Inhibition of the Thermal Decomposition of Ammonium Nitrate

George H. Madany[1] and George Burnet[2]

As part of a continuing study of nitrogen loss during the drying of mixed fertilizers, the rate of decomposition of NH_4NO_3 at 225° C. was investigated by determining the loss in weight, the composition of the residue, and the change in pH for pure NH_4NO_3 and simple mixtures containing NH_4NO_3. The decomposition rate of pure NH_4NO_3 climbed during the first 2 hours until it was equivalent to a weight loss per hour of about 5.5% of the original sample. The rate then dropped to about 2.5% per hour with a slight increase as the heating period progressed.

The pH of the salt decreased from 5.2 to 3.5 during the first 2 hours of heating and then remained essentially constant. The increase in acidity resulted in a corresponding increase in rate of decomposition. Several amphoteric and basic oxides and salts as well as some neutral salts were added in varying amounts to control pH. The alkali and ammonium bromides and iodides proved to be effective inhibitors in concentrations as low as 0.5%. Mechanisms for the reactions of interest are proposed.

Ammonium nitrate is a relatively stable compound which decomposes at higher temperatures and explodes if heated while confined (Van Dolah et al., 1966). Nitrogen losses which occur during the manufacture of many mixed fertilizers have been traced to the decomposition of ammonium nitrate (TVA, 1959). While this investigation was prompted by the desire to locate additives which would reduce these losses, further understanding of the mechanism of decomposition of ammonium nitrate and factors that influence it were also important objectives.

Pure ammonium nitrate starts to decompose at its melting point of 169.6° C. according to the following main reaction (Saunders, 1922):

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad (1)$$
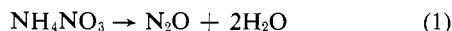
Nitrogen constitutes 2% of the product up to 260° C. and is accompanied by traces of NO, NO_2, O_2 (Kretzschmar, 1934; Rozman, 1960a; Saunders, 1922; Shah and Oza, 1932). Above this temperature the N_2 increases appreciably. The source of nitrogen in the decomposition products according to Saunders (1922) is as follows:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \qquad (2)$$

$$5NH_3 + 3HNO_3 \rightarrow 9H_2O + 4N_2 \qquad (3)$$
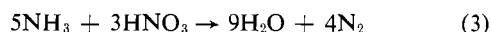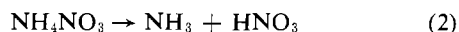
Most investigators are agreed that Reaction 2 is a precursor to Reaction 1. Feick (1954) confirmed that the vapor is completely dissociated according to Reaction 2 between 190° and 270° C. Ammonium nitrate tends to explode when confined and ignited or heated because the heat of decomposition is not absorbed by the endothermic dissociation reaction which is inhibited by the pressure which develops (Sykes et al., 1963).

Delsemme (1950) noted that dry ammonium nitrate explodes at 290° C. while Feick and Hainer (1954) found that the decomposition reaction at 315° C. (2 atm.) was perfectly smooth and regular and the brown color of NO_2 absent. This difference is attributed (Delsemme, 1950)

to water which catalyzes dissociation of the salt. Friedman and Bigeleisen (1950) reported that dry NH_4NO_3 does not decompose up to 300° C. but simply sublimes. On the other hand Rosser et al. (1963) concluded that H_2O inhibits the decomposition of NH_4NO_3. While H_2O promotes the first stage of dissociation, it may possibly inhibit the second stage which consists of the decomposition of HNO_3. An optimum amount of water may be required to act as a positive catalyst.

Kummer (1947) and Friedman and Bigeleisen (1950) have verified by isotopic experiments that the N—N bond in N_2O produced by decomposition of NH_4NO_3 is between a nitrogen from NH_4^+ and another from NO_3^- exclusively. Rozman's (Rozman et al., 1958; Rozman, 1960a, 1961) mechanism for the decomposition of ammonium nitrate consists essentially of three principal stages: hydrolysis of the nitrate with the formation of ammonia and nitric acid; thermal decomposition of nitric acid to form nitrogen dioxide, water, and oxygen; and reaction of nitrogen dioxide with ammonia to form the decomposition products which may vary qualitatively and quantitatively according to the decomposition conditions, primarily the temperature.

