

COMBUSTION OF MIXTURES CONTAINING NaClO₄, S AND CARBON

G. Hussain and G. J. Rees

DEPARTMENT OF SCIENCE AND CHEMICAL ENGINEERING, THE POLYTECHNIC OF WALES, PONTYPRIDD, MID GLAMORGAN, CF37 1DL, U.K.

The thermoanalytical techniques e.g. DSC, TG/DTG and Hot Stage Microscopy have been used to examine the system of NaClO₄, S and charcoal mixtures. The results show that there is no reaction between NaClO₄ and S alone, but the presence of charcoal activates their reaction. Charcoal is oxidised by NaClO₄ prior to the melting of NaClO₄, showing a solid phase reaction. The presence of S activates the whole of the reaction to such a level that the mixture burns around 300°C.

Introduction

In black powder, KNO₃ is used as an oxidizer [1-3] for the combustion of charcoal. K₂SO₄ is formed as a major solid product and about 56-57% solids are formed [1] along with CO₂ as the major gaseous product [3, 4]. In the search for a better oxidizer which could produce less solids but effective force of propulsion also, NaClO₄ is being investigated. In this paper we report results obtained, by thermoanalytical techniques such as DSC, DTG/TG and Hot Stage Microscopy (HSM) from the combustion of mixtures containing NaClO₄, S and carbon.

Experimental

In this study the binary or ternary mixtures of NaClO₄ (Aldrich Chemical Co Ltd.) S (99.99% purity, Aldrich Chemical Co. Ltd.) and charcoal (Activated Granular, Sigma Chemical Co., Poole) were prepared [5] by mixing the sieved powdered samples (<125 μm). NaClO₄ was weighed in a china crucible and 20% (by weight) water was mixed with a glass rod followed by addition of other components. Water was added to oxidiser first

for the better distribution of the oxidiser and for safety during mixture preparations. The paste was dried at room temperature. The methods of recording DSC and TG/DTG curves are described in earlier papers [5, 6]. In all of the DSC and TG/DTG experiments, 2.0 mg of samples were used except in the case of pure NaClO_4 when 3.1 mg was used. Heating rates in DSC and TG/DTG experiments were 20 and 40 deg/min respectively.

Results and discussion

The DSC curve 'a' in Fig. 1 was obtained when 3.1 mg of pure NaClO_4 was used. A small endothermic peak at 310° along with very strong endothermic peak at 472° is observed. The small peak at 310° is associated with the previously reported [7, 8] orthorhombic-to-cubic phase transition and is reversible if the sample is not allowed to decompose after 550° [7] (shown by mixture of weak peaks in the DSC curve in the temperature range $550\text{--}580^\circ$). The strong peak at 472° has been assigned to fusion/melting of the sample [7, 8]. The process of melting at $471\text{--}472^\circ$ was also observed visually in the HSM.

When the binary mixture of NaClO_4 and Charcoal (75:25) was heated, the DSC curve 'b' from 2.0 mg sample, shown in Fig. 1 was obtained. An en-

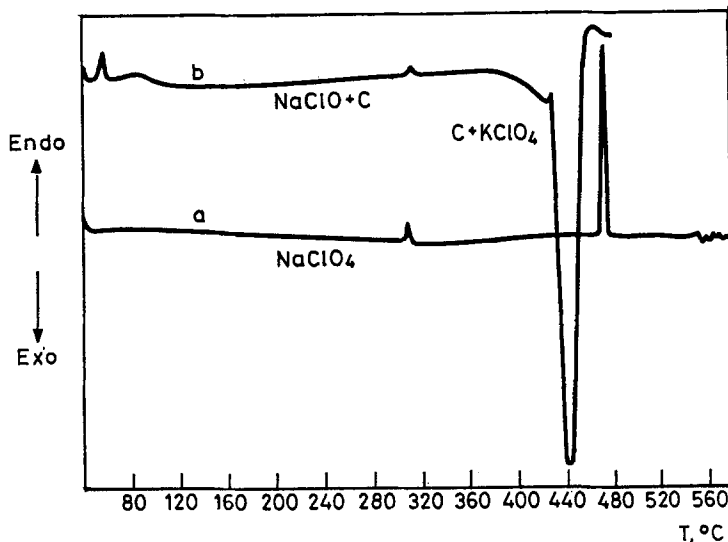


Fig. 1 DSC heating curves from : a) 3.1 mg of pure NaClO_4 ; b) 2.0 mg of the binary mixture of NaClO_4 and charcoal (75:25)

dothermic peak at 50° followed by a broad endothermic peak at 95° , assigned to the removal of water of hydration [7, 8] was observed. The absence of these peaks from pure NaClO_4 (Fig. 1) also confirms that the added water to binary mixture during preparation remained as water of hydration after drying at $25\text{--}30^{\circ}$. This was clearly observed when water was added to the pure NaClO_4 followed by drying at $25\text{--}30^{\circ}$ and heating in the HSM.

