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Combustion reactions of antimony + potassium permanganate mixtures. Rate of propagation and influence of loading pressure

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Abstract

Combustion reactions of $Sb + KMnO_4$ mixtures were studied in consolidated application form when they were ignited linearly, and in loose powdered form when they were studied by DSC, TG/DTG, and hot-stage microscopy. The influence of fuel content and loading pressure on burning rate were examined. From the results, a mechanism for the combustion wave is suggested.

INTRODUCTION

Combustion reactions of small samples of pyrotechnic compositions under controlled conditions, when studied by thermal methods of analysis, have been the subject of extensive investigations [1–4]. The resulting mechanism is then correlated to the combustion behavior of the mixtures in compressed application form [5–8]. Antimony/potassium permanganate mixtures in pelleted form have industrial application as delay compositions [9]. Beck and Brown have made a detailed thermoanalytical investigation of the reactions of the $Sb/KMnO_4$ system. By combining XRD, IR, and optical and electron microscope results, they identified reaction intermediates and products in the combustion process [2]. In the present work, mixtures of $Sb + KMnO_4$ in compressed application form were examined and the influence of fuel content and loading pressure on the propagation behavior was tested. Attempts are made to correlate the propagation behavior of the compositions to the mechanism suggested by the thermoanalytical results.

EXPERIMENTAL

Materials and apparatus

Potassium permanganate was supplied by B.D.H. Chemicals Ltd. with 99.5% minimum purity. For the kinetic and thermal studies of $KMnO_4$,

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fresh crystals were prepared using a procedure described by Hill [10]. Powdered $KMnO_4$ was prepared by grinding crystals in an agate mortar; the sample was then sieved and its surface area was measured as $0.46\,m^2\,g^{-1}$. Antimony powder with 98.5% purity was also supplied by B.D.H. Chemicals Ltd.; the mean particle size was 4.6 micron with $0.509\,m^2\,g^{-1}$ surface area. The major instrumentation was a Perkin-Elmer TGS-2 thermogravimeter, a Perkin-Elmer DSC2 differential scanning calorimeter, a Stanton-Redcroft HSM-5 hot-stage microscope, a Strohlein OPI-Bb 119-E surface-area meter and a Coulter-Counter TA for measuring the particle size.

Procedure

The preparation of $Sb + KMnO_4$ mixtures was carried out in a portakabin located outside the main laboratory, because pyrotechnic mixtures are sensitive to accidental ignition by static electricity, impact and friction. Therefore, adequate safety measures are necessary in mixing and pelleting the compositions. The firing of delay elements was carried out behind an armored screen and away from other ignitable materials. The experimental techniques used were similar to those described previously [11, 12]. $Sb + KMnO_4$ mixtures with 20–80% antimony were prepared using carboxymethyl cellulose as a binder. Because $KMnO_4$ is soluble in water, a small amount of binder was added to the thoroughly mixed composition in order to prepare granules of the mixture. The final mixture contained less than 0.3% binder and was compacted into 10 mm die-cast delay tubes under 60×10^{-6} to $240 \times 10^{-6}\,N\,m^{-2}$ pressing loads.

RESULTS AND DISCUSSION

Rate of propagation

The variation in burning time of the compositions with fuel content is given in Fig. 1. The maximum burning time is with 30% antimony; the burning time decreases as the fuel content increases, and reaches a minimum at 65% antimony. With further increase in Sb, burning time increases up to 80% Sb, above which the compositions fail to propagate. XRD analysis of the products showed the formation of Mn_2O_3, Mn_3O_4 and α-Mn with the mixtures containing excess oxidizer. Identification of the main reaction responsible for the propagation is difficult, due to the variable valances of manganese and the presence of a number of stable oxides of antimony. For the reaction of the $Fe/KMnO_4$ system, Hill [10] suggested formation of $K_2O_{0.2}MnO_{1.89}$. For the thermal decomposition of $KMnO_4$, Herbstien and Weissman [14] detected the formation of oxides of manganese with an intermediate amount of oxygen. For the oxidation of antimony, Cody et al. [15] and Golunski et al. [16] made detailed studies indicating three stable oxides of antimony, Sb_2O_3, Sb_2O_4 and Sb_2O_5. Sb_2O_3

