KINETIC STUDIES OF DOUBLE-BASE PROPELLANTS BY DIFFERENTIAL SCANNING CALORIMETRY: EFFECT OF BALLISTIC MODIFIERS

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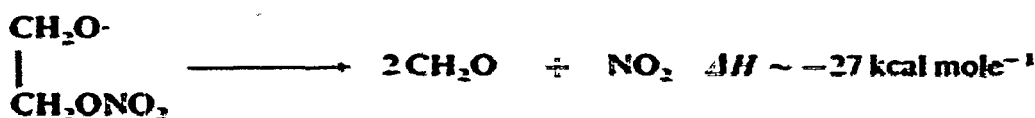(Received 7 January 1978)

ABSTRACT

The decomposition reactions of two typical double-base propellants, with and without ballistic modifiers, have been studied at different heating rates employing DSC. The heating rates and ballistic modifiers did not affect the activation energy calculated for the condensed phase reaction (53 ± 4 kcal mole^{-1}). The coincidence between activation energies of both propellants and a comparative study of a series of thermograms, suggest that ballistic modifiers act on gas phase or heterogeneous reactions occurring near the burning surface, probably in the fizz zone.

INTRODUCTION

Following the investigation on thermal decomposition of solid propellants, initiated with composite propellants[1], we present here a study of the kinetics and of the effects of ballistic modifiers on the decomposition reaction of double-base propellants. Kubota[2] has extensively reviewed the work done on the mechanism of these reactions. From his excellent analysis one can conclude that at present there is no clear understanding either of the weight that condensed phase reactions play, nor of the magnitude of the involved heat of reactions of these propellants. Generally it is recognized that the initial stage of the combustion reactions starts with the breakage of the O-NO$_2$ bond from nitrate esters, since it is the weakest of the chemical bonds present. The initial products of these reactions are NO$_2$ and aldehyde molecules and apparently, the decomposition process occurs in the condensed phase or at least at the burning surface. The following step would be the reaction between these aldehydes, other organic compounds and NO$_2$, giving NO; finally the last stage is the exothermic oxidation of the organic molecules by NO giving N$_2$, CO$_2$, CO, H$_2$O, etc.[2]

Kubota[2] took into account that for low pressures and lead-catalyzed propellants, solid carbon particles were observed at the burning surface, and suggested that the catalytic action of the lead salts took place on the condensed phase, giving active gaseous species and carbon. This solid carbon production reduces the effective fuel/oxidized (aldehyde/NO$_2$) ratio, shifting it to the stoichiometric ratio, and increasing the oxidation reaction rate in platonized propellants.

Kubota[2] and Wilfong et al.[3] considered the breakage of the O–N bond in nitric esters as an endothermic reaction; in other work, for ethylene glycol dinitrate, Adams and Wiseman[4] proposed a two stage decomposition as follows:

$$\begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \longrightarrow \begin{array}{c} CH_2O \cdot \\ | \\ CH_2ONO_2 \end{array} + NO_2 \quad \Delta H \sim 35 \text{ kcal mole}^{-1}$$

$$\begin{array}{c} CH_2O \cdot \\ | \\ CH_2ONO_2 \end{array} \longrightarrow 2 CH_2O + NO_2 \quad \Delta H \sim -27 \text{ kcal mole}^{-1}$$

As the mechanism of decomposition for this simple ester involves an endothermic and an exothermic reaction, it could happen that for the very complex reaction of nitrocellulose–nitroglycerin propellants, one may obtain a net production of heat.

Wilfong et al.[3] proposed a unimolecular reaction for the endothermic breakage of the O–N bond. Further, in the study of the nitrocellulose decomposition, since there is a great number of molecules available at the surface, and they are immediately replaced when they are decomposed to gaseous products, they consider an apparent zero order. In the already mentioned work by Adams and Wiseman[4], they suggested an exothermic reaction of zero order at the burning surface, giving gaseous products.

