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Thermal decomposition of high-nitrogen energetic compounds—dihydrazido-*S*-tetrazine salts

Jimmie C. Oxley*, James L. Smith, Heng Chen

Chemistry Department, University of Rhode Island, Kingston, RI 02881, USA

Abstract

The thermal stabilities of 3,6-dihydrazido-1,2,4,5-tetrazine (Hz_2Tz) and its salts with diperchlorate [$Hz_2Tz(HClO_4)_2$], dinitrate [$Hz_2Tz(HNO_3)_2$], bisdintramidate [$Hz_2Tz(HDN)_2$], and bisdinitroimidazolate [Hz_2TzBim] have been examined and compared to other 3,6-disubstituted tetrazines. The neutral tetrazines exhibited two principal modes of decomposition: elimination of N_2 from the tetrazine ring followed by cleavage of the remaining N–N bond, and loss of the substituent group, in some cases assisted by proton transfer. The salts Hz_2TzX_2 undergo reversible equilibrium with the parent Hz_2Tz and HX, thus, in several cases the decomposition rate of the parent tetrazine and the salt are essentially identical. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 3,6-Dihydrazido-1,2,4,5-tetrazine (Hz_2Tz); Tetrazine; Thermal stability; Thermal decomposition

1. Introduction

Traditional explosives, nitrate esters, nitroarenes, nitramines, must contain sufficient NO_2 groups to self-oxidize the carbon and hydrogen atoms of the molecule. In designing new energetic materials, one area of emphasis has been on increasing the nitrogen content at the expense of carbon/hydrogen content. This has two advantages: lowering C/H content lowers the oxygen requirement, substituting N–N for C–N usually increases the heat of formation. Central to these efforts have been the study of nitrogen-containing rings. In some cases the effort was successful, as in the case of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO) [1–6]. Other compounds, such as 2,4,6-trinitro-1,3,5-triazine have been proposed, but not successfully synthesized [7,8]. Tetrazine, a high-nitrogen ring compound, is one of the frameworks on which new energetic materials are based. The spectroscopic and photodissociation properties of known tetrazines have long been an area of interest to the theoretician. Synthesis efforts at Los Alamos National Laboratory (LANL) have resulted in a series of new 3,6-substituted-1,2,4,5-tetrazines, both neutral species and salts [9–14]. We have examined and reported the thermal stability of the neutral tetrazines—3,6-substituted-1,2,4,5-tetrazines, where the substituents were Cl, NH_2, NH_3NH_2 and 3,5-dimethylpyrazole [15]. Now, we report thermal studies on one of the salts of these tetrazines—3,6-dihydrazino-1,2,4,5-tetrazine.

2. Experimental section

3,6-Dihydrazido-1,2,4,5-tetrazine (Hz_2Tz) and its diperchlorate [$Hz_2Tz(HClO_4)_2$], dinitrate [$Hz_2Tz(HNO_3)_2$], bisdintramidate [$Hz_2Tz{\cdot}2HN(NO_2)_2$], and bisdinitroimidazolate [Hz_2TzBim] salts were synthesized and provided by Dr. Michael Hiskey of LANL

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* Corresponding author.
E-mail address: joxley@chm.uri.edu (J.C. Oxley).

