Thermochimica Acta, 54 (1982) 141–146
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

CALORIMETRIC VALUES OF COMPOSITE SOLID PROPELLANTS

K. KISHORE, V.R. PAI VERNEKER and A. SAMEENA BEGUM

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012 (India)

(Received 30 September 1981)

ABSTRACT

The calorimetric values of composite solid propellant based on polystyrene, polyphenolformaldehyde, poly(vinyl chloride) and carboxy-terminated polybutadiene were determined using combustion calorimetry in order to assess the uncertainities in their measurements. The dependence of the calorimetric values on various propellant composition was obtained. The stoichiometry of oxidizer and fuel in the propellant for complete combustion obtained experimentally were compared with the theoretical stoichiometry calculated based on the oxidizer decomposition.

INTRODUCTION

It is well known that energetics of propellants play a very vital role in the selection of their formulation and performance. A scan of the literature reveals that not much attention has been paid to obtaining reliable calorimetric data. In addition, the values available are on homogeneous propellants [1–5] and very few values have been reported for composite solid propellants [6–9].

In the present work an attempt has been made to determine the calorimetric values of composite solid propellants based on polystyrene (PS), polyphenolformaldehyde (PPF), poly(vinyl chloride) (PVC) and carboxy-terminated polybutadiene (CTPB) as binders with a view to assessing the uncertainties in enthalpy measurements and obtaining their dependence on the propellant composition.

EXPERIMENTAL

Calorimetric procedure

A bomb calorimeter (Toshniwal India) was used in the present work. The jacket temperature of the bomb calorimeter was maintained constant by circulating thermostated water. The Beckmann thermometer was replaced by a ten junction teflon coated (o.d. = 0.01 in. Omega U.S.A.) chromel–alumel thermocouple, one end of which was kept in a Dewar flask filled with water whose temperature was precisely

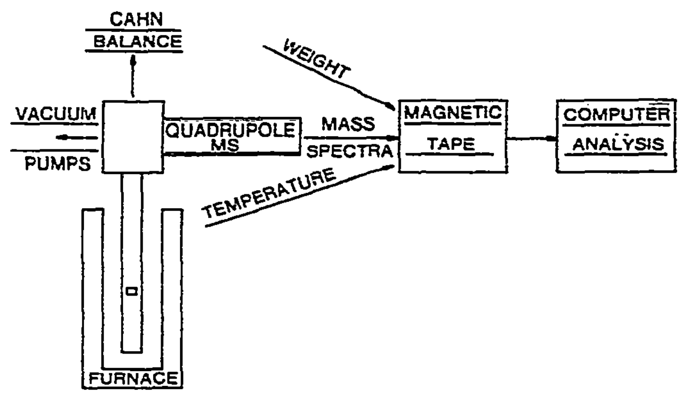
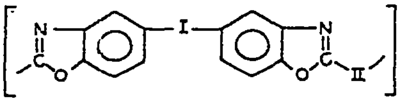


Fig. 1. Schematic of apparatus.

10^{-7} Torr. Samples are heated from 30 to 1000°C at $4\,\mathrm{deg\,min}^{-1}$ with system pressures less than 1×10^{-5} Torr at the maximum rate of product evolution. For each analysis, a quadrupole mass spectrometer (Granville-Phillips Spectroscan 400) completes 100 scans from m/e 1 to 400. Mass spectral intensities, I, sample temperature, T, and weight loss, W, are stored on magnetic tape and subsequently analyzed on a CDC 6600 computer to give plots of I for each m/e, total ionization current, ΣI, W, and first derivative of the weight loss, $\mathrm{d}W/\mathrm{d}T$ as a function of T. The system is shown schematically in Fig. 1. The mass spectrometer is situated with no line-of-sight between the ion-source and the sample hot zone, thus tending to discriminate strongly against condensible products. The present geometry emphasizes the detection of evolved gases, thus oligomers tend to condense on the walls of the hangdown tube without detection. The complex mixture of volatile products is sorted according to the characteristic mass spectral fragmentation patterns and the unique shapes of the intensity–temperature profiles.

