THERMAL ANALYSIS OF EXPLOSIVES AND SOLID PROPELLANT INGREDIENTS*

J. NORMAN MAYCOCK

Research Institute for Advanced Studies (RIAS), Martin Marietta Corporation, 1450 South Rolling Road, Baltimore, Maryland 21227 (U. S. A.)

(Received February 26th, 1970)

ABSTRACT

The application of thermoanalytical techniques to explosives and propellant ingredients is now well established. Since sample preparation, age, packing, and geometry can drastically affect collected data, it is not surprising that thermoanalytical results reported in the literature, even for relatively simple systems, are somewhat inconsistent. Standardization of technique and reporting of the complete details of the experimental method should make data from different sources consistent. Sound theoretical models for propellant burning and decomposition-to-detonation transformations will also aid in providing a more valid basis for correlating thermal analysis data with such practical measurements as burning rate, shock, and thermal stability.

INTRODUCTION

Probably the most important characteristic of military and commercial explosives and solid rocket propellants is performance as related to end use and safety. Performance can be described by a variety of conventional properties such as thermal stability, shock sensitivity, friction sensitivity, explosive power, burning or detonation rate, *etc.*[1,2]. Modern methods of thermal analysis show great promise for providing information in both these conventional properties and other parameters of explosive and propellant systems.

Thermal properties of pseudo-stable materials have been determined mainly by differential thermal analysis (DTA), thermogravimetry (TG), and isothermal or adiabatic constant volume decomposition. Each technique is valuable by itself, but the combination of any two or even all three simultaneously has proved to be invaluable for the study of explosives, propellants, and other systems. Physical processes in pseudo-stable materials which may be observed by DTA can often be interpreted only with a knowledge of TG or gas evolution (constant volume decomposition) data. This can be seen in Table I where a selection of physical processes and the method by which thermal techniques will register them are listed.

TABLE I[a]

PHYSICAL PROCESSES DETECTABLE BY THERMAL ANALYSIS

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

[a]Key: + process is indicated; — process is not indicated.

The correct interpretation of the wealth of experimental data obtained by thermoanalytical techniques is a problem not to be taken lightly, since many important decisions relative to the use of a particular material will be based on these interpretations. It is obvious that these techniques can be used both for quality control and as an approach to the basic science of pseudo-stable materials. In the last two decades, many theoretical treatments of DTA, TG, DSC, and conventional decomposition data have appeared. Unfortunately, only isothermal decomposition has received very detailed analysis with accompanying success when applied to real systems[4,5]. The need for good theoretical treatments of DTA, TG, and DSC techniques remains clearly outstanding.

DECOMPOSITION KINETICS

Characterization of pseudo-stable solids by specification of exo- or endo-therm temperature is sufficiently well established that these values are available for almost all materials. A representative list has been published by Krien[3]. The kinetics of these decompositions have only recently been investigated by DTA, TG, or DSC. However, kinetic analysis of these data is relatively meaningless unless it can be correlated with a realistic physical model of the process.

There are essentially three possible approaches to deriving the kinetics of the decomposition of pseudo-stable solids: (1) normal isothermal decomposition using the TG technique, (2) shift in DTA exo- or endo-therm temperature as a function of heating rate, and (3) analysis of dynamic TG traces as a function of heating rate. Of the three, the first is the most reliable provided that the temperature of the test sample can be raised to the degree desired without any decomposition taking place. This is possible only for high melting-point explosives, e.g., HMX[6], and relatively thermally

stable propellant ingredients such as ammonium perchlorate[7]. Successive decompositions and poor thermal stability. *e.g.*, NO_2ClO_4[8], require combined DTA–TG and supplementary information before any reliability can be attached to the kinetic data.

Prior to a kinetic analysis by isothermal TG. it is useful to know the characteristic DTA–TG curve for the sample. In the case of HMX[6], Fig. 1 shows that a meaningful temperature range for isothermal studies is about 220–280°C, where
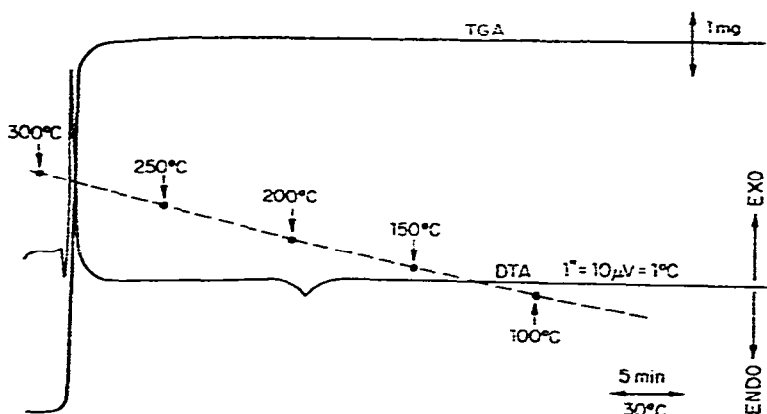

Fig. 1. DTA–TG trace for 15-mg β-HMX in flowing dry He atmosphere (10 l. hr⁻¹) at a heating rate of 6°C. min⁻¹. The sample holder was a 3-mm diam, 4-mm high platinum crucible.

