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A THERMO-ANALYTICAL STUDY OF THE PYROTECHNIC REACTIONS OF BLACK POWDER AND ITS CONSTITUENTS

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ABSTRACT

Simultaneous TG-DTA studies of black powder compositions, as well as of binary mixtures of the constituents, in nitrogen, showed no reaction between sulphur and charcoal. The charcoal/KNO_3 combination undergoes a strongly exothermic reaction between 380 and 550°C.

During normal thermal analysis of sulphur-containing mixtures, sulphur vaporizes above its liquid-liquid transition (171°C) and below the melting point of KNO_3 (315°C) so there is no significant reaction between sulphur vapour and solid KNO_3. If the escape of sulphur vapour is reduced, through use of high heating rates, or a preheated furnace, some of the sulphur can be induced to react with molten KNO_3. The reaction between sulphur vapour and molten KNO_3 in ternary systems is regarded as the "pre-ignition" reaction, and the higher temperature oxidation of solid charcoal by molten KNO_3 propagates the combustion of black powder. In air, sulphur oxidizes at temperatures below the melting-point of KNO_3.

INTRODUCTION

Although black powder has a long and intriguing history [1,2], relatively few thermo-analytical studies have been reported [3,4]. The thermal properties of its individual constituents are, however, well documented [5-9].

KNO_3 undergoes a rhombic-to-trigonal phase transition at 116°C and melts at 325°C. Decomposition occurs above 650°C. Sulphur changes from an initially rhombic to a monoclinic structure at 90°C and melts at 101°C. In an

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inert atmosphere, at a heating rate of $20^{o}C\ min^{-1}$, vaporization of sulphur begins just above its liquid-liquid transition at $171^{o}C$. In air, at the same heating rate, vaporization is accompanied by partial oxidation. Charcoal is the constituent with the most-variable properties [8]. In an inert atmosphere, moisture is lost below $120^{o}C$, and organic volatiles below $800^{o}C$. Combustion in air begins above $300^{o}C$.

EXPERIMENTAL

Powdered sulphur, KNO_3 and charcoal (moisture 4.5%, volatiles 16.0%, fixed carbon 77.2% and ash 2.2%) were supplied by AECI Explosives and Chemicals Ltd. Dry sieved (<53 μm) powders were mixed by end-over-end tumbling. Pastes were prepared by adding the required amount of water to the mixed powder and mixing further by hand.

Thermal analyses using a Stanton Redcroft STA-780 simultaneous TG-DTA and a Perkin-Elmer DSC2, were supplemented by hot-stage optical microscopy, scanning electron microscopy, infrared spectroscopy and X-ray diffraction.

RESULTS

Low-temperature processes observed in the TG-DTA traces of the mixtures included the removal of water, the phase transitions of sulphur and of KNO_3, and the melting of sulphur, as observed in the traces of the individual constituents. In air, at $202 \pm 5^{o}C$, a broad exothermic reaction between sulphur and atmospheric oxygen ($\Delta H = -3.84 \pm 0.25\ kJ\ g^{-1}$, compared to the value predicted from thermodynamic data, of $-9.27\ kJ\ g^{-1}$) was observed.

The charcoal/sulphur mixture, heated in nitrogen, showed only melting and vaporization of the sulphur below $300^{o}C$, followed by devolatilization of the charcoal. A reported reaction between sulphur and the charcoal volatiles [4] was not observed.

The charcoal/KNO_3 mixture undergoes a strongly exothermic reaction between solid charcoal and molten KNO_3 (m.pt $315^{o}C$) between 380 and $550^{o}C$. Atmospheric oxygen, if present, also contributes to this reaction. The solid residue contains K_2CO_3. The reaction scheme suggested [3] is:

$$3C(s) + 2KNO_3(\ell) \rightarrow K_2CO_3(s) + N_2(g) + CO_2(g) + CO(g)$$

ΔH of reaction, calculated from standard enthalpies of formation, is $-2.78\ kJ\ g^{-1}$ and is in good agreement with the experimental value ($-2.83 \pm 0.20\ kJ\ g^{-1}$) obtained in N_2. The composition of the mixture (87.5% KNO_3), corresponds to the above reaction limited by the carbon present. The mass of the residue in N_2 of 49.7 ± 2.6% is greater than that predicted if all the potassium was finally present as K_2O (40.8%). The DTA traces confirm the melting of K_2CO_3 at 891°C.

