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A Reinvestigation of the Thermal Decomposition of Methylammonium Nitrate

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Introduction

Methylammonium nitrate (MAN) is an explosive compound which is used as a sensitizer for slurry and emulsion explosives containing ammonium nitrate (AN). The sensitizing effect can be ascribed in a general way to a lowering of the decomposition temperature and an improvement in the oxygen balance:

$$CH_3NH_3NO_3 + 2NH_4NO_3 \rightarrow CO_2 + 7H_2O + 3N_2$$

MAN forms prismatic crystals, mp 109−11 °C, which are very hygroscropic.[1]

Analysis of MAN by differential scanning calorimetry[2,3] has shown an endothermic solid phase change at 86 °C and the onset of exothermic decomposition at 260 °C. In the two papers cited above, it was proposed that MAN dissociates into nitric acid and methylamine prior to decomposition. The major products at 200 °C were said to be H_2O, NO_2, NO, and N_2. Other components present in small quantities were CH_3NH_2, CO, and N_2O. At 300 °C the formation of N_2, NO, CO_2, and N_2O increased relative to NO_2, CO, and H_2O, and CH_3NH_2 was no longer detectable. A mass spectral peak with $m/z = 61$ was suspected to be CH_3NO_2. The investigation by Jain and Rao[3] of the gaseous products of MAN decomposition at 225 °C showed H_2O, N_2, NO, NO_2, CH_3NH_2, and NH_3. There was no mention of CO and CO_2 which have the same mass numbers as N_2 and N_2O, respectively. The identification of NH_3 cannot be relied upon because H_2O also gives a peak with $m/z = 17$.

Another study of thermal decomposition[4] confirmed the dissociation of MAN into nitric acid and methylamine and proposed a reaction mechanism as follows:

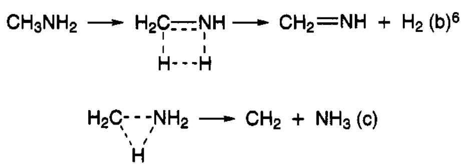
$$CH_3NH_3NO_3 \rightarrow CH_3NH_2 + HNO_3 \xrightarrow{\text{many steps}} HCONH_2 + {}^1\!/_2NO_2 + {}^1\!/_2NO + {}^1\!/_2H_2O + 2H^\bullet$$

$$H^\bullet + NO \rightarrow HNO \rightarrow {}^1\!/_2N_2O + {}^1\!/_2H_2O$$

At a higher temperature the gaseous products detected by FTIR were CO_2, N_2O, HCN, NO, CO, and trace amounts of NH_3 and CH_4.

A shock-tube study of the decomposition of methylamine alone[5] reported a unimolecular mechanism with three possible pathways:

$$CH_3{-}NH_2 \rightarrow CH_3 + NH_2 \text{ (a)}$$



Pathway a was said to be the most reasonable. Pathway b is prohibited as a concerted reaction by the orbital symmetry rules. The proposed complete mechanism is:

$$CH_3NH_2 \rightarrow CH_3 + NH_2;\ CH_3 + CH_3NH_2 \rightarrow CH_4 + CH_2NH_2$$

$$CH_3 + CH_2NH_2 \rightarrow CH_4 + CH_2{=}NH;\ NH_2 + CH_3NH_2 \rightarrow NH_3 + CH_2NH_2$$

$$NH_2 + CH_2NH_2 \rightarrow NH_3 + CH_2{=}NH;\ CH_2{=}NH \rightarrow H_2 + HCN$$

MAN is a simple derivative of AN, and the chemistry of its decomposition is probably similar in many respects to that of AN. At low temperature AN decomposes by a series of steps with ionic mechanisms:[7]

$$NH_4{}^+NO_3{}^- \rightleftharpoons NH_3 + HONO_2$$

$$2HONO_2 \rightleftharpoons NO_2{}^+ + NO_3{}^- + HOH$$

$$NH_3 + NO_2{}^+ \rightarrow NH_2NO_2 + H^+$$

$$NH_2NO_2 \rightarrow N_2O + HOH$$

Above 290 °C a free radical mechanism begins to intervene:[8]

