Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazines under Nonignition Conditions

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Products formed by reaction of nitrogen tetroxide and hydrazine or methylhydrazines at low temperatures were collected and analyzed, using mass spectroscopy, gas chromatography and infrared absorption spectroscopy. It was found that hydrazine and nitrogen tetroxide form water, nitrogen, nitric oxide, hydrazinium nitrate, and ammonia. When monomethylhydrazine is used instead of hydrazine, the products include methylamine, dimethylamine, methanol, methylnitrosamine, dimethylnitrosamine, N-methylformamide, water, methylhydrazinium nitrate, nitrogen, and dissolved oxides of carbon and nitrogen. When 1,1-dimethylhydrazine is used in place of hydrazine, the products include methylamine, dimethylamine, methanol, dimethylnitrosamine, dimethylformamide, formamide, nitrogen, water, dimethylhydrazinium nitrate, and dissolved oxides of carbon and nitrogen. Between 60% and 80% of the liquid portion of the products is dimethylnitrosamine. Based on the evidence provided by these analyses, reaction mechanisms are proposed.

1. Introduction

A HYPERGOLIC propellant combination frequently used in aerospace vehicles is nitrogen tetroxide as oxidizer and hydrazine, momethylhydrazine or unsymmetrical dimethylhydrazine as the fuel. Spontaneous ignition occurs readily at atmospheric pressure, but when the pressure is very low these propellants may undergo a different reaction and ignition may not occur. Instead, other, less volatile reaction products are formed. An accumulation of reaction products in the combustion chamber can be dangerous, since they are potentially explosive and have been known to detonate.

Sawyer and Glassman[1] have studied the gas-phase reactions of nitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4) by means of a rapid adiabatic flow reactor. They proposed a multistep reaction, each step having a different rate, with nitrosamine (NH_2NO) and ammonia as intermediates. Mayer, Taylor, and Schieler[2] analyzed preignition residues of N_2O_4 and several hydrazines. Analysis of the N_2O_4-UDMH reaction products by time-of-flight mass spectrometry detected dimethylnitrosamine and monomethylnitrosamine. The mass spectra of the reaction products from N_2O_4 and MMH also showed the presence of monomethylnitrosamine. Infrared spectra detected hydrazinium nitrate from hydrazine oxidation, monomethylhydrazinium nitrate from MMH oxidation, and dimethylnitrosamine from UDMH oxidation. Other researchers[3,4] have reported on the products formed from the reaction of N_2O_4 with Aerozine-50, with N_2H_4, and with alkylated hydrazines at low temperatures. Red fuming nitric acid, rather than N_2O_4, was also made to react with N_2H_4 under nonignition conditions.[5] The solid intermediate products formed in this case were found to consist almost completely of hydrazinium nitrate ($N_2H_5NO_3$).

Analysis of these substances serves, first, to determine their nature and, second, to aid in understanding the chemical mechanism and the sequence of events which occur during hypergolic ignition.

2. Preparation of Reaction Products from N_2O_4 and Hydrazines

The reactions of N_2O_4 with different hydrazines were carried out at −20°C in carbon tetrachloride. This solvent is inert to N_2O_4 and hydrazines, and was used to dilute the reactants and to insure the fluidity of the reaction mixture. It is assumed that the presence of the CCl_4 solvent has little effect on the reaction.

Low temperatures were attained by means of a cryogenic bath of dry ice in isopropanol. The mixture was kept well agitated to avoid any local concentration of hydrazines, which might cause ignition.

The hydrazine was added dropwise to the N_2O_4/CCl_4 solution, and was protected from moisture contamination by means of a drying tube. Approximate stoichiometric quantities of the reactants were used. The temperature rose after each addition, and no further addition was made until the temperature decreased to −20°C. The concentration of N_2O_4 in CCl_4 was approximately 4% by weight, or 0.6 molar.

The reaction proceeds with the formation of two liquid phases. The less-dense phase is a red-colored, water soluble liquid containing many substances, including dissolved gases. This liquid changes composition over a period of time, with some loss of dissolved gases. The other, heavier phase is a carbon tetrachloride solution of some of the reaction products.

Three analytical techniques have been used to investigate the composition of the reaction products: mass spectroscopy, gas chromatography, and infrared absorption spectroscopy.

3. Mass Spectroscopy

The red liquid phases produced during the low-temperature reactions of nitrogen tetroxide with hydrazine (N_2H_4), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) were analyzed on a Consolidated Engineering Corporation Model 491 mass spectrometer. Each sample was introduced directly into the instrument as a liquid. The resultant mass spectra of a typical set of samples are shown in Figs. 1–3.