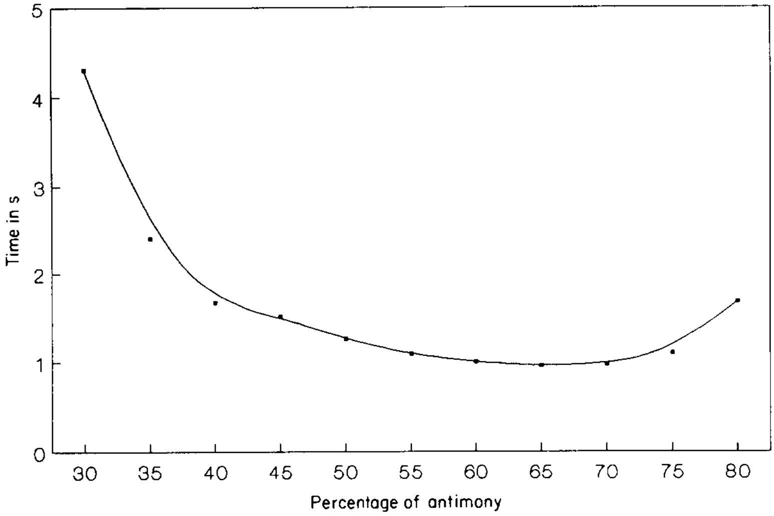

Fig. 1. Variation of delay time with fuel content.

is stable up to 360°C; above this temperature it vaporizes and in the presence of oxygen oxidizes to Sb_2O_4 and Sb_2O_5. Sb_2O_5 is stable up to 400°C where it begins to lose oxygen, and by 950°C it decomposes to α-Sb_2O_4. XRD analysis of combustion slags did not show strong patterns relating to the oxides of antimony; one possibility is that at high combustion temperatures they form inorganic glass undetectable by XRD. These results are in agreement with the earlier work of Beck and Brown [2]; their XRD and IR analyses of the thermoanalytical products of $Sb + KMnO_4$ mixtures showed that K_2MnO_4 is the product of first stage of decomposition of $KMnO_4$.

Thermoanalytical studies

The $Sb + KMnO_4$ compositions and their individual components were studied by DSC and TG/DTG. Figure 2 shows the DSC trace of $KMnO_4$. Two thermal events take place; the first is indicated by an exothermic peak at 300°C relating to the thermal decomposition of $KMnO_4$; the second is indicated by an endothermic peak at 640°C relating to further decomposition of the products. The thermogravimetry results showed that, in the first decomposition stage of $KMnO_4$, 10.7–12.8% weight loss occurs depending on the sample atmosphere, air or nitrogen. The weight loss is higher in air and is due to the release of oxygen. In the second stage, depending on the weight loss in the first stage, between 3.7 and 5.2% weight loss occurs, again due to oxygen release. The decomposition of $KMnO_4$ has been the subject of many investigations. So far, there has been no agreement on the chemical nature of the products, except that oxygen is released [14, 17].

Figure 3 shows the DSC trace of powdered Sb under static air atmosphere at a heating rate of 5°C min^{-1}. Two exothermic peaks at 505

