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Hypergolic Ignition of Various Hydrazones with Nitric Acid

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Solid hydrazones obtained by the reaction of various aldehydes with phenyl and dimethylhydrazines have been found to be hypergolic with nitric acid. The hypergolicity appears to be related to the chemical structure of these compounds. The observed ignition delays have been accounted for by assuming the role of nitration, neutralization and oxidation reactions occurring simultaneously in the preignition stage. p-Nitrobenzoic acid and benzoic acid have been isolated as preignition reaction intermediates in the benzaldehydephenylhydrazone-nitric acid system

Introduction

THE hypergolic nature of solid hydrazones on coming into contact with red fuming nitric acid (RFNA) was established in our earlier studies.[1,2] The short ignition delays of these systems indicate the potential use of the hydrazones as hybrid rocket fuels. The ignition delay of a hybrid system depends upon various physicochemical parameters. The effect of some of these parameters like oxidizer-to-fuel ratio, particle size, and concentration of NO_2 in RFNA on the ignition delay of a phenylhydrazone-RFNA system was reported earlier.[2] The ignition delay, however, primarily depends upon the chemical reactivity of the fuel with the oxidizer. The chemical reactions leading to ignition being extremely fast, their mechanism is not clearly understood. No study has been made so far on hydrazone-nitric acid systems which reveals the nature of basic chemical reactions leading to ignition.

When a liquid oxidizer like RFNA comes into contact with a solid fuel, exothermic reactions start at the surface of the fuel. In amine-RFNA systems, presumably, a Lewis-type acid-base reaction with the formation of a salt occurs.[3-5] The heat released may decompose the intermediate products with the evolution of gases leading to ignition. Apart from this, the oxidation and nitration reactions of concentrated nitric acid with organic compounds are well known[6] and may be taking place simultaneously. The role of nitration in the preignition reactions of amine-RFNA[3,7] and anilineformaldehyde-RFNA[8] systems has been mentioned. Recently, in the furfurylidine ketones-RFNA system,[9] the observed ignition delays have been examined in the light of preignition reactions involving mainly nitration, oxidation, and polymerization reactions. It is apparent therefore that various types of reactions may be occurring simultaneously during the preignition stage.

In the present study a comparison of the minimum ignition delays with HNO_3 of hydrazones having different substituents has been made under identical conditions. It is envisaged that, depending upon the reactivity of the substituent, a particular reaction leading to ignition may become more prominent than the remaining reactions and, thus, the ignition delay may show a certain trend depending upon the functional group. An attempt has been made to isolate the reaction intermediates by quenching the preignition reaction.

Experimental

Ignition Delays

Several methods[10-15] have been used to measure the ignition delay (ID) of hybrid propellants. A simple device for measuring ignition delay was designed and fabricated in the laboratory. It essentially consists of three parts (Fig. 1); 1) a device to receive the "start" signal, 2) a phototransister circuit to sense the presence of flame and to give the "stop" signal, and 3) an electronic counter.

As shown in Fig. 1, the fuel was placed in a porcelain crucible. The oxidizer, RFNA, was sucked into the graduated tube by means of the propipetter labelled A. This also pushed the mercury toward the probe. The probe was adjusted so that it just touched the mercury surface. In this position the counter showed a reading of zero. After carefully adjusting the amount of the oxidizer with the propipetter labelled B, the oxidizer was allowed to fall on the fuel by rapidly opening the stopcock. As soon as the contact of mercury with the probe was broken, the counter started counting. The oxidizer on reacting with the fuel gave a flame which was sensed by the phototransister, which, in turn, stopped the counter. The time indicated by the counter gave the oxidizer drop time plus the ID. The oxidizer drop time as obtained by a separate experiment, was found to be 101 ± 0.5 ms. This value was subtracted from the total time to get the actual ignition delay. All ignition delays were determined at room temperature (25 ± 2° C). The delays reported in this investigation are an average of at least the four closest readings for a particular set of conditions.

The solid-fuel particles were seived through stainless steel seives. Fuel particles passing through 297-μm but not through 210-μm mesh sieves were used.

