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AUTOIGNITION TEMPERATURES OF MILITARY HIGH EXPLOSIVES BY DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

Autoignition temperatures were determined for military high explosives TNT, RDX, PETN and HMX by differential thermal analysis (DTA). A method was developed in which several heating rates were utilized and the related data extrapolated to a near zero heating rate to obtain the autoignition temperatures. The first order exponential equation derived by Kissinger[1] $\frac{d(\ln \varnothing / T_m^2}{d\, 1/T_m} = -\frac{E}{R}$ as used for the extrapolation.

Only HMX did not obey this relationship due to the hypothesized secondary reaction. A different relationship of rate and temperature was found for HMX to determine its ignition temperature at a minimum rate of heating.

The autoignition temperatures of the explosives obtained with the developed DTA methods are

		Autoignition temp. (°C)	*Apparent activation energy E(cal mol^{-1})*
JAN-T-248	TNT, Grade 1	275 Confined	24 000
MIL-R-00398B,	RDX, Type B, Class C	197	34 000
MIL-P-00387B,	PETN	160	33 000
MIL-H-45444A,	HMX, Type B. Class C	234	—
Values for additional explosives are:			
MIL-N-244A	Nitrocellulose 12.6%	176	49 000
MIL-C-401C	Composition B 60% RDX, 40% TNT, 1% wax	174	39 000
MIL-T-0039	Tetryl	166	34 000
	Tritonal 80/20 TNT/Al	250 Confined	22 000
MIL-O-45445	Octol 75/25 HMX/TNT	236	80 000
JAN-P-408	Pentolite 50/50 PETN/TNT	156	26 000
MIL-6-21723	CH-6 97.5% RDX, 2.5% inert	193	41 000
	PBX 90%, RDX 10%, inert	189	33 000

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INTRODUCTION

Military explosives are materials which are thermodynamically unstable; they are always decomposing at temperatures above 0 K. The rate of decomposition is imperceptible at room temperature but increases exponentially as the temperature rises. The products of decomposition (gas and energy) are dissipated to the surroundings. At an elevated temperature a point is reached where more energy is released by the decomposition than can be dissipated to the surroundings. The explosive then begins to self-heat. The lowest temperature at which self-heating occurs followed by ignition is considered to be the autoignition temperature. The autoignition temperature will vary slightly due to particle size and environment. The purpose of these experiments was to establish the autoignition temperature for high explosives TNT, RDX, PETN and HMX.

The study was initiated as part of the mission to upgrade Safety Statements pertaining to explosives. The explosive parameter autoignition was found to be largely omitted on these statements. A literature search of army and navy sources revealed that most data available were ignition temperatures after varying short incubation periods. As many values appeared as there were test apparatus. As an example ignition values for TNT differing by as much as 200°C can be found in the literature for Russian and U.S. references[7].

An attempt to clarify this situation was made by the navy at China Lake, Calif.[3]. Thermal apparatus incorporating DTA was used to obtain the critical temperature of propellants, but no compilation of autoignition for explosives could be found. It was decided to incorporate data obtained from a recently purchased miniaturized DTA apparatus in order to obtain accurate, repeatable, and reliable ignition temperatures. The method was to obtain values at four or five heating rates and extrapolate back to almost a zero heating rate in order to approach a true autoignition temperature.

EXPERIMENTAL PROCEDURE

DTA was conducted on a Deltatherm III DTA accessory. Two thermocups sit within an open cylindrical steel sample block separated by a few millimeters of air. The explosive sample and the reference material are placed within 0.14-in. steel cups and placed into these thermocups. The thermocups consist of a steel cup to which an alumel and a chromel wire are welded. Thermograms were recorded on a Mosely 7100 B two-pen time-base recorder. One pen recorded the temperature of the reference material; the other pen recorded the ΔT of the two cups at a space of 1/10 in. ahead of the temperature pen.

Explosives for these tests were used as is from their containers.

Explosives were tested at nominally 20, 10, 5 and 2½°C per minute heating rate. HMX was also tested at 1¼°C per minute.

STUDY

Values for ignition temperatures of explosives vary widely according to the apparatus used to obtain the values. A test procedure using a small sample of explosive and DTA apparatus should increase the accuracy and reliability of autoignition temperature determinations. The small sample would minimize temperature differentials in the sample. Since the ignition temperature is measured in the center of the sample whereas thermocups measure the surface temperature, the minimization of temperature differentials is necessary.

Autocatalytic activity (gaseous products reacting with the undecomposed explosive) results in lower ignition temperatures and steeper slopes. To minimize the autocatalytic activity a constant flow of argon was passed across the sample holder while the sample was heated at a constant rate. If the gas products are removed, a first order reaction should result where the rate of decomposition is based only on simple bond breaking. The application of a theoretical equation derived by Kis-

