Compatibility of Ammonium Nitrate with Monomolecular Explosives
Part II: Nitroarenes[1,2]

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Abstract

Ammonium nitrate/ fuel mixtures are widely used commercially; however, for military application it is often deemed necessary to enhance their performance by addition of conventional organic explosives. It is unreasonable to assume that such mixtures would retain the same thermal properties as the parent ammonium nitrate formulations. This paper presents a study of the thermal stability of such mixtures. Mixtures of ammonium nitrate and nitroaromatic compounds in various ratios have been decomposed isothermally in the temperature range 216° to 360°C. The thermal decomposition kinetics of both ammonium nitrate and the nitroarenes have been followed by liquid chromatography. Markedly enhanced decomposition of the nitroarenes was observed. Products of decomposition have been identified, and possible decomposition mechanisms are discussed.

Background

Ammonium nitrate mixtures with TNT were extensively used during World Wars I and II; aluminum was also sometimes added.[3] In this study we are investigating whether mixtures of ammonium nitrate with nitroarenes possess the same thermal characteristics as their individual components, or whether incompatibilities render the mixture significantly less stable. For example, it has been shown that when ammonium nitrate is added to TNT, the impact sensitivity of the mix is much greater than TNT alone.[3]

The nitroarenes examined included not only the military explosives 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitroaniline (picramide or TNA), and 1,3,5-triaminotrinitrobenzene (TATB), but also less complex nitroarenes which in some studies may yield themselves more readily to analysis: ortho-nitrotoluene, ortho- nitroaniline, nitrobenzene.

Experimental Section

o-Nitroaniline (o-NA), o-nitrotoluene (o-NT), nitrobenzene (NB) and ammonium nitrate (AN) were used as received from Aldrich Chemical Company. 1,3,5-Trinitroaniline (TNA) was purchased ina concentrated sulfuric acid solution, and the solid was precipitated by neutralization with aqueous NaOH.[2] 1,3,5- Trinitrotoluene (TNT) was obtained as production grade and recrystallized from benzene to a final melting point of 79-80°C. 1,3-5-Triaminotrinitrobenzene (TATB) was obtained from Los Alamos National Laboratory and used as received.

Solid/solid mixtures were prepared as previously discussed.[2] Samples were prepared in 100 mg batches by grinding neat ammonium nitrate together with solid nitroarenes. Individual samples (0.4 to 1.2 mg) were sealed in 200 uL glass capillaries. For the solid-liquid mixtures, the two components were weighed separately into reaction tubes; the tubes were centrifuged in order to mix the two ingredients before reaction.

The thermal stability of the samples was probed by examining differential scanning calorimetric (DSC) thermograms and by analysis of the residue from isothermally heated samples. A Perkin Elmer DSC-4 equipped with a TADS software data station was used in the DSC studies. DSC samples were sealed in glass capillaries as previously described.[2] Unless otherwise stated, scans were performed at 20°/min and were calibrated against the melting endotherm of indium. DSC results were primarily used for qualitative thermal stability assessment. The interpretation was that the lower the temperature of the exothermic maximum, the lower the thermal stability of the sample. Both qualitative and quantitative assessment of thermal stability was derived from isothermal thermolyses at 270° and 360°C. Ammonium nitrate decomposition was quantified by ion chromatography.[2] The nitroarene decomposition was analyzed by extraction of the samples with acetone. The extracts were analyzed by gas chromatography (GC) using a Varian 3600 GC equipped with an Alltech fused silica 5-BP capillary column (8 foot length) and a flame-ionization detector (FID). With injection port set at 250°C, the column at 80°C one minute then ramped to 210°C at 15°/min, and the detector set at 300°C, the retention times of TNT and of trinitroaniline were about 5 minutes, of o- nitrotoluene and of o-nitroaniline, about 3 minutes. To examine the condensed-phase products a Hewlett-Packard GC (5891A) with a HP 5971 mass selective (MS) detector was used. Acetone extracts of the thermolyzed samples were injected onto the DB-5 capillary column (9 foot length). The ionization source was set at 70eV; the injection port temperature was 250°C; the column temperature was raised from 80°C at 10°C/min to 180°C where it was held 2 minutes before it was ramped to 210°C. Some of the products were identified by comparison with authentic samples which were either purchased from Aldrich Chemicals or obtained from the High Explosives Research and Development group at Eglin Air Force Base. Those for which authentic samples were not available were tentatively assigned on the basis of their highest observed mass peak and their fragmentation pattern.

Results

With the exception of nitrobenzene, all nitroarenes examined promoted the decomposition of ammonium nitrate at 270°C (Table I). The effect of nitrobenzene was slight, presumably because the thermal decomposition of nitrobenzene itself is insignificant at 270°C. At 360°C the accelerating effect of the nitroarenes was still noticeable but much less marked than at 270°C (Table I). The thermal decompositions of o-nitrotoluene (o-NT), trinitrotoluene (TNT), o-nitroaniline (o-NA), and trinitroaniline (TNA) were all enhanced by the presence of ammonium nitrate (Table II). It is notable that the thermal decompositions of o- nitrotoluene and o-nitroaniline were much more adversely affected by the presence of ammonium nitrate than were those of the trinitro-analogs TNT and trinitroaniline.

