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THE THERMOCHEMISTRY OF EXPLOSIVES:
A REVIEW

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ABSTRACT

The application of traditional thermal analysis techniques as well as specialized thermal techniques to the characterization of explosives is reviewed. Topics included are general references, pressure measurement techniques, gaseous product analysis, DTA, DSC, TG, combined TG–DTA, and miscellaneous techniques as applied to a variety of explosive materials. The bibliography includes 135 references.

INTRODUCTION

The characterization of the thermal chemistry of explosive materials constitutes an important and growing discipline within the field of thermal analysis. Qualitative knowledge of the thermal behavior of explosive materials based on intuition is no longer sufficiently reassuring to the worker handling these materials on a daily basis. Fortunately, the techniques of thermal analysis have proved amenable to the quantitative study of the thermal properties of explosives while presenting challenges in both experimental design and interpretation. Although large quantities of thermal data have been generated and reported over the last few years, the study of the thermochemistry of explosives is still in its infancy and remains an active area of investigation. Therefore, it was rather surprising to discover the scarcity of basic reviews covering the literature of this important field.

With the exception of the few limited reviews described later, the authors were unable to find a summary of the techniques, procedures, and applications utilized

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in the study of the thermal properties of explosives as reported in the literature. This paper seeks to at least partially rectify this situation. Although no claims are made as to the completeness of the review, or even that the best papers were selected, we do feel that the review adequately represents the major thrust of work currently being done in the field and provides references which the interested reader can consult for further details.

GLOSSARY OF TERMS

The study of explosives, as with most scientific disciplines, consists of a myriad of acronyms, abbreviations, and other abuses of the language which can intimidate if not discourage the uninitiated. To help alleviate the confusion, we offer the following list of common terms as a guide to the remainder of the paper.

PETN = pentaerythritol tetranitrate
RDX = 1,3,5-trinitro-s-triazine; cyclotrimethylenetrinatramine; hexogen
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; cyclotetramethylenetetranitramine; octogen
PETriN = pentraerythritol trinitrate
CN = cellulose nitrate
HEM = highly energetic material
TNT = trinitrotoluene
TNB = 1,3,5-trinitrobenzene
Pentolite = mixture of PETN and TNT
Tetryl = N-methyl-N,2,4,6-tetranitroaniline; trinitrophenylmethylnitramine

GENERAL REFERENCES

Although texts devoted exclusively to the thermal properties of explosives could not be found, the thermal behavior of explosive materials is discussed to a limited extent in several reference works. An excellent book entitled *Chemistry of the Solid State*, edited by Garner[48], describes much of the early work on the theory of solid state thermal decomposition with numerous examples relating to explosive materials. The chapters on the "Kinetics of Exothermic Solid Reactions" by Garner and Bircumshaw, the "Decomposition of Organic Solids" by Bawn, and "Explosion and Detonation in Solids" by Ubbelohde are especially significant. *The Decomposition of Solids* by Young[133] also deals with the solid state decomposition of explosive materials although in a less explicit manner than Garner's book. Thermal decomposition of pyrotechnic constituents and blends is treated in some detail in excellent reference books by Ellern[40] and by Shidlovsky[122] and in the *Engineering Design*

TABLE 1

PHYSICAL PROCESSES DETECTABLE BY THERMAL ANALYSIS[a]

Physical process	*Indicated by*				*Conventional thermal decomposition rate*
	TG		*DTA*		
	Increase	*Decrease*	*Endothermic*	*Exothermic*	
Melting	—		+		
Sublimation		+	+		+
Boiling		+	+		+
Phase transformation	—		+	+	+
Desorption		+	+		+
Adsorption	+			+	+
Solid reaction			+	+	—
Decomposition	—	+	+	+	+
Explosion		+		+	+
Oxidation, reduction	+	+	+	+	+

Key: +, process is indicated; —, process is not indicated.

[a] Table 1 is reprinted from ref. 81 with permission from the author and *Thermochimica Acta*.

Handbook—Military Pyrotechnics Series produced by the US Army Materiel Command[125]. General reference books describing thermoanalytical methods which may be useful include *Thermal Methods of Analysis* by Wendlandt[129] and *Thermal Analysis* by Schwenker and Garn[121].

The application of thermoanalytical techniques to explosives and propellant ingredients was reviewed by Maycock[81]. The chart reproduced in Table 1 served as a guide to the selection of applicable thermal techniques and the interpretation of the data was discussed in some detail. Three techniques commonly used in decomposition kinetics studies were reviewed: (1) normal isothermal decomposition using TG techniques; (2) shifts in DTA traces as a function of heating rate; and (3) analysis of dynamic TG traces as a function of heating rate. Other topics discussed include phase changes of explosives and experimental techniques with reference to sample preparation, atmosphere control, and particle size. Routine test procedures, propellant characterization, radiation damage studies, and heats of explosion measurements were mentioned as applications of thermoanalytical techniques.

The stability of explosives, including thermal stability, was reviewed by Aubertein[11]. Definitions and procedures for routine stability tests were described and a selection of testing standards was discussed. After establishing the distinction between chemical stability as used in general chemistry (e.g., dissociation) and stability of explosives, meaning their storage life without deterioration under practical conditions, Aubertein pointed out that most stability tests applied to explosives have little or no meaning since the specific properties of the explosive under consideration are not taken into account in the procedural test conditions. Some interesting historical background on the thermal stability of explosives and the development of stability tests is also given in the article.

Decomposition kinetics procedures and mechanisms for the thermal decomposition of explosives were reviewed in an article by Andreyev[1c]. Although detailed experimental procedures were not considered, general techniques were discussed with the expected thermal behavior for several classes of explosives. This paper provides a general description of kinetics procedures but does not delve into the mathematical derivation of the equations used to calculate the kinetic parameters.

The application of DTA and TG to the examination of explosives was reviewed by Krien[70] (in German). The generation and interpretation of data by these traditional thermal techniques was reviewed in some detail. Several new applications to explosive materials were also mentioned.

PRESSURE MEASUREMENT TECHNIQUES

The monitoring of pressure variation as a function of time or temperature is a classical technique currently used for observing the progress of thermal decomposition reactions of explosive materials. This technique was developed primarily during the 1920's with significant refinements during the 1940's leading to a considerable quantity of high quality kinetics data on the thermal decomposition of explosives. The original method, described by Farmer[41] in 1920, consisted of decomposing a compound into a vacuum system while following the progress of decomposition by means of the gas evolution(pressure)-time curve. Several significant modifications and refinements of the technique have since been made and will be described as applicable.

Vaughan and Phillips[126] were among the first to report the application of the gas evolution technique to the study of explosives with their investigation of the thermal decomposition of certain nitrobenzenediazo-oxides in the temperature range of 50 to 120°C. Sigmoidal volume–time curves were reported but little kinetic interpretation was attempted due to the complexity of the reactions and the limited accuracy of the data. Microscopic examination of the decomposition products and chemical analysis of the gaseous products were also included in the study.

In a 1947 communication to *Nature*, Phillips[91] reported kinetic data obtained from pressure–time study analyses for the thermal degradation of some organic nitrates. However, this apparently represented work performed as part of the war effort; therefore, few details were disclosed although there were several references to unpublished Scientific Advisory Council Reports and implications that a considerable endeavor was underway to unravel the thermal decomposition processes of explosives. The order of thermal stability of the O–N bonds in alkyl nitrates was reported as methyl > ethyl > n-propyl with the order attributed to resonance stabilization effects.

The utilization of the pressure–time technique to determine kinetic parameters for the thermal decomposition of explosives received considerable impetus from the series of papers published by Robertson[100–102] in the late 1940's. The confining system utilized in this study consisted of an Apiezon oil manometer to measure slow reactions or a membrane type manometer consisting of a glass gas handling system and photographic recording to measure fast reactions. Sample heating was accomplished by two different mechanisms—a glass apparatus and an "ovens" apparatus. In the glass apparatus, the sample of explosive was placed in a small glass spoon rotating on a horizontal ground joint so that the sample could be dropped into the heated bulb. The Pyrex bulb was directly immersed in a eutectic mixture of sodium, potassium and calcium nitrates which was controlled to within 1/2°C. The "ovens" apparatus consisted of heated parallel copper plates designed to suddenly close on a thin layer of the explosive sample mounted on a thin mica slide. Either of the heating devices could be incorporated into the closed system.

Robertson investigated the decomposition kinetics of several explosives by utilizing the pressure–time technique. The thermal decomposition reaction of ethylenedinitramine was found[100] to be first order between 184 and 254°C with a half-life of 43 sec at 184°C and 0.5 sec at 254°C. Decomposition was said to occur through a homogeneous reaction since variation of the quantity of sample produced no change in the kinetic results. Studies[100] of the decomposition of tetryl showed some acceleration of the reaction rate during decomposition and the expression for the unimolecular constant of initial decomposition was determined to be $k = 10^{15.4}\exp(-38{,}500/RT)$. PETN pressure–time curves over the temperature range of 161 to 233°C showed a very nearly constant rate of gas evolution for about the first half of decomposition after which the rate diminished in accordance with the unimolecular rate equation. The initial decomposition rate expression was determined to be $k = 10^{19.8}\exp(-47{,}000/RT)$ with the final rates being two or three times greater. Decomposition of PETN dissolved in dicyclohexyl phthalate was also investigated as well as the decomposition of ethylenediamine dinitrate and ammonium nitrate.

Kinetics data have been reported for some cyclic nitroamines which were determined to undergo a liquid phase decomposition in accordance with the unimolecular equation[101]. Solutions of RDX in dicyclohexyl phthalate and TNT were found to exhibit a decreased rate relative to the decomposition of the fused explosive. This suggests that short chain reactions are involved in the decomposition of the pure material.

An interesting series of papers was published by Batten[16, 17] and Batten and Murdie[14, 15] which characterize the thermal decomposition of RDX at temperatures below the melting point. The pressure measurement systems used in these studies are illustrated in Figure 1. The authors discussed several factors which influence the decomposition process, postulated a decomposition mechanism, calculated activation energies, and considered the catalytic effect of formaldehyde on the decomposition reaction. The sigmoidal decomposition process was divided into three stages—an induction period, an acceleration region, and a maximum rate region. The induction period was attributed to negative catalysis by the decomposition products, the acceleration region was thought to involve competing reactions of positive and negative catalytic gaseous decomposition products with the undecomposed RDX, and the maximum rate region represents the condition where negative catalytic action is minimized. It was reported that the presence of formaldehyde substantially accelerated

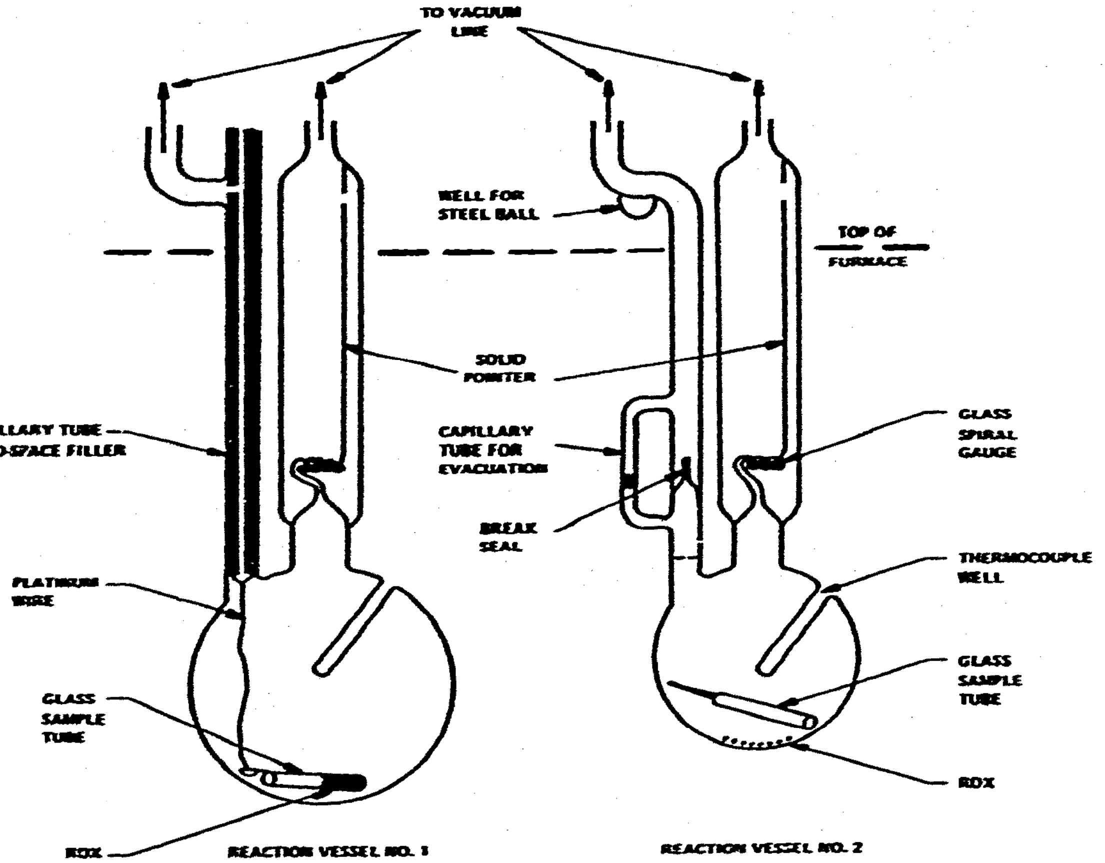

Fig. 1. Reaction vessels used by Batten and Murdie[14] for the study of the thermal decomposition of RDX. (Reproduced from ref. 14 with permission from the authors and the *Australian Journal of Chemistry*.)

the rate of reaction with the duration and degree of the acceleratory process increasing steadily with decreasing reaction temperature to about a six-fold increase at the lowest temperature relative to the highest. Typical decomposition–time curves for the decomposition of RDX below its melting point are shown in Fig. 2. These curves display the sigmoidal shape which is characteristic of most data generated by the pressure–time technique.