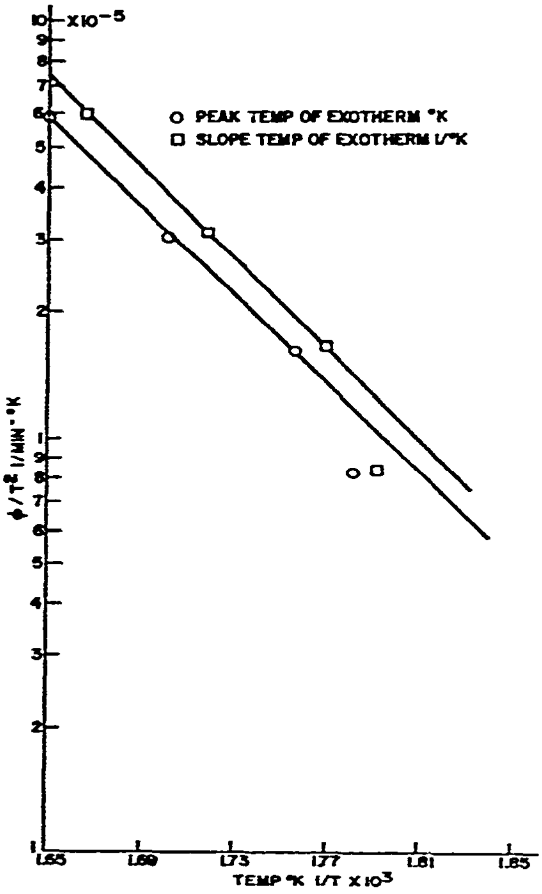

Fig. 1. Graph of DTA data from TNT KNK 11-270 confined heating rate vs. absolute temperature of exotherm.

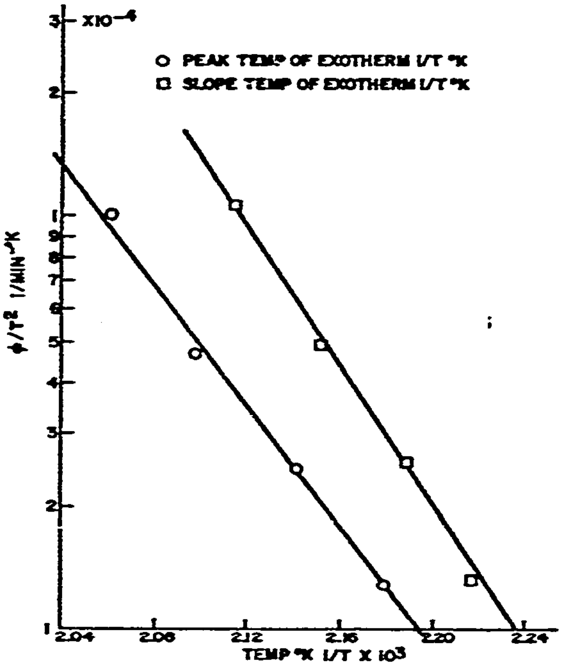

Fig. 2. Graph of DTA data for PETN PA 2-267T heating rate vs. absolute temperature of exotherm

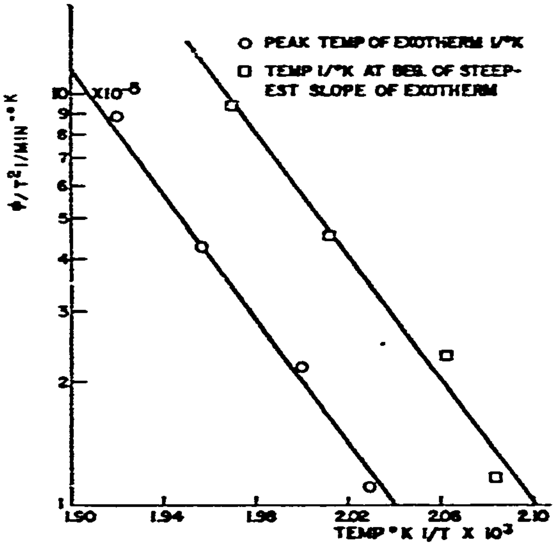

Fig. 3. Plot of DTA data RDX Type B class C HOL 8-84 heating rate vs. absolute temperature of exotherm.

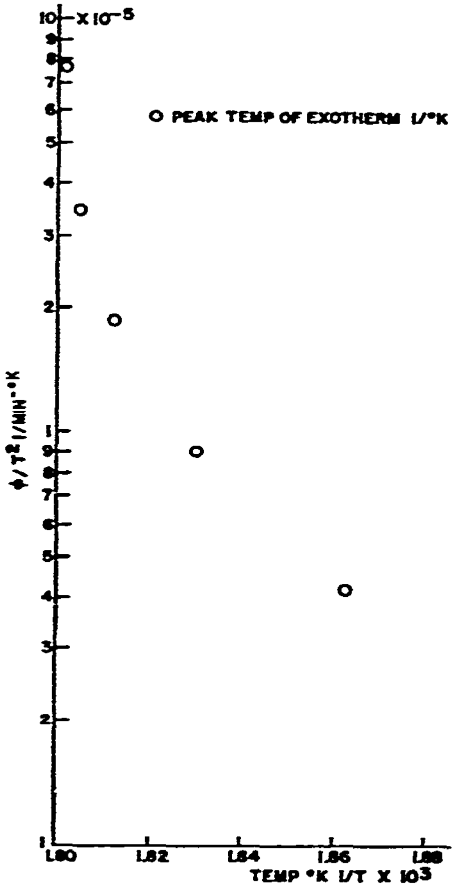

Fig. 4. Plot of DTA data of HMX HOL 701-19 grade II class A heating rate vs. absolute temperature of exotherm.

singer[1,2] could then be made. A straight line based on this equation would make possible the calculation of ignition temperature as the rate of heating approached zero. The slope of the straight line would be equal to E/R (E being the activation energy). The methods and procedures for obtaining activation energies are based on previous applications[3] of the Kissinger equation to propellants and explosives.