The figures show an interesting trend. Sawyer and Glassman,[1] who studied the gaseous phase reaction of N_2O_4 and N_2H_4, have proposed that a reaction intermediate for these two compounds is the unstable molecule, nitrosamine, NH_2NO. If this is true, then one would expect the reaction of N_2O_4 with methylhydrazine and dimethylhydrazine to produce the methyl-substituted analogs of the proposed intermediate: methylnitrosamine, CH_3NHNO, and dimethylnitrosamine, $(CH_3)_2NNO$,

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respectively. In the mass spectra of the reaction products, then, one might naturally expect to find the fragmentation ions of these compounds. However, both nitrosamine and methylnitrosamine are unstable and decompose according to the equations:

$$NH_2NO \rightarrow H_2O + N_2$$

$$CH_3NHNO \rightarrow CH_3N{=}NOH \rightarrow CH_3OH + N_2$$

So, in the mass spectra of the reaction products of hydrazine and methylhydrazine with N_2O_4, the fragmentation ions of the decomposition products—water, methanol and nitrogen—are more likely to appear rather than those of nitrosamines.

In the fragmentation pattern of dimethylnitrosamine, which was synthesized for this study, the largest peak (parent) is at *m/e* 74, with smaller peaks at *m/e* 43, 28, and 15. Figure 1 shows all of these peaks and indicates a substantial concentration of dimethylnitrosamine in the reaction products. This supports the mechanism proposed by Sawyer and Glassman.

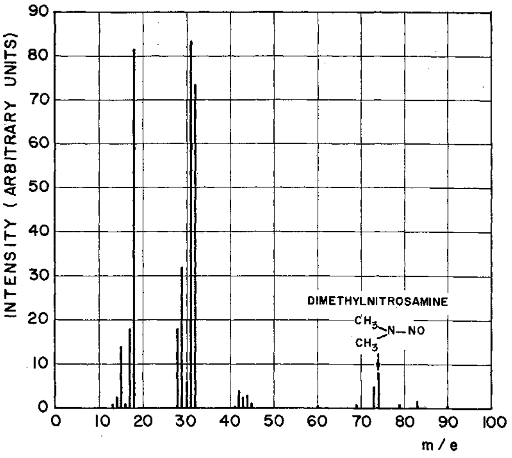

Fig. 1 Mass spectrogram of reaction products of UDMH and N_2O_4.

The large peaks at *m/e* 31 and 32 indicate methanol, and this fact, taken together with the substantial peak at *m/e* 28 (for nitrogen), may mean that a large amount of methylnitrosamine was also formed in the reaction but subsequently decomposed into methanol and nitrogen. The peaks at *m/e* 44 and 45 are due to dimethylamine, and possibly formamide. The results of the gas chromatographic analysis which follow indicate that dimethylamine and not formamide is the major contributor toward these peaks. Formamide is rapidly oxidized by N_2O_4.

Other peaks in Fig. 1 are due to additional reaction products, such as oxides of nitrogen, CO_2, NH_3, H_2O, and perhaps some CO.

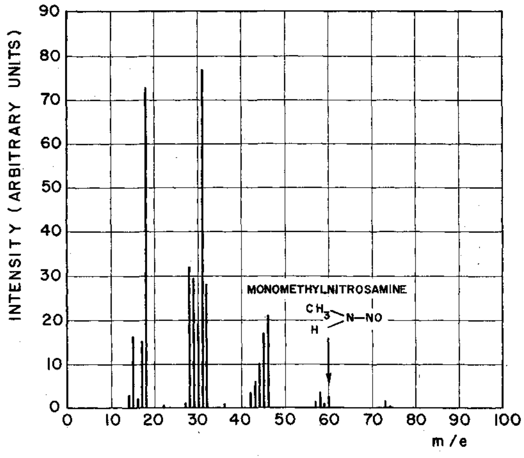

Fig. 2 Mass spectrogram of reaction products of MMH and N_2O_4.

Figure 2 shows the mass spectrum of the reaction products of methylhydrazine (MMH) and N_2O_4. There is no *m/e* 74 peak, indicating no dimethylnitrosamine. The large peaks at *m/e* 31 and 32 again suggest methanol, and as there is also a large peak at *m/e* 28, the implication is that methylnitrosamine, CH_3NHNO, was initially formed in the reaction and then decomposed into methanol and nitrogen. This is further borne out by the presence of a small peak at *m/e* 60, which is the parent peak of methylnitrosamine, some of which has apparently survived in the reaction mixture.

Figure 2 also shows sizeable peaks from *m/e* 42–46. These peaks are from the decomposition of the nonvolatile salt, methylhydrazinium nitrate. The infrared spectra show the presence of this salt in the reaction products. It was shown[5] that in the mass spectrometer the salt hydrazinium nitrate decomposes to give large peaks at *m/e* 30, 31, 32, and 46 corresponding to $N_2H_2{}^+$, $N_2H_3{}^+$, $N_2H_4{}^+$, and NO_2 ions. By analogy, the decomposition of methylhydrazinium nitrate should give $CH_3NHNH_2{}^+$ (*m/e* 46), CH_3NHNH^+ (*m/e* 45), etc. An alternative explanation for these peaks would be the presence of methylhydrazine reagent in the products. The gas chromatogram, however, shows no such contamination, and the N_2O_4 was in excess. Other peaks in the spectrum can be explained by the presence of volatile oxidation products: N_2O, CO_2, H_2O.

