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PROCESS FOR THE MANUFACTURE OF NITROFORM AND ITS SALTS

Donald J. Glover, Bowie, Md., Joseph C. Dacons and Darrell V. Sickman, Washington, D.C., and Marion E. Hill, Kensington, and Mortimer J. Kamlet, Silver Spring, Md., assignors to the United States of America as represented by the Secretary of the Navy

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to a new and improved process for the preparation of nitroform and the salts of nitroform. More specifically, the invention relates to a process whereby one of the nitro groups of tetranitromethane is replaced by a hydrogen, sodium or potassium or other light metal to produce nitroform or a salt of nitroform.

Nitroform, trinitromethane, $CH[NO_2]_3$, has been found useful as an intermediate in the preparation of a wide variety of compounds which have been found useful as high explosives and propellants. For example, 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate has been prepared by first reacting free nitroform with formaldehyde and an acrylic compound such as acrylic acid or acrylamide and then reacting the mixture of 2,2,2-trinitroethanol and 4,4,4-trinitrobutyric acid obtained as one of the products of the first reaction with sulfuric acid. This compound, 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate, hereinafter referred to as TNETB, is a castable explosive having a melting point of 93° C. and may be employed alone or in explosive mixtures as a substitute for TNT with improved results as may be seen from the following table comparing the two compounds.

Table I

	TNETB	TNT	Improvement TNETB/TNT, percent
Crystal density, g./cc.	1.78	1.65	8
Cast density, g./cc.	1.70	1.56	9
Percent oxygen	58.0	42.3	32
G. oxygen/cc.	1.03	0.70	47
Oxygen balance:			
to CO, percent	+21	−8	29
to CO_2, percent	−4	−47	43
Detonation velocity meters/sec.	8,450	7,054	20
Fragmentation velocity ft./sec.	4,440	3,680	21
Heat of detonation, cal. lg. [computed]	1,524	984	55
Underwater effects, equivalent weights:			
Shock wave	1.18	0.87	36
Bubble energy	1.16	1.00	16

The salts of nitroform are useful as intermediates in the preparation of TNETB and in the preparation of nitroform itself as hereinafter described.

Several methods are known for the preparation of nitroform and the salts of nitroform. Orton and McKee [Journ. Chem. Soc., 1920, 283] prepared tetranitromethane by the nitration of acetylene and in so doing isolated small amounts of nitroform which they suggested might be an intermediate in their process. Schulteiss and Schimmelschmidt [PB 47730, B.I.O.S. 709] adapted this process to the production of nitroform by stopping the reaction at the nitroform stage and extracting the mixture with nitrogen dioxide at 0° C. Because of the extreme conditions and complex equipment required, however, this process has never been effectively utilized for the production of nitroform.

Another method for producing nitroform and its salts

involves the reduction of tetranitromethane which is readily available from the nitration of acetylene, ketene [Dargens and Levy, Compt. rend., 229, 1081 [1949]], or acetic anhydride [Org. Syn., vol. 21, p. 105] or as a by-product in the manufacture of trinitrotoluene in accordance with the process described in U.S. Patent No. 1,632,959 to R. H. Gärtner. A variety of reagents have been employed in this reduction of the tetranitromethane but there are disadvantages attendant to the use of each. Thus potassium ethylate [Hantzsch and Rickenberger, Ber., 32, 629 [1899]] and sodium methylate [Macbeth, Ber., 46, 2537 [1913]] give the corresponding alkyl nitrates as hazardous by-products. The use of hydrazine is attended by the formation of toxic hydrazoic acid [Schultheis and Schimmelschmidt, supra] while alkaline hydrogen peroxide involves the use of an expensive and dangerous reagent. High cost or poor yields militate against the use of ammonia [Pietet and Genequard, Ber., 36, 2225 [1903]], sodium sulfite [Muraour, Bull. soc. chim., [4]35, 367 [1924]], potassium ferrocyanide [Chattaway and Harrison, Journ. Chem. Soc., 1916. 171] or aqueous alkaline solutions of glycerol [Macbeth and Orr, Journ. Chem. Soc., 1932, 534].

