Hypergolic Reactions of TNT

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Abstract:

One way being considered to destroy trinitrotoluene (TNT) land or surf mines is to exploit its reactivity using darts containing chemicals, which, upon contact with TNT, cause instantaneous decomposition, but not detonation. To determine the best candidates to fill the darts, liquids, specifically amines, which react in a hypergolic fashion with TNT were examined for both the rate of reaction and amount of energy released. Micro-calorimetry was used to measure heat release while spectroscopy and conventional peak intensity monitoring by chromatography were used to examine the rate of reaction. Calorimetry measurements showed little variation between different amines reacting with TNT (about 110-130 kJ/mole TNT). TNT reaction with hydride actually produced more heat than with amines. Further, dinitrotoluene (DNT), which generates substantial heat, does not undergo a hypergolic reaction with amines suggesting heat release is not the controlling factor for the hypergolic reactions. Rate constants, determined for the loss of TNT in dilute acetonitrile solution, clearly showed distinctions among the amines. The more primary amine functionalities in the amine compound, the faster it destroyed TNT. Hydrides or amine mixtures spiked with hydride decomposed substantially faster than the amines alone. However, a direct correlation between reaction rate and time-to-ignition was not observed.

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Introduction

Reactions of 2,4,6-trinitrotoluene (TNT) with bases are well known. Nucleophilic attack at the methyl carbon or one of the meta positions (Fig. 1) can result in the formation of Meisenheimer complexes and other colored species(1-10). In the 1970's there was an effort to chemically neutralize TNT with species that would react quickly with TNT, but not detonate it. Candidate compounds, which ignite spontaneously on contact with TNT (i.e. so-called hypergolic compounds), included metal alkyls, inter-halogen compounds, and various organic amines. Since the metal alkyls and the inter-halogen compounds were difficult to handle, amines were chosen as reactive fills. Specifically a device, called the Venom Penetrator was designed to inject diethylene triamine (DETA) into land and surf mines (11-14)

To provide a basic understanding of the reaction chemistry of TNT with hypergolic compounds, a study of parameters influencing ignition and rate of ignition of TNT was undertaken. Included were (a) amount of heat released, rate of heat release, intermediate formation and extent of reaction progress.

Materials and Method

Munitions-grade 2,4,6-trinitrotoluene (TNT) was obtained from NAVSEA, Naval Surface Warfare Center, Indian Head Division and used without purification. Reagent grade 2,4-dinitrotoluene (DNT), diethylene triamine (DETA), ethylene diamine (EDA), propylamine, di(propylamine, tripropylamine, propyl diamine (PDA), hexamethylene diamine (HMDA), tris (2-aminoethyl)amine (tris), and acetonitrile (ACN) were purchased from Aldrich. ACN was dried over molecular sieve and de-aerated with argon prior to use. Heats of reaction were determined using a Thermal Hazards Technology micro-reaction calorimeter (Model μRC). Powdered nitroarene (5 to 10 mg), of varying grain size, was sealed in a septum cap vial along with a magnetic stirring bar and placed in the calorimeter at 25°C. No special precautions were taken to keep the reaction dry or inert. In a typical reaction, 100 or 200 μL of amine were added by syringe over a few seconds. The start time was when the syringe punctured the septum. The syringe remained inside the vial for the duration of the run, typically 4000 seconds, with the initial 400 seconds being used to establish a baseline. The volume of added amine was such that all the powdered nitroarene was wetted. Stirring was at 180 revolutions per minute; however, solubility issues prevented complete homogeneity in some cases.

Automatic instrumental integrations were used. Spectrophotometric observations of the progress of reaction were made using a Perkin-Elmer Lambda 2 uv-vis spectrometer. Liquid chromatography (LC) (Agilent Model 1100) was used to follow disappearance of the nitroarene and, thus, determine the rate of TNT or DNT reaction. The LC was equipped with a Agilent Hypersil BDS column and photodiode array detector (LC/PDA). A modification of a procedure developed by Agilent using acetonitrile solvent was employed (Agilent Pub. #5091-7626E). TNT or DNT peak areas were compared against standards of known concentration. At least four standard solutions were prepared and analyzed to construct a standard curve. A typical procedure for determining reaction rates was as follows: TNT was dissolved and DETA was diluted with dry, de-aerated acetonitrile. The two solutions were mixed in a flask under argon. At various time intervals a portion (100 uL) was removed, diluted in fresh acetonitrile to 1 mL and analyzed by LC for quantification of TNT remaining. A portion (300 uL) of the sample was further diluted (2.5 mL acetonitrile) and scanned on the uv-vis spectrometer. Calorimetry measurements were taken with a Thermal Hazards Technology Micro-Reaction Calorimeter. The differential scanning calorimeter (DSC) exothermic data in Table 6 was obtained using a TA Instruments Model Q100. The scan rate was 20ºC per minute from 50ºC to 450ºC. The exothermic data was reported as replicate averages. The number of replicates is given by the Run # column.