Cosgrove and Owen[33–35] have also made a substantial contribution toward elucidation of the thermal decomposition reactions of RDX. These authors reported that the rate of decomposition was directly proportional to the volume of the reaction vessel, independent of the amount of RDX at a constant volume, and retarded by the presence of inert gases. Data were presented which indicated that gas phase decomposition of RDX was dominant during the initial stages of the reaction. The effects of the products—nitrogen, nitrous oxide, nitric oxide, carbon dioxide, carbon monoxide, water, formaldehyde, hydroxymethyl formamide, and methylene diformamide—as well as a small quantity of TNT, on the decomposition process was discussed.

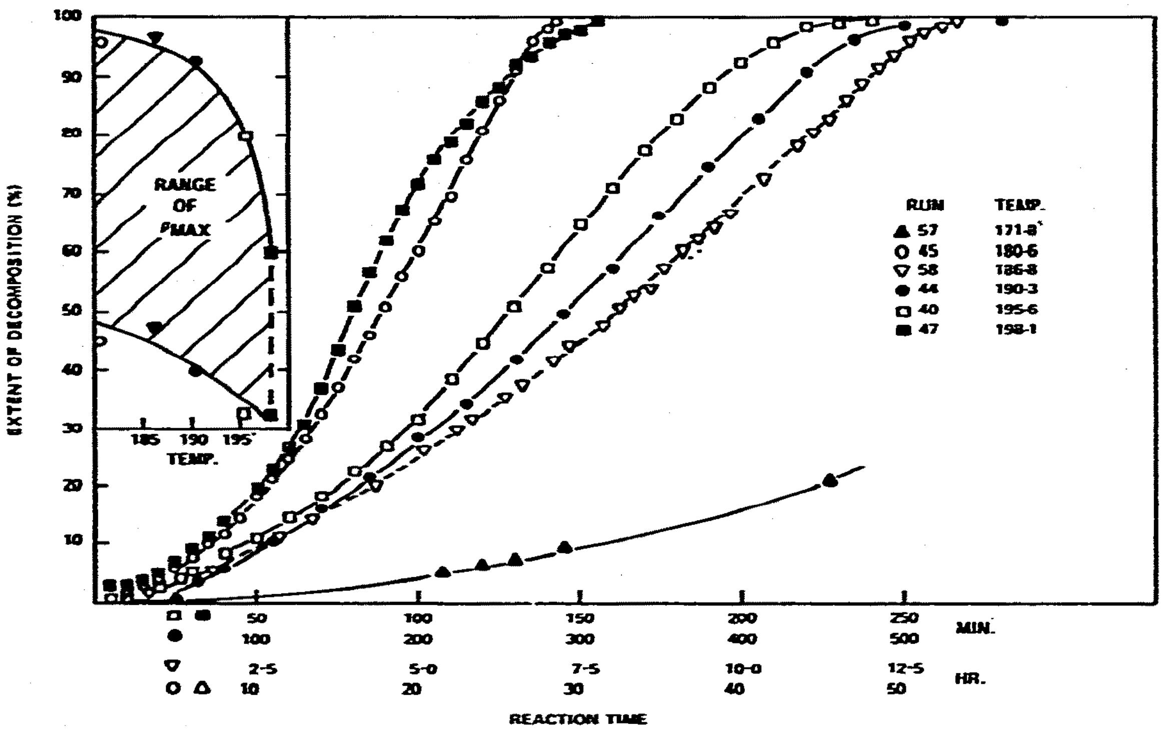

Fig. 2. Typical decomposition–time curves for 0.2-g samples of RDX in the spread condition, at temperatures below its melting point. Inset: Range of the maximum rate plotted against temperature[15]. (Reproduced from ref. 15 with permission from the authors and the *Australian Journal of Chemistry*.)

The thermal decomposition and explosion of azides was studied by Yoffe[132] using the apparatus illustrated in Fig. 3. Topics which were investigated and discussed include autocatalysis of the reaction by the products, self-heating of the sample during decomposition, and the explosive decomposition of the samples. It was noted that the explosion temperature of silver azide was a function of the inert gas pressure above the sample, the mass of the sample and the thermal conductivity of the container vessel and the bath. It was determined that some of the azides decomposed after melting while others decomposed from the solid state.

In the mid-fifties, Bircumshaw and Newman published two papers[20, 21] which represent a rather thorough investigation of the thermal decomposition of ammonium perchlorate. It was found that ammonium perchlorate decomposed to the extent of 28 to 30% when heated at temperatures below 290°C in an inert gas stream or in vacuo and left a residue which was chemically identical to the starting material. The effect of crystal transformation on the decomposition curves was reported as were impurity and particle size effects. Calculations of kinetic parameters were shown using various methods. An extension of this study to higher temperatures (above 350°C) has been reported by Galway and Jacobs[47].

Some interesting information on the processes which control the reaction rate in the burning process was afforded by an investigation of the thermal decomposition

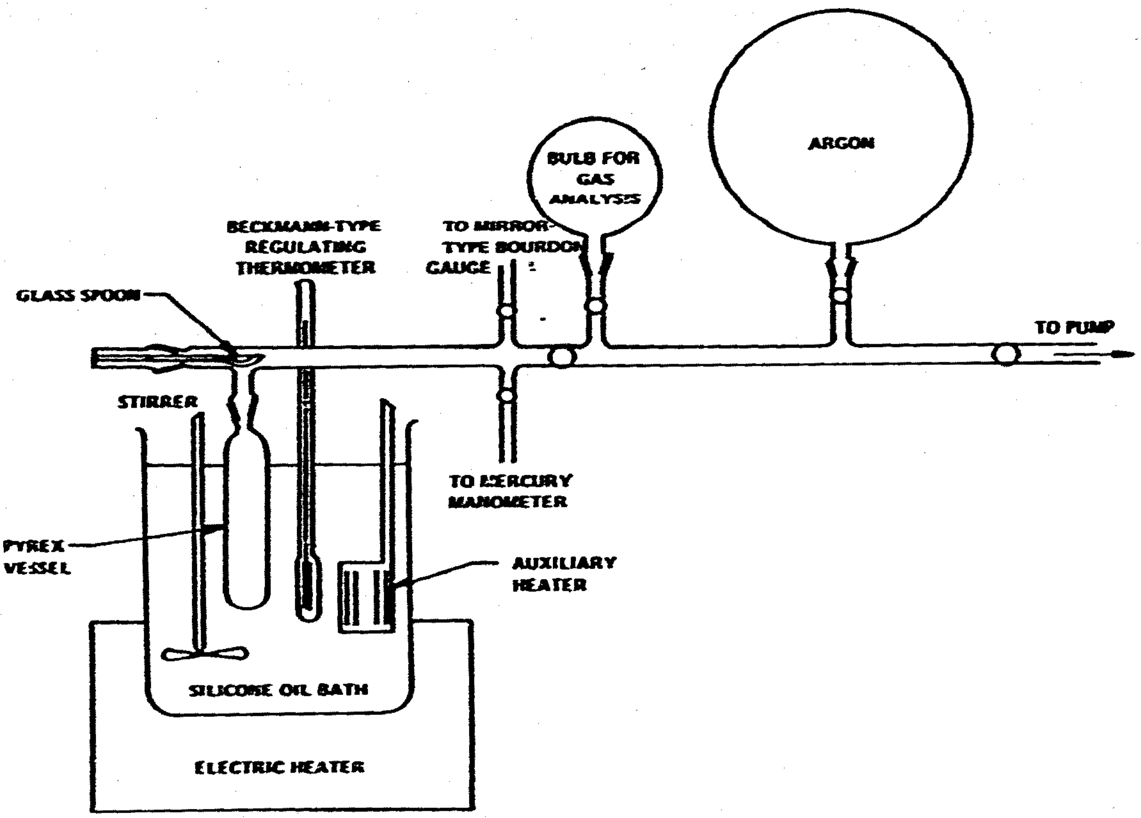

Fig. 3. Apparatus used by Yoffe[132] for studying the decomposition of azides. (Reproduced from ref. 132 with permission from the author and the Royal Society of London.)

of gunpowder[22]. Based upon data obtained by the volume–time technique, the following reactions were postulated for the decomposition process:

$S + \text{organic} \rightarrow H_2S$
$KNO_3 + \text{organic} \rightarrow NO_2$
$2KNO_3 + S \rightarrow K_2SO_4 + 2NO$
$KNO_3 + 2NO \rightarrow KNO_2 + NO + NO_2$
$H_2S + NO_2 \rightarrow H_2O + S + NO$
$2NO_2 + 2S \rightarrow 2SO_2 + N_2$
$2KNO_3 + SO_2 \rightarrow K_2SO_4 + 2NO_2$

These reactions apply essentially to the pre-ignition stages of reaction; once the reaction gets underway and sufficient heat is evolved, then the primary process of the oxidation of carbon by potassium nitrate dominates with propagation of the process through the material. It was suggested that the formation of a liquid phase produced by the melting of sulfur at about 130°C is a necessary condition for initiation of the thermal decomposition process.

The thermal stability of seven structurally related explosive compounds dissolved in TNT was determined by pressure measurements[116]. Large differences in thermal stability were found and were accounted for by the ease of oxidative attack of the substituent by the nitro group. Compounds with easily oxidizable groups are least stable.

Additional studies which utilized the pressure monitoring technique as a portion of the investigation include the decomposition of ethyl nitrate by Pollard et al.[93], the decomposition of nitryl perchlorate by Cordes[32], and the decomposition of solid *trans*-diazidotetraaminecobalt(III) azide by Joyner[68]. A modified version of the pressure rise technique was used by Griffiths and Groocock[54] to study the very rapid gas evolution from the thermal decomposition of α-lead azide. Jach[66] also reported on the decomposition of α-lead azide using a pressure measurement technique and Muellar[84] has studied the decomposition of molten silver azide. Additional studies utilizing pressure techniques include those of Maycock and Pai Verneker[77], Urakawa and Masutomi[124], Pai Verneker and Avrami[89], and Rosen and Dacons[116].

