1971-06

The thermal decomposition of (Beta)-HMX.

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THESIS

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June 1971

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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL
June 1971

ABSTRACT

Although HMX exists in four conformational forms, α, β, γ, and δ, in the crystalline state, the most stable polymorph at room temperature is the β form [1]. Therefore, this form was used for this study.

Kinetic data obtained from Differential Thermal Analysis (DTA) changes in heating rates and at isothermal conditions showed differences in the observed activation energies in the three temperature ranges, namely, 473°-506°K, 506°-514°K, and above 514°K at one atmosphere.

Calculations have been made of the rate of reaction as a function of time in each of these temperature regimes based upon the best available model and compared with the experimental result.

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TABLE OF SYMBOLS

$\frac{dx}{dt}$	=	The rate of reaction.
x	=	Fraction of reacted material.
n	=	The empirical order of reaction.
T	=	Temperature in °K.
R	=	Gas constant = 1.987 cal/mole - °K.
E_a	=	Activation energy in calories/mole.
DTA	=	Differential Thermal Analysis.
T_m	=	The sample temperature at which the peak differential thermal analysis deflection occurs.
T_f	=	Final temperature on isothermal conditions.
$\frac{dT}{dt}$	=	Heating rate of sample explosive °K/sec.
A	=	Constant.
k	=	Observed self-heating rate.

ACKNOWLEDGEMENT

I express my gratitude to Professor J. E. Sinclair for his advice and assistance in preparing this work. We are also grateful for the help of Mr. Robert Smith as Electronics Technician and Mr. Robert Scheile as glass-blower. The conferences with Dr. H. J. Mueller have been expecially helpful. This project has been sponsored by the Naval Air Systems Command.

I. INTRODUCTION

Tetramethylene tetranitramine (HMX) has four polymorphs, α, β, γ, and δ. These are stable at different temperature ranges and have different impact sensitivities. The most stable form at normal room temperatures is the β polymorph. It has been reported that near its melting point, β-HMX obeys a first-order rate law but at lower temperatures it obeys the sigmoid pressure-time relationships displayed by solids undergoing autocatalysis [2]. For β-HMX activation energies obtained in this report were:

Temperature °K	Activation Energy Kcal/mole
473°-506°	44.20
506°-514°	63.23
Above 514°	52.65

Suryanarayana and Graybush [2] also reported a variation in composition as a function of temperature from a mass spectrometric analysis of the decomposition products.

II. REACTION KINETICS IN DIFFERENTIAL THERMAL ANALYSIS [3]

Differential Thermal Analysis is the measurement of changes in heat content and other thermal properties of a material. These changes are indicated by a deflection or peak on the plot. If the reaction rate is proportional to temperature, the position of the peak is also a function of temperature. This peak temperature variation can be used to calculate the energy of activation with the temperature of maximum deflection being the temperature at which the reaction rate is greatest.

Solid → Solid + gas reactions can be described by

$$\frac{dx}{dt} = A(1-x)^n e^{-E_a/RT} \tag{2.1}$$

If the temperature rises during the reaction, the reaction rate dx/dt will rise to a maximum and return to zero when the reactant is expended. At the peak d/dT [dx/dt]=0. If the temperature rises at a constant rate dT/dt, differentiation of (2.1) gives

$$\frac{d}{dT}\left[\frac{dx}{dt}\right] = \frac{dx}{dt}\left[\frac{E_a\left(\frac{dT}{dt}\right)}{RT^2} - An(1-x)^{n-1} e^{-E_a/RT}\right] = 0 \tag{2.2}$$

If the temperature at which the peak deflection occurs is labeled T_m equation (2.2) can be rearranged to give:

$$\frac{E_a\left[\frac{dT}{dt}\right]}{RT_m^2} = An(1-x)_m^{n-1} e^{-E_a/RT_m} \tag{2.3}$$

The temperature, T_m, is the sample temperature at which the peak DTA deflection occurs [3] so that

$$\frac{dT}{dt} = \frac{A\ R\ T_m^2}{E_a}\ n(1-x)_m^{n-1}\ e^{-E_a/RT_m} \qquad (2.4)$$

From the peak shape of DTA data and comparing it with information in Reference 3, it can be predicted that it follows the first-order rate law which agrees with the results in Reference 2. From equation (2.4) we obtain

$$\frac{dT}{dt} = \frac{A\ R\ T_m^2}{E_a}\ e^{-E_a/RT_m} \qquad (2.5)$$

when n = 1

Taking the ln $\left(\frac{dT/dt}{T_m^2}\right)$ and differentiating on both sides

$$\frac{d\ \ln\left(\frac{dT/dt}{T_m^2}\right)}{d(1/T_m)} = -\frac{E_a}{R} \qquad (2.6)$$

The plot of $\ln(dT/dt\,/T_m^2)$ versus $1/T_m$ should give a straight line which has a slope $-E_a/R$ and an intercept of $\ln(AR/E_a)$.

From Reference 3 the following equation is obtained for the solution of "x":

$$\ln\left(\frac{1}{1-x}\right) = \frac{ART^2}{E_a(dT/dt)}\ e^{-E_a/RT}\left(1 - \frac{2RT}{E_a}\right) \qquad (2.7)$$

III. EXPERIMENTAL

A. MATERIAL

Since the β-HMX form is the most stable of the four polymorphs of HMX it was used in this work. The commercial salt was purified by recrystallization from an acetone solution using water precipitation. This was repeated until no trace of RDX was detectable by thin layer chromatography techniques which use diphenylamine exposed to ultraviolet light as the indicators [4].

B. APPARATUS

The apparatus used to study thermal decomposition of β-HMX was a "du Pont 900 Differential Thermal Analyzer" capable of measuring exotherms or endotherms as a function of sample temperature with variable starting temperatures and heating rates.

C. CHANGE IN HEATING RATE

In the DTA measurements the sample of 0.4 mg. of β-HMX and also the reference glass beads were loaded in a capillary tube 2 mm. in diameter. The reaction then proceeds in 1 atmosphere of air with the change in heating rate at a starting temperature of 220°C, measured by a chromel-alumel thermocouple.

D. ISOTHERMAL EXPERIMENT

A time base accessory adapted to the 900 DTA was used in order to change the sample temperature on the X-axis to

the time scale. The temperatures that were used in this experiment were between 505° and 549°K.

IV. RESULTS

In Figure 1, the sample β-HMX has been "analyzed" in 1 atm. of air with a heating rate of 2°C/min. The most significant features are the endothermic and exothermic process at 192°C and 276°C respectively. The endothermic process is the crystal phase change β-δ transformation of the β-polymorph [6] and it is an irreversible transformation [9].

Examination of the DTA trace shows that the decomposition of δ-HMX is very exothermic. These thermal decomposition exotherms also exhibit very small endotherms which are due to the formation of a liquid phase during thermal decomposition and at the phase change β-δ it also exhibits very small endotherms. This phenomenon of the formation of a liquid phase during solid state decomposition has been observed in the other organic solids [6].

Figure 2 shows the DTA traces of α, β, γ, and δ-HMX [5].

Figures 3-3A show that the T_m values increase with increase in heating rate.

In Figures 4-12, curves are shown plotting the temperature of β-HMX in °K versus time-in-seconds for the heating rates 0.5°, 1.0°, 1.5°, 2.0°, 2.5°, 3.0°, 3.5°, and 4.5°C/min. From these plots, three separate slopes can be seen. These are at the temperature ranges of 473°-506°K, 506°-514°K, and above 514°K.

In Figure 13 the curve of $\ln(dT/dt \big/ T_m^2)$ versus $1000/T_m$ is shown for Figures 4-12. From the first portion of 473°-506°K is obtained E_a = 44.20 Kcal/mole.

$$\frac{dx}{dt} = 10^{15.21}(1-x)e^{-E_a/RT}$$

$$\frac{dT}{dt} = 10^{15.21} \cdot \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$$

Figure 14 shows the data from Figures 4-12, the second portion of 506°-514°K from which is obtained E_a = 63.23 Kcal/mole.

$$\frac{dx}{dt} = 10^{22.89}(1-x)e^{-E_a/RT}$$

$$\frac{dT}{dt} = 10^{22.89} \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$$

Figure 15 shows the data from Figures 4-12, the result of the third portion of the temperature above 514°K from which is obtained E_a = 52.65 Kcal/mole.

$$\frac{dx}{dt} = 10^{18.67}(1-x)e^{-E_a/RT}$$

$$\frac{dT}{dt} = 10^{18.67} \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$$

From Reference 2 the mass spectrometric study of the thermal products from β-HMX was found. The observed activation energies reported are 499°-518°K, 45 Kcal/mole;

518°-541°K, 10-15 Kcal/mole; and 541°-533°K, 52 Kcal/mole by gas accumulation and gas removal to prevent further reaction. Comparing these data with our values is difficult but the general range is good and our values of 44.20 Kcal/mole in the range of 473°-506°K agrees with the authors' value of 45 Kcal/mole in the range of 499°-518°K.

V. DISCUSSION

Reference 2 states: "Several causes for the acceleration of the decomposition of β-HMX to a constant rate have, therefore, to be considered:

1. Progressive melting as a result of lowered melting point by the products.

2. Self-heating.

3. Autocatalysis by-products, both solid and gaseous.

4. Acceleration due to structural factors such as an increase in the number of nuclei or in the surface area analogous to the inorganic solids.

Either 1 or 3 can account for the increasing rate which would compensate for the fall in rate as the material is consumed."

From Reference 2 the observed activation energies on the middle range did not agree with the author. Isothermal experiments were used to prove activation energies between 505°-514°K. An activation energy of 65.79 Kcal/mole was observed which agrees with the change in heating rate experiment and Reference 9, which was found to be 63 ± 2 Kcal/mole.

In the isothermal experiment, three different observed activation energies are found which are due to the acceleratory period, intermediate period and decay period agreeing with Reference 10. These three periods are shown very clearly in the temperature range of 505°-514°K, but above

514°K only the intermediate period is shown because the reaction is very fast at high temperatures. The activation energy from the isothermal experiment is 52.67 Kcal/mole which agrees with the change in heating rate and with A. J. B. Robertson [8].

The calculations were performed on the WANG 700A and the IBM 360/67. Intercept and slope in the Figures 4-15 and the Figures 17-20 were calculated by the WANG 700A n^{th} order regression and in the Figures 4-12 the n^{th} order regression to get the equation T = f(t) was also used. When the time is known this equation can be used to predict the temperature for a known heating rate.

When the decomposition of β-HMX is accelerated, the DTA plots show three separate peaks indicating a change of reaction mechanism. This is also indicated by the activation energy plots which contain three different slopes and three different activation energies.

TABLE I.

Temperature between 473°-506°K

$\frac{dT}{dt}$ Experimental	T_m °K	$\frac{dT}{dt}$ Calculation	% Deviation From Experiment
0.0214	536	0.0198	7.48
0.0275	541	0.0296	- 7.64
0.0390	545.5	0.0423	- 8.46
0.0416	545.5	0.0423	- 2.64
0.0555	547.5	0.0495	10.09
0.0494	548.1	0.0518	- 5.87
0.0677	551.1	0.0654	3.40
0.0830	551.9	0.0695	16.26
0.0765	554.5	0.0848	- 10.85

TABLE II.

Temperature between 506°-514°K

$\frac{dT}{dt}$ Experimental	T_m °K	$\frac{dT}{dt}$ Calculation	% Deviation From Experiment
0.0146	537	0.0129	11.64
0.0212	543	0.0254	-19.81
0.0288	545	0.0318	- 10.42
0.0406	547	0.0396	2.46
0.0505	550.9	0.0607	- 20.20
0.0491	548.8	0.0483	1.63
0.0617	550	0.0550	10.86
0.0727	551.9	0.0676	7.01
0.0929	554.5	0.0895	3.66

TABLE III.

Temperature above 514°K

$\frac{dT}{dt}$ Experimental	T_m °K	$\frac{dT}{dt}$ Calculation	% Deviation From Experiment
0.0229	538.9	0.0227	0.87
0.0324	542.5	0.0319	1.54
0.0386	545.4	0.0418	- 8.29
0.0517	547.2	0.0493	4.64
0.0557	550.5	0.0667	- 19.75
0.0625	549.8	0.0626	- 0.16
0.0703	550.5	0.0667	5.12
0.0858	551.5	0.0731	14.80
0.0929	554.5	0.0958	- 3.12

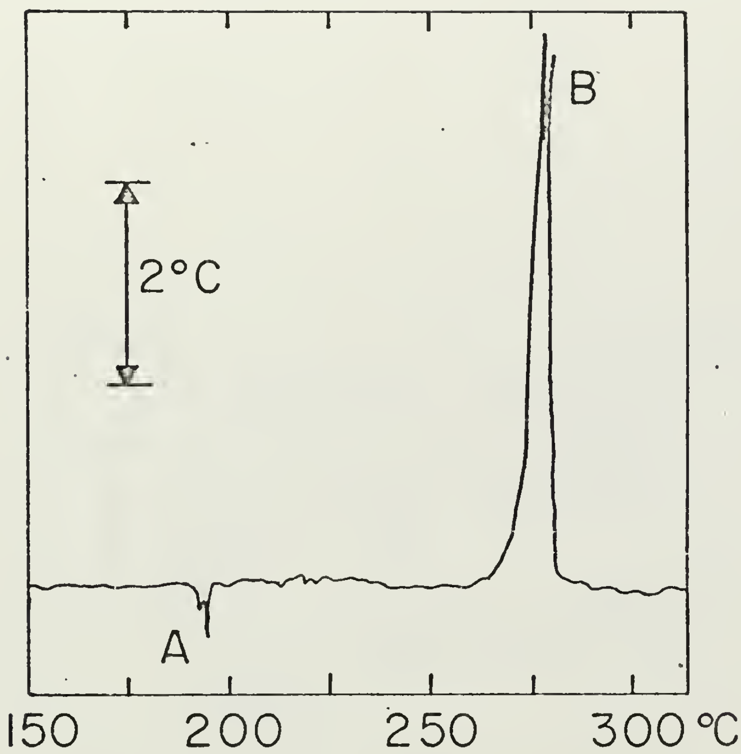

Figure I. The DTA traces of β−HMX (experimental) at I atmosphere, heating rate 2°C/min shows endotherm at A and exotherm at B.

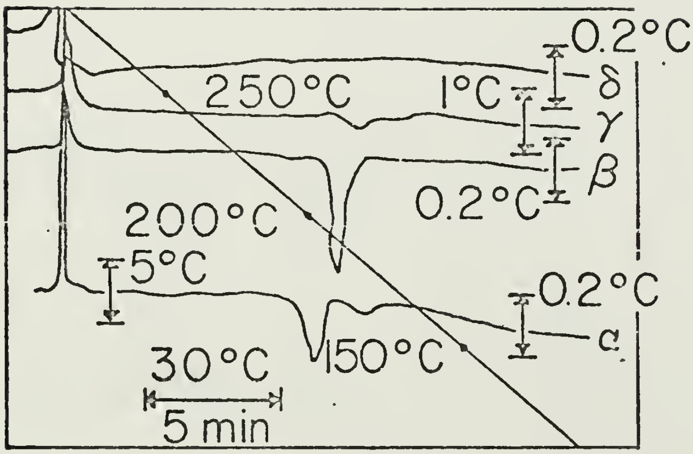

Figure 2. The DTA traces of α, β, γ, δ-HMX using a heating rate 6°C/min and a flowing (10 liter/h) atmosphere of dry He [5].

