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APPARATUS
FOR
GENERATING GASEOUS HYDROGEN AZIDE AND METHODS OF PREPARING SOME SELECTED AZIDES

BRUNO REITZNER
RALPH P. MANNO

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APPARATUS FOR GENERATING GASEOUS HYDROGEN AZIDE AND METHODS OF PREPARING SOME SELECTED AZIDES

by

Bruno Reitzner and Ralph P. Manno

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Reviewed by: H. J. Matsuguma
H. J. MATSUGUMA
Chief, Explosives
Research Section

Approved by: LHEriksen
L. H. ERIKSEN
Chief, Explosives and
Propellants Laboratory

Feltman Research Laboratories
Picatinny Arsenal
Dover, New Jersey

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ABSTRACT

An apparatus for preparing relatively large quantities of gaseous hydrogen azide has been designed. The hydrogen azide thus prepared can be used for reactions in the gas phase as well as in solutions. Methods for preparing sodium, potassium, ammonium, calcium, strontium and barium azides have been developed. An attempt was made to prepare lead azide by reacting hydrogen azide with lead oxide. The formation of hydrazine sulfate was observed when hydrazoic acid was passed through concentrated sulfuric acid.

INTRODUCTION

The need for various metal azides in relatively large quantities and with very high purity for explosives research studies has been realized for some time. In general, these azides are prepared by reacting hydrazoic acid with the respective bases and, due to the explosive nature of hydrogen azide, this compound is commonly prepared in dilute aqueous solutions. It was, however, felt that the necessity of using dilute aqueous solutions would be a serious obstacle for performing certain reactions. It was, therefore, decided to develop a method which would yield gaseous hydrogen azide suitable for reactions in the gas phase but which could also be used to carry out reactions in aqueous and non-aqueous solutions.

EXPERIMENTAL PROCEDURE

A. Preliminary Experiments

The reaction of a metal azide with a strong acid produces hydrogen azide according to the equation:

$$MeN_3 + HX = HN_3 + MeX$$

In the standard method described in Inorganic Syntheses(1) a solution of sodium azide is dropped into 40% sulfuric acid and the hydrogen azide thus formed is distilled off together with water. The distillate contains 3% HN_3. In order to obtain water-free hydrogen azide it was first tried to add a concentrated sodium azide solution to 50% sulfuric acid at a temperature ranging from 80 to 90°C. With nitrogen as a carrier gas and diluent, the hydrogen azide-water mixture was passed through concentrated sulfuric acid kept at room temperature. The pre-dried mixture was then passed through a drying tower containing phosphorus pentoxide. A certain time after the reaction had started the temperature in the wash bottle containing the concentrated sulfuric acid began to rise, frothing was observed and the effluent gas contained SO_2. On continuatation of the reaction a white precipitate started to form in the wash bottle. The wash bottle was then detached from the apparatus, allowed to cool, and its contents poured in cold water, thereby increasing the amount of precipitate. Preliminary investigation of the precipitate (infrared absorbtion spectrum, reaction with $BaCl_2$, and reaction with ammoniacal silver nitrate) showed that the precipitate was hydrazine sulfate.(a)

These observations necessitated the substitution for the sulfuric acid of an acid which was not reduced by HN_3 but had enough drying capability to render the effluent HN_3 essentially water-free. A mixture of phosphoric acid and P_2O_5 was selected as the best choice both for releasing HN_3 and for removing the water.

(a) An investigation of the reaction leading to this compound will be the object of a separate report.

