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THERMOCHEMISTRY OF EXPLOSIVES

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ABSTRACT

The kinetics constants for the decomposition reaction of an explosive can be used to calculate the lowest temperature (critical temperature, T_m) at which any specific size and shape of explosive can self heat to explosion; however, the accuracy of the calculation is in doubt without an independent experimental determination of a critical temperature for a known size and shape of the explosive. A method is presented for the experimental determination of critical temperatures on a routine basis, and it is shown that agreement between calculated and experimental values is excellent for most common explosives.

INTRODUCTION

An explosive decomposes exothermally at a definite rate at every temperature above absolute zero. When the physical characteristics of the mass of explosive are such that the heat produced by chemical decomposition cannot be transferred to the surroundings as rapidly as it is produced, the mass of explosive will self heat to explosion. The lowest constant surface temperature above which a thermal explosion is produced is called the critical temperature, T_m. The heat-balance problem has been considered[1–3], and a relatively simple expression has been derived for the critical temperature in terms of the related chemical and physical parameters, as follows:

$$\frac{E}{T_m} = R \ln\left[\frac{a^2 \rho Q Z E}{T_m^2 \lambda \delta R}\right] \qquad (1)$$

where R is the gas constant (1.9872 cal mol^{-1} K^{-1}), a is the radius of a sphere or cylinder or the half-thickness of a slab, ρ is the density, Q is the heat of reaction during the self-heating process, Z is the pre-exponential and E the activation energy from the Arrhenius expression, λ is the thermal conductivity, and δ is the shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, and 3.32 for spheres).

As shown in Fig. 1, an infinite number of compensating pairs of activation energies and pre-exponentials will give the correct critical temperature for a charge of specified size and shape; however, each set will give different values for every other size or shape. Only the correct set of kinetics constants will give the correct critical

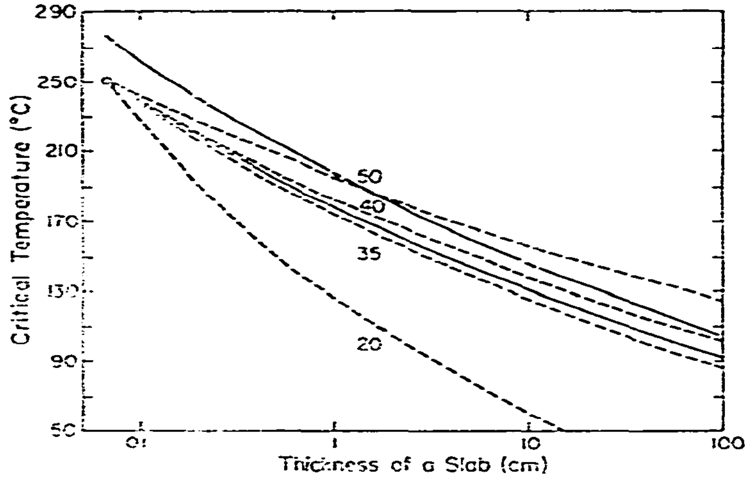

Fig. 1. Compensation of E and Z. The circle is the experimental T_m for BTF (benzenetrifuroxan); the dashed lines are calculated curves, using compensating pairs of activation energies and pre-exponentials at the experimental point. Compensating pairs are the following: $E = 50$ kcal mol^{-1}, $Z = 3.16 \times 10^{18}$ sec^{-1}; $E = 40$ kcal mol^{-1}, $Z = 2.62 \times 10^{14}$ sec^{-1}; $E = 37.2$ kcal mol^{-1}, $Z = 1.92 \times 10^{13}$ sec^{-1}; $E = 35$ kcal mol^{-1}, $Z = 2.44 \times 10^{12}$ sec^{-1}; $E = 20$ kcal mol^{-1}, $Z = 2.3 \times 10^{6}$ sec^{-1}. The upper solid line is the theoretical curve from the data of Table 2 ($E = 37.2$ kcal mol^{-1}, $Z = 4.11 \times 10^{12}$ sec^{-1}); for the lower solid line the same E was used, but the Z (1.92×10^{13} sec^{-1}) was chosen to give the correct T_m at the experimental point.

temperature for every size and shape. Therefore, it is important to make accurate determinations of kinetics constants and to have an independent method for the determination of critical temperatures for at least one specific size and shape. When the calculated and experimental critical temperatures are found to agree, it should be possible to use the kinetics constants to calculate critical temperatures for other sizes and shapes with some confidence.

