Thermochimica Acta, 166 (1990) 231–239
Elsevier Science Publishers B.V., Amsterdam

ADIABATIC CALORIMETRY FOR EVALUATION OF THERMALLY INDUCED REACTIONS IN LIQUID PROPELLANTS *

NATHAN KLEIN and CHARLES S. LEVERITT

Interior Ballistics Division, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005 (U.S.A.)

(Received 9 January 1990)

ABSTRACT

The gun propellants that are aqueous mixtures of the nitrate salts of hydroxylamine (HAN) and triethanolamine (TEAN) are homogeneous, ionic liquids and are susceptible to damage by a variety of contaminants. Reaction initiation that results from the absorption of thermal energy is a method for determination of propellant stability. An adiabatic calorimetry based, diagnostic system utilizes a commercially available accelerating rate calorimeter (ARC) that has been modified to make it suitable for use with liquid gun propellants. The effects of contaminants and impurities on reaction onset temperature which is related to safe storage temperature are readily determined using the ARC. In addition to propellant safety studies, the ARC data also provide insight into propellant efficacy, since ignition and combustion are observed. Reaction onset temperatures, as determined with the ARC, are independent of the quantity of material being stored, thereby eliminating the extrapolation from small laboratory samples that is a common uncertainty in many stability evaluation test methods. The presence of nitric acid, a common propellant contaminant, affects both storage stability and propellant efficacy in the gun. The data indicate that storage stability is adversely affected to a much greater extent than efficacy.

INTRODUCTION

Aqueous mixtures of the nitrate salts of hydroxylamine (HAN) and triethanolamine (TEAN) produce gun propellants that are colorless, odorless, homogeneous liquids with a very large liquidus range, solidifying to homogeneous glasses at temperatures below −80 °C [1]. The HAN and TEAN are mixed in such proportion as to produce N_2, CO_2, H_2O stoichiometry at equilibrium. The role of water in the formulated propellant is

---

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

essentially that of solvent and diluent. Thermochemical calculations clearly show the effect both of water and the HAN : TEAN ratio on impetus [2]; and although maximum impetus is obtained in mixtures that are slightly fuel-rich, the propellants are compounded at N_2, CO_2 stoichiometry in order to reduce the probability of secondary muzzle flash. The effect of water content on impetus is far greater than variation in HAN : TEAN ratio. The nature of both the physical and chemical properties is such that one would reasonably expect that the presence of impurities will cause changes to be observed. These changes will probably be deleterious.

Evaluation of the thermal stability of the propellants and of the effects of impurities and contaminants on both storage stability and efficacy are major topics in the overall development of liquid propellant weapon systems. A reasonable value for propellant storage life is 20 years; but because the laboratory investigator usually is faced with time constraints that do not permit such extended studies, techniques must be devised that will produce experimental data quickly and that are suitable for extrapolation. This last point is, by no means, trivial since many of the experimental methods that have been used in the past and are collectively referred to as "accelerated storage testing" do not possess the scientific foundation to permit extrapolation. A second requirement that is frequently placed on accelerated aging tests is that the samples used for testing be much smaller than the propellant packages actually in storage. Although the need for such a requirement is intuitively obvious, one consequence can lead to serious errors in storage lifetime prediction because small samples attenuate the effect of sample self-heating that is the result of slow, exothermic reaction. Since reaction rates increase when temperature is raised, the effects of self-heating are amplified as some function of sample size. Failure to take this effect into account could result in serious overestimation of the thermal stability of the material being evaluated.

Neither HAN nor TEAN is commercially available in the quantities needed to maintain operation of a fielded artillery system, and both are synthesized specifically for use in propellant production. HAN is prepared by the electrolysis of nitric acid [3], and TEAN is prepared by neutralization of triethanolamine with nitric acid followed by isolation and recrystallization. Both components should be pure and free of starting materials before propellant compounding is undertaken, although inadvertent noncompliance with processing procedures creates the possibility that some nitric acid will be present as an impurity in the propellant. Nitric acid is also one of the major products obtained from the thermal decomposition of HAN, which is the first step in the thermal degradation of the HAN-based propellants [4,5]. Since nitric acid also enhances propellant decomposition [6], deterioration of the stored samples should accelerate. Thus, the presence of nitric acid, regardless of its source, could affect storage stability and possibly gun performance.

