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**Rosco Bodine**

February 4th, 2004, 04:46 PM

Having obtained the full texts for two old British patents related to a simplified method for producing azides , I am sharing this obscure and interesting information with others who may wish to experiment with and elaborate upon this process .

GB128014 , Complete Specification ,  
Improvements in and relating to the Production of Azides  
application date: June 17 , 1918 No. 9952 / 18  
complete accepted : June 17 , 1919

I , William Richard Hodgkinson , C.B.E. , of Ordnance College , Woolwich , London , S.E. 18 , Professor of Chemistry and Metallurgy , do hereby declare the nature of this invention and in what manner the same is to be performed , to be particularly described and ascertained in and by the following statement :

This invention relates to the production of azides .

The object of the invention is to provide a process of producing azides from salts of hydrazine without the employment of ethyl benzoate or the like , and the formation of benzoyl hydrazine . According to the invention , salts of hydrazine are diazotised by means of a suitable nitrite under such conditions that the reaction mass is at no time so distinctly acid as to redden litmus paper , but appears on the border line of acidity and alkalinity . The conditions of acidity under which the reaction is carried out according to the invention , are preferably comparable with the conditions of acidity as indicated by litmus paper , of , for instance a solution of boric acid . Thus in accordance with the invention , the nitrite solution is brought together with a salt of hydrazine in approximately the proportions required on the basis of theory to diazotise the hydrazine , under such conditions that the acidity never exceeds the degree of acidity indicated above , and an acidified salt of the metal of which the azide is required , is introduced into the mixture , or alternatively the mixture is added to the solution of the salt of the metal .

For example , silver azide is formed by adding a neutral solution of hydrazine sulphate and sodium nitrite in molecular proportions to a solution of silver nitrate of a degree of acidity with nitric acid enabling the conditions in regard to acidity set forth above to be realised , while avoiding the precipitation of silver sulphate . Thus , for example 130 grams of hydrazine sulphate is converted to the neutral hydrazine ammonium sulphate , which is more soluble in water than is the simple hydrazine sulphate , by the addition of ammonia solution , the mixture being made up to about 500 ccs . To this solution contained in a vessel in which it can be violently agitated , the calculated amount of sodium nitrite dissolved in 500 ccs. of water is added slowly so that the temperature does not rise much above 30 degrees Centigrade .

The reaction resulting in the formation of sodium azide may be represented by the following equation :



From this equation it will be seen that the solution would become acid as the result of the reaction were it not for the fact that sodium nitrite is never pure but is alkaline , the alkali in the nitrite ordinarily being sufficient to maintain the solution on the border line of acidity and alkalinity , and addition of a small quantity of alkali being made should such not be the case . The solution thus made contains sodium azide , some unchanged reagents , and the by-products of the reaction .

The sodium sulphate and sodium azide contained in the solution may be separated by crystallisation but preferably the solution is added gradually to an acidified solution of silver nitrate produced by adding 1.0 cc. of 70% of nitric acid to 1000 ccs. of a normal solution of silver nitrate which is violently agitated during such adding, the temperature of the reaction mass being prevented from rising much higher than 30 - 40 degrees Centigrade. With adequate cooling and agitation the yield of silver azide may be obtained equivalent to 85 % of the calculated possible amount. Instead of adding the diazotised solution to the acidified silver nitrate solution, the latter may be added to the former.

When starting from hydrazine nitrate which is also an acid salt, a solution of ammonia should be added in order to form the neutral hydrazine ammonium salt or, if desired, the neutral hydrazine sodium salt may be produced, the remaining steps of the process being then carried out as above described.

In producing lead azide, a solution of a hydrazine salt of an acid which will not result in the precipitation of an insoluble lead salt of the acid in question, for instance hydrazine nitrate, is employed, and the reaction mass in this case should be only just acid, as lead azide is particularly easily acted on by acids, while in producing silver azide the acidity of the reaction mass may be greater in order to avoid the precipitation of silver sulphate and agitation indicated in the foregoing example.