For practical purposes, the experimental method for the determination of critical temperatures should be adaptable to laboratory operations. It must, therefore, be a compromise between accuracy of definition of conditions and violence of reaction. Henkin and McGill[4] presented a time-to-explosion method, designed for the determination of kinetics constants, that could be adapted for the experimental determination of critical temperatures on a laboratory scale. A modified procedure[5] was used in earlier attempts to verify eqn (1) (ref. 6). The method has been further modified to increase the accuracy with which physical conditions can be specified, but it must be recognized that a small-scale, routine test has limitations with regard to accuracy.

It is fortunate from al practica standpoint that the chemical and physical parameters of eqn (1) appear within a log term, making moderate errors in the various parameters more tolerable. E, Z, and λ are the largest and smallest values normally appearing in eqn (1); therefore, they are the most critical to know accurately, but they are the most difficult to obtain. It is almost impossible to obtain thermal conductivity data under the conditions of the experiment; therefore, it has been my approach to make the most accurate measurements possible of E and Z, to use measured values for λ where available, to make "reasonable guesses" for λ where no data are available, and to absorb the resulting error in the log term. Results appear to justify this approach.

EXPERIMENTAL

All of the new kinetics constants reported were determined by use of the Perkin-Elmer DSC-1B or DSC-2[7,8].

The time-to-explosion test for the determination of T_m uses empty aluminum blasting-cap shells (DuPont E-83, approximately 0.25-in. ID × 1.625-in. long, weighing approximately 0.719 g empty). The explosive sample (40 mg in the "standard" test) is placed in the shell, and it is confined with an aluminum plug. The plugs in use are hollow anodized aluminum plugs 6.55-mm OD × 5.33-mm ID and 5.64-mm long. Standard Lee plugs have also been used. The sample and confining shell and plug are pressed with a conical punch in a suitable die body to a pressure somewhat less than 6,100 p.s.i. (400 pounds force), as required to expand the aluminum plug to form a positive seal. Assembled cells and component parts are shown in Fig. 2. After pressing, sample thickness can be measured and density can be calculated. The assembly is