EXPERIMENTAL DESIGN

Thermal reaction assessment techniques such as differential scanning calorimetry (DSC), which rely on temperature ramp heating of the sample, all suffer from the deficiency that the effect of slow exothermic reactions is suppressed. This effect is supplementary to a similar shortcoming associated with the use of small samples. These limitations have been discussed in some detail [7] and have led to the development and use of adiabatic calorimeters for the evaluation of thermal hazards in chemical systems. Such calorimeters can produce both thermodynamic and kinetic data for chemical systems that react slowly although no commercially available system is fast enough to accurately acquire the kinetics data associated with propellant ignition and/or combustion. An accelerating rate calorimeter (ARC), produced by Columbia Scientific Instruments Corp., Austin, TX, has been modified to make it suitable for certain liquid propellant studies.

The ARC consists of a very well insulated chamber containing several heating elements, that holds a small sample container, usually a spherical bomblet, with a length of tubing attached. The tube serves as sample inlet and provides a means for connection of the bomblet to the rest of the apparatus. A sensitive Nicrosil–Nisil thermocouple (type N) attached to the sample container monitors the evolution of heat from the sample and thus detects the onset of exothermic reaction. If heat production is detected, the chamber heaters are activated and attempt to minimize any temperature difference between the sample and the chamber, thus eliminating heat transfer from the sample container and creating the equivalent of adiabatic conditions. The heaters are programmed so that the chamber and sample are heated to some preset temperature and then held at that temperature for a predetermined time. During the temperature-hold period the output of the thermocouple is monitored; if no heat production is detected, the chamber is heated to a higher temperature. The sequence is repeated until the maximum programmed temperature is obtained. Since the mass and heat capacity of the sample container is known, the amount of heat necessary to produce a change in temperature is readily determined and is one of the criteria for sample size selection. Thermocouple response, typically 0.01° C, determines the accuracy and error band of the measurement. Prudent selection of operating parameters results in data that are independent of sample size and can therefore be extrapolated to large samples.

Selection of a proper sample container was one problem associated with use of the ARC for HAN-based propellants. Passivated ANSI 316 stainless steel had been successfully used in the past, but sample bomblets made of this alloy gave results that were not reproducible. Used bomblets revealed the presence of rust and corrosion in the vicinity of the electron-beam welds used to join the hemispheres and the filling tube, apparently because the welding process changed the composition and/or structure of the alloy enough to make it unusable. A pure metal, rather than an alloy, was selected for the sample bomblet construction. Since tantalum had been shown [8] to be unreactive to the HAN-based propellants and their decomposition products, bomblets, diameter 1.3 cm, with walls 0.76 mm thick were fabricated. Safe operating pressure of the container is 55 MPa, a value that exceeds the limitations of other ARC components. The bomblet is joined to the ARC via a tube fitting, and care is required to assure that this fitting remains gas tight during the entire experimental cycle. The difference in properties between tantalum and the ARC fitting to which the bomblet is joined mandates that tantalum ferrules be used at this connection.

The response time of the bomb thermocouple, the data sampling rate of the ARC electronics, and the maximum output of the heating elements in the calorimeter limit its applicability to reactions that evolve heat at a slow to moderate rate. Although adequate for most thermal stability evaluations, the data sampling and heating rates are too slow to accurately track a rapidly burning propellant. Data related to the combustion event were obtained from a fast, piezoelectric pressure transducer and charge amplifier (Kistler Models 601b and 5004), the output of which was recorded by a digital storage oscilloscope sampling at a rate of 0.05 ms point^{-1}. Reaction initiation temperatures, the heat produced during reaction, and the nature of the reactions that take place when reaction is initiated are required for proper thermal stability assessment. A block diagram of the calorimeter showing the modifications is presented in Fig. 1.

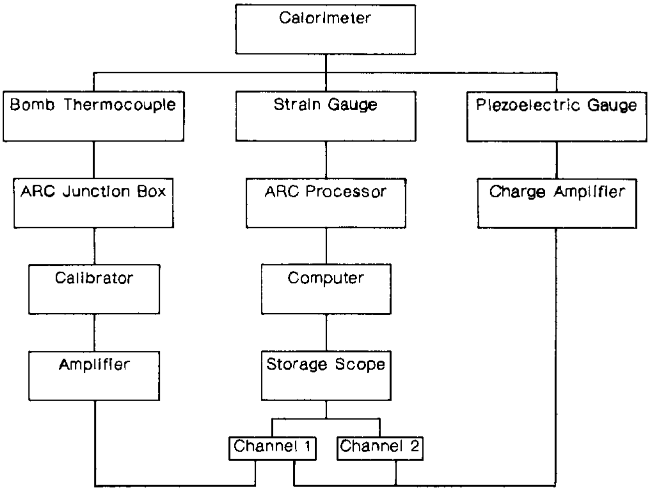

Fig. 1. Calorimeter arranged for fast temperature and pressure recording.

