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Catalytic Decomposition of Ammonium Nitrate in Superheated Aqueous Solutions

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Abstract: The decomposition of aqueous ammonium nitrate at elevated temperatures and pressures is examined as a function of chloride, nitrate, and total acidity. Catalysis requiring both chloride and acid was observed in solutions containing 20% (w/w) NH_4NO_3 at 180 °C. Nitrous oxide and dinitrogen were generated in a 4:1 ratio below 0.2 M H^+. Dinitrogen formation correlated with the production of additional acidity by the reaction $5NH_4NO_3 \rightarrow 4N_2 + 2HNO_3 + 9H_2O$. The second-order dependence of the decomposition reaction on $[H^+]$ is consistent with the reversible formation of NO_2^+. Incorporation of ^{18}O into the N_2O product, as well as the inverse deuterium isotope effect, supports this conclusion. A novel mechanism based on the intermediacy of NO_2Cl is proposed for the chloride catalysis and contrasted to the radical-based pathways operational in molten NH_4NO_3 decompositions. Isotope-labeling experiments using $^{15}NH_4NO_3$ lead to the formation of $^{15}N{=}N{=}O$-labeled nitrous oxide and the dinitrogen products $^{15}N{\equiv}^{15}N$ and $N{\equiv}^{15}N$ in a 1:3 ratio. Decomposition of $NH_4{}^{15}NO_3$ produces only $N{=}^{15}N{=}O$ and $N{\equiv}^{15}N$. This agrees with the reaction sequences: $NO_2Cl + NH_4^+ \rightarrow \{O_2N{-}NH_3\}^+ + H^+ + Cl^-$, $\{O_2N{-}NH_3\}^+ \rightarrow N_2O + H_3O^+$ and $3NO_2Cl + 3NH_3 \rightarrow 3NH_2Cl + 3NO_2^- + 3H^+$, $3NH_2Cl \rightarrow N_2 + NH_4^+ + 3Cl^- + 2H^+$, $3NO_2^- + 3NH_4^+ \rightarrow 3N_2 + 6H_2O$. These results bear on the industrial preparation of NH_4NO_3 and suggest conditions under which nitrous oxide emissions might be important to the global N_2O budget.

Introduction

The environmental implications of increasing atmospheric nitrous oxide (N_2O) are well recognized.[1] Atmospheric N_2O is the predominant source of stratospheric NO, which catalyzes the $O_3 + O \rightarrow 2O_2$ reaction[2] (a stratospheric ozone sink). In the lower stratosphere, NO_2, formed by the reaction of NO with ozone, may also sequester ClO as $ClONO_2$.[3] This can diminish the effect of NO and ClO radicals on ozone loss. Nitrous oxide has an atmospheric lifetime of 120−150 years,[4] and it has a greenhouse forcing factor 315 times as great as that of CO_2.[5] Accumulation of atmospheric N_2O has been estimated at 0.3% per year over the past several decades, and N_2O is currently 10−15% above its preindustrial value.[6] About 30% of the sources in the global nitrous oxide budget are uncertain.[7,8] Most N_2O evolution involves terrestrial or oceanic bacterial action;[9] however, global distribution patterns suggest that there are also significant anthropogenic sources.[10] For example, industrial production of adipic acid (a precursor to nylon-66) is a point source of nitrous oxide that accounted for 10−15% of the annual increase in N_2O levels and about 45% of the excess observed in the northern hemisphere.[11] This realization led to a voluntary phase-out of the industrial emissions.[12]

As part of an effort to identify various mechanisms of nitrous oxide formation,[11,13,14] we have examined the stability of hot aqueous solutions of ammonium nitrate. Nitrous oxide emissions from soils treated with ammonium nitrate have been studied in some detail;[15] however, N_2O releases during fertilizer manufacture have not been considered. In one widely used method of NH_4NO_3 manufacturing, hot aqueous NH_3 and HNO_3 are combined in a titanium sparger; temperatures of 180 °C may arise from the exothermicity of this neutralization reaction. Global capacity for producing ammonium nitrate was 66 billion kg/yr in 1985,[16] about half of which was marketed as a solid. Prilling is a drying method which sprays an ammonium nitrate solution into a countercurrent air stream heated to 180 °C. Water evaporates as the solution droplets fall. Some nitrogen loss is known to occur during this step.[17]

Molten ammonium nitrate decomposes at temperatures above 200 °C according to eqs 1 and 2. During NH_4NO_3 synthesis, low pH is often employed to suppress the second reaction. Pure ammonium nitrate is known to present an explosion hazard when it is contaminated with chloride or organics. Previous mechanistic studies of NH_4NO_3 decomposition have focused on the

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$$NH_4NO_3(l) \rightarrow N_2O(g) + 2H_2O(g) \quad (1)$$

$$NH_4NO_3(l) \rightarrow NH_3(g) + HNO_3(g) \quad (2)$$

solid and its anhydrous melt, while comparatively little is known of ammonium nitrate's reactivity in solution. The tragic explosion[18] at the Terra Industries ammonium nitrate plant in Port Neal, Iowa, underscored the fact that superheated, aqueous NH_4NO_3 can also be violently reactive. When fundamental information is obtained about the solution mechanisms underlying one of the largest scale industrial processes, its potential contribution to the nitrous oxide budget may be evaluated. In addition, a study of solution decomposition reactions may provide new insight into the explosion hazards present during the manufacture and use of this important fertilizer.

