

THERMAL DECOMPOSITION OF MONOMETHYLAMINE NITRATE

Yael Miron

Pittsburgh Mining and Safety Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, PA (U.S.A.)

(Received May 13, 1979; accepted in revised form November 2, 1979)

Summary

Experimental thermal analysis and mass spectrometric results indicate that, when heated, monomethylamine nitrate dissociates to form monomethylamine and nitric acid, which then react further or decompose to form other varied compounds, including nitrogen oxides and nitrous acid. Reaction products of nitrous acid and methylamine — such as nitromethane, which has an m/e value of 61 — are suggested in the mass spectra fragmentation profiles. A trace of hydrazoic acid was also recorded.

Monomethylamine, one of the dissociation products, is a flammable gas. In dry air, at room temperature, its lower limit of flammability is 4.9%. Its autoignition temperature is 430°C; the experimental results suggest that in the presence of other decomposition products, most probably nitrogen dioxide, the autoignition temperature is lowered to 300°C or less. Small amounts of iron oxide — especially if in the form of rust — act as a catalyst, accelerate dissociation, and may possibly initiate another decomposition path. Copper powder is also a very efficient decomposition catalyst.

Preventing acid build-up and rust formation is important for the safe handling and transport of monomethylamine nitrate.

Introduction

Nitrate salts — such as ammonium nitrate (AN), sodium nitrate (SN), and hydrazine nitrate (HN) — are used extensively as propellant and explosive ingredients, both as fuel and oxidant. For these reasons, their decomposition and combustion modes, under various conditions, have been studied in detail.

Another such salt is monomethylamine nitrate (MMAN). During World War II, it was used as an ingredient for bomb and shell loading. Now it is used as a component in some commercial water gel formulations. Knowledge of its dissociation and/or decomposition mode would be desirable, but none was found in the open literature.

MMAN decomposition was observed via differential scanning calorimetry, thermogravimetric analysis, and mass spectrometry. The effect of small amounts of iron oxide, rust, and copper on MMAN decomposition was also assessed. These compounds have shown catalytic activity in the decomposition of ammonium and hydrazine nitrates.

Experimental work

Reagents

MMAN — a white, crystalline, highly hygroscopic salt — was available as an aqueous slurry (Bureau key No. L-1482; supplied by E.I. du Pont de Nemours & Company, Inc., Falling Waters, West Virginia). It was recovered from the slurry by filtration, washed with alcohol, and vacuum-dried. Dried samples were kept in a dessicator. Additional oven drying, at 70–80°C, was done as desired. In spite of attempts to keep samples dry, most of them picked up some moisture during transfer and preparation. Unless otherwise specified, samples designated dry are only nominally dry. Both dry and wet crystals were used in the tests; when wet, the crystals were removed directly from the slurry, excess liquid was drained off, and the drained crystals were surface-dried with tissue paper.

Reagent-grade red anhydrous ferric oxide powder (Baker's Analyzed; Lot No.92041) was used in the tests in which the catalytic activity of iron oxide was evaluated. Rust was obtained from various surfaces in the laboratory and the office.

Paint-grade fine copper powder* was utilized in tests in which the catalytic activity of copper was evaluated.

Instruments

A differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA), Du Pont model 990 instruments, were used in thermal analysis tests. Aluminum sample pans and covers were employed in the DSC tests; the covers were hand-pressed into the pans. A platinum pan was used in the TGA tests. In the TGA tests, the thermocouple, positioned just above the sample, measured events in the gas phase. Various heating rates were used in both thermal instruments. The starting atmosphere was static air in the DSC tests; slowly flowing air was used in the TGA tests. During the tests, the gaseous decomposition products generated by the samples altered the atmosphere in both the DSC cell and the TGA tests. In several of the TGA tests, the end opening of the oven was constricted to slow down the outflow of gaseous products.

The mass spectrometer used was a Consolidated Engineering Corp. model 21-103 instrument; it is a single-focussing, magnetic deflection type. MMAN samples were contained in a 120-cc round-bottom glass flask, which was directly connected to the mass spectrometer inlet valve. Following evacuation, the container was heated with a heating mantle. The temperature of the sample was monitored with a Chromel-Alumel thermocouple placed inside a sealed thin-walled glass well, positioned directly above the sample. The response rate of the thermocouple for the experimental conditions was premonitored and found adequate.

* A product of United States Bronze Powders, Inc. Grade: Copper 8000, Lot No. FO-1318-73. (Reference to specific brands in this report is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.)

This mass spectrometer is used routinely in the analysis of hydrocarbons. To measure blends of nitrogen oxides or of nitric acid and its decomposition products with a high degree of accuracy, the instrument requires conditioning with nitrogen oxides; however, the accuracy is sufficient for our purpose without this conditioning. A few of the decomposition products of MMAN are hydrocarbon amines themselves, and their presence might nullify any pretreatment.

Experimental results of thermal analysis

DSC

When crystalline MMAN, contained in a covered sample pan, is heated in the DSC at $10^{\circ}\text{C}/\text{min}$, a solid-phase transition takes place between 78°C and 85°C . A second peak usually follows at around 110 – 112°C , although a few were recorded at temperatures as low as 98°C . Sample position, size, and other geometrical factors affect peak temperatures. The reported melting temperature of MMAN is 100 – 112°C . [1]. These two phase changes are endothermic.

A typical thermogram for dry crystals is presented in Fig. 1. In a few thermograms, the second endotherm is missing, as it is in Fig. 2. The samples giving rise to these latter thermograms were kept in a heated oven up to the start of the DSC test. They were also prepared in the oven (loading into sample pan, etc.) in an attempt to minimize water adsorption. Thus, the second endotherm at 110°C may be due to the desorption of water with concurrent dissolution of MMAN in its desorbed water, which is almost always present in the hygroscopic MMAN crystals if exposed to the ambient air even for a very short time. Verifying this observation would require hot-stage microscopy, or quantitative calorimetry to measure heat of melting and heat of solution of MMAN in water. The variation in the ratio of lengths (or areas) of the first two endothermic peaks from thermogram to thermogram — which would be constant if the second peak were due only to heat of melting — also suggests a relationship to amount of adsorbed water, which differs from sample to sample. If this is the case, then the melting point of dry MMAN remains unknown.