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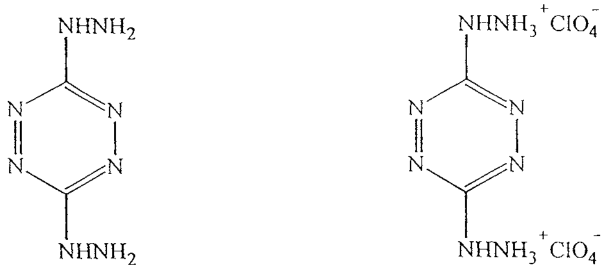
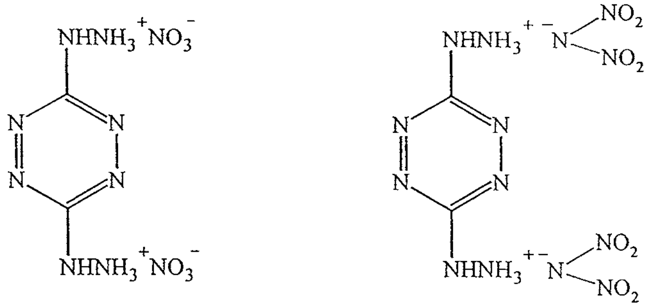
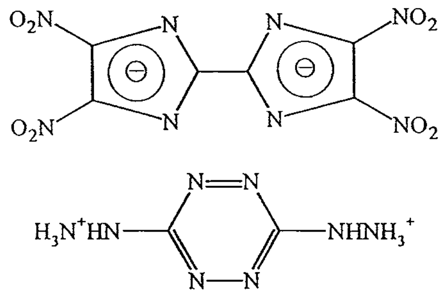


3,6-dihydrazino-1,2,4,5-tetrazine Hz_2Tz 3,6-dihydrazino-1,2,4,5-tetrazine diperchlorate $Hz_2Tz(HClO_4)_2$



3,6-dihydrazino-1,2,4,5-tetrazine dinitrate $Hz_2Tz(HNO_3)_2$ 3,6-dihydrazino-1,2,4,5-tetrazine bis-dinitramide $Hz_2Tz(HDN)_2$



3,6-dihydrazino-1,2,4,5-tetrazine bis-dinitroimidazolate Hz_2TzBim

Fig. 1. The tetrazine salts.

[15]. Properties of these salts (Fig. 1) are listed in Table 1. Thermal stability was initially evaluated using differential scanning calorimetry (DSC). Samples (0.1–0.4 mg) were sealed in capillary tubes (1.5 mm o.d. × 10 mm), which were held in an aluminum cradle [16] under nitrogen flow inside the head of a TA Instruments 2910 (calibrated against indium). Thermograms used for the comparison were obtained over the temperature range 40–500 °C at a scan rate of 20 °C/min. In some cases, the American Society for Testing and Materials (ASTM), differential heating rate method was used to calculate Arrhenius parameters [17]. Thermograms were collected at heating rates (β) of 1, 2.5, 5, 10, and 20 °C/min, and activation

Table 1
Properties of dihydrazido-tetrazine salts[a]

Sample	Color			Solubility					
	Unheated color	DSC residue	Isothermal residue	Water	Acetonitrile	Methanol	Acetone	Density (g/cm^3)	H_{50}
Hz_2Tz	Dark red powder	Yellow residue	Dark yellow or black residue	Fair	Insoluble	Insoluble	Insoluble	1.69	65
$Hz_2Tz(HClO_4)_2$	Yellow powder	None	Black residue	Good	Good	Good	Good	1.96	14
$Hz_2Tz(HNO_3)_2$	Orange powder	None	Black residue	Good	Insoluble	Good	Good	1.80	17
$Hz_2Tz(HDN)_2$	Yellowish green powder	None	Black residue	Good	Insoluble	Good	Good	1.82	11
Hz_2TzBim	Orange powder	Dark gray residue	Black residue	Insoluble	Insoluble	Insoluble	Insoluble	1.83	60

[a] Densitry and H_{50} from LANL data [15].

energy (E_a) was calculated from the slope of the plot of $\log_{10}\beta$ versus $1/T$ (T is the exothermic peak temperature (exo. T) in K), as follows:

$$E_a = -2.19R\left[\frac{d(\log_{10}\beta)}{d(1/T)}\right]$$

where R is the gas constant.

