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THERMOCHEMICAL EVALUATION OF ZERO-ORDER PROCESSES INVOLVING EXPLOSIVES

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INTRODUCTION

An accidental explosion occurred at a government laboratory in March 1960 during a pressing operation involving a mixture that contained both lead and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane). The incompatibility between Pb and HMX had not been observed with the vacuum stability test, but it can easily be observed with a DTA test. RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) is the major impurity in HMX, and the solidus temperature of the RDX/HMX system appears to be near 180°C. A sharp exotherm is observed in the DTA record at about 180°C when Pb is added to impure HMX. Explosions are often obtained in the DTA apparatus at higher temperatures with HMX/Pb mixtures.

Both RDX and HMX decompose in the liquid phase to produce largely formaldehyde and N₂O. Observations on the HMX/Pb system indicate that one of the major contributions made by Pb to the overall reaction is a secondary reaction loop involving N₂O and formaldehyde. N₂O oxidizes Pb, and lead oxide oxidizes formaldehyde. The redox cycle increases the overall energy evolution rate during thermal decomposition. The heterogeneous reaction should be zero order, the rate depending on the surface area of the catalyst. The (impure) HMX/Pb reaction is extremely complex, but a zero-order reaction can be observed.

Several heavy metals other than Pb have been found to be dangerously incompatible with RDX and HMX, and it has become important to develop a general method for making quantitative predictions of the thermal hazards of such systems. All heavy metals with close-lying oxidation states appear to be incompatible with the nitramines. The metals, oxides, and salts of these elements all appear to be equally incompatible with HMX and RDX.

Although it has long been possible to detect incompatibilities between metals and explosives, it has not been possible to produce quantitative predictive models for hazards. We report here methods for identifying zero-order reactions and assessing their hazard potential. The general method proposed involves the following steps: (1) production of isothermal DSC rate curves, (2) identification of the parts of the reactions that obey a zero-order rate law by producing "order plots" of the rate data, (3) measurement of zero-order rates at different temperatures, (4) normalization of the rates to identical surface areas of catalyst, (5) determination of kinetics constants from an Arrhenius plot of the zero-order rate data, (6)

measurement of critical temperatures for known mixtures with a time-to-explosion test, and (7) production of a mathematical predictive model for the critical temperature of any size, shape, and composition of mixture.

EXPERIMENTAL

All of the rate measurements were made with a Ferkin-Elmer Model DSC-1B differential-scanning calorimeter. General methods for the production and evaluation of isothermal DSC rate curves are described in an accompanying paper by Janney and in reference [1]. We found that an 8-mg sample of 1/1-HMX/Pb was a convenient size for measurements on range 8 of the DSC at 535 K. We filled the excess free volume in the sample cell with aluminum-disc spacers.

A description of the time-to-explosion test apparatus and the general method for the measurement of a critical temperature (T_c) can be found in reference [2] and the accompanying paper by Janney. The critical temperature is the lowest constant surface temperature at which a material of a specific size, shape, and composition can self heat to explosion.

Samples. The HMX sample was obtained from the Holston Defense Corporation, Kingsport, TN, and it was identified as Lot 920-32. It is relatively pure (<0.5% RDX). The lead powder is nominally spherical and shows a measured surface area of $0.11 \text{ m}^2 \text{ g}^{-1}$.

RESULTS AND DISCUSSION

Figure 1 shows a comparison between an isothermal DSC rate curve obtained from the HMX sample alone and a rate curve obtained from the same amount of HMX with an equal volume of Pb powder added. The HMX sample shows an "autocatalytic-type" rate curve. Its initial rate is relatively low, but the rate increases with time. The HMX/Pb rate curve shows a significant initial rate, and the rate does not change greatly for approximately 300 s. The nearly constant rate indicates a significant contribution from a zero-order reaction.

Figure 2 shows the order plots obtained from the rate curves of Figure 1. The fraction decomposed at any time, α , is determined by integration of the rate curves. The slope through any range of reactant depletion is the reaction order for that reaction regime. Reaction regimes showing negative slopes or curved lines on the order plot involve complexity. Causes for complexity can be chemical autocatalysis, melting with decomposition, and/or solid-state reactions. Suitable autocatalytic or nucleation-growth rate laws must be used for the evaluation of reaction regimes showing complexity.

