Studies on Thermal Decomposition of Double-Base Propellants

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The scanning thermogram of a block sample of a double-base propellant shows a shoulder around 200°C which is not observed in a powder sample of the sample propellant. The heat of decomposition was also found to be different in the two cases. Product analysis and activation energy calculations show that nitroglycerine undergoes decomposition in the block sample, whereas it vaporizes in the powder sample.

Introduction

KNOWLEDGE about the thermal decomposition of double-base propellants greatly helps in understanding the aging phenomena. Kirby[1] studied the thermal decomposition of double-base propellants (DBP) using differential scanning calorimetry (DSC). He noticed a dip in the ascending portion of the exotherm in DSC thermogram. He attributed this dip to the desorption or vaporization of nitroglycerine (NG). He further observed an oily liquid deposited on the dome cover of the sample holder assembly which by infrared (IR) spectral analysis was shown to be NG. In the present investigation an attempt was made to study the process associated with the endothermic dip observed in the DSC thermogram.

Experiment

The composition of the DBP used was: 26.5% NG, 57.5% nitrocellulose (NC), 5.0% dibutylphthalate, 6.0% dinitrotoluene (DNT)/trinitrotoluene (TNT), 1.5% 2-nitrodiphenylamine (2-n DPA) and 3.5% inorganic salts. The experimental details about the use of differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are given in Ref. 2.

Results and Discussion

The DSC thermograms of DBP decomposition are shown under two different conditions, i.e., block and powdery samples, in Fig. 1. The DSC experiments were carried out under nitrogen gas flow (30 ml/min). It is seen from Fig. 1 that the shoulder appears only in the block sample and not in the powder. The actual temperature at which the shoulder appeared in the present investigation is slightly different from Kirby and Ayres' work.[1,3] This may be due to the difference in the heating rate, N_2 gas flow rate, or composition of the propellant. The heat of decomposition for these two samples is found to be different: the heat of decomposition of the block sample is less than the powder sample. An oily liquid (sublimate) was also noticed on the inside dome cover of the sample holder, which was subjected to analysis.

Simulating the conditions followed in DSC runs, an oily liquid was also collected by thermally heating the propellant sample in a specially designed assembly (shown in Fig. 2). N_2 was bubbled through the sample tube. The sample was heated in the furnace for 10 min at about 140°C, and the sublimate collected in the air condenser was examined. The sample was found to contain two layers: one slightly yellowish in color, the other dark brownish. The light yellowish colored layer contained primarily water. This water formation could possibly be due to the decomposition of a part of the NG. A reddish yellow vapor with a pungent smell, which may be NO_2 gas, was also noticed during decomposition. A substantial quantity of the oily liquid sublimate was collected by repeatedly introducing fresh samples into the sample holder. During experiment it was impossible to prevent the partial decomposition of the NG, giving water and NO_2 during sampling. The IR spectra of the oily liquid sublimate was taken. The IR spectra of the oily liquid in the present investigation and in Kirby's work are shown in Fig. 3. It can be seen that the two IR spectra are similar.

The oily sample was subjected to thin-layer chromatographic (TLC) analysis as well as a concentration zone analysis, which is a dependable means of identifying the components present in the sample without destroying the components. The solvent system used in the separation was chloroform and benzene (1/1 by volume). The spots were identified by spraying with various spot testing reagents. The sample was also separated by column chromatography in order to characterize the components present. Different colored bands were seen on the column. The effluent was collected in batches and tested for the identity of components. These fractions were finally identified by using IR, mass spectroscopy, etc., in addition to simple spot testing. The analysis of the oily liquid/sublimate was found to contain the following compounds: NG, DNT, 2/4/6 trinitro DPA, 2-n DPA, 2/4 dinitro DPA, and nitroso DPA. These results clearly indicate that the oily liquid contains not only NG but several other components as well.

