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Combustion of liquid gun propellants in an adiabatic calorimeter [1]

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Abstract

An accelerating rate calorimeter (ARC) was used to evaluate the effect of chemical composition on the thermal stability and burning rate of the liquid propellants currently being considered for use in medium-to-large caliber guns. The most effective propellants to date have been stoichiometric, aqueous mixtures of hydroxylammonium nitrate (HAN) and the nitrate salt of an organic amine, triethanolammonium nitrate (TEAN). Because these propellants do not burn at atmospheric pressure, but instead react slowly enough to maintain thermal pseudo-equilibrium, such experiments provide information regarding the stability of the mixtures in storage. Thermal stability is directly related to the nitrate ion concentration of the mixtures, and propellant composition can be modified to change energy release rates without affecting thermal stability. Replacement of the TEAN component with *N*,*N*-diethylhydroxylammonium nitrate (DEHAN) increases burning rate as much as 17-fold without adversely affecting thermal stability because the total nitrate concentration of the HAN–TEAN and HAN–DEHAN mixtures is the same.

INTRODUCTION

The use of an accelerating rate calorimeter (ARC) for evaluation of the storage and performance characteristics of liquid propellants designed for use in guns has been described previously [1]. The corrosivity of the propellants and their reaction intermediates makes it necessary that tantalum bomblets be used as sample containers and, because experiments are conducted both at ambient and elevated pressure, gas-tight seals between the bomblets and the stainless steel calorimeter fittings are required. Tantalum is quite soft and galls easily and a thin film of uncured 3145RTV silicone rubber is used as sealant at the dissimilar metal junction. The

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rubber readily withstands the 225°C maximum temperature used and does not interfere with the reactions that take place. All of the special features needed for propellant studies, such as the tantalum bomblets and fast pressure transducers, are added externally and the calorimeter is essentially unmodified, making the technique readily portable.

The gun propellants being investigated are homogeneous, aqueous mixtures of hydroxylammonium nitrate (HAN) and one or more nitrate salts. All of the mixtures are formulated so as to obtain N_2, CO_2 and H_2O stoichiometry. These mixtures will undergo thermal decomposition but will not burn at atmospheric pressure, a situation that greatly reduces the risk associated with the use of these highly energetic liquids. Thermal decomposition relates directly to storage stability, and burning characteristics play a major part in evaluating gun performance. Because either thermal decomposition or burning can be achieved depending on the pressure at which reaction is initiated, the ARC can be used for both types of experimental study. The earliest stages of thermal decomposition of the HAN-based propellants involve only the HAN component [2] and reaction is essentially pressure independent [3], indicating that reaction is occurring in the liquid phase because gas phase or gas–liquid reactions are usually strongly pressure dependent. If impurities are absent, the reaction initiation temperature is inversely proportional to the total nitrate concentration of the mixture [4], again supporting the proposition that reaction is taking place in a homogeneous liquid.

The size of propellant samples evaluated in the ARC is quite small, typically 30 μl, and the effect of sample size on the data obtained must be considered if the apparatus is to be used for evaluation of thermal stability. This problem was thoroughly considered when the apparatus was designed [5] and should be either insignificant or of minor importance if the sample is homogeneous and reaction takes place within the sample rather than in the gas space that comprises the majority of the volume of the sample container. This requirement is so crucial to the use of the technique for thermal stability assessment that experimental verification was felt to be essential. All tests were conducted at atmospheric pressure in order to avoid combustion with its concomitant rapid gas and heat release. Avoidance of a significant pressure increase in the ARC, the result of the gas evolution associated with HAN decomposition, is difficult because of the small-diameter tubing used, and a 20-fold variation in sample size (5 to 100 μl) was the range covered. No variation in reaction initiation temperature was observed. The ARC data obtained in this manner are directly comparable with slow cook-off tests conducted on much larger samples and indicate that the reaction initiation temperature is indeed sample size independent.