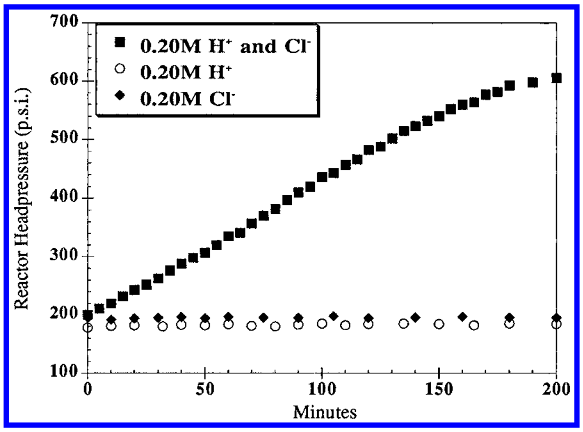

Figure 1. Synergistic catalysis of 20% (w/w) of ammonium nitrate in water. Solutions were sealed within a Ti reactor, purged with agron, and heated to 180 °C. Time zero for each reaction was defined as the time when the target temperature was first reached. H^+ was added as HNO_3, and Cl^- was introduced as NH_4Cl.

Experimental Section

All reactions were performed within a 300 mL Parr titanium pressure reactor, which was purged and pressurized to 50 psi with argon. Gas samples were extracted from the headspace periodically and analyzed on a Hewlett Packard 5890 gas chromatograph with a thermal conductivity detector and a 3392A integrator. Calibration curves were used to determine the quantities of nitrogen, nitrous oxide, and argon present in a 50 μL injection, from which the composition of the bulk headspace was calculated. The volume and mass of solution remaining at the end of the reaction were recorded, and aliquots were titrated with a standard NaOH solution to determine total acidity. All solutions were prepared with HPLC-grade H_2O. Ammonium nitrate, ammonium chloride, nitric acid, hydrochloric acid, 12 M DCl, $^{15}NH_4NO_3$ (99% ^{15}N), $NH_4{}^{15}NO_3$ (99% ^{15}N), and $H_2{}^{18}O$ (70% ^{18}O) were all used as received. ND_4NO_3 was prepared by triple recrystallization of NH_4NO_3 from D_2O (99.9%).

Reactions of 20% (w/w) Aqueous Ammonium Nitrate. Solutions of ammonium nitrate (18.0 g) in water (75 g) were sealed within the titanium reactor and heated to 180 °C. The decomposition of the ammonium nitrate solution was monitored both by the total headspace pressure and the changing headspace gas composition. The influences of free chloride and total acidity on the rate and course of the decomposition were evaluated independently. Ammonium chloride was added to ammonium nitrate solutions prepared in 0.191 M nitric acid to vary the chloride concentration between 0.000 and 0.298 M. Conversely, the ammonium chloride concentration was kept fixed at 0.20 M as the acid concentration was adjusted from 0.000 to 0.512 M. The nitrate dependence was established by the addition of $NaNO_3$. Ammonium concentration studies were not conducted due to the difficulty of finding a suitable anion, which neither buffered the solution pH nor was chemically incompatible under the reaction conditions. Ammonium nitrate solutions containing 0.20 M Cl^- and 0.20 M H^+ were also examined at temperatures between 170 and 200 °C to determine the effects of temperature on the decomposition profile.

Reactions at High Ammonium Nitrate Concentrations. Ammonium nitrate (18 g) solutions ranging from 15% (w/w) to 50% (w/w) in water were prepared with 0.20 M Cl^- and 0.20 M H^+. Above 50% (w/w), the chloride loading had to be substantially lowered, and no initial acid was added. *Warning: ammonium nitrate, either dry or as a concentrated aqueous solution, presents a significant explosion hazard when contaminated by chloride and/or organics.*

Isotope-Labeling Experiments. Ammonium nitrate solutions (20% w/w) labeled with ^{15}N (either as $^{15}NH_4NO_3$ or as $NH_4{}^{15}NO_3$) and containing 0.20 M Cl^- and 0.20 M H^+ were decomposed at 180 °C. After the reactor was allowed to cool, the nitrous oxide and dinitrogen were analyzed on a Hewlett Packard gas chromatograph/mass spectrometer (GC/MS) to determine the nature and the extent of ^{15}N incorporation into both products. Water and CO_2 were first removed with a dry ice/acetone bath and NaOH, respectively. As N_2 is a mass spectral fragmentation product of N_2O, the pretreated gases were then separated by freezing out the N_2O at 77 K and Toepler pumping the N_2 on a vacuum line. ND_4NO_3 (18 g) was decomposed at 180 °C in a solution of 0.20 M DCl/D_2O to investigate deuterium isotope effects. NH_4NO_3 (1.27 g) was also decomposed in a 0.20 M solution (5.60 g) of HCl prepared with $H_2{}^{18}O$. GC/MS analysis was used to calculate the degree of ^{18}O exchange as determined from the $N_2{}^{16}O/N_2{}^{18}O$ product ratio.

Results and Discussion

Decomposition of 20% (w/w) Solutions of Ammonium Nitrate at 180 °C. Solutions containing 20% by weight certified ACS-grade ammonium nitrate in HPLC purity water were sealed into a 300 mL titanium pressure reactor. No detectable decomposition occurred after heating at 180 °C for 10 h. Neither 0.20 M H^+ (as HNO_3) nor 0.20 M Cl^- (as NH_4Cl) catalyzed decomposition individually; however, when they were added together catalysis was observed. Figure 1 depicts the headspace pressure profile for these experiments. A plateau above 600 psi was coincident with complete depletion of ammonium nitrate. The gaseous products evolved consisted of 78% N_2O and 22% N_2.