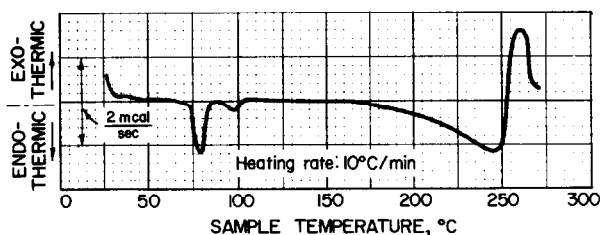


Fig. 1. MMAN crystals, dry; Differential Scanning Calorimeter thermogram for dry MMAN crystals.

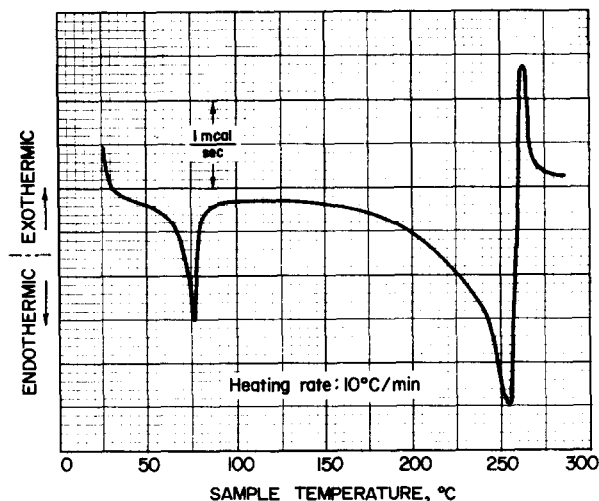


Fig.2. MMAN crystals, dry; sample was prepared in the oven to avoid moisture pickup. Differential Scanning Calorimeter thermogram for dry MMAN crystals.

A large endotherm, indicative of dissociation, starts at about 150°C. An exotherm occurs immediately after the maximum rate of dissociation is attained at about 250°C; this is probably due to reaction of monomethylamine with oxygen (air) as well as to reactions between gaseous products, and possibly to reactions between gaseous products and residual condensed material. Of course, it is impossible to tell from the DSC thermograms by themselves exactly when endothermic behavior ends and exothermic behaviour begins, or if the two processes occur simultaneously. In some DSC tests, the sample was larger and the exothermic reaction was energetic enough to propel the sealed sample pan onto the cover of the DSC oven, where it adhered. This is evident in the shape of the exothermic risetime of Fig.3.

All three compounds that were tested for catalytic activity enhanced MMAN decomposition, as is observed in the DSC thermograms. The effect of copper powder on drained, pat-dried crystals can be seen in Fig.4, whereas the results of adding small amounts of ferric oxide to dry MMAN crystals are shown in Figs. 5 and 6. Fig. 7 shows the consequent decomposition of dry MMAN containing a small amount of rust powder. The source of the rust did not affect the results. The propellant-like activity described above, which was dependent on sample size, was much more pronounced in the presence of the additives. Even more dramatic was the effect of rust on a moist crystal of MMAN. The crystal was removed from the aqueous slurry of MMAN, drained of excess liquid, and pat-dried just before the test. A fast, sharp increase in temperature denotes an ignition, as recorded in Fig.8.

In the presence of copper or rust, the endothermic dissociation does not take place at all; instead, a very fast exothermic event starts at about 160°C and 190°C, respectively. When small amounts of iron oxide are present, some

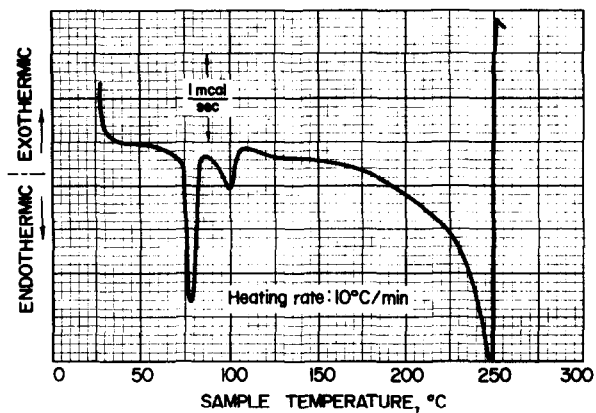


Fig. 3. MMAN crystals, dry; Differential Scanning Calorimeter thermogram for dry MMAN crystals.

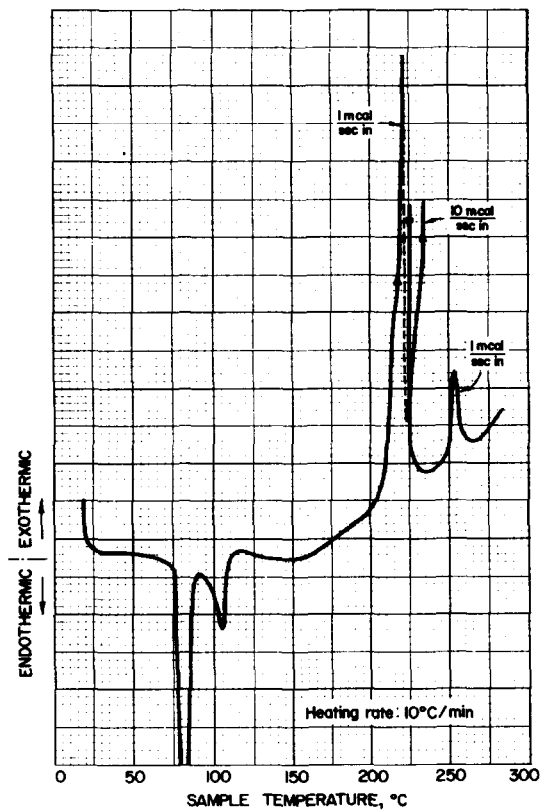


Fig. 4. Differential Scanning Calorimeter thermogram of wet MMAN crystals (drained and pat-dried) containing fine copper powder.

