United States Patent Office

3,066,479

Patented Dec. 4, 1962

3,066,479

STABILIZED AZIDE FUEL AND COMBUSTION PROCESS

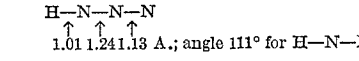
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No Drawing. Filed July 14, 1959, Ser. No. 826,905
16 Claims. (Cl. 60—35.4)

The present invention relates to a process for the controlled decomposition of azides in the presence of excess volatile base whereby the decomposed azide may be used as a fuel gas in a rocket, gas turbine or the like. Such controlled decomposition may be initiated and promoted by electrical or thermal ignition, contact with an oxidizer, contact with a catalyst, or by combinations of these and other procedures.

Azides have found little use because of the violently explosive character thereof and the attendant danger in handling them. A process for the controlled decomposition of azides is valuable because of the highly exothermic character of the decomposition reaction of the azides and the low molecular weight of the decomposition gas. These two characteristics make azides very valuable as fuel gases for mono-propellent rocket and gas turbine systems.

Azides exist either as anions or as parts of covalent molecules; this has been demonstrated on the basis of infrared analysis and electron and -ray diffraction. The following structure has been demonstrated on the basis of infrared bands and bond lengths of hydrazoic acid:



Both the azide ion and covalent azides have been shown to contain three nitrogen atoms in a straight line and, in the case of covalent azides, the bond length between the middle nitrogen and the unattached nitrogen is regularly shorter than the bond length between the other two nitrogens. This is believed to be largely responsible for the explosive character of covalent azides. In the case of hydrazoic acid, the 1.24 Angstrom link is an unstable one but, on the other hand, ionic azides have the azide ion stabilized by resonance, so that the two N—N bond lengths are the same. For example, in sodium azide, both N—N lengths are 1.15 Angstrom units.

Generally speaking, azides of alkali and alkaline earth metals are not very explosive. Azides of sodium, potassium, rubidium and cesium are colorless salts and may be heated to 300° C., or higher, without decomposition. All of the alkali and alkaline earth azides which have been examined have ionic azide structures. However, hydrazoic acid, organic azides, and azides of heavy metals such as silver and lead, have the covalent azide linkage as described above, and are highly explosive.

One apparent exception to the rule that ionic azides are not explosive is the compound ammonium azide, which is ionic but expodes at about 130° C. upon heating. It is believed that this exception is apparent rather than real and that the actual mechanism is loss of ammonia followed by explosion of the residual hydrazoic acid. This is substantiated by the observation that ammonium salts of weak acids generally drop in pH value, upon boiling in water solution, evidently as the result of loss of ammonia.

In accordance with the present invention, it is shown that azide salts of volatile bases, e.g. ammonium azide, which contain the azide ion, are sufficiently stable to

permit handling under carefully controlled conditions, provided the cation is present in excess.

Thus, ammonium azide in the presence of anhydrous ammonia liquefied under pressure is stabilized. Similarly, hydrazoimide (or hydrazinium azide, $N_2H_5{+}N_3^-$) is stabilized in the presence of excess hydrazine. Unsymmetrical dimethylhydrazinium azide ($(CH_3)_2N_2H){+}N_3^-$, in the present of dimethylhydrazine is also stabilized.

In each of these cases the base is strong enough to maintain the azide in the ionic form. An examination of the pH of approximately one-tenth molar solutions in water of the compounds ammonia, hydrazine, and unsymmetrical dimethylhydrazine (UDMH) shows values for the ammonia and dimethylhydrazine of about 11.5 and of about 11 for hydrazine.

Other volatile bases which may be used are substituted ammonias such as tetramethyl ammonium hydroxide, for example, and other substituted hydrazines such as methylhydrazine, for example. In general any volatile base may be used which vaporizes below 300° C. The advantages of using azide salts, in the presence of excess base as rocket fuels, is shown by the following discussion of heats of decomposition of various materials:

Some Physical Properties of Volatile Bases and Their Azides

	M.P.	B.P.	Density
NH_3	−78° C.	−33° C.	.077
H_2NNH_2	1	114	1.01
$(CH_3)_2NNH_2$		63 / 717 mm.	
HN_3	−80	+37	

There are three variables, depending upon the inherent properties of a rocket propellant, which are important in rating the efficiency thereof as a fuel, i.e. combustion temperature, combustion gas molecular weight, and specific heat ratio. The specific heat ratio varies very little between fuels and so may be omitted from consideration. The combustion temperature largely depends upon the heat of the fuel reaction and, secondarily, on the heat capacity of the products at constant pressure which, like the specific heat ratio, varies little from one reaction to another. The combustion gas molecular weight is highly important, as the lower the molecular weight, the greater the volume of gas product resulting from the particular reaction.