Influence of [H^+]. Reactions were performed in which the chloride concentration was maintained at 0.20 M while the acidity was varied. In these experiments, the amount of N_2 produced was proportional to the increase in solution acidity; a ratio approaching 2:1 (N_2/produced H^+) was observed consistently (Table 1). Decomposition rates were sensitive to the initial acid concentration below 0.2 M H^+, where product H^+ acceleration dominated the reaction profile (Figure 2). Since nitrogen generation was quantified throughout each reaction, the acidity of the solution at any time could be calculated by using the 2:1 N_2/H^+ ratio to estimate how much additional acid had been created. Each of the decomposition profiles of Figure 2 were broken down into a series of smaller segments, such that the headspace pressure increase rate was linear over each segment. The total solution acidity was determined at the first and last point for each segment and averaged. Rate data from each of the experiments agree within experimental error and show that the reproducible apparent induction times seen at low initial acid concentrations reflect rate acceleration by the generation of additional H^+ during the reaction. Above 0.2 M H^+, the decomposition rates are linear throughout approximately 80−90% of the reaction. This originates in the offsetting effects of rate acceleration (from additional acid generation) and rate inhibition (as the ammonium nitrate is consumed). Rate data derived from the initial linear portion of five experiments with acid concentrations at or above 0.2 M are plotted in Figure 3.

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Table 1. Product Distributions from the Complete Decomposition of 20% Ammonium Nitrate Solutions

	$[H^+]^a$						
$[Cl^-]^a$ (M)	(init M)	(final M)	moles of H^+ produced	moles of N_2 produced	ratio of N_2:H^+	moles of N_2O produced	ratio of N_2O:N_2
0.200	0.0300	0.363	0.027	0.056	2.1:1	0.146	2.6:1
0.200	0.0616	0.383	0.026	0.046	1.8:1	0.138	3.0:1
0.200	0.0900	0.377	0.025	0.045	1.8:1	0.137	3.0:1
0.200	0.124	0.407	0.024	0.042	1.8:1	0.141	3.4:1
0.200	0.166	0.425	0.022	0.042	1.9:1	0.153	3.6:1
0.199	0.191			0.040		0.142	3.6:1
0.206	0.192	0.446	0.021	0.043	2.0:1	0.158	3.7:1
0.206	0.282	0.498	0.020	0.039	2.0:1	0.162	4.2:1
0.206	0.410	0.572	0.017	0.033	1.9:1	0.165	5.1:1
0.205	0.40			0.031		0.16	5.1:1
0.207	0.512	0.637	0.017	0.031	1.8:1	0.174	5.7:1
0.0502	0.191	0.431	0.021				
0.0773	0.191	0.430	0.020	0.032	1.6:1	0.113	3.5:1
0.100	0.191	0.436	0.021	0.038	1.8:1	0.129	3.4:1
0.124	0.191	0.434	0.021	0.037	1.8:1	0.129	3.5:1
0.150	0.191	0.439	0.022	0.040	1.8:1	0.144	3.6:1
0.199	0.191			0.040		0.142	3.6:1
0.298	0.191	0.457	0.023	0.045	2.0:1	0.166	3.7:1

[a] Chloride and acid concentrations were determined at room temperature and atmospheric pressure.

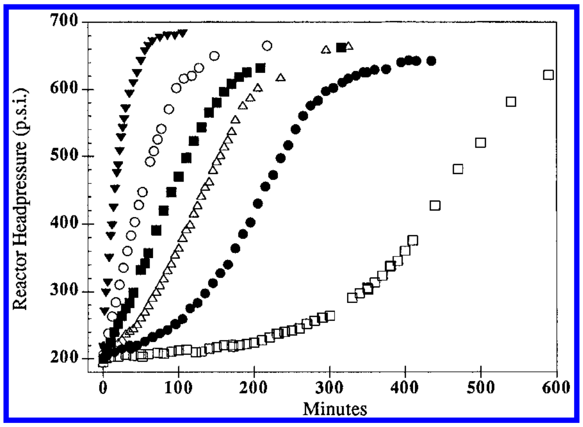


Figure 2. Reaction profiles for 20% ammonium nitrate solutions in 0.20 M chloride at 180 °C, plotted as a function of time for various initial acid concentrations: (□) 0.030 M H^+, (●) 0.062 M H^+, (△) 0.124 M H^+, (■) 0.192 M H^+, (○) 0.282 M H^+, and (▼) 0.512 M H^+. The leveling of the curves at extended times represents complete decomposition.

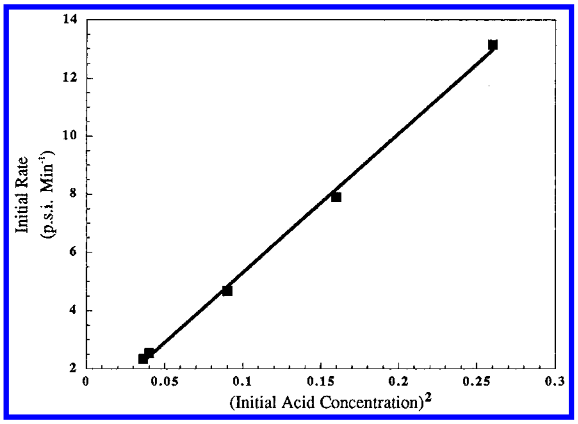


Figure 3. Plot of the second-order rate dependence on the acid concentration, as determined by the method of initial rates. Initial rate data for five experiments are plotted against the square of the initial acid concentration. All reactions were performed in 0.20 M chloride at 180 °C.