endothermic dissociation does occur, which then gives place to a fast exotherm at about 265°C. Endothermic peaks above 200°C can be seen in Figs. 5–8. For samples containing ferric oxide these peaks are at 265°C and 244°C (Figs. 5 and 6, respectively); for samples containing rust they are at 226°C and 214°C (Figs. 7 and 8, respectively). The causes for these endothermic peaks could be various. Based on past DSC results with other materials, they could be due to:

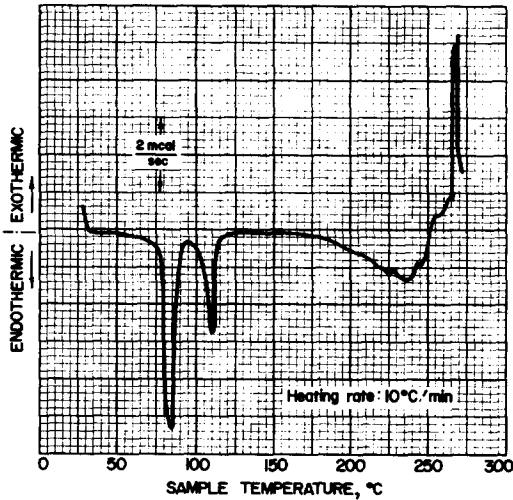


Fig. 5. Differential Scanning Calorimeter thermogram of dry MMAN crystals containing Fe_2O_3 powder.

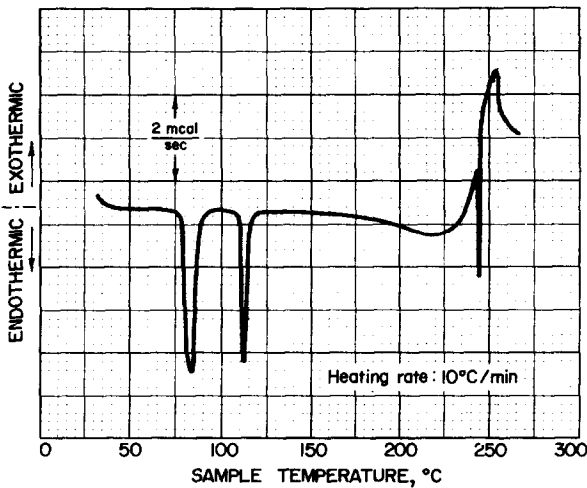


Fig. 6. Differential Scanning Calorimeter thermogram of dry MMAN crystals plus Fe_2O_3 powder.

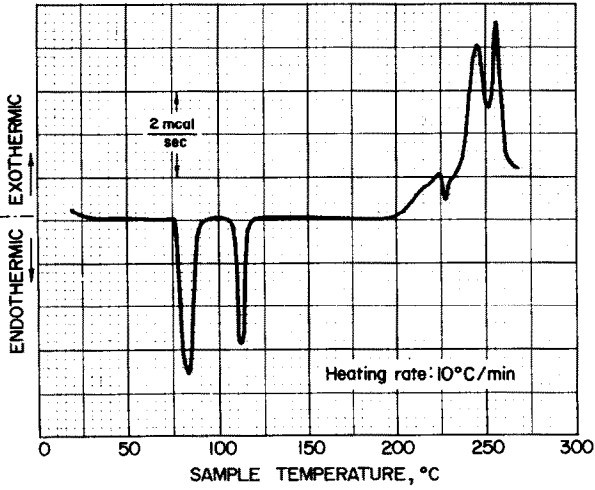


Fig.7. Differential Scanning Calorimeter thermogram of dry MMAN crystals plus rust powder.

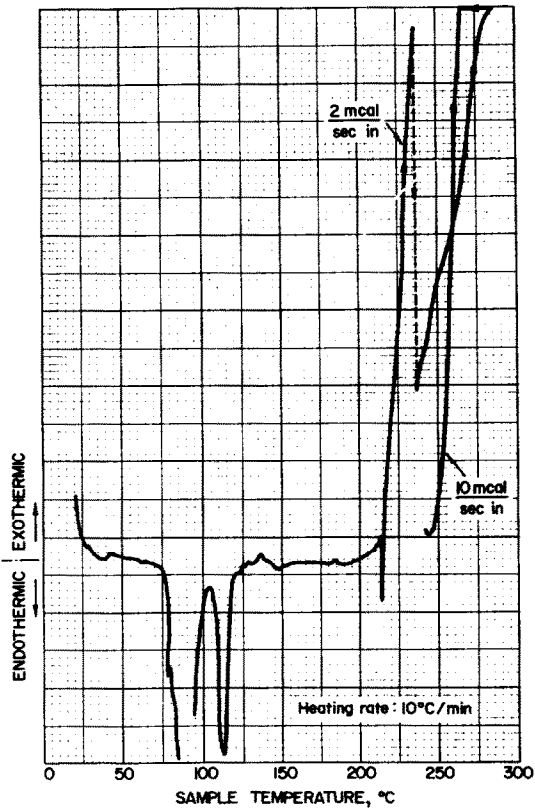


Fig.8. Differential Scanning Calorimeter thermogram of wet MMAN crystals (drained and pat-dried) plus rust powder.

(a) Fast release of vapor that has accumulated in the closed sample pan by popping off of the sample pan cover. This happened in the test whose results are shown in Fig.8.

(b) Propelling of the sample pan away from the DSC base to the inner silver cover of the DSC oven and back to the DSC base platform. This happened in the test depicted in Fig. 6.

(c) A reaction of a very small amount of iron oxide with hot nitric acid to form either ferrous or ferric nitrate. This reaction, depending on the salt formed and its degree of hydration, can be essentially thermally neutral. The size of the endothermic peak in Figs. 5 and 7 is indeed small.

Another common phenomenon, seen in Figs. 4, 6 and 7, is the presence of two close exothermic peaks in the vicinity of 250°C. These peaks suggest consecutive reactions and could be due to reactions between gaseous products and/or between gaseous products and residual condensed material.

The sharp increases in temperature in Figs. 4 and 8 required an immediate change in the sensitivity settings of the DSC. The concurrent change in pen position of the recorder is shown by the dashed lines.

