Flammability Characteristics of Hydrazine Fuels in Nitrogen Tetroxide Atmospheres

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HYPERGOLIC SYSTEMS used as missile propellants have introduced handling problems not associated with ordinary fuel-oxidant systems. Of particular interest here are the hypergolic systems in which hydrazine fuels are combined with nitrogen tetroxide. The flammability characteristics of such systems have been studied extensively by the Federal Bureau of Mines. This report contains the results obtained with hydrazine, monomethyl hydrazine, and unsymmetrical dimethylhydrazine at the Explosives Research Laboratory.

EXPERIMENTAL RESULTS

NO_2*-Air Mixtures. Minimum spontaneous ignition temperatures (S.I.T.) of liquid hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) at 25° C. were determined in contact with NO_2*-air mixtures (NO_2* represents the equilibrium mixture of NO_2 and N_2O_4.) in a modified ASTM autoignition temperature apparatus (*1*, *3*). These tests were conducted by injecting the liquid fuel into a heated atmosphere of NO_2* and air contained in a uniformly heated 250 cc. borosilicate glass erlenmeyer flask. The results of these tests are given in Figure 1, where the S.I.T. is plotted as a function of NO_2* content. In every test the fuel and oxidant reacted on contact, producing a white cloud of fine particles; however, as noted in the figure, this reaction did not always culminate in an ignition. Although 70 μliters of liquid fuel was normally used in each test, preliminary studies showed that the S.I.T. was independent of the fuel volume down to at least 10 μliters. Time delays between injection of the liquid and ignition, when it occurred, were imperceptible to the observer. The short horizontal lines appearing on the curves in Figure 1 indicate the uncertainty in the NO_2* concentration (±0.80 volume % at 100° C.). Approximately 100 separate tests were conducted to establish each curve with a repeatability of about ± 2 C°.

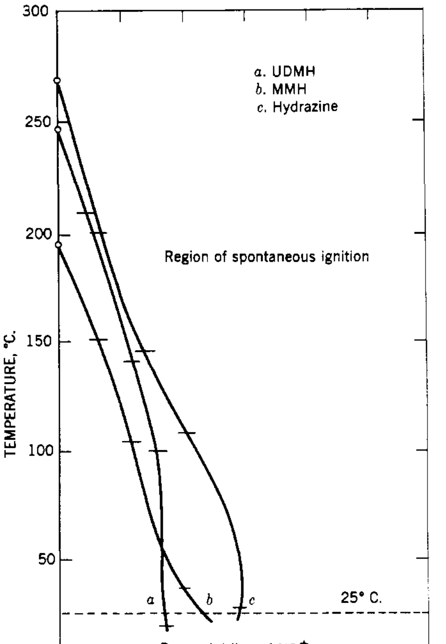

Figure 1. Minimum spontaneous ignition temperatures of liquid hydrazine, MMH, and UDMH, at an initial temperature of 25° C. in contact with NO_2*-air mixtures at 740± 10 mm. Hg pressure as a function of NO_2* concentration

The results of Figure 1 show that at ambient temperature (25° C.) liquid UDMH ignites spontaneously in those NO_2*-air mixtures containing more than about 8 volume % NO_2*; similarly, MMH and hydrazine ignite in NO_2*-air mixtures containing more than about 11 and 14 volume %, respectively. At temperatures above 50° C. the MMH ignites in the presence of lower concentrations of NO_2* than does UDMH.

In the first experiments, the liquid fuel temperature was maintained at 25° C.; however, since higher ambient temperatures are encountered in practice, we determined the effect of liquid temperature on the S.I.T. of the fuels. Figures 2, 3, and 4 show the results of this study. For both liquid hydrazine and UDMH at any fixed concentration of NO_2* in air, the S.I.T. was found to increase with decreasing liquid temperature. This appears to be in