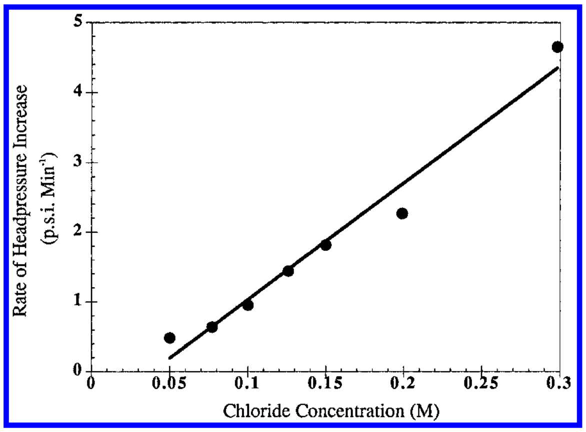


Figure 4. Plotting the linear correlation between the overall rate of decomposition and the chloride concentration used. Reactions were carried out at 180 °C in the presence of 0.191 M H^+.

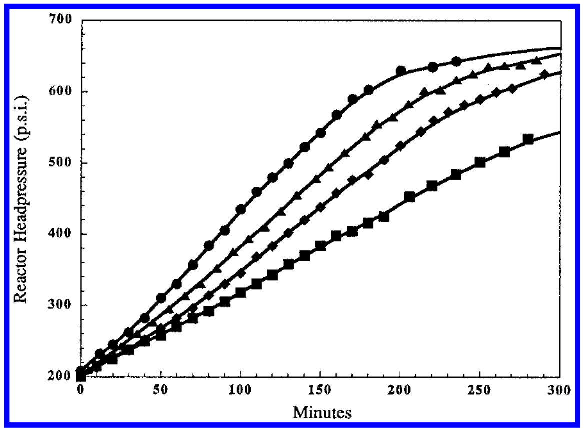


Figure 5. Reaction profiles for experiments with elevated nitrate levels, in 0.20 M chloride and 0.20 M acid, at 180 °C: (■) 0.00 g $NaNO_3$ (0.225 mol total nitrate), (◆) 3.05 g of $NaNO_3$ (0.261 mol total of nitrate), (▲) 6.05 g of $NaNO_3$ (0.297 mol total of nitrate), (●) 12.05 g of $NaNO_3$ (0.367 mol total of nitrate).

This shows a second-order rate dependence on initial acid concentration.

Influence of $[Cl^-]$. When the initial acid concentration was held constant at 0.191 M and the chloride concentration was varied, both the N_2O:N_2 ratio and the total moles of H^+ generated remained invariant (Table 1). Plotting the rate of increase in total headspace pressure versus the chloride concentration (Figure 4) shows an approximate first-order dependence. Gas chromatography data were used to quantify first-order relationships for the rates of production of both N_2 and N_2O in 0.191 M HNO_3 as a function of the chloride concentration, from which the following empirical rate equations were derived at 180 °C:

$$d(N_2)/dt = k_{obsd}[Cl^-],$$
$$k_{obsd} = 3.2(\pm 0.4) \times 10^{-5} \text{ mol of } N_2 \text{ s}^{-1} \text{ M}^{-1}$$

$$d(N_2O)/dt = k_{obsd}[Cl^-],$$
$$k_{obsd} = 1.0(\pm 0.2) \times 10^{-4} \text{ mol of } N_2O \text{ s}^{-1} \text{ M}^{-1}$$

Influence of Additional Nitrate. A number of experiments were performed with both the H^+ and Cl^- concentrations maintained at 0.20 M while nitrate (as $NaNO_3$) was added (Figure 5). The additional NO_3^- modestly enhanced the ammonium nitrate decomposition rates; an empirical data fit suggested an approximate $\sqrt{3}$ dependence. Note that at higher nitrate concentrations evidence for rate acceleration from acid autocatalysis can be observed early in the reaction profile.

Decomposition Mechanisms of Aqueous Ammonium Nitrate Solutions. The decomposition of pure and chloride-contaminated ammonium nitrate melts has been studied in some detail;[19−21] however, far less is known about decomposition behavior in aqueous solutions. Ammonium nitrate decomposition is inhibited by small quantities of water added to the melt.[22] This effect has been attributed to the ionization of nitric acid and its subsequent inability to generate NO_2^+,[22] which is believed to be a key intermediate in the decomposition pathway.[19−21] It is incorrect to infer that water can completely block NO_2^+ formation; however, as the nitric acid dissociation equilibrium shifts toward the undissociated form as temperature and pressure are increased.[23] Above 150 °C the ionization constant is less than one.[23] Therefore, appreciable amounts of undissociated HNO_3 exist in aqueous solution under the conditions of our kinetics experiments.

In their classic studies of organic nitration reactions, Ingold et al. were the first to show conclusively the intermediacy of $H_2NO_3^+$ during the generation of the nitryl cation.[24,25] They identified two limiting cases for these reactions. When anhydrous nitric acid was used as a nitrating agent, the reaction was best expressed as eq 3.

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \rightleftharpoons NO_2^+ + H_2O + NO_3^- \quad (3)$$

When stronger acids were used, a significant increase in the rate of nitration was observed, and the formation of NO_2^+ was attributed to eq 4.