Pressurization of the propellant samples results in ignition and combustion when the reaction is thermally initiated. Heat generation is sufficiently fast that adiabatic conditions cannot be maintained and kinetic evaluation of data in which the heat release rate is equated to reaction rate is not valid. In fact, combustion is fast enough to be approximated by a thermal spike and the combustion products produce an exponential cooling curve. Extrapolation of this curve to reaction onset time results in data of some theoretical interest. The ARC is thus a powerful tool for evaluation of propellant performance because it provides a well-controlled and reproducible set of experimental conditions under which reaction is observed. Because heat release and gas generation are coincident, it is reasonable to assume that gas generation rate and burning rate are closely related and variations in gas generation rate can be used as an indicator of propellant performance. This paper addresses the effect of propellant composition on gas generation rates and, by extension, on combustion characteristics.

EXPERIMENTAL RESULTS AND DISCUSSION

A nitrate salt, usually that of an aliphatic amine, must be added to the mixture to produce an N_2, CO_2 and H_2O stoichiometric propellant because HAN is oxygen rich. The rate of gas generation observed when the propellant burns is dependent on the chemical structure of this second salt [6], and the nitrate salts of tertiary amines produce gases more rapidly and at a more uniform rate than do the salts of primary or secondary amines. Product analysis indicates that the salts of primary or secondary amines produce reasonably stable organic intermediates during the earlier stages of reaction. The concentrations of such intermediates are able to build up before finally reacting, and pressure waves and irregular and uncontrollable combustion are obtained [6]. Because tertiary amines are more readily oxidized to small, reactive fragments and thus do not accumulate, they are the organic component of choice. Triethanolammonium nitrate (TEAN) is the amine nitrate component of the propellant mixtures presently in use and an example of a pressure trace obtained in the ARC when burning an HAN–TEAN mixture containing 20% water (the gun propellant LGP1846) is shown in Fig. 1. The smoothness and regularity of gas generation is evident from the figure but the gas generation rate is fairly slow and maximum pressure is not achieved until 32.5 ms after reaction initiation. Because TEAN is the nitrate salt of a tertiary amine, the data presented in Fig. 1 represent the fastest burning rate obtainable with this type of propellant mixture.

In view of the fact that reactions are sequential, with HAN reacting first [2], an attempt to increase the burning rate further was made by introducing the nitrate salt of an alkyl-substituted hydroxylamine, *N,N*-diethylhydroxylammonium nitrate (DEHAN), as a component of the propellant. Because DEHAN is a derivative of HAN, it would be reasonable to expect that it begins reacting at approximately the same time that HAN decompo-

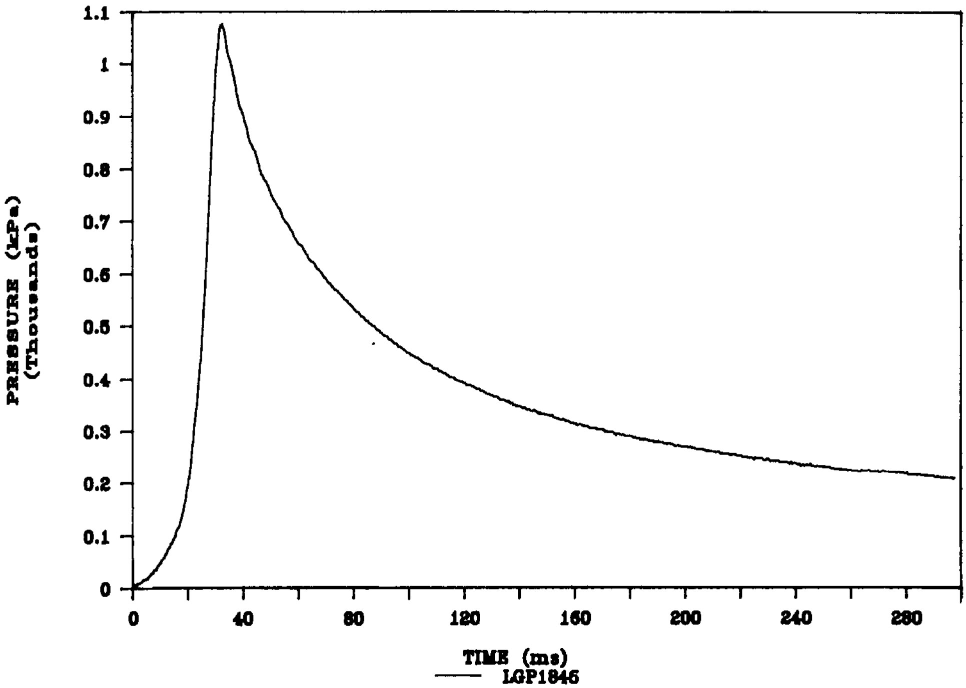

Fig. 1. Pressure-time record of the burning of an HAN-TEAN mixture.

