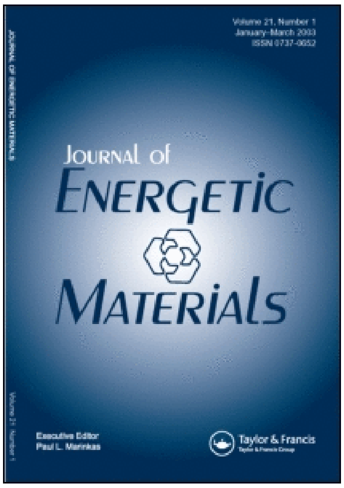

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AMMONIUM PERCHLORATE DECOMPOSITION: NEAT AND SOLUTION[1]

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ABSTRACT

The thermal decomposition of ammonium perchlorate (AP) was examined over a broad temperature range (215°C to 385°C) in solution and condensed phase. Over the entire temperature range, the decomposition, as monitored by loss of ammonium ion, appeared first-order out to 70% decomposition. Up to about 350°C the decomposition of AP in methanol (5wt% AP) proceeded at a rate similar to neat AP, but the AP in aqueous solution (20wt%) decomposed considerably slower than the neat material. Activation energies and frequency factors were determined for each experimental condition. In addition, decomposition

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products, both gaseous and condensed phase, were identified and quantified. For neat AP decomposition, the following reaction stoichiometries were determined.

at 250C:

$10\ AP \rightarrow 4\ N_2O + 1\ N_2 + 7\ O_2 + 1\ Cl_2 + 2\ HClO_3 + 6\ HCl + 16\ H_2O$

at 380C:

$10\ AP \rightarrow 3\ N_2O + 2\ N_2 + 7\ O_2 + 1\ Cl_2 + 2\ 1/3\ HClO_3 + 5\ 2/3\ HCl + 16\ H_2O$

At low temperatures, decomposition of ammonium perchlorate in methanol proceeded at a similar rate to that of neat AP. In contrast to decomposition of neat AP, the only nitrogen-containing decomposition product was nitrogen gas, while chlorine appeared only as chloride. The presence of CO and CO_2 as decomposition gases and chromatographic analysis of the solvent indicated interaction between methanol and AP. The decomposition of AP in water was slowed, but product distribution was not significantly different than that of neat AP.

Obvious structural similarities between AP and ammonium nitrate and the fact that decompositions were slowed by the presence of water, led to examination of the effect acids and bases have on AP decomposition rate. Previous decomposition studies of ammonium nitrate indicated acids accelerated the thermal decomposition, while bases retarded it. These observations along with the observed decomposition products led us to concur with previous researchers that the initial step in AP decomposition is proton transfer to form ammonia and perchloric acid. Subsequently, the decomposition products of perchloric acid facilitate the oxidation of ammonia.

AP decomposition rate with addition of 5wt% various chlorine oxide salts [perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), and chloride (Cl^-)] was examined. Stoichiometry of decomposition was not noticeably perturbed. Chlorate had a slight acceleratory effect on the decomposition of AP at all temperatures, while added sodium perchlorate had no effect on rate. Differential scanning calorimetry (DSC) indicated chlorite and chloride retarded decomposition, but isothermal results were less definitive.

BACKGROUND

AP is an energetic salt used primarily as the oxidizer in solid rocket propellants. Its thermal behavior has been examined by a number of researchers.[2] In 1988 a detonation occurred destroying one of two U.S. manufacturers of AP. This prompted renewed efforts to better characterize the stability of AP.[3]

Previous studies of AP, report condensed-phase decomposition was particle size and surface area dependent[4,5] and decomposition occurred only to 30% and then ceased. If the AP were recrystallized and its original density restored decomposition could again be initiated. To study AP decomposition without concern for such solid-phase factors, we examined the decomposition of AP in solution in addition to the condensed phase. AP was sufficiently soluble in water and in methanol that 20% and 5% solutions could be prepared, respectively.[6] In the two solutions and in the condensed phase, decomposition kinetics were measured and condensed- and gas-phase products were identified and quantified. It is possible that the decomposition route of AP in the solution is not comparable to the condensed phase path, and this concern is addressed.

EXPERIMENTAL SECTION

AP used in these studies was 200 micron rotary-round, Kerr-McGee lot # 7765, manufactured September 1986 and donated by Edwards Air Force Base.[7] In most tests 1 to 1.3 mg samples of AP were weighed into 40 uL melting point capillary tubes (1.5-1.8 x 90 mm), and the open end of the capillary was flame sealed under air. Aqueous solutions of AP (20% by weight) were prepared by dissolving 0.2 grams of AP in 0.8 mL of distilled deionized water. In methanol (HPLC grade), the highest concentration of ammonium perchlorate that could readily be dissolved was 5 weight percent. Solid additives, such as $NaClO_4$, $NaClO_3$, $NaClO_2$ and NaCl were added to AP at the 5 wt% level; using a wooden spatula, AP (0.95 g) was stirred with 0.05 g of each additive for 10 minutes until the mixtures appeared homogeneous. The mixtures were not ground together because there was concern that changing the particle size of the ammonium perchlorate might affect its decomposition rate.