Materials and Characterization

The RFNA used in the investigation was supplied by M/s. Purex Lab, and was analyzed[16] for the acid as well as for NO_2 content. The acid which contained 6 to 7% NO_2 was actually pure nitric acid, NO_2 having been formed during storage. The water content of the acid was obtained by a subtraction method. The phenylhydrazones[17] and dimethylhydrazones[18] were prepared by reacting phenyl or dimethylhydrazine with the appropriate aldehyde or ketone in 1:1 mole ratio and were recrystallized from alcohol. The compounds were characterized by comparing their melting points with those reported in the literature.[17,18] The thermal behavior of the hydrazones was ascertained by differential thermal analysis using platinum cups at 10°C/min heating rate in air. Each

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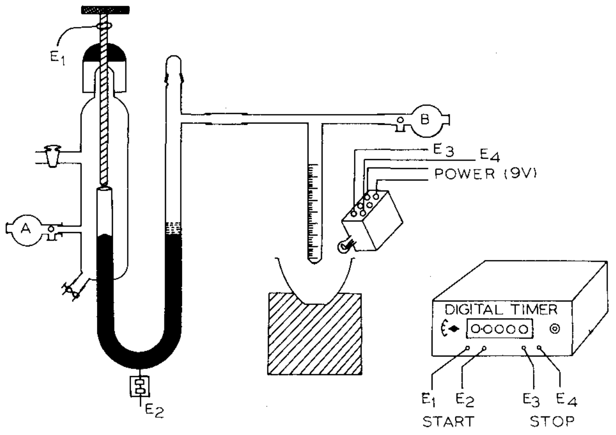


Fig. 1 Schematic diagram of the ignition delay setup.

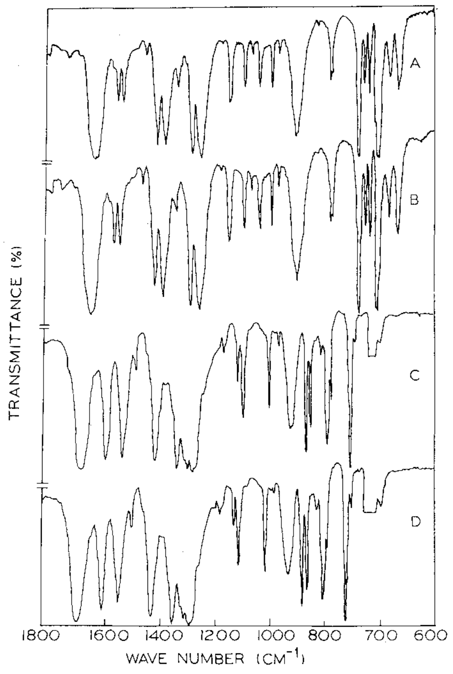


Fig. 2 Infrared spectra of A—intermediate product melting at 122°C, B—authenticated sample of benzoic acid, C—intermediate product melting at 241°C, and D—authenticated sample of p-nitrobenzoic acid. The IR of samples A and B were taken in Nujol mull and those of C and D were taken in KBr.

hydrazone gave an endotherm corresponding to the melting and an exotherm corresponding to the decomposition of the compound. These data are listed in Table 1.

Isolation of Intermediate Products

The preignition reaction mixture was prepared by adding 40 g of benzaldehydephenylhydrazone in small portions at regular intervals to 120 ml of HNO_3 (having 7% NO_2 conc.) at -10°C over a period of 3 h. After the addition, the reaction was arrested by diluting the acid with ice-cold water. The brown spongy mass obtained was washed several times with distilled water and dried.

To isolate the intermediates, a portion of the reaction mixture was dissolved in ether and the soluble portion was extracted repeatedly with 10% sodium bicarbonate. The deep red sodium bicarbonate extract was neutralized by the addition of HCl. A brown solid separated out and was filtered and dried. A portion of this mixture was subjected to sublimation. The major portion sublimed at 115-120°C and the remainder at 200-205°C. The sublimate obtained in the low-temperature range was pale yellow, which after repeated sublimations collected as white leaflets melting sharply at 121-122°C. It was found to be a carboxylic acid. An analysis of this compound gave 68.60% C and 5.37% H. The values calculated for benzoic acid are 68.84% C and 4.95% H. The infrared spectrum of this compound (Fig. 2) matched very well with that of an authenticated sample of benzoic acid.

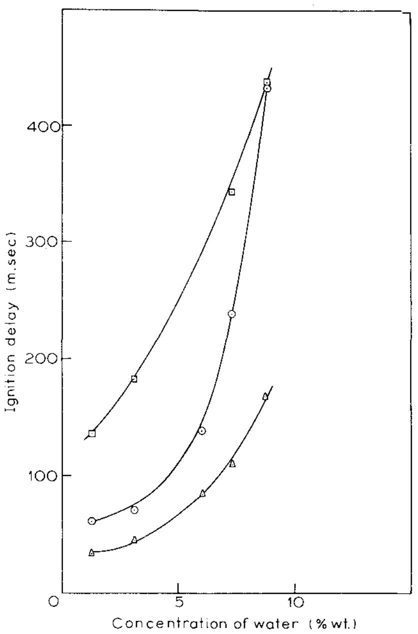


Fig. 3 Effect of concentration of water in nitric acid on the ignition delay: ⊡ —p-dimethylaminobenzaldehydephenylhydrazone (compound 3), ▽ —p-hydroxybenzaldehydedimethylhydrazone (compound 11), and ⊙ —p-chlorobenzaldehydedimethylhydrazone (compound 12).