A refinement of the activation energy and an estimation of the Arrhenius pre-exponential factor (A) were calculated according to the ASTM protocol, where a table of D factors is given [17].

$$A = \beta E_a \frac{e^{E_a/RT}}{RT^2}, \quad \text{refined}$$

$$E_a = \left(-2.303\frac{R}{D}\right)\left[\frac{d(\log_{10}\beta)}{d(1/T)}\right]$$

Isothermal thermolyses were performed on samples (0.1–0.6 mg) in tubes 4 mm o.d. × 50 mm to measure kinetics or in narrower tubes (1.2–1.5 mm o.d.× 50 mm) to determine decomposition gases. The constant temperature bath consisted of an aluminum block with four chambers containing molten Wood's metal, a hot plate acted as the main heating source, while the temperature was maintained within 1 °C with a 250 W immersion heater, an Omega (CA/500/J1) temperature controlling sensor and Omega 651 resistance thermometer. Rate constants were calculated by determining the fraction of sample remaining at various times during the isothermal heating. After the sample was heated for a specified time interval, the tube was broken, and the sample was transferred to a 10 ml volumetric flask using distilled, dionized water. The remaining quantity of dihydrazido-tetrazine (Hz_2Tz) was assessed by a Hewlett Packard (HP) 1084B high performance liquid chromatograph (HPLC). The LC was equipped with a 20 μl injection sample loop, a Waters 486 Tunable Absorbance Detector (set to 250 nm), an Alltech Econosphere C18 5U column (4.6 mm × 250 mm), and a HP 3396 series III integrator. The mobile phase consisted of water and methanol or acetonitrile, details are shown in Table 2.

To identify the decomposition gases, the sample was sealed under vacuum or air and heated to complete decomposition. The decomposition gases were analyzed by gas chromatography/mass spectrometry (GC/MS) [18]. A HP Model 5890 Series II GC, equipped with Model 5971 electron impact quadruple mass spectrometer was run in scan mode (mass range 12–200) with a threshold of 150 and a sampling of 2 (3.5 scans per second). Helium was used as the carrier gas, and the GC column was a PoraPLOT Q

Table 2
HPLC solvents and flows for 3,6-dihydrazino-tetrazine salts

Sample Solvents	$Hz_2Tz(HClO_4)_2$ 10% CH_3OH in water	$Hz_2Tz(HClO_4)_2$ 50% CH_3OH in water	$Hz_2Tz(HDN)_2$ 10% CH_3CN in water	$Hz_2TzHz_2Tz(HNO_3)_2$ 10% CH_3CN in water
Flow rate (ml/min)	0.4	1.0	0.4	0.6
Retention time (min)	9.6	3.3	8.3	5.8

(0.25 mm × 25 mm) from Chrompack. The GC injector temperature was 100 °C, and the detector/transfer line temperature was 180 °C. Initially, the oven temperature was held for 5 min at −80 °C, it was then increased at a rate of 15 °C/min up to 190 °C. Decomposition gases were identified by comparing their GC retention times and mass spectra to authentic samples. When authentic samples were not available, sample spectra were compared with the NIST MS library for tentative assignment.

Total amount of decomposition gases was initially assessed by heating the tetrazine salts to complete decomposition, inside a sealed capillary tube and breaking the tube into a mercury manometer. To quantify each of the decomposition gases, a HP 5890 series II GC with a thermal conductivity detector (GC/TCD) and Hayesep DB 100/120 (30′ × 1/8″) column (Alltech) was used. A standard gas mixture—40% N_2, 5% CO, 30% CO_2, and 25% N_2O (Scott Specialty Gases)—and gas sample loops of 10, 50, 100, 250 and 500 µl volume were used for calibration. The injector temperature was set at 120 °C, the detector temperature at 200 °C, flow of helium carrier gas was at 20 ml/min. The oven was held for 6 min at 35 °C and then ramped (40 °C/min) to 180 °C, where it was held 28 min.

Injection of the gaseous decomposition products was accomplished by placing the sealed tubes in a Nalgene (870 PFA, i.d. 1/8″), sample loop in line with the carrier gas and injector of the GCTCD or GC/MS. The sample loop was purged with helium, the oven was cooled to −80 °C, the sample tube was broken by bending the flexible loop, and the loop was switched in line. Although the Nalgene 870 PFA loop was permeable to air, because it was continuously under helium gas pressure, air contamination was constant and relatively low. To check the baseline, an empty capillary tube, sealed according to the procedures for samples, was broken in the GC loop [18].

