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Thermal Stability Studies on a Homologous Series of Nitroarenes[1]

Jimmie C. Oxley,* James L. Smith, and Hong Ye

Chemistry Department, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801

Robert L. McKenney and Paul R. Bolduc

WL/MNME, 2306 Perimeter Rd., Suite 9, Eglin Air Force Base, Florida 32542-5910

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The thermal stabilities of a number of nitroarenes were examined in solution and in condensed phase. In general, increasing the number of nitro groups decreased thermal stability. Changing the substituent on 1-X-2,4,6-trinitrobenzene from X = H to NH_2 to CH_3 to OH accelerated decomposition; this effect was attributed to increased ease of intramolecular proton transfer to an ortho nitro group, thus weakening the carbon−nitrogen bond. In solution, the effect of increasing substitution from $n = 1$ to $n = 3$ on $X_n(NO_2)_3C_6H_{3-n}$ was uniformly that of decreasing the thermal stability of the species. However, in condensed phase, results suggested that crystal habit may be more important than molecular structure; for X = Br, CH_3, and NH_2, the more substituted species was the more stable.

Introduction

For a number of years researchers have attempted to correlate the chemical structure of energetic materials to their sensitivity to a variety of stimuli (e.g., heat, impact, and friction) (Table 1); the difficulty with that approach as applied to nitroarenes is thoroughly explored in ref 2. Although many factors affect thermal stability, one obvious structural effect is the general trend for nitroarenes to be more stable than nitramines which, in turn, are more stable than nitrate esters. At temperatures over which thermal stability is normally examined, each of these classes of explosives has a common mode of decomposition available—loss of NO_2.[3−13] Therefore, the trend in thermal stabilities is in line with the X−NO_2 bond dissociation energies: nitrate ester O−NO_2, 40 kcal/mol; nitramine N−NO_2, 47 kcal/mol; nitroarene C−NO_2, 70 kcal/mol.[10]

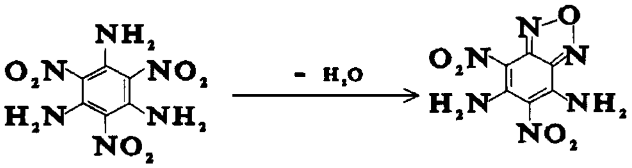
Among energetic materials commonly used as explosives, one stands out in terms of exceptional stability—1,3,5-triamino-2,4,6-trinitrobenzene (TATB). TATB has unusually high thermal and impact stabilities yet retains acceptable performance (Table 1). Like 2,4,6-trinitrotoluene (TNT), TATB is a nitroarene, but unlike TNT, TATB is not melt castable, nor is it readily solubilized. This makes TATB difficult to process. In an effort to understand the exceptional stability of TATB and perhaps find alternatives, we examined the thermal stabilities of five homologous series: 2,4,6-trinitroaniline (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), and TATB; TNT, 2,4,6-trinitroxylene (TNX), and 2,4,6-trinitromesitylene (TNM); 2,4,6-trinitrophenol (picric acid, HO−TNB), 2,4,6-trinitroresorcinol [styphnic acid, $(HO)_2$−TNB], and 2,4,6-trinitrophloroglucinol [$(HO)_3$−TNB]; 1-bromo-2,4,6-trinitrobenzene (Br−TNB), 1,3-dibromo-2,4,6-trinitrobenzene (Br_2−TNB), and 1,3,5-tribromo-2,4,6-trinitrobenzene (Br_3−TNB); TNT, 3-amino-2,4,6-trinitrotoluene (ATNT), and 3,5-diamino-2,4,6-trinitrotoluene (DATNT).

The thermal decomposition mechanisms of nitrotoluenes and TNT have received much attention,[3−6] while the thermal decomposition studies of nitroaniline and TATB have been comparatively neglected.[7−9] It has been suggested that the key to TATB insensitivity is the thermoneutral formation of benzofurazan and benzofuroxan rings in the first step of its decomposition.[9]

TABLE 1: Performance vs Sensitivity[a]

	critical temp, °C	H50 drop height, cm[b]	mp, °C	detonation velocity, m/s	density, g/cm^3
TNT	288	212	81	7045	1.62
TATB	347	>320	448	7660	1.85
HMX	253	26	247	9110	1.89
RDX	217	22	204	8639	1.77
PETN	192	12	143	8160	1.77

[a] Data from ref 16. [b] Type 12.



Owing to the insolubility of TATB, thorough analysis of its decomposition behavior has been hampered, and much of its behavior is inferred by analogy. Politzer et al.[13] have carried out extensive theoretical analyses on the hydroxy−trinitrobenzene derivatives for which the thermal stability decreases as the number of hydroxyl groups increases. They suggested that proton transfer from hydroxyl to nitro results in formation of nitronic acid and that an increased number of hydroxyl-substituents facilitate this reaction. This same mode of reactivity is available to nitrotoluenes and nitroanilines;[5] yet it is widely known that triaminotrinitrobenzene (TATB) is more, rather than less, thermally stable than the monoamino substituted 1-amino-2,4,6-trinitrobenzene. The reason for this difference in substituent effect is not immediately obvious.

At temperatures over which the thermal stability of nitroarenes is normally studied, two modes of decomposition are generally postulated: homolysis of the C−NO_2 bond and proton transfer to the nitro group, resulting in formation of nitronic acid. The latter reaction may be inter- or intramolecular, and several subsequent decomposition pathways are available. The relative dominance of these decomposition pathways changes with

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temperature; Brill has reviewed the manner in which this affects observed sensitivities.[2]

The use of solution eliminates the sometimes confusing effects of particle size, crystal habit, and melting point. In solution, the intrinsic chemistry of the molecule can be followed in a pseudo-first-order fashion. Furthermore, solute/solute interactions are minimized, and reactive intermediates can sometimes be trapped before they undergo subsequent reactions.

Experimental Section

A few nitroarenes were commercially (Aldrich) available, but most were obtained from Eglin Air Force Base. A sample of d_3-TNT was synthesized by methods previously discussed.[14] The thermal stabilities of the nitroarenes were initially assessed by differential scanning calorimetry (DSC). Activation energies and frequency factors were determined by the ASTM[15] variable heating rate method; by use of these values and the Arrhenius relationship, the rate constants at 340 °C were calculated. Nitroarenes were also examined by isothermal thermolysis of neat samples and of 1.2 wt % benzene solutions. Thermal stability was assessed from the rate constants determined from first-order plots. Amino-, bromo-, and methyl-substituted trinitrobenzenes exhibited first-order behavior in both solution and condensed phase out to 50% or 70% conversion. Hydroxy- and methoxytrinitrobenzenes usually exhibited first-order behavior only out to 20% conversion; accordingly, their rate constants were calculated only from the initial part of the first-order plot.