A different type of pressure monitoring technique which utilizes simultaneous thermogravimetry and pressure measurements, known as thermobarogravimetric analysis (TBGA), has been applied to the study of nitronium perchlorate[79] and other explosives[82]. The modified Mettler thermoanalyzer system used to obtain these measurements is illustrated in Fig. 4. By simultaneously recording p vs. t and w vs. t at 10°C intervals in the temperature range from 80 to 150°C, sublimation and decomposition processes for nitronium perchlorate were characterized. Sublimation processes were observed for both nitronium perchlorate and for nitrosonium perchlorate which is formed as a decomposition product of nitronium perchlorate. The

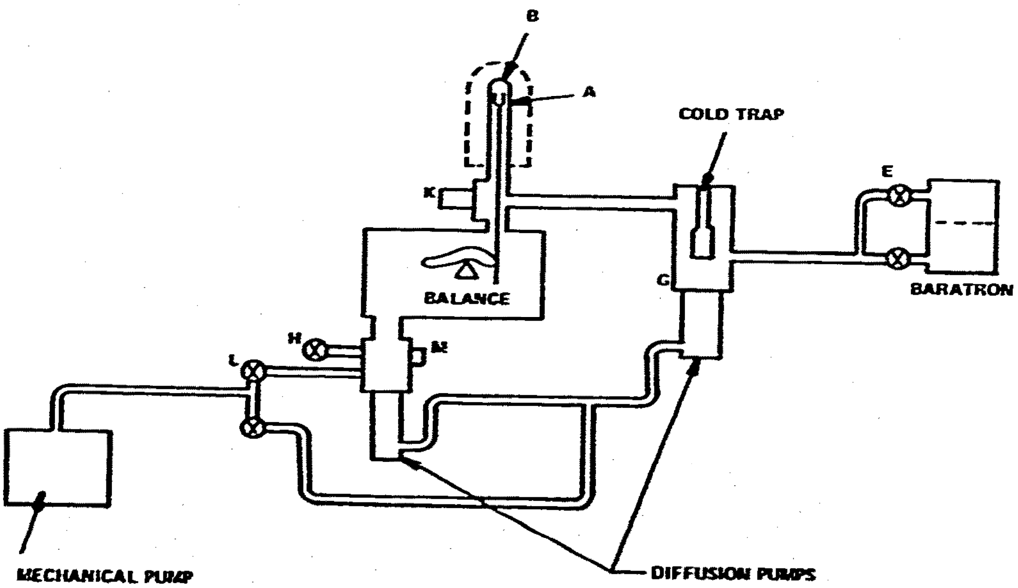

Fig. 4. Diagrammatic section through balance and vacuums system of the Mettler thermoanalyzer used by Maycock and Pai Verneker[79]. (Reprinted with permission from the authors and from J. N. Maycock and V. R. Pai Verneker, *Thermobarogravimetric (TBGA) Technique to Characterize Sublimation Processes, Nitronium Perchlorate, Analytical Chemistry*, 40 (1968) 1935. Copyright by the American Chemical Society.)

sensitivity of the sublimation process to an overpressure of an inert gas was also demonstrated by the technique.

The thermobarogravimetric technique was used to characterize the thermal and photosublimation processes of PETN, RDX, and TNT[82]. A compilation of the activation energies of sublimation and evaporation of the materials compares favorably with previously reported enthalpies of sublimation and evaporation. Photosublimation rates for these explosives were found to be pressure-dependent and proportional to the intensity of the radiant energy; on the other hand, they were independent of radiant wavelength in the spectral region from 200 to 600 nm.

While these pressure–time studies make an important contribution toward the characterization of the thermal properties of explosives, it should be noted that all studies were performed at elevated temperatures. As Aubertein[11] pointed out, the stability of explosives is defined in terms of deterioration under practical storage conditions. Since extrapolation of data from high temperatures to low temperatures is of dubious validity, there is a definite need for modification of the pressure–time or other techniques to include low or ambient temperature decomposition processes.

GASEOUS PRODUCT ANALYSIS

Many studies of the thermal decomposition of explosives utilize analytical techniques to characterize the distribution of evolved gaseous products either as a supplementary technique or as the primary thrust of the research. The procedures and techniques range from minimal classical analysis to elegant instrumental designs. Both trapping or cumulative methods and real time analyses have been used to advantage. It may also be of historical interest to note that a paper by Rogers et al.[110] describing the pyrolysis of some explosive compounds is regarded as a classic in gas evolution studies and is often acknowledged as the birth of gas evolution detection (GED) due to the thoroughness of the investigation.

Gas analysis was often included in pressure–time studies of thermal decomposition to aid in the interpretation of the data. Vaughan and Phillips[126] separated the evolved gases from some nitrobenzenediazo-oxides by fractional condensation with subsequent analysis of the individual fractions. Three fractions were collected: Fraction I, gases volatile at $-186^\circ C$, contained O_2, NO, H_2, CO, and CH_4; Fraction II, gases volatile at $-120^\circ C$, contained CO_2 and N_2O; the residue consisted of organic vapors, NO_2, etc. According to the authors, "accepted chemical methods" were used to analyze the individual fractions.

Robertson[100–102] also utilized fractional separation and analysis of decomposition products in his thermal studies. Analytical methods used include absorption of NO in chromous chloride and determination of CO and H_2 by copper oxide combustion with the residue assumed to be nitrogen. Carbosorb was used to separate and gravimetrically determine the quantity of CO_2 present. Robertson also found that the product distribution from the thermal decomposition of PETN at 210°C varied with heating time.

Bircumshaw and Newman[20, 21] used fractional separation in their study of ammonium perchlorate decomposition. The oxygen and nitrogen fraction was collected with a Toepler pump, transferred to an Ambler gas analysis apparatus, exploded with pure hydrogen, and the oxygen/hydrogen content calculated from the pressure difference. Chlorine and chlorine dioxide were determined by sweeping the evolved gases through a set of absorber bulbs containing a neutral potassium iodide solution followed by titration of the released iodine with thiosulphate. Nitrosyl chloride concentration was determined by measuring the volume decrease of a nitric oxide/oxygen mixture produced by conversion to nitrogen tetroxide in the presence of nitrosyl chloride.

Hermoni and Gruenwald[60] also utilized fractionation with subsequent chemical analysis to study the high-pressure thermal decomposition of nitroethane. However, the residue left at −70°C was dissolved in 0.1 N potassium hydroxide and the nitroparaffins were determined polarographically.

Infrared spectroscopy was used for the analysis of gaseous products from the thermal decomposition of ethyl nitrate[72, 73]. Ethyl nitrate was sealed in bulbs, immersed in a hot bath for a measured time interval, quenched in a cold-water bath, the gaseous contents transferred to an IR cell, and the spectrum recorded. Gaseous products were identified as ethyl nitrite, nitromethane, and methyl nitrite. Nitrogen dioxide and nitric oxide were determined qualitatively by visual observation of color and quantitatively by measurements of absorption intensity at 4050 Å using a visible wavelength spectrophotometer.

Pollard et al.[93] measured the gaseous evolution of nitrogen dioxide from the thermal decomposition of ethyl nitrate by a photometric technique. The intensity of a filtered waveband from 5000 to 5450 Å, in which region nitrogen dioxide absorbs strongly, was measured with a photocell at suitable intervals with concentrations calculated from Beer's Law. Fractionation and analysis was used to determine the other products reported to be CO_2, CO, NO, N_2O, and N_2 with a possible trace of hydrogen.

A fractionation analysis technique was used by Cordes[32] to study the thermal decomposition of nitryl perchlorate. The fraction non-condensable at liquid nitrogen temperature was analyzed on a mass spectrometer and found to be at least 99% oxygen with no nitrogen present. The fraction volatile at −112°C was analyzed spectrophotometrically before and after sparking with a Tesla coil. The only spectral species observable before sparking were ClO_2 and Cl_2 whereas only Cl_2 and NO_2 were observed after sparking. Based upon these data, the original composition of this fraction was deduced to be Cl_2, ClO_2 and NO_3Cl with Cl_2 comprising about 90% of the mixture.

Waring and Krastins[127] identified the gaseous products from nitroglycerin by IR analysis. The decomposition reaction was quenched by quick cooling at timed intervals and the gaseous products were transferred to an IR cell and spectra recorded. Species identified included CO, NO, CO_2, NO_2, and H_2COOH as well as traces of formaldehyde. In that portion of the study designed to determine the sequence of

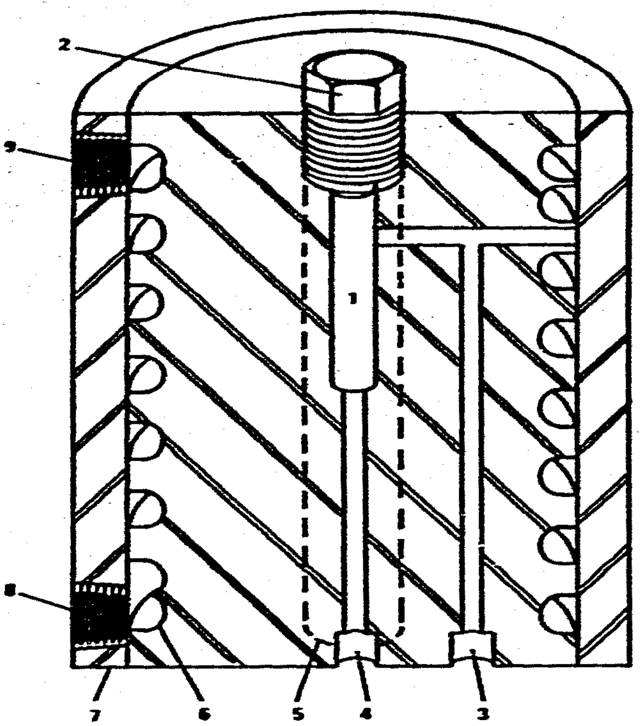

Fig. 5. Schematic of pyrolysis block used in gas evolution detection apparatus developed by Rogers et al.[110]. 1 = Pyrolysis chamber; 2 = nickel plug; 3 = carrier gas inlet; 4 = carrier gas outlet; 5 = cartridge heater wells (2); 6 = helical threads cut in inner body of block; 7 = outer shell of block; 8 = cooling jacket inlet; 9 = cooling jacket outlet. (Reprinted with permission from the authors and from R. N. Rogers, S. K. Yasuda and J. Zinn, *Pyrolysis as an Analytical Tool, Analytical Chemistry*, 32 (1960) 672. Copyright by the American Chemical Society.)

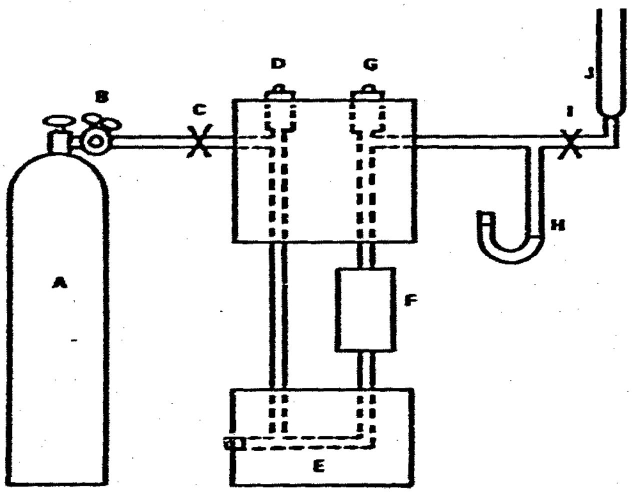

Fig. 6. Schematic drawing of the pyrolysis apparatus developed by Rogers et al.[110]. A = Carrier gas supply; B = pressure regulator; C = flow-control needle valve; D = reference thermal conductivity; E = pyrolysis chamber; F = combustion tube; G = active cell; H = manometer; I = pressure-control needle valve; J = rotameter. (Reprinted with permission from the authors and from R. N. Rogers, S. K. Yasuda and J. Zinn, *Pyrolysis as an Analytical Tool, Analytical Chemistry*, 32 (1960) 672. Copyright by the American Chemical Society.)

product evolution, Waring and Krastins introduced 5 to 10 mg of nitroglycerin into a high-temperature IR absorption cell, brought the system to a requisite temperature, and continuously scanned the spectrum between 2 and 9 μm.

Cosgrove and Owen[33—35] studied the decomposition of RDX at 195°C using a static system with product analysis by mass spectroscopy, IR spectroscopy, and wet chemical methods. Products of decomposition were identified as N_2, NO, N_2O, CO_2, CO, H_2O, methylol formamide and similar compounds, formaldehyde, HCN, a nitrate and a nitrite.

