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A THERMOANALYTICAL STUDY OF THE DECOMPOSITION OF A DOUBLE-BASE PROPELLANT

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ABSTRACT

The thermal decomposition of a double-base propellant was investigated by isothermal and dynamic DSC and by dynamic TG. In addition the rate constant and the order of the reaction of the decomposition process were determined by DSC analysis. The kinetic parameters (activation energy E and Arrhenius pre-exponential term A) for the thermal decomposition were confirmed by half-life test. Thus they can be used as a screening technique to predict potential explosive hazards due to self-heating during storage at lower temperatures than those of the peak temperatures.

An attempt has been made to compare the behaviour of the double-base propellant with those of the two components. It is suggested that the thermal combustion of nitroglycerin is the driving kinetic process of the overall thermal decomposition.

INTRODUCTION

Nitrocellulose, NC (13.35% N), and glycerol trinitrate, NG, are the essential ingredients of the smokeless double-base propellant which is mostly used in small arms ammunitions. The kinetics and the mechanism of its thermal decomposition are of considerable importance since they relate to the stability of this propellant and may also be involved in its combustion process.

The thermal decomposition of this double-base powder was investigated by isothermal and dynamic DSC and by dynamic TG. In addition, the rate constant and the order of the reaction of decomposition and half-life test were determined by DSC analysis. An attempt was also made to compare the behaviour of the double-base propellant with those of the two components.

EXPERIMENTAL

A Perkin-Elmer DSC-2 thermal analyser with DSC and TG modules was used. Samples were weighed on a Sartorious Electronic Analytical Balance

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1601 MP8. Aluminium pans were used. The lids were placed (not crimped) over the samples.

Weights of the samples were about 0.15 mg and 0.3–0.8 mg respectively, for two different calibres of double-base powder. The DSC scans were carried out at 2.5, 5, 10, 20 and 40 K min^{-1} heating rates, over the temperature range 465.16 to 488.16 K (with range full scale from 5 to 10 mcal s^{-1}). For the larger calibre, at the higher heating rates, the thermal decomposition often generates a large output of heat quickly with a consequent loss of thermal equilibrium. The following "ignition" and the thermal explosion of the double-base propellant caused the DSC peaks to run "off scale" and the lids to blow off the pans.

MATERIALS

The double-base propellant (OLIN W 874) used has the following composition: 80% nitrocellulose, 10% nitroglycerin, 0.4% graphite, 1% KNO_3 0.5% Na_2SO_4, 1% $CaCO_3$, 1% diphenylamine, 5.1% dibutylphthalate and 1% SnO_2.

RESULTS AND DISCUSSION

The parameters which define the sensitivity of explosives can be divided into thermodynamic parameters (critical mass and peak temperature) and kinetic parameters (activation energy and pre-exponential factor).

Thermodynamic parameters

The critical mass [1] is the minimum weight of sample which would explode in fixed and specified conditions of temperature and pressure. Peak temperature (T_m) [2] can be defined as the temperature at which the rate of heat dissipation from an exothermic reaction is maximum under thermal equilibrium conditions or as the lowest constant surface temperature above which thermal explosion occurs.

Kinetic parameters

E is the activation energy of the thermal decomposition process. A is the first-order Arrhenius pre-exponential term in the same process. The pre-exponential term A has the dimensions of time^{-1}. Kissinger [3,4] and other authors [5,6] have found that the peak temperature is a function of the heating rate of the sample through the following (pseudo) first-order reaction

$$\ln\left(\mathrm{d}T/\mathrm{d}t/T_m^2\right) = \ln(RA/E) - E/RT_m$$

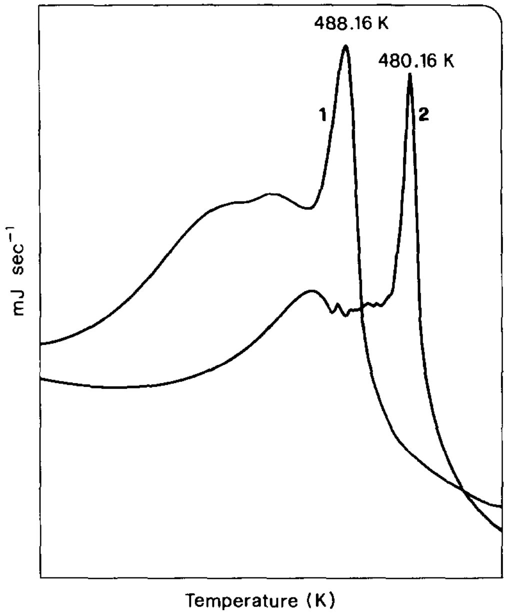


Fig. 1. DSC traces of double-base propellant decomposition: (1) heating rate 40 K min^{-1}; (2) heating rate 20 K min^{-1}.

where dT/dt is the time rate of sample heating and R the gas constant. This equation can be applied with a reasonable approximation even to an nth-order reaction, regardless of the reaction order.