kinetic data can be obtained without the problems of decomposition prior to test temperature equilibration. Isothermal TG curves for HMX are shown as a function of temperature in Fig. 2. With these data available, an analytical treatment must now be chosen. If a topochemical description of the decomposition process is not available,
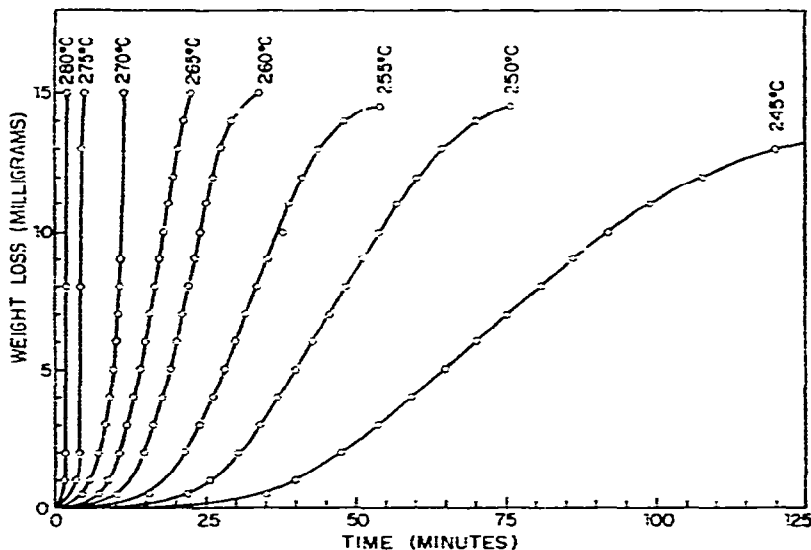

Fig. 2. Isothermal weight loss for 15-mg samples of δ-HMX at various temperatures in a flowing helium atmosphere.

a more general analytical model should be used. This is possible if the rate equation can be expressed in the general form

$$f(\alpha) = kt$$

k being the rate constant and α_n, α_{n+1} values of the fractional decomposition α at times t_n and t_{n+1}. Thus,

$$F(\alpha_{n+1}) - F(\alpha_n) = k(t_{n+1} - t_n)$$

For a different temperature, but the same values of α

$$F(\alpha_{n+1}) - F(\alpha_n) = k'(t'_{n+1} - t'_n)$$

A plot of log $(t_{n+1} - t_n)$ against T^{-1} should be linear with a slope of 2.303R. This approach has been applied to HMX to elucidate the rate constants k and the activation energy of decomposition E. Typical values obtained are on the order of 62 kcal.mole^{-1}.

The reliability of the value obtained for E can be verified by supplementary experiments or by calculation from first principles where possible. If a mechanistic model of the decomposition is available, the various analytic expressions for vaporization of an ion pair, branching nuclei with or without interference, etc., can be used[5].

Several kinetic treatments related to the shift in exo- or endo-therm temperature as a function of heating rate exist[9], although none were derived for fast solid decompositions of the type exhibited by explosives. Further, the underlying assumptions of the existing treatments are unrealistic when dealing with fast reactions. A study of the thermal decomposition of LiAlH$_4$ illustrates the confusion that can occur when the Kissinger approach is used[10]. By the Kissinger technique[9], the activation energy calculated from DTA peaks corresponding to the reactions

$$LiAlH_2 \rightarrow LiH + Al + \tfrac{1}{2}H_2$$

$$LiH \rightarrow Li + \tfrac{1}{2}H_2$$

was 24 kcal.mole^{-1}, whereas the activation energy found from isothermal runs using a modified Prout–Tompkins equation[7] was 46.9 kcal.mole^{-1}. These results indicate that care should be exercised in using activation energies derived from DTA, particularly for very rapid processes.

· All kinetic treatments based on differential enthalpic measurements require knowledge of sample size, heat of reaction, and rate of heat evolution so that the rate constant at any temperature and hence the activation energy can be calculated. Data from DSC is in the form of distance between the reaction curve and a base line at the associated temperature. This distance is proportional to the rate of heat evolution or absorption and thus proportional to the rate constant[11]. If a linear Arrhenius plot is assumed, the activation energy can be calculated from

$$-E = R\frac{\ln d_1 - \ln d_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} = \frac{4.58 \log \dfrac{d_1}{d_2}}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

where d_1 and d_2 are the rates of heat evolution at T_1 and T_2 in Fig. 3a. This approach assumes a zero reaction order and, as with methods based on DTA, should be used with care. Rogers and Morris[11] have used this technique with RDX, HMX, Tetryl,
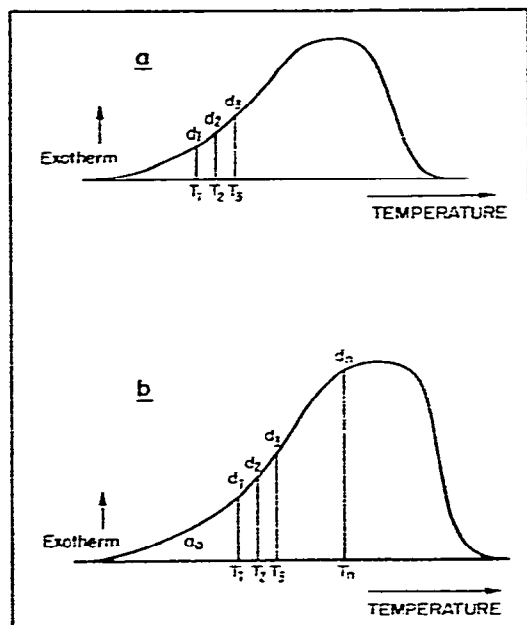

Fig. 3. Approach to kinetic calculations based on DSC data.

PETN, and $KMnO_4$ with reasonably good success. Their value of 48.4 kcal.mole[-1] for the activation energy for decomposition of RDX compares well with the literature value of 47.5[13], although the respective values[14] for PETN are 28.5 and 47.0 kcal.mole[-1].