Sample: α (15 mg)
β (15 mg)
γ (15 mg)
δ (2 mg)

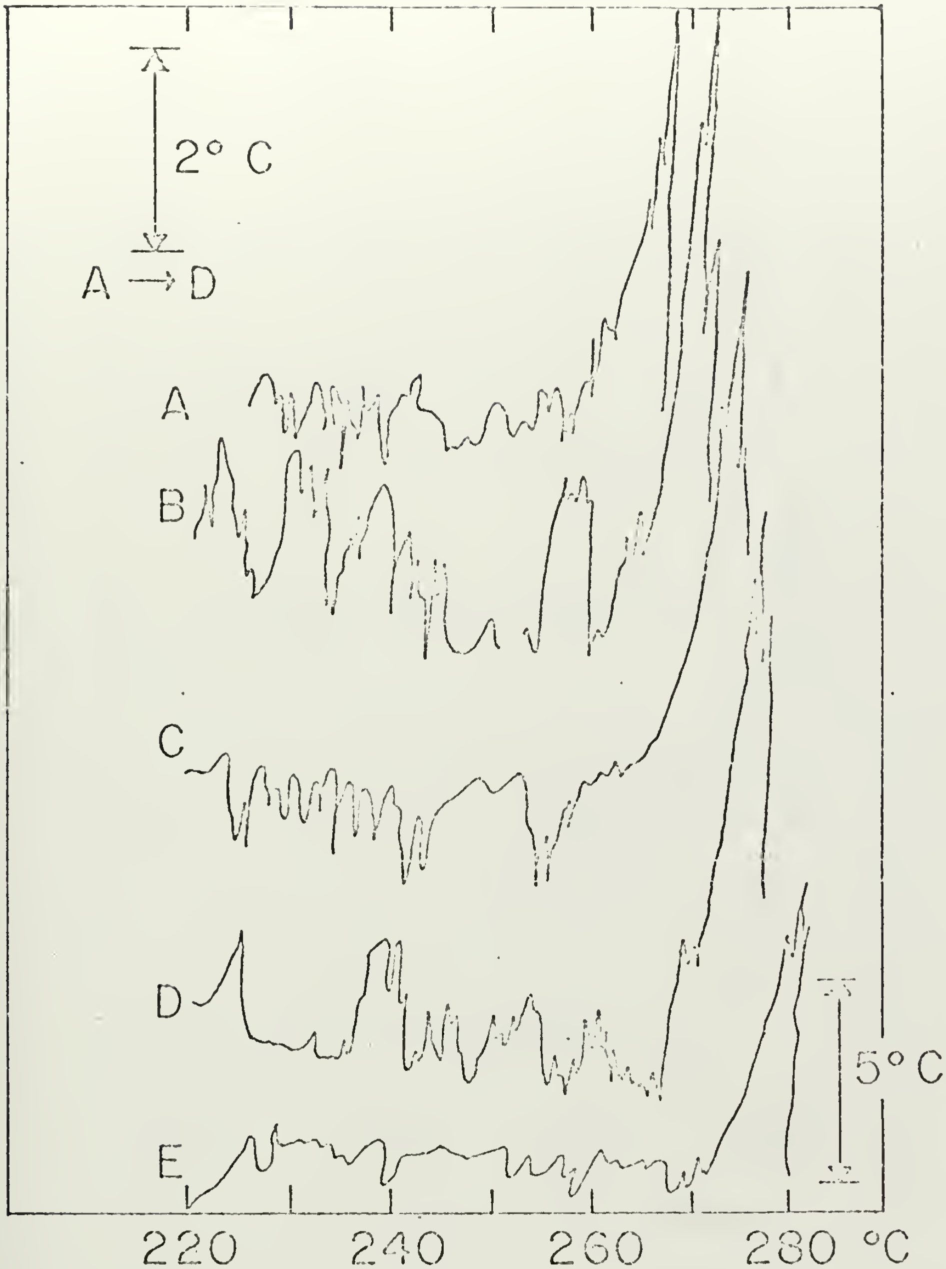

Figure 3. Experimental for β-HMX at different heating rates: A : heating rate = 0.5° C/min.
B : heating rate = 1.0° C/min.
C : heating rate = 1.5° C/min.
D : heating rate = 2.0° C/min.
E : heating rate = 2.5° C/min.

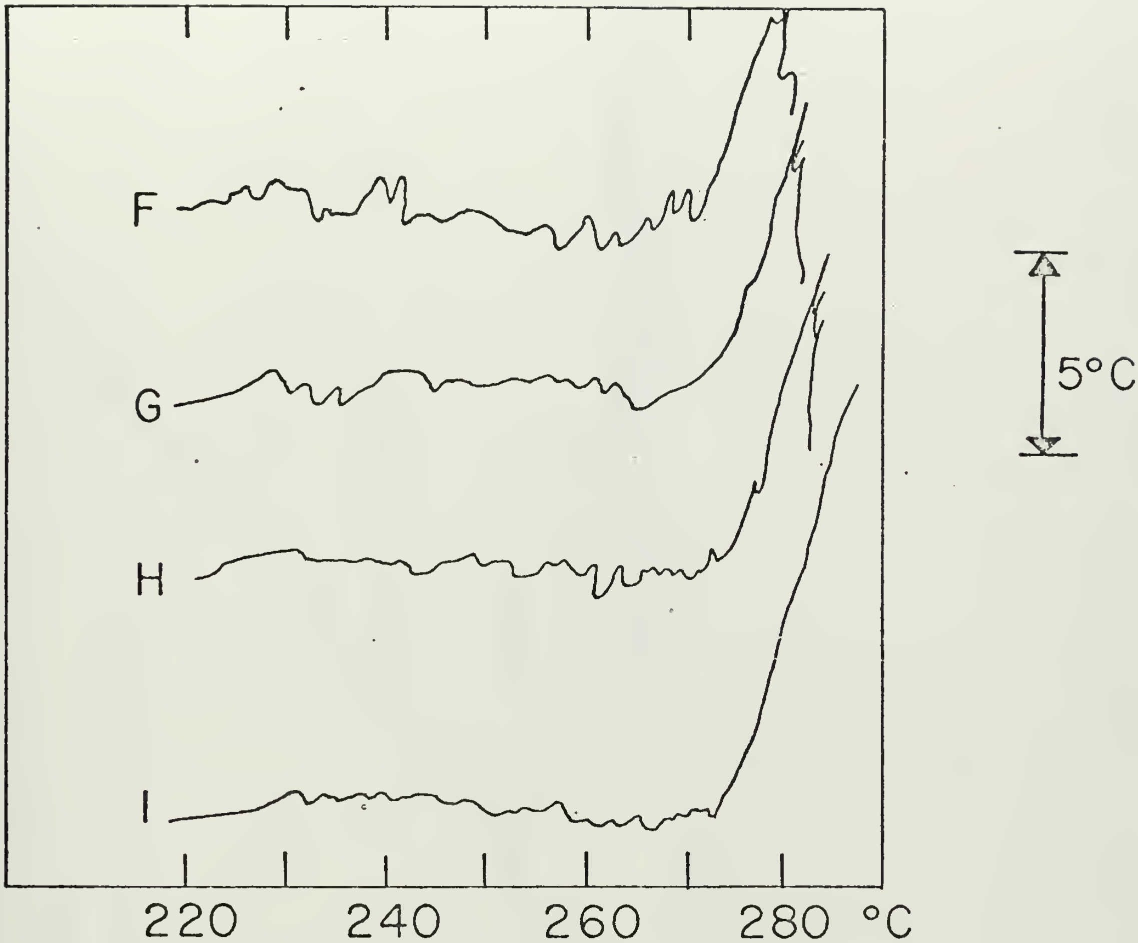

Figure 3A. Experimental DTA traces for β-HMX at different rates:

F: heating rate = 3.0° C/min.
G: heating rate = 3.5° C/min.
H: heating rate = 4.5° C/min.
I: heating rate = 5.0° C/min.

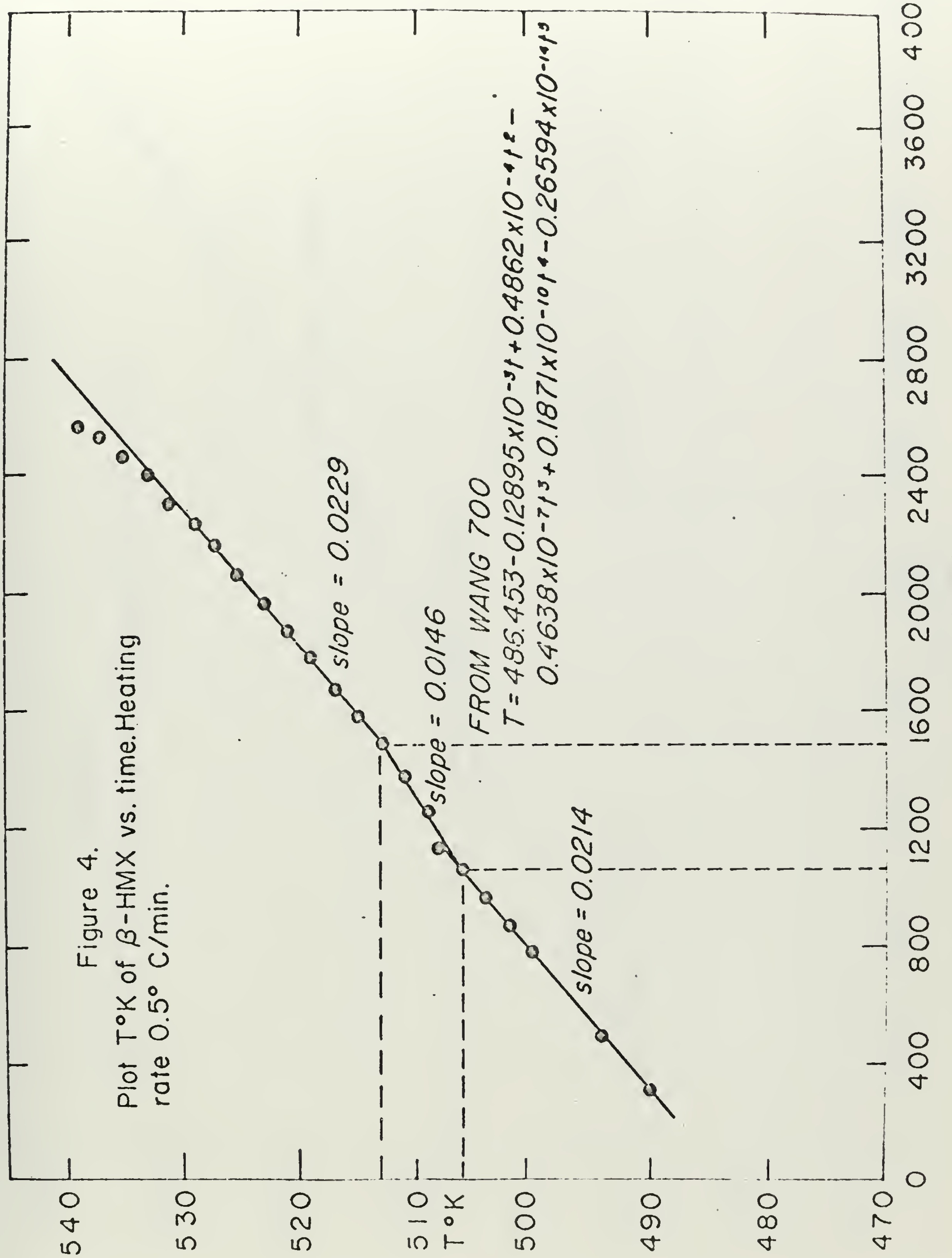

Figure 4.
Plot T°K of β-HMX vs. time. Heating rate 0.5° C/min.

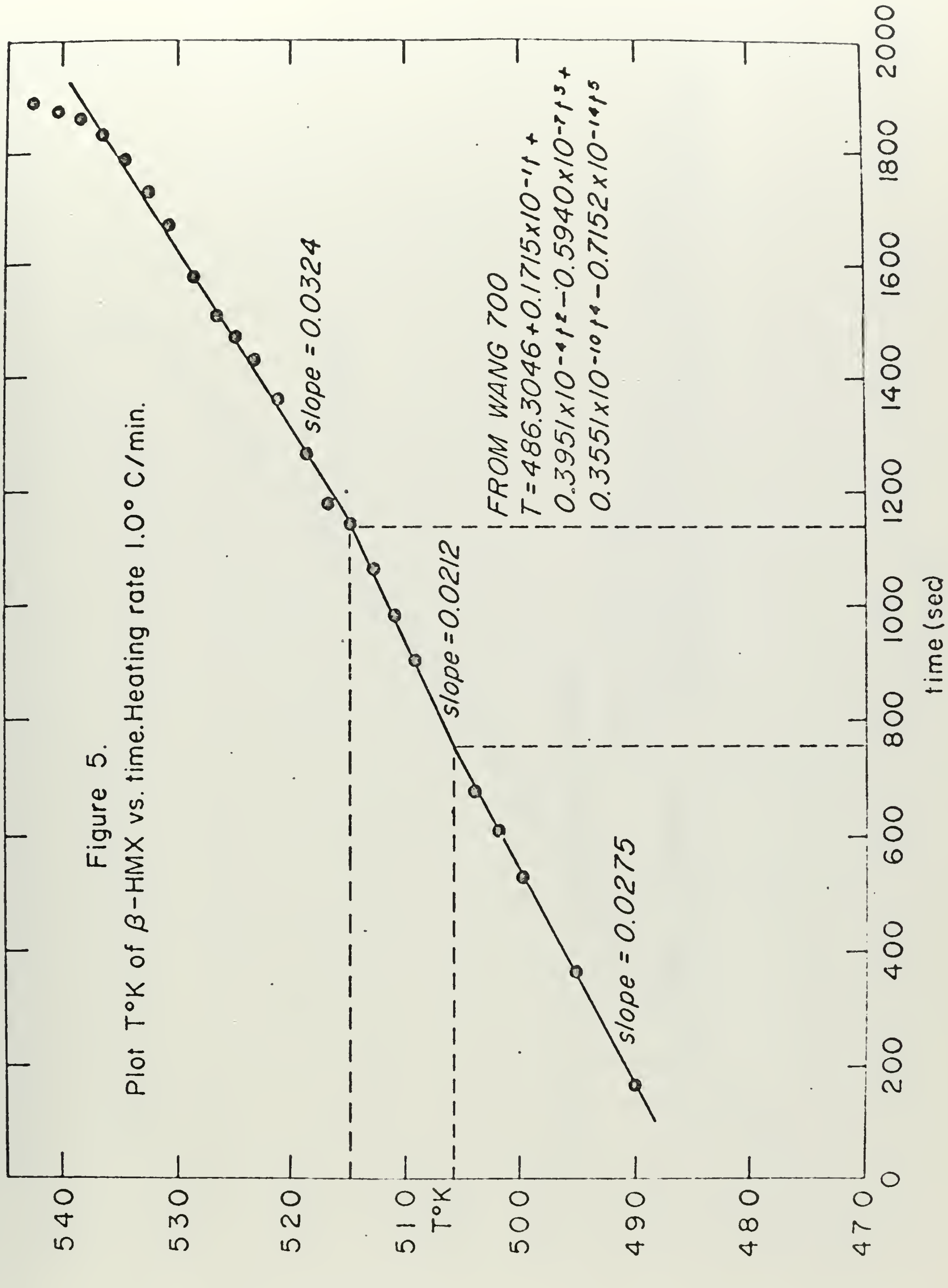

Figure 5.
Plot T°K of β-HMX vs. time. Heating rate 1.0° C/min.