$$NH_4{}^+NO_3{}^- \rightleftharpoons NH_3 + HONO_2$$

$$HONO_2 \rightarrow HO^\bullet + NO_2$$

$$HO^\bullet + NH_3 \rightarrow NH_2{}^\bullet + HOH$$

$$NH_2{}^\bullet + NO_2 \rightarrow NH_2NO_2$$

$$NH_2NO_2 \rightarrow N_2O + HOH$$

In the discussion section we postulate the intermediacy of methylnitramine, CH_3NHNO_2, in the decomposition of MAN, and it will be helpful to review the chemistry of its decomposition here. Melius and Binkley speculated that the weakest bond ($N{-}NO_2$) should break first in thermolysis but they also entertained the possibility of elimination:

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[2] Miron, Y. *J. Hazard. Mater.* **1980**, *3*, 83.

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[4] Russel, T. P.; Brill, T. B. *Propellants, Explos., Pyrotech.* **1990**, *15*, 66.

[5] Dorko, E. A.; Pchelkin, N. R.; Wert, J. C.; Mueller, G. W. *J. Phys. Chem.* **1979**, *83*, 297.

[6] Smith, O. I.; Sawyer, R. F., West. States Sect., Combust. Inst. [Pap.], **1976**, 76, Pt. 1.

[7] Rosser, W. S.; Inami, S. H.; Wise, J. *J. Phys. Chem.* **1963**, *67*, 1753.

[8] Brower, K. R.; Oxley, J. C.; Tewari, M. *J. Phys. Chem.* **1989**, *93*, 4029.

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$$CH_3NHNO_2 \rightarrow CH_2{=}NH + HONO$$

In the presence of aqueous acid[10,11] nitramines decompose with a second-order rate law presumed to have the rate-limiting step:

$$RNHNO_2 + H^+ \rightarrow R^+ + N_2O + H_2O$$

Electron donation by R appears to be an important factor. The intermediacy of R^+ was indicated by the formation of RCl in the presence of hydrochloric acid.

Experimental Section

Sealed mp capillary tubes containing 2–8 mg of sample were used for thermal decomposition at temperatures up to 300 °C. The samples were heated in a thermostatically controlled bath of Wood's metal. The rate of decomposition was followed by measurement of the volume of gas released when the tubes were quenched and opened. The tubes were scored and placed in a short closed-end section of glass tubing which was connected by a rubber tubing joint to an inverted 6-mm U-tube dipping into water. The tube was broken by bending the rubber tubing, and the change in water level was measured before any of the released gas could diffuse into contact with the water. Rapid decomposition under estimated conditions of 1200 K and 1 kbar was studied by transient adiabatic compression of an atmosphere of argon surrounding the sample.[12]

Gaseous products other than N_2 and H_2 were quantitatively analyzed by Fourier transform infrared spectrometry with a resolution of 1 cm^{-1}. Liquid products and some gases were analyzed by GC/MS.

MAN was prepared by neutralizing an aqueous solution of methylamine with nitric acid. The water was evaporated, and the residue was recrystallized from *tert*-butyl alcohol, mp 109 °C, 83% yield. Isotopically labeled $CH_3NH_3{}^{+15}NO_3{}^-$ was prepared in the same way using $H^{15}NO_3$. N-Deuterated MAN was prepared by equilibration of MAN with excess deuterium oxide. The product was isolated by evaporation and drying in a vacuum desiccator. C-Deuterated methylamine was prepared by hydrogenation of CD_3NO_2 (Aldrich Chem. Co.) with Pd catalyst. The amine was isolated as the hydrochloride. The aqueous free base was obtained by neutralization with aqueous NaOH and distillation. The base was converted to nitrate as described above. Methylnitramine, mp 38 °C, 43%, was obtained according to the procedure of Shiino and Oinuma[13] by nitration of *N,N'*-dimethylurea.