B. Description of Apparatus

The apparatus in its final form is shown in Figure 1. The reaction vessel (1) is a 2 liter round bottom flask with a thermometer well and an outlet stopcock at the bottom. The flask is filled with approximately 1 liter of a solution containing 750 cc of 85% phosphoric acid (reagent grade) and 250 g of phosphorus pentoxide. The flask is surrounded by an electric heating mantle (2). A three-neck connection piece (3) is inserted into the neck of the flask. The necks provide connections for (4) water to flush the system after the reaction is completed, (5) nitrogen, (6) sodium azide solution and a condenser. Connection (6) is attached to a head tank (7) containing a sodium azide solution. The concentration of this solution is about 5M. About 50 cc of a 5% barium hydroxide solution were added to 1.5 liters of the azide solution to precipitate carbonate which is present in the sodium azide. This eliminates carbon dioxide impurities in the gaseous hydrogen azide. The sodium azide solution flows into the reaction vessel due to gravity and a glass fritt (8) prevents the barium carbonate slurry from entering the reaction flask. The head tank is provided with an air inlet (9) to which a tube containing ascarite (10) is attached to keep out carbon dioxide. The flow of the sodium azide solution is controlled by stopcock (11). The hydrogen azide formed by the reaction is carried with the nitrogen stream through the condenser into the receiving flask (12) containing the solution or suspension of the hydroxide or carbonate to be reacted and a Teflon covered magnetic stirrer. It was found necessary to wash the stirrer with HCl to remove iron particles which were adhering to the magnet and which caused pink discoloration in the product. The reaction vessel was separated from the receiving flask by a plexiglas shield (14). The receiving flask was omitted when ammonium azide was prepared; the arrangement for this reaction is described later. Provisions are made to attach a phosphorus pentoxide tower in place of the receiving flask if very dry hydrogen azide is needed.

The whole apparatus is enclosed in an explosion-proof hood. Stopcocks (13) and (11) which control the flow of the spent phosphoric acid and the sodium azide solution, respectively, can be operated from outside the hood by means of a grooved wooden rod.

In the early stage of the experiments two explosions occurred which destroyed the apparatus. The explosions always occurred when greased joints on the outlet tube (6) which had been in contact with gaseous hydrogen azide were turned. It is assumed that hydrogen azide accumulates in the grease and is then ignited by friction. The greased joints were, therefore, replaced by polyethylene couplings and no explosions occurred thereafter.

C. Determination of the Water Content in the Hydrogen Azide

Shortly after the addition of the sodium azide solution to the phosphoric acid - P_2O_5 mixture, small droplets appeared in the condenser indicating that the hydrogen azide contained some water. The water content was determined in the following manner: The generated gas was passed through two weighed absorption tubes, the first containing calcium chloride, to absorb the water, and the second containing ascarite in its first three quarters and calcium chloride in its fourth quarter to absorb the hydrogen azide. The nitrogen carrier gas was freed from water and carbon dioxide by passing it through absorption tubes containing ascarite and calcium chloride. During the entire experiment the heating mantle was maintained at a constant voltage. The flow rate of the nitrogen and the dropping rate of the azide solution (12 drops/min) were also kept constant. The absorption tubes were weighed at 30-minute intervals of attachment. The results are shown in Table I. These results show that the ratio between water and hydrogen azide, after about 30 minutes achieves a fairly constant value of 1:100. The percentage of water was considered sufficiently low and no further drying was attempted.