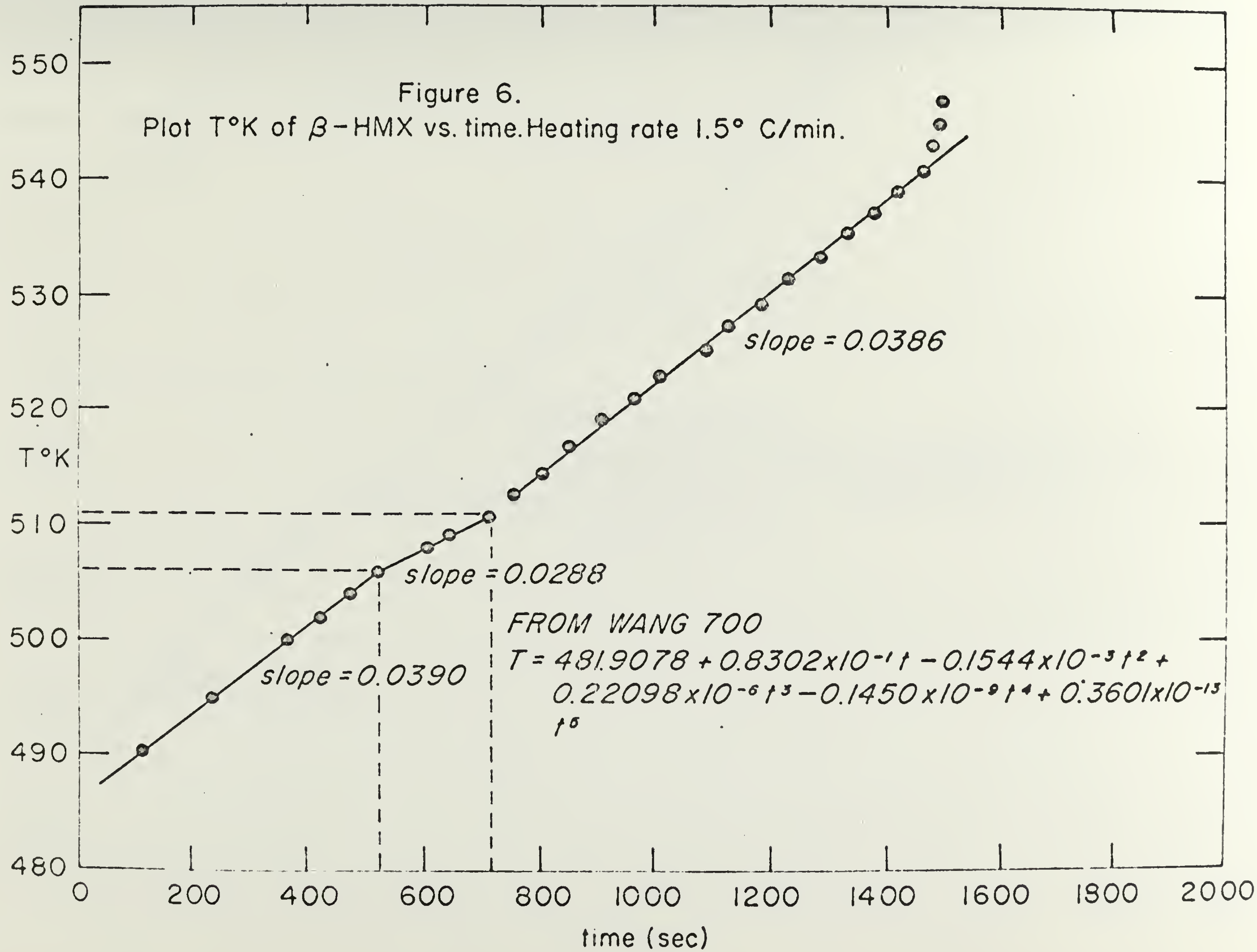

Figure 6.
Plot T°K of β-HMX vs. time. Heating rate 1.5° C/min.

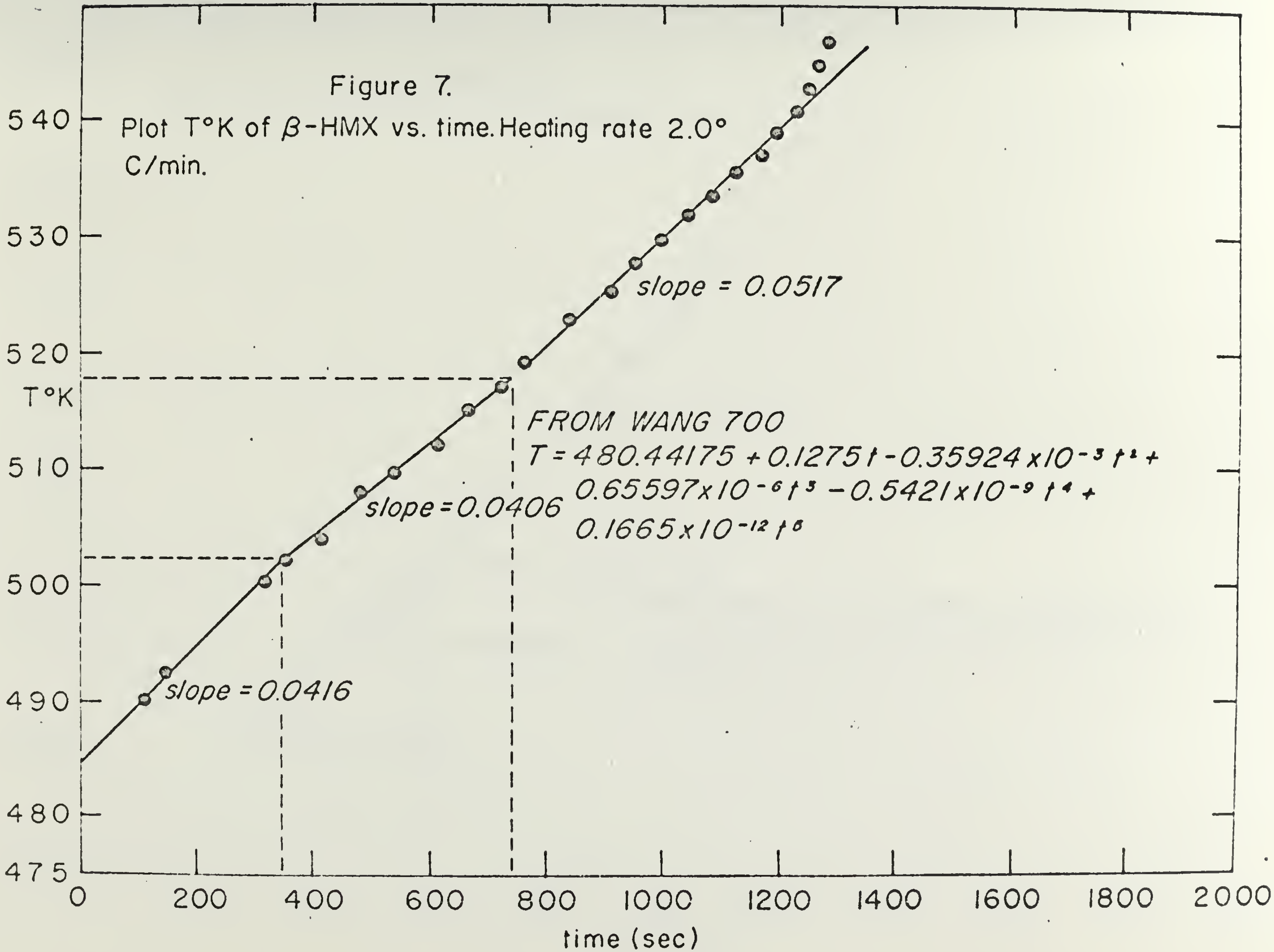

Figure 7.
Plot T°K of β-HMX vs. time. Heating rate 2.0° C/min.

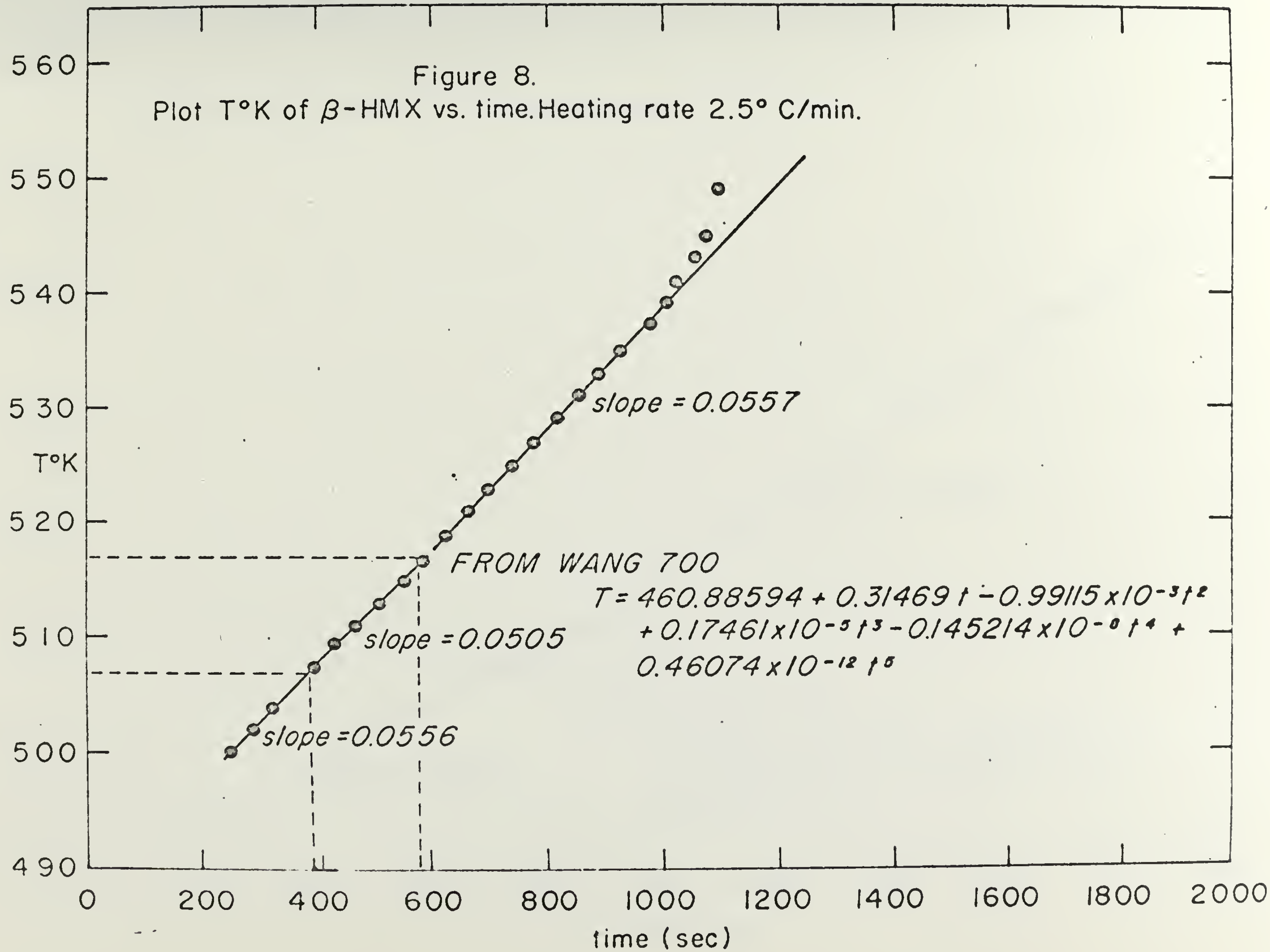

Figure 8.
Plot T°K of β-HMX vs. time. Heating rate 2.5° C/min.

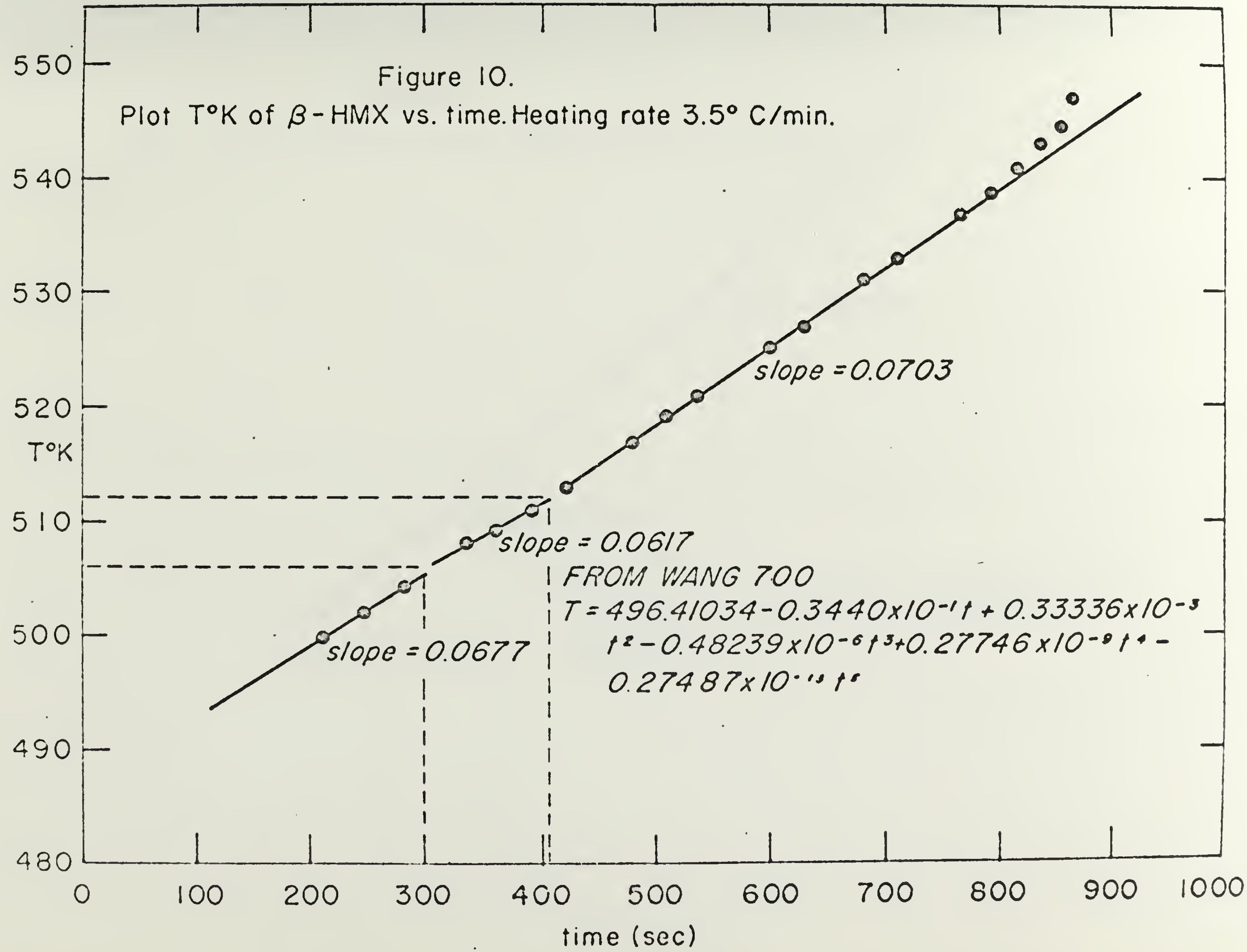

Figure 10.
Plot T°K of β-HMX vs. time. Heating rate 3.5° C/min.