The dynamic thermograms of DNT, NG, etc., are shown in Fig. 4. It is seen from Fig. 4 that NG and DNT are more volatile than the other components. Evaporation of NG and DNT begins at 100°C. It should be mentioned here that the formation of the oily liquid begins much earlier, close to the temperature where the shoulder/dip is noticed in the DSC thermogram (Fig. 5 below). The thermogram of DBP also indicates that the weight loss begins before significant heat generation is noticed from the DSC curve. A similar observation was made by Kirby,[1] for which he offered the explanation that the reaction products involved in heat-producing reactions that do not produce gases are either insignificant or are not detectable by DSC because they occur at the same temperature at which the gas-producing reaction

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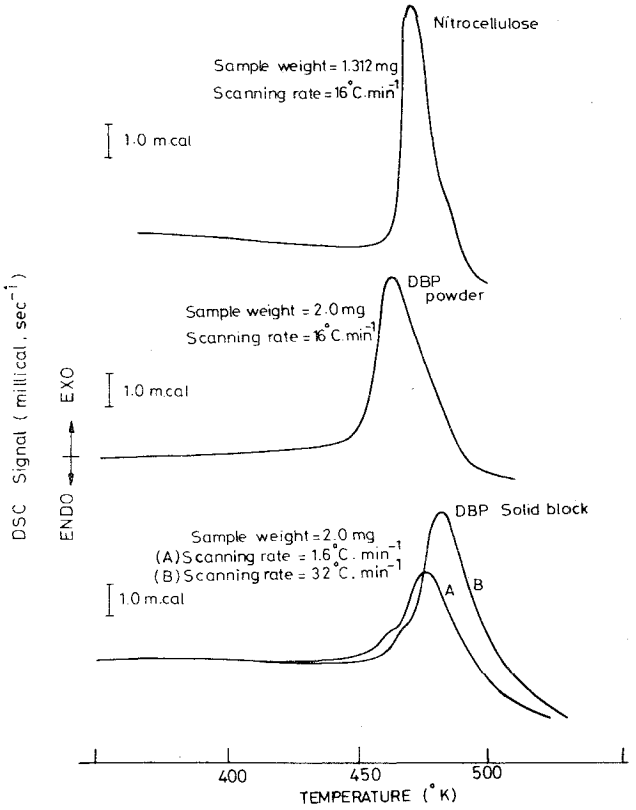

Fig. 1 DSC thermograms of DBP and nitrocellulose.

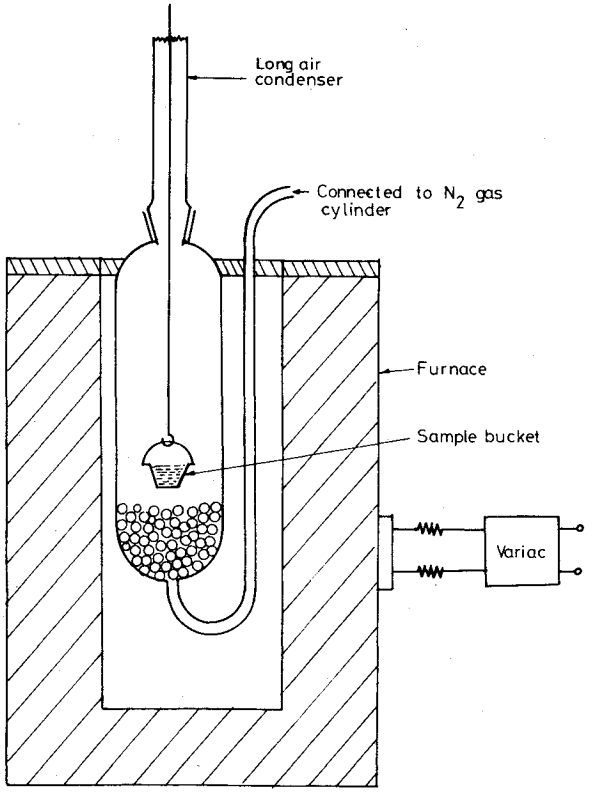

Fig. 2 Sample tube for partial heating of DBP.

occurs for DBP. It is also predicted that, before any significant decomposition of the propellant can take place, the breaking of NC chains could be the endothermic process.