If the reaction proceeds under conditions where thermal equilibrium is always maintained, and the samples are below the minimum weight, then a plot of $\ln[(dT/dt)/T_m^2]$ vs. $1/T_m$ gives a straight line of slope $-E/R$. The activation energy was also calculated using Ozawa's method [7,8]

$$\ln(dT/dt) = 0.4567E/RT_m = \text{a constant}$$

The DSC traces for the double-base propellant at various heating rates are given in Fig. 1. Kissinger's method is very useful for studying a reaction which consists of only a single exotherm corresponding to T_m. T_m, activation energy E and factor A are reported in Tables 1–4. It was found that the minimum weight is below 0.28 mg (indeed for the larger calibre the temperature peaks often run "off scale" at higher temperature rates). The E values obtained using Kissinger's and Ozawa's methods are very similar.

It is noteworthy that the activation energy values for the decomposition of the nitrocellulose 164.12 [9], 171.6–292.95 [10], 172.62 [11] and of the nitroglycerin 163.3 kJ mol^{-1} [12] were found to be much smaller (with the exception of the value 292.95) than those of the double-base powder decomposition. This could be attributed to a synergic process. For testing E values, a very useful method is represented by a half-life experiment for thermal decomposition [10].

TABLE 1

Heating rates and peak temperatures for thermal decomposition of double-base propellant (minor calibre)

Peak temperatures T_m (K)	Heating temperatures (K min^{-1})
469.16	40
473.16	20
477.16	10
480.16	5
488.16	2.5

TABLE 2

Heating rates and peak temperatures for thermal decomposition of double-base propellant (major calibre)

Peak temperatures T_m (K)	Heating temperatures (K min^{-1})
465.16	40
468.16	20
470.16	10
475.16	5
483.16	2.5

TABLE 3

Kinetic parameters for thermal decomposition of double-base propellant (minor calibre)

Method: dynamic DSC	E (kJ mol^{-1})	A (s^{-1})
Kissinger	275.41	3.16×10^{28}
Ozawa	269.47	1.39×10^{31}

Half-life

The half-life equation for first-order decay is $t_{1/2} = 0.693/k$ where k is the decomposition rate value at a fixed temperature. For a temperature equal to 453.16 K the $t_{1/2}$ value is 9.43 min. A sample was then aged in a DSC pan at 453.16 K for 9.43 min, cooled to room temperature and run at 5

TABLE 4

Kinetic parameters for thermal decomposition of double-base propellant (major calibre)

Method: dynamic DSC	E (kJ mol^{-1})	A (s^{-1})
Kissinger	266.76	7.01×10^{27}
Ozawa	261.0	$3 \quad \times 10^{30}$

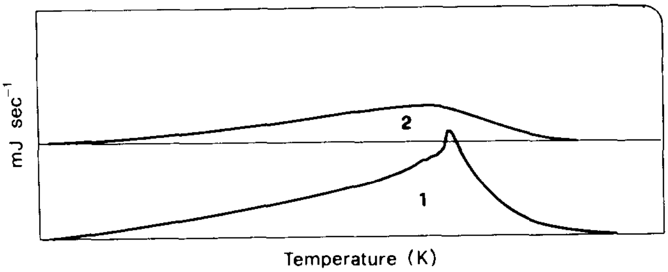


Fig. 2. Half-life after thermal aging in DSC (5 K min^{-1}): (1) unaged sample; (2) aged sample at 453.16 K for 9.43 min.

K min^{-1} with the method used to obtain T_m values. The ratio between the half and zero time values was equal to 0.56 (Fig. 2). Thus the excellent agreement between found and theoretical values, allows us to suppose that the kinetic values calculated by means of the Kissinger equation are reliable. The fact that less than 50% of the sample had reacted after the predicted half-life had elapsed indicates that, at temperatures lower than T_m, the propellant is less reactive than would be predicted by the calculated kinetic data. The kinetic parameters are also very useful as a screening technique to predict potential explosive hazards due to self-heating during storage at lower temperatures than those at which the T_m data were obtained. Half-life values at various temperatures are given in Table 5.