Results and Discussion

Heats of Reaction: Heats associated with reactions of amines on neat TNT were measured by reaction calorimeter (Table 1). Because a liquid consistency was necessary in order to stir the mixture, the amine was added in a 30-fold to 60-fold molar excess. In cases where the amine (HMDA) or hydride ($NaBH_4$ or $LiAlH_4$) was a solid, it was premixed with the nitroarene, and the reaction was initiated by addition of a liquid amine or ACN. Baseline runs showed that the addition of ACN to the nitroarene or hydride was slightly endothermic, but no correction was applied to the exotherm following addition of the amine. Typical integrations, to determine heats of reaction, were made over 1 hour following addition of 100uL of amine to 5-10 mg of TNT. For the choice of amines used in this study, there was no apparent dependence on the nature of added amine. The major factor affecting the quantity of heat released was the amount of nitroarene available. Hhowever for both TNT and DNT, addition of a small weight percent borohydride to the nitroarene/amine reaction dramatically increased heat released (Table 1).

Rates of Reaction: Three approaches were taken in following the rate of the nitroarene/amine reaction. To examine the effect of substitution on the reactivity of the amine, a homologous series of amines [propyl ($PrNH_2$), dipropyl (Pr_2NH) and tripropyl amine (Pr_3N)] were visually observed reacting with TNT. It was found that the mono-alkyl amine reacted with TNT far faster than the tri-alkyl amine. Figure 2 shows qualitative results of adding a drop of each amine to acetonitrile solutions of TNT.

In an attempt to provide better quantification, uv-vis spectroscopy was used to monitor the nitroarene/amine reaction. The initial uv-vis studies examined the reaction of 2,4-dinitrotoluene (DNT) and DETA. Figure 3 shows the start and end spectra, as well as blanks (DNT and DETA alone). As soon as DETA was added, DNT solutions became light blue and, with time, red. Figure 4 shows the change in peak intensities with time—peaks at 650 nm and 400 nm decreased, while one at 527 increased. Similar experiments were performed with TNT and DETA (Fig. 5). As DETA was added to the TNT solution in acetonitrile, the peak at ~650 nm disappeared; the peak at 520 nm shifted to 500 nm, and a new peak grew in at 440 nm.

Quantification of the rate of TNT/DETA reaction was accomplished monitoring nitroarene loss by LC with PDA (214 nm). Data was plotted as first-order, and rate constants are given in Tables 2 to 4. Initially, an attempt was made to follow the reaction of the amine with the neat nitroarene (Table 2). The rate of TNT loss was roughly the same regardless of whether the amine was DETA or EDA. However, to achieve sample homogeneity, it was necessary to use a large excess of the amine (~100-fold).

In order to control the ratio of amine to nitroarene, it was necessary to perform the reactions in acetonitrile. Thus, for TNT and a single amine, this created an additional variable to be considered--nitroarene concentration in acetonitrile—in addition to nitroarene to amine ratio and temperature. Thus, depending on these ratios, the solution reaction of TNT and DETA (Table 3) may proceed faster than the reaction of the neat reagents (Table 2). A typical plot obtained is shown in Figure 6; the first-order rate constants are listed in Table 3. It was found that the ratio of amine to TNT was not nearly as important (cf. run 2 to 4) as the TNT concentration in acetonitrile (cf. run 2 to 3).

The effect of temperature on the reaction was rather surprising (Fig 7). For reactions at 25°C and 40°C the rate increased with temperature (Table 4). However, the reaction at 0°C was actually faster than the reaction at 25°C. One possibility was that the low temperature allowed moisture to condense into the reaction flask. To test this hypothesis a reaction was performed at room temperature with two drops of water added. The rate of this moist reaction was slightly faster than the normal room temperature reaction, but not the order of magnitude increase observed at 0°C. Another observation which required consideration was that fact that at room temperature the reactions were not first-order, but the reaction performed at 0°C and the one started at room temperature and cooled to 0°C after 4 hours appeared to approximate first-order (Fig. 7). We speculate that the nitroarene-amine reaction path proceeds through a TNT-amine complex and that the intermediate formation is enhanced at low temperature. We have not succeeded in isolating the intermediate. The only species recognizable in a GC/MS (gas chromatography with mass selective detector) analysis of the acetonitrile solutions of TNT/ DETA is 3,5-dinitro-p-toluidine, an expected reduction product.