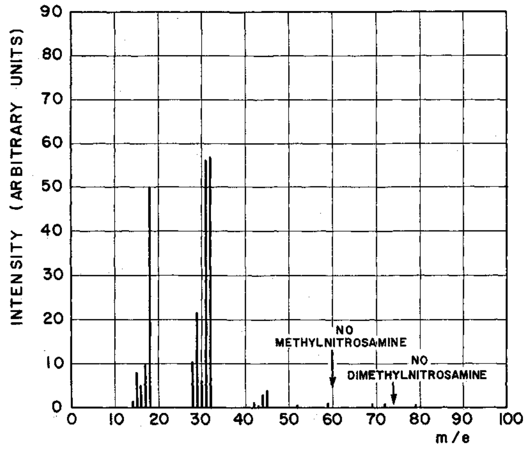

Fig. 3 Mass spectrogram of reaction products of N_2H_4 and N_2O_4.

Figure 3 shows the mass spectrum of the reaction products formed from hydrazine and nitrogen tetroxide. There are virtually no high-molecular weight peaks. Since the postulated intermediate, nitrosamine, NH_2NO, is unstable, it does not appear in the spectrum, and a *m/e* 46 peak is missing. On the other hand, peaks corresponding to its decomposition products, water (*m/e* 18) and nitrogen (*m/e* 28) do appear. The series of large peaks starting at *m/e* 28 and culminating in the largest peaks at *m/e* 31 and 32 can be attributed mainly to the presence of hydrazinium nitrate, $N_2H_5{}^+NO_3{}^-$, in the manner of the argument used above for methylhydrazinium nitrate. Hydrazinium nitrate appears in the infrared spectra (see Sec. 5) but would decompose in the mass spectrometer to form hydrazine and nitric acid. Hydrazine gives a series of peaks[5] from *m/e* 28 to 32. Other peaks due to H_2O, N_2, NO, N_2O, and possibly $H_2N_2O_2$, O_2 and NH_3, complete the spectrum.

4. Gas Chromatographic Analysis

The red liquid layers obtained from the reactions of N_2O_4 with UDMH, MMH, and N_2H_4 have also been analyzed by gas chromatography. The instrument used for these analyses was a Hewlett-Packard Model 700 gas chromatograph equipped with dual flame ionization detectors. The column of the chromatograph was a 6-ft, coiled aluminum tube (0.125 in.) filled with Porapak Q, 80/100 mesh.

Figure 4 shows the chromatogram for the reaction products of UDMH and N_2O_4. Identification of each compound was made by comparison of the elution times for each peak with the elution times for authentic standards. The main peak in the

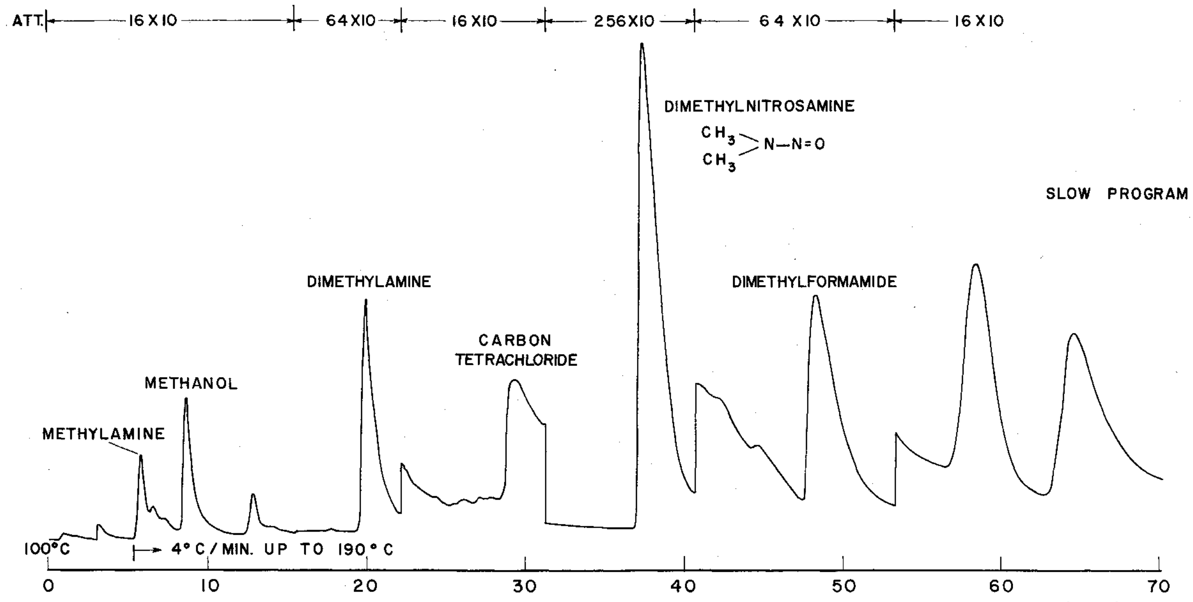

Fig. 4 Chromatogram of reaction products of UDMH and N_2O_4.