Samples were thermolyzed using a constant temperature (±1°C) molten metal bath (Wood's metal). DSC experiments used a Perkin Elmer DSC-4 equipped with TADS database software. Analyses were carried out under N_2 flow, and scans calibrated against the melting endotherm of indium. The samples were approximately 0.2 mg, sealed in thin walled capillaries and placed in aluminum cradles in the DSC head.[8] American Standard Testing Methods (ASTM) variable heating method was employed to determine gross activation energy and a preexponential factor.[9] DSC thermograms were also obtained for AP mixed with various additives. Relative thermal stability was assessed from comparing thermograms obtained at identical scan rates; samples with exotherms at substantially lower or higher temperatures were deemed, less or more thermally stable, respectively. For such comparisons, scan rate was 20°/minute, unless otherwise noted.

Isothermal decomposition kinetics were determined either by monitoring the amount of decomposition gas released or by following the losses of ammonium or perchlorate ion. A mercury manometer was used to determine gas evolved during AP thermolysis. The fraction of AP reacted was computed from the ratio of amount of gas formed with time during isothermal thermolysis to amount of gas formed upon complete AP decomposition. Determining the amount of gas formed upon complete decomposition at each temperature was necessary because the stoichiometry of the decomposition and, hence, the total gas released was temperature dependent.

The total amount of decomposition gases formed at 215° and 370°C was 1.2 and 1.6 mole gas per mole AP, respectively.

At most temperatures, AP decomposition was followed by monitoring loss of ammonium ion using chemically suppressed ion chromatography (IC). A Dionex IC model 2000i/SP system with a 750 uL sample loop was used. The cation separation system consisted of a Dionex HPIC-CS1 (P/N 030831) column and a Dionex HPIC-CG2 (P/N 035370) cation guard column. In front of these two column was a Dionex HPIC-Guard 2 organic guard column. The eluent used was 0.005 M (5mM) HCl. The suppressor regenerant was tetrabutyl ammonium hydroxide (TBAOH) (approximately 1.0mM). A flow rate of the eluent (1.2 mL/min) produced a pump pressure of approximately 800 psi; the regenerant flow rate was 5 mL/min. Detector output range was typically 30 microsiemens with integrator attenuation of 1024, and chart speed of 0.1 cm/min. Standards (0.1 to 10 ppm) were prepared by dilution of a 100 ppm ammonium nitrate stock solution.

To quantify the anions, perchlorate (ClO_4^-), chlorate(ClO_3^-) and chloride (Cl^-), a Beckman Model 110A high pressure liquid chromatograph (HPLC) was used in conjunction with a Waters 486 tunable absorbance detector (wavelength 280 nm) and a Vydac 302IC (Cat# 302IC4.6, 24 cm length) column.[10] The eluent 1mM isophthalic acid was adjusted to pH 4.9 using sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$). Both 20 and 100 microliter sample loops were used, depending on the concentrations of interest. Standard and sample concentrations ranged between 5 and 200 ppm. Standards were prepared using NaCl, $NaClO_2$, $NaClO_3$, and $NaClO_4$; typical retention times using the conditions cited were 4, 5, 6, and 10 minutes, respectively.

Samples were prepared for HPLC analysis by one of the following methods. Either a thick glass rod was used to crush a melting point capillary tube into a fine powder under a small amount of deionized distilled water. Or the tip of the melting point capillary tube was broken off and the entire contents removed by washing with five 40 uL aliquots of deionized distilled water. In both methods, aqueous AP solutions were transferred quantitatively into a volumetric flask and the solution was brought up to volume with distilled deionized water. Samples prepared for ammonium (Dionex) analyses were diluted 1/50, while those prepared for anion (Vydac) analyses were diluted 1/10. If crushed glass was still present, the solutions were filtered.

Analysis of decomposition gases, nitrogen, oxygen, nitrogen dioxide, nitrous oxide and chlorine, were conducted using a Varian 3600 gas chromatograph equipped with a thermal conductivity detector (TCD) and a Haysep DB (Cat# C-5000) stainless steel column (length 30′, o.d. 1/8", i.d. 0.085"). Helium carrier gas was used at a flow rate of 20 mL/min; the injector temperature was 50°C, and the detector temperature, 150°C; oven temperature was ramped from 0°C to 80°C at 10°C/min. Gas standards (10 to 250 microliters in volume) nitrogen (N_2), oxygen (O_2), chlorine (Cl_2) and nitrous oxide (N_2O) exhibited retention times of approximately 7, 8, 21, and 25 minutes, respectively. Quantification and identification of gases in thermolyzed samples were compared with standards of known amounts. Since the reaction capillary tubes were sealed under air, to evaluate the amount of nitrogen and oxygen formed during ammonium perchlorate thermolysis, it was necessary to quantify the amount of these gases in the headspace of these tubes. Using three empty capillary tubes, the quantity of nitrogen and oxygen filling these tubes was quantified by gas chromatography (GC) in the same manner in which subsequent thermolysis samples were analyzed.

