1,1,3,3-Tetraoxo-1,2,3-triazapropene Anion, a New Oxy Anion of Nitrogen: The Dinitramide Anion and Its Salts

Jeffrey C. Bottaro,* Paul E. Penwell, and Robert J. Schmitt*

Contribution from the Functionally Designed Materials Program, Chemistry and Chemical Engineering Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025

Received March 24, 1997[⊗]

Abstract: We report the synthesis of a completely new, stable class of inorganic salts named the dinitramide salts. These salts are based on a newly discovered nitrogen oxide anion known as the dinitramide anion. The dinitramide anion is a uniquely stable, high oxygen density grouping that can be prepared in many salt combinations including the ammonium or hydrazinium salts. The dinitramide anion has both fundamental scientific interest and practical applications. We describe here the synthesis of dinitramide salts and give a preliminary report on their properties.

Introduction and Background

The field of nitrogen oxide chemistry is considered a mature, well-developed area where breakthroughs are not expected to occur.[1,2] We report here the synthesis of a completely new, stable oxy acid of nitrogen that has both fundamental scientific interest and practical applications.[3−14] These salts are based on a newly discovered inorganic anion, as shown in Figure 1, which we named the dinitramide anion.

Dinitramide salts, a uniquely stable oxy anion of nitrogen, were first discovered in our laboratory in 1988,[6,11] with the subsequent allowance of a composition of matter patent in 1993.[6] This article is the first open literature report of the work done in our laboratory. Since our initial report of the synthesis of dinitraminic acid and dinitramide salts, both theoretical and experimental studies of the stability of dinitramide salts have been undertaken.[15−22]
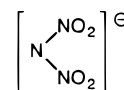

Figure 1. The dinitramide anion.

Following the publication of our patents, Russian workers at the Zelinsky Institute in Moscow on the whole and at the LNPO Soyuz facility and at the Zelinsky Institute in Moscow presented accounts of their independent research on the synthesis and use of dinitraminic acid and dinitramide salts.[3,7,9,13,23−28]

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Table 1. Nomenclature of the Dinitramides and Dinitramines

compound name	structure
methyldinitramine	$CH_3N(NO_2)_2$
nitramide	NH_2NO_2
dinitraminic acid	$HN(NO_2)_2$
ammonium dinitramide	$NH_4N(NO_2)_2$

The choice of names for dinitramide salts is based on an extension of the well-established nomenclature for nitramide. The free acid, $HN(NO_2)_2$, should be named dinitraminic acid. Table 1 shows the proposed nomenclature for the various alkyldinitramines and other oxides of nitrogen in the dinitramide family.

The dinitramide salts are high oxygen density groupings prepared with many different counterions including the proton, cesium, ammonium, or hydrazinium salts. The ammonium salt of the dinitramide anion is more thermally labile and impact sensitive than ammonium nitrate, but considerably more stable than the related, covalently bound, *N,N*-dinitro derivatives such as alkyldinitramines ($R-N(NO_2)_2$) or nitramide.

The fundamental impact of our work at SRI and the Russian work is to extend the range of stable oxides of nitrogen that can be formed. A potential practical use for this compound is as a replacement for oxidizers (such as ammonium perchlorate) to give an environmentally benign solid rocket propellant system, eliminating the emission of chloride from rocket motors.[39] A second potential use for dinitraminic acid and dinitramide salts is as a cationic phase-transfer agent due to the dinitramide anion's inherent ability to increase the solubility of cationic agents in organic solvents.

The synthesis of dinitraminic acid and dinitramide salts are described in this paper and a summary of the properties of dinitraminic acid and dinitramide salts is presented. The following paper by Gilardi et al. presents the crystallography of dinitramide salts.[40]

Results and Discussion

Conceptual Basis for the Dinitramide Anion. The concept for dinitraminic acid and dinitramide salts synthesis came from comparing the stability of the covalently bound oxides of nitrogen and chlorine with the stability of their ionic salts. As expected, the ionic derivatives of nitrogen oxides are appreciably more stable (thermal, acid, base) than the corresponding covalent

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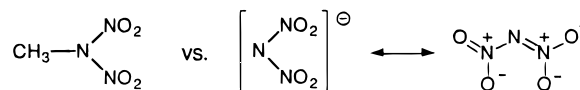
Figure 2. Bonding in an alkyldinitramine vs dinitramide.

compounds. The relative stability of alkyl nitrates $(R-ONO_2)$[45] vs nitrate salts, alkylnitrites $(R-ONO)$[46] vs nitrite salts, serves as an example. The enhanced stability of ionic salts led us to consider whether it was possible to obtain a similarly stable derivative from the ionic counterpart of an alkyldinitramine.