The above mechanism was confirmed by Dobychin and Smirnov (1963). Patry et al. (1947) detected hydrazine in the reaction products between ammonia and nitrogen dioxide up to 100° C. This supports Rozman's postulate which suggests transient existence of $NH_2 \cdot$ free radicals in the third stage.

Veley (1883) noted that acidity increased the rate of decomposition. Wood and Wise (1955) found that the rate is proportional to the product of the mass of salt and the concentration of the acid. Inhibition may thus be affected by controlling the acidity of the melt. Rosser et al. (1963) concurred that HNO_3 promotes decomposition, while Rozman et al. (1958) and Dobychin and Smirnov (1963) believe that the real catalysts are nitrogen dioxide and water, which are the products of the decomposition of nitric acid. Tramm and Velde (1934) reported that chloride-free acidic ammonium nitrate did not decompose at 175° C. Guiochon (1960) states that the effect of nitric acid on pure ammonium nitrate in the liquid phase is negligible. He notes that the N_2 formed in the experiments of Wood and Wise probably comes from the gas phase reaction of HNO_3 and NH_3 since sealed ampoules were used.

---

[1] Division of Science, Minot State College, Minot, N.D. 58701.

[2] Chemical Engineering Department, Iowa State University, Ames, Iowa 50010.

Saunders (1922) investigated the effect of addition of NH_4Cl on the decomposition of ammonium nitrate. He noted that when any mixture is raised to a particular temperature, there is first a passive period varying from a few minutes to 1.5 hours, depending on the amount of impurity, temperature, and free acid present. Then follows a rapid but brief rise in temperature and evolution of gas which contains chlorine. The percentage of N_2 in the decomposition gases increases to 52.6% at a temperature of 235° C. Guiochon and Jaque (1957) reported that addition of small quantities of Cl_2 or HNO_3 reduces the induction period from 1 hour to 12 seconds at 190° C. Guiochon (1960) found that ammonium bromide and iodide accelerate the decomposition of the nitrate but cause longer induction periods. When NH_4I and NH_4Cl are added together to the NH_4NO_3, the induction period is nearer to that of the NH_4I but the decomposition rate soon approaches that of the Cl^--catalyzed mixture. When Br^- and Cl^- are mixed, the induction period is nearer to that of the Cl^-. Tramm and Velde (1934) report that Cl^- does not accelerate decomposition in neutral or basic melts, but does so in acidic NH_4NO_3 even at 140° C.

Veley (1883), Wood and Wise (1955), Rosser et al. (1963), and Rozman et al. (1958) all reported that ammonia inhibits the decomposition reaction completely even at elevated temperatures. Rozman and Borodkina (1959, a and b) showed that both urea and urotropine are effective inhibitors. They liberate NH_3 which neutralizes the acid and reacts with NO_2.

The sulfate ion in large amounts has some inhibiting effect below 240° C., but catalyzes the decomposition above that temperature (Robertson, 1948; Saunders, 1922; Shah and Oza, 1932). Zinc oxide (Rozman, 1960b), litharge (Veley, 1883), thoria (Shah and Oza, 1932), sodium metaphosphate and pyrophosphate (Guiochon, 1960) have some inhibiting effect too. When As_2O_5, $CuSO_4$ (Shah and Oza, 1932), CaO, Fe_2O_3, MnO_2, MgO, NiO_2, UO_2, molybidic acid, potassium persulfate, ammonium thiocyanate, or chromium compounds (Guiochon, 1960; Robertson, 1948) were added, decomposition was catalyzed. Guiochon (1960) reports that graphite had little effect, while sulfur burned in NH_4NO_3. Reducing salts such as sulfamate, thiosulfate, thiocyanate, acetate, formate, hypophosphite, ammonium nitrite, and sodium nitrite are oxidized, sometimes explosively, while nonreducing salts have little effect.

INVESTIGATIVE APPROACH AND PROCEDURE

From the review of the literature, the authors concluded that thermal decomposition of ammonium nitrate might best be inhibited by controlling the acidity of the melt through addition of a buffer. A pH range of 5 to 6 was deemed most desirable since a higher value would cause liberation and loss of NH_3. The pH was measured potentiometrically by dissolving 0.01 gram ion weight per 10 ml. of distilled water. This method provides a reliable basis for comparing the concentration of hydrogen ion in various mixtures.