The DSC thermograms of the mixtures of ammonium nitrate with o-nitrotoluene, o-nitroaniline, and trinitroaniline showed a single exotherm which appeared at a substantially lower temperature than those of the neat nitroarenes (Figs. 1-3). Only for trinitroaniline was the exotherm of the mixture substantially lower than that of neat ammonium nitrate (AN) (Fig. 3). For o- nitrotoluene and o-nitroaniline (Figs. 1 and 2), it would be difficult to recognize that ammonium nitrate was destabilized without reference to the isothermal results. The thermogram of the AN/TATB mixture showed a new exotherm between that of neat ammonium nitrate (328°C) and that of neat TATB (397°C), which is consistent with destabilization of TATB, but suggests stabilization of ammonium nitrate (Fig. 4).[2] The mixture of TNT with ammonium nitrate produced two exotherms, one lower than neat ammonium nitrate and one lower than neat TNT (Fig. 5). On the basis of the isothermal decomposition data we conclude that both species have been destabilized.

GC/MS data were collected on the decomposition products from the thermolysis of TNT and TNA under various conditions; these are shown in Tables III-IV. Relative amounts only are indicated; values are the relative peak heights with the largest decomposition peak set equal to one. Some of the species were positively identified by comparison of the GC retention time and the mass spectral fragmentation pattern to authentic samples; these are noted. Others were assigned on the basis of their highest mass peak and fragmentation pattern. Assignments are recorded in Table III. It should be noted that authentic samples of 1,3,5-trinitrobenzene and 2,4,6-trinitrobenzoic acid gave peaks of the same retention time and the same parent mass (213). We suspect this is due to decomposition of 2,4,6-trinitrobenzoic acid in the injection port. Peaks J (Table III, m/e 213) has been tentatively assigned as 1,3,5-trinitrobenzene. Since trinitrobenzoic acid would be an intermediate in the formation of trinitrobenzene, the assignment does not affect the kinetic rationale. Another assignment open to question is that of peaks Q and T as 2-amino-4,6-dinitrobenzoic acid (m.w. 227) and dinitroaminotoluene (m.w. 197), respectively. For both of these, the highest molecular weight (m.w.) usually observed in the mass spectrum is 197. Because in a few spectra, peak Q shows a mass unit 210, it is assigned as the 2-amino-4,6-dinitrobenzoic acid, loss of 17 (OH) being a common mode of fragmentation.[4] In no case can isomers be differentiated; peak F is assigned as 2,4- dinitrotoluene because an authentic sample produced the same retention time and fragmentation pattern. Since peak E, which has a retention time a minute less than that of F, exhibits the same highest mass and fragmentation pattern, we have assigned it as the other likely isomer, 2,6-dinitrotoluene.

Two TNT decomposition products produced only in the thermolyses in methanol proved particularly difficult to identify. Peak H, for which the highest mass fragment was 198, could be assigned as dinitrobenzyl alcohol or dinitrocresol based on that mass; or it could be trinitrobenzyl alcohol, assuming that species did not exhibit a parent peak. Indeed, under the conditions of this study, TNT usually did not exhibit a parent mass of 227; 210 was usually the highest peak observed. As can be seen from the Tables (III and IV), most of the nitroarene fragmentation patterns are based on the losses of 17 (OH), 30 (NO), 46 (NO_2), 47 (HNO_2), 63 (HNO_3) or combinations of these. Peak V (highest m/e 241) may be assigned as 2,4,6- trinitrobenzaldehyde from its mass, but from its fragmentation pattern the more likely assignment is methyl 2-amino-4,6- dinitrobenzoate, which has the same parent mass.

Discussion

Kinetics of Ammonium Nitrate Decomposition

The first step in ammonium nitrate decomposition is dissociation into ammonia and nitric acid.

$$NH_4NO_3 \Longleftrightarrow NH_3 + HNO_3$$

At low temperature the subsequent decomposition steps involve an ionic mechanism, the slow step being the protonation of nitric acid.[2,5] As a result, added acidic species, such as ammonium salts, nitric acid, nitrogen dioxide, accelerate ammonium nitrate decomposition. Conversely, added basic species, such as the salts of weak acids, retard ammonium nitrate decomposition. At temperatures above 300°C, the important ammonium nitrate decomposition mechanism is the homolysis of the O-N bond in nitric acid.

