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Title: BASE HYDROLYSIS KINETICS OF HMX-BASED EXPLOSIVES
USING SODIUM CARBONATE

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Base Hydrolysis Kinetics of HMX-Based Explosives Using Sodium Carbonate

Robert L. Bishop, Cary Skidmore, Raymond L. Flesner, Philip Dell'Orco, Terry Spontarelli, John Kramer and David Bell

Sodium carbonate has been identified as a possible hydrolysis reagent for decomposing HMX-based explosives to water soluble, non-energetic products. In this study, the reaction kinetics of sodium carbonate hydrolysis are examined and a reaction model is developed. The rate of hydrolysis is reaction-rate limited, opposed to mass transfer limited, up to 150°C. Greater than 99% of the explosive solids in powder form are destroyed in less than 10 minutes at a temperature of 150°C. The primary products from sodium carbonate hydrolysis are sodium nitrite, formate, nitrate, acetate, glycolate, hexamine, nitrogen gas, nitrous oxide, and ammonia.

Introduction

The Department of Defense and the Department of Energy must dispose of a large volume of high explosive (HE) material,¹ including unexploded ordnance and bulk explosives recovered from aging munitions stockpiles. Traditionally, open burning/open detonation (OB/OD) is used to dispose of these materials, but environmental concerns have forced the development of new technologies.² High explosives are usually characterized as compounds or mixtures containing both a fuel and an oxidizer which react violently with small impact, thermal, or electrical stimulus. Due to noise concerns and the dispersion of undesirable burning products, OB/OD has recently fallen out of favor with state and federal regulatory agencies. This has prompted the development of safe and environmentally benign disposal alternatives. One high explosive disposal alternative being developed in parallel by industry and Los Alamos National Laboratory is base hydrolysis.

Base hydrolysis is a method of breaking down high explosives to organic and inorganic salts, soluble organic compounds, and benign nitrogen gases (primarily nitrous oxide, nitrogen and ammonia). The process operates at relatively low pressures and temperatures compared to OB/OD, is easy to control and implement, and is a closed system. Depending on the high explosive treated, the aqueous products are still considered hazardous waste that require further treatment. Several papers have been written with research being performed by both private and government laboratories.³⁻⁷

Currently, an ammonia-based hydrolysis process is operational at Thiokol to treat CYH rocket propellant.⁷ A large-scale unit is scheduled for implementation later this year at both Eglin Air Force Base and the Pantex Plant in Amarillo, Texas. In addition, Chemical Systems Division, a propellant manufacturer in northern California, is using base hydrolysis to destroy waste energetic materials.⁶ It has been determined that base hydrolysis using sodium hydroxide at either 90°C or 150°C is an effective method for the disposal of many explosives. Furthermore, the hydrolysis reaction using sodium hydroxide is mass transfer limited above a temperature of 70°C.⁸

The base used most often in this process is sodium hydroxide. The feasibility of using sodium carbonate as an alternative base to sodium hydroxide was investigated. To better understand the effectiveness of sodium carbonate as an agent for the hydrolysis of HMX, and PBX 9404 (94% HMX, 3% nitrocellulose, 3% chloro-ethyl phosphate, and 0.1% diphenylamine), kinetic studies were performed. PBX 9404 is a plastic bonded explosive developed by Los Alamos National Laboratory and used in DOE munitions. The HMX used in our experiments was in a coarse powder, which had an average particle diameter of 125 microns. For the PBX 9404 experiments, molding powder was used, except for one experiment in which a consolidated piece was used. The consolidated piece was a cube approximately 1.5 inches per side, and weighed 127 grams. Molding powder consisted of small particles or pieces of plastic-covered explosive up to 0.5-1 cm in diameter. The consolidated piece was manufactured by pressing molding powder in a high

pressure hydrostatic press at an elevated temperature. Kinetic studies are needed to quantitatively evaluate the performance of sodium carbonate as a hydrolysis agent.

The explosives were converted into non-explosive, aqueous compounds by treatment with either 1, 1.5 or 2.5 molar sodium carbonate at elevated pressure. The fraction of the solids converted to soluble compounds, and the experimental time-temperature profile was used to determine the rate. The overall rate was determined and a first order rate equation was developed with an Arrhenius rate constant.

Experimental

Two reactors were used to perform the kinetic studies. Most of the experiments were carried out in a 100 ml Hastelloy "C" reactor that was heated and stirred with a VWR Scientific series 400HPS hot plate/stirrer. The hot plate/stirrer was equipped with an automatic temperature control system. The temperature and pressure of the reactor were recorded every five seconds using a LabView data acquisition program. The reactor was heated to a setpoint temperature and held there for several minutes, then rapidly quenched in an ice bath. One sample port was used to take gas samples and to vent the off-gas at each experiment's completion. The whole apparatus was placed in a fume hood behind an explosive blast shield.