Tetranitromethane has also been reduced to nitroform by the agency of aqueous potassium hydroxide [Schmidt, Ber., 52, 400 [1919]]. The usefulness of this process is reduced, however, by the simultaneous hydrolysis of the tetranitromethane to potassium carbonate with the corresponding reduction in the yield of the desired nitroform product in accordance with the following equations:

$$C[NO_2]_4+2KOH\rightarrow KC[NO_2]_3+KNO_3+H_2O \quad [I]$$

$$C[NO_2]_4+2KOH\rightarrow K_2CO_3+4KNO_2+3H_2O \quad [II]$$

The relative yields of the two sets of products formed in these competing reactions depends on the concentrations of the tetranitromethane and the potassium hydroxide and it has been found that a potassium hydroxide concentration greater than 7 N and a molar ratio of potassium hydroxide to tetranitromethane greater than 100 to 1 is required to obtain a potassium nitroform yield higher than 80% while a 92.3 yield of potassium nitroform requires 14 N KOH. Such high concentrations of KOH are clearly prohibitive.

It is, therefore, an object of the present invention to provide a new and useful process for the production of nitroform and the salts of nitroform which is commercially feasible and which does not involve the use of extreme ambient conditions or hazardous or expensive reagents and does not produce hazardous by-products.

Another object is to provide a new and useful process for the production of nitroform and the salts of nitroform in high yield from low cost reagents.

Other objects and the attendant advantages of the invention will become apparent to those skilled in the art as the invention is disclosed in the following detailed description.

The above objects are achieved in accordance with the invention by subjecting tetranitromethane to the action of a light metal salt of nitrous acid in aqueous or aqueous alkaline solution. Applicants have discovered that the nitrite anion, alone or in conjunction with other alkaline materials converts tetranitromethane to nitroform anion in aqueous or aqueous organic solvents in accordance with the following equation:

$$C[NO_2]_4+NO_2^-\rightarrow C[NO_2]_3^-+N_2O_4 \quad [III]$$

In the presence of alkali, the nitrite anion is catalytic in its effect and is regenerated in accordance with the following equation:

$$N_2O_4+2OH^-\rightarrow NO_2^-+NO_3^-+H_2O \quad [IV]$$

In the presence of chemically equivalent quantities of

hydroxide and nitrite ions, the rate of the reaction leading to the nitroform salt is many orders of magnitude greater than the reaction leading to the formation of the carbonate. The conversion of the tetranitromethane under these conditions to the nitroform salt is, therefore, essentially quantitative with only negligible by-product formation of potassium carbonate. The reaction proceeds rapidly in good yields so as to minimize the effects of undesirable side reactions.

The reaction of the invention proceeds in aqueous solvents but most rapidly in mixed aqueous organic solvents in which the tetranitromethane is soluble. The reaction of the invention for example gives equally good yields in aqueous and in aqueous methanolic solutions but since the solubility of tetranitromethane in water is limited the reaction proceeds more slowly in this medium. The incorporation of an organic solvent, such as methanol, enhances the rate of the reaction by increasing the solubility of the tetranitromethane. However, above an optimum concentration of the organic solvent, e.g. 40 to 50 percent by volume of methanol, the inorganic reactants become insoluble. Since the function of the organic solvent is merely to increase solubility, any solvent for tetranitromethane which is also miscible with water may be employed. Aqueous solutions of methanol and dioxane have been employed in the reaction of the invention with equally good results. Other solvents such as butanol, ethanol, isopropanol, n-propanol and ethylene glycol may also be employed.

Any commercially available nitrite salt of a light metal which by dissociation furnishes nitrite ion in solution such as sodium or potassium nitrite may be employed in the reaction of the invention. When it is desired to isolate the nitroform salt, a nitrite such as potassium nitrite may be employed to form a relatively insoluble salt such as potassium nitroform. When it is desired to react the nitroform salt in situ a more soluble nitroform salt may be formed using a nitrite such as sodium nitrite as the starting reagent.

