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PROCESS FOR PREPARING HYDRAZINIUM DIPERCHLORATE

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This invention relates to a process for preparing anhydrous hydrazinium diperchlorate from inexpensive materials in good yield and in a high state of purity.

More particularly, this invention concerns a process for preparing hydrazinium diperchlorate through the reaction of a perchlorate salt with a hydrazinium dihalide in a non-aqueous reaction environment.

Recently it has been disclosed that hydrazinium diperchlorate, a known and potent oxidizing agent has utility as an oxidizer in high energy solid propellant compositions. This information has appeared among other places in U.S. Pat 3,006,743.

When hydrazinium diperchlorate is utilized as a propellant oxidizer, the control of certain of its physical characteristics is essential to satisfactory performance. For example, seemingly trivial properties such as residual moisture, the amount of water of hydration, crystal structure and the type and amount of contaminants are all critical factors in the oxidizers performance.

A particularly critical factor in the preparation of propellant-grade hydrazinium diperchlorate is control of the residual moisture in the product. Surprisingly enough, complete absence of residual moisture is a necessity when hydrazinium diperchlorate is used as a propellant oxidizer. While the presence of excess moisture in the oxidizer is disadvantageous in most propellant compositions, when hydrazinium diperchlorate is used as an oxidizer, the presence of excess moisture is dangerous. This is because hydrazinium diperchlorate acquires hypersensitivity to detonation by shock when even a trace of moisture is present. This hypersensitivity, which is imparted by even small amounts of residual moisture, renders the oxidizer extremely hazardous to produce, handle and store, particularly in the presence of other easily oxidable components commonly found in propellant compositions. The hazards introduced by the presence of residual water can be avoided by isolating the hydrazinium diperchlorate as the hydrate. However, the hydrate is less advantageous than the anhydrous salt in other respects; for example, it is less energetic and less dense and is much more sensitive to detonation by shock than is anhydrous salt. The use of a denser oxidizer offers a substantial advantage in propellant compositions. Not only is the oxidizing power of the salt per unit weight increased but the use of the more dense form of the oxidizer permits the use of a larger propellant charge in the rocket motor. This in turn increases the range of the rocket without increasing its size. A gain of this type is especially important in manned aerospace travel.

Freedom from contaminants is also especially desirable when hydrazinium diperchlorate is to be used as an oxidizer in propellant compositions. Again, it has been found that the presence of contaminants or even of reaction by-products is to be avoided where possible. For example, the hydrazinium monoperchlorate, a by-product in some preparations of the diperchlorate, is an undesirable contaminant in propellant compositions. Not only is the monoperchlorate much less energetic as an oxidizer than the hydrazinium diperchlorate, but it is much more sensitive to detonation by shock than the diperchlorate.

While there are several prior art processes for preparing the hydrazinium diperchlorate, all of them have distinct disadvantages. For example, some of the processes involve the direct neutralization of hydrazine base with concentrated perchloric acid. These processes involve the use of an expensive and hazardous reagent, anhydrous perchloric acid, as well as the preparation of the undesirable monoperchlorate as a contaminating by-product. As indicated earlier not only is the monoperchlorate hypersensitive to detonation but is also difficult to remove from the diperchlorate product.

While it is possible to obviate some of these process defects by neutralizing the hydrazine base with dilute perchloride acid in an aqueous system, other problems arise. For example, in processes where an aqueous system is used, it is essential to avoid the formation of the less energetic, less dense hydrazinium diperchlorate hydrate and to remove all the traces of residual moisture from the product. In either event some type of dehydration step is required. Since the dehydration of a powerful oxidizing agent by direct drying is hazardous, alternative and more expensive drying procedures such as azeotropic or vacuum distillation must be resorted to. These and other drying methods require more extensive drying and distillation equipment, more handling of hazardous materials, and extending the number of process steps and the time required for their completion.

For these reasons, the direct preparation of an anhydrous form of hydrazinium diperchlorate substantially free from residual moisture and contaminants is an important advance in the propellant art.

Thus, it is an object of this invention among others to directly prepare anhydrous hydrazinium diperchlorate in good yield by a non-hazardous preparative process.

It is another object of this invention to prepare hydrazinium diperchlorate sufficiently free from residual moisture to obviate further drying steps.