Table 5 reports first-order rate constants for the reaction of acetonitrile solutions of various amines and TNT. Several observations can be made. As observed in the visual experiments (Fig.2), tertiary amines react more slowly with TNT than do secondary amines, and secondary amines react more slowly than primary. Thus, in tris, the teriary amine group is not considered reactive with TNT; and in DETA, the secondary amine is unreactive compared to the two primary amines. Indeed, the rate of reaction can be correlated with the number of primary amines in a compound--the more primary amine functionalities in a compound, the faster it reacts with TNT. Thus, among the primary amines, propyl ($PrNH_2$) and isopropyl ($iPrNH_2$) amines reacted slowest, while the tri-functional amine tris(3-aminoethyl)amine (tris) reacted most quickly.

Conclusions

Methods have been developed to track the reaction of the nitroarenes TNT and DNT with amines. The goal of this study was to elucidate the hypergolic reactions of TNT with various reducing agents. However, little difference among the amines, in terms of heats of reaction, was observed; all released about 110-130 kJ/mol TNT (Table 6, Fig. 8). The reaction of TNT with hydride produced more heat than with amines. However, if heat release were the controlling feature, DNT would be expected to react in a hypergolic fashion, and it does not. The heat released in the DNT/amine reaction is substantial; possibly more than the analogous reaction with TNT. Therefore, we conclude heat release is not the controlling feature. Rate constants, determined for the loss of TNT in dilute acetonitrile solution, clearly showed distinctions among the amines. The more primary amine functionalities in the amine compound, the faster it destroyed TNT. Hydrides or amine mixtures spiked with hydride decomposed substantially faster than the amines alone. However, a direct correlation between reaction rate and time-to-ignition was not observed. Most striking are the slow inflammation of TNT with DETA and the lack of inflammation of DNT with DETA. Possibly the high viscosity of DETA slows its neat reaction to the point that viscosity becomes more important than kinetics. In conclusion, the controlling feature of these reactions appear not to be heat release, but a combination of reaction rate and diffusion of the species, governed by the viscosity of the liquid reactant.

Acknowledgements

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Reference

1. F. Terrier, Rate and Equilibrium Studies in Jackson-Meisenheimer Complexes. Chem. Rev., **1982**, 82 (2), 77.

2. M.R. Crampton, Meisenheimer Complexes. Adv. Phys. Org. Chem., **1969**, 7, 211.

3. F. Fant, A. De Sloovere, K. Matthijsen, C. Marle, S. El Frantroussi, The use of amino compounds for binding 2,4,6-tritoluene in water. Environmental Pollution, **2001**, 111, 503.

4. E. Buncel, The role of Meisenheimer or σ-complexes in nitroarene-base interactions. The chemistry of functional groups supplement F: "The chemistry of amino, nitroso, and nitro compounds and their derivatives." (Part 2), Wiley, Chichester, UK 1982, 1225.

14. A.J. Tulis, A. Snelson, J.L. Austing, R.J. Dihu, D.L. Patel, B.D. Briggs, D.C. Heberlein, "Hypergolic Chemical Initiation of Non-Detonative Autocatalytic Self-consumption/Destruction of TNT, RDX, and TNT-Based Explosives;" International Annual Conf. Fraunhofer, 1996; EDIT 27, V41.