The amount of nitrogen and oxygen thus determined was subtracted from the amount of nitrogen and oxygen found in all thermolyzed AP samples.

To check for possible solvent degradation when methanol was the solvation medium for AP thermolyses, a Hewlett Packard series II 5890 GC equipped with a HP5971 mass selective detector, a crosslinked methyl silicon capillary column (HP1, 25 m x 0.2 mm x 0.33 uL film thickness) was used. The carrier gas was helium. The temperatures of the injector port, oven, and detector were 240°, 80°, and 250°C, respectively.

RESULTS

Kinetics

Decomposition of AP in the condensed phase was examined from 215°C to 385°C. Rate constants are listed in Table I. At all temperatures the decomposition as followed by loss of ammonium ion, appeared first-order out to 70% decomposition. Decomposition kinetics by monitoring evolved gas, showed considerable scatter of data (Fig. 1). The latter method of determining rate constants was employed only at four temperatures; they are also in Table I. At most temperatures fraction of ammonium perchlorate remaining at a given time was determined by using ion chromatographic analysis to quantify remaining ammonium ion. At two temperatures 250°C and 380°C, the progress of the reaction was also assessed by monitoring perchlorate ion remaining. Rate constants determined by all three methods were comparable (Table I). The Arrhenius plot for neat AP (Fig. 2) showed slight curvature suggesting a change in the dominant decomposition mechanism over the 170°C range. Gross activation energy was determined using all the temperatures in this range, with the exception of the points at 250° which appeared to be too low. A value of 21.3 kcal/mol (Table II) was obtained. Activation parameters were also determined by the ASTM programmed DSC method;[9] these are also given in Table II. The activation energy (22.7 kcal/mol) determined by programmed DSC is almost identical to the isothermal value obtained over the entire 170° temperature range. These values are within the broad range of values reported by previous workers[2] and agree best with those of Kraeutle.[7,11]

Our studies involving ammonium nitrate decomposition indicated effects due to the presence of acids and bases.[12] Since in many ways ammonium perchlorate can be considered analogous to ammonium nitrate, we examined the effects of acids and bases upon the decomposition of AP at both the high and low end of the temperature range. As expected nitric acid accelerated the decomposition of ammonium perchlorate, while ammonia retarded it (Table III). At high temperature (380°C) the acceleration (1.8 times faster) and deceleration (2.0 times slower) effects were slightly less than those same effects (2.3 times faster and 5.0 times slower, respectively) at 250°C. DSC scans also indicated that the addition of sodium salts of weak acids stabilized AP. The addition of 5wt% oxalate, carbonate, formate, or fluoride, increased the temperature at which the exothermic maximum was observed by at least 35°C. This same stabilization effect was observed when these salts were mixed with ammonium nitrate. In that case, the effect was rationalized in terms of the intrinsic basicity of the salts of weak acids.[12]

At temperatures below 300°C, AP in methanol solution (5wt%) decomposed at about the same rate as did neat AP. Above 300°C, AP in methanol decomposed slightly faster than neat AP. In contrast, aqueous AP (20wt%) decomposed much more slowly than neat AP. Rate constants were determined for the decomposition of AP in water at only a few temperatures since it was soon obvious that aqueous decomposition of AP would not be directly comparable to that of neat (Table I).

In an attempt to shed light on the decomposition mechanism of AP, we examined its decomposition in the presence of potential reaction intermediates, 5wt% chlorine oxides salts: perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), and chloride (Cl^-). The effect of these salts was first examined by differential scanning calorimetry (DSC) and then by isothermal thermolyses. DSC indicated that chlorate accelerated decomposition of AP, while chlorite and chloride retarded it and perchlorate had no effect (Fig. 3,4). Isothermal results confirmed the acceleratory effect of chlorate and the fact that perchlorate had no effect, but only at 235°C did it appear that chlorite and chloride retarded the decomposition of AP (Table III).

Products

Products of AP under various conditions were determined at 250°C and at 380°C (Table IV). Regardless of the decomposition phase or the presence of additives, the fate of the ammonium nitrogen was to form either nitrous oxide or N_2; no nitrate was observed. Although the ratio of N_2 to nitrous oxide was independent of the presence or absence of chlorine oxides, it showed a marked temperature dependence. At the low end of the temperature range (250°C) little N_2 was formed; the ratio of N_2 to nitrous oxide was approximately one to four. This is in line with the product distribution reported by previous researchers.[2] At 380°C, the ratio of N_2 to N_2O increased so that it was close to two to three. However, one of the few studies to report decomposition products as high as 380°C does not report formation of N_2.[13] The distribution of other decomposition products did not appear to vary with temperature. The oxygen from the perchlorate anion formed molecular oxygen, the dominate decomposition gas at both temperatures examined. Some oxygen was also found as chlorate, and any unaccounted for oxygen was assumed to form water. Chlorine from perchlorate was found as either chlorate, chloride, or chlorine gas, its fate dependent upon the temperature and presence of chlorine oxide salts. Chloride was the predominant decomposition fate of perchlorate from neat AP at both 250°C and 380°C. At both temperatures examined, product distribution was not greatly affected by the addition of 5wt% chlorine oxide salts (Table IV).

