DEGRADATION PROFILE OF PROPELLANT SYSTEMS WITH ANALYTICAL PYROLYSIS/CONCENTRATOR/GC TECHNOLOGY*

S.A. LIEBMAN**, P.J. DUFF, K.D. FICKIE, M.A. SCHROEDER and R.A. FIFER

U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005-5066 (U.S.A.)

Summary

Instrumentation that provides trace organic analysis for complex polymer and nitramine-containing materials has been shown effective in many studies [1—8]. Development of a degradation profile provides concerted analytical information on ingredients alone or in the final formulation matrix. Laboratory studies on a few milligrams of material may be correlated to larger-scale tests and finally to full-scale performance using appropriate simulation conditions [8]. Because of the complexity of the pyrolysis/combustion behavior of materials, multivariate experimental designs are employed to aid in the interpretation. Optimized formulations may then be developed toward desired performance criteria.

Introduction

Propellant performance critically depends on its structure, formulation, and processing conditions. Minor components may be present as unwanted contaminants (such as residual solvents, monomers, etc.) or as important additives that serve to improve processing or combustion behavior of the final product. It is therefore important that accurate, detailed analysis of complex propellants can be efficiently conducted. This report describes the development of a degradation profile of selected propellants emphasizing dynamic headspace analysis (DHS) and pyrolysis gas chromatography (PGC) with packed and capillary column separations. Earlier work, reported in part [7], included other analytical aspects in this program; namely, high pressure liquid chromatography (HPLC), differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy.

Nitramines (RDX, HMX), polymeric binders, and catalysts were examined under thermal conditions that are appropriate for determination of their respective purities and thermal decomposition behavior. In an initial

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**National Research Council Senior Associate.

screening of factors influencing RDX degradation, a five-factor Box-Behnken experimental design was followed. The relative influence of thermal and compositional factors was thus examined.

Experimental

Samples
RDX was purified by recrystallization from acetone and shown by HPLC to have about 0.2% HMX impurity. Reference nitrosamines were supplied through the courtesy of Prof. T.S. Brill, Univ. Delaware, and Dr. J.C. Hoffsommer, NSWC. These and related compounds are suspected RDX degradation products.

Pyrolysis/concentrator/GC analyses
Detailed experimental conditions and method development were previously reported [7] in studies using a Pyroprobe Model 123 (Chemical Data Systems, Inc., Oxford, PA 19363). This system consists of a programmable pyrolyzer interfaced to the Model 320 sample concentrator. For the experimental design series of 46 separate runs, the concentrator internal trap contained 5A molecular sieve (100—120 mesh) at the sample inlet followed by Carbosieve B (60—80 mesh). This trap retained the fixed and reactive gases, water, and other small molecular weight species for analysis on the packed column/thermal conductivity detector (TCD) GC analysis line. Simultaneously, other trapped volatiles were analyzed on the fused silica capillary column/flame ionization detector (FID) GC line. Therefore, each degradation condition resulted in two GC traces as can be seen in Fig. 1.

Dynamic headspace analysis (DHS)
Propellant formulations and components were examined in ~10 mg amounts for trace volatiles (solvents, monomers, impurities, or low-level degradation) at thermal desorption temperatures typically about 120°C for 10—15 min. DHS experiments are conducted in the CDS 320 concentrator by sweeping inert (or oxidative) gas over the sample held in a cartridge within the thermal desorber module. The evolved vapors are trapped on the internal sorbent bed and subsequently pulse-heated from the trap into a heated (250°C) transfer line and injected into the on-line GC for separation and detection as described above. All time, temperatures, and flows are controlled by the microprocessor-based concentrator system.

Pulse and programmed pyrolysis experiments were conducted between 400°C to 800°C in He or air (combustion) in the Pyroprobe Model 123 system. Heating rates ranged from fast (ms) rise times to slow (min) controlled thermal treatments. Since the Pt coil element with the quartz tube insert was used, temperatures set at the controller must be calibrated to determine actual sample temperature. For this series, the latter is about 30°C lower than the former; i.e., setting 230°C results in a 200°C sample

temperature which is just in the RDX melting range of 205°C. Hence, the RDX decomposition was closely followed at the melting point and 10 degrees above and below it for this study.

