Safe Operating Temperatures for Pressurized Alkaline Hydrolysis of HMX-Based Explosives

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Alkaline hydrolysis is used to convert high explosives to nonenergetic, aqueous compounds. Base hydrolysis of high explosives is exothermic (ΔH_{RXN} = 2.3 kJ/g), and thermal runaway of the reaction is a possibility at elevated temperatures (>120 °C) where the rate of reaction is large. Thermal runaway could result in an accidental detonation of the energetic material being treated, so safe operating parameters for base hydrolysis need to be determined. To measure the safe operating temperature, base hydrolysis was performed at temperatures ramped from 20 to 300 °C. The results show that PBX 9501 molding powder detonates at a 185 °C bulk temperature in 1.5 M NaOH with a 4.5 °C/min linear temperature ramp and no agitation. The reaction of pressed PBX 9501 with 0.75, 1.5, and 3.0 M NaOH and water and both pressed and nonpressed PBX 9404 with 0.75, 1.5 M, and 3.0 M NaOH and water did not produce a detonation with a 4.5 °C/min linear temperature ramp. A previously developed reaction rate model was used to show that thermal runaway should occur when the base hydrolysis reaction rate reached a maximum at a bulk temperature between 185 and 225 °C.

Introduction

HMX-based (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) PBX 9404 and PBX 9501 are U.S. Department of Energy (DOE) explosives developed at Los Alamos National Laboratory for nuclear ordnance. Because of both stockpile rebuilding and weapon retirement activities, a large amount of surplus explosive needs to be destroyed. Alkaline hydrolysis is an alternative to the traditional method of explosive destruction, open burn/open detonation (OB/OD).[1−27] Alkaline hydrolysis destroys high explosives by degrading nitramine explosives, such as HMX, into organic and inorganic salts, soluble organic compounds, and benign nitrogen gases (nitrous oxide (N_2O), nitrogen (N_2), and ammonia (NH_3)). The process operates at relatively low temperatures compared to incineration, is easy to implement and control, and is conducted in a closed system.

Recently, reaction rate models were developed for the treatment of HMX-based explosives with aqueous 1.0−3.0 M NaOH or Na_2CO_3 up to 160 °C in a pressurized reactor.[20,27] However, the possibility of thermal runaway during the reaction has not been thoroughly investigated. Therefore, small-scale (5 mL) experiments were performed using a 4.5 °C/min linear temperature ramp that started at ambient temperature and ended at 300 °C. The temperature at which a detonation occurs gives an upper bound on a safe operating temperature for the base hydrolysis reaction. A linear temperature ramp allowed a range of temperatures to be studied in each run and minimized both the total amount of explosive needed and the damage to the reactor due to detonation of the explosive.

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Experimental Procedure

The studies included two HMX-based formulations, PBX 9404 and PBX 9501, produced by the Holston Defense Corp. Both formulations contain two sizes of HMX crystals. Coarse HMX (class 1) has a mean diameter of 234 μm[28] and resembles table salt or granular sugar. Fine HMX (class 2) has a mean diameter of 5 μm[8] and resembles talc or powdered sugar. In both formulations, coarse and fine HMX are blended in a 3:1 weight ratio, respectively. The formulation PBX 9404 consists of 93.9 wt % HMX, 3 wt % nitrocellulose (NC) binder, and 3 wt % tris-β chloroethyl phosphate (CEF) plasticizer. Diphenylamine (DPA; 0.1 wt %) was added to stabilize NC. PBX 9501 consists of the identical bimodial distribution of 94.9 wt % HMX bonded with 2.5 wt % polyurethane elastomer (Estane 5703), and 2.5 wt % of the low-melting eutectic mixture of bis(2,2-dinitopropyl)acetal and bis(2,2-dinitropropyl)formal (BDNPA/BDNPF). Irganox 1010 [Ciba-Geigy; tetrakis-(methylene 3-(3−5-di-*tert*-butyl-4-hydroxyphenol)propionate] methane; 0.1 wt % is added to stabilize Estane.

