Thermal Decomposition Studies on Ammonium Dinitramide (ADN) and ^{15}N and ^{2}H Isotopomers

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The thermal decomposition of ammonium dinitramide (ADN) and potassium dinitramide (KDN) were examined neat and in solution. Isothermal kinetics were measured (160−220 °C) by monitoring dinitramidate loss and were found to be first-order. Ammonium ion loss and gas formation were not good measurements of ADN decomposition since they reflect the fate of the ADN decomposition product ammonium nitrate. Kinetics of decomposition were nearly identical for ADN neat (proteo- and deutero-), ADN in water (1 or 20 wt %), ADN in various pH aqueous buffers, and for aqueous KDN (1 wt % in water or deuterium oxide). The activation energy, calculated for ADN, was about 40 kcal/mol (167 kJ/mol) for neat ADN and 37 kcal/mol (155 kJ/mol) for aqueous solutions of ADN. Decomposition of ADN in aqueous buffers suggested that under the conditions of these studies decomposition of dinitramidate or its parent acid proceeds at about the same rate at pH 3, pH 5, and unbuffered but decreased by about 40% at pH 9. Neat KDN was unique in that it decomposed about an order of magnitude slower than ADN, but its decomposition increased to be comparable to that of ADN when KDN was aqueous or when any ammonium salt was mixed with KDN. Nitrous oxide and nitrate (or nitric acid) were the principal decomposition products of dinitramide. Nitrogen gas was also formed, to a significant extent in the decomposition of ADN and to a small extent in that of KDN. Nitrogen gas resulted from the interaction of ammonium or ammonia with the nitrate or gaseous nitrogen oxides. Studies of ^{15}N-labeled ADN confirm that one $N-NO_2$ bond remains intact, forming nitrous oxide, while the other nitro group combines with the nitrogen from ammonium to form nitrogen gas. Several decomposition pathways consistent with these findings are considered.

Introduction

Certain inorganic species, such as the ammonium salts of strong acids—nitrate (NO_3^-, AN), perchlorate (ClO_4^-, AP), and dinitramide [$N(NO_2)_2^-$, ADN]—find use in both explosives and propellant fill. The ammonium salts of nitrite (NO_2^-) and chlorate (ClO_3^-) are similarly energetic but more unstable than nitrate or perchlorate, respectively, presumably due to the availability of an electron pair on the central atom. Only the latter finds limited use. Because AN[1] and AP[2] are produced in bulk and have been the subject of major accident investigations in this century (AN, Texas City, TX, April 1947; AP, Henderson, NV, May 1988), they have been studied in depth by us and others.[3,4] In contrast, the synthesis of ADN has been only recently reported,[5] and it is not yet widely available. With the view of preventing major incidents in the manufacture, formulation, and storage of ADN, we have embarked on a study of its thermal decomposition characteristics, comparing our results with the behavior of other energetic ammonium salts.

The initial step in the decomposition of AN and AP is dissociation into ammonia and the corresponding acid ($X^- = NO_3^-$ or ClO_4^-):[1]

$$NH_4^+X^- \rightarrow NH_3 + HX \qquad (1)$$

The next step depends on the temperature. Over the temperature ranges examined, both AN (200−380 °C) and AP (215−385 °C) appear to change decomposition pathways. AN exhibited a curved Arrhenius plot, which was interpreted as a discontinuity at 290 °C and ascribed to a change in decomposition mechanism, predominately ionic below 290 °C and free radical above that temperature. The two mechanisms we proposed for AN decomposition are shown below. The effect of the low-temperature mechanism is that acids accelerate the decomposition of AN, while bases (such as ammonia and the salts of weak acids NaF or $NaHCO_3$) retard it.

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

Low-Temperature (<290 °C) AN Decomposition:

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

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

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

High-Temperature AN Decomposition:

$$HNO_3 \rightarrow NO_2 + HO^\bullet \qquad (2b)$$

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

$$NO_2 + {}^\bullet NH_2 \rightarrow NH_2NO_2 \rightarrow N_2O + H_2O \qquad (4b)$$

Overall: $$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Nitrogen production was observed over the entire temperature range. However, it was over 4 times more prominent in the low-temperature regime (26% N_2 at 290 °C and 6% at 340 °C).

$$NO + {}^\bullet NH_2 \rightarrow NH_2NO \rightarrow N_2 + H_2O$$

Experimental Section

Ammonium and potassium dinitramide were provided by SRI[5] and Thiokol, and ammonium dinitramide-^{15}N [$NH_4{}^{15}N$-

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TABLE 1: Rate Constants of Decomposition (s^{-1})