Kirby and Suh[5] have carried out a study on M-2 propellant, using differential calorimetry. One of their conclusions was that DSC is not suitable for the determination of the heat of reaction at the condensed phase, since the measurements are affected by heterogeneous and/or gas phase reactions which occur at or near the surface. We agree with Kirby and Suh's[5] conclusions about the restrictions of DSC, but taking into account our experimental results, we believe that the first region of the thermograms is indeed related to condensed phase reactions, and the middle and final zones are related to heterogeneous and/or gas phase reactions.

EXPERIMENTAL

We have attempted to study the effect of lead salts using films prepared in the laboratory by solvent evaporation (ethyl acetate/dimethylsulphoxide) from solutions with the propellant compositions. Neither the thermograms, nor the activation energies calculated with these samples showed differences produced by the lead salts, and the activation energies were much smaller than those calculated for the extruded propellants. The different behaviour produced by the solvent treatment was mentioned by Swotinsky et al.[6], who pointed out that the metallic salts used as ballistic modifiers produce "plateau" effects only with propellants obtained by solventless processes.

For this reason, we used two double-base extruded propellants. The composition of both propellants was: nitrocellulose, nitroglycerin, stabilisers and plasticisers (propellant A) and with the additional lead salts for propellant B. The composition was slightly modified between propellants A and B in order to obtain the same heat
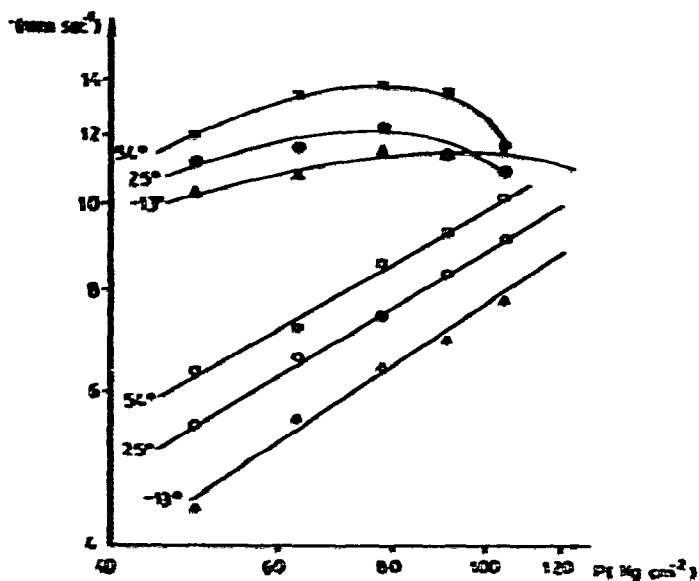
Fig. 1. Effect of ballistic modifiers on burning rate. Propellant A: ⚏. −13 °C; ◌. 25 °C; ◻. 54 °C. Propellant B: ▲. −13 °C; ●. 25 °C; ■. 54 °C.

of explosion (830 cal g^{-1}). In Fig. 1 one can see the "plateau" effect of the ballistic modifiers on the curve log r vs. log P (r, burning rate; P, pressure), plotted for both propellants.

The thermograms were run with filings and disc samples. The discs were prepared by slicing the propellants with a microtome and cutting them out with a cork borer (diameter 3 mm). The weight of the samples used varied between 0.8 and 2.5 mg, according to the heating rate employed. The samples were encapsuled 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. The nitrogen flux during the sample heating was approximately 20 ml min^{-1}, at atmospheric pressure. The heating rates were 4, 8, 16, 32 and 64 K min^{-1}. The measurement of the thermogram areas was carried out by the Gregory's numerical integration method[7] for propellant A, and using a planimeter for propellant B.

RESULTS AND DISCUSSION

Thermograms obtained with propellant A, using discs or filings, showed only one reaction peak for all heating rates (Fig. 2). The same was observed with propellant B in the case of filings. For discs, this propellant showed one peak for 4 and 8 K min^{-1} (low heating rates), but for 16, 32 and 64 K min^{-1} (high heating rates) another small peak is seen just before the maximum is reached (Fig. 2).