Choice of solvents for nitroarene thermolyses was limited. The ideal solvent would have the following characteristics: (1) would dissolve sufficient nitroarene to allow analytical detection; (2) would, itself, be inert at elevated temperatures; (3) would not interact with the nitroarenes. No solvent met all criteria, and few met the first two requirements. Arenes are the least polar solvents in which the nitroarenes dissolve, but during thermolyses nitroarenes abstract hydrogen from the arene ring or substituents, if available.[3] Benzene was the solvent of choice since its role as a hydrogen donor is well documented, and its decomposition products are primarily biphenyl.[3] Because some of the nitroarenes exhibited limited solubility in benzene, 1.2 wt % nitroarene was set as the standard concentration for the solutions examined. DATB and TATB were the only nitroarenes examined which did not dissolve in benzene. The very limited solubility of TATB was a problem. It is reported to range from a high of 820 ppm in methanesulfonic acid to 100 ppm in dimethyl sulfoxide (DMSO) to 26 ppm in dimethylformamide.[16] DMSO was suitable for dissolving DATB and TATB for analytical purposes, but its decomposition at elevated temperature precluded its use in most of the thermolysis studies. The majority of the DATB and TATB thermolyses were performed in *N,N*-dimethylacetamide.

Samples (0.5−0.8 mg neat and 20 μL solution) were heated in 200 μL reaction tubes (inside diameter 2.4 mm and length 60 mm). For the compounds insoluble in benzene, DATB and TATB, 40 ppm solutions in *N,N*-dimethylacetamide were prepared; and 40 μL was transferred into an 80 μL capillary (inside diameter 1.5 mm and length 60 mm). Tubes were flame sealed and heated in a molten metal bath (180 to 390 °C) for the desired length of time. At the completion of heating, the tip of the tube was broken. For neat samples, 60 μL of acetone was added and the tube was resealed and heated in a boiling water bath until no more sample appeared to dissolve. To analyze relatively insoluble compounds such as trinitroaniline, DATB, and TATB, the entire capillary was ground into pieces in a beaker, 20 mL of DMSO was added, and the samples were sonicated at 70 °C for 48 h. In some cases, the reproducibility of the condensed-phase data is constrained by our ability to extract all the remaining reactant from the resulting residue.

The fraction of sample remaining was determined by gas chromatography with a flame ionization detector (GC-FID) or mass selective detector (GC−MS) or by high performance liquid chromatography (HPLC). Most samples could be quantified by GC-FID; a Varian 3600 gas chromatograph equipped with an Alltech fused silica 5-BP capillary column (inside diameter 0.32 mm and length 30 m) was used. Typical settings were an injector temperature of 250 °C, detector temperature at 300 °C, hold times of 1 to 5 min, and heating rates of 5 to 15 °C/min over a temperature range of 65 to 210 °C; these gave retention times of 2 to 8 min.[1] For 2,4-dinitroaniline and trinitrophloroglucinol and for all compounds which had to be dissolved in DMSO[17] or *N,N*-dimethylacetamide, a Beckman 110A HPLC was used for quantification. The HPLC was equipped with a C-18 reverse-phase column (25 cm × 0.46 cm), a 20 μL sample loop, and a Waters 486 tunable absorbance UV detector (410 nm for the phenols, 254 nm for the anilines). A one-to-one mixture of methanol/water was used as the mobile phase.

A Hewlett-Packard 5890A GC equipped with a 5970B mass selective detector was used for product identification. The column was a DB-5 narrow-bore. The GC oven was initially held at 80 °C (5 min) and then ramped to 210 °C at 15 °C/min. The injector and detector were set at 240 and 280 °C, respectively. With these conditions retention times were typically 10 to 28 min. When possible, products were identified by comparison of fragmentation patterns and retention times with an authentic sample. These identifications are noted. Most products were deduced from their parent mass and fragmentation pattern.

Results

Products. In samples thermolyzed in benzene, products resulting from solute/solvent interactions were observed. Biphenyl, the result of hydrogen abstraction from benzene, was the principal product in the thermolyses of all the nitrobenzene species. Nitrobenzene, phenol, nitrophenol, nitrobiphenyl, and terphenyl were also observed in some spectra (Table 2). For several nitroarenes, decomposition products at various stages during the decomposition were examined. Those shown in Tables 2−9 give the relative amounts of decomposition products produced at about 40% decomposition at 340 °C; the largest peak (total ion count) is assigned as 1.

1,3,5-Trinitrobenzene was the only pure nitrobenzene examined neat. Loss and reduction of the nitro group produced the observed products—1,3-dinitrobenzene, dinitrophenol, and dinitronitrosobenzene. In benzene, the products of 1,3- and 1,4-dinitrobenzene were also examined. In addition to the benzene-derived products discussed above, only nitrobenzene was observed (Table 3).

Decomposition products observed for the mono-, di-, and tribromotrinitrobenzene series are shown in Figure 1. For all three the common products were the result of the replacement of nitro with bromo. Although trinitrobenzene was the only observed product of bromine homolysis, bromine loss must have been facile since bromine radicals were available for this replacement (Table 4).

The nitroanilines *p*- and *o*-nitroaniline, 2,4- and 2,6-dinitroaniline, and 2,4,6-trinitroaniline were thermolyzed neat and in benzene solution (1.2 wt %). The products of DATB and TATB were not amenable to GC−MS analysis. Furazan-containing species was the major decomposition product of the nitroanilines which possessed ortho amine and nitro groups. DATB and

TABLE 2: Major Decomposition Products of Nitroarene in Benzene Solution at 340 °C

