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Hypergolic Ignition of Rocket Propellants with Nitric Acid Containing Dissolved Nitrogen Tetroxide

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Introduction

LOW ignition delay in hypergolic bipropellants is a great advantage in the design of liquid rocket engines as it helps to eliminate undesirable pressure peaks. Red fuming nitric acid (RFNA) is hypergolic with a number of fuels and many investigations have been carried out to determine the manner in which the ignition delay is influenced by added catalysts, water content of the acid, temperature of the propellants, etc.[1–4] However, no data has been reported on the effect of concentration of dissolved nitrogen tetroxide (N_2O_4) on the ignition delay. The present investigation was carried out mainly for that purpose. Results presented herein show that increase in the concentration of dissolved N_2O_4 in nitric acid invariably results in a decrease in ignition delay. The magnitude of the effect depends on the chemical nature of the fuel which determines the mechanism of preignition reactions.

Materials

The fuels selected for study were an aromatic amine xylidine (mixed isomers), an aliphatic amine triethylamine (TEA) and a hydrazine derivative, unsymmetrical dimethyl hydrazine (UDMH). Chemically pure samples of these fuels were used. Commercial nitric acid containing 1.97% by weight of dissolved N_2O_4 was used as such as oxidizer. N_2O_4-free oxidizer was prepared by heating the commercial acid in an open dish at 60°C for half an hour. Oxidizer containing higher percentage of N_2O_4 was prepared by bubbling dry N_2O_4 through chilled commercial acid, the dry N_2O_4 being obtained by heating concentrated nitric acid with copper turnings in a flask and passing the gas produced in the reaction over phosphorous pentoxide. Different concentrations of dissolved N_2O_4 were obtained by passing the gas for different lengths of time through the chilled acid. The concentration of N_2O_4 in the acid samples was determined by a method described by Welcher.[5]

Ignition Delay Measurements

A simplified form of the modified open cup tester described by Ladanyi and Miller[6] was used for these experiments. All testing was done at room temperature (21° ± 2°C) and therefore the cooling arrangement was not provided. The fuel was loaded in the test tube and the oxidizer was kept in the ampule; the advantage being that once the ampule was flame sealed there was no possibility of escape of N_2O_4 and consequent change in composition of the oxidizer. To ensure uniformity, as soon as a particular sample of acid was prepared, a large number of ampules were filled up and sealed. Some of these were used for chemical analysis to determine the concentration of dissolved N_2O_4 and the rest were used for ignition delay experiments. Ignition delay was measured using a photocell and oscilloscope arrangement. The starting signal was obtained at the instant of contact by impact of the drop weight on the head of crush rod. The fore end of the drop weight carried a metal pin which made contact in a mercury well provided on the head of the crush rod to ensure stable electrical contact. It was found that in the absence of such an arrangement the oscilloscope trace was unsteady and difficult to read due to vibrations accompanying the impact.

Results and Discussion

The experimental results are given in Table 1. In case of xylidine a slow uniform decrease in ignition delay is observed with an increase in concentration of N_2O_4 in the oxidizer. It was also observed that ignition was preceded by the evolution of a lot of smoke. A large carbonaceous residue was left which decreased with increase in concentration of N_2O_4. In case of TEA, the presence of a small amount of N_2O_4 in nitric acid brings down the ignition delay enormously and a further increase in concentration of N_2O_4 does not have any effect. In the case of UDMH, though the ignition delay was reduced but the effect was not at all significant. The ignition in the case of UDMH was accompanied by a loud report, like the sound of a small explosion, the intensity of this sound increasing noticeably with an increase in concentration of N_2O_4. This may be similar to the popping phenomena[7] observed in case of N_2O_4-Hydrazine system due to extreme reactivity of the propellants and may be significant from the point of view of injector design in practical systems using UDMH-RFNA combination.

The cause for the different effects on the ignition delay in the three cases most probably lies in the difference in the manner in which N_2O_4 influences the mechanism of the preignition processes. It would therefore be interesting to analyse the relative importance of nitric acid and N_2O_4 in these processes.

Table 1 Ignition delay data

Concentration of N_2O_4 dissolved in nitric acid, wt %	Average Ignition Delay[a]		
	Xylidine[b] $F/O = 1.5$ sec	TEA $F/O = 4$ m sec	UDMH $F/O = 0.25$ m sec
0	2.1	68.66	4.83
1.97	2.0	24.66	4.76
8.35	1.5	23.66	4.70
15.23	1.33	23.52	4.40
21.30	1.17	23.33	4.20

[a] In all cases 1 ml of oxidizer was taken in the ampule. The fuel to oxidizer ratios (F/O) used are those which gave minimum ignition delay in diagnostic measurements with acid containing 1.97% N_2O_4.

[b] In case of Xylidine a stop watch was used for measurement, because of long time intervals involved and because of the fact that a large amount of smoke was evolved prior to ignition, fouling the inner wall of the test tube and rendering the signal to photocell very weak.