The fraction subliming at 200-205°C was also subjected to repeated sublimations, with white crystals melting at 241°C obtained. Qualitative analysis of this compound showed the presence of nitrogen and a —COOH functional group. The methylester of this compound melted at 95°C, which corresponded to that of the methylester of p-nitrobenzoic acid. Furthermore, the infrared spectrum of this compound was found to be identical to that of an authenticated sample of p-nitrobenzoic acid (Fig. 2). It therefore appears that apart from many other intermediate products which remain unidentified, benzoic acid and p-nitrobenzoic acid are definitely preignition reaction products.

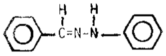
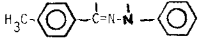
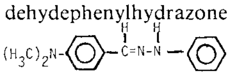
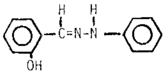
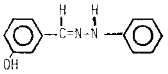
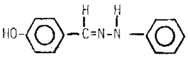
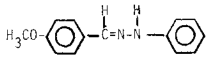
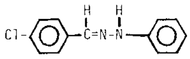
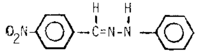
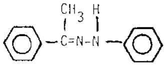
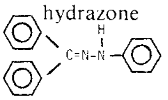
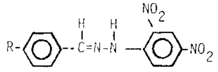
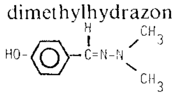
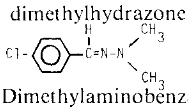
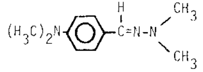
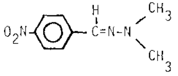
Results

The average minimum ignition delays of various hydrazones are reported in Table 1. The ignition delays obtained using pure nitric acid (containing 6-7% NO_2) are much smaller than those with RFNA (containing 21-24% NO_2). In many cases, the ignition becomes inconsistent, or no flame appears with RFNA. The amount of water in nitric acid has a drastic effect on the ignition delay (Fig. 3). The delay becomes longer with an increase in the water content. At 12% water concentration, no ignition takes place. It appears, therefore, that the ignition delays are determined largely by the concentration of HNO_3. The addition of fuming sulfuric acid in small amounts further decreases the ignition delays (Table 2) of phenylhydrazones, but has virtually no effect on the dimethylhydrazones. The 2,4-dinitrophenylhydrazones as well as acetophenone- and benzophenone-phenylhydrazones are found to be nonhypergolic.

Discussion

The hydrazones are known to be attacked by electrophilic reagents.[19] The electrophilic attack may take place theoretically at the basic NH nitrogen atom or at the

Table 1 Ignition and thermal properties of hydrazones

No.	Compound	Melting point/decomposition point, °C	Optimum fuel/oxider	Average minimum ignition delay, ms	
				Acid[a] A	Acid[a] B (RFNA)
1	Benzaldehydephenylhydrazone 	159/290	0.24	102	1280 (inconsistent flame)
2	p-Tolulaldehydephenylhydrazone 	115/290	0.24	83	650 (inconsistent flame)
3	p-Dimethylaminobenzaldehydephenylhydrazone 	144/295	0.24	108	181
4	Hydroxybenzaldehydephenylhydrazone				
a)		143/295	0.47	86	(no flame, vigorous reaction)
b)		144/298	0.47	103	189
c)		179/278	0.47	297	1730 (inconsistent flame)
5	p-Methoxybenzaldehydephenylhydrazone 	122/295	0.39	158 (inconsistent flame)	418 (inconsistent flame)
6	p-Chlorobenzaldehydephenylhydrazone 	127/270	0.26	420 (inconsistent flame)	(no flame, very little reaction)
7	p-Nitrobenzaldehydephenylhydrazone 	160/258	...	(no flame, very little reaction)	
8	Acetophenonephenylhydrazone 	104/295	...	(no flame, vigorous reaction)	
9	Benzophenonephenylhydrazone 	138/319	...	(no flame, little reaction)	
10	2,4-Dinitrophenyl- hydrazone  R = H,CH_3,$N(CH_3)_2$,OH,OCH_3,NO_2	...	...	(no flame, vigorous reaction)	
11	p-Hydroxybenzaldehydedimethylhydrazone 	150/235	0.39	37	103
12	p-Chlorobenzaldehydedimethylhydrazone 	64/248	0.39	60	218 (inconsistent flame)
13	p-Dimethylaminobenzaldehydedimethylhydrazone 	70/307	0.26	164	195
14	p-Nitrobenzaldehydedimethylhydrazone 	108/301	0.39	69 (inconsistent flame)	230 (inconsistent flame)