Another model based on the theory of Borchardt and Daniels[15] requires

$$\ln \frac{d}{(1-\alpha)^x} = \ln CA - \frac{E}{RT}$$

where x = area of the exotherm to d_n divided by the total area of the exotherm, C = calibration factor relating d to the rate of heat produced multiplied by the weight of the sample, x = the order of reaction; and A = the frequency factor; see Fig. 3b. This modification has been applied to the thermal decomposition of ammonium perchlorate[16] with good results although the activation energy of 120 kcal.mole[-1] for the high temperature region is not supported by other workers[7]. Possibly the assumption of temperature uniformity throughout the sample[15], which is unlikely with rapid processes, may be a contributing factor.

Models for deriving kinetics from nonisothermal thermogravimetry have been derived and used with some success in studying the decomposition of relatively stable solids (cf. Ref. 12). However, examples of such approaches applied to explosives or even propellant components have not been reported, and our attempts to use these techniques have been negative. It is probable that the reactions are proceeding too

fast for existing analytical models. And in many instances the underlying assumptions (*e.g.*, temperature uniformity within the sample, independence of interfacial reaction area, independence of sample atmosphere, *etc.*) are not valid. Appropriate analytical treatments of the nonisothermal description would be particularly valuable in view of the small amount of thermoanalytical data necessary for the description of a system.

PHASE CHANGES

Conformational and crystallographic phase changes, as well as changes of state, are important parameters to know in characterizing metastable solids. Phase changes can be determined by DTA and DSC. whereas changes of state can be determined by TG in addition to DTA and DSC.

Conformational changes in the structure of organic explosives are not uncommon, and a knowledge of their transformation energies is valuable in describing the various phases. Probably the most well known example is HMX which exhibits the four conformational forms: α, β, γ, and δ shown in Fig. 4. By prior calibration of the instrument it was possible to determine transition energies[17] for $\beta \rightarrow \delta$ 2.74 kcal.mole^{-1} and $\alpha \rightarrow \beta$ 0.75 kcal.mole^{-1}. These values, derived from DTA at 6°C. min^{-1} and found to be independent of heating rate, agree quite well with values determined by conventional calorimetry[18]: $\beta \rightarrow \delta$ 2.9 kcal.mole^{-1} and $\alpha \rightarrow \beta$ 0.6 kcal.mole^{-1}.

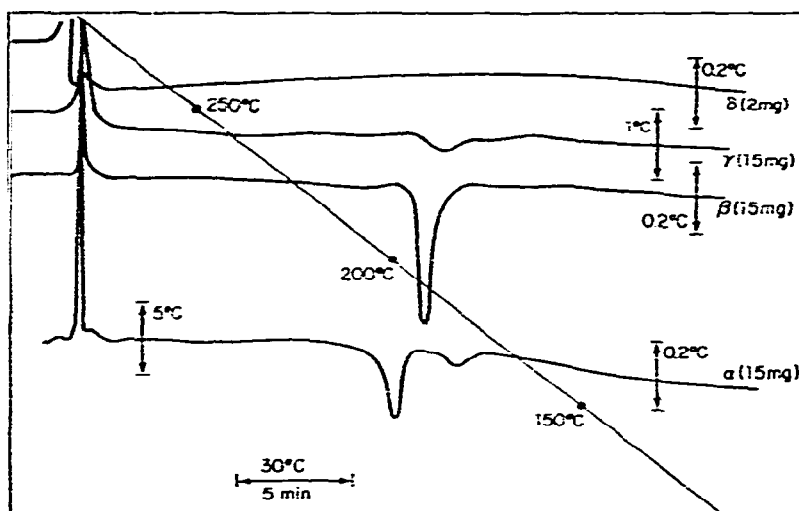
Fig. 4. DTA traces of α, β, γ, and δ HMX at a 6 °C. min^{-1} heating rate and in a flowing atmosphere of dry He (10 l. h^{-1}).

Sublimation of a solid can be complicated by the simultaneous thermal decomposition of the parent solid. This is well known for such materials as nitronium perchlorate, PETN. HMX, ammonium perchlorate, and metallic picrates. When the two processes are competitive, normal thermogravimetry or isothermal constant volume decomposition methods cannot, alone, show a distinction between the two processes.

Jacobs and Russell–Jones[19] have recently applied thermogravimetry to the sublimation of ammonium perchlorate pellets in a temperature range where they assumed complete sublimation and no thermal decomposition. Their study over a fairly wide temperature range involved an elaborate kinetic model to take into account both surface diffusion and gas phase diffusion. They were able to fit the experimental data extremely well by adjusting some variable parameters. Their rigorous kinetic analysis can be approximated to

$$1-(1-\alpha)^{1/3} = kt$$

which describes a surface reaction taking place at a rate proportional to the surface area and propagating inward at a rate $a_0 k$, where a_0 is the initial value of some characteristic size parameter (e.g., the radius of a sphere of reactant).

Recently, a Mettler thermoanalyzer has been used to determine the kinetics of sublimation of nitronium perchlorate[20]. The decomposition gas pressure and the sample weight loss can be recorded simultaneously for the same sample on this instrument (Fig. 5). The amount of sublimation as a function of time or temperature
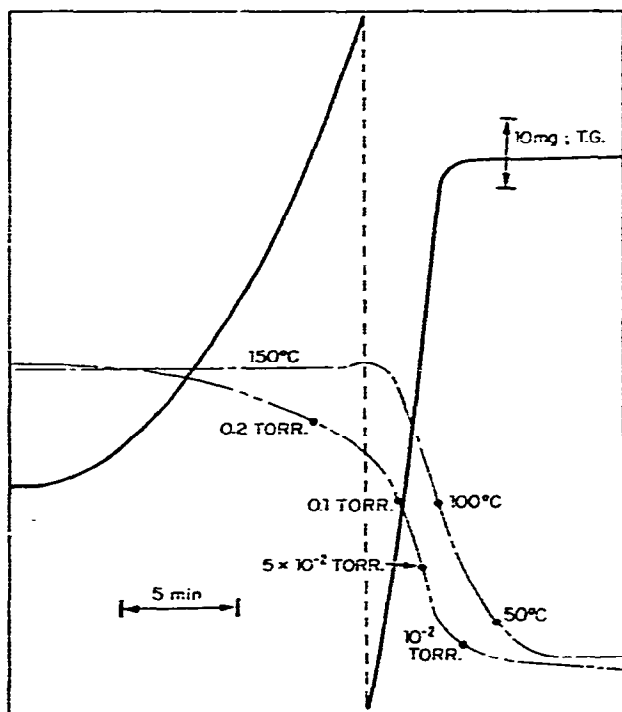