It is a further object of this invention to prepare hydrazinium diperchlorate anhydrous substantially free from reaction by-products and troublesome contaminants such as the hazardous hydrazinium monoperchlorate.

Yet a further object of this invention is the preparation of hydrazinium diperchlorate product relatively insensitive to detonation by shock.

Still another object of this invention is the preparation of a stable, high density, anhydrous hydrazinium diperchlorate capable of producing more thrust per unit weight of propellant composition than is possible with hydrated forms of the product.

The above objects and many others are achieved by a novel synthetic process conducted in an anhydrous reaction environment. The preparative reaction involves contacting a hydrogen fluoride solution of ammonium perchlorate or certain alkali metal perchlorates with a hydrazinium dihalide salt under substantially anhydrous reaction conditions. The diperchlorate product which is formed is insoluble in anhydrous hydrogen fluoride and can be removed by filtration or decantation. While the inventive process is not intended to be dependent upon or limited to any specific reaction mechanism or reaction intermediates, the following equation is presently believed to represent the overall reaction course.

$$2MClO_4 + N_2H_6X_2 + 2HF \xrightarrow[HF]{\text{excess}} N_2H_6(ClO_4)_2 + 2MF + 2HX$$

wherein M is selected from the group of perchlorate salts consisting of sodium, potassium, rubidium, cesium, and ammonium perchlorates, and X is a halogen.

In the preferred process embodiment the perchlorate salt, preferably sodium perchlorate and the hydrazinium dihalide, preferably hydrazinium dichloride are intimately mixed and placed in a suitable corrosion resistant reactor fitted with stirring and cooling means, and a means of introducing inert gas atmosphere into the system. Anhy-

drous liquid hydrogen fluoride in excess is introduced to a chilled mixture of the reactants and the admixed reactants are slurried in the excess of anhydrous hydrogen fluoride solvent. The reaction is conveniently initiated by allowing the chilled reaction vessel to warm up, preferably to about room temperature. The amount of hydrogen fluoride used is not critical as long as at least a slight excess over what is required to solubilize the reactants is present. A larger excess of HF, while not necessary for the success of the reaction, is not detrimental to its success.

The first stage of the reaction (solvolysis of the hydrazinium perchlorate) can be followed visually by the evolution of the insoluble gaseous hydrogen halide by-product from the reaction mixture. The insoluble hydrogen halide gas is removed by slowly introducing an inert carrier gas such as nitrogen, argon, helium, or the like to the system. After the evolution of hydrogen halide gas has ceased, the stirring of the reactants in the excess of hydrogen fluoride reaction liquor is continued for at least an hour for up to 18 hours or more depending upon the size of the batch being produced. The smaller batches taking a shorter time and the larger batches taking a proportionately longer reaction time. The soluble fluoride salt is removed by filtrations, decantation or centrifugation after reducing the volume of the reaction liquor until the amount of hydrogen fluoride present is only slightly greater than that required to keep all the fluoride salt in solution. To minimize the contamination of the hydrazinium diperchlorate by the soluble fluoride salt by-product, it is desirable to wash the product several times with additional anhydrous hydrogen fluoride in which the product is only slightly soluble. Residual hydrogen fluoride is removed from the product by evacuating the system at room temperature. For most purposes the above obtained hydrazinium diperchlorate product containing only traces of hydrogen fluoride is satisfactory. However, where complete freedom from hydrogen fluoride is necessary, the last traces of hydrogen fluoride can be removed by exposing the product to a high vacuum at moderate temperatures (from about 50° C. and upwards). The required high vacuum can be obtained using an ordinary high capacity vacuum pump. Again, the length of time required for these operations is a variable limited primarily by batch size and the equipment available. Ordinarily, however, 16–48 hours evacuation of the system suffices to produce a product completely free from hydrogen fluoride.