[a] The compositions of the acids used for phenylhdrazones were A—93.63% HNO_3 and 6.29% NO_2, and B—75.75% HNO_3, 21.26% NO_2, and 2.92% H_2O. Those for dimethylhydrazones were A—91.3% HNO_3, 7.3% NO_2, and 1.33% H_2O, and B—72.67% HNO_3, 24.55% NO_2, and 2.71% H_2O. Each acid had 0.07% soluble impurity. The quantity of the acid used in each experiment was 0.55 ml in the case of phenylhydrazones and 0.5 ml in the case of dimethylhydrazones.

Table 2 Effect of fuming sulfuric acid on the ignition delay

	Ignition delay,[a] ms			
Compound no.:	1	3	11	13
No H_2SO_4	149	154	37	164
1% H_2SO_4	121	104	37	164

[a] The composition of nitric acid used was 91.3% HNO_3, 7.3% NO_2, and 1.33% H_2O.

hydrazone carbon atom, as well as at the ortho and para positions of the aryl rings. Hydrazones are amphoteric in nature and form salts with strong acids and bases. Hydrazones are very susceptible to oxidation; mild oxidizing agents like MnO_2 [20] oxidize them by removal of hydrogens at carbon and nitrogen atoms. Strong oxidizing agents oxidize arylhydrazones to diazonium ions.[19] The exothermic preignition reactions of concentrated HNO_3 with hydrazones may, therefore, primarily be considered in the light of the nitration, acid-base, and oxidation reactions.

As seen from Table 1, smaller ignition delays for phenylhydrazones are observed with concentrated HNO_3 than with RFNA. An increase of NO_2 content results not only in longer ignition delays, but the consistency of the flame is also affected in certain cases. In the discussion, therefore, only ignition delays of various hydrazones obtained using concentrated HNO_3 (having 6-7% NO_2) have been considered.

The introduction of various groups in the para position of the phenyl ring at the carbon atom of phenylhydrazones has a significant effect on the ignition delay. It is seen that electron-releasing (ortho, para directing) groups decrease the ignition delay, whereas, the electron-withdrawing group, e.g., nitro group, makes the system nonhypergolic. The ignition delays increase with the substituent in the following order:

$$CH_3 < H < N(CH_3)_2 < OCH_3 < OH < Cl < NO_2$$

It may be recalled that the effect of substitution on nitration of benzene with HNO_3 follows more or less a similar trend. The velocity of nitration [21] appears to decrease with the substituent in the following order:

$$CH_3 > NR_2 > OH > OR > H > Cl > NO_2$$

In nitration reactions of aromatic systems, $NO_2{}^+$ has been shown to be the reactive species.[22] The electrophilic substitution in phenylhydrazones may take place at both of the phenyl rings and also possibly at the hydrazone carbon atom, as in the case of halogenation reactions of phenylhydrazone.[19] However, the effect of substitution on nitration at the phenyl ring attached to the hydrazone carbon atom is expected to be a maximum because of the proximity of the substituent group. The isolation of p-nitrobenzoic acid as one of the reaction intermediates in the benzaldehydephenylhydrazone-HNO_3 system provides strong evidence of a nitration reaction in the preignition stage. Furthermore, it is interesting to note that the ignition delays of the various phenylhydrazones decrease in the presence of a small amount of fuming H_2SO_4. It has been shown by various authors[22] that a mixture of concentrated HNO_3 and H_2SO_4 is an exceptionally strong nitrating agent for aromatic compounds. Indeed, the lowering of the ignition delay in the presence of H_2SO_4 in an aromatic liquid amine-HNO_3 system has been accounted for on the basis of a nitration reaction.[3] It therefore appears that nitration is one of the important preignition reactions in a phenylhydrazone-HNO_3 system. The increase of ignition delays with increases in water content of the acid may also be understood in terms of a nitration reaction. The active component responsible for hypergolic reaction with nitric acid has been shown to be the $NO_2{}^+$ ion,[5] which is in a state of dissociation equilibrium with nitric acid,

$$2\,HNO_3 \rightleftharpoons NO_2{}^+ + NO_3{}^- + H_2O$$

The considerable increase in ignition delay with the addition of water to the system may be understood in terms of dilution of the acid. It is also possible that the presence of water shifts the equilibrum to the left, thus reducing the concentration of $NO_2{}^+$ ions. A similar effect on the ignition delay of the addition of water to the acid was observed in the p-phenylenediamine-HNO_3 system, where it was also shown that the addition of a nitronium salt decreases the ignition delay and the addition of KNO_3 increases the ignition delay.[5]