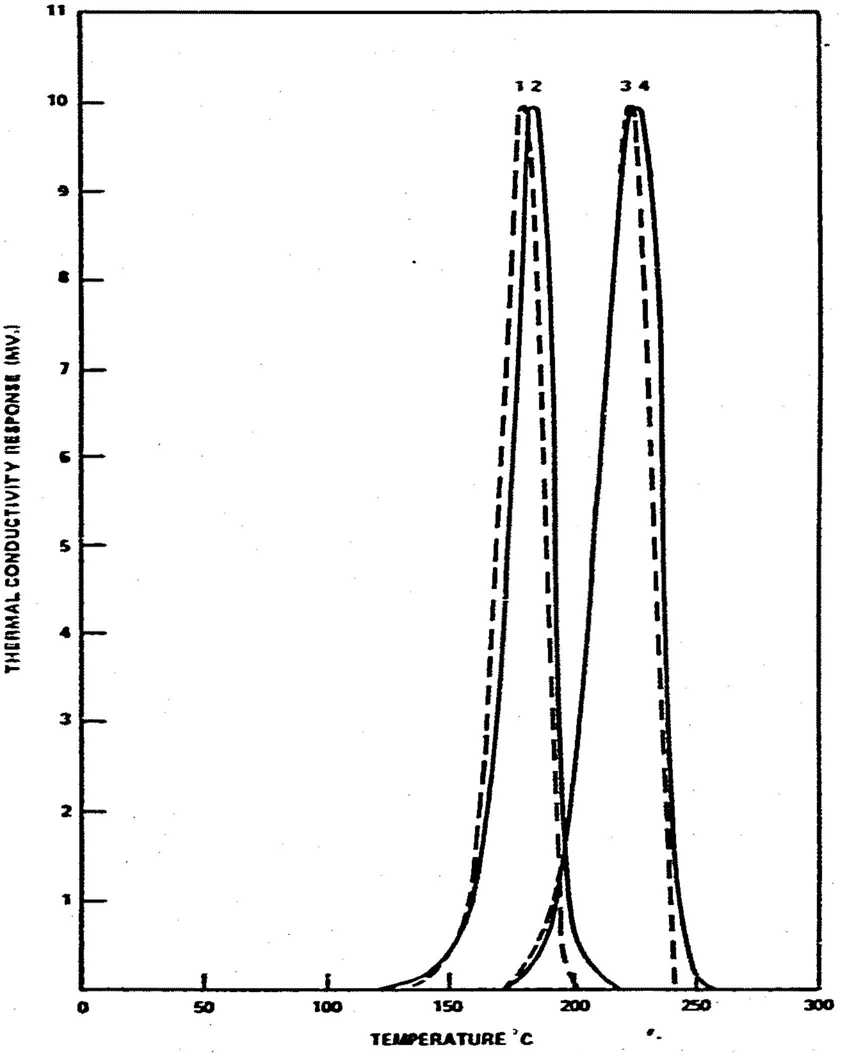

Fig. 7. Comparison of theoretical and experimental pyrolysis curves for PETN and RDX[110]. 1 = Theoretical curve for PETN; 2 = experimental curve for PETN, uncorrected for gas flow time lag; 3 = theoretical curve for RDX; 4 = experimental curve for RDX, uncorrected for gas flow time lag. (Reprinted with permission from the authors and from R. N. Rogers, S. K. Yasuda and J. Zinn, *Pyrolysis as an Analytical Tool, Analytical Chemistry*, 32 (1960) 672. Copyright by the American Chemical Society.)

A classic paper published by Rogers et al.[110] in 1960 describes the construction and theory of operation of a pyrolysis apparatus with applications related to the study of explosive materials. The pyrolysis block and schematic of the apparatus are illustrated in Figs. 5 and 6, respectively. Basically, the technique involves heating a sample at a linear rate in a flowing inert gas stream and measuring the changes in thermal conductivity of the gas stream due to the presence of gaseous decomposition products. The response of a thermal conductivity cell is recorded as a function of sample temperature as shown in the curves for PETN and RDX in Fig. 7. This technique is now known as gas evolution detection (GED). Rogers et al. investigated the effect of carrier gas flow-rate, heating rate, sample weight, thermal conductivity bridge voltage, pressure, and composition of carrier gas on the resulting pyrolysis curves for some explosives. Theoretical arguments were developed to demonstrate the application of pyrolysis data to kinetic studies. It was also observed that the curves obtained were approximately the derivative of the thermogravimetry curve.

Rogers later described a modification of the pyrolysis apparatus to utilize thin-layer chromatography (TLC) as an evolved gas analyzer[111]. As the sample was heated at a linear rate in a dynamic gas atmosphere, an activated TLC plate moved in front of the outlet orifice on a trolley whose speed was coordinated with the heating rate. At the end of a run, the plate was developed and the position of the spots was measured to determine the temperature range in which each decomposition species was evolved. The application of the apparatus to the study of the thermal decomposition of TNT was described in some detail. Relative retention values and characteristic colors produced by developing the plate with *p*-DEAB reagent indicated the presence of 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrobenzyl alcohol (TNB-OH), 4,6-dinitroanthranil (DNA), 2,4,6-trinitrobenzoic acid (TNB-a), and a trace of an unidentified compound. The TLC data, together with DTA and pyrolysis curves for TNT, are shown in Fig. 8.

Dacons et al.[36] also used TLC to study the thermal decomposition of TNT. The TNT was decomposed in Pyrex test tubes held at 200°C for 16 h. The residue was dissolved in benzene with individual fractions identified by elution on the TLC plate. A brown powder remained after dissolution of the residue in benzene which did not melt below 300°C and burned with infumescence when ignited by a flame. No effort was made to identify this substance although exploratory chromatography indicated that it was a mixture of several components rather than a single compound.

A very useful and practical form of gas analysis was described by Frazer and Ernst[43] in the development of the chemical reactivity test (CRT). In this test, a sample of the pure explosive or a mixture of explosive with a foreign material was sealed in a specially designed container and heated in an oil-bath for a specified period of time. The sample container was then connected to a three-stage gas chromatograph for quantitative analysis of gaseous decomposition products. This method allowed the progress of reaction to be studied as a function of time, temperature, and material environment and was an expedient method for determining material incompatibility. The method has now become the standard test for materials incompatibility although

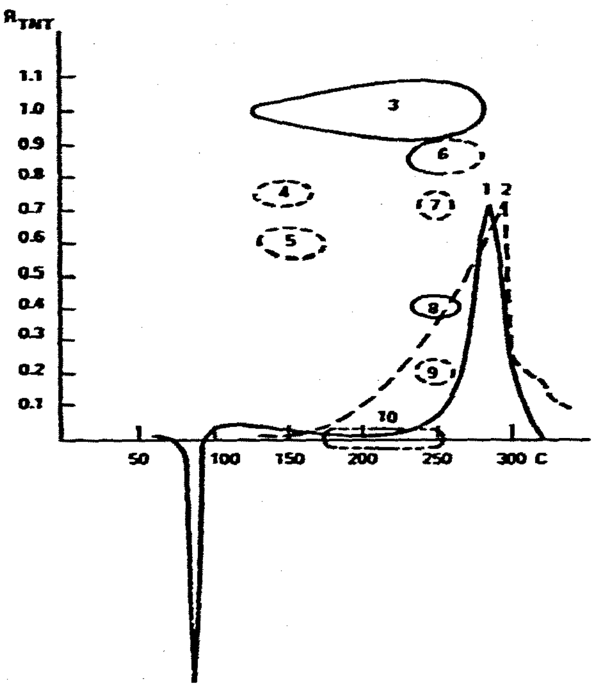

Fig. 8. Graphical compilation of thermal data for a 0.284 mg sample of TNT; heating rate, 11 °C min^{-1}; carrier gas, air[111]. 1 = DTA curve; 2 = pyrolysis curve; 3 = TNT zone; 4 = 2,6- and 3,5-DNT zone; 5 = 2,4-DNT zone; 6 = TNB zone; 7 = DNA zone; 8 = TNB-OH zone; 9 = unidentified zone; 10 = TNB-a zone. (Reprinted with permission from the author and from R. N. Rogers, *Combined Pyrolysis and Thin-Layer Chromatography. A Method for the Study of Decomposition Mechanisms, Analytical Chemistry*, 39 (1967) 730. Copyright by the American Chemical Society.)

several subtle refinements such as elimination of the three-stage gas chromatograph in favor of improved single stage instruments have evolved through extensive laboratory use.

A GC determination of the explosion and decomposition gases of explosives has also been reported by Schubert and Volk[120]. A theoretical consideration of the chemistry of thermal decomposition was used to postulate probable product distributions from the dissociation of organic nitrates. Techniques for determining these postulated decomposition products gas chromatographically were then discussed and evaluated. When the GC technique was applied to PETN at 140°C and nitrocellulose at 132°C, a change in product distribution as a function of the duration of decomposition was found to occur.

GC was also used by Rauch and Fanelli[95] to identify the products of decomposition of RDX in the temperature range of 207–227°C. The GC analyses were supplemented by ultraviolet, infrared, and mass spectrometric measurements. Other investigations utilizing GC for product analysis include determination of the heat stability of pentolite by Urakawa and Masutomi[124].

The thermal decomposition of ammonium perchlorate has been studied mass spectroscopically by several investigators. Heath and Majer[58] found the decomposi-

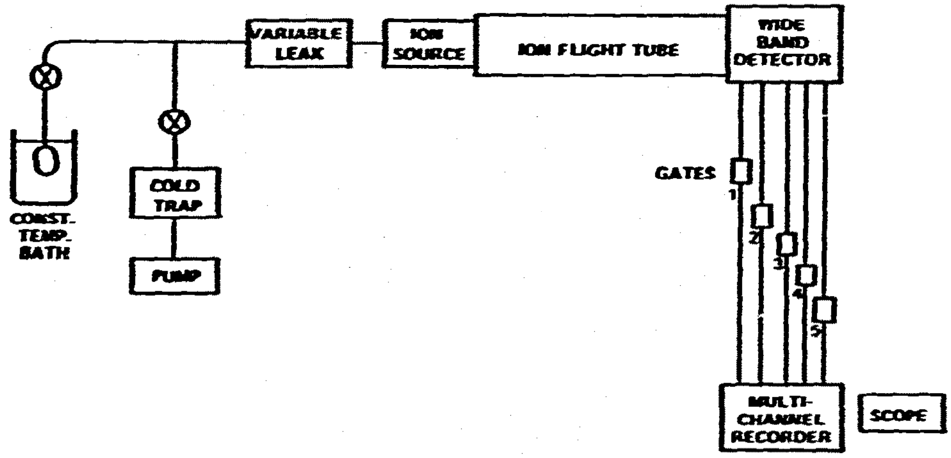

Fig. 9. A diagrammatic display of the constant volume apparatus connected via a variable leak to the Bendix time-of-flight mass spectrometer used by Maycock and Pai Verneker[75]. (Reprinted with permission from the authors and from J. N. Maycock and V. R. Pai Verneker, *The Thermal Decomposition of Nitronium Perchlorate*, *Journal of Physical Chemistry*, 71 (1967) 4077. Copyright by the American Chemical Society.)

tion products to consist primarily of H_2O, NO, NO_2, O_2 and Cl_2, but Goshgarian and Walton[52] found the major products to be H_2O, NO, O_2, Cl_2, HCl, N_2O, and N_2. Maycock, et al.[76] used isotopically labeled $^{15}NH_4ClO_4$ and found the same product distribution as Goshgarian and Walton except that the NO was determined to be a fragmentation product of N_2O. A later study[87] used isotopically labeled $NH_xD_{4-x}ClO_4$ and a Knudsen cell to further clarify the product distribution.

Maycock and Pai Verneker[75] have studied the decomposition of nitronium perchlorate using mass spectroscopy. The isothermal decomposition process was monitored with a Bendix time-of-flight mass spectrometer which was gated simultaneously on five different chemical species as a function of time. The experimental apparatus is illustrated in Fig. 9. The primary products were reported to be O_2, NO, and Cl_2 and kinetics constants were calculated for the formation of these products.

At least one paper describes the investigation of a pyrotechnic mixture by mass spectrometric analysis in combination with other techniques[118]. Simultaneous DTA/EGA experiments provided semiquantitative data on the thermal decomposition of a potassium chlorate/lactose mixture.

DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used to considerable advantage in the study of the thermal properties of explosives. Unique instrumentation suitable for the hazards and special problems presented by explosive materials has been developed and described in the literature. Thermal data generated by these techniques have been used in applications ranging from kinetic studies to quality control to reliability testing.