Results and Discussion

Analysis of the vapors produced by thermal decomposition of MAN in sealed glass tubes revealed substantial amounts of products which had not been previously reported. Even more surprising was the observation of an abrupt *qualitative* change in the products when the temperature was increased from 240 °C to 280 °C. At 240 °C the order of abundance was the following: H_2O, N_2, CO_2, CH_3ONO_2, N_2O, CO, $HCONH_2$, CH_3ONO, CH_3OH, NO. At 280 °C the order was the following: H_2O, N_2, CO, CO_2, CH_4, N_2O, CH_3ONO, CH_3ONO_2, CH_3OH, HCN. At the lower reaction temperature CH_4 and HCN could not be detected, but their IR absorption lines were very prominent when the temperature was 280 °C. The products obtained at very high temperature and pressure from the adiabatic gas compression apparatus with a reaction time of 10^{-3} s were the following: H_2O, N_2, CO, CO_2, CH_4, NO, HCN. Apparently, there are no further qualitative changes beyond 280 °C. Figure 1 shows the rate of evolution of gas from MAN at 240 °C in the form of a first-order rate plot. The decomposition is clearly autocatalytic. Figure 2 shows that the initial rate of decomposition at 280 °C is moderate, although it should be noted that condensible products do not contribute to the analysis by measurement of gas volume after quenching. After approximately 12 s a flame appears in the vapor space. Several tubes were quenched at 10 s without any sign of ignition, and analysis by FTIR showed sufficient methyl nitrate to give a partial pressure of approximately 1 atm. We believe that the accumulation of methyl nitrate is responsible for the ignition. Because it is liquid at ambient conditions (like water and methanol) it makes no contribution to the early part of Figure 2. Most nitrate esters[14] have half-lives less than 1 s at 280 °C. The mechanism of formation of methyl nitrate from MAN will be discussed below.

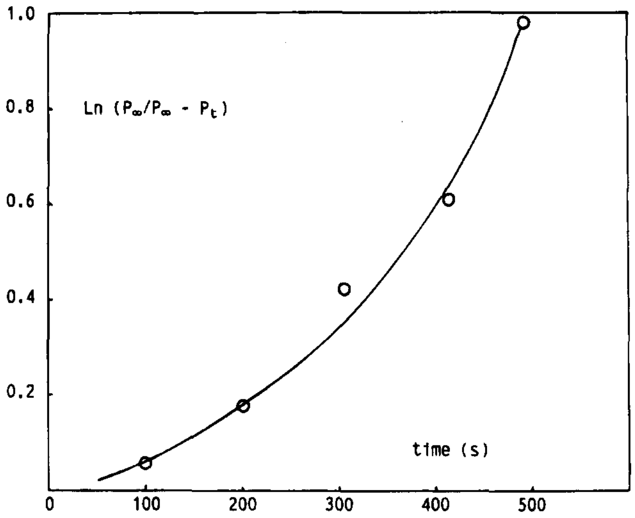

Figure 1. Decomposition of MAN at 240 °C.

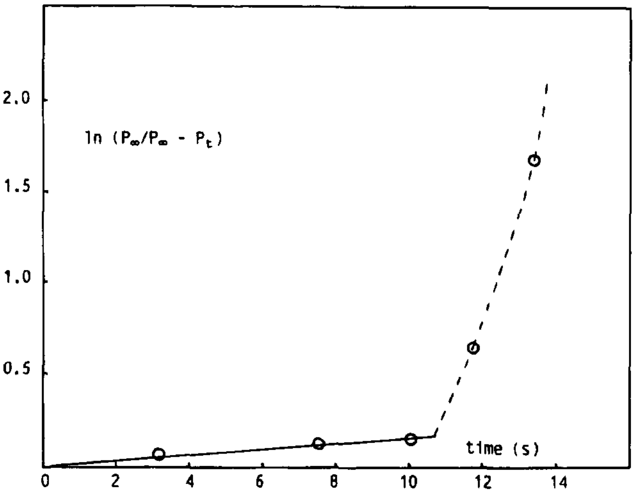

Figure 2. Decomposition of MAN at 280 °C.

Formation of Methane. Methane is one of the more surprising products of decomposition at the higher temperature. Alkanes are not formed from pyrolysis of alkyl nitrates or nitrites. Methane is formed by unimolecular decomposition of methylamine at extremely high tem-

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[10] Barrot, J.; Denton, I. N.; Lamberton, A. H. *J. Chem. Soc.* **1953**, 1998.