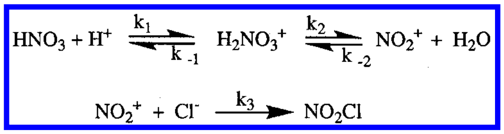
$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \quad (4)$$

The exact K_A for nitric acid under the current reaction conditions can be estimated to lie within the range $1 > K_A > 0.1$.[23] Under the dilute aqueous conditions of these experiments, eq 4 is a better representation of the equilibria responsible for generating NO_2^+. In support of this, Ingold noted that the reaction identified in eq 3 was inhibited by the addition of nitrate;[24] however, excess nitrate (as $NaNO_3$) slightly accelerated decomposition rates in the current study. Equation 4 mirrors the initiation step previously reported for molten NH_4NO_3 salts.[19−21]

Further support for the validity of the equilibria proposed in eq 4 was obtained when NH_4NO_3 was decomposed in 70% $H_2{}^{18}O$. Both $N_2{}^{16}O$ and $N_2{}^{18}O$ were generated in a 4:3 ratio. The quantity of $N_2{}^{18}O$ observed represented 75−80% of that anticipated from total oxygen scrambling. Control reactions showed that no ^{18}O exchange occurred between N_2O and $H_2{}^{18}O$. The dehydration/rehydration equilibrium of eq 4 must occur repeatedly to generate the observed level of exchange. This agrees with previous kinetic studies, which found that this near pre-equilibrium proceeded more quickly then subsequent nitration events and causes ^{18}O incorporation into NO_3^-.[26]

It was also observed that ND_4NO_3 in 0.2 M DCl/D_2O decomposed at rates approximately double those of analogous protonated samples. This inverse kinetic isotope effect is consistent with an equilibrium isotope effect favoring undissociated nitric acid.[27] The O−D bond is stronger than the O−H bond, and this drives the equilibria of eq 4 toward higher NO_2^+ concentrations, thereby accelerating decomposition.

Scheme 1



The synergistic catalytic behavior of H^+ and Cl^- in dilute aqueous ammonium nitrate solutions shows that the generation of NO_2^+ alone is insufficient for catalysis. Previous mechanistic studies of anhydrous ammonium nitrate melts have shown that NO_2^+ can abstract an electron from chloride to initiate radical chain mechanisms.[28] In aqueous solution, however, chloride may stabilize NO_2^+ as NO_2Cl. Nitryl chloride has been postulated recently as a reactive intermediate in the aqueous, ionic redox chemistry of other nitrogen species.[29,30] The first-order kinetic dependence on chloride at 0.2 M $[H^+]$ for both N_2O and N_2 formation implicates eq 5 as a common, rate-determining step in the mechanism.

$$NO_2^+ + Cl^- \rightarrow NO_2Cl \quad (5)$$

In contrast, experimental rate laws determined for the production of N_2O and N_2 from the chlorine-radical-catalyzed decomposition of NH_4NO_3 melts express a square-root dependence on chloride concentrations and yield highly variable N_2O/N_2 product distributions.[17]

Scheme 1 depicts the formation of the nitryl chloride intermediate. Ingold[24] and Bunton[26] have reported the equilibrium k_1/k_{-1} to be fast for organic nitration steps. They have also reported that k_{-2} is more rapid than k_2; the aqueous conditions of the current experiments may shift the second equilibrium even further to the left. Given that the first two equilibria are fast, the expression for the rate determining step is $d(\text{products})/dt = k_3[NO_2^+][Cl^-]$. If one assumes steady state behavior for $[NO_2^+]$, the rate expression becomes:

$$d(\text{products})/dt = (k_2k_3[Cl^-][H_2NO_3^+])/(k_{-2} + k_3[Cl^-])$$

Inverting both sides yields

$$(\text{rate})^{-1} = k_{-2}/(k_2k_3[Cl^-][H_2NO_3^+]) + 1/(k_2[H_2NO_3^+])$$

As $[HNO_3]$ can be approximated as $[H^+][NO_3^-]/K_{A(HNO_3)}$, this rate expression is consistent with the second-order acid dependence (Figure 3) and the first-order chloride dependence (Figure 4). Figure 6 was constructed by plotting $(\text{rate})^{-1}$ as a function of $[Cl^-]^{-1}$. It should be possible to obtain a direct measure of the ratio k_{-2}/k_3 by dividing the slope of Figure 6 by its intercept value. A small, positive intercept was anticipated, and the observed small negative value (−0.15 ± 0.18, 95% confidence level) is not statistically significant. The observed dependency upon nitrate is lower than predicted; however, it is also important to recognize that the high salt concentration involved, as well

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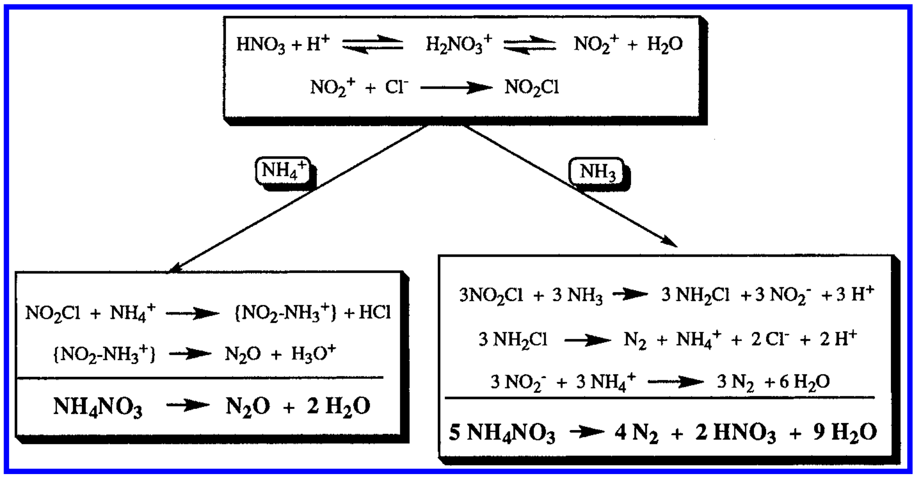
Scheme 2



