Thermochimica Acta, 18 (1977) 113–123

EFFECT OF DIFFERENT CARBONS ON IGNITION TEMPERATURE AND ACTIVATION ENERGY OF BLACK POWDER*

ABRAHAM D. KIRSHENBAUM

Ballistic & Combustion Research Branch, Propellants Division, Feltman Research Laboratories, Picatinny Arsenal, Dover, N. J. 07801 (U. S. A.)

ABSTRACT

By means of TG, DTG, and DTA, it was shown that the source of carbon can affect the decomposition and reaction characteristics of black powder compositions. Carbons with high volatile content lower the activation energy and reduce the ignition temperature of black powder. The removal of these volatiles causes an increase in ignition temperature and activation energy. It also showed that although sulfur has no effect on the ignition temperature, it does affect the preignition reaction. Sulfurless black powder also has larger activation energies than regular black powder. Compositions of black powder containing channel black have lower activation energies than those with charcoal.

INTRODUCTION

Black powder has been known for a long time to be an excellent igniter, but no information is available as to why it performs so well. The specifications for black powder are very broad so that different sources of black powder using different charcoals may be used, without knowledge of their effect. A literature search showed that very little is known of the preignition reaction, the ignition process and the fundamentals of black powder combustion. Even the work reported by different investigators conflict[1,2]. Laboratory experiments showed that black powder manufactured with different carbons had different ignition and combustion properties. Thermogravimetric analysis of the different carbons used, show that they vary in volatile content from 3 to 30%. (Volatile content is defined as the loss in weight when the carbon is heated to 950°C in an inert atmosphere.) The volatiles are normally present as water and oxyhydrocarbon functional groups attached to the carbon lattice and upon heating come off mainly as H_2O, CO, CO_2 and CH_4. Thus, it was deemed advisable to obtain a better definition of the role of the various ingredients and impurities in black powder in order to understand why black powder performs the way it does. This paper deals with the effect sulfur, carbon and the volatile functional groups have on the ignition temperature and activation energy of black powder.

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*Presented at the 6th North American Thermal Analysis Society Conference, Princeton, N. J., June 20–23, 1976.

APPARATUS AND PROCEDURE

The Mettler Thermoanalyzer was used in these studies. Simultaneous DTA and TG analyses were obtained by heating 10 mg samples of sulfurless ($C+KNO_3$) and regular ($C+S+KNO_3$) black powders in a helium atmosphere at a rate of 10°C min^{-1} in Al_2O_3 crucibles. Heating rates of 4 and 6°C min^{-1} were also used in the activation energy studies. The percent volatiles in the different carbons were determined by thermogravimetric analyses. Samples of carbon (100 mg) were heated in Al_2O_3 crucibles in a helium atmosphere to 950°C at a rate of 15°C min^{-1}.

Three types of carbon were used in these studies, namely charcoal, channel black and furnace black. The commercial method of preparation and the carbon content of these carbons are shown in Table 1.

TABLE 1

TYPES OF CARBON

	Preparation	*% Carbon*
Charcoal	Destructive distillation of vegetable substance	50–90%
Channel black	Natural gas flame impinged on cool iron surface	85–95%
Furnace black	Burn natural gas or oil in furnace with 50% of air required for complete combustion	99%

The carbon content of charcoal can vary from 50–90%. Water, volatile content, and ash are the impurities. Different wood charcoals having similar chemical composition are difficult to obtain since the charcoals are obtained from different types of wood or mixtures thereof, and is generally obtained as a by-product. Channel and furnace blacks can be obtained with more reproducible properties.

The carbons used in the $C+KNO_3$ mixtures consisted of (a) the original carbons, (b) carbons heated in vacuo for 100 h at 490°C, and (c) carbons heated in helium to 950°C in the thermogravimetric analyses. Only the original carbon was used in the $C+S+KNO_3$ mixtures. The binary and tertiary mixtures of the various ingredients were made by thoroughly blending the ingredients in a mortar and pestle, and used in powder form.