Twelve substituted bibenzoxazole polymers with degree of polymerization in the range 20–50 [5], were analyzed in this study. All had been synthesized [6,7] as part of a program to develop new high-temperature elastomers. The polymers have the common structure

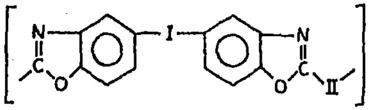


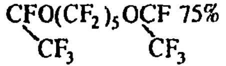
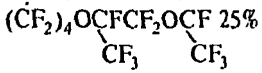
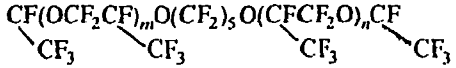
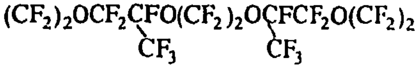
(1)

with substitution I and II at the locations shown, joining the heterocyclic units at the 6-membered and 5-membered rings, respectively. Table 1 summarizes the polymers and assigns an identification number for each. Perfluoroalkyl substitution of the form $-(CF_2)_3-$ or $-(CF_2)_8-$ introduces desirable high-temperature properties; whereas perfluoroether substitution provides enhanced low-temperature elastomeric properties. Ideally, the correct admixture of substitution may yield the best combination of thermal and mechanical properties. A wide range of perfluoroalkylether substitution is represented in Table 1. The simplest, of the form $-CF_2O(CF_2)_2OCF_2-$, is categorized (1, 2, 1) according to the number of CF_2 links between O atoms.

TABLE I

Fluoro-substituted benzoxazole structures



I	II	Identification number
	$(CF_2)_8$	1
$(CF_2)_3$	$(CF_2)_8$	2
$(CF_2)_8$	$(CF_2)_8$	3
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_8$	4
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	5
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_4O(CF_2)_2O(CF_2)$	6
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	 $\underset{CF_3}{CF}O(CF_2)_5O\underset{CF_3}{CF}$ 75%  $(CF_2)_4O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}$ 25%	7
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	 $\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})_mO(CF_2)_5O(\underset{CF_3}{CF}CF_2O)_n\underset{CF_3}{CF}$ $m+n=5$	8
$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	$CF_2(OCF_2CF_2)_mO(CF_2)_5O(CF_2CF_2O)_nCF_2$ $m+n=7$	9
$(CF_2)_3$	$CF_2O(CF_2)_2OCF_2$	10
$(CF_2)_8$	$CF_2O(CF_2)_2OCF_2$	11
 $(CF_2)_2OCF_2\underset{CF_3}{CF}O(CF_2)_2O\underset{CF_3}{CF}CF_2O(CF_2)_2$	$(CF_2)_4O(CF_2)_4O(CF_2)_4$	12

Similarly, $-(CF_2)_4O(CF_2)_4O(CF_2)_4-$ is categorized (4, 4, 4). Using this scheme, substitution of the simple forms (1, 2, 1), (1, 2, 4), (2, 5, 2), (4, 4, 4) as well as other, more-complicated types with CF_3 branches and long perfluoroalkylether chains are represented. The set outlined in Table 1 has sufficient diversity to permit assessment of effects arising from specific changes in the substitution at locations I and II.

RESULTS AND DISCUSSION

General results

The maximum in the degradation rate—as evidenced by the maximum in dW/dT —occurs within the interval 450–600°C for all samples. The data given in Fig. 2 for sample 8 indicates rapid thermal degradation over a fairly narrow temperature range. The full-width-half-maximum (FWHM) of the dW/dT curves never exceeds 70 degrees. Major detected products include COF_2, HF, CO, a series of simple perfluorocarbons, and a corresponding series of fluorocarbons containing one H atom. Some of the other detected products are HCN, CF_3CN and CF_4. Characteristic of the simple perfluorocarbons are a series of fragment ions F^+, CF^+, CF_2^+, $C_2F_3^+$, $C_2F_4^+$, $C_2F_5^+$... having the same temperature dependency. In samples with $-(CF_2)_8-$substitution, the highest mass ions contained 8 C atoms. Samples 1, 2, 3, 4 and 11 having this substitution had characteristically greater abundance of the higher mass ions. Based upon the ratio of the intensities $C_2F_5^+/C_3F_5^+$, these perfluorocarbons are predominantly cyclic [9]. A series of ions CF_2H^+, $C_2F_4H^+$,