spectrum is due to dimethylnitrosamine, $(CH_3)_2NNO$, in agreement with mass spectroscopic data. Because of its significance, the identification of the peak was verified by injection of a mixture of reaction product and authentic dimethylnitrosamine. No new peaks appeared in the chromatogram, but the dimethylnitrosamine peak became much larger. Assuming equal sensitivities for all components, the concentration of dimethylnitrosamine in the reaction products is approximately 80%. This agrees well with mass spectral data. Other peaks in the chromatogram are methanol, dimethylamine, and dimethylformamide. All of these components are in small concentration and are reasonable reaction products. Carbon tetrachloride, the solvent, also appears. Several other small peaks remain unidentified and seem to be heavier, higher molecular weight compounds.

The gas chromatogram of the reaction products of MMH and N_2O_4 is shown in Fig. 5. A small amount of dimethylnitrosamine is present, in addition to small amounts of carbon tetrachloride, N-methylformamide, and larger amounts of methylamine and dimethylamine. Significant quantities of methanol are found. As explained earlier, the decomposition of methylnitrosamine, CH_3NHNO, produces methanol and nitrogen. Thus, the presence of a relatively large amount of methanol may indicate that a sizeable quantity of methylnitrosamine was formed in the reaction, and then decomposed. There is a large peak in the chromatogram which may be methylnitrosamine. Although no standard is available for this compound, its elution time was estimated from the elution time of dimethylnitrosamine and the effect of methyl-substitution on the elution time of similar compounds, such as the methylformamides. This estimated elution time is similar to that of the unknown peak; however, this is not sufficient evidence upon which to base an identification.

There are virtually no large peaks in the chromatogram of the reaction products of hydrazine and N_2O_4. The conclusion is that hydrazine is oxidized mainly to simple, inorganic compounds to which the detector does not respond.

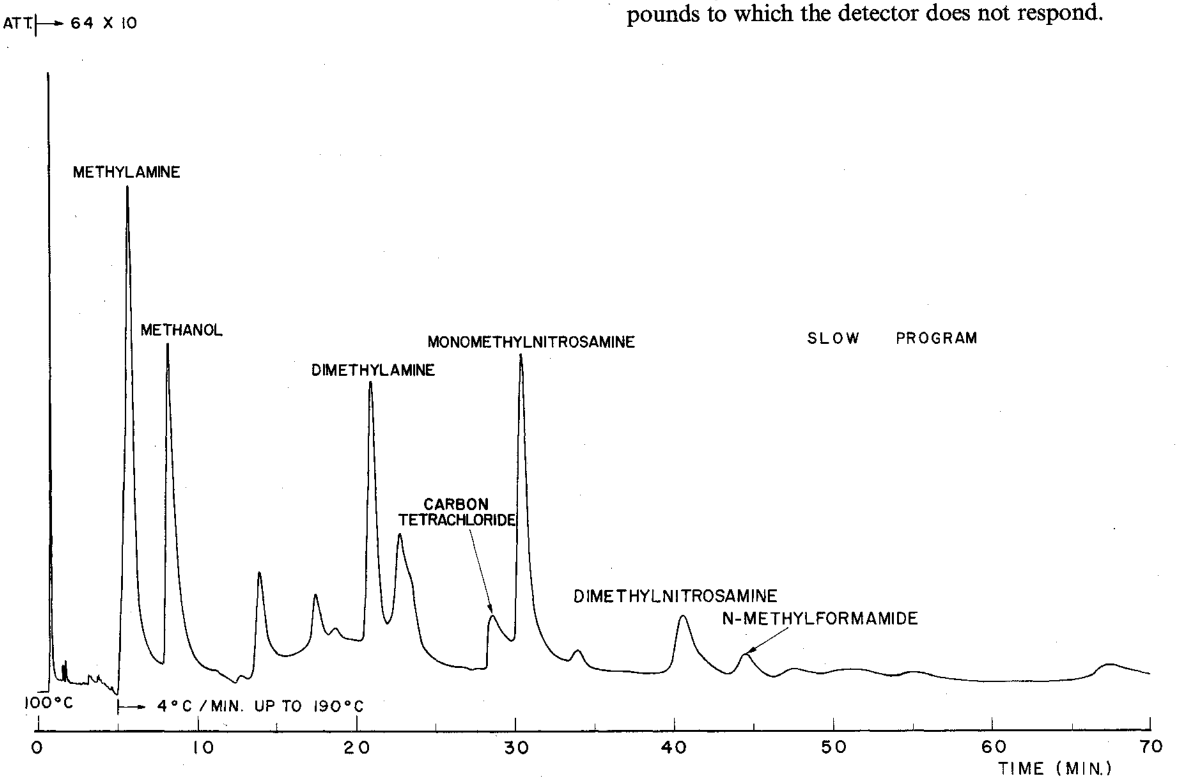

Fig. 5 Chromatogram of reaction products of MMH and N_2O_4.

