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INVESTIGATION OF THERMAL DECOMPOSITION OF HMX AND RDX BY PYROLYSIS–GAS CHROMATOGRAPHY

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ABSTRACT

Cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX) were investigated by means of pyrolysis–gas chromatography (PGC) and their pyrogenic products were identified by pyrolysis capillary gas chromatography–mass spectrometry (PCGC–MS). As an application, the composition of mixed explosive composed of HMX and RDX was also determined.

INTRODUCTION

Cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX) are two widely used explosives and energetic ingredients of propellants. There have been many papers on their thermal decompositon [1] and other properties, but until this study, pyrolysis–gas chromatography (PGC) has not been used to investigate them. PGC is a combination of thermal pyrolysis with gas chromatography and has been widely used in both laboratories and industry [2], especially in polymer analysis [3]. In previous works [4–6], qualitative identification of explosives and propellants by PGC, and thermal decomposition of nitrocellulose by PCGC–MS were carried out. It is demonstrated here that PGC can play a significant role in the analysis of explosives and propellants because of its unique advantages of speed, simplicity and sensitivity. In this work, HMX and RDX were pyrolysed at 1023 K for 20 s using PGC, and their pyrogenic products were identified by PCGC–MS. As an example of practical application, the composition of mixed explosive containing HMX and RDX was determined by PCGC.

EXPERIMENTAL

Chemicals

HMX and RDX were industrially procured and were purified by recrystallization in acetone before use, following which no impurity peak appeared

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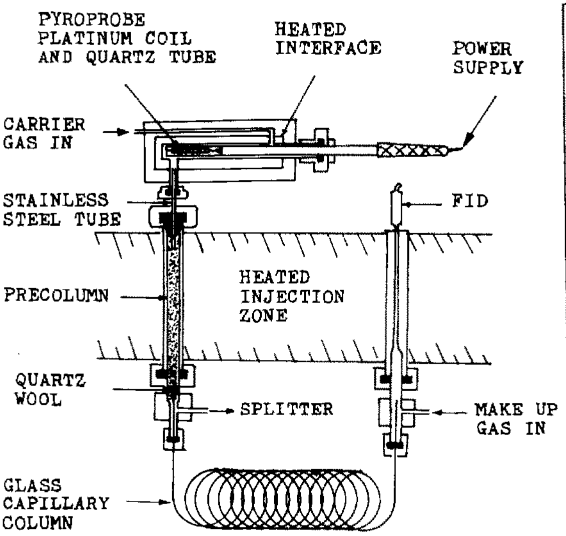
on their liquid chromatograms. HMX and RDX crystals were directly pyrolysed. Mixed explosive samples were prepared by mixing varying amounts of HMX and RDX and dissolving them in acetone to form homogeneous mixtures. The weight percentages of RDX in these mixtures were 0, 20, 40, 60, 80 and 100%. The solvent was first driven out of the sample at 373 K for 20 s in the pyrolyser; then the mixed explosive was pyrolysed after the acetone had eluted from the chromatographic column.

Instruments

The pyrolyser used in this work was CDS 150 Pyroprobe (Chemical Data Systems, U.S.A.) consisting of a heated interface, a platinum coil probe and a quartz sample tube. The interface was connected through a stainless steel tube to a GC-5A gas chromatograph (Shimadzu, Japan) with flame ionization detection (FID). A 3 m × 4 mm stainless steel column packed with 8.3% OV-101 on Celite (80–100 mesh) was employed in the qualitative experiments, and a 50 m × 0.28 mm glass capillary column coated with OV-101 by a static method [7] was used in quantitative analysis. The PCGC system is shown in Fig. 1. Nitrogen was used as the carrier gas. The experimental conditions were as follows: pyrolysis temperature (T_p), 1023 K; pyrolysis interval (I_p), 20 s; heating rate (R), "off"; interface temperature, 423 K; column temperature (T_c), 348 K; carrier gas flow, 20 ml min^{-1}; hydrogen flow, 45 ml min^{-1}; air, 400 ml min^{-1}. Sample size was about 0.03 mg.



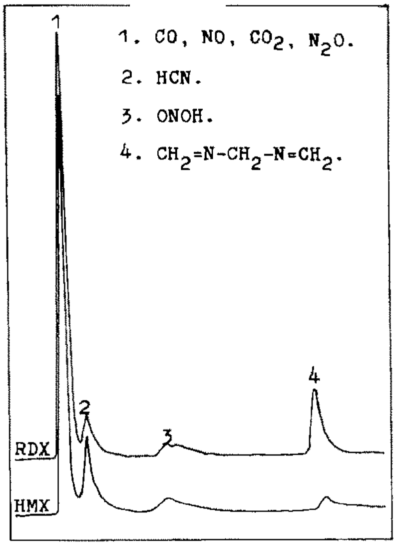


Fig. 1. Schematic diagram of the pyrolysis system.

Fig. 2. Total ion chromatograms of the pyrolysates of HMX and RDX.

The pyrolysates were identified by PCGC–MS using a CDS 190 Pyroprobe with coil probe. The interface of the pyrolyser was directly attached to a Finnigan 1020 GC–MS–DS instrument with electron ionization (EI) source under 70 eV. A 30 m × 0.25 mm fused-silica capillary column coated with SE-54 was used and the carrier gas was helium. The pyrolysis conditions were the same as mentioned above. T_c was 303 K.