Table 1 shows detail of parameters such as temperature range and peak temperature for both propellants and all heating rates. It also shows that there is no significant difference between the peak temperatures for all cases at each heating rate.
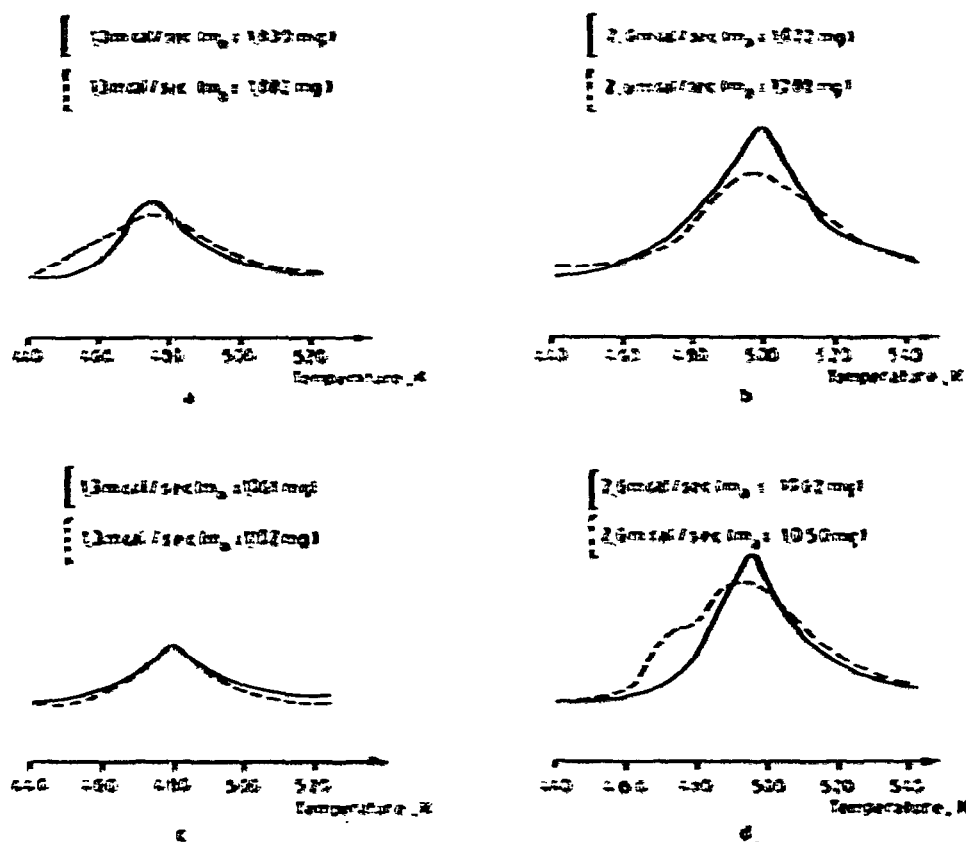
Fig. 2. Typical thermograms of propellants A (———) and B (- - - -). (a) filings. 8 K min⁻¹: (b) filings. 64 K min⁻¹: (c) discs. 8 K min⁻¹: (d) discs. 64 K min⁻¹.

In order to study the thermograms, the Uricheck's method[8] was applied to all experiments. This method implies an order of reaction $n = 1$ and calculates the decomposed fraction z to a fixed temperature using the relationship: area under the curve up to that temperature/total area. This method was used to analyze the different slopes obtained during the development of the reaction: since taking into account that the area under the curve does not represent only the heat generated in the condensed phase[5].

TABLE I

COMPARISON OF PEAK TEMPERATURE (T_p), INITIAL TEMPERATURE (T_i) AND FINAL TEMPERATURE (T_f) (DEGREE KELVIN) OF THERMOGRAMS AT DIFFERENT HEATING RATES

Heating rate K min⁻¹	Propellant A						Propellant B					
	Discs			Filings			Discs			Filings		
	T_p	T_i	T_f	T_p	T_i	T_f	T_p	T_i	T_f	T_p	T_i	T_f
4	472	438	507	467	430	512	470	431	507	469	420	517
8	479	446	511	475	440	523	476	437	520	475	426	523
16	482	432	535	483	450	535	480	430	534	485	437	534
32	490	445	535	492	459	536	489	434	541	489	439	535
64	498	451	547	501	462	551	496	443	549	495	449	549