Figures 1–4 are graphs of rate of heating divided by the square of the absolute peak temperature versus the reciprocal of the absolute peak temperature on semilogarithmic graph paper. Figure 5 is a graph of the reciprocal of these values on rectangular paper for HMX, for which a straight line could not be obtained on logarithmic paper. The graphs represent values obtained from DTA exothermic peaks conducted at four and five heating rates. Typical DTA curves for each explosive are shown in Figs. 6–9.

Good straight lines were obtained for TNT (Fig. 1), PETN (Fig. 2) and RDX (Fig. 3) which shows good agreement with the theoretical equations derived in refs. 1–3. The data from HMX produced a hyperbolic curve on both semilogarithmic

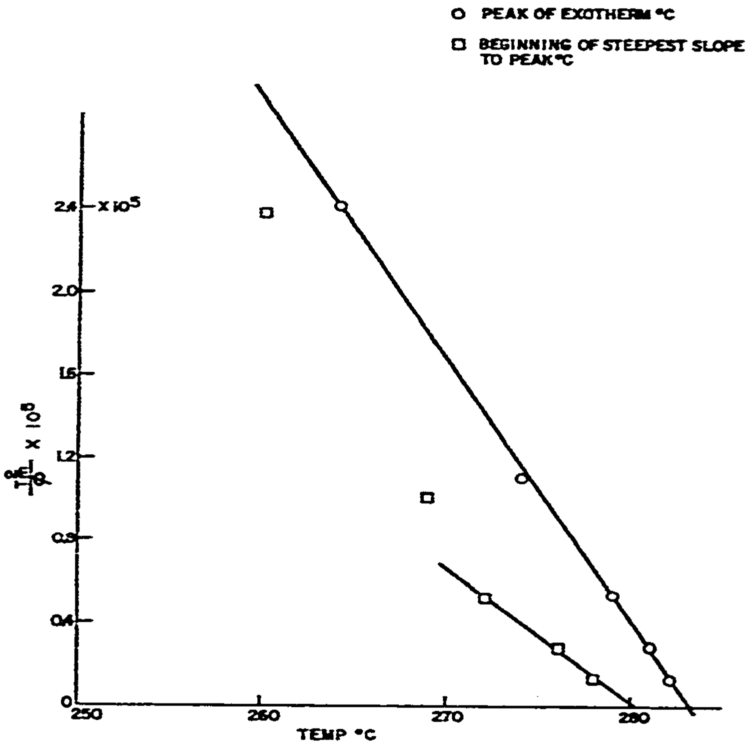

Fig. 5. Plot of DTA data of a HMX HOL 701-19 grade II class A heating rate vs. absolute temperature of exotherm.

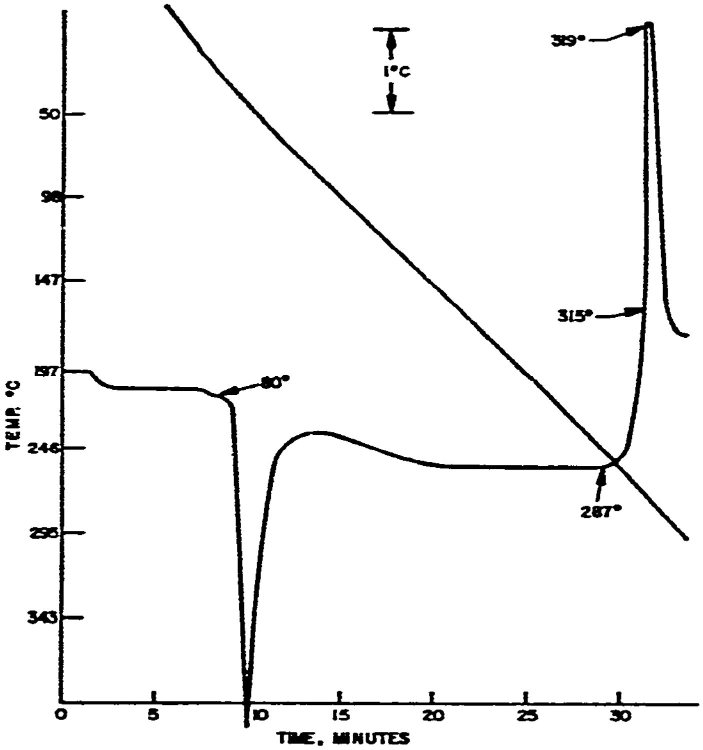

Fig. 6. DTA TNT in argon 10 ml min^{-1} heating rate 10°C min^{-1}; Dec. 16, 1971.