D. Preparation of Sodium Azide

1. NaOH Procedure

One liter of the H_3PO_4-P_2O_5 reaction mixture as described above was placed in the reaction vessel. 50 gms (0.8 mole) of NaOH (reagent grade) were dissolved in 100 cc of distilled water and placed in the receiving flask. The reaction vessel was heated to 100°C and approximately 300 cc of a 5 molar solution of NaN_3 treated with $Ba(OH)_2$ were added dropwise to the phosphoric acid. Addition was stopped after 4 hours. The sodium hydroxide solution was neutralized after about 72 hours. 900 cc of ethanol were then added to the receiving flask causing sodium azide to precipitate. The precipitation was completed by cooling the reaction mixture with dry ice until frost appeared on the walls of the receiving flask. The precipitate was filtered, washed 3 times with about 100 cc of ethanol and 3 times with about 100 cc of ether, sucked to dryness, and finally dried in a vacuum desiccator. [Yield 47 gms NaN_3 (58%).] The addition of $Ba(OH)_2$ to a 300 mg sample of the product dissolved in distilled water caused no precipitate indicating freedom from carbonate, fluoride, and phosphate. A small sample of the slightly pink material was dissolved in H_2O which was slightly acidified with HN_3 and the spectrum was determined in a Beckman DK-1 Spectrometer. An absorption maximum was found at 460 $m\mu$ and this increased when a drop of $FeCl_3$ solution was added. It is, therefore, assumed that the pink color is due to Fe^{+++} impurities which form the complex $[Fe(N_3)]^{++}$ reported by Wallace and Dukes(2). This complex was found to have an absorption maximum at 460 $m\mu$ and it is stable in slightly acid solutions. Since it is very difficult to recrystallize sodium hydroxide, it was therefore decided to try sodium carbonate which can be obtained in a purer form.

2. Na_2CO_3 Procedure

The reaction flask was charged with 1 liter of the H_3PO_4-P_2O_5 mixture described above. 25 gms of Na_2CO_3 (reagent grade) were dissolved in 100 cc of triply-distilled water and placed into the receiving flask. 200 cc of a 5 molar NaN_3 solution treated with $Ba(OH)_2$ were added dropwise

Table I

Percentage of H_2O in HN_3

	Gain in Weight			
Time of Attachment (min)	$CaCl_2$ Tube mg	Ascarite Tube mg	% Water	Temperature of the Acid °C
0-30	3.825	38.08	10	80°
40-70	0.535	35.19	1.4	92°
90-120	0.290	70.36	0.41	114°
135-165	0.350	34.49	1.01	107°
175-205	0.510	58.53	0.87	106°

to the phosphoric acid heated at 100°C. The hydrogen azide reacting with the Na_2CO_3 causes the initial formation of $NaHCO_3$ which, due to its lower solubility precipitates and tends to clog the inlet tube. As soon as $HaHCO_3$ started to precipitate the solution was heated on a steam bath to drive off CO_2. The reaction was completed after 30 hours as no carbonate was detected with $Ba(OH)_2$. 900 cc of ethanol were added to the solution to precipitate NaN_3. Precipitation was completed by cooling the reaction mixture until frost appeared on the flask. The precipitate was filtered, washed with ethanol and ether and sucked to dryness. The yield was 30 gms of NaN_3 (98%). No pink discoloration could be detected.

E. Preparation of KN_3, $Ca(N_3)_2$, $Sr(N_3)_2$ and $Ba(N_3)_2$

The method for preparing these compounds was essentially the same as described under sodium azide. All compounds were prepared from both the hydroxides and the carbonates. The results are summarized in Table II.

F. Preparation of Ammonium Azide

Ammonium azide was prepared in the gas phase by reacting the gaseous HN_3 with gaseous ammonia. The apparatus is shown in Figure 2. It consists of a horizontal glass tube (1) (36" x 1") with two inlet tubes (2 and 3) and an outlet tube (4). Tube 2 was used for introducing the hydrogen azide nitrogen mixture from the generator, and tube 3 was used for introducing ammonia. The orifices of the tube had to be kept about 20" apart in order to prevent the clogging of tube 2 with ammonium azide. Ammonia was always used in excess. Sodium azide solution was added to the H_3PO_4-P_2O_5 mixture in the HN_3 generator in such a way that about 2 g/hr of ammonium azide formed. The ammonium azide was needle shaped and colorless.

G. Attempts to Prepare Lead Azide from Lead Oxide and Hydrogen Azide

10 gms of lead oxide (reagent grade) were suspended in 50 cc of water, and stirred vigorously. Gaseous HN_3 prepared in the manner described in Chapter D was passed through the suspension. The reaction was stopped after 4 hours. The resulting product was inhomogeneous. Besides crystals of dirty brown lead azide, lumps of unreacted lead oxide coated with lead azide were observed. This indicated that the precipitation of the almost insoluble lead azide on the lead oxide prevented further reaction.