Product							
phenol ($m/z = 94$)	nitrobenzene ($m/z = 123$)	no. assignment ($m/z = 128$)	nitrophenol ($m/z = 139$)	biphenyl ($m/z = 154$)	no. assignment ($m/z = 8$)	nitrobiphenyl ($m/z = 199$)	terphenyl ($m/z = 230$)
				parent molecules			
13DNB	13DNB	13DNB		13DNB	13DNB	13DNB	13DNB
14DNB	14DNB	14DNB		14DNB	14DNB	14DNB	14DNB
TNB	TNB	TNB	TNB	TNB	TNB	TNB	TNB
*o*NT	*o*NT			*o*NT	*o*NT	*o*NT	*o*NT
*p*NT	*p*NT			*p*NT	*p*NT	*p*NT	*p*NT
24DNT		24DNT		24DNT	24DNT	24DNT	24DNT
26DNT		26DNT		26DNT	26DNT	26DNT	26DNT
		TNT	TNT	TNT	TNT	TNT	TNT
TNX		TNX	TNX	TNX	TNX		
TNM		TNM	TNM	TNM			
*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA
*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA	*o*NA
24DNA		24DNA		24DNA	24DNA	24DNA	24DNA
26DNA	26DNA		26DNA	26DNA	26DNA		
	TNA	TNA	TNA	TNA	TNA		
	OHTNB	OHTNB	HOTNB	OHTNB	OHTNB		
	CH3OTNB	CH3OTNB	CH3OTNB	CH3OTNB	CH3OTNB		
	ATNT		ATNT	ATNT			
	DATNT	DATNT	DATNT	DATNT	DATNT		
	BrTNB	BrTNB	BrTNB	BrTNB	BrTNB		
	Br2TNB	Br2TNB	Br2TNB	Br2TNB	Br2TNB		
	Br3TNB	Br3TNB	Br3TNB	Br3TNB	Br3TNB		

TABLE 3: Decomposition Products of Nitrobenzenes

products	neat TNB	1.2 wt % in benzene		
		TNB	13DNB	14DNB
$P-NO_2 + H$	1.00	1.00	1.00	1.00
$P-2NO_2 + 2H$		0.25		
$P-2NO_2 + OH$			0.43	0.83
$P-NO_2 + OH$	0.33			
$(2NO_2)C6H5(NO)$	0.18			

TATB are also thought to undergo such ring formation. In the decomposition of *p*-nitroaniline, which lacked ortho nitro and amino groups, only the oxidation products nitrobenzene and aniline were detected. Nitrobenzene was also a minor product in the decomposition of the other nitroanilines in benzene, and neat trinitroaniline produced an analogous product—trinitrobenzene (Table 5).

The thermolyses of *p*- and *o*-nitrotoluenes and 2,4- and 2,6-dinitrotoluene formed products resulting from oxidation of methyl: nitrobenzaldehyde (151), nitrobenzene (123), and dinitrobenzene (168) from *p*-nitrotoluene; aminobenzaldehyde (121) and aminobenzoic acid (137) from *o*-nitrotoluene; aminonitrobenzaldehyde (166) and aminonitrobenzoic acid (182) from the dinitrotoluenes (Table 6). It should be noted that in the case of *p*-nitrotoluene the oxidation is intermolecular; the nitro group within the molecule is not reduced. For the other nitrotoluenes oxidation of methyl is obviously intramolecular with the ortho nitro group reduced to an amine. For the trinitrotoluenes, TNT, TNX, and TNM, products resulting from intramolecular oxidation of methyl were also observed (Table 7). In addition, for all the di- and trinitrotoluenes, loss of one molecule of water resulted in formation of an 1,2-oxazolo ring (Figure 2). For trinitromesitylene a product with *m/e* 201 suggested loss of three water molecules and the formation of di[1,2]oxazolo[3,4-*g*]benzo[1,2]oxazole. For each trinitrotoluene, a product representing loss of NO_2 was detected; but only for TNM and TNX was such a species produced in significant amounts.

The thermolyses products of both aminotrinitrotoluene (ATNT) and diaminotrinitrotoluene (DATNT) were examined. Both exhibited loss of one or two molecules of water, presumably due to ring closure. From our mass spectral data alone, it is impossible to say whether two furazan or one furazan and one

TABLE 4: Decomposition Products of Bromotrinitrobenzenes

products	neat			1.2 wt % in benzene		
	BrTNB	Br2TNB	Br3TNB	BrTNB	Br2TNB	Br3TNB
$P-Br + H$	0.027		0.011			
$P-NO_2 + H$	0.27	0.012		0.11		0.30
$P-NO_2 + Br$	1.00	1.00	1.00	1.00	1.00	1.00
$P-2NO_2 + 2Br$		0.11	0.11		0.17	0.11
$P-2NO_2 + 2Br$ isomer		0.24			0.39	
$P-3NO_2 + 3Br$		0.50			0.57	
$P-2NO_2 + H + Br$						0.077

TABLE 5: Decomposition Products of Aminonitrobenzenes

products	neat			1.2 wt % in benzene				
	*p*NA	*o*NA	TNA	*p*NA	*o*NA	24DNA	26DNA	TNA
nitrobenzene	1.00			0.48	0.12		0.082	0.31
$(HO)C6H5(NO_2)$				0.024	0.17		0.017	1.00
$P-H_2O$		1.00	1.00		0.51	0.14	1.00	0.77
$P-NO_2 + H$	0.36							0.34
trinitrobenzene			0.39					

TABLE 6: Decomposition Products of Methylnitrobenzenes

	neat				1.2 wt % in benzene			
products	*p*NT	*o*NT	24DNT	26DNT	*p*NT	*o*NT	24DNT	26DNT
nitrobenzene	0.46				0.28	0.14		
nitrobenzaldehyde	1.00				1.00	0.28		
dinitrobenzene	0.073		0.095	0.004				0.25
o-cresol		0.20						
$P-NO_2-CH_3 + NH_2 + CHO$		1.00	1.00	0.15		0.4		
$P-NO_2-CH_3 + NH_2 + COOH$		0.86	0.38	1.00		1.00	0.43	0.096
$P-H_2O$			0.067	0.02			1.00	1.00
$P-NO_2 + H$			0.064					0.021
$P-2NO_2 + OH$								0.055

TABLE 7: Decomposition Products of Methyltrinitrobenzenes

	neat			1.2 wt % in benzene		
products	TNT	TNX	TNM	TNT	TNX	TNM
$P-NO_2 + H$	0.067	1.00	1.00	0.078	1.00	1.00
$P-NO_2 + H$ isomer		0.32				
$P-NO_2 + OH$			0.36			
$P-H_2O$	1.00	0.30	0.76	1.00	0.039	0.25
$P-NO_2-CH_3 + NH_2 + CHO$	0.045			0.014		
$P-NO_2-CH_3 + NH_2 + COOH$	0.034		0.022			0.023
$P-CH_3-NO_2 + NH_2 + H$	0.015			0.007		0.007
$P-NO_2 + NH_2$	0.12			0.0	0.060	
$P-H_2O-NO_2 + NH_2$		0.037			0.093	
$P-3H_2O$						0.08
trinitrobenzene	0.089			0.008		