RESULTS AND DISCUSSION

Figure 2 illustrates the total ion chromatograms of the pyrolysates of HMX and RDX as well as the identification of the major peaks. Most of the pyrolysis products are the same as the thermal decomposition products reported in the literature [1]. This proves that the pyrolysis of HMX and RDX is comparable with their thermal decomposition. The main difference between pyrolysis and thermal decomposition is that the major nitrogen oxide of the pyrogenic products of HMX and RDX is not NO_2 but NO because NO_2 is not stable at high temperatures.

From Fig. 2 it can be seen that the major pyrolysates of HMX and RDX are the same. This indicates that the molecular structures of HMX and RDX and their pyrolysis mechanisms are similar. In other words, the first step in the pyrolysis of HMX is transformation into RDX. However, the disparities in their structures are also apparent in Fig. 2, i.e. the distribution of each product is different. This shows that HMX and RDX have different thermostabilities. RDX is more stable than HMX because its hexa-atomic ring structure has minimum tension. Therefore, the yield of small molecular weight or volatile pyrolysates of HMX is greater than that of RDX at the same T_p. On the contrary, the yield of larger molecular weight pyrolysates of RDX is greater than that of HMX.

Assuming that the pyrolysis fraction of sample (F_p) is 100% at 1273 K for 20 s, the relationships between F_p and T_p for HMX and RDX are shown in Fig. 3. In this way, the differences between the thermostabilities of HMX and RDX are obvious. When T_p is below 573 K, the pyrolysis of HMX is slower than that of RDX. But when T_p is above 573 K, the situation is reversed and the pyrolysis of HMX is quicker than that of RDX. This proves that the pyrolysis is accelerated with the increase of temperature, and accelerates at a higher rate for HMX than for RDX. Consequently, it can be concluded that PGC is a useful method to study the thermostability, pyrolysis and thermal decomposition of explosives.

The experiments above demonstrated that the major pyrolysates of HMX and RDX are the same, but the distribution of each product is different. Hence, the concentration of each pyrolysate of the mixed explosive composed of HMX and RDX varies with the composition of the mixture as indicated in Fig. 4. It is observed that the areas (peak area normalized to

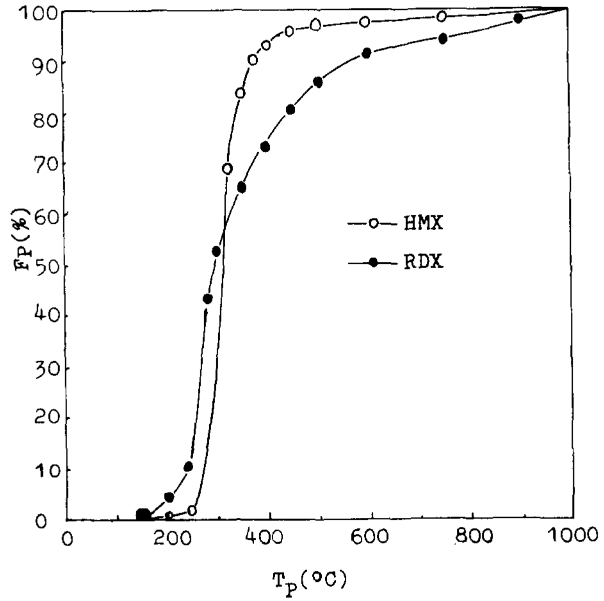


Fig. 3. Relationship between pyrolysis temperature (T_p) and pyrolysed percentage of samples (F_p) of HMX and RDX.

100%) of peak 1 and peak 4 vary regularly, i.e. the content of peak 1 is decreased and peak 4 is increased when the RDX content in the mixture increases. Content changes of the other peaks are not obvious. For this

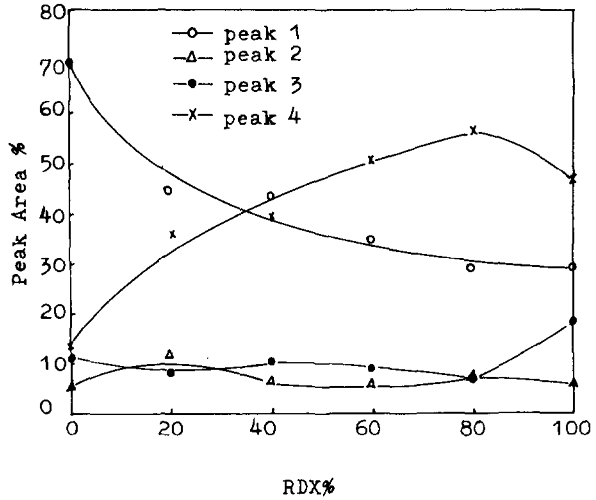


Fig. 4. Relationship between the content of each peak of the pyrolysates and the composition of mixed explosive composed of HMX and RDX. (The peak numbers are the same as those in Fig. 2.)

reason, the composition of the mixed explosive can be quantitatively determined by PCGC using the curve of peak 1 and/or peak 4 shown in Fig. 4, as a calibration. The accuracy and precision of this method are sufficient for the needs of industrial analysis.

CONCLUSION

PGC is a useful tool not only in the study of the thermostability, pyrolysis and thermal decomposition of explosives, but also in the quantitative determination of the composition of mixed explosives. The major nitrogen oxide in the pyrolysates of HMX and RDX is not NO_2 but NO, and NO_2 can catalyse the pyrolysis of HMX and RDX. The pyrolysis of HMX is slower than that of RDX when pyrolysis temperature is below 573 K, and quicker above 573 K.

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