	ADN neat					ADN aqueous [DN]		KDN 1% aq	KDN neat
Temp (C)	DN	NH4	gas	N2	N2O	20% H2O	1%H2O	DN	DN
120	8.19E-05	3.80E-05				1.17E-05	1.36E-05	1.36E-05	
140	2.70E-04	1.20E-04	6.50E-05	4.4E-05	9.0E-05	1.37E-04	1.37E-04	1.36E-04	b
160	6.88E-04	2.98E-04	3.84E-04	4.3E-04	4.6E-04	1.05E-03	1.02E-03	9.76E-04	b
180	4.74E-03	2.04E-03	1.88E-03	2.3E-03	3.6E-03	7.28E-03	6.69E-03	6.28E-03	2.66E-04
200	3.47E-02	1.22E-02	1.19E-02	9.1E-03	1.5E-02	4.14E-02	3.53E-02	3.32E-02	1.34E-03
220			7.25E-02	5.9E-02	8.4E-02				6.66E-03
240									3.45E-02
E kcal/mol	39.9 (a)	37.8 (a)	35.3			37.6	36.3	35.9	37.4
A s-1	8.8E+16	3.6E+15	2.5E+14			9.9E+15	2.1E+15	1.4E+15	2.6E+14
R^2	1.00	1.00	1.00			1.00	1.00	1.00	1.00

a Activation Energies (E) for neat ADN were calculated using temperatures 160 C and above
b Fraction remaining plotted as first-order was non-linear.

Aqueous ADN (1%) Decomposition Rate s-1 at 160C in Various pH Buffers				
pH	3	5 unbuff H2O	9	Ion Measured
	9.89E-04	8.99E-04 1.00E-03	6.19E-04	Dinitramidate [DN]
	2.32E-04	2.71E-04 6.9E-05	5.22E-05	Ammonium [NH4]
	0.23	0.30 0.07	0.08	rate NH4/rate DN

$(NO_2)_2$] was provided by the naval lab at China Lake. To prepare ammonium-^{15}N dinitramide [$^{15}NH_4N(NO_2)_2$], a solution of ammonium dinitramide (0.25 g, 2 mmol) in acetonitrile (4 mL) was introduced to a column of Amberlyst 15 (15 mL). (For the preparation of ammonium-^{15}N dinitramide ^{15}N [$^{15}NH_4{}^{15}N(NO_2)_2$] the same procedure was followed using ammonium dinitramide-^{15}N, as a starting material.) The dinitramidic acid, thus formed, was eluted with acetonitrile into 6.4 N ammonium-^{15}N hydroxide (0.32 mL, 2.05 mmol). The solvents were removed under reduced pressure at 40 °C. The oily residue was redissolved in acetonitrile (5 mL), and methylene chloride was added to precipitate ammonium-^{15}N dinitramide (0.21 g, 84%) or ammonium-^{15}N dinitramide-^{15}N (0.24 g, 96%). To prepare ammonium-d_4 dinitramide [$ND_4N(NO_2)_2$], a concentrated solution of ADN was prepared in deuterium oxide and allowed to stir 6 h in the dark before the water was removed by evaporation. The residue was redissolved in deuterium oxide and stirred another 1.5 h before the water was evaporated, and the sample was placed in a desiccator.

ADN and KDN were dried under vacuum for 24 h, then weighed (0.2−0.5 mg), sealed into glass tubes (2.4 mm x 6−7 cm long, 200 uL), and heated in a constant temperature bath. After the desired length of time, the glass tubes were removed from the bath, and the contents of the tube were examined by chromatography. The gaseous products [nitrogen (N_2), nitrous oxide (N_2O), and nitric oxide (NO)] were separated and quantitatively identified using a Varian 3600 gas chromatograph equipped with thermal conductivity detector (GC-TCD) and Hayesep DB 100/120 (30 ft x 1/8 in.) column (column temperature, 35 °C; helium flow, 20 mL/min). A HP 5890 gas chromatograph equipped with an electronic pressure control system, a poraPLOT Q (Chrompack) capillary collumn (25 m × 0.25 mm i.d.), and a HP 5971 electron impact quadrupole mass spectrometer was used for analysis of gases produced from the decomposition of labeled ADN. The glass tubes were broken directly into a plastic sample tube inserted into the carrier gas line just before the injector. For condensed-phase products, 20 or 50 uL samples containing 50−500 ppm ADN or KDN were injected at ambient temperature into a Hewlett Packard 1084B liquid chromatograph (LC) equipped with a Waters 486 tunable absorbance detector or a Waters 431 conductivity detector. The separation column for dinitramidate, nitrate, and nitrite anions was an AS11 4 mm anion column (Dionex) and for ammonium cation a 3.9 × 150 mm IC-Pak Cation M/D column (Waters). For the anions, a mobile phase of 2 mM NaOH (pump A, 60%) and acetonitrile (pump B, 40%) with a total flow rate of 1.0 mL/min was used with UV detection (214 nm).[6] For ammonium ions, a mobile phase of 0.1 mM EDTA/3 mM HNO_3 (flow, 1.0 mL/min) and a conductivity detector were used. Differential scanning calorimetry (DSC) experiments were run on a Perkin Elmer DSC 4 or a TA 2910 using a 20 °C/min heating rate for standard runs and calibrating to indium. The variable heating rate DSC method (ASTM)[7] (20, 15, 10, 7, 5, 3 °C/min) for determining Arrhenius parameters was performed on ADN and KDN. All DSC samples were contained in sealed glass sample tubes.