The acidity of small samples of MMAN — heated in the DSC in both open and covered sample pans — was checked with pH paper* immediately after they reached 120°C and 150°C; pH values were 4 and 2, respectively, indicative of acid formation

TGA

MMAN decomposition was also observed in the TGA. Complete results are given in Table 1. Some water loss was recorded in almost all of the samples. Weight loss was recorded continuously so that it was not possible to distinguish where water loss ended and MMAN dissociation started. Fig.9 represents test results in which ignition did not take place, whereas Figs. 10 and 11 show results in which it did, at about 300°C. A sharp temperature rise, due to ignition, is seen in Fig. 10. In Fig. 11, the rise in temperature is not as pronounced. Fig.12 is at most a borderline case, not an ignition. The dashed lines in Fig.10 show recorder pen movement due to changes in sensitivity settings. The turbulence caused by the ignition has led to momentary vibrations of sample pan and thermocouple. Calculated fuel-lean-limit flame temperatures for monomethylamine and air are 1470°C [2]. This large jump in temperature, though of short duration, upsets the preset heating rate. As a result of the combined vibrations and temperature fluctuations, the portions of the thermograms past the ignition temperature jump in Figs. 10 and 11 are "wild" and should be discounted.

In many of the tests, the end opening of the TGA oven tube was constricted so as to retain some of the gaseous reaction products, but during periods of high weight loss rate, product escaped through the end opening in the form of white vapor.

*Alkacid tester. Fisher Scientific Corporation. Range pH 2—pH 10. The paper indicates the approximate hydrogen ion concentration; good to ± 1 pH.

TABLE 1
TGA ANALYSIS OF MMAN DECOMPOSITION^a

Test No.	Initial weight of MMAN (mg)	Max. wt. loss (mg/min)	Specific wt. loss rate (min ⁻¹)	Temp. at max. wt. loss rate (°C)	Heating rate (°C/min)	MMAN crystals	TGA tube exit	Comments
1	7.20	3.09	0.43	251	10	dry ^b	open	
2	10.92	5.28	0.48	254	10	dry	open	
3	5.66	2.25	0.40	260	10	dry	constricted	
4	5.76	4.00	0.69	271	10	dry	constricted	
5	8.55	3.62	0.42	266	10	dry	constricted	
6	6.64	2.09	0.32	257	10	dry	constricted	Fe ₂ O ₃ powder added; 1.0 mg
7	17.20				10	wet ^c	constricted	Wild behavior throughout
8	6.34	2.21	0.35	260	10	wet	not recorded	
9	6.12	10.8	1.76	296	50	dry	constricted	
10	7.78	15.2	1.95	305	50	dry	constricted	
11	5.58	8.76	1.57	290	50	wet	constricted	see Fig. 9
12	6.42	7.20	1.12	300	50	wet	constricted	
13	6.46	9.70	1.50	300	50	wet	constricted	
14	7.30	13.2	1.81	300	50	wet	constricted	
15	8.70	14.8	1.70	297	50	wet	constricted	
16	14.60	>20.0	>1.37	333	50	wet	constricted	
17	16.04	28.7	1.79	338	50	wet	constricted	
18	9.60	18.0	1.88	300	50	wet	open	Fe ₂ O ₃ powder added; see Fig. 12
19	8.16	19.5	2.39	297	50	wet	open	Rust powder added; 0.46 mg; see Fig. 11d
20	6.40	>20.0	>3.13	313	50	dry	open	Rust powder added; 0.48 mg
21	7.36	>20.0	>2.72	292	50	wet	constricted	See Fig. 10
22	9.98	1.96	0.20	235	5	not recorded	constricted	Rust powder added; 0.96 mg

^a The atmosphere in all the tests was of slowly flowing air.

^b Dry crystals usually contain a small amount of adsorbed water.

^c Wet crystals were obtained from slurries of 86% MMAN in water. excess liquid was drained, and crystals were pat-dried.

^d Rust scraped from various surfaces in laboratory.

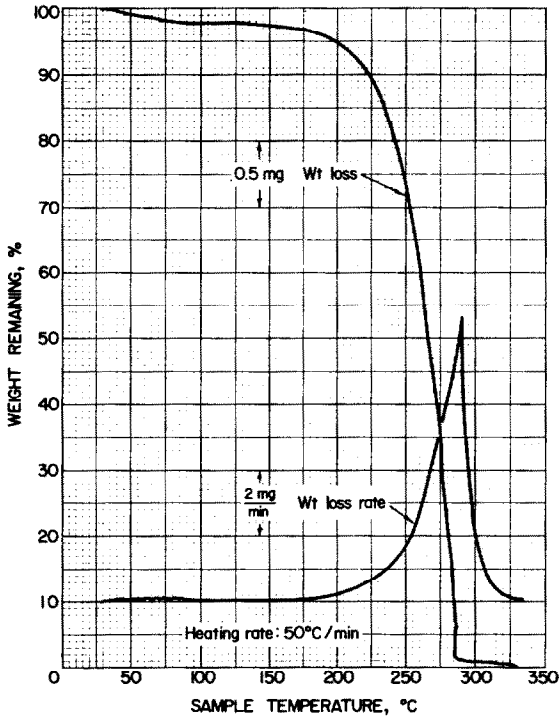


Fig.9. TGA thermogram of a wet MMAN crystal (drained and pat-dried).

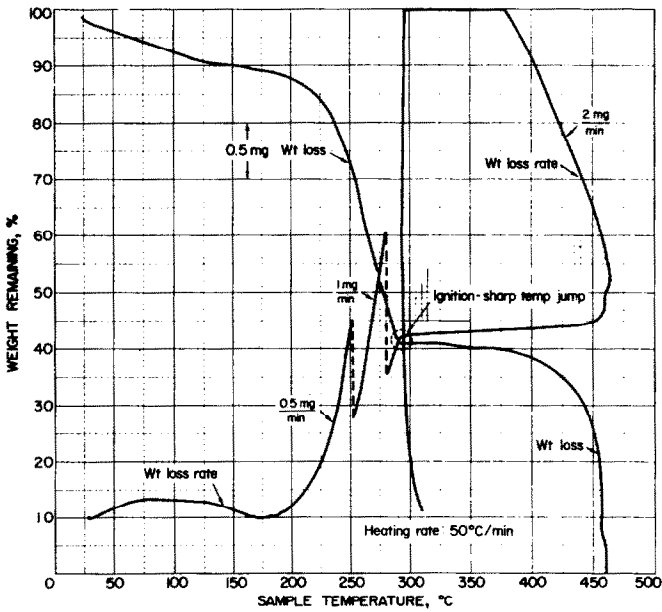


Fig.10. TGA thermogram of wet MMAN crystals (drained and pat-dried).