The azides produced in accordance with the invention are usually amorphous, and in this state they are safer to handle than when crystalline.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

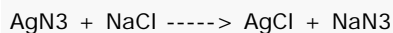
1. The process of producing azides from salts of hydrazine in which salts of hydrazine are diazotised by means of a suitable nitrite under such conditions that the reaction mass is at no time so distinctly acid as to redden litmus paper, but appears on the border line of acidity and alkalinity.

2. The process as claimed in Claim 1 in which the conditions of acidity under which the reaction is carried out according to the invention are preferably comparable with conditions of acidity as indicated by litmus paper, of, for instance, a solution of boric acid.

3. The process of producing azides from salts of hydrazine, substantially as hereinbefore described.

Dated this 10th day of December, 1918

Regarding the second patent GB129152, It simply states that another method of isolating sodium azide is to agitate in cool water a suspension of silver azide with slightly less than the theoretical amount of sodium chloride for a few minutes, and filter the precipitated silver chloride. The residual solution of sodium azide is evaporated on a steam bath to yield a concentrated solution of sodium azide. The reaction proceeds according to the equation



The sodium azide produced may be used in double decomposition reactions to form whatever other azides are desired.

**megalomania**

February 6th, 2004, 03:25 PM

Wow, that's a fascinating process if it works as it says. Preparing sodium azide in this way sure beats bubbling ammonia into liquid sodium metal to make the amide, and then reacting that to form the azide. It looks like lead azide will still have to be made from sodium azide in the usual way.

Hydrazine salts should be well within the means of amateur experimentors. In fact the procedure to make hydrazine on my website is derived from the procedure to make hydrazine sulfate; instead of concentrating the hydrazine hydrate thus formed from ammonia and bleach, one adds sulfuric acid. The full procedure has been posted on The Forum before.

I don't much care for purifying the sodium azide with silver nitrate... too expensive. I suppose by "The sodium sulphate and sodium azide contained in the solution may be separated by crystallisation" is fractional crystallization?

**Rosco Bodine**

February 6th, 2004, 05:33 PM

Yes , the "Hodgkinson Process" for azides would sure greatly simplify things when going the synthetic route from OTC precursors .

Hydrazine is more easily made from urea and 10 percent sodium hypochlorite pool chlorinator . I have done it a dozen times . The hydrazine is isolated as the monohydrazine sulfate . There is a fully detailed description of the method and its refinements posted at the Hive and also over at Mad Science . Feel free to import those files here if you wish .

The more modern but more difficult route to sodium azide requires freebasing the hydrazine from the sulfate and extracting the hydrazine hydrate with methanol portions . Then the methanolic extract of hydrazine hydrate is basified with a slight equimolar excess of sodium hydroxide , and treated dropwise with a slight equimolar excess of isopropyl nitrite , the reaction being performed over about two hours with the reaction flask in a plain ice bath . A closed glass system that can maintain a slight pressurization also complicates things for the more modern method , although it works very well and yields pure crystalline sodium azide directly .

The Hodgkinson patent describes a method which requires no elaborate glassware or volatile precursors . A good stirrer and some ventilation is about all that is required in the way of special equipment .

The only complication is that close control of pH is absolutely essential for the reaction to work . A good narrow range color indicator and perhaps a pH buffer scheme of some sort would be refinements which could be the basis for experiments .

The Hodgkinson patent method is probably general and there is room for many experiments to elaborate on the process .

For many purposes it will not be needed to isolate the sodium azide but only to use its solution . Or the sodium azide could be isolated by fractional crystallization . The silver azide double decomposition method is simply a shortcut route to a solution of pure sodium azide , and the silver is recyclable in the process .

Regarding the production of lead azide by Hodgkinsons method , the hydrazine sulfate must be first converted to neutral hydrazine nitrate and diazotised , and the solution treated with lead nitrate . Hydrazine sulfate can be treated with calcium nitrate and the calcium sulfate filtered , to leave a solution of hydrazine dinitrate . This is neutralized and then treated with sodium nitrite , to form a solution of sodium azide useful for producing lead azide .