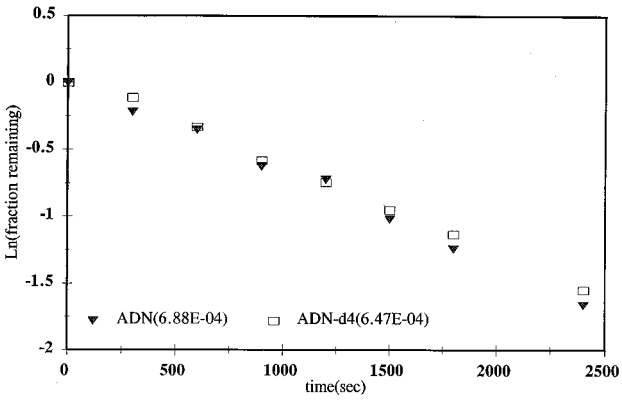

Figure 1. First-order plots of neat ADN and ADN-d_4 thermolysis at 160 °C and analyzed by dinitramidate loss.

Results

The isothermal decomposition of ADN was followed by monitoring the disappearance of ammonium and dinitramidate ions or the formation of decomposition gases. Rate constants were determined in all cases using first-order plots consisting of 6−16 data points. Regardless of the observation method, the decomposition of ADN, both neat and in solution, was first-order out to 55−90% decomposition (Figure 1), and with the exception of the gas formations rates, the R^2 values were usually 0.99, occasionally as low as 0.95. Rate constants and Arrhenius parameters based on these methods are given in Table 1 along with similar values for KDN (Figure 2). Activation energies with frequency factors measured over the temperature range 160−200 °C agree with recent presentations by Russian scientists [148 kJ/mol (35.5 kcal/mol) with 2.5×10^{14} s^{-1}; and 151 kJ/mol (36.2 kcal/mol) with 5.0×10^{13} s^{-1}][8] and with DSC analyses using the ASTM variable heating rate method (Table 2).[7] Below 160 °C the Arrhenius plot of neat ADN bends,

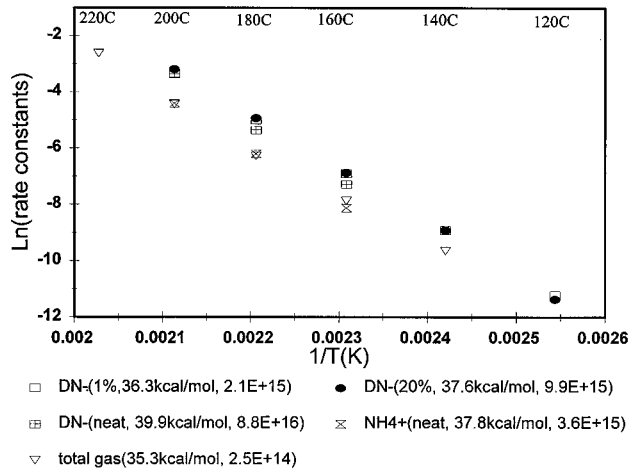

Figure 2. Arrhenius plots of ADN thermolysis neat and in water, with various monitoring methods.

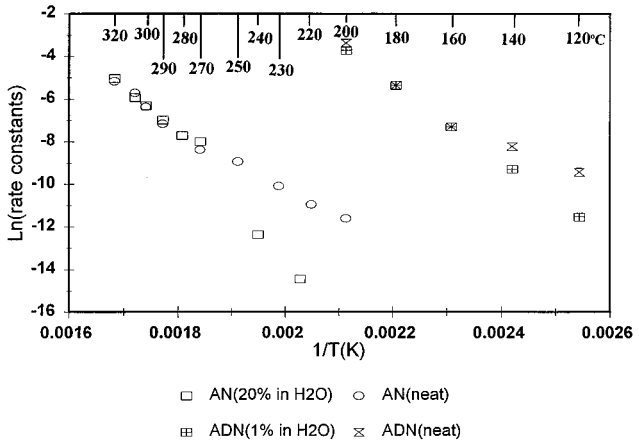

Figure 3. Arrhenius plots of AN and ADN decompositions, neat and in water.

TABLE 2: DSC Maximum Temperature (°C) Scanned at 20 °C/min from 50 to 450 °C

	ADN	KDN	AN	AP
neat	189s,274w	239	318	357s,369w
+ NH3	188	222	387	446
+ 5% NaF	198	239	392	428
+ 5% NaHCO3	177w,199s	238	375	
+ 5% diphenylamine		238		
+ 5% NaHSO4	184			
+ 5% (NH4)2SO4		210		
+ 5% HNO3	188s,252w	189,243		331s, 360w
+ NO2	77w, 242	100,132, 324 all endotherms		
+ 5% water	190	240		
+ 5% KDN	179	---	222w, 292s	
+ 10% ADN	---	201	220w,298s	
+ 30% AN	191	190		
+ 5% min. oil	184s,235w	243,248	297w,384s	
DSC m.p.	94	130	169	not obs.
endotherm	301	325		
				w=weak, s= strong
ASTM Arrhenius Parameters of Neat Salts				
E kcal/mol	27	39	29	23
A s-1	1.8E+11	1.1E+15	6.5E+08	8.3E+05

suggesting a change in decomposition mechanism and a lower activation energy (75.1 kJ/mol, 18.0 kcal/mol with 7.7×10^5 s^{-1}, Figure 3). The Arrhenius plot for aqueous ADN does not show such a shift, at least not down to 120 °C. This difference in behavior between neat and aqueous ADN matches one we have previously reported for AN.[1]