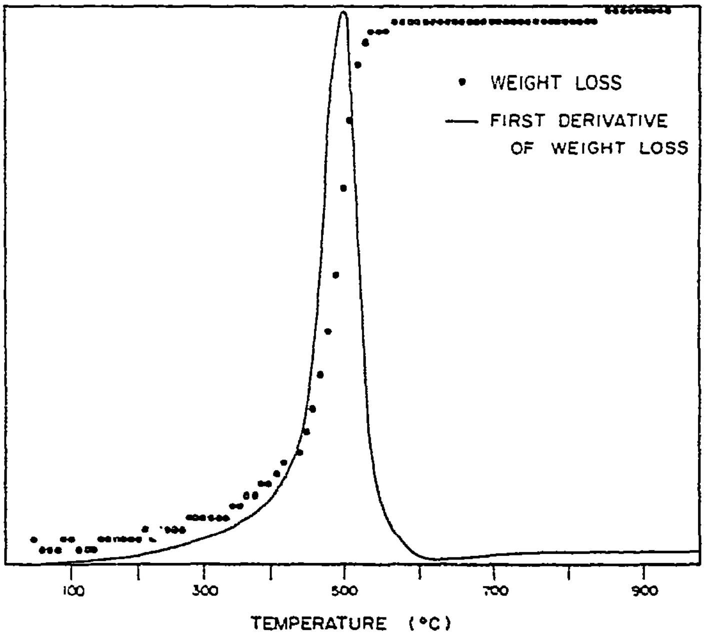


Fig. 2. Dependency of W and dW/dT on T for sample 8 (4 deg min^{-1}).

$C_3F_6H^+$... are detected indicating the release of CF_3H, C_2F_5H, C_3F_7H... during sample heating. The temperature profiles for these products are indistinguishable; however, there are some small, but reproducible, differences in the shape and position of the maximum in the profiles compared with those for the simple perfluorocarbons.

Hydrogen fluoride is a major product (m/e is 10–20% of ΣI) for polymers with $-(CF_2)_n-(n = 3,8)$ substitution at either location I or II. Accompanying HF is SiF_4 produced in the surface reaction

$$4\,HF + SiO_2 \rightarrow SiF_4 + 2\,H_2O \tag{2}$$

The SiF_3^+ ion, identified unambiguously from Si isotope ratios, amounts to only a few percent of the HF^+ ion intensity. Carbon monoxide is released from all samples indicating decomposition of the 5-membered ring. The temperature profiles for CO are very similar to those for HF. Temperature dependencies of several of the volatile products from sample 10 are shown in Fig. 3. Although CF_3CN is not a major product, its presence (CF_2CN^+, CF_3CN^+) gives further confirmation of decomposition of the 5-membered rings. Clearly from Fig. 3, CF_4 is not a primary degradation product. Its temperature profile indicates a rearrangement involving products of the primary degradation.

Carbonyl difluoride is a major degradation product from all samples including those with no perfluoroalkylether substitution. Thus, COF_2 can be formed using the O atom in the 5-membered oxazole ring. The ratio COF^+/COF_2^+ is relatively higher in samples 8, 9 and 12 for which there is extensive fluoroether substitution.

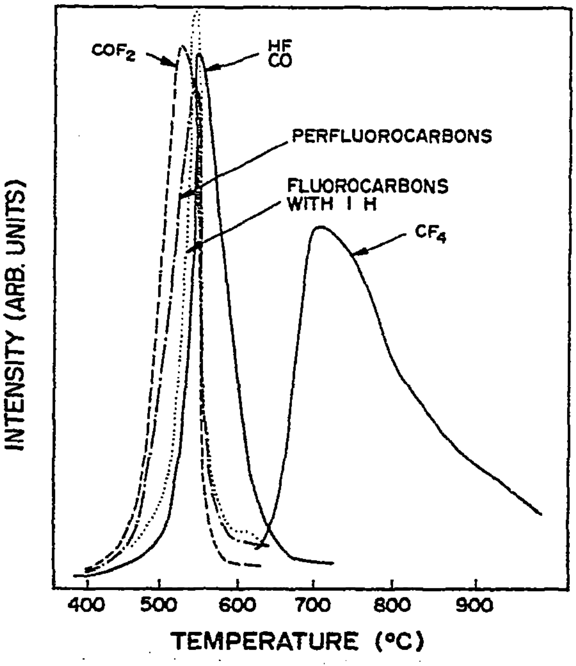


Fig. 3. Dependency of major volatile products on T for sample 10 (4 deg min^{-1}).