The covalently bound alkyldinitramines have been well studied.[32,41,42] All covalently bound alkyldinitramines suffer instability problems that presumably originate from a combination of the steric hindrance between the two nitro groups and the high electonegativity of the *N,N*-dinitro group. A *N,N*-dinitro group leaves the alkyldinitramine electron deficient, especially at the central nitrogen. These effects destabilize alkyldinitramines and the instability can be observed in their thermal properties; all known alkyldinitramines thermally decompose at temperatures less than 70 °C and are highly shock and impact sensitive.

The effects on the stability of nitrogen oxides discussed above can be observed in the relative stability of the ionic and covalent nitrogen oxides. The observed relative stability of nitrogen oxides (as Na^+ salts as measured by thermal analysis) is

$$NO_3^- > NO_2^- > N(NO_2)_2^- \gg alkyl-N(NO_2)_2$$

The relative stability of nitrogen oxides (as NH_4^+ salts as measured by thermal analysis) is

$$NO_3^- > N(NO_2)_2^- > NO_2^- \gg alkyl-N(NO_2)_2$$
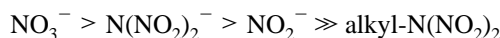
The corresponding dinitramide salts have less steric hindrance between the nitro groups (at least partial sp^2 hybridization at the central nitrogen) and a higher N−N bond order due to the overall negative charge (Figure 2).

Synthesis of the Dinitramide Anion. Dinitramide salts were first synthesized in our laboratory by a β-elimination reaction of 1-(*N,N*-dinitramino)-2-trimethylsilylethane catalyzed by cesium fluoride.[6,11] Fluoride ion catalyzes an elimination yielding trimethylsilyl fluoride, ethylene, and the desired cesium dinitramide as the products (eq 1).

(1)
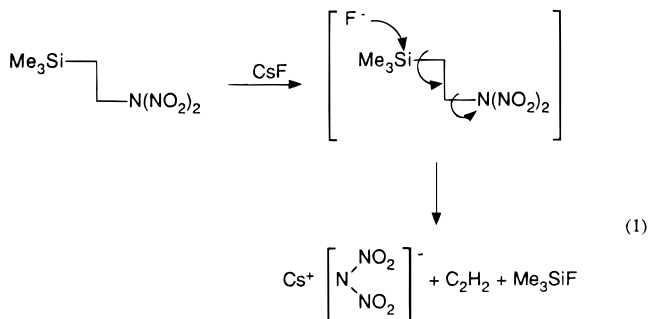
1-(*N,N*-Dinitramino)-2−(trimethylsilyl)ethane is synthesized by a recently discovered reaction between an isocyanate and a mixture of nitric acid and nitronium tetrafluoroborate (eq 3).[41] This route is not an efficient synthesis of dinitramide salts for bulk use, but it did provide us with an initial synthesis of cesium dinitramide. The crystal structure of cesium dinitramide

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prepared this way was determined by X-ray crystallography by Gilardi and co-workers.

Preparation of other salts of dinitramide can be easily done by ion exchange of the cesium ion with other cations such as ammonium (eq 2) or by the use of alternative metal fluoride salts (M^+F^-) in the elimination reaction. Many other dinitramide salts have been prepared by ion exchange including the protio (dinitraminic acid), ammonium, hydrazinium, sodium, and potassium dinitramide:

$$CsN(NO_2)_2 \xrightarrow[\text{Ion Exchange}]{M^+} M^{+n}(N(NO_2)_2^-)_n \qquad (2)$$
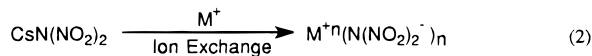
where M^+ = H^+, Li^+, Na^+, K^+, Cs^+, Ba^+, Ca^{+2}, $NH_2N=C-(NH_2)_2^+$, $C_2N_5H_9^{2+}$, $(NH_2)_3C^{+,}$ cubane$-1,4-(NH_3^+)_2$, cubane$-1,2,4,7-(NH_3^+)_4$, Me_4N^+, NH_3OH^+, $^+H_3NCH_2CH_2NH_3^+$, plus many others.