Above 160 °C the decomposition rate of ADN was similar neat and in solution. The decomposition kinetics of ADN in water were followed at two concentrations (20 and 1 wt %); the rate of ADN decomposition was not concentration dependent (Table 1). Rate as monitored by dintramidate anion disappearance was larger than as monitored by ammonium cation loss; this difference was especially dramatic in aqueous solution. In 1% aqueous solutions of ADN and KDN (shown in Table 1) and even 3,3-dinitroazetidium dinitramide (DNAZ DN)[17] dinitramidate was lost at about the same rate: 1.02×10^{-3}/s, 0.976 $\times 10^{-3}$/s, and 0.898×10^{-3}/s at 160 °C, respectively. For KDN, this rate was unchanged even when it was thermolyzed in deuterium oxide. However, neat KDN decomposed an order of magnitude slower than neat ADN. This enhanced stability of KDN is confirmed by the position of the DSC exotherm of KDN (239 °C) relative to ADN (189 °C) (Table 2).

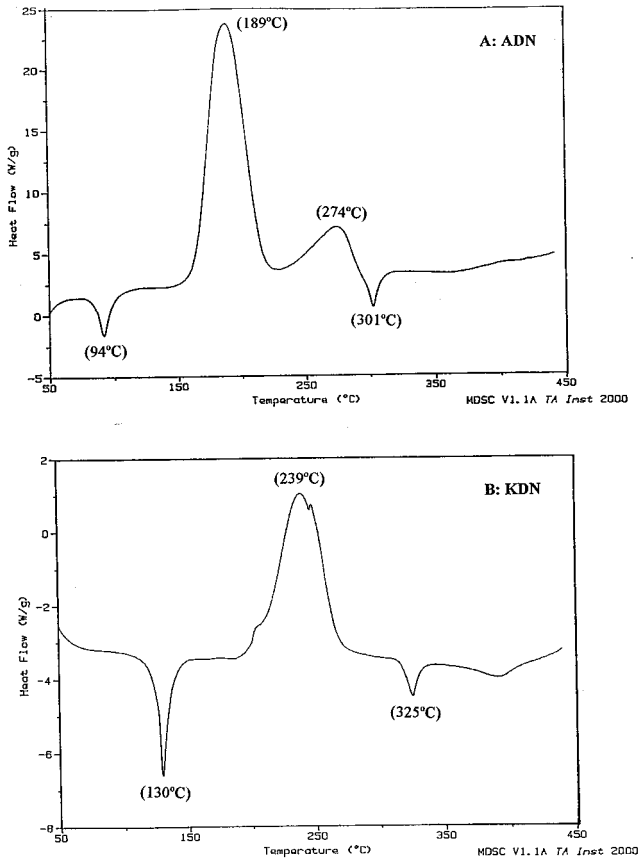

Figure 4. DSC traces at 20 °C/min: (a) ADN (endotherm 92 °C, exotherm 189 °C, exotherm 274 °C, endotherm 302 °C) and (b) KDN (endotherm 130 °C, exotherm 239 °C, endotherm 325 °C).

The DSC trace of neat KDN (Figure 4) exhibited two endotherms, the first (130 °C) corresponding to the KDN melt and the second (325 °C) to the melting of KNO_3. The exotherm of KDN (239 °C) is not a single sharp peak (530 J/g); slower scan rates reveal a small initial exotherm just prior to the main peak; and the main peak appears to have two maxima. As shown in Figure 4, some scans of neat ADN revealed a second exotherm (274 °C, 190 J/g) following the major exotherm at 189 °C (1700 J/g). The DSC trace of ADN also indicated two endotherms. The first endotherm (94 °C) is melting of ADN. The second endotherm (301 °C) followed the exotherm at 274 °C. The latter exotherm is attributed to the decomposition of ammonium nitrate formed during ADN decomposition. The endotherm that follows the exotherm at 274 °C resulted from the formation and vaporization of water during ammonium nitrate decomposition. This phenomenon was reported previously for ammonium nitrate decomposition in sealed glass tubes.[1]

