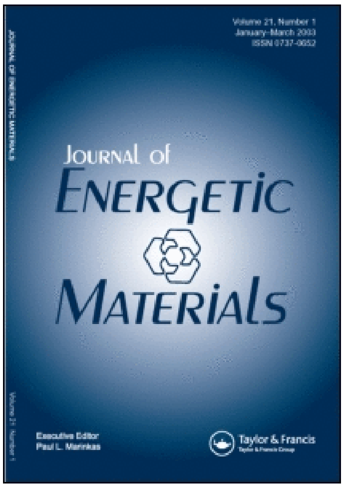

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Gas production from thermal decomposition of explosives: Assessing the thermal stabilities of energetic materials from gas production data

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GAS PRODUCTION FROM THERMAL DECOMPOSITION OF EXPLOSIVES: ASSESSING THE THERMAL STABILITIES OF ENERGETIC MATERIALS FROM GAS PRODUCTION DATA

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ABSTRACT

The gas formation associated with the thermal decompositions of nineteen energetic materials was determined at three temperatures (120°C, 220°C and 320°C). Although there was considerable variability within classes, among the largest producers of gas were the nitrate esters. PETN (pentaerythritol nitrate) generated about 6.3mole gas per mole, while nitrocellulose, produced almost no gas. Second in gas production were the nitramines, followed by nitroarenes and lastly, energetic salts. NTO (5-nitro-2, 4-dihydro-3H-1, 2, 4-triazol-3-one), which does not fit into the four main classes of energetic materials, exhibited gas production (2.13 mole gas per mole NTO) comparable with some nitroarenes and

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the energetic salt, ammonium dinitramide (ADN). For selected compounds gas evolution data was used to construct first-order plots, from which Arrhenius parameters were determined and compared with previously reported values.

INTRODUCTION

The safe manufacture, storage and transport of energetic materials depend on their thermal stability. A wide variety of sophisticated thermal analysis instruments are available to assess thermal stability of energetic materials. The advantages, disadvantages and limitations of these instruments have been considered elsewhere.[1,2] Less costly and well established techniques such as gas evolution tests have withstood the tests of time and still remain useful indicators of thermal stability. One of the earliest tests, the Abel Test, was developed in 1875 to determine the thermal stability of nitrocellulose, nitroglycerin and nitroglycol. This test was based on the fact the nitrate esters produce nitrogen dioxide (NO_2) upon decomposition. The original protocol involved heating one gram samples at 180°F and observing the time required to change paper permeated with starch and iodine from white to blue. While this test was aimed at energetic materials producing large amounts of NO_2, tests were soon developed which examined total volumes of gases produced. The Taliani test (1904) [3] and the so-called "65.5°C" test used constant volume containers and monitored the build-up of pressure. The vacuum stability test [3] heated five gram samples of energetic materials for 40 hours at 90°C (double-based propellants), 100°C (single-base propellants) or 200°C (high explosives) and measured the volume of gas produced by means of a mercury manometer attached directly to the reaction tube. These tests and modernized versions are still being used. One such version is the chemical reactivity test (CRT) where samples are heated at 120°C and atmospheric pressure for 22 hours.[4] The volume of gas produced is determined and the gaseous components identified and quantified by gas chromatography.[5] The above mentioned tests are relatively inexpensive, reliable, and frequently used in quality control to evaluate lot to lot variations for specific formulations. However, they can be subject to misinterpretation when attempts are made to rigorously correlate experimental data between unrelated classes of explosives. The purpose of this study was to present gas production data for a wide variety of different explosives and consider the advantages and limitations of this data when used to evaluate thermal stability.

EXPERIMENTAL SECTION

The energetic materials used for this study can be classified into four categories. The energetic salts (Figure 1) were ammonium dinitramide (ADN),[6] ammonium nitrate (AN),[7] and ammonium perchlorate (AP).[8] The nitrate esters (Figure 2) were nitroglycerin (NG), ethylene glycol dinitrate (EGDN), pentaerythritol tetranitrate (PETN), [9] and nitrocellulose (NC). The nitramines[10] (Figure 3) include 1,3,5-trinitrohexahydro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 1,3,3-trinitroazetidine (TNAZ), and dimethylnitramine (DMN). The nitroarenes (Figure 4) were 2,4,6-trinitrotoluene

(TNT), trinitroxylene (TNX), trinitromesitylene (TNM), amino-2,4,6-trinitrobenzene (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 2,4,6-trinitrophenol (picric acid).[11] We also report data for 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO),[12] shown in Figure 5, which is a candidate for an insensitive high explosive but does not fit into any of the above mentioned categories. With the exceptions of NG and EGDN, the above energetic materials were obtained from government laboratories.