Fig. 5. Simultaneous weight loss, pressure increase, and temperature profile for nitronium perchlorate at 150 °C.

can be obtained by converting the pressure curve into mass units. Since the stoichiometric decomposition of nitronium perchlorate is known, a kinetic analysis of the data obtained by this simultaneous method is possible. It shows the process to fit the rate law

$$1-(1-\alpha)^{1/3} = kt$$

The current liability of this experimental method is the finite time required for the sample to reach its equilibrium isothermal condition. However, this instrumental problem should readily be overcome, and this technique has recently been applied to the organic explosives RDX, PETN, and TNT[21].

EXPERIMENTAL TECHNIQUE

Sample preparation

Sample preparation and history are necessary but often overlooked parameters in the interpretation of thermoanalytical data, despite the fact these problems are well respected by solid-state physicists for their frequent influence upon the properties of materials being investigated. The problem is no less for the thermal analyst interested in pseudo-stable materials, many of which can show completely different properties if they undergo aging, different growth techniques, mechanical deformation, different sample packing, etc.

Consider the effect of preparation in the case of ammonium perchlorate[22]. Three methods of crystallization were studied from: (*1*) a solution at 60–70°C cooled to room temperature. (*2*) an aqueous solution cooled to 5°C, and (*3*) single crystals grown from a saturated aqueous solution at 45°C cooled at the rate of 0.1–0.01 °C. day^{-1} and crushed to the desired particle size of about 100 μm. Throughout this investigation the particle size was kept constant and the reactivity study conducted on preparations having the same age. In Fig. 6, DTA thermograms clearly show
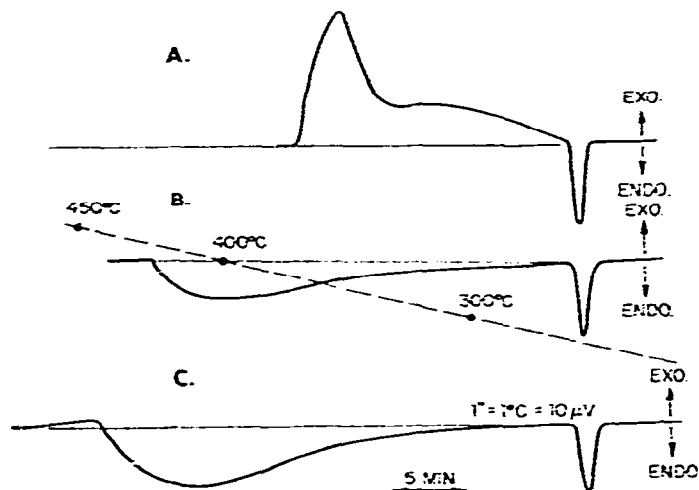

Fig. 6. DTA traces for three preparations of NH$_4$ClO$_4$ conducted on samples in a platinum crucible at a heating rate of 6°C. min^{-1} and in a flowing dry He atmosphere (10 l. h^{-1}).

differences for these nominally identical materials. The differences are thought to be due to the possibility of trace quantities of perchloric acid monohydrate diffusing into the NH$_4$ClO$_4$ crystal lattice. The suspected extent of this diffusion is C>B>A.

Aging studies on explosives are usually confined to changes in shock sensitivity

measurements; aging studies of propellants are usually measured by burning rate techniques. However, a recent study of the aging characteristics of lead azide, PbN_6. using DTA and TG has shown the applicability of these measurement techniques[23]. Here DTA has provided the means for detecting the presence of a metastable modification influencing long-term properties of a material.

Atmosphere control

The gas atmosphere around the test sample should also be carefully controlled in investigating pseudostable solids. This is well documented for the isothermal decomposition of ammonium perchlorate where traces of water can drastically alter reaction rates[24] and, to a lesser extent, the shape of the DTA peaks. Similarly, solid hydrides can exhibit exothermal decomposition peaks instead of endothermal ones if traces of oxygen are present in the test atmosphere[25]. The effect of trace quantities of oxygen on the thermal decomposition of potassium azide is illustrated[26] in Figs. 7 and 8. The large discrepancy in the DTA traces is probably due to oxidation of the
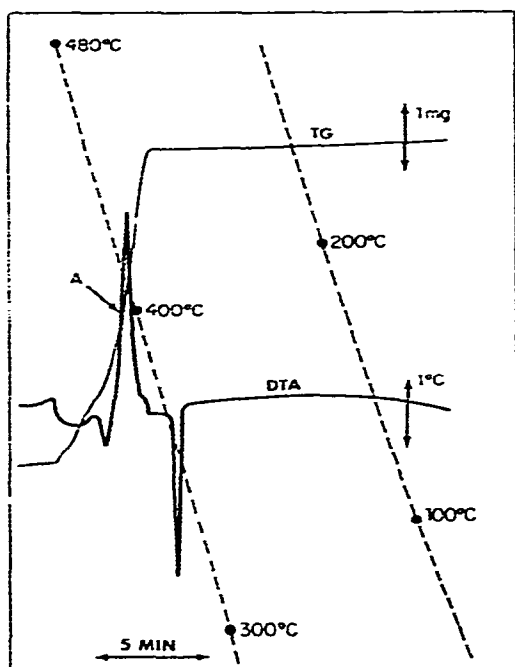