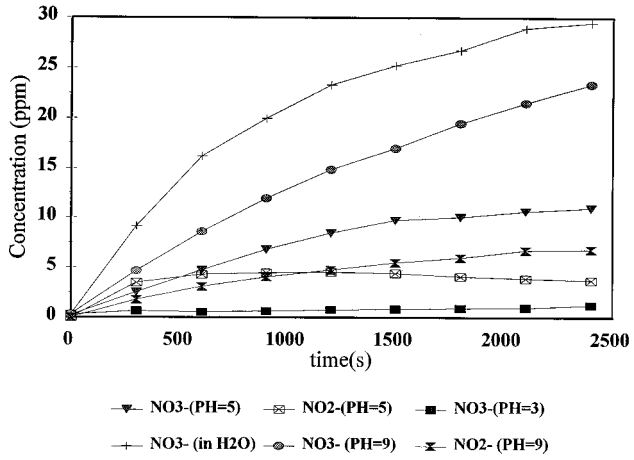

Figure 5. Concentration of NO_3^- and NO_2^- formed in ADN aqueous thermolysis at 160 °C in pH buffer solutions.

The effects of selected additives on DSC thermograms (temperature range 50−450 °C) of ADN, AN, and AP are summarized in Table 2. ADN was not stabilized by basic species (NH_3, NaF, $NaHCO_3$) nor significantly destabilized by acid (HNO_3), as was observed in analogous DSC experiments with AN and AP. In contrast, though KDN was not stabilized by basic species, it was destabilized by acid or any ammonium salt [ADN, AN, $(NH_4)_2SO_4$, Table 2].

Both ADN and KDN were examined under a NO_2 atmosphere. KDN exhibited an initial endotherm consistent with its melt (133 °C) and another high-temperature endotherm (326 °C) attributed to the melt of KNO_3, but no exotherm was observed. ADN under NO_2 produced a small exotherm at 77 °C and a large one at 242 °C immediately followed by a small endotherm, suggesting AN decomposition.

The effect of pH on ADN kinetics was examined for 1% aqueous solutions using Aldrich Hydrion buffers (pH 3, 5, 9) and compared with the unbuffered 1% aqueous solution of ADN in Table 1. Although we do not know the precise pH at elevated temperature, calculations indicate a shift of less than a pH unit. Replicates of the unbuffered solution varied with a standard deviation of about 2%. Using two standard deviations (i.e. about ±4%) as an estimate of the uncertainty in these measurements suggests that variations in the rate constants for DN^- decomposition are probably not significant when comparing the pH 3 and pH 5 solutions with the unbuffered solution. On the other hand, it is noteworthy that for the pH 9 solution the rate constant is reduced by about 40% when compared with the unbuffered solution. The effects of pH on the rate of ammonium ion loss and product ratios were more dramatic. In neat ADN, the rate of loss of the ammonium cation was about half that of the dinitramidate anion. In acidic solution, the ammonium cation disappeared at less than one-third the rate of the dinitramidate anion; and in neutral or basic solution, the rate of cation disappearance was less than one-tenth the rate of dinitramide anion loss. Under all experimental conditions, nitrate was the major condensed-phase product. The amount of nitrate was a function of both time and pH. As ADN decomposition progressed, nitrate concentration increased; nitrate production increased with increasing pH (Figure 5). In neutral aqueous solution at 90% ADN decomposition, 0.77 mole nitrate per mole of ADN and roughly the same amount of ammonium ion remained. (This also illustrates the extremely slow disappearance of ammonium ion.) In contrast, at the 90% decomposition point of neat ADN, only 0.57 mole nitrate per mole ADN was observed. In buffered aqueous solutions, at pH 5 and 9, some nitrite was observed at concentrations less than a third that of nitrate. It formed early, and as the reaction progressed, its concentration plateaued and began to decrease. In buffered solution, pH 3, and in the unbuffered neutral water, no nitrite was observed.

The decomposition of neat ADN formed N_2 and N_2O in roughly equal ratios (0.85 mol each gas/1 mol ADN at 230 °C). The exact ratio shifts during the course of the reaction and with temperature, but generally falls in the range of N_2/N_2O about 0.6−0.8, with the total amount of gas being about 1.6−1.7 moles per mole ADN. In aqueous solution ADN forms primarily nitrous oxide (200 °C, N_2, 0.15 mol/mol; N_2O, 0.69 mol/mol) as does neat or aqueous KDN (200 °C, N_2, 0.1 mol/mol; N_2O, 0.66 mol/mol). A trace amount of NO was occasionally observed, but amounts were not sufficient to quantify. Quenching a neat ADN sample thermolyzed at 200 °C to 78% decomposition, we found roughly the following stoichiometry:

$$NH_4^+N(NO_2)_2^- \rightarrow 0.44N_2 + 0.65N_2O + 0.68NH_4^+ + 0.22\ N(NO_2)_2^- + 0.46NO_3^-$$

Mass spectral analysis of the decomposition gases of the ^{15}N-labeled ADN showed around 90% of the observed N_2 came from the interaction of the ammonium nitrogen with the nitrogen of one of the nitro groups. At the same time, about 90% of the N_2O was made up of one nitrogen originating from a nitro group and one from the amine nitrogen. Thermolyses were conducted at 200 °C and 140 °C. At the lower temperature the 90% figures were closer to 80% (N_2) or 85% (N_2O). NO was observed in some experiments and found to be at least 92% from the nitro groups on the amine nitrogen (Table 3).