RESULTS AND DISCUSSION

A. Ignition temperature

1. The carbon–potassium nitrate binary mixture (sulfurless black powder). Thermal analysis of the binary mixture at a heating rate of 10°C min^{-1} produced DTA curves (Fig. 1), consisting of 2 endotherms, (rhombic to trigonal phase change of KNO_3 at 132±2°C and the melting of KNO_3 at 335±3°C), and a large exotherm starting at 380–395°C with ignition between 415 and 500°C depending upon the carbon used. Thermogravimetric analysis of the carbons used showed them to vary in volatile content from 3–30 wt.%. A comparison of the ignition temperatures and volatile contents of the carbons are presented in Table 2, and show that the greater the percent volatiles in the carbon, the lower the ignition temperature.

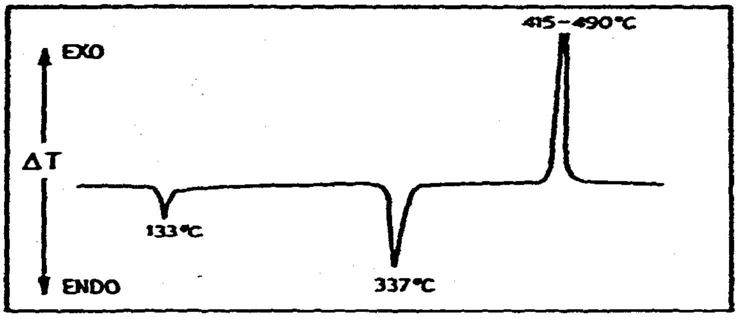

Fig. 1. DTA curve of $C+KNO_3$.

TABLE 2

EFFECT OF % VOLATILES ON DTA IGNITION TEMPERATURE FOR THE $C+KNO_3$ REACTION

Carbon used	*% Volatiles in carbon*	*DTA ignition temp. (°C)*
Cannel coal	33.7	410
Charcoal		
No. 1	28.9	413
No. 2	26.1	408
No. 3	20.4	421
No. 4	20.2	418
No. 5	19.3	413
No. 6	12.2	432
No. 7	9.1	451
No. 8	6.4	455
Channel black		
No. 1	23.1	422
No. 2	13.7	424
No. 3	10.7	436
No. 4	4.6	455
Furnace black		
No. 1	4.8	450
No. 2	3.9	492

Partial or total removal of the volatiles from the carbons, by thermal means in vacuum or inert atmosphere, increased the ignition temperature of the binary mixture as the volatile content decreased as shown in Table 3. A plot of ignition temperature vs. % volatiles (Fig. 2) showed that there is a linear relationship between 2–15% volatiles—the greater the volatile content, the lower the ignition temperature. Using carbons with volatile contents greater than 15% did no further decrease the ignition temperature.

TABLE 3

EFFECT OF REMOVING VOLATILES ON DTA IGNITION TEMPERATURE FOR THE C+KNO_3 REACTION

Carbon sample	*% Volatiles in carbon*	*DTA ignition temp. (°C)*
Charcoal 1	28.9	415
	9.40[a]	436
	0[b]	443
Channel black 1	23.1	422
	9.43[a]	438
	0[b]	445
Channel black 2	13.7	424
	7.45[a]	445
	0[b]	460
Channel black 3	10.65	436
	8.10[a]	444
	0[b]	460

[a] Heated 100 h at 490°C in vacuo. [b] Heated to 950°C at 15°C min^{-1} in helium flowing atmosphere in DTA apparatus and cooled in helium atmosphere.