This indicates that there are additional sources of COF^+ from higher mass fluorocarbonyl products. Since COF_2 is the first major product to be detected during programmed heating (see Fig. 3), the mechanism for its formation may be important in determining the thermal stability of the polymer samples. This will be discussed later.

No evidence for release of F_2 was obtained; however, its extreme reactivity [10] would lend support to the hypothesis that it reacts before leaving the sample. It is doubtful that F_2 reacts with trapped water according to the reaction

$$2\,F_2 + 2\,H_2O \rightarrow 4\,HF + O_2 \qquad (3)$$

since no product O_2 was detected.

In summary, evolved gas analyses point to primary fragmentation at the substitution sites I and II and at the 5-membered oxazole rings. There is little mass spectral evidence for any products derived from the original 6-membered rings. It is inferred, therefore, that C from the two 6-membered rings remains in the char. On this basis, one would estimate the ratio of char weight to original sample weight to be given by C_{12}/M, where C_{12} is the molecular weight of 12 C atoms and M is the molecular weight of one mer. The experimental and calculated ratios are summarized in Fig. 4 for nine samples for which absolute weight data were available. Considering the experimental uncertainty and the assumptions involved, the correlation between calculated and observed ratios is fairly good.

COF_2 Production

As discussed above, the release of COF_2 occurs at the lowest temperature. Its production is reviewed empirically for the 12 samples in the following discussion. In

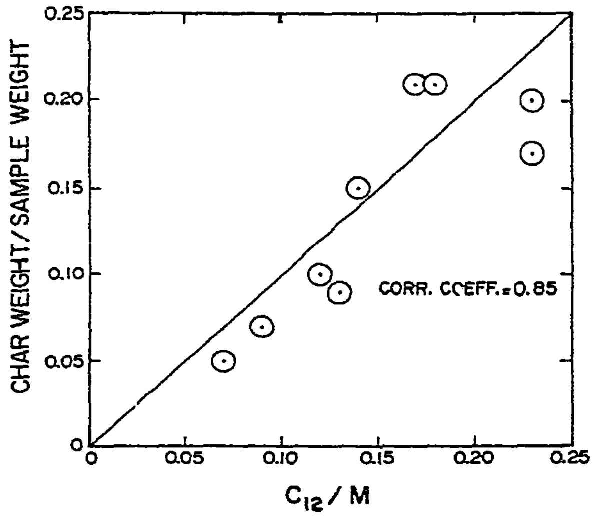


Fig. 4. Plot of the ratio char weight/sample weight as a function of the ratio C_{12}/M where C_{12} and M are the molecular weights of 12 C atoms (144) and one mer of bibenzoxazole sample, respectively. The line is drawn to show the correspondence expected if the char is C originating from the two 6-membered rings.

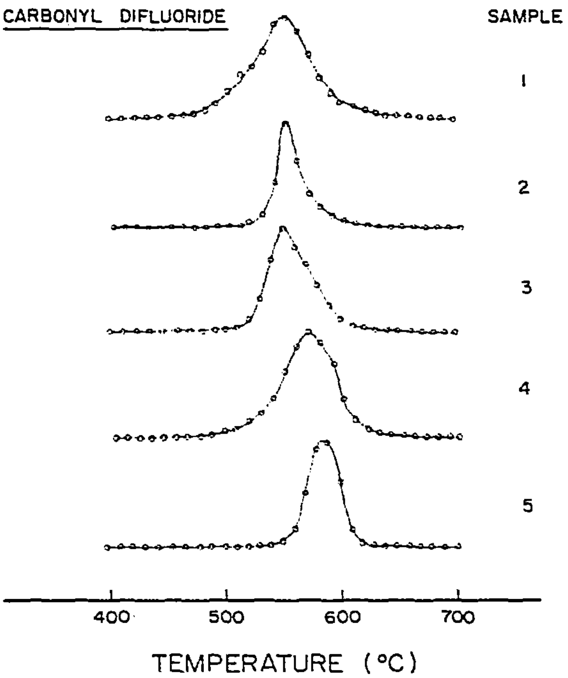


Fig. 5. Temperature dependence of COF_2 production in samples 1–5.