Another way to look at the preparation of the dinitramide anion is that dinitraminic acid is simply a product of further nitration of nitramide (eq 3). Nitramide can be formed by several methods including the direct nitration of ammonia.[11,12] Thus, in principle, any reaction that forms nitramide can form dinitraminic acid by further nitration. For example, in our laboratory, it was found that the dinitramide anion can simply be prepared by the reaction of nitronium salts with nitramide followed by neutralization of dinitraminic acid to give a dinitramide salt at low temperatures, as shown in eq 3:[6]

$$NH_2NO_2 \xrightarrow[\text{(2) } NH_3]{\text{(1) } NO_2X/CH_3CN} NH_4N(NO_2)_2 \qquad (3)$$
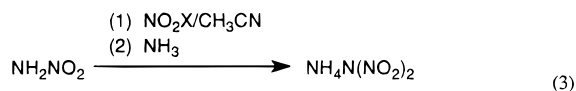
where X = BF_4^- and $HS_2O_7^-$.

The yield of this reaction can range up to 95% for the reaction of nitramide with well-purified NO_2BF_4. The ammonium salt is prepared by neutralizing the intermediate dinitraminic acid by reaction with ammonia. Other alkylammonium salts can be similarly prepared by direct reaction with the alkylamine or by ion exchange. N_2O_5 is ineffective for the nitration of nitramide, giving only a low yield of dinitramide salts. The major byproducts from the N_2O_5 reaction are ammonium nitrate and ammonium nitrite. These reactions proceed by an initial nitration of nitramide by the nitrating agent, followed by the loss of a proton to a base.

A known route to nitramide is the direct nitration of ammonia at liquid nitrogen temperatures (eq 4).[29] Nitramide can be isolated in a low yield. This led to a study of the direct dinitration reaction of ammonia with nitrating agents to prepare dinitramide salts. This reaction is generally successful for the synthesis of dinitramide salts:[43]

$$NH_3 + NO_2X \xrightarrow{NH_3 \text{ (excess)}} NH_4N\begin{smallmatrix} NO_2 \\ \\ NO_2 \end{smallmatrix} \qquad (4)$$

where X = BF_4^-, NO_3^-, $HS_2O_7^-$.

The yield of this reaction is generally 15% for the reaction of ammonia with N_2O_5, 25% for the reaction with NO_2BF_4 at $-7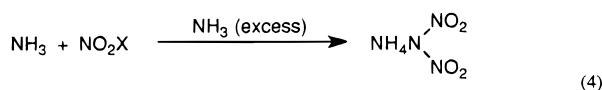8$ °C, and 20% for the reaction with $(NO_2)HS_2O_7$ at -60 °C. Again, the reaction is believed to proceed by a direct nitration of ammonia to give nitramide, followed by a second nitration of nitramide by the nitrating agent, and followed by the loss of a proton to ammonia to give ammonium dinitramide. Several side reactions are possible in this reaction sequence that limit the overall yield, including the destruction of the intermediate nitramide by reaction with ammonia. A curious paradox was observed in these studies. Although NH_3 reacted

Table 2. Yield vs Nitrating Agent

substrate	nitrating agent	yield (%)
NH_3	NO_2BF_4	25
NH_3	$NO_2HS_2O_7$	15
NH_3	NO_2NO_3	15
NH_2NO_2	NO_2BF_4	90
NH_2NO_2	NO_2NO_3	trace
$EtOC(O)NNO_2^- \ NH_4+$	NO_2NO_3	70

directly with N_2O_5 to give ADN in approximately 15% yield, nitramide only gave a trace ($<1\%$) of ADN upon reaction with N_2O_5. We attribute the nitration of nitramide to the catalysis of the nitration of NH_2NO_2 to $HN(NO_2)_2$ by excess NH_3 in a manner reminiscent of the catalysis of the acylation of amines by ternary amines.

More recently, we found that ammonium nitrourethane (ANU) can be used as the substrate for preparing dinitramide salts.[44] In this reaction, a nitronium ion source (such as N_2O_5 or NO_2BF_4) is used to give a dinitrourethane (DNU) as the initially nonisolated intermediate. DNU then is reacted with ammonia to give ammonium dinitramide. The reaction is done at -20 °C in methylene chloride. This reaction is shown in eq 5. Table 2 summarizes the yield of dinitramide salts with respect to the different substrates and nitrating agents.