Fig. 7. Simultaneous DTA–TG for a 5-mg sample of KN_3 at 25 °C. min^{-1} in a flowing atmosphere of O_2-free He (10 l. h^{-1}).

colloidal potassium formed during the decomposition. In such cases, atmospheric problems can generally be overcome by providing good scrubbing lines for the trace contaminants in the gases. Atmosphere contaminants in the reaction zone can best be removed by evacuating the complete system prior to filling with a well scrubbed inert gas.
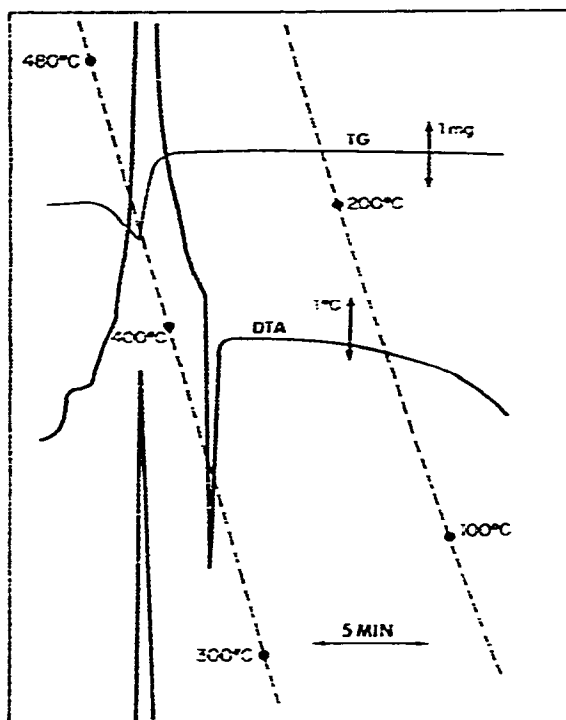
Fig. 8. Simultaneous DTA–TG for KN_3 showing the weight increase after decomposition. Sample size 5 mg, heating rate 25 C. min^{-1}, flowing He atmosphere containing traces of O_2.

Several of the more exotic oxidizers and fuels are extremely hygroscopic and require especially careful handling. These problems can be overcome by loading the thermal analysis sample holders in a dry box, transporting them to the test instrument in sealed jars, and loading them into the instrument under an inert atmosphere using a bell-jar arrangement. One arrangement with a Mettler Thermoanalyzer is shown in Fig. 9. It has been employed successfully in studies of nitronium perchlorate[20], and hydroxylammonium perchlorate.

Particle size

Sample particle size is also an important parameter to keep constant, especially when comparing data. As a general rule most materials exhibit an increase in reactivity as the particle size is decreased. This is usually seen as a sharpening of the DTA peak, a steeper TG trace, and also occasionally an increase in shock sensitivity for explosives and an increase in burning rate for monopropellant systems. An example is the work of Mayer et al. on propellant grade ammonium perchlorate[27], see Fig. 10.

Of particular interest in the Mayer data is the DTA dependence on particle size. For ammonium perchlorate to be used as the oxidizer in a high burning rate propellant then, at first approximation, the sample showing decomposition at the lowest temperature is the most appropriate choice. Inspection of these data would suggest the
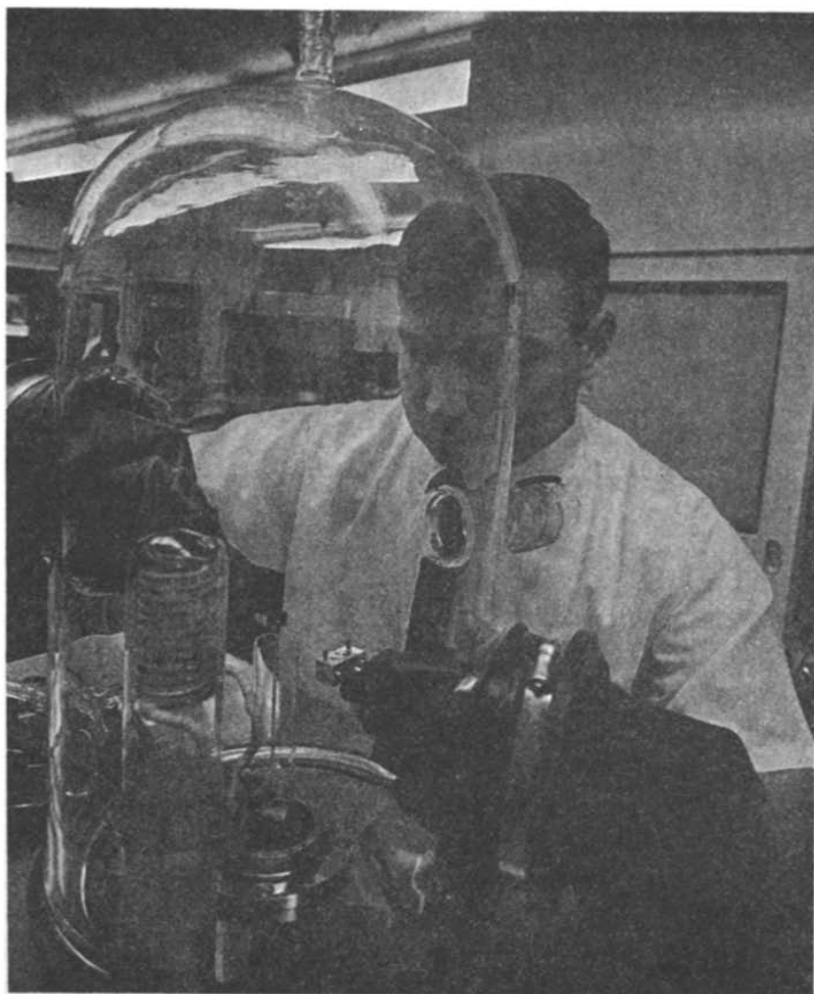
Fig. 9. Bell-jar arrangement for working with extremely hygroscopic samples.

choice of the 5 μm AP as the best oxidizer to use. This oxidizer would give a higher burning rate than the other samples shown in Fig. 10.