The present investigation shows that the powder sample does not show any shoulder/dip in the thermal decomposition curve obtained with DSC. This suggests that special reactions

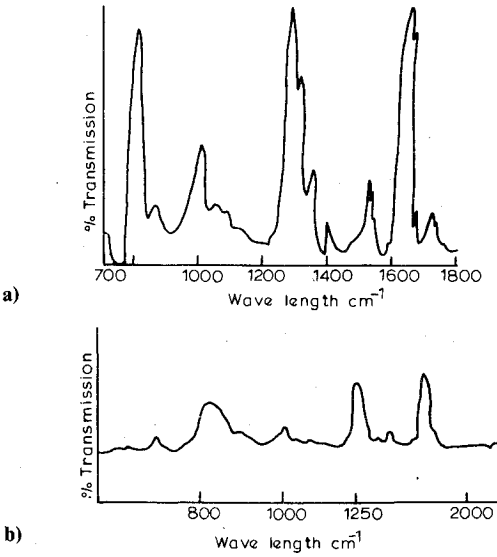

Fig. 3 Infrared spectra of oily liquid: a) present work, b) Ref. 1.

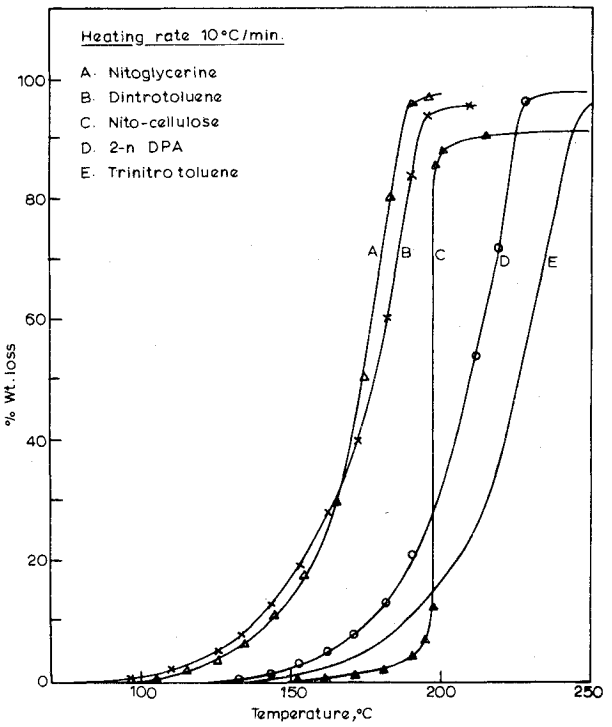

Fig. 4 Thermogram traces of DBP ingredients.

occur in the block which do not occur in the powder sample. If one considers the dip as due to the vaporization of NG, it should be more pronounced in the case of powder, as the surface area is greater compared to the block sample. If one considers that the dip is due to the breaking of long chains to shorter ones of NC, it should be seen more clearly in the NC decomposition curve of DSC. There was no such observation in the DSC thermogram in Fig. 1. Hence, the process taking place seems to be neither vaporization of NG, nor the breaking of NC as assumed by Kirby.[1] It can also be pointed out that the Ayres and Bens' interpretation[3] on the step observed in their thermogram is also wrong, since the amount of ethyl centralite in DBP is so low that it cannot cause such an endothermic effect by just evaporation.