The decomposition runs were conducted by placing 0.5 mole of reagent grade ammonium nitrate in a 250-ml. flask with various amounts of additives. The mixtures were ground thoroughly to effect intimate mixing before

being placed in the flasks which were then immersed in a constant temperature bath for various periods of time. The flasks were weighed before and after the heating period, and the loss in weight was noted. Most tests were conducted at 225° C. which is about the maximum encountered in commercial operations and corresponds closely to that used by previous investigators.

The sample residues were analyzed and the change in acidity was followed by determining the pH. During the early runs, the pH was determined before the sample was heated and at the end of the 8-hour period only. In later runs, intermediate pH values were determined and graphed to show the interrelationship between acidity and rate of decomposition.

RESULTS

Effect of Drying. Figure 1a indicates the cumulative percentage loss and the rate of decomposition in two samples of reagent grade ammonium nitrate when heated at 225° C. for 8 hours. Sample II was predried, while sample I was not predried before heating. Apparently, drying tends to inhibit decomposition. However, since H_2O is one of the by-products of decomposition, the effect of starting with dry salt should vanish as soon as enough water is generated by the decomposition reaction.

A peak appears in each rate curve toward the end of the second hour of heating. The same phenomenon was observed in several succeeding samples. This maximum indicates an autocatalytic effect, and is probably accompanied by a rise in temperature of the melt above its
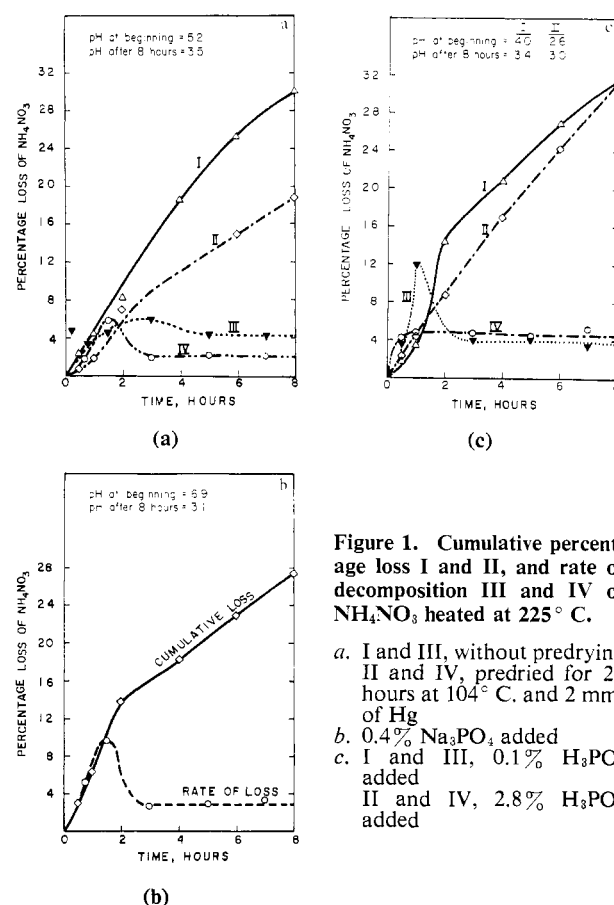

(a)

(c)

(b)

Figure 1. Cumulative percentage loss I and II, and rate of decomposition III and IV of NH_4NO_3 heated at 225° C.

a. I and III, without predrying II and IV, predried for 24 hours at 104° C. and 2 mm. of Hg
b. 0.4% Na_3PO_4 added
c. I and III, 0.1% H_3PO_4 added
II and IV, 2.8% H_3PO_4 added

subsequent equilibrium value. If this is the case, then the amount of melt, the geometry, and thermal characteristics of the container may influence the height and width of this peak.

Effect of Acidity. Figure 1b shows the cumulative and rate of loss of NH_4NO_3 to which 0.4% Na_3PO_4 was added to raise its pH to 6.9. In the process of grinding the sample, the odor of NH_3 was clearly detectable. The salts were dried before mixing for 24 hours at 105° C. then, while still warm, put in a vacuum desiccator at 2 mm. of Hg absolute pressure.

