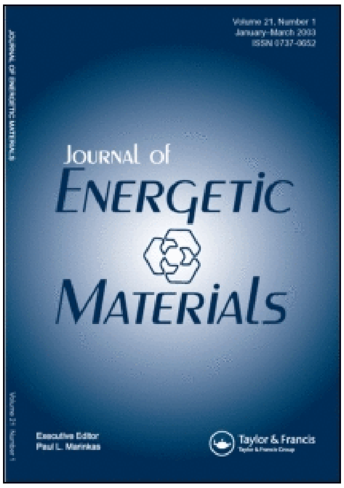

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BASE HYDROLYSIS OF TNT-BASED EXPLOSIVES

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Four TNT explosive formulations were treated with 1.5 M and 3 M solutions of sodium hydroxide (NaOH) at temperatures between 90°C and 150°C. The reaction time needed for over 99% conversion of the explosive compound was less than 5 minutes at 150°C for both Octol and Comp B, and less than 30 minutes at 90°C for Tritonal and Tetrytol. The TNT and Tetryl fractions of the explosive produced negligible gas and liquid products were ammonia, sodium acetate, sodium formate, and sodium nitrite. The RDX and HMX fractions produced a substantial amount of gas and the major products were nitrous oxide, nitrogen, and ammonia. The aluminum used in Tritonal was converted to aluminum hydroxide and hydrogen gas.

INTRODUCTION

The base hydrolysis of 1,3,5,7-tetraaza, 1,3,5,7-tetranitrocyclooctane (HMX) based explosives at temperatures above 90°C has been previously described in detail.[2,3] In this process, waste explosives are treated with an aqueous base, such as sodium hydroxide, to convert the explosives into non-energetic compounds and gases. The reaction may be carried out at elevated temperatures in a pressurized reactor to obtain shorter reaction times. The aqueous product is then oxidized using techniques such as hydrothermal oxidation prior to release to the environment.

In this paper, the hydrolysis of melt castable explosives is studied. Melt castables are explosives that usually contain 2,4,6-trinitotoluene (TNT). They make up the majority of the explosives used by both DoD and DOE.[4,5] The low melting point of TNT allows the mixture to be melt cast into molds and aids in achieving uniform dispersal of the more energetic components.

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To determine if base hydrolysis is a useful method for the destruction of melt castable explosives, TNT, Octol[6] (30 wt% TNT, 70 wt% HMX), Comp B[7] (40 wt% TNT, 60 wt% RDX, some formulations contain 1% wax), Tetrytol (75 wt% Tetryl, 25 wt% TNT), and Tritonal[7] (80 wt% TNT, 20 wt% aluminum) were treated with aqueous NaOH. The overall reaction time was determined along with some of the chief products formed during reaction.

EXPERIMENTAL METHODS

Base hydrolysis was carried out using TNT, Octol, Comp B, Tetrytol and Tritonal. The majority of the explosives were provided as cast pieces from Eglin Air Force Base's High Explosive Research and Development (HERD) facility. Mason and Hanger's Pantex Plant provided the Tetrytol. Some neat, powdered TNT provided by Los Alamos was used for determining the products of TNT hydrolysis. The size of the explosive pieces ranged from scrap (<5 g) to 2 kg cast pieces.

The experiments with TNT powder were carried out in a 100 ml and a 2 L reactor that have been described in previous papers.[2,3] For the other explosives, the experiments were performed in either the 2 L reactor, or by using a large beaker and a hot plate. The reactors were heated and held at the set point temperature for the desired processing time. Afterwards, the reaction liquid was cooled by either immersing the reactor in ice water or by flowing tap water through internal cooling coils (2 L reactor). The liquid was filtered using a Buchner funnel with an 8 µm filter paper, and the solids were dried and weighed. Gas and liquid samples were taken at the completion of some experiments.

