A Comparison of the Thermal Decomposition of Nitramines and Difluoramines

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The decomposition rates and product distributions of a number of nitro- and difluoramino-substituted six-membered rings were compared: nitrocyclohexane (I); 1,1-dinitro-cyclohexane (II); 1,1,4,4-tetranitrocyclohexane (III), 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV); 1,4-dinitropiperazine (V); 1,4,4-trinitropiperidine (VI), and 4,4-bis(difluoramino)-1-nitropiperidine (VII). The study suggested the following order for susceptibility to decomposition: $N-NO_2 > C-(NO_2)_2 > C-(NF_2)_2$ The difference in bond energies among the compounds is small. Geminal bis(difluoramino) compounds appeared to be somewhat more stable than the corresponding gem-dinitro compounds though they released more heat during decomposition. Where a nitramine functionality was present, the nitroso analogue was observed as a major decomposition product. The decomposition of gem-bis(difluoramino) and gem-dinitro compounds exhibited similarities. Both experienced loss of one geminal NX_2 group followed by the rearrangement of the remaining NX_2. Where X was oxygen, loss of the initial nitro by homolysis was favored; rearrangement of the remaining nitro followed by homolysis of NO resulted in a C═O bond. Where X was fluorine, the initial difluoramino may have been lost as HNF_2. The remaining difluoramino reacted by losing fluorine, leaving C═NF or by losing HNF, resulting in ═C−F; the latter was mainly observed.

Introduction

The presence of a nitro group signals a compound that decomposes exothermically and which may require special handling precautions. Indeed, most explosives contain NO_2 groups. Another moiety with the same oxidizing and energetic potential is the NF_2 group. Since new routes for synthesizing these NF_2 compounds have become available,[1,2] we have examined the thermal stability of several new difluoramines and their nitro analogues.

The $N-NO_2$ linkage has frequently been studied in dimethylnitramine and the cyclic nitramines[3−7] RDX and HMX. In the latter two, alternating CH_2N-NO_2 groups make depolymerization with formation of N_2O and CH_2O an important decomposition pathway.[3−7] Proposed decomposition pathways for RDX and HMX are shown in Figures1 and 2, respectively.[6,7] Common to the thermolysis of all nitramines is the formation of nitrosamine formed via $N-NO_2$ homolysis, subsequent reduction to NO, and reaction of NO with the amine:

$$R_2N-NO_2 \xrightarrow{-NO_2} R_2N \xrightarrow{+NO} R_2N-NO \qquad (1)$$

Indeed, the observed activation energies for decomposition of secondary nitramines falls in a range comparable to the $N-NO_2$ bond energy (Table 1).

The $C-NO_2$ linkage is found in a variety of nitroarenes and in a more limited number of nitroalkanes. Three modes of decomposition are generally postulated: (a) homolysis of the $C-NO_2$ bond; (b) inter- or intramolecular hydrogen transfer to the nitro group, resulting in HONO loss; and (c) nitro/nitrite isomerization.[8−11] The relative dominance of these pathways depends on temperature; and since homolysis requires the most energy, it is favored at high temperatures (Table 1).[12,13] However, the isokinetic point between homolysis and elimination has been estimated to be much lower for gem-dinitro species (370 K) as compared to mononitro- and vicinal dinitro-alkanes (770 K).[14] Cleavage of the gem-dinitro species is several orders of magnitude faster than that of mononitroalkanes[15] because the bond is weaker due to inductive effects.[16] Thus, homolysis is considered to be the principal decomposition pathway in the thermolysis of 2,2-dinitropropane and hexanitroethane.[10]

$$\rightarrow RCH_2\bullet + NO_2 \qquad (2a)$$

$$RCH_2\_NO_2 \rightarrow \bullet R{=}CH_2 + HONO \qquad (2b)$$

$$\rightarrow RCH_2\_ONO \rightarrow RCH_2O\bullet + NO \qquad (2c)$$

Few gem-dinitroalkyl nitramines are known. One that has found practical use is 1,3,3-trinitroazetidine (TNAZ).[16,17] Unlike many energetic materials, it is stable well above its melting point (101 °C). In a theoretical study of its stability, only a 2 kcal/mol energy difference was found between the products of $N-NO_2$ (44.6 kcal/mol) and $C-NO_2$ scission (46.6 kcal/mol).[18] We observed products from both decomposition pathways.[19] Under the experimental conditions (neat thermolyses, 160 to 280 °C), $N-NO_2$ was favored although its dominance is not huge, 66% of the initial 10% decomposition. NO formed was observed (by ^{15}N-labeling experiments) to come from the N-nitro group. A small DKIE (1.4) was observed as well as a

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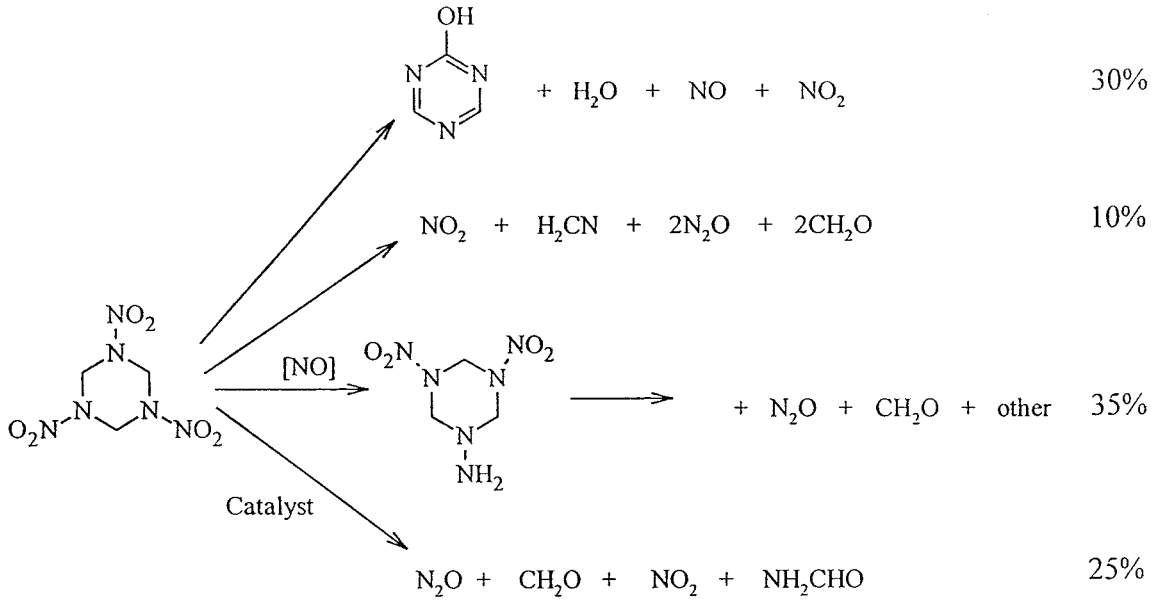


Figure 1. Decomposition pathway of RDX (ref 6).

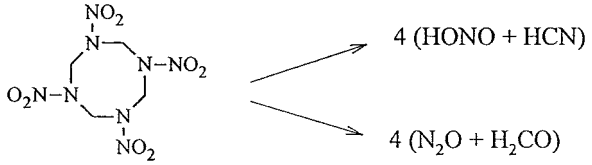


Figure 2. Decomposition pathway of HMX (ref 7).

sensitivity to ammonia; it was speculated that this resulted from the C−NO_2 cleavage pathway in which hydrogen transfer to the nitro group assisted in bond breakage.[19] Brill examined the decomposition of TNAZ, DNNC, and HNDZ (Figure 3), anticipating the weaker C−$(NO_2)_2$ linkage would be the site of initial homolysis.[20,21] This was the case for DNNC and HNDZ, but results were unclear for TNAZ.