[11] Denton, I. N.; Lamberton, S. H. *J. Chem. Soc.* **1955**, 1655.

[12] Brower, K. R. Proceedings of the 16th International Pyrotechnics Seminar, Jonkoping, Sweden, 1991, p 185. van Niekerk, A. P.; Brower, K. R. *Propellants, Explos., Pyrotech.*, in press.

[13] Shiino, K.; Oinuma, S. *Kogyo, Kayaku Kyokaishi* **1960**, *21*, 351.

[14] Hiskey, M. A.; Brower, K. R.; Oxley, J. C. *J. Phys. Chem.* **1991**, *95*, 3955.

perature as noted earlier,[5] but we will argue for another pathway which is accessible at moderate temperature. In any case its precursor must be the methyl radical which abstracts hydrogen from a variety of donors. To demonstrate this point we pyrolyzed N-deuterated MAN at 280 °C and in the adiabatic gas compression apparatus. In both cases the methane contained 50% CH_4 and 50% CH_3D with only a trace of CH_2D_2. All three hydrogen atoms are retained when the methyl radical is formed, and CH_3 has equal probability of abstracting H or D from the pool of potential donors which contains 50 atom% D.

The C—N bond of methylamine must be broken in order to form CH_3. The pathway of lowest energy would appear to be as follows:

$$HNO_3 \xrightarrow{\text{partial reduction}} HNO_2$$

$$CH_3NH_2 + HNO_2 \rightarrow CH_3N{=}NOH \rightarrow CH_3^{\bullet} + N_2 + HO^{\bullet}$$

The reaction proposed above is closely related to the Gomberg reaction:[15]

$$ArN{=}NZ \rightarrow Ar^{\bullet} + N_2 + Z^{\bullet}$$

and the Sandmeyer reaction:[15]

$$ArN_2^{+}X^{-} + CuX \rightarrow Ar^{\bullet} + N_2 + CuX_2$$

Formation of Hydrogen Cyanide. Hydrogen cyanide like methane makes an abrupt appearance when the temperature is increased from 240 °C to 280 °C. In order to find out whether the original C—N bond in MAN remains intact in HCN, we pyrolyzed $CH_3NH_3^{+15}NO_3^{-}$ at 280 °C. Analysis of the HCN by GC/MS showed 95% $HC^{14}N$, 5% $HC^{15}N$. The formation of HCN can therefore be represented in a general way as:

$$CH_3NH_2 \xrightarrow[\text{dehydrogenation}]{\text{oxidative}} HCN$$

The small amount of $HC^{15}N$ can probably be explained by the sequence:

$$CH_3^{\bullet} + {}^{15}NO \rightarrow CH_3{}^{15}NO \rightarrow H_2C{=}{}^{15}NOH \rightarrow HC^{15}N + HOH$$

Methylamine could be oxidized either by a free-radical chain dehydrogenation or by hydride abstraction. In the latter case there should be a substantial H/D kinetic isotope effect for CD_3NH_2 but not for CH_3ND_2. In agreement with the prediction it has been found that N-deuterated MAN has $k_H/k_D = 1.06$ and C-deuterated MAN has $k_H/k_D = 2.5$. Both reactions were followed up to one half-life, and their rate plots are qualitatively similar to Figure 1. Competition among possible oxidizing agents (NO_2^{+}, NO_2, $H_2NO_3^{+}$, etc.) depends on concentration as well as reactivity, and we cannot reliably guess which is the most effective. In a general way, however, the reaction can be represented as follows:

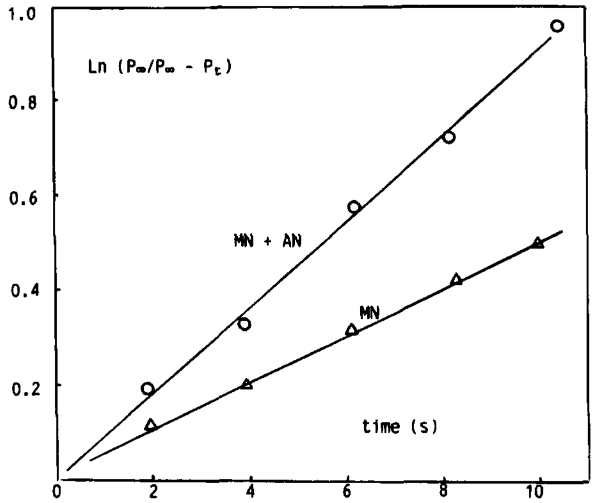


Figure 3. Decomposition of methylnitramine (MN) and ammonium nitrate (AN) + MN at 240 °C.