TABLE 8: Decomposition Products of Aminotrinitrotoluenes

	neat		1.2 wt % in benzene	
products	ATNT	DATNT	ATNT	DATNT
$P-NO_2 + H$			0.055	
$P-H_2O$	1.00		1.00	
$P-NO_2-CH_3 + NH_2 + COOH$	0.25		0.059	
$P-NH_2 + H$		1.00		0.084
$P-NH_2-NO_2 + 2H$		0.18		
$P-2H_2O$		0.097	0.034	1.00

TABLE 9: Decomposition Products of Picric Acid and 2,4,6-Trinitroanisole

	neat		1.2 wt % in benzene	
products	HOTNB	CH_3OTNB	HOTNB	CH_3OTNB
$P-NO_2 + H$	1.00	1.00	1.00	0.015
dinitrophenol		0.95		0.19
211, 209	0.097	0.62	0.14	1.00
dinitrobenzene			0.033	0.058
trinitrobenzene			0.012	
$P-CH3 + H$				0.20

oxazolone ring formed. We speculate the latter is the case although the distinction is not critical to this study. Our reason for this assumption is the presence of the methyl intramolecular oxidation product diaminodinitrobenzoic acid (242) in the thermolysis of ATNT. Minor products resulting from the loss of nitro from ATNT (197) and amino from DATNT (242) and loss of both from DATNT (197) were also observed (Table 8).

Thermolyses of 2,4,6-trinitrophenol and 2,4,6-trinitroanisole both produced dinitrophenol (184) and a product of mass 209 (Table 9). Trinitroanisole also formed dinitroanisole (198). The formation of the dinitro species shows that each trinitro compound can decompose by loss of NO_2, a route common to all the nitroarenes examined. However, the fact that both form dinitrophenol demonstrates CH_3 loss as a decomposition route for trinitroanisole.

In summary, at 340 °C all the nitroarenes exhibited NO_2 loss; this was the major product of the nitrobenzenes and *p*-nitrotoluene and *p*-nitroaniline. The bromonitrobenzenes exhibited NO_2 loss and/or addition of bromine. Aminonitrobenzenes and nitrotoluenes, with hydrogen-containing substituents ortho to nitro groups, lost water to form a five-membered ring. In the case of the nitrotoluenes many products were observed resulting from intramolecular reduction of NO_2 and oxidation of CH_3.

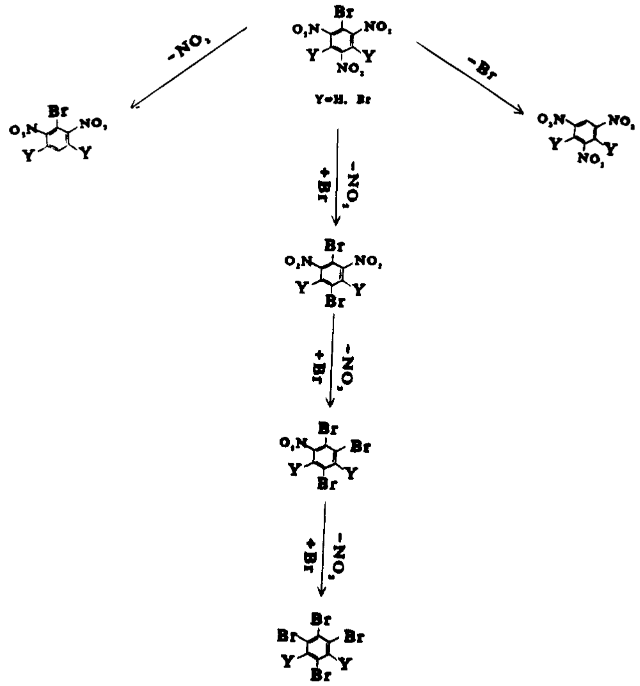


Figure 1. Thermal decomposition of bromotrinitrobenzenes.

Kinetics. Relative thermal stability of energetic materials is assessed in a variety of ways, e.g., comparing DSC exotherms, Henkin critical temperatures, and total gas evolution.[18] The rankings are subject to the temperature regime of the comparison. In this study we have chosen to determine the rate constants for each energetic material over as wide a temperature range as could conveniently be measured by our isothermal decomposition method. Since most of the materials exhibited similar activation energies, comparison of their rate of thermal

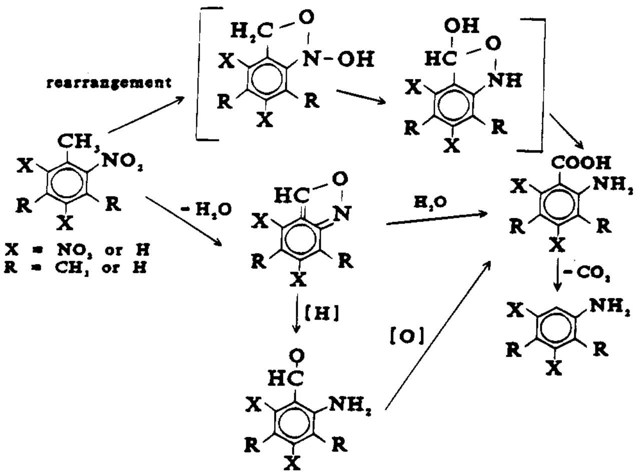


Figure 2. Thermal decomposition of methyltrinitrobenzenes.

decomposition at any temperature in the range examined would have yielded the same relative ordering. The materials were compared using their 340 °C rate constants, which for some nitroarenes was the lowest and for some the highest temperature at which their thermolyses could conveniently be examined. However, for some compounds the activation energies were sufficiently different that it is obvious that had a different temperature range been chosen, the relative ordering would change. In fact, in a few cases thermal stabilities ordered by the temperature of the DSC exothermic maximum (20 °C/min) were not consistent with those obtained by ordering the compounds by the 340 °C isothermal rate constants. Usually, the rate of decomposition was slower in solution than that in condensed phase for although the nitroarenes primarily decompose by intramolecular hydrogen abstraction, intermolecular hydrogen abstraction also occurs.[3] The importance of intermolecular hydrogen abstraction is seen in the fact that condensed-phase thermolyses could be as much as 10 times faster than those where the nitroarene was 1.2 wt % in benzene and the observation that TNT at 10 wt % in benzene decomposed about 10 times faster than the 1.2 wt % solution.