The effects of heating rate, reactor size, and mixing properties on the kinetics of the reaction were determined by comparing results obtained using two different reactors. A 2L stainless steel Parr reactor was used as the second reactor. The reactor was heated with electrical coil heaters that were in contact with the walls of the reactor, and cooled by an internal cooling coil that used tap water as the coolant. The electric heaters and cooling water were controlled by a Watlow series 945 controller. Similar to the 100 ml reactor, the pressure and temperature were recorded every five seconds using a LabView data acquisition program. The reactor was agitated by a stirrer shaft with two flat impellers, and the rotational speed of the stirrer was recorded every five seconds. A gas sampling/vent port and a liquid sampling port were both available, allowing for liquid and gas samples to be taken during experiments. The temperature control system on the Parr reactor was capable of controlling the heat generated from the reaction by internal cooling, whereas, the 100 ml reactor did not have this feature. The coolant feature provided better temperature control in the Parr reactor. Both reactors were batch loaded and sealed air tight before the beginning of each experiment. At the end of each experiment, the liquid was filtered using a Buchner funnel with 1.2 micron paper filter, and the remaining solids were dried and weighed.

In some experiments, gas and liquid samples were taken. Samples were taken at the completion of the experiments in the 100 ml reactor, while intermediate samples were taken in the 2L Parr reactor experiments. The gas samples were analyzed by gas chromatography. The liquid samples were analyzed for pH, ion content, and total organic and inorganic carbon.

Similar experiments were grouped for data analysis purposes. The criterion used for grouping was based on similar solids loading, base concentration, and reactor size. An Arrhenius type model was used to predict the final solids mass using the experimental temperature profile. The same Arrhenius parameters were used for all the experiments within each group. The differences between the experimental mass remaining and the predicted mass was then minimized to find the optimum Arrhenius parameters to use. The coefficients for each group were then compared and a mean was determined along with an error term. The error term represents a two-tailed, 95% confidence interval.

Results and Discussion

Experiments were performed varying the initial sodium carbonate concentration, the setpoint temperature, the time the solution was left at the setpoint, the explosive solid loading, and the size of the reactor. By varying these factors, the major parameters that could affect the reaction were studied. In two experiments, the rotational speed of the

stirrer was varied. A summary of the range over which these parameters were varied is shown in Table 1.

Table 1:
Experimental Summary

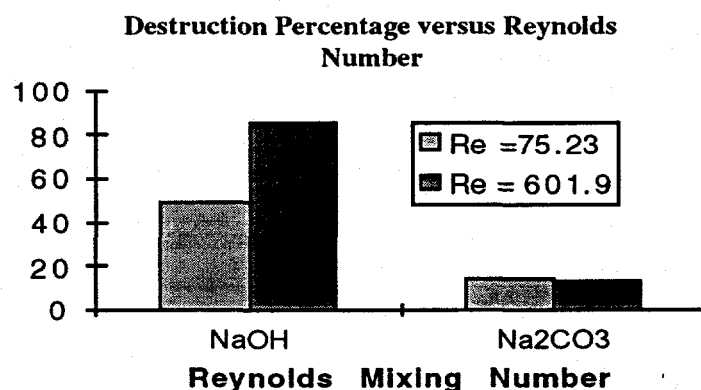
Parameter	HMX Experiments	PBX 9404 Experiments
Temperature	120-154°C	110-142.8°C
Base Concentration	1.0-1.5M	1.0M-2.5M
Solids Loading (g explosive/g liquid)	0.05-0.34	0.066-0.3
Time at Temperature	3-18 min	4-30 min

Over 60 experiments were performed. At a temperature of 150°C, a base concentration of 1.5M and a solids loading of 0.1 grams explosive per ml of liquid, over 99% of the explosive was destroyed after only five minutes. Significant destruction efficiency was observed for experiments done at temperatures as low as 130°C, with the reaction rate being more than double at 150°C than at 130°C. The pressure in the reactor due to the accumulation of gaseous products was as high as 300 psig in the 100ml reactor and 70 psig in the 2L Parr reactor. Although the pressure effect on the rate was not determined, no major change was observed when the pressure was varied by either venting or by having a larger fraction of head space in the 2 L reactor.