(5)
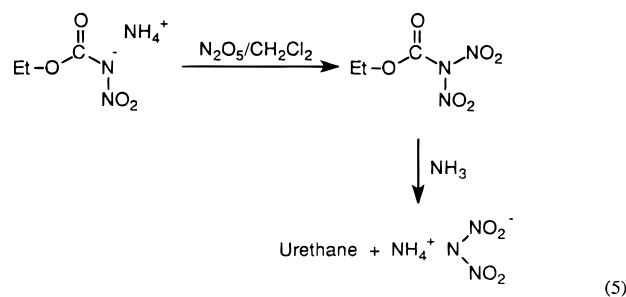
We think of the mechanism for the reaction of DNU with ammonia as being a simple displacement reaction occurring at the carbonyl center to yield initially a dinitramide anion and protonated urethane, as shown in eq 6. Possible side reactions that lower the yield include the transfer of a nitro group from *N,N*-dinitrourethane to ammonia. This would give nitramide that would be rapidly decomposed upon further reaction with ammonia or any adventitious base.

(6)
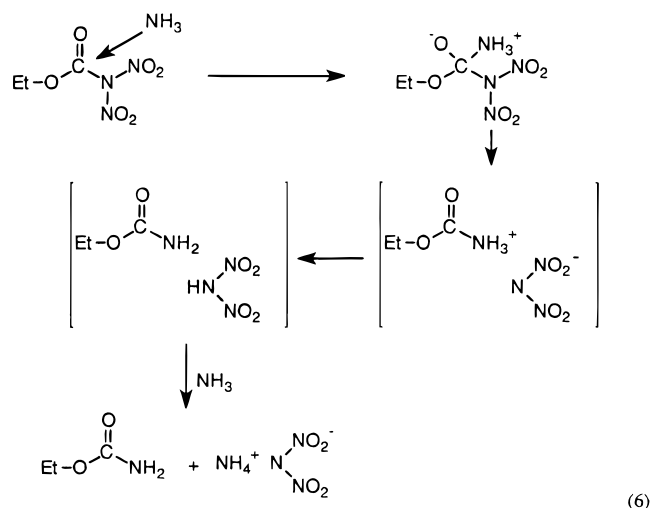
Crystallographic Analysis of Dinitramide Salts. Gilardi and co-workers at NRL used X-ray crystallography to extensively study the structure of ammonium dinitramide. The crystal-
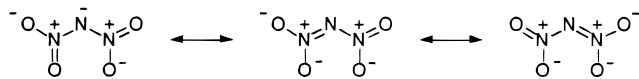
Figure 3. Representative resonance structures of the dinitramide ion.
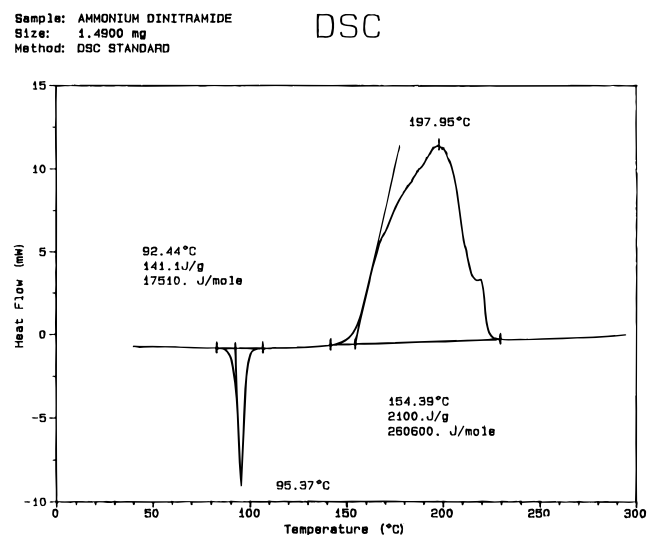
Figure 4. Thermal analysis of the ammonium dinitramide (ADN).

lographic data and analysis will be presented in detail in the following paper by Gilardi and co-workers.

Physical and Chemical Properties of Dinitramide. The dinitramide anion has significantly improved acid, base, oxidative, thermal, and shock stability when compared with alkyldinitramines or nitramide, but is generally less stable than the nitrate or nitrite ions (the exception being $R_3NH^+NO_2^-$). We believe that the observed stability is due to the presence of an overall negative charge that is distributed by resonance over the entire molecular system, thus strengthening those $N-NO_2$ bonds most susceptible to rupture. Some of the possible resonance forms are shown in Figure 3.