order to study the rate of COF_2 production, the behavior of the molecular ion COF_2^+ (*m/e* 66) with temperature can be considered. Temperature profiles are given in Figs. 5–7. Comparison of samples 1–4, for which the substitution at II is constant, provides a method for assessing the effects of altering substitution at I. Carbonyl

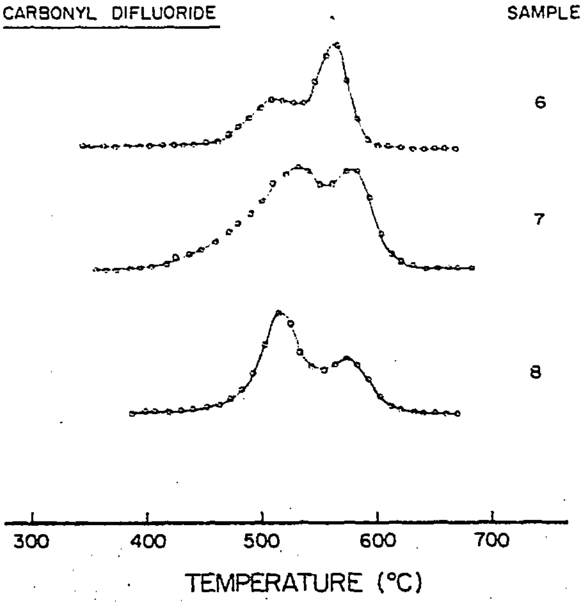


Fig. 6. Temperature dependence of COF_2 production in samples 6–8.

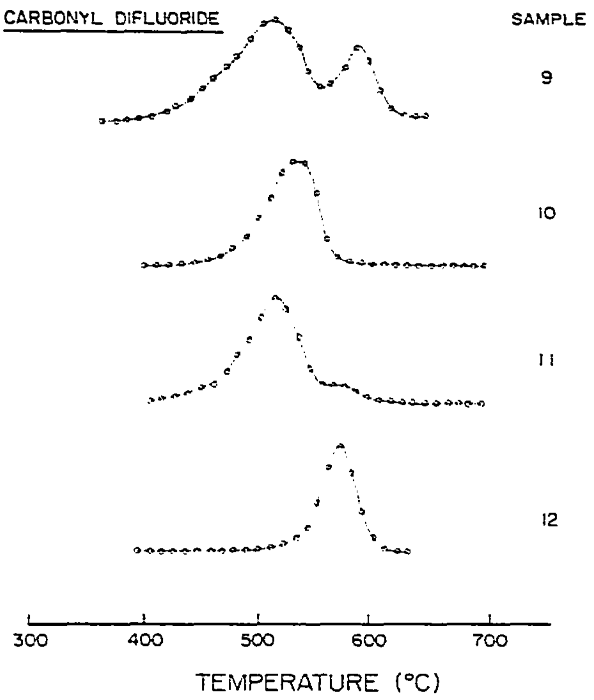
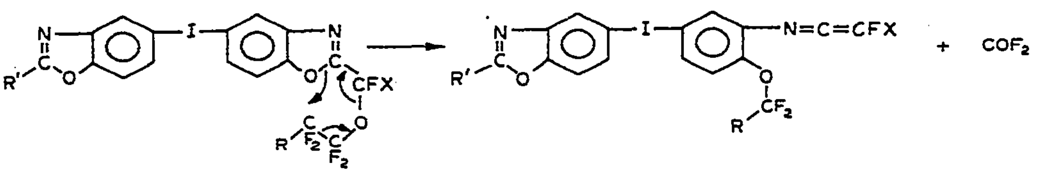