sition is observed, thereby introducing combustible organic fragments into the mixture at an earlier stage of the reaction sequence. The HAN-TEAN stoichiometry requires an HAN : TEAN molar ratio of 7, whereas HAN-DEHAN stoichiometry requires an HAN : DEHAN molar ratio of 5 so that oxygen-balanced mixtures of the three salts covering a wide concentration range can be formulated. Stoichiometric mixtures of HAN, TEAN and DEHAN, each containing 20 wt.% water, were prepared, with the compositions shown in Table 1. The mixture notation indicates the percentage of TEAN replaced by DEHAN.

TABLE 1

HAN-TEAN-DEHAN mixtures (wt.%) used for burning rate studies

Mixture	HAN	TEAN	DEHAN
0	60.81	19.19	0.00
5	60.81	18.23	0.96
10	60.81	17.26	1.93
20	60.80	15.35	3.85
80	60.77	3.84	15.39
100	60.76	0.00	19.24

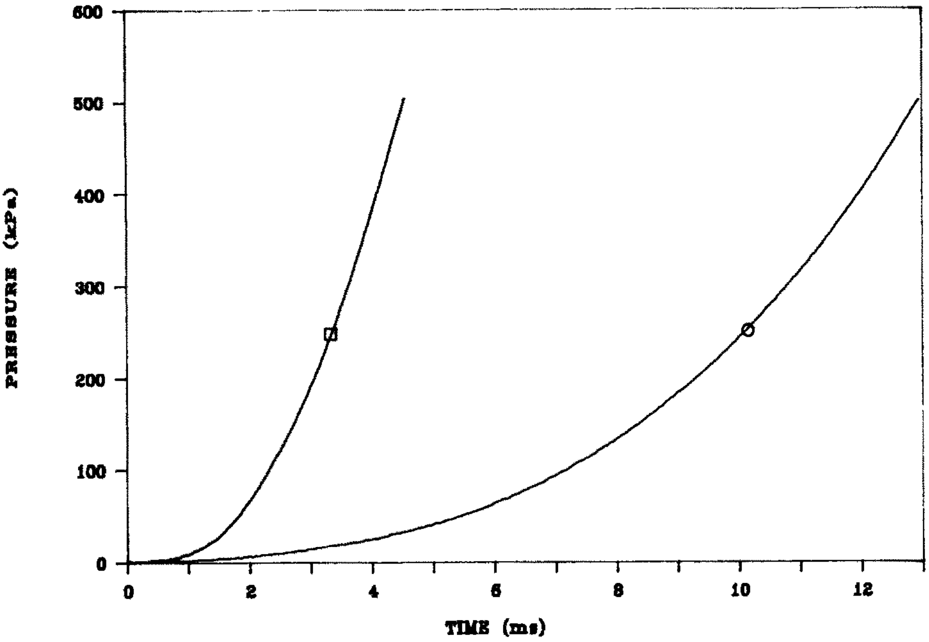

Fig. 2. Pressure–time records of the HAN–TEAN and HAN–DEHAN mixtures: -ө-, mixture 0; □, mixture 100.

All the data were obtained under essentially identical experimental conditions. The tantalum bomblet volume was 1.1 ml and contained a 30 μl propellant sample under 4 MPa nitrogen pressure. The starting temperature was 50°C, increasing in 5°C steps with a 5 min wait and 1 min search between steps. The nitrate concentration range of the propellant samples was 10.5–10.7 M and, as expected, the reaction initiation temperature was the same for all the samples, within experimental error.