The reaction conditions of the novel preparative process of this invention offer a fair degree of latitude. For example, while the liquid fluoride is conveniently added to the reaction mixture at low temperatures, the reaction itself proceeds readily at temperatures between 10–60° C., although about room temperature is preferred. Additional points of flexibility are in the optional use of a vacuum or inert atmosphere and in the order of adding reactants. For example, while the removal of hydrogen fluoride from the product is customarily expedited by the use of a strong vacuum, the same results can be obtained over a longer period of time by using a stream of dry inert gas to carry off the hydrogen fluoride. Similarly although the use of an inert gas atmosphere throughout the reaction is desirable to minimize contamination by atmospheric moisture, it is not essential to the success of the reaction. The use of an inert gas atmosphere can be avoided if suitable precautions are taken to keep the reaction free of moisture. For instance, the air can be dried by contacting it with a conventional drying agent such as phosphorous pentoxide or the like. Ordinarily, however, to minimize accidental contamination, the use of an inert atmosphere is desirable. Suitable and typical inert gases which can be used for this purpose include nitrogen, carbon dioxide, argon and the like.

The reaction will proceed satisfactorily when any of the disclosed alternative reactants are used. For example, while sodium perchlorate is the preferred perchlorate salt

reactant, other perchlorates such as potassium, rubidium, cesium and ammonium perchlorates in the form of their anhydrous salts are satisfactory reactants. Similarly, while hydrazinium dichloride is the preferred hydrazinium dihalide reactant, other dihalides such as the dibromide are alternative reactants. The critical factor in the choice of reactants and upon which the success of the process depends is the great difference in solubility of the hydrazinium diperchlorate product and the fluoride salt by-products in the anhydrous hydrogen fluoride reaction liquor. The hydrazinium diperchlorate product is soluble only to the extent of about 4 g. in 100 g. of hydrogen fluoride, while the solubility of the fluorides of sodium, potassium, rubidium, cesium and ammonium in hydrogen fluoride are all greater than 30 g./100 g. HF. Since lithium fluoride is relatively insoluble in anhydrous hydrogen fluoride it cannot be easily separated from the hydrazinium diperchlorate product. For this reason lithium perchlorate is not a satisfactory reactant in the inventive process. Because of the products freedom from contaminating by-products, the low cost and availability of the reactants, as well as the good yields obtained, the preferred reactants are sodium perchlorate and hydrazinium dichloride.

The novel process of this invention is advantageous in several respects. For example, the hydrazinium diperchlorate product obtained is in the anhydrous form rather than as a hydrate. As indicated earlier, the anhydrous product is a much more energetic oxidizer per unit volume of weight than the hydrates. An ancillary advantage in this respect is the higher density of the anhydrous product which facilitates handling, formulation and packing in propellant mixtures. An important advantage of the process is that the need for further drying of the product is eliminated. The drying steps are avoided since the hydrazinium diperchlorate product is obtained in the desired anhydrous form. Since the product is violently combustible with a variety of commonly encountered substances, reducing the number of process steps is a substantial advantage of the process.

Less important but significant advantages of the novel process are the low cost and availability of the reactants, the use of a less hazardous reactant (perchlorate salts rather than concentrated perchloric acid) and no significant contamination of the product by reaction by-products. The neutralization-type processes of the prior art produce a product containing significant amounts of the hydrazinium mono-diperchlorate. This by-product is difficult to remove from the product and is less energetic, and more shock sensitive than the diperchlorate.

Additional advantages of this invention will be gleaned by a perusal of the following examples which give more detailed illustrations of this inventive process.

EXAMPLE 1

Preparation of hydrazinium diperchlorate using sodium perchlorate and hydrazinium dichloride

In a reaction vessel equipped with stirring means, a cooling device and inlets for supplying nitrogen and liquid hydrogen fluoride, the following reactants are added; a pulverized and intimately admixed mixture of 2.45 parts by weight of anhydrous sodium perchlorate and 1.05 parts by weight of hydrazinium dichloride. The mixture is chilled to −80° C., purged with a nitrogen atmosphere, evacuated and 9.88 parts by weight of anhydrous liquid hydrogen fluoride is added to the reaction mixture. The system is brought back to atmospheric pressure by reintroducing nitrogen to the system and the reaction is initiated by allowing the reaction mixture to warm to room temperature. The solvolysis of the hydrazinium dichloride to the fluoride salt is evidenced by the evolution of bubbles of hydrogen chloride gas. The hydrogen fluoride suspension is stirred vigorously for 5 hours and allowed to settle. The insoluble fraction is hydrazinium diperchlorate and the soluble fraction is principally sodium fluoride, which has a solubility in hydrogen fluoride of