In contrast to the decomposition of neat AP, when AP was decomposed in methanol, N_2 was the only nitrogen-containing decomposition product; and chloride was the only chlorine-containing species. The amount of N_2 and chloride formed accounted for all the AP initially present (Table IV). No oxygen gas was observed, but both carbon monoxide and dioxide were detected. At 250°C and at 380°C, methanol in which AP had been thermolyzed to decomposition levels of 20% and 70% was examined by GC/MS, and in all cases a small peak immediately after the methanol peak was observed. The fragmentation pattern at 250°C (69 s, 59 l, 58 m, 57 s, 45 m, 44 l, 43,l 42 m, 40 m, 32 m, 28 l, 18 s) indicates a different species than that observed at 380°C (93 s, 59 l, 58 l, 45 m, 43 m, 40 l, 32 l 31 l, 29 l, 28 l).

In water, the decomposition rate of AP was substantially slower (Table I) so that after fourteen days at 250°C, no appreciable decomposition products were detected. Analysis of ammonium and perchlorate indicated about 6% loss. At 380°C after 60 hours, about 60% of the AP had decomposed. Surprisingly, the distribution of N_2, nitrous oxide, and oxygen was similar to that produced by neat AP. Chlorine produced was slightly higher, while chloride was slightly lower than the neat decomposition (Table IV).

DISCUSSION

The progress of ammonium perchlorate thermolysis, as ammonium ion remaining, appeared to be well-behaved and first-order out to 70% decomposition over the entire temperature range 215°C to 385°C. The Arrhenius plot constructed from the rate constants measured over the temperature range 215°C to 385°C was slightly curved. This curvature in the Arrhenius plot and the change in the N_2 to nitrous oxide ratio at 380°C (Table IV) suggests a shift in the dominant AP decomposition mechanism at high temperatures. Like the decomposition ammonium nitrate, the decomposition rate of AP was sensitive to the presence of both acids and bases. For both ammonium salts, the effect on decomposition rate was more pronounced at low temperature than at high temperature (Table IV), although the difference in the effect was not nearly as great in the case of AP as it was in the case of ammonium nitrate.[12] For ammonium nitrate, the acceleratory effect of acids and the retarding effect of bases has been explained in terms of a mechanism where the protonated oxidizing species ($H_2NO_3^+$) is involved in the rate determining step.[12]

Over the years, three routes have been considered as the initial step in AP decomposition: electron transfer forming NH_4^+ and ClO_4^-, decomposition of perchlorate anion, and dissociation of ammonium into ammonia and perchloric acid (eq.1).[4,16-19] The preponderance of experimental evidence supports the latter mechanism as does this study. This decomposition route is in line with that of other energetic ammonium salts (NH_4NO_3, $HONH_3NO_3$, $NH_4N(NO_2)_2$).[12,14,15]

$$NH_4ClO_4 \quad <==> \quad NH_3 \quad + \quad HClO_4 \qquad (1)$$

The next step in the decomposition of AP must involve oxidation of ammonia, but whether perchloric acid or a decomposition product of perchloric acid is the oxidizing species is the question. Since acids were observed to accelerate the decomposition of AP and bases retard it, we have postulated a decomposition mechanism analogous to that proposed for ammonium nitrate.[12] After dissociation of the salt to form the free acid and ammonia, protonation of the acid leads to further decomposition.

$2\,HClO_4 \quad --> H_2ClO_4^+ + ClO_4^-$ (a)

$H_2ClO_4^+ \quad --> ClO_3^+ + H_2O$ (b)

$NH_3 + ClO_3^+ --> [NH_3ClO_3^+] --> NO_2Cl + H_3O^+$ (c)

$H_3O^+ + ClO_4^- --> HClO_4 + H_2O$ (d)

$NO_2Cl --> Cl + NO_2$ (e)

$NH_3 + Cl --> NH_2 + HCl$ (f)

$NH_2 + NO_2 --> NH_2NO_2 --> N_2O + H_2O$ (g)

Scheme I

Sum Scheme I: $2\,NH_4ClO_4 \; -> \; N_2O + HClO_4 + HCl + 3\,H_2O$ (2)

Since rate studies show that perchlorate ion and ammonium ion disappear at approximately the same rate, a mechanism which consumes all perchlorate during the oxidation of ammonia would seem appropriate. However, since ammonium perchlorate is over oxidized, all the perchlorate need not be consumed in the oxidation of ammonia. If the rate-determining step in perchloric acid decomposition were the same as that above, then it would be expected that the loss of ammonium and perchlorate ions would occur at comparable rates.