The experiments in which the mixing Reynolds number was varied from 75 to 600 showed that the reaction rate was not affected (see Figure 2). This is a clear indication that the reaction is kinetically limited in this temperature range. The same experiments were performed using a sodium hydroxide solution, which has been shown to be mass transfer limited above 70°C.⁸ A change in the mixing Reynolds number from 75 to 600, corresponded to a doubling of the reaction rate. The sodium carbonate system appears to be kinetically limited due to the lower hydroxide ion concentration when compared to sodium hydroxide hydrolysis.

Table 2 shows the average aqueous and gaseous reaction products formed. Of the remaining carbon, 33.5% is formate, 7% is acetate, and 60% was not identified by either ion or gas chromatography. The 60% unknown for the total carbon is most likely in the form of hexamine and other organic carbon species. The 35% unknown for the total nitrogen is most likely made up of hexamine, ammonia gas, and other amines.

Figure 2:



Reaction Rate Modeling.

Once it was confirmed that the reaction was kinetically limited, a first order model in hydroxide ion was used to fit the experimental data. Previous researchers have indicated that the hydrolysis of HMX is fit by a second order overall rate equation, first order in HMX and first order in OH⁻ concentration.⁹⁻¹² The second order rate constant is then fit by

using an Arrhenius equation. The following chemical equilibrium equations and data were used to determine the hydroxide ion concentration in the rate law. Hydroxide ion is formed by two reactions with water.

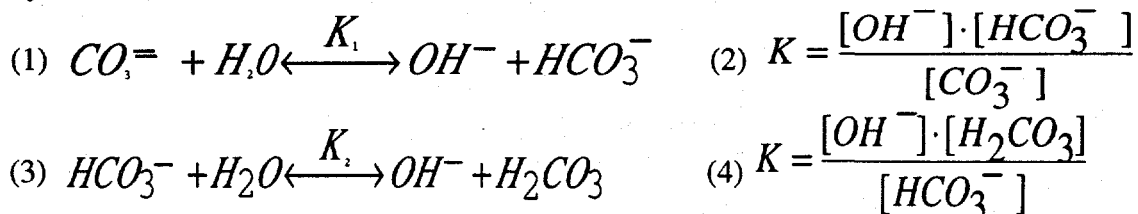


Table 2:
Hydrolysate Products

	Concentration (ppm)	% Total Carbon or Nitrogen in Explosive Processed
Carbon Bearing Species		
Inorganic Carbon	4,700	24.5
Organic Carbon	14,500	75.5
Formate	24134	~33.5
Acetate	2286	~7.4
Carbon (Not detected by IC or GC)		~59
Nitrogen Bearing Species		
Nitrite	21069	17
Nitrate	trace	trace
Nitrogen gas	~ 1735	~4.6
Nitrous Oxide	~25487	~43
Other (Not detected by IC or GC)		~35.4

The concentration of the hydroxide ion in these equations was calculated as a function of temperature using a known equilibrium constant, K_{298} , and compensating for the temperature effect using standard thermodynamic relationships.¹³ The values of the heat of reaction and the equilibrium constant, K_{298} , are listed in Table 3.^{14,15}

Table 3:
Heat of Reaction and Equilibrium Constants for
Hydroxide Reactions

Reaction	K_{298}	ΔH (J/mole)
1	$2.083 \cdot 10^{-4}$	41057
2	$2.38 \cdot 10^{-8}$	48295.8

The solubility of HMX is affected by temperature and the other species present in solution. To effectively describe the HMX aqueous concentration, all these factors must be taken into account. For these results the assumption was made that the aqueous HMX concentration was either relatively constant for the temperature range studied, or that it could be absorbed into the reaction rate constant. Using this assumption, a good estimate could be obtained by using a first order model with respect to hydroxide. The results show that this model does give a good estimate.

In order to model both the HMX and the PBX 9404 using the same equation, the 6% of the mass of PBX 9404 that was nitrocellulose and chloro-ethyl-phosphate had to be taken into account. The analysis of the PBX 9404 data was performed under the following assumptions: The 6% of the mass that was not HMX did not affect the HMX-carbonate reaction rate, and the non-HMX components either reacted quickly or were completely soluble immediately after the reaction started. The nitrocellulose in the PBX 9404 was also assumed to react quickly, causing the PBX 9404 to fall apart into small particles with size distribution similar to that for HMX. These assumptions allowed for 6% of the mass of PBX 9404 to be destroyed immediately, with no effect on the remaining HMX. The amount of carbonate ion consumed by the nitrocellulose was taken into account.