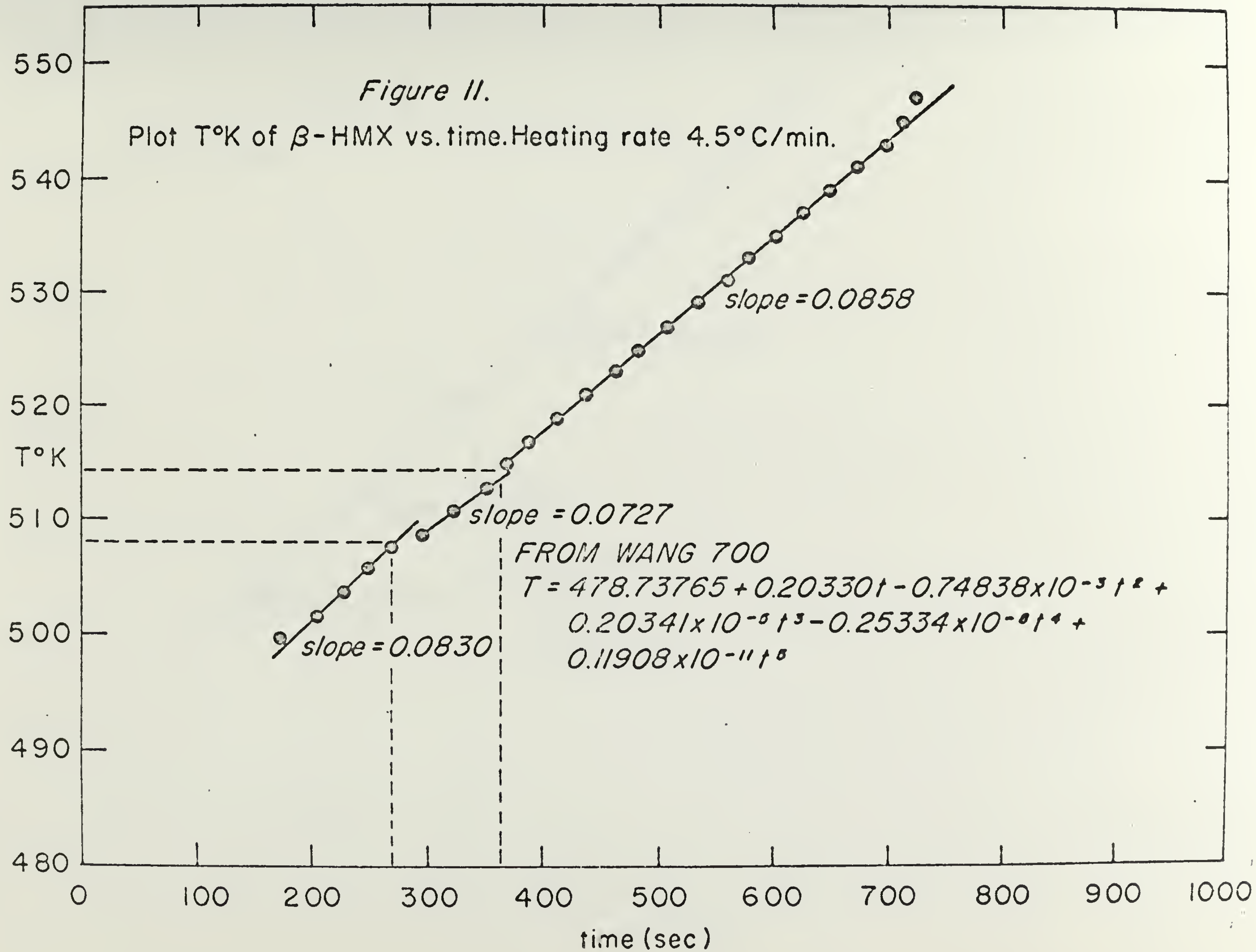

Figure 11.

Plot T°K of β-HMX vs. time. Heating rate 4.5°C/min.

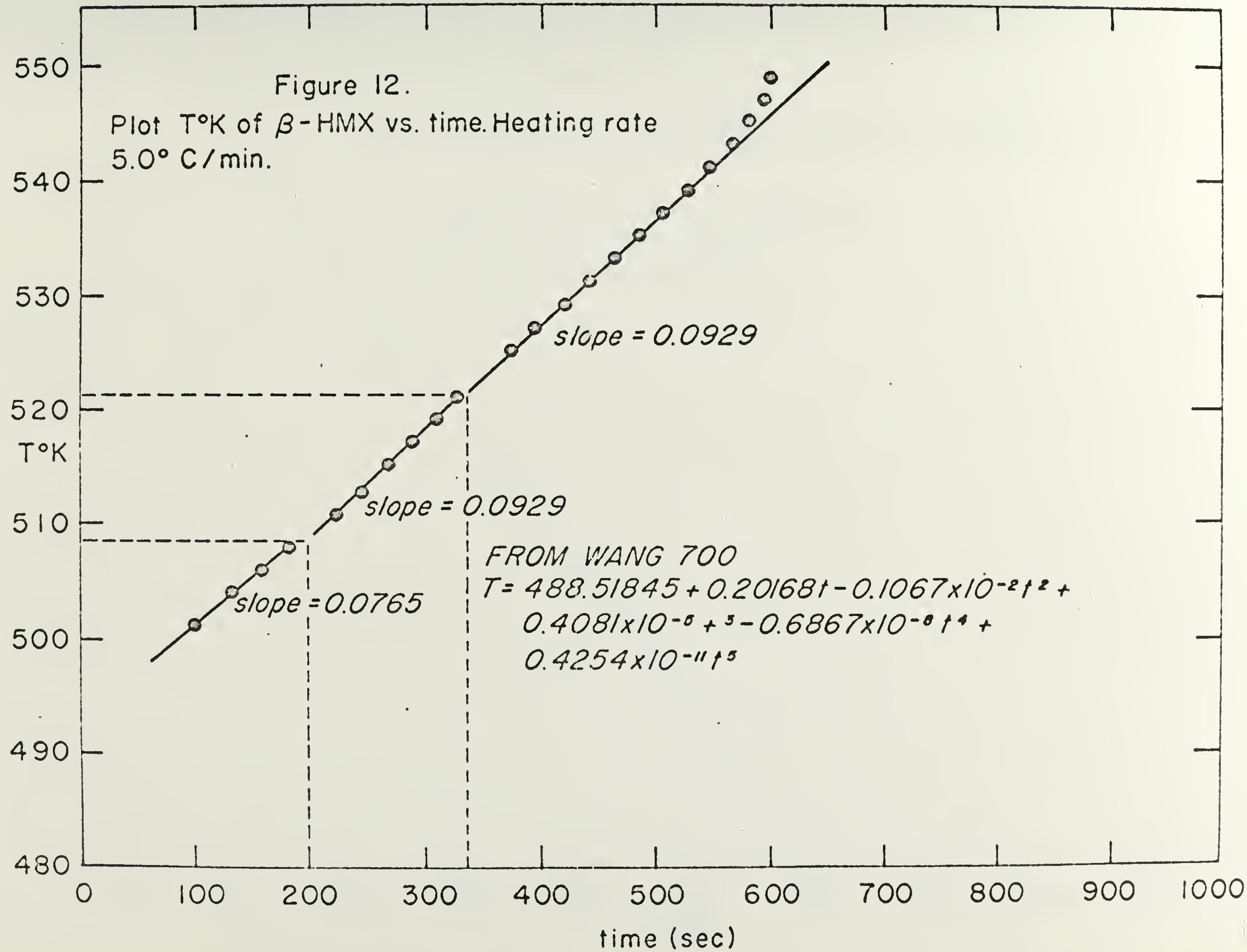

Figure 12.
Plot T°K of β-HMX vs. time. Heating rate 5.0° C/min.

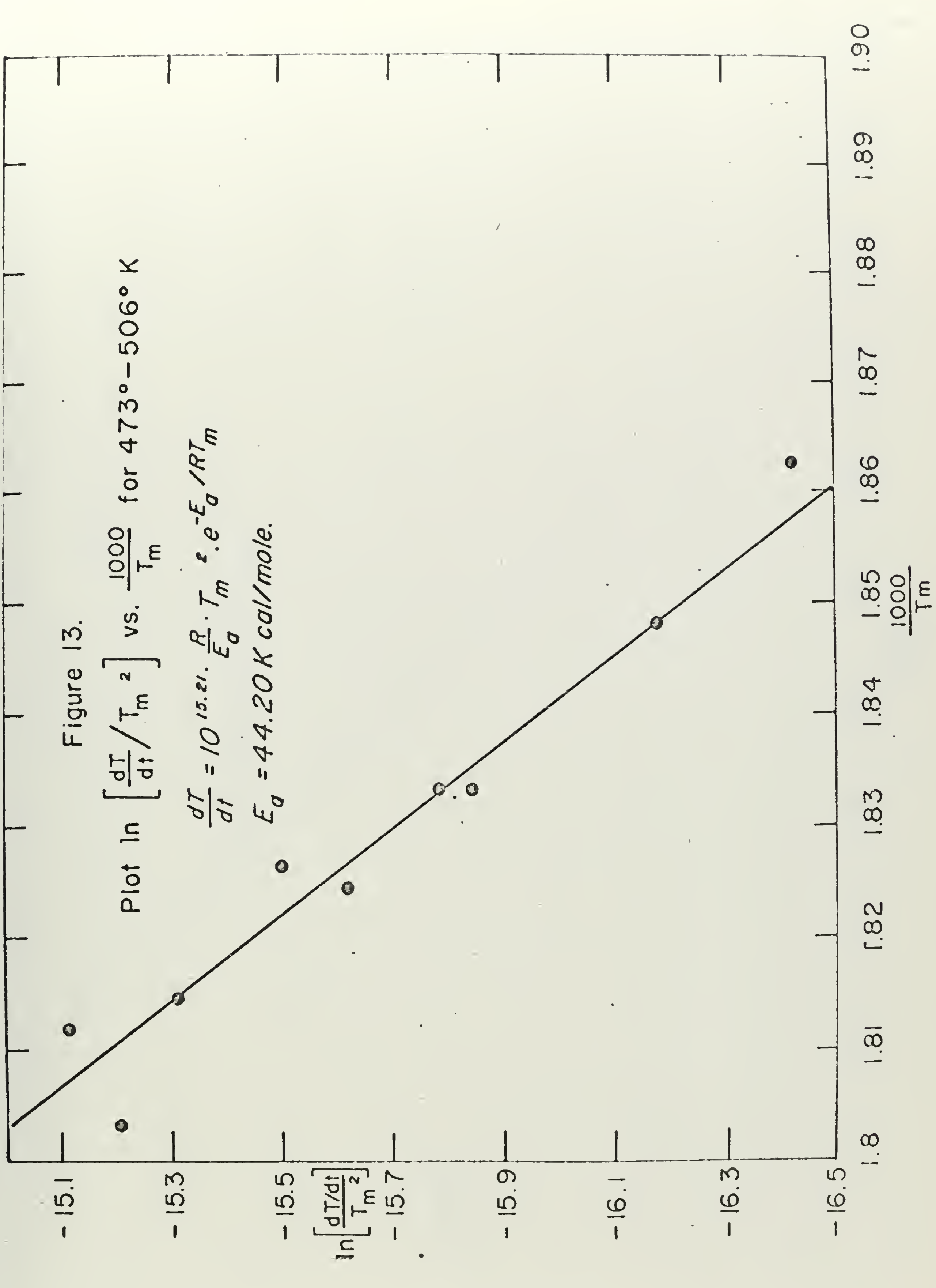

Figure 13.

Plot $\ln\left[\frac{dT}{dt}/T_m^2\right]$ vs. $\frac{1000}{T_m}$ for 473°–506° K

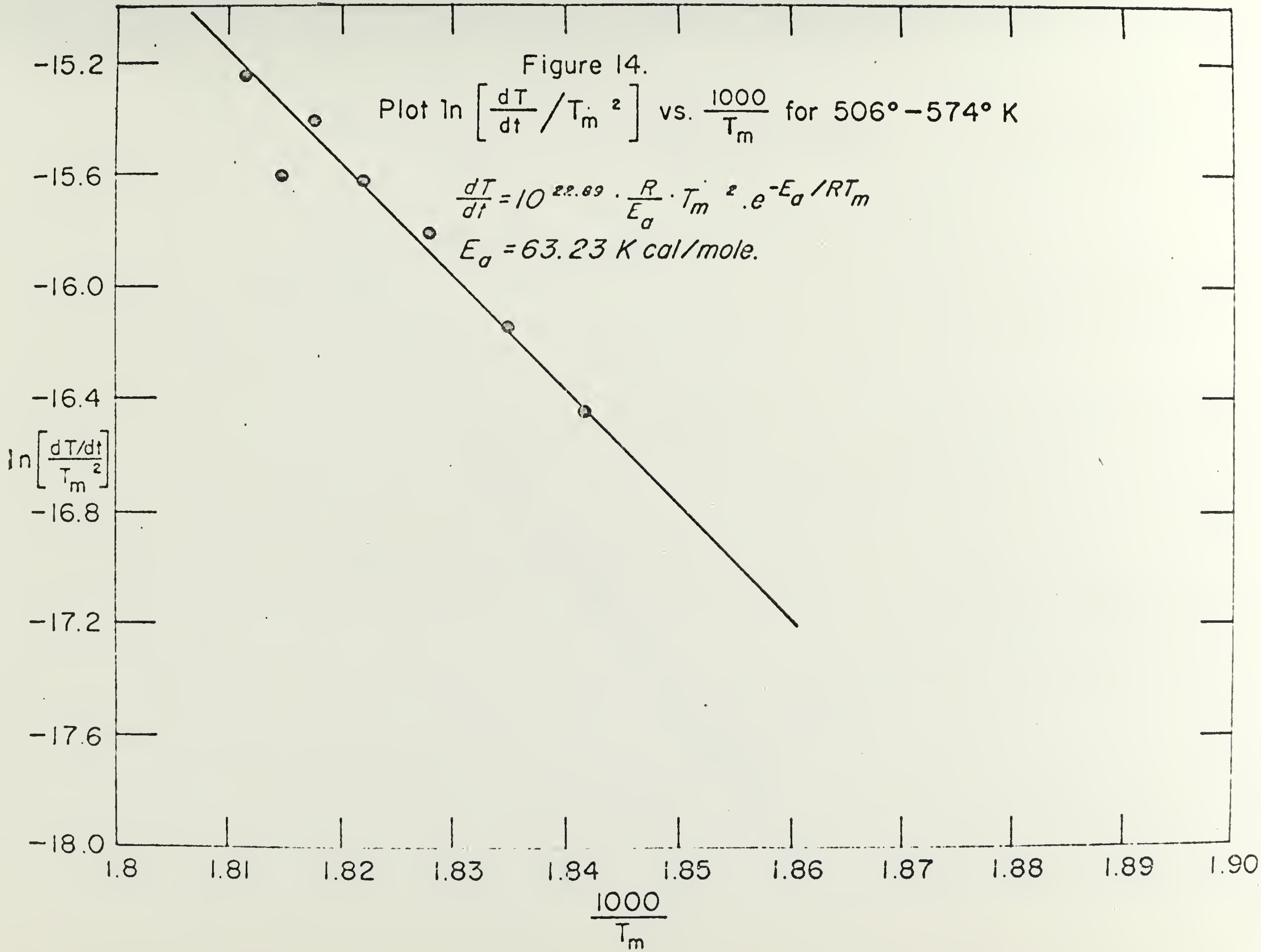

Figure 14.

Plot $\ln\left[\frac{dT}{dt}/T_m^2\right]$ vs. $\frac{1000}{T_m}$ for 506°–574° K

$\frac{dT}{dt} = 10^{22.89} \cdot \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$

$E_a = 63.23$ K cal/mole.