Synthesis of NG was accomplished in a 25mL round bottomed flask equipped with a magnetic stir bar and cooled in an ice bath. To the 25mL flask 9mL concentrated sulfuric acid (H_2SO_4) and 3mL of 69% nitric acid (HNO_3) were added. The mixture was stirred vigorously for 15 minutes and then 1mL of glycerin was added at a rate of one drop per minute. The resulting mixture was stirred for an additional 30 minutes while being cooled in an ice bath and then poured onto approximately 80mL of crushed ice in a 100mL beaker. The top layer, containing the NG, was removed by pipette and washed with distilled water until the wash solution was pH7. The resulting nitrate ester was dried in an open beaker for four to five days in a hood. The yield was about 0.5mL of NG. It was stored in a refrigerator until used. The same procedure was used for the preparation of EGDN from ethylene glycol. The drying time for EGDN was only 24 hours.

Replicate samples (at least 5) of each energetic material (1-2.5 mg) were weighed into glass capillary tubes and sealed at ambient pressure. Each energetic material was heated at three different temperatures (120°C, 220°C and 320°C) using various reaction times, one of which represented complete decomposition. Following thermal decomposition and cooling to ambient temperature, the sealed capillary tubes were broken into a calibrated mercury manometer. The calibration procedure involved determination of the radius of the manometer tube using standard volumes of gas (50uL, 100uL, 150uL and 200uL) introduced into the manometer with a gas tight syringe. For four of the nitroarenes (TNT, TNX, TNM, and picric acid) and two of the energetic salts (AN and AP), gas volume data versus time were obtained at various temperatures. This data was used to generate first-order plots and calculate rate constants and Arrhenius parameters.

A TA Instruments Model 2910 differential scanning calorimeter (DSC) was used to obtain the exothermic maximums given in Table I. Analyses were carried out under nitrogen gas flow with approximately 0.2 mg samples sealed in quartz micro-capillary tubes placed in an aluminum cradle.[13] The scan rate was 20°C/min over a range 50°C to 450°C; melting points were read from these curves.

RESULTS AND DISCUSSION

For the three main classes of mono-molecular explosives (nitrate esters, nitramines and nitroarenes), some energetic salts and NTO the total gas productions, expressed as mole gas per mole compound at 120°C, 220°C and

320°C, are summarized in Table I. From Table I it is evident that the total amount of gas produced is dependent on temperature and compound. Also included in this table are additional thermal parameters: melting points; the differential scanning calorimeter (DSC) exothermic maximum temperatures (scanned at 20°/minute); and rate constants either measured isothermally (three significant figures) or calculated (two significant figures) from the references indicated. In Table II the activation energy (E_a) and pre-exponential factor (A) determined herein by gas evolution are compared with literature values obtained using other methods.

Trends by Temperature

Decomposition at 120°C: At 120°C only the energetic salt, ADN, and the nitrate esters, NG and EGDN, were observed to produce gas. For NG and ADN, gas was observed as early as 22 hours, while for EGDN, gas not observed until 72 hours. The largest producer of gas at 120°C was NG (3.15mole gas/mole compound). At 120°C, only five of the nineteen compounds were in the liquid state; three of these produced gas at 120°C (ADN, NG, and EGDN). Also in the liquid state at 120°C, but not evolving measurable gas, were TNAZ and TNT. At the next temperature studied, 220°C, only six of the nineteen were not in the liquid state; of these, only three did not produced any decomposition gas after 72 hours. These results point out the inherent instability of a mobile liquid species relative to a solid species.[13] The fact that TNAZ and TNT are molten at 120°C, yet do not undergo appreciable decomposition, indicates their relatively high thermal stability.