$$NH_4NO_3 \Longleftrightarrow NH_3 + HNO_3$$

$$HNO_3 \xrightarrow{\text{slow}} NO_2 + HO^{\cdot}$$

$$HO^{\cdot} + NH_3 \longrightarrow {}^{\cdot}NH_2 + H_2O$$

$$NO_2 + {}^{\cdot}NH_2 \longrightarrow NH_2NO_2$$

$$NH_2NO_2 \longrightarrow N_2O + H_2O$$

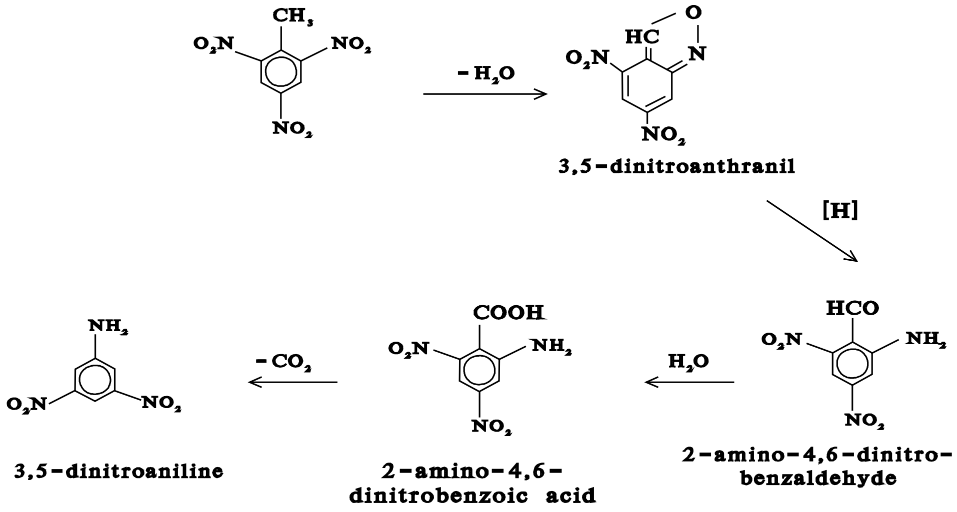
Scheme I

This free radical mechanism is unaffected by acids and bases. As a result of the change in decomposition mechanism, basic species, which stabilize ammonium nitrate, and acidic species, which destabilize it, have been observed to have a dramatic effect at 270°C, but little effect at 360°C. Addition of 16M nitric acid solution to ammonium nitrate increased the rate of decomposition 40-fold at 230°C, but only 5-fold at 340°C. Similarly, nitrogen dioxide accelerated ammonium nitrate decomposition, increasing the rate 3-fold at 230°C but only 1.3- fold at 340°C.[5]

Homolysis of the C-NO_2 bond, thus producing NO_2, has been established as one mode of nitroarene decomposition. It is the dominant mode in the vapor phase.[6] We have speculated the destabilizing effect of nitroarenes on ammonium nitrate is due to the production of small amounts of nitrogen dioxide upon decomposition.[2] We have observed that the destabilizing is more pronounced at 270°C than at 360°C. This decrease in the destabilizing effect is probably due to the change in mechanism in ammonium nitrate decomposition from ionic to free radical, rather than a change in the nitroarene decomposition (which might be expected to produce more nitrogen dioxide at higher temperatures). The addition of TATB raises, rather than lowers, the ammonium nitrate DSC exotherm; this is a stabilizing effect observed only in isothermal studies at low temperatures (<270°C). At higher temperatures, TATB destabilized ammonium nitrate as did the other nitroarenes. We have speculated that only at high temperature does TATB produce sufficient NO_2 to destabilize ammonium nitrate, and at low temperatures it stabilizes ammonium nitrate by reacting with nitric acid.[2]

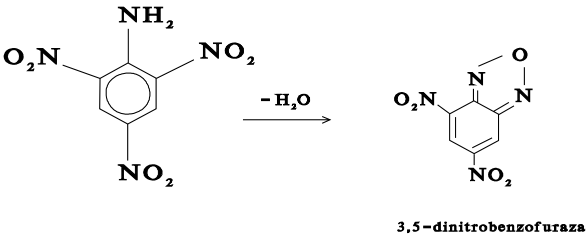
Kinetics of Nitroarene Thermal Decomposition

Generally the nitroarenes with no other functional group (mono-, di-, tri-nitrobenzenes) are more thermally stable than nitroanilines, which in turn are more stable than nitrotoluenes.[7] The thermal decomposition of nitrotoluenes has been a matter of study for many years and to a lesser extent that of nitroanilines. In the vapor phase, the decomposition of nitrotoluenes and nitrobenzenes appears to proceed by homolysis of the C-NO_2 bond, thus producing NO_2.[6] However, in the condensed phase, hydrogen transfer to the NO_2 group lowers the bond energy of the C-NO_2 bond, facilitating its cleavage.[8] Homolysis of the C-NO_2H bond results in loss of nitrous acid rather than NO_2. In nitrotoluenes where one or more nitro groups sit ortho to the methyl group, hydrogen transfer may be intramolecular as well as intermolecular (from either nitroarene or a solvent). Intermolecular hydrogen transfer may also result in loss of HONO, in which case the free radical arene species may dimerize or polymerize, or hydroxyl loss may occur, formingthe nitrosoarene, which can undergo further reduction to species such as toluidene.[8] The intramolecular pathway is thought to proceed through an intermediate anthranil.[9,10] In the decomposition of o- nitrotoluene, anthranil is difficult to isolate since it readily undergoes further decomposition.[9] In TNT, dinitroanthranil (O) has been isolated,[11] but it also decomposes further to products such as 2-amino-4,6-dinitrobenzaldehyde (S), 2-amino-4,6- dinitrobenzoic acid (Q) and dinitroaniline (R) where the methyl group has been oxidized (Scheme II).