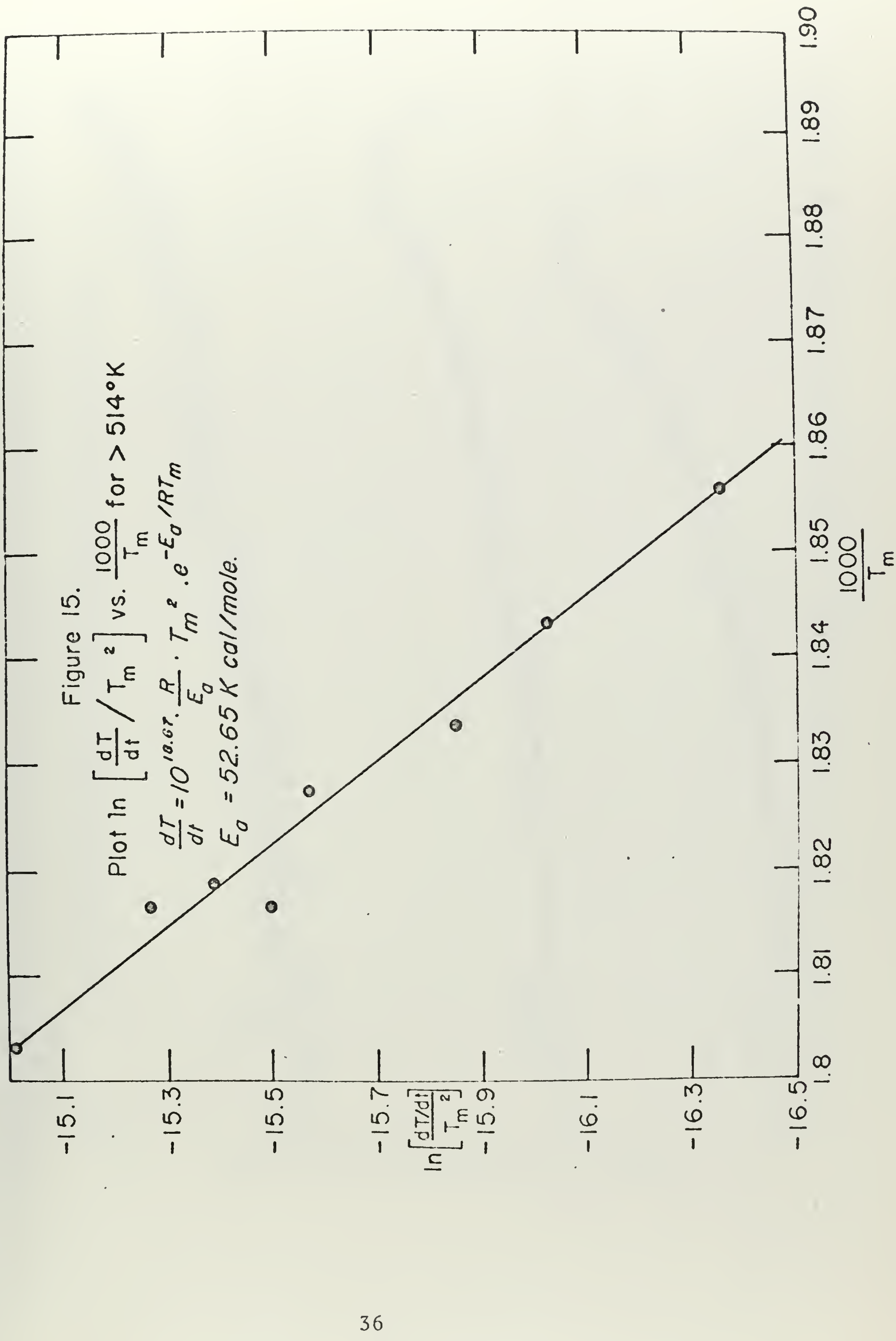

Figure 15.

Plot $\ln\left[\frac{dT}{dt} / T_m^{\,2}\right]$ vs. $\frac{1000}{T_m}$ for > 514°K

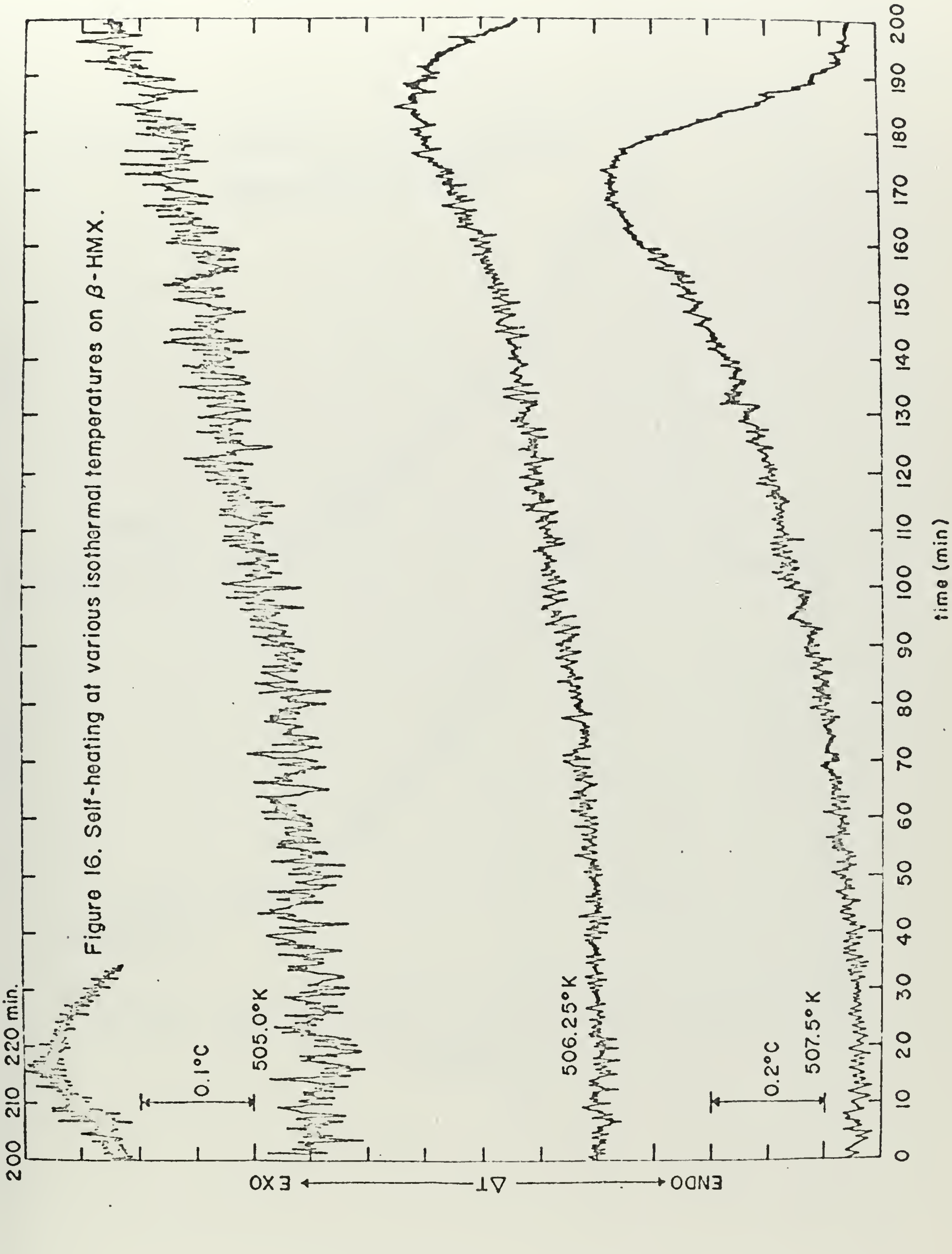

Figure 16. Self-heating at various isothermal temperatures on β-HMX.

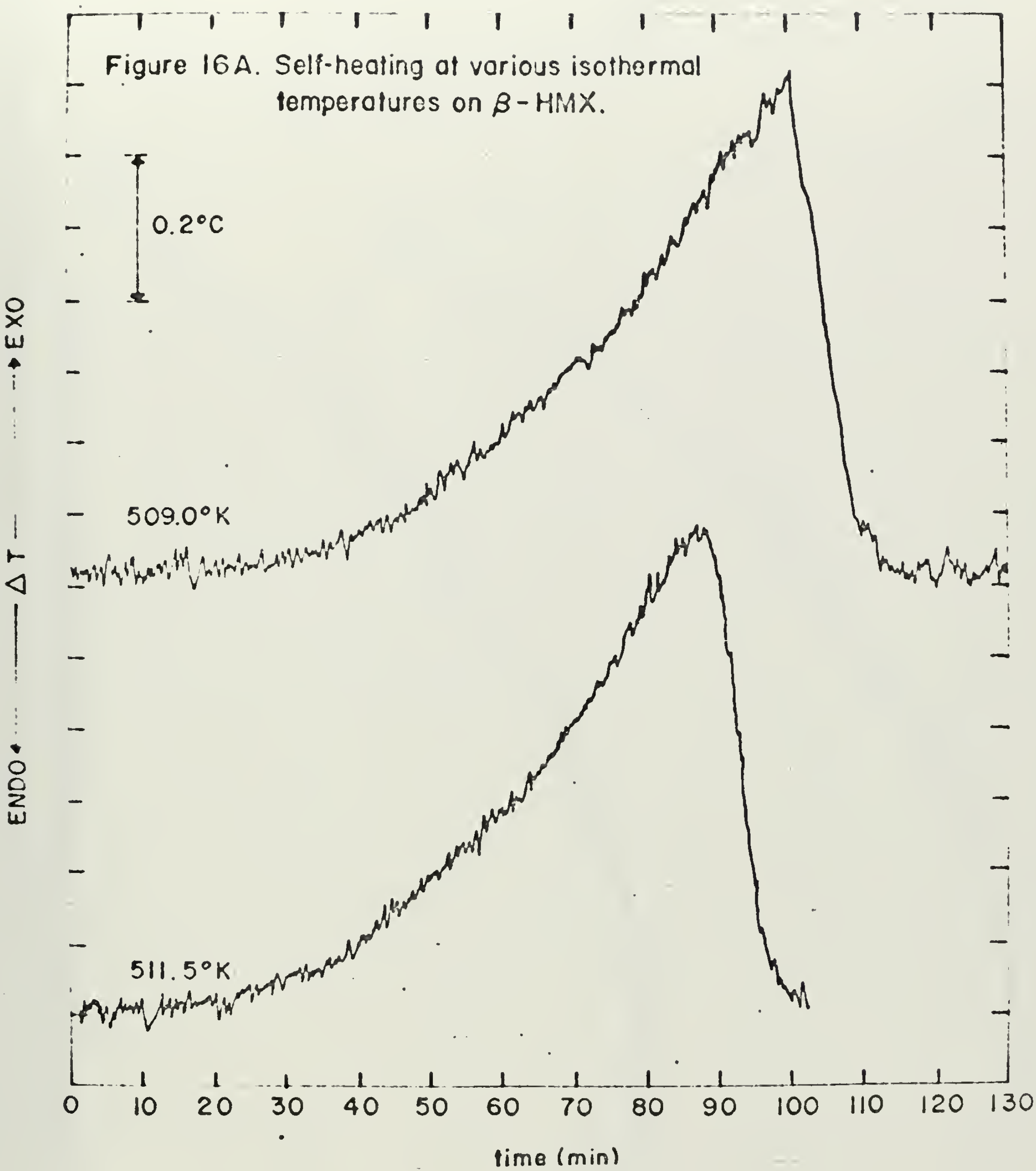

Figure 16A. Self-heating at various isothermal temperatures on β-HMX.
0.2°C
ENDO ← ΔT → EXO
509.0°K
511.5°K
0
10
20
30
40
50
60
70
80
90
100
110
120
130
time (min)

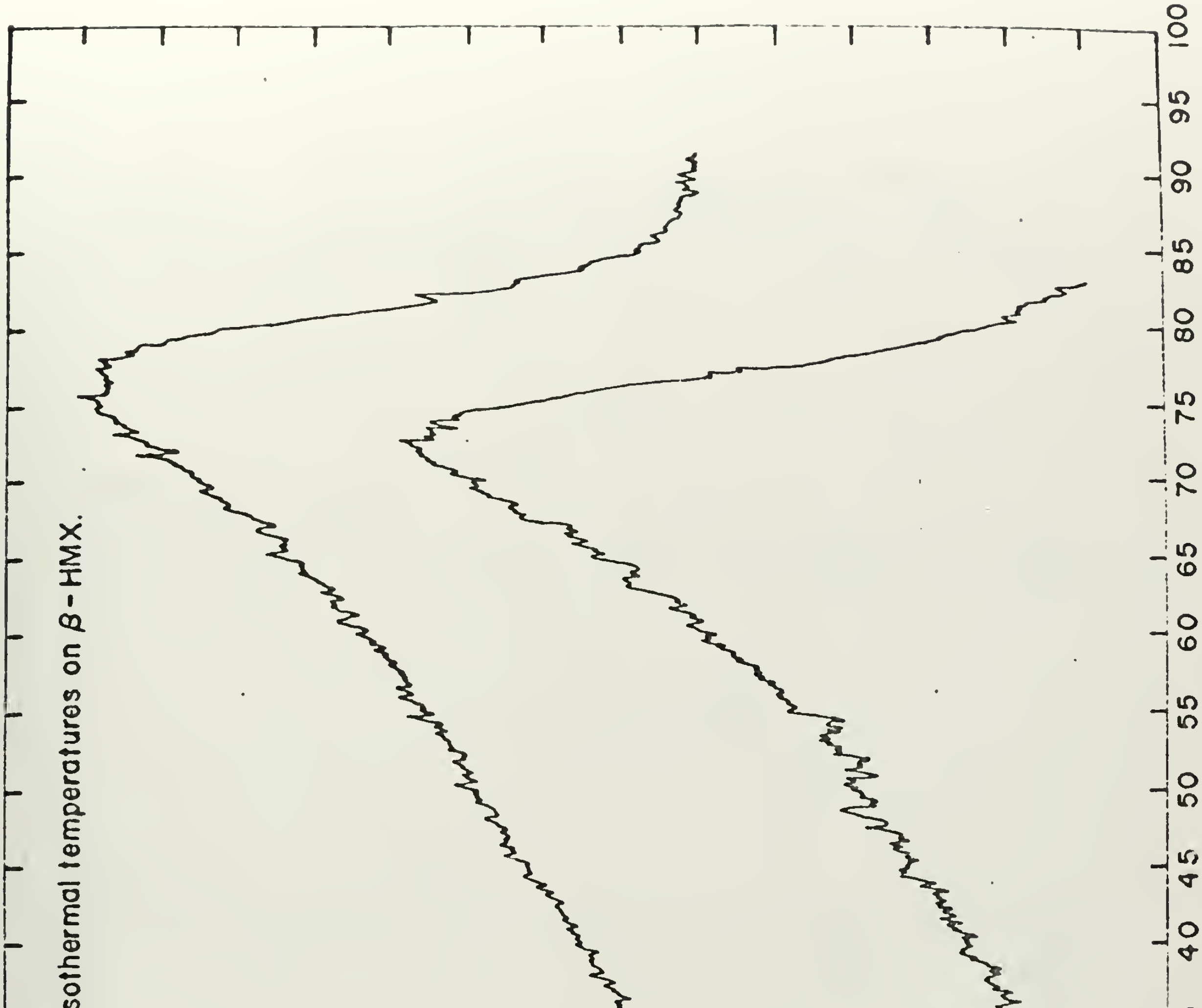

Figure 16B. Self-heating at various isothermal temperatures on β-HMX.