RESULTS AND DISCUSSION

The propellant mixture defined as "pure" is 60.79% HAN, 19.19% TEAN and 20.02% water. Nitric acid content is $\leq 0.05\%$ and the concentration of all transition metals is < 5 ppm. Since the effect of sample size on storage lifetime predictions is a matter of concern, preliminary investigations using this "pure" propellant revealed that reaction initiation temperature became independent of sample size above 0.015 ml.

The HAN-based propellants will not ignite and burn if kept at atmospheric pressure. Instead, decomposition of the HAN component is observed producing water, nitric acid, nitrogen and its oxides. The TEAN is recovered essentially unreacted. In order to observe ignition and combustion, the sample must either be confined (loading density ≥ 0.05 g ml^{-1}) or pressurized.

The first indication of reaction is seen at 118 °C in 0.030 ml samples of acid-free propellant at 20 atm nitrogen pressure, and a vigorous reaction is observed at 122 °C. A typical pressure curve associated with this vigorous reaction is shown in Fig. 2. A pressure maximum is seen 7.3 ms after reaction commences, and a regular oscillation at a frequency of 250 Hz is also apparent. The origin of the oscillation is an acoustic resonance produced in the tubing that connects the bomblet to the piezoelectric pressure transducer since frequency is dependent on length and diameter of the

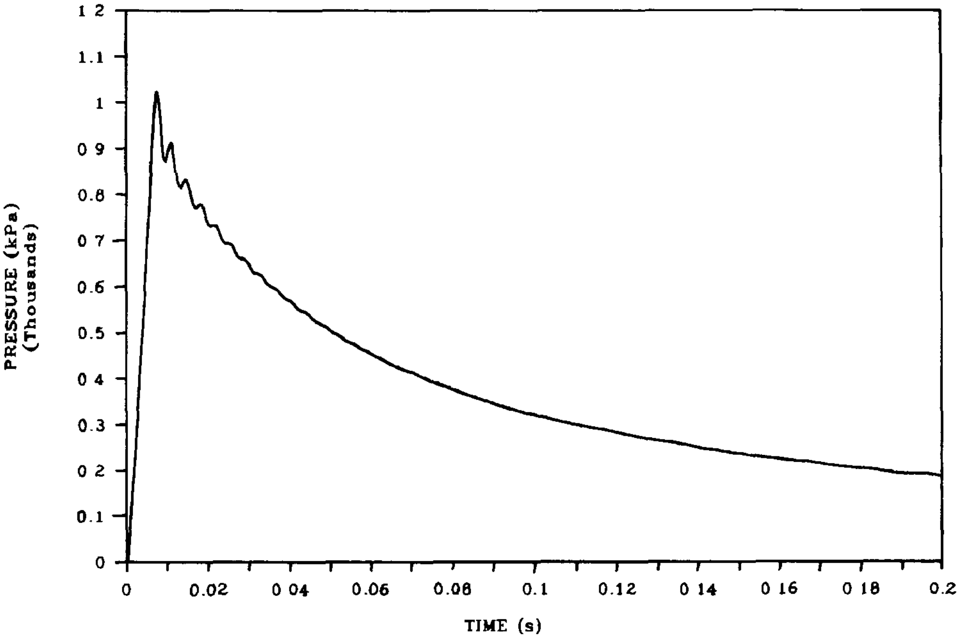

Fig. 2. Pressure–time history of the reaction of an HAN-based propellant in an ARC bomblet.

