Thermochimica Acta, 16 (1976) 365–376
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KINETIC STUDIES OF COMPOSITE PROPELLANTS BY DIFFERENTIAL SCANNING CALORIMETRY

EFFECT OF HEATING RATE AND SAMPLE GEOMETRY

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(Received 19 January 1976)

ABSTRACT

Differential scanning calorimetry has been used to calculate some kinetic parameters of a typical composite solid propellant (PBAA based). The heating-rate affects the development of thermograms and also the apparent activation energy. Sample geometry has a definitive influence on thermograms and on sample ignition but seems to have no effect on activation energy calculations.

INTRODUCTION

Research carried out applying thermoanalytical techniques for the determination of the activation energy in the combustion process of solid propellants, has been done[1–3] at heating rates (B) in the range 10 to 20 K min^{-1}. To our knowledge, no detailed studies concerning the influence of the heating rate on the activation energy are reported in the literature. However, if there is a relationship between these two parameters, it should be established, since it is common practice to employ thermoanalytical data in real motor combustion calculations. The composite solid propellant combustion mechanism is very complicated and only a general outline can be postulated. It is recognized that parallel and consecutive reactions may occur; thus it is quite reasonable to assume that the reaction mechanism may change with different heating conditions. In addition, the heating rates used in thermoanalytical methods are much lower than those which ignite the propellant in the motor. Heating rate variations may change the reaction path and consequently the activation energy may be changed and may take values quite different from those obtained by thermoanalytical techniques. Waesche and Wenograd[1], working with DSC and a propellant of the same composition as the one used in the present research work, did not find variation of the activation energy over the range they tested (isothermal to 20 K min^{-1}). From their findings, they justify the use of kinetic parameters obtained by thermoanalytical methods in solid propellant combustion calculations, where the heating rates are always considerably higher[4].

In the same publication[1] the authors describe a two-step propellant decomposition, which is also observed with ammonium perchlorate (AP) alone. However, when they work with a propellant with AP particles of 15 μm the first reaction peak does not appear. Assuming that an induction period exists, they consider that this low temperature reaction would not influence the extrapolation to high heating rates.

These conclusions seem to be confirmed by the research done with pure AP by Bircumshaw and Phillips[5]. They found that when working isothermally there was no induction period at a high temperature (420°C). However, this effect was observed when the experiments were run at 280°C.

Similar studies reported by Sammons[6] demonstrated that the decomposition of AP alone at low temperatures (600 K) generally reach 30%. Working with DSC, and comparing the exothermic peaks at low and high temperatures, he found that the amount of AP which has reacted varies between 15 to 50%. Nevertheless, Sammons[6] reported in his paper, that it has been demonstrated by thermogravimetric methods that the decomposition of AP never reaches values higher than 30%, depending on its purity. For high purity AP the thermograms show almost no decomposition at low temperatures, but even when using these samples in isothermal studies, the decomposition may be extended to 30%, which would confirm the existence of an induction period. Waesche and Wenograd[1] studying the high temperature decomposition (AP particle size: 15 μm) have found two peaks, but they did not explain this behavior. They stated that the reaction which corresponds to the first peak indicates a larger heat release rate at high temperatures. This would indicate that this reaction is the controlling step in the combustion process.

The present work, using DSC, has studied the influence of the heating rate on the kinetic parameters in the range 4 to 64 K min^{-1}. Taking into account the results obtained by other authors[1,5,6] this investigation is mainly concerned with the kinetics of the high temperature decomposition. The induction period associated with the reaction at lower temperatures, appears to eliminate any influence of this process on the real combustion.

The effect of the sample geometry on thermograms was also investigated. Some results were already reported by Sammons[6] and we analysed the possible effects on experimentally determined activation energies.

EXPERIMENTAL

The solid propellant composition was: AP 75% (particle size 16 μm) and polybutadiene-acrylic acid (PBAA) 25%.

The samples were prepared by slicing propellant with a microtome. The slice thickness was measured with a dial gauge (± 10 μm) and then discs were cut out (diameter 3 mm) with a cork borer. These were encapsulated in sealed aluminum pans with 7 holes (diameter 0.1–0.2 mm) pierced in the lid to allow gaseous decomposition products to escape. The samples were weighed with a Cahn electrobalance. The differential calorimeter employed was a Perkin-Elmer DSC-1B.