TNT hydrolysate liquid has two phases (aqueous and organic), while HMX hydrolysate liquid has only one (aqueous). The TNT hydrolysate was acidified (pH = 2) to precipitate the oily phase components from the hydrolysate. The solution was then centrifuged and filtered. The filter cake was washed with water and methanol, and dried. The solid was analyzed by both proton and carbon-13 NMR.

RESULTS AND DISCUSSION

Base Hydrolysis of Neat TNT

The chemistry involved in the base hydrolysis of TNT and Tetryl is different than for HMX or RDX. Since TNT and Tetryl are nitroaromatic explosives, the aromatic ring in the molecule is difficult to degrade, and base hydrolysis alone does not appear to completely break it down.[9] Therefore, the hydrolysates of TNT, Tetryl and melt castables have more than one phase. The aqueous phase contains the base hydrolysate salts (formate, acetate), while the organic phase contains the aromatic TNT and Tetryl breakdown products. Although both phases pass through an

8 µm filter, the solution appears cloudy and an non-aqueous layer will form on the bottom of hydrolysate solutions if given time to settle.

If the solution is acidified, a solid precipitate can be centrifuged out of solution. A proton NMR of the hydrolysate precipitate, Figure 1, shows three peaks near 7 ppm, which are indicative of the presence of an aromatic ring. A C-13 NMR of the hydrolysate (not shown) had characteristics which were typical of polymeric species. Saupe *et al.*[8] determined that the majority of the carbon in TNT hydrolysate (over 90%) was either in polymeric substances having a molecular weight between 3,000-30,000 (40%) or greater than 30,000 (60%). Saupe *et al.* performed their hydrolysis experiments at 80°C and pH 14.

Even though the benzene ring does not completely degrade during the reaction, base hydrolysis can still convert TNT to a non-explosive solution. The known products of TNT hydrolysate are shown in Table 1. A total organic carbon (TOC) and total inorganic carbon (TIC) analysis of the TNT liquid effluent yields a total carbon balance of 105%. No gas formation was detected. The high amounts of unidentified carbon and nitrogen are contained in TNT fragments that have polymerized into large molecules. The table shows that for every mole of TNT, only approximately 0.5 mole of carbon and approximately 1 mole of nitrogen are converted into ions. The rest of the carbon and nitrogen is probably still attached to the aromatic ring. Since less than one mole of carbon is converted to ions, we deduce that the methyl carbon is being removed from the aromatic structure, leaving the aromatic ring intact.

A Total Carbon (TC) analysis was performed on the aqueous and on the organic phases of the base hydrolysate. The results showed that 76% of the total carbon contained in the organic phase. This is consistent with the concept that the majority of the carbon products are polyaromatic species, which would reside in the organic phase.

TABLE 1
Products from TNT Hydrolysate

	% Total Carbon or Nitrogen in Explosive Processed
Carbon Bearing Species	
Formate (aqueous)	8
Acetate (aqueous)	3
Unidentified Carbon	89
Nitrogen Bearing Species	
Nitrite (aqueous)	34
Nitrate (aqueous)	0.6
Ammonia (aqueous)	9
Unidentified Nitrogen	57

The nitrogen products from Table 1 were consistent with Saupe *et al.*[9] who determined that approximately 40% of the nitrogen in TNT was converted to nitrite, and approximately 3% to ammonia.

Base Hydrolysis of TNT-containing Explosives

The gaseous product compositions for Octol, Comp B, Tetrytol and Tritonal are shown in Table 2. The aqueous product compositions are also given for Comp B and Tetrytol. No gaseous products were detected in the hydrolysis of TNT. The N_2O and N_2 gasses from the hydrolysis of Comp B and Tetrytol are due to the hydrolysis of the RDX or HMX component. The principle aqueous products are acetate, nitrite, and formate. These products are similar to those previously found in HMX and RDX base hydrolysis.[2,3,9-21] For Tritonal, hydrogen gas was produced by the reaction of NaOH with aluminum (Equation 1). If a milder base such as ammonium hydroxide were used instead of NaOH, the production of hydrogen gas would be nearly eliminated.