Effect of Substituent Type. In symmetrical trinitrobenzene (TNB) with one non-nitro substituent, the nature of the non-nitro substituent had a direct effect on the rate constant (k). At 340 °C the relative ordering of thermal stabilities was the same in benzene solution (benz.) or condensed (cond.) phase. For amino-, methyl-, and hydroxy-substituted trinitrobenzene, the thermal stability appeared to be directly related to the acidity of the hydrogen contained in the substituent.

stability:

$$\mathrm{TNB} \gg \mathrm{Br{-}TNB} > \mathrm{NH_2{-}TNB} > \mathrm{CH_3{-}TNB} > \mathrm{CH_3O{-}TNB} > \mathrm{HO{-}TNB}$$

Rate Constants (E-03, s^{-1})

	TNB	Br–TNB	NH$_2$–TNB	CH$_3$–TNB	CH$_3$O–TNB	HO–TNB
k_{340C} cond.	0.08	2.3	4.4	9.8	23	191
k_{340C} benz.	0.06	0.45	0.54	0.97	2.0	7.6

Effect of Nitro Groups. At 340 °C, in the condensed phase and solution we found that the thermal stability decreased as the number of nitro substituents on the ring increased.

stability	$(NO_2)C_6H_5$ >	$1,3\text{-}(NO_2)_2C_6H_4$	$1,4\text{-}(NO_2)_2C_6H_4$ >	$(NO_2)_3C_6H_3$
k_{340C} cond. (E-04, s^{-1})	0.15	0.30	0.37	0.76
k_{340C} benz. (E-04, s^{-1})	0.05	0.18	0.18	0.56

When the nitroarenes were substituted with amino or methyl groups, the relative position of the nitro group to the substituent affected thermal stability. This has frequently been observed in nitrotoluenes;[2] we observed it in nitroanilines, as well.

stability nitroanilines	*p*-NA >	*o*-NA >	2,4-DNA	2,6-DNA >	TNA
k_{340C} cond. (E-03, s^{-1})	0.10	0.14	0.59	0.45	4.4
k_{340C} benz. (E-03, s^{-1})	0.096	0.14	0.14	0.36	0.54

stability nitrotoluenes	*p*-NT >	*o*-NT >	2,4-DNT	2,6-DNT >	TNT
k_{340C} cond. (E-03, s^{-1})	0.11	0.49	0.50	0.42	9.8
k_{340C} benz. (E-03, s^{-1})	0.096	0.13	0.19	0.78	0.97

Effect of Multiple Heterosubstituents. In both benzene solution and condensed phase, the effect on thermal stability of the addition of multiple heterosubstituents to trinitrobenzene was examined. In addition to comparing the 340 °C rate constants, the positions of the DSC exothermic maxima (DSC exo.) were compared and found to give the same thermal stability ranking as the 340 °C isothermal rate constants.

Di- and trihydroxy-substituted trinitrobenzenes decomposed too quickly at 340 °C to allow their decomposition rate constants to be accurately measured; therefore, the hydroxytrinitrobenzenes were compared at lower temperatures. Successive hydroxy substitution of trinitrobenzene (mono-, di-, and trihydroxytrinitrobenzene) (Table 10) or successive amino substitution of trinitrotoluene (amino- and diaminotrinitrotoluene) decreased thermal stability in both solution and condensed-phase decomposition studies (Table 11).

stability	HO–TNB >	(HO)$_2$–TNB >	(HO)$_3$–TNB
k_{260C} cond. (E-03, s^{-1})	0.36	21	1000
DSC exo. (°C)	332	300	215
k_{280C} benz. (E-03, s^{-1})	0.009	2.5	54
mp (°C)	124	180	163

stability	(CH$_3$)–TNB >	(NH$_2$)(CH$_3$)–TNB >	(NH$_2$)$_2$(CH$_3$)–TNB
k_{340C} cond. (E-03, s^{-1})	9.8	22	82
DSC exo. (°C)	328	323	306
k_{340C} benz. (E-03, s^{-1})	0.97	1.5	4.7
mp (°C)	80	140	228

When the homologous series of methyl- and bromotrinitrobenzenes were examined, the thermal stability trends in solution and in condensed phase diverged. In solution addition of methyl groups decreased thermal stability (Table 12); addition of bromo groups had no effect (Table 13). However, when the condensed-phase series were examined, a smooth increase in thermal stability with increased non-nitro substitution was observed in both homologous series.

	TNT	TNX	TNM
k_{340C} cond. (E-03, s^{-1})	9.8	6.0	1.7
DSC exo. (°C)	328	351	368
k_{340C} benz. (E-03, s^{-1})	0.97	1.6	2.3
mp (°C)	80	187	240

	Br–TNB	Br$_2$–TNB	Br$_3$–TNB
k_{340} cond. (E-03, s^{-1})	2.3	1.4	1.0
DSC exo. (°C)	374	399	400
k_{340} benz. (E-03, s^{-1})	0.45	0.41	0.45
mp (°C)	124	140	160

The general observation for thermolyses performed in benzene solution was that the addition of hydrogen-containing substit-

TABLE 10: Arrhenius Parameters of Hydroxytrinitrobenzenes

Rate Constants (s^{-1})

	neat			in benzene		
T (°C)	HOTNB	(HO)2TNB	(HO)3TNB	HOTNB	(HO)2TNB	(HO)3TNB
180		4.12E−05	3.60E−04			
		3.02E−04	2.05E−03			
220	2.67E−05	8.28E−04			2.57E−05	8.98E−04
240			2.32E−04		7.27E−05	3.79E−03
260	3.63E−04	2.07E−02	1.00		6.71E−04	2.43E−02
270	1.77E−03	1.32E−01				
280	3.22E−03	1.14E−01		8.81E−05	2.51E−03	1.51E−01
280		1.12E−01				5.40E−02
290	7.15E−03					
300	9.19E−03	2.99E−01		5.19E−04	3.20E−02	4.83E−01
300				6.09E−04		
300				5.03E−04		
310	2.63E−02					
320				2.07E−03		
340	1.91E−01	1.19		7.06E−03	7.06E−03	
340				8.23E−03		