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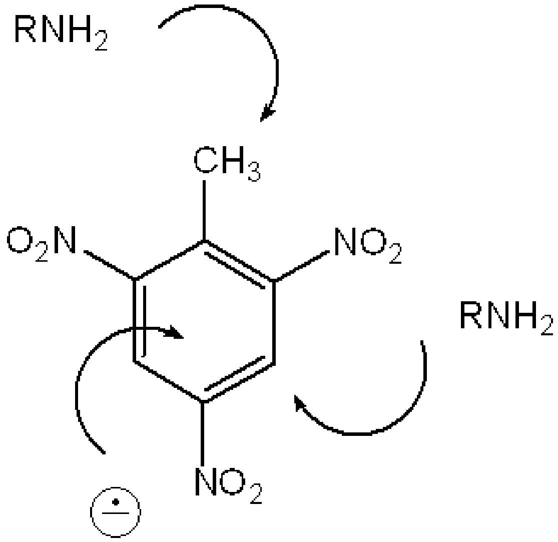
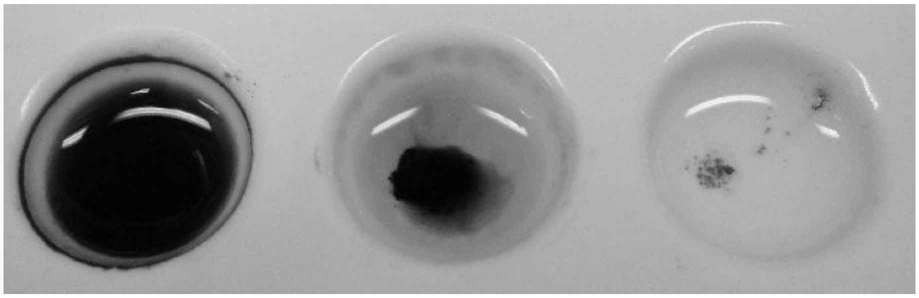


Figure 1: Sites of Amine Attack on TNT



$PrNH_2$ > Pr_2NH > Pr_3N

Figure 2. Picture of Reaction of TNT solution with propylamines

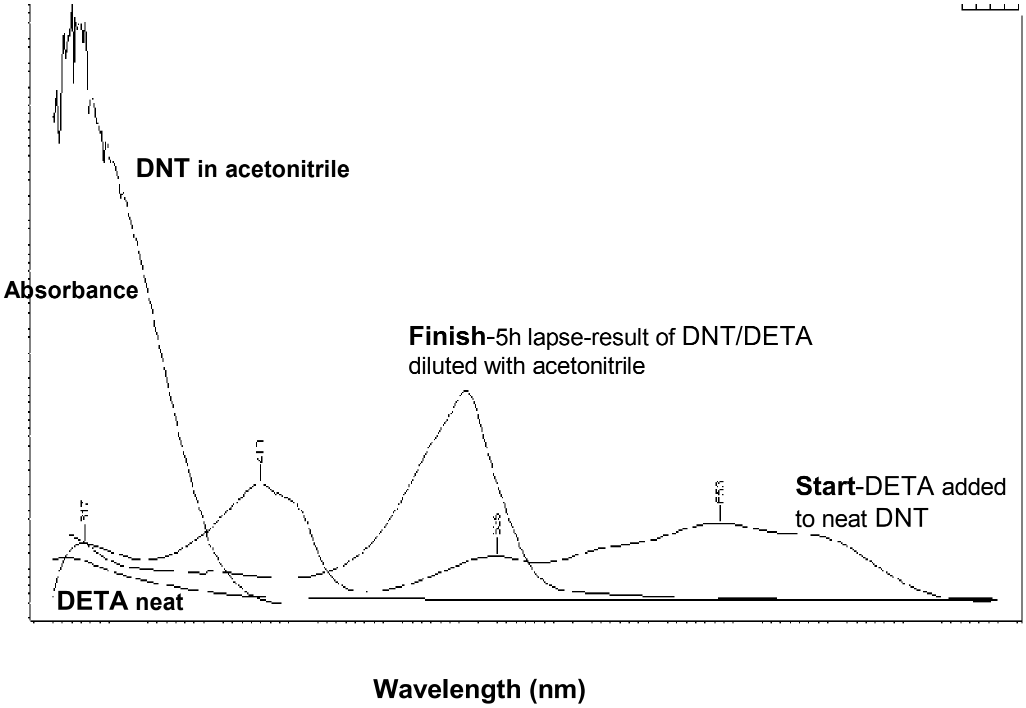


Figure 3: Spectra of reaction of neat DNT (red line) with addition of excess DETA (neat)