EQUATION 1

$$2Al+2OH^-+6H_2O\longrightarrow 2Al(OH)_4^-+3H_{2(g)}$$

The reaction of aluminum with NaOH is very exothermic, and temperature control can be difficult. In preliminary experiments performed in an open beaker, the heat from the reaction of NaOH and Al caused the solution to boil off leaving a potentially dangerous, hot, dry piece of TNT on the bottom of the reactor. In the 2 L pressure reactor the NaOH solution did not boil off, but the solution temperature rose due to the reaction, as shown in Figure 2.

A pressure and temperature versus time plot for Octol hydrolysis is shown in Figure 3. The figure shows that little head pressure is generated below a temperature of 90°C (20 KPa due to water vapor), but above that temperature, the head pressure increases rapidly. This is further verification that the product gas was generated by HMX, and not TNT, since HMX does not react at a significant rate (producing gas) at temperatures less than 80°C.[2,3]

Table 3 shows the overall reaction time for the explosives with NaOH. Above 90°C, these results show at least a 94% conversion in 30 min or less.

Reaction Rate Studies

Comp B and Tetrytol were studied in more detail to determine reaction rate relations. Figure 4 plots the melting/hydrolysis rate and the overall reaction rate of the TNT

TABLE 2
Gaseous and Aqueous Effluent from the Base Hydrolysate of TNT-containing Explosives

Gaseous Products

Explosive	**N_2O (%N in Explosive)**	**N_2 (%N in Explosive)**	**CO (%C in Explosive)**
TNT	None	None	None
Tetrytol	None	None	None
Octol	42	3.0	<0.1
Comp B	16	0.11	<0.1
Tritonal	Hydrogen was formed from the Al reaction. No other gas detected		

Aqueous Product Ions

Explosive	**Acetate**	**Formate**	**Nitrite**	**Nitrate**
Comp B	3.5	25	27	0.09
Tetrytol	1.6	3.4	39	1.0

TABLE 3
Overall Reaction Times for TNT-containing Explosives

Explosive	**Concentration of Base**	**% Explosive Loading**	**T**	**Time at Temperature**	**% reacted**
Octol	3M NaOH	10 wt%	150°C	<1 minute	99.0
Octol	3M NaOH	18 wt%	95°C	28 minutes	94.6
Comp B	3M NaOH	18 wt%	85°C	28 minutes*	74.4
Comp B	3M NaOH	18 wt%	150°C	5 minutes	98.0
Tritonal	1.5M NaOH	5 wt%	95°C	30 minutes	99.5
Tetrytol	1.5M NaOH	10 wt%	90°C	30 minutes	99%

*no mixing

in the Comp B as a function of temperature. The melting rate was determined by measuring the time required for the piece of Comp B to no longer be observable as a large solid. The overall reaction rate was determined by measuring the remaining total mass after various processing times at two different temperatures. In all the experimental runs, RDX powder was still present after the TNT melted and reacted.

Figure 4 shows that the melt rate and the overall reaction rate show the same temperature trend, and that the melting step accounts for about 75% of the overall rate. This leads to a conclusion that the RDX hydrolysis rate is slightly slower than the TNT melt rate, and that conversion of the RDX component sets the time required for complete conversion. Furthermore, when several small pieces of Comp B were used, instead of one large piece, the melting rate was more than double. The increase in melting rate is due to the increase in the initial surface area of the Comp B.

The effect of processing time and reaction conditions on conversion for Comp B are shown in Figure 5. The temperature was 88°C-94°C and the experiment was performed in an open beaker on a hot plate. The base concentration or mass loading did not appear to have a large effect on the reaction rate. A conversion of 100% was achieved in less than 30 minutes (not shown). The reaction appears to slow down slightly over time. In HMX hydrolysis,[2,3] the reaction rate slows because the rate of HMX dissolution decreases due to declining HMX surface area. The declining reaction rate with Comp B maybe due to a similar effect with RDX.