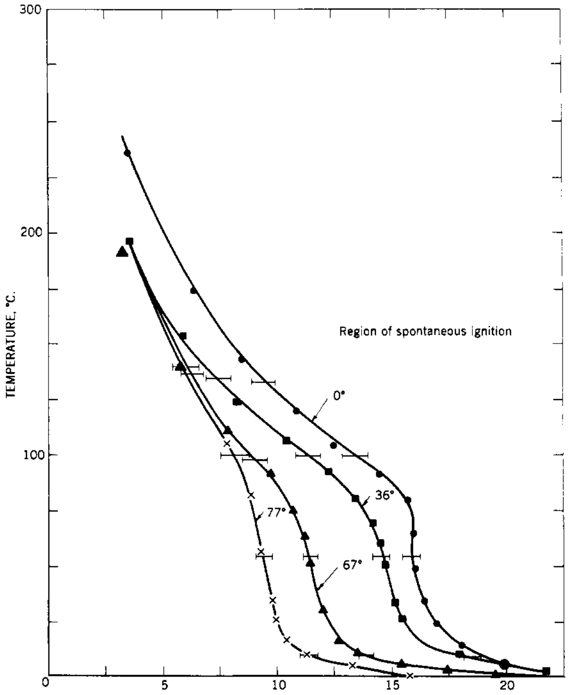

Figure 2. Minimum spontaneous ignition temperatures of liquid hydrazine at various temperatures in NO_2*-air mixtures at 740± 10 mm. Hg pressure as a function of NO_2* concentration

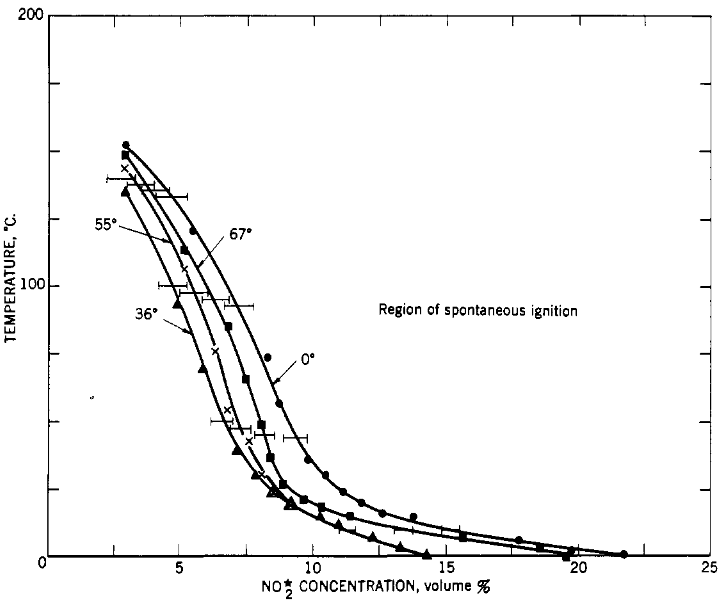

Figure 3. Minimum spontaneous ignition temperatures of liquid MMH at various initial temperatures in NO_2^*-air mixtures at 740± 10 mm. Hg pressure as a function of NO_2^* concentration

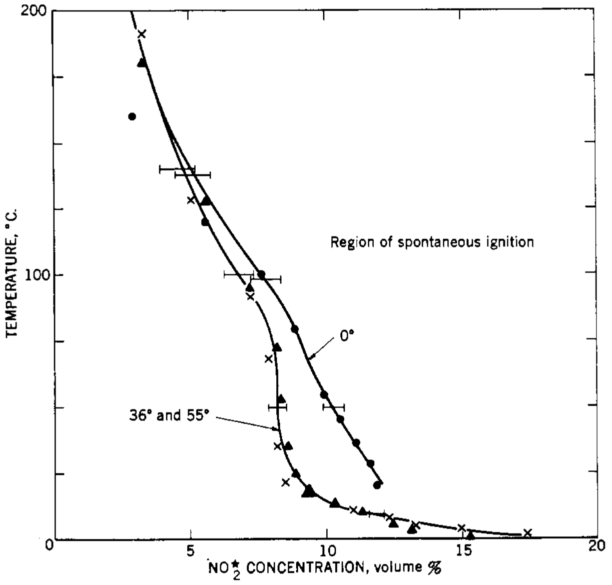

Figure 4. Minimum spontaneous ignition temperatures of liquid UDMH at various initial temperatures in NO_2^*-air mixtures at 740± 10 mm. Hg pressure as a function of NO_2^* concentration

agreement with the results predicted by the thermal theory of ignition since an increase in the fuel vapor concentration (due to an increase in the liquid temperature) increases the reaction rate at any specified oxidant temperature and concentration and thereby lowers the S.I.T. However, the corresponding results for liquid MMH at 36°, 55°, and 67° C. appear to be anomalous and further study is indicated.

NO_2^*-O_2-He Mixtures. To determine the effect of thermal conductivity of the gaseous medium on the S.I.T. of UDMH, a series of ignition temperature tests was conducted with an He-O_2 atmosphere. The S.I.T. curve obtained under these conditions is given in Figure 5, curve *a*, *b* (upper branch). Comparison of this curve with Figure 1, curve *a* shows that the S.I.T. of UDMH in NO_2^*-He-O_2 is the same as that in NO_2^*-air.

