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A STUDY ON COMBUSTION BEHAVIOUR OF CARBON-SULPHUR-SODIUM NITRATE MIXTURES

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The effect of substitution of KNO_3 by $NaNO_3$ in black powder has been studied by DSC, TG/DTG and FTIR emission spectroscopy. Unlike KNO_3, there is no visible exothermic reaction between S and $NaNO_3$, immediately after the melting of $NaNO_3$. Instead a minor exothermic reaction is observed at higher temperature between melted $NaNO_3$ and adsorbed S on carbon. However, there is an increase in such reaction, when carbon black instead of charcoal is used. Infrared spectra show that CO_2 and Na_2SO_4 are major gaseous and solid products respectively. This shows that the combustion of ternary mixtures in air is different from that in N_2, with slower heating rate, in DSC or TG apparatus.

The combustion of black powder [1–3] which has a traditional composition of KNO_3 (75%), charcoal (15%) and S (10%) [4–5] has been studied in our laboratories. Although black powder is the oldest explosive known, it is still being used due to its peculiar properties [6]. Extensive studies [7–9] have been carried out and a substitute has been sought [10].

Sodium nitrate is used as an oxidizer in propellants for air-augmented rocket applications [11–12] and trip flare or ignition mixtures [13].

In our study the KNO_3 has been substituted by $NaNO_3$ and the combustion behaviour of mixtures containing $NaNO_3$, carbon black/charcoal and S has been studied by DSC, TG/DTG and FTIR emission spectroscopy.

Experimental

The sieved powdered samples of ($<125\,\mu m$) $NaNO_3$ (Aldrich Chemical Co), S (99.99% purity, Aldrich Chemical Co) and Charcoal (Activated Granular, Sigma Chemical Co, Poole, Dorset)/carbon black (Activated

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china crucible and 20% water was mixed with a glass rod followed by addition of other components. Water was added to oxidizer first for the better distribution of oxidizer and for safety during mixture preparations. The composition of various mixtures is presented in Table 1.

Table 1 The composition of various mixtures containing $NaNO_3$

Mixture	$NaNO_3$, mg	Charcoal/carbon black, mg	Sulphur, mg
(N–S)	80	–	20
(N–Ch)	75	15Ch	–
(N–Ch–S10)	75	15Ch	10
(N–Ch–S15)	75	15Ch	15
(N–Ch–S25)	75	15Ch	25
(N–C–S10)	75	15C	10

Ch = charcoal, C = Carbon black, N = $NaNO_3$

One of the samples (N–Ch–S15) was pressed in a die as explained earlier [3]. The pressed was essential to give a flash for FTIR emission spectroscopy. The methods of recording infrared emission spectra and DSC/TG curves have also been provided earlier [2,1]. However in the case of DSC, no crimping press was used and in TG, the Pt pan without any cover was used in all experiments. In all of the DSC and TG/DTG experiments, 2.4 mg of each sample, except for pure $NaNO_3$, was used.

Results

DSC

The DSC curves in Fig. 1 (a-d) were obtained when pure $NaNO_3$ (1.8 mg) and mixtures (N–S, N–Ch, N–Ch–S10) were heated. A strong endothermic peak at 306° along with a weak endothermic peak at 272° are observed in the four curves. The strong endothermic peak can be assigned to the melting of $NaNO_3$ [14]. The weak peak at 272° could be due to any impurity or any transition for $NaNO_3$. Two additional weak endothermic peaks at 106° and 115° in curve b have been assigned [1, 15] to the rhombic to monoclinic transition and melting of S. There is no visible effect on the main peak of $NaNO_3$. The curve c shows a very strong exothermic peak at 458° in addition to peaks from $NaNO_3$, due to oxidation of carbon [1, 8] whereas the curve d shows peaks due to $NaNO_3$ and carbon oxidation along with a broad and weak exothermic peak at 365°. This peak could be due to interaction of melted $NaNO_3$ and adsorbed S on charcoal as reported for a $KClO_4$ system

[16]. There is no visible reaction immediately after the melting of $NaNO_3$ with what is called free S and no effect on the $NaNO_3$ melting peak like KNO_3 [1,9]. The peaks due to S at 106° and 115° could not be seen, due to the smaller amount of S.