The peak due to orthorhombic-to-cubic phase transition is comparatively weaker due to a smaller amount of NaClO_4 . There is a weak endothermic peak at 430° associated with melting of NaClO_4 probably depressed to lower temperature. The strong exothermic peak at 440° could be due to the oxidation of charcoal as in the case of KClO_4 [5] thus showing an oxidation/reduction reaction between NaClO_4 and charcoal.

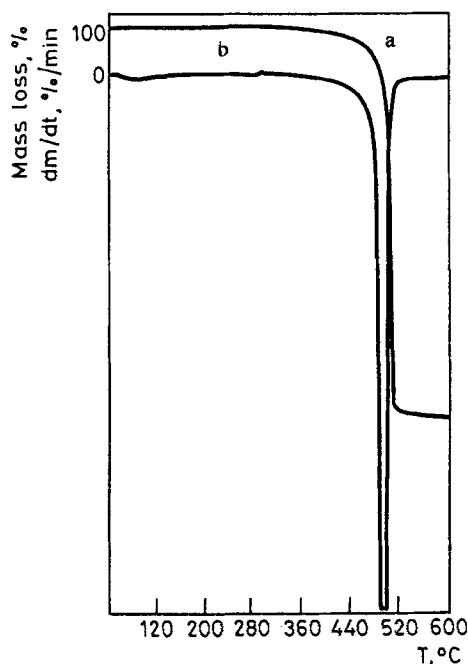


Fig. 2 TG (a) and DTG (b) curves of the binary mixture of NaClO_4 and charcoal

The TG/DTG curves (Fig. 2) also show a very strong DTG peak at 495° from the oxidation of carbon. The overall weight loss of 70% corresponds roughly to the removal of Charcoal and oxygen from NaClO_4 as NaClO_4 decomposes to NaCl and O_2 [8]. The oxidation of carbon takes place far below the temperature of decomposition of NaClO_4 (580° , DTG curve not shown) thus showing that the presence of fuel i.e. charcoal, catalyses the

decomposition of NaClO_4 and the decomposition of NaClO_4 and oxidation of carbon takes place simultaneously. The difference in DTG and DSC peak values could be due to different heating rates and the fact that in DTG, the Pt cup was open while in DSC, the Al cup was covered.

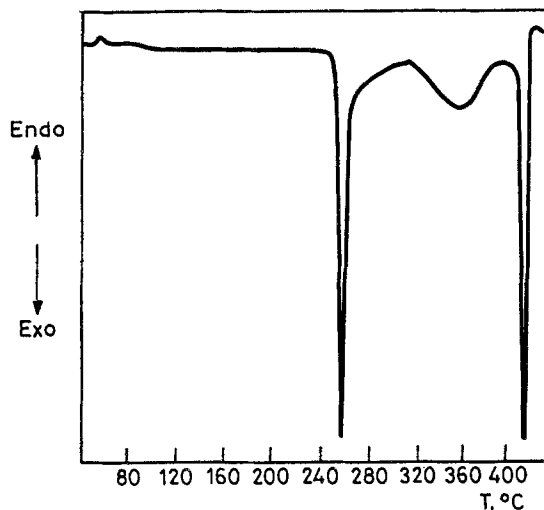


Fig. 3 DSC heating curve from 2.0 mg of the ternary mixture of NaClO_4 , S and charcoal (75:10:15)

When 2.0 mg of a ternary mixture of NaClO_4 -ch-S (75:15:10) was heated, the DSC curve in Fig. 3 was observed. The peaks due to dehydration of NaClO_4 and phase transition are observed at the usual position. Two very sharp and strong peaks at 255° and 408° along with a broad and strong peak at 355° are observed. The first could be due to the oxidation of free S by NaClO_4 in the presence of charcoal whereas the broad peak at 355° could be due to the oxidation of adsorbed S [9]. There was no such exothermic reaction between NaClO_4 and S after or prior to the melting of NaClO_4 in case of a binary mixture of NaClO_4 and S (75:25) as evidenced in the case of KNO_3 [1, 10]. In the HSM it was also observed that during heating of this binary mixture all of the yellow sulphur just evaporated leaving white NaClO_4 crystals thus showing no reaction between S and NaClO_4 similar to KClO_4 [5]. This was also supported by the fact that almost all of the S was removed up to 300° (the peak at 285° (not shown) corresponding to the removal of S [5]). However, in case of the ternary mixture of KClO_4 [5] no such reaction KClO_4 and S in the presence of charcoal was observed. The peak at 408° due to oxidation of carbon was comparatively at lower temperature.