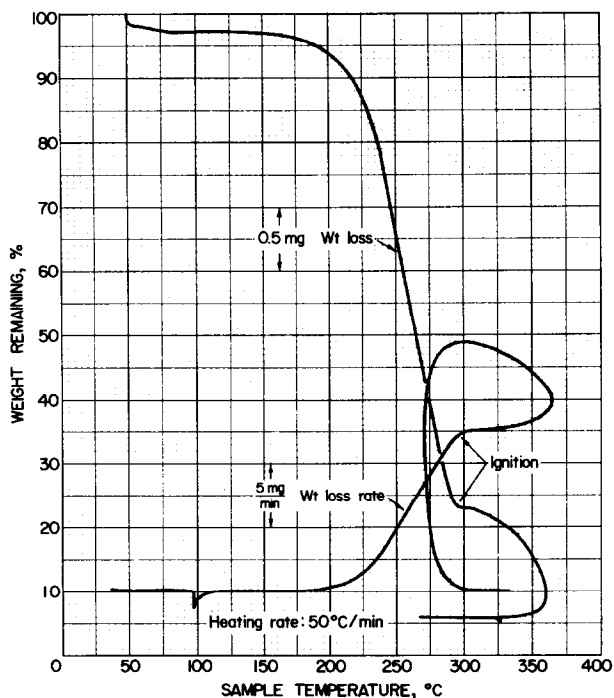


Fig.11. TGA thermogram of a wet MMAN crystal (drained and pat-dried) plus rust powder.

Weight loss rate was usually proportional to sample weight. When the average value of the specific maximum weight loss rate* is compared with the energy input, a roughly linear relationship is observed (Table 2). Thus, essentially the same process, such as dissociative vaporization, which usually is surface-dependent, occurs in all the non-ignition tests at the different heating rates.

In the three tests in which ignition occurred (tests 19, 20 and 21, shown in Table 1), the average maximum weight loss rate was higher than in tests at the same heating rate (50°C/min) that did not result in ignition. Therefore, either catalysis of dissociation or another decomposition mode are implied. It also signifies the formation of larger amounts of gaseous products and their partial accumulation in the TGA oven tube. In tests 19 and 20, the end opening of the tube was not constricted but rust was present; in test 21, the end opening was constricted, whereas a catalyst was not used. Even when not constricted, the end diameter opening, 6 mm in diameter, could have slowed down the outflow of larger amounts of gases. The constricted end

*Where specific maximum weight loss rate is the maximum weight loss rate per unit weight.

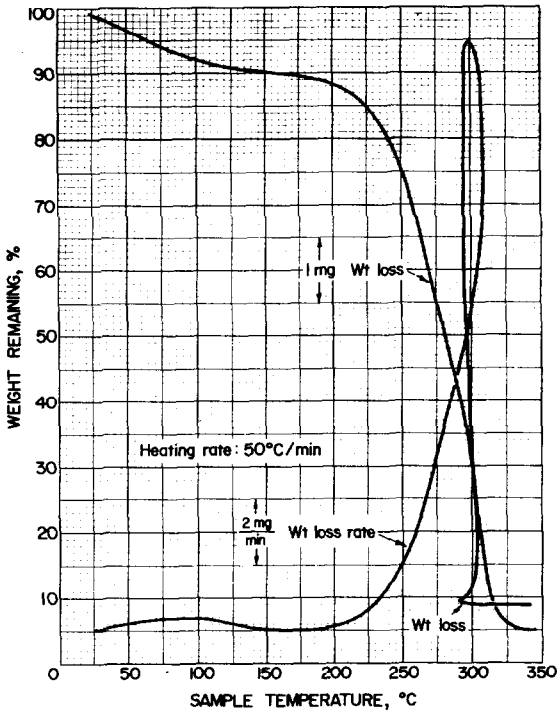


Fig.12. TGA thermogram of a wet MMAN crystal (drained and pat-dried) plus Fe_2O_3 powder.

TABLE 2

Heating rate ($^{\circ}\text{C}/\text{min}$)	Average specific weight loss rate (min^{-1})	Number of tests
5	0.2	1
10	0.44	7
50	1.61	10
50	>2.4 with resultant ignition	3

was 2 mm in diameter. For ignition to take place, enough flammable gas, such as monomethylamine, had to be generated and present in the oven tube.

Experimental results of mass spectrometry

The results of thermal analysis indicated that MMAN dissociates in a fashion similar to that of other nitrate salts to form an acid and a base.

Verification of this dissociation mode was desirable, and mass spectrometry of MMAN was undertaken.

A mass spectrum is a representation of the products of ionization and/or dissociation of gas molecules by electron impact. Each compound entering the mass spectrometer is broken into fragments of specific intensity and thus has its own fragmentation pattern, or profile, for the specific instrument. When only NO_2 is introduced into the mass spectrometer in question, the fragmentation pattern formed is such that the $\text{NO}_2^+/\text{NO}^+$ ratio is approximately 1/3 at a pressure of 70μ – 100μ [3]. When nitric acid is introduced into the instrument, the $\text{NO}_2^+/\text{NO}^+$ ratio is $\sim 5/4$ at the same pressure range. Thus, when NO_2^+ ($m/e = 46$) is present in larger amounts than NO^+ ($m/e = 30$), the presence of HNO_3 is strongly indicated.