A product with decreased gas molecular weight is especially desirable in providing thrust with a higher volume of gas output for a given temperature of rocket exhaust parts than is possible with any oxidation reaction from bi-propellent systems. For example, the decomposition of the mono-propellent hydrazine and the oxidation of ethyl alcohol are shown in the following two equations:

$$N_2H_4 \rightarrow 2H_2 + N_2 + 12 \text{ kilocalories}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + 328 \text{ kilocalories}$$

Disregarding for the moment the difference in exothermic heat of the two reactions, the complete decomposition of hydrazine to its elements converts one mole of liquid to three moles of gas, whereas the reaction of alcohol and lox, i.e. liquefied oxygen, converts four moles of liquid to five moles of gas. The gas molecules are larger in the latter case and fewer of them result from a given amount of the liquid needed for the reaction.

The two cited reactions, plus five other relevant reactions, are as follows:

$NH_3 \rightarrow \frac{3}{2}H_2 + \frac{1}{2}N_2 - 10.9$ kilocalories	1 mole to 2 moles (1)
$HN_3 \rightarrow \frac{1}{2}H_2 + \frac{3}{2}N_2 + 70.9$ kilocalories	1 mole to 2 moles (2)
$NH_4N_3 \rightarrow 2H_2 + 2N_2 +$ about 41 kilocalories (density 1.35)	1 mole to 4 moles (3)
$N_2H_4 \rightarrow 2H_2 + N_2 + 12$ kc. (density 1.01)	1 mole to 3 moles (4)
$H_2NNH_2 \cdot HN_3 \rightarrow \frac{5}{2}H_2 + \frac{5}{2}N_2 +$ about 64 kc. (density 1.2)	1 mole to 5 moles (5)
$H_2NNH_2 + O_2 \rightarrow 2H_2O + N_2 + 128$ kc. (density 1.01) (density 1.14)	2 moles to 3 moles (6)
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + 328$ kc. (density 0.79) (density 1.14)	4 moles to 5 moles (7)

Heats of decomposition for ammonium azide and hydrazinium azide are not available, but it is known that ammonia and acetic acid neutralize with evolution of about 19 kilocalories of heat. On the basis of heat of neutralization for these two azides of 10 kc. per mole and heats of formation as follows: ammonia +10.9 kc., hydrazine −12 kc., hydrazoic acid −70.9 kc., the above heats of decomposition were estimated.

An examination of the above tabulation shows that, like the decomposition of hydrazine, the decompositions of ammonium azide and hydrazinium azide produces high percentages of hydrogen and large volumes of gaseous products compared to the volume of liquid decomposed. In fact, the relative amounts of gaseous products are even greater. Unlike hydrazine, these two decompositions (Equations 3 and 5) show high heats of decomposition so that the heats of decomposition are comparable to the heats per mole of the bi-propellant systems, alcohol and oxygen, and hydrazine and oxygen (Equations 6 and 7), on a basis of one mole of material placed in a rocket. Thus, comparing the decomposition of one mole of hydrazinium azide with the reaction of one mole of hydrazine and one mole of oxygen, the heat of combustion of the latter reaction should be divided by two to be on a basis comparable to one mole of reacting material. Similarly, the heat of combustion of one mole of alcohol and 3 moles of oxygen should be divided by four to be on a basis of reaction of one mole of material.

From the foregoing, it will be seen that the heat of decomposition of azides is comparable to the heat of oxidation of oxidizable compounds. Further, the unusually low product gas molecular weights of the decomposition products of azides and volatile bases are much more favorable for rocket operation than the corresponding products of oxidation reactions.

It is also within the scope of this invention to combine the decomposition of azides in the presence of excess volatile bases, with partial or complete oxidation, with an oxidizing agent, of the fuel.

The operational advantage of the use of hydrazine and an oxidizer for rocket fuel, i.e. a specific impulse higher by about 20 than that resulting from the oxidation of carbon-containing fuels, has led to an extensive program for the development of methods for manufacturing hydrazine. However, hydrazine remains expensive and difficult to manufacture. Manufacture of the safer UDMH likewise presents difficulties.

