

BRIEF COMMUNICATION

Ignition and Thermal Behaviour of Solid Hydrazones

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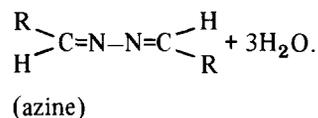
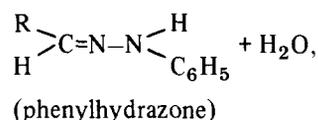
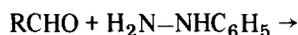
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In a hybrid rocket system, a solid fuel is chosen which ignites spontaneously on coming into contact with a liquid oxidizer such as red fuming nitric acid (RFNA). Solid amines, such as p-phenylenediamine, p-toluidine and xylydines [1], and amine-formaldehyde compositions [2] have been considered as fuels for this purpose. However, compounds having N-N bonds are generally more energetic and are therefore preferred for high energy propellant formulations. It is well known that hydrazines, particularly phenylhydrazine, form solid condensation products with aldehydes and ketones, which contain N-N bonds. We have considered the use of these products, the hydrazones, as solid fuels for hybrid systems. It is interesting to note that often compounds containing N-N bonds, such as tetraformaltrisazine [3] and furfuraldazine [4], have recently been investigated for a similar purpose.

The various hydrazones prepared during the course of this investigation were found to have tolerable ignition delays with RFNA. These compounds decompose exothermally on heating, as shown by differential thermal analysis (DTA). The thermal stability of these compounds has been compared with those of the azines, the analogous condensation products of hydrazine hydrate.

The phenylhydrazones were prepared by reacting phenylhydrazine with various aldehydes following established procedures [5]. In the case of benzophenone, the hydrazones were prepared by refluxing alcoholic solutions of benzophenone with phenylhydrazine and hydrazine hydrate, respectively. Benzalazine and formaldazine were

prepared by mixing 0.2 mole of hydrazine hydrate with 0.5 mole of the respective aldehyde and recrystallizing with alcohol. These reactions could be represented as follows:



With the exception of formaldehyde, which gives polymeric products with both phenylhydrazine and hydrazine hydrate, the condensation products were crystalline, nonhygroscopic materials. Some assessment of the purity of these compounds was obtained by comparing their melting points with those reported in the literature, as shown in Table 1. The infrared spectra of the various hydrazones showed a C=N stretching band at ca. 1620 cm^{-1} . DTA was carried out over the temperature range 35 to 400°C on an apparatus similar to that described earlier [6]. Platinum cups were employed and a heating rate of $12.5^\circ/\text{min}$ was chosen for these experiments. The peak temperatures reported in Table 1 correspond to the temperature of the maximum peak height. Thermogravimetric

TABLE I
DTA and Ignition Delay Results

Hydrazone/azine	Melting point (°C)		DTA ^a Peak temperatures in air (°C)	Ignition delay (m.sec.)
	Observed	Reported ^b		
Benzaldehyde phenylhydrazone	157	157-8	155(-) 282(+)	300
Furfuraldehyde phenylhydrazone	98	97-8	98(-) 258(+)	100
Formaldehyde phenylhydrazone	-	-	100(-) 210(+) 250(+)	480
Benzophenone phenylhydrazone	139	137	140(-) 305(+)	Vigorous reaction no flame
Tetraformaltrisazine	-	-	240(-)	590
Benzalazine	96	93	98(-) 322(-)	Vigorous reaction no flame
Furfuraldazine	112	111-12.5	110(-) 280(-)	80
Benzophenone hydrazone	98	98	98(-) 330(-)	Vigorous reaction no flame

^a (+) and (-) after temperature represent exotherm and endotherm, respectively.

^b Reported in Refs. [11] and [12].

analysis (TGA) was carried out on a conventional McBain-Bakr type quartz-spring balance [7]. Ignition delays were determined at room temperature by the cup test method using RFNA with a 10-12% NO₂ content.

The results presented in Table 1 show that some of the phenylhydrazones are hypergolic with RFNA with ignition delays comparable to those of the azines and other hybrid systems [2,4,8]. Careful examination of these systems suggests that the phenylhydrazones formed by the reaction of an aldehyde rather than a ketone appear to be hypergolic with RFNA. This is shown by the failure of the hydrazones of benzophenone and other systems [9] to ignite on reacting with RFNA.

The thermal stability of these compounds could be estimated from the DTA results. The first (endothermic) peak observed in all cases corresponds to melting of the compound. The second (exothermic) peak observed in the case of the phenylhydrazones is due to the decomposition of the compound. These exotherms are not affected by a nitrogen atmosphere. On the other hand, the second (endothermic) peak observed in the case of the azines and benzophenone hydrazone is due to

boiling of these compounds. The TGA weight losses corresponding to the second peak temperature in the DTA exceed 95% in the case of the azines and 75-90% in the case of the hydrazones. In order to study the decomposition which may accompany boiling, these compounds were sublimed at atmospheric pressure. While benzalazine and benzophenone hydrazone could be sublimed almost quantitatively, furfuraldazine sublimed with considerable decomposition leaving a residue behind. Similarly, tetraformaltrisazine is reported to decompose on heating [10].

These results show that the aldehyde phenylhydrazones that are hypergolic with RFNA all decompose on heating. Similarly the azines that were found to be hypergolic, i.e., furfuraldazine and tetraformaltrisazine, decompose to a certain extent on heating. However, benzalazine and benzophenone hydrazone, which boil without decomposition, were found to be nonhypergolic with RFNA, under identical experimental conditions. In the present series of compounds, it therefore appears that those which decompose on heating are likely to ignite more readily when brought in contact with an oxidizer than those which volatilize.

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