The DSC thermogram of NG is shown in Fig. 5. It is seen that there are two endothermic peaks: the first begins at 145°C and peaks at 187°C; the second peaks at 204°C. It

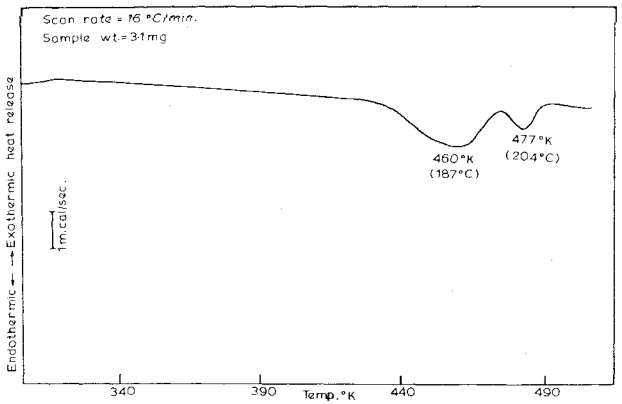

Fig. 5 DSC trace of nitroglycerine.

seems that the first peak is due to the vaporization of NG (reported boiling point around 145°C) and the second peak must be due to the decomposition of the distilled NG collected on the relatively cooler part of the sample cell or unvaporized NG present at the bottom of the pan. Partial decomposition of NG has been shown by Ayres and Bens[3] in their DTA/gas evolution measurement of NG decomposition. Ayres and Bens[3] reported only one endothermic change, which they attributed to the evaporation of NG. The second endotherm in the present investigation has not been reported previously. This may be due to the fact that the pattern of the thermogram depends strongly upon the thermal technique employed and upon whether the sample cup is completely or partially sealed or open. In NG decomposition, this factor will be particularly strong, since NG undergoes both vaporization and decomposition. Most of the reported work on the thermal analysis of NG is about differential thermal analysis (DTA). Hence, it is probable that the second endotherm, which is due to the decomposition of NG, must be taking place in the block sample of DBP, whereas the powder samples give rise only to the vaporization step. In the present work the shoulder in the DSC thermogram appeared around the temperature 204°C at a scan rate of 32°C/min^{-1}. This temperature coincides with the decomposition temperature of NG. Hence, the appearance of the shoulder, although endothermic, may be due to decomposition of NG and not to vaporization. The appearance of the shoulder in the DSC thermogram in the block sample and the absence of the shoulder in the powder sample can now be explained as follows. In the block sample NG vaporizes, but it has to diffuse toward the surface through the NC polymeric matrix before it leaves the system. The diffusion may involve a definite time, and therefore the NG can undergo decomposition in the block sample as a temperature of 203°C is attained, causing a significant amount of heat absorption. In the powder sample, vaporization and diffusion are closely linked and hence no endothermic dip is observed. This also supports the fact that the dip is due to NG decomposition and not to vaporization.

Evidence is also sought from energy (E) calculations of the DBP decomposition from the DSC thermograms. The E values for the endothermic dip on the DSC curve and for the main reaction in the solid block were obtained using Kissinger's method.[4] The value is 31 kcal/mole for the main reaction (corresponding to the exothermic peak) in the block. The E value for the endothermic dip (42 kcal/mole) matches very well with the endothermic decomposition of NG. The E value for the powdered DBP sample was calculated using the same Kissinger method[4] as used for the block sample. The E value is found to be 45 kcal/mole for the main process. It may be seen from the above results that the E value for the main decomposition in the powdered sample (45 kcal/mole) is greater than the E value for the main decomposition observed for the block sample (31 kcal/mole). The most plausible explanation for the decrease (by 14 kcal/mole) in the E value for the main decomposition in the block sample is as follows: the reaction products, formed due to the significant endothermic NG decomposition in the block sample, catalyzes the main decomposition in DBP.

Conclusions

It may be concluded that the decomposition behavior of the block and powder samples of double-base propellant are different, and that this difference arises due to the occurrence of exothermic NG decomposition in the condensed-phase, as compared to NG vaporization in the powder sample.

References

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