Table 4 lists the Arrhenius parameters for the HMX and PBX 9404 experiments. These data were taken for a series of experiments, and 95% confidence bounds are given in the table. The data show that there is no statistical difference between the parameters for the HMX experiments and those for the PBX 9404 experiments. This confirms that the assumptions used in the analysis of the PBX 9404 compounds are consistent with the results.

The model can be used in the design of reactors and in scale-up to production. Since the difference in the reactor size did not seem to have an effect on the rate, the kinetic equation can be applied to any size reactor. The use of a first order model also eliminated the immediate need to try to evaluate the solubility properties of HMX in base solutions at high temperatures.

Table 4
Arrhenius Coefficients for HMX-Carbonate Reaction

Explosive ($\pm 95\%$ confidence)	Activation Energy ($\text{KJ} \cdot \text{mol}^{-1}$) E	Natural Log of the Pre-Exponential Factor ($\ln \text{ sec}^{-1}$) $\ln A$
HMX	92.4 ± 0.7	20.8 ± 0.8
PBX 9404	91.5 ± 0.8	22.1 ± 0.5

Predictions for different reaction conditions were carried out based on the model developed from the experimental results. Figure 3 shows the effect that the initial base concentration and the temperature have on the rate. The data represent a theoretical isothermal run using different starting carbonate concentrations. The plot shows that the effect of temperature on the reaction is quite substantial. The time until total destruction of the explosive varies from roughly 8 minutes at 150°C to 37 minutes at 130°C for a starting carbonate concentration of 1.5M. The initial carbonate concentration can also greatly affect the rate. The total destruction time changes from roughly 12 minutes for a 2.5M solution at 140°C to almost 24 minutes for a 1M solution at the same temperature.

However, the temperature profile does not need to be isothermal for the model to be useful. Figure 4 shows predictions based on an experimental temperature profile. The fluctuation in the temperature at its setpoint is due to the control system used in the Parr reactor. The model was used to predict the hydroxide ion concentration, the carbonate ion concentration, and the HMX fraction remaining. The figure shows that the hydroxide ion concentration increases with the temperature until the peak temperature is reached, and then the concentration falls. The increase is due to the effect that the temperature has on the equilibrium constant (Clausius/Clapeyron Equation).¹³ The graph shows the effect is very sizable. The subsequent decrease in the hydroxide ion concentration is due to the change in the equilibrium (equations 2, 4) from the consumption of the hydroxide ion in the reaction. As hydroxide ion is consumed, so is the carbonate ion (see Reaction 1 and 3). This is also shown on the graph. The HMX fraction remaining also shows the effect that the temperature has on the reaction rate, with virtually no reaction taking place at temperatures

below 100°C and rapid destruction at 150°C. The agreement between the predicted and experimental results for the experiment used to generate Figure 4 was $\pm 1.2\%$.