Ammonium dinitramide (ADN) has a melting point of 92 °C, followed by an onset of decomposition at 130 °C. The thermal behavior of unstabilized dinitramide anion can be seen in the DSC presented in Figure 4. The density of ADN is 1.801 g/cm^3 (X-ray). Ammonium dinitramide shows UV maximums in water at 212 and 284 nm with $E_{284} = 5.207 \times 10^3$ L mol^{-1} cm^{-1} (Figure 5). We have determined that dinitraminic acid is a strong acid with a pK_a of approximately −5.

The dinitramide anion is stable to decomposition between pH 0 and 15. Dinitramide salts decompose slowly in concentrated acid at room temperature, but appear to be stable to base. We used UV spectroscopy to measure the decay of ammonium dinitramide at room temperature in sulfuric acid. In 8.0 molar sulfuric acid, no loss was seen after 8 h, but in concentrations of 11.0 M and above decay was observed in minutes. The rate of acid-catalyzed decomposition increases directly with acidity. In sulfuric acid, decomposition is quite rapid in 18 M (concentrated) H_2SO_4 and slower at lower acid concentrations. Spectral changes are observed in the UV−vis between 10 and 12 M H_2SO_4. Between 10 and 12 M H_2SO_4, the dinitramide anion absorption at 284 nm is significantly reduced.

We believe that a protonation of the dinitramide anion is occurring over this acid range, giving $HN(NO_2)_2$. At lower concentrations, the compound exists as the separated ion pair $M^+/N(NO_2)_2^-$ in solution. Dilution of these concentrated acid solutions returns the UV−vis to its original form, by converting the acid form to the separated ion pair (when we allow for the dilution effects and some decomposition of the dinitramide anion
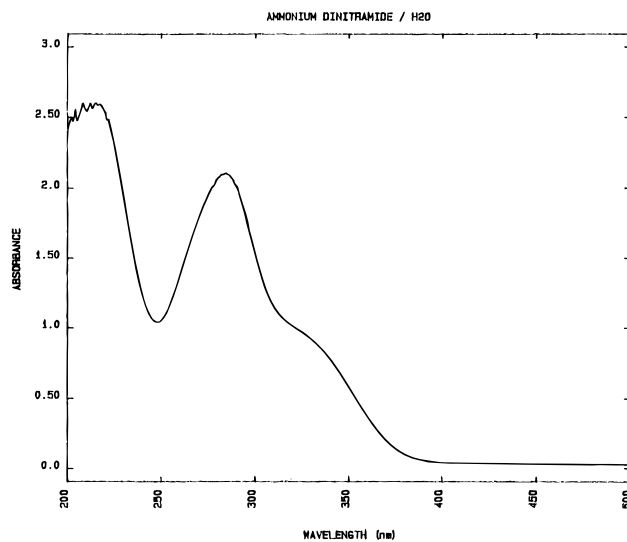
Figure 5. UV−vis of the dinitramide (ADN).

Table 3. Decomposition of ADN in H_2SO_4 at Room Temperature

concentration (M/l)	k (min^{-1})	$t_{1/2}$ (min)
11.0	0.00742	93
12.0	0.0252	28
13.0	0.335	2.1

Table 4. Decomposition of Cesium Dinitramide HNO$_3$ at Room Temperature

concentration (%)	k (h^{-1})	$t_{1/2}$ (h)
70	0.228	3.04
70[a]	0.048	14.4
90	1.81	0.38

[a] Added urea to eliminate NO$_x$.

caused by the acid). A first-order analysis of the decay data gave the results summarized in Table 3.

We used the cesium salt of dinitramide to measure the decay in nitric acid. In one experiment, a small amount of urea was added to the nitric acid to remove NO^+ or NO_x species. In 70% nitric acid that had been stabilized using urea which is known to scavenge NO^+ and NO_2, known as one-electron oxidants, the half-life of the dinitramide anion increased from 3 to 14 h. This result indicates a greater susceptibility to a one-electron oxidation than to an acid-catalyzed decomposition in nitric acid. Table 4 summarizes the results of the decomposition measurements in nitric acid.