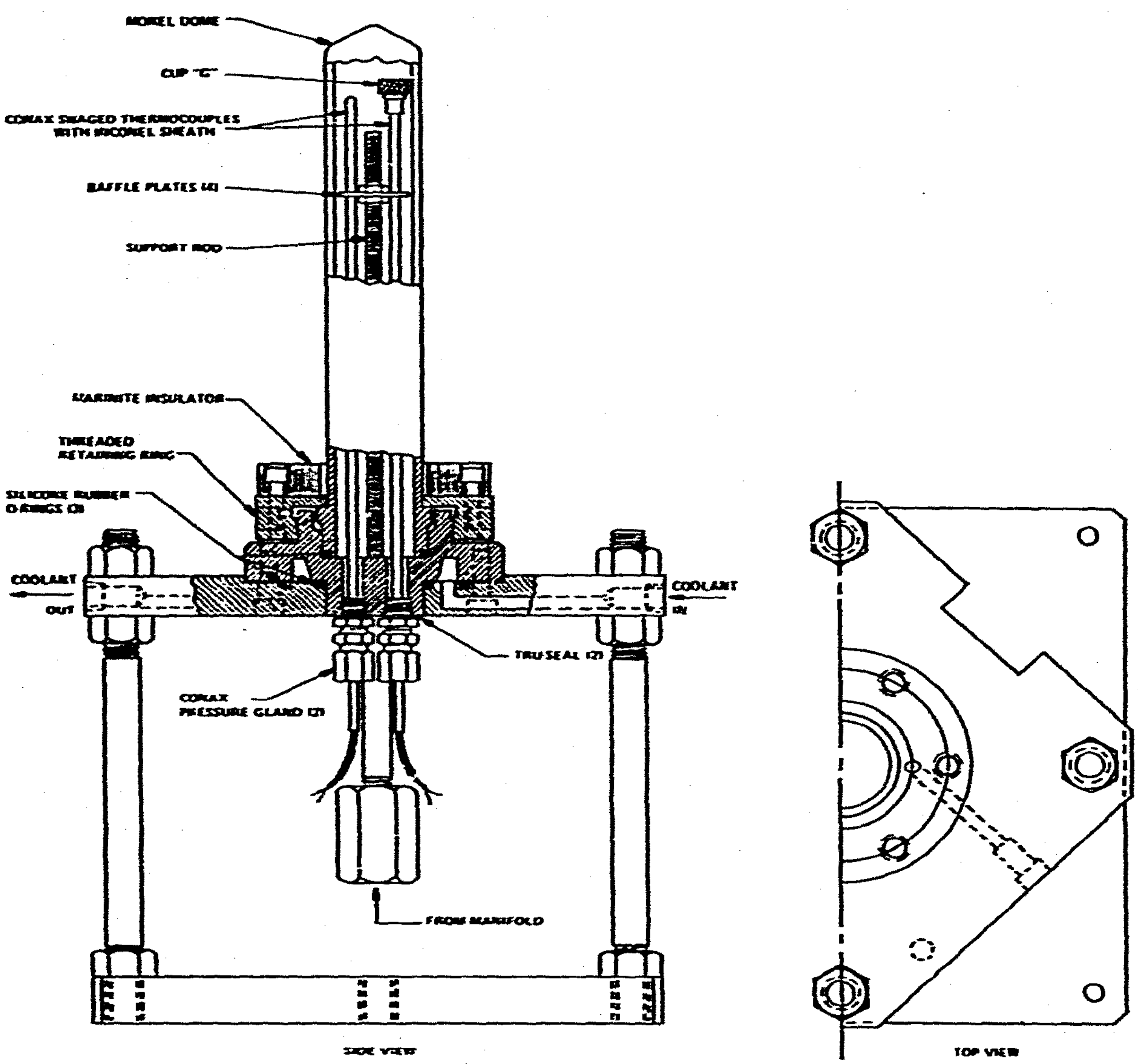

Fig. 10. Schematic diagram of the DTA apparatus designed by Bohon[26]. (Reprinted with permission from the author and from R. L. Bohon, *Differential Thermal Analysis of Explosives and Propellants Under Controlled Atmosphere, Analytical Chemistry*, 33 (1961) 1451. Copyright by the American Chemical Society.)

A thermistorized DTA apparatus was described by Pakulak and Leonard[90] and applied to the study of the thermal behavior of the nitrate esters of cellulose and pentaerythritol. The thermistor bridge arrangement used in the instrument reportedly gave high sensitivity while maintaining acceptable reproducibility. DTA curves of cellulose, cellulose acetate, cellulose nitrate, pentaerythritol, PETriN, PETN, and 3,3-bis-(nitratomethyl) oxetane which were generated by the instrument are reproduced in the article.

Bohon[26] described a DTA apparatus design which stressed versatility, ruggedness, chemical inertness to fluorine-containing samples, and easy replacement of thermocouples for use in studying explosives and propellants under controlled atmospheres. The system featured a tiny pressure tight constant volume bomb, the "f-cup" cell, as well as "g-cup" cell with a porous metal cap. The apparatus could sustain detonations and could operate at pressures of over 400 psig with internal temperatures up to 500°C. Construction details for the apparatus are shown in Fig. 10.

Techniques for obtaining approximate heats of explosion on milligram quantities of propellants and explosives using the instrument described above were reported by Bohon[25]. The success of these techniques was mixed—single-compound explosives which ignite and homogeneous double-base propellants generally yielded acceptable results, but composite, heterogeneous propellants produced less satisfactory results. Problems encountered included errors introduced by sample impurities, incomplete combustion, reaction with the cup, calibration errors, and small sample size necessitated by strength limitations of the container. Still, the method gave surprisingly good results for some materials and seems to warrant consideration when sample quantities are limited and for preliminary screening of new highly energetic materials.

High pressure DTA was used by David[38] to study the reactions of dinitrotoluene and tolylenediamine. A sample container design was described which would accommodate pressure changes up to 3000 psig at 500°C and could be used with a standard DTA apparatus such as that marketed by the Robert L. Stone Company. The cell was used to study the thermal stability of dinitrotoluene, the reduction temperature of dinitrotoluene with Raney nickel, decomposition reactions of dinitrotoluene with tolylenediamine, and the parameters affecting the violent decomposition of reduction mixtures.

Graybush et al.[58] have reported modifications to the remote cell used in conjunction with the DuPont 900 DTA which allows its utilization for the study of primary explosives. The modifications were primarily concerned with achieving a vacuum of 10^{-6} torr and protecting thermocouples from exposure to stray thermal currents. The high vacuum allowed complete removal of trace amounts of oxygen which were suspected of interfering with the decomposition reaction mechanisms of the explosives. When lead azide specimens were placed in the modified cell at varying vacuum pressures prior to backfilling and purging with helium, deformation of the exothermic trace was observed to occur as a function of pressure with peak shape becoming constant at 10^{-6} torr. The article reproduces curves for lead azide, lead azide doped with ferric halides, lead styphnate, mercury fulminate, and potassium dinitrobenzfuroxan although only the lead azide data are discussed in any detail.

Duswalt[39] described the analysis of DSC (or DTA) curves of highly exothermic reactions to obtain useful information concerning the thermal properties of the material. It was suggested that comparison of "starting" and maximum peak temperatures of two similar materials, for one of which the stability is known under the conditions in question, might detect gross differences, changes during storage, effects of solvent, and so forth. Another suggested test consisted of heating a portion of a sample isothermally for a period of time at an appropriate temperature, then decomposing it in the DSC and comparing the decomposition exotherm with that of the untreated sample. The difference between the two exotherms is a measure of the extent of decomposition at the isothermal temperature. Other topics discussed include peak shape analysis, critical temperature determination, four different methods for obtaining kinetics data from DSC measurements, and experimental considerations such as sample characteristics and baseline positioning.

The thermal behavior of solid propellants was studied by Sammons[117] using DSC techniques. Activation energies for the thermal decomposition of a carboxy-terminated polybutadiene binder, ammonium perchlorate, and a propellant were calculated using established kinetics procedures. A combustion model for solid state propellants was discussed and, based on the model, additives were selected that were likely to alter the temperature sensitivity of the burn rate. These preliminary studies indicated that DSC can be used as a tool for selection of additives to achieve variation in ballistic characteristics of a solid propellant.

Freeman and Anderson[44] used DTA to investigate the effects of X-radiation on crystalline ammonium perchlorate. Two endotherms and one exotherm were recorded for irradiated samples prior to the crystalline transition; these were not present in untreated samples. Additional exotherms were also observed after the crystalline transition for the treated material. The DTA curves showed that irradiated samples displayed decomposition characteristics similar to ammonium perchlorate sublimate. It was postulated, with some experimental support, that the presence of ClO_3^- ion was responsible for the anomalous behavior of the irradiated sample. It was also noted that X-ray diffraction patterns and IR analysis did not indicate any differences between the treated and untreated materials.

Compatibility of highly energetic materials with various polymers was studied by Reich[97] using DTA. Explosive materials such as CN, RDX, and HMX were mixed with various polymers including Teflon, polyethylene, Epon 828, polymethylmethacrylate, polyisobutylmethacrylate, etc., to determine effects on ignition sensitivity and/or thermal stability. A novel kinetics method was developed and used in the interpretation and evaluation of DTA data obtained. A summary of the data obtained for CN and RDX is presented in Table 2. The calculated values of activation energy and reaction order were used as indices for judging compatibility of the HEM with the polymeric materials. It is interesting to note in Table 2 that decomposing RDX in the presence of HMX (also a cyclonitramine) produced a decrease in the measured activation energy from 80 to about 66 kcal mol^{-1} and a decrease in reaction order from 0.8 to 0.7. The study of the thermal behavior of RDX–HMX mixtures was extended by Reich[98]. Data from cyclic and non-cyclic heating programs indicated that solid solutions of RDX–HMX occurred in the composition range of about 55 to 83 weight percent RDX. These data were used to construct approximate phase diagrams for the melting and decomposition of RDX–HMX mixtures.

The autoignition temperatures of some military high explosives were determined by a method using DTA data with a modified form of the Kissinger equation[56]. By

TABLE 2

SUMMARY OF COMPATIBILITY DATA FOR CELLULOSE NITRATE AND CYCLOTRIMETHYLENE TRINITRAMINE[a]

Run No.	*HEM*	*Polymer*	*W, % HEM*	*Decomp. peak temp. (°C)*	*n*	*E (kcal mol⁻¹)*	*ΔH_{dec} (kcal g⁻¹)*	*ΔH_f (cal g⁻¹)*
CN-1	cellulose nitrate	—	100	204	4.6	180	0.40	—
CN-2 to 6		T	32–75	203–206	5.0 ±	187 ±	0.37 ±	—
CN-7 to 10		PE	34–50	204–208	4.8 ±	170 ±	0.38 ±	—
CN-11 to 12		PST	34–48	204–205	4.7 ±	177 ±	0.33	—
CN-13		Epon 828 (anh. cured)	35	205	4.4	170	0.42	—
RDX-1, 1B	RDX	—	100	240	0.8 ±	80 ±	0.49	30 ±
RDX-2		PE	42	237	0.7	81	0.25	20
RDX-3, 3A		Epon 828 (anh. cured)	42	220 ±	1.9 ±	107 ±	0.54 ±	—
RDX-4		Epon 828 (anh., extracted)	43	—	—	—	—	8
RDX-4A		Epon 828 (anh., extracted)	42	224	1.7	105	—	6
RDX-5		PST	47	241	0.9	84	0.51	23
RDX-6		Epon 828 (BF_3-cured)	33	238	0.8	79	0.52	29
RDX-7		PAA	51	241	0.8_5	88	0.65	33
RDX-8		PMMA	47	239	1.1_5	66	0.58	—
RDX-9		PIBM	54	237	1.0	76	0.48	20
RDX-10		PEMA	38	238	1.3_8	70	0.66	—
RDX-11		Gantrez	55	219	—	—	—	—
RDX-12		PODA	53	238	0.6	76	0.48	22
RDX-13		(HMX)	82	245	0.7	66	—	16

[a] Table 2 is reprinted from ref. 97 with permission from the author and *Thermochimica Acta*.

obtaining DTA traces at several heating rates and extrapolating the related data to a near zero heating rate, reproducible autoignition temperatures were obtained for TNT (275°C), RDX (197°C), PETN (160°C), and HMX (234°C).