RESULTS AND DISCUSSION

Thermogram characteristics

Figures 1–4 show series of thermograms which present some similar features and may be summarized as follows:

(1) The typical endothermic peak (I) of the crystal phase change of AP is observed at about 526 K. It is known that this peak corresponds with the orthorhombic to cubic transformation.

(2) A sort of plateau (II) follows peak (I); this corresponds to the low temperature decomposition of AP.

(3) An exothermic peak (III) appears in the range 600–640 K, depending on the sample thickness and on the heating rate employed. Immediately after peak (III) the figures show a second exothermic reaction, which will be called peak (IV) in this publication. Sometimes this peak coincides with the former. These two exothermic peaks correspond to what is generally known as the high temperature decomposition. In general, we will refer to them as the lower and higher temperature peaks.

Reaction kinetics

In order to calculate activation energies of solid propellants from thermoanalytical experiments, Waesche and Wenograd[1] applied a method based on the calculation of the fractions decomposed at each temperature, using the relationship: *area under the curve to any given temperature/total area*. This method assumes that

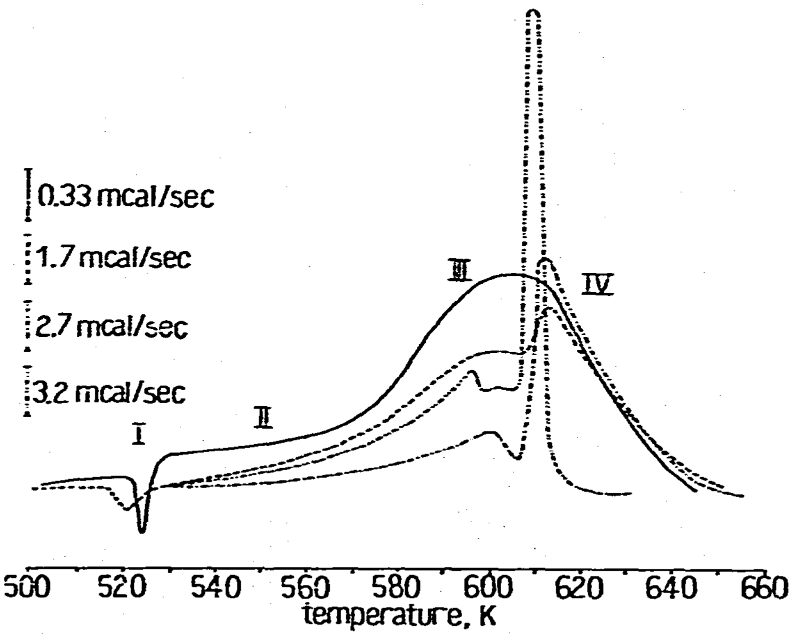


Fig. 1. Thermograms for different sample thicknesses; $B = 8$ K min^{-1}, (———) thickness = 110 μm, $m = 1.053$ mg; (— — —) thickness = 230 μm, $m = 2.190$ mg; (—·—·) thickness = 310 μm, $m = 3.398$ mg; (—··—) thickness = 330 μm, $m = 3.460$ mg.