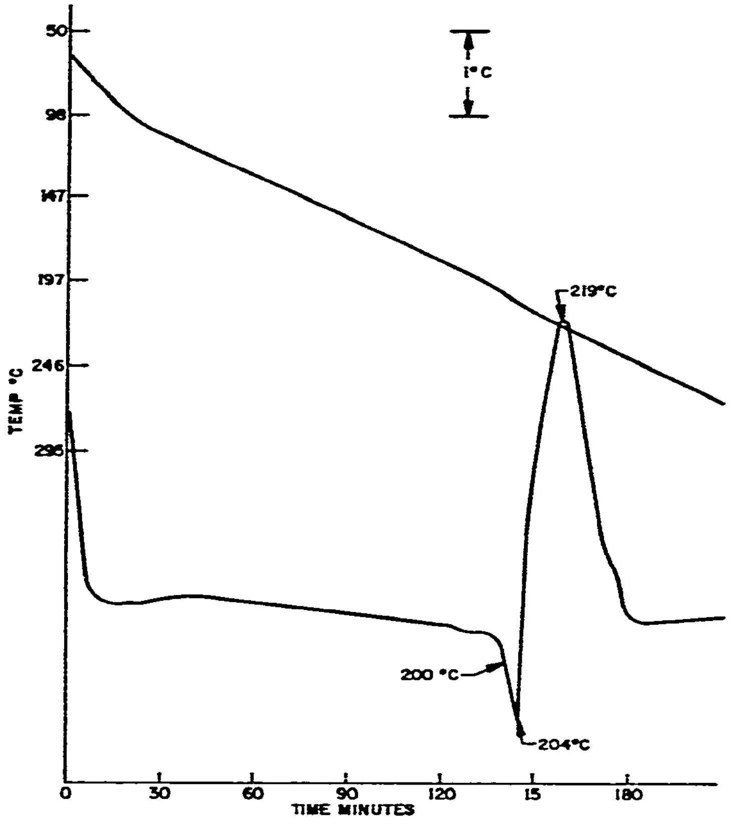

Fig. 7. DTA RDX 5.2 mg 2½ °C min^{-1} in argon 30 ml min^{-1}; Nov. 28, 1971.

paper and rectangular paper (Fig. 4). A straight line relationship was obtained by graphing the reciprocal of the data on rectangular paper (Fig. 5).

Tables 1, 3, 5 and 7 list the DTA obtained from each experiment. Tables 2, 4, 6 and 8 list the compiled data used to plot the graphs of Figs. 1–5 and include the calculations of activation energies calculated from this equation:

$$\frac{d(\ln \varnothing/T_m^2)}{d\,1/T_m} = -\frac{E}{R} \tag{1}$$

$\varnothing$ = constant heating rate (°C min^{-1})
T_m = temperature maximum or peak temperature (K)
E = activation energy, cal mol^{-1}
R = gas constant, 1.987 cal mol^{-1}.

Equation (1) was derived by Kissinger[1,2] from the equation for solid → solid + gas reaction as follows:

$$dx/dt = A(1-x)^n e^{-E/RT} \tag{2}$$

A = frequency factor (sec^{-1})
x = fraction of explosive reacted
n = empirical order of reaction
$\mathrm{d}x/\mathrm{d}t$ = rate of reaction
t = time (min)

At the maxima the exotherm peak $(\mathrm{d}/\mathrm{d}t)/(\mathrm{d}x/\mathrm{d}t) = 0$, $x = 1$ the first derivative of eqn (2) is:

$$0 = -E/RT^2 \, \mathrm{d}T/\mathrm{d}t \, A\mathrm{e}^{-E/RT} \tag{3}$$

Rearrangement of eqn (3) results in eqn (1) where $\varnothing = \mathrm{d}T/\mathrm{d}t$.

The derivation is only valid at the exotherm peak. The ignition temperatures correspond to the temperature where the exotherm would begin even if heat sources were removed. This point would occur on a DTA exotherm at the beginning of the steepest slope—for at that point the majority of molecules are activated and a straight line to the peak results. The autoignition temperature can be calculated by utilizing the peak temperature activation energy obtained from eqn (1); the slope temperature

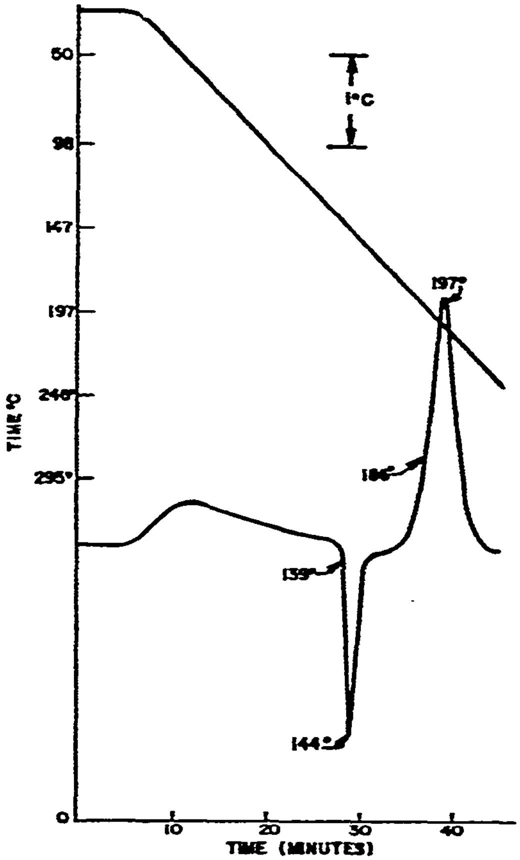

Fig. 8. DTA 3.8 mg PETN 5 °C min^{-1} in argon 30 ml min^{-1}; Dec. 2, 1971.