Scheme II

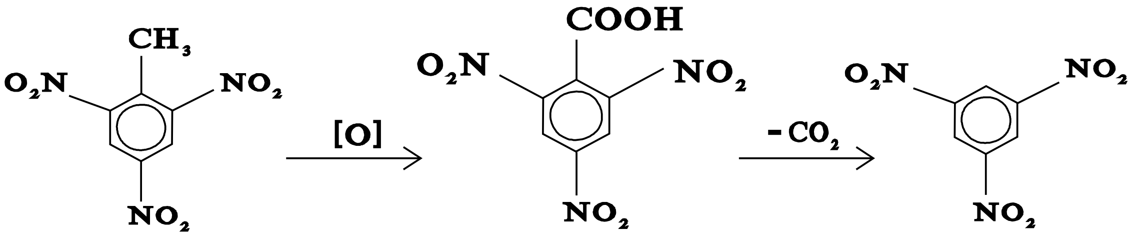
For trinitroaniline the decomposition pathway is thought to be similar to that of TNT. However, intramolecular hydrogen transfer produces a benzofurazan ring.[12] From our observations it appears that benzofurazan is considerably more stable to further decomposition than its carbon analog, anthranil.



Scheme III

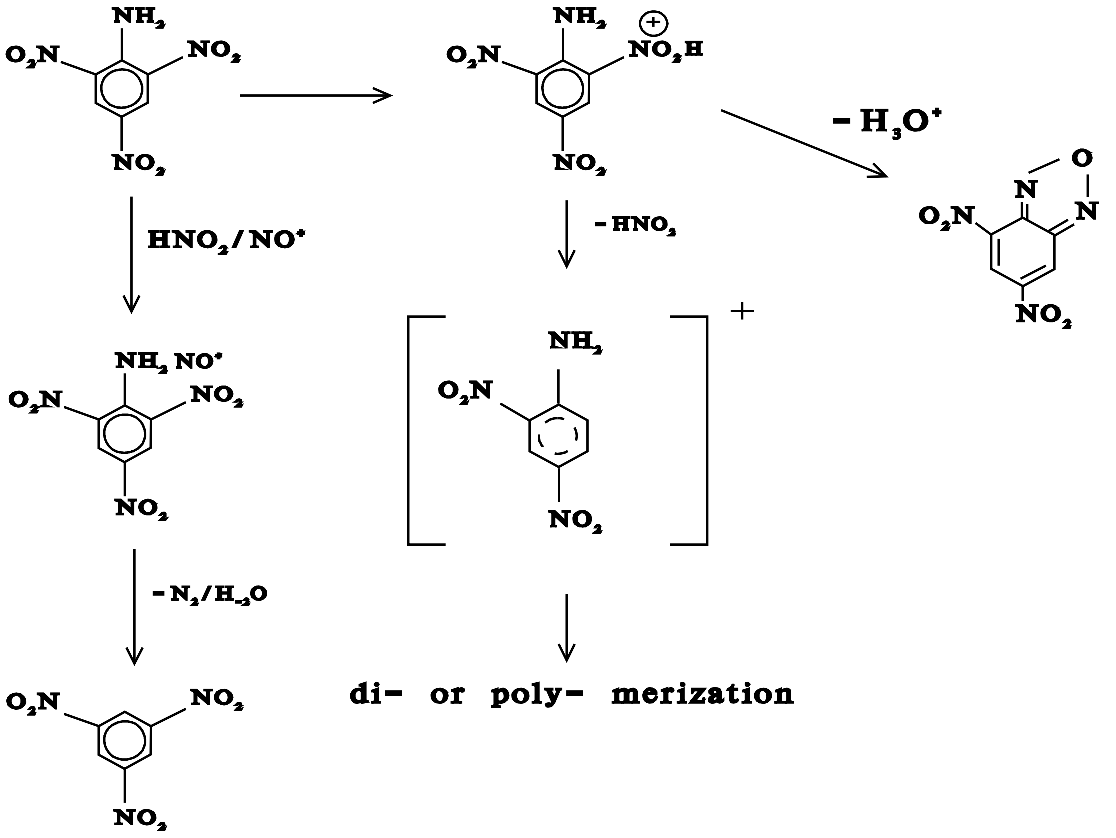
Effect of Nitric Acid and Ammonia on Nitroarenes