Further studies of the thermal and solution properties of this anion are under way. The proposed, acid-catalyzed, decomposition pathways are shown in eqs 7 and 8. The products of the decomposition of dinitramide have been observed in other studies.[19] We speculate that decomposition of the dinitramide anion occurs upon the second protonation of the anion, as shown in eqs 7 and 8. Protonation can occur at either the oxygens or the central nitrogen. Protonation on the oxygen should follow the mechanism in eq 7, with initial elimination of nitrous oxide, nitronium ion, and water. This mechanism is consistent with the observed products of decomposition. We cannot distinguish the first route from the second proposed decomposition pathway (eq 8), where the protonation occurs at the central nitrogen. We favor the first route (with protonation at oxygen), because the electron densities on the nitro groups suggest that this route would be favored. The decomposition products in either case should be the same. Further studies are required to distinguish these routes.

$$N_2O + NO_2^+ + H_2O$$

$$\downarrow$$

$$N_2O + HNO_3 + H^+ \tag{7}$$

$$Products\ (N_2O,\ H_2O,\ HNO_3) \longleftarrow H_2NNO_2 + NO_2^+ \tag{8}$$

Reactions of the Dinitramide Anion. We have begun investigations of the chemical reactions of the dinitramide anion.[44] The reaction of cesium dinitramide with methyl triflate gives a 40% yield of methyl dinitramine, identified by comparison with a known sample (eq 9). To a large extent, the dinitramide anion reacts at the central nitrogen, demonstrating a significant electron density at this site. The other products have not yet been analyzed in detail but are believed to result from reaction via attack at the oxygens.

$$CsN(NO_2)_2 + CH_3OSO_2CF_3 \longrightarrow CH_3-N(NO_2)_2 \tag{9}$$

Experimental Procedures

Caution: *All* dinitramide salts and alkyl dinitramines are potentially hazardous materials that are both thermally and impact sensitive. These compounds are strong oxidizers and can be explosive under certain conditions. Use extreme care when handling these materials. Dinitramide salts exhibit instability to light and acids.

Synthesis of [2−(Trimethylsilyl)ethyl)-*N,N*-dinitramine. To form the [2−(trimethylsilyl)ethyl]−*N,N*−dinitramine precursor, an ice-cooled mixture of 1.45 g (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO_3 (under argon) was formed, and then 10 mmol of 2−(trimethylsilyl)ethyl isocyanate was added, with fume-off avoided by controlling the rate of addition as appropriate. The reaction was stirred for 15 min at 0 °C, diluted to 25 mL with $CHCl_3$, and filtered rapidly through a l in. × 3 in. plug of SiO_2, eluting with 100 mL of $CHCl_3$. Chromatography of the crude product, eluting $CHCl_3$ over SiO_2 and collecting the fastest-moving, UV-active material ($R_f = 0.5$), resulted in the collection of 500 mg of the desired [2−(trimethylsilyl)ethyl]−*N,N*−dinitramine precursor (25% yield).

Synthesis of Cesium Dinitramide. Cesium fluoride, 1 g, 7 mmol, was added to about 2.5 mL of [2−(trimethylsilyl)ethyl]−*N,N*−dinitramine, dissolved in 20 mL of acetonitrile and maintained at 20 °C. The solution was stirred for about 120 min, filtered through a plug of silica, and washed with a small amount of acetonitrile. The cesium dinitramide salt product was then recovered by crystallization from ethyl acetate. The product yield was 900 mg (50% yield), mp 80 °C.

Synthesis of ADN from Nitramide. Nitramide (120 mg, 2 mmol) was dissolved in 4 mL of anhydrous acetonitrile cooled under argon to a temperature of −l0° C and then treated the solution with 300 mg (2.3 mmol) of nitronium tetrafluoroborate. The reaction mixture was stirred for 10 min and then added to a stirred mixture of 8 mL of 1 molar NH_3/2−propanol in 100 mL of ethyl ether. The mixture was stirred for 5 min. The mixture was evaporated to dryness, triturated with 10 mL of 1:1 acetone/ethyl acetate, filtered, and evaporated to dryness. The residue was crystallized from 2 mL of 1-butanol to give 150 mg of ADN (60% yield, first crop).

Synthesis of ADN from Ammonia. N_2O_5 was made from the ozonolysis of 12.3 g of N_2O_4 (0.13 mol) dissolved in 300 mL of dry CH_2Cl_2 and cooled to −78 °C. An ozone stream was passed through the solution, under stirring, until the solution was dark blue, resulting in the formation of a solid precipitate of nitronium nitrate.