MMAN samples weighing 180–200 mg were heated to 500°C , and gaseous products were analyzed in the range of 100 – 500°C , at 100°C intervals. Experimental values for one sample, representative of the results, are given in Table 3. To obtain quantitative results, in addition to preconditioning of the mass spectrometer, calibration curves are needed for each individual ion found in the spectrum. This is especially the case when many of the m/e peaks of the various ions overlap. Calibration curves provide sensitivity values that are used in solving a set of simultaneous equations to obtain the contribution of each ion to the m/e peaks of its fragmentation pattern. Once the contribution of each ion is known, final quantitative calculations are possible. Since this was not done, the results are qualitative and are reported in divisions of peak height or intensity. Calibration curves obtained at various other times show similar sensitivities for most of the ions of interest in this study. (The sensitivities of nitrogen dioxide and methylamine, though similar,

TABLE 3

MASS SPECTROMETER TEST. PRESSURE RANGE: 55–80 μmHg

m/e	Species or ions	Peak intensity (divisions)				
		100°C	200°C	300°C	400°C	500°C
18	H_2O	^a	900	500	250	171
28	CO		108	283	242	368
28	N_2		772	1705	1816	1475
30	NO		500	750	460	920
31	CH_3NH_2		180	163	60	24
44	CO_2		11	146	253	424
44	N_2O		111	164	97	126
46	NO_2		800	690	55	21
61	$\text{CH}_3\text{NH}_2\text{NO}^{\text{b}}$		1	52	16	1
	CH_3NO_2					
	other peaks also present					

^a Present; small amount.

^b Probable ions.

differ from those of the other ions.) Calculations based on all these sensitivities suggest that the peak intensities can be used, at best, as a very rough gauge of the relative amounts of most of the ions; for nitrogen dioxide and methylamine the peak intensities are low, namely, relatively more nitrogen dioxide and methylamine were present than indicated by peak intensities. At 100°C, only water was found in the gaseous phase. At 200°C, water was still a major component, but so were nitrogen dioxide, nitric oxide, and nitrogen. Monomethylamine, carbon monoxide, and nitrous oxide were also observed. At this temperature, the ratio of nitrogen dioxide to nitric oxide is approximately 1.6. At 300°C, the amount of nitrogen is much larger than it is at 200°C; also increased are the amounts of nitrogen dioxide, nitric oxide, carbon monoxide, carbon dioxide, and nitrous oxide. A peak at $m/e = 61$ is also noted.

In general, for all temperatures the ratios of carbon monoxide to carbon dioxide and of nitrogen dioxide to nitric oxide decrease with increasing temperature. The amount of monomethylamine and of water decreases with increasing temperature. Nitrogen is present in large quantities throughout the temperature range.

The peak of $m/e = 61$ could be due to nitromethane. Although the molecular weight of methylnitrite is also 61, its fragmentation pattern does not contain a peak at $m/e = 61$. Nonetheless, peaks at m/e values such as 18, 30, and 31 are present in its pattern. Thus, its presence among the products is possible. A nitroso compound of methylamine, $\text{CH}_3\text{NH}_2\text{NO}$, with a molecular weight of 61, is a possible intermediate product, but there is no published fragmentation pattern for such a compound. Traces of hydrazoic acid were also recorded.

Discussion

Decomposition mode

The formation of monomethylamine and nitric acid in the endothermic dissociation of MMAN was indicated by the results of thermal analysis and essentially substantiated by the results of mass spectrometry. The presence of monomethylamine ($m/e = 31$) is registered at 200°C. At the same temperature, the ratio of nitrogen dioxide to nitric oxide is ~ 1.6 , indicative of nitric acid for the mass spectrometer that was used. The presence of acid was also noted in the DSC tests with pH paper and in aqueous slurries of MMAN that were repeatedly heated to facilitate sampling. After a few heating cycles, the liquid portion of the slurry turned acidic and pale yellow in color, owing to the presence of NO_2 from dissociating nitric acid. The slurry is usually heated to about 90–100°C and is kept hot until all MMAN dissolves, at which time a sample is taken. Thus, dissociation can start at this relatively low temperature, if enough time is allowed.

In the DSC tests, at a heating rate of 10°C/min, dissociation was first noted between 135 and 140°C, as seen in Fig.2. And in TGA test 22, in

which the sample was heated at 5°C/min, initial weight loss was recorded at 130°C.

Both nitric acid and monomethylamine can decompose or react further in the gaseous phase. Whenever nitric acid and water are present together, and temperature and pressure conditions vary, other nitrogen-oxygen compounds form such as nitric oxide, nitrogen dioxide, nitrous acid, and nitrogen trioxide.

When monomethylamine is exposed to nitrogen dioxide, nitromethane and methylnitrite can form [4], and some nitromethane probably did form, as indicated by the mass spectrometer. Possibly, some methylnitrite also formed.

When monomethylamine is oxidized by oxygen at temperatures above 250°C, some of the following reactions are suggested as taking place [5]:



These reactions can be summed up as follows:



Carbon monoxide, carbon dioxides, water, and nitrogen are among the reaction products. The results from the mass spectrometer suggest that thermal oxidation of monomethylamine by nitrogen oxides leads to the same products. The qualitative nature of the results of the mass spectrometer prevents one from assuming any quantitative kinetic scheme, but they do indicate that initial dissociation to HNO_3 and CH_3NH_2 does take place and is followed by reaction of the dissociation products in the gaseous phase. Monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) have properties similar to those of aliphatic amines, such as monomethylamine. When reacting with nitrous acid, MMH forms an azide [6],



while UDMH forms *N*-nitroso and nitrosamine compounds [7]. An *m/e* peak at 61 was detected in the mass spectrometer. It is probably the known reaction product nitromethane, but it could also be $\text{CH}_3\text{NH}_2\text{NO}$, a nitroso compound of monomethylamine with *m/e* also equal to 61. Of similar interest, in one of the mass spectrometer tests, a small amount of hydrogen azide (N_3H), a very powerful explosive gas, was noted.

Ignition of methylamine depends on the ratio of methylamine to oxygen, on methylamine concentration, on mixture temperature, and on surface-

to-volume ratio of the reaction vessel. The amount of MMAN decomposition products introduced into the mass spectrometer was kept low so as to avoid an ignition and explosion. Similarly, the trace amounts of hydrogen azide were too small to cause an explosion.

