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# Methylhydrazinium Nitrate

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**Methylhydrazinium nitrate was synthesized by the reaction of dilute nitric acid with methylhydrazine in water and in methanol. The white needles formed are extremely hygroscopic and melt at 37.5–40.5 °C. The IR spectrum differs from that reported elsewhere. The mass spectrum exhibited no parent peak at 109 *m/z* and thermogravimetric analysis indicated that the compound decomposed slowly at 63–103 °C to give ammonium and methylammonium nitrate. The density is near 1.55 g/cm$^3$.**

## Introduction

Methylhydrazinium nitrate was observed by Seamans and Dawson (*1*) to be a component of plume deposits formed on burning monomethylhydrazine (MMH) with dinitrogen tetroxide in small rocket thrusters under vacuum. Since then several publications have referred to the salt as the primary component in the exhaust plumes (*2–4*), but the chemical literature contains no mention of the physical and chemical properties of this simple salt. Since the plume deposits can have a deleterious effect on spacecraft instrumentation, sensors, solar panels, and thermal control surfaces, methylhydrazinium nitrate was synthesized and some properties were determined.

## Experimental Section

The monomethylhydrazine, nitric acid, and methanol were reagent grade and were used without further purification. The methylhydrazinium nitrate was handled in a nitrogen-filled glovebag or under a nitrogen blanket. The melting points were taken in Pyrex capillaries and are uncorrected. The infrared spectra were taken on a Digilab, FTS-15C FTIR. The DSC and TGA scans were taken on a Du Pont Model 900 under vacuum after loading under nitrogen. The mass spectra were obtained on a Finnigan Model 3200 mass spectrometer.

***Synthesis of Methylhydrazinium Nitrate.*** To a 250-mL round-bottom flask, containing a magnetic stirring bar and fitted for nitrogen purge, was added 7.5 g of MMH (0.17 mol) dissolved in 50 mL of $H_2O$. The flask and contents were chilled in an ice bath. A solution of 14 mL of concentrated $HNO_3$ (0.17 mol) in 50 mL of $H_2O$ was chilled in an ice bath and then poured into a 100-mL addition funnel.

The acid was slowly added to the MMH solution over a 15-min period. The mixture was allowed to warm slowly to ambient temperature.

The water was then removed by vacuum pumping over a period of 10–12 h. The residue—a white paste—was recrystallized from 50 mL of anhydrous methanol chilled to -30 °C. This resulted in clear, needle-shaped crystals. Filtration was accomplished under a dry nitrogen blanket. The yield was ca. 5.5 g (0.050 mol, 30% yield).

The compound is deliquescent and, exposed to the laboratory atmosphere, absorbed enough water vapor to form a solution in 10–20 s. All transfer operations were carried out in a glovebag filled with dry nitrogen.

The melting point was determined to be 37.5–40.5 °C, with a slight softening of the crystals at 35–37 °C. Cooling of the melted crystals resulted in resolidification at 36 °C.

A more convenient synthesis was found by dissolving the same quantities of MMH and nitric acid in anhydrous methanol and using the same conditions. In this case, the methanol was stripped off in 2 h and the clear, syrupy liquid was recrystallized twice from methanol chilled to -30 °C. The resultant crystals softened at 37 °C and melted from 38 to 40.5 °C. Miron and Perlee (*5*) reported an endotherm at 41.5 °C which they correctly ascribed to the melting point. Anal. Calcd for $CH_7N_3O_3$: C, 11.01; H, 6.48; N, 38.52. Found: C, 11.20, 11.16; H, 6.26, 6.27; N, 38.22, 38.33.

***Infrared Spectra.*** The infrared spectra were determined by FT-IR in a Nujol (mineral oil) mull and the Nujol absorptions were subtracted. The spectrum of the methylhydrazinium nitrate is given in Figure 1. The methylhydrazinium nitrate spectrum is close to that of MMH with the exception of the intense peak at 1375 cm$^{-1}$ which is due to the nitrate ion. The absorptions between 3200 and 3000 cm$^{-1}$ and the absence of the strong peaks near 2600 cm$^{-1}$ indicate that the methylhydrazinium ion has the extra hydrogen on the nitrogen next to the methyl group. This is by analogy to the work of Evans and Kynaston (*6*) on the hydrochlorides of hydrazine and substituted hydrazines.

The spectrum of methylhydrazinium nitrate was identical with that of Seamans and Dawson (*1*) when differences in the instrument are accounted for. The spectra reported by Takimoto and Denault (*2*) and Maag, Jeffrey, and Millard (*4*) were different but these were taken in KBr pellets where the nitrate salt would be expected to react with the KBr.

***Differential Scanning Calorimetry Data.*** The DSC curve was taken at a slow heating rate of 2 °C/min. An endotherm was found starting at 34 °C which peaked rapidly at 41 °C. A strong exotherm occurred at 208 °C. The temperature of this exotherm varies with the heating rate. The curve took a definite trend downward above 140 °C which may have been due to vaporization of the salt.

***Thermogravimetric Analysis.*** Several attempts were made to determine the percent of evaporation of samples on our TGA apparatus at various temperatures. However, the data were not reproducible at temperatures between 61 to 103 °C. Examination of the sample after it had been maintained at these temperatures showed that the methylhydrazinium nitrate had partially decomposed to ammonium nitrate and methylammonium nitrate. These samples had been maintained at these temperatures as much as 25 h in order to obtain measurable weight changes.