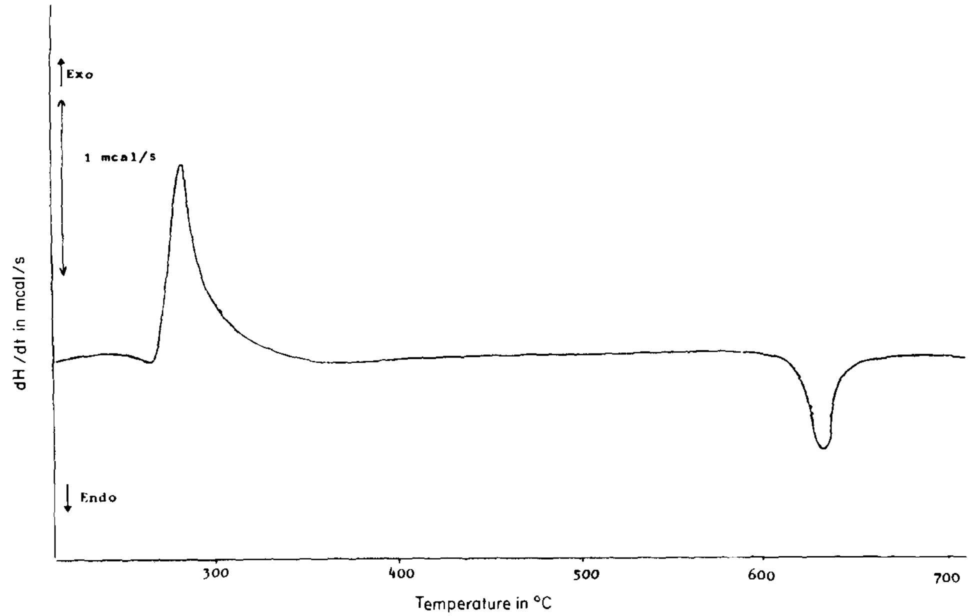

Fig. 2. DSC trace of the decomposition of $KMnO_4$ under static air atmosphere at 5°C min^{-1} heating rate.

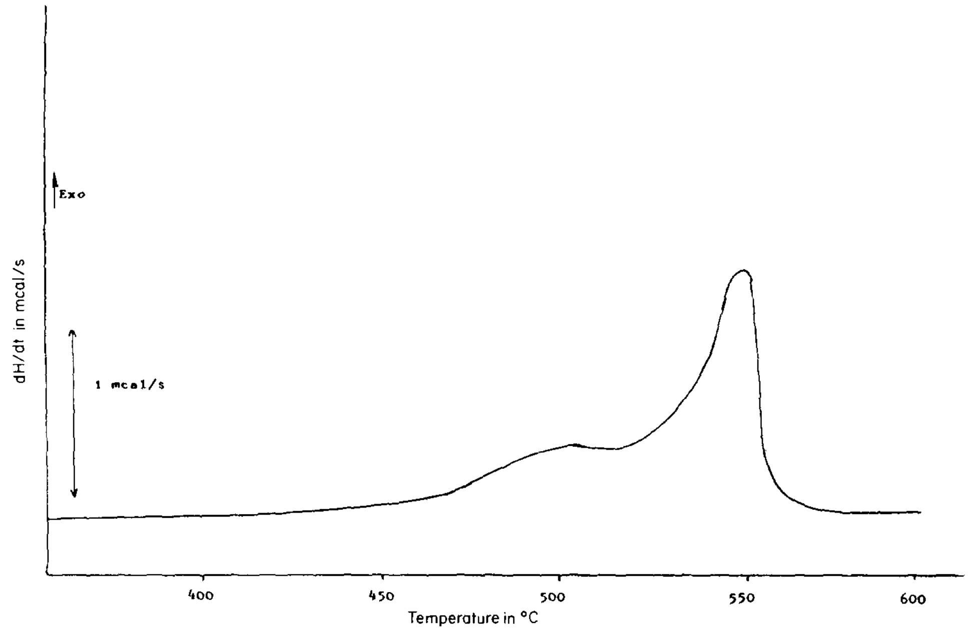

Fig. 3. DSC trace of the oxidation of antimony under static air atmosphere at a 5°C min^{-1} heating rate.