Perchloric and hydrochloric acid shown as decomposition products in equation (2) do not necessarily form. Those species which interact to produce HCl and $HClO_4$ would instead form the observed oxygen, chlorine, chloric acid, hydrochloric acid, and water, depending on the reaction conditions (eq. 3-5).

$$HCl + HClO_4 \rightarrow HClO_3 + HCl + 1/2\,O_2 \qquad (3)$$

$$HCl + HClO_4 \rightarrow 2\,HCl + 2\,O_2 \qquad (4)$$

$$HCl + HClO_4 \rightarrow 3/2\,O_2 + Cl_2 + H_2O \qquad (5)$$

Nitrogen gas was also formed in the decomposition of AP at 250°C. This means that NH_2 must undergo further oxidation to NH before interaction with NO_2 in a reaction analogous to Scheme I g to form N_2 and water. The overall reaction would be that shown in equation (6).

$$2\ NH_4ClO_4 \rightarrow N_2 + HClO_4 + HCl + 1/2\ O_2 + 3\ H_2O \qquad (6)$$

To account for the stoichiometry of AP decomposition observed at 250°C, the equations (2), (3), (4), (5), and (6) would be multiplied by 4, 2, 2, 1, and 1, respectively.

$$10\ AP \rightarrow 4\ N_2O + 1\ N_2 + 7\ O_2 + 1\ Cl_2 + 2\ HClO_3 + 6\ HCl + 16\ H_2O \qquad (7)$$

The curvature of the Arrhenius plot, the change in the stoichiometry of the nitrogen-containing decomposition products, and the change in the degree to which acids and bases affect the decomposition rate of AP suggest a change in the predominant pathway for AP decomposition. A likely alternative pathway would be the homolytic cleavage of the O-Cl bond in perchloric acid (Scheme II). Since the Cl-O bond energy in perchloric acid is estimated to be about 48 kcal/mol,[16] this would be a higher activation energy process. Although at higher temperatures, it is usual for reactions with higher activation energies to become dominant, the curvature of the Arrhenius plot (Fig. 2) makes this assumption questionable.

$HClO_4$ --> HO + ClO_3

NH_3 + HO --> NH_2 + H_2O

NH_2 + ClO_3 --> $[NH_2ClO_3]$ --> NO_2Cl + H_2O

NO_2Cl + NH_3 --> NH_2NO_2 + HCl

NH_2NO_2 --> N_2O + H_2O

Scheme II

Sum Scheme II: 2 NH_4ClO_4 -> N_2O + $HClO_4$ + HCl + 3 H_2O (2)

At 380°C nitrogen became a significant decomposition product. A proposed mechanism for that reaction is shown in Scheme III.

$HClO_4$ --> HO + ClO_3

NH_3 + ClO_3 --> NH_2 + $HClO_3$

$HClO_3$ --> HO + ClO_2

NH_3 + HO --> NH_2 + H_2O

NH_2 + ClO_2 -> NOCl + H_2O

NH_2 + NOCl --> NH_2NO + Cl

NH_2NO --> N_2 + H_2O

HO + Cl --> HOCl --> HCl + 1/2 O_2

Scheme III

Sum Scheme III: 2 NH_4ClO_4 -> N_2 + $HClO_4$ + HCl + 1/2 O_2 + 3 H_2O (6)

To account for the stoichiometry of decomposition observed at 380°C, the equations (2), (3), (4), (5), and (6) would be multiplied by 9, 7, 5, 3, and 6, respectively.

$$30\ AP \rightarrow 9\ N_2O + 6\ N_2 + 21\ O_2 + 3\ Cl_2 + 7\ HClO_3 + 17\ HCl + 48\ H_2O \qquad (8)$$

The fact that only the relative ratio of N_2/N_2O changed with temperature suggests that the other decomposition products arise directly from perchloric acid decomposition, a decomposition which is not affected by the 170° temperature change.

That excess perchlorate ion did not affect the rate of AP decomposition was not surprising since AP is an over-oxidized species. That chlorate accelerated ammonium perchlorate decomposition was also expected. It is well known that ammonium chlorate is much less thermally stable than AP.[20,21] What was not anticipated was the stabilizing effect of chlorite and chloride as observed by DSC (Figs. 3, 4) and in the 235°C isothermal decomposition (Table III). It should be noted that DSC comparative scans indicated that chlorate, chlorite, and chloride, added at the 5wt% level, all destabilized ammonium nitrate decomposition. One might argue that in

AP, chlorate and chloride serve as radical traps and that reduction of these species is much more difficult than reduction of perchlorate.[22]

Below 300°C, AP in methanol solution (5wt%) decomposed at about the same rate as it did neat. However, at higher temperatures AP decomposed faster in methanol than it did neat (Fig. 2). With the possible exception of water, which at no time was directly observed, none of the oxygen-containing decomposition products shown in equations (7) or (8) were detected when AP was decomposed in methanol. The only chlorine-containing product found was chloride. This result was expected since methanol degradation was observed, and carbon monoxide and carbon dioxide were detected. The presence of CO_2 and a trace of CO indicated oxidization of methanol. Almost two moles of carbon dioxide were evolved for every mole of AP decomposed. This essentially accounts for all the oxygen contained in the perchlorate anion. Therefore, it is reasonable that the nitrogen and chlorine of AP were found exclusively as N_2 and chloride.

$$2\ NH_4ClO_4 \xrightarrow[-H_2O]{CH_3OH} N_2 + 2\ HCl + 4\ CO_2 + \text{organic}$$

Although the organic decomposition products of methanol observed by GC/MS have not yet been identified, at both 250°C and 380°C the decomposition products are higher molecular weight than methanol. This would suggest polymerization and/or oxidation of methanol occurred. There are a number of species containing oxygen and chlorine radicals which could promote methanol polymerization. However, it should be noted that only a minor amount of methanol was degraded, even after 70% of the AP had decomposed.