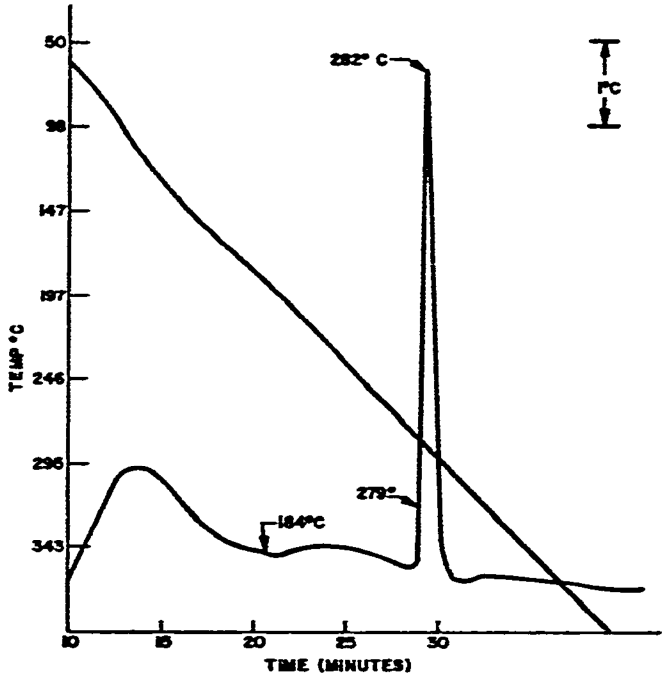

Fig. 9. DTA 1.5 mg HMX in argon 20 ml min^{-1} grade II class A HOL 701-19, rate 10 °C min^{-1}; Dec. 17, 1971.

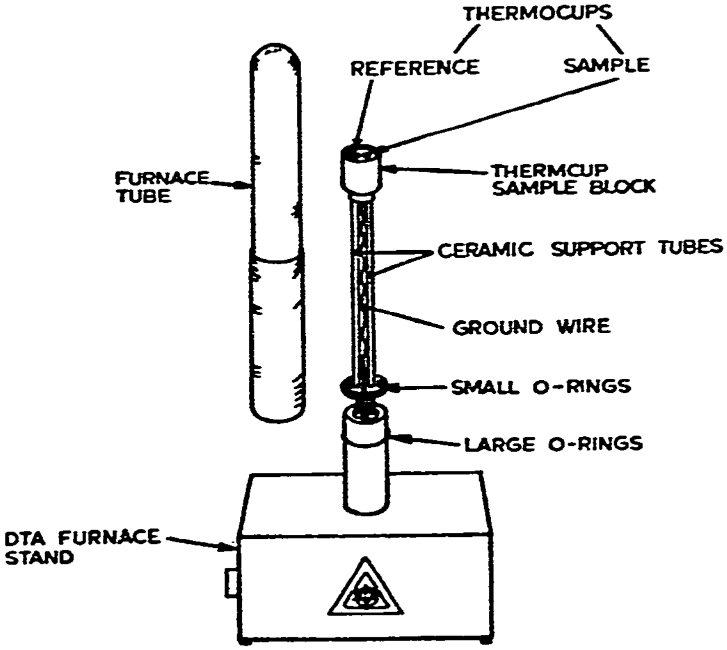

Fig. 10. Differential thermal analysis accessory of Deltatherm III.

frequency factor obtained from eqn (3) ($E\varnothing/RT_2^m = Ae^{-E/RT}$) and by setting $\varnothing$ equal to a small number.

This procedure consists of:

Obtaining the energy of activation from the curve of $\varnothing/T_m^2$ versus $1/T_m$.

Calculating an average frequency factor from eqn (3) for slope temperatures and also for peak temperatures.

Setting the therm $E\varnothing/RT_m^2$ equal to 0.1 as $\varnothing \rightarrow 0$ and solving for the autoignition temperature from T in the exponent.

Military explosives TNT, RDX and PETN obeyed the exponential relationship. Thus, the above procedure was followed, and autoignition temperatures of 275 °C for confined TNT, 197 °C for RDX Type B Class A, and 166 °C for PETN were obtained. The explosive TNT melted at 79–80 °C and began to evaporate soon after that. Unconfined TNT evaporated before it could be ignited except at the fastest nominal heating rate of 20 °C min^{-1}. To obtain ignition data, a second 0.14-in. steel cup was

TABLE 1

DTA DATA TNT KNK 11-270 CONFINED SAMPLE SIZE 3–10 mg

Nominal rate (°C min^{-1})	*Actual rate (°C min^{-1})*	*Exotherm*			*Argon flow-rate (ml min^{-1})*
		Initial (°C)	*Slope (°C)*	*Peak (°C)*	
20	22	302	322	331	10
20	21	—	324	330	10
20	21	309	332	336	10
20	23	312	326	333	10
20	22	309	328	333	10
Average	22	—	326	333	
10	10.3	301	307	312	10
10	10.8	295	312	317	10
10	10.6	287	315	319	10
10	10.8	300	312	316	10
10	11.0	299	300	312	10
Average	10.7	—	309	312	
5	5.3	276	292	297	10
5	5.2	278	295	299	30
5	5.0	288	297	299	30
5	5.3	256	278	284	23
5	5.4	283	295	300	10
5	5.3	271	293	295	10
Average	5.3		292	296	
2½	2.5	266	280	283	10
2½	2.6	273	287	290	10
2½	2.6	268	286	288	10
2½	2.7	271	286	287	10
Average	2.6		285	287	