The PBX 9404 and PBX 9501 molding powders are made by dissolving the binder in an organic solvent, such as 2-butanone, and then adding this solution to a HMX−water slurry. The organic solvent is then removed by an air sweep.[29,30] Consolidated pieces (5.5 × 6 mm) were made by pressing the molding powder. The PBX 9404 pieces used in this study were pressed at 3.3 × 10^8 Pa and 80 °C. The PBX 9501 pieces were pressed at the same pressure and 85−95 °C. This study included the hydrolysis of both molding powder and pressed pieces.

Figure 1 shows a schematic of the 5 mL Inconel 625 (high nickel alloy) reactor designed to perform thermal safety studies. The reactor was loaded with approximately 320 ± 10 mg of explosive and 3.2 mL of solution. Clamshell resistance heaters increased the reactor

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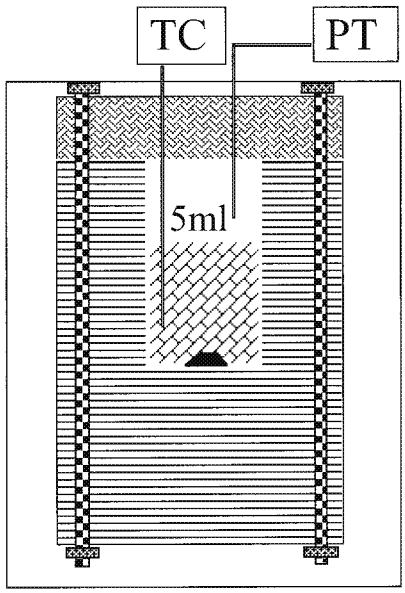

Figure 1. Thermal stability reactor (5 mL volume). Material of construction is Inconel 625. The bulk liquid temperature is measured with a thermocouple (TC), and the headspace pressure is measured with a pressure transducer (PT).

temperature at a rate of 4.5 °C/min (the maximum rate where a stable, linear ramp could be maintained), from 50 to 300 °C. Two type K stainless steel thermocouples were used to measure both the bulk liquid and the reactor outer wall temperature. The wall temperature was used for the feedback temperature control. Because of the small cell size and the clamshell heaters, stirring was unavailable for these experiments. In large-scale reactors, agitation would be used. A pressure transducer was used to measure the reactor head pressure. A computer running Labview software (National Instruments) recorded pressure, time, and temperature. A temperature controller (model 3000, Omega Engineering) regulated the reactor temperature. The pressure was measured to track the conversion of the explosive to gaseous products through either base hydrolysis or other reactions. A point discontinuity of pressure versus time indicated detonation of the explosive, and detonation was clearly heard in the laboratory. The reactor was designed to withstand the detonation of the explosive charge.

Results

Figure 2 shows temperature versus pressure plots for the base hydrolysis of PBX 9404 and PBX 9501 molding powders. In each plot, the pressure rise due to water vapor pressure was subtracted from the experimental pressure. Parts a–d of Figure 2 show that PBX 9404 began reacting at a lower temperature than PBX 9501 and at a faster rate. Furthermore, the reaction rates for PBX 9501 and PBX 9404 are similar between 190 and 250 °C for all cases except 1.5 M NaOH (Figure 2b). This is because above approximately 200 °C HMX can thermally degrade and may undergo hydrolysis with water. The reaction between water and HMX leads to a very fast reaction rate and, therefore, a rapid pressure increase. The final pressure in the water hydrolysis case (Figure 2d) is much lower than that in the other experiments. This is probably due to a smaller amount of gaseous products from the reaction with water than from base hydrolysis. Finally, in the 1.5 M NaOH case, PBX 9501 detonated at 185 °C. This experiment was repeated, and an identical detonation temperature was observed.