5. Infrared Absorption Spectroscopy

The infrared absorption spectra of the reaction products of hydrazine, methylhydrazine, and dimethylhydrazine with nitrogen tetroxide were obtained using a Beckman IR-8 infrared spectrophotometer. The red liquid samples were introduced into the beam as a film between disks of irtran-2 (a polished magnesium fluoride crystal). It should be noted, however, that some of the comparison standards used (the two nitrates of MMH and N_2H_4) in this paper were run as potassium bromide pellets, and were obtained from Henry Perlee[4] of the U.S. Department of Interior, Bureau of Mines.

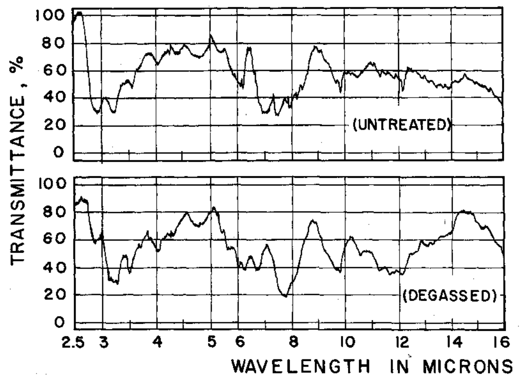

Fig. 6 Infrared spectra of reaction products of UDMH and N_2O_4.

The infrared spectra obtained from the reaction products of N_2O_4 and dimethylhydrazine are shown in Fig. 6. In order to help resolve the complexity, a portion of the reaction products was placed under vacuum for 48 hr. The lower spectrum of Fig. 6 shows the resulting degassed products. From the wave lengths of those peaks which decreased in intensity the structure of the molecule(s) which caused the absorptions can be determined. The peaks which decreased in size after degassing are those at 2.9, 3.4, 6.1, 6.9, 9.8, and 12.1 μ. Taken together, these peaks correspond to the combined overlapping absorptions of methylamine, CH_3NH_2, and dimethylamine, $(CH_3)_2NH$. Thus, we conclude that these two amines were present in the original reaction products. There may also be some trimethylamine present, but since its few absorptions would be obscured by those of the previous amines, its presence or absence is uncertain from the infrared spectra alone. The shifting and splitting of other peaks indicates that there is much overlapping of the spectra of the various compounds.

The general appearance of the spectra in Fig. 6 resembles (though it does not match) that of dimethylhydrazinium nitrate, $(CH_3)_2NNH_3{}^+NO_3{}^-$. However, the absorption peak at 7.5-8.0 μ is more indicative of an organic (covalent) nitrate. Thus, the mixture could contain methyl nitrate, CH_3ONO_2. Also present are peaks which could result from the presence of dimethylnitrosamine (Fig. 7). This compound has three major absorption peaks at 6.9, at 7.57–7.73 and at 9.48 μ due to N=O, C—N and N—N vibrations, respectively. The spectra of the UDMH-N_2O_4 reaction products show absorptions in all three of these regions.

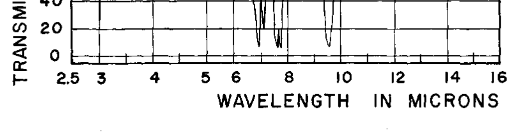

Fig. 7 Infrared spectrum of dimethylnitrosamine.

From other analytical methods it is known that this is indeed a major component of the reaction products. Thus, although the infrared spectra support (or do not contradict) the presence of many substances, one cannot assign a firm identification on this basis.

Perhaps of equal importance are those compounds whose absence can be confirmed. Aliphatic nitro compounds absorb very strongly at 6.45 μ. Since this peak is absent in all the spectra, the reaction products do not contain any nitromethane, CH_3NO_2, or similar compounds. Azides, isocyanates, isocyanides, nitriles (cyanides), and carbodiimides, all absorb very strongly between 4.0 and 5.0 μ so that none of these compounds are present in any significant quantity. Such compounds are expected to be soluble in both liquid phases.

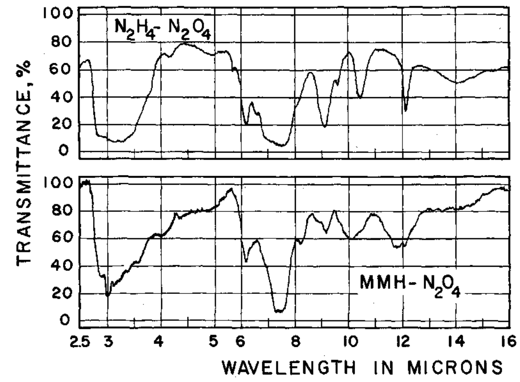

Fig. 8 Infrared spectra of the reaction products of N_2H_4 and N_2O_4 (upper), and MMH and N_2O_4 (lower).