Arrhenius Parameters

	neat			in benzene		
T (°C)	HOTNB	(HO)2TNB	(HO)3TNB	HOTNB	(HO)2TNB	(HO)3TNB
E_a (kcal/mol)	44.3	37.5	49.4	48.6	50.1	43.9
E_a (kJ/mol)	185	157	207	203	209	183
A (s^{-1})	1.56E+15	5.78E+13	2.05E+20	2.05E+15	2.49E+17	2.16E+16
R^2	0.99	0.98	0.99	0.99	0.99	0.98
T range (°C)	220−340	180−340	180−260	280−340	220−340	220−330

TABLE 11: Arrhenius Parameters of Aminotrinitrotoluenes

Rate Constants (s^{-1})

	neat			in benzene		
T (°C)	TNT	ATNT	DATNT	TNT	ATNT	DATNT
240			3.99E−04			
260	1.24E−04	4.81E−04	1.66E−03	1.23E−05		
280	2.91E−04	1.61E−03		3.24E−05	3.33E−05	1.28E−04
300	1.17E−03	5.09E−03	1.26E−02		1.79E−04	7.08E−04
300		4.39E−03		1.51E−04		
320	2.55E−03	1.42E−02			4.76E−04	1.98E−03
340	1.09E−02	2.19E−02	8.E−02	1.00E−03	1.38E−03	4.67E−03
340	9.61E−03			9.34E−04	1.62E−03	
340	8.88E−03					
350				2.E−03		
360	4.01E−02			3.96E−03	6.18E−03	2.67E−02
370				7.48E−03		
370				7.08E−03		

Arrhenius Parameters

	neat			in benzene		
T (°C)	TNT	ATNT	DATNT	TNT	ATNT	DATNT
E_a (kcal/mol)	38.1	32.0	32.8	53.0	43.3	43.6
E_a (kJ/mol)	159	134	137	221	181	182
A (s^{-1})	3.87E+11	7.29E+09	4.22E+10	7.15E+15	4.61E+12	2.58E+13
R^2	0.99	0.99	1.00	0.99	0.99	0.98
T range (°C)	260−360	260−340	240−340	280−370	280−360	280−360

uents decreased thermal stability. However, the thermal stability of the aminotrinitrobenzene series could not be compared in benzene solution due to the insolubility of DATB and TATB. Accordingly, condensed-phase studies of the aminotrinitrobenzene series were conducted while we sought a method by which to study the entire series in solution. As expected, we found that the fully substituted trinitrobenzene, TATB, was substantially more stable than the other two, DATB and trinitroaniline (Table 14).

Since DMSO was used to solubilize the residue of the condensed-phase decomposition, we attempted to use it as the solvent for the thermolysis of the aminotrinitrobenzene series at 200 °C. In 2 min, 14% of the TATB had reacted compared to 7% of the DATB and 5% of the trinitroaniline (TNA). Longer reaction times could not be examined since DMSO began to exhibit substantial decomposition after 20 min. When it was discovered that *N,N*-dimethylacetamide (DMA) dissolved small quantities (40 ppm) of the aminotrinitrobenzenes and was

TABLE 12: Arrhenius Parameters of Methyltrinitrobenzenes

Rate Constants (s^{-1})

	neat			in benzene		
T (°C)	TNT	TNX	TNM	TNT	TNX	TNM
260	1.24E−04	3.54E−05	2.12E−05			
280	2.91E−04	1.80E−04	9.85E−05	1.23E−05	1.50E−05	2.10E−05
300	1.17E−03	6.36E−04	1.25E−04	3.24E−05	5.03E−05	9.01E−05
320	2.55E−03	1.31E−03	4.63E−04	1.51E−04	2.34E−04	6.94E−04
340	1.09E−02	7.59E−03	1.36E−03	1.00E−03	1.81E−03	1.87E−04
340	9.61E−03	5.74E−03	2.01E−03	9.34E−04	1.51E−03	2.66E−03
340	8.88E−03	4.74E−03			1.49E−03	
350				2.E−03	3.46E−03	3.69E−03
360	4.01E−02	2.29E−02	7.20E−03	3.96E−03	7.33E−03	8.95E−03
360						
370				7.48E−03	1.15E−02	1.22E−02
370				7.08E−03		

Arrhenius Parameters

	neat			in benzene		
T (°C)	TNT	TNX	TNM	TNT	TNX	TNM
E_a (kcal/mol)	38.1	41.5	36.6	53.0	55.1	51.3
E_a (kJ/mol)	159	174	153	221	230	215
A (s^{-1})	3.87E+11	3.88E+12	1.88E+10	7.15E+15	6.73E+16	4.12E+15
R^2	0.99	0.99	0.97	0.99	0.99	0.99
T range (°C)	260−360	260−360	260−360	280−370	280−370	280−370

TABLE 13: Arrhenius Parameters of Bromotrinitrobenzenes

Rate Constants (s^{-1})

	neat			in benzene		
T (°C)	BrTNB	Br2TNB	Br3TNB	BrTNB	Br2TNB	Br3TNB
280	4.24E−05	4.02E−05	2.17E−05			
280			1.88E−05			
300	2.39E−04	1.50E−04	9.60E−05			
320	6.35E−04	3.44E−04		1.47E−04	1.63E−04	1.46E−04
330				2.72E−04		2.11E−04
330						1.70E−04
340	2.34E−03	1.44E−04	1.10E−03	4.23E−04	3.27E−04	4.89E−04
340			1.30E−03	4.84E−04	4.99E−04	4.05E−04
340			7.64E−04			
350	5.72E−03			8.02E−04		6.59E−04
360	8.34E−03	4.00E−03	4.15E−03	1.84E−03	1.26E−03	9.27E−04
360						9.14E−04
370	9.35E−03			2.24E−03		1.70E−03
380	1.34E−02			4.37E−03	2.78E−03	2.39E−03

Arrhenius Parameters

	neat			in benzene		
T (°C)	BrTNB	Br2TNB	Br3TNB	BrTNB	Br2TNB	Br3TNB
E_a (kcal/mol)	42.1	39.8	44.9	44.0	37.4	37.4
E_a (kJ/mol)	176	7	188	184	156	156
A (s^{-1})	2.21E+12	2.14E+11	1.11E+13	2.32E+12	9.17E+09	8.64E+09
R^2	0.99	0.99	0.99	0.99	0.98	0.98
T range (°C)	280−380	280−360	280−360	320−380	320−380	320−380

itself inert to at least 340 °C, the aminotrinitrobenzenes were thermolyzed in that solvent. However, it became obvious that interaction between the nitroarenes and solvent occurred; at 340 °C the decomposition rate of TNA increased 1000-fold in dimethylacetamide compared to its rate in benzene.