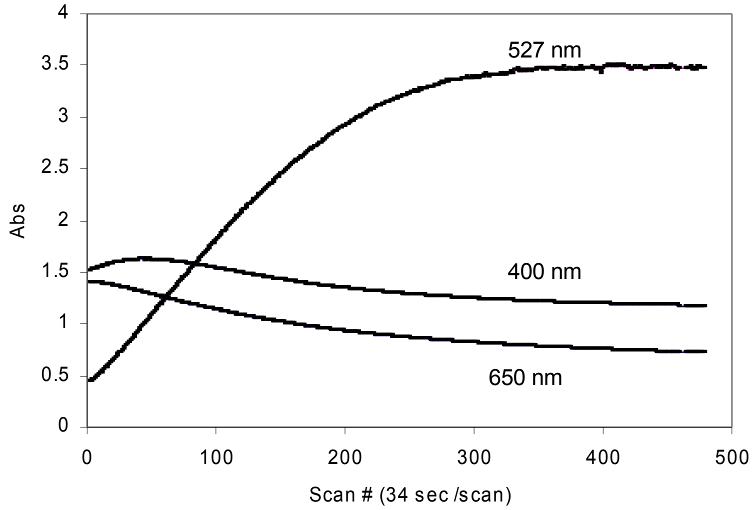


Figure 4: Change in uv-vis of neat DNT/DETA reaction

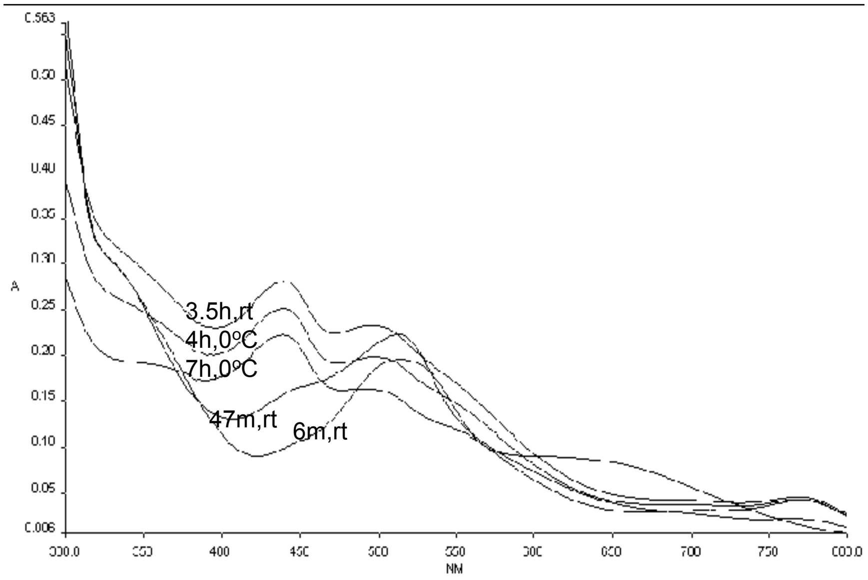


Figure 5: Spectra of reaction of TNT (2% acetonitrile) with DETA (2% in acetonitrile)