Figure 8 (lower) shows the spectrum of the reaction products (untreated) of methylhydrazine and N_2O_4. As is seen from Fig. 9 (lower), it resembles that of methylhydrazinium nitrate. This nitrate, $CH_3NHNH_3{}^+NO_3{}^-$, is then one of the major components. However, the blurring of the peaks indicates that there are other compounds present as well. The peaks for nitrate ions (5.7, 7.0–7.5, and 12.1 μ) and the N-N bond (9.5 μ) are clear. From the blurred absorption (Fig. 8) at 2.9 μ (not present in the authentic standard, Fig. 9) we can deduce that amines are present.

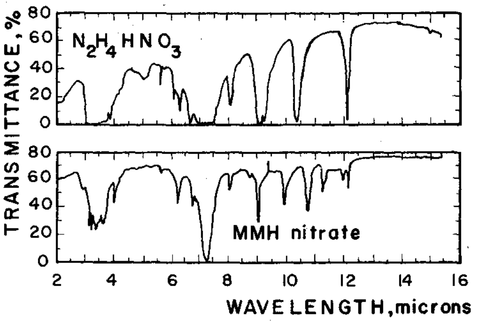

Fig. 9 Infrared spectra of hydrazinium nitrate (upper), and methylhydrazinium nitrate (lower).[4]

In Fig. 8 (upper) is shown the infrared spectrum of the reaction products of hydrazine and N_2O_4. Comparison of this with Fig. 9 (upper), pure hydrazinium nitrate, shows that the products contain large amounts of hydrazinium nitrate, $N_2H_5{}^+NO_3{}^-$. Peaks are clearly seen for hydrazinium ion (3.0–3.9 μ), nitrate ion (7.0–7.5, 12.1, and 5.7 μ), and the N-N bond in the hydrazinium ion (9.2 μ). The peak at 8.0 μ is not sharply isolated from the peak at 7.0–7.5 μ, suggesting that other materials are also present.

Again, since there are virtually no absorptions between 4 and 5 μ in Fig. 8, there are practically no azides, isocyanates, isocyanides, nitriles, or carbodiimides present in the reaction products of methylhydrazine and N_2O_4 or of hydrazine and N_2O_4.

6. Proposed Mechanisms of Reaction of Nitrogen Tetroxide with Hydrazines

The identification of the major products allows the formulation of a reaction mechanism. The proposed mechanism is based upon reactions which are already known, and upon analogous reactions of similar reagents.

The main product from the nonignition reaction of UDMH and N_2O_4 is dimethylnitrosamine $(CH_3)_2NNO$. Figure 10 gives a likely mechanism for its formation. There is a free radical interaction between N_2O_4 and a generalized hydrazine, where *R* and *R′* may be hydrogen or methyl. The abstraction of a hydrogen atom by NO_2 radical is a step proposed by other researchers, including Sawyer and Glassman.[1] Further reaction and decomposition of (*B*) gives an amine (*E*). The amine (*E*) so formed would either constitute a reaction product in itself, as has been indicated by the results of our various analytical methods, or would react further. The nitrosation of amines by nitrous acid produced in the formation of (*B*), or by nitrosonium ion (see Fig. 11) is a well-known reaction. The nitrosation of amines by N_2O_4 at low temperatures in carbon tetrachloride is also known,[6] and is stated to give products (*F*), a nitrosamine, and (*G*), an alkylammonium nitrate, at temperatures near 0°C. The products (*E*) and (*G*) are stable. The nitrosamine (*F*) is stable only if both *R* and *R′* are methyl groups. Thus, dimethylnitrosamine is an expected (and confirmed) product from the N_2O_4-dimethylhydrazine reaction. But in the case of methylhydrazine ($R = H$, $R' = CH_3$), the methylnitrosamine formed decomposes into methanol and nitrogen (as presented in Sec. 3), and when hydrazine itself is used, the nitrosamine (NH_2NO) formed decomposes to water and nitrogen.