APPLICATIONS

Routine test procedures for explosives

It has been shown how different methods of thermal analysis can be used to study kinetics, phase changes, and as "fingerprinting" devices. These techniques are sufficient justification for routine application of thermal analysis to explosives and propellants. If these dynamic techniques can be correlated to the more "engineering-type" tests currently used, the use of thermal analysis will save time and provide additional information on explosives and propellants.
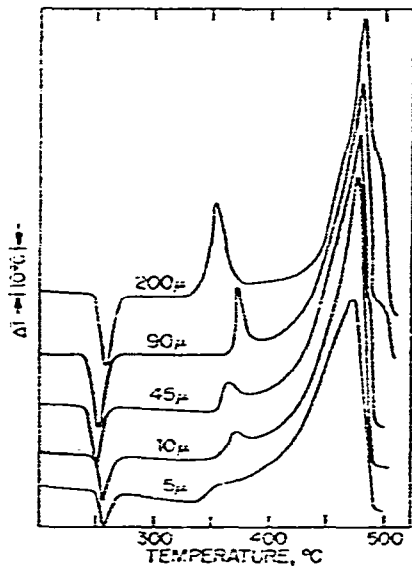
Fig. 10. Typical DTA curves for propellant grade NH_4ClO_4 (AP): particle sizes 5, 10, 45, 90, and 200 μ.

Applications to explosives

According to Copp *et al.*[28], there are two main variants in routine engineering-type tests for determining the thermal sensitivity of explosives: (*1*) the explosive is heated in a suitable container from room temperature to the ignition point with ignition occurring above a limiting temperature dependent on the heating rate and (*2*) the container is suddenly plunged into a bath maintained at a constant temperature, and the time interval before ignition occurs is measured. The possibility of using thermogravimetry as a general method for determining the thermal sensitivity of lead azide by differentiating between a detonation and a fast decomposition is seen in Tables II and III.

TABLE II

DETONATION AS A FUNCTION OF CRITICAL MASS OF PbN_6[a]

Mass (mg)	Visual criterion	Mass loss (mg)	Inference: temperature of reaction (°C)
1.0	Decomposition	0.25	<1515
1.6	Decomposition	0.35	<1515
2.0	Decomposition	0.50	<1515
3.0	Detonation	3.0	>1515
4.0	Violent detonation	4.0	>1515

[a]Heating rate: 15 °C/min; atmosphere: flowing He 10 l/h.

Table II shows that a critical mass is required to proceed from decomposition to detonation (keeping the heating rate and other experimental variables constant),

and reveals that during decomposition only 25–30 percent of PbN_6 is lost. A 100-percent loss is observed during detonation.

TABLE III

DETONATION OF PbN_6 AS A FUNCTION OF CRITICAL HEATING RATE[a]

Heating rate ($°C/min$)	Visible criterion	Mass loss (mg)	Sensitivity, height/half width	Inference: temperature of reaction ($°C$)
10	Decomposition	0.50	10/3.5 = 2.9	<1515
15	Decomposition	0.55	15/2.0 = 7.5	<1515
25	Detonation	2.0	25/1.0 = 25.0	>1515

[a]Sample mass: 2.0 mg; atmosphere: flowing He 10 l/h.

When the heating rate is varied from a low to a high value (Table III), the reaction goes from decomposition to detonation with a 25–30-percent weight loss for decomposition and a 100-percent weight loss for detonation. The fourth column of Table III gives the sensitivity of the DTA exotherm associated with the weight loss, as calculated from the ratio of the height of the exotherm to its half width. As will be seen later, this sensitivity calculated from the DTA exotherm can lead to the same conclusions as data from thermogravimetry.

The differences in weight loss corresponding to decomposition and detonation can be explained on the basis that when lead azide is thermally decomposed, the reaction products are gaseous nitrogen and metallic lead. The nitrogen content of lead azide is about 28 percent; therefore, thermogravimetry shows this loss. However, when the thermal reaction leads to an explosive decomposition (detonation), thermogravimetry shows a 100-percent weight loss, since the detonation of PbN_6 creates temperatures of the order of 3300 °C. At these temperatures, the metallic lead formed during the detonation is completely vaporized.

A simple thermogravimetric technique thus provides a reliable method for differentiating between decomposition and detonation, eliminating the need for visual observation and allowing the use of very small samples. At a constant heating rate, the sample mass is the critical factor deciding whether the reaction leads to decomposition or detonation (Table II). In order to differentiate between the sensitivities of different samples of PbN_6, it is correct to say that the sample which requires the minimum weight to detonate is the most sensitive and vice versa. This is in complete agreement with earlier knowledge that a critical mass is required for detonation[3]. The results in Tables II and III show that this critical mass is very much dependent on the heating rate. Therefore, if constant mass is maintained, the heating rate can be used to differentiate between lead azide samples varying sensitivities. The lower the heating rate at which a given mass of PbN_6 detonates, the higher its sensitivity and vice versa.

As a function of heating rate, the DTA sensitivity is seen to change from a low

arbitrary value to a high one as the reaction changes from a decomposition process to one of detonation. By prior correlation with thermogravimetry, this arbitrary sensitivity value can be used as a test parameter.