The autocatalytic decomposition rate and the total loss were slightly greater than that of pure ammonium nitrate, and the acidity of the sample at the end of the run was higher. This is contrary to what might be expected for a sample with a 6.9 starting pH. The higher acidity results from the reaction between ammonium nitrate and the trisodium phosphate which causes loss of ammonia and a rise of acidity early in the heating period. The reactions are as follows:

$$Na_3PO_4 + 3NH_4NO_3 \rightarrow (NH_4)_3PO_4 + 3NaNO_3 \quad (4)$$

$$(NH_4)_3PO_4 \rightarrow NH_4H_2PO_4 + 2NH_3 \quad (5)$$
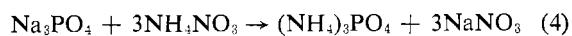
The ammonium dihydrogen phosphate is acidic and thus speeds decomposition of the nitrate. Another sample of the mixture to which water was added showed a higher autocatalytic peak and greater total loss. This is an indication that both H_2O and H^+ are involved in catalysis. Increasing the percentage of Na_3PO_4 or, in other tests, K_3PO_4 from 0.02 to 1.0% led to a corresponding increase in the rate of decomposition.

Figure 1c shows the cumulative loss and the rate of decomposition of $NH_4NO_3-H_3PO_4$ mixtures. Apparently, 0.1% H_3PO_4 speeds the decomposition mainly during the autocatalytic period, while the addition of 2.8% H_3PO_4 nearly eliminates the autocatalytic peak. This means that the autocatalytic reaction takes place at pH which is lower than that of the pure ammonium nitrate melt but higher than a melt where the H^+ concentration has reached equilibrium conditions. Addition of 20 ml. of H_2O to the dry raw samples gave identical results on heating after the water had evaporated.

Figure 2 shows the changes in pH of an NH_4NO_3 sample containing 9.5% $Na_3PO_4 \cdot 12H_2O$ as it is heated at 225° C. for 8 hours. The second curve describes a sample containing 9.5% concentrated H_3PO_4. Both curves meet at pH = 2.7. At higher pH values, NH_3 is liberated as described by Equations 4 and 5 and the pH value falls. At a pH lower than 2.7, the ammonia is stabilized by the hydrogen ion, while nitric acid decomposes.

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (6)$$
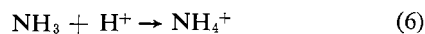
Apparently at a pH of 2.7, the rate of decomposition of the NO_3^- is equal to the rate of the decomposition of NH_4^+. The curves depart from each other after the fourth hour of heating and curve in the direction of their original pH. This happens because, as the NH_4NO_3 is depleted by decomposition, the original additives—i.e., Na_3PO_4 and H_3PO_4—tend to be regenerated and their effect starts to be impressed on the pH again.
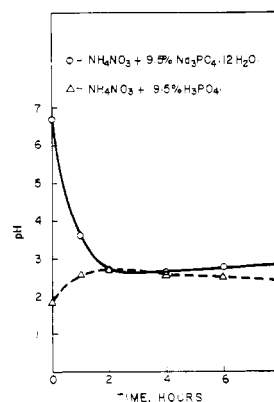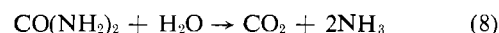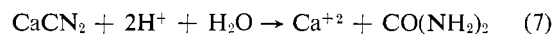

Figure 2. Changes in pH of $NH_4NO_3-Na_3PO_4 \cdot 12H_2O$ and $NH_4NO_3-H_3PO_4$ heated at 225° C.