Figure 3 contains temperature versus pressure traces comparing the different physical forms of the explosive studied. Figure 3a shows that only the PBX 9501 molding powder, and not the pressed pieces or the HMX crystals, detonates. Figure 3b shows that there are only slight differences in the pressure curves for the PBX 9404 molding powder and the PBX 9404 pressed pieces.

Discussion

To analyze the results of these experiments, the heat of reaction for the base hydrolysis of HMX was measured. The heat of reaction, calculated from differential scanning calorimetry of NaOH hydrolysis of HMX dissolved in DMSO at room temperature, was 2.3 kJ/g of HMX.[31] In a simple calorimetry experiment, the value was 1.5 kJ/g of HMX for base hydrolysis in aqueous NaOH. The following reaction equation is based both on experimental results and on reaction pathways found in the literature:[1,2,7,12,14,22,32]

$$C_4H_8N_8O_8 + 5OH^- \rightarrow 2N_2O(g) + 2NH_3 + 2NO_2^- + 2HCOO^- + CH_3COO^- + H_2O \quad (1)$$

The heat of reaction at 298 K, based on this equation, was calculated to be 2.1 kJ/g. This is consistent with the previous values from both calorimetry and the differential temperature reactor experiment. However, because both the concentration and the type of base can influence the reaction pathways, a conservative value of 2.3 kJ/g of explosive was used for the thermal stability analysis of base hydrolysis.

A reaction rate model from prior studies[20,27] (eq 2) was

$$q''_{\text{generated}}\ (\text{W/cm}^2) = k_L[\text{HMX}]_{aq}E\Delta H_{RXN}$$

$$q''_{\text{removed}}\ (\text{W/cm}^2) = \frac{k_{COND}}{\delta_T}(T_{RXN} - T_{BULK})$$

$$\delta_T = \frac{D_{HMX}}{k_L}\left(\frac{Sc}{Pr}\right)^{1/3} \qquad k_L = 0.13(\epsilon\nu)^{1/4}Sc^{-2/3}$$

$$\epsilon = \frac{PoN^3Ds^5}{\nu_L\rho_L}$$

$$Po = f\{Re\} \qquad k_{COND} = f\{T\}$$

$$E = f\{k_L, D_{HMX}, [OH], k_{RXN}\} \quad (2)$$

used for thermal calculations. This model is a coupled kinetic/mass-transfer model based on gas–liquid film theory.[33–37] The reaction appears to occur entirely within the solution phase. The local kinetic model given by Heilmann et al.,[7] which is first order in hydroxide ion concentration and first order in dissolved HMX concentration, was used. Mass-transfer coefficients were estimated using the method developed by Kawase and Moo-Young.[38] The solution thermal and transport properties were assumed to be the same as the properties of water.[39] The model predictions were compared to experimental data obtained at 1–6 M NaOH concentration, 5–15 wt % initial solid explosive concentration, 0.5–3 W/kg mixing energy, and 100–155 °C reaction temperature. A single adjustable parameter, related to