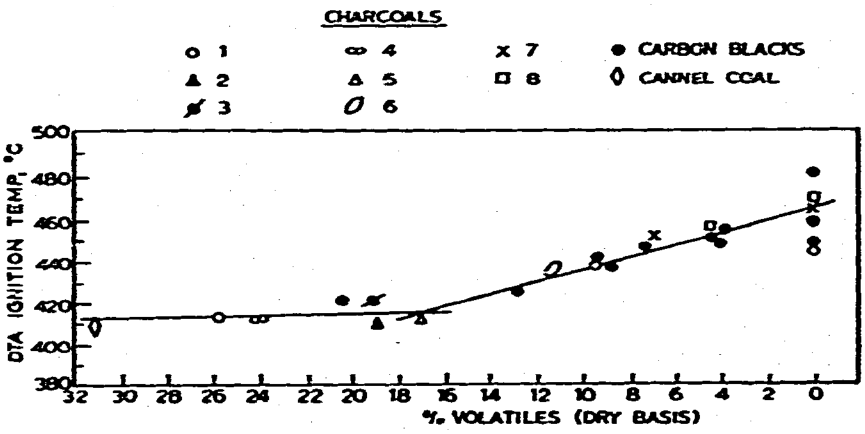

Fig. 2. Effect of % volatiles on binary mixture ignition temperature.

The ignition temperature of mixtures containing carbons freed of volatile matter varied between 443 and 482°C. A comparison of these data with those obtained for the mixtures containing the original carbons is presented in Table 4 and shows that although their ignition temperatures are lower, the order for those containing the thermally treated carbons is the same as that of the original carbon–KNO_3 samples. These results indicate that other parameters besides volatile content affect the ignition of black powder.

TABLE 4

COMPARISON OF DTA IGNITION TEMPERATURE OF BINARY MIXTURES USING THE ORIGINAL CARBONS AND CARBONS HEATED TO 950°C (VOLATILE FREE)

Carbon used	*DTA ignition temp. (°C)*	
	Original carbon	*Volatile free carbon*
Charcoal 1	415	443
Channel black 1	422	445
Channel black 2	424	460
Channel black 3	436	460
Charcoal 7	451	462
Charcoal 8	455	467
Furnace black 1	450	475
Channel black 4	455	480
Furnace black 2	490	482

The surface area of the different carbons used in these studies and the DTA ignition temperatures obtained for the binary mixtures containing the carbons which were thermally freed of volatile matter are tabulated in Table 5. A study of the data shows that for the furnace blacks, the greater the surface area of the carbon, the lower the DTA ignition temperature of the black powder. However, for channel blacks and charcoals which have larger surface areas, no correlation exists. Even with surface areas of 1000 $m^2\ g^{-1}$, ignition temperatures of less than 460°C were not attainable.

TABLE 5

EFFECT OF SURFACE AREA OF VOLATILE FREE CARBONS ON IGNITION TEMPERATURE OF BLACK POWDER MIXTURES

Carbon	*Surface area of carbon ($m^2\ g^{-1}$)*	*DTA ignition temp. (°C)*
Furnace black	29	498
	72	484
	120	480
	130	475
	143	475
Channel black	150	480
	460	460
	695	460
Charcoal	950	462
	1000	467

The possibility of the ash content of the carbons affecting the ignition temperature of the mixtures by acting as a catalyst or deterrent was investigated. Analysis of the carbons showed that channel blacks (prepared from natural gas) have almost no ash content (0.02%), furnace blacks (prepared from oils) contained 0.75% ash, whereas charcoals have ash contents between 1–15%. A comparison between the ash content of the carbon and ignition temperature of the binary mixture is presented in Table 6. The data show that no correlation exists between percent ash and ignition temperature.

TABLE 6

CARBON ASH CONTENT VS. BINARY IGNITION TEMPERATURE

Charcoal	*% Ash*	*Ignition temp. (°C)*
No. 1	1.1	413
No. 5	1.5	413
No. 8	2.7	455
No. 2	4.3	408
No. 9	4.8	435
No. 4	6.1	418
No. 7	6.8	451
No. 3	11.2	421
No. 6	14.6	432
Channel black	0.02	422–455
Furnace blacks	0.75	450–490

2. *The $C+S+KNO_3$ tertiary mixture (black powder).* The effect of sulfur on the ignition temperature of the $C+KNO_3$ mixture was determined by thermal analyzing tertiary mixtures containing some of the different carbons. The ignition temperatures obtained are compared to those obtained for the binary mixtures in Table 7 and show that sulfur has little or no effect on the ignition temperature. If