For both the PGC and DHS experiments, a Perkin-Elmer (Norwalk, CT) Sigma 2000 GC was used with the column oven (containing the Porapak column and the fused silica capillary (OV-1701 WCOT 0.32 mm × 25 m, 0.3 micron film thickness)) programmed for −30°C, 1 min hold, 30°C/min to 200°C, hold 7 min.

Results from DSC, HPLC, and Fourier transform infrared spectroscopy on propellant components and mixtures were obtained in the manner described in the earlier work [7].

Results and discussion

DHS examination of RDX and HMX showed minimal content of volatiles (purification residuals, etc.). However, at a temperature of only 120°C, very low-level thermal degradation was detected in the RDX sample. In general, formulation components may be heated to various time/temperature/atmospheres (simulating process or exposure conditions) to determine short or long-term aging. Likewise, mixtures of ingredients, such as binders, antioxidant, stabilizer, and catalyst were probed to reveal thermally-induced reactions or decompositions. When combined with GC peak identification and kinetic data, such DHS analysis aids formulation optimization. Extension to QC method development is direct with the highly automated concentrator/GC system. Figure 1 illustrates a purity analysis by DHS for ethyl centralite samples from two vendors. Small, but potentially significant differences are noted in both the TCD and FID patterns.

DSC thermal analyses under careful thermal pretreatments showed that the presence of two endothermic peaks in the melting point region for RDX could be used as a rapid purity check. Purified RDX containing less than 0.2% HMX impurity showed only a single endotherm in the 200°C melting point region. Other variations in thermal pretreatments and heating rates resulted in exothermic peaks below 200°C, in addition to the major exotherm above 220°C.

Residues from selected thermal treatments of RDX were examined by FTIR both as solids and as extracts to detect the presence of minor, but significant degradation products. Nitrosamines were specifically targeted by FTIR spectral substraction and HPLC separation methods. Further work should improve detection and identification to permit structural and mechanistic inferences to be made in concert with the pyrolysis/combustion simulation data.