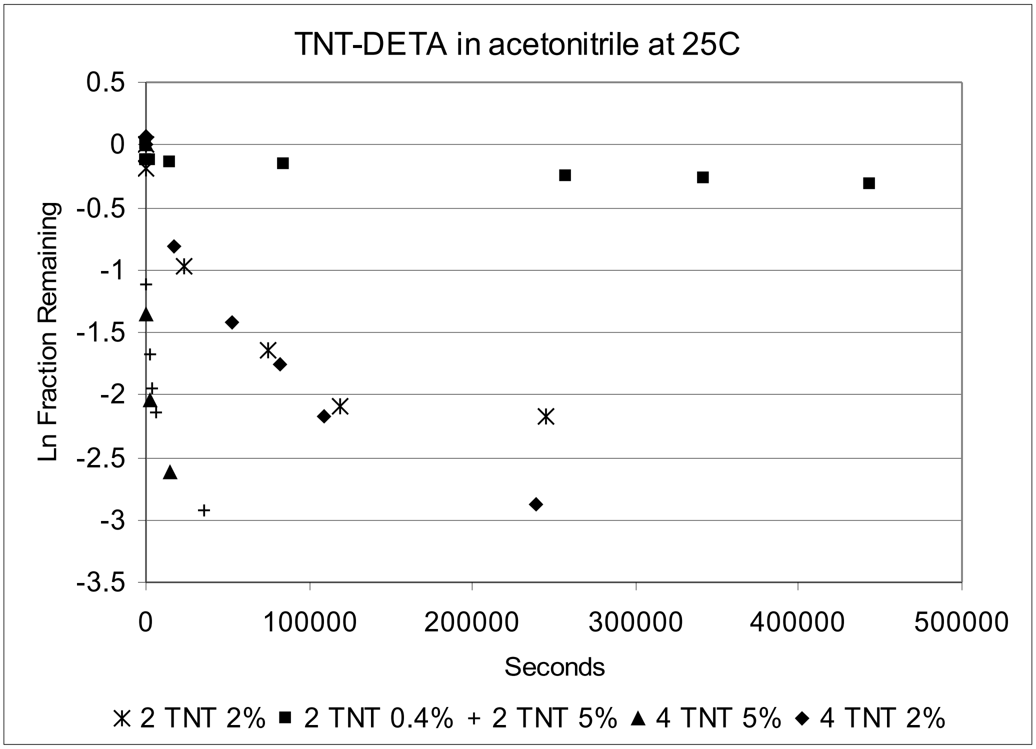


Figure 6: First-order plots: TNT-DETA at 25ºC

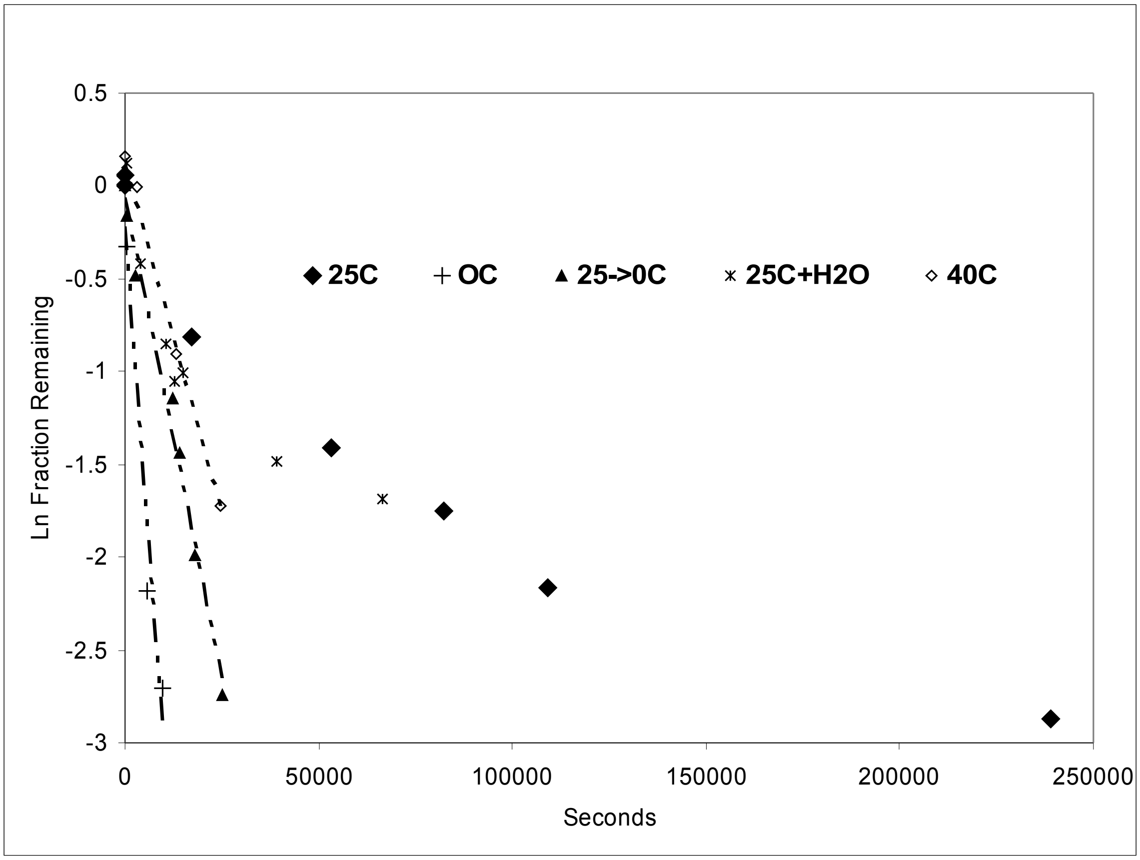


Figure 7: First-order plots of TNT reactions with DETA at various temperatures

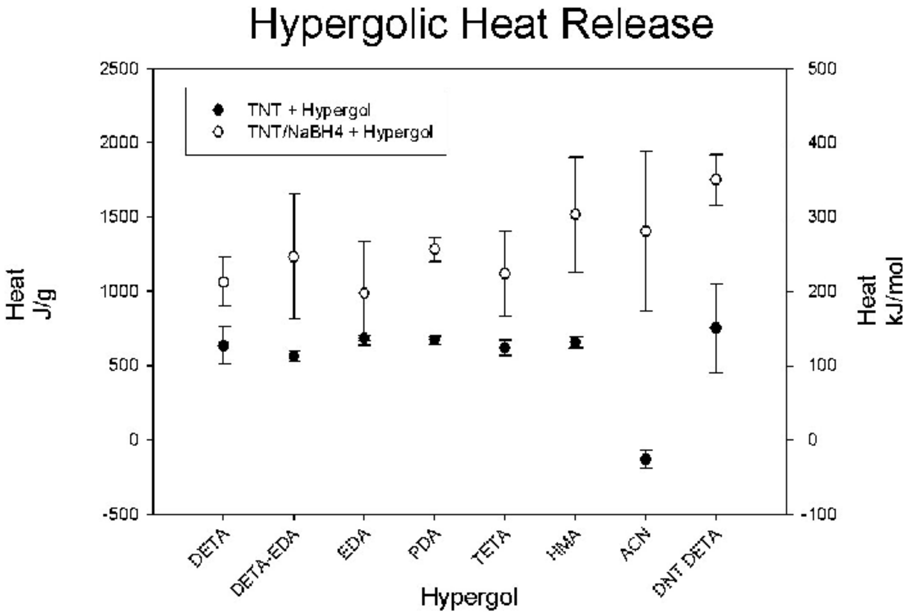


Fig. 8 Heat Release of Amine or Hydride with TNT

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						With Added Hydride				
Arene	Amine	arene:amine ratio	J/g	kJ/mol	# runs	arene:hydride ratio	$NaBH_4$	J/g	kJ/mol	# runs
TNT	ACN dripped in					0.66	10%	963 ± 12	218 ± 3	2
TNT	ACN dripped in					1.05	15%	1787	406	1
TNT	tris	26	544 ± 46	123 ± 10	8	0.66	10%	984 ± 256	223 ± 58	4
TNT	PDA	47	590 ± 26	134 ± 6	3	0.66	10%	1129 ± 70	256 ± 16	2
TNT	PDA	47				1.05	15%	1539 ± 129	349 ± 29	4
TNT	HMDA		575 ± 33	131 ± 7	4	1.05	15%	1335 ± 343	303 ± 78	5
TNT	DETA	50	557 ± 110	126 ± 25	13	0.66	10%	935 ± 147	212 ± 33	4
TNT	EDA	69	600 ± 18	136 ± 4	5	0.66	10%	868 ± 307	197 ± 70	4