Azides are also expensive, but this is, apparently, due primarily to the hazardous nature thereof and the consequent slight demand therefor. Other azides are normally prepared from non-explosive azides by a simple procedure; sodium azide, in turn, is prepared from non-explosive low cost materials, according to the following equations:

(1) $NH_4NO_3 \rightarrow N_2O + 2H_2O$

(2) $N_2O + NaNH_2 \rightarrow NaN_3 + H_2O$

For liquid and vaporizing liquid fuel operation in a rocket or gas turbine, the fuel escapes through, or is pumped into, an ignition zone where ignition may take place by electrical or thermal means, by contact with an oxidizer either for start-up or throughout the course of the reaction, by a catalytic method, for example, using a platinum group metal-containing catalyst, or by a combination of these procedures.

For example, the reaction is initiated by contact of 100 percent nitric acid and an azide with excess volatile base, using either spark or heat ignition. After the reaction is initiated, the nitric acid flow is shut off and the reaction continues, being supported by its own heat of decomposition. The reaction may also be initiated by a spark, without the use of an oxidizer. Further, the azide with excess volatile base may be ignited by passage over a catalyst, for either decomposition or oxidation reactions, with use, in the latter reaction, of additional oxidizing materials. Suitable catalysts include mixed copper oxide-manganese oxide mixtures, platinum metals and the like.

The invention will be further illustrated by reference to the following specific example:

Example I

A fuel containing 20 percent hydrazine and 80 percent hydrazinium azide is thoroughly mixed at a temperature of about 70° C., in order that both the hydrazine and hydrazinium azide are maintained in the liquid form. It is essential, in order for the hydrazine to provide the basic environment for the hydrazinium azide, that the two materials be mixed together as completely as possible.

It is essential that the fuel chamber to which this fuel is to be added contains no materials inducing decomposition of hydrazine; thus, the fuel chamber must be entirely free of any iron rust, for example.

The fuel is then charged to the second stage of a rocket, the first stage consisting solely of the oxidizer IRFNA (fuming HNO_3 containing 22 percent NO_2), together with the necessary equipment to pressurize the oxidizer. Suitable quantities of fuel and oxidizer are 2,000 lbs. of IRFNA in the first stage, and 12,000 lbs. of the fuel in the second stage.

In operation, the oxidizer is used to burn part of the fuel in the initial blast-off, after which the first stage is dropped from the rocket and the remainder of the rocket power is provided by the fuel as a mono-propellant.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A composition comprising an azide of a volatile base, and an excess of the base forming the basic cation sufficient to stabilize the azide.

2. A composition according to claim 1 in which the azide is ammonium azide.

3. A composition according to claim 1 in which the azide is hydrazinium azide.

4. A composition according to claim 1 in which the azide is unsymmetrical dimethylhydrazinium azide.

5. A composition comprising an azide of a volatile base, and an excess of the base forming the basic cation sufficient to stabilize the azide, the volatile base being one that vaporizes at a temperature below 300° C.

6. A method for producing thrust or driving force, which comprises burning in a combustion zone a composition comprising an azide of a volatile base, and an excess of the base forming the basic cation sufficient to stabilize the azide, to decompose the composition to obtain combustion product gases for producing the thrust or driving force.

7. A method for producing thrust or driving force, which comprises burning in a combustion chamber a composition comprising an azide of a volatile base, and

an excess of the base forming the basic cation sufficient to stabilize the azide, the volatile base being one that vaporizes at a temperature below 300° C., to decompose the composition to obtain combustion product gases for producing the thrust or driving force.

8. A method according to claim 6 in which the combustion decomposition is effected by electrical ignition.

9. A method according to claim 6 in which the combustion decomposition is effected by thermal ignition.

10. A method according to claim 6 in which the combustion decomposition is effected by contact with an oxidizer.

11. A method according to claim 6 in which the combustion decomposition is effected by electrical ignition and contact with an oxidizer.

12. A method according to claim 6 in which the combustion decomposition is effected by heat and contact with an oxidizer.

13. A method according to claim 6 in which the combustion decomposition is effected by contacting the composition with a catalyst selected from the group consisting of a platinum group metal-containing catalyst and a copper oxide-manganese oxide catalyst.

14. A method according to claim 13 in which the catalyst is a platinum group metal-containing catalyst.

15. A method according to claim 6 in which the combustion decomposition is effected by contacting the composition with a catalyst selected from the group consisting of a platinum group metal-containing catalyst and a copper oxide-manganese oxide catalyst, and an oxidizer.

16. A method according to claim 6 in which the combustion decomposition is effected by heating and contacting the composition with a catalyst selected from the group consisting of a platinum group metal-containing catalyst and a copper oxide-manganese oxide catalyst.

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