Figure 2 shows that the first 15% of the energy from the 1/1-HMX/Pb system is evolved according to a zero-order rate law up to $\ln(1 - \alpha) = -0.16$. Experiments with HMX samples of different purity indicate that the zero-order process is a result of reactions involving the RDX/HMX mixed melt. The rate is a function of the surface area of the catalyst, and the extent is a function of the amount of impurity (RDX) present.

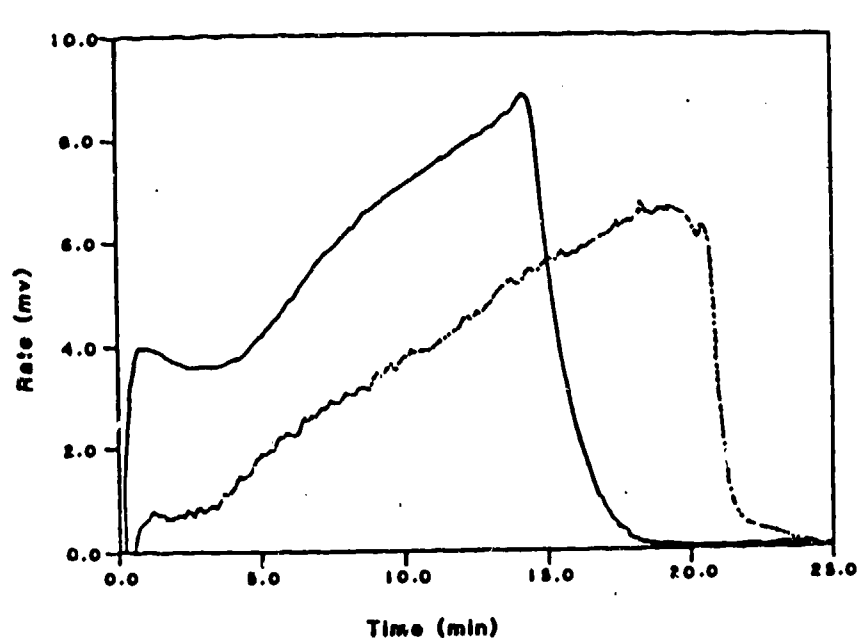


Figure 1. Isothermal DSC rate curves for 1.272 mg HMX (dashed) and 7.761 mg 1/1-HMX/Pb, containing 1.242 mg HMX, (solid) at 535 K. Curves normalized to 1 mg HMX at DSC Range 1.

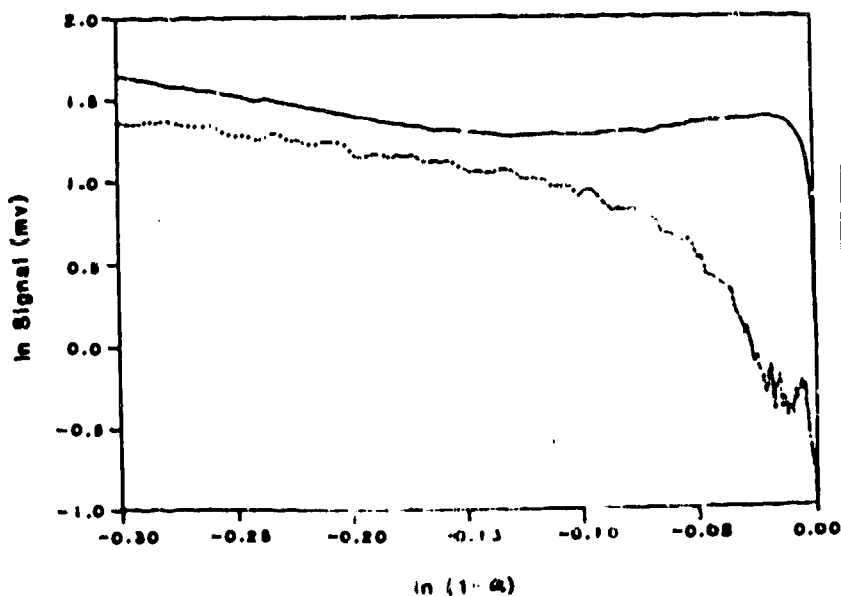


Figure 2. Order plots of rate data from Figure 1. HMX (dashed) and 1/1-HMX/Pb (solid) to 26% depletion [$\ln(1 - \alpha) = -0.3$].