The maximum amount of nitrogen in the lead azide (from 4 determinations) was found to be 25.61% (theory 28.86%). Due to the impurity of the product further work on this method was stopped.

CONCLUSIONS

The apparatus offers a convenient way of obtaining hydrogen azide which can be used for gas phase reactions as well as for reactions in aqueous and non-aqueous media.

Table II

Product	Starting Material	Amount of 5M NaN_3 Solution Added to H_3PO_4-P_2O_5 Mixture	Time of Reaction	Yield	Remarks
KN_3	50 g KOH in 200 cc H_2O	500 cc	5 hours	35 g (48.6%)	slightly pink
	30 g K_2CO_3 in 80 cc H_2O	200 cc	10 hours	32 g (91.4%)	colorless
$Ca(N_3)_2$	5 g $Ca(OH_2)$ in 25 cc H_2O	100 cc	2 hours	2 g (23.9%)	colorless
	25 g $CaCO_3$ in 100 cc H_2O	300 cc	10 hours	10 g (32.3%)	slightly pink
$Sr(N_3)_2$	20 g $SrCO_3$ in 100 cc H_2O	300 cc	5 hours	13 g (39%)	slightly pink
$Ba(N_3)_2$	35 g $Ba(OH)2$ in 150 cc H_2O	300 cc	10 hours	31 g (68.7%)	pink
	13 g $BaCO_3$ in 100 cc H_2O	200 cc	5 hours	13 g (89.4%)	pink

A variety of metal azides can be prepared using this apparatus. The azides prepared so far were obtained from reagent grade starting materials. The pink color of the mother liquor observed when NaOH, KOH, $Ca(OH)_2$, $CaCO_3$, $SrCO_3$, $BaOH_2$ and $BaCO_3$ were used indicates that the purity of these reagent grade materials may not be sufficient for super pure azides, and further efforts must be directed towards purification of the starting materials. The recrystallization or re-precipitation of the respective carbonates appears to be the most promising way to achieve this purpose.

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2. Wallace, R. M., and Dukes, E. K., J. Phys. Chem. 65, 2094 (1961)