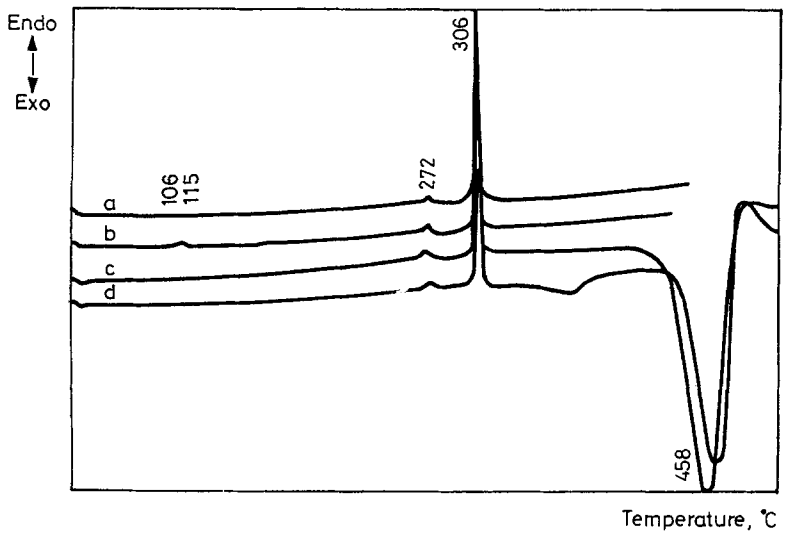

Fig. 1 DSC curves from (a) 1.8 mg of pure $NaNO_3$ (b) 2.4 mg of N–S (c) 2.4 mg of N–Ch (d) 2.4 mg of N–Ch–S10

For comparison, the DSC curve for sample N–C–S10 showed the peak previously at 365°, shifted to 338° but with increased intensity, thus showing a reaction of an increased amount of adsorbed S. The peak due to the oxidation of carbon has shifted to 432° and has decreased its intensity. A strong shoulder at 458° is also observed.

TG/DTG

In Fig. 2, the TG curve (a), and DTG curve (b) for the sample N–Ch–S10 show a broad DTG peak at 250° due to removal of S [8] and a very weak and broad peak centred at 360° due to possibly adsorbed S [16]. The peak due to carbon oxidation [1], observed at 470° for N–Ch–mixture, is not much affected. When more S was present in the sample N–Ch–S25, the peak due to removal of free S at 255° was stronger but the peak due to adsorbed S was slightly weaker, thus confirming our assignment of this peak to adsorbed S on charcoal, as the amount of charcoal was slightly changed. The peak due to carbon oxidation has been much reduced. This could be due to a smaller amount of $NaNO_3$ – charcoal in total weight of 2.4 mg and possibly in-

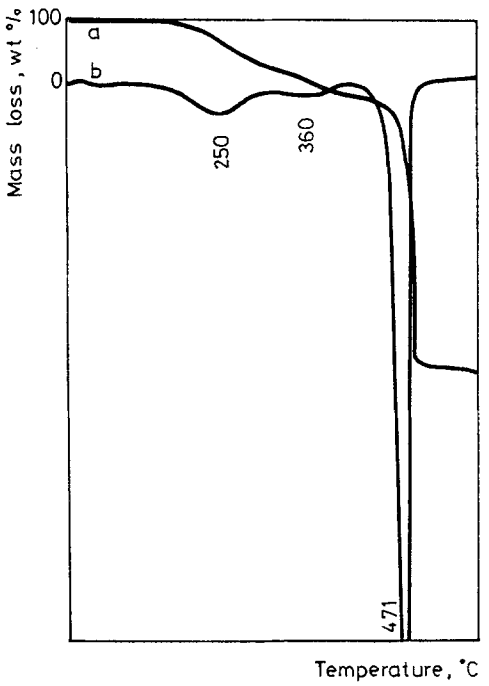

Fig. 2 TG (a) and DTG (b) curves from N–Ch–S10

creased amount of S [17]. The mixture (N–C–S10) containing carbon black shows a very broad DTG peak centred at 283° but a sharper and comparatively stronger peak at lower temperature of 342° due to greater adsorption of S on carbon black, which has a larger surface area. The DTG peak due to carbon oxidation has shifted to 440°, affected by the stronger exothermic reaction of adsorbed S and melted $NaNO_3$.

Spectroscopic studies

Single beam emission spectra in Fig. 3 (a-c) were recorded when 50 mg of sample (N–Ch–S15) was ignited, and belong to the same flash in order of increasing time. A very strong band at 2272 cm^{-1} with a shoulder of 2365 cm^{-1} and very strong band at 1097 cm^{-1} are observed. The strongest band at 2272 cm^{-1} along with a weak band at 664 cm^{-1} has been assigned [2, 16] to CO_2 molecules produced in the combustion. The shoulder at 2365 cm^{-1} is due to hot atmospheric CO_2 molecules and is completely removed by rationing against the background. The weaker bands in the region of 3750-3300 cm^{-1} could be due to combination bands of CO_2 [16, 18].

The other strong band at 1097 cm^{-1}, with a weak band at 618 cm^{-1} can be assigned to sulphate [2] from Na_2SO_4. The broad band centred at 1335 cm^{-1} with other weaker features at 950 and 525 cm^{-1} could be due to carbonate [2] from Na_2CO_3. This band may have some contribution from the small amount of SO_2 and residual $NaNO_3$.