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Index categories: Fuels and Propellants, Properties of; Liquid Rocket Engines.

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The mechanism of reaction of nitric acid and N_2O_4 with both aromatic and aliphatic compounds has been reviewed by Urbanski.[8] In the absence of N_2O_4, the only nitrating agent in nitric acid is NO_2^+ ion. It will attack the benzene ring of xylidine [Formula $C_6H_3.(CH_3)_2.NH_2$] at a position decided by the directive influence of the two $-CH_3$ and one $-NH_2$ groups already present in the molecule, to form a mononitro derivative. Further attack on the ring and formation of dinitro derivative along with production of heat will result in the cleavage of benzene ring, i.e., the ring after substitution will be unstable at the prevailing thermal environment. When N_2O_4 is present, there is the additional possibility of N_2O_4 directly attacking all the double bonds of the benzene ring making the whole system unstable. From the trend of the data it can be presumed that ignition delay with 100% N_2O_4 will be much less than that for 100% nitric acid, thus showing that attack by N_2O_4 is faster, taking less time to produce unstable compounds during the preignition phase.

In case of triethylamine [Formula: $(CH_3.CH_2)_3N$], the most probable position of attack by nitric acid is the nitrogen atom itself, because the three ethyl groups are directly linked to the electronegative element nitrogen and because of the electron releasing nature of the ethyl group, this nitrogen will be surrounded by a high electron density cloud thus facilitating the electrophillic attack. Once the NO_2 is attached to nitrogen, the three $-CH_2-$ of the ethyl groups will become active and will be susceptible to attack by nitric acid leading to the formation of unstable compounds and free radicals. When N_2O_4 is present, simultaneous attack on all ethyl groups and on the nitrogen atom is possible. The very considerable decrease in ignition delay in presence of small concentrations of N_2O_4 and the fact that larger concentrations of N_2O_4 do not produce further decrease in ignition delay, indicate that oxidative attack by N_2O_4 may be very vigorous and highly energetic. Small quantities of N_2O_4, therefore, are enough to start this attack, which can then be sustained by nitric acid alone under the prevalent thermal environment.

The chemical structure of UDMH [Formula: $NH_2.N(CH_3)_2$], is such that NO_2^+ ion can attack only the nitrogen atoms. The reactivity of methyl group with N_2O_4 is very low[9] and even when N_2O_4 is present, attack is mainly on nitrogen atoms. Hence, there is practically no difference in ignition delay with or without N_2O_4. The very small decrease in presence of N_2O_4 may be attributed to the slight increase in reactivity of $-CH_3$ in presence of N_2O_4.

From the preceding discussion, it is clear that the action of N_2O_4 depends on the chemical structure of the fuel, particularly on the positions of the various functional groups in its molecule. There are a number of other fuels which are hypergolic with nitric acid. It may be expected that because of its stronger action, presence of N_2O_4 in the acid will reduce the ignition delay in all cases. The quantitative effects, however, could be quite different, as shown in the present study and can best be determined only by experiment.

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Surface Reaction Model for Metal Particle Combustion

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Nomenclature

c, λ, D = heat capacity, thermal conductivity coefficient, binary diffusion coefficient
ρ, T = gas density and temperature
$\hat{T}$ = cT/L
L = specific heat of vaporization or sublimation
m = fuel consumption rate
M = $m/(4\pi r_s \rho D)$
r = radial distance
$\hat{r}$ = r/r_s
Q_1 = heat of reaction, per unit mass of fuel, to form gaseous products from gaseous reactants
Q_2 = heat of condensation for the products per unit mass of fuel
$\hat{Q}_1, \hat{Q}_2$ = Q_1/L, Q_2/L
Y = mass fraction
ν_1 = stoichiometric mass ratio of oxidizer to fuel
O, s, ∞ = subscripts for oxidizer, particle surface, and infinity

Introduction

VARIOUS models have been postulated to describe the vapor-phase combustion of metal particles.[1,2] However under many situations this combustion mode does not always occur. For nonvolatile metals it is simply not favored. For volatile metals the absence of this burning mode maybe caused by the difficulty either in achieving ignition or in maintaining combustion in an ambient atmosphere of low temperature T_∞ and oxidizer concentration $Y_{O,\infty}$. Under these circumstances it has been observed that chemical reactions between fuel and oxidizer may take place on the particle surface.[3] We shall formulate in the following a surface reaction model in which the gas-phase diffusion of heat and species are the rate-limiting processes.

Formulation

The combustion process is assumed to be quasi-steady, isobaric, and spherically symmetric. Oxidizer gas diffuses from infinity to react stoichiometrically and completely with the fuel at the particle surface, producing either condensed oxides that reside on the surface or vaporized oxides that are transported to the ambient. The spherical particle, which can

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