TABLE 2

MAXIMUM DECOMPOSED FRACTION WHERE LINEARITY IS ACCOMPLISHED IN THE URICHECK'S PLOTS

Heating rate $K min^{-1}$	Propellant A		Propellant B	
	Discs	Filings	Discs	Filings
4	0.63	0.50	0.37	0.10
8	0.62	0.46	0.44	0.14
16	0.55	0.50	0.14	0.10
32	0.66	0.60	0.14	0.14
64	0.57	0.59	0.04	0.12

it is impossible to calculate the real decomposed fraction of the reaction working only with the area under the curve.

The Kishore's method[7] was also used. In this case the decomposed fraction is plotted versus a reduced time $t/t_x = 0.5$ (real time/time for $x = 0.5$). If for different heating rates all the points fall on the same curve, the order of reaction is the same. In addition, from the slope of the plot log $(r \, b \, A^{-1})$ vs. T^{-1} (r, chart speed; b, height of the curve; A, total area; T, absolute temperature) for a fixed x and different heating rates, one can calculate the activation energies at several extents of reaction.

Finally, a third method by Rogers and Morris[10], was applied on each thermogram in order to calculate activation energies. We used here only the first points of the curve, where the reagent consumption is not important, and at 4 K intervals. The calculations were done for $b \geqslant 5$ mm for the purpose of eliminating points affected with a large error. The results obtained showed that there is no significant difference in activation energy with the heating rate, contrary to what we found with composite propellants[1]; therefore we decided to take an average of the values for each sample.

Using Uricheck's method[8], practically all the experiments with filings showed a deviation from linearity at lower apparent decomposed fractions, than those with discs (Table 2). This difference is very significant for propellant B, which has ballistic modifiers. The fact that this deviation occurs at a lower decomposed fraction for filings, where it is expected that gaseous and/or heterogeneous reactions may have an earlier effect, suggests that these reactions are responsible for the deviation. Since for the case of filings of propellant B linearity is effective only in a narrow range, we think that ballistic modifiers act mainly on the mechanism of gas phase reactions or at least on reactions which develop just at the burning surface. In the case of discs of propellant B the low decomposed fraction obtained at heating rates of 16, 32 and 64 K min^{-1} agrees with the small peak present in these thermograms, which causes the deviation from linearity.

Applying the Kishore's method[9], the plots $1 - \alpha$ vs. $t/t_x = 0.5$ for all samples and heating rates are concurrent. The activation energies calculated for $x = 0.1, 0.2, 0.6$ and 0.8 are detailed in Table 3. Figure 3, which shows experimental results of discs of both propellants at $x = 0.1$ and 0.2, gives evidence of a discontinuity for the points obtained at low heating rates against those at high heating rates. At present we are not
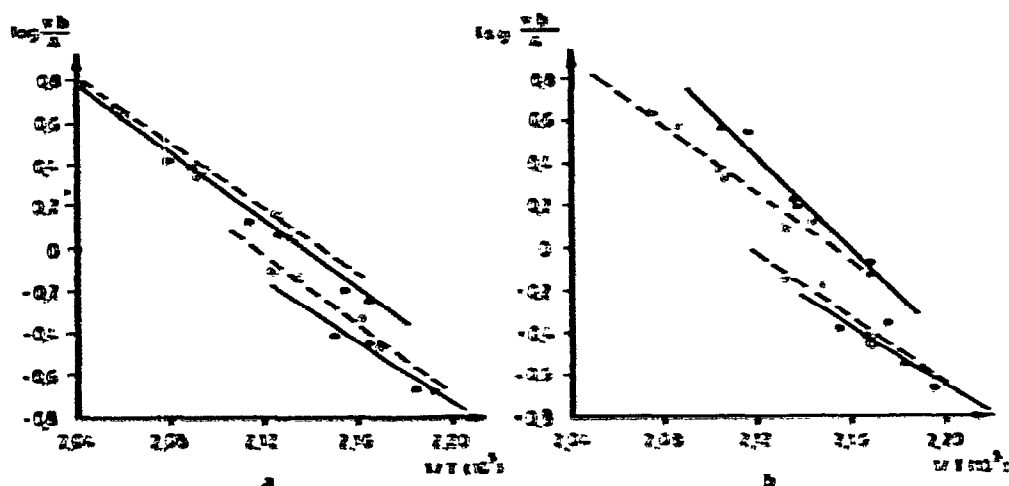
TABLE 3

