

[54] **1-AZIDO-1,1-DINITROALKANES, USEFUL
AS PROPELLANTS**

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260/349**

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[58] Field of Search **149/88; 260/349, 32.4;
204/72**

[56] **References Cited**

UNITED STATES PATENTS

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OTHER PUBLICATIONS

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(1964).

Primary Examiner—Leland A. Sebastian

[57] **ABSTRACT**

Azido nitro paraffin, a method for its preparation by
electrolysis of the corresponding nitroparaffin salt and
sodium azide and its uses as a plasticizer, propellant or
propellant component.

8 Claims, No Drawings

1-AZIDO-1,1-DINITROALKANES, USEFUL AS PROPELLANTS

BACKGROUND OF THE INVENTION

This invention relates generally to an energetic composition, a method for its preparation and its uses. More particularly, it relates to azido gem-dinitroparaffin. The nitro alkanes are commonly regarded as being a good source for energetic material and this particular nitroalkane is of special interest because its relative insensitivity to impact and thermal stability makes it a good choice as a propellant or as a component in a propellant system.

The process of making azido compounds has always caused chemists difficulty especially when the reaction is an attempt to add reactive groups to an already reactive and unstable compound. In the past, this reaction, if it proceeded at all, was likely to result in an explosion.

SUMMARY OF THE INVENTION

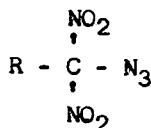
Accordingly, it is an object of this invention to provide an energetic material which is relatively insensitive to impact and is thermally stable.

Another object of this invention is to provide a method of preparation of an energetic material with the aforementioned properties.

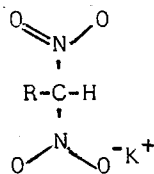
A further object is to provide a plasticizer for a polymer.

Still another object of this invention is to provide a propellant composition.

According to the invention these and other objects are attained by providing a new class of compounds which are represented by the following structural formula:



where R is a straight or branched chain containing up to approximately eight carbons including lower alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and pentyl among others. The method or preparation for the various energetic compounds consists of reacting a salt of the gem-dinitroparaffin with an azide in an electrolysis cell. For example, a salt having the formula



where R is aliphatic and contains up to eight carbons is reacted with an acid to form $\text{RCH}(\text{NO}_2)_2$ whereupon an azide in a basic solution is added thereto and the resulting solution is then electrolyzed to form the desired compound.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Although the compounds may be prepared as described above, there are some recommended steps to be followed if a good yield is desired. For example, in order to obtain a relatively pure starting material, the dinitro salt may first be made as a salt which is insoluble in water such as the potassium salt the preparation of which was previously reported by C. M. Wright and D. R. Levering in *Tetrahedron* 19 Supp. 1, 3 (1963). Another method of preparation for the potassium salt which can be used was suggested by Dr. Levering who used 1-chloro-1-nitroethane as a reactant in the Ter-Meer Process.

The limited solubility of the potassium salt which allows it to be prepared in a relatively pure form is disadvantageous in that it does not react effectively with the azide. But, it was found that the soluble dinitro salt does produce the azido derivative in good amounts and therefore, in the practice of this invention the potassium salt is converted into the soluble sodium salt. This may be accomplished by first converting the potassium salt into the dinitroalkane by the addition of hydrochloric acid and then reacting the alkane with the azide in a sodium hydroxide solution.

The products and processes of the invention are further described and illustrated by the examples hereinafter set forth.

EXAMPLE I

The potassium salt of 1,1-dinitroethane was prepared according to the Wright and Levering method which has already been disclosed. This salt was then converted to 1,1-dinitroethane in approximately 90% yield by the addition of aqueous 5% HCl and extracting with chloroform. A 10% HCl solution can also be used although the yield of the alkane was less than with the 5% solution.

A 100 ml aqueous solution of approximately 7% of the dinitroethane was adjusted to pH of approximately 8 with NaOH and 5% solution of sodium azide. The solution was then electrolyzed at a current of 3 amps. for 1 hour in a conventional electrolysis cell having a smooth platinum anode. The electrolysis was stopped every 15 minutes, the product 1-azido-1,1-dinitroethane (DNZE) removed and the electrolysis retrated. The crude electrolysis product was then purified by preparative-scale gas chromatography. The electrolysis proceeded smoothly and the overall yield was about 25%.