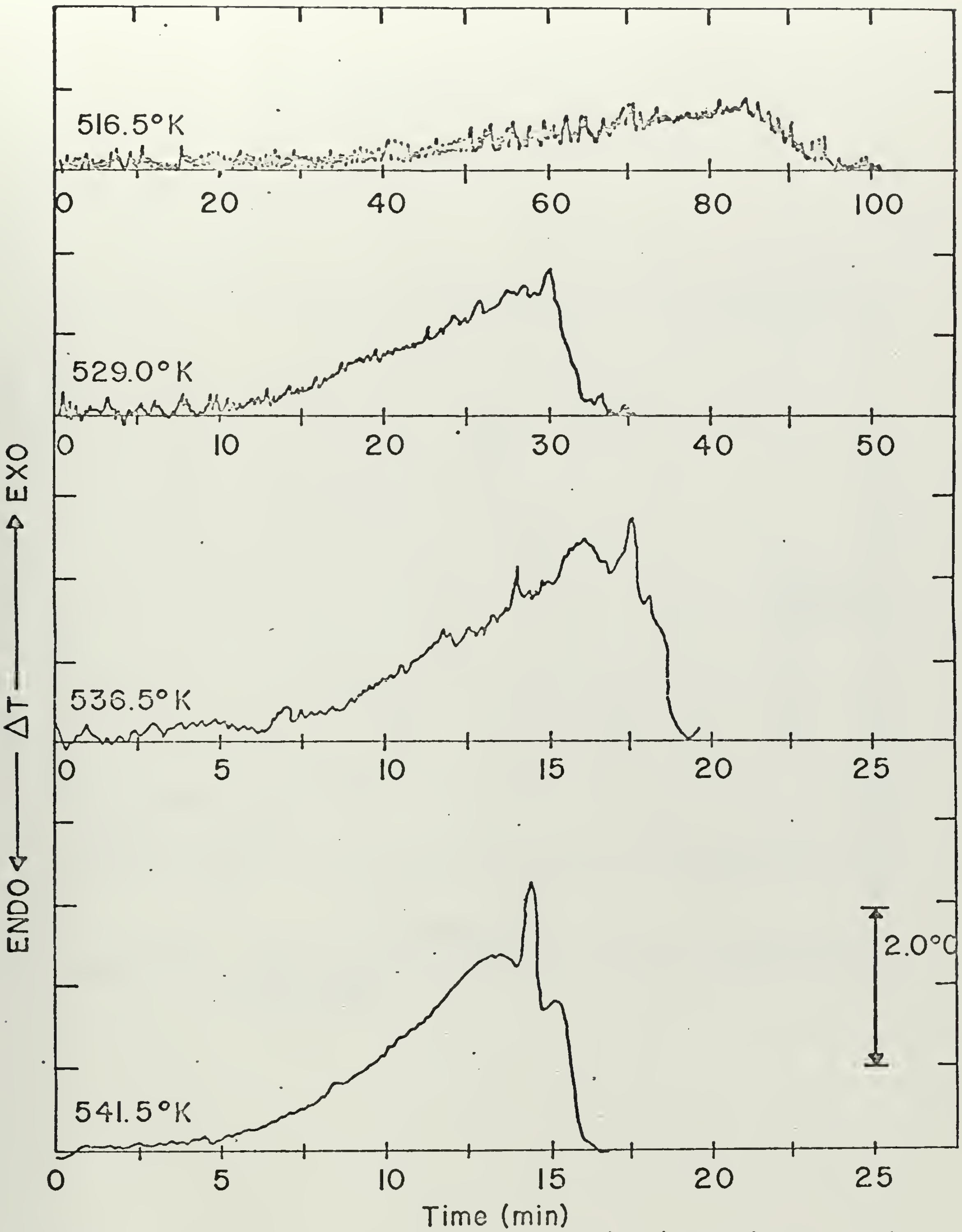

Figure 16C. Self-heating at various isothermal temperatures on β-HMX.

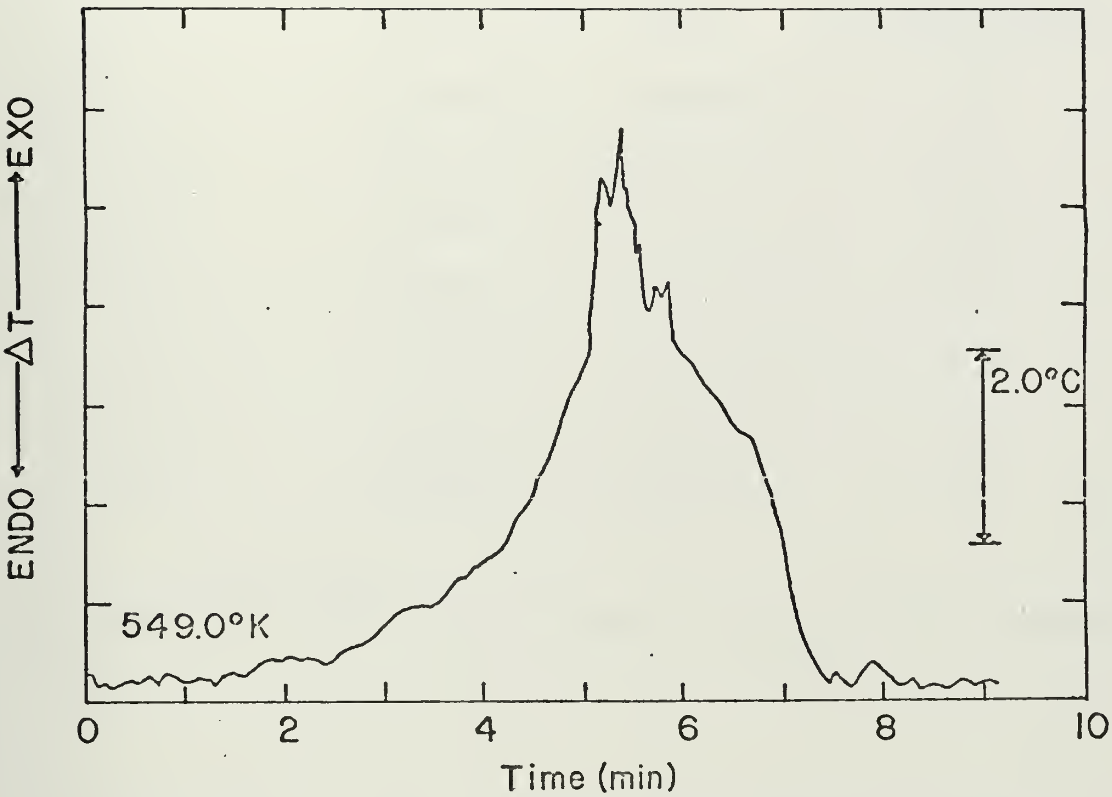

Figure 16D. Self-heating at various isothermal temperatures on β-HMX.

TABLE IV-A

Temperature 505°-514°K

ISOTHERMAL EXPERIMENT

ACCELERATORY PERIOD

T°K	k_1	k_{1cal}	% Deviation From Experiment
505.0	$.9083x10^{-4}$	$.9113x10^{-4}$	- 0.33
506.25	$.9528x10^{-4}$	$.1077x10^{-3}$	- 13.04
507.5	$.1316x10^{-3}$	$.1271x10^{-3}$	3.42
509.0	$.1825x10^{-3}$	$.1550x10^{-3}$	15.07
511.5	$.2121x10^{-3}$	$.2152x10^{-3}$	- 1.46
513.0	$.2694x10^{-3}$	$.2616x10^{-3}$	2.89
514.0	$.2763x10^{-3}$	$.2978x10^{-3}$	- 7.78

$k_1 = 10^{25.33} e^{-E_a/RT}$, from Figure 17, E_a = 67.86 Kcal/mole.

TABLE IV-B

Temperature 505°-514°K

ISOTHERMAL EXPERIMENT

INTERMEDIATE PERIOD

T°K	k_2	k_{2cal}	% Deviation From Experiment
505.0	$.4631 \times 10^{-3}$	$.4818 \times 10^{-3}$	- 4.04
506.25	$.5800 \times 10^{-3}$	$.5674 \times 10^{-3}$	2.17
507.5	$.6607 \times 10^{-3}$	$.6676 \times 10^{-3}$	- 1.04
509.0	$.8248 \times 10^{-3}$	$.8106 \times 10^{-3}$	1.72
511.5	$.1169 \times 10^{-2}$	$.1117 \times 10^{-2}$	4.45
513.0	$.1371 \times 10^{-2}$	$.1353 \times 10^{-2}$	1.31
514.0	$.1443 \times 10^{-2}$	$.1535 \times 10^{-2}$	- 6.37

$k_2 = 10^{25.43} e^{-E_a/RT}$, from Figure 18, $E_a = 66.42$ Kcal/mole.

TABLE IV-C

Temperature 505°-514°K

ISOTHERMAL EXPERIMENT

DECAY PERIOD

T°K	k_3	k_{3cal}	% Deviation From Experiment
505.0	$.2404 \times 10^{-3}$	$.2422 \times 10^{-3}$	- 0.75
506.25	$.2995 \times 10^{-3}$	$.2829 \times 10^{-3}$	5.54
507.5	$.3170 \times 10^{-3}$	$.3301 \times 10^{-3}$	- 4.13
509.0	$.4140 \times 10^{-3}$	$.3969 \times 10^{-3}$	4.13
511.5	$.5251 \times 10^{-3}$	$.5384 \times 10^{-3}$	- 2.53
513.0	$.6532 \times 10^{-3}$	$.6456 \times 10^{-3}$	1.16
514.0	$.7441 \times 10^{-3}$	$.7282 \times 10^{-3}$	2.14

$k_3 = 10^{23.69} e^{-E_a/RT}$, from Figure 19, $E_a = 63.09$ Kcal/mole.

TABLE V.

Temperature 516.5°-549.0°K

ISOTHERMAL EXPERIMENT

INTERMEDIATE PERIOD

T°K	k_2	k_{2cal}	% Deviation From Experiment
516.5	0.7245×10^{-3}	0.7440×10^{-3}	- 2.69
529.0	0.2736×10^{-2}	0.2502×10^{-2}	8.55
536.5	0.4868×10^{-2}	0.5040×10^{-2}	- 3.53
541.5	0.7094×10^{-2}	0.7954×10^{-2}	- 12.12
549.0	0.1653×10^{-1}	0.1552×10^{-1}	6.11

$k = 10^{19.16} e^{-E_a/RT}$, from Figure 20, E_a = 52.67 Kcal/mole

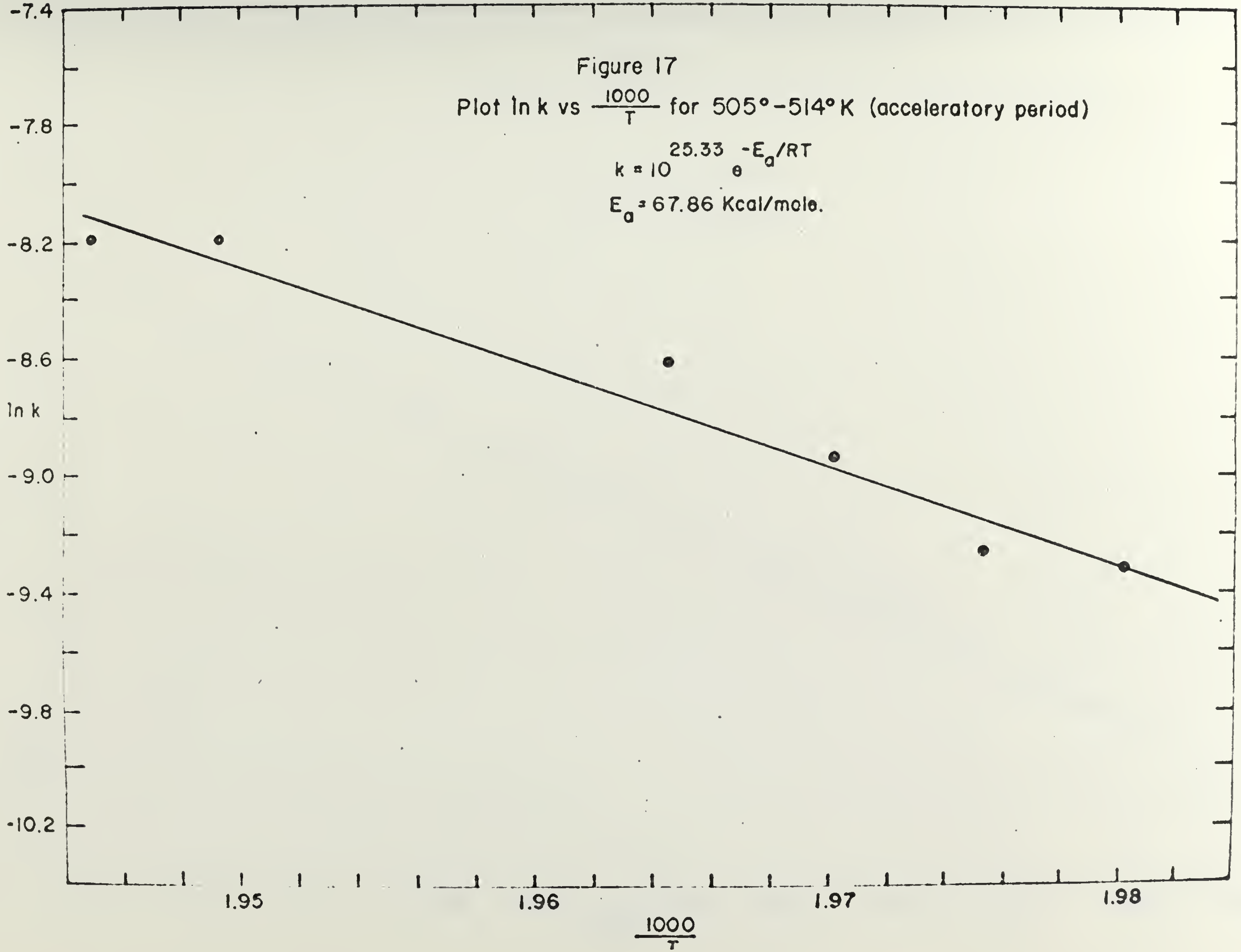

Figure 17

Plot ln k vs $\frac{1000}{T}$ for 505°-514°K (acceleratory period)

$k = 10^{25.33} e^{-E_a/RT}$

E_a = 67.86 Kcal/mole.