3. Results

3.1. Kinetics

DSC was used to rate the relative thermal stabilities of Hz_2Tz and its nitrate [$Hz_2Tz(NO_3)_2$], dintramidate [Hz_2TzDN_2], perchlorate [$Hz_2Tz(ClO_4)_2$], and imidazole [Hz_2TzBim], salts. Three of the five exhibited their major exotherm between 152 and 164 °C [Hz_2Tz, $Hz_2Tz(NO_3)_2$, and Hz_2TzDN_2], the perchlorate salt exhibited an exotherm about 30° higher (190 °C), and the imidazole, even higher (220 °C) (Table 3). All the salts released more heat than the parent neutral species. Isothermal heating followed by LC analysis of fraction of remaining tetrazine was used to determine decomposition rate constants. The decompositions were not first-order very far into their decompositions, Hz_2Tz and $Hz_2Tz(ClO_4)_2$, were first-order to 40% conversion, $Hz_2Tz(NO_3)_2$ and Hz_2TzDN_2, only to about 10%. The rate constants were calculated from the linear portion of the curve, they are used for comparison purposes only. The extent of the decomposition curve used to calculate the rate constant is shown as percent fraction reacted "F.R.%" in Table 3. In line with the DSC results, Hz_2Tz, $Hz_2Tz(NO_3)_2$, and $Hz_2Tz[N(NO_2)_2]_2$ exhibit similar rate constants (0.002–0.003 s^{-1} at 140 °C), while the perchlorate salt decomposed significantly slower. The decomposition kinetics of Hz_2TzBim were not determined by LC, because it was insoluble in common LC solvents (acetone, acetonitrile, methanol, water), although it was soluble in DMF and DMSO. The decomposition kinetics of Hz_2TzBim were determined by the DSC ASTM method [17]. Using Arrhenius parameters, a rate constant of 3×10^{-6} s^{-1} could be calculated for Hz_2TzBim at 140 °C. The decomposition rate constant was also estimated using gas manometry to determine the total amount of gas produced with time relative to the total amount of gas produced upon 100% decomposition. That value was in good agreement (2×10^{-6} s^{-1}) with the one calculated from the DSC data.

To examine the possible involvement of hydrogen transfer during the decomposition process, some of the tetrazine salts were decomposed in solution. Solutions of $Hz_2Tz(NO_3)_2$ and Hz_2TzDN_2 (∼0.02 M) were prepared in methanol and in water. The decomposition of Hz_2TzDN_2 was first-order out to 60% conversion in methanol and water, while it appeared autocatalytic in the melt. This observation is not unusual. Autocatalytic behavior in the neat melt becomes first-order in the presence of a solvent which removes the catalytic decomposition product. Hz_2TzDN_2 was thermolyzed in both proteo and deutero water. An external solvent deuterium kinetic isotope effect (DKIE) of 1.8 was observed.