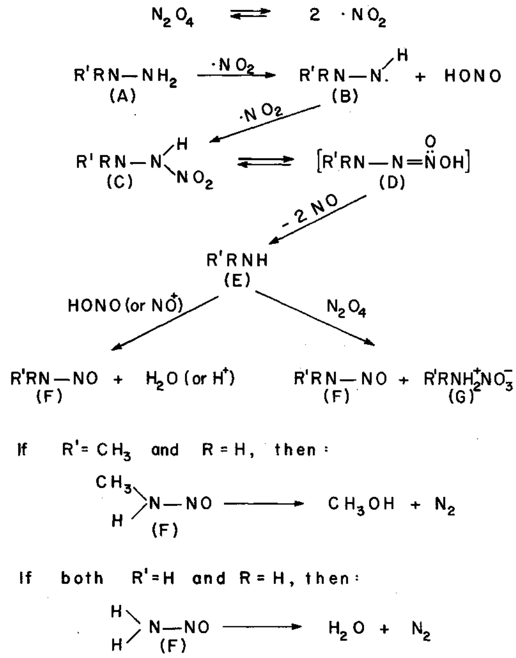

Fig. 10 Proposed free radical mechanism for reaction of N_2O_4 with hydrazines.

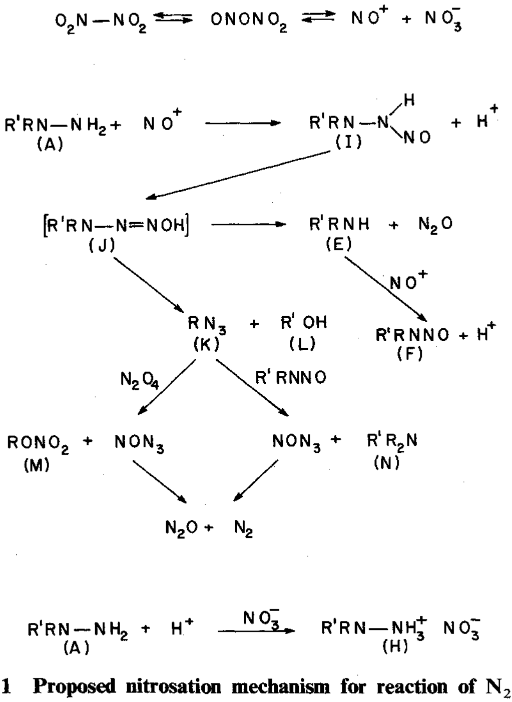

Fig. 11 Proposed nitrosation mechanism for reaction of N_2O_4 with hydrazines.

In Fig. 11 is shown the proposed mechanism and products resulting from the nitrosation of hydrazines (*A*) by nitrosonium ion (NO^+) or by nitrous acid (HONO) produced as in Fig. 10. Although ionization of pure N_2O_4 is insignificant, the formation of NO^+ is promoted by donor solvents: nitrosamines, and especially amines and hydrazines. The nitrosohydrazine (*I*) is formed and tautomerizes to form an intermediate (*J*) which decomposes, according to Sidgwick,[7] to form the amine (*E*) and nitrous oxide. The amine formed would then be expected to react with NO^+ ion or with N_2O_4 as in Fig. 10 to produce nitrosamines (*F*) and alkylammonium nitrates (*G*). However, (*J*) may also decompose to form azides. It is well known that hydrazine itself may be oxidized by nitrous acid to an azide, hydrazoic acid, and water[8]

$$N_2H_5{}^+ + HONO \rightarrow HN_3 + H_2O + H^+$$

the reaction being acid catalyzed. If the same mechanism operates for substituted hydrazines, then this reaction would give methyl azide (*K*) and methanol (*L*) from dimethylhydrazine, and hydrazoic acid and methanol (or methyl azide and water) from methylhydrazine.

The preceding conclusions are of notable significance, since the explosive decomposition of azides has been suspected of being the cause of occasional violent detonations and hard starts in rocket engines using hydrazine-N_2O_4 propellants.

It appears that azide formation, if it occurs at all, could be remedied by flushing the combustion chamber with nitrogen tetroxide after each engine shutdown in order to destroy any azides. Hydrazoic acid and azide ion are known[6] to react completely with N_2O_4 to give nitric acid, nitrous oxide, and nitrogen. The intermediate nitrosyl azide, NON_3, decomposes to nitrous oxide and nitrogen. Since the reaction of N_2O_4 and HN_3 occurs in the gaseous phase, the implication is that ionization to form azide ion is unnecessary, and a similar reaction may occur with alkyl azides, e.g., methyl azide, giving methyl nitrate (*M*) and the same gases. Nitrosamines are also known to react rapidly with azides to give amines (*N*), nitrous oxide, and nitrogen. Thus, it seems very unlikely that hydrazoic acid or azides would survive in the reaction mixture, which is saturated with N_2O_4 and contains nitrosamines as well. The final reaction products would be the nitrate (*M*), the amine (*N*), and methanol (*L*) and/or water. If UDMH is used the amine (*N*) may be trimethylamine, which may not survive the reaction mixture due to further nitrosation with loss of a methyl group and the production of more dimethylnitrosamine.[9]

Note that whenever a hydrogen ion is produced, as in the formation of compounds (*I*) and (*F*), shown in Figs. 10 and 11, it can add to a hydrazine molecule giving a hydrazinium ion. This ion and the nitrate already present from N_2O_4 ionization, easily account for the hydrazinium nitrates (*H*) observed as products.