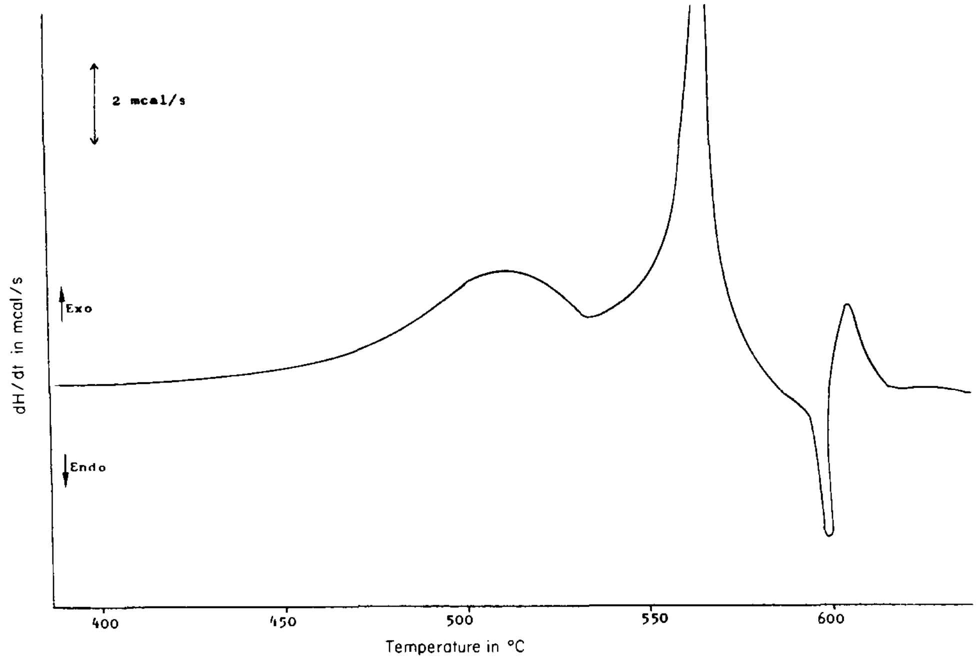

Fig. 4. DSC trace of the oxidation of antimony under static air atmosphere at a 20°C min^{-1} heating rate.

and 550°C are present. Ignition of Sb occurs in the temperature range of the second peak. Figure 4 shows the DSC trace of Sb under static air with a 20°C min^{-1} heating rate; the ignition is clear. The occurrence and temperature of the ignition depends on the rate of heating and sample weight. Thermogravimetry traces of antimony under static air atmosphere recorded at 5°C min^{-1} are presented in Fig. 5. Oxidation takes place in two stages, probably due to the surface and bulk oxidation [13]. The first stage of oxidation takes place in the temperature range 370–500°C with a 7% weight gain; the second stage takes place in the range 500–615°C with a 11% weight increase. Nakahara [9] found a total of 25% weight gain occurring in two approximately equal stages; Beck and Brown [2] found a 1% weight increase at 300°C, followed by a $16 \pm 2\%$ weight increase from 300 to 500°C, the final stable products being formed at around 600°C. The weight gain due to the oxidation of Sb is countered by the loss of Sb_2O_3 in vapor form as an intermediate product leading to the variable TG results. XRD analysis of the final products showed that Sb_2O_4 was formed; a weak pattern corresponding to the formation of cubic Sb_2O_5 was also present.

When a mixture of $KMnO_4$ and Sb was examined by thermogravimetry, a curve similar to that of pure $KMnO_4$ was obtained (Fig. 6); 10.12% weight loss occurred at 300°C, indicating that gaseous oxygen leaves the mixture without reacting with Sb. In order to determine whether a similar mechanism is followed in the confined form of pressed pellets, a large