Aqueous (20wt%) AP decomposed much more slowly than neat AP or AP in methanol. Ammonium nitrate in water decomposed somewhat more slowly than neat ammonium nitrate,[12] but the difference is not nearly as dramatic as it is for AP. The severe inhibitory effect of water on AP decomposition may be attributed to the fact that formation of radical species was suppressed. Even in decomposition Scheme I, some radicals were postulated. Dilution effects may also contribute to the retardation of the decomposition. Surprisingly, the decomposition products found in the aqueous decomposition of AP did not differ significantly from those found in neat decomposition. Therefore, we conclude that there is not direct reaction with the solvent.

CONCLUSION

The first step in the decomposition of neat AP is dissociation of AP into ammonia and perchloric acid. One mechanism by which perchloric acid may decompose is through protonation; the subsequent decomposition products oxidize the ammonia. Identification and quantification of the AP decomposition products allowed us to write stoichiometry for decomposition at two temperatures. Since curvature was observed in the Arrhenius plot of the decomposition rate constants for neat AP and since product distribution changed with temperature, it is likely that the principal decomposition mode changes. Rate constants and activation parameters were determined for the decomposition of AP both in the condensed phase and in solution.

It was thought that studying the decomposition of AP in solution would eliminate potential problems with particle size and surface area effects. However, neither AP decomposition in water (20 wt%) nor its decomposition in methanol (5wt%) proved to be completely analogous to its neat decomposition. Although decomposition products were similar, AP decomposition in water was significantly slower than that of neat. This was attributed to the fact that in water, formation of radical intermediates was not energetically favorable. Below 300°C, the thermolysis of in methanol proceeded at a rate comparable to that of neat AP. The decomposition of AP in methanol caused some oxidation of methanol; almost two moles of carbon dioxide were formed per mole of thermolyzed AP. Since this accounted for most of the oxygen contained in perchlorate, the nitrogen and chlorine of AP formed exclusively N_2 and chloride.

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TABLE I
AP Thermolysis Rate Constants

T(°C)	Neat k (1/s)	Analysis Method	5% in Methanol k (1/s)	20% in Water k (1/s)
215	7.70E-06	gas		
235	4.17E-05	gas	2.00E-05	1.94E-06
235	2.52E-05	NH_4^+		3.06E-06
250	1.38E-05	NH_4^+	7.33E-05	
250	8.55E-06	NH_4^+		
250	6.45E-06	ClO_4^-		
270	3.08E-04	NH_4^+	2.33E-04	
290	1.85E-04	NH_4^+	3.33E-04	6.67E-06
310	1.11E-03	NH_4^+	2.19E-03	
330	1.78E-03	NH_4^+	6.79E-03	2.22E-05
330				9.44E-05
350	2.39E-03	NH_4^+	1.60E-02	
350			1.55E-02	
370	1.67E-03	gas	1.43E-02	
370	2.61E-03	gas		
370	2.38E-03	gas		
370	1.33E-03	NH_4^+		
380	3.33E-03	gas		1.28E-04
380	3.70E-03	NH_4^+		
380	5.30E-03	NH_4^+		
380	2.60E-03	ClO_4^-		
385	5.00E-03	NH_4^+		

For solution thermolyses, all analyses were ammonium cation.
Rate constants were determined by linear regression.

TABLE II
AP Arrhenius Parameters

AP Composition Analysis	Temperature Range °C	# Temps.	R^2	Activation Energy		A
				kcal/mol	kJ/mol	sec^{-1}
Neat ion chromat.	235-385*	9	0.90	20.5	85	2.80E+04
Neat gas evolved	215-380	4	0.98	21.2	89	3.43E+04
Neat ion + gas	215-385*	10	0.94	21.3	89	4.81E+04
Neat programmed DSC		6		22.7	95	8.32E+05
5wt% in Methanol **	235-370	8	0.98	34.1	143	1.08E+10
20 wt% in Water **	235-380	4	0.97	18.8	79	1.78E+02

* data at 250°C excluded ** analysis by NH_4^+ chromatography

TABLE III
Rate Constants of AP with Additives (ClOx, HNO_3, NH_3)