Difluoramines have several decomposition routes possible; the principal two are analogous to those of the nitro analogues. Homolysis of C−NF_2 (3a), like homolysis of C−NO_2 (2a), requires considerable energy. It is not usually favored in monodifluoramines unless temperatures are above 400 °C. Where hydrogen is available, transfer to the X (X = O or F) of R−NX_2 provides a lower energy decomposition pathway. In nitro compounds, the next step is usually loss of HONO (2b); in difluoramines, HF is eliminated (3b). The compound resulting from HF loss might be considered analogous to the nitroso species formed by nitramine compounds (1). Grebennikov[22,23] and Ross[24] have shown that loss of HF is favored at low temperatures for monodifluoramines with alpha hydrogen.

$$RCH_2 - NF_2 \rightarrow RCH_2\bullet + NF_2$$
$$E_a = 214 \text{ kJ/mol (51 kcal/mol)}^{23} \quad (3a)$$

$$RCH_2 - NF_2 \rightarrow R'CH_2{=}NF + HF$$
$$E_a = 176 \text{ kJ/mol (42 kcal/mol, gas phase)}^{23} \quad (3b)$$

In compounds containing no hydrogen, $F_xC(NF_2)_{4-x}$ (x = 0 to 2), Sullivan[25] postulated a mechanism involving first-order dissociation of NF_2 followed by loss of one fluorine from a second NF_2 ligand. Added N_2F_4 did not affect the reaction rate; therefore, researchers concluded that NF_2 did not abstract F from $FC(NF_2)_3$. Also of note is the fact that $C(NF_2)_4$ did not form $FC(NF_2)_3$, nor did $FC(NF_2)_3$ form $F_2C(NF_2)_2$. From these and other observations a mechanism was postulated:

$$C(NF_2)_4 \xrightarrow{-NF_2} [\cdot C(NF_2)_3 \rightarrow (NF_2)_2C(F)NF] \xrightarrow{-F} (NF_2)_2C{=}NF$$

$$FC(NF_2)_3 \xrightarrow{-NF_2} [F\_C(NF_2)_2 \xrightarrow{\downarrow -NF} (NF_2)CF_2(NF)] \xrightarrow{-F} F(NF_2)C{=}NF \rightarrow\rightarrow N_2 + CF_4 + NF_3 \quad (4)$$

$$F_2C(NF_2)_2 \xrightarrow{-NF_2} [F_2\_C(NF_2) \xrightarrow{\downarrow -NF} (NF)CF_3] \xrightarrow{-F} F_2C{=}NF$$

In the series $XC(NO_2)_2(NF_2)$, where X = NO_2, CH_3, or F, C−NO_2 homolysis was found to be the first step in thermal decomposition.[22] The thermolysis of these compounds, in both gas and liquid phase, was first-order and independent of phase, pressure, surface-to-volume ratio, or inhibitors. Because the C−NF_2 bond energy is generally higher than that of C−NO_2 in gem(dinitro) alkanes,[22,26] it is not surprising that C−NO_2 homolysis occurred first (Table 1). After NO_2 loss, several possible decomposition routes were postulated:[22]

$$(NO_2)XC(NO_2)(NF_2) \xrightarrow{-NO_2} X\dot{C}(NO_2)(NF_2) \rightarrow \begin{cases} XC(=O)(NF_2) + \text{NO oxidation} \\ XC(=NF)(NO_2) + \text{F ejection of F} \\ XC(=NF)F + NO_2 \text{ rearrangement} \end{cases} \quad (5)$$

Examining a series of compounds where difluoramino groups were attached to primary, secondary, or tertiary carbons, Grebennikov et al. observed that solution decomposition was 6 orders of magnitude faster than in gas phase; and the activation energy of 110−120 kJ/mol (26−28 kcal/mol) was significantly lower than observed for HF loss in the gas phase (176 kJ/mol or 42 kcal/mol).[23] On the basis of these observations, they proposed that the liquid-phase decomposition involved ionic dissociation of the N−F bond:

$$RCH_2NF_2 \Leftrightarrow [RCH_2NF^+][F-] \rightarrow RCH{=}NF + HF \quad (6)$$

TABLE 1: Summary of Arrhenius Parameters[a]

bond	reaction	E_a kJ/mol range		average[b]	E_a (kcal/m ol)	log A s^{-1}	ref
C−ONO				40	168		13
N−NO_2	homolysis	43	49	44	184	12−18	5
		38	53	44	184	13−20	5
		37	47	45	188	13−17	44
				46	192	16	45
				47	196		18
				53	222	20	3
				50	210		8
				47	197		13
C−NO_2 arene	homolysis	61	72	66	276		8
				70	294		8
	isomerization			56	234	13	12
	−HONO from CH or NH			48	201		8
C−NO_2 alkane	homolysis	39	61	50	209		10
				62	259	17.5	14
				60	252		8
	−HONO	41	46	45	188	11.5	14
		39	50	44	184		10
C−NO_2 gem,di	homolysis	39	43	41	171		22
				51	213	18.0	3
				49	205	17.5	14
				45	188		18
	−HONO	39	47	43	180	11.5	14
C−NF_2	homolysis			60	251	17.5	24
	−HF	24	29	27	113		23
				42	176	13.5	24
C−NF_2 gem[c],di	homolysis	40	54	47	196	16.0	25
				45	188		29

[a] Range of activation energies (Ea) are given for papers reporting multiple compounds. Average is also given. [b] A single entry in the "average" compound means only one compound was reported. [c] Ross says gem NF_2 should be 10 kcals less.

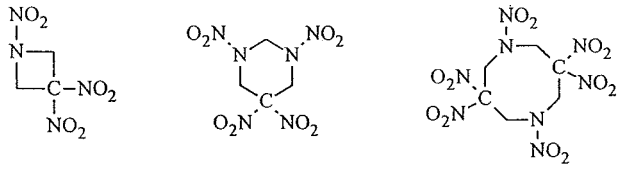


Figure 3. Structures of nitramines (ref 21).

Such a mechanism is supported by the observations that difluoramine decomposition is accelerated by bases and the decomposition of bis(2,2-dinitropropyl)-*N*-fluoramine is accelerated by acids, bases, and polar solvents.[27] However, as pointed out, a purely heterolytic E1 mechanism fails to explain HF loss in nonpolar solvents and gas-phase decompositions.[27] Gem-bis(difluoramines) without alpha hydrogen do not undergo HF elimination. Probably the electron-withdrawing difluoramino group makes the carbon less likely to support a positive charge:[25]

$$(CH_3)_2C{=}N^+(CH_3)F \leftrightarrow (CH_3)_2C^{+-}N(CH_3)F \quad \text{(ref 28)} \quad (7)$$

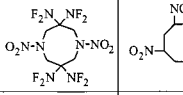
Ross et al. compared the thermal decomposition of bis-(difluoramino)propanes where the difluoramino moieties were vicinal and geminal.[29] Pyrolyses were conducted at low pressure in the range of 650 to 750 °C for the vicinal compound and in the range of 450 to 550 °C for the geminal one. For 1,2-bis-(difluoramino)propane the principal decomposition product was propylene, suggesting the decomposition pathway reversed the stepwise addition of N_2F_4 to propylene. For 2,2-bis(difluoramino)propane, the major products were (a) $CH_3C(NF)F$ (62%) and (b) $(CH_2)_2C{=}NF$ (21%). The initial step was thought to be homolysis of C−NF_2 followed by (a) loss of methyl and rearrangement of the NF_2 group or (b) loss of fluorine from the NF_2 group.