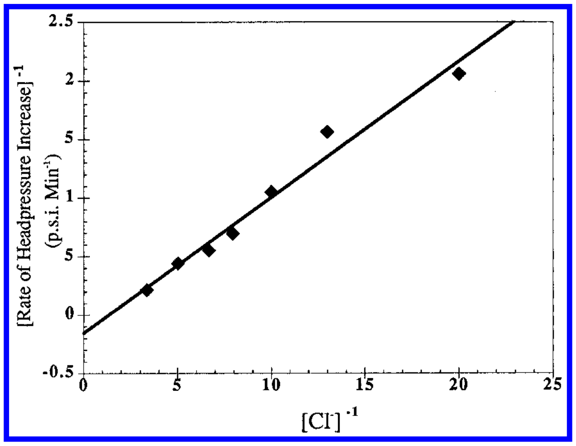


Figure 6. Plotting the inverse of the decomposition rate as a function of inverse chloride concentration. Rate data were taken from the study of chloride dependence. The initial acid concentration was held invariant at 0.191 M.

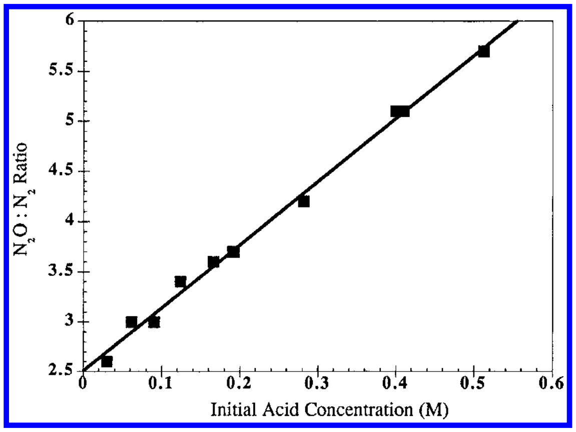


Figure 7. Plot of the final ratio of nitrous oxide to dinitrogen evolved during ammonium nitrate decomposition, as a function of initial acid concentration. Reactions were carried out at 180 °C in the presence of 0.20 M Cl^-.

as the reduced dielectric constant of H_2O at 180 °C, will introduce activity coefficient corrections of unknown magnitude. In spite of these limitations, the experimental data fit the kinetic model reasonably well.

Several lines of evidence point toward NO_2Cl as a common intermediate in the generation of both N_2O and N_2. The Coulombic barrier inhibiting direct attack of NO_2^+ on NH_4^+ is avoided by initial formation of nitryl chloride, which can generate nitrous oxide through the mechanism of eqs 6 and 7.

$$NO_2Cl + NH_4^+ \rightarrow \{O_2N{-}NH_3\}^+ + H^+ + Cl^- \quad (6)$$

$$\{O_2N{-}NH_3\}^+ \rightarrow N_2O + H_3O^+ \quad (7)$$

Nitryl chloride is also known to react with ammonia.[31] Both the nitrite[32] and the chloramine[31] produced in eq 8 react further to yield dinitrogen.

$$3NO_2Cl + 3NH_3 \rightarrow 3NH_2Cl + 3NO_2^- + 3H^+ \quad (8)$$

$$3NH_2Cl \rightarrow N_2 + NH_4^+ + 3Cl^- + 2H^+ \quad (9)$$

$$3NO_2^- + 3NH_4^+ \rightarrow 3N_2 + 6H_2O \quad (10)$$

Nitrous oxide prepared from the decomposition of $^{15}NH_4NO_3$ contained the label exclusively (>98%) on the terminal nitrogen ($^{15}N{=}N{=}O$), while N_2O prepared from $NH_4{}^{15}NO_3$ was labeled only at the central nitrogen ($N{=}^{15}N{=}O$). Neither $N{=}N{=}O$ nor $^{15}N{=}^{15}N{=}O$ were observed in detectable quantities. This is consistent with the mechanism of eqs 6 and 7. The dinitrogen gas produced from $^{15}NH_4NO_3$ contained both $^{15}N{\equiv}^{15}N$ and $N{\equiv}^{15}N$ in a 1:3 (±5%) ratio, while only $N{\equiv}^{15}N$ was recovered from the decomposition of $NH_4{}^{15}NO_3$. Background N_2 in the mass spectrometer prevented reliable quantification of the unlabeled dinitrogen. The 1:3 ratio of $^{15}N{\equiv}^{15}N$ and $N{\equiv}^{15}N$ prepared from $^{15}NH_4NO_3$ is inconsistent with the radical mechanism;[21] however, the stoichiometries of eqs 9 and 10 in the current mechanism satisfy this isotope distribution.