The S.I.T. curves obtained in NO_2^*-O_2, NO_2^*-He and various NO_2^*-O_2-He mixtures are also given in Figure 5.

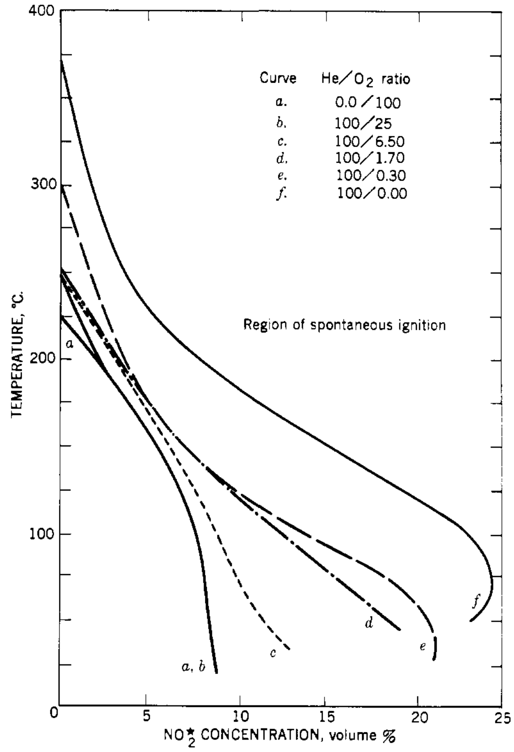

Figure 5. Minimum spontaneous ignition temperatures of 0.05 cc. of liquid UDMH in He–O_2–NO_2^* atmospheres at 1 atm. pressure for various He/O_2 ratios

These results show that very small (0.3%) quantities of oxygen in helium have a substantial effect on lowering the S.I.T. One would therefore suspect from these results that oxygen contributes to the initiation steps of the chemical kinetics. The addition of further quantities of O_2 has a less pronounced effect on the S.I.T. of UDMH.

Effect of Pressure. To determine the effect of moderate pressure changes on the S.I.T. of these liquids, a series of experiments was conducted on UDMH in a borosilicate glass-lined steel container at 15 and 45 p.s.i.a. initial pressure; the container was equipped with suitable hardware for pressure measurement and introduction of the gases and liquids. The results obtained at these pressures are given in Figure 6. The results obtained here at 15 p.s.i.a. agree fairly well with those obtained at atmospheric pressure in the modified ASTM apparatus (Figure 1). Normally the S.I.T. of a fuel is not affected appreciably by moderate changes in pressure. For example, an increase in pressure from 15 to 45 p.s.i.a. lowers the S.I.T. of UDMH in air by 4° C. (Figure 6). However, as NO_2^* is added to the air, the difference between the S.I.T. values at these two pressures increases and then eventually decreases again. This is illustrated in Figure 7 where the S.I.T. is plotted as a function of the changes in the ratio of N_2O_4 to NO_2^* and the NO_2^* concentration (ΔNO_2^*) for 30 p.s.i. change in pressure. This figure shows that within experimental uncertainties the S.I.T.'s of liquid UDMH in NO_2^*-air atmoshperes above 200° C. and below 25° C. are not affected by these changes in pressure. Because above 200° C. NO_2^* consists of essentially pure nitrogen dioxide and below 25° C. of pure nitrogen tetroxide, we have concluded that the S.I.T. of UDMH in a nitrogen dioxide-air or nitrogen tetroxide-air atmosphere is not affected by these changes in pressure. Therefore, since the S.I.T's between these two temperatures appear to be pressure dependent, we conclude *a priori* that this pressure dependence is due to the change in the concentration ratio of nitrogen tetroxide to nitrogen dioxide. In other words, we have suggested that for a

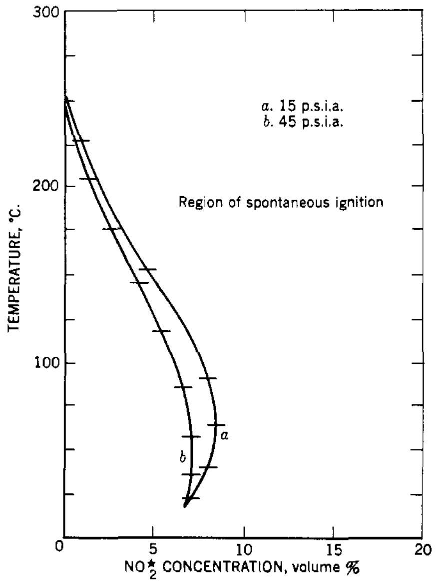

Figure 6. Minimum spontaneous ignition temperatures of 0.05 cc. of liquid UDMH in NO_2^*-air mixtures at 15 and 45 psia. pressure as a function of NO_2^* concentration