Experimental Section

Mono- and dinitrocyclohexanes (I and II) were purchased from Aldrich. 1,1,4,4-Tetranitrocyclohexane (III),[30] 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV),[31] and 1,4-dinitropiperazine (V)[32,33] were synthesized following literature procedures. The syntheses of 1,3,3-trinitropiperidine (VI) and 3,3-bis(difluoramino)-1-nitropiperidine (VII) have been described elsewhere.[34] 3,3,7,7-Tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (VIII, HNFX) was synthesized and provided by Chapman.[1] Compounds are shown at the top of Table 2. Differential scanning calorimetric (DSC) analyses were performed to determine the endothermic and exothermic activity of the compounds; a TA 2910 DSC was used to record the change in heat flux from the sample while its temperature was raised at a constant rate (usually 20°/min.). Samples were run under nitrogen flow and calibrated against indium. A typical experiment involved heating from 50 °C to 500 °C samples (0.2−0.5 mg) in sealed glass capillary tubes (1.5 mm o.d., 0.28 mm wall thickness, and 8 mm length) held in the DSC head by an aluminum support. In other analyses, sample size was held about the same, but glass tube size varied: for kinetics and condensed-phase products analysis, tubes with inner diameters of 2.0 mm and total volumes of 150 to 200 uL were used; for gas chromatography (GC) evacuated tubes of inner diameters 0.9−1.1 mm and 40−50 uL total volumes were employed. Solution studies used 40 to 60 uL samples of 1% (by weight) solutions (in benzene, d6 benzene, or acetone). When tetra-substituted cyclohexanes were heated at 320 °C in the presence of acid or base, 0.5 uL nitric acid or pyridine was added to 0.3−0.5 mg samples.

Gas products were identified by gas chromatography with mass selective detection (GC/MS): a Hewlett-Packard (HP) model 5890 GC, equipped with electronic pressure control and a model 5971 electron impact quadrupole MS; a PoraPLOT Q

TABLE 2: Rate Constants and Arrhenius Parameters

Table II Rate Constants & Arrhenius Parameters									
	I	II	III	IV	V	VI	VII	VIII	IX
									
			DSC Exotherms & Enotherms						
T (Endo, oC)			196	109	216	116	63	190(exo)	280
E (Endo, kcal/mol)			26	11	48	24	12	460	
T (Exo, oC)	350	291	270	282	304	271	273	240(exo)	285
E (Exo, kcal/mol)	305	308	1135	1739	723	967	1375	304	
			Isothermal Rate Constants in 1/s						
340	5.65E-04								
320	1.73E-04					6.46E-01	1.81E+00		
300	1.17E-04								
280	5.43E-05					6.90E-02	6.89E-02		
260		1.20E-03	1.26E-02	2.72E-03	4.80E-03	1.03E-02	1.17E-02		
240	1.63E-05	3.17E-04	2.27E-03	6.08E-04	9.51E-04	2.97E-03	2.76E-03		
220		7.19E-05	3.81E-04	1.60E-04	1.11E-04	3.85E-04	4.51E-04		
200			7.24E-05	2.97E-05	7.71E-06	8.66E-05	8.40E-05		
180						2.00E-05			
			Arrhenius Parameters			**200C-280C**			
Ea(kcal/mol)	21.1	36.6	43.0	37.2	53.7	43.1	43.2		
Ea(kJ/mol)	88.6	153.7	180.7	156.2	225.6	181.0	181.4		
A (s-1)	1.33E+04	1.39E+12	5.93E+15	5.26E+12	7.33E+19	6.93E+15	7.94E+15		
R2	0.970	1.000	0.998	0.999	0.995	0.994	0.998		
			Isothermal Rate Constants in 1/s						
a) 240C in benzene	4.46E-06	2.20E-04	1.67E-03	4.35E-04	1.52E-03	1.64E-03	1.04E-03		
b) 240C in d6 benzene		2.67E-04	1.69E-03	4.21E-04		1.69E-03	1.20E-03		
ratio a/b		0.8	1.0	1.0		1.0	0.9		
in HNO3 (240C)			2.41E-03	3.40E-04					
in pyridine (240C)			5.39E-03	3.69E-04					

(Chrompack Co.) capillary column (25 mm × 0.25 mm i.d.); and helium carrier gas. Column temperature was ramped at 15 °C/min from −80 °C to 180 °C and held for 5 min for gas identification.[35] Permanent gases (N_2, CO, CO_2, and N_2O) were quantified using GC with a thermal conductivity detector (GC/TCD). The HP 5890 GC was equipped with a Heyesep DB 100/120 (30′ × 1/8″) column. The oven temperature was held at 35 °C for 5 min, then ramped to 190 °C at 10 °C/min. Authentic gases were used for calibration.

After thermolysis, the residue in the sample tubes was dissolved in either acetonitrile for high-performance liquid chromatography (HPLC) or acetone for GC analyses. To quantify the amount of sample remaining, an HP 1100 HPLC with autosampler (10 uL injection), photodiode array detector, and Hypersil BDS C18 (4.0 mm i.d. × 100 mm) column were used. The column temperature was 38 °C. For compounds I and II, the eluent flow rate was 0.8 mL/min. The initial mobile phase was 15% acetonitrile and 85% water; the acetonitrile was ramped to 40% in 5 min and to 100% by 10 min. For compounds III, V, and VI, the flow rate was 1.0 mL/min, and an isocratic mobile phase was used; acetonitrile was fixed at 30%, 48%, and 55% respectively. For compounds IV and VII, GC (HP 5890) with flame ionization detection (FID) and a J&W DB5 column (0.32 mm × 50 mm) was used to quantify remaining sample. The injector temperature was 220 °C; the detector temperature was 300 °C; and the column temperature was held at 35 °C for 1 min, ramped at 10 °C/min to 75 °C, then to 280 °C at 25 °C/min. Fraction remaining versus time at temperature was assessed on average at eight different time intervals. Data were plotted as zero-, first-, and second-order; first-order plotting of the data had the best fit. Typically, linear regression yielded 0.99 R^2 values.

To identify the condensed phase decomposition products, a Varian 3400 GC with J&W DB-5MS, (30 m × 0.25 mm i.d.) coupled to a Finnigan-MAT TSQ-700 tandem MS was used. The injector temperature was 220 °C; the transfer line was 260 °C; and the column temperature was ramped from 50 °C to 260 °C at 15 °C/min. The electron energy was 70 eV, with emission current 200 uA; and the ion source was operated at 150 °C. In the chemical ionization (CI) mode, methane was used as reagent gas. The thermolyzed samples were examined by electron impact (EI), CI positive, and CI negative ionization modes. Product assignments were based on the M+1 or M−1 ions in CI and/or fragmentation patterns. MS/MS was used to study the fragmentation pathways of the compounds. Detailed experimental conditions are published elsewhere.[34]

Results

Thermal Stability. Most of the substituted cyclohexanes and nitropiperidines exhibited melting endotherms well below their decomposition exotherms. This is surprising because many energetic materials, such as RDX and HMX, do not show a melt distinct from decomposition. The decomposition exotherm

TABLE 3: Gaseous Decomposition Products

(samples decomposed at 320°C for 24 hr)

		Area Percent (mol gas/mol compound)					
	retention time						
		II	III	IV	V	VI	VII
N_2	3.3	7.9 (0.22)	12.0 (0.96)	15.9 (0.63)	10.7 (0.35)	12.6 (0.59)	12.4 (0.41)
CO	4.5	6.3 (0.18)	3.8 (0.36)	3.5 (0.13)	5.4 (0.19)	4.3 (0.23)	22.6 (0.24)
CO_2	12.3	45.7 (0.43)	77.8 (1.41)	44.7 (0.45)	7.0 (0.15)	61.9 (0.94)	39.4 (0.32)
N_2O	13.1	7.9 (0.00)	1.4 (0.00)	0.9 (0.00)	18.9 (0.14)	2.9 (0.06)	5.7 (0.11)
Total (moles gas/ mole compound)		'(0.83)	'(2.73)	'(1.21)	'(0.83)	'(1.82)	'(1.08)
C_2H_4	14.2						0.7
CF_2CH_2	14.9						1.3
FC_2H_3	15.6						1.5
H_2O	16.2	7.2	4.5	13.1	1.7	4.8	2.2
CH_3CN	21.6	1.2	0.4	1.3	2	1.7	6
Cyclopentene	23.6	2.4					
propanenitrile	23.8						0.7
cyclobutane-methyl	24	1					
$FCH_2C(O)NH_2$	27.4						0.9
benzene	27.4	4.9	trace				
1,2,4-trifluorobenzene	27.5			2.1			
1,4-difluorobenzene	27.8			18.4			
cyclohexene	28.2	8.9					
pyrazine($C_4H_4N_2$)	29.5				54.3	1	
pyridine	31.1					10.9	12.1