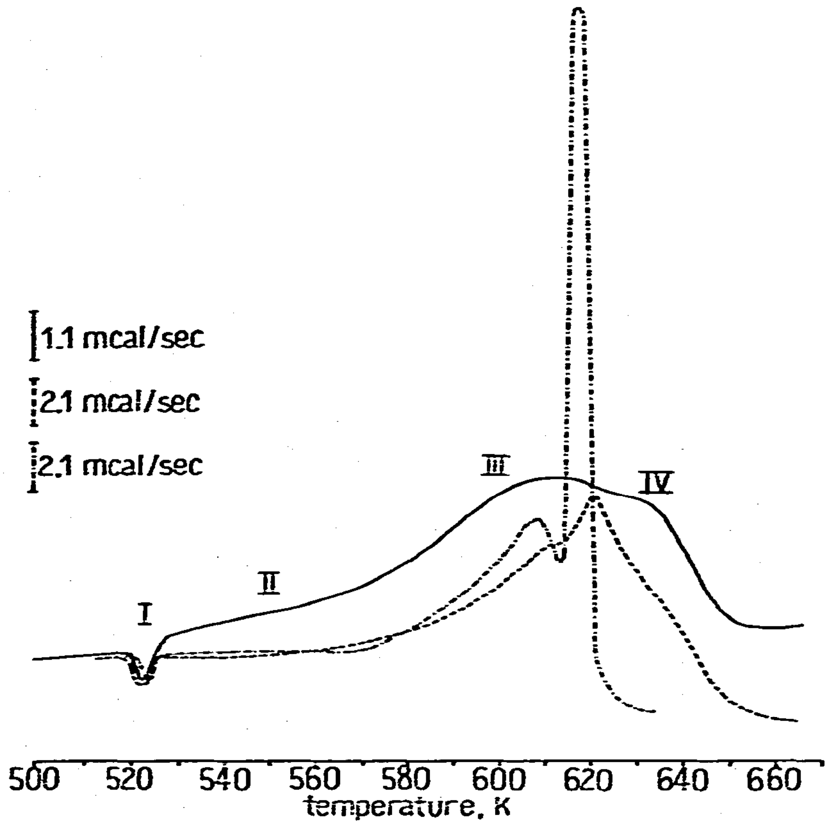


Fig. 2. Thermograms for different sample thicknesses, $B = 16$ K min^{-1}; (———) thickness = 110 µm, $m = 1.058$ mg; (— — —) thickness = 180 µm, $m = 1.804$ mg; (— · — ·) thickness = 200 µm, $m = 1.942$ mg.

the heat of reaction of both processes is the same. These authors[1] employed pre-decomposed samples at approximately 570 K to obtain more accurate determinations in the high temperature region. Comparison of activation energies obtained with pre-decomposed and with regular samples for a propellant with 90 µm particle size, showed that the decomposition kinetics is not affected by that process. However, the authors did not indicate if they found the same results with samples of a smaller particle size. In order to compare results with those of Waesche and Wenograd[1] we did a similar experiment using our propellant (particle size 16 µm) but pre-heating the sample at 8 K min^{-1} to 573 K. After cooling it, the final thermogram was run using the same heating rate (Fig. 5). Comparing plateaus (II), it is evident that the low temperature decomposition has disappeared. However, the endothermic peak areas (I) showed no significant differences in either case. Figure 5 also shows that in the high temperature region, there is only one exothermic peak which corresponds to peak (III) in a regular thermogram.

The fact that peak (IV) is not observed after the pre-heating treatment would indicate a change in the overall kinetic reaction. This leads us to decide that for