Under the conditions applying during normal thermal analysis of the sulphur/KNO_3 mixture, sulphur vaporizes below the melting point of KNO_3 (315°C) and there is no significant reaction between sulphur vapour and solid KNO_3. If the escape of sulphur vapour is reduced, through use of high heating rates, or by preheating the furnace (to 460°C) before introducing the sample, up to 20% of the sulphur in the mixture can be induced to react with molten KNO_3. The solid residue contains K_2SO_4 and unreacted KNO_3. In air, sulphur is oxidized below the melting-point of KNO_3.

The behaviour of sulphur in the ternary mixtures is similar to that described above. The TG-DTA traces of black powder (composition: 70% KNO_3, 10% charcoal by mass, 20% sulphur) in N_2 are shown in Fig. 1. The usual endotherms of sulphur and KNO_3 are observed. Vaporization of sulphur occurs between 165 and 276°C, and at higher heating rates (50°C min^{-1}) and large sample masses, the range was extended to 310°C. The mass loss (20.7 ± 0.5%) confirms the complete removal of unreacted sulphur. The oxidation of charcoal by KNO_3 (mass loss 29.2 ± 0.9%) follows between 390 and 550°C and is then followed between 600 and 1000°C by decomposition of unreacted KNO_3 (mass loss of 17.2 ± 1.2%). DSC traces of black powder heated at 80°C min^{-1} in N_2 showed only a slight exotherm beginning at 334°C due to the reaction between sulphur and KNO_3. This reaction could be enhanced by introducing the sample into a preheated (460°C) furnace. In air, sulphur oxidizes between 190 and 290°C (mass loss 21.4 ± 0.8%) (Fig. 2). TG shows that some charcoal is

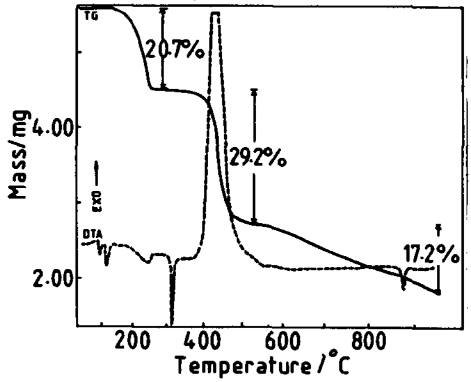

Fig.1 TG-DTA of black powder in N_2 at 20°C min^{-1}.

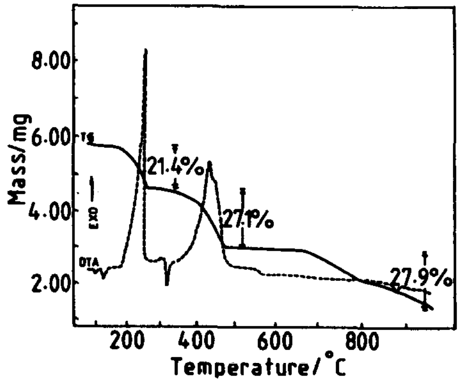

Fig.2 TG-DTA of black powder in air at 20°C min^{-1}.

oxidized by air at 300°C, but that oxidation becomes more rapid at temperatures above the melting point of KNO_3 (mass loss 21.4 ± 0.4%).

DTA traces of black powder paste, heated at 20°C min^{-1} in an inert atmosphere, or in air, showed that water vaporizes completely between 25 and 130°C without influencing the higher-temperature reactions. DSC traces of ternary mixtures, with a constant charcoal/KNO_3 ratio, but increasing proportion of sulphur, were recorded in N_2 and in air (Figs. 3 and 4, respectively). The first exotherm in N_2 arises from the S/KNO_3 reaction and, in air, from the S/O_2 reaction. Enthalpies calculated from DSC curves are given in Table 1.

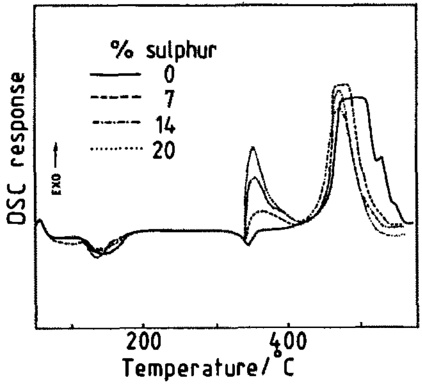

Fig.3 DSC traces in N_2 of ternary mixtures with increasing sulphur content.