TABLE 7

EFFECT OF SULFUR ON THE IGNITION TEMPERATURE OF $C+KNO_3$

Carbon	*DTA ignition temp. (°C)*	
	$C+KNO_3$	$C+S+KNO_3$
Charcoal 1	415	420
Channel black 1	422	435
Channel black 2	424	435
Channel black 3	436	438
Furnace black 1	450	450
Channel black 4	455	460
Furnace black 2	490	475

anything, the presence of sulfur increased the temperature required for ignition. However, sulfur did play a great role in the pre-ignition reaction as evidenced by an exotherm about 100°C before ignition as can be seen in Fig. 3. The exotherm can occur before, during, or after the melting of KNO_3 depending upon the carbon used.

From their study on the initiation, burning and thermal decomposition of black powder, Blackwood and Bowden[1] concluded that the exothermic preignition reaction is between sulfur and oxyhydrocarbons functional groups (the volatiles) in the

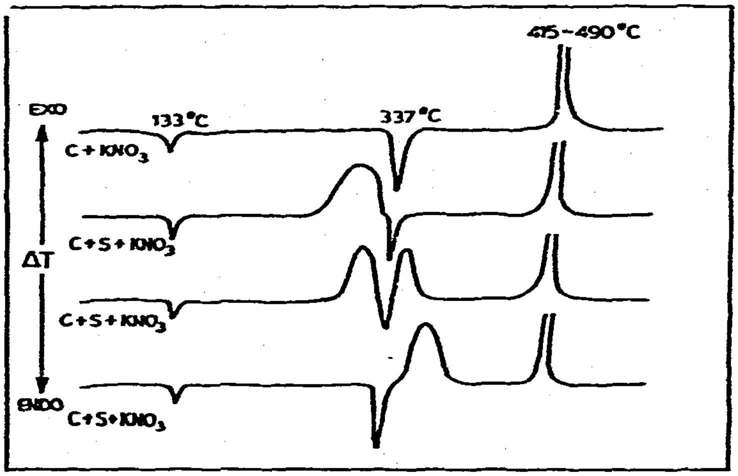

Fig. 3. Effect of S on C+KNO_3 reaction.

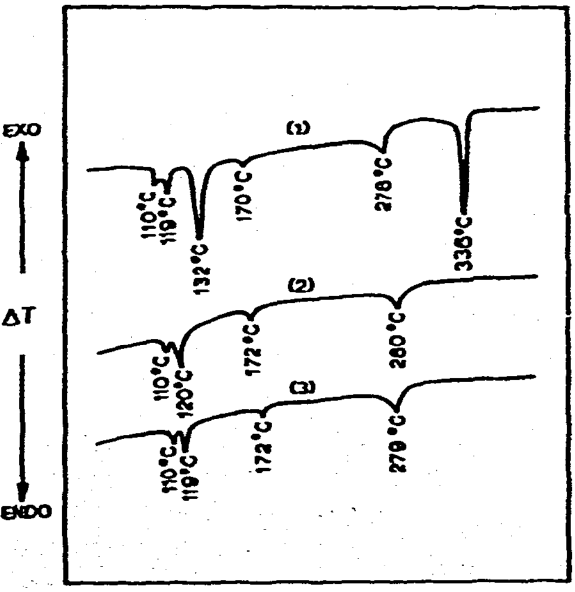

Fig. 4. DTA curves of (1) KNO_3+S; (2) C+S; (3) S.

charcoal. Their work was questioned by Campbell and Weingarten[2]. These investigators reported that the pre-ignition reaction was between sulfur and potassium nitrate. In order to shed some light on this discrepancy, the reactions between $S+KNO_3$ and $C+S$ were studied by thermal analysis. From the DTA curves obtained, as shown in Fig. 4, it can be seen that neither $S+KNO_3$, nor $C+S$, produce exotherms on heating. This indicates that the pre-ignition reaction is more than what either pair of investigators claim since the presence of all 3 components ($S+C+KNO_3$) have to be present in order to get the pre-ignition exothermic reaction.