DSC and TGA results show that fine copper powder and active iron oxide, such as rust, affect the decomposition path of MMAN. In their presence, MMAN does not go through an endothermic dissociation phase; rather it only undergoes an exothermic decomposition phase (see Fig. 4, 7 and 8). Initiation of the exothermic phase, which in the absence of a sensitizer becomes prominent at $\sim 250^{\circ}\text{C}$, is noted at $\sim 190^{\circ}\text{C}$ in the presence of a sensitizer. At present, the species formed via exothermic decomposition of MMAN are not known.

The experimental results enhance the idea of similarity between MMAN and nitrate salts, such as ammonium nitrate (AN) and hydrazine nitrate (HN). All three are highly hygroscopic. All three can dissociate and/or decompose, depending on conditions, and they are all sensitized by small amounts of some transition metals and their salts.

These nitrates dissociate to nitric acid and another compound, which is usually less soluble in the parent salt; at the temperatures at which the compound forms, it is desorbed, leaving a melt enriched in nitric acid. The acid catalyzes additional dissociation and/or decomposition. To illustrate, AN undergoes the following reactions [8]:



$\Delta H = +30$ kcal/mole; endothermic dissociation;



$\Delta H = -18.8$ kcal/mole; exothermic decomposition.

Other decomposition schemes in which various gases are released are known, but eqn. (7) forms the major path. Besides nitric acid, water is cited as a catalyst for the dissociation of AN. HN likewise dissociates into nitric acid and hydrazine and decomposes by various routes [9]. In all these cases, low pressure favors dissociation, as does high heat input at higher temperatures. These tests show that dissociation into acid and an amine, and the enrichment of the melt with the acid, is likewise a trait of MMAN.

Ignition in the TGA and DSC tests

If we accept the premise of MMAN dissociative evaporation to methylamine and nitric acid, then a few simple calculations are of interest. In TGA test 21 (Table 1), at the point of ignition, over 4 mg of the sample was in the vapor phase, 1.45 mg as CH_3NH_2 . Assuming ideal gas behavior, essentially no loss of gaseous products through the constricted end opening, and approximate atmospheric pressure, the partial pressure of CH_3NH_2 in the

system (volume = 50 ml, temperature $\sim 297^\circ\text{C}$) is

$$P = \frac{0.00145}{31} \times \frac{82 \times 570}{50} = 0.044 \text{ atm or about 4.5\%}.$$

The lower limit of flammability of CH_3NH_2 , in dry air at room temperature and atmospheric pressure, is 4.9% [10]. It is somewhat lower at higher temperatures. The minimum autoignition temperature is 430°C , yet we have observed ignition at 292°C in test 21, in which no catalyst was used. At least one of the compounds present must lower the ignition temperature of methylamine; nitrogen dioxide immediately comes to mind. Mass spectrometric results show that nitrogen dioxide is abundant at 200°C . It is also present at 300°C . More important, nitrogen dioxide is a powerful sensitizer of ignition in many flammable gaseous mixtures because it is capable of lowering ignition temperatures and reducing ignition delay times.

To cite a few examples, nitrogen dioxide lowered the ignition temperature of methane-oxygen mixtures in argon by about 200°C and also reduced the ignition delay time [11]. In another study of methane-air systems, 1% to 2% nitrogen dioxide effectively reduced ignition delay times [12]; it also lowered the activation energy of ignition of the mixture.

The autoignition temperatures of n-butane and n-heptane were lower in oxygen than in air, and lower in nitrogen dioxide than in oxygen [13]. Of additional interest are the data regarding the spontaneous ignition temperature (SIT) of aniline and UDMH in air-nitrogen dioxide atmospheres [14]. The SIT is strongly reduced as a function of nitrogen dioxide concentration. Results for aniline are seen in Fig.13, reproduced from ref. 14. Monomethylamine, containing both a hydrocarbon and an amine moiety, will likely be sensitized in similar manner by nitrogen dioxide.

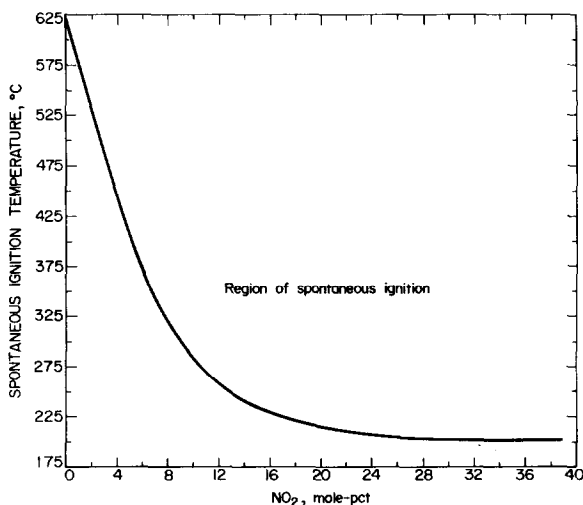


Fig.13. Effect of NO_2 concentration on the minimum spontaneous ignition temperature of aniline vapor in red fuming nitric acid vapor-air mixtures at atmospheric pressures.

Burning speeds of aqueous MMAN solution also were affected by the presence of nitrogen dioxide, as shown in Table 4. Aqueous MMAN solutions, obtained by heating a slurry of MMAN once, had a lower burning speed than solutions obtained from large batches of slurry that were heated a few times. Burning speeds of once-heated MMAN solutions were lower not only at the same pressure but also at much higher pressures, which usually increase burning speeds dramatically. As has been mentioned earlier, the aqueous portion of such slurries becomes acidic and acquires a yellow color, indicative of the presence of nitrogen dioxide, when heated a few times.

The examples cited display the ability of nitrogen dioxide to sensitize the ignition of varied gaseous mixtures, including materials containing amine groups. It is proposed here that nitrogen dioxide lowers the SIT of monomethylamine in air as well.