These same technique of determining the critical mass and critical heating rate have been applied to a series of azides and the data compared with the shock sensitivity values[26]. They have also been used to distinguish between samples of lead azide having slightly different shock sensitivity values.

This new method of determining the thermal stability of explosives applies to any explosive with a metal component in its structure, e.g., metallic azides, picrates, fulminates, etc. The application of this technique to nonmetallic salts could conceivably be achieved by the addition of some vaporizable small particle size metal to the test sample. This may also be practical with the organic explosives, although the secondary explosives (HMX, RDX, etc.) will require extremely high heating rates. With all the wealth of information appearing in the literature on explosives characterization, it is now apparent that methods of thermal analysis applied to measurement of performance parameters can yield more information than just a "signature" of the material.

Propellant characterization

Today's demand for better oxidizers and fuels as propellant ingredients is being met by the synthesis chemist. Unfortunately, many of the better materials are inherently unstable because of their extreme oxidative powers. Thus propellant ingredient workers must solve instability problems without sacrificing the usefulness of the new ingredient. Frequently, the addition of carefully selected impurities to the host ingredient or the use of some form of inert encapsulation technique will overcome the problem. DTA can be used to screen the selected impurities for their effect on the host material. For example, Fig. 11 shows the effect of selected impurities on
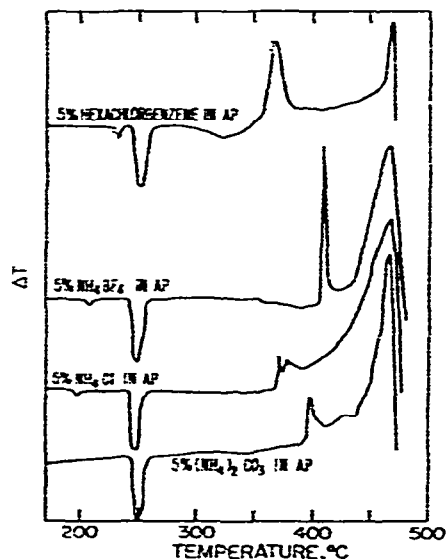

Fig. 11. DTA curves for AP containing a 5 percent additive.

the thermal characteristics of propellant grade 90-μm ammonium perchlorate. Compare Fig. 11 with the thermogram for the pure material in Fig. 10.

The application of thermal analysis to a study of propellants unfortunately provides no information concerning the burning characteristics. Burning temperatures are in the 3000°K range; while the normal ammonium perchlorate decomposition occurs at about 700°K. Thus a very important question yet to be resolved is the correlation between conventional thermal analysis data and actual propellant burning rate data. Using thermoanalytical techniques, the entire sample of ammonium perchlorate is heated slowly or held at constant temperature. By contrast, in the deflagration process, temperatures above 3000°K are attained in the flame, high pressures are generated, and the sample is subjected to interacting combinations of temperature, pressure, and time. In the burning propellant, the ammonium perchlorate grains experience a large temperature gradient between the surface and interior for very short times compared with the normal thermal decomposition. The large discrepancy which thus exists between the decomposition and deflagration modes suggests that any correlation may be only superficial at best.

Pittman et al.[29] have made a fairly exhaustive study of a possible correlation between thermal decomposition data obtained by DTA and actual burning rate measurements. The initial attempt to correlate decomposition and deflagration of ammonium perchlorate plus catalyst and a complete propellant containing the same stoichiometric amount of catalyst was not successful (Fig. 12). Clearly, from these data, a catalyst which loweres the DTA decomposition temperature of ammonium perchlorate does not indicate that a composite propellant employing the same catalyst will burn faster. In the acetylacetonate series, Mn^{II} and Mn^{III} are excellent decomposition catalysts producing low DTA peak temperatures; but they are poor burning rate catalysts. The converse is true for Cr^{III} and Al.
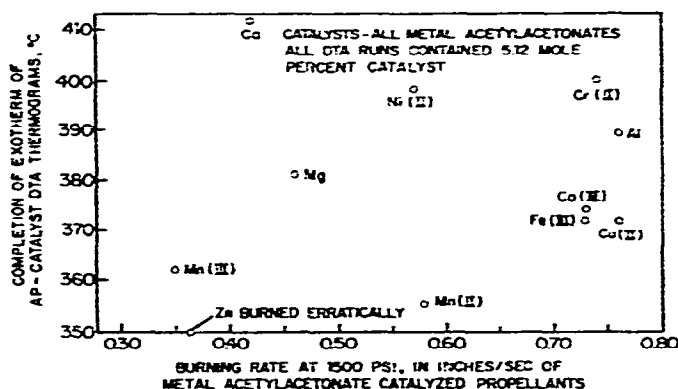

Fig. 12. Correlation of DTA parameters of AP-catalyst mixtures with burning rates of propellants containing the corresponding catalyst.

A trend in thermal decomposition catalysts, particularly the oxides, is revealed in the survey of ammonium perchlorate data in Table IV.

TABLE IV

THERMAL DECOMPOSITION CATALYSTS

Very good	Good	Poor
Zn, Mn, Cu	Cd, Pb	Mg, K, Na
Ni, Co	Fe, Ag, Ca	Ba, Ti, Ge
	Cr, Al, Th	Sr

This order contrasts strongly with the burning rates since Cu and Fe are the best burning rate catalysts, while Zn and Mg oxides are poor catalysts for this process and can, under certain circumstances, retard the burning.

Considering the vastly more complex processes involved in the burning of a composite propellant than in the thermal decomposition of the relatively simple oxidizer-catalyst system, the apparent inconsistency of data is not surprising.