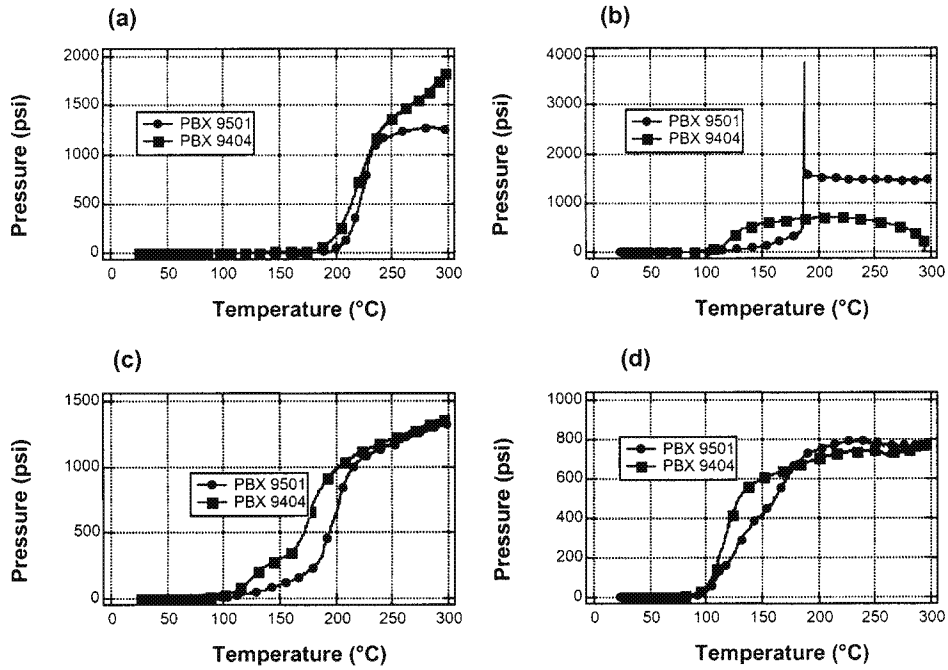

Figure 2. Temperature−pressure plots at different NaOH concentrations. PBX 9501 and PBX 9404 were in the form of a molding powder. A 4.5 °C/min linear temperature ramp was used. (a) Reaction with 3.0 M NaOH. (b) Reaction with 1.5 M NaOH. (c) Reaction with 0.75 M NaOH. (d) Reaction with water.

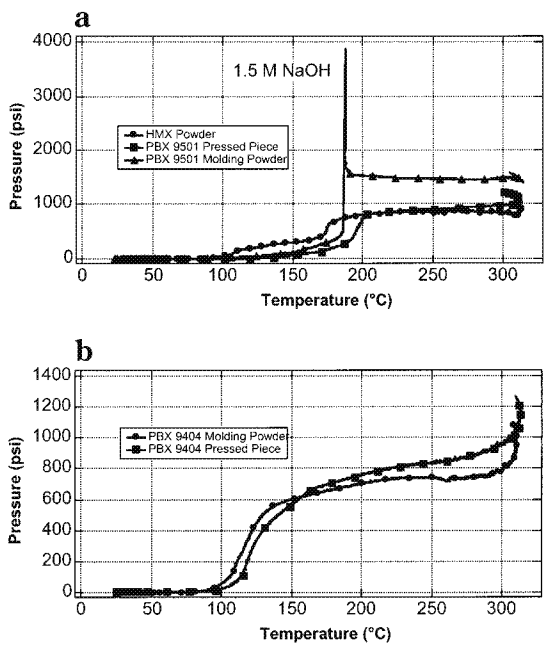

Figure 3. Temperature−pressure plots comparing molding powder to pressed pieces. The NaOH concentration is 1.5 M. The pressed pieces were 5.5 × 6 mm in size. (a) Hydrolysis of the HMX powder, PBX 9501 molding powder, and PBX 9501 pressed pieces. (b) Hydrolysis of the PBX 9404 molding powder and PBX 9404 pressed pieces.

the particle surface/volume ratio, was adjusted to minimize the error between predicted and experimental results.

For the range of conditions in this study, the reaction rate model predicts that nearly all of the reaction occurs very close to the solid/liquid interface. No variations in solution temperature, as a function of position within the reactor, were considered during the development of the reaction rate model. For the thermal stability analysis in this study, all of the reaction is assumed to occur at the solid/liquid interface temperature.