B. Activation energy

Activation energies can be obtained from both the thermogravimetric and differential thermal analysis data. If there is a loss in weight during the reaction, the thermogravimetric method is considered more accurate. With this method, one uses the derivative curve of the weight loss which is obtainable directly with the Mettler thermoanalyzer, Fig. 5A, for which the following form of the Arrhenius equation can be used:

$$\Delta \ln(-\mathrm{d}w/\mathrm{d}t) = -(E/R)\Delta(1/T) + nC$$

where C is a constant, T is absolute temperate and $\mathrm{d}w/\mathrm{d}t$ is the rate of weight loss with time. If the equation holds, a plot of $\Delta \ln(-\mathrm{d}w/\mathrm{d}t)$ vs. $\Delta(1/T)$ will produce a straight line, the slope of which equals E/R (E = activation energy, R = gas constant).

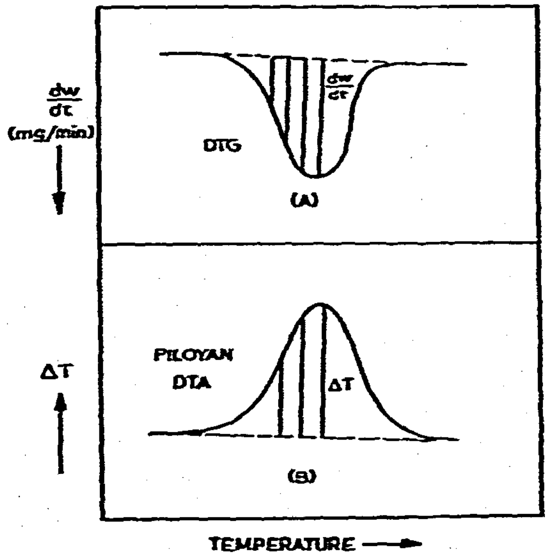

Fig. 5. (A) DTG and (B) DTA curves obtained with Mettler thermoanalyzer.

There are several methods used to determine the activation energy from the DTA data[3–6]. Kirshenbaum and Beardell[7] have found that Piloyan's method[5] worked very well for $Zr+M_0O_3$ delays while Rogers and Morris[8] have used this technique with RDX, HMX, Tetryl and PETN with good success. In this method, the Arrhenius equation can be written as

$$\ln \Delta T = C - \ln f(\alpha) - E/RT$$

where C is a constant, ΔT is the difference in heat between reference cell and reaction cell at given T(K) and f(α) is a function of the extent of reaction. Under normal isothermal conditions, the only variable determining the reaction rate is α. In DTA, however, the temperature also varies. According to Piloyan et al.[5], under normal heating rates, the change in temperature has a greater effect on ΔT than the change in α. Thus f(α) can be neglected and the equation becomes:

$$\ln (\Delta T) = C - E/RT)$$

Plotting ln ΔT vs. $1/T$(K) produces straight lines the slope of which equals E/R.

In these studies, the thermogravimetric method and the DTA Piloyan techniques were used, and the reproducibility of the data are demonstrated in Table 8. The

TABLE 8

REPRODUCIBILITY OF ACTIVATION ENERGIES BY DTG AND DTA METHODS (kcal mol^{-1})

Carbon in mixture		*Tertiary mixture*		*Binary mixture*	
		DTG	*DTA*	*DTG*	*DTA*
Channel black 1		28.0	29.9	54.9	61.9
		27.9	26.9	61.0	64.3
		28.5	28.7	55.4	63.2
		27.5	29.5	57.3	—
	Average	28.0	28.7	57.1	63.1
Channel black 2		63.8	70.0	55.8	
		58.6	61.1	64.0	
		64.6	60.6	72.1	
	Average	62.3	63.8	64.0	
Channel black 3		39.7	34.8	74.8	
		37.1	36.8	73.5	
		36.5	33.2	73.7	
		39.7	—	—	
	Average	38.3	34.9	74.0	
Furnace black 1				52.8	57.1
				52.3	58.3
				53.0	57.6
	Average			52.7	57.7