Scheme 2 summarizes the reaction pathways proposed for the decomposition of aqueous ammonium nitrate solutions. Both acid and chloride are required to generate NO_2Cl, which subsequently reacts along parallel pathways, producing N_2O and N_2. The data presented in Table 1 show that the nitrous oxide/dinitrogen product ratio is directly proportional to the acidity of the reaction, although no such correlation was found in the chloride dependency studies. The linear response of the N_2O/N_2 ratio to the initial acidity of the reaction (Figure 7) is a direct consequence of the common intermediacy of NO_2Cl. The rates of formation of N_2O and N_2 can be expressed as $d(N_2O)/dt = k_{N_2O}[NO_2Cl][NH_4^+]$ and $d(N_2)/dt = k_{N_2}[NO_2Cl][NH_3]$. Since $K_{A(NH_4^+)} = [H^+]\,[NH_3]\,[NH_4^+]^{-1}$, the ratio of the rate expressions is as follows:

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(31) Jander, J.; Engelhardt, U. *Developments in Inorganic Nitrogen Chemistry*; Elsevier Scientific Publishing Company: New York, 1973; Vol. 2, p 228.

(32) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 1st ed.; Pergamon Press: New York, 1984; pp 1542.

$$\frac{d(N_2O)/dt}{d(N_2)/dt} = \frac{k_{N_2O}[NO_2Cl][NH_4^+]}{k_{N_2}[NO_2Cl]\,[NH_3]} = \frac{k_{N_2O}[NO_2Cl][NH_4^+]}{k_{N_2}[NO_2Cl]K_{A(NH_4^+)}[NH_4^+][H^+]^{-1}}$$

This simplifies to yield the expression

$$\frac{d(N_2O)/dt}{d(N_2)/dt} = \frac{k_{N_2O}}{k_{N_2}K_{A(NH_4^+)}}[H^+]$$

The excellent linear correlation depicted in Figure 7 provides strong evidence for this mechanistic proposal. Further experimental support for the intermediacy of free NH_3 in the N_2 evolution pathway was found in the product distribution of the ND_4NO_3 decomposition experiments outlined previously. The greater strength of N−D bonds would be anticipated to favor ND_4^+.[27] Therefore, free ND_3 concentrations in solution would be lowered and N_2 formation would be inhibited. The N_2O/N_2 ratio from ND_4NO_3 decomposition rose to over 4.0:1 as compared to the 3.5:1 ratio observed in analogous NH_4NO_3 decompositions.

The chloride-catalyzed decomposition of ammonium nitrate at 100 °C in strongly acidic solutions (1−8 M HNO_3) has been examined.[33] This was proposed to occur through a mechanism based on the initial formation of HOCl. An empirical fit of the kinetics data showed a third-order dependence on nitrate concentration, in contrast to the much weaker dependence observed under the current conditions. It is significant to note that at 100 °C the generation of NO_2^+ via eq 4 would be a less viable reaction pathway, because of the large dissociation constant for nitric acid at the lower temperature.

Influence of Increased Ammonium Nitrate Loading. It is interesting to consider the reaction conditions involved in fertilizer manufacturing, where the ammonium nitrate loading of superheated aqueous solutions may be 70−95%. A series of reactions were performed at elevated ammonium nitrate concentrations. Figure 8 depicts the increase in reaction rate as the ammonium nitrate loading is increased from 20 to 50% by weight. Above 50% (w/w) NH_4NO_3, decomposition is exquisitely sensitive to chloride. At 60% NH_4NO_3, solutions heated to 180 °C were decomposed by the presence of chloride even in the absence of added acid. This may reflect the dehydrating nature of concentrated salt solutions, which would favor NO_2^+ formation in eq 4 as well as product catalysis by H^+. Figure 9 depicts the reaction profiles for three experiments performed on 70% ammonium nitrate at 180 °C. The decomposition was very rapid at the highest chloride loading used, and more severe conditions were not tested to alleviate the risk of accidental explosion.

The rate of ammonium nitrate decomposition was also studied as a function of temperature. Figure 10 shows the data obtained from decomposition experiments conducted on 70% ammonium nitrate solutions contaminated with 900 ppm chloride. No initial acidity was introduced. At temperatures below 170 °C, the rate of decomposition was slow. An Eyring plot was used to estimate the apparent activation energy under these conditions at 180 kJ mol^{-1}. Temperatures above 180 °C also increased the proportion of nitrous oxide evolved. Decomposition of 20% ammonium nitrate at 220 °C generated a headspace that was greater than 95% N_2O.

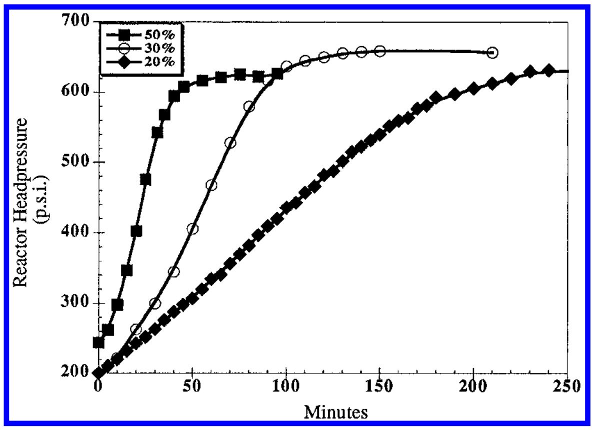

Figure 8. The effect of increased ammonium nitrate loading on the rate of decomposition. All reactions were performed at 180 °C with 0.20 M H^+ and 0.20 M Cl^-.