	TNA	DATB	TATB
k_{340C} cond. (E-03, s^{-1})	4.4	10	0.18
DSC exo. (°C)	387	360	397
k_{340C} benz. (E-03, s^{-1})	0.54		
k_{340C} DMA (E-03, s^{-1})	451	617	> 1000
mp (°C)	192	286	449

We assumed that the interaction between TNA and dimethylacetamide was formation of a Meisenheimer complex, a complex much studied in the case of TNT and basic species.[19] Accordingly, we examined the methyltrinitrobenzene series in dimethylacetamide. Simple dissolution to form 1.2 wt % solutions revealed a stability ordering which was maintained upon heating. TNT formed a pink solution; dimethyltrinitrobenzene (TNX) formed a yellow solution; the trimethyltrinitrobenzene (TNM) remained colorless. After 2 min of heating at 240 °C, 46% of the TNT, 14% of the TNX, and 11% of the TNM had reacted. This experiment suggested that interaction of the trinitroarene with dimethylacetamide decreases with increased heterosubstitution. As a result, we assume the relative

TABLE 14: Arrhenius Parameters of Aminotrinitrobenzenes

Rate Constants (s^{-1})

	neat			in benzene	dimethylacetamide		
T (°C)	TNA	DATB	TATB	TNA	TNA	DATB	TATB
220		4.12E−06					
220		2.32E−06					
230							4.62E−02
240		3.40E−06				4.93E−02	
250							1.11E−01
259							1.82E−01
259							1.55E−01
260	1.27E−05	1.98E−05					
270					8.73E−02	1.01E−01	2.30E−01
280	5.57E−05	1.06E−04	4.92E−06	1.20E−05			
290		4.84E−04					
300	3.50E−04	1.75E−03	1.61E−05		1.54E−01	2.77E−01	
300	2.23E−04	1.04E−03					
308		3.35E−03					
318		5.28E−03					
320	8.48E−04	2.73E−03	1.06E−04	1.14E−04	2.95E−01		
320	8.20E−04						
328		8.85E−03					
330			1.51E−04				
340	4.53E−03	8.56E−03	1.80E−04	6.02E−04	4.51E−01	6.17E−01	
340	4.30E−03	1.23E−02		4.73E−04			
352				1.32E−03			
360	1.71E−02		1.24E−03	2.27E−03			

Arrhenius Parameters

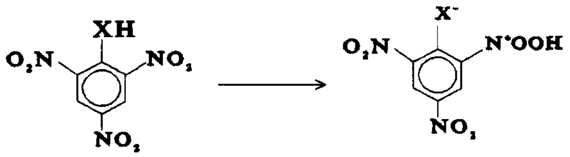
	neat			in benzene	dimethylacetamide		
T (°C)	TNA	DATB	TATB	TNA	TNA	DATB	TATB
E_a (kcal/mol)	48.0	47.9	46.8	45.5	15.8	18.1	22.4
E_a (kJ/mol)	201	196	190	66	75	94	
A (s^{-1})	5.12E+14	1.79E+15	1.41E+13	9.82E+13	1.92E+05	1.83E+06	2.51E+08
R^2	0.99	0.97	0.98	0.99	0.98	0.99	0.99
T range (°C)	260−360	220−340	280−360	280−360	270−340	250−340	230−270

order of thermal stabilities among the aminotrinitrobenzenes, which was observed both in dimethylacetamide and DMSO, is parallel to the ordering observed for the other trinitroarenes in benzene. Like the other trinitroarenes, increased substitution of the ring increased the thermal decomposition rate in solution.

Discussion

Effect of Nitro Groups. Within the nitrobenzene group, thermal stability decreased slightly as the number of nitro groups increased. Presumably, since the C$-$NO$_2$ is subject to homolysis, the more C$-$NO$_2$ bonds, the more rapid the decomposition. Within the nitrotoluene and nitroaniline classes, there was also a trend for thermal stability to decrease with increasing number of nitro groups; but the relative position of the nitro groups appeared to be more important than the total number of nitro groups. *p*-Nitrotoluene and nitroaniline were much more stable than the ortho analogs. These observations were applicable to both solution and condensed-phase decompositions.

Effect of Substituent Type. Both in solution and in condensed phase, nitrobenzenes, as a class, are more thermally stable than the heterosubstituted nitrobenzenes. Since trinitroaniline (NH_2−TNB) is more thermally stable than TNT (CH_3−TNB), and TNT is more stable than picric acid (HO−TNB), thermal stability appears to correlate with the acidity of the hydrogen-containing substituent. This type of correlation would be in line with a decomposition mode where the rate-determining step is intramolecular proton transfer from the hydrogen-containing substituent to a neighboring NO_2 group:



XH = OH, NH$_2$, or CH$_3$

This would explain the stability of unsubstituted nitrobenzenes since the major mode of decomposition available to them would be homolysis of the C$-$NO$_2$ bond rather than C$-$NO$_2$H formed by intramolecular proton transfer. The latter homolysis has an activation energy roughly half of the former. (Note formation of C$-$NO$_2$H would still be available by intermolecular pathways, but the accessibility of intramolecular vs intermolecular routes has been adequately demonstrated in the enhanced thermal stability of *p*-nitrotoluene compared to that of *o*-nitrotoluene.[3])

Hydrogen transfer to the nitro group of the nitroarene has been supported by the observation of deuterium kinetic isotope effects (DKIE).[3,20] For example, TNT thermolyzed at 340 °C in proteo- and deuterobenzene exhibited a DKIE of 2.0 attributable to intermolecular hydrogen transfer from benzene to TNT. When the decomposition of TNT at 340 °C in benzene was compared to that of d^3-TNT, a DKIE of 3.4 was found, indicating the greater importance of intramolecular hydrogen transfer.

Even if proton acidity explains some of the thermal stability trends observed with singly-substituted trinitrobenzenes, this rationale cannot be applied to 2,4,6-trinitroanisole (CH_3O-TNB), one of the most unstable of the monosubstituent trinitrobenzenes, nor to 1-bromo-2,4,6-trinitrobenzene (Br−TNB), one of the most stable. It might be argued that the poor thermal stability of trinitroanisole is not a result of proton transfer but of CH_3^+ transfer to the neighboring nitro group. Indeed, CH_3^+ is labile. The reason that trinitrobromobenzene is somewhat less thermally stable than trinitrobenzene is not obvious, but it is likely an electronic effect.