The spectrum b shows similar bands but with reduced intensities. The band at 2272 cm^{-1} is now weaker than the band at 1097 cm^{-1}. This trend is further observed from spectrum c where the intensity of the band at 1097 cm^{-1}, shifted to 1112 cm^{-1}, remained more than the band at 2272 cm^{-1} which shifted to 2287 cm^{-1}.

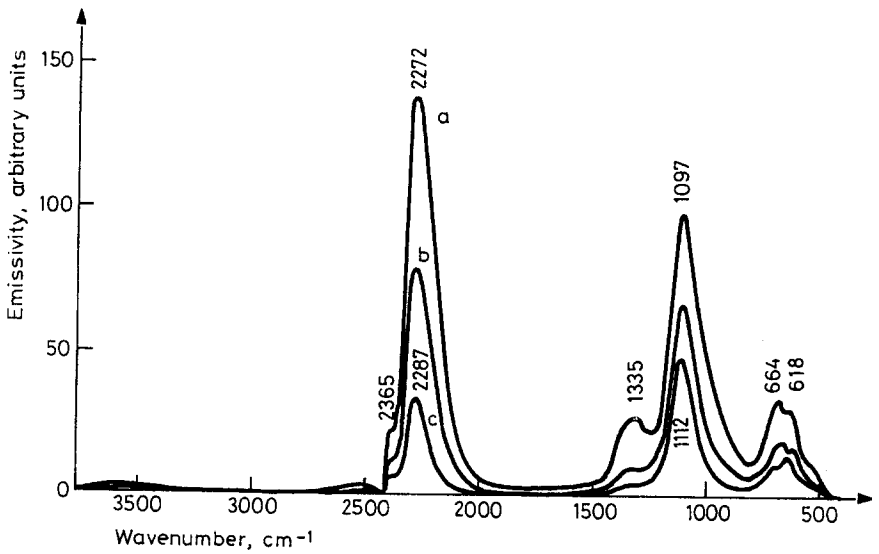

Fig. 3 Single beam emission spectra (i.r.) from 50 mg of N–Ch–S15 (a–c, inorder of increasing time)

This trend also confirms that the bands at 2272 cm^{-1} and 1097 cm^{-1} are due to gaseous CO_2 molecules and solid Na_2SO_4 respectively [2]. The shift of bands to higher frequencies is due to cooling of the molecule.

Discussion

$NaNO_3$ has a melting point of 306°, shown by the endothermic peak in the DSC curve (Fig. 1a). This peak is neither affected by the presence of carbon (Fig. 1b) nor S (Fig. 1c). Unlike KNO_3 [1], there is no exothermic reaction observed between S and $NaNO_3$ immediately after the melting of $NaNO_3$. Even the presence of carbon in the $NaNO_3$-S mixture does not markedly af-

fect this process. The only evidence of a minor reaction is observed between melted $NaNO_3$ and adsorbed S. This reaction is increased when carbon black is substituted in place of charcoal. As $NaNO_3$ and KNO_3 belong to the same alkali metal nitrate group, some similarities were expected. The marked difference observed in our results, is thought to be due to the nitrate ion in $NaNO_3$, not being available at the melting point of $NaNO_3$, but only at higher temperature.

The infrared spectra in Fig. 3 show that the combustion of a pressed ternary mixture in air produced CO_2 and Na_2SO_4 as major gaseous and solid species, similar to those produced by black powder [2]. This shows that the burning of a ternary mixture in air and in N_2 with slower heating rate are different processes [16]. The large amount of Na_2SO_4 cannot be accounted for by the adsorbed S only.

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Zusammenfassung — Mittels DSC, TG/DTG und FTIR Emissionsspektroskopie wurde der Effekt des Ersatzes von KNO_3 gegen $NaNO_3$ in Sprengpulver untersucht. Im Gegensatz zu KNO_3 gibt es unmittelbar nach dem Schmelzen von $NaNO_3$ keine wahrnehmbare exotherme Reaktion zwischen S und $NaNO_3$. Dafür wurde bei höheren Temperaturen eine geringe exotherme Reaktion zwischen geschmolzenem $NaNO_3$ und an C adsorbiertem S beobachtet. Unabhängig davon werden Reaktionen begünstigt, in denen man anstelle von Holzkohle Ruß verwendet. IR-Spektren zeigen, daß die hauptsächlichen gasförmigen und festen Produkte CO_2 bzw. Na_2SO_4 sind. Dies zeigt, daß sich die Verbrennung ternärer Gemische in Luft von der in Stickstoff unterscheidet.