Pittman et al.[29] also examined the effect of varying the proportion of a single catalyst, e.g., Fe_2O_3, in the oxidizer and then in the composite propellant. Fig. 13 shows a relatively good correlation between the lowering of the DTA exotherm temperature (decomposition) and the deflagration rate. Both catalysts, Fe_2O_3 and n-butyl ferrocene, show this correlation, although the Fe_2O_3 data cannot be compared directly with n-butyl ferrocene data. While not quantitative, these results indicate that thermoanalytical techniques can be used as a guide to expected burning rates provided that they are not loosely interpreted and not compared directly in different systems.
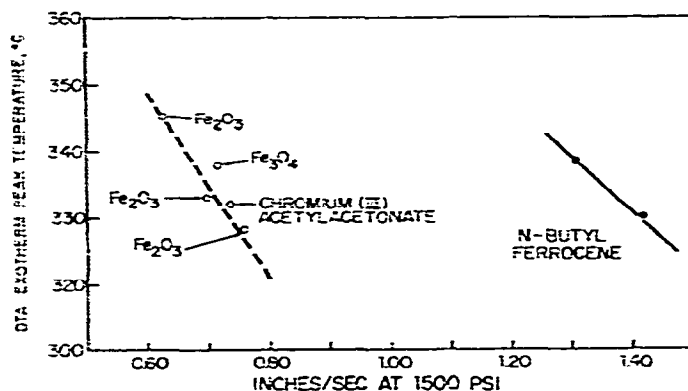

Fig. 13. Correlation of DTA parameters with the burning rates of propellant samples.

Radiation damage studies

Most explosives and propellant ingredients are susceptible to damage by X and γ radiation. Some may even be damaged by the less energetic u.v. It is important to know the effect of radiation on such parameters as thermal stability, shock sensitivity, burning rate, etc. Generally radiation damage can cause one or more of the following

effects: (*1*) production of new molecules in the solid. (*2*) change in phase transformation behavior, and (*3*) production of local defect structures, *e.g.*, color centers.

Probably the most intensively studied material of interest is the oxidizer ammonium perchlorate. The most complete work on the effect of X-and γ-rays on the thermal decomposition of ammonium perchlorate[30-33] showed by DTA and TG that the thermal decomposition of irradiated ammonium perchlorate proceeded much more readily than the unirradiated samples. By comparing changes in the thermoanalytical data from the irradiated samples with electron spin resonance measurements and the DTA of ammonium perchlorate containing known impurities, a mechanism for radiation damage was formulated involving the production of foreign chemical species in the host lattice. [60]Co γ-radiation damage effects in ammonium perchlorate have been reinvestigated[34] by isothermal decomposition techniques and show relatively large increases (threefold) in the rate of decomposition of the irradiated solid. These data are comparable to those obtained by TG. and it would be expected that the DTA exotherm peak temperature would also be lowered as found by Freeman *et al.*[30-33].

From the previous discussion of the relationship between lowering of DTA exotherm temperatures, it would be natural to expect that irradiated ammonium perchlorate would provide a faster burning propellant. Cavey and Pittman[35] have recently investigated the burning rate over a pressure range of 500–1500 psi. They found no indication of an enhancement by using the irradiated oxidizer. Again this illustrates the point that a higher rate of weight loss, or the shift of a DTA exotherm to a lower temperature, does not necessarily mean a higher propellant burning rate.

Ultraviolet radiation damage of HMX has also been investigated by thermal analysis[36,37]. A shift in the temperature of the endothermal processes associated with the conformational changes observed in HMX was reported in both studies. A shift in the decomposition exotherm temperature has also been correlated with changes in reaction rates using the simultaneous DTA–TG technique[36].

Heats of explosion

In the search for new and highly energetic explosives and propellant ingredients, many new compounds with unknown fundamental parameters have been prepared. Many of these materials are toxic and extremely sensitive to shock and friction. The heat of explosion of an unknown, newly synthesized material can be a guideline to its destructive power and its potential use as an explosive or as a propellant ingredient. Bohon[38,39] has successfully utilized a modified DTA technique to determine heats of explosion. His major problem was to find a method to establish equilibrium between the extremely hot product gases and the DTA sample cup and measuring thermocouple. Of several designs, the most successful was a constant volume container. The DTA curves obtained using this closed volume technique are similar to those obtained from more conventional techniques, and the method was found to be particularly good for single-compound explosives or double-base propellants. Typical of the results obtained was the determination of the heat of explosion for JPN propellant

samples as 1110 ± 140 cal.g^{-1} at about 250°C. Similar studies have been conducted on the explosives NG, TNT, RDX. Tetryl. and PETN, the N-5 double-base propellant, and also on aluminized double-base propellant ABL-2056.

Clearly this technique merits further attention, since it may be possible that pressures developed in the burning of a solid propellant can be simulated with the result that a more meaningful relationship between DTA and burning rate can be established.

TABLE V

DTA TESTS ON MATERIALS CAPABLE OF EXPLOSION

Substance	Melting point (°C)	Crystal transformation (°C)	Ignition temperature (°C)	Exotherm temperature (°C)
2,4,6-Trinitrotoluene (TNT)	81	—	295–300	250
2,3,4-Trinitrotoluene	112	—	295–300	—
2,4,5-Trinitrotoluene	104	—	295–300	—
Ammonium picrate	280 (decomposition)	200	313	280
Trinitrophenylmethylnitramine (Tetryl)	129	—	201–212	162
1,3,5-Trinitro-1,3,5 triazacyclohexane hexogen (RDX)	205	—	229	215
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane octagen (HMX)	275	186	279–281	260
Pentaerythritol tetranitrate (PETN)	140	—	203	160
Nitroguanidine	264	—	210–240	168
Ammonium nitrate	169	32.5 84.2 125.2	No ignition up to 360	— (endothermic)

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