Decomposition at 220°C: After 22 hours, at 220°C, most of the energetic materials studied produced some gas. The exceptions were NC, TNM and TATB. Three of the nitrate esters (NG, EGDN and PETN), three nitramines (HMX, RDX and TNAZ), one nitroarene (DATB) and all the energetic salts appeared to have achieved maximum gas production after 22 hours at 220°C. None of the other nitrtoarenes had achieved maximum gas production. At 220°C most of the species should have been in the liquid state; the exceptions were the polymeric nitrate ester (NC), three nitroarenes (TNM, DATB, TATB), the nitramine, HMX, and one energetic salt (AP). Three of these six (NC, TNM, TATB) produced no decomposition gases at this temperature. HMX, which melts at about 280°C and has a decomposition rate at 240°C which is much lower than the other three nitramines (Table I), produced a substantial amount of decomposition gas at 220°C.

Decomposition at 320°C: This temperature is substantially above the melting point of all compounds studied except TATB (449°C) and NC (no melting point). After 22 hours, at 320°C, eighteen of the nineteen samples produced appreciable amounts of gas. Most of the nitroarenes produced substantially more gas at 320°C and 22 hours than at 220°C. However, none appeared to have achieved maximum gas production. On the other hand, the nitrate esters and energetic salts appeared to have reached maximum gas production after 22 hours at 320°C. Even at the higher temperature, NC produced barely detectable quantities of gas (about

0.001mole gas per mole NC).

With the exception of RDX, HMX and AN, which exhibited no change, the total amount of gas evolved per mole energetic material was somewhat larger at 320°C than at 220°C. DMN, TNM, TNA, DATB, and TATB produced considerably less gas at 220°C, even after long heating times, than they did at 320°C. While it is tempting to associate the maximum gas volumes at higher temperatures with more complete decomposition, (e.g. decomposition) of intermediates, care must be taken not to rule out the possibility of alternate mechanisms over a given temperature range. Alternatively, a change in mechanism may not manifest itself as a change in gas volume for a given time interval. Ammonium nitrate decomposition changes from a predominantly ionic to a mostly free-radical mechanism around 290°C but still produces about one mole of gas per mole AN.[7]

$$NH_4^+\,NO_3^- \rightleftharpoons NH_3 + HNO_3 \qquad (1)$$

Low Temperature (< 290°C) AN Decomposition:

$$HNO_3 + HNO_3 \rightleftharpoons H_2ONO_2^+ + NO_3^- \qquad (2a)$$

$$H_2ONO_2^+ \rightleftharpoons NO_2^+ + H_2O \qquad (3a)$$

$$NO_2^+ + NH_3 \rightarrow NH_3NO_2^+ \rightarrow N_2O + H_3O^+ \qquad (4a)$$

High Temperature (>290°C) AN Decomposition:

$HNO_3 \rightarrow NO_2 + HO^{\cdot}$ (2b)

$HO^{\cdot} + NH_3 \rightarrow {}^{\cdot}NH_2 + H_2O$ (3b)

$NO_2 + {}^{\cdot}NH_2 \rightarrow NH_2NO_2 \text{ -> } N_2O + H_2O$ (4b)

Overall: $NH_4NO_3 \rightarrow N_2O + 2\,H_2O$ (5)

Each decomposition mode leads to the production of nitrous oxide, but the amount of nitrogen produced in a side reaction is temperature dependent (26% N_2 at 290°C and 6% at 340°C):

$NO + {}^{\cdot}NH_2 \rightarrow NH_2NO \rightarrow N_2 + H_2O$ (6)

Nevertheless, as Table I shows, the total amount of gas evolved remains the same, about 0.9 mole/mole AN, at 220°C and 320°C.

Trends by Explosive Class

Energetic Salts: As a class the energetic salts (ADN, AN, AP), on average, formed the least gas; ranging from 0.9 mole gas per mole AN to 2.3 mole gas per mole ADN. The decomposition pathway for each proceeds via proton transfer to form ammonia and the parent acid ($X^- = N(NO_2)_2^-$, NO_3^- or ClO_4^-):

$NH_4^+X^- \rightarrow NH_3 + HX$ (7)

Further oxidation of the ammonia by the acid produces gases. In the mechanism shown for AN (Eq. 1-6), it is evident that one mole of gas is the maximum expected (since total gas measurements were performed at room temperature, where water was condensed). The oxidation of the ammonium ion of AP by perchloric acid forms predominately nitrous oxide at low temperatures (Eq. 8) and nitrogen at high temperature (Eq. 9): [8]

$2\ NH_4ClO_4 \rightarrow N_2O + HClO_4 + HCl + 3\ H_2O$ (8)