The nitrite salt may be used alone or in conjunction with other alkaline salts capable of neutralizing the acidic products of the reaction such as sodium or potassium carbonate, sodium or potassium bicarbonate, sodium or potassium hydroxide, or sodium or potassium acetate.

When the nitrite salt alone is used two equivalents per mole of tetranitromethane should be employed for best results. For example, when potassium nitrite is employed the stoichiometry of the reaction is expressed as follows:

$$C[NO_2]_4+2KNO_2+H_2O\rightarrow KC[NO_2]_3+KNO_3+2HNO_2$$

When used in conjunction with other alkaline salts smaller amounts of the nitrite salt may be employed. With one equivalent of potassium bicarbonate and one equivalent of potassium nitrite the stoichiometry is as follows:

$$C[NO_2]_4+KHCO_3+KNO_2 \rightarrow KC[NO_2]_3+KNO_3+CO_2+HNO_2$$

In this reaction the nitrite anion is not catalytic in its effect since it is converted to unionized nitrous acid. When two or more equivalents of the alkaline salt are present in the reaction solution the reaction is as follows:

$$C[NO_2]_4+KNO_2\rightarrow KC[NO_2]_3+N_2O_4$$
$$N_2O_4+K_2CO_3\rightarrow KNO_2+KNO_3+CO_2$$
$$\overline{C[NO_2]_4+K_2CO_3\rightarrow KC[NO_2]_3+KNO_3+CO_2}$$

Under these conditions the nitrite anion is truly catalytic inasmuch as it does not appear in the stoichiometry of the reaction.

The reaction of the invention will proceed at any temperature between the freezing point and the reflux temperature of the solvent. However, a temperature between about 45° and about 55° C., is preferred. At lower temperatures the rate of the reaction is diminished while at higher temperatures there is an increased tendency for

decomposition of the product to take place. A typical reaction gives yields of 95 to 100% in 2½ to 3½ hours at the preferred temperatures. Since the reduction is not strongly exothermic, no difficulty is involved in temperature control.

The reaction of the invention goes equally well in dilute or concentrated solutions but high concentrations are preferred in order to make maximum use of available reactor capacity. For a typical preparation in a solvent consisting of 50% methanol and 50% water at 50° C. the optimum concentrations are 2⅔ moles each of sodium nitrite, sodium bicarbonate and tetranitromethane per liter of solvent. Two factors determine the upper limit of the concentrations which can be used. These are [1] the solubility of the inorganic reactants and [2] the explosive nature of the intimate mixtures of tetranitromethane with organic fuels at higher concentrations of tetranitromethane. In the typical preparation described above the tetranitromethane is initially not completely miscible with the remainder of the mixture and vigorous stirring is required. However, after from about 15 to about 45 minutes the reaction mixture coalesces to a single phase and the stirring may be discontinued.

The order of addition of the reactants to the reaction mixture is not important, however, if an alkaline salt is employed in conjunction with the nitrous acid salt the preliminary mixing of the tetranitromethane with a solution of the alkaline salt followed by a delay in the addition of the nitrite is not desirable since this will result in a dimunition of the yield due to the side reaction represented by Equation II above.

The reaction of the invention may be employed to produce nitroform or a nitroform salt as desired. The nitroform salt may be isolated by precipitation, retained in solution for further reaction or, converted to free nitroform by reaction with a mineral acid such as hydrochloric, sulfuric, nitric or phosphoric acid.

Where free nitroform is the desired product the preferred procedure is to generate sodium nitroform through the reaction of tetranitromethane with sodium nitrite and sodium bicarbonate in a methanol/water solvent as previously described, and then to add to the reaction mixture an excess of a mineral acid to convert the sodium salt to free nitroform. The free nitroform may then be extracted from the aqueous solution with methylene chloride or chloroform, azeotropically distilling the extract or drying it over a drying agent to remove the water, concentrating the extract and chilling the extract to precipitate the free nitroform. Methylene chloride and chloroform are particularly convenient for the extraction, however, any low boiling solvent which will dissolve nitroform and which is immiscible with water may be employed.