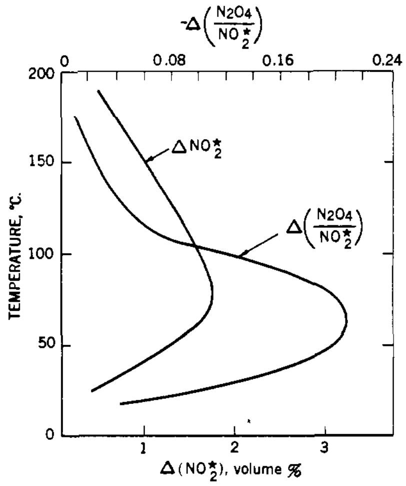

Figure 7. Comparison of the change in NO_2^* for the spontaneous ignition of liquid UDMH (Figure 6) with the corresponding change in the (calculated) ratio of N_2O_4/NO_2^* for the same pressure change (from 15 to 45 p.s.i.a.)

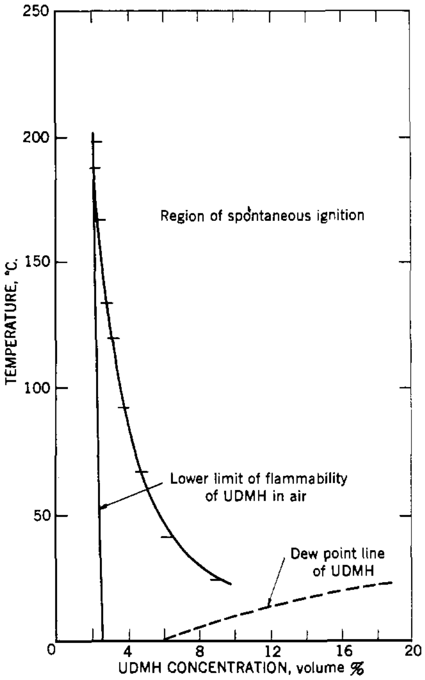

Figure 8. Minimum spontaneous ignition temperatures of vaporized UDMH-air mixtures in contact with 100% NO_2^* at 25° C. and 740± 10 mm. Hg pressure as a function of UDMH concentration in air

given NO_2^*-air mixture the S.I.T. decreases with increasing pressure because the NO_2^* equilibrium shifts towards increasing concentration of the more reactive N_2O_4.

Vaporized Fuel. The above investigations were conducted with liquid fuel; however, similar results can be obtained with gaseous fuel. Such data were obtained for UDMH by vaporizing a measured volume of liquid in air in the modified ASTM apparatus. NO_2^* was then injected into this heated mixture to determine if an ignition would result. Figure 8 shows the results of this study; the S.I.T. is given here as a function of the UDMH concentration in the UDMH-air mixture. From this figure we see that at 25° C. a UDMH-air mixture containing greater than 9 volume % UDMH will ignite spontaneously on contact with NO_2^* at the same temperature.

The lower limit of flammability (L.L.) line of UDMH-air mixtures is included in Figure 8. Mixtures with UDMH concentrations below the L.L. line are considered nonflammable so that we would not expect them to ignite spontaneously on contact with NO_2^*. However, there is also a range of mixture compositions between the L.L. line and the S.I.T. curve that are not ignited in this manner; an external ignition source (flame, spark, etc.) would be required to ignite these mixtures.

CONCLUSIONS

At ambient temperature (25° C.) and pressure, liquid hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine ignite spontaneously in NO_2^*-air atmospheres containing NO_2^* concentrations greater than about 8, 11, and 14 volume %, respectively. These results appear to be independent of the fuel volume down to at least 10 μliters. An increase in the liquid fuel temperature appears to decrease the NO_2^*-air mixture temperature required for spontaneous ignition.

The addition of small quantities (0.3%) of oxygen to an He-NO_2^* mixture lowers the S.I.T. of UDMH considerably (as much as 50° C.). This indicates that oxygen is a contributing factor in the initiation steps of the oxidation process.

A moderate increase in pressure tends to decrease the S.I.T. of UDMH in NO_2^*-air. The amount of decrease depends on the pressure and NO_2^* content.

At ambient temperature and pressure, mixtures of UDMH vapor and air ignite spontaneously on contact with NO_2^*, provided the UDMH concentration in the UDMH-air mixture exceeds about 9 volume %.

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