ACTIVATION ENERGIES (KCAL MOLE^{-1}) CALCULATED BY THE KISHORE'S METHOD[1]

z	Propellant A			Propellant B		
	Discs		Filings	Discs		Filings
	(a)	(b)	(c)	(a)	(b)	(c)
0.10	33.6	37.2	37.3	32.6	50.8	47.5
0.20	36.7	35.1	37.4	34.9	37.2	52.5
0.60	46.1(c)		40.4	41.2(c)		49.9
0.80	42.4(c)		42.1	39.7(c)		56.8

(a) 4 and 8 K min^{-1}.
(b) 16, 32 and 64 K min^{-1}.
(c) All heating rates.

Fig. 3. Discontinuity in Kishore's plots for discs at $z = 0.1$ (●, ———) and 0.2 (○, - - -). (a) propellant A; (b) propellant B.

able to give an explanation of this change in the ordinate to the origin, but as it was confirmed in several runs of the experiments, we decided to calculate each of the activation energies (low and high heating rates) separately for both decomposed fractions.

In order to compare, at least qualitatively, the evolution of the reaction at different heating rates, we plotted the apparent not decomposed fraction $(1 - z)$ vs. temperature for all kinds of samples (Figs. 4 and 5). In the case of discs (Fig. 4), one can see that the shape of the curves is modified varying the heating rate. The curves at low heating rates (4 and 8 K min^{-1}) are steeper than at higher heating rates. As the slope of the curve represents the evolution of the rate of reaction, its change may suggest that at low heating rates an induction period exists. These plots and the thermograms for discs of both propellants coincide at 4 K min^{-1} and they begin to differ at increasing heating rates (Fig. 2).
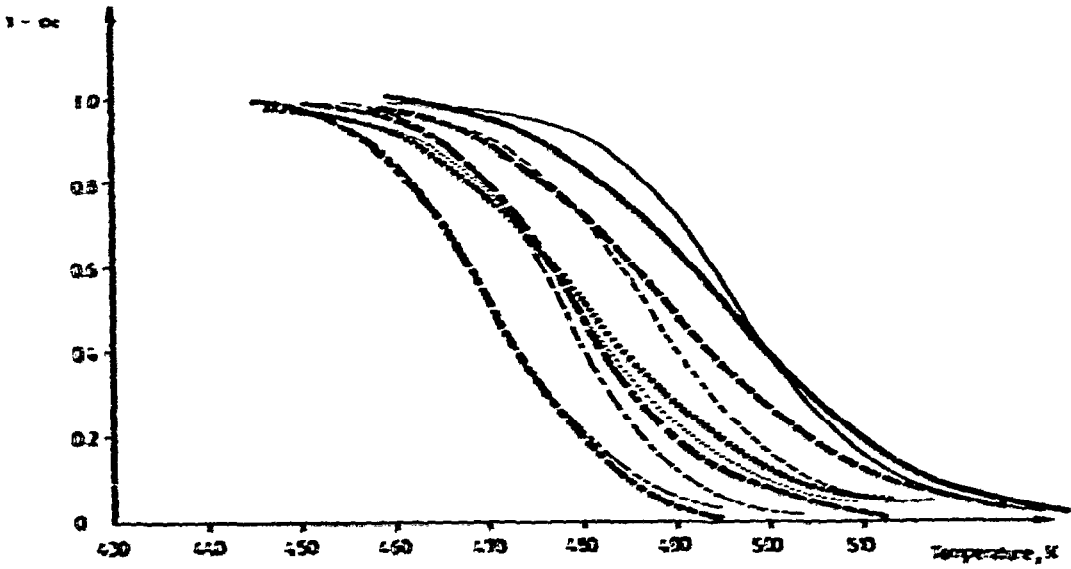