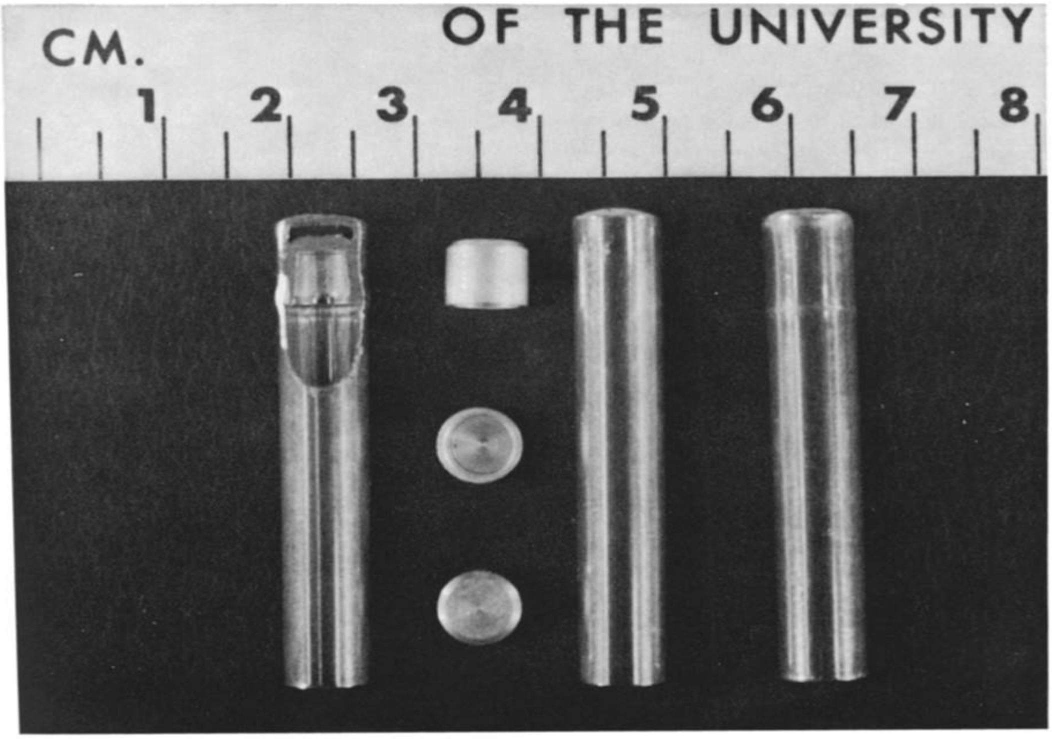

Fig. 2. Time-to-explosion cells and component parts. From right to left: (1) loaded cell, showing wall deformation over flared plug; (2) empty, unused, DuPont E-83 blasting-cap shell; (3) three views of the plug; and (4) cutaway view of loaded cell, sample black for visibility.

dropped into a preheated metal bath, and the time to explosion is measured. With the sample completely confined in an aluminum system, we find that the explosion often ruptures the shell at the bottom; therefore, time is measured from insertion to the sound of the reaction. Explosions tend to throw hot metal in all directions; therefore, the assembly shown in Fig. 3 is used to confine the metal bath. When explosions are obtained with a given explosive, the metal bath temperature is lowered until explosions are not obtained. The lowest temperature at which an explosion can be obtained is T_m. It often requires a relatively large number of tests (10 or more) to determine T_m with confidence. Any thermal-runaway reaction is considered to be an explosion, whether it ruptures the shell or not.

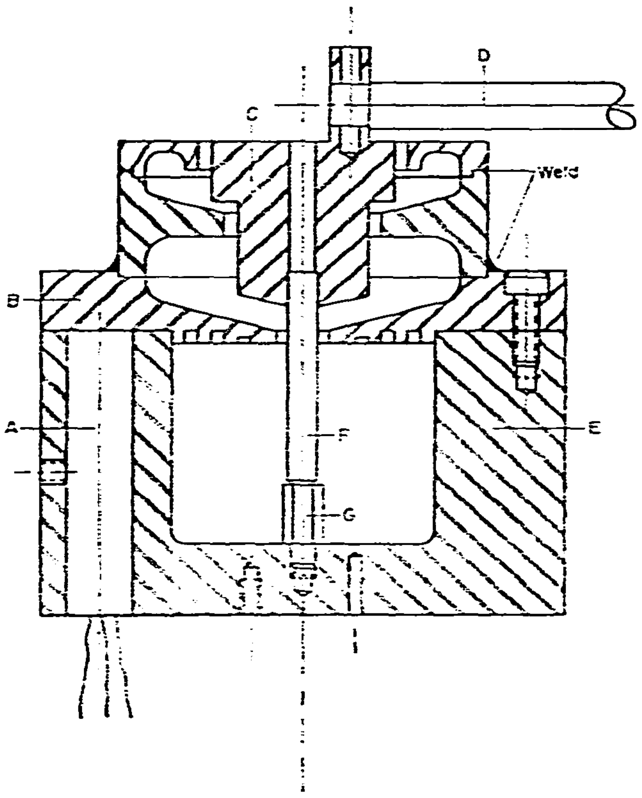

Fig. 3. Experimental assembly for time-to-explosion test. Parts are the following: A = cartridge heaters (3 each); B = top assembly, bolted to base; C = sample-cell holder assembly, the sample cell being insulated from the holder with a band of glass tape around its top; D = sample-cell-holder pivot arm, allows cell and holder to be inserted into the lower assembly remotely; E = metal-bath container, made from mild steel for stability with molten metal; F = sample cell; and G = sample-cell support pedestal, length adjusted according to length of sample cell. Also shown in the base are a grounding lug and a thermocouple well.