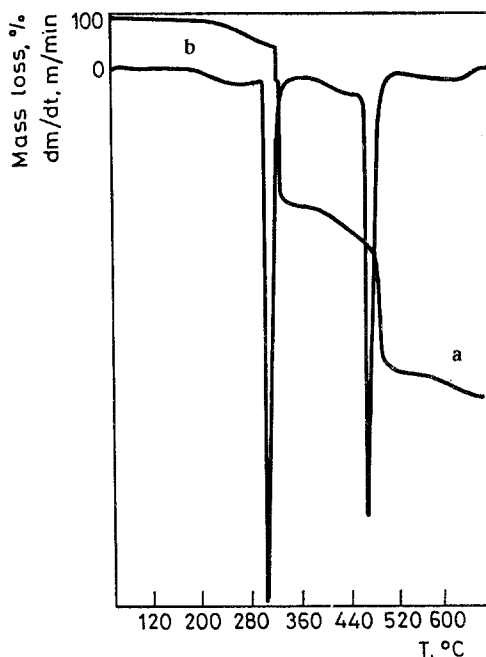


Fig. 4 TG (a) and DTG (b) curves from 2.0 mg of the ternary mixture of NaClO_4 , S and charcoal

When 2.0 mg of this mixture was heated, the TG and DTG curves in Fig. 4, were obtained. The DTG curve shows the partial removal of S around 250° followed by a very very strong and sharp peak at 302° from the oxidation of S. The other strong peak at 465° from the oxidation of carbon along with residual NaClO_4 (around 600°) are observed. The strong shoulder to the main peak at 465° could be from the oxidation of adsorbed S. The overall weight loss in TG from the peak at 302° was 32%. As the amount of S was 10% in the mixture, the removal of S only, by oxidation would have resulted in a loss less than 20%. The additional weight loss could only be accounted for by the partial oxidation of carbon. This was supported by the fact that in one experiment, when 4 mg of sample was used, the flash occurred around 300° and most of the mixture had burnt. No strong peak but a weak peak from residual mixture, after 360° , was observed. A similar process was also observed in the HSM.

These results show that although S does not react alone with NaClO_4 , the presence of carbon facilitates their reaction. The oxidation of carbon (charcoal) by NaClO_4 takes place around 495° (Fig. 2) but the presence of S also

activates this reaction. Thus the presence of both the S and carbon causes the activation of the whole of the pyrotechnic reaction to take place around 300°.

As some of the water from the sample preparation stage is retained by NaClO₄, the ignition with nichrome wire [1, 5] was not so abrupt as in the case of KClO₄ [5]. However, if the ternary mixture is heated to 95° first, then ignition by nichrome wire produces a sudden flash.

The infrared emission spectra (not shown) from the burning of ternary mixture were similar to those observed from KClO₄ [5], thus showing CO₂ and SO₂ as the major gaseous products.

* * *

We wish to express our thanks to the Procurement Executive of the Ministry of Defence, UK for providing financial support for the research.

References

- 1 G. Hussain and G. J. Rees, *Propellants, Explosives, Pyrotechnics*, 15 (1990) 43.
- 2 M. E. Brown and R. A. Rugunaman, *Propellants, Explosives, Pyrotechnics*, 14 (1989) 69.
- 3 G. Hussain and G. J. Rees, *Propellants, Explosives, Pyrotechnics*, 16 (1991) 6.
- 4 G. Hussain and G. J. Rees, *Fuel*, 70 (1991) 667.
- 5 G. Hussain and G. J. Rees, *Fuel* (in press).
- 6 G. Hussain and G. J. Rees, *J. Thermal Anal.*, (in press).
- 7 S. Shimada and R. Furuichi, *Thermochim. Acta*, 163 (1990) 313.
- 8 D. J. Devlin and P. J. Herley, *Reactivity of Solids*, 3 (1987) 75.
- 9 G. Hussain and G. J. Rees, *Propellants, Explosives, Pyrotechnics*, (in press).
- 10 *Chem. Eng. News*, 30 (1981).

Zusammenfassung — Mittels DSC, TG/DTG und HSM wurde das System von Gemischen aus NaClO₄, S und Holzkohle untersucht. Die Ergebnisse zeigen, daß sich zwischen NaClO₄ und S allein keine Reaktion abspielt, daß diese Reaktion aber durch Gegenwart von Holzkohle aktiviert wird. Noch vor dem Schmelzen von NaClO₄ wird Holzkohle in einer Feststoffreaktion von NaClO₄ oxydiert. Die Gegenwart von S aktiviert die gesamte Reaktion in dem Maße, daß das Gemisch bei 300°C verbrennt.