Effect of Salts Other than Halides. The authors reasoned that calcium cyanamide should be a good negative catalyst because it has a great affinity for water and acids. Probable reactions with urea as an intermediate would be as follows:

$$CaCN_2 + 2H^+ + H_2O \rightarrow Ca^{+2} + CO(NH_2)_2 \quad (7)$$

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \quad (8)$$

Urea has been shown to be a good inhibitor, so it was logical to expect that calcium cyanamide should be as good as urea if not better. However, 1% $CaCN_2$ in NH_4NO_3 resulted in poorer stability characteristics than NH_4NO_3 alone after the first 2 hours. The odor of ammonia was readily apparent upon mixing the cyanamide and the ammonium nitrate. A corresponding sample with water added to it had identical decomposition rate curves. A 10% $CaCN_2$ in NH_4NO_3 sample, to which water was added, showed appreciable inhibition, cutting the nitrogen losses by 50% over those of pure NH_4NO_3. Significant amounts of ammonia were lost very early in the heating period owing to the high pH.

One per cent Calgon [sodium metaphosphate $(NaPO_3)_n$, where n can be as high as 1000] raised the initial pH to 6.0 but had a negligible inhibition effect; 10% Calgon decreased the decomposition 15% compared with pure NH_4NO_3. Ten per cent Calgon and 20% $CaSO_4$ decreased the decomposition by 40% and eliminated the autocatalytic period.

Effect of Some Metallic Oxides. Amphoteric or slightly basic oxides were expected to show inhibition. The contrary proved to be the case, however, as they catalyzed the hydrolysis step in the decomposition of NH_4NO_3 and thus acted as positive catalysts.

Ten per cent anhydrous Fe_2O_3 had a mild inhibiting effect, while a similar percentage of hydrated ferric oxide had a strong positive catalytic effect. When traces of $FeCl_3$ were present in the hydrated oxide the decomposition approached an explosive rate at 225° C.

Ten per cent BeO raised the pH to a constant level of 6; but owing to side reactions, the inhibiting effect was not pronounced. One per cent BeO had a similar but correspondingly weaker action.

Addition of As_2O_3 lowered the pH and increased the decomposition rate. Arsenic pentoxide was more acidic and was an even stronger positive catalyst.

Effect of Halide Salts. When hydrated KF was mixed

with ammonium nitrate, decomposition started at room temperature and went very rapidly to completion at higher temperatures. The reaction is the following:

$$NH_4NO_3 + KF \rightarrow KNO_3 + NH_3 + HF \qquad (9)$$
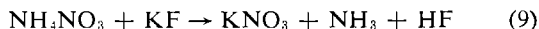
NH_4NO_3 and KCl mixed in a 1 to 1 mole ratio seemed to be sensitive to the history of the sample preparation. The pH of the mixture was usually high (around 5.5). A sample dried at 105° C. for 8 hours and then heated at 225° C. had a very pronounced autocatalytic period where the rate of decomposition reached 55% per hour accompanied by a sharp drop in pH to a value of 3.5. This was followed by a period during which there was a rise in pH and the decomposition rate was only 2%. A similar sample that was dissolved in water and only partially taken to dryness before being put in the heating bath showed no autocatalytic period and the pH remained constant at 5.5. The loss of ammoniacal nitrogen was in all cases higher than that of nitrate nitrogen.

A 1 to 1 mole ratio of NH_4NO_3-KBr heated at 225° C. without predrying had a cumulative weight loss of only 7% after 8 hours. Its pH was 6.0 throughout the heating period, and no significant autocatalytic peak was present in its rate of decomposition. A similar mixture that had been predried for 48 hours at 105° C. and 0.1 mm. of Hg lost only 1.7% of its weight after 8 hours of heating (Figure 3a). No inhibitor that approaches this effectiveness has been previously reported. The bromide appears definitely to inhibit decomposition and not only to lengthen the induction period as Guiochon (1960) reported. As free bromine was liberated early in the heating period, the induction period should have been correspondingly short.

When KI is mixed with NH_4NO_3, the iodide ion is slowly liberated as free iodine even at room temperature. In the process of its oxidation, it inhibits the decomposition of ammonium nitrate, raises its pH, and is even more effective than the bromide. When an equimolecular mixture of NH_4NO_3 and KI was heated for 8 hours at 225° C. without being predried, the total loss was 5.2% only, and the pH remained at a steady 5.3.