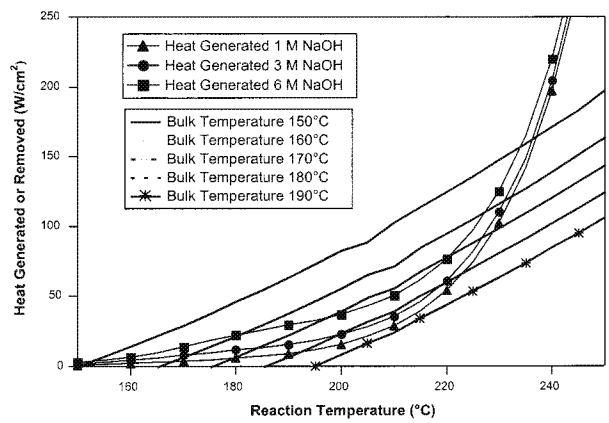

Figure 4. Thermal stability plot for NaOH hydrolysis of HMX-based explosives. The reaction temperature is the assumed solid/liquid interface temperature.

Figure 4 compares the heat of reaction that would be generated at an assumed solid/liquid interface temperature (the three sharply rising curves) with the heat that would be lost to the bulk solution by convection (the four lines of near unity slope). When the heat lost to the bulk liquid is greater than the heat generated near the solid/liquid interface, the system is thermally stable. The plot shows that a stable condition occurs below a bulk temperature of 180 °C for 1.0 and 3.0 M NaOH. For 6.0 M, 180 °C is just slightly above the stability point. Above 185 °C, the reaction is thermally unstable. This value coincided with the temperature at which the PBX 9501 molding powder detonated (see Figure 2).

Figure 5 shows a simulation of the PBX 9501 molding powder experiments. The molding powder particle diameter varied between 1 and 2 mm. For this simulation, a 1.5 mm diameter was assumed. A 20 °C temperature difference between the outside of the reactor wall and the bulk solution was measured. Because the temperature of the solid/liquid interface was not measured, a

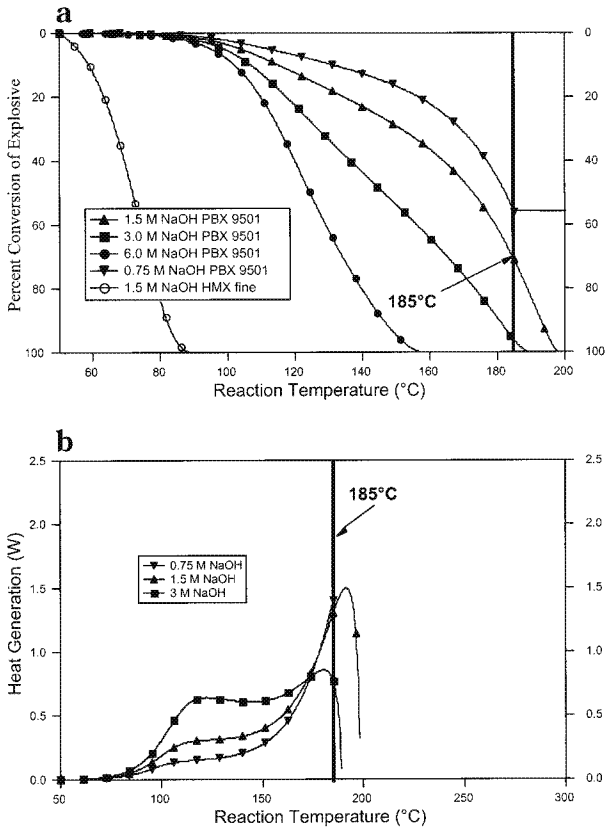

Figure 5. Modeling simulations of the base hydrolysis of the PBX 9501 molding powder. The reaction rate model used was from Bishop et al.[20,27] (a) Percent conversion of explosive. (b) Heat generated near the solid/liquid interface.