Figure 3:
Isothermal Plots

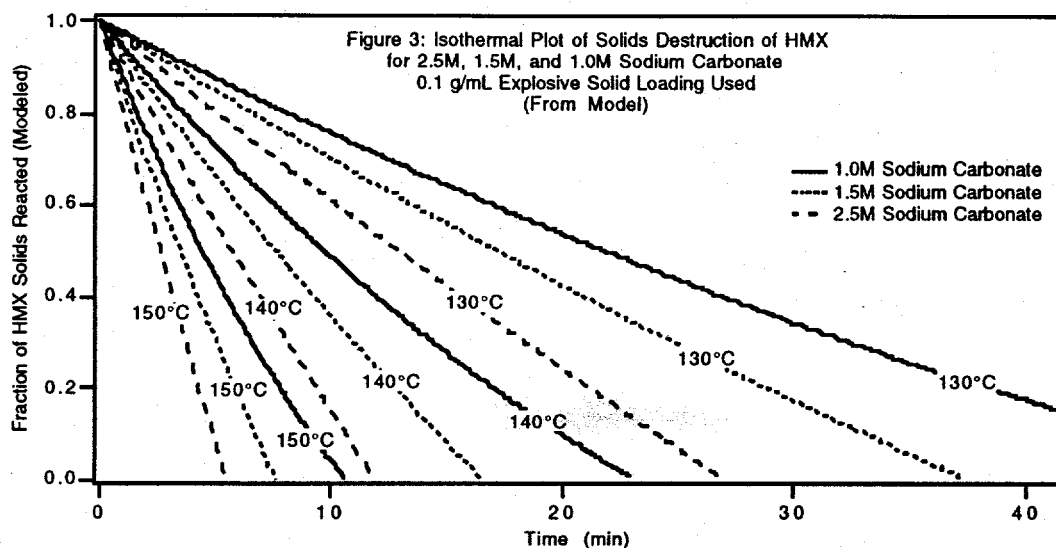
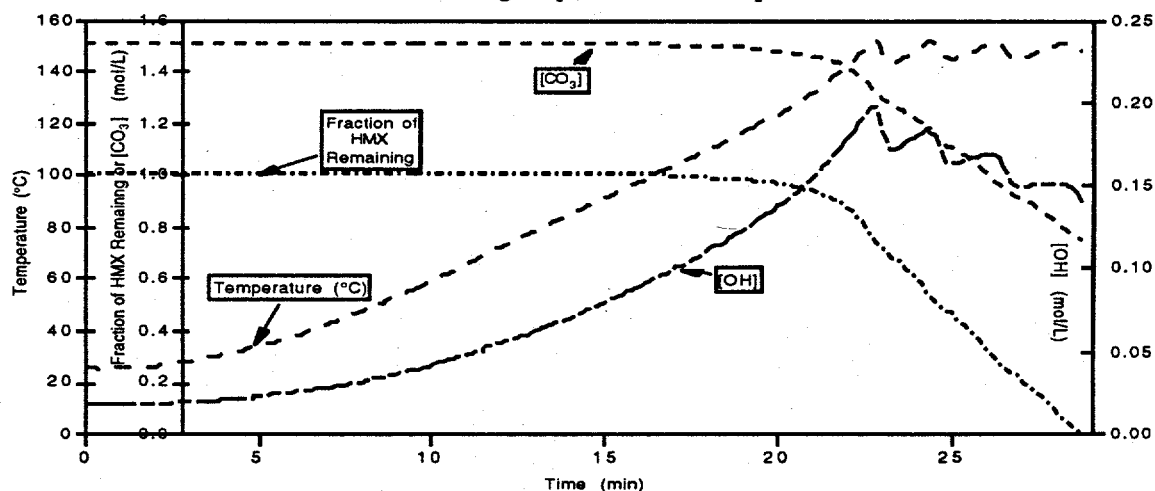


Figure 4:
Model Predictions using Experimental Temperature Profile

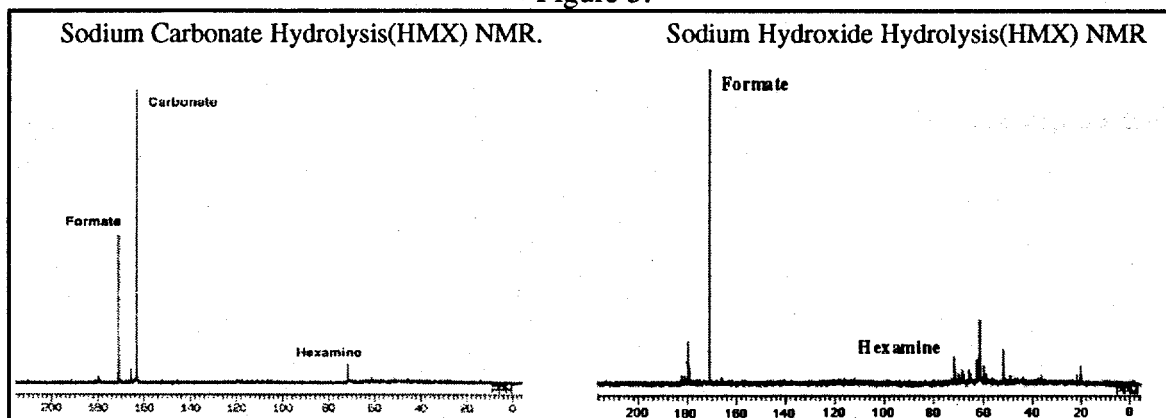


In the experiment in which the PBX 9404 was in the form of a consolidated piece instead of molding powder, after reacting for ten minutes at 150°C using 3M Na_2CO_3 , only 43.9% of the total starting mass had reacted. The reaction rate limited model predicts that 75.6% of the total mass should have reacted. It appears that in consolidated pieces, mass transfer resistance begins to compete with reaction kinetics thereby rendering the kinetic model less accurate. The majority of the remaining solid was still in one piece, with HMX powder surrounding it. The presence of both a large central piece, and a large amount of HMX powder suggests that the reaction is occurring in a transitional regime. When NaOH is used on a large piece, the remaining mass is in one piece, with little or no HMX powder present. The reaction model developed is only valid as long as the reaction stays in the reaction rate limited regime.