Table 3
DSC peaks and isothermal kinetics for tetrazine salts

	Sample											
	Hz_2Tz0		$Hz_2Tz(HNO_3)_2$ in CH_3OH		$Hz_2Tz(HDN)_2$				$Hz_2Tz(HClO_4)_2$		Hz_2TzBim	
					CH_3OH		H_2O	D_2O				
DSC exo max	164 °C	1409 J/g	161 °C	5012 J/g	152 °C	5773 J/g			191 °C	279 J/g	222 °C	3998 J/g
20°/min	299 °C	365 J/g							288 °C	1487 J/g		
Temperature (°C)									434, 457	1500	ASTM	Gas
170												
k (s^{-1})									2.80E−04		1.4E−04	4.0E−05
F.R. (%)									37			
160												
k (s^{-1})							9.60E−04					
F.R. (%)							43					
140												
k (s^{-1})	2.30E−03		2.80E−03	1.50E−04	1.80E−03	1.60E−03	1.40E−04		4.80E−05		4.8E−06	3.9E−06
F.R. (%)	63		90	95	88	34	37		59			
130												
k (s^{-1})					2.70E−04	6.00E−04	6.00E−05	3.3E−05				
F.R. (%)					90	41	45	41				
120												
k (s^{-1})	3.30E−04		3.80E−04	2.00E−05					1.00E−05			
F.R. (%)	65		92	95					75			
110												
k (s^{-1})					2.30E−05	5.20E−05						
F.R. (%)					94	45						
100												
k (s^{-1})	5.00E−05		6.20E−05		2.10E−06				2.70E−06			
F.R. (%)	64		90		96				78			
80			2.50E−06									
k (s^{-1})	4.10E−06											
F.R. (%)	81		91									
E_a (kJ/ml) isothermal	126		139		205	151	135		92.5			
E_a (kcal/mol)	30		34		49	36	33		22			
A (s^{-1})	2.20E+13		1.10E+15		1.20E+23	1.90E+16	2.00E+13		2.30E+07			
R^2	0.998		0.99		0.987	0.998	0.998		0.998			
E_a (kJ/ml) ASTM					155						172	
E_a (kcal/mol)					37.0						41	
A (s^{-1})					2.51E+17						2.33E+16	
R^2					0.995						0.996	

3.2. Products

Three of the tetrazine salts, [$Hz_2Tz(NO_3)_2$], [Hz_2TzDN_2], and [$Hz_2Tz(ClO_4)_2$], left no residue when heated in the sealed DSC tubes. The other two, containing significantly less oxygen in their structure, left a black residue. Isothermal heating of the salts, even when taken to complete decomposition, left a blackened residue in every case. Presumably, a residue remained because the high temperatures used in the DSC scans were never approached in any of the isothermal tests. No remainder of the original tetrazine ring was detected. However, each salt formed gaseous decomposition products, and these were identified by GC/MS and quantified by GC/TCD (Table 4). As in the case of the neutral tetrazines [15], the principle decomposition gas was N_2. However, the neutral tetrazines formed 0.5–1.5 mol gas per molecule, three of the salts formed 6–13 mol of gas. We attribute the extra gas to the anion itself, nitrate and dinitramidate [8] make nitrogen and nitrous oxide, while Bim makes CO. The anion does not oxidize more of the tetrazine residue, otherwise the perchlorate salt would have produced large quantities of gas, too (Table 4).

4. Discussion

Table 5 compares some of the observations we made during the thermolysis of the tetrazine salts to those we

Table 4
Moles of decomposition gas per mole tetrazine salt at complete decomposition

		Hz_2Tz		$Hz_2Tz{\cdot}2HNO_3$		$Hz_2Tz{\cdot}2HDN$		$Hz_2Tz{\cdot}2HClO_4$		$Hz_2Tz{\cdot}Bim$	
Sample amount (mg)		0.78	0.70	0.55	0.60	0.17	0.19	1.42	1.00	0.74	0.65
Heating temperature (°C)		240	240	240	240	145	145	150	150	240	240
Heating time (min)		60	45	1560	210	210	50	1440	1200	30	50
Moles gas/mole Tz Salt											
N_2		0.64	0.65	4.27	4.79	6.46	7.27	1.13	1.03	6.93	6.88
CO_2		0.14	0.17	0.98	0.85	1.30	1.40	0.47	0.67	0.50	0.64
N_2O				0.04		0.38	0.32				
CO				0.71	1.24	1.20	1.35			5.94	5.87
NO											
Total gas by GC		0.79	0.83	6.0	6.9	9.5	10.4	1.6	1.7	13.4	13.3
Total gas by manometer		0.73	0.76	5.7	7.0	8.2	8.2	1.6	1.5	13.9	12.7
GC/MS	Ret. time (min)		Area of chromatogram (%)								
N_2	3.4	240 °C	27.4	240 °C	16.3	145 °C	20.8	150 °C	15.7	240 °C	28.3
O_2	3.9	40 min	–	210 min	1.3	50 min	4.7	1440 min	2.9	30 min	–
CO	4.8		Trace		1.7		1.5				11.8
CO_2	14.1		72.6		63.1		66.9		81.3		51.3
N_2O	14.8		Some		15.6		3.9				1.8
H_2O	19.5		Some		1.9		2.2		Some		Some
HCN	21		–		–		–				6.9
CH_3CN	25.5		Some		Trace		–				Trace