Warren and Wilson[128] combined the techniques of hot-stage microscopy and DSC to study the thermodynamic properties of the esters of 2,4,6-trinitrobenzoic acid. Entropies of fusion and α to β transition were calculated from the respective endotherms and correlated with alkyl chain length.

Other studies which reported DTA data as a supplementary technique included a study of the explosive behavior of barium azide by Pai Verneker and Avrami[89] and a study of the heat stability of pentolite by Urakawa and Masutomi[124]. DTA curves for several organic explosives were reported by Piazzi[92] and an apparatus has been described for DTA studies of explosives which features an aluminum-foil-covered asbestos oven with a blow-off top and sample holders that disintegrate to dust upon detonation[12]. DTA was used by Boddington et al.[24] to study pyrotechnic reactions of tungsten-potassium dichromate.

Perhaps the most active investigator of the thermal properties of explosives through the use of DSC techniques is R. N. Rogers of Los Alamos Scientific Laboratory. Numerous articles have appeared in the literature either authored or co-authored by Rogers which describe applications of DSC to explosives research with an especially significant contribution to thermal decomposition kinetics. Many of these articles are reviewed while others which do not explicitly mention explosives applications are neglected even though they have utility in explosives research.

Rogers and Morris[105] reported a method of estimating activation energies with a DSC. Detailed procedures were outlined as well as helpful hints on technique and anticipation of potential problems that the investigator may encounter. Activation energies were calculated for HMX, RDX, tetryl, PETN, and $KMnO_4$, pure and in solution, and were compared with previously reported literature values. The primary advantages cited for their method of determining activation energies were the small sample size required and the fact that the DSC method negates the necessity to assume a proportionality between gas evolution rate and reaction rate as is done in gasometric determinations.

Rogers and Smith[103] discussed a method of estimating pre-exponential factors from the DSC curve of an unweighed sample. The equation $A = BE\exp(-E/RT_{\max})/RT_{\max}^2$ is developed where B is the heating rate, $T_{\max}$ is the temperature of maximum deflection, and E is the activation energy (calculated by the method described in ref. 105). Although the actual heating rate is not known accurately at the maximum with highly exothermic materials, the value of A is relatively insensitive to this parameter so that an estimated rate suffices for calculations. The pre-exponential factors calculated for RDX, HMX, tetryl, and PETN using the method compared favorably with values obtained from alternative sources.

Differential scanning calorimetry has been successfully applied to the study of the chemical kinetics for simple homogeneous decomposition of a pure compound in a condensed phase[106]. However, it was stressed that kinetics theories developed for DSC apply only if the reaction is first order. If the fraction of material decomposed at T_{max} is not constant with different heating rates, the reaction must be complex and does not conform to the kinetics models. When the kinetics theories were applied to the thermal decomposition of RDX, both autocatalysis and inhibition were exhibited since the calculated activation energy both increased (inhibitor effect) and decreased (catalytic effect) in different regions of the DSC curve.

The DSC determination of kinetics constants for systems that melt with decomposition was discussed by Rogers[107]. It was suggested that systems that melt with decomposition could be detected by one of several observations, namely: (1) the capillary melting point as a function of heating rate; (2) the size of the DTA or DSC melting endotherm as a function of heating rate; or (3) the decomposition rate curves show an induction period at temperatures below the nominal melting point. Kinetics curves corresponding to decomposition in the solid phase, the mixed solid and liquid phases, and the homogeneous liquid phase are illustrated in the article for cupferron tosylate and HMX.

A simplified determination of rate constants by DSC was described by Rogers[104] based on the fact that many explosives decompose in a homogeneous liquid phase which implies a first order reaction. In such cases, DSC yields rate data directly; this obviously simplifies the kinetics work. Plots of the natural logarithm of the deflection from baseline in millimeters versus time gave values for the rate constants for cupferron tosylate and HMX from the measured slope of the curve. The rate constant for the decomposition for HMX at 271°C was calculated to be 0.0015 sec^{-1} as compared with a value of 0.0013 sec^{-1} calculated by more traditional methods.

The observation that isothermal rate curves determined for some compounds by DSC varied with the volume of the sample cell led to a method for the determination of vapor-phase kinetics data[112]. By integration of decomposition curves for RDX, the fraction of the original sample present in the vapor phase at the instant the last liquid disappeared was determined. A Clausius–Clapeyron plot was constructed from these data with the slope being the heat of vaporization of the compound. Arrhenius plots of RDX and HMX vapor-phase data were presented with calculated values of activation energies and pre-exponentials. The vapor phase technique also allowed corrections to be made to kinetics constants for reactions in the condensed phase[114]. In studying thermal decompositions, it is usually assumed that DSC recorder deflection is due to reactions in the condensed phase when in fact, there are usually vapor phase decomposition contributions. Rogers discussed techniques to establish an accurate baseline to compensate for the vapor phase contribution and demonstrated the corrected calculation for RDX.

DSC was used in combination with X-ray data and microscopy to establish crystal imperfections as the source of anomalous behavior in the heat of fusion of PETN recrystallized by different methods[113]. Microscopy showed at least three general crystal habits of PETN: (1) "tetragonal" showing characteristic apex angles and little evidence of strain; (2) "needle" having re-entrant cavities from the ends and/or a high length-to-width ratio; and (3) "superfine" composed largely of irregular

TABLE 3

HEATS OF FUSION OF DIFFERENT PETN CRYSTAL HABITS[a]

Habit and sample No.	*Surface* *($cm^2\ g^{-1}$)*[b]	*ΔH_f* *($cal\ g^{-1}$)*
Superfine		
25-9	4700	31.7±0.1
2689	4300	31.8±0.2
2909	5400	33.2±0.2
Needle		
25-88	3250	36.5±0.3
25-159[c]	4400	37.0±0.1
25-81	16400	36.6±0.3
25-157[c]	18600	37.7±1.2
Tetragonal		
RPS-3518	1000	36.8±0.4
DB-2	1000	36.5±0.5
Single crystals		37.4±0.3

[a] Table 3 reprinted from ref. 113 with permission from the authors and *Thermochimica Acta*.
[b] Determined by gas permeability.
[c] Prepared by reprecipitation of superfine 2689.

plates. The heats of fusion for these forms are given in Table 3. Factors investigated include the effect of precipitation temperature and of sample purity on ΔH_f. The formation of a metastable polymorph, PETN II, was studied and crystal orientations were discussed. Differences in the heat of fusion were attributed to the lattice energy increase resulting from random inclusion within the lattice of inverted and strained PETN molecules.

Rogers has also reported using DSC data to calculate the lowest temperature (critical temperature, T_m) at which any specific size and shape of explosive composition can self-heat to explosion and correlated these data with time-to-explosion tests[108].

THERMOGRAVIMETRY

While thermogravimetry (TG) can provide useful data relating to the thermal properties of explosives, there is a surprising scarcity of experimental studies based solely on this technique. Many papers include TG in combination with other thermal methods but few papers have been published describing specialized apparatus or techniques as are available for DTA. Therefore, those few papers devoted exclusively to TG are discussed in this section, but the majority of the TG work will be discussed in the next section on TG–DTA techniques.

Cook and Abegg[31] presented a method employing the direct measurement of weight loss by use of a sensitive quartz spring balance to study the isothermal decomposition of explosives. The method assumed that weight loss resulted only from decomposition and was thus applicable only for systems where the vapor pressure was sufficiently low that no appreciable weight was lost from vaporization. Experimental values were determined for pre-exponential factors and activation energies of the decomposition process by applying a least-squares fit to experimental log $k'(T)$ vs. $1/T$ curves. Ammonium nitrate, PETN, EDNA, tetryl, hydrazine nitrate, and TNT were studied. For the decomposition of TNT in the temperature interval of 250 to 301 °C, there was no measureable vapor phase decomposition—only liquid phase decomposition. Comparisons of calculated kinetics values with previously reported values were generally rather poor. Autocatalysis was thought to be appreciable for some substances at the higher temperatures of the experiment.

The sublimation of ammonium perchlorate was studied by Jacobs and Russell-Jones[67] using a Stanton thermogravimetric balance. Calculations of activation energy for the decomposition of ammonium perchlorate in the temperature range of 304–375°C indicated that gas-phase reactions were rate-determining, so that weight loss measurements were attributable to a sublimation process. The sublimation process was found to fit the equation

$$1 - (1 - a)^{1/\gamma} = kt$$

where a is fractional decomposition, $\gamma = 2$ or 3, k is the rate constant, and t is time. Based on a theoretical model, another more complex expression was derived and tested with experimental data. The evaporation coefficient varied from about 4×10^{-2} for sublimation in vacuo to about 5×10^{-4} for sublimation under one atmosphere. The chemistry of the sublimation process was also discussed.

Thermogravimetric solid decomposition results for isothiocyanatopentamminecobalt(III) perchlorate (ICCP) were analyzed by a geometric model based upon growing spherical nuclei and burning sphere relations[99]. Activation energies were calculated from the TG curves in air and in vacuo.

COMBINED THERMOGRAVIMETRY–DIFFERENTIAL THERMAL ANALYSIS

Although both TG and DTA are extremely useful in the study of thermal decomposition, each technique has limitations with regard to the physical processes that can be observed. Therefore, a common practice has been to combine the two techniques to furnish complementary data for a more complete view of thermal occurrences. Combination of TG–DTA with yet another technique such as evolved gas analysis is also being used to provide an even wider perspective of the thermal processes. Although several combined techniques have already been discussed, this section is devoted exclusively to combined TG–DTA as applied to explosive compounds.

In 1957, Hogan and Gordon[63] reported a study of the thermal properties of a barium peroxide–magnesium–calcium resinate system using TG and DTA. However, to prevent damage to the instrument, only the individual ingredients rather than the

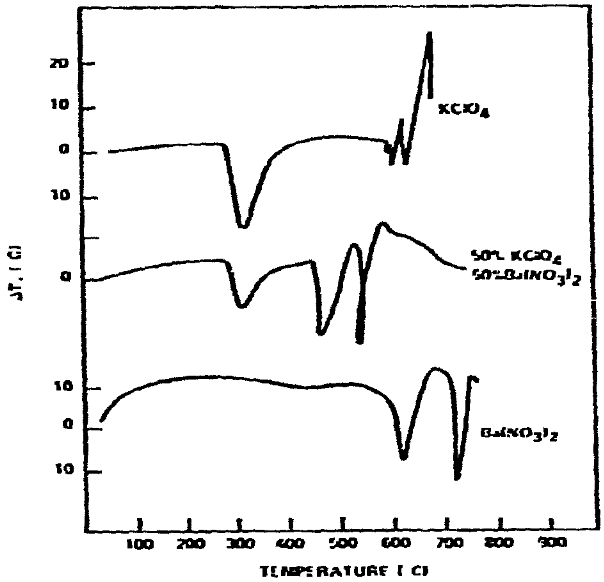

Fig. 11. Differential thermal analysis curves for potassium perchlorate, barium nitrate, and a potassium perchlorate-barium nitrate binary mixture as reported by Hogan and Gordon[64]. Heating rate is 15°C min^{-1} and sample size is 4 g. (Reprinted with permission from the authors and from V. D. Hogan, S. Gordon and C. Campbell, *Differential Thermal Analysis and Thermogravimetry Applied to Potassium Perchlorate–Aluminum–Barium Nitrate Mixtures, Analytical Chemistry*, 29 (1957) 306. Copyright by the American Chemical Society.)

mixture were run on the thermobalance. TG curves showed a weight loss corresponding to the loss of one atom of oxygen from BaO_2 at 600°C, a continuous weight gain beginning at 600°C with changes in slope at 650 and 675°C for magnesium, and a continuous weight loss from 110 to 560°C with a change in slope in the 350 to 450°C region for calcium resinate. The DTA curves showed no thermal effects for BaO_2, an exotherm beginning at 496°C followed by the fusion endotherm at 637°C and a second exotherm for magnesium, and an endotherm at 214°C followed by several changes in baseline for calcium resinate. DTA curves for Mg–BaO_2, Mg–CaR_2, BaO_2–CaR_2, and BaO_2–Mg–CaR_2 systems were also obtained and discussed. From the data, it was concluded that ignitions involving calcium resinate occur after it has begun to decompose but before any of the other ingredients undergo any thermal reactions. Time-to-ignition data were also obtained and showed that the thermal degradation products of calcium resinate vary with temperature and determine the ignition parameters for compositions containing this material.