Isothermal DSC

It is also possible to define the rate constant and the order of the decomposition reaction by means of isothermal DSC (Fig. 3) [13]. The rate of decomposition, at any time, is represented by the vertical displacement from the baseline to the decay portion of the DSC curve. The peak maximum is taken as the starting point and the time at this point is taken as zero. As shown in Fig. 3 the rate of decomposition decreases as the

TABLE 5

Half-life times of double-base at various temperatures (major calibre)

Temperature (K)	Half-life
333.16	2.093×10^6 years
373.16	68 years
458.16	4.275 min
473.16	27.88 s
573.16	2×10^{-4} s
873.16	9×10^{-13} s

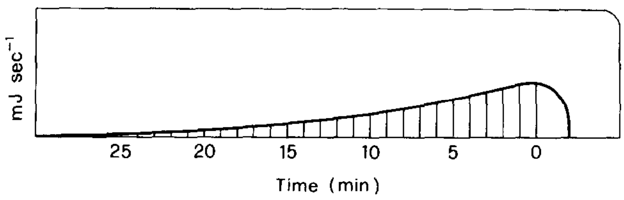
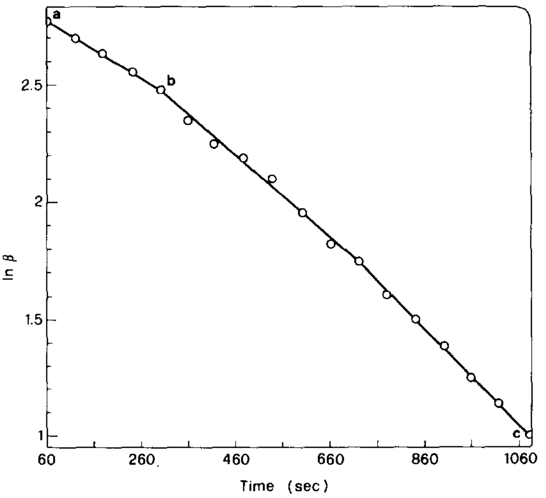


Fig. 3. Isothermal DSC curve of double-base propellant decomposition at 463.16 K.

decomposition reaction proceeds. By plotting ln (displacement) versus time, the reaction rate constant can be obtained from the slope (Fig. 4).

The order of the reaction is obtained from the slope of the plot of ln (rate of reaction) versus the reactant fraction remaining at the end of each time interval (Fig. 5). The rate constant is equal to 7.36×10^{-4} s^{-1} during the initial stage of decomposition, while after 50% of the sample had reacted, the rate constant becomes 1.88×10^{-3} s^{-1}. The order of reaction is 0.7. These values show that a very homogeneous thermal decomposition process is a feature of this propellant.

Using isothermal DSC values at various temperatures, an Arrhenius plot of ln k vs. $1/T$ is obtained (Fig. 6). The activation energy found (262.774 kJ mol^{-1}) is in very good agreement with the dynamic DSC data.



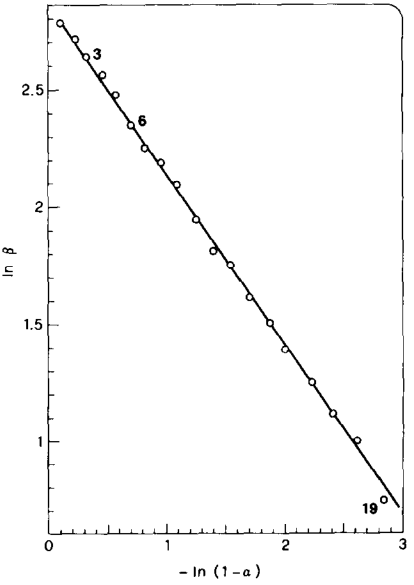
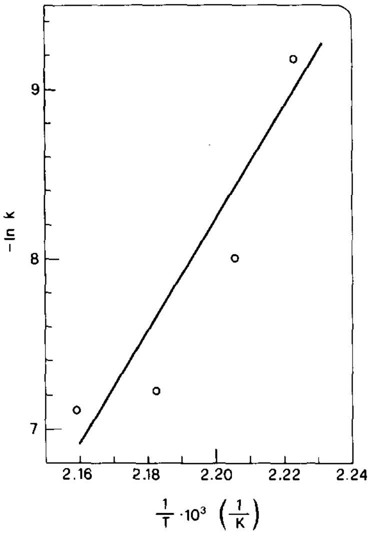


Fig. 4. Rate constant plot for double-base propellant decomposition from isothermal DSC data at 463.16 K: ab, $k = 7.36 \times 10^{-4}$ s^{-1}; bc, $k = 1.88 \times 10^{-3}$ s^{-1}.