Discussion

Ammonium nitrate, nitrous oxide, and nitrogen gas are the principal equilibrium decomposition products of ADN. The first two arise from the ADN, and the last, from the decomposition of ammonium nitrate:

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

$$NH_4^+NO_3^- \rightarrow N_2 + 2H_2O$$

Our labeling studies clearly show that N_2O is derived almost exclusively (98% from experiment B at 200 °C, Table 3) from dinitramide. Nitrogen gas is formed by a combination of the ammonium nitrogen and one of the nitrogens of the dinitramidate nitro groups. This is shown both by the observation that KDN formed little N_2 and by the study of ^{15}N-labeled ADN. The nitrogen gas labeling studies are not as conclusive as the N_2O data because we did not prepare $*NH_4N(*NO_2)_2$, which could give rise to nitrogen exclusively from $*NH_4$ and $*NO_2$. However, if one considers the possible reactions shown in Table 3, one sees from the *NN results in experiment C that the sum of the two reactions (amine N)$*N + NO_2$ and $*N + NH_4$ cannot be more than about 9% at 200 °C. Since *NN in experiment A is 93% (200 °C) of the nitrogen and could result from only two reactions, $*NH_4 + NO_2$ or $*N + NO_2$, while *NN in experiment B is 92% (200 °C) of the nitrogen and could result from only two reactions, $*NH_4 + NO_2$ or $N + *NH_4$, then simple analysis suggests $NH_4 + NO_2$ produces at least 88% of the nitrogen gas observed. Formation of nitrogen gas does not require the formation of ammonium nitrate, but it is a reasonable speculation.

In our studies ammonium nitrate was not directly detected in the decomposition of ADN. However, AN has been reported

TABLE 3: Distribution of Label in ADN Decomposition Gases (50% dec)

	A: *NH4*N(NO2)2		B: *NH4N(NO2)2)			C: NH4*N(NO2)2		
	200C	140C	200C		140C	200C		140C
Nitrogen								
NN	1.1	0.6	7.9		16.4	90.6		80.3
Possible Rx	NO2+NO2		N+NO2	NO2+NO2	N+N	NH4+NO2	NO2+NO2	NH4+NH4
N*N	92.4	92.9	91.7		83.2	8.7		15.2
Possible Rx	*NH4+NO2	*N+NO2	*NH4+NO2	*NH4+N		*N+NO2	*N+NH4	
***N*N**	6.5	6.5	0.4		0.4	0.7		4.5
Possible Rx	*N+*N	N+NH4 NH4+NH4	*NH4+*NH4			*N+*N		
Nitrous Oxide								
NNO	0.9	1	98.3		84.7	2.3		20.4
Possible Rx	NO2+NO2		N+NO2	NO2+NO2	N+N	NH4+NO2	NO2+NO2	NH4+NH4
N*NO	96.4	96.3	1.3		15.1	95.2		77.6
Possible Rx	*N+NO2	*NH4+NO2	*NH4+NO2	*NH4+N		*N+NO2	*N+NH4	
***N*NO**	2.7	2.6	0.2		0.2	2.5		2
Possible Rx	*N+*N *N+*NH4	*NH4 +*NH4	*NH4+*NH4			*N+*N		

NO from Labeled ADN at 200C (50% decomposed)

	*NH4*N(NO2)2	*NH4N(NO)2)	NH4*N(NO2)2
NO	93.3	98.5	93.2
N*O	6.7	1.5	6.8

*NH4*N(NO2)2 at 200C

	12 s (20% dec.)	40 s (50% dec)	400 s (10 1/2 lives)
NO	95.7	93.3	91.7
*NO	4.3	6.7	8.3

to sublime from thermolyzed ADN starting at temperatures as low as 80 °C (N_2O appearing as early as 60 °C), is joined by the sublimation of ADN at 95 °C, and is still evolving at 188 °C along with N_2O, NH_3, and NO_2.[10] Our analyses of neat or aqueous decompositions of ADN or KDN yielded the expected stoichiometric balance of ammonium or potassium cations to the sum of nitrate and dinitramidate anions. The fact that more nitrate is observed in aqueous or basic decompositions of ADN than in the neat or acidic decomposition of ADN can be related to the behavior of AN. Both water and base stabilized AN to thermal decomposition; thus, the nitrate disappears more slowly under these conditions. Further evidence of nitrate formation comes from the DSC data. The DSC scan of KDN showed an endotherm (325 °C) after the decomposition exotherm, which was consistent with the melt of KNO_3 (333 °C), while the DSC scan of ADN showed a second small exotherm (274 °C). One might argue that this exotherm is too low for AN (normally 318 °C) and that at the temperatures of the isothermal ADN studies AN should be relatively stable. However, DSC observations indicate that ADN destabilizes AN when the two are mixed (Table 2). This destabilization probably arises from two sources. Acids catalyze AN decomposition; since dinitramidic acid ($pK_a = -5.62$)[8] is a much stronger acid than nitric acid ($pK_a = -1.34$), AN in admixture with ADN is in a more acidic environment than pure AN. AN in admixture with ADN has a lower melting point than pure AN, and in its molten state AN undergoes more rapid decomposition than as a solid.