TABLE 2

CALCULATION OF ACTIVATION ENERGY AND AUTOIGNATION TEMPERATURE FOR TNT (CONFINED) KNK 11-270

Temperature (°C)	*Temperature* (K)	*Rate* = $\varnothing$ (°C min^{-1})	$1/T+10^3$ (K)	$\varnothing/T^2 \times 10^{-5}$
Temperature at the peak of the exotherm				
333	606	22.0	1.650	5.847
315	588	10.7	1.701	3.058
296	569	5.3	1.757	1.637
287	560	2.6	1.786	0.829
Temperature at the beginning of the slope to the exotherm peak				
326	599	22.0	1.666	5.988
309	582	10.7	1.718	3.121
292	565	5.3	1.770	1.660
285	558	2.6	1.792	0.835

$$\text{slope} = \frac{E}{\ln R} = \frac{\log(\varnothing/T^2)_1 - (\varnothing/T^2)_2}{1/T_1 - 1/T_2}$$

$E_p = 24\,200$ cal mol^{-1}; $E_s = 24\,900$ cal mol^{-1}.
E_p = activation energy at peak; E_s = activation energy at slope; $\varnothing$ = constant heating rate; T = temperature (K); R = gas constant; A = frequency factor (sec^{-1}).

Peak temp. (K)	$\varnothing/T^2 \times 10^{-5}$	$\frac{E\varnothing}{RT^2}$	$e^{-E/RT} \times 10^{-9}$	$A \times 10^8$
606	5.991	0.72965	1.865	3.912
588	3.095	0.37695	1.013	3.721
568	1.642	0.1998	0.488	4.094
560	0.829	0.10096	0.358	(2.821)
				average (3) = 3.90×10^8
Slope temp. (K)				
599	6.131	0.76799	0.830	9.253
582	3.159	0.39571	0.451	8.774
565	1.660	0.20794	0.235	8.849
558	0.834	0.10447	0.178	(5.869)
				average (3) = 8.96×10^8

$$\frac{E\varnothing}{RT^2} = A\,e^{-E/RT}$$

as $\varnothing \to 0$
$E\varnothing/RT^2 \to 0.1$

$$\log 0.1 = \log 3.90 \times 10^8 - \frac{E}{RT \times 2.303}$$

$T = 552$ K
279.0 °C peak temperature

$$\log 0.1 = \log 8.96 \times 10^8 - \frac{E}{RT \times 2.303}$$

$T = 547.6$ K
= 274.6 °C autoignition temperature confined.

placed atop the one which contained the TNT—resulting in confinement and successful ignitions at even $2\frac{1}{2}$°C min^{-1}.

The data from HMX exotherm did not produce a straight line. A hyperbola resulted on both semilogarithmic paper and rectangular paper. A hyperbolic function can be of the nature of $(e^{x}-e^{-x})/2$, which would be indicative of a second exponential reaction of rate versus the reciprocal of absolute temperature. Thus a normal calculation of activation energy was precluded.

Although a constant flow of argon was intended to prevent autocatalysis, it would not prevent autocatalysis of an instantaneous reaction. Nitric oxide has been found to accelerate the decomposition of HMX. The flow of argon would even have aggravated the condition by blowing away other decomposition products such as formaldehyde which could have competed with the HMX for the nitric oxide. In any case the reciprocal of data producing a hyperbola is a straight line on rectangular paper. A very good straight line (Fig. 5) resulted when $T_m^2/\varnothing$ versus T was graphed.

TABLE 3

DTA DATA FOR RDX TYPE B CLASS A HOL 8-84[a]

Nominal rate (°C min^{-1})	*Actual rate (°C min^{-1})*	*Exotherm temp. (°C)*			*Sample weight (mg)*
		Initial	*Slope*	*Peak*	
20	25.0	207	234	250	0.9
20	27.5	210	234	245	2.8
20	20.0	207	236	249	1.2
20	24.0	208	236	246	1.6
average			235	248	
10	11.0	211	222	231	3.2
10	11.0	205	225	239	1.6
10	10.7	209	223	239	2.3
10	12.8	209	226	244	1.7
10	10.6	207	224	239	1.0
average	11.2		224	238	
5	5.0	208	209	222	
5	5.4	202	211	226	
5	5.3	206	210	230	5.8
5	5.4	206	214	225	3.7
5	5.3	196	214	234	1.4
average	5.5		212	227	
$2\frac{1}{2}$		202	206	223	
$2\frac{1}{2}$		206	207	219	
$2\frac{1}{2}$		204	207	219	
$2\frac{1}{2}$		202	207	221	
$2\frac{1}{2}$		199	207	219	
$2\frac{1}{2}$		203	207	217	
average			207	220	

[a] Argon flow of 28–30 ml min^{-1} across sample.

TABLE 4

CALCULATION OF ACTIVATION ENERGY AND AUTOIGNITION TEMPERATURE FOR RDX TYPE B CLASS C HOL 8-84

Temperature °C	*Temperature* K	*Rate* = $\varnothing$ (°C min^{-1})	$T^2 \times 10^5$	$\varnothing/T^2 \times 10^{-5}$	$1/T \times 10^{-3}$
Temperature at peak of exotherm					
248	521	24.1	2.7144	8.878	1.919
238	511	11.2	2.6112	4.289	1.957
227	500	5.5	2.5000	2.200	2.000
220	493	2.7	2.4305	1.111	2.208
Temperature at slope of exotherm					
235	508	24.1	2.5808	9.339	1.969
224	497	11.2	2.4701	4.534	2.012
212	485	5.5	2.3523	2.338	2.062
207	480	2.7	2.3040	1.172	2.083