Sodium Carbonate as a Hydrolysis Agent

There are three chief advantages of using sodium carbonate for base hydrolysis. The first is the significantly lower pH value when compared to sodium hydroxide. The lower pH allows for easier handling. In sodium hydroxide hydrolysis, the product stream has an average pH of 13,¹⁶ whereas for sodium carbonate the pH is around 9.5 or lower. Second, the cost of sodium carbonate is less than NaOH. The cost of NaOH is \$300/ton for a 50% by weight solution in water.¹⁷ The cost of sodium carbonate is only \$106/ton,¹⁸ a cost savings of 28% when compared to sodium hydroxide at a solid loading of 0.1 grams explosive per ml of solution and a base concentration of 1.5M. Finally, sodium carbonate has a simpler reaction products than the sodium hydroxide process. In the sodium carbonate process very few aqueous products are made, with the majority being carbonate, formate, nitrate, nitrite, and hexamine. A Carbon 13 NMR scan of the products from 1.5M sodium carbonate and 1.5M sodium hydroxide hydrolysis of HMX are presented below in figures 5.

Figure 5:



Conclusions

The reaction kinetics of HMX and PBX 9404 base hydrolysis using sodium carbonate were investigated. Several experiments were performed using different size reaction vessels, and different concentrations of both base and explosive. The reactions were carried out in sealed vessels and performed in the temperature range between 100°C and 150°C.

The use of sodium carbonate for base hydrolysis of HMX or PBX 9404 is a viable method. At a temperature of 150°C, a base concentration of 1.5M, and a 1:10 mass ratio of explosive to base solution, 100% percent of all the solids are destroyed in less than ten minutes. Furthermore, the products from the reaction contain fewer components than when sodium hydroxide is used as the hydrolysis agent, and the solution has a final pH below the RCRA corrosive level. The availability of sodium carbonate as a cheap solid can have a cost saving over sodium hydroxide. Sodium carbonate is a useful and practical alternative to sodium hydroxide.

The hydrolysis of HMX and PBX 9404 using sodium carbonate can be modeled using a first order rate equation in hydroxide ion. Both PBX 9404 and HMX hydrolysis follow the same rate law. This fact could enable sodium carbonate to be used effectively in other plastic bonded explosives where the majority of the compound is HMX. The fact that the reaction can be modeled effectively ignoring the concentration of HMX in solution leads to the conclusion that the solubility either changes slightly over the temperature range studied, or that the solubility can be taken into account using the Arrhenius parameters in the rate law. The knowledge of the kinetics of this reaction will help in modeling and designing a production scale operation in the near future.

Acknowledgments

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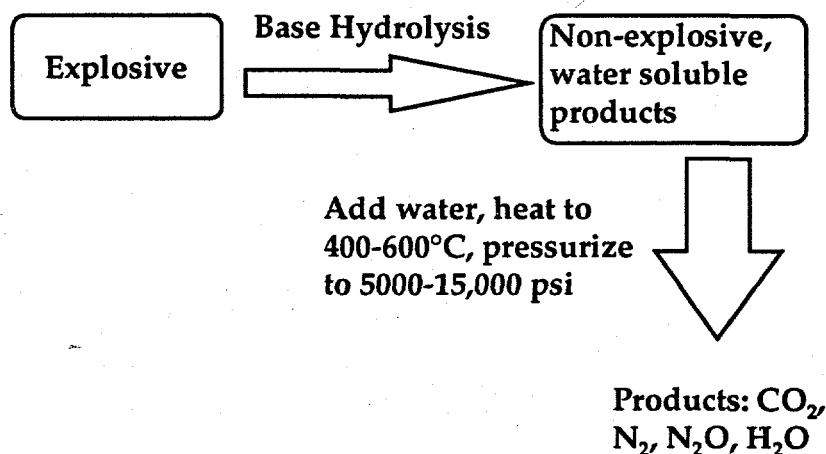
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Base Hydrolysis Kinetics of HMX-Based Explosives Using Sodium Carbonate

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International Workshop on Peaceful Utilization of
Energetic Materials,
St Petersburg, Russia, June 3-6, 1996

Base Hydrolysis/Hydrothermal Processing Technology Summary



Introduction, Base Hydrolysis

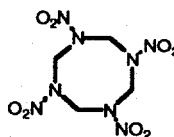
- ◆ Reactions with NaOH NH_3 “de-energize” and solubilize many explosive materials
- ◆ Typical operating temperatures - 80 to 150°C
- ◆ Base Hydrolysis Implementation:
 - Large Rocket Motor Demil Program (General Atomics, Thiokol, Tyndall AFB)
 - Eglin AFB (High Explosives Research and Development Facility)
 - DOE (Pantex)