Fig. 4. Discs: change in decomposed fraction (expressed as $1 - z$) with temperature. Light trace: propellant A; heavy trace: propellant B. Heating rate (— - - —) 4 K min⁻¹; (— - — -) 8 K min⁻¹; (. . . . . .) 16 K min⁻¹; (- - - -) 32 K min⁻¹; (———) 64 K min⁻¹.
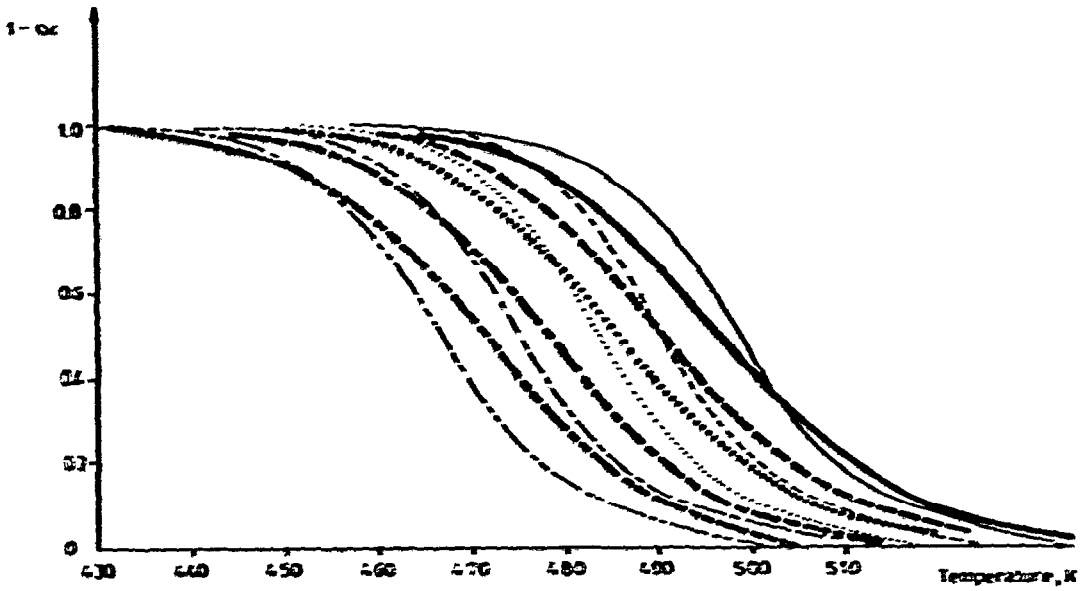

Fig. 5. Filings: change in decomposed fraction (expressed as $1 - z$) with temperature. Light trace: propellant A; heavy trace: propellant B. Heating rate: (— - - —) 4 K min⁻¹; (— - — -) 8 K min⁻¹; (. . . . . .) 16 K min⁻¹; (- - - -) 32 K min⁻¹; (———) 64 K min⁻¹.

As has been described before, thermograms of discs of propellant B at heating rates over 16 K min⁻¹ showed a small peak before the maximum. This peak is not obtained with propellants without ballistic modifiers. Thus, it seems quite reasonable to believe that this alteration in the thermogram is related to the catalytic activity of the modifiers.

Comparing the thermograms of filings, one can see that the peak shape of propellant B is wider and lower than that of propellant A. This fact affects the plot of Fig. 5, showing that the reaction rate of catalyzed propellant B varies slower than the rate of non-catalyzed propellant A.

Following the study of both figures, one finds that the shape of $1 - \alpha$ vs. T plots for high heating rates of discs of both propellants is similar to those of filings for each of them. This similarity in the evolution of the reaction seems to suggest that at high heating rates the influence of the gas phase reactions is dominant. One can explain this idea by supposing that at higher heating rates there is less time available for diffusion and the reactions will occur in a narrow region, very close to the surface, which will be detected to a large extent by the equipment.