The 0–500 KPa portion of the pressure traces obtained with mixtures 0 and 100 are shown in Fig. 2. The equation $P = At^B$ fits the curves very well and the value of A for mixture 100 is 17 times the mixture 0 value. A constant value of B applies to all the mixtures listed in Table 1. The gas generation rate increases as DEHAN replaces TEAN and Fig. 3 shows the gas generation rate, normalized to mixture 0, as a function of the weight fraction of DEHAN in the mixture. The reasonably good fit of the experimental data to this rather simple model implies that the reactions of TEAN and DEHAN proceed independently of one another as the sample burns.

The energy content of the mixtures, calculated with the thermochemistry code BLAKE [7], indicates that energy increases as the TEAN is replaced, the HAN–DEHAN mixture (100) containing 6.3% more energy than the HAN–TEAN mixture (0). However, volumetric impetus (the quantity di-

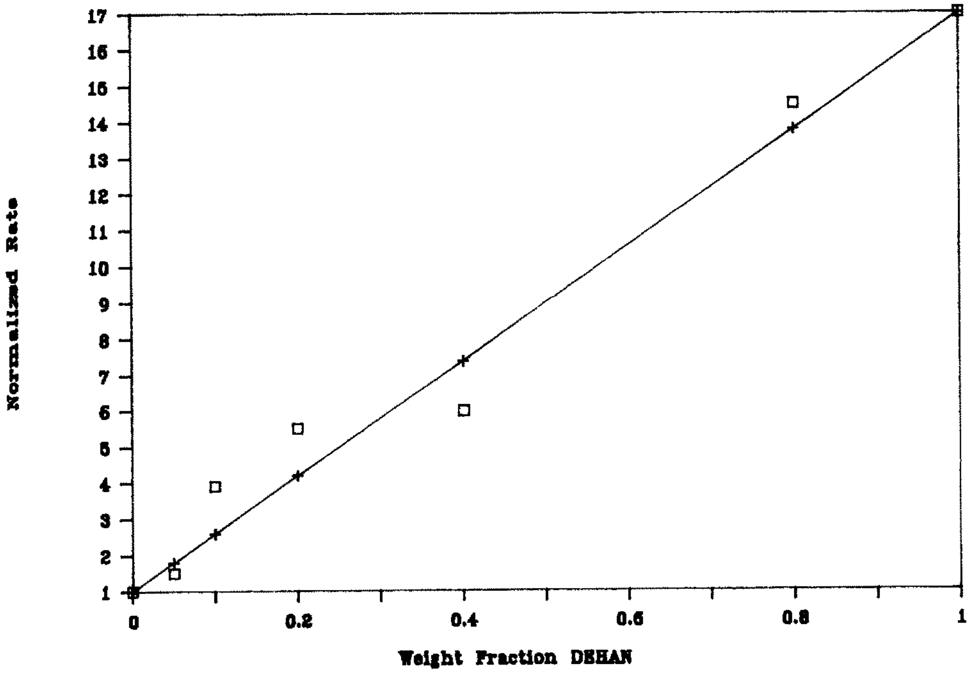

Fig. 3. The effect of DEHAN content on the burning rate of HAN–TEAN–DEHAN mixtures: □, found; +, calculated.

rectly related to the Fig. 3 data because sample volume was kept constant) increases by only 3.3% because the density of the mixtures decreases as TEAN is replaced by DEHAN. The increase in gas generation rate is well above this 3.3% and would indicate that the kinetics rather than the thermodynamics of the process is responsible for the difference in performance.

CONCLUSIONS

Results obtained with an adiabatic calorimeter for HAN–TEAN–DEHAN gun propellant mixtures indicate that the energy required to initiate reaction remains a function of the total nitrate concentration of the mixture. Thus the thermal stability of the mixtures should not be affected as DEHAN replaces TEAN, although the burning rate increases significantly. Because the ARC data show sufficient indication of changed and possibly improved performance, the mixtures are currently being evaluated in larger experimental fixtures that more closely simulate the conditions found in the liquid propellant gun. The size and complexity of these fixtures makes experimentation difficult and quite expensive and underscore the value of the ARC for preliminary evaluation of candidate propellant systems.

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