3

PBX 9404 definition

- ◆ DOE Plastic-Bonded Explosive
- ◆ 94% HMX, 3% Nitrocellulose (binder), 3% Tris (2-chloro ethyl) phosphate (plasticizer, 0.1% Diphenylamine (stabilizer for NC)

HMX



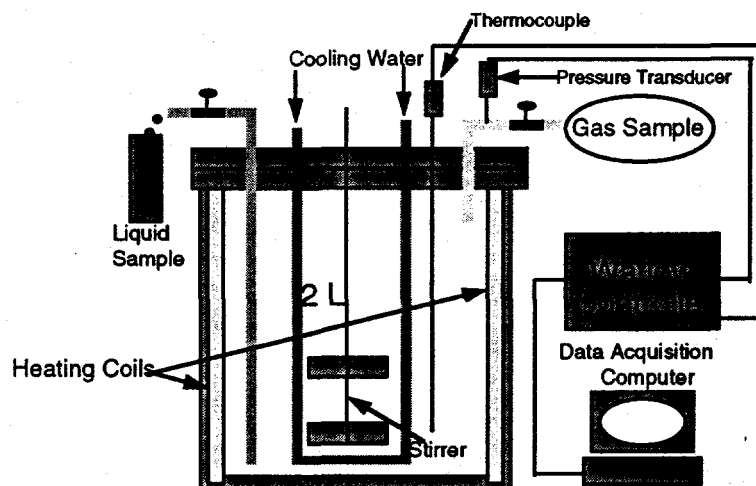
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Lab Scale Base Hydrolysis

- ◆ 2 Liter Parr reactor, 100 cc reactor
- ◆ Temperatures up to 150°C
- ◆ NaOH, NH₄OH, Na₂CO₃, 1-3 M
- ◆ Characterize rate of reaction
 - Kinetics and/or mass transfer limitations
- ◆ Reaction mechanisms
- ◆ Product analysis

5

2 Liter Parr Reactor



6

Lab-Scale Experiments

- ◆ Over 60 experiments performed on PBX 9404 molding powder, pressed pieces, and HMX powder
- ◆ Na_2CO_3 at 1 M to 2.5 M
- ◆ 93 to 150°C, 14 to 300 psi, 3 to 30 minutes time, different mixing intensities
 - Re mixing range: 75 to 600

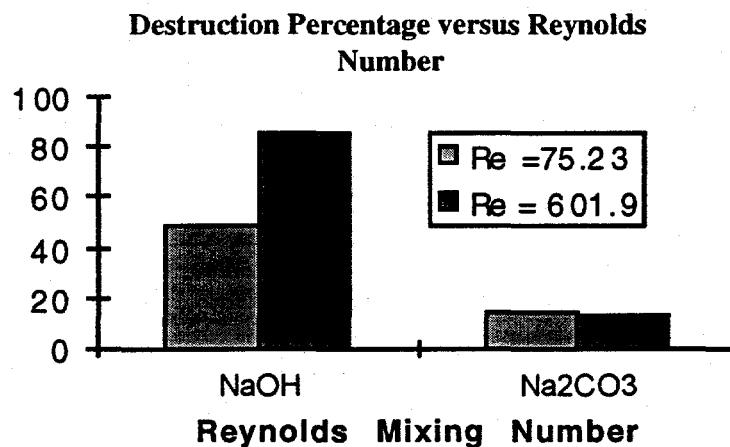
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Lab Scale Expts.: Reaction Products

- ◆ Aqueous Carbon Products: Sodium Acetate, Formate, Glycolate, Carbonate, Methylamine
- ◆ Aqueous Nitrogen Products: Sodium Nitrite, Nitrate, Ammonia, Methylamine
- ◆ Gas Products: N_2O , N_2 , NH_3 , Trace CO

8

Kinetics vs Mass Transfer



9

Kinetic model

- ◆ Literature: 1st order in [HMX] and [OH⁻] for homogeneous reaction
- ◆ Our assumption for heterogeneous reaction:
 - Overall reaction rate: pseudo 1st order, [OH⁻] only
 - [HMX] does not change or is included in reaction constant at changing Temp