made for the neutral tetrazines [15]. Four of the compounds [Hz_2Tz, $Hz_2Tz{\cdot}2HNO_3$, $Hz_2Tz{\cdot}2HDN$, and HzTzP (where P is 3,5-dimethylpyrazole)] exhibited DSC exotherms around 160 °C, and their rate constants at 140 °C were very similar ($(2.5–5.2) \times 10^{-3}\ s^{-1}$). For the neutral tetrazines, we found that one mode of thermal decomposition was the same observed under electron impact: elimination of two nitrogen atoms as N_2 and cleavage of the remaining N–N bond (Fig. 2). However, we observed that two of 3,6-substituted neutral tetrazines, both of which had hydrazido substitutents in the 3/6-positions were far less stable than the other tetrazines. This observation led us to conclude that the main decomposition pathway involved dissociation of the substituent group, in some cases assisted by proton transfer. In the study of neutral tetrazines, we found an external deuterium kinetic isotope effect (DKIE) in cases where one substituent was amino. We attributed this behavior to protonation enhancing the rate of amino loss as NH_3. Neither the diamino nor

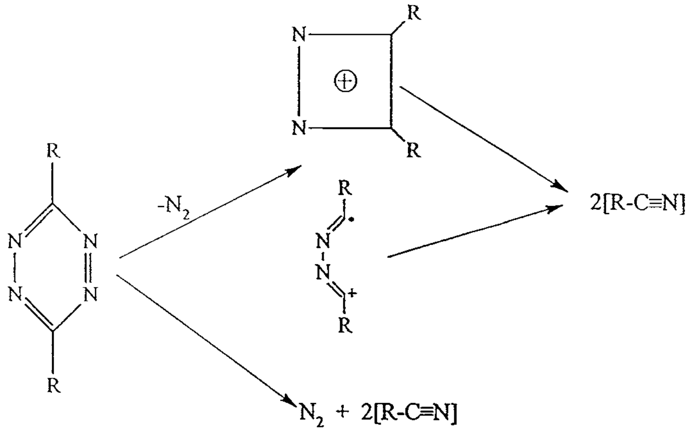


Fig. 2. Decomposition scheme of 1,2,4,5-tetrazines.

Table 5
Comparison of neutral tetrazines & salts

	Salts of NH_2NH-Tz-$NHNH_2$				Group 1		Group 2				Group 3	
	$2HNO_3$	$2HN(NO_2)_2$	$2HClO_4$	Bim	NH_2NH-Tz-X		$P2TzH_2$	P_2Tz	$PTzNH_2$	$ClTzNH_2$	Cl_2Tz	$(NH_2)_2Tz$
					X = $NHNH_2$	X = P						
DSC exo (°C)	161	152	191, 288 434, 457	222 Estimate	164	164 299	273	297	297	238 305	341	347
Rate 140 °C × 10^{-3}	2.8	1.8	4.8E−02	2.0E−06	2.5	5.2	1.2E−01			6.3E−02		
DKIE	Water 130 °C	1.8		Acetone 240 °C	1.4	1.2	1	2	1.5	–	–	
Total gas/Tz	6.4	8.2	1.6	13	0.8	1.2	0.6	0.7	0.7	0.9	1.5	1.2
N_2/Tz	4.5	6.9	1.08	6.9	0.7	0.6	0.3	0.6	0.6	0.3	0.4	0.6
CO_2/Tz	0.9	1.4	0.6	0.6	0							
N_2O/Tz	0.04	0.4	CO/Tz	5.9	0							
Other products observed in GC/MS												
CH_3CN	Trace	Trace			Some	Small	Small	Small	Small			
HCN	–	7%			–	Trace			Trace			Trace
NH_3/water	2%	Some			Trace							