***Mass Spectra.*** Samples were run at the normal ionizing potential of 70 eV and at the reduced potential of 20 eV to determine if the fragmentation pattern was different and thereby obtain evidence whether a molecule such as methylhydrazinium nitrate which would be expected to dissociate in the vapor would have its parent peak at 109 mass/charge units (*m/z*). No parent peak was found nor were there significant differences in the mass spectra. The mass spectrum at 70 eV is given in Table I.

The principal conclusion is that there are no significant peaks corresponding to methylhydrazinium nitrate, but there are those of MMH alone and $HNO_3$ alone. The MMH peaks are all present in the methylhydrazinium nitrate in approximately the same ratios, when compared with a standard methylhydrazine spectrum, and the deviations can be approximately accounted for by the nitric acid fragments. A weak parent peak at *m/z* 63 is that of nitric acid. These data are consistent with the complete dissociation of the salt as expected from the known behavior of other amine salts (*7*).

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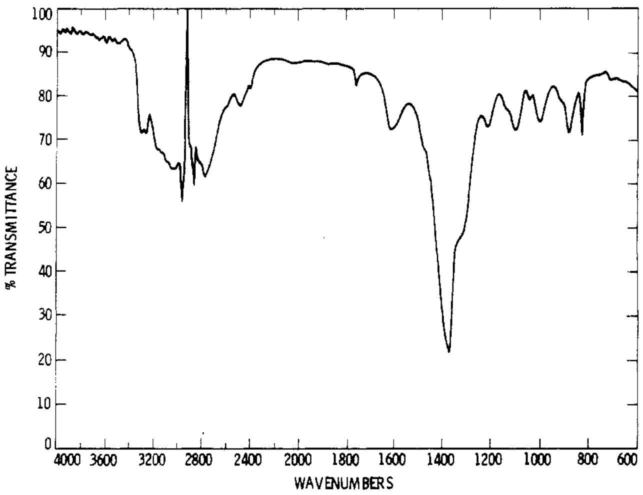

**Figure 1.** Infrared spectrum of methylhydrazinium nitrate.

**Table I. Mass Spectrum of Methylhydrazinium Nitrate**

| $m/z$ | % of base | + ion |
|---|---|---|
| 14 | 5.61 | N, $CH_2$ |
| 15 | 8.80 | NH, $CH_3$ |
| 16 | 6.67 | $NH_2$, O |
| 17 | 13.74 | OH, $NH_3$ |
| 18 | 31.75 | $H_2O$ |
| 26 | 1.54 | CN |
| 27 | 10.26 | CNH |
| 28 | 59.63 | $CNH_2$, $N_2$, CO |
| 29 | 20.03 | $HCNH_2$, $N_2H$, HCO |
| 30 | 45.01 | NO, $N_2H_2$ |
| 31 | 36.88 | HNO, $N_2H_3$, $CH_3NH_2$ |
| 36 | 2.51 | |
| 41 | 1.45 | $CH_2H$ |
| 42 | 3.00 | $CN_2H_2$ |
| 43 | 5.71 | $CN_2H_3$ |
| 44 | 2.51 | $CH_3N_2H$ |
| 45 | 47.62 | $CH_3NHNH$ |
| 46 | 100.00 | $CH_3NHNH_2$, $NO_2$ |
| 47 | 2.12 | $CH_3NH_2NH_2$, $HNO_2$ |
| 56 | 0.87 | |
| 63 | 0.77 | $HNO_3$ |

***Density***. The density was determined by sink–float techniques. Crystals floated in carbon tetrachloride ($d^{20}{}_4$ 1.594) but sank in chloroform ($d^{20}{}_4$ 1.483). In trichlorotrifluoroethane (Freon TF, FC-113; $d^{25}$ 1.565) the crystals just barely floated, most of the crystals being submerged. The density was estimated to be approximately 1.55 g/cm$^3$.

The most unusual property of methylhydrazinium nitrate is its tendency to form strong solvates. Pumping at $<10^{-5}$ torr for 5 days did not remove water of solution nor did similar pumping for 4 days on a methanol solution. However, chilling to about $-30$ °C allowed the salt to drop out of solution and crystals did form. Methylhydrazine hydrate has also been reported to form similarly stable solvates (*8*). In air the nitrate salt rapidly attacked aluminum.

***Safety***. Methylhydrazinium nitrate is toxic (*9*) even when applied to the skin. The impact sensitivity is comparable to that of ammonium perchlorate (*8*).

## Acknowledgment

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**Registry No.** Methylhydrazinium nitrate, 29674-96-2; methylhydrazine, 60-34-4.

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# Preparation and Molecular Structure of New Cyclic $\beta$-Diketone Schiff Bases

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**The molecular structure of new Schiff bases derived from cyclic $\beta$-diketones was investigated by kinetic analysis and mass, IR, and UV spectroscopy. The study indicates that these Schiff bases exist as a tautomeric mixture of the enolimine–ketamine–ketimine forms.**

## Introduction

Previous spectral studies, IR, UV, NMR, and mass spectrometry, have clearly shown that Schiff bases derived from $\beta$-diketones are tautomerized mainly into both the ketamine and enolimine forms (*1–9*). Schiff bases derived from diamines and