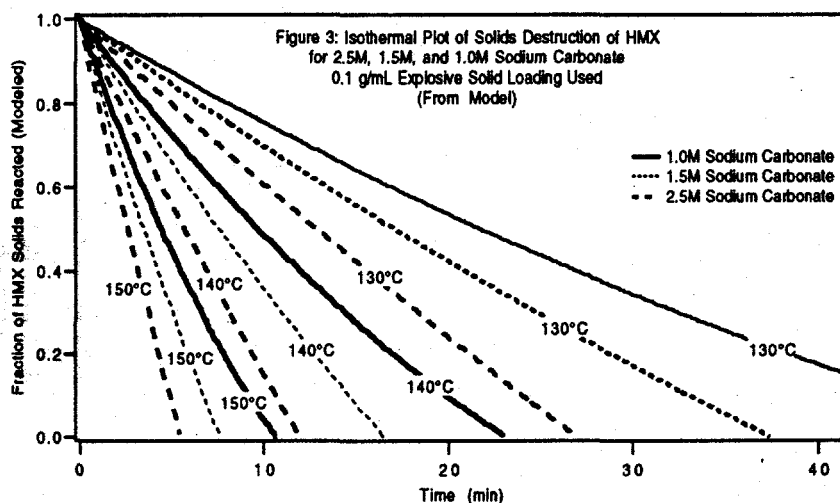
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Kinetic Model Results

Explosive ($\pm 95\%$ confidence)	Activation Energy ($\text{KJ} \cdot \text{mol}^{-1}$) E	Natural Log of the Pre-Exponential Factor ($\ln \text{sec}^{-1}$) $\ln A$
HMX	92.4 ± 0.7	20.8 ± 0.8
PBX 9404	91.5 ± 0.8	22.1 ± 0.5

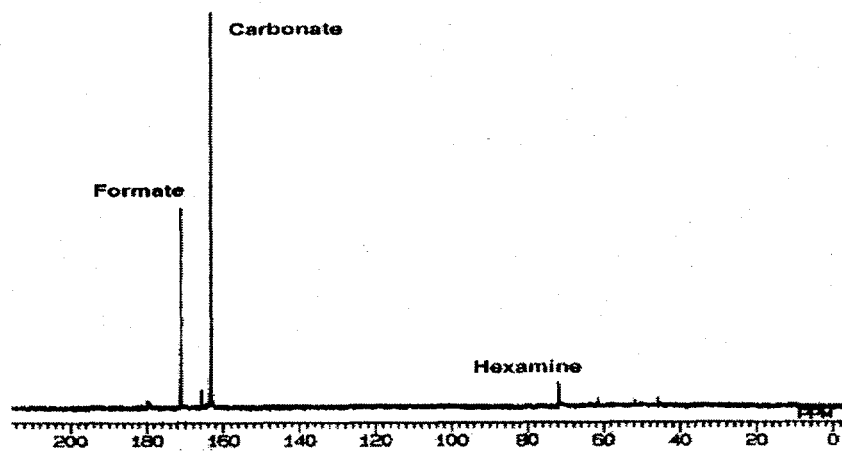
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Model Predictions



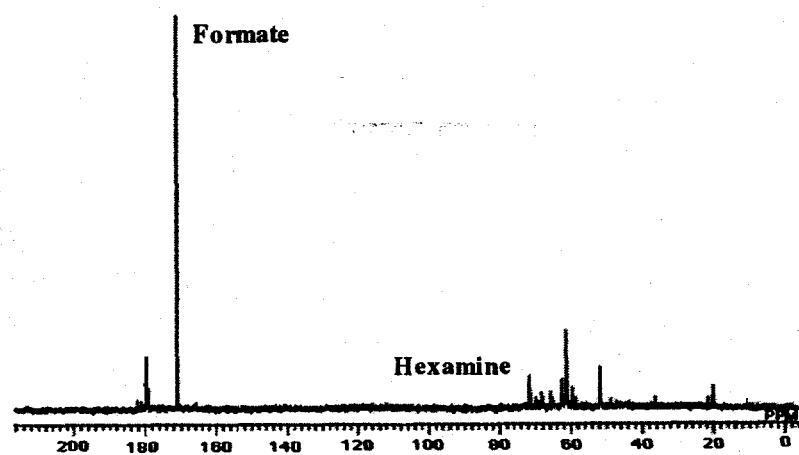
12

Sodium Carbonate NMR



13

Sodium Hydroxide NMR



14

Summary

- ◆ Sodium Carbonate - viable alternative to NaOH
 - Cheaper, cleaner products, lower final pH
 - Slower, not amenable to hydrothermal processing
- ◆ Heterogeneous Kinetic model:
 - Arrhenius rate constant coeffs determined
- ◆ Rate relatively fast at 150°C

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Acknowledgments

- ◆ DOE, Joint DoD/DOE Munitions Technology Program

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