Table 6
Comparison of thermal stabilities of DNAZ and dihydrazido tetrazine salts

Acid	pK_a	X^-	$DNAZ^+$		Hz_2Tz^+		
			k (s^{-1}) at 140 °C	DSC exo (°C)	k (s^{-1}) at 140 °C	DSC exo (°C)	
$HClO_4$	>-7	ClO_4^-	aq. (1%) dec.		4.80E−05	191, 288	ClO_4^-
HCl	−7	Cl^-	1.30E−03	191			
$HN(NO_2)_2$	−5.62	$N(NO_2)_2^-$	2.00E−03	151	1.80E−03	152	$N(NO_2)_2^-$
HNO_3	−1.34	NO_3^-	1.30E−03	152	2.80E−03	161	NO_3^-
NTO	3.67	NTO^-	5.80E−03	180	2.00E−06	222	Bim-

the dihydrazido were tested, but undoubtedly both would also have exhibited an external DKIE.

In this study of the salts of the dihydrazido-tetrazine, we found two ($Hz_2Tz \cdot 2HNO_3$, $Hz_2Tz \cdot 2HDN$) of the four salts had thermal stabilities similar to the parent tetrazine, but two were substantially more stable. If the decomposition pathway were totally dependent upon loss of the substituent in the 3/6-position, all should decompose at about the same rate. As with the neutral tetrazines, we observed an external DKIE when the bisdinitramidate salt was thermolyzed in D_2O and H_2O. This could be due to protonation of the hydrazido substituent as postulated for the neutral tetrazines, but it could also be due to protonation of the anion resulting in the reformation of the neutral dihydrazido-tetrazine. Since loss of a 3/6 substituent does not explain all the experimental results, the effect of the anion must be considered.

We have previously reported a thermal stability study conducted on a series of salts [NO_3^-, $N(NO_2)_2^-$, Cl^-, NTO^-] of the nitrogen-heterocycle 3,3-dinitroazetidine (DNAZ) [19]. In that study, we found their relative thermal stability in water roughly followed the acidity of the parent acid. The results suggested a mechanism that involved proton transfer from the dinitroazetidium cation to form DNAZ. DNAZ, regardless of the salt of origin, then decomposed at approximately the same rate. Table 6 shows some of the kinetics data from the DNAZ study along with similar data from the dihydrazido-tetrazine salts examined herein. The similarities are obvious. The salts of nitrate and dinitramidate, which have similar acidities, decomposed at about the same rate regardless of whether the cation was $DNAZ^+$ or Hz_2Tz^{2+}. In fact, one mode by which the dinitramidate anion decomposes formed nitrous oxide and nitrate [20]. Perhaps in studying $Hz_2Tz \cdot 2HDN$, we are really examining the decomposition of $Hz_2Tz(HNO_3)_2$. The overall mechanism we envision is shown below. Step 1 is an equilibrium for strong acids, such as $HClO_4$ and HCl, leans strongly to the left, little of the neutral organic species is available. Once formed the organic species $DNAZ^+$ or Hz_2Tz^+ rapidly decomposes. In the case of the tetrazine, loss of a 3 or 6 substituent may be the mode of decomposition (step 2). However, another possibility for 1,2,4,5-tetrazine decomposition is shown in Fig. 2. In this case, we think loss of the hydrazido ligand more likely though a few cyanide species were observed in the decomposition products.

$$[HL - Tz - LH]^{2+} + 2X^- \Leftrightarrow L - Tz - L + 2HX \tag{1}$$

$$L - Tz - L \xrightarrow{-L \text{ or } HL} N_2, + L - CN, \text{decomposition products} \tag{2}$$

5. Conclusion

The salts Hz_2TzX_2 undergo a reversible equilibrium with the parent Hz_2Tz and HX, thus, in several cases the decomposition rate of the parent and the salt are essentially identical. The parent tetrazine compound, once formed, can decompose by loss of N_2 or by the loss of the exocyclic substituent. The latter reaction is aided by proton transfer, an external DKIE was found.

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