Peak $\frac{E}{2.303R} = \log \frac{(\varnothing/T^2)_1 - (\varnothing/T^2)_2}{1/T_1 - 1/T_2}$

$E_p = 34\,680$ cal mol^{-1}

$E_s = 34\,000$ cal mol^{-1}

RDX TYPE B CLASS A HOL-8-84

Peak temp. (*K*)	$\varnothing/T^2 \times 10^{-5}$	$E\varnothing/RT^2$	E/RT	$e^{-E/RT} \times 10^{-15}$	$A \times 10^{14}$
521	8.878	1.5480	33.467	0.2912	5.3159
511	4.289	0.7478	34.122	0.1520	4.919
500	2.200	0.3836	34.873	0.0718	5.343
493	1.111	0.1937	35.368	0.04355	4.448
		average $A = 5.017 \times 10^{14}$			
Slope temp.					
508	9.339	1.6284	34.324	0.12352	13.18
497	4.534	0.7906	35.084	0.05820	13.58
485	2.338	0.4077	35.951	0.02442	16.70
480	1.172	0.2044	36.326	0.01684	12.14
		average $A = 1.390 \times 10^{15}$			

Peak $\frac{E\varnothing}{RT^2} = A\,e^{-E/RT}$

as $\varnothing \to 0$ $\log 0.1 = \log 5.017 \times 10^{14} = \frac{34680}{4.567T}$

$E\varnothing/RT^2 \to 0.1$

$T = 483$ K $= 210$ °C peak temperature

Slope $\log 0.1 = \log 1.390 \times 10^{15} = \frac{34680}{4.567T}$

$T = 470$ K

$T = 197$ °C autoignition temperature

The autoignition temperature as $\varnothing \to 0$ was obtained for HMX Grade II Class A (β HMX) from the slope of the straight line (Table 8). The slope value of 12500 does not have any apparent functional value. An autoignition temperature of 234 °C was obtained by calculating the peak temperature at a heating rate of 0.1 °C and extrapolating the ignition temperature.

The calculated activation energies of 27,000 cal mol^{-1} for PETN and 35,000 cal mol^{-1} for RDX are low in comparison with the values of other researchers. Activation energy values listed in refs. 4 and 5, particularly those done isothermally in a static atmosphere, are all considerably higher. It is very possible that autocatalysis is responsible for the high values, particularly if the products of decomposition from these explosives were not removed. It is also probable that purer recrystallized material results in higher energies of activation. The samples tested in this report were specification grade materials used as manufactured.

Since TNT evaporates rapidly above 220 °C, thus cooling the liquid TNT, ignition is very difficult to obtain by DTA except at the fastest rate. To obtain meaningful data (exotherms) the samples of TNT were capped. The capping slowed

TABLE 5

DTA DATA PETN PA 2-267T[a]

Nominal rate (°C min^{-1})	*Actual rate (°C min^{-1})*	*Exotherm temp. (°C)*		*Sample weight (mg)*
		Slope	*Peak*	
20	21	197	209	0.8
20	24	199	212	1.6
20	23	201	212	1.8
20	24	202	213	2.0
20	27	203	214	3.8
average	23.8	200	212	
10	10.4	194	203	3.4
10	10.0	190	204	2.7
10	10.4	192	204	2.7
10	11.4	189	199	5.0
10	11.4	193	202	3.6
average	10.7	192	202	
5	5.2	184	194	3.5
5	5.2	181	192	2.5
5	5.0	186	197	3.8
5	5.5	181	193	1.9
5	5.9	185	194	3.1
average	5.4	183	194	
2.5	2.7	177	185	2.7
2.5	2.6	180	187	4.1
2.5	2.6	176	184	4.2
2.5	2.7	177	188	4.1
2.5	2.9	172	189	4.0
average	2.7	176	187	

[a] Argon flow across sample = 28–30 ml min^{-1}.

TABLE 6

CALCULATION OF ACTIVATION ENERGY AND AUTOIGNITION TEMPERATURE FOR PETN PA 2-267T

Temperature		*Rate* $\varnothing$ ($^\circ C\ min^{-1}$)	$T^2 \times 10^5$	$\varnothing / T^2 \times 10^{-5}$	$1/T \times 10^{-3}$
°*C*	*K*				
Temperature at the peak of the exotherm					
212	485	23.8	2.352	10.1190	2.061
202	475	10.7	2.275	4.7033	2.096
194	467	5.4	2.181	2.4759	2.141
187	460	2.7	2.107	1.2814	2.178
Temperature at the slope to the exotherm peak					
200	473	23.8	2.237	10.6392	2.114
192	465	10.7	2.162	4.9491	2.150
183	456	5.4	2.098	2.5739	2.188
176	449	2.7	2.034	1.3274	2.217

$$\text{slope} = \frac{E}{2.303R} = \frac{\log(\varnothing/T^2)-(\varnothing/T^2)_2}{1/T_1 - 1/T_2}$$