$2\ NH_4ClO_4 \rightarrow N_2 + HClO_4 + HCl + 1/2\ O_2 + 3\ H_2O$ (9)

The remaining perchloric acid and HCl undergo further reaction to form oxygen and a trace of chlorine. The gas composition varies with temperature, but the total amount of gas remains about 1.3 mole gas per mole AP:

At 250°C

$10\ NH_4ClO_3 \rightarrow 4\ N_2O + 1\ N_2 + 7\ O_2 + 1\ Cl_2 + 2\ HClO_3 + 6\ HCl + 16\ H_2O$ (10)

At 380°C

$10\ NH_4ClO_3 \rightarrow 3\ N_2O + 2\ N_2 + 7\ O_2 + 1\ Cl_2 + 2\ 1/3\ HClO_3 + 5\ 2/3 HCl + 16\ H_2O$ (11)

The only energetic salt to produce as much as 2 mole gas per mole salt was ADN. The early evolution of gases from ADN is evidence that this material is much less thermally stable than some of the other energetic materials examined. It has been previously shown that the dinitramidate anion decomposes first, forming N_2O and AN and that subsequent decomposition of AN results primarily in N_2 formation.[6]

$NH_4^+\ N(NO_2)_2^- \rightarrow N_2O + NH_4^+NO_3^-$ (12)

$NH_4^+\ NO_3^- \rightarrow N_2 + 2\ H_2O$ (13)

Nitrate Esters: Among the nitrate esters examined was the compound that formed the least amount of gas (NC-- 0.001 mole gas per mole NC) and the compound that formed the most gas (PETN--6.3 mole gas per mole PETN at 320°C). With the exception of the polymer NC, among the nitrate esters the relative order of gas production EGDN < NG < PETN correlated with the number of nitro groups in each compound, 2, 3, and 4, respectively. It was previously reported that the first step in nitrate ester decomposition is loss of NO_2 leaving RH_2CO.[9] Depending on the stability of the beta carbon fragment, the next step is probably loss of formaldehyde (H_2CO).

$$O_2N\text{-}O(CH_2)_nO\text{-}NO_2 \rightarrow NO_2 + O_2N\text{-}O(CH_2)_nO\bullet \qquad (14)$$

PETN loses all four nitro groups and two molecules of formaldehyde to undergo a double ring closure to form a spiral-ketal. This unstable species decomposes to produce a polymeric residue (Scheme 1).[9]

Nitramines: Like the nitrate esters, the nitramines formed substantial amounts of gas. Among the nitramines, HMX produced the most gas (5.4 mole gas per mole HMX at 320°C) and DMN the least (about 1 mole gas per mole DMN at 320°C). Multifunctional nitramines have been shown to fall apart in a different fashion than mono-functional nitramines.[10,12] Initial decomposition of nitramines involves N-NO_2 bond homolysis. Frequently the nitrogen dioxide is reduced and forms nitroso species and a minimum amount of gas:

$$(CH_3)_2N\text{-}NO_2 \rightarrow (CH_3)_2N\bullet + NO_2 \qquad (15)$$

$$(CH_3)_2N + NO \rightarrow (CH_3)_2NNO\bullet \qquad (16)$$

However, in some cases, the amine radical undergoes further break down before the lost NO_2 can return as reduced NO, and little nitrosamine is formed. For simple nitramines, such as DMN initial decomposition forms dimethylnitrosamine and little gas; only at higher temperature (320°C) does the nitrosamine break down to produce more gases. In the case of RDX and HMX with alternating CH_2-NNO_2 groups, the loss of only one NO_2 group triggers the unraveling of the entire heterocycle and total gas production is high. In mono-functional nitramines, N-N scission means the most likely fate of each nitrogen atom is formation of nitrogen gas. In RDX and HMX, once the first N-N bond is broken, the rest of the heterocycle unravels and the extra nitramine functionality forms nitrous oxide rather than nitrogen gas.

$$\text{HMX} \rightarrow NO_2 + HCN + 3\,H_2C{=}N{-}NO_2 \qquad (17)$$

$$H_2C{=}N{-}NO_2 \rightarrow NNO + H_2CO \qquad (18)$$

In solution, the decomposition gases are predominately nitrogen gas, and more nitrosamine is observed than in the neat melt because the amine radical remaining after initial NO_2 loss is stabilized by the solvent, preventing further unraveling of the ring.