Effect of Multiple Heterosubstituents. It has been speculated that TATB possesses its unusually high thermal stability because there are no hydrogen atoms directly attached to the aromatic ring or because it is necessary for it to undergo loss of three molecules of water before becoming an explosive species. However, in solution studies, we found that as the number of heterosubstituents on the trinitrobenzene (TNB) ring increased, the thermal stability decreased. This was true in the benzene thermolyses of the hydroxy- and methyltrinitrobenzenes and the aminotrinitrotoluenes as well as for the aminotrinitrobenzene series heated in *N,N*-dimethylacetamide or DMSO. For trinitroarenes with substituents possessing labile protons, increased reactivity with increased substitution is understandable since intramolecular hydrogen transfer to form C−NOOH is facilitated. Only the bromotrinitrobenzene series, where hydrogen transfer to nitro groups cannot be a factor, showed no change in thermal stability with increased number of non-nitro substituents.

The observation in solution that addition of substituents to trinitrobenzene (TNB) decreased thermal stability indicates that TATB was actually less thermally stable than aminotrinitrobenzene (TNA) or DATB, a conclusion at odds with conventional perceptions of this molecule. However, when the condensed-phase series were examined, it was found that the completely substituted arenes were indeed the most stable. For the methyl- and bromo-substituted series, there was a smooth increase in condensed-phase thermal stability with increased non-nitro substitution. For the amino-substituted trinitrobenzenes, the thermal stability trend in the condensed phase was not smooth; DATB exhibited a higher rate of decomposition at 340 °C than either trinitroaniline or TATB.

The intriguing difference between solution-phase and condensed-phase thermal stability studies is in the effect of multiple heterosubstituents. In condensed phase, the methyl-, bromo-, and aminotrinitrobenzene series showed increased thermal stability with added substituents, in opposition to the relative thermal stability order observed in solution—decreased thermal stability with increased substitution. In contrast, the hydroxytrinitrobenzene and aminotrinitrotoluene series in condensed phase thermolyses maintained the thermal stability order observed in benzene solution.

The stability trends observed in the methyl-, bromo-, and amino-substituted homologous series suggest that, in the condensed phase, intermolecular attractive forces may be more important than the structure of the individual molecule. In fact, their rate of decomposition decreased as the melting point increased. Although TATB was the least stable of the aminotrinitrobenzene homologues in solution (dimethylacetamide or DMSO), in condensed phase it was the slowest to decompose. Due to its high molecular weight, symmetry, and hydrogen bonding, TATB melts at a temperature substantially higher than the other two aminotrinitrobenzenes. It may be that the high thermal stability of TATB is simply a result of an inability to disrupt its crystal lattice either by melting or by dissolution. Generally, the more mobile liquid phase decomposes more rapidly than the solid phase; therefore, the species which melt first begin to decompose much faster than those which remain solid. In series where the melting points differ widely, those species with higher melting points may withstand higher temperatures, thus overcoming their "intrinsic" or solution reactivity and reversing the order of stability dictated by the chemistry of the isolated molecule.

In the amino-substituted trinitrobenzene series, the thermal stabiity trend in the condensed phase was not smooth; diamino-substituted species decomposed most quickly. Like the other series, the triamino-substituted trinitrobenzene TATB was the least stable in solution (dimethylacetamide or DMSO). In condensed phase, however, the strong intermolecular attractive forces partially reversed that trend. In TATB, these forces overcome the "intrinsic" instability of the molecule; therefore, it decomposed most slowly. In DATB, however, which has a substantially lower melting point than TATB, the "intrinsic" chemistry of the molecule was not overwhelmed by these forces, and it decomposed the fastest in the series.

The hydroxytrinitrobenzene homologous series exhibited condensed-phase thermal stabilities in the same relative order as the solution stabilities. This is not surprising in view of the large differences observed in their solution rate constants and the small differences in their melting points. The aminotrinitrotoluene series is not a true homologous series, but it is interesting to note that their condensed-phase rate constants also follow those observed in solution. Like the hydroxytrinitrobenzene series, these species have such high intrinsic rate constants that intermolecular attractions are overwhelmed. It is obvious diaminotrinitrotoluene DATNT would not make a good replacement for the difficult to process TATB.

Conclusions

Most of the trends observed in solution appeared to apply to the condensed-phase decomposition, though, of course, the condensed-phase decompositions were faster than those in benzene solution. Both in solution and in the condensed phase, the thermal stability of the nitroarenes decreased as the number of nitro groups was increased from one to three and as another substituent capable of attack on the ortho nitro group was added. In the solution studies, increasing the number of hydroxy, methyl, or amino groups on trinitrobenzene decreased the thermal stability. The destabilization is due to the presence of groups ortho to the nitro groups which can transfer a proton to the nitro group, thus, lowering the $C-NO_2$ bond strength.

In some cases, the thermal stability of the homologous series followed the solution trend of decreased stability with increased substitution; in others, it did not. The trend was maintained in the hydroxytrinitrobenzene series and in the aminotrinitrotoluene series. However, in condensed-phase studies the thermal stability of the series $(CH_3)_n-$TNB, $(NH_2)_n-$TNB, Br_n-TNB, where $n = 1, 2,$ or 3, increased with substitution. This increased stability was attributed not to a change in the elementary chemistry but to an increase in the intermolecular attractive forces as molecular weight and symmetry increased. Since melting point reflects lattice stability, we observed that in condensed-phase thermolyses, high-melting species, such as TATB, exhibited the highest thermal stability in their homologous series, even though the intrinsic molecular stability of the high-melting species is lower. The overall balance of the thermal stability of the molecular structures and of the lattice forces leads to homologous series which show stability trends both parallel and opposed to those in solution. In cases where the trisubstituted trinitrobenzene evidenced low thermal stability in solution and only a moderately higher melting point than its homologs, the ordering in the condensed phase may be the same as that in solution with the most substituted species being the least stable [$(HO)_3$TNB and DATNT]. These species have such high "intrinsic" rate constants that intermolecular attractive forces are overwhelmed. These observations suggest that, in the condensed phase, intermolecular attractive forces may be more important than the intrinsic molecular structure. The knowledge that the thermal stability of TATB may be more a function of its lattice stability than an intrinsic property of the isolated molecule should be considered in the design of future insensitive explosives.

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