Anhydrous NH_3 (6 g, 0.35 mol) was added over a 30 min period to the solution of N_2O_5 in CH_2Cl2 while maintaining the mixture at −78 °C with stirring. Stirring was continued for 2 h at −78 °C and then the reaction was allowed to warm to room temperature. The CH_2Cl_2 was taken off, and the remaining solids were washed with 100 mL of CH_2Cl_2. The ADN product was extracted twice with 50 mL of acetone, each extraction lasting 20 min. The acetone extractions were concentrated to dryness to yield 1.77 g of a light yellow solid, which was recrystallized from 1-butanol to give 1.16 g of ADN (15% yield). The reaction between N_2O_5 and NH_3 to form ADN was repeated at a temperature of −30 °C in CH_2Cl_2, resulting in a yield of about 5%; and at −40 °C in a 2:1 CH_3CN/CH_2Cl_2 mixture, resulting in a yield of about 12%.

Synthesis of Other Dinitramide Salts by Ion Exchange. All desired dinitramide salts can be prepared by ion exchange starting from cesium dinitramide and using AMBERLYST 15 sulfonic acid resin charged with the appropriate cation: Elution is performed using a methanolic solution of cesium dinitramide over a large excess of the charged resin.

In a typical example, 10 g of AMBERLYST 15 (sulfonic acid resin) was suspended in 100 mL of CH_3OH, treated with 5 mL of 95% hydrazine, filtered, and washed with 100 mL of CH_3OH. This material was then placed into a 4 in. × 0.5 in. column and eluted with a solution of 200 mg of cesium dinitramide in 5 mL of CH_3OH, followed by washing with an additional 20 mL of CH_3OH. Concentration of the effluent gave approximately 100 mg of pure hydrazinium dinitramide (SRI−13) after crystallization from CH_3CN, mp 80 °C. **This material is shock sensitive and one should exercise caution in handling it.**

Synthesis of ADN from N_2O_5 and Ammonium Nitrourethane. Two hundered milliters of a 0.5 M solution of N_2O_5 in CH_2Cl_2 (see above) was treated at −30 °C with 100 mmol of ANU, stirred for 3 h, cooled to −60 °C, and treated with excess (5 g) anhydrous ammonia gas over a 5 min period. The resulting suspension was warmed to room temperature, concentrated in vacuo, and digested with 150 mL of 1:1 isopropyl alcohol/ethyl acetate. The triturate was passed through a 3 × 1 inch plug of silica gel, concentrated, and crystallized (CH_3-CN/CHCl$_3$) to give 6.5 g (50%) of ADN.

Kinetics, Spectra, and Thermal Analysis of Ammonium Dinitramide. UV−vis spectra and decomposition kinetics data were obtained with a Hewlett-Packard 8450A UV−vis spectrophotometer. A constant temperature cell accessory was used for the kinetics experiments, and these were run at 22 °C. In a typical ADN acid decomposition experiment 50 ul of an aqueous ADN stock solution was added to a UV/vis cell containing 3000 ul of the desired sulfuric acid concentration at 22 °C. This gave an initial ADN concentration of about 0.1 mM. The solution was mixed: and then the instrument measured the absorbance at preprogramed regular intervals observing the decomposition of ADN. The wavelength chosen for the absorbance measurement varied depending on the acid concentration. For the 11, 12, and 13 M sulfuric acid, 235 nm was used. Any background absorbances of the cell and acid solution were compensated for automatically by making and storing balancing/background measurements before the kinetic runs were made. First-order analysis of the absorbance−time data was used to generate rate constants. The same procedures were used for cesium dinitramide in nitric acid. The nitric acid decomposition was measured with and without the presence of urea. Urea is known to eliminate NO^+ and NO_2, both one-electron oxidants. All water was from a Millipore purification system. Sulfuric and nitric acids were Mallinckrodt reagent grade and ADN was synthsized in our lab with a purity greater than 99%.

Thermal analysis of ADN was done on a TA Instruments 2100-910 differential scanning calorimetry (DSC) system. The sample was run in an aluminum pan under inert atmosphere with a heating rate of 10 °C/min. The instrument was calibrated according to the manufacturer's instructions using common standards.

JA9709278