Condensed-Phase Thermolyses *

	Temperature °C			
Samples	215°	235°	370°	380°
Neat AP	5.6E-06	1.1E-04	2.6E-03	3.6E-03
@ $NaClO_4$	1.7E-05	1.2E-04	3.5E-03	3.6E-03
@ $NaClO_3$	2.2E-04	2.0E-04	5.0E-03	1.6E-02
@ $NaClO_2$		4.1E-05	3.7E-03	3.6E-03
@ NaCl		5.3E-05	2.1E-03	2.0E-03

Thermolyses:	Aqueous (20wt%) AP **	
Samples	235°C	330°C
Aqueous AP	3.4E-06	2.2E-05
@ $NaClO_4$	2.9E-06	
@ $NaClO_3$	5.6E-06	5.0E-05
@ $NaClO_2$	2.0E-06	
@ NaCl	1.9E-06	

Condensed-Phase Thermolyses

	250°C	380°C
Neat AP	4.0E-06	5.0E-03
@ HNO_3	9.3E-06	8.8E-03
@ NH_3	7.9E-07	2.5E-03

* Rate constants determined graphically from gas evolution data.

** Rate constants determined graphically from ammonium ion remaining.

Table IV

Product Distribution in AP Thermolysis (neat, in MeOH, Water)

	Thermolysis Products of AP									Atomic Balance			
	N_2	N_2O	O_2	Cl_2	NH_4^+	ClO_4^-	ClO_3^-	Cl^-	H_2O*	N	Cl	O	H
		at 250°C for 144 hours											
Neat	0.12	0.43	0.61	0.11	0.10	0.00	0.20	0.60	1.2	1.2	1.0	4	3.5
$NaClO_4$	.074	0.47	0.61	0.14	0.14	0.15		0.20	1.5	1.2	0.6	4	3.8
$NaClO_3$	.079	0.43	0.63	0.28	0.13	0.16		0.15	1.5	1.2	0.9	4	3.8
$NaClO_2$	0.16	0.36	0.52	0.17	0.05	0.14		0.16	1.9	1.1	0.6	4	4.2
NaCl	0.19	0.19	0.55	0.13	0.11	0.15		0.18	2.0	0.9	0.6	4	4.6
	N_2	N_2O	O_2	Cl_2	NH_4^+	ClO_4^-	ClO_3^-	Cl^-	H_2O*	N	Cl	O	H
		at 380°C for 35 minutes											
Neat	0.19	0.31	0.71	0.084	0	0	0.23	0.51	1.1	1.0	0.9	4	2.8
$NaClO_4$	0.23	0.23	0.82	0.22		0.00	.094	0.41	1.4	0.9	0.9	4	3.3
$NaClO_3$	0.20	0.30	0.91	0.20		0.00	.090	0.42	1.2	1.0	0.9	4	2.8
$NaClO_2$	0.21	0.35	0.74	0.22		0.00	0.10	0.38	1.5	1.1	0.9	4	3.4
NaCl	0.22	0.38	0.42	0.086		0.00	.078	0.38	2.2	1.2	0.6	4	4.7

	N_2	N_2O	O_2	Cl_2	NH_4^+	ClO_4^-	ClO_3^-	Cl^-	H_2O*	CO_2	CO
	at 250°C for 9 days										
5% @MeOH	0.55	--	--	--	--	0.00	0.00	0.97		1.8	.11
	at 380°C for 1 hour										
5% @MeOH	0.52	--	--	--	--	0.00	0.00	0.95		1.8	.12
20% @H_2O at 270°C for 14 days											
	0.02	--	--	--	0.94	0.93					
20% @H_2O at 380°C for 60 hour											
	0.11	0.18	0.35	0.15	0.41	0.37	0.00	0.26	1.6*		

* H_2O was not measured; it was calculated to adjust oxygen balance to 4.

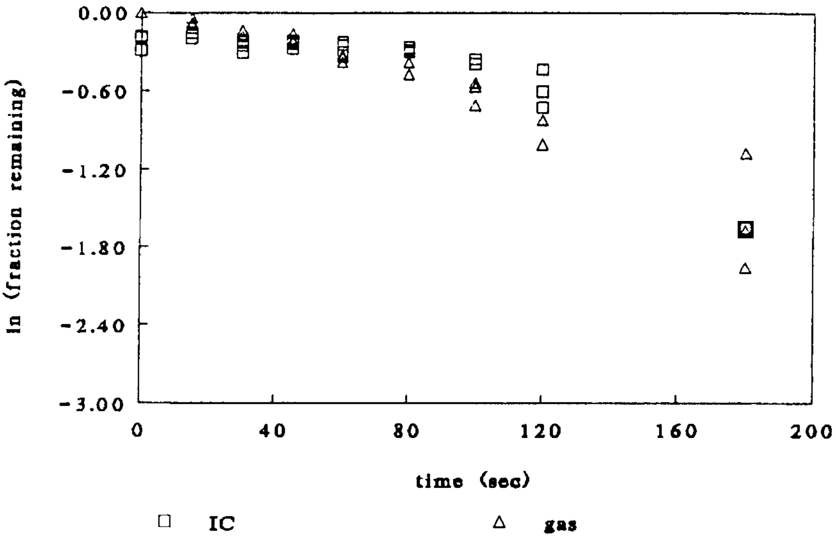

Figure 1: First-order Plot of Ammonium Perchlorate Decomposition at 370°C Monitored by Evolved Gas and By Ammonium Ion Loss.