Effects of thermal and reactive conditions on RDX decomposition were monitored in the concentrator/GC system. The multivariate study included the heating rate (three levels), final temperature (three levels), varied at-
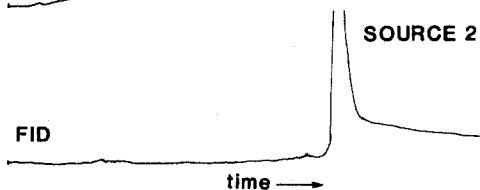
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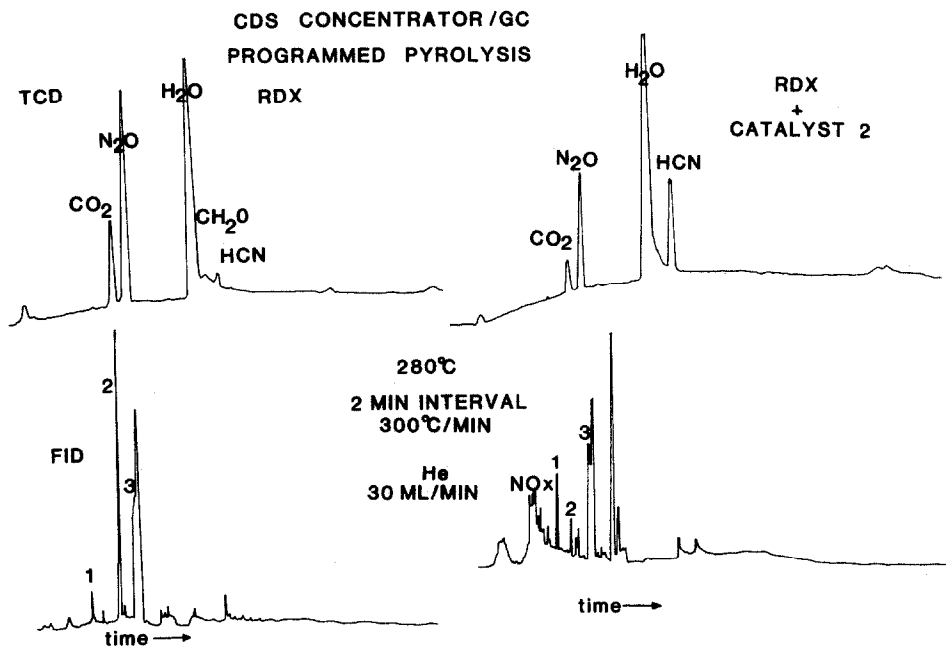
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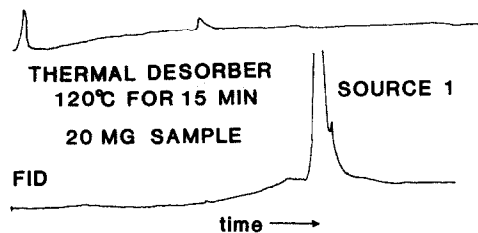
Fig. 1. Dynamic headspace analysis.
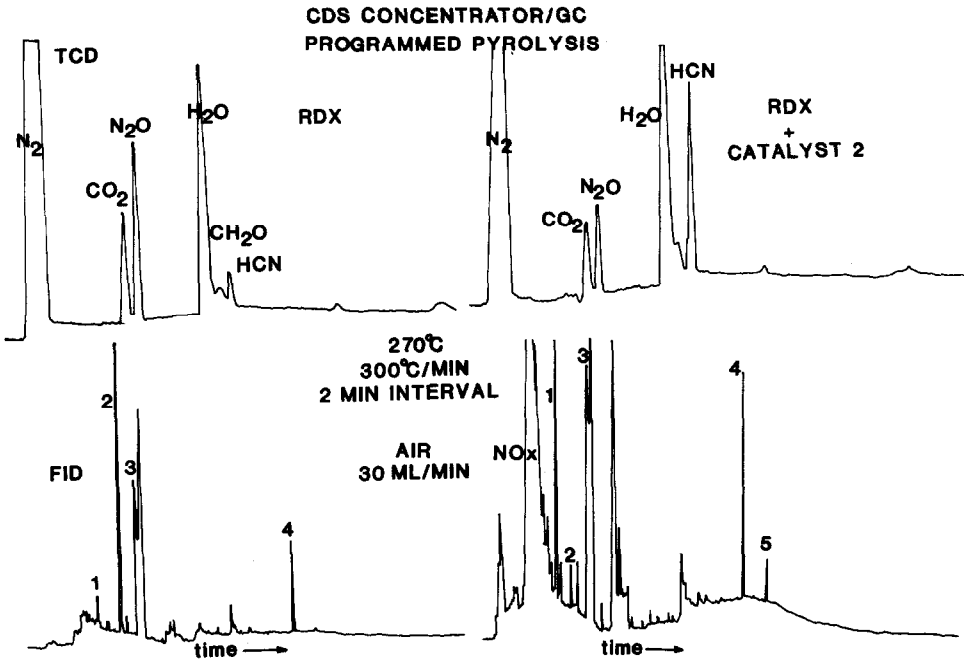

Fig. 2a. Concentrator/GC programmed pyrolysis in He.

CDS CONCENTRATOR/GC
PROGRAMMED PYROLYSIS

TCD

N$_2$ CO$_2$ N$_2$O H$_2$O RDX CH$_2$O HCN

HCN H$_2$O N$_2$ RDX + CATALYST 2 N$_2$O CO$_2$

270°C
300°C/MIN
2 MIN INTERVAL

AIR
30 ML/MIN

FID 2 3 1 4

1 2 3 NOx 4 5

time ⟶   time ⟶

Fig. 2b. Concentrator/GC programmed pyrolysis in air.