The ignition delays of hydroxybenzaldehydephenylhydrazones with the hydroxy group in the ortho, meta, or para position to the hydrazone carbon atom are in the order, ortho < meta < para, respectively. This order can also be explained by assuming nitration at the phenyl ring attached to the hydrazone carbon atom. A hydroxy group being ortho-para directing, nitration would take place in the ortho and para positions with respect to the OH group. Of the two, the para position is favored. When the OH group is in the para position with respect to the hydrazone carbon atom, the para position for nitration is not available and, hence, the nitration reaction may take place at the ortho position only. However, when the OH group is in the ortho or meta position, the nitration can take place in the para as well as in the ortho position with respect to the OH group. Thus, with the OH group in the ortho or meta position, the nitration reaction is facilitated, resulting in lower ignition delays. This argument may be extended to account for the low ignition delay observed in the case of benzaldehydephenylhydrazone. In this case nitration can take place in the para position itself with respect to the hydrazone carbon atom.

Another exception to the nitration rule appears to be the higher ignition delay of p-hydroxybenzaldehydephenylhydrazone than that of p-methoxybenzaldehydephenylhydrazone. Apart from reactivity if it is assumed that low melting/decomposition point of the compound helps in reducing the ignition delay, it may be seen that the former compound has a considerably high melting point, which may result in a longer ignition delay.

The nonhypergolicity of 2,4-dinitrophenylhydrazones may again be understood to some extent on the basis of a nitration reaction. However, it may be that the acid-base (neutralization) reactions in these systems are also important. The introduction of two nitro groups in the phenyl ring attached to the nitrogen atom actually makes the hydrazones acidic[23] and thus lowers the reactivity towards HNO_3.

It is interesting to note that the phenylhydrazones obtained by the reaction of a ketone with phenylhydrazine are nonhypergolic. This fact points to the reactivity of the hydrogen atom at the hydrazone carbon atom. Electrophilic substitutions are reported[19] to take place at this carbon atom. It may be that in ketone-phenylhydrazones, the hydrogen atom at carbon, the favored site for electrophilic attack, is replaced by a methyl or phenyl group, making the attack more difficult, probably because of steric hindrance.

The effect of substitution (on the phenyl ring) on the ignition delay can not be explained in a similar manner in the case of dimethylhydrazones. The presence of methyl groups increases the basicity of the nitrogen atom to which they are attached to such an extent that the Lewis acid-base type reactions may become primarily responsible for the exothermicity and, therefore, for the observed ignition delays. The electrophilic attack of $NO_2{}^+$ ions on the basic nitrogen may also play an important role.[7] The nitration at the phenyl ring may not be a prominent reaction as the ignition delays do not show the expected order. The ignition takes place even if NO_2 group is present on the phenyl ring. Further, there is no effect of fuming H_2SO_4 on the ignition delay in these cases (Table 2). The trend in the ignition delay with various groups, however, appears to be dependent on the decomposition temperature of the various hydrazones. Excepting nitrobenzaldehydedimethylhydrazone, the ignition delay varies linearly with the decomposition temperature.

It is well known that concentrated HNO_3 can simultaneously nitrate and oxidize a variety of organic compounds. The oxidation predominates nitration if the HNO_3 is diluted, and vice versa.[6] The effect of oxidation reactions of concentrated HNO_3 with hydrazones is not apparent as far as their ignition delays are concerned. Nevertheless, oxidation appears to be significant and may be taking place simultaneously along with nitration and acid-base reactions. This is evident from an analysis of the preignition reaction products of the benzaldehydephenylhydrazone-HNO_3 system which shows one of the products to be benzoic acid. This must have been formed by the oxidation of benzaldehyde. The arylhydrazones are known [24] to become oxidized to their parent aldehydes on heating, which accounts for the formation of benzaldehyde in the present case.

Conclusions

1) Solid hydrazones formed by the reaction of aldehydes with phenyl and dimethylhydrazines are hypergolic with concentrated HNO_3 and RFNA. The extent of hypergolicity depends upon the chemical structure and strength of the acid, if other physical factors are kept constant.

2) Nitration and neutralization appear to be the most important preignition reactions, although oxidation reactions may also be taking place simultaneously.

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