Figure 3b shows the results obtained when NH_4NO_3 with 2% NH_4I added was heated at 225° C. without being predried. No autocatalytic peak materializes, but, as the I^- is oxidized and depleted, the pH starts to drop and the rate of decomposition climbs correspondingly. When the amount of NH_4I was decreased to 0.5%, the period of active inhibition lasted for a proportionally shorter time and an autocatalytic peak appeared at the third hour of heating. In another test at 180° C., 0.5% NH_4I maintained the pH of the melt slightly over 5 for 8 hours, while a total loss in weight of only 0.7% occurred. The losses when 2% NH_4I was added at 180° C. were a little more than one half those when 0.5% ammonium iodide was added.

Also at 180° C., 0.5% NH_4Cl showed a strong positive catalytic effect as is seen in Figure 3c. There is a steady fall in the pH during the first 2 hours of heating. When the pH reaches 3.5, autocatalysis sets in. The pH then continues down to 2.7 where it holds steady during the time the reaction rate drops off. The total loss in 8 hours was 34% compared with 0.6% for pure NH_4NO_3.
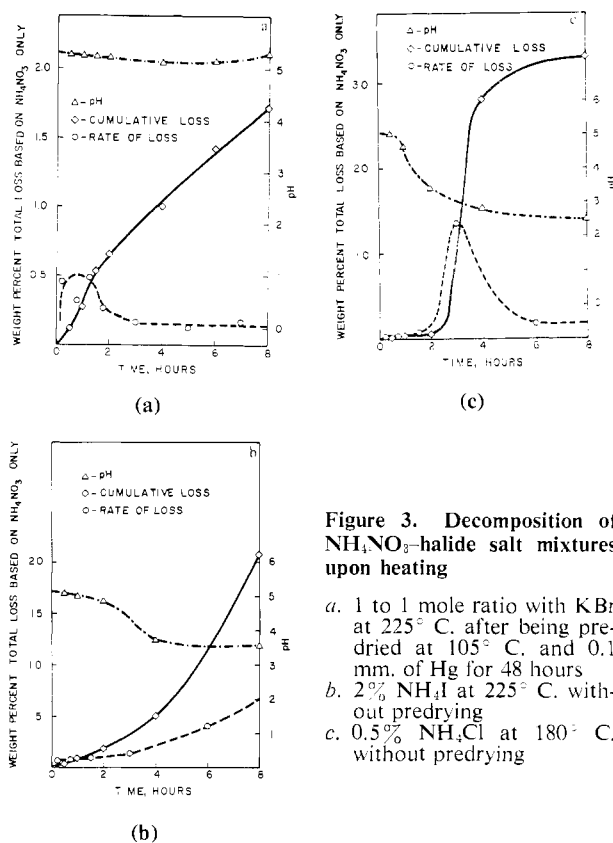

(a)

(c)

(b)

Figure 3. Decomposition of NH_4NO_3-halide salt mixtures upon heating

a. 1 to 1 mole ratio with KBr at 225° C. after being predried at 105° C. and 0.1 mm. of Hg for 48 hours
b. 2% NH_4I at 225° C. without predrying
c. 0.5% NH_4Cl at 180° C. without predrying

When 0.5% NH_4Cl and 0.5% NH_4I were simultaneously added to NH_4NO_3 and the mixture was heated at 180° C. for 8 hours, loss was nearly double that observed when iodide alone was added, but only 4.5% of that with the chloride alone. Therefore, the iodide has a strong inhibiting effect on ammonium nitrate which contains chloride ion. The pH of the mixture remains at a steady value of 5.0 throughout the run.

When this test was repeated with the NH_4I replaced by NH_4Br, the total loss was five times that when iodide alone was used. The increase in rate of loss paralleled the drop in pH. Analysis showed that some bromide remained in the residue at the end of the run.

In all runs reported thus far, the gases produced in the flasks during heating were allowed to leave freely. An interesting result was observed in a special series of runs where each flask was equipped with a small air-cooled condenser. When NH_4NO_3 to which 2% NH_4I had been added was heated in these flasks, moisture and iodine were trapped in the condensers and returned (refluxed) to the flasks. This resulted in the concentration of iodine remaining high in the flasks which in turn increased the overall inhibiting effect (Table I).

