Thermochimica Acta, 191 (1991) 131–134
Elsevier Science Publishers B.V., Amsterdam

A study of the thermal stabilities of nitramon propellants by pyrolysis gas chromatography

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(Received March 20 1991)

Abstract

The thermostabilities of nitramon propellants of different compositions were studied by pyrolysis gas chromatography (PGC), and the effect of the components on the pyrolysis profile of the propellant is discussed. Because the pyrolysis behaviour is related to the combustion and, thus, to the ballistic property of the propellant, a propellant can be assessed on the basis of a PGC investigation. The results show that nitroguanidine (NGU) not only improves the thermal stability, but also stabilises the decomposition process of nitramon propellant.

INTRODUCTION

Pyrolysis gas chromatography (PGC) is a powerful tool used in the study of the thermal degradation and characterisation of synthetic polymers, biopolymers and geopolymers [1,2]; it is also a feasible and informative technique for explosive and propellant analysis. Duff [3] has reported a PGC–FTIR method for the investigation of propellant decomposition mechanisms. The identification of explosives and the thermal decomposition of HMX, RDX and NC by PGC have been reported in our previous papers [4–6]. Nitramon propellants are now used worldwide, and their thermal stabilities greatly affect their manufacture and practical use. Zhao et al. [7] have investigated the thermal decomposition of nitramons by thermal analysis methods including DSC and TG. In this work, the thermostabilities of three kinds of nitramon propellant of different compositions were studied by PGC. The influence of their compositions on the pyrolysis profile of the propellants is discussed on the basis of the PGC data, indicating that the PGC results are comparable with those obtained from DSC analysis.

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EXPERIMENTAL

Samples

The main ingredients of the nitramon propellants used in this work are listed in Table 1.

Instruments

The pyrolyser used was a Model 150 Pyroprobe with a platinum coil probe, a quartz sample tube and a heated interface (Chemical data systems, USA), which was attached directly through a stainless steel tube to a GC-5A gas chromatograph with a flame ionization detector (FID) (Shimadzu, Japan), as described in our previous report [6]. A 3 m × 4 mm (i.d.) stainless steel column packed with 8.3% OV-101 on Celite (80–100 mesh) was employed, with nitrogen as the carrier gas. The PGC data were handled by a Model CDMC-1B chromatographic data processor.

Experimental conditions

The pyrolysis temperature (T_p) was set from 523 to 1273 K. The pyrolysis interval (I_p) was 20 s, with the heating rate (R) at "off". The interface temperature was 433 K and the column temperature (T_c) was 433 K. These conditions ensured that the samples were pyrolysed as completely as possible, and that most of the pyrolysates were eluted from the column.

RESULTS AND DISCUSSION

In order to compare the thermostabilities of the three samples, it was assumed that the pyrolysis fractions of the samples (F_p) were 100% at 1273 K after 20 s. The F_p–T_p relationships for the three nitramon propellants and for pure RDX were obtained as shown in Fig. 1, according to the total peak area on each pyrogram at different values of T_p. From these curves, it can be seen that all the nitramons tested are more stable than pure RDX. This is natural as the other ingredients in these samples inhibit the decomposition

TABLE 1

Main ingredients of the nitramons used in this study

Sample	Main components
R-1	NC, NG, RDX, C_2, PB
R-2	NC, NG, RDX, C_2
R-3	NC, NG, RDX, C_2, NGU

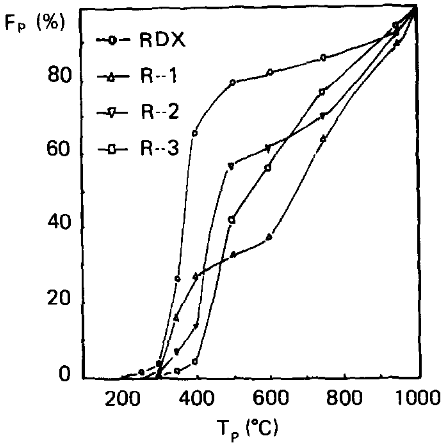

Fig. 1. The pyrolysis fraction of sample (F_p) as a function of pyrolysis temperature (T_p) for the three nitramons and pure RDX.

of RDX. From the point of view of the initial decomposition T_p, R-3 is the most stable, and R-1 the most unstable. This proves that NGU has a pronounced inhibiting effect on the RDX decomposition, so that it can improve the thermostability of R-3. In contrast, PB decreases the stability of R-1.

To make further comparison, the data from Fig. 1 were processed, yielding $\Delta F_p/\Delta T_p$ against T_p curves, as illustrated in Fig. 2. It is obvious that not only the initial decomposition T_p but also the pyrolysis characteristics of the different samples can be obtained from these curves. Although its initial decomposition T_p is the lowest of the three propellants, R-1 has a relatively stable decomposition process because of its lower maximum and shallow "trough" between the two peaks of its curve. However, R-2 has the most unstable decomposition process because of its two greater maxima and

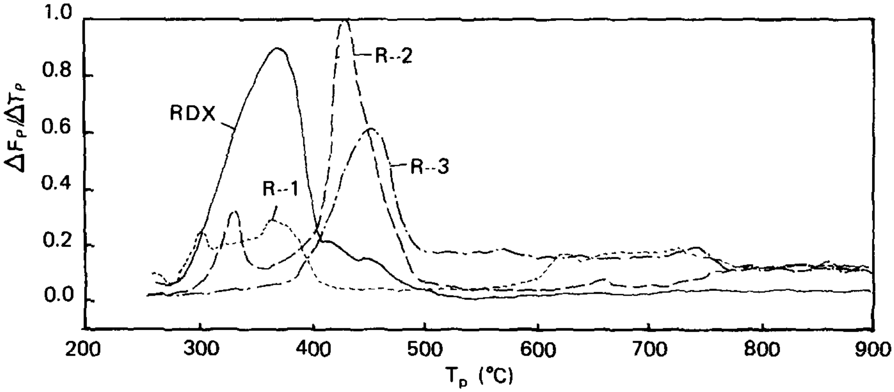

Fig. 2. $\Delta F_p/\Delta T_p$ vs. T_p curves for the three nitramons and pure RDX.

a wide, deep "trough" on its curve. This type of pyrolysis profile is unfavourable to the ballistic property of the nitramon. As compared with R-1 and R-2, R-3 is most favourable to the ballistic property of the nitramon due to its relatively high initial decomposition T_p and because it has only one maximum on its curve. From these results, it can be concluded that PB cannot enhance the thermostability, but can stabilise the decomposition process of the powder, and that NGU can not only improve the thermal stability, but also stabilise the decomposition process. Because the sample was thoroughly pyrolysed under the PGC conditions, the decomposition process is similar to the combustion of the propellant. As a result, R-3 appears to have a consistent ballistic property. These conclusions are the same as those obtained from the DSC analysis [7].

Therefore, PGC is an effective method for the study of the thermal decomposition of multicomponent propellants. Furthermore, the identification of the pyrolysates, which can be achieved by PGC–MS and/or PGC–FTIR, can help us to understand the decomposition mechanisms of the propellants. This is in progress.

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