TG and DTA were also used to characterize a series of potassium perchlorate–aluminum–barium nitrate mixtures[64]. TG curves for the individual oxidants and a series of potassium perchlorate–barium nitrate binary mixtures were reported. The curves for potassium perchlorate and barium nitrate show stoichiometric decomposition to potassium chloride and barium oxide at about 600 and 650°C, respectively.

The DTA curves obtained for the oxidants are shown in Fig. 11. TG curves of the ternary mixtures exhibited weight losses equivalent to the quantitative decomposition of potassium perchlorate to potassium chloride at about 540°C and a further loss due to decomposition of the nitrate ion. The DTA curve for the ternary mixture exhibited the potassium perchlorate transition, the fusion of the eutectic mixture of $KClO_4$ and $BaNO_3$ at 465°C, the fusion of aluminum, and the decomposition of nitrate ion.

Campbell and Weingarten[29] studied the ignition and combustion reactions of black powder using TG and DTA. DTA curves were obtained for each of the ingredients and then for the black powder mixture. Overlapping endothermal bands from the crystalline transition of potassium nitrate, transition and fusion of sulphur, and the vaporization of volatile matter from the charcoal were resolved in the DTA curve for black powder. The TG curves showed a slight weight loss beginning at 250°C followed by an extremely rapid weight loss at 275°C due to ignition. All possible binary combinations of the ingredients were also examined by DTA and TG. These data showed that an exothermal reaction between sulfur and potassium nitrate occurred at the temperature at which black powder ignites and that there is no heat evolution from a pre-ignition reaction between molten sulfur and the oxyhydrocarbons present in the charcoal as proposed by Blackwood and Bowden[22].

DTA and TG studies of some salts of guanidine and related compounds have been reported by Fauth[42]. For six picrates examined, the order of increasing thermal stability under rapid heating rates was determined to be hydrazine > aminoguanidine > N-methylguanidine > guanylurea > N-ethylguanidine > guanidine. The styphnates were observed to detonate with the relative stability in terms of increasing temperature of detonation being hydrazine > N-methylguanidine > N-ethylguanidine > guanidine > guanylurea > aminoguanidine.

A wide variety of military explosives were analyzed by TG and DTA in order to establish the feasibility of developing thermal stability tests utilizing these techniques[74]. DTA and TG curves were given, along with some interpretation, for twelve different explosive materials. The use of derivative DTA was recommended to improve resolution of points of inflection and clarify the temperature at which the thermal event occurs.

The thermal decomposition reaction of ammonium perchlorate after irradiation with X-rays and γ-rays was monitored in DTA and TG experiments conducted under ambient and reduced pressure by Freeman et al.[44, 45]. Four principal changes in the details of the decomposition of ammonium perchlorate due to pre-irradiation were listed as: (1) more extensive reaction prior to and during crystalline transition: (2) highly exothermal decomposition immediately following crystalline transition: (3) more extensive reaction over the temperature range of 310 to 385°C; and (4) a decrease in the extent of the final stage of decomposition at temperatures higher than 385°C. The importance of the various stages of reaction was found to be a function of radiation exposure dose. It was suggested that the radiation produces positive holes which favor an electron transfer mechanism of decomposition.

Scanes[118] has applied DTA–TG to the study of pyrotechnic compositions containing potassium chlorate and lactose. The compositions were examined under a variety of conditions and it was determined that the most significant peaks in the DTA curve were exotherms at about 200°C, corresponding to the fusion of lactose, and at about 340°C, corresponding to the oxidation of the organic residues. The tendency of the composition toward explosion was demonstrated to be a function of heating rate and temperature. Mass spectrometric gas analysis was also performed to complement the DTA–TG data.

Simultaneous DTA–TG was used by Pai Verneker and Maycock[88] to characterize the explosivity of lead azide. The TG curve was used to distinguish between decomposition and detonation since decomposition gives a mass loss of 25 to 30% while detonation gives a 100% mass loss. It was shown that a critical mass was necessary for detonation and that increased heating rates lead to detonation. Examination of the DTA data generated on samples aged for various time intervals at different temperatures revealed a small exotherm which sometimes occurred around 120°C, was independent of the system in which PbN_6 was stored, and was never observed after four weeks of storage. Several possible explanations were offered although the effect was not further investigated. Reactivity changes as a function of aging were investigated in three different ways: the thermogravimetric method, which can differentiate between decomposition and detonation, as a function of heating rate; the DTA method of shift in the exotherm temperature; and the DTA method whereby sensitivity in arbitrary units was defined as the height of the exotherm over the half width. Copper was found to desensitize the decomposition reaction in the initial four weeks after which a sensitization was observed.

Simultaneous TG–DTA techniques have also been used to determine the characteristics of the decomposition of nitronium perchlorate[78]. The three-step weight loss was deduced to follow the reaction steps:

$$NO_2ClO_4 \rightarrow NOClO_4 + 1/2O_2$$
$$2NOClO_4 \rightarrow NO_2ClO_4 + ClO_2 + NO_2$$
$$NO_2ClO_4 \rightarrow NO_2 + O_2 + ClO_2$$

An endotherm peaking at 156°C which was not associated with a weight loss was observed and attributed to a crystal phase change in nitronium perchlorate.

An endotherm at 190–200°C and an exotherm accompanied by a sharp weight loss at 290–300°C was revealed by the TG–DTA curves for HMX[80]. The endotherm was attributed to the crystal phase change of monoclinic β-HMX going to hexagonal δ-HMX. Thermal cycling around the transition temperature showed that the conversion process was irreversible.

Simultaneous TG–DTA has been used in conjunction with other techniques such as pressure–time measurements, visible range absorption spectroscopy, and electrical conductivity to study the role of point defects in the thermal decomposition of ammonium perchlorate[77].

MISCELLANEOUS TECHNIQUES

The study of the thermochemistry of explosives has provided a plethora of unusual special purpose techniques and instrumentation to generate data on thermal behavior. Therefore, this section is a catch-all in which widely diverse studies will be described. But the central theme of all the studies is the same—to obtain information on the thermal behavior of explosive materials in a safe, scientifically acceptable manner.

IR techniques have been used with some success in the study of explosives. The thermal decomposition of di-t-butyl peroxide (DTBP) and some nitrate esters was studied by heating a dispersion of the material in potassium halide pellets and monitoring changes in the IR spectra[19]. The gradual disappearance of the O–O stretch at 875 cm^{-1} was used to calculate rate constants for the decomposition of the DTBP. An activation energy of 38 kcal mol^{-1} was calculated as compared with 39.1 kcal mol^{-1} previously reported for the gas phase decomposition. In the decomposition of nitrate esters, it was found that NOX (X = Cl or Br) is formed by reaction of the KX matrix and NO_2 formed from the homolytic cleavage of the $RO–NO_2$ bond. The thermal decomposition of NO_3^- formed by the heterolytic cleavage of the $R–ONO_2$ bond in KX was assessed by considering the free energy of possible reactions and studying the oxygen donor–acceptor tendencies for various species.

The alkali metal halide matrix technique has also been used by Hartman and Musso[57] in their study of the thermal decomposition of nitroglycerin. Pressed disks of the matrix material and nitroglycerin were heated isothermally with the IR spectrum recorded at specified intervals. As the nitroglycerin bands decreased, product bands due to ionic nitrate, carbon dioxide, formaldehyde, water, and metastable products or intermediates appeared in the spectrum. Effects due to differences in matrix material were discussed and it was pointed out that the matrix acts as a scavenger for reactive intermediates. Two possible problems were noted for the technique: (1) diffusion of products from the pellet, and (2) reactions with the matrix material. Decomposition kinetics constants were calculated and a mechanistic description of the dissociation process was considered.

An IR investigation of ammonium nitrate melts showed that the melts had an ionogeneous character, in which the ammonium could not move freely, probably because of hydrogen bridges[69]. The melts were contained in pyrex cells with silver chloride windows at 215°C. The spectra of the gas phase showed an immediate increase in the partial pressure of ammonia as decomposition began followed by a pressure decrease and the formation of N_2O. The HNO_3 and H_2O pressures increased slowly and NO_2 was formed later in the reaction. Based on these qualitative observations, a rather complex dissociation mechanism was proposed.

An apparatus has been designed to automatically measure the time-to-explosion for HEM and is shown schematically in Fig. 12[59]. The explosive is placed in a copper cylinder which is quickly immersed into a thermostated Wood's metal-bath. The

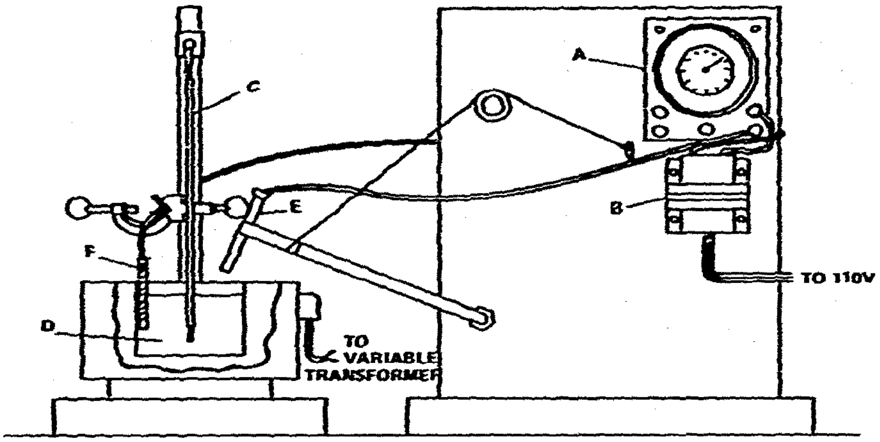

Figure 12. Diagram of the time-to-explosion apparatus developed by Henkin and McGill[59]. A = Impulse counter and interval timer; B = step-down transformer; C = mercury thermometer; D = Wood's metal-bath; E = hollow copper cylinder; F = wire connecting bath and timer. (Reprinted with permission from the authors and from H. Henkin and R. McGill, *Rates of Explosive Decomposition of Explosives, Industrial and Engineering Chemistry*, 44 (1952) 1391. Copyright by the American Chemical Society.)

instant the cylinder touches the molten metal, electrical contact is made which initiates the impulse counter until the explosion of the sample blows off the cap and interrupts the electrical circuit. Data obtained by this method are illustrated in Table 4.

Rogers[108] described a modified time-to-explosion method utilizing the apparatus in Fig. 13. The apparatus encloses the metal-bath and is thus safer to the operator. Comparisons of critical temperatures in standard gilding-metal blasting cap shells and in aluminum cells showed that several explosives, TATB, DATB, and BTF, were incompatible with the gilding-metal cells. Experimental data were compared with calculated critical temperature values based upon kinetics constants obtained from DSC curves and substituted into the equation

$$E/T_m = R \ln(a^2 \rho Q Z E / T_m^2 \lambda \delta R)$$

where T_m is the critical temperature, R is the gas constant, a is a geometric factor, ρ is the density, Q is the heat of reaction during the self-heating process, Z is the pre-exponential, E is the activation energy, λ is the thermal conductivity, and δ is the shape factor. Comparison of the experimental and theoretical critical temperatures for several explosives are shown in Table 5.

Rogers[109] described the use of time-to-explosion data to detect incompatibility in explosive systems through significant decreases in the critical temperature of the pure explosive and shorter time-to-explosion after addition of the material in question. The low temperature, long explosion time region of the thermal initiation curve was considered of primary importance. Hazardous mixtures identified by the method included ammonium nitrate–zinc powder and HMX–RDX.