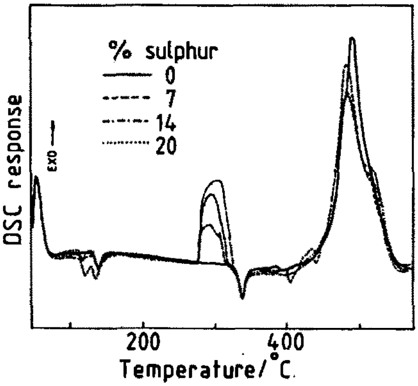

Fig.4 DSC traces in air of ternary mixtures with increasing sulphur content.

TABLE 1

Enthalpies of reaction for ternary mixtures with increasing sulphur content

% Sulphur	- ΔH oxid of S /kJ g^{-1}	- ΔH oxid of charcoal /kJ g^{-1}	- ΔH total /kJ g^{-1}
In N_2			
0	-	2.89 ± 0.13	2.89
7	0.21 ± 0.04	2.10 ± 0.06	2.31
14	0.32 ± 0.05	1.96 ± 0.09	2.28
20	0.44 ± 0.03	1.81 ± 0.09	2.24
In air			
0	-	2.30 ± 0.13	2.30
7	0.19 ± 0.01	2.05 ± 0.05	2.24
14	0.39 ± 0.02	1.97 ± 0.06	2.36
20	0.54 ± 0.04	2.00 ± 0.06	2.54

In N_2, the contribution to the total ΔH from the first exotherm increases as the sulphur content increases, while the ΔH from the second exotherm decreases on account of the KNO_3 consumed in the first exotherm. The total enthalpy change therefore generally decreases with increasing sulphur content. In air, a slight decrease in the total ΔH occurs from 0 to 7% sulphur, but then increases with further increase in the sulphur content. The contribution to ΔH from the S/O_2 exotherm increases with increasing sulphur but the contribution from the second exotherm remains constant for mixtures between 7 and 20% sulphur.

At heating rates of 80°C min^{-1}, a single and not very reproducible exotherm, in which the S/KNO_3 and charcoal/KNO_3 exotherms merge to form a single exotherm with onset temperature just above the m.pt of KNO_3, was observed (Fig. 5).

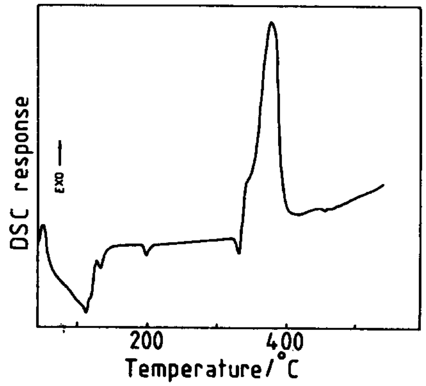

Fig.5 DSC trace of black powder at 80°C min^{-1} in N_2.

CONCLUSIONS

DSC, TG and DTA of black powder (composition 70% KNO_3, 20% sulphur and 10% charcoal), as used for the manufacture of safety fuse, has shown that two exothermic reactions occur at temperatures above the melting point of KNO_3 (315°C). Through examination of the binary mixtures of the constituents of black powder, it was confirmed that the first exothermic process is a reaction between sulphur and KNO_3. This reaction was found to depend very much on the prevention of the escape of sulphur vapour from the reaction system. The second exothermic process is the oxidation of solid charcoal by molten KNO_3.

The presence of the water in the paste does not appear to alter or affect any of the high-temperature rections as it is readily removed from the low mass samples in a broad endothermic process which overlaps some of the lower temperature transitions of the constituents.

The reaction between sulphur vapour and molten KNO_3 has been called "the pre-ignition reaction" [3] because it is presumed that the heat evolved in this reaction raises the temperature of the system to a high enough value for the exothermic reaction between charcoal and molten KNO_3 to take place. This latter reaction is called the "propagation reaction" [3]. These processes were seen to merge at high heating-rates.

The reactions occurring during thermal analysis at slow heating rates are not necessarily those which take place during the ignition and combustion of black powder, but thermal analysis does provide insights into the main factors which have to be taken into account in studying the combustion [10].

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