We have previously observed in AN decomposition over the temperature range 200−300 °C, the lower the temperature, the greater the ratio of N_2/N_2O produced.[1] This suggests that at the low temperatures of this study (140−200 °C) AN decomposition might produce almost exclusively N_2. Since we ascribe AN responsible for forming N_2, making up just under half the total decomposition gases, the slower rate of AN decomposition explains the reason that rate, as measured by total gas evolution or by ammonium loss, is slower than that measured by dinitramidate loss (Table 1). Rate constants in Table 1 clearly show N_2O forms at a faster rate [tracking the rate of dinitramidate (ADN) disappearance] than N_2 forms [tracking the rate of ammonium (AN) disappearance]. Rates derived from total gas evolved are a combination of the ADN and AN decomposition reactions. We are not speculating as to the manner in which AN forms nitrogen gas nor claiming AN *per se* must form. What we have observed is that the elements of AN, ammonium and nitrate, are present in 1:1 ratio in the thermolysis mixture and that the labeling studies show most of the nitrogen gas contains one nitrogen from ammonium and one nitrogen from the nitro group of dinitramide (whether that nitro group has become nitrate, nitrogen dioxide, or nitric oxide). Some researchers have not observed nitrogen gas among ADN decomposition products,[11] while others have.[13] This could be a matter of experimental conditions.

Our experimental conditions usually do not permit the observation of nitrogen dioxide, and we do not observe it in the thermolysis of ADN. A number of other researchers have reported the observation of nitrogen dioxide.[9−11,14] However, under our experimental conditions, sealed glass capillary, ADN decomposition is first-order out to high degrees of conversion. The conclusion must be either that nitrogen dioxide does not catalyze ADN decomposition or that it is not formed in large amounts. Since our DSC experiments suggest NO_2 does catalyze ADN decomposition, we must conclude that ADN does not produce large amounts of this gas.

The absence of a primary deuterium kinetic isotope effect (DKIE) when KDN was thermolyzed in water versus deuterium oxide (ratio of the rates 1.07) or when the neat decomposition rates of ammonium-d_4 dinitramide and ADN were compared (factor of 1.06) does not rule out step 1 or 2a, but suggests they are not rate controlling. However, the fact that ADN decomposition is not retarded by the presence of water nor bases [isothermal (Table 1) and DSC (Table 2) evidence] nor accelerated by acid (DSC, Table 2) does exclude step 2a. The low-temperature decomposition of AN is highly susceptible to acids and bases as a result of step 2a. We observed that in various pH aqueous buffers the rate of dinitramidate loss is little changed, while as the pH increased, the rate of ammonium loss slowed. These observations clearly show that the loss of dinitramidate and ammonium proceed independently. They also

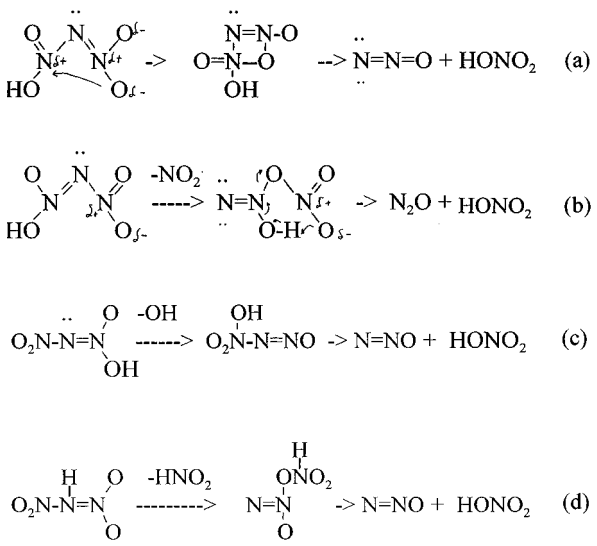

Figure 6. Possible decomposition pathways for ADN decomposition. Mechanisms a and b have been proposed and discussed by a number of researchers.

show that at the temperature regime of this study the decomposition of dinitramidate proceeds at the same rate whether it is the charged dinitramidate anion (unbuffered or basic solutions) or the neutral dinitramidic acid (acidic solution). Comparison of the AN and the ADN Arrhenius plots neat and in aqueous solution (Figure 3) indicates that like AN, ADN experiences a shift in its dominant decomposition mechanism. While AN decomposition changes from a predominately ionic mechanism to a predominately free radical mechanism as the temperature is raised above 270 °C,[1] ADN undergoes such a change at a much lower temperature (160 °C). We found in the high-temperature regime that acids, bases, and water had little effect on AN, while in the low-temperature regime they affected the decomposition rate. This ADN study is apparently in the high-temperature regime. Researchers studying ADN decomposition at 75 °C have reported that bases do stabilize it.[10]