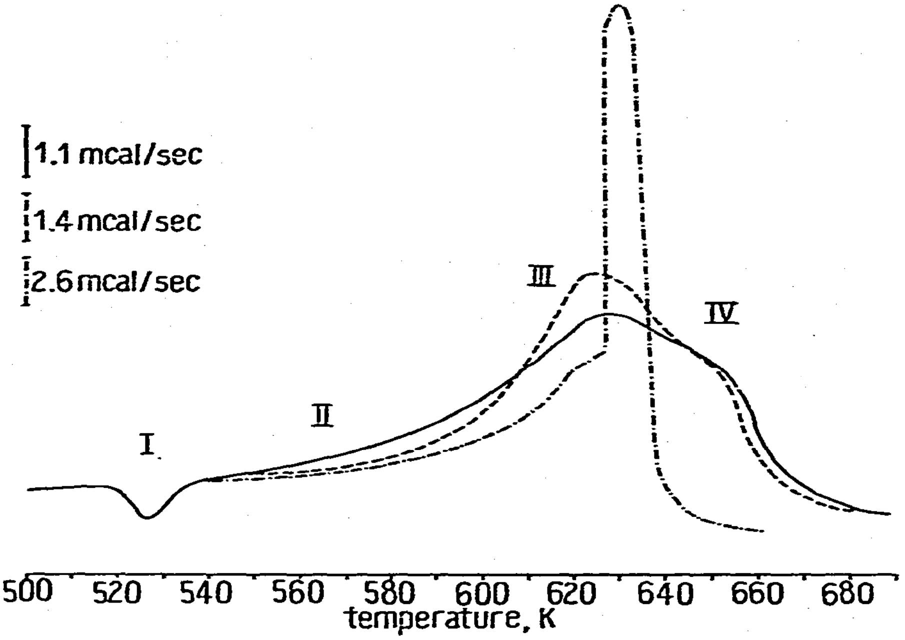


Fig. 3. Thermograms for different sample thicknesses, $B = 32$ K min^{-1}; (——) thickness = 60 μm, $m = 0.652$ mg; (– – –) thickness = 100 μm, $m = 0.978$ mg; (–·–·) thickness = 110 μm, $m = 1.088$ mg.

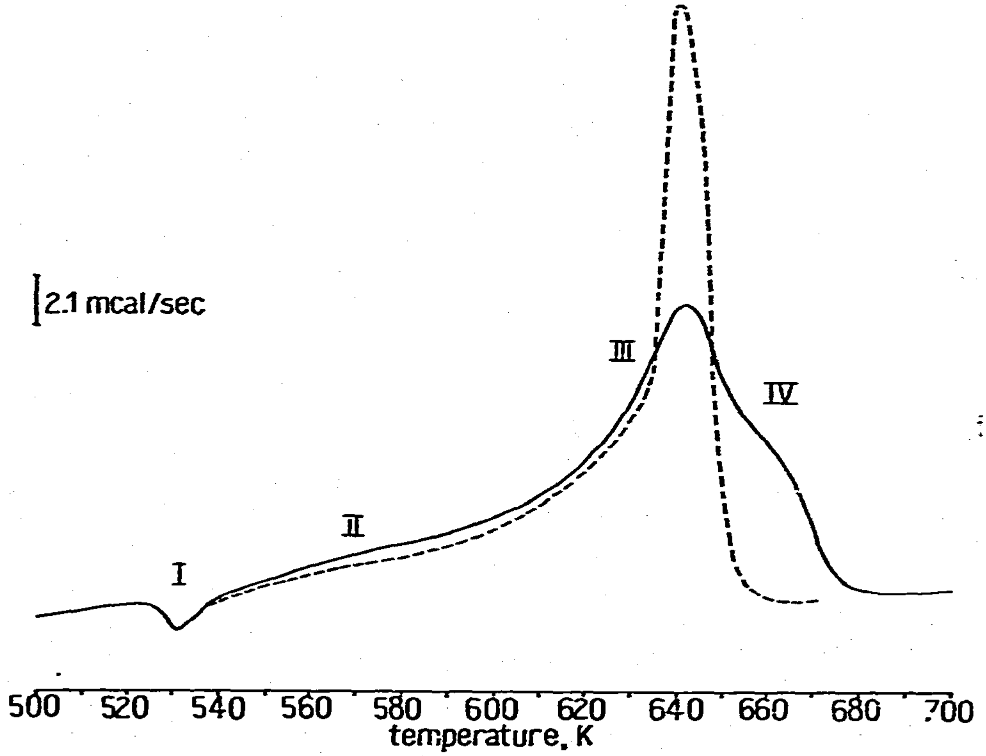


Fig. 4. Thermograms for different sample thicknesses, $B = 64$ K min^{-1}; (——) thickness = 60 μm, $m = 0.622$ mg; (– – –) thickness = 60 μm, $m = 0.640$ mg.