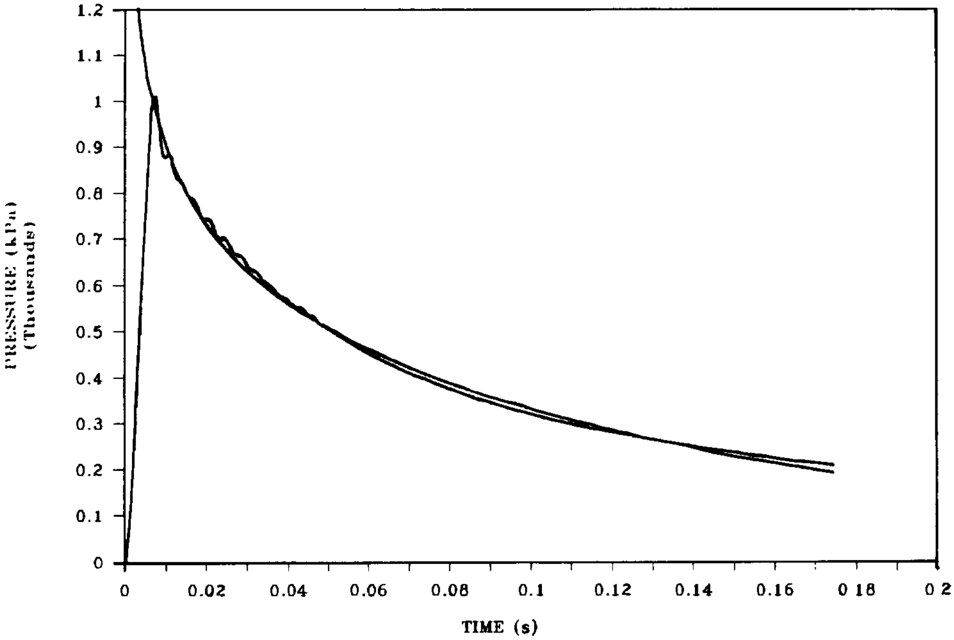

Fig. 3. Filtered and extrapolated pressure history of the reaction.

tubing used. The oscillation is readily removed by filtering the data with a digital, narrow-band, rejection filter. A pressure maximum is seen because the gas that is rapidly evolved is at a much higher temperature than the sample container. Gas and heat evolution is completed by the time the pressure maximum is seen, and the pressure decay, caused by contraction due to cooling, is expressed fairly precisely by a logarithmic function. The maximum pressure recorded will be less than the peak pressure because gas and heat production, although very rapid, is not instantaneous. Extrapolation of the logarithmic cooling curve should result in a value of the peak pressure that is free of the effect of heat transfer during reaction. The effect of processing using a digital filter, and the fit of the pressure data obtained between 10 ms and 175 ms to the function

$$P(t) = A + B\ln(t - t_0) \tag{1}$$

where P is pressure, t is time and A and B are constants (in appropriate units), are shown in Fig. 3. Calculation of peak pressure under these experimental conditions using the BLAKE thermochemical code [9] results in a value of 2.29 MPa, and extrapolation of the cooling curve fit results in a value of 2.24 MPa at $t = 0$. The agreement between extrapolated and calculated values of maximum pressure is indicative of complete combustion, as is the shape of the pressure curve. The data record produced by the calorimeter shows that the temperature rise associated with the exothermic event recorded was 36 °C.

TABLE 1

First observation of heat production in acid contaminated propellant

Acid content (wt.%)	Reaction onset temperature (° C)
0.0	118
0.1	85
0.2	80
0.5	64
1.0	37
2.0	62
5.0	68

Propellant mixtures containing nitric acid were prepared and both their reaction onset temperature and their rate of gas production measured. Thermal initiation temperature data are presented in Table 1. One sees that reaction onset temperature decreases as acid concentration increases, reaching a minimum at 1.0% acid. This would indicate that the thermal stability of the mixtures is decreasing as acid is increased. Since 65 ° C is the long-term storage temperature requirement, propellants containing nitric acid at concentrations of 0.5% or higher are unacceptable for military use.

The pressure curves that are companion to the data in Table 1 indicate that reaction rates and reaction sequences are also changing; and, at the higher acid concentrations, the propellant no longer burns. At acid concentrations of 0.2% or less, the pressure data obtained were indistinguishable from one another indicating that propellant efficacy is unaffected by these small acid concentrations. Although both storage stability and efficacy are adversely affected by the presence of nitric acid in these mixtures, it would seem that the effect on storage stability is more readily evident. Whether variations in gas production are as sensitive an indicator of efficacy as reaction initiation temperature is of storage stability is not known with certainty even though it appears that measured gas production rates correlate well with gun performance.