of most of the compounds was in the range 270−300 °C (Table 2). Comparing the nitrocyclohexanes, it is obvious that the fewer functional groups attached to the ring, the more stable the compound (i.e., the higher the temperature of the exothermic maximum). As nitro groups are added to cyclohexane, the DSC exothermic maximum drops from 350 °C to 270 °C. Comparison of the nitro- and difluoramino- analogues suggests that the difluoramino compounds may be slightly more stable, but upon decomposition they release more heat. The isothermal rate constants at 240 °C showed the same trends observed in the DSC data. The decomposition of the tetra-substituted cyclohexanes and the nitropiperidines appeared first-order out to 50% decomposition; 1,4,4-trinitropiperidine followed first-order kinetics to over three half-lives. The decomposition of nitrocyclohexane and dinitrocyclohexane deviated from first-order after about 40% decomposition. Since these two compounds were used only for purposes of comparison, their first-order rate constants were calculated using only the first 40% data. The four compounds of interest were thermolyzed neat or in benzene, in deutero or proteo benzene, or neat in the presence of acidic or basic species (Table 2). Little variation in rate was observed, suggesting both first-order reaction and one where proton transfer was not a critical factor in the rate-determining step. At low fraction reacted, the reaction products were soluble in acetone or acetonitrile; at high levels of decomposition, an insoluble tar was formed.

Neat samples of 1,1-dinitrocyclohexane (II); 1,1,4,4-tetranitrocyclohexane (III); 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV); 1,4-dinitropiperazine (V); 1,3,3-trinitropiperidine (VI); and 3,3-bis(difluoramino)nitropiperidine (VII) were heated at 320 °C for 24 h to effect complete decomposition. Most of the decomposition products were condensed; only 1,1,4,4-tetranitrocyclohexane (III) formed more than 2 mol of permanent gas per mole compound. Decomposition gases were identified by GC/MS; the major decomposition gases, (nitrogen, nitrous oxide, carbon monoxide, and carbon dioxide) were quantified by GC/TCD (Table 3). Nitrogen gas was the primary fate of the nitrogen atoms. Nitrous oxide was observed mainly in the decomposition of the nitramines, suggesting that it arises directly from the nitramine functionality or from its decomposition product nitrosamine. Water and acetonitrile were formed by all compounds examined (Table 3). All three nitramines exhibited the aromatized parent ring as a product; 1,1,4,4-tetrakis-(difluoramino)cyclohexane formed fluorinated benzenes; and the nitrocyclohexanes formed small quantities of benzene. The surprising observation was the presence of oxygenated decomposition gases (carbon monoxide, carbon dioxide and nitrous oxide) in the thermolysis of tetrakis(difluoramino)cyclohexane. After ruling out the possibility of a GC leak or an impurity in the starting material, we surmised that the compound was reacting with residual air in the "evacuated" reaction tube. This supposition is supported by the fact that when the sample was sealed under air the quantities of all oxygenated decomposition gases increased. In some runs, silicon tetrafluoride rather than HF was observed. The SiF_4 would be directly formed from the reaction of HF with the glass reaction vessel:

$$4HF + SiO_2 = 2H_2O + SiF_4 \qquad (8)$$

TABLE 4: GC/MS Analysis of the Decomposition Products

GC/MS Analysis of the Decomposition Products of 1,1-Dinitrocyclohexane, 1,1,4,4-Tetranitrocyclohexane, and 1,1,4,4-Tetrakis(difluoramino)cyclohexane

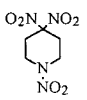
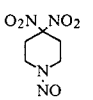
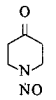
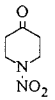
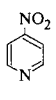
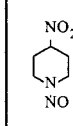
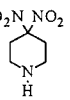
Tetranitrocyclohexane	III			confirmed III.1			confirmed III.2		III.3			III.4			confirmed III.5			III.6		III.7			III.8			III.9	III.10		not confirmed III.11		III.12		III.13			III.14		
amount (1)	M,L	M	M	L	L	L	L	S	L,M	L	L	L	M	S	M,M	S	S	S	S	S	S	S	S	S	S	S	T		S		T		S			S		
found in (2)	n3,n2	b	a	n3	b	a	n3	b	n3,n2	b	a	n3	b	a	n3,n2	b	a	n	b	n3	b	a	n2	b	a	a	b		b		a		a			a		
minute retention	12:20			6:28			4:30		9:54			11:47			10:05			10:43		11:22			5:36			5:08	7:38		7:46		7:44		12:33			10:00		
molecular weight	264			112			108		188			207			168			184		170			110			109	128		128		143		174			?		
264	EI+	CI+	CI-	EI	CI+		EI	CI+	EI	CI+		EI	CI+	CI-	EI	CI+	CI-	EI	CI+	EI	CI+	CI-	EI	CI+		EI	CI+	EI	CI+	EI	CI+	EI	CI+	Cl-	EI	CI+	CI-
	172	265	218	112	113		108	109	188	189		207	209	209	168	169	168	184	186	170	171	170	110	141		109	110	128	129	128	129	143	144	186	234		102	110	108
	171	247	170	83	112		82	95	142	171		160	207	207	122	152	159	154	185	153	169	168	82	111		82	101	92	119	98	99	115	126	170	216		82	82	46
	142	218	141	56	85		81	80	112	143		130	162	141	92	124	138	139	184	124	141	152	68	101		55	82	91	101	68	87	97	111	169	187		55	55	
	125	171	125		71		54		111	142		114	160	125	76			107	167	94	126	140	54	73		54	67	90	92	67	86	96	97	156	171		54		
	124	142	46		56				100	112		115	131		75			93	155	92	124	125		55		52	55	74	91	54	71	83	79	141	142		30		
	108								83	111		95	113		64			92	110	77	110	46				46	54			53	61	69	69	139	141				
	95								70	96		79			50			91		66	94					30				52		55	55	109	112				
	78								67			77						79		51	77													94	111				
	77								60			67						63		50	51													66	110				
	67								55			53						53		30														65	96				

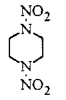
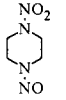
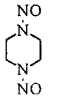
Tetrakis(NF_2)cyclohexane	IV			S2. S IV.1			Q IV.2			X IV.3			U IV.4			V IV.5		W IV.6		S1 IV.7		T IV.8			Q1 IV.9			S4 IV.10			Dinitrocyclohexane	II		II.1		II.2		III.3	
amount (1)	L, L	L	L	L,S	L	L	S,S	S	S	S	S		T	S		S	S	S	M	S		S			M			S			amount	M		L		M		M	
found in (2)	n3,n2	b	a	n3,n2	b	a	n3,n2	b	a	b	a		b	a		b	a	b	a	b		a			n3			n3			found in	n3		n3		n3		n3	
minute retention	5:23			4:45			4:08			9:29			5:00			7:14		7:45		4:35		5:34			4:08						retent. min.	9:03		4:35		7:51		10:22	
molecular weight	288			202			202			215			217			149		129		129		200			149			149			M.W.	174		98		127		?	
288	EI+	CI+	CI-	EI+	CI+	CI-	EI+	CI-	CI-	EI+	CI+	CI-	EI-	CI+	CI-	EI+	CI+	EI+	CI+	EI+	CI+	EI+	CI-	CI-	EI+	CI+	CI-	EI-	CI+	CI-		EI-	CI+	EI+	CI+	EI	CI+	EI-	CI-
	236	269	77	202	203	130	170	203	150	215	216	162	165	218	145	149	150	129	130	129	131	200	201	128	149	150	127	149	150	148		97	175	98	100	127	129	96	285
	198	236	72	150	202	110	150	170	130	163	173	143	116	198	104	121	149	109	129	110	130	148	200	111	130	148	109	130	158	139		82	158	83	99	97	128	69	238
	183	198	65	130	183	109	132	151	110	143	163	123	96	165	88	100	130	100	100	109	111	82	166	108	110	130	107	120	121	128		81	157	70	81	81	115	55	183
	151	183	52	112	150	90	117	132	90	115	145	70	77	145	52	92	121	86	85	96	110	55	153	93	103	112	39	105	107	127		79	144	69	69	79	98		171
	131	165	39	98	131	52	97	117	72	97	128	19		127	39	85	92	85	82	84	96	54	148	66	102	92		103	105	122		69	142	55	55	77	81		144
	112	151	26	97	112	39	77	97	52	86	115			112	26	77	77	74	74	83	83	53	144	52	98			79	79	109		67	129			53			143
	85	131	19	83	98	26	59	77	39	82	99			94	19	56	56	59	59	70		47	134	39	90			77	43	108		55	128						96
	65	112		59	97	19		59	19	55	82			65		42		53		63		42	112	26	83					97			99						
	54				84					54	55			54		30				57		28	96	19	80					90			97						
					59					30										51			73		76					77			82						
																														39			81						