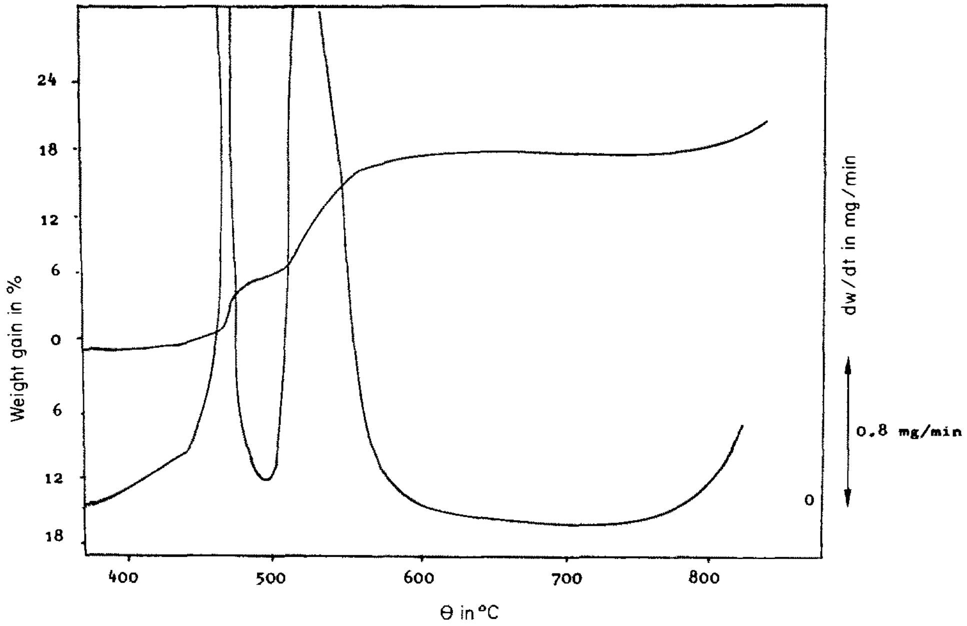

Fig. 5. TG/DTG traces of oxidation of antimony in static air atmosphere at a 20°C min^{-1} heating rate.

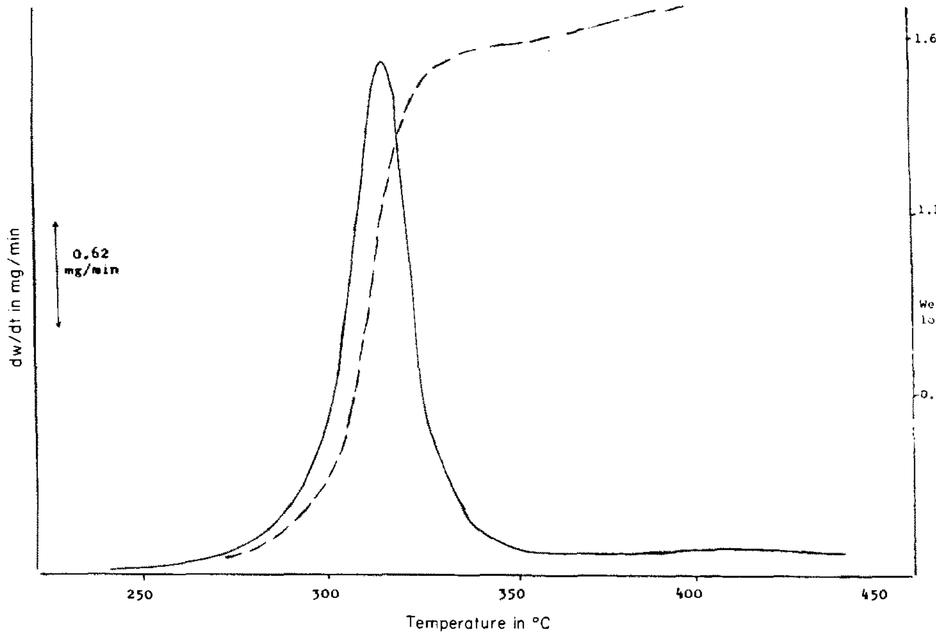

Fig. 6. TG/DTG traces of a 40/60 mixture of Sb + $KMnO_4$, 27.5 mg sample weight. The maximum weight loss due to the decomposition of $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ is calculated to be 1.673 mg.