TABLE 9

COMPARISON OF VOLATILE CONTENT OF CARBON WITH ACTIVATION OF ENERGY OF BINARY AND TERTIARY MIXTURES

Type of carbon	*% Volatiles*	*Activation energy (kcal mol^{-1})*			
		Binary		*Tertiary*	
		DTG	*DTA*	*DTG*	*DTA*
Cannel coal	33.7	—	—	42.5	41.5
Charcoal 1	28.9	51.6	—	68.4	73.4
Charcoal 2	26.1	51.2	—	57.4	68.4
Channel black 1	23.1	57.1	63.1	28.0	28.7
Charcoal 3	20.4	58.9	—	60.0	77.7
Charcoal 4	20.2	75.9	—	94.2	88.9
Channel black 2	13.7	64.0	—	62.3	63.8
Charcoal 5	12.2	43.8	50.6	70.4	82.8
Channel black 3	10.6	74.0	—	38.3	34.9
Charcoal 6	9.1	74.0	—	81.5	95.1
Charcoal 7	6.4	72.2	—	—	—
Furnace black 1	4.8	52.7	57.7	49.0	42.5
Channel black 4	4.6	99.9	—	—	48.1
Furnace black 2	3.8	104.3	—	97.0	110
Graphite	2	—	—	64.3	58.5

TABLE 10

COMPARISON OF VOLATILE CONTENT OF CARBON WITH ACTIVATION ENERGY OF BINARY AND TERTIARY MIXTURES

Type of carbon	*% Volatiles*	*Activation energy (kcal mol^{-1})*			
		Binary		*Tertiary*	
		DTG	*DTA*	*DTG*	*DTA*
Charcoal					
1	28.9	51.6	—	68.4	73.4
2	26.1	51.2	—	57.4	68.4
3	20.4	58.9	—	60.0	77.7
4	20.2	75.9	—	94.2	88.9
5	12.2	43.8	50.6	70.4	82.8
6	9.1	74.0	—	81.5	95.1
7	6.4	72.2	—	—	—
Channel black					
1	23.1	57.1	63.1	28.0	28.7
2	13.7	64.0		62.3	63.8
3	10.6	74.0	—	38.3	34.9
4	4.6	99.9	—	55.5	48.1
Furnace black					
1	4.8	52.7	57.7	49.0	42.5
2	3.8	104	—	97	110

thermal analysis activation energy data obtained for the various different carbon containing binary and tertiary mixtures are compared with the volatile content of the carbons in Table 9. No correlation exists when all the different types of carbon are put together in one table. The data are divided into charcoals, channel blacks and furnace blacks in Table 10. A study of these data shows that for channel and furnace blacks the binary mixtures have larger activation energies than the tertiary ones, i.e., presence of sulfur lowers the activation energy. It also shows that on the whole, the higher the volatile content of the carbon, the lower the activation energy, except for the tertiary mixture containing channel black 3. No correlation could be observed for the charcoal containing mixtures. It was also observed that for tertiary mixtures, the activation energies of mixtures containing charcoals were greater than for those using channel or furnace black. When some of the volatile content is removed from the channel and furnace black, the activation energies of the binary mixtures increased as shown in Table 11. No such phenomena was observed with the charcoal mixtures.

TABLE 11

EFFECT OF REMOVING VOLATILES FROM CARBON ON THE ACTIVATION OF BINARY MIXTURES

Type carbon	*Condition*	*% volatiles in carbon*	*DTG activation energy (kcal mol⁻¹)*
Charcoal 1	Original	28.9	51.6
	500°C	9.5	49.3
	950°C	0	56.8
6	Original	9.1	74.6
	950°C	0	50.8
Channel black 1	Original	23.1	57.1
	500°C	9.4	64.1
2	Original	13.7	64.0
	500°C	7.5	69.8
3	Original	10.6	74.0
	950°C	0	104.3
Furnace black 1	Original	4.8	52.7
	950°C	0	75.5

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