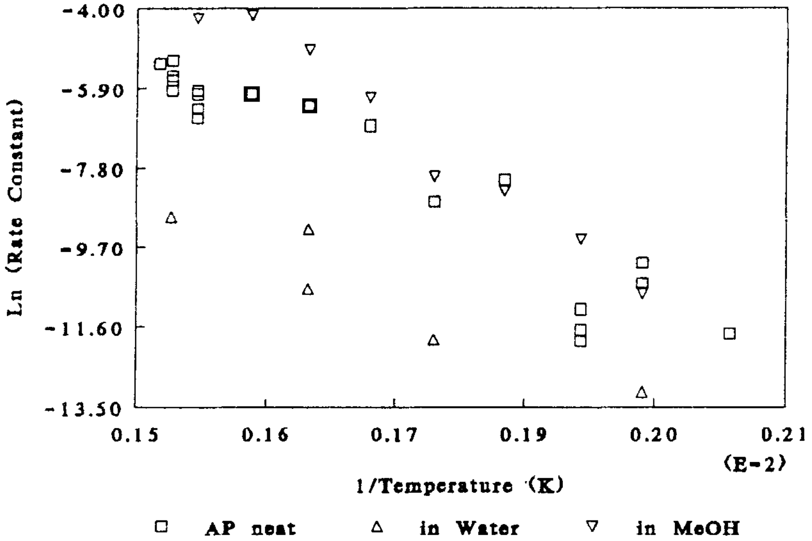

Figure 2: Arrhenius Plot for Ammonium Perchlorate, Neat, in MeOH, in Water

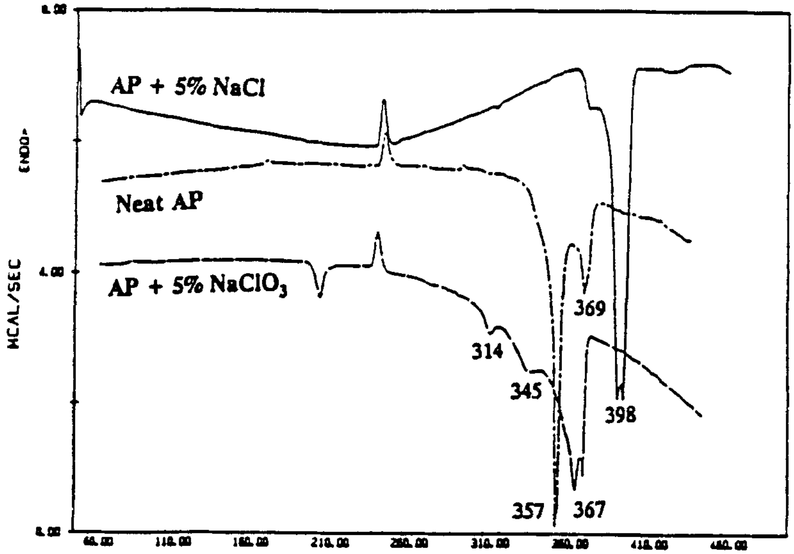

Fig 3. DSC of Ammonium Perchlorate with ClOx Salts

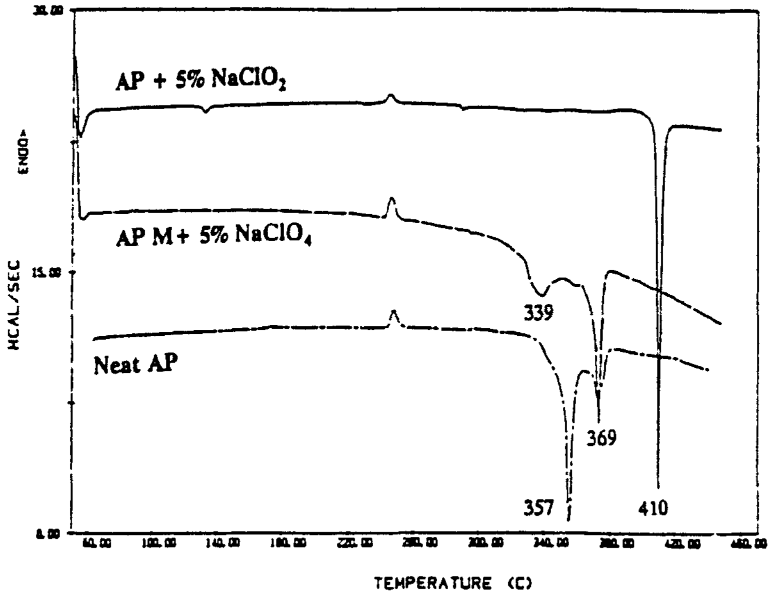

Fig 4. DSC of Ammonium Perchlorate with ClOx Salts