The rate of conversion for Tetrytol is shown in Figure 6. The temperature of the solution was 90°C and the experiments were performed in an open beaker on a hot plate. The rate of conversion for Tetrytol hydrolysis appears to be linear over the time scale studied with an average fractional conversion rate of 0.034 min^{-1}. The hydrolysis of Tetrytol does not show a slowing of the conversion rate over time because the entire Tetrytol mixture melts at temperatures below 89°C.

4.0 CONCLUSION

The products of TNT hydrolysis are much more complex than those of HMX or RDX hydrolysis, and experimental conditions such as temperature, base concentration, and agitation may have a significant influence on the products formed. The rate of hydrolysis of TNT is faster than either HMX or RDX, and neat TNT and Tritonal have short reaction times even at 95°C. Therefore, the slower rate of RDX and HMX hydrolysis rather than the rate of TNT destruction define the overall rate of hydrolysis of Octol and Comp B. For Tetrytol, the fractional conversion rate was constant at approximately 0.034 min^{-1}.

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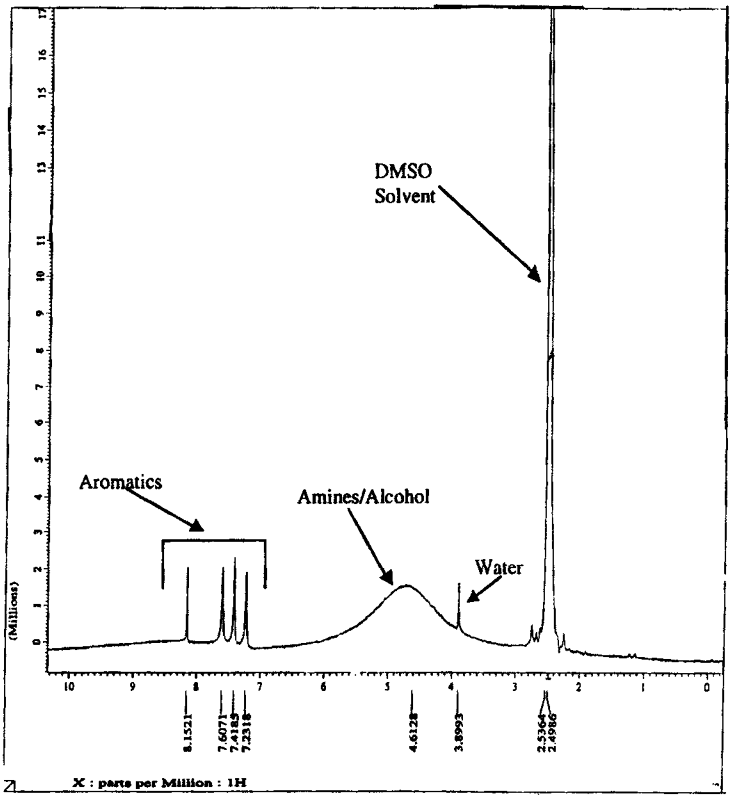

FIGURE 1
Proton NMR of the TNT hydrolysate, oily phase. The phase was separated from solution by acidification and centrifugation.