DISCUSSION

Earlier time-to-explosion tests were run in gilding-metal blasting cap shells; however, it was found that a number of explosives were quite incompatible with the gilding metal. A comparison between results obtained in gilding-metal and aluminum shells for the "worst" explosives identified to date is shown in Table 1. It is possible that a few explosives may be slightly incompatible with aluminum, but the effects were not observed during kinetics constants determinations in aluminum DSC cells.

TABLE 1

COMPARISON OF CRITICAL TEMPERATURES IN GILDING-METAL AND ALUMINUM TIME-TO-EXPLOSION CELLS

Explosive	T_m (°C)	
	Gilding-metal	*Aluminum*
TATB	312	331
DATB	298	321
BTF	196	250

A comparison between critical temperature values determined with the experimental time-to-explosion method and calculated with eqn (1) is shown in Table 2. Half-thickness values, a, and densities, ρ, are typical for the explosives as pressed into the test assemblies. The pressed sample is very thin, approximating a slab better than a cylinder; therefore, 0.88 is used for δ.

Robertson's kinetics constants for HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane)[9] were checked with the DSC[7,8], and the check was excellent. However, HMX decomposition rates are high, and I feel more confidence in Robertson's numbers.

RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) kinetics constants show an almost perfect check between Robertson's values[9] and DSC values; however, a very large number of data points was available from DSC work, leading to use of the DSC values for the calculations.

No attempt has been made to determine kinetics constants for TNT (2,4,6-trinitrotoluene) by the DSC method. Robertson's constants[10] give by far the best check with experimental time-to-explosion data of any literature values.

There was no difference between Robertson's values[11] and DSC values for the constants of PETN (pentaerythritol tetranitrate).

Kinetics constants for TATB (1,3,5-triamino-2,4,6-trinitrobenzene), BTF (benzenetrifuroxan), NQ (nitroguanidine), PATO (3-picrylaminotriazole), and HNS (2,2′,4,4′,6,6′-hexanitrostilbene) were determined by the DSC method.

The kinetics constants for DATB (1,3-diamino-2,4,6-trinitrobenzene) were determined by the DSC method, and the results agree very well with those reported by Maksimov[12], $E = 50$ kcal mol^{-1} and $Z = 10^{15}$ sec^{-1}.

TABLE 2

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED CRITICAL TEMPERATURES

	T_m (°C)		*Values used*					
	Exp.	*Calc.*	*a* (*cm*)	ρ (*g cm*$^{-3}$)	*Q* (*cal g*$^{-1}$)	*Z* (*sec*$^{-1}$)	*E* (*kcal mol*$^{-1}$)	$\lambda \times 10^4$ (*cal cm*$^{-1}$ *sec*$^{-1}$ °*C*$^{-1}$)
HMX	253–255	253	0.033	1.81	500	5×10^{19}	52.7	7.0
RDX	215–217	217	0.035	1.72	500	2.02×10^{18}	47.1	2.5
TNT	287–289	291	0.038	1.57	300	2.51×10^{11}	34.4	5.0
PETN	200–203	196	0.034	1.74	300	6.3×10^{19}	47.0	6.0
TATB	331–332	334	0.033	1.84	600	3.18×10^{19}	59.9	10.0
DATB	320–323	323	0.035	1.74	300	1.17×10^{15}	46.3	6.0
BTF	248–251	275	0.033	1.81	600	4.11×10^{12}	37.2	5.0
NQ	200–204	204	0.039	1.63	500	2.84×10^{7}	20.9	5.0
PATO	280–282	288	0.037	1.70	500	1.51×10^{10}	32.2	3.0
HNS	320–321	316	0.037	1.65	500	1.53×10^{9}	30.3	5.0

All pressed charges of organic explosives reported to date have shown thermal conductivities (λ) between 2 and 13×10^{-4} cal cm^{-1} sec^{-1} °C^{-1}; however, charge densities have not always been reported. Changes in phase should not affect the values greatly; organic liquids and frothy organic liquids would be expected to have thermal conductivities in the indicated range. Guessed values are weighted for differences in density, tending to keep the result in the middle of the reported range of values. It is impractical to attempt to measure λ under the conditions of the time-to-explosion test; therefore, it is doubtful that values better than the guesses will be obtained in the near future. Note that an error is commonly found in reported values for the λ of RDX in the open literature: the best value is 2.53×10^{-4} cal cm^{-1} sec^{-1} °C^{-1} at a density of 1.533 g cm^{-3}. The value for DATB was obtained from ref. 13, and the value for HMX was weighted from the same source and local measurements on plastic-bonded explosives.