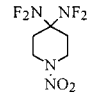
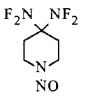
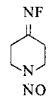
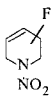
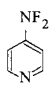
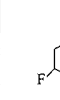
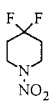
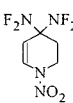
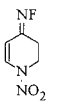
* Also observed in benzene--biphenyl and in acetone--2,4-hexane-dione

TABLE 4 (Continued)

GC/MS Analysis of the Decomposition Products of Dinitropiperazine, Trinitropiperidine, & Bis(difluoramino)nitropiperidine

Trinitropiperidine	**VI**			**VI.1**			**VI.2**			**VI.3**			**VI.4**			**VI.5**		**VI.6**
																		
amount (1)	L,L	L	L	L,L	L	L	L,T	L	L	M, T	M	M	S,T	S	T	T		S
found in (2)	n3,n2	b	a	n3,n2	b	a	n3,n2	b	a	n3,n2	b	a	n3,n2	b	a	a		n2
minute retention	12:05			11:19			8:21			9:16			5:12			9:36		12:30
molecular weight	220			204			128			144			124			159		175
220	EI+	CI+	CI-	EI	CI+	CI-	EI	CI+	CI-	EI	CI+	CI-	EI	CI+	CI-	EI	CI+	EI	CI+
	174	221	220	204	205	204	128	129	127	144	145	143	124	124	124	159	160	175	176
	128	174	174	158	187	126	111	111		127	111		78	107	70	113	159	129	129
	111		126	128	158		97	99	98	97	99	96	51		52	82	147	99	100
	100		93	111	128		56			70	97				46	55	128	83	83
	98		46	100	112		42			56	83					42	113	82	47
	80			82	82		30			55	55						84	55	
	42			80						42		46					83		
	30			42		46				28							82		
				30															

Dinitropiperazine	**V**		**V.1**		**V.2**	
						
amount	L		L		M	
found in	n3		n3		n3	
retent. min.	12:48		11:39		10:48	
M.W.	176		160		144	
176	EI	CI+	EI	CI+	EI	CI+
	176	177	160	161	144	145
	160	159	130	115	114	115
	130	131	100	85	84	
	113	85	84		57	
	100		57		56	
	84		56		55	
	57		55			
	56					
	55					

Bis(NF2)nitropiperidine	**VII**			**N** **VII.1**			**O** **VII.2**			**M** **VII.3**			**L** **VII.4**			**K** **VII.5**			**L1** **VII.6**		**L2** **VII.7**		**O1** **VII.8**		**P1** **VII.9**		**P** **VII.10**		
																													
amount (1)	M,M	M	M	L,L	L	L	T	T	S	S	S	S	M	M	M	T	T	T	T		T	T	T		T		S		
found in (2)	n3,n2	b	a	n3,n2	b	a	n2	b	a	n3	b	a	n3	b	a	n3	b	a	a		b	a	a		a		a		
minute retention	9:12			8:26			8:55			7:36			6:32			5:44			5:31		6:42		8:36		11:54		10:55		
molecular weight	232			216			145			146			130			150			168		166		230		159		143		
232	EI+	CI+	CI-	EI	CI+	CI-	EI	CI+	CI-	EI	CI+	CI-	EI	CI+		EI	CI+	CI-	EI	CI+	EI	CI+	EI	CI+	EI	CI+	EI	CI+	CI-
	180	234	115	216	217	144	145	146	146	128	147	148	130	131		150	151	46	148	168	166	167	230	231	159	160	143	144	141
	115	233	95	197	197	113	126	116	115	99	129	98	98	130		133	131		130	148	149	147	229	230	142	142	113	114	46
	42	180	19	186	186	93	115	115	99	98	99	46	85	111		119	100		96	129	136	131	210	210	113	114	84	84	
		115		164	174	71	96	96	95	80	85		53	85		100			54	96	119	119	186	187	84	84	55	69	
				145	164	52	56		52	72	55			75		80			47	54	100	100	164	177	55		42	55	
				115	146	46	42		46	53						56					80	80	115	168	42				
				96	145	39			19							30					60		96	115	30				
				42	115	19															56		43	97					

(1) L = large; M= moderate; S=small; T=tiny; relative amounts of product based strictly on size of chromatographic peak.

(2) n3 = neat heated at 320C; n2= neat heated at 240C; b = 1% in benzene*; a = 1% in acetone, a,b heated at 320C

* Also observed in benzene: biphenyl, nitrobenzene, nitrophenol

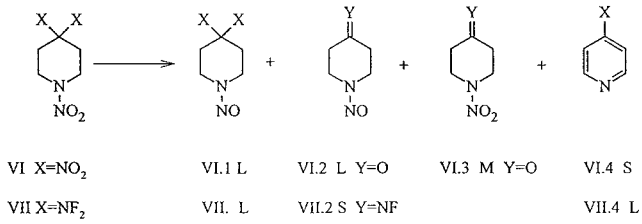


Figure 4. Decomposition products of nitramines VI and VII compared.

Condensed Phase Products. *Mass Fragmentation.* Mass fragmentation studies were performed on the neat compounds (III, IV, VI, VII, VIII). The MS/MS studies indicated that six-membered rings (III, IV, VI, VII) shared the same initial fragmentation step: loss of one of the geminal ($C-NX_2$) groups, where X = F or O. In the case of the eight-membered ring, HNFX (VIII), the initial step was $N-NO_2$ fragmentation. The second fragmentation step for the other two nitramines (VI, VII) was cleavage of $N-NO_2$. For the two cyclohexanes (III, IV), the second major fragmentation was loss of another NX_2 group, probably para to the first. A common fate of the gem-dinitro groups in compounds III and VI was loss of NO to form a ketone. The gem-NF_2 groups in the difluoramines (IV, VII, and VIII) formed fluorinated compounds or fluoroimine (=NF). Further details of these studies are published elsewhere.[34]

Thermolysis Products. GC/MS (EI+, CI+, and/or CI− detection) was used to identify thermolysis products of neat (240 °C and 320 °C) or solution (benzene or acetone 320 °C) samples. At 240 °C, products were examined as a function of percent decomposition (10 to 90%). A wider variety of products were formed at 320 °C though the principal products remained the same. Product assignments were based on the apparent molecular mass and fragmentation patterns, and in some cases, comparison with authentic samples (Table 4). For the nitramines at high or low temperature, neat or in solvent (benzene or acetone), the corresponding nitrosoamine was the principle product. Dinitropiperazine (V) when heated at 320 °C for 3 s (95% decomposition) formed both the mono- and dinitroso analogues (Table 4). In addition to nitrosamine (VI.1), trinitropiperidine (VI) formed products resulting from the loss of the geminal nitro groups: a large amount of *N*-nitrosopiperidin-4-one (VI.2); a moderate amount of N-nitropiperidin-4-one (VI.3); and small amounts of nitropyridine (VI.4) and *N*-nitroso-4-nitropiperidine (VI.5). At 240 °C 4,4-dinitropiperidine (VI.6) was also a major product; it was not observed at 320 °C. 4,4-Bis-(difluoramino)-1-nitropiperidine (VII) formed a large amount of the parent nitrosamine (VII.1), moderate amounts of (difluoramino)pyridine (VII.4), and small quantities of 4-fluoroimino-*N*-nitrosopiperidine (VII.2) and VII.3, where reaction occurred at the difluoramine site (Figure 4). A small amount of a species (III.6) with *m*/*z* of 184 was observed in the decomposition of both nitropiperidines (VI and VII) and tetranitrocyclohexane (III). This species was only observed in the thermolysis of the nitropiperidines when they were heated in benzene, but for tetranitrocyclohexane it was observed in the neat thermolysis as well as the one in benzene. The fragmentation pattern of the compound, which was identical in the thermolysis of all three species, was consistent with a dinitrophenol or a dinitrocyclohexadiene-4-one. The former would appear more likely than the latter, but the fragmentation pattern differed significantly from that of the commercially available 2,5-dinitrophenol.