TNT	DETA-EDA		493 ± 30	112 ± 7	3	0.66	10%	715 ± 207	162 ± 47	2
TNT	DETA-EDA					1.05	15%	1269 ± 278	288 ± 63	4
	average		**560** ± 39	**127** ± 9				**1152** ± 194	**262** ± 44	
TNT	EDA:DETA:NaBH4:HMDA	40/40/15/5					15%	351 ± 51	80 ± 12	7
TNT	EDA:DETA:NaBH4:HMDA	45/45/5/5					5%	1371 ± 314	311 ± 71	7
TNT	ACN dripped in						$LiAlH_4$	1253 ± 1673	228 ± 305	5
DNT	tris		1229 ± 66	224 ± 12	4					
DNT	DETA	29	660 ± 260	120 ± 47	9		10%	1921 ± 190	350 ± 35	7
DNT	EDA		1535 ± 97	280 ± 18	4					
DNT	ACN dripped in						10%	847 ± 56	154 ± 10	3

Table 1: Summary of Average Reaction Calorimetry Results: Nitroarenes with Various Amines

nitroarene	amine	mg arene	uL amine	ratio amine/ arene	rate constant s^{-1}	R^2
TNT	DETA	40	2000	105	2.12E-05	-0.50
TNT	DETA	40	2000	105	1.90E-05	0.91
TNT	DETA	40	2000	105	2.78E-05	0.98
TNT	EDA	40	2000	170	2.07E-05	0.87
DNT	DETA	20	1000	84	7.02E-05	0.99
DNT	DETA	20	1000	84	6.77E-05	0.99