Since it is the ammonium nitrate which undergoes decomposition most readily and the nitroarene which is most adversely affected, the effect of the initial ammonium nitrate decomposition products, ammonia and nitric acid, on nitroarene thermolysis was examined. Measurement of the isothermal rate constants indicated that the decompositions of all the nitroarenes were enhanced by nitric acid. Acid catalysis can be envisioned as the result of the attack of H^+ on one of the nitro groups, thus facilitating its loss. However, toluene, itself, is subject to oxidation by strong acids; therefore, direct oxidation of the methyl group in TNT or diazotization of the amino group in trinitroaniline is also likely. The fact that 1,3,5- trinitrobenzene is the major decomposition product of TNT when heated with nitric acid vide infra suggests that direct attack on the methyl group is the preferred mode of reaction (Scheme IV). For trinitroaniline possible modes of acid attack are shown in Scheme V.

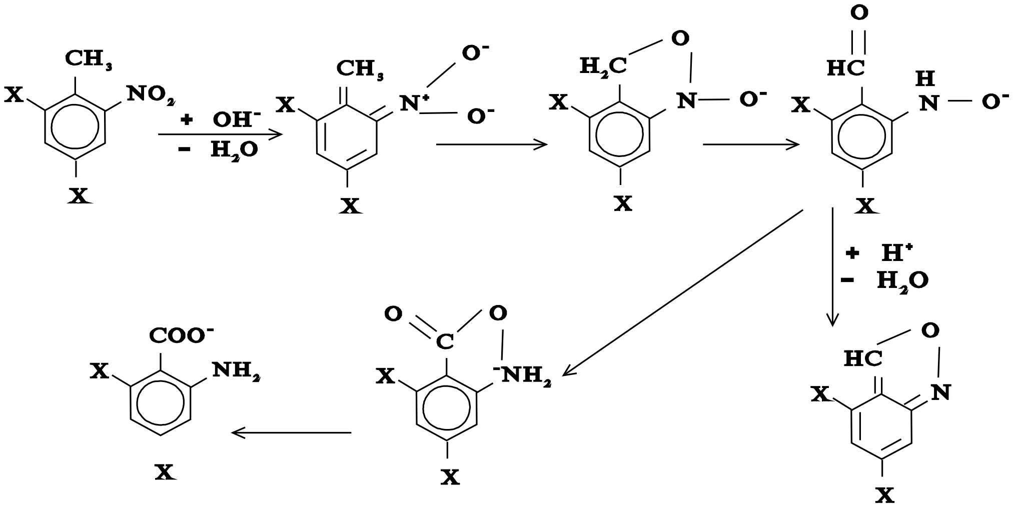


Scheme IV

Only the decomposition of TNT was significantly enhanced by the presence of ammonia (Table II). Base catalyzed decomposition of nitrotoluenes has been discussed by a number of researchers.[13] The base assists in the removal of the methyl hydrogen (scheme VI). It is not surprising that TNT with three electron-withdrawing nitro groups is more sensitive to the presence of base than is o-nitrotoluene.



Scheme V



X = H anthranilate
X = NO₂ dinitroanthranilate

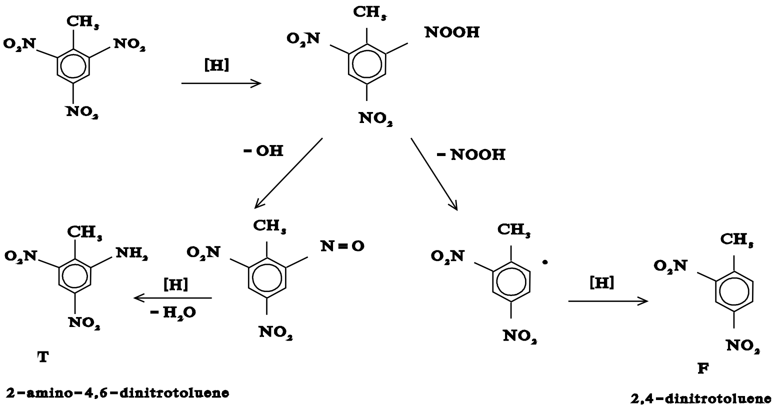
X = H anthranil
X = NO₂ dinitroanthranil

Scheme VI

Identification of Decomposition Products

Normally both thermal decomposition of TNT and of trinitroaniline resulted in a large amount of intractable black film on the thermolysis tube. However, in the presence ammonium nitrate less residue and more gases were observed.[2] The black residue was extracted by slurrying in acetone and analyzed by GC/MS. The products observed are shown in Tables III and IV.