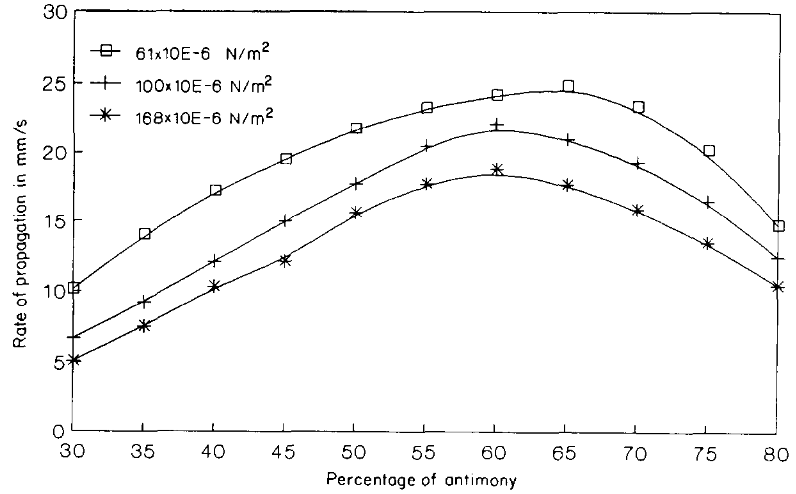

Fig. 7. Effect of loading pressure on the rate of propagation.

amount of $KMnO_4$ was decomposed at 350°C and the solid residue was then mixed with Sb in various proportions. Ignition tests were carried out on these compositions and they were found to be non-propagative. Therefore, it can be concluded that in the propagation wave of the $Sb + KMnO_4$ system, both gas and solid phase reactions are involved.

Effects of loading pressure on propagation rate

Figure 7 shows the rate of propagation at various loading pressures. In all compositions, the rate of burning decreases as the loading pressure increases. However, the effect of pressing load on compositions containing a high excess of fuel was found to be different from those containing a high excess of oxidant. Wilth high $KMnO_4$ mixtures, at higher densities the resulting gases from the decomposition of unreacted oxidant causes a pressure build-up inside the delay tube leading to erratic burning rates and causing bursts in the delay tubes.

When the loading pressure of a self-contained pyrotechnic mixture is increased, depending on the mechanism of the propagation wave, it either increases or decreases the rate of burning. Propagation waves involving only solid-phase reactions without gaseous products are expected to increase the burning rate due to the better surface contact between reactant particles at higher densities. However, when a gas phase reaction is also involved or the reaction results in vapor phase products, the increase in density causes the rate of propagation to fall, and in this case the heat transfer is carried out by the gaseous phase diffusing through the voids to raise the temperature of the next layer to that of the ignition temperature. Therefore, an increase in the loading pressure which reduces the voidage will inhibit the rate of burning of the composition [18]. In the combustion of

$Sb + KMnO_4$ mixtures, as described previously, there is a very strong possibility of gas–solid oxidation of Sb to form Sb_2O_3 in vapor form and its further oxidation in the gas phase to form Sb_2O_4. Further evidence for the presence of a gas-phase reaction in the combustion wave was obtained when the propagative mixtures of $Sb + KMnO_4$ were heated while being observed under hot-stage microscope. Under an inert atmosphere, none of the compositions ignited, whereas in air atmosphere, ignition took place. Ignition originated from a hot spot and advanced with a glow front through the mixture. When the effect of loading pressure was tested on mixtures with a large excess of Sb, because there is just enough oxidizer in the mixture to sustain combustion, at high densities restricting the gas-phase reactions causes the propagation to cease; therefore, ignition failures were observed.

CONCLUSIONS

The results indicate that the amount of oxygen released in the first stage of decomposition of $KMnO_4$ is influenced by the sample atmosphere; weight loss is always higher in air than in nitrogen atmosphere. In the combustion of $Sb + KMnO_4$ mixtures in pelleted form, both gas and solid phase reactions are present. The increase of density in all compositions results in a lower propagation rate due to the restriction on gas phase reactions.

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