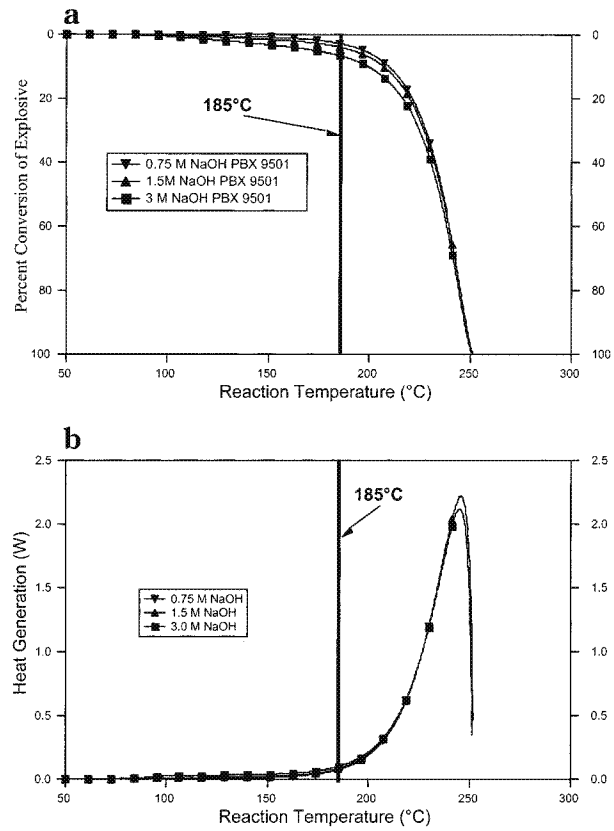

Figure 6. Modeling simulations of the base hydrolysis of the PBX 9501 pressed pieces. The reaction rate model used was from Bishop et al.[20,27] (a) Percent conversion of explosive. (b) Heat generated at the solid/liquid interface.

20 °C temperature difference between the solid/liquid interface and the bulk solution was assumed. A temperature differential of 20 °C matches the value predicted from a simple heat balance around the solid particle at a bulk temperature of 185 °C (where detonation occurs). Figure 5a shows that, for concentrations above 3.0 M NaOH, there is little or no mass of PBX 9501 remaining when the temperature reaches 185 °C. This explains why no detonations occurred in the 3.0 M samples. For the case where the concentration of NaOH was 0.75 M, the base is completely consumed before the solution reaches 185 °C. However, there would still be PBX 9501 molding powder present at this temperature. This is also true of the reaction of PBX 9501 molding powder with water. Therefore, just having explosive present in the solution above a temperature of 185 °C is not sufficient to cause a detonation.

Figure 5b shows how the rate of heat generation changes as the solution temperature changes. This plot shows that, for 1.5 and 0.75 M NaOH, the maximum heat production occurs near 185 °C. For the 3.0 M NaOH solution, the heat generation drops at 180 °C as PBX 9501 is depleted. For 0.75 M, the heat generation stops at 185 °C as the hydroxide ion concentration drops to zero, halting the reaction. This simulation shows why a detonation was observed only with 1.5 M NaOH. At higher and lower base concentrations, the reaction slowed near 185 °C because of depletion of one of the reactants.

Pressed PBX 9501 pellets did not detonate in 0.75–3.0 M NaOH at temperatures to 300 °C using a heating ramp of 4.5 °C/min. A simulation of the experiments, shown in Figure 6, shows that, although there is an excess of base and some explosive remaining at 185 °C, the reaction due to hydrolysis does not begin to produce a significant amount of heat until the reaction temperature is close to 240 °C. The lower reaction rate, compared to the PBX 9501 molding powder, is due to the lower surface area of the pressed pellets. The water decomposition/hydrolysis reaction becomes significant above 200 °C. Therefore, by the time the base hydrolysis reaction becomes significant, the water decomposition/hydrolysis reaction has already consumed the explosive.