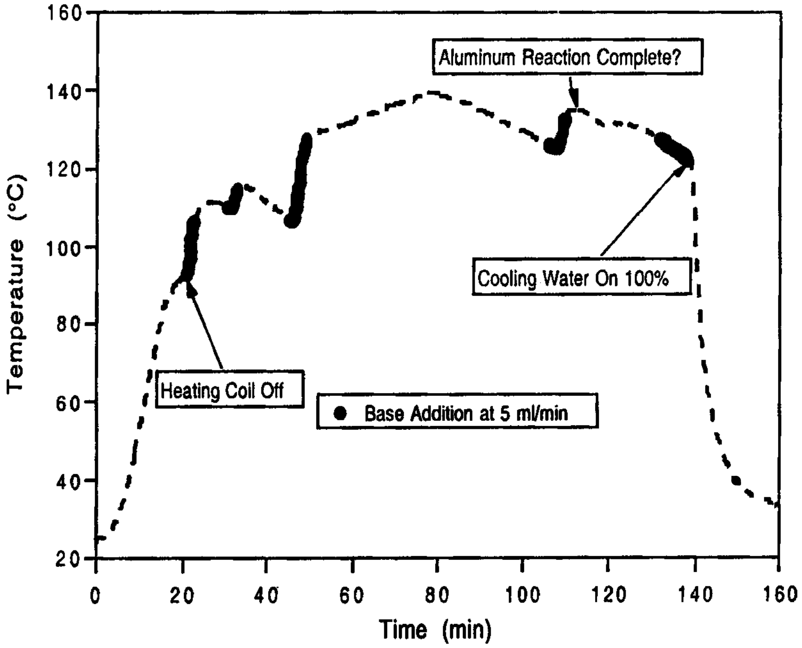

FIGURE 2
Temperature-time profile for Tritonal hydrolysis. Experiment was performed in the 2 L reactor using a HPLC pump to add a 15 M NaOH solution at 5 mL/min. All external heating was turned off before base addition.

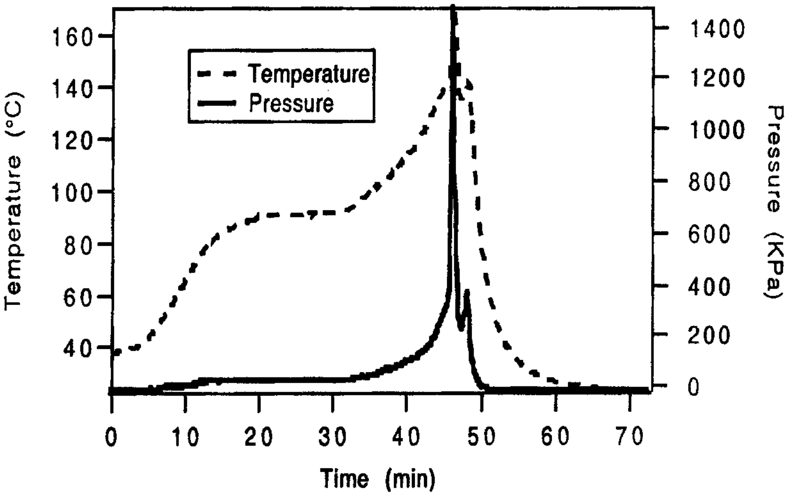

FIGURE 3
Pressure and temperature profile for Octol hydrolysis. The experiment was performed in the 2 L reactor using a starting solution of 1.5 M NaOH.