The heat of reaction, Q, should be the heat effect that obtains during the self-heating phase of the process: it is not the heat of combustion, heat of detonation, or even the heat effect during the thermal explosion. It is usually found that heat effects, as measured with a DSC, vary widely as a function of confinement or heating rate, but, to a first approximation, the assumption can be made that all explosives have a Q of about 500 cal g^{-1}. The values presented in Table 2, however, have been weighted into three groups according to DSC measurements: compounds showing measured values at different degrees of confinement that are significantly below "normal" are assigned a Q of 300 cal g^{-1}, and those with experimental values above "normal" are assigned a value of 600 cal g^{-1}. An absolutely accurate value for Q is not required, because Q appears in the log term of eqn (1).

The values of Q listed in Table 2 for PETN and TATB may appear to be at variance with experience, but DSC measurements on PETN have been as low as 140 cal g^{-1} and values for TATB have been as high as 750 cal g^{-1}.

Most common high explosives melt with decomposition, but a few appear to decompose completely in the solid state; however, phase changes, changes in composition, and changes in crystal perfection change decomposition rates as a function of extent of decomposition. When the critical temperature of an explosive is below its nominal melting point, it must decompose in the solid state, usually a slow process, until some change allows its decomposition rate to increase sufficiently for it to self-heat to explosion. Therefore, the *time to explosion* may be largely determined by the low-rate, solid-state reactions, but the *critical temperature* will be determined by the process showing the maximum rate attainable in a condensed-phase reaction for the explosive in question. This is an important distinction, because we can usually measure the kinetics constants for the most rapid reaction quite accurately, and, consequently, we can calculate a critical temperature with some confidence. However, the solid-state reactions involved in time-to-explosion estimations are difficult to measure accurately, and the solid-state rates can vary tremendously with changes in purity and crystal perfection.

TATB appears to decompose entirely in the solid state, and it shows a maximum in its rate curve. The most rapid condensed-phase reaction occurs after the disappearance of the TATB X-ray diffraction pattern, that is, the most rapid reaction occurs in an amorphous phase. Kinetics constants obtained from the reaction in the amorphous phase predict the critical temperature perfectly.

Temperatures involved in the kinetics measurements and the self-heating reaction are within the same range; therefore, critical-temperature predictions should be quite accurate. However, the DSC sample does not see the same confinement as a real charge. Changes in mechanism or contributions from heterogeneous reactions could change the observed maximum-rate process, a fact that emphasizes the importance of an independent time-to-explosion determination of the critical temperature.

The data on BTF show how it is possible to detect potentially hazardous systems. The measured kinetics constants give a critical temperature that is much higher than the observed value; therefore, the DSC measurement obviously missed the most rapid reaction. Order plots[7] for BTF taken *above* the melting point showed that the reaction order did not become positive until approximately 21% decomposition, and the reaction did not approach first order until approximately 63% decomposition. There is definitely complexity in the reaction, suggesting caution in handling BTF until more is known about its chemistry.

With the exception of BTF, the excellent agreement between calculated and experimental values makes it appear possible to make valid calculations for other shapes, sizes, and densities of the explosives listed in Table 2, using the values presented.

CONCLUSION

Kinetics constants (the activation energy, E, and pre-exponential, Z, of the Arrhenius equation) can be determined for the decomposition reactions of many explosives with a differential scanning calorimeter[7,8]. The kinetics constants can be used to estimate the lowest temperature (critical temperature) at which any specified size and shape of explosive can self-heat to explosion; however, the accuracy of the calculation is in doubt without an independent experimental determination of a critical temperature for a known size and shape of the explosive. A method is presented for the experimental determination of critical temperatures on a routine basis, and it is shown that agreement between calculated and experimental values is excellent for most common explosives.

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