Products observed in the decomposition of TNT, neat and in admixture with ammonium nitrate, are shown in Table III. Despite a variety of products, certain trends are evident. When TNT is decomposed neat, the major decomposition product was 2-amino-4,6- dinitrobenzaldehyde (S). 2-Amino-4,6-dinitrobenzoic acid (Q) and 3,5-dinitroaniline (R assigned from authentic sample) were also important decomposition products. These three, as discussed above, are the result of an intramolecular decomposition pathway (Scheme II). Intramolecular reactions would be expected to be important in the neat condensed-phase thermolysis. The intermediate for this reaction would be dinitroanthranil (O), and this is occasionally observed in the thermolyses (Table III). Two additional products were also predominant: 2-amino-4,6- dinitrotoluene (T) and 2,4-dinitrotoluene (F assigned from authentic sample). These are thought to arise from an intermolecular decomposition pathway as shown below:



Scheme VII

Dinitrotoluene may also be a product of direct C-NO_2 homolysis. This mode of decomposition is expected to be dominant in the vapor phase but is still a viable pathway in the condensed phase. It is this decomposition route which we have postulated to be the common mode by which all the monomolecular explosives destabilized ammonium nitrate.[2]

When ammonium nitrate was mixed with TNT (one-to-one weight ratio), all the decomposition products (S, Q, R, T, F) observed in the neat TNT decomposition were formed, but the major decomposition product was one of two new decomposition products. 1,3,5-Trinitrobenzene (J), a result of complete removal of the methyl group by oxidation to CO_2, is the major product of decomposition (Scheme IV). 2,4,6-Trinitroaniline (U) is the other new product not observed in the neat TNT thermolysis. This would appear to be an alternate end product for the trinitrobenzene radical after loss of CO_2; the radical is capped by combination with the amine radical produced in the ammonium nitrate high temperature decomposition (Scheme I). 3,5- Dinitroaniline (R), another result of complete oxidation of the methyl group, appears to be a more abundant product in the ammonium nitrate/TNT mixture than in the neat TNT melt. The observation of these highly oxidized products is in line with what might be expected with the added oxidizing power of ammonium nitrate. The methyl group is more likely to be oxidized intermolecularly (as evidenced by the presence of large quantities of trinitrobenzene) than intramolecularly (as in the neat TNT decomposition).

Because the predominant role of ammonium nitrate in the TNT mixture appeared to be oxidation, TNT was heated (270°, 1.66 min) in the presence of 50 wt% concentrated nitric acid. As in the decomposition of TNT in admixture with ammonium nitrate, 1,3,5- trinitrobenzene (J) is the principle decomposition product. The other species detected (D, F, R, S) are also the same observed in the TNT/ammonium nitrate mix. The only products observed in the TNT/ammonium nitrate mixture but not found in the TNT/nitric acid thermolysis are 2-amino-4,6-dinitrobenzoic acid (Q) and 2,4,6- trinitroaniline (U). The lack of the latter is expected if it is formed, as we argue, from combination with the amine radical produced in ammonium nitrate decomposition. The former might also be expected to be missing since it is a result of TNT rearrangement, a pathway overwhelmed by the abundance of oxidizing power.

To aid in the identification of the decomposition products of the neat organic explosives, which tend to form intractable residues, TNT and trinitroaniline were decomposed in methanol solution. To ascertain whether the basic reaction was dramatically different in methanol, the thermolysis rate constants in the solvent were determined (Table V). Methanol was not an "inert" solvent; not only did TNT decompose a bit more quickly, but new decomposition products were observed. In this case, the presence of methanol appeared to be more important than the presence of added ammonium nitrate. Although the presence of ammonium nitrate still accelerated the TNT decomposition, in methanol the products of TNT decomposition were basically the same whether neat TNT or TNT in admixture with ammonium nitrate was thermolyzed. This is most likely a dilution effect, since both TNT and ammonium nitrate where present only at the 1.0% level. The dominant decomposition products in methanol were methyl 2-amino-4,6-dinitrobenzoate (V) and a peak H (m/e 198), assigned as dinitrobenzyl alcohol or dinitrocresol. These were not observed in the condensed-phase thermolyses; they appear to be products of intermolecular oxidation by the solvent. Trinitroanisole was considered a possible decomposition product in methanol, but no observed peaks matched the retention time nor fragmentation pattern of an authentic sample. 2-Amino-4,6- dinitrobenzoic acid (Q), a result of internal rearrangement in the TNT molecule, was also an important product in methanol. Two dinitrotoluene isomers (E, F) (from C-NO_2 homolysis) and dinitrobenzoic acid (L) (from intermolecular oxidation) were common, but less abundant, decomposition products. The products of neat TNT decomposition (S, R, T) were also detected. 2,4,6- Trinitroaniline (U), formed in the decomposition of the TNT/ammonium nitrate melt, was not produced. In an attempt to clarify the unique decomposition products, a dilute methanol solution of o-nitrotoluene (2%) was heated 9 minutes at 320°C. The principle decompositions were analogs of V [(m/e 151) methyl aminobenzoate], of Q [(m/e 137) aminobenzoic acid], and of S [(m/e 121) aminobenzaldehyde].