Fig. 7. Temperature dependence of COF_2 production in samples 9–12.

difluoride is released over a narrow temperature interval (FWHM = 60 degrees) with a rate maximizing in the temperature range 550–590°C. The similarity of the profiles suggests that the release of COF_2 is relatively independent of the type of substitution at location I. Similarly, in samples 4–9, substitution at I is of the same form, predominantly (2, 5, 2), thereby permitting an assessment of the effects of changes in substitution at location II. It is apparent from the profiles in Figs. 5–7 that some significant effects are operative. For example, the COF_2 production rates for samples 4 and 5 maximize within the range 550–590°C; however the rates for samples 6–9 pass through two maxima as the temperature is raised. One falls into the temperature interval discussed above, while the second occurs at approximately 50 degrees lower temperature in the interval 500–540°C. Samples 10 and 11 display primarily a single profile falling within the lower temperature interval, but there is a hint of a second process for sample 11 in the vicinity of 580°C. Sample 12 behaves like samples 1–5.

Concerning substitution at II, samples 1–5 and sample 12 fall into one category, while samples 6–11 fall into another. In the first, substitution is of the form $-(CF_2)_n-R-(CF_2)_n-$where $n \geq 2$ and in the second, of the form $-CF_2-O-R-$ or $-CF(CF_3)-O-R-$. This could be summarized by stating that any samples with an O atom β to the 5-membered ring have reduced thermal stability evidenced by the release of COF_2 at approximately 50 degrees lower temperature. We associate the apparent loss in stability with a lower energy process and propose the following rearrangement to explain the observations.



(4)

X = F, CF_3

This step initially releases COF_2 and opens the 5-membered oxazole ring. Once completed, subsequent elimination of fluorocarbons and more COF_2 is to be expected. Symmetric 6-membered ring intermediates are possible only when O is β to the oxazole ring. Symmetry may be the reason why COF_2 is not observed when O is γ to the oxazole ring. We have looked carefully, without success, for evidence of C_2F_4 production from an analogous rearrangement for polymers with $-(CF_2)_8-$ substitution.

The two samples 10 and 11 possessing (1, 2, 1) ether substitution at position II do not display a resolved maximum in the temperature region 550–580°C. Possibly two rearrangements (4) take place to eliminate COF_2, thus reducing the probability of its further release at higher temperatures.

Summary of thermal degradation at heating rate of 4 deg min^{-1}

When the temperature is raised above 400°C, the lowest energy process (4) can commence provided that the substitution at II has an O atom β to the 5-membered ring. The rate for this process increases and passes through a maximum at 500–540°C. As the number of available reaction centers decreases, the rate of COF_2 production drops. At temperatures of 550°C, the C–C, C–F, and C–O bonds within the substitution at I and II acquire sufficient energy to rapidly cleave with the concurrent release of stable perfluorocarbons such as C_2F_4, C_3F_6, C_4F_8... The perfluorocarbon radicals can abstract an H to form HF and a series of stable fluorocarbons CF_3H, C_2F_5H... Other products such as CO, COF_2, CF_3CN, and HCN are also produced at this temperature. The maxima in the rate for these processes are well defined within the temperature interval 550–590°C. Most of the fluorosubstitution and the 5-membered rings are rapidly degraded leading to completion of the primary phase of thermal degradation around 600°C. Secondary degradation products, primarily CF_4, are slowly evolved (see Fig. 3). Mass spectral and thermogravimetric data indicate that the char consists of C atoms that probably originated as the 6-membered rings in the samples.

CONCLUSIONS

Thermogravimetric and evolved gas analyses have been applied to the study of the thermal degradation of a series of 12 perfluoroalkyl- and perfluoroalkylether-substituted bibenzoxazole samples. Thermal stability has been found to depend more strongly upon the type of substitution linking the 5-membered rings than that linking the 6-membered rings. A mechanism has been proposed to account for the loss in thermal stability of some of the samples.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. R.C. Evers for providing the samples and to P.A. Benadum for technical assistance. This research was supported in part by the Air Force Systems Command, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio under Contract F33615-77-C-5175.

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