In other tests, thioacetamide did not inhibit decomposition when added at a 2% level followed by heating at 225° C. but did have some inhibiting effect at a 0.5% level when heated at either 180° or 225° C. Mixtures of materials which individually acted as inhibitors were tried. A mixture of 0.25% each of thioacetamide, ammonium bromide, and urea proved ineffective as an inhibitor at 180° and 225° C. Ammonium bromide and urea, and ammonium bromide, ammonium iodide, and

Table I. Cumulative Percentage Loss of Weight during Heating at 225° C.

Heating Time, Hr.	Percentage Weight Loss		
	Pure NH₄NO₃	2% NH₄I, open flask	2% NH₄I, with reflux
0.5	2.0	0.3	0.2
1.0	4.2	0.7	0.4
2.0	8.3	2.0	0.7
4.0	18.3	5.0	1.2
6.0	25.5	11.0	1.7
8.0	29.5	20.8	2.0

Table II. Effect of Acetamide on Decomposition

Weight % of CH₃CONH₂ Added	Loss, Weight % NH₄NO₃ Present, upon Heating at 225° C. for 8 Hr., No Predrying
None	30
0.3	18
0.5	15
1.0	12
1.5	10
2.0	10

urea mixtures showed less effect than the individual components and not a cumulative effect at 180° and 225° C. More inhibition was observed at the lower temperature. These tests raise the question as to whether or not urea is an effective inhibitor to thermal decomposition of NH_4NO_3 when halides are an impurity and whether or not the bromides and iodides will be less effective inhibitors when organic compounds are also mixed with the ammonium nitrate.

Acetamide alone proved to be a fairly good inhibitor at 225° C. when added in various percentages to ammonium nitrate (Table II).

It is of interest to speculate about the mechanism through which Br^- and I^- act as inhibitors. The chief chemical difference between Cl, Br, and I is the decrease in their electronegativity as the size of the atom gets larger. Therefore, the ease of oxidation increases from the chloride to the iodide ion. Rozman (1961) and Keenan and Dimitriodes (1962) postulate that the chloride ion acts as a catalyst by being oxidized to Cl by the nitrosonium ion NO^+ and nitrite ion NO_2^- that are intermediates in the decomposition of ammonium nitrate. The Cl abstracts hydrogen from NH_3 or NH_4^+ to become HCl, according to the following reactions.
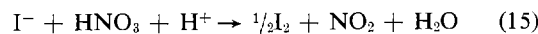
$$NO^+ + Cl^- \rightarrow NO + Cl \tag{10}$$

$$NH_3 + Cl \rightarrow NH_2\cdot + HCl \tag{11}$$
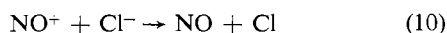
Thus Cl acts as an activating agent by attacking NH_3, and contributes to an increase in H^+ that also catalyzes the decomposition.

The I^- raises the pH of ammonium nitrate by the following possible mechanism.

$$HNO_3 \rightarrow NO_2 + \cdot OH \tag{12}$$

$$I^- + \cdot OH \rightarrow I + OH^- \tag{13}$$

$$OH^- + H^+ \rightarrow H_2O \tag{14}$$
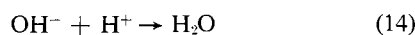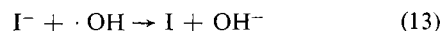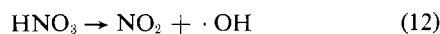
The sum of the above reactions is

$$I^- + HNO_3 + H^+ \rightarrow \frac{1}{2}I_2 + NO_2 + H_2O \tag{15}$$

Reaction 12 has been confirmed by Johnston et al. (1951, 1953) as the first step in the thermal decomposition of nitric acid. Iodine's ability to abstract hydrogen from NH_3 is appreciably weaker than that of Cl. Bromine's characteristics are intermediate between those of chlorine and iodine.

The fact that I^- inhibits the decomposition of NH_4NO_3

in the presence of Cl^- may be explained through the observation that the induction period, when Cl^- is present, can be terminated within a few seconds when a small amount of Cl_2 or acid is injected into the hot sample. This means that either an acid or a certain amount of Cl_2 must accumulate in the sample before Cl^- starts its cycle of positive catalysis. Since I^- raises the pH of the sample, the accumulation of acid is prevented. The accumulation of Cl_2 is also prevented by the following reaction.