When the data from both the PBX 9501 molding powder and the PBX 9501 pressed pellet experiment are analyzed together, three phenomena appear to be affecting the stability of the system. One, the exothermic reaction heats the particle and promotes thermal runaway. Two, heat transfer from the explosive solid to the bulk liquid cools the particle and promotes thermal stability. Three, mass consumption through the water decomposition/hydrolysis reaction consumes the HMX, preventing thermal runaway and possible detonation. This causes a window of instability to exist when the heat generation is greater than the cooling heat transfer, but the water decomposition/hydrolysis reaction is too slow to prevent thermal runaway by decomposing the explosive. This occurs when the hydrolysis reaction rate peaks at a temperature between 185 and 225 °C. Thermal stability is also affected by the heating rate. At higher heating rates, reactant depletion is less likely before the mixture reaches 185 °C, so there is greater risk of a detonation.

For the PBX 9404 molding powder and pressed pieces, Figure 3 shows that the base hydrolysis reaction is completed before the temperature reached 185 °C. This

is because the nitrocellulose binder in PBX 9404 quickly degrades at 70 °C, freeing the HMX crystals and thereby rapidly increasing the surface area-to-volume ratio. At a temperature ramp of 4.5 °C/min, the PBX 9404 molding powder cannot explode because there is no PBX 9404 left at the instability temperature of 185 °C. However, if the temperature ramp was changed or if larger pieces of pressed PBX 9404 were used, then the base hydrolysis reaction could become unstable above 185 °C.

To validate the model predictions, one experiment was performed at a heating rate of 2 °C/min. In that case, PBX 9501 did not detonate at a 1.5 M NaOH concentration. This is consistent with the model because, with a slower heating rate, the majority of PBX 9501 would be consumed by reaction before the temperature reached 185 °C. However, more experiments at different heating rates need to be performed to further validate the model.

Scale-up of the Process

Only very small amounts of explosive (300 mg) were investigated in this study. Research on the thermal stability of large pieces of explosive has not been specifically studied, but large pieces of explosive have undergone base hydrolysis at temperatures up to 125 °C at Los Alamos National Laboratory without incident.

Conclusions

The safe operating conditions for the base hydrolysis of PBX 9404 and PBX 9501 were studied. To ensure safe operation, the bulk reaction temperature should be kept at or below a temperature of 180 °C. Above 185 °C, a thermal runaway of the reaction can cause a detonation.

Three different phenomena were found to affect the thermal stability of the system. (1) The heat of reaction, which was found to be about 2.3 kJ/g of HMX, causes the system to heat, decreasing its thermal stability. (2) The cooling of the explosive particle through convection to the bulk liquid lowered the surface reaction temperature, increasing the thermal stability. (3) A previously undetermined effect, the reaction of HMX with water, occurs at temperatures above 200 °C. These three effects create a window of instability when the hydrolysis reaction rate peaks between 185 and 225 °C.

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Nomenclature

D_{HMX}: diffusivity of HMX in water (cm^2/s)
D_S: diameter of the stir bar or agitator blade (m)
DMSO: dimethyl sulfoxide
E: enhancement factor
HMX: 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
$[HMX]_{aq}$: aqueous concentration of HMX (g/cm^3)
k_{COND}: thermal conductivity of water [W/(cm K)]
k_L: mass-transfer coefficient (cm/s)
N: rotation speed of the stir bar or agitator (1/s)
[OH]: aqueous concentration of OH^- (mol/L)
PBX: plastic-bonded explosives
Po: Power number
Pr: Prandtl number
$q''_{generated}$: flux of heat generated due to reaction (W/cm^2)
$q''_{removed}$: flux of heat removed due to convection/conduction to bulk liquid (W/cm^2)
Sc: Schmidt number
T_{BULK}: temperature in the bulk fluid (°C)
T_{RXN}: temperature in the reaction zone (°C)
v_L: liquid volume in the reactor (m^3)
δ_T: length of the thermal boundary layer (cm)
ΔH_{RXN}: heat of reaction (kJ/g)
ϵ: energy dissipation per unit mass (W/kg)
ρ_L: density of the fluid (kg/m^3)

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