The MS fragmentation patterns for the thermal decomposition products of dinitro-, tetranitro- and tetrakis(difluoramino)-cyclohexanes indicated that the ring remained intact (Table 4). The major products of the nitrocyclohexanes involved the replacement of the geminal nitro groups by a ketone functionality; thus, 1,1-dinitrocyclohexane, heated for 15 s at 320 °C formed cyclohexanone (II.1, confirmed with an authentic sample); and 1,1,4,4-tetranitrocyclohexane compounds III.1, III.2, and III.3 (Table 4). It is difficult to assign with certainty the other products of dinitrocyclohexane. Two assignments fit equally well the fragmentation patterns of II.2 and II.3: nitrocyclohexene or the dimer, di(nitrocyclohexane) and di-(nitrosocyclohexane), or nitrosocyclohexyl-dinitrocyclohexane. 1,1-Gem-dinitrocyclohexane is known to undergo electrochemical reduction to form 1,1′-dinitrobicyclohexyl[15] and to replace one of the g*em*-nitro groups with certain nucleophiles;[36] therefore, such reactivity may occur during the thermolysis or in the MS instrument.

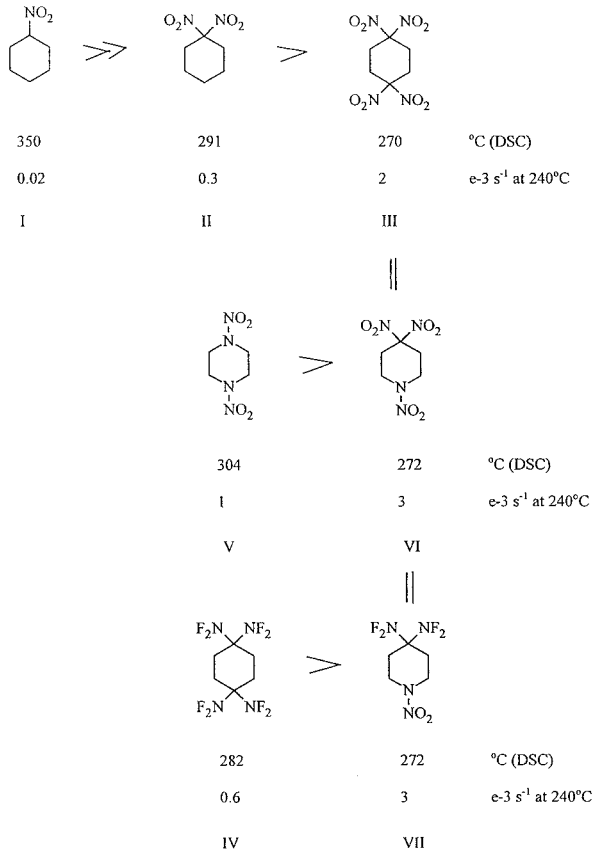


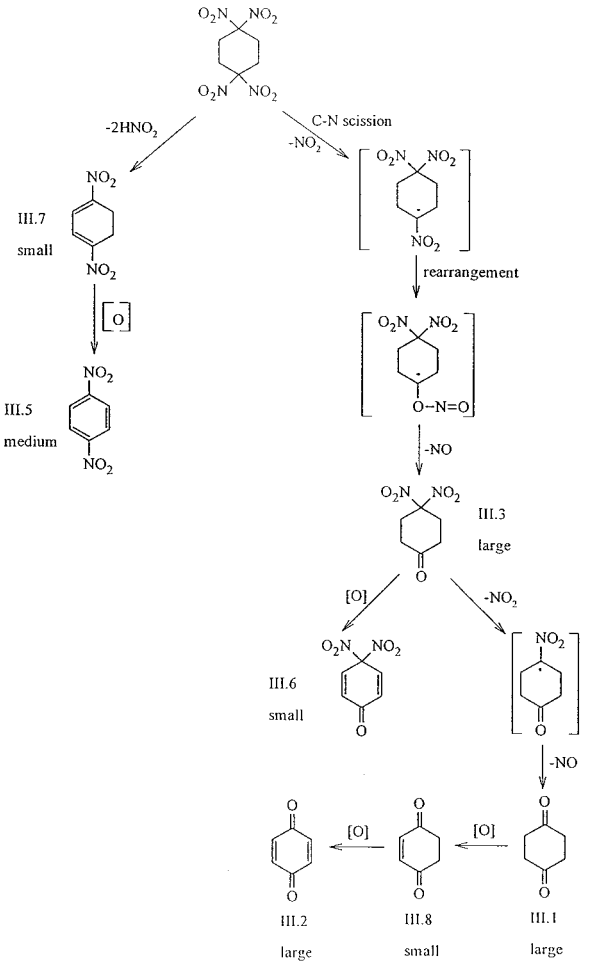
Figure 5. Thermal stability comparison of compounds studied.

Neat or in solvent, at high or low temperatures 1,1,4,4-tetranitrocyclohexane formed dinitrocyclohexanone (III.3) as a major product and dinitrobenzene (III.5) as a minor one. At 320 °C cyclohexanedione (III.1) and benzoquinone (III.2) were also major decomposition products. (The chlorine containing species (III.4) was an impurity found in some batches of the tetranitrocyclohexane.) The two principal decomposition products of neat 1,1,4,4-tetrakis(difluoramino)cyclohexane had GC/MS peaks with *m*/*z* of 202 and a fragmentation pattern consistent with the formula $C_6H_7(NF_2)_2F$. In solvent several other peaks were observed. Possible structural assignments are shown in Table 4. Three peaks (IV.5, IV.9, IV.10) with *m*/*z* of 149 and fragmentation pattern suggesting $C_6H_6(NF_2)F$ were observed. Difluorobenzene and trifluorobenzene were identified in the decomposition gases (Table 3).

Discussion

The decomposition rates of nitrocyclohexane, 1,1-dinitrocyclohexane, and 1,1,4,4-tetranitrocyclohexane increased as the

SCHEME 1: Thermal Decomposition Mechanism of 1,1,4,4-Tetranitrocyclohexane

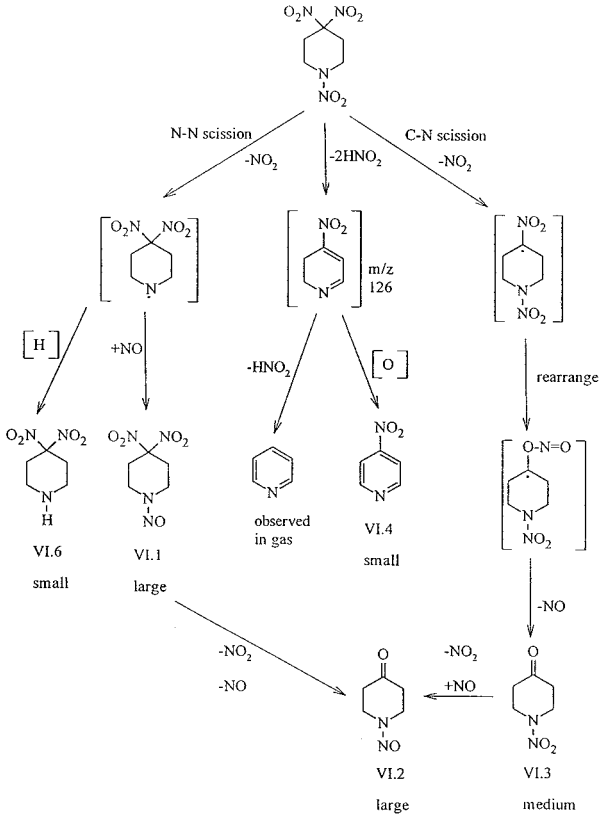


number of nitro groups increased. The increase in rate and decrease in the DSC exothermic maximum are especially dramatic between nitrocyclohexane and 1,1-dinitrocyclohexane illustrating lower energy decomposition routes available to gem dinitro species. Inductive effects should weaken C−N bond in gem dinitro species relative to mononitro compounds,[3] and steric effects should also make loss of a nitro more energetically favorable. Figure 5 is a schematic of the relative thermal stabilities of the various species.