Fig. 5. Order plot of isothermal DSC decomposition data at 463.16 K; $n = 0.7$; 28.5%, 50.6% and 94.2% of decomposition at points 3.6 and 19 respectively.



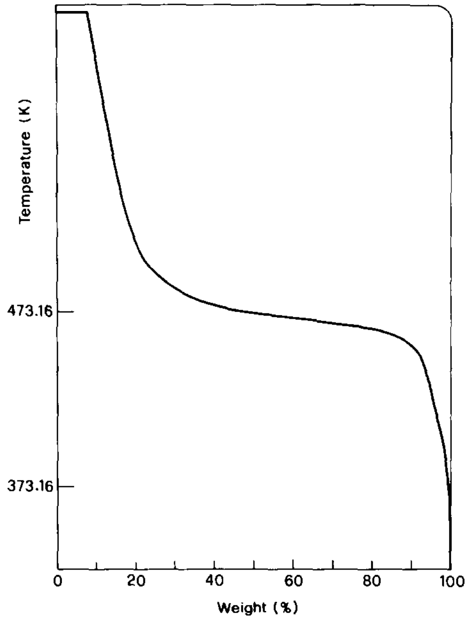


Fig. 6. Arrhenius plot of isothermal DSC decomposition data for double-base propellant; $E = 262.744$ kJ mol^{-1}.

Fig. 7. TG curve of double-base propellant at a heating rate of 10 K min^{-1}.

Thermogravimetry

A TG curve at a heating rate of 10 K min^{-1} was obtained (Fig. 7). The curve inflexion is at 467.16 K, which is in agreement with the temperature peak of 470.16 K found in the DSC curve obtained under the same conditions. Loss of 50% of weight occurs over a 10 K range, with the greatest rate (of loss) from 75 to 65% of weight. It is noteworthy that there is ~ 10% by weight of nitroglycerin in the double-base powder and that the temperature of inflexion occurs in this range of weight loss.

Chemically, explosives can be subdivided into two classes [14]: those with complete combustion and those with incomplete combustion. Using the empirical formula $C_aH_bO_cN_d$, for the former the following relation was found: $c \geq 2a + b/2$ while for the latter the relation is $c < 2a + b/2$. Thus the chemical reaction for nitroglycerin is

$$2C_3H_5(ONO_2)_3 = 6CO_2 + 5H_2O + 3N_2 + 1/2O_2$$

and it can be seen that the combustible elements (C and H) are completely oxidized to CO_2 and H_2O by the oxygen atoms of nitroglycerin. This is not true for nitrocellulose. However, nitrocellulose is an explosive substance fully convertible into gases as follows

$$C_{12}H_{14}O_{22}N_6 = 5CO_2 + 7CO + 2H_2 + 5H_2O + 3N_2$$

Furthermore, in the presence of atmospheric oxygen, there is competition [15] between nitrogen monoxide and dioxide ($2NO + O = 2NO_2$) for the nitrocellulose combustion. Indeed the former hinders the rearrangement of the chains of nitrocellulose to permit the formation of stable gaseous species, while the latter favours this process.

These reasons allow us to suppose that the nitroglycerin combustion is the driving kinetic process of the overall thermal decomposition.

As previously shown, the greater activation energy E of the double-base propellant with respect to those of the two essential components, was attributed to a synergic phenomenon. Comparing the temperature peaks of the double-base powder with those of the major component (nitrocellulose) [11], under the same conditions, it can be seen that this phenomenon appears at high heating rates.

CONCLUSIONS

The analysis of DSC and TG data, obtained from the thermal decomposition reaction near to the ignition temperature, is very useful. Indeed the rate of energy release in the thermal decomposition is directly connected with the net amount of energy released in the explosive decomposition.

The kinetic parameters E and A also permit prediction of potential explosive hazards at various temperatures. However it is reasonable to assume that, at much lower temperatures than T_m, the double-base powder displays a mechanism of thermal decomposition differing from that predicted by kinetic data.

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