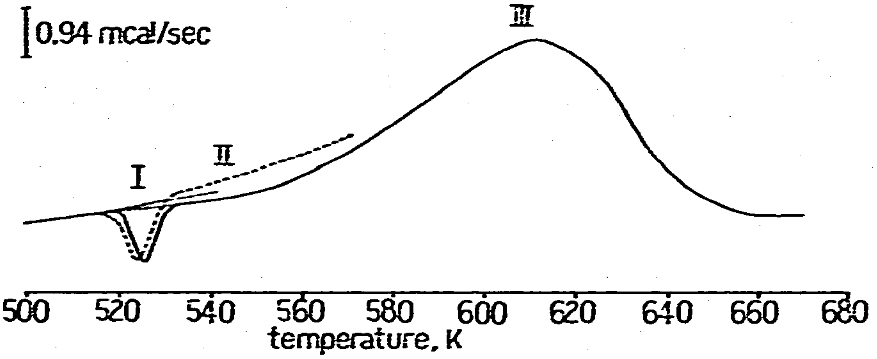


Fig. 5. Thermograms obtained during pre-heating to 573 K (— — —) and on the pre-heated sample (———). $B = 8$ K min^{-1}; thickness = 230 μm; $m = 2.112$ mg.

calculations of kinetic parameters, it would not be reasonable to apply the method used by Waesche and Wenograd[1].

To obtain a better understanding of the reactions which generate peaks (III) and (IV), we programmed the following experiment: first we ran a thermogram ($B = 8$ K min^{-1}) up to completion of peak (III) (approximately 620 K). Then the sample was cooled and a new thermogram was obtained under the same experimental conditions. Both thermograms are shown in Fig. 6. The second thermogram still shows the AP crystal phase change (I), thus it was considered of interest to calculate the decomposition percentage measuring the change of the endothermic peak area. Two different experiments, applying this methodology gave 52 and 62%. These values of the AP decomposition indicate that, since even at the beginning of peak (IV) the AP has not been completely used, one may think of the possibility of parallel reactions. According to the temperature, one of these reactions may predominate, depending on their activation energies. Unfortunately we were not able to find a thermoanalytical method which allowed us to determine the kinetic parameters of the second reaction (peak IV). This would give us the chance to get an idea of the importance of this reaction in the overall combustion process.

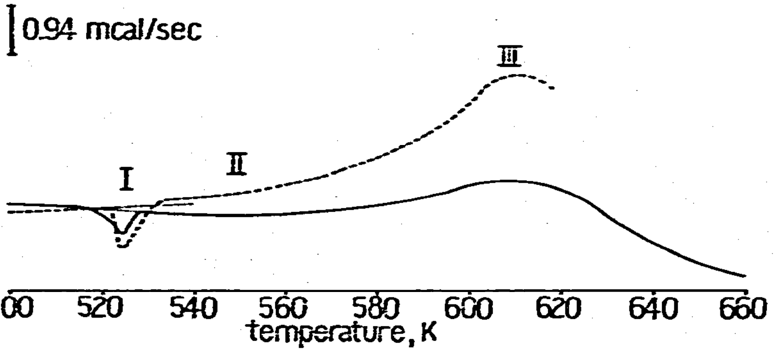


Fig. 6. Thermograms obtained during pre-heating to 620 K (— — —) and on the pre-heated sample (———). $B = 8$ K min^{-1}; thickness = 230 μm; $m = 2.176$ mg.

Several methods are known[2,7–9] for the calculation of kinetic parameters, apparent activation energy (E), pre-exponential factor (Z) and pseudo-order of reaction (n), employing these techniques. We attempt to compare them in quantitative calculations of peak (III). Figure 7 shows the thermogram used for this comparison ($B = 4$ K min^{-1}) and Table 1 shows the results obtained. This table shows first the value of E using method (a) for the whole thermogram, e.i., peaks (III) and (IV). The values for peak (III) alone are also shown for methods (a) and (c). In these cases, in order to eliminate the effect of peak (IV), a curve following the assumed shape which should give peak (III), in absence of peak IV, was traced on the thermogram (Fig. 7). Then we were able to calculate the relative areas in order to obtain the decomposed fraction.