$$CH_3ND_2 + \text{electrophile} \rightarrow CH_2{=}ND_2^{+} + [\text{H:electrophile}]^{-} \text{ (no KIE)}$$

Formation of Methanol and Methyl Nitrite. The diazotization which was invoked to explain formation of methyl radical can also account for the formation of methanol and methyl nitrite:

$$CH_3N_2^{+} + HOH \rightarrow CH_3OH_2^{+} + N_2$$

$$CH_3OH + HONO \rightarrow CH_3ONO + HOH$$

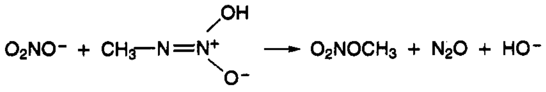
Methanol is known to be esterified very rapidly by nitrous acid even in a medium which is highly aqueous.

Formation of Methyl Nitrate and Nitrous Oxide. The presence of methyl nitrate cannot be explained as easily as that of methyl nitrite. The formation of alkyl nitrate esters does not go well in highly aqueous media. Even the position of equilibrium is probably unfavorable although it is impossible to verify this point experimentally because of the intervention of redox reactions. As a test of the proposition that methanol is not a precursor of methyl nitrate we added methanol to MAN before heating and found that the rate and extent of accumulation of methyl nitrate was not increased.

An alternative hypothesis which also explains the formation of nitrous oxide is that methylnitramine is an intermediate in analogy to the accepted intermediacy of nitramine[7] in the decomposition of AN.

$$CH_3NH_2 + NO_2^{+} \rightarrow CH_3NHNO_2 + H^{+}$$

$$CH_3NHNO_2 \rightleftharpoons CH_3N{=}NO_2H$$



$$O_2NO^{-} + CH_3{-}N{=}N^{+}(OH)(O^{-}) \rightarrow O_2NOCH_3 + N_2O + HO^{-}$$

Catalysis by H^{+} leading to HOH in place of HO^{-} is also possible and perhaps likely.

The validity of the hypothesis above was checked by the classical test of adding a suspected intermediate to the reaction. The intermediate should give the proper products and be consumed more rapidly than the starting material. An additional requirement in the present case

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(15) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 641, 647.

is that methylnitramine should form nitrous oxide by itself but fail to form methyl nitrate unless nitrate ion is present. Experimentation with pure methylnitramine and also with a mixture of methylnitramine and AN as a source of NO_3^- showed that all three requirements were satisfied. Pure methylnitramine decomposed rapidly at 240 °C and gave nitrous oxide but no methyl nitrate. An equimolar mixture with AN decomposed even more rapidly and gave 10% of the theoretical yield of methyl nitrate after quenching. This seems remarkable in view of the short half-life expected for nitrate esters at 240 °C. The rate of decomposition of methylnitramine and its mixture with AN is shown in Figure 3. There is no indication of autocatalysis.

Formation of Formamide, Nitrogen, Carbon Monoxide, and Carbon Dioxide. Formamide, like hydrogen cyanide, is presumed to arise from further oxidation of the imine produced by hydride abstraction from methylamine. Hydrolysis of the imine would give formaldehyde to be further oxidized to carbon monoxide and carbon dioxide. The chemistry of the low oxidation states of nitrogen in aqueous media is extraordinarily complex as described by Bonner and Hughes.[16] A variety of paths can lead to dinitrogen, N_2.

Acknowledgment. This work was supported by the Research Center for Energetic Materials, a consortium administered by the New Mexico Institute of Mining and Technology.

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[16] Bonner, F. T.; Hughes, M. N. *Comments Inorg. Chem.* **1988**, 7, 215.