The above procedure may be modified by the use of other nitrites such as potassium nitrite so that insoluble nitroform salts such as potassium nitroform are generated and reacted in situ with a mineral acid other than nitrous acid such as hydrochloric, sulfuric or nitric acid. The insoluble nitroform salts such as potassium nitroform are initially insoluble in the reaction mixture but with good stirring this does not impede the process.

A variation of the above procedure is to prepare and isolate the insoluble nitroform salt such as potassium nitroform. The insoluble nitroform salt is then suspended in an organic solvent in which free nitroform is soluble and dry hydrogen chloride gas bubbled into the mixture to convert the salt to free nitroform. The insoluble chloride which is formed may then be filtered off and the nitroform precipitated from the organic solution by concentrating and chilling the solution.

Analysis of solutions of salts of nitroform may be conveniently accomplished by diluting the solutions to suitable concentrations and measuring the absorbance at 350 millimicrons in the ultraviolet. The molar absorbency index of nitroform ion at this wave length has been accurately measured and found to be 14,418±30.

The invention will be more completely understood by reference to the following examples which are given by way of illustration only and are not to be considered as limiting the invention in any manner.

Example I

A vigorously stirred mixture of 31.1 g. [0.45 mole] of sodium nitrite and 37.8 g. [0.45 mole] of sodium bicarbonate in 150 cc. of 50 volume percent methanol-water was heated to 50° C. and 48.0 cc. [78.4 g., 0.40 mole] of tetranitromethane was added dropwise over a ten minute period. The initially colorless mixture soon turned yellow and then red, and within twenty minutes the multiphase system had coalesced to a single phase. The temperature was maintained between 45 and 55° C. for an additional three hours with continued stirring, after which time the system was allowed to cool. The yield of sodium nitroform, as determined by spectrophotometric analysis of the reaction mixture was 69 g. or 100% of the amount theoretically anticipated.

Example II

The initial procedure was identical with that of Example I with the exception that the temperature remained between 23 and 27° during the course of the reaction. The same color changes were observed, but they took place more slowly. In six hours, the mixture had not yet coalesced to a single phase, but after twenty two hours the system had become homogeneous. Spectrophotometric analysis after twenty four hours reaction time indicated the presence of 65.5 g. of sodium nitroform [95% of theory].

Example III

To a vigorously stirred solution of 61.2 g. [0.88 mole] of sodium nitrite in 200 cc. of methanol and 150 cc. of water at 22° C. was added in a single portion 48.0 cc. [78.4 g., 0.40 mole] of tetranitromethane. The system initially comprised two colorless phases but over a six hour period these coalesced to a homogeneously red solution. Stirring was continued for a total of twenty two hours. Spectrophotometric analysis of the reaction mixture indicated the presence of 65.5 g. of sodium nitroform [95% yield].

Example IV

The procedure was identical with that of Example III with the exception that the reaction temperature was 50° C. and the reaction time 45 minutes. The formation of a single phase required twenty minutes and the yield of sodium nitroform, determined spectrophotometrically was 62 g. [90% of theory].

Example V

In 25 cc. of 33⅓ volume percent dioxane were dissolved 2.12 g. [0.025 mole] of potassium nitrite and 2.50 g. [0.025 mole] of potassium bicarbonate. To this solution was added with vigorous stirring 1.96 g. [0.010 mole] of tetranitromethane. The mixture was heated at 45° C. for 2¼ hours during which time the usual color changes were observed and potassium nitroform began to precipitate. On cooling the reaction mixture to 6° C. and filtering, there was obtained 1.46 g. [78%] of pure potassium nitroform. Spectrophotometric analysis of the filtrate indicated the presence of an additional 0.38 g. [20%] of potassium nitroform.