EXAMPLE II

The procedure followed with the propane derivative was substantially the same as described above except that the starting material was the potassium salt of dinitropropane prepared according to the Wright and Levering method. 15.3 g of the resulting yellow crystals were neutralized with 500 ml. of 5% HCl solution. Some of the salt formed did not dissolve and was removed and dried by vacuum (6.79g. obtained — purity 99.7% by G.C.). The HCl solution was extracted with three 100-ml portions of chloroform which was removed and 4.2g of dinitropropane (DNP) (95.8% by G.C.) was recovered at 91% yield. Eight ml. of DNP was dissolved in 100 ml. of distilled water with the aid of NaOH resulting in a pH of 9.2. Then 7.5g% sodium

azide was added. This solution was then placed in an electrolysis cell in which the dinitropropane solution prepared above was used as the anode solution and a few milliliters of 1% NaOH was added to the cathode compartment to serve as a catholyte. The entire assembly was immersed in an ice bath and a current of 3 amps. was passed through the solution. Electrolysis was stopped every 15 minutes and the product which had been formed was removed from the cell. This was continued until no appreciable product formed during a 15 minute period. The total electrolysis time took 1.5 hours and yielded 4.34 grams of 1-azido-1,1-dinitropropane (DNZP) which constituted 27% yield based on the amount of DNP at the start and assuming that there is no recoverable DNP in the anode solution. This product analyzed 81% pure by gas chromatography.

EXAMPLE III

A sample of 3 parts of DNZP (Example II) was mixed with 1 part of polynitropropene. The propane derivative plasticized the polymer. A differential thermal analysis was run and the mixture was found to be stable to over 120°C.

EXAMPLE IV

The effectiveness of the compounds in propellant compositions was further tested by calculating the specific impulse (I_{sp}) of the compositions. Accordingly as demonstrated in the Table set forth below, the compositions containing the compounds of the invention exhibit higher values than those containing nitroglycerine (NG) for which the compounds were substituted.

For purposes of reference, nitrocellulose is referred to as NC, aluminum Al, cyclotetramethylenetetranitramine HMX and nitrodiphenyl amine as NDPA. The percentages are in weight percentages.

TABLE

	NC	Al	HMX	DNZP	DNZE	NG	2-NDPA	I_{sp}
1.	10	16	44	30				275.8
2.	10	18	42		30			278.1
3.	10	18	42			30	1	273.2
4.	10	16	43					278.1
5.					100			

Run number 5 in the Table sets forth that DNZE exhibits a high I_{sp} which indicates that it would also be good monopropellant as well as a plasticizer and a component in a propellant composition.

PROOF OF STRUCTURE

The structure of the azide dinitroparaffins was proven by a combination of infrared, nuclear magnetic resonance (NMR), gas chromatography and elemental analysis. For example, a purified sample of 1-azido-1,1-dinitroethane (Example I) yielded an NMR spectrum of a single peak at 130 cycles/sec. due to the $-\text{CH}_3$, the only protons in the sample. The same sample, on analysis was found to contain 43.4% N (theoretical 43.5%). Infrared showed complex absorption in the azide region, bands at 2,117 cm^{-1} , 2,150 cm^{-1} and 2,190 cm^{-1} , and strong absorption in the nitro region (1,588 cm^{-1}). Gas chromatography indicated that the sample contained only one major component that accounted

for more than 98% of the sample. These data thus proved the structure of the resultant product.

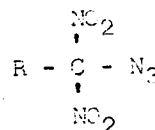
PROPERTIES OF THE AZIDO DINITROPARAFFINS

Both the ethane and the propane derivatives are dense, oily and faintly yellow liquids. One milliliter of the ethane derivative was found to weigh 1.456g at room temperature and boils at 44°C (1.75mm.). Also both compounds are extremely irritating to the eyes, nose and skin even in small quantities and therefore find use as a tear gas. In addition, these compounds exhibited relative insensitivity to impact. For example, the ethane has a sensitivity of approximately 80 cm (2-kg. weight, 50%) and the propane a sensitivity of approximately 100 cm. (2-kg. weight, 50%). On differential thermal analysis (DTA), both compounds were found to be stable to over 100°C at a heating rate of 10°/min. The Examples set forth herein for the preparation of the azido dinitroparaffins were performed with a smooth platinum. However, anodes made from other materials such as graphite or nickel can be used without departing from the scope of the invention. In addition, the aqueous solutions of the Examples can be replaced by solutions containing other solvents such as methanol or acetonitrile and the electrolysis process would produce the same product.

As will be apparent to those skilled in the art, various other modifications of the invention can be made or followed in view of the above disclosure without departing from the spirit and scope of said invention.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A compound of the structure



wherein R is alkyl and contains up to eight carbons.

2. A compound according to claim 1 wherein R is lower alkyl.

3. 1-azido-1,1-dinitroethane.

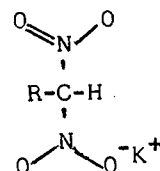
4. 1-azido-1,1-dinitropropane.

5. A method of making an azido gem-dinitroparaffin which comprises the steps of reacting a soluble salt of the gem-dinitroparaffin with sodium azide in an electrolysis cell.

6. A method according to claim 5 wherein the electrolysis cell contains a smooth platinum anode.

7. A method of preparing the compound of claim 1 which comprises the steps of

reacting



where R has the same significance as in claim 1 with hydrochloric acid to form $\text{RCH}(\text{NO}_2)_2$;

adding sodium azide in a basic solution; and electrolyzing the solution.

8. The method of plasticizing polynitropropene by adding to said polymer the compound of claim 1.

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