We found that we could not make suitably homogeneous mixtures of HMX and Pb; composition varied from sample to sample. Consequently, considerable scatter was observed in the absolute rate data obtained from the different samples, but the overall characteristics of the rate curves remained the same. As a result of the data scatter, we cannot present accurate values for the kinetics constants for the zero-order reaction; however, the values obtained are in the RDX and HMX region. Our preliminary numbers for the zero-order reaction are the following: $E = 52 \text{ kcal mole}^{-1}$ and $Z = 1.2 \times 10^{18} \text{ s}^{-1}$. Our critical temperature predictive models for RDX and HMX are based on the following values: RDX, $E = 47.1 \text{ kcal mole}^{-1}$ and $Z = 2.02 \times 10^{18} \text{ s}^{-1}$; HMX, $E = 52.7 \text{ kcal mole}^{-1}$ and $Z = 3 \times 10^{19} \text{ s}^{-1}$. The important observation is that Pb does not catalyze the elementary decomposition reaction during the zero-order process: there is no significant reduction in E . The only significant effect must be the increased energy-evolution rate that results from the heterogeneous redox cycle.

RDX and HMX are partially miscible in the solid state, and they show an apparent eutectic composition near 62.5 wt.% RDX. The heat of formation of RDX is $14.7 \text{ kcal mole}^{-1}$; that for HMX is $17.9 \text{ kcal mole}^{-1}$. The heat of reaction of the mixed melt should be 1075 cal g^{-1} when the products are $\text{H}_2\text{O}(\text{g})$, N_2 , and CO . The decomposition of RDX in the mixed melt should be the predominant reaction; therefore, RDX kinetics should best model the rate at moderate temperatures.

The thermal conductivities of HMX/Pb systems have not been measured; however, measurements have been made on RDX systems containing granular Fe and Cu. The thermal conductivity of metal loaded explosives increases slightly as the metal content is increased, depending on particle size and shape. Assuming the same slope for the thermal conductivity versus volume-percent-metal functions for RDX and HMX systems, we have used the following expression to estimate thermal conductivities for HMX/Pb mixtures:

$$\lambda = 9 \times 10^{-4} V + 1 \times 10^{-3} \quad (1)$$

where λ is the thermal conductivity in $\text{cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ and V is the volume fraction of metal.

Since the presence of Pb appears to convert an RDX/HMX melt nearly quantitatively to H_2O , CO , and N_2 without making an appreciable change in the rate of the elementary reaction, we can estimate a heat of reaction and kinetics constants for the zero-order reaction. Given those values, thermal conductivity, and density, we can produce a predictive model for catastrophic self heating according to the Frank-Kamenetskii equation [3],

$$\frac{E}{T_c} = R \ln \left[\frac{a^2 \rho Q Z E}{T_c^2 \delta \lambda R} \right] \quad (2)$$

where E and Z are the Arrhenius activation energy and pre-exponential, R is the gas constant, T_c is the critical temperature, a is a dimension (radius of a sphere or infinite cylinder or half thickness of an infinite slab), ρ is the mass of explosive per unit volume of Q is the heat of reaction, λ is the thermal conductivity, and δ is a shape factor (0.88 for infinite slabs, 2.0 for infinite cylinders, and 3.32 for spheres).

If predictions made from the model agree with experimental critical temperatures for HMX/Pb systems of known size and shape, it can be assumed that the increased energy-evolution rate during the zero-order process is responsible for the observed hazard. It should also be possible to use the predictive model for predicting critical temperatures for other sizes and shapes of HMX/Pb charges under similar confinement. A comparison between experimental and predicted values is shown in Table 1.

TABLE 1. CRITICAL TEMPERATURE AS A FUNCTION OF LEAD CONTENT FOR HMX/Pb SYSTEMS.