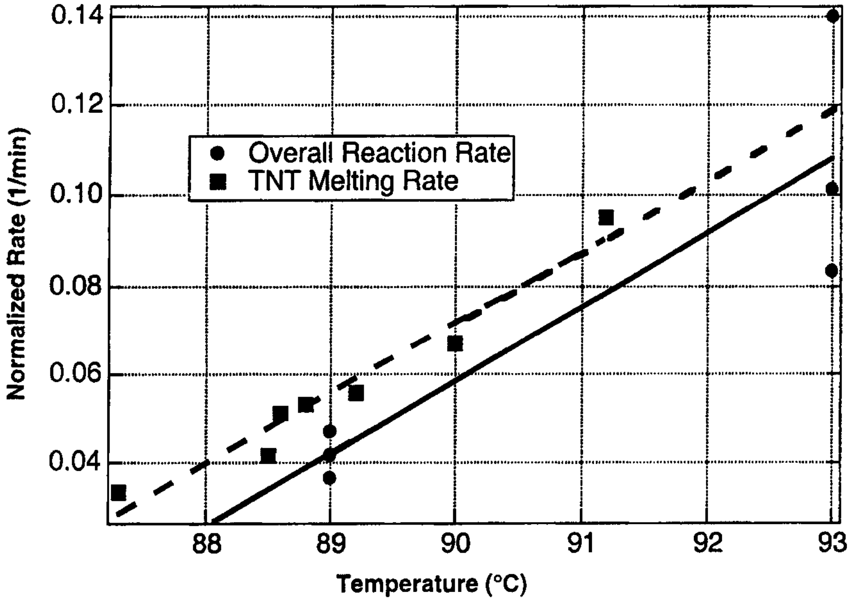

FIGURE 4
Melting and Reaction Rate of Comp B as a function of Temperature. Performed in an open beaker on a hot plate with a starting solution of 1.5 M or 3 M NaOH.

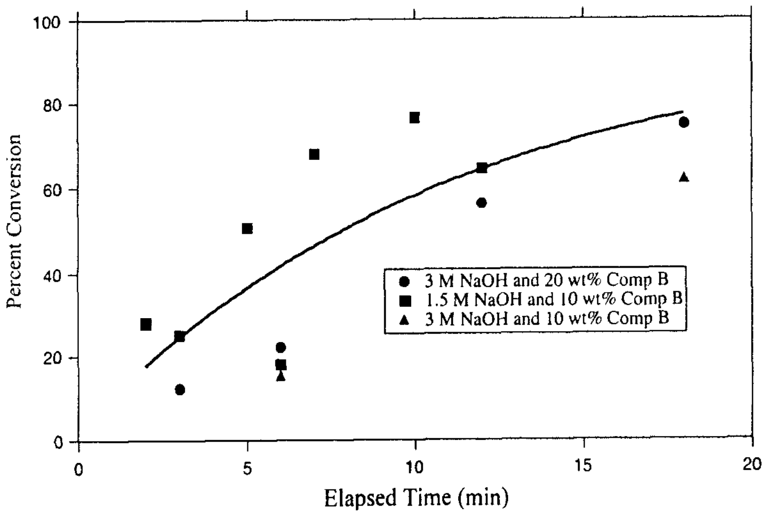

FIGURE 5
Conversion of Comp B as a function of time. Performed in an open beaker on a hot plate with a starting solution of 1.5 M or 3 M NaOH.

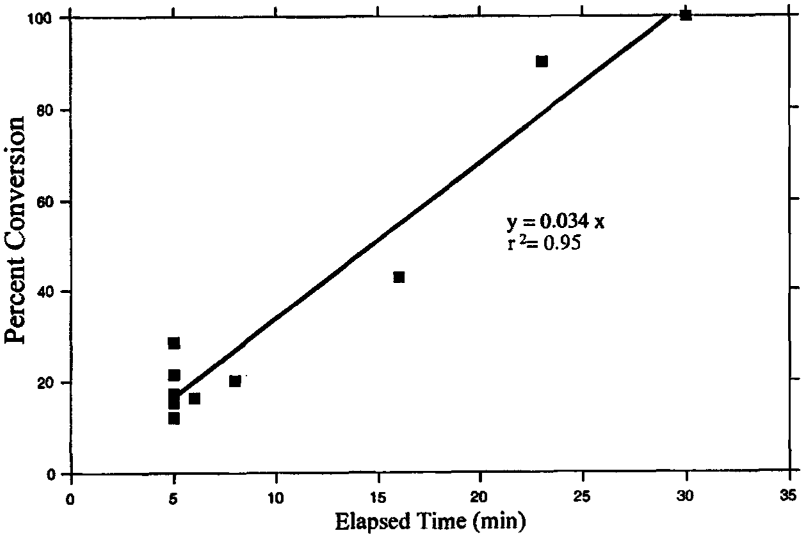

FIGURE 6

Conversion of Tertytol as a function of time. Performed in an open beaker on a hot plate with a starting solution of 1.5 M or 3 M NaOH.