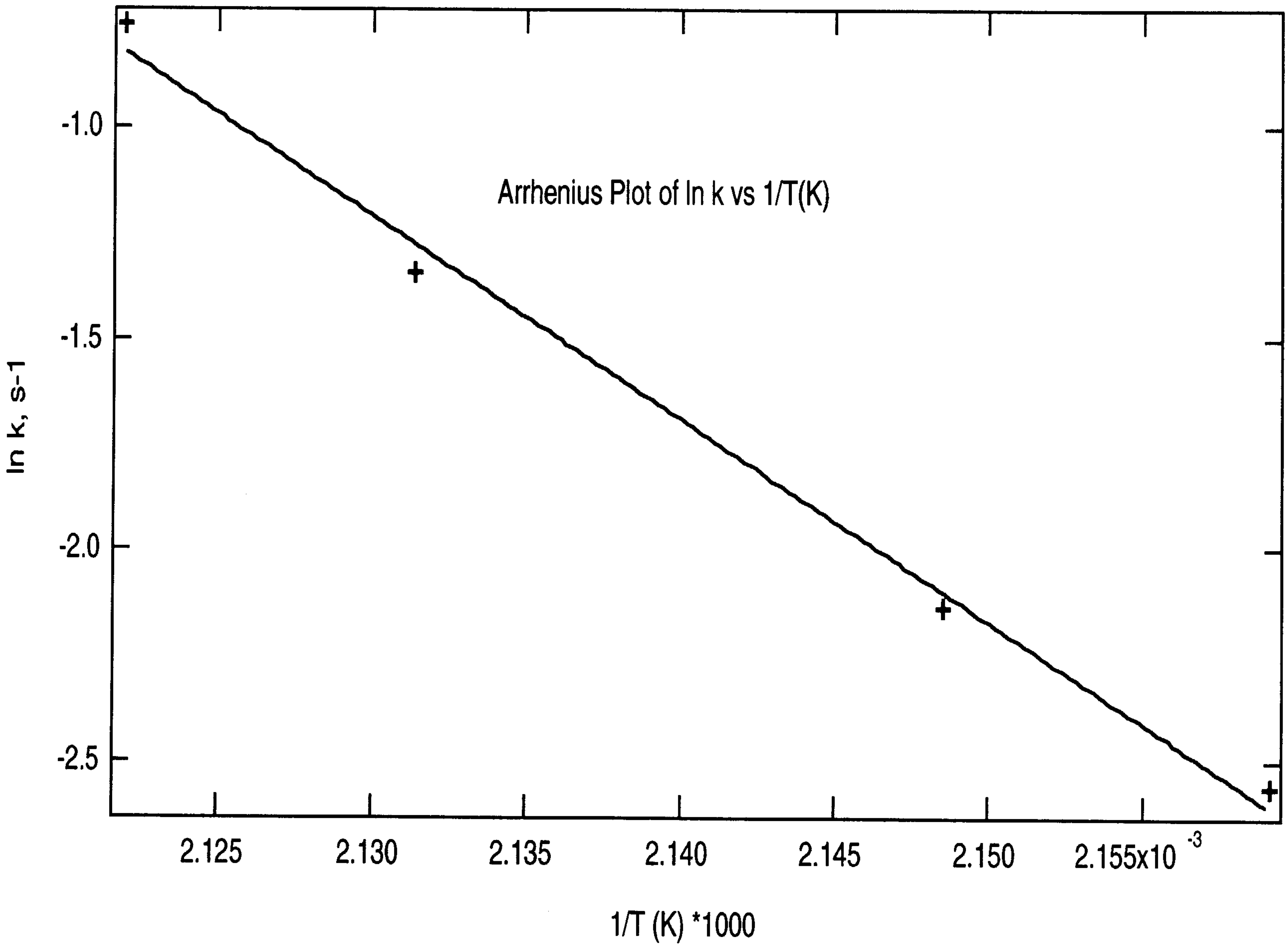
Table 4: Kinetic Data

Ramp Rate	k ,s^{-1} (mean)	ln k	Temp. (K)	1/T (K)
1°C/min	0.20794	-1.5705	463.145	$2.159 *10^{-3}$
2°C/min	0.36270	-1.0142	465.429	$2.148*10^{-3}$
5°C/min	0.84299	-0.1708	468.710	$2.1335*10^{-3}$
10°C/min	1.40761	0.3419	471.257	$2.1187*10^{-3}$

Table 5: Arrhenius Data for the β→δ Solid-Solid Phase Transition of HMX

E_a, kJ mol^{-1}	ln A	Temp °C
402 ± 8 kJ	12.1 ± 1	189-198

$$k = 1.75*10^5 e^{-48,446/RT}$$


Arrhenius Plot of ln k vs 1/T(K)
ln k, s-1
-1.0
-1.5
-2.0
-2.5
2.125
2.130
2.135
2.140
2.145
2.150
2.155x10 -3
1/T (K) *1000

Chapter V DISCUSSION and CONCLUSIONS

In order to calculate the kinetic parameters from DSC data, we have used the generally accepted methods of Bershtein [13]. We have calculated the rate constants for 4 temperatures and the activation energy based on the shift in the transition temperature, $\beta \rightarrow \delta$ for HMX. The values of E_a from this work is 402 kJ/mol compared to previous results by Brill [9] of 204 kJ/mol. Brill and associates measured the phase transition of HMX using FTIR, sodium chloride plates and silicon oil. Given the differences in technique between FTIR and DSC the results found in this work are reasonable.

In this investigation a large sample set (16) proved to be statistically valid for the determinations of k. Linear regressions were performed, observed and good fits were obtained, for each temperature. The enthalpy determination of ΔH_o, for the $\beta \rightarrow \delta$ phase transition was reproducible with in 3 parts in 100 over the range of this experiment. Thus, the data derived from this experiment k, E_a, and ΔH_o are valid parameters for the solid-solid phase transition.

Obtaining pure β phase HMX was very important for this investigation. Related to the phase change is the particle size distribution and is presented in Figure 3. Compared to previous work on HMX, this study utilized very pure β phase material. In addition, the particle size was controlled more rigorously at about 160 μm, giving a more consistent result for α. Thus, these kinetic results should have less scatter than results with less control of HMX purity and particle size.

The kinetic basis of the polymorphic conversion is due to the cohesive forces in the HMX crystal lattice [21]. The energy required to bring about change from chair to chair-chair conformation has been reported by Brill [21] as ring torsion and is essentially a normal mode of the molecule that requires about 4 kJ mol^{-1}. For the purpose of this investigation the energy of activation found in this work relates to the disruption of the intermolecular interactions with in the crystal lattice of β phase HMX and is much larger (100X) than that of simple conformational changes.

The evidence of a straightforward one step mechanism is not supported by this research. Solid–solid phase transition kinetics is very complexed. There are many factors that contribute to an overall reaction mechanism. The initial assumptions that were chosen to allow simple manipulation of the HMX phase transition data prove to be too limiting. The rate constant by definition should in fact be constant, however, our data reflects it is not (refer to k vs time plot in Appendix 2). The assumption of a first order, simple single step reaction is a good starting point for the study of HMX phase transition kinetics, but further analysis should be done with other reaction orders and multiple step mechanisms.

Understanding the kinetics of β phase HMX will clearly help the custodian understand the limitations of storage and use of this compound.

In conclusion, the measurement of E_a of the β→δ transformation of HMX from this experiment has been determined. This information is crucial to the understanding of the conversion of the β crystal phase of HMX. The time and temperature relationships with respect to β phase HMX are better understood.

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