Sample	a (cm)	Expt. T_c ($^{\circ}\text{C}$)	Calc. T_c ($^{\circ}\text{C}$)
HMX	0.048	257	---
95/5-HMX/Pb	0.041	222	222
75/25-HMX/Pb	0.046	226	227
50/50-HMX/Pb	0.045	239	239

Compositions are given in volume percent. The experimental time-to-explosion method 2 can be modeled as a slab ($\delta = 0.88$). Estimated thermal conductivities used in the predictive model are the following: for 95/5, 1×10^{-3} ; for 75/25, 1.2×10^{-3} ; and for 50/50, 1.5×10^{-3} . The crystal density for HMX is 1.91 g cm^{-3} , and all of the samples were pressed to about 90% maximum density. Therefore, the following density values were used in the predictive model: for

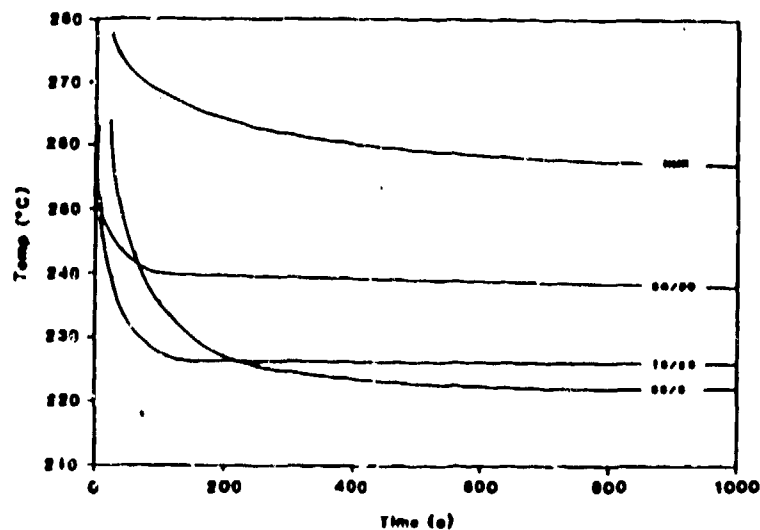


Figure 3. Time to explosion as a function of temperature and lead content for HMX/Pb systems.

95/5, 1.63 g cm⁻³; for 75/25, 1.3 g cm⁻³; and for 50/50, 0.86 g cm⁻³. Heats of reaction were simply scaled according to the volume percent of HMX, as follows: for 95/5, 1021 cal g⁻¹; for 75/25, 806 cal g⁻¹; and for 50/50, 537.5 cal g⁻¹. The following kinetics constants for the decomposition of RDX in the liquid phase were used: $E = 47.1 \text{ kcal mole}^{-1}$ and $Z = 2.02 \times 10^{18} \text{ s}^{-1}$. As a result of the log function, predictions are not very sensitive to moderate errors in ρ , λ , and Q .

The experimental time-to-explosion curves are shown in Figure 3. It can be seen that the samples that contained lead had reduced times to explosion as well as lowered critical temperatures.

We normally determine kinetics constants in a self-generated atmosphere at ambient pressure (approximately 76 kPa in Los Alamos). The time-to-explosion test is run in a self generated atmosphere under significant confinement. A lack of agreement between predicted and experimental values is usually a result of pressure effects on secondary gas-phase and/or heterogeneous reactions. When agreement is achieved, it can be assumed that the system modeled is not very sensitive to pressure effects. In the case of the HMX/Pb system, the secondary reactions with Pb must be extremely fast; however, heavily confined systems may be significantly more hazardous than predicted by our model.

CONCLUSIONS

We believe that quantitative predictive models can be made for thermal hazards of explosives systems involving zero-order reactions. The zero-order reactions can be identified by making order plots of isothermal DSC rate data. Kinetics constants can be measured for the zero order reactions of complex processes (if homogeneous mixtures can be produced), and critical temperatures can be predicted. Predictions can be tested against experimental values.

Incompatibilities between explosives and materials that provide hazardous zero-order contributions to the self-heating process can easily be detected with a time-to-explosion test. However, because increasing the amounts of catalyst will increase the dilution as well as increasing catalyst surface area, tests at different compositions are required for greatest confidence. Predictions of hazards for sizes and shapes other than those tested require a kinetics-based predictive model.

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