TABLE 4

BURNING SPEEDS OF AQUEOUS MMAN SOLUTIONS^a

Freshly-heated MMAN sample		Repeatedly-heated MMAN sample	
Pressure (p.s.i.)	Average burning speed (cm/s)	Pressure (p.s.i.)	Average burning speed (cm/s)
1000	0.03	1000	1.5
1200	0.32		
1400	0.52		
1600	0.58		
1800	0.53		
2000	0.56		
2200	0.57—very fast		
2400	0.77—0.89		

^a K.R. Becker, PMSRC, U.S. Bureau of Mines (unpublished data).

Activation energy of dissociation of MMAN

An attempt was made to calculate the activation energy of dissociation and/or decomposition of MMAN from the TGA data. The procedure used is described by Horowitz and Metzger [15] for TGA weight-temperature curves common to many decomposition schemes. In these curves, the weight first drops slowly, then drops precipitously over a relatively narrow temperature range, and finally turns back to a zero slope as the reactant is consumed. If all the products are gases that escape from the decomposing mass, a simplified equation results that relates activation energy to experimental parameters. A plot of these experimental data should yield a straight line, from which slope the activation energy is determined.

Many of the TGA curves of this study resemble those described by Horo-

witz; hence, this relatively simple method was chosen for assessing the activation energy values for MMAN dissociation. Results are given in Table 5.

Although activation energies vary widely (from about 13 kcal/mole to more than 40 kcal/mole), some trends are noted, as follows:

(1) Activation energy values for the dry samples are larger than activation energies for the initially wet samples.

(2) Activation energy values are lower for the higher heating rates.

(3) In a few of the tests, two activation energies were indicated for different temperature ranges.

(4) Tests that recorded high specific weight loss rates showed lower activation energies (Table 6).

In general, it can only be stated that more than one dissociation and/or decomposition scheme is indicated for MMAN.

TABLE 5

ACTIVATION ENERGIES FOR DECOMPOSITION OF MMAN CALCULATED FROM TGA CURVES^a

Test no.	Sample wt. (mg)	MMAN state	Heating rate (°C/min)	T_g^b (°C)	Additive	E (kcal/mole)
1	7.20	dry	10	244		28.8 to 220°C ^c 44.0 above 220°C
2	10.92	dry	10	249		35.6
3	5.66	dry	10	253		31.3
4	5.76	dry	10	263		28.0
6	6.64	dry	10	248		27.6
8	6.34	wet	10	248		18.1 to 230°C ^c 39.0 above 230°C
9	6.12	dry	50	292		29.0
10	7.78	dry	50	299		30.9
11	5.58	wet	50	279		26.1
12	6.42	wet	50	281		20.6
13	6.46	wet	50	286		21.7
15	8.70	wet	50	288		23.5 at 240–290°C ^d
16	14.60	wet	50	327		14.0 at 230–295°C ^d
17	16.04	wet	50	328		15.7 at 245–295°C ^d
18	9.60	wet	50	294		17.5
19	6.12	wet	50	270	Rust	23.2 to 260°C 16.1 above 260°C
20	6.40	dry	50	306	Rust	12.3 to 250°C ^c 39.0 above 250°C
21	7.36	wet	50	298		17.8

^a Calculations based on a procedure described by Horowitz and Metzger [15].

^b T_g is defined as the temperature at which $W/W_0 = 1/e$; W_0 = initial sample weight; $W = W_t$ = sample weight at time t .

^c Where two activation energies are given, the plotted data did not yield a straight line; rather, the data could be represented by two straight parts.

^d Plotted data did not fit a straight line although deviation from linearity was not very large. The slope was determined from the data points in the indicated temperature range, which was linear.

TABLE 6

Test no.	Specific maximum wt. loss rate (min ⁻¹)	Activation energy (kcal/mole)
16	> 1.4	14.0
17	1.8	15.7
18	1.9	17.5
19	2.4	16.1; above 260°C
20	> 3.9	12.3
21	> 2.7	17.7

Catalysis by copper and iron oxide

The transition metals — which can exist in more than one valence state, and which take place in redox reactions — act as catalysts in many decomposition schemes, especially for ammonium salts. They also catalyze decomposition of MMAN. Copper powder is specifically active and influences decomposition rate drastically. Rust, a specific form of iron oxide, is also highly active. In addition to increased rate, generation of sensitive species, able to enhance ignition phenomena, is also possible.

Conclusions

MMAN can dissociate to form nitric acid and monomethylamine, with the acid probably acting autocatalytically to bring about further dissociation and/or decomposition. If a saturated aqueous slurry is kept heated in a container, in time an acidic solution forms; the pH can reach a value of 2. Monomethylamine and other dissociation products diffuse to the upper surface of the liquid contents and hence to the ullage space of the container; there they can form a combustible mixture which might be hazardous.

Old remedies to eliminate autocatalytic decomposition due to nitric acid or nitrogen dioxide include the use of urea as a neutralizer. Urea combines with nitric acid and forms N₂, CO₂ and H₂O. Nitric acid mixed with urea does not oxidize organic compounds but only nitrates them [16]. Substituted ureas, acetanilide, carbonic esters, diphenyl amine, and calcium carbonate are used in the explosives industry for similar purposes. Increasing ullage in containers may prevent the formation of a minimum combustible mixture. Special stainless steels such as 304 or 316, that resist attack by dilute nitric acid, will eliminate any possibility of rust formation. At 30°C the corrosion rate of stainless steel 304 or 316 by a 5% nitric acid solution is less than 0.1 mils per year, at higher temperatures it increases slightly [17]. This is still a very low corrosion rate; nonetheless, some iron ions will go into solution. Preventing acid buildup and rust formation is important for the safe handling and transport of MMAN.

Acknowledgements

I wish to thank Mr. Joseph Malli, Mr. Ben Thames and Ms. Janet Shultz for the mass spectrometry results, and Mr. Robert E. Higgin for editorial assistance. I express my appreciation to Mr. Richard W. Watson, Dr. O.R. Bergman (Du Pont, Martinsburg, WV) and Dr. Charles P. Lazzara for reading the manuscript. I also wish to express my special thanks to Dr. Lazzara for valuable discussions on mass spectrometry results.

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