The manner by which dinitramidic acid or dinitramidate ion may convert to nitrous oxide and nitric acid has been discussed by others.[10−13,15,16] Oxygen transfer from one nitro group to another would produce nitrous oxide and nitric acid or nitrate; such a route requires a four-membered cyclic transition state (Figure 6a) and has been observed in the gas phase.[12] Politzer et al., using density functional procedures, have calculated an activation barrier for this mechanism of about 56 kcal/mol.[18] Our experimental activation energies for ADN (Table 1) are 37−40 kcal/mol, considerably less than Politzer's calculated value. The same products would result from $N-NO_2$ scission with subsequent attack by the free NO_2 on one oxygen of the remaining $N-NO_2$ (Figure 6b).[10] Politzer has calculated the energy difference between homolytic and heterolytic loss of NO_2 radical or ion and has shown that NO_2 radical is favored energetically by 40 kcal/mol.[15]

Each of the reaction mechanisms in Figure 6 begins with the assumption that, like AN and AP, the first step in ADN decomposition is hydrogen transfer to form ammonia and dinitramidic acid. Brill has observed the evolution of ammonia during T-jump IR experiments where the temperature was at least 260 °C;[9] McMillen has observed free dinitramidic acid at 90 °C; [13] and Russell has reported AN sublimation at 80 °C and ADN sublimation at 95 °C.[10] Lin[16] performed *ab initio* calculations that showed that in the gas phase ADN is 12.1 kcal/mol more stable as $NH_3[HN(NO_2)_2]$ rather than $NH_4^+[N(NO_2)_2]^-$. Undoubtedly the gas-phase reaction proceeds via the following:

SCHEME 1

$$NH_4^+N(NO_2)_2^- \leftrightarrow NH_3 + HN(NO_2)_2$$

$$HN(NO_2)_2 \rightarrow N_2O + HNO_3$$

$$NH_3 + HNO_3 \rightarrow \text{AN and further decomposition products}$$

The question is whether the condensed-phase reaction must begin with the formation of dinitramidic acid or can proceed directly from dinitramidate:

SCHEME 2

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

Wight[11] did not observe ammonia evolved from a thermogravimetric scan until the temperature reached nearly the melting point of AN. This observation and the similarity in rate of ADN decomposition in acidic and basic aqueous media indicate that decomposition may proceed through dinitramidate and dinitramidic acid. However, we observe that neat KDN decomposed an order of magnitude more slowly than neat ADN. When dissolved in water, KDN decomposed at the same rate as ADN. Furthermore, DSC scans showed that neat KDN was more stable than ADN, but when nitric acid, AN, ADN, or $(NH_4)_2SO_4$ was added to KDN, the exotherm was lowered to a temperature similar to the exotherm of ADN. These observations indicate that protons assists the decomposition of dinitramide. Possibly such assistance does not require release of ammonia and the free acid (Scheme 1). Lin has done *ab initio* calculations addressing the location of the proton on dinitramide.[16] He found that $HN(NO_2)_2$ was 4 kcal/mol more stable than $HON(O)NNO_2$ but that $NH_3[HN(NO_2)_2]$ was only 2.3 kcal/mol more stable than $NH_3[HON(O)NNO_2]$. Clearly crystal effects are important. Figure 6 shows two previously proposed ADN decomposition mechanisms. Lin[16] has examined the energetics of 6a and 6b. He concluded they are competitive, but as the temperature increases, 6b, NO_2 loss, would be favored. Either mechanism is in line with our observations. The bond energy 38−40 kcal/mol is similar to the activation energy (37−40 kcal/mol) we report herein. There are two other possible pathways that match experimental observations; these are shown in Figure 6c,d and await theoretical calculations.

Conclusions

ADN decomposition kinetics (120−200 °C) were first-order to over 50% decomposition. In the temperature range 160−200 °C, neither acids nor bases significantly altered the rate of ADN decomposition, nor did ADN exhibit an intra- or inter-deuterium kinetic isotope effect. We conclude that above 160 °C the dominant decomposition mode is free radical; below that temperature an ionic decomposition mode affected by acidity may become important. Decomposition of dinitramide results in nitrous oxide and nitric acid (or nitrate). Any of the mechanisms shown in Figure 6 would be consistent with our experimental observations. That nitrous oxide derives both of its nitrogen atoms from dinitramide (one from the central nitrogen and one from a nitro group) has been demonstrated using ^{15}N-labeled ADN in thermolysis studies. Nitrate was detected in the aqueous and neat decomposition of ADN, and the DSC scan of KDN exhibited an endotherm after the decomposition exotherm, which was consistent with the melting of KNO_3. In the thermolysis of ADN, the resulting nitrate salt is AN, a species that can decompose on its own to form N_2 and water. While neat KDN is more thermally stable than ADN,

its decomposition behavior in solution or neat in the presence of ammonium salts is identical to that of ADN (neat or in water). The enhanced stability of neat KDN relative to ADN is ascribed to its lack of a protonic species.

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