Although it contains a nitramine functionality, TNAZ cannot be considered a simple nitramine because it contains a $C(NO_2)_2$ group. Nevertheless, one of the first decomposition products observed is the nitroso species 1-nitroso-3,3-dinitroazetidine.[10] A number of decomposition products in which the azetidine ring is intact have been identified; among these are 1,3-dinitroazetidine and 3,3-dinitroazetidine. Upon heating, at high temperature, one mole of TNAZ forms about 3 moles of gas. This is consistent with findings that the three nitro groups ultimately end up as nitrogen gases, while the ring forms insoluble residue.[10]

Nitroarenes: After 22 hours at 220°C the range of gas production varied from no gas to about 3.5 mole gas per mole picric acid. No gas evolution was detected for either TNM or TATB after 22 hours at 220°C. At 320°C and 22 hours all nitroarenes produced gas. In general, nitroarenes appeared to evolve 2 to 4 moles gas per mole arene at 320°C. Early in the decomposition arene-related compounds were observed. For species with exocyclic methyl groups, arene products with various oxidation states of the methyl (CH_2OH, COH) and/or amine groups formed by the reduction of nitro groups. Late in the decomposition insoluble polymeric residues formed.

CONCLUSIONS

This study showed that gas production was roughly correlated with the number of nitro groups. As shown is Table I, the complete decomposition of 14 of the 19 energetic materials resulted in moles of gas equivalent to or about one mole greater than the number of nitro groups present. The extra gas production was probably due to gasification of the carbon backbone. This is especially evident for PETN and HMX which both formed substantially more gas than their number of nitro groups. Although the amount of gas produced cannot be used as an acrossthe-board estimate of thermal stability, within a given class of energetic materials, such measurements appear to be related to thermal stability. Among the nineteen compounds examined, only the nitrate esters and ADN exhibited significant decomposition at 120°C. With the exception of NC all appeared to undergo substantial decomposition at 220°C, although the nitramines did not decompose completely. Most of the nitroarenes produced more gas at 320°C than 220°C suggesting that intermediate arenes are formed at 220°C. The results of this study also point out the inherent instability of mobile liquid species relative to solid species.

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Table I. Moles of Gas per Mole Compound Formed at Various Temperatures & Times

Temp $^{\circ}$C	120				220				320				#	m.p.	DSC	constant (1/s)		Eact kcal/	log A /sec	
Hours	22	72	hours*	561	22	72	hours*	550	22	72	hours*	>416	NO_2	$^{\circ}$C	$^{\circ}$C	240 $^{\circ}$C	320 $^{\circ}$C	mole		Refs.
NG	2.54	3.2			3.55	3.50			3.96	4			3	13						
EGDN	0	2.17			2.3	2.3			2.74	2.75			2	-23						
PETN	0	0	120		5.04	5.19			6.32	6.3			4	143	210	2.0E-01	3.68E+01	39.4	16.1	9
NC	0	0	360		0	0	360		0.001	0.001	360			none	220					
ADN	1.25	1.45		2.53	2.13	2.2	46		2.4	2.3			2	94	189	3.7E-01	5.2E+01	37.3	15.5	6
AN	0	0			0.88	0.9	46		0.89	0.9		0.96	1	169	328	3.E-05	5.71E-03	30.4	9.04	7
AP	0	0			0.87	0.9	47		1.25	1.25				**	340	2.00E-05	1.6E-03	20.5	4.68	8
RDX	0	0	240		2.92	3.9			3.84	3.9		4.8	3	204	285	1.70E-02	2.3E+00	37.8	14.3	10
HMX	0	0	240		4.33	4.3			4.24	5.4		8.39	4	280	244	7.13E-05	7.8E-02	52.8	18.4	10
TNAZ	0	0			3.01	3			3.46	3.77		4.44	3	101	278	4.60E-03	1.4E+00	43.7	16.3	10
DMN	0	0	560		0.57	0.57		0.79				1	1	57	292	1.00E-03	1.7E-01	38.0	13.2	10
NTO	0	0			2.13	2.2			2.4	2.3	48	2.42	1	none	267	1.00E-04	2.7E+00	78.5	29.4	12
PA	0	0	120		3.47	3.64			3.89	4.09		4.62	3	124	332	1.E-05	7.3E-02	44.3	15.2	11
TNT	0	0	120		1.83	2.18			2.68	3.23		3.27	3	80	328	2.3E-05	2.55E-03	38.1	11.6	11
TNX	0	0	120		1.01	1.66			2.13	2.22		2.45	3	187	351	8.1E-06	1.31E-03	41.5	12.6	11
TNM	0	0	170		0	0			1.77	1.92		2.16	3	240	368	4.8E-06	4.63E-04	36.6	10.3	11
TNA	0	0			0.25	0.50		3.03	3.21	3.41			3	192	387	1.8E-06	8.48E-04	48.0	14.7	11
DATB	0	0			0.24	0.24		1.34	3.19	3.45		3.98	3	286	360	3.40E-06	2.73E-03	47.9	15.3	11
TATB	0	0	170		0	0			3.23	3.40		3.84	3	449	397	1.6E-07	1.06E-04	46.8	13.1	11