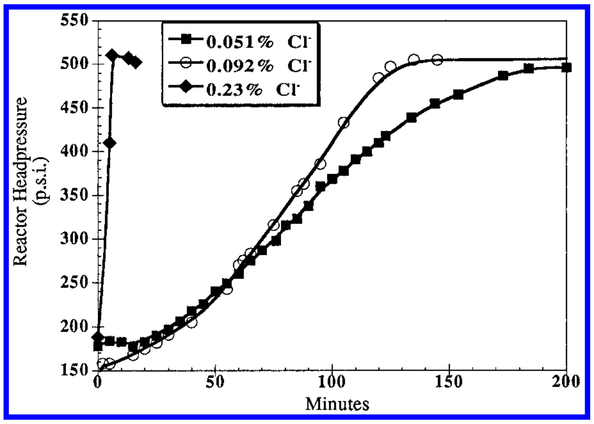

Figure 9. Reaction profiles for the decomposition of 70% ammonium nitrate solutions contaminated with different levels of chloride (as NH_4Cl) at 180 °C.

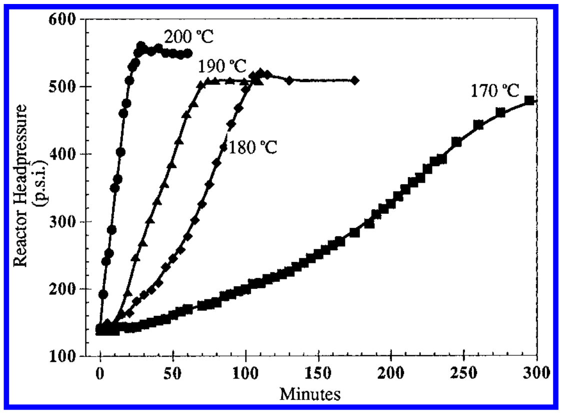

Figure 10. Reaction profile as a function of temperature; 70% ammonium nitrate solutions initially free of acid were contaminated with 900 ppm NH_4Cl and heated to temperatures ranging from 170 to 200 °C.

Ammonium Nitrate Manufacture as a Potential Source of Atmospheric Nitrous Oxide. Ammonium nitrate is prepared by mixing ammonia and nitric acid, resulting in a hot aqueous solution approximately 60% (w/w) in ammonium nitrate. To produce solid NH_4NO_3, the remaining water must be driven off. One of the two common drying methods is known as prilling; in this procedure the solution is sprayed into the top of a prilling tower and encounters a countercurrent of hot air as it falls. Temperatures in the prilling tower can surpass 180 °C, and a residence time of 15 s is typical. The data suggest the presence of elevated chloride concentrations (above approximately 500 ppm) would be sufficient to initiate decomposition of am-

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(33) Kelmers, A. D.; Maya, L.; Browning, D. N.; Davis, W., Jr. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1583−1588.

monium nitrate and generate nitrous oxide under these conditions. The dangers of chloride-contaminated ammonium nitrate solids are well-known within the industry, and Cl^- standards have been adopted; the currently accepted chloride limit for manufacture of ammonium nitrate in Europe is 200 ppm. The rate measurements show that when chloride-limited operating conditions are maintained, it is unlikely that ammonium nitrate decomposition could produce globally significant quantities of nitrous oxide. Higher levels of chloride contamination will generate nitrous oxide, and monitoring effluent emissions from neutralizers and prilling towers may be informative.

Relevance to the Commercial Manufacture of NH_4NO_3. Ammonium nitrate is a commodity chemical manufactured primarily as a agricultural fertilizer and for producing explosives. Although often regarded as safe, incidents still occur during its production and handling. The largest accidental explosion in the U.S. occurred in Texas City on April 16, 1947, when a fire aboard the *S. S. Grandcamp* caused the detonation of 2280 tons of solid ammonium nitrate fertilizer. Over 600 people were killed, and the Associated Press war correspondent likened the destruction to the atomic-bombing of Nagasaki.[34] The exact cause of the Texas City explosion was never determined. Some fertilizer bags were known to have ruptured, spilling granulated ammonium nitrate onto the floor of the hold, where seawater residue may have provided chloride. The water used in an attempt to extinguish the *Grandcamp* fire could have exacerbated the problem by redissolving accumulated chloride salts and mixing them with the dissolved ammonium nitrate. It is unclear whether seawater was used directly to fight the blaze that preceded the explosion.[35]

During a scheduled plant shutdown in December 1994, 164 000 lbs of NH_4NO_3 detonated at a fertilizer plant in Port Neal, Iowa, killing four people and injuring 18 others. An EPA report concluded that the ammonium nitrate had been manufactured from nitric acid contaminated with chlorides.[36] Before the explosion, an aqueous solution of 85−90% ammonium nitrate, with a pH estimated to be less than one, was sprayed with steam above 220 °C at 200 psig for 9.5 h.[36] The aqueous decomposition reactions outlined in this paper involve similar species and conditions, and present a plausible mechanism for the buildup of pressure in the titanium reactor and the ensuing explosion. Although “dry” ammonium nitrate decomposes more rapidly than concentrated aqueous solutions at similar levels of chloride contamination, the current data indicate that at temperatures exceeding 170 °C aqueous decomposition may proceed rapidly.

Acknowledgment. The authors thank Prof. Charles L. Perrin for helpful suggestions. Funding was provided by the National Science Foundation, grant number CHE-9632311.

JA971618K

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[34] Gray, H. B.; Simon, J. D.; Trogler, W. C. *Braving the Elements*; University Science Books: Sausalito, CA, 1995; p 418.

[35] *Natl. Fire Protection Assoc. Quarterly* **1947**, *41*, 25−57.

[36] Thomas, M. J.; Cummings, A.; Gomez, M. Chemical Accident Investigation Report: Terra Industries, Inc. Nitrogen Fertilizer Facility, Port Neal, Iowa, U.S.E.P.A., Region 7, 1996.