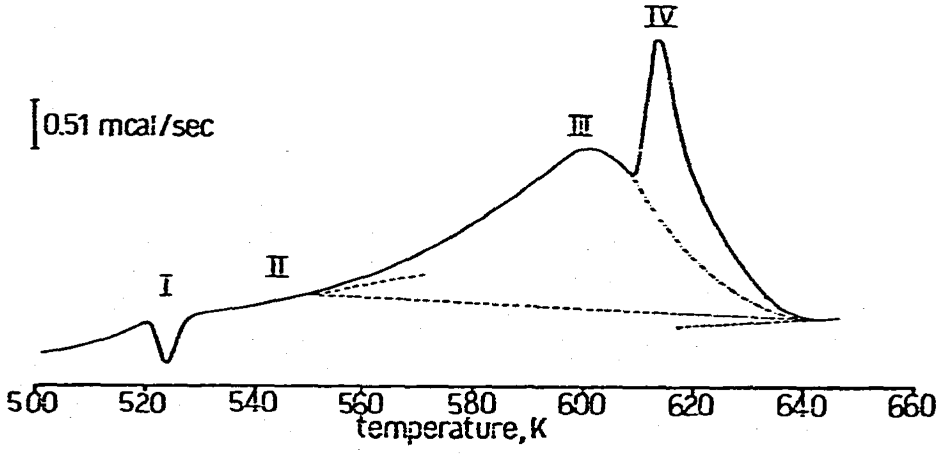


Fig. 7. Thermogram of the composite propellant at $B = 4$ K min^{-1}. Thickness = 230 μm; m = 2.378 mg.

TABLE 1

COMPARISON OF ACTIVATION ENERGIES OBTAINED USING DIFFERENT ANALYTICAL METHODS

r = Correlation coefficient.

Method	*E* (*kcal mol*$^{-1}$)	*n*	*r*	*Peaks considered*
(a) Waesche and Wenograd[2]	40.5	1[a]	−0.9995	III, IV
(a) Waesche and Wenograd[2]	45.2	1[a]	−0.9998	III
(b) Rogers and Morris[7]	34.4	—	−0.9977	—
(c) Rogers and Smith[8]	36.6	0.60	0.9985	III

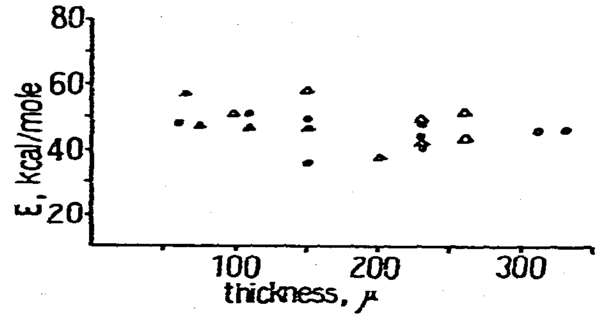
[a] Assumed.

It is quite reasonable to think that the differences found between method (a) and (b), (c) are due to the assumption that $n = 1$. It is interesting to note that including in method (a) (peak (III) alone) $n = 0.6$ from method (c), the E obtained is 39.4 kcal mol^{-1} ($r = -0.9995$).

Activation energy vs. heating rate

The results presented in this publication are average values of series of thermograms. These thermograms correspond to samples of different thickness, but we have found that apparently there is no specific relation between thickness and activation energy as is shown in Fig. 8, where only the results at 8 K min^{-1} were plotted.

For the highest heating rate applied, 64 K min^{-1}, it was impossible to use sample thicknesses over 60 μm, since in these cases the propellant ignited very often. When this phenomenon occurred a very sharp peak was observed at temperatures close to peak (III) (Fig. 4). For the calculations only those thermograms which did not show ignition were employed.



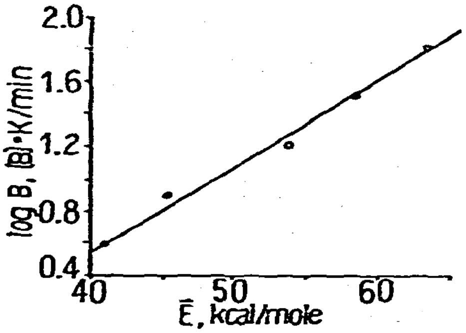


Fig. 8. Activation energy (E) vs. sample thickness for $B = 8$ K min^{-1}. ○ = Different mass and equal sample diameter; △ = equal mass and different sample diameter.

Fig. 9. Log heating rate (B) vs. average activation energy ($\bar{E}$).