hours* denotes longest time for which this sample was heated with no results differing from the previous column.

* * the AP does not melt; an endothermic phase change occurs at 240 $^{\circ}$C

DSC heating rate 20 $^{\circ}$C per minute

Table II. Activation energy and pre-exponential factors of selected energetic materials obtained from total gas evolution data and compared with results using other methods.

Compound	Total gas		Other			reference
	Ea (kcal/mol)	A sec^{-1}	Ea (kcal/mol)	A sec^{-1}	method	
TNT	44.05	3.0E+13	38.1	3.87E+11	HPLC	11
TNX	42.32	3.7E+11	41.5	3.88E+12	HPLC	11
TNM	33.14	3.3E+08	36.6	1.88E+10	HPLC	11
Picric Acid	24.40	4.8E+06	44.3	1.58E+15	HPLC	11
AN	29.11	3.5E+08	30.4	1.10E+09	IC	11
AP	26.40	7.7E+06	20.5	4.81E+04	IC	8

$NH_4N(NO_2)_2$

Ammonium Dinitroamide

ADN

$NH_4\ NO_3$

Ammonium Nitrate

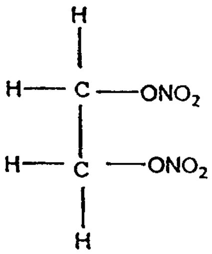
AN

NH_4ClO_4

Ammonium Perchlorate

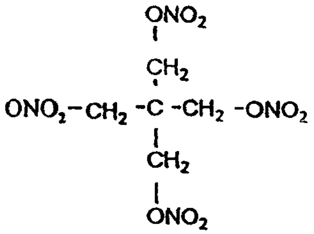
AP

Figure 1. Chemical structures of energetic salts.



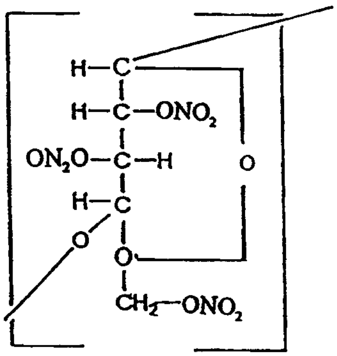
Ethylene Glycol Dintrate

EGDN



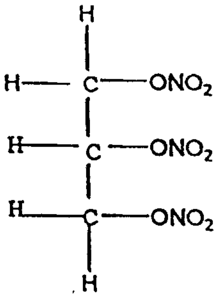
Pentaerythritol Tetranitrate

PETN



Nitrocellulose

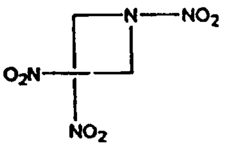
NC



Nitroglycerin

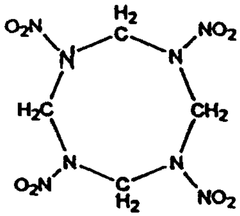
NG

Figure 2. Chemical structures of nitrate esters.



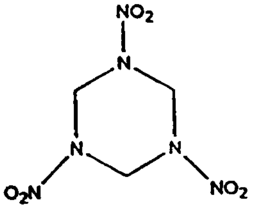
1,3,3-Trinitroazetidine

TNAZ



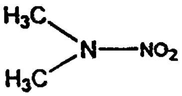
1,3,5,7-Tetranitro-1,3,5,7-tetrazocine

HMX



Hexahydro-1,3,5-trinitro-s-triazine

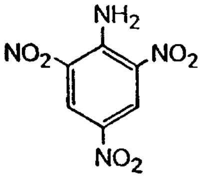
RDX



Dimethylnitramine

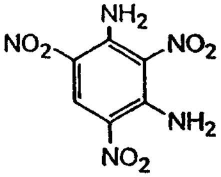
DMN

Figure 3. Chemical structures of nitramines.