The ARC produces data that are of considerable value in developing an understanding of the thermal reactions of the propellants. The propellant will not burn at atmospheric pressure, and 20–30 mg samples produce exothermic sequences at 122° C, 180° C, and 227° C. Samples of 10.4 M HAN (the concentration having been selected so that nitrate ion concentration is the same as it is in the propellant) produce exothermic sequences at 122° C and 180° C, and TEAN samples exhibit exotherms at 180° C and 227° C. Samples of nitric acid also produce the 180° C exotherm. The data available suggest that the exothermic reactions observed are the decomposition of the hydroxylammonium ion at 122° C, the decomposition of nitrate at 180° C, and the partial decomposition of the triethanolammonium ion at

227 ° C. TEAN decomposition is incomplete, and a tarry residue is recovered from the bomblet when TEAN or unpressurized propellant is the reacting sample. If the propellant sample is pressurized, a vigorous reaction is seen only at 122 ° C, and water is the only condensed product recovered after the bomblet is cooled.

Propellants containing small amounts of nitric acid are essentially identical to the acid-free samples in terms of the reactions observed. However, at atmospheric pressure, a new feature appears at nitric acid concentrations above 0.5%. The exotherms previously seen are suppressed and are replaced by a slow exothermic reaction that begins at approximately 60 ° C and continues for the duration of the experiment (225 ° C). When pressurized, these mixtures do not burn as vigorously in the ARC as the uncontaminated propellants, and an organic residue is frequently obtained. These data suggest that propellant performance in the gun may be adversely affected by the presence of $> 0.5\%$ acid. Although propellant efficacy data are not usually obtained in accelerated aging studies, the data indicate that the effects of this particular impurity may be more pervasive than simply a lowering of storage life. TEAN is a primary alcohol, and the incomplete evidence presently available suggests that nitrate esters are being produced in the acid-containing propellant samples. Nitrate esters are thermally unstable and their production and thermal decomposition could well account for the slow exothermic reactions observed. A caveat is offered regarding the data obtained from the acid-containing samples. The ARC is designed to detect and follow exothermic reactions, and the detection of the slow exotherm sets the ARC heating rate so that adiabatic conditions are maintained. The heat release rate observed for these samples is dependent on the conditions of the experiment and is not necessarily independent of sample size. It is not clear that the data can be extrapolated to other experimental conditions.

CONCLUSIONS

The ARC, with small modifications, is well suited for evaluation of both the thermal stability and performance of the HAN-based liquid propellants. The presence of nitric acid decreases their thermal stability and, at sufficiently high concentration, adversely affects both stability and performance to the point where the mixtures are no longer suited for their intended use.

REFERENCES

1 M.M. Decker, E. Freedman, N. Klein, C.S. Leveritt and J.Q. Wojciechowski, HAN-based Liquid Gun Propellants: Physical Properties, BRL-TR-2864, November 1987, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

2 N. Klein, C.A. Spiegel and N.A. Messina, The Effect of Oxidizer-to-Fuel Ratio Variation on Liquid Propellant Combustion, Proc. 1987 JANNAF Prop. Meet., Vol. I, CPIA Pub 480, Chemical Propulsion Information Agency, Laurel, MD, 1987, p. 201.

3 J.H. Barnatt, R.L. Dotson and J.A. Leistra, Development of a Production Process for Hydroxylammonium Nitrate by Electrolytic Reduction of Nitric Acid, Final Report for Contract DAAA 15-87-C-0007, March 1988, Olin Corp., New Haven, CT.

4 N. Klein, R.A. Sasse and K.E. Travis, Reactions of Liquid Monopropellants at Atmospheric Pressure, BRL Report No. 1855, February 1976, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

5 N. Klein, R.A. Sasse, R.L. Scott and K.E. Travis, Thermal Decomposition of Liquid Monopropellants, BRL Report No. 1970, March 1977, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

6 N. Klein and R.A. Sasse, Ignition Studies of Aqueous Monopropellants, ARBRL-TR-02232, April 1980, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

7 D.L. Townsend and J.C. Tou, Thermochim. Acta, 37 (1980) 1.

8 M.M. Decker, E. Freedman, N. Klein, C.S. Leveritt, J.Q. Wojciechowski, O. Briles and L. Joesten, Compatibility Assessment of HAN-Based Propellants, Proc. 1987 JANNAF Prop. Char. Meet., CPIA Pub 470, Chemical Propulsion Information Agency, Laurel, MD, 1987, p. 119.

9 E. Freedman, personal communication.