Example VI

A solution of 76.0 g. [0.55 mole] of potassium carbonate and 94.0 g. [1.10 mole] of potassium nitrite in 300 cc. of 50% methanol-water was heated to 50° C. and 119 ml. [196 g., 1.0 mole] of tetranitromethane was added dropwise over a twenty minute period with vigorous stirring. After an additional three hours at 45–55° C., the mixture was cooled to 0° C. and the precipitate was filtered off, washed well first with cold methanol and then with ether, and air dried for two hours. The dried crude product weighed 229.2 g. of which spectrophotometric analysis indicated that 151.6 g. [80.0% of theory] was potassium nitroform.

Example VIII

To a solution of sodium nitroform in aqueous methanol prepared as in Example I was added 125 cc. of concentrated hydrochloric acid. The solution was continuously extracted with methylene chloride for 18 hours and the extract dried over anhydrous calcium sulfate. Removal of the methylene chloride by evaporation in vacuo left 11.5 g. of crude nitroform. The yield, based on tetranitromethane initially used, was 91% of theory.

Example VIII

Two hundred grams of a crude product containing 80% potassium nitroform was prepared as in Example VI and suspended in 1000 cc. of methylene chloride. With external cooling and vigorous agitation anhydrous hydrogen chloride was bubbled into the mixture until the color of the suspended material had changed from yellow to almost white. The inorganic salts were filtered off and the methylene chloride solution evaporated in vacuo to remove the solvent. The residue was nitroform. Conversion of the potassium salt to the free acid was almost quantitative.

From the foregoing it may be seen that there has been disclosed a new and useful commercially feasible process for the preparation of nitroform and the salts thereof under mild ambient conditions which process employs only easily available, inexpensive, safe reagents and produces a high yield of product without the formation of hazardous byproducts.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

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

1. The process of producing light metal salts of nitroform consisting essentially of reacting tetranitromethane with a nitrite salt of a light metal in the ratio of at least two equivalents of salt per equivalent of tetranitromethane.

2. The process of producing light metal salts of nitroform consisting essentially of reacting tetranitromethane with a nitrite salt of a light metal in the ratio of at least two equivalents of salt per equivalent of tetranitromethane in aqueous solution.

3. The process of producing light metal salts of nitroform consisting essentially of reacting tetranitromethane with a nitrite salt of a light metal in aqueous alkaline solution the sum total of the equivalents of nitrite and alkaline material being two per equivalent of tetranitromethane.

4. The process of producing nitroform consisting essentially of reacting tetranitromethane with a nitrite salt of a light metal in aqueous alkaline solution the sum total of the equivalents of nitrite and alkaline material being two per equivalent of tetranitromethane and reacting the product of the reaction with a mineral acid.

5. The process of producing nitroform consisting essentially of treating an aqueous alkaline solution of tetranitromethane in which one equivalent of trinitromethane is present per two equivalents of alkaline material with substantially two equivalents of a light metal salt per equivalent of tetranitromethane whereby the aqueous alkaline solution is sufficient to neutralize the acidic products of the reaction between the nitrite salt and the tetranitromethane, said last-named reaction resulting in a light metal salt of nitroform; and treating the said salt with a mineral acid whereby nitroform is produced.

6. The process of reducing tetranitromethane by treating the tetranitromethane in an aqueous alkaline solution containing at least two equivalents of alkaline material

per equivalent of tetranitromethane with nitrite anion furnished by a light metal nitrite salt, whereby a light metal salt of nitroform is produced.

7. The process of claim 6 wherein the ratio of chemical equivalents of the nitrite anion to the tetranitromethane is at least 2.0.

References Cited in the file of this patent

Chattaway et al.: J. Chem. Soc. (Lond), 1916, 171–74.
Schmidt: Ber. Deut. Chem., 52, 400–12 (1919).
Muraour: Bull. Soc. Chem. (4), 35, 367–79 (1924).
Kornblum et al.: J.A.C.S., 73, 4041–43 (1951).