TABLE 4

EXPLOSIVES EXPLODING BELOW 360°C* (25-mg sample)

	Temp. (°C)	*Explosion time (sec)*
Pentaerythritol tetranitrate	350	0.050
	324	0.091
	272	0.475
	256	1.03
	244	1.57
	229	2.93
	220	4.55
	215	No explosion
Trinitrophenylmethylnitramine (tetryl)	360	0.325
	346	0.425
	329	0.582
	314	1.45
	285	1.45
	269	2.22
	264	No explosion
N,N′-Dinitro-N,N′-di-(β-nitroxyethyl) oxamide	356	0.080
	322	0.183
	300	0.316
	270	0.650
	243	1.69
	229	2.70
	213	4.75
	208	No explosion
Tetramethylolcyclopentanone tetranitrate	350	0.300
	320	0.490
	300	0.760
	270	1.35
	249	2.40
	232	3.35
	225	No explosion
Tetramethylolcyclohexanol pentanitrate	350	0.088
	317	0.112
	287	0.459
	261	0.910
	238	1.63
	230	2.02
	221	2.48
	210	3.40
	200	No explosion
Ethylenedinitramine	314	0.166
	286	0.242
	266	0.333
Ethyltrimethylolmethane trinitrate	351	0.077
	277	0.551
	260	0.880
	246	1.16
	228	2.05
	221	2.54
	215	No explosion
Black powder	359	12.0
	356	13.5
	350	15.4
	341	21.1
	325	29.0
	320	34.1
	315	No explosion
Nitrocellulose (13.4% N)	358	0.074
	331	0.100
	292	0.383
	264	1.30
	242	3.99
	234	5.80
	225	10.2
	210	21.5
	198	41.1
	185	201
	180	440
	174	1200
	170	No explosion
Nitrocellulose (12.6% N)	325	0.143
	287	0.442
	246	2.87
	243	4.20
	227	8.17
	218	13.7
	210	21.5
	192	76.5
	188	102
	180	458
	170	No explosion
Picric acid	350	1.48
	330	2.96
	312	5.50
	294	11.8
	286	16.6

TABLE 4 (continued)

Temp. (°C)	*Explosion time (sec)*	*Temp. (°C)*	*Explosion time (sec)*
251	0.450	277	26.3
232	0.554	273	29.6
221	0.750	267	50.3
192	2.08	260	No explosion
180	4.88		
176	6.80		
169	13.5		
162	37.1		
158	120		
149	793		
142	No explosion		

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[a] Table 4 is reprinted with permission from the authors and from H. Henkin and R. McGill, *Rates of Explosive Decomposition of Explosives, Industrial and Engineering Chemistry*, 44 (1952) 1391. Copyright by the American Chemical Society.

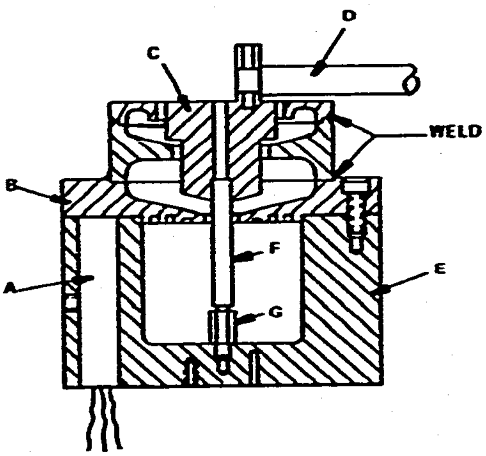

Fig. 13. Experimental assembly for the time-to-explosion test as described by Rogers[108]. A = Cartridge heaters (three); B = top assembly, bolted to base; C = sample-cell holder assembly, the sample cell being insulated from the holder with a band of glass tape around its top; D = sample-cell-holder 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; G = sample cell support pedestal, length adjusted according to length of sample cell. (Reprinted from ref. 108 with permission from the author and *Thermochimica Acta*.)

Time-to-explosion measurements were used to determine the effects of various adsorbates on the explosive decomposition of RDX[30]. It was found that neither a radical nor an ion scavenger in contact with RDX as a gas or adsorbate produced an effect on the activation energy relative to vacuum-exposed material. Shifts in the rate curves were found to be independent of chemical processes and were solely a function of the physical adsorption of vapors. Desorption of the adsorbed vapors retarded

TABLE 5

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED CRITICAL TEMPERATURES[a]

	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

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the onset of initiation due to the endothermicity of the process and, therefore, shifted rate curves toward longer times to explosion. Time-to-explosion data have also been reported, in combination with data from other thermal techniques, in papers by Pai Verneker and Avrami[89] and by Popolato[94].

Time-to-explosion measurements were made for several explosives under static pressures up to 50 Kbar at various temperatures[71]. PETN and HMX showed inhibition with increasing pressure as evidenced by a reduction in the rate of decomposition while TNT showed no effect from the pressure increase. A diamond high-pressure IR cell was used to obtain spectra of the thermal decomposition of nitromethane. Band shifts were noted with increasing pressure which were attributed to stronger hydrogen bonds between the methyl group and neighboring nitro groups and to the contraction of certain bond lengths.

A rather unique method for studying the behavior of explosives at temperatures between 300 and 1000°C was developed by Wenograd[130]. The explosive was loaded into fine hypodermic needle tubing which was heated essentially instantaneously by a capacitor discharge. The temperature and explosive event was recorded by monitoring the resistance of the tube and using the temperature coefficient of resistance of the material to determine the temperature. The oscillographic output obtained by the method is illustrated by the record of explosion of a TNETB sample in Fig. 14. The explosives studied showed time delays varying between 50 msec and 50 μsec. Using the temperature at which a time-to-explosion of 250 μsec was obtained as the critical temperature of the explosive, a plot of critical temperature as a function of impact sensitivities was made. With the exception of tetryl and DNPTB, the data fit a smooth curve fairly well.

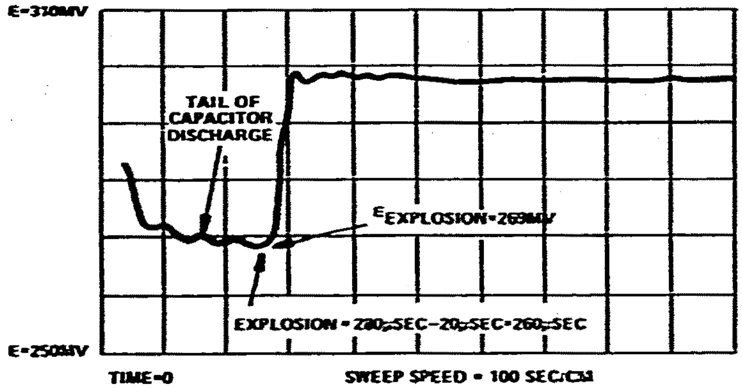

Fig. 14. Oscillographic record of explosion of TNETB sample using the method of Wenograd[130]. (Reprinted from ref. 130 with permission from the author and The Faraday Society.)

A theoretical treatment of thermal initiation has been developed by Zinn and Mader[134]. Numerical solutions were obtained for non-linear heat conduction equations arising in the theory of thermal explosions and explosion times were calculated for several explosive materials assuming various geometric sample shapes. Experimental explosion time data for most explosives were in reasonable agreement with theoretical values. The steady-state heat conduction equation obeyed by explosive materials was also studied mathematically by Bailey[13] in order to be able to guarantee the existence of steady-state solutions when the boundary temperature is low enough, and to obtain information about the onset of thermal instability.

The theoretical development of the thermal initiation of explosives was later extended by Zinn and Rogers[135] to include the effects of pressure accumulation and reactant depletion. Time-to-explosion measurements were made for several explosives and results were compared with theory and with previously published data. All data were in reasonably close agreement with the calculations. The determination of rate parameters for the decomposition of TNT from the experimental time-to-explosion data was also discussed.

The effect of particle-size distribution on the thermal decomposition of α-lead azide was studied by Hutchinson et al.[65] using a gravimetric method. Decomposition was monitored by continuously weighing activated charcoal which was maintained at liquid nitrogen temperatures and adsorbed the nitrogen released from the reaction. The decomposition data, recorded as weight of released nitrogen adsorbed on the charcoal vs. time, were transformed into rate curves. A model of lead azide decomposition was discussed which exhibited a fair degree of correlation with experimental results. The data showed that fine particles decomposed at a faster rate than coarse particles and that the explosive decomposition yielded a stoichiometric quantity of nitrogen confirming lead and nitrogen gas as the products.

Dacons et al.[37] studied the decomposition of TNT by heating at 200°C for 16 h in air and then analyzing the residues. The residues were dissolved in hot benzene and separated by column chromatography. At least 25 discrete species were indicated by the chromatographic process; in addition, a polymeric material of indefinite composition and insoluble in hot benzene was also observed. It was also noted that no trinitrobenzene was detected although Rogers[111] has identified TNB as the primary TNT decomposition product between 233 and 285°C. A number of possible explanations were offered for the contrasting results of the two investigations.

The influence of high pressure on thermal explosion and the decomposition and detonation of single crystals has been investigated by Bowden et al.[28]. The data for high-pressure studies indicated that the effect of pressure on the thermal decomposition of PETN, cyanuric triazide, and lead azide was small but caused a slight reduction in the rate of decomposition. A high-speed ciné microscope was used in the second part of the study to follow the combustion and explosion of single crystals of silver azide, thallous azide, mercury fulminate, lead styphnate, trinitrotriazidobenzene and cyanuric triazide. Burning speeds were determined and physical effects such as propagation of cracks ahead of the flame front were described. The experiments indicated that the explosion of crystals is not a uniform process and demonstrated that increases in crystal size or initial temperature lead to increased burning rates.

The combustion of ethyl nitrate was studied by Needham and Pawling[86] by stabilizing an ethyl nitrate flame on a burner and sampling the flame with a fine silica probe. The products were collected in a trap at −80°C, fractionally distilled, and identified by IR spectroscopy. Products identified include H_2O, CO, NO, CH_4, CO_2, C_2H_4, N_2O, CH_3ONO, CH_3NO_2, CH_3OH, H_2CO, CH_3CHO, HCN, C_2H_2, H_2, N_2, and more complex materials. Reactions were discussed to account for the product distribution.

The heats of reaction of a number of mixtures containing potassium chlorate and lactose have been determined by bomb calorimetry[119]. The maximum heat of reaction was obtained for a mixture of 74% potassium chlorate–26% lactose. Stoichiometric equations were considered for various mixtures and correlated with the measured heats of reaction. Heats of reaction of potassium chlorate with various other fuels were also determined calorimetrically and found to show little variation. Therefore, heat of reaction cannot be the sole criterion when selecting a fuel.

The thermal stabilities of HNAB and HNB were studied by Hoffsommer and Feiffer[62] in the temperature range of 215 to 280°C by analysis for undecomposed explosive. TLC was used to measure the residual explosive. HNAB decomposed at 1.3% per hour at 230°C, about 18 times faster than HNB, and 60% per hour at 280°C, about 4 times faster than HNB.

A high-heating-rate thermoanalytical technique has been reported for use in the study of propellants[27]. Samples were prepared as thin films which were uniformly heated by radiant energy on one side while the temperature of the opposite side was monitored by a rapid response IR detector. Heating rates of 50 to 300°C sec^{-1} were used. The IR detector output was digitized, converted into time–temperature results by use of calibration data, and reduced to a form similar to DTA curves by differencing the experimental values against a hypothetical inert sample.

The effusion process of measuring vapor pressure developed by Knudsen has been used to determine the energy of activation of the decomposition of cellulose nitrate[61]. Other studies on the thermal behavior of explosives include a description of an improved apparatus and technique for the measurement of the vacuum stability of explosives at elevated temperatures[115] and measurements of the electrical conductance of $KClO_3$ and $KClO_3$-primary explosive mixtures to determine thermal stability[131]. A study which compares theoretical burn models to experimental data for some composite rocket propellants has been performed by Mihlfeith[83].

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CONCLUSIONS

Although the general areas of study within the broad field encompassing the thermochemistry of explosives have been mentioned, many significant studies were regrettably neglected. Almost all of the considerable quantity of thermal work emanating from the Russian school of thermal analysis has been neglected due to the inaccessibility of much of the work and the language barrier. However, translated abstracts indicate a considerable effort toward the elucidation of the thermal behavior of explosives by Andreyev[1–9], Belyayev[18], Bobolev[23], Gorbunov[49–51], Grishin[55], Rayevskiy[96], Svetlov[123], and many more investigators. Many studies which were performed for the military were also omitted because of classification problems or inaccessibility. There was also the problem of defining an explosive in a sufficiently general manner to demonstrate the significant techniques without having to review the major portion of the chemical literature. While numerous explosives were not mentioned, several compositions not normally regarded as explosives in the traditional sense, such as some of the pyrotechnic mixtures and propellants, were included due to their rising importance.

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