Table 2: First-Order Rate Constants for Neat Nitroarene with Amine at 25°C

	nitroarene	amine	mg arene	uL amine	ratio amine/ arene	% TNT in ACN	% amine ACN	rate constant s^{-1}	R^2
1	TNT	DETA	40	40	2	0.4%	0.4%	8.00E-07	-0.87
2	TNT	DETA	201	200	2	2.0%	100%	1.94E-05	0.88
3	TNT	DETA	101	100	2	5.0%	100%	4.11E-04	-2.11
4	TNT	DETA	201	400	4	2.0%	4.0%	2.15E-05	0.90
5	TNT	DETA	200	400	4	5.0%	10.0%	1.3E-04	-3.80

Table 3: First-Order Rate Constants for Reactions of TNT Acetonitrile Solutions with DETA at 25°C

nitroarene	amine	mg arene	uL amine	ratio amine/ arene	% TNT in ACN	% amine ACN	temp ^{o}C	rate constant s^{-1}	R^2
TNT	DETA	201	400	4	2.0%	4.0%	0	3.09E-04	0.88
TNT	DETA	201	400	4	2.0%	4.0%	25->0	1.07E-04	0.97
TNT	DETA	201	400	4	2.0%	4.0%	25	2.15E-05	0.90
TNT	DETA	201	400	4	2.0%	4.0%	25*	3.23E-05	0.42
TNT	DETA	200	400	4	2.0%	4.0%	40	6.90E-05	0.97
TNT	DETA	40	100	5	0.4%	1.0%	-10	1.10E-05	0.92
TNT	DETA	40	100	5	0.4%	1.0%	25	1.77E-06	0.76

* two drops of water were added

Table 4: First-order Rate Constants for Reactions of TNT-DETA Acetonitrile Solutions

amine	% amine ACN	rate constant s^{-1}	R^2
$NaBH_4$	--	> 0.02	
tris	5.5%	7.93E-04	0.84
PDA	3.0%	1.60E-04	0.90
DETA/EDA/$NaBH_4$	--	9.50E-05	0.92
DETA	4.0%	2.15E-05	0.90
HMDA	--	1.97E-05	0.93
HMDA*	--	5.91E-06	0.97
EDA	2.4%	3.39E-06	0.91
$iPrNH_2$	3.0%	8.09E-07	0.95
$PrNH_2$	3.0%	8.12E-07	0.98
Pr3N	7.0%	<E-13	

*TNT toHMDA ratio1:2.5

Table 5: Rate Constants at 25ºC for TNT 2% in ACN in 1:4 Ratio with Amines

	melting point °C	density g/cm^3	viscosity cST	arene: amine ratio	Rx calorimeter J/g	±	kJ/mol	±	# run	DSC exotherm °C	DSC heat release J/g	# run	arene: amine ratio	rate constant s^{-1}	R^2 fit
TNT	81	1.65			Reaction Calorimeter					DSC			Kinetics		
$LiAlH_4$					1253	1673	228	305	5						
$NaBH_4$					963	12	218	3	2	286	2600	6	4	> 0.02	
tris		0.977		26	544	46	123	10	8	158	800	3	4	7.93E-04	0.84
PDA	-12	0.888		47	590	26	134	6	3	163	553	2	4	1.60E-04	0.90
DETA/EDA/$NaBH_4$ (45/45/10)										83	700	2	4	9.50E-05	0.92
HMDA													4	1.97E-05	0.93
HMDA	42	0.848	1.5 (50C)		575	33	131	7	4				2.5	5.91E-06	0.97
DETA	-39	0.955	5.8	50	557	110	126	25	13	169	393	5	4	2.15E-05	0.90
EDA	8.5	0.899	1.6	69	600	18	136	4	5	178	950	4	4	3.39E-06	0.91
DETA/EDA 50/50					493	30	112	7	3						
$iPrNH_2$	-32	0.694											4	8.09E-07	0.95
$PrNH_2$	-83	0.719								158	400	3	4	8.12E-07	0.98
Pr3N	-93.5	0.753											4	<E-13	
2,4-DNT	70	1.52													
tris		0.977			1229	66	224	12	4	145	2300	3			
DETA	-39	0.955	5.8	29	660	260	120	47	9	174	1500	3			
EDA	8.5	0.899	1.6		1535	97	280	18	4	164	400	2			
$NaBH_4$										110	300	3			

Calorimetry used neat reactants unless reducing agent was solid then ACN was used; DSC used neat reactants.

Table 6: A Summary of Thermal and Kinetic Examinations of Nitroarenes with Amines. The DSC run# refers to the number of replicate DSC thermograms used to calculate the DSC exotherm temperature.