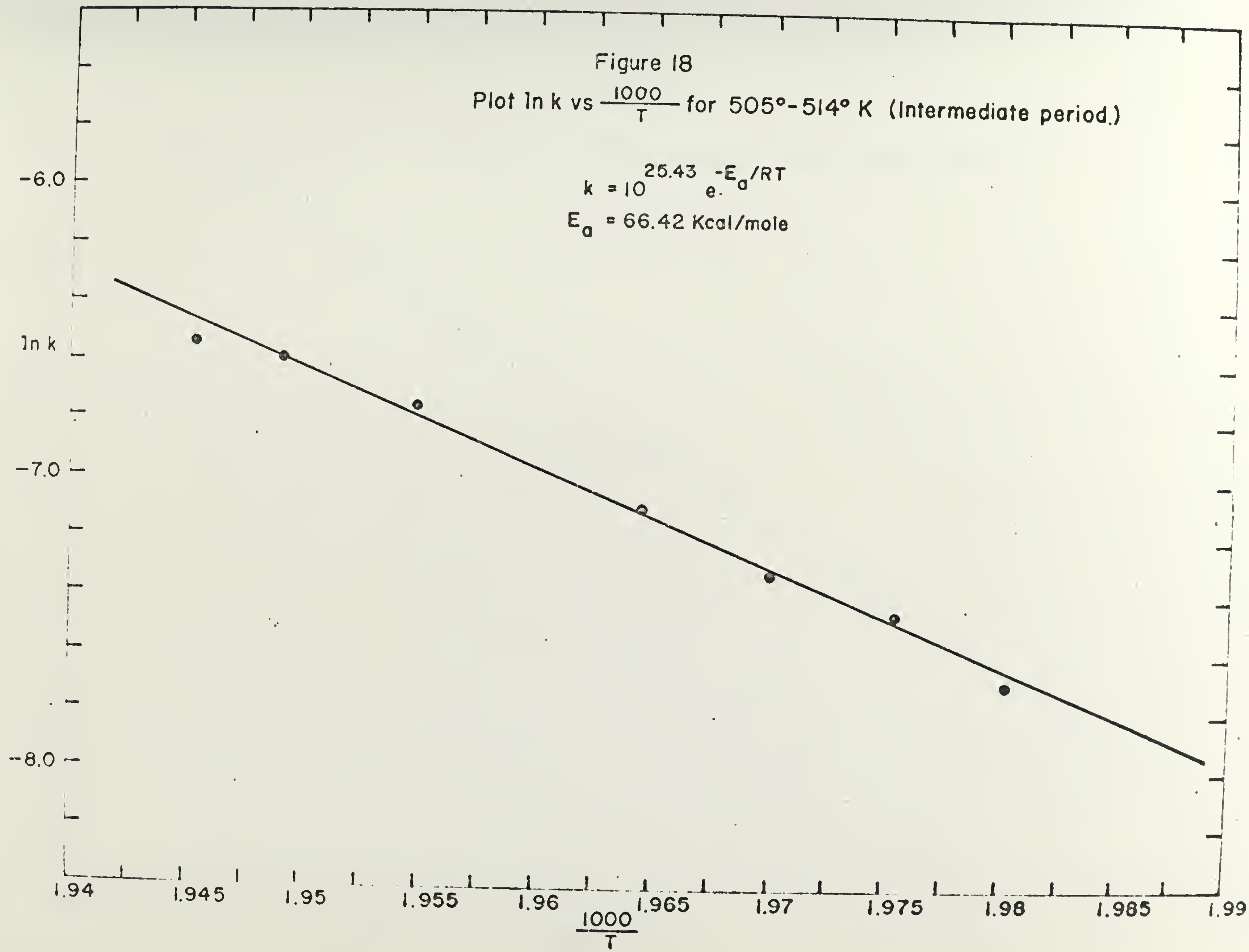

Figure 18

Plot ln k vs $\frac{1000}{T}$ for 505°-514° K (Intermediate period.)

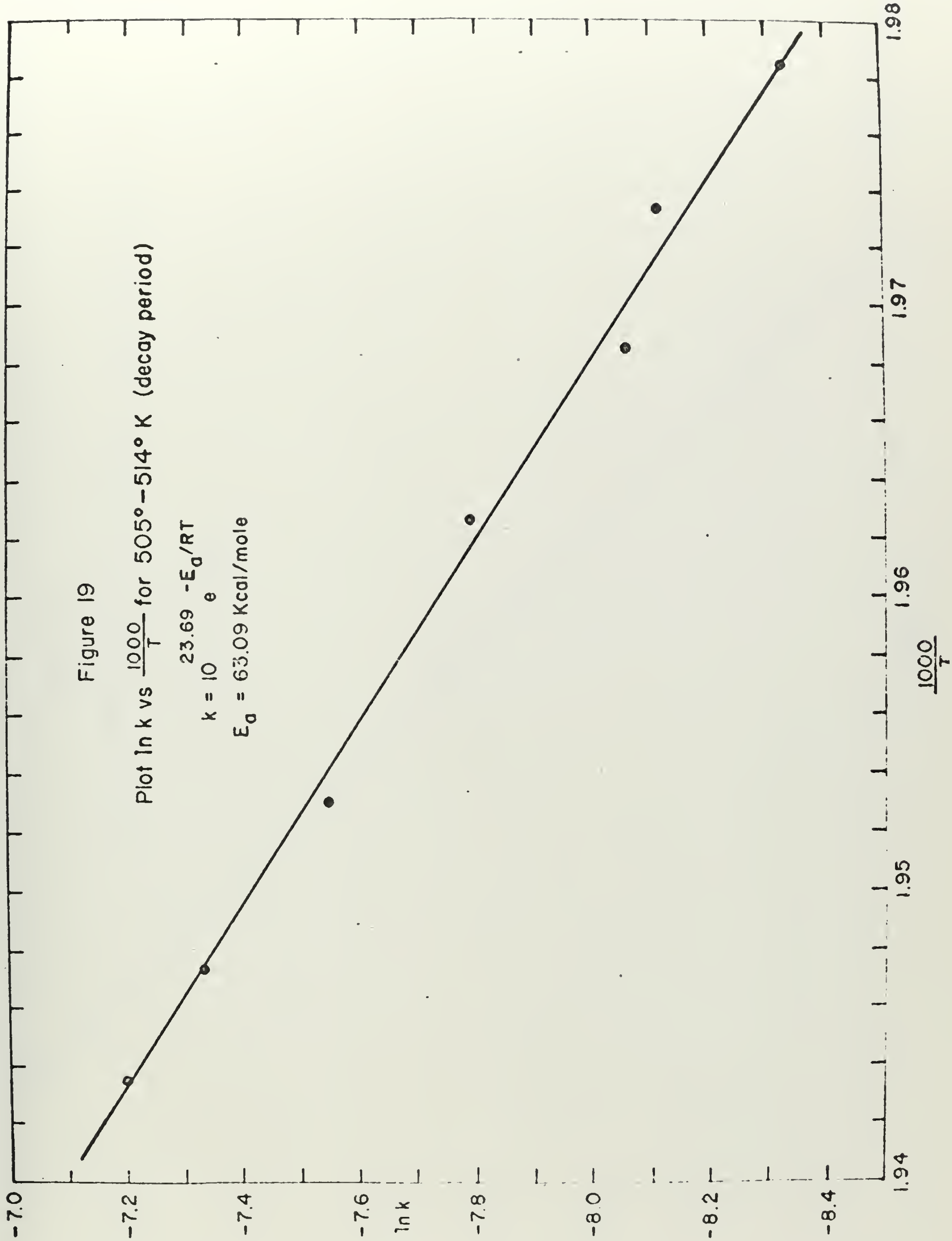

Figure 19

Plot ln k vs $\frac{1000}{T}$ for 505°–514° K (decay period)

$k = 10^{23.69}\ e^{-E_a/RT}$

E_a = 63.09 Kcal/mole

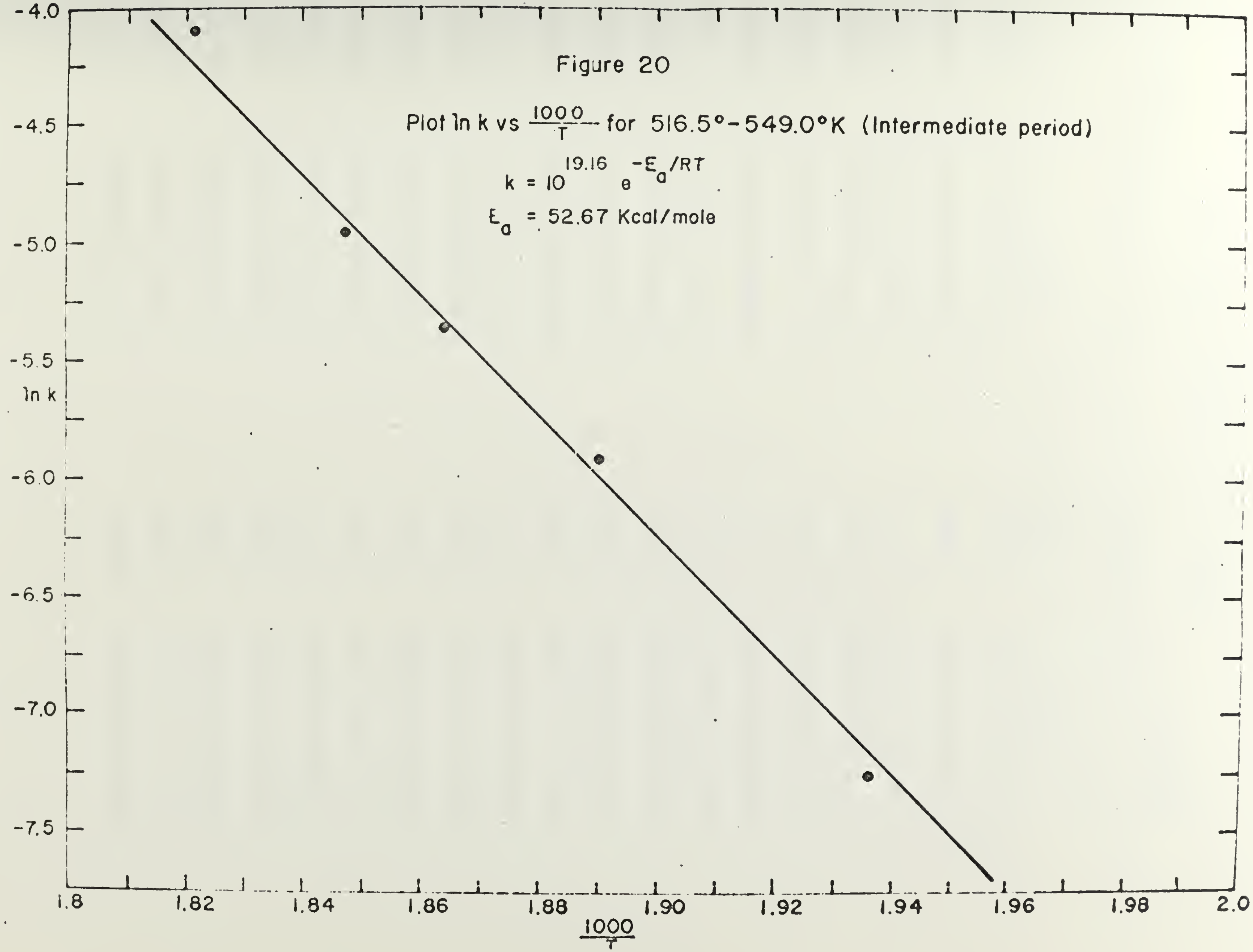

Figure 20

Plot ln k vs $\frac{1000}{T}$ for 516.5°-549.0°K (Intermediate period)

$k = 10^{19.16} e^{-E_a/RT}$

E_a = 52.67 Kcal/mole

APPENDIX A

Temperature between 473°-506°K

For known T_m, $dT/dt = 10^{15.21} \cdot \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$

E_a = 44.20 Kcal/mole.

T_m	dT/dt	T_m	dT/dt
536.00	.198338153111ex-01	540.75	.290664267870ex-01
536.25	.202401605280ex-01	541.00	.296516482511ex-01
536.50	.206544493279ex-01	541.25	.302481084239ex-01
536.75	.210768293901ex-01	541.50	.308560124634ex-01
537.00	.215074509914ex-01	541.75	.314755690817ex-01
537.25	.219464670478ex-01	542.00	.321069905809ex-01
537.50	.223940331741ex-01	542.25	.327504929568ex-01
537.75	.228503077087ex-01	542.50	.334062958762ex-01
538.00	.233154517670ex-01	542.75	.340746228424ex-01
538.25	.237896293008ex-01	543.00	.347557011570ex-01
538.50	.242730071109ex-01	543.25	.354497620611ex-01
538.75	.247657549274ex-01	543.50	.361570407417ex-01
539.00	.252680454520ex-01	543.75	.368777764288ex-01
539.25	.257800543858ex-01	544.00	.376122124525ex-01
539.50	.263019605111ex-01	544.25	.383605963090ex-01
539.75	.268339456969ex-01	544.50	.391231797101ex-01
540.00	.273761950143ex-01	544.75	.399002186962ex-01
540.25	.279288967160ex-01	545.00	.406919736417ex-01
540.50	.284922423576ex-01	545.25	.414987093897ex-01

T_m	dT/dt
545.50	.423206952865ex-01
545.75	.431582052431ex-01
546.00	.440115178487ex-01
546.25	.448809164045ex-01
546.50	.457666890403ex-01
546.75	.466691287513ex-01
547.00	.475885335051ex-01
547.25	.485252062905ex-01
547.50	.494794552516ex-01
547.75	.504515937042ex-01
548.00	.514419402494ex-01
548.25	.524508188705ex-01
548.50	.534785590074ex-01
548.75	.545254956182ex-01
549.00	.555919693153ex-01
549.25	.566783264057ex-01
549.50	.577849190178ex-01
549.75	.589121051830ex-01
550.00	.600602488984ex-01

T_m	dT/dt
550.25	.612297202640ex-01
550.50	.624208955924ex-01
550.75	.636341574219ex-01
551.00	.648698946850ex-01
551.25	.661285028239ex-01
551.50	.674103838180ex-01
551.75	.687159463479ex-01
552.00	.700456058993ex-01
552.25	.713997848059ex-01
552.50	.727789124540ex-01
552.75	.741834252926ex-01
553.00	.756137670110ex-01
553.25	.770703886513ex-01
553.50	.785537486905ex-01
553.75	.800643131343ex-01
554.00	.816025557253ex-01
554.25	.831689579741ex-01
554.50	.847640092937ex-01

APPENDIX B

Temperature between 506°-514°K

For known T_m, $dT/dt = 10^{22.89} \cdot \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$

$E_a = 63.23$ Kcal/mole

T_m	dT/dt	T_m	dT/dt
537.00	.129288972052ex-01	541.50	.215119410159ex-01
537.25	.133027492434ex-01	541.75	.221237118451ex-01
537.50	.136870545695ex-01	542.00	.227523017131ex-01
537.75	.140820953405ex-01	542.25	.233981568832ex-01
538.00	.144881610495ex-01	542.50	.240617349989ex-01
538.25	.149055487260ex-01	542.75	.247435054120ex-01
538.50	.153345630870ex-01	543.00	.254439494200ex-01
538.75	.157755167657ex-01	543.25	.261635606090ex-01
539.00	.162287304999ex-01	543.50	.269028451162ex-01
539.25	.166945333113ex-01	543.75	.276623219585ex-01
539.50	.171732627450ex-01	544.00	.284425233300ex-01
539.75	.176652650589ex-01	544.25	.292439949623ex-01
540.00	.181708954480ex-01	544.50	.300672963888ex-01
540.25	.186905182566ex-01	544.75	.309130013481ex-01
540.50	.192245072238ex-01	545.00	.317816980814ex-01
540.75	.197732457059ex-01	545.25	.326739897217ex-01
541.00	.203371269022ex-01	545.50	.335904946328ex-01
541.25	.209165541249ex-01	545.75	.345318467801ex-01

T_m	dT/dt	T_m	dT/dt
546.00	.354986961239ex-01	550.50	.581095254383ex-01
546.25	.364917089739ex-01	550.75	.597086579399ex-01
546.50	.375115684348ex-01	551.00	.613503113220ex-01
546.75	.385589747716ex-01	551.25	.630355761312ex-01
547.00	.396346458493ex-01	551.50	.647655697993ex-01
547.25	.407393175207ex-01	551.75	.665414373511ex-01
547.50	.418737441262ex-01	552.00	.683643520174ex-01
547.75	.430386988533ex-01	552.25	.702355158988ex-01
548.00	.442349742770ex-01	552.50	.721561606815ex-01
548.25	.454633827467ex-01	552.75	.741275483043ex-01
548.50	.467247569331ex-01	553.00	.761509716855ex-01
548.75	.480199502511ex-01	553.25	.782277554608ex-01
549.00	.493498374134ex-01	553.50	.803592566862ex-01
549.25	.507153149045ex-01	553.75	.825468656964ex-01
549.50	.521173015047ex-01	554.00	.847920067558ex-01
549.75	.535567388317ex-01	554.25	.870961390088ex-01
550.00	.550345918743ex-01	554.50	.894607571429ex-01
550.25	.565518495997ex-01		

APPENDIX C

Temperature above 514°K

For known T_m, $dT/dt = 10^{18.67} \cdot \frac{R}{E_a} \cdot T_m^2 \cdot e^{-E_a/RT_m}$

E_a = 52.65 Kcal/mole.