The thermolysis of trinitroaniline produced significantly fewer decomposition products than that of TNT. Only three were identified in the thermolysis of trinitroaniline neat or in admixture with ammonium nitrate; two are common to both decompositions. The two products common to the thermolysis of trinitroaniline neat and with ammonium nitrate are dinitrobenzofurazan and 1,3,5-trinitrobenzene. These are the result of two important decomposition pathways. Dinitrobenzofurazan is produced by an intramolecular rearrangement between the neighboring nitro and amino groups (Scheme III). A similar reaction is responsible for the formation of dinitroanthranil during TNT decomposition; but in this case, since dinitrobenzofurazan is significantly more stable than dinitroanthranil, the decomposition stops here, not producing the variety of intramolecular products observed from in TNT decomposition. 1,3,5-Trinitrobenzene is the other major decomposition product common to both neat and mixed trinitroaniline thermolyses. This is a result of loss of the amino group. Presumably, it is lost by intermolecular oxidation to nitro and subsequent loss of NO_2. This hypothesis is supported by the observation that in the oxidizing melt with ammonium nitrate the relative ratio of trinitrobenzene to dinitrobenzofurazan increases substantially. The product unique to the ammonium nitrate/trinitrobenzene melt is dinitrobenzofuroxan. Again, it is not surprising that this more highly oxidized product is formed in the ammonium nitrate mixture. A third, but minor product, in the neat trinitroaniline decomposition has yet to be identified.

Conclusions

Ammonium nitrate is less thermally stable in admixture with nitroarenes. It is postulated that NO_2 or HONO produced during nitroarene decomposition destabilizes ammonium nitrate. Nitroarenes are destabilized by the presence of ammonium nitrate. Since the first step in ammonium nitrate decomposition is the formation of ammonia and nitric acid, these species were examined to determine their effect on nitroarene decomposition. The decomposition of all nitroarenes was catalyzed by nitric acid. In addition, decomposition of nitrotoluenes was found to be catalyzed by ammonia. These findings address important concerns when considering safe storage of large batches of ammonium nitrate/TNT mixtures. The stability of these mixtures is significantly less than either of the ingredients alone.

Acknowledgments

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Table I
Isothermal Rate Constant* (sec-1) of Ammonium Nitrate in one-to-one Weight Mixtures

	neat	NB	oNT	TNT	oNA	TNA
270°C	6.3	4.6	8.4	27	20	33 x 10^{-4}
360°C	13	18		18	23	21 X 10^{-2}

NB = nitrobenzene, oNT = o-nitrotoluene, oNA = o-nitroaniline
TNA = trinitroaniline, TNT = trinitrotoluene

* Values at 270°C are from first-order plots; those at 360°C are estimated from three samples each, heated for 11 seconds.

Table II
Isothermal Rate Constants (k x 10^4 sec^{-1}) of Organics with Additives

	Temperature		1st-order k	k constant time*	
	°C	neat	50% AN	HNO3	NH3
oNT	360	4.8	127	88	6.2
TNT	270	5.3	22	19	28
oNA	360	4.7	305	too fast	2.2
TNA	270	2.4	7.3	600	9.7

AN = ammonium nitrate, oNT = o-nitrotoluene, oNA = o-nitroaniline
TNA = trinitroaniline, TNT = trinitrotoluene

* Rate constant for neat compounds and those mixed with AN are from first-order plots(with the exception of oNT/AN); those for mixtures with acid and base (and for oNT/AN) are estimated from fraction remaining from three samples heated for a set time.

Table III A

Relative Amounts of Decomposition Products of TNT

Time min.	Fraction Remaining	A	D	E	F	G	H	J	K	TNT	L	O	Q	R	S	T	U	V	W
TNT neat, 270°C																			
4	.88		.03	0.1	0.2							0.2	1.0	0.9	1.0	0.3			
4	.88				0.3								0.5	0.3	1.0	0.2			
5	.85				0.2							0.1	0.3	0.3	1.0	0.1			
8	.77				0.2								0.2	0.7	1.0	0.2			
TNT/AN, 270°C																			
1.6	.81		.04		.03			1.0				.02	0.1	0.1	0.2	0.1	0.2		
9	.31							1.0						.004			.003		
9	.31		0.2	.02	.02			1.0							0.1	.01	.01		
120C 23h			.02	.01	1.0								0.1		0.2	0.1			
TNT/HNO3, 270°C																			
1.6	.83		.005		.004			1.0						.004	.004				
TNT/NH3, 270°C																			
1.7	.76			.05	0.1								0.36	1	0.72	0.32	.001		
3.3	.58		0.3	0.5	0.8			1.0					0.33		0.11				
TNT in methanol, 270°C																			
2.5	.85						0.1						1.0	.01	0.8	0.4		0.3	
12	.47			0.3	0.2	0.1	0.7		0.2		0.1		1.0	0.1	0.5	0.3		0.8	
17	.34			0.2	0.2		1.0		0.2			0.2	0.5			0.1		0.8	
17	.34			0.2	0.1		0.7		0.2		0.2		0.4	.01		0.1		1.0	
TNT/AN in methanol, 270°C																			
0.4	.73	1.0		0.6	0.9	0.2	0.2		0.3		0.5		0.1			0.1			0.3
2	.22	0.1	0.1	0.4	1.0	0.1	0.6		0.3		0.6		0.3	.02		0.4		0.1	0.7
17	0			0.7	0.4		0.8				0.4	0.3	1.0			0.3		1.0	