$E_p = 33260$ cal mol^{-1} peak
$E_s = 38360$ cal mol^{-1} slope

PETN PA 267T

Peak temp. (*K*)	$\varnothing / T^2 \times 10^{-5}$	$E\varnothing / RT^2$	E/RT	$e^{-E/RT} \times 10^{-15}$	$A \times 10^{15}$
485	10.1190	1.6939	34.514	1.0293	1.6456
475	4.7033	0.7873	35.241	0.4960	1.5872
467	2.4759	0.4145	35.845	0.2695	1.5380
460	1.2814	0.2145	36.390	0.1553	1.3811
					average $A = 1.5380 \times 10^{15}$
Slope temp. (*K*)					
473	10.6392	1.7809	35.390	0.4170	4.2707
465	4.9491	0.8285	35.997	0.2321	3.5695
456	2.5739	0.4309	36.709	0.1151	3.7440
449	1.3274	0.2222	37.282	0.0636	3.4937
					average $A = 3.770 \times 10^{15}$

as $\varnothing \to 0$ *Peak* $\dfrac{E\varnothing}{RT^2} = A\,e^{-E/RT}$

$E\varnothing/RT^2 \to 0.1$ $\log 0.1 = \log 1.538 \times 10^{15} - \dfrac{33260}{RT \times 2.303}$

$T = 450$ K
$T = 177\,^\circ$C peak temperature

Slope $\log 0.1 = \log 3.770 \times 10^{15} - \dfrac{33260}{RT \times 2.303}$

$T = 439$ K
$T = 166\,^\circ$C autoignition temperature

the escape of the gases—raising the vapor pressure and diminishing the evaporation rate. Ignition could then take place at lower temperatures than if the small samples of TNT were heated unconfined.

Peak temperatures from TNT exotherm produced a straight line relationship from the logarithm of $\varnothing/T^2$ versus $1/T$. The straight line is indicative that a first order reaction exists and that the evaporation had a negligible effect once ignition took place.

TABLE 7

DTA DATA FOR HMX GRADE II CLASS A HOL 701-19[a]

Nominal rate (°C min^{-1})	*Actual rate (°C min^{-1})*	*Exotherm temp. (°C)*			*Sample weight (mg)*
		Initial	*Slope*	*Peak*	
20	23.0	273	279	283	—
20	24.5	276	278	282	4.0
20	20.0	276	279	283	3.7
20	27.0	275	277	280	3.3
20	23.0	275	278	283	2.3
average	23.5	275	278	282	
10	10.5	271	275	280	3.6
10	10.3	270	275	280	2.6
10	12.0	270	275	280	2.3
10	10.0	273	277	282	1.5
10	10.3	—	278	282	1.4
average	10.6	271	276	281	
5	5.5	266	274	280	4.9
5	5.9	268	273	280	2.2
5	5.3	267	272	280	4.8
5	5.7	267	271	276	5.8
5	5.9	267	271	278	3.7
5	5.7	263	271	278	3.2
average	5.7	266	272	279	
2.5	2.6	251	267	273	3.6
2.5	2.8	247	270	275	3.2
2.5	3.0	246	269	275	2.7
2.5	2.6	251	270	275	2.7
2.5	2.7	256	268	272	2.7
2.5	2.7	261	272	275	2.9
2.5	2.4	252	268	275	3.4
average	2.7	252	269	274	
1.25	1.20	241	260	263	
1.25	1.10	248	262	268	
1.25	1.20	—	254	256	
1.25	1.30	246	263	266	
1.25	1.10	246	261	266	
1.25	1.30	249	259	263	
average	1.20	246	260	264	

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[a] Argon flow of 28–30 ml min^{-1} for all experiments.

TABLE 8

CALCULATION OF ACTIVATION ENERGY AND AUTOIGNITION TEMPERATURE FOR HMX GRADE 11 CLASS A HOL 701-19

From Fig. 5: $\frac{y_2 - y_1}{x_2 - x_1} = m = -1.25 \times 10^4$

$$
\begin{aligned}
y &= mx + b \\
T^2/\varnothing &= -1.25 \times 10^4\, T_p + b \\
b &= 3.54 \times 10^6 \\
m &= \text{slope}
\end{aligned}
$$

if $\varnothing = 0.1\,^\circ\mathrm{C\ min^{-1}}$, then solving the quadratic equation for $T = 238\,^\circ\mathrm{C}$ for the peak; the ignition temperature would be 4–5 °C less or 234 ± 10 °C.

Temp. (°C)	*Abs. temp.* (K)	$\varnothing$ = *rate* (°C min^{-1})	$1/T \times 10^3$	$\varnothing/T^2 \times 10^{-5}$	$T^2/\varnothing \times 10^5$
Temperature at the peak of exotherm					
282	555	23.5	1.801	7.660	0.131
281	554	10.6	1.805	3.470	0.288
279	552	5.7	1.812	1.870	0.535
274	547	2.7	1.830	0.903	1.107
264	537	1.2	1.862	0.416	2.404
Temperature at the slope to the exotherm peak					
278	551	23.5	1.815	7.730	0.129
276	549	10.6	1.821	3.540	0.282
272	545	5.7	1.838	1.910	0.524
299	542	2.7	1.848	0.918	1.089
260	533	1.2	1.826	0.422	2.370

Since the autoignition temperatures reported here are based on a minimal heating rate, it is theoretically possible for ignition to take place at lower temperatures. Since explosives do decompose below their autoignition temperature, it is possible, that an explosive of large enough critical diameter with proper confinement, and surrounded by sufficient gaseous decomposition products could ignite. Heating large samples of explosives in closed ovens at temperatures approaching the autoignition temperatures are not advised. The DTA experiments do indicate that explosives heated to temperatures below the autoignition temperatures and then cooled will not spontaneously explode.

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