The fact that compounds III through VII all decompose at about the same rate (within an order of magnitude at 240 °C) reflects the similarity in activation energies for gem-dinitro, gem-bis(difluoramino), and nitramine functionalities (Table 1). In the temperature range 200 to 280 °C the two nitramines (VI and VII) decomposed at almost identical rates and with essentially identical activation energies, and trinitropiperidine (VI) decomposed more quickly than dinitrocyclohexane (II).[37] These two observations are taken to indicate that in this temperature range homolysis of the nitramine functionality is the rate-determining step. This is in line with the lower bond energy for N−NO_2 compared to gem C−NO_2 (e.g., 44.6 and 46.6 kcal/mol, respectively, as calculated for TNAZ.[18] The initial loss of *N*-nitro also agrees with the observations of Grebennikov.[22] Comparing compounds III and IV, it appears species with gem-bis(difluoramino) groups may be slightly more stable than those with gem-dinitro groups.

The gem-dinitro groups in piperidine (VI) or cyclohexane (III or II) decomposed to leave a single nitro group or a =O

SCHEME 2: Thermal Decomposition Mechanism of 1,4,4-Trinitropiperidine



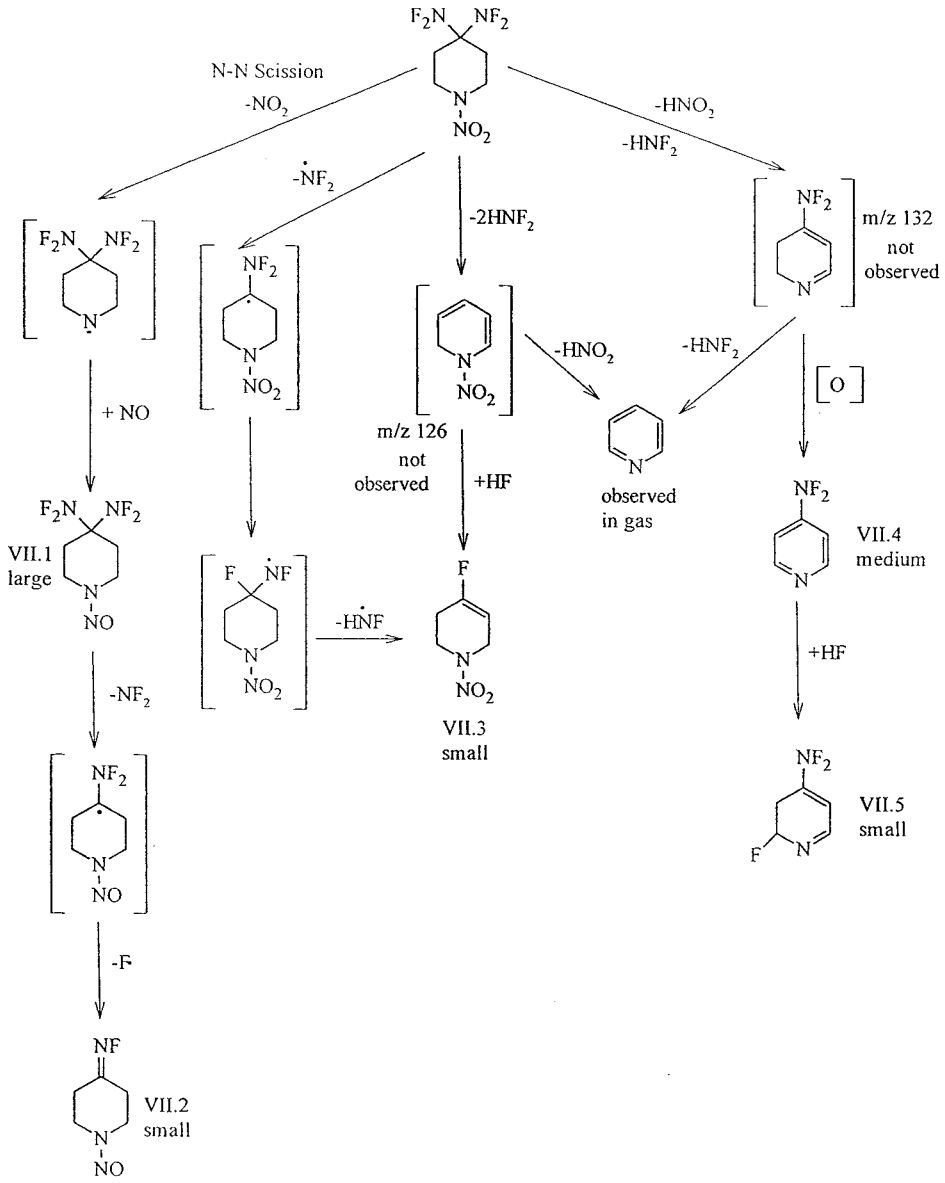
group in their place. At 320 °C, neat or in solution, 1,1,4,4,-tetranitrocyclohexane (III) formed 1,4-cyclohexanedione (III.1), 1,4-benzoquinone (III.2), and dinitrocyclohexanone (III.3) as the major decomposition products. Of these, only III.3 was observed at 240 °C. It is likely that the ketone functionality is formed via bond homolysis:

$$>C-(NO_2)_2 \xrightarrow{-NO_2} >C-NO_2 \rightarrow >C-O-NO \xrightarrow{-NO} >C{=}O \quad (9)$$

At lower temperature (240 °C versus 320 °C) such homolysis would be less favored, and HNO_2 elimination would dominate. Indeed, at 240 °C, 1,4-dinitrobenzene (III.5), a modest product at 320 °C, became a major product (identified by comparison with an authentic sample). This species (III.5) and dinitrocyclohexadiene (III.7) apparently resulted from HNO_2 loss (see Scheme 1). While we speculate that these products are the result of a five-centered monomolecular reaction, the multitude of oxidized ring species attest to the availability of oxidizing species. Nitrogen dioxide is a likely oxidizing agent; indeed, nitrobenzene and nitrophenol were observed when the thermolysis was performed in benzene solution (1%). Interestingly, neat tetranitrocyclohexane formed dinitrobenzene (III.5) but not nitrobenzene. The reason that aromatization is achieved via loss of two rather than three molecules of HNO_2 is not obvious. The same trend was observed in the nitramines (VI and VII); they formed substituted pyridines (VI.4 and VII.4) resulting from the loss of two NX_2 groups (X = O or F) and subsequent oxidation; however, in these cases, pyridine was also observed.

The major decomposition products of the nitramines (V, VI, and VII) are the nitrosamine analogues,[5] supporting N−NO_2 homolysis as a major decomposition route. However, for both VI and VII, loss of one or both of the gem NX_2 groups is also

SCHEME 3: Thermal Decomposition Mechanism of 4,4-bis(Difluoramino)-1-nitropiperidine



an important decomposition route. The fates of the gem-dinitro groups on the nitropiperidine (VI) ring are similar to the fates observed for these groups on the cyclohexane ring (III). Like compound III, at 320 °C the gem-dinitro functionality of trinitropiperidine (VI) appeared to favor C−NO_2 homolysis over HNO_2 elimination, producing as major products the nitrosamine (VI.1), *N*-nitrosopiperidin-4-one (VI.2) and *N*-nitropiperidin-4-one (VI.3) (Scheme 2).