T_m	dT/dt	T_m	dT/dt
538.75	.223746688366ex-01	543.25	.341912611705ex-01
539.00	.229121968118ex-01	543.50	.349992295378ex-01
539.25	.234621319673ex-01	543.75	.358255366055ex-01
539.50	.240247487940ex-01	544.00	.366705812033ex-01
539.75	.246003275887ex-01	544.25	.375347704242ex-01
540.00	.251891545656ex-01	544.50	.384185198216ex-01
540.25	.257915219805ex-01	544.75	.393222535702ex-01
540.50	.264077282528ex-01	545.00	.402464046337ex-01
540.75	.270380780769ex-01	545.25	.411914149401ex-01
541.00	.276828825787ex-01	545.50	.421577355291ex-01
541.25	.283424594141ex-01	545.75	.431458267992ex-01
541.50	.290171329122ex-01	546.00	.441561586226ex-01
541.75	.297072341949ex-01	546.25	.451892105622ex-01
542.00	.304131013396ex-01	546.50	.462454720816ex-01
542.25	.311350795055ex-01	546.75	.473254426778ex-01
542.50	.318735210598ex-01	547.00	.484296321498ex-01
542.75	.326287857437ex-01	547.25	.495585607500ex-01
543.00	.334012408110ex-01	547.50	.507127594161ex-01

T_m	dT/dt	T_m	dT/dt
547.75	.518927699523ex-01	552.25	.782354990822ex-01
548.00	.530991452937ex-01	552.50	.800250182024ex-01
548.25	.543324496461ex-01	552.75	.818538288519ex-01
548.50	.555932587842ex-01	553.00	.837227570243ex-01
548.75	.568821601939ex-01	553.25	.856326453302ex-01
549.00	.581997534123ex-01	553.50	.875843532827ex-01
549.25	.595466501210ex-01	553.75	.895787575765ex-01
549.50	.609234745243ex-01	554.00	.916167524747ex-01
549.75	.623308634746ex-01	554.25	.936992501278ex-01
550.00	.637694667803ex-01	554.50	.958271809103ex-01
550.25	.652399474629ex-01		
550.50	.667429819794ex-01		
550.75	.682792604838ex-01		
551.00	.698494871036ex-01		
551.25	.714543802259ex-01		
551.50	.730946727435ex-01		
551.75	.747711123111ex-01		
552.00	.764844617155ex-01		

APPENDIX D

For temperature between 505°K-514°K (acceleratory period)

$$k = 10^{25.33} e^{-E_a/RT}$$

$$E_a = 67.86 \text{ Kcal/mole.}$$

T°K	k_1	T°K	k_1
505.00	.911304602995ex-04	509.75	.171137416866ex-03
505.25	.942315077286ex-04	510.00	.176851211276ex-03
505.50	.974348546887ex-04	510.25	.182749891758ex-03
505.75	.100743768016ex-03	510.50	.188839247867ex-03
506.00	.104161615502ex-03	510.75	.195125244427ex-03
506.25	.107691868717ex-03	511.00	.201614026476ex-03
506.50	.111338106142ex-03	511.25	.208311924697ex-03
506.75	.115104016395ex-03	511.50	.215225460492ex-03
507.00	.118993401478ex-03	511.75	.222361351913ex-03
507.25	.123010180056ex-03	512.00	.229726519235ex-03
507.50	.127158391079ex-03	512.25	.237328090723ex-03
507.75	.131442197141ex-03	512.50	.245173408816ex-03
508.00	.135865888307ex-03	512.75	.253270036116ex-03
508.25	.140433885792ex-03	513.00	.261625762086ex-03
508.50	.145150745891ex-03	513.25	.270248609204ex-03
508.75	.150021163795ex-03	513.50	.279146840185ex-03
509.00	.155049977910ex-03	513.75	.288328964329ex-03
509.25	.160242173931ex-03	514.00	.297803745221ex-03
509.50	.165602889100ex-03		

For temperature between 505°-514°K (intermediate period)

$$k = 10^{25.43} e^{-E_a/RT}$$

$$E_a = 66.42 \text{ Kcal/mole.}$$

T°K	k_2	T°K	k_2
505.00	.481844357201ex-03	509.75	.892854358520ex-03
505.25	.497887209858ex-03	510.00	.922021450124ex-03
505.50	.514447537937ex-03	510.25	.952111358642ex-03
505.75	.531541487831ex-03	510.50	.983152319590ex-03
506.00	.549185692775ex-03	510.75	.101517340123ex-02
506.25	.567397286355ex-03	511.00	.104820453035ex-02
506.50	.586193917940ex-03	511.25	.108227651569ex-02
506.75	.605593766593ex-03	511.50	.111742107328ex-02
507.00	.625615556912ex-03	511.75	.115367085165ex-02
507.25	.646278574822ex-03	512.00	.119105945904ex-02
507.50	.667602683955ex-03	512.25	.122962149003ex-02
507.75	.689608341860ex-03	512.50	.126939255370ex-02
508.00	.712316617275ex-03	512.75	.131040930264ex-02
508.25	.735749208215ex-03	513.00	.135270946056ex-02
508.50	.759928459245ex-03	513.25	.139633185550ex-02
508.75	.784877380742ex-03	513.50	.144131644853ex-02
509.00	.810619667841ex-03	513.75	.148770436618ex-02
509.25	.837179719686ex-03	514.00	.153553793420ex-02
509.50	.864582660179ex-03		

For temperature between 505°-514°K (decay period)

$$k = 10^{23.69} e^{-E_a/RT}$$

$$E_a = 63.09 \text{ Kcal/mole.}$$

T°K	k_3	T°K	k_3
505.00	.242190279609ex-03	509.75	.435111502853ex-03
505.25	.249843332536ex-03	510.00	.448601844163ex-03
505.50	.257730286007ex-03	510.25	.462496606374ex-03
505.75	.265858042599ex-03	510.50	.476807492454ex-03
506.00	.274233701601ex-03	510.75	.491546531570ex-03
506.25	.282864563669ex-03	511.00	.506726088071ex-03
506.50	.291758136892ex-03	511.25	.522358870100ex-03
506.75	.300922142125ex-03	511.50	.538457939041ex-03
507.00	.310364518999ex-03	511.75	.555036719059ex-03
507.25	.320093431746ex-03	512.00	.572109006686ex-03
507.50	.330117275298ex-03	512.25	.589688980082ex-03
507.75	.340444681636ex-03	512.50	.607791210507ex-03
508.00	.351084526224ex-03	512.75	.626430671731ex-03
508.25	.362045934460ex-03	513.00	.645622751264ex-03
508.50	.373338288842ex-03	513.25	.665383260915ex-03
508.75	.384971235359ex-03	513.50	.685728448473ex-03
509.00	.396954691205ex-03	513.75	.706675008825ex-03
509.25	.409298851397ex-03	514.00	.728240096375ex-03
509.50	.422014197166ex-03		

APPENDIX E

For temperature between 514°-554.5°K (intermediate period)

$$k = 10^{19.16} e^{-E_a/RT}$$

$$E_a = 52.67 \text{ Kcal/mole.}$$

T°K	k	T°K	k
514.00	.579649357880ex-03	518.25	.884778435032ex-03
514.25	.594365325615ex-03	518.50	.906869572309ex-03
514.50	.609440049372ex-03	518.75	.929490186551ex-03
514.75	.624881906326ex-03	519.00	.952652428724ex-03
515.00	.640699460655ex-03	519.25	.976368716308ex-03
515.25	.656901467545ex-03	519.50	.100065173795ex-02
515.50	.673496876624ex-03	519.75	.102551446022ex-02
515.75	.690494836841ex-03	520.00	.105097013298ex-02
516.00	.707904699912ex-03	520.25	.107703229478ex-02
516.25	.725736025547ex-03	520.50	.110371477926ex-02
516.50	.743998585055ex-03	520.75	.113103172164ex-02
516.75	.762702365951ex-03	521.00	.115899756412ex-02
517.00	.781857576676ex-03	521.25	.118762706299ex-02
517.25	.801474651621ex-03	521.50	.121693529497ex-02
517.50	.821564254973ex-03	521.75	.124693766346ex-02
517.75	.842137286082ex-03	522.00	.127764990529ex-02
518.00	.863204884569ex-03	522.25	.130908809785ex-02

T°K	k	T°K	k
522.50	.134126866646ex-02	526.75	.201967473439ex-02
522.75	.137420839118ex-02	527.00	.206846866451ex-02
523.00	.140792441321ex-02	527.25	.211839346493ex-02
523.25	.144243424376ex-02	527.50	.216947421177ex-02
523.50	.147775577082ex-02	527.75	.222173651312ex-02
523.75	.151390726710ex-02	528.00	.227520651738ex-02
524.00	.155090739794ex-02	528.25	.232991092447ex-02
524.25	.158877522859ex-02	528.50	.238587699852ex-02
524.50	.162753023386ex-02	528.75	.244313257713ex-02
524.75	.166719230531ex-02	529.00	.250170608379ex-02
525.00	.170778175979ex-02	529.25	.256162653968ex-02
525.25	.174931934801ex-02	529.50	.262292357505ex-02
525.50	.179182626544ex-02	529.75	.268562744308ex-02
525.75	.183532415725ex-02	530.00	.274976902937ex-02
526.00	.187983513106ex-02	530.25	.281537986756ex-02
526.25	.192538176473ex-02	530.50	.288249214909ex-02
526.50	.197198711669ex-02	530.75	.295113873940ex-02

T°K	k	T°K	k
531.00	.302135319017ex-02	535.25	.449100723282ex-02
531.25	.309316975145ex-02	535.50	.459604928470ex-02
531.50	.316662338765ex-02	535.75	.470344672044ex-02
531.75	.324174979087ex-02	536.00	.481325003547ex-02
532.00	.331858539393ex-02	536.25	.492551075839ex-02
532.25	.339716738715ex-02	536.50	.504028146526ex-02
532.50	.347753373255ex-02	536.75	.515761581026ex-02
532.75	.355972317833ex-02	537.00	.527756853617ex-02
533.00	.364377527507ex-02	537.25	.540019550116ex-02
533.25	.372973039243ex-02	537.50	.552555369935ex-02
533.50	.381762973181ex-02	537.75	.565370128136ex-02
533.75	.390751534779ex-02	538.00	.578469757781ex-02
534.00	.399943015881ex-02	538.25	.591860312353ex-02
534.25	.409341797119ex-02	538.50	.605547967535ex-02
534.50	.418952348918ex-02	538.75	.619539024216ex-02
534.75	.428779233914ex-02	539.00	.633839910800ex-02
535.00	.438827108067ex-02	539.25	.648457184909ex-02

T°K	k	T°K	k
539.50	.663397536880ex-02	543.75	.973992005912ex-02
539.75	.678667791422ex-02	544.00	.996058661844ex-02
540.00	.694274911084ex-02	544.25	.101860429296ex-01
540.25	.710225997812ex-02	544.50	.104163883176ex-01
540.50	.726528297053ex-02	544.75	.106517240667ex-01
540.75	.743189198495ex-02	545.00	.108921534624ex-01
541.00	.760216240852ex-02	545.25	.111377818234ex-01
541.25	.777617113664ex-02	545.50	.113887165428ex-01
541.50	.795399659806ex-02	545.75	.116450671315ex-01
541.75	.813571879480ex-02	546.00	.119069452424ex-01
542.00	.832141932284ex-02	546.25	.121744647258ex-01
542.25	.851118140605ex-02	546.50	.124477416627ex-01
542.50	.870508992684ex-02	546.75	.127268944113ex-01
542.75	.890323145780ex-02	547.00	.130120436383ex-01
543.00	.910569429355ex-02	547.25	.133033123820ex-01
543.25	.931256847671ex-02	547.50	.136008260728ex-01
543.50	.952394584812ex-02	547.75	.139047125951ex-01

T°K	k	T°K	k
548.00	.142151023207ex-01	552.50	.210789883587ex-01
548.25	.145321281671ex-01	552.75	.215413849674ex-01
548.50	.148559256326ex-01	553.00	.220134929809ex-01
548.75	.151866328455ex-01	553.25	.224955071104ex-01
549.00	.155243906310ex-01	553.50	.229876257770ex-01
549.25	.158693425292ex-01	553.75	.234900511899ex-01
549.50	.162216348657ex-01	554.00	.240029893923ex-01
549.75	.165814168109ex-01	554.25	.245266503637ex-01
550.00	.169488404022ex-01	554.50	.250612480696ex-01
550.25	.173240606225ex-01	554.75	.256070005261ex-01
550.50	.177072354555ex-01	555.00	.261641298966ex-01
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551.00	.184980961241ex-01	555.50	.273134291171ex-01
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APPENDIX F

PROCEDURE TO OBTAIN THE OBSERVED SELF-HEATING RATE.

There are three kinetic laws which have been advanced to account for the three different parts of the curve obtained under isothermal conditions. These laws fall into three main types, namely [10]:

$$T = kt^{4.078} + C \quad \text{for the acceleratory period}$$

$$\ln\left[\frac{T}{T_f - T}\right] = kt + C \quad \text{for the intermediate period}$$

$$\ln T = kt + C \quad \text{for the decay period .}$$

1. For the acceleratory period, the observed self-heating rate was obtained from the plot of T versus $t^{4.078}$, then the $(\text{slope})^{1/4.078}$ is the observed self-heating rate at that temperature.

2. For the intermediate period, the observed self-heating rate was obtained from the slope of the plot $\ln[T/(T_f - T)]$ versus time(sec).

3. For the decay period, the observed self-heating rate was obtained from the slope of the plot ln T versus time(sec).

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UNCLASSIFIED
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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Postgraduate School Monterey, California 93940	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

THE THERMAL DECOMPOSITION OF β-HMX

4. DESCRIPTIVE NOTES *(Type of report and, inclusive dates)*

Master's Thesis, June 1971

5. AUTHOR(S) *(First name, middle initial, last name)*

Weera Hoondee

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 1971	68	10

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

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13. ABSTRACT

Although HMX exists in four conformational forms α, β, γ, and δ, in the crystalline state, the most stable polymorph at room temperature is the β form [1]. Therefore, this form was used for this study.

Kinetic data obtained from Differential Thermal Analysis (DTA) changes in heating rates and at isothermal conditions showed differences in the observed activation energies in the three temperature ranges, namely, 473°-506°K, 506°-514°K, and above 514°K at one atmosphere.

Calculations have been made of the rate of reaction as a function of time in each of these temperature regimes based upon the best available model and compared with the experimental result.

DD FORM 1473 1 NOV 65 (PAGE 1)

S/N 0101-807-6811

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
HMX						
Differential Thermal Analysis						
Thermal Decomposition						

Thesis 128466
H72935 Hoondee
c.1 The thermal decomposition of β-HMX.