Taking into account the observations just described and the coincidence between thermograms of disc samples at low heating rates (less influence of gas phase reactions) one can agree with the hypothesis of Powling and co-workers[11] that ballistic modifiers affect the reactions which take place in the gas phase. Figure 5 is an interesting example which shows a definite sequence in the reactions when filings of both propellants are studied. Superposition of curves at each heating rate intersect each other and this intersection takes place at higher decomposed fractions as the heating rate increases. In this case no curve can be superimposed on another, as happened with some disc experiments. This seems to show that when working with filings, gas phase reactions always have an effect, regardless of the heating rate employed.

TABLE 4

ACTIVATION ENERGIES (KCAL MOLE^{-1}) CALCULATED BY THE ROGERS AND MORRIS' METHOD[10]

Heating rate ($K\,min^{-1}$)	Propellant A		Propellant B	
	Discs	Filings	Discs	Filings
4	58.5	53.1	44.2	49.7
	62.4	56.3	42.2	50.1
8	53.7	58.1	60.0	45.5
	57.6	54.1	52.5	45.6
16	45.6	59.2	55.2	50.6
	43.8	61.5	56.1	49.5
32	50.5	67.9	55.9	55.2
	58.8	52.5	53.0	55.0
64	45.7	52.2	56.9	49.7
	53.1	66.3	55.9	59.4
$\bar{E}$	53.6 ± 4.1	58.1 ± 4.0	53.2 ± 4.0	51.6 ± 3.2
s	5.77	5.64	5.67	4.42
s^2	33.29	31.81	32.16	19.54

$\bar{E}$ = average activation energy.
s = standard deviation.
s^2 = variance.

The average activation energies calculated by the Rogers and Morris[10] method, which are detailed in Table 4, were compared using the Student test. Taking a significance level of 0.05, we accept that average activation energies from discs of both propellants agree. For discs and filings of propellant B, we must reject the hypothesis for a significance level 0.05, but we may risk the acceptance of results for values larger than 0.01 and smaller than 0.05. For filings of both propellants, the hypothesis does not agree with the experimental data with a significance level 0.01.

As one can infer from Table 4, filings of propellant A show a general tendency to have larger calculated activation energies. This difference may be explained considering that gas phase reactions begin to affect the development of the thermograms at an earlier stage ($x \approx 0.1$-0.2) as happens with the experiments of propellant B. For propellant A, which has no lead salts, and accepting that ballistic modifiers do not affect condensed phase reactions, one can admit that gas concentration on the reactive surface could be high enough to initiate gas phase reactions at decomposed fractions of the same order. However, these gaseous reactions, as they are not affected by the catalyst, would have a light effect on the linearity of Uricheck's plot[8]. In the calculation employing the Rogers and Morris method[10] it is quite possible that some points, which really are affected by the gaseous reactions, are included giving an activation energy which really cannot be assigned only to condensed phase reactions.

The agreement of the average activation energies for discs of both propellants, calculated by the Rogers and Morris method[10], which consider only the first region of the thermograms, denotes that the first region can be assigned to the condensed phase reactions and that they are not affected by the ballistic modifiers.

The modification of the $1 - x$ vs. T curves at low and high heating rates, already discussed above, produces the discontinuity in the Arrhenius' plots used to calculate the activation energy by the Kishore's method[9]. For this reason, we consider that in this particular situation, where for a fixed fraction of decomposed material different reactions can take place according to the heating rate employed, the method is not fully reliable.

To the contrary of what happens with discs, the results of activation energies obtained with filings for both propellants show the largest difference in the data described (Table 3). It is interesting to note that in these cases one should expect to obtain much more influence of reactions in the gas phase, and consequently of catalytic effects.

Finally, reviewing all the experimental data just described in this paper, and keeping in mind the limitations which one should expect for DSC in combustion studies, we are tempted to believe that our work seems to show that ballistic modifiers affect fundamentally gas phase reactions occurring very close to the burning surface, quite probably in the fizz zone, and that they do not have an important effect on condensed phase reactions, since the calculated activation energies agree quite well for both propellants in the case of disc samples and at the beginning of the thermograms.

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