Loss of one NF_2 group appears to be a major pathway for the difluoramines IV and VII. Abstraction of HF, common in the decomposition of difluoramines containing alpha hydrogen,[23,24] is not an option for geminal bis(difluoramino) groups; and we observed no solvent or pH effect on the decomposition rate of 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV) which might support an E1 type ionic decomposition process.[23] Nevertheless, product distribution suggests loss of HNF_2 is an important decomposition pathway. Although the gem-dinitro groups favor homolysis at the temperatures of this study, the C−NF_2 linkage may be sufficiently stronger that homolysis is not preferred.

Once one gem-difluoramino group is lost, literature suggests the remaining difluoramine would rearrange to form a fluoroimine C═NF, via loss of fluorine or another ligand:[25,29]

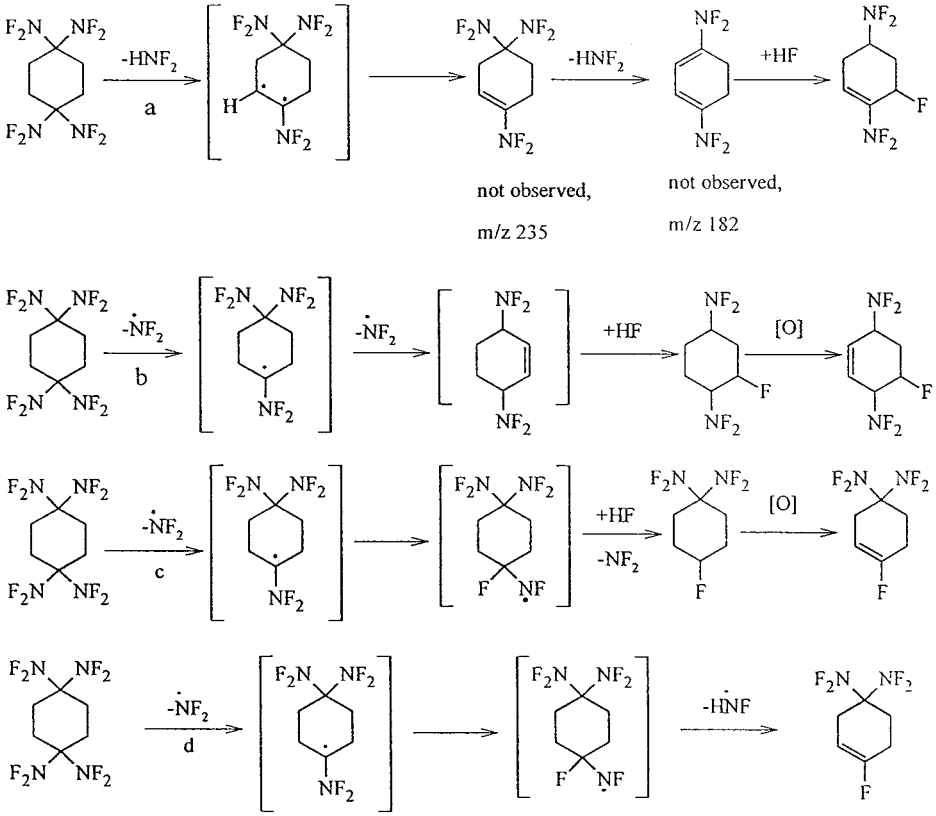
$$F_xC(NF_2)_{4-x}\ (\text{where } x = 0-2) \xrightarrow{-NF_2} (F_x)(NF_2)_{2-x}C{=}NF + F\bullet \quad (10)$$

$$2,2\text{-}(NF_2)_2C_3H_6 \rightarrow (CH_3)_2C{=}NF\ (21\%) + CH_3(F)C{=}NF\ (62\%) \quad (11)$$

However, only minor products appeared to contain fluoroimine (Table 4). As geminal dinitro compounds decompose to leave "═O", geminal difluoramino groups decompose to the "−F" analogues.

While the principal fate of 4,4-bis(difluoramino)-1-nitropiperidine (VII) was formation of the nitrosamine (VII.1), indicating the importance of N−NO_2 homolysis, a considerable amount of 4-difluoraminopyridine (VII.4) was formed. The most straightforward way to form difluoraminopyridine (VII.4) would be by the loss of two hydrogen during the elimination of NF_2 and NO_2 and a final oxidation by an external molecule such as NO_2 or NF_2 (Scheme 3). The five-centered elimination of HNO_2 is well-known though it is not favored in unsubstituted piperidine

SCHEME 4: Thermal Decomposition Mechanism of 1,1,4,4-tetrakis(Difluoramino)Cyclohexane



at these temperatures.[5] Indeed, trinitropiperidine formed only minor amounts of the analogous product VI.4 (Figure 4). Loss of HNF_2 has not previously been postulated, but HNF_2 is an isolatable species.[38] Because HNF_2 is known to add across double bonds, the reverse reaction is probable; furthermore, NF_2 is known to abstract hydrogen.[39,40] Thus, it is possible that HNF_2 is formed and undergoes subsequent reaction.[41] (NF exists; it is isoelectronic with molecular oxygen; and, like NF_2, it is known to dimerize.[42])

$$HNF_2 \rightarrow HF + NF$$
$$NF + NF \rightarrow FN{=}NF \qquad (12)$$

Minor decomposition products of 4,4-bis(difluoramino)-1-nitropiperidine (VII), such as VII.5 or VII.3, appeared to have fluorine but not "═NF" attached directly to the ring; thermolysis products of 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV) also appeared to have fluorine attached to the ring without an accompanying ═NF group. In Scheme 3 we speculate that VII.3 could have formed by one of two routes: addition of HF across a point of unsaturation or by rearrangement of NF_2 followed by loss of HNF. The troubling aspect of the first route is that the precursor unsaturated ring (*m*/*z* 126) was not observed, even though among the decomposition gases was pyridine, which we envision was formed via loss of three molecules of HNX_2 (where X = O or F, Scheme 3). The presence of F unpaired with NF is also difficult to rationalize in the decomposition products of 1,1,4,4-tetrakis(difluoramino)cyclohexane (IV), where the two principal decomposition products have *m*/*z* of 202. Four possible reaction modes were considered (Scheme 4) though none is entirely satisfactory: (a) loss of two molecules of HNF_2; (b) loss of two NF_2 radicals; (c) loss of one NF_2 radical, rearrangement of the remaining NF_2, subsequent addition of HF; (d) loss of one NF_2 radical, rearrangement of the remaining NF_2, subsequent loss of HNF. One would think that if route (a) were followed, the -ene and/or -diene would be observed. They are not. This is the same objection we have to the proposed formation of VII.3 and VII.5 in Scheme 3. The loss of two radicals in route (b) would be energetically disfavored. Routes (c) and (d) both begin with NF_2 homolysis; but by analogy to 4,4-bis(difluoramino)-1-nitropiperidine (VII), loss of HNF_2 should be favored.

Conclusions

Because the bond energies of $N{-}NO_2$, $C{-}(NO_2)_2$, and $C{-}(NF_2)_2$ are close in magnitude (Table 1), decomposition kinetics alone do not allow us to determine the initial site of decomposition. However, comparing analogues of $C{-}(NX_2)_2$, where X = F or O, it appears that $C{-}(NF_2)_2$ is the most stable. This trend in stability has also been calculated for $N{-}NX_2$ compounds.[43] For the various nitramines, nitroso-nitramines were always the principal products, strongly suggesting that $N{-}NO_2$ homolysis was the first step in their decomposition. (In the case of the four-membered ring TNAZ with both $N{-}NO_2$ and $C{-}(NO_2)_2$ functionalities, we had previously observed the product distribution favored $N{-}NO_2$ scission.)[19] In the decomposition of 1,1,4,4-tetranitrocyclohexane, where the formation of thermodynamically stable nitrobenzene would indicate consecutive lose of HNO_2, that product was not observed. The replacement of $C{-}(NO_2)_2$ with C═O again suggests $C{-}NO_2$ homolysis is important for compounds containing gem-dinitro groups. In contrast, the major decomposition products of 1,1,4,4-tetrakis(difluoramino)cyclohexane and 4,4-bis(difluoramino)-1-nitropiperidine appear to result from HNF_2 loss.

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