Retention Times of Decomposition Products and Major Fragments for TNT

5.4	7.9	8.1	9.1	9.5	10.5	10.8	11	11.5	12	14.7	15.5	15.6	16.1	16.5	16.9	17.4	22
A	D	E	F	G	H	J	K	TNT	L	O	Q	R	S	T	U	V	W
								227							228	241	
								226					211		210	209*	221
						213*	213	212	212	209	210	181	197	198	149	191	
							212	210*	195*	192	197	164	180*	195	119	175	
			182		198	197	195*	193	179	89	180*	183*	146	152	167		145
	168	165	165*	161	168	183	178	180	164	77	163	137	135*	134	136		129
140	122	148	148	160*	152	167	165	164	149	75	150	107	90	133	90		
131	92	135	119	158	122	120	120	149	137	74	104	91	63	104			
104	76	121	89	145	63	77	75	134	89	30	78	64		78			
77	75	90	63	144		30		89	77		52			77			
42		89		130				63	75					18			
		63		129					63								
				117					51								
				102													
				63													

*Indicates largest peak in spectrum if not that of the highest m/e.

**For the two shortest heating times for TNT/AN in methanol, small peaks were observed at 6.8 min. (B, m/e 145), at 7.3 min. (C, m/e 152), at 24 min. (X, m/e 251), and at 27 min. (Y, m/e 207). These were not assigned.

Table III B

GC/MS Decomposition Products Assignments

code	mol. wt.	compound	
D	168	1,3-dinitrobenzene	(by authentic sample)
E	182	2,6-dinitrotoluene	
F	182	2,4-dinitrotoluene	(by authentic sample)
H	198	dinitrobenzyl alcohol or dinitrocresol	
J	213	trinitrobenzene	(by authentic sample)
L	212	dinitrobenzoic acid	
O	209	dinitroanthranil	
Q	227	amino-dinitrobenzoic acid	
R	183	3,5-dinitroaniline	(by authentic sample)
S	211	amino-dinitrobenzaldehyde	
T	197	amino-dinitrotoluene	
U	228	trinitroaniline	(by authentic sample)
V	241	methyl amino-dinitrobenzoate	

Time Min.	Fraction Remaining	Code of Decomposition Product Decreasing Abundance --->																
		Major																
neat TNT, 270°C																		
4	0.88	S	Q	R				T		O	F	E	E	D				
4	0.88	S			Q	R	F	T										
5	0.85	S						Q	R	F	O	T						
8	0.77	S	R					T	Q	F								
TNT/AN, 270°C																		
1.6	0.81	J							S	U	R	T	Q	D	F	O		
9	0.31	J														R	U	
9	0.31	J							D		S					E	F	T V
120C	23h	F							S	Q			Z	T		D	E	
TNT/nitric acid, 270°C																		
1.6	.83	J														D	F	R S
TNT/NH3, 270°C																		
1.7	.76	R	S			Q	T				F					U		
3.3	.58	J	F		E		Q	D			S							
TNT in methanol, 270°C																		
2.5	0.85	Q	S			T	V				H	R						
12	0.47	Q	V	H	S			T	E	F	K	G	L					
17	0.34	H	V		Q		E	K	O	F	T							
17	0.34	V		H		Q			E	L	K		F	T		R		
TNT/AN in methanol, 270°C																		
0.4	0.73	A	N	F	E	L	W	K	H	G	C	B	Q	T	X			
2	0.22		F		W	X	Y	L	H	E	T	Q	K	D	G	A B C V R S		
17	0	Q	V	H	E		I	L	F	T	O							

Table IV
Retention Times of Decomposition Products and Major Fragments
for Trinitroaniline (TNA)

	TNA heated 270C for 12 min				TNA/AN heated 270C for 3.7 min			
minute	10.4	10.5	12.6	17	10.4	10.5	17	20.6
	210	213	209	TNA	TNA	225		
	180	197	179	228				195
	150	167	163	212				165
	134	137	133	198				132
	120	120	117	166				52
	87	91	90	136				
	74	75	78	90				
	61	63	62	78				
	30	30	30	63				

Time	Compound
10.4	dinitrobenzfurazan
10.5	1,3,5-trinitrobenzene
12.6	?
20.6	dinitrobenzofuroxan

Table V
Rate Constants at 270°C
Neat and Methanol Solutions of Nitroarenes and Mixtures

	TNT	TNT/AN
neat	5.25E-04	2.15E-03
MeOH Solution	1.06E-03	1.26E-02
	TNA	TNA/AN
neat	2.43E-04	7.34E-04
MeOH Solution	7.00E-04	6.02E-03