about 7 times greater than that of the hydrazinium diperchlorate product. The product is isolated by decanting the hydrogen fluoride solution containing solubilized sodium fluoride to a second tube. It is further purified by washing four times with small portions of anhydrous hydrogen fluoride. The yield of product is reduced somewhat during the washing and decanting steps because of its slight solubility in hydrogen fluoride. However, if desired, it is possible to recover that portion of the product which dissolves in the hydrogen fluoride from the sodium fluoride by fractionally crystallizing the product from the hydrogen fluoride wash liquor.

The hydrogen fluoride insoluble fraction containing the product is placed under reduced pressure for several hours to remove the residual hydrogen fluoride left in the product. A comparison of the products infra-red spectrum with that of a known sample confirms the identity of the product as hydrazinium diperchlorate. Analysis of a sample establishes that the product contains less than 0.3% sodium. The hydrazinium diperchlorate product melts with vigorous decomposition at about 200° C.

EXAMPLE 2

Preparation of hydrazinium diperchlorate using potassium perchlorate and hydrazinium dibromide as reactants

In this example the same equipment and procedure is followed as described in Example 1, except that 2.77 parts by weight of anhydrous potassium perchlorate, 1.94 parts by weight of hydrazinium dibromide and 10.65 parts by weight of anhydrous liquid hydrogen fluoride are used as reactants. Again a solid product is obtained which the melting point and infra-red analysis established to be the desired product.

EXAMPLE 3

Preparation of hydrazinium diperchlorate using ammonium perchlorate and hydrazinium dichloride as reactants

In this example the same equipment and reaction procedures are used as described in Examples 1 and 2 except that 2.34 parts by weight of anhydrous ammonium perchlorate, 1.05 parts by weight of hydrazinium dichloride, and 8.60 parts by weight of anhydrous liquid hydrogen fluoride are used as reactants. Infrared analysis and the melting point confirm the identity of the product as hydrazinium diperchlorate.

It is to be understood that the foregoing examples are for the sake of illustration only and that numerous changes and variations can be made in the ingredients, proportions and conditions specifically set forth therein without departing from the spirit of the invention as defined in the following claims.

We claim:

1. A process for preparing anhydrous hydrazinium diperchlorate substantially free from contaminants comprising the steps of contacting a hydrazinium dihalide with a perchlorate salt selected from the group consisting of sodium, potassium, rubidium, cesium, and ammonium perchlorates, in the presence of a stoichiometric excess of anhydrous hydrogen fluoride reaction liquor under substantially anhydrous conditions until insoluble hydrazinium diperchlorate product precipitates out and separating the precipitated product contained therein from the reaction liquor.

2. The process of claim 1 wherein the perchlorate salt is sodium perchlorate.

3. The process of claim 1 wherein the perchlorate salt is potassium perchlorate.

4. The process of claim 1 wherein the perchlorate salt is ammonium perchlorate.

5. The process of claim 1 wherein the hydrazinium dihalide is hydrazinium dichloride.

6. The process of claim 1 wherein the hydrazinium dihalide is hydrazinium dibromide.

7. The process of claim 1 wherein the perchlorate salt is sodium perchlorate and the hydrazinium dihalide is hydrazinium dichloride.

8. The process of claim 1 wherein the perchlorate salt is potassium perchlorate and the hydrazinium dihalide is hydrazinium dichloride.

9. The process of claim 1 wherein the perchlorate is sodium perchlorate and the hydrazinium dihalide is hydrazinium dibromide.

10. The process of claim 1 wherein the perchlorate is potassium perchlorate and the hydrazinium dihalide is hydrazinium dibromide.

11. The process of claim 1 wherein the perchlorate is ammonium perchlorate and the hydrazinium dihalide is hydrazinium dibromide.

12. The process of claim 1 wherein the reaction is conducted in an inert gas atmosphere.

References Cited

UNITED STATES PATENTS

3,131,997 5/1964 Stern ..... 149—36 X

OTHER REFERENCES

Turrentine: Journal of American Chem. Soc., vol. 37, pp. 1122–1128 (1915).

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