In Fig. 12 are shown the reactions to be expected from the presence of methanol (*L*) and the amines (*E*) (*N*), formed in the previous reactions. Oxidation of the methanol by NO_2 (or N_2O_4) would produce formaldehyde (O), which can interact in several ways with the various species present: formaldehyde can react with secondary amines (as dimethylamine) to form an aminocarbinol (*P*), the first (an equilibrium) step in the well-known Mannich reaction.[9] Oxidation of this intermediate carbinol (by NO_2, with elimination of water and NO) would give formamide or an N-substituted formamide (*S*), depending on the initial hydrazine used. In the likely event that much of the formaldehyde

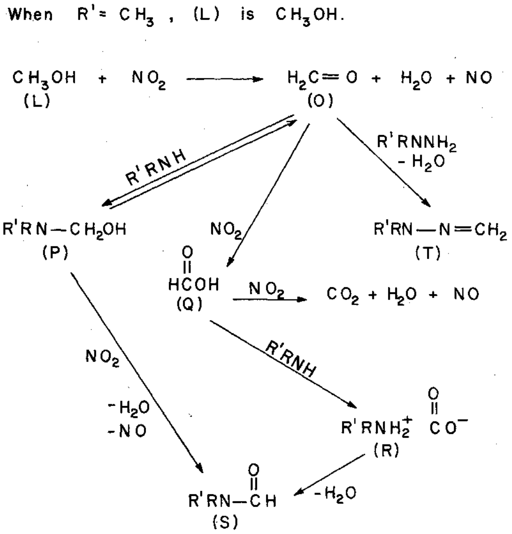

Fig. 12 Proposed mechanism for interaction of some reaction products of N_2O_4 and hydrazines.

is further oxidized to formic acid (*Q*) before it can react with the amine present (*R'R*NH), the reaction of this acid with the amine would produce ammonium formate or an alkylammonium formate (*R*), which through loss of water (induced by the hydrazines and N_2O_4 present) also gives the formamide or N-substituted formamide (*S*). N,N-dimethylformamide, N-methylformamide, and formamide (in very small amounts) are in fact observed products of the reaction of N_2O_4 with hydrazines.

Formamides which are N,N-disubstituted are resistant to N_2O_4 oxidation, while the presence of one or more N-H bonds in the molecule renders the formamide susceptible to attack. For UDMH reaction, N,N-dimethylformamide was observed in significant amounts. For MMH reaction, a much smaller amount of N-methylformamide was found. For hydrazine, no formamide was detected, since neither hydrazine nor N_2O_4 contain any carbon. But a very small amount of formamide was found in the N_2O_4-UDMH products, probably produced by reaction of some ammonia with formic acid (*Q*), according to Fig. 12 ($R'=R=H$).

Another reaction is the production of a formaldehyde hydrazone (*T*) from formaldehyde and the methylhydrazines. In the UDMH reaction, the expected product would thus be formaldehyde dimethylhydrazone, $(CH_3)_2N-N=CH_2$. Zung et al.,[10] did detect, by mass spectroscopy, "significant" amounts of this material in the reaction products of N_2O_4 and UDMH. The detection of this compound may be taken as evidence for the presence of formaldehyde in the reaction mixture.

7. Summary and Conclusions

The proposed mechanisms account for nearly all of the observed reaction products of N_2O_4 with hydrazine, methylhydrazine (MMH), and dimethylhydrazine (UDMH). For UDMH, the predicted products are dimethylnitrosamine, dimethylamine, dimethylhydrazinium nitrate, methanol, dimethylformamide, water, nitric oxide, nitrous oxide, nitrogen, carbon dioxide, formaldehyde dimethylhydrazone, trimathylamine, methyl nitrate, and dimethylammonium nitrate. All of these except the last four have been detected, and one of these four has been found by another researcher.[10] The trimethylamine, methyl nitrate, and dimethylammonium nitrate not discovered as yet are quite compatible with the present data.

For MMH, the predicted products are methylamine, dimethylamine, small amounts of mono and dimethylnitrosamines, N-methylformamide, large amounts of methanol and methylhydrazinium nitrate, water, nitric oxide, nitrous oxide, nitrogen, carbon dioxide, methylammonium nitrate and methyl nitrate. All but the last two have been found, and they are not incompatible with the data.

For hydrazine, the predicted products are water, nitrogen, nitric oxide, nitrous oxide, hydrazinium nitrate, ammonium nitrate, and ammonia. All but ammonium nitrate have been detected.

The authors do not claim that the mechanisms presented in this paper must be the actual manner in which N_2O_4 interacts with hydrazines, nor are they intended to encompass all the possible interactions of the reactants and their products. The mechanisms are presented as a plausible manner of interaction of the reagents which accounts for the major reaction products which have so far been discovered, and is based on a combination of sound chemical theory and well-documented reactions.

References

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