CDS SAMPLE CONCENTRATOR/GC
PROGRAMMED PYROLYSIS

TCD

TCD 60°C/MIN TO 360°C
9 MIN INTERVAL

He 30 ML/MIN

FID PROPELLANT A

FID PROPELLANT B

time ⟶   time ⟶

TCD TCD

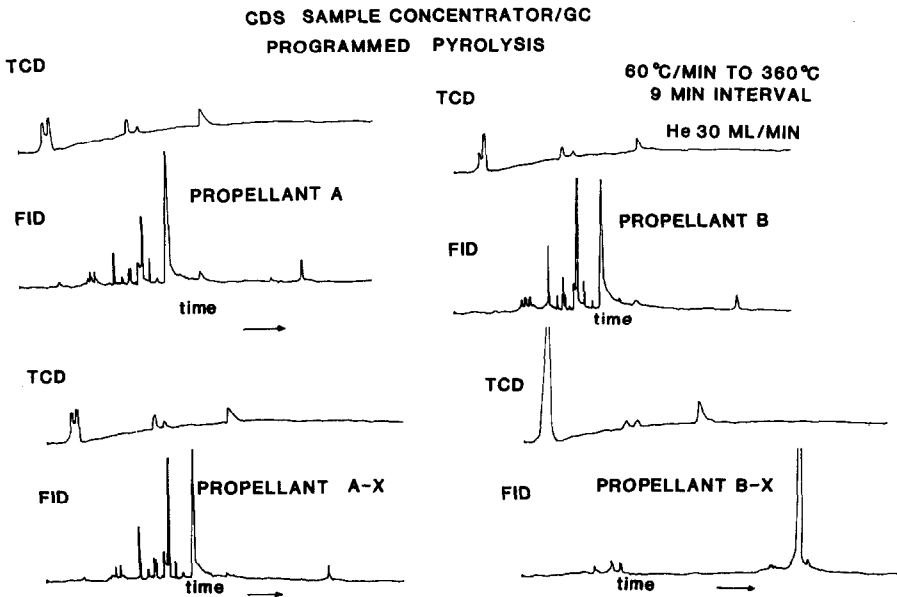FID PROPELLANT A-X

FID PROPELLANT B-X

time ⟶   time ⟶

Fig. 2c. Programmed pyrolysis of four propellants.

mospheres (inert, reactive, oxidative), removal rate of volatile degradation products, and catalytic additives ($NaBH_4$, TaH_2, Ta_2O_5). Major changes in the relative ratios of HCN, CH_2O, and NO_x were seen as a function of these variables. Unidentified peaks 1, 2, and 3 in the FID pattern change significantly with the addition of catalyst 2. Results are shown in Fig. 2 from typical analyses conducted within the total 46 runs in the experimental design. Figures 2a and 2b compare patterns produced from programmed pyrolysis conducted under He and air atmospheres, respectively. Figure 2c gives typical TCD/FID patterns from controlled degradations under He for four propellant samples. Propellant B-X was shown to be significantly different in its behavior from the other formulated propellants. This result correlated with larger-scale comparisons in which propellant B-X exhibited poor ballistic performance.

Conclusion

The integrated analytical instrumentation used in this study has generated detailed information for components and propellant formulations at a laboratory (mini-scale) level. Controlled thermal degradation parameters were chosen to simulate short and long-term exposure conditions and to probe complex, low-level chemical interactions. Sensitivity of nitramines to imposed thermal conditions and to certain catalysts has been demonstrated.

Development of a full degradation profile requires correlation of these mini-scale results to required performance tests in mid-scale and final field assessments. Concerted organic analysis with this selected analytical instrumentation permits detailed, reliable information to be safely established in the laboratory, aids optimization of propellant formulations at the R&D stage, and provides a means to improve processing/QC operations.

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