In order to apply the simplified method of Rogers and Morris[7], all the thermograms were analysed taking only the first points of the curve at 4 K temperature intervals, where reaction is not important.

Table 2 summarizes the results at different heating rates and shows how the activation energy is affected. In Fig. 9 one can observe the relationship between both parameters plotting the log of the heating rate. In the range which is covered by this figure equation:

$$\log B = 0.054\bar{E} - 1.6 \tag{1}$$

gives the relationship between $\bar{E}$ and B. The thermograms are affected by a great dispersion of data (Fig. 8), but nevertheless the activation energy rise obtained with increasing heating rate, is a clear indication that the reaction path is modified. This effect may suggest that it is not very convenient to predict the behavior of solid propellant combustion in real motors from thermoanalytical data since the heating rates in actual combustion conditions are much higher[4] than those used in conventional thermoanalytical methods.

TABLE 2

AVERAGE ACTIVATION ENERGIES FOR DIFFERENT HEATING RATES

s = Standard deviation.

B (K min^{-1})	$\bar{E}$ (kcal mol^{-1})	s (kcal mol^{-1})
4	41.0	7.2
8	45.2	4.6
16	53.8	6.9
32	58.4	1.7
64	63.6	4.4

Waesche and Wenograd[1] did not find that the kinetic data obtained from thermograms were affected by the heating rates over the range they tested (isothermal to 20 K min^{-1}). This conclusion favors their assumption that an extrapolation is correct. As we have demonstrated, working in a wider scan rate, it may be adventurous to make such an approximation. In fact, the optimum approach would be the development of quantitative thermoanalytical methods employing compatible heating rates with actual solid propellants ignition processes as was attempted qualitatively by Bouck et al.[10]. Actually this in one of our main present objectives, and the results will be reported in the future.

Effect of the sample geometry on the activation energy

In order to determine if the sample geometry may have some sort of effect on activation energy determinations by DSC, we decided to run several series of thermograms using $B = 8$ and 32 K min^{-1}. During these experiments sample disc weights were kept constant but thickness and diameter were changed accordingly. The average activation energies obtained were: 48.2 kcal mol^{-1} ($s = 5.9$ kcal mol^{-1}) for $B = 8$ K min^{-1} and 58.4 kcal mol^{-1} ($s = 4.4$ kcal mol^{-1}) for $B = 32$ K min^{-1}. These results agree reasonably with those shown in Table 2, where the diameter was kept constant but not the weight. All the data obtained for $B = 8$ K min^{-1} are included in Fig. 8. As we have generally observed throughout our work, data dispersion is high. However, Fig. 8 does not indicate that one may think of a simple activation energy–geometry relationship.

Reaction order calculation

Table 2 shows the value of the reaction order obtained employing the method developed by Rogers and Smith[8] and for a heating rate of 4 K min^{-1}. In order to explore the possibility that n may also be affected by B, we determined the value of n in an experiment run at 64 K min^{-1} employing the same method. For this case the results were: $E = 59.0$ kcal mol^{-1}; $n = 0.63$; $r = 0.9979$. The value obtained agrees quite well with that in Table 2. We have not made a complete study of n, mainly because knowing that the activation energy is affected by B, results of n would not help much in the kinetics studies, at least under our present research conditions.

Sample thickness

A definitive trend observed throughout the present work was, that at all scan rates applied, when the sample thickness was increased, peak (IV) became sharper and finally ignition of the sample was obtained. In addition, the critical ignition thickness (D) became smaller at higher heating rates. Figures 1 to 4 show the shape which the thermograms develop at different sample thicknesses and scan rates. These modifications appear to be due to the principal exothermic reaction which generates heat, increasing the temperature of the center of the sample disc, since conduction is not high enough to permit a homogeneous distribution. Thus, one of the basic assumptions of thermoanalysis is not fulfilled. When these effects reach extreme conditions, ignition with a flame is observed and the thermogram curve falls down indicating total consumption of the reactive species.

Duswalt[11] has derived the critical conditions of heating, starting from the Frank-Kamenetskii equation[12]. This expression was modified for programmed heating rates, since the reactive species concentration changes with the sample temperature reached at each instant of the experiment. This change in reactive concentration is a function of the heating rate.