**Rosco Bodine**

February 12th, 2004, 01:30 PM

Since obtaining copies of these patents I have been studying carefully the texts in preparation for experiments with Hodgkinsons patent process .

Marvin , or others who may be knowledgeable about the chemistry involved , I invite your input and ideas .

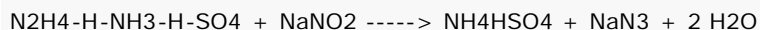
I have two significant , ( yet reconcilable ) issues concerning the Hodgkinson patent .

In the above patent there is information which I must legitimately question , regarding both the mechanism of the reaction and the pH .

According to Hodgkinsons description of the reaction ,

[QUOTE]

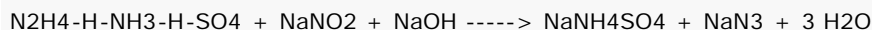
The reaction resulting in the formation of sodium azide may be represented by the following equation :



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[END QUOTE]

The observation I can make is that even \*if\* the Sodium Nitrite used by Hodgkinson was alkaline due to the presence of an "impurity" of an \*added\* equimolar amount of Sodium Hydroxide , ( which is certainly a great deal more than a "small quantity" of added alkali like Hodgkinson describes ) ..... the reaction product would still be so acid as to be more than sufficient to redden litmus . Let us consider the reaction equation for the situation I describe and this will be evident .



The NaNH<sub>4</sub>SO<sub>4</sub> is a "stipulated compound" to illustrate acidity , but in reality would probably be an indeterminate mixture of normal and acid sulfates of Sodium and Ammonia .

There is a ( possible ? ) way of reconciling this discrepancy . Where Hodgkinson describes preparing a solution of \*neutral\* hydrazine ammonium sulfate , no particular quantity of ammonia is specified as being added to achieve that \*neutral\* solution . There may be actually present in such a "neutral" solution an "excess" of alkali not accurately reflected by the simplified equation for the reaction as written by Hodgkinson . This excess alkali , together with the unspecified amount of alkali described as being present in Hodgkinsons "impure nitrite" , may satisfy the accounting for some of the missing amount of additional alkali not detailed by Hodgkinson .

The second issue regarding pH as described by Hodgkinson relates to the comparison of the pH required for the reaction as being comparable to the pH for a solution of Boric Acid . The pH for a .1 M solution of Boric Acid is pH 5.2 . The color change range for Litmus is pH 6 to pH 8 , so at pH 5.2 , the reaction mixture would already be quite red to litmus .....in direct contradiction with Hodgkinsons description .

In spite of these discrepancies which seem most obvious and somewhat perplexing , I believe that Hodgkinsons process probably does indeed work , although not all of the finer details are disclosed completely by the patent .

It would be nice to have a more detailed and modern description of the process after the subtleties are worked out from experiments . Only from experiments shall we know "the rest of the story" about Hodgkinsons patent process for producing azides from hydrazine salts .

Rosco

**Rosco Bodine**

March 14th, 2004, 09:47 PM

Update :

After many careful experiments have been done without success at reproducing the results described by GB128014 , I am reasonably

sure the method described by the patent is BOGUS and unworkable .

I used pure chemicals , accurately measured and controlled conditions of pH in different experiments , in increments of two tenths of a pH across the range from pH 5 to pH 7.2 .

I tried following the patents process description exactly , and I tried variations of every sort I could contemplate , with no joy in producing azides except in useless trace quantity mixed with inert undesired by products .

On rare occasion I have encountered this scenario before , where a patent makes disclosure of a technology which does not withstand scrutiny . There is no way of being sure about the validity of what is reported by a patent except to experiment and thereby put the matter to the test , which I have done .

My "finding" regarding GB128014 is that the information it discloses is either incorrect or incomplete , and the process it describes is \*NOT\* a straightforward nor valid method for the synthesis of azides .

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