$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2 \tag{16}$$
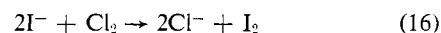
Thus both avenues are blocked and the Cl^- ceases to be an effective positive catalyst.

CONCLUSIONS

Losses from NH_4NO_3 due to heating can be reduced by first drying the salt, which nearly eliminates autocatalysis, or by adding an inhibitor to control pH. Whether initially on the alkaline or acid side, NH_4NO_3 reaches a pH of 2.7 upon heating at 225° C. All effective inhibitors raise the pH to about 5.3.

Certain bromide and iodide salts are effective inhibitors at concentrations as low as 0.5%. They reduce the H^+ concentration and control decomposition until the halide ions are oxidized to free Br_2 or I_2. The fact that chloride salts catalyze the decomposition of NH_4NO_3 upon heating was confirmed, but this effect can be neutralized by adding compounds which provide either bromide or iodide ions. The latter are less effective in the presence of urea or thioacetamide. An inhibiting effect comparable with that already known to exist for urea alone is obtained with acetamide.

LITERATURE CITED

Delsemme, A. H., Compt. Rend. 230, 1858 (1950).
Dobychin, S. L., Smirnov, V. M., Zh. Prikl. Khim. 36, 215 (1963).
Feick, G., J. Am. Chem. Soc. 76, 5858 (1954).
Feick, G., Hainer, R. M., J. Am. Chem. Soc. 76, 5860 (1954).
Friedman, L., Bigeleisen, J., J. Chem. Phys. 18, 1325 (1950).
Guiochon, G., Ann. Chim. (Paris) (13) 5, 295 (1960).
Guiochon, G., Jacque, L., Compt. Rend. 244, 1927 (1957).
Johnston, H. S., Foering, L., Tao, Y., Messerly, G. H., J. Am. Chem. Soc. 73, 2319 (1951).
Johnston, H. S., Froering, L., Thompson, R. J., J. Phys. Chem. 57, 390 (1953).
Keenan, A. G., Dimitriodes, B., J. Chem. Phys. 37, 1583 (1962).
Kretzschmar, W., Z. Anorg. Allgem. Chem. 219, 17 (1934).
Kummer, J. T., J. Am. Chem. Soc. 69, 2559 (1947).
Patry, M., Garlet, R., Pupko, S., Compt. Rend. 225, 941 (1947).

Robertson, A. J. B., *J. Soc. Chem. Ind.* **67**, 221 (1948).

Rosser, W. A., Inami, S. H., Wise, H., *J. Phys. Chem.* **67**, 1753 (1963).

Rozman, B. Yu., *J. Appl. Chem. USSR* **33**, 1048 (1960a).

Rozman, B. Yu., *Zh. Prikl. Khim.* **33**, 1258 (1960b).

Rozman, B. Yu., *J. Inorg. Chem. USSR* **6**, 399 (1961).

Rozman, B. Yu., Borodkina, L. I., *Zh. Prikl. Khim.* **32**, 271 (1959a).

Rozman, B. Yu., Borodkina, L. I., *Zh. Prikl. Khim.* **32**, 2585 (1959b).

Rozman, B. Yu., Sivoladshi, E. A., Davydov, Y. A., Bystrov, A. N., *Zh. Prikl. Khim.* **31**, 1101 (1958).

Saunders, H. L., *J. Chem. Soc.* **1922**, pp. 121, 698.

Shah, M. S., Oza, T. M., *J. Chem. Soc.* **1932**, p. 725.

Sykes, W. G., Johnson, R. H., Hainer, R. M., *Chem. Eng. Progr.* **59**, 66 (1963).

Tennessee Valley Authority, *Farm Chem.* **122**, 24–8 (July 1959).

Tramm, H., Velde, H., *Angew. Chem.* **47**, 782 (1934).

Van Dolah, R. W., Mason, C. M., Perzak, F. J. P., Hay, J. E., Forshey, D. R., *U. S. Bur. Mines, Rept. Invest.* No. **6773** (1966).

Veley, V. H., *J. Chem. Soc.* **43**, 370 (1883).

Wood, B. J., Wise, H., *J. Chem. Phys.* **23**, 693 (1955).