Duswalt[11,13] has proposed the following expression for the critical thickness:

$$D = 2\left(\frac{\delta\lambda RT^2}{EQC_0 Ze^{-X}}\right)^{1/2} \bigg/ \left[1 - \frac{ZE}{BR}(1-n)\rho(X)\right]^{\frac{1}{2(1-n)}}$$

where δ = critical constant depending on geometric configuration of the sample (0.88 for slab); λ = thermal conductivity; R = gas constant; T = absolute temperature;

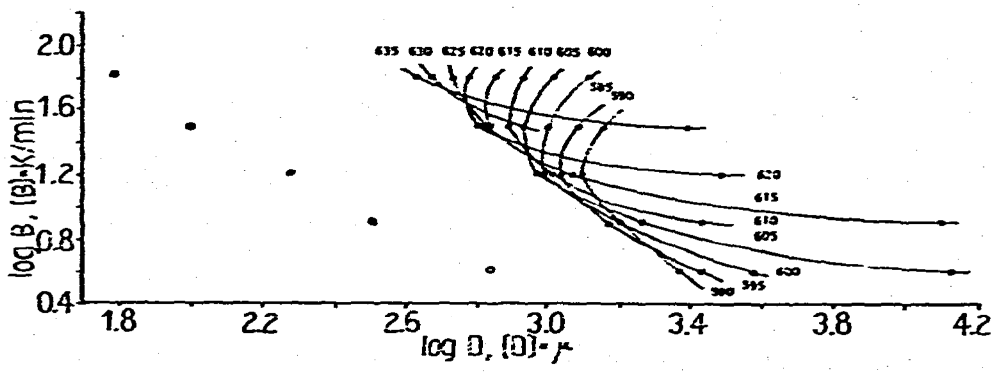


Fig. 10. Log heating rate (B) vs. log critical thickness (D) for different surface temperatures (in K); ●: calculated critical thicknesses, O = Experimental critical thicknesses.

Q = heat of reaction; C_0 = density (concentration) of reactant; $X = E/RT$ and $\rho(X)$ is a tabulated function[14] for $X = 10$ to 50. This equation has been derived for $n \neq 1$. We have applied this equation to our results plotting log B vs. log D. The representation is shown in Fig. 10. The values of the parameters included in the equation were calculated from our experimental thermograms at each heating rate. From Duswalt's studies the tangent of the isothermals obtained, should give the critical sample thickness. Below this curve the thermograms should not ignite. However, as Fig. 10 also shows, the critical sample thickness obtained experimentally—for example by running consecutive thermograms with increasing sample thickness and detecting flame development—is much smaller than that expected from Duswalt's plotting. The difference ranges from a factor of 3 ($B = 4$ K min^{-1}) to 7 for the higher scan rate tested ($B = 64$ K min^{-1}). To our knowledge Duswalt's equation has not been tested before experimentally by other investigators and at present we are not able to explain such a marked difference.

CONCLUSIONS

Though dispersion data in DSC experiments with solid propellants are high, we think that a definitive effect on activation energy by the heating rate has been demonstrated, at least in the range covered. Data dispersion may be due to the relatively heterogeneous composition of the sample, considering the small amounts used in DSC experiments. The above effect makes it reasonable to use thermoanalytical data with some restrictions when they are extrapolated to actual combustion calculations.

For the high temperature reaction (peak III and IV) it has been shown that even with a pre-heating treatment which covered even peak (III), AP was not completely decomposed, giving one more evidence of the complexity of the pre-ignition reactions of the solid propellants.

Apparently there is no simple relationship between activation energy and sample geometry; however, sample thickness plays an important role in DSC thermograms, since at each scan rate there is a critical thickness above which propellant ignition is observed. Critical thickness calculations from Duswalt's[11,13] studies, did not agree with the experimental data.

ACKNOWLEDGMENTS

Helpfull discussions and partial experimental cooperation of Dr. R. Podestá, Lic. R. Jiménez Rebagliati and Lic. M. Kaupert, members of our Institute, are gratefully acknowledged.

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