Fig. 1

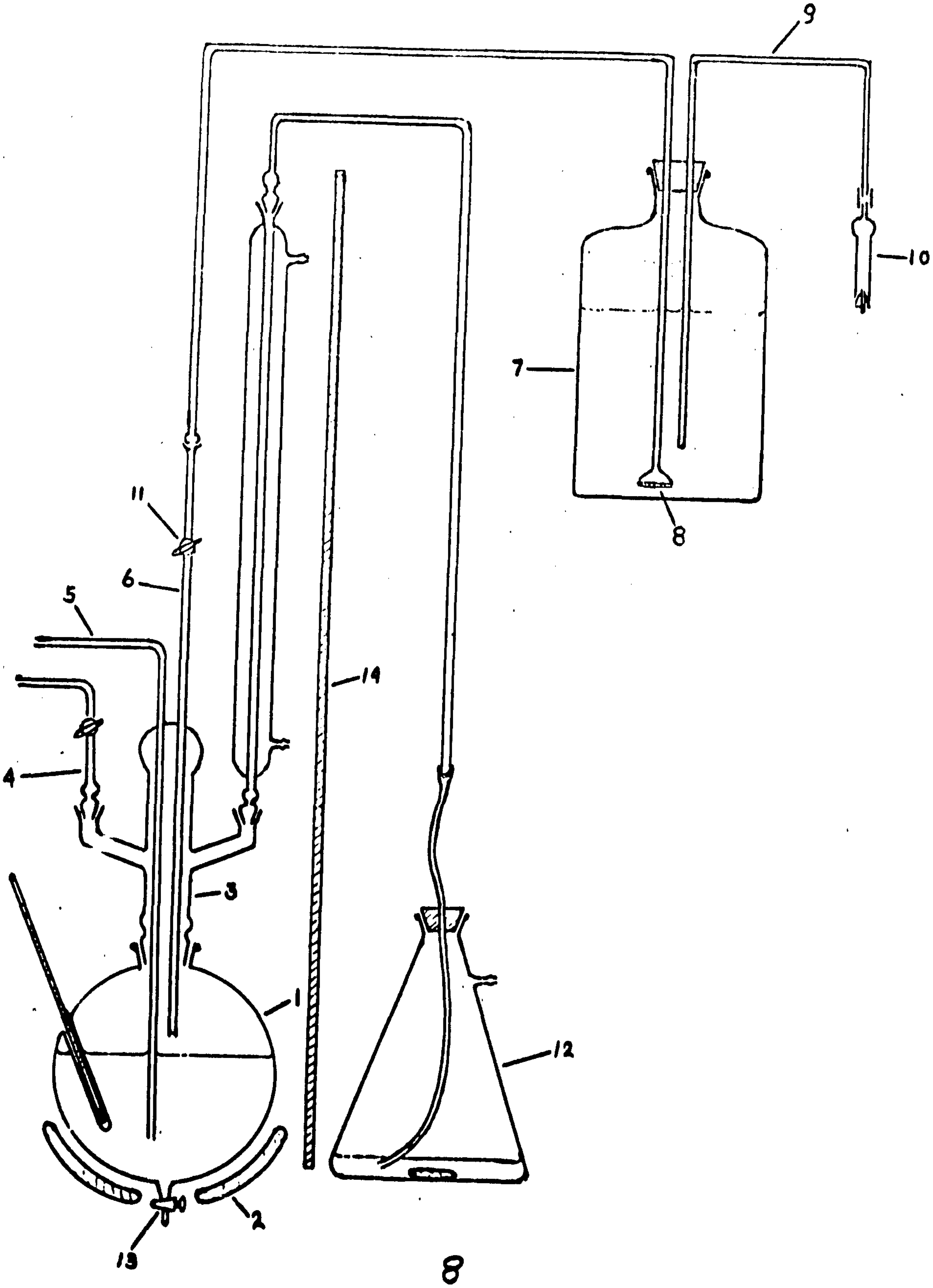
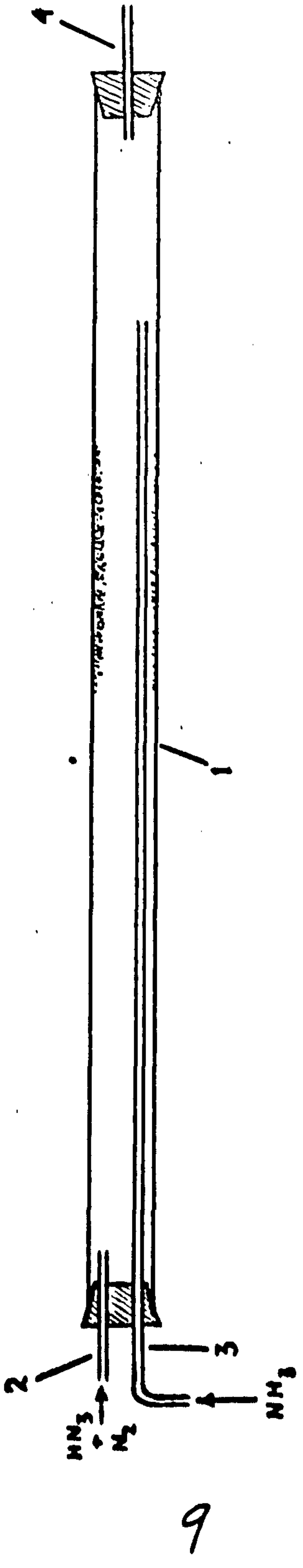


Fig. 2



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