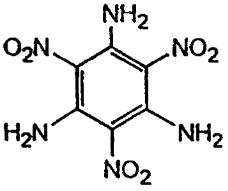
Amino-2,4,6-trinitrobenzene

TNA



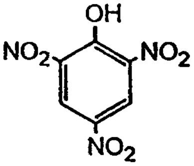
1,3-Diamino-2,4,6-trinitrobenzene

DATB



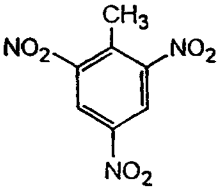
1,3,5-Triamino-2,4,6-trinitrobenzene

TATB



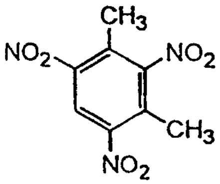
Picric Acid

PA



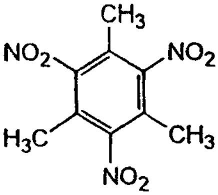
Trinitrotoluene

TNT



2,4,6-Trinitroxylene

TNX



Trinitromesitylene

TNM

Figure 4. Chemical structures of nitrarenes.

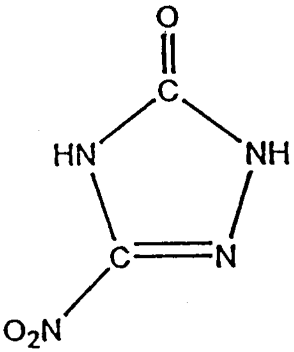
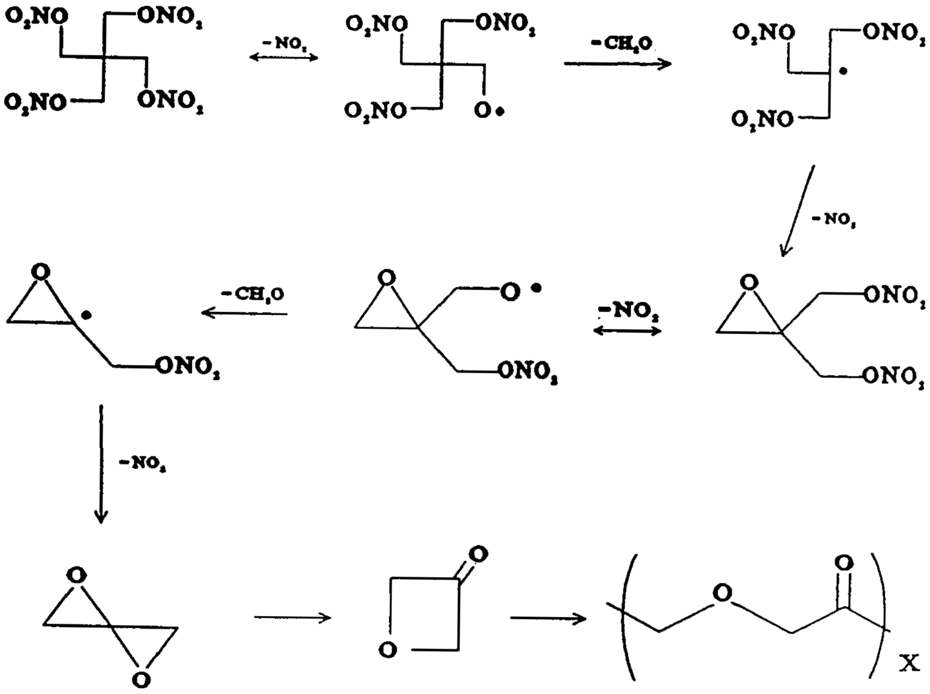


Figure 5. Chemical structure of NTO.

SCHEME 1


O₂NO
ONO₂
O₂NO
ONO₂
-NO₂
O₂NO
ONO₂
O₂NO
O•
-CH₂O
O₂NO
ONO₂
O₂NO
-NO₂
O
ONO₂
ONO₂
-NO₂
O
O•
ONO₂
-CH₂O
O
ONO₂
-NO₂
O
O
O
O
O
O
X