

diborane, with a probable trace of diborane itself. The course of the whole process can be recognized by occasional measurement of the vapor tension of the mixture at  $-78.5^{\circ}$ ; Table X presents such data for 8.1 cc. of symmetrical dimethyldiborane, decomposing during eight days at room temperature, in a space of 33 cc. The gradual rise of the vapor tension to a value above that of the unsymmetrical dimethyldiborane (10 mm.) demonstrates the formation of more volatile material. At the end of eight days, the process still had not reached equilibrium. The mixture now was fractionated, yielding 0.5 cc. of monomethyldiborane, 0.5 cc. of trimethyldiborane, and 7.1 cc. of a mixture of symmetrical and unsymmetrical dimethyldiborane. This mixture was hydrolyzed, producing 28.3 cc. of hydrogen (3.98 volumes) and 4.9 cc. of dimethylboric acid (boric and methylboric acids not determined). Hence the 7.1-cc. portion consisted of 4.9 cc. of the unsymmetrical derivative and 2.2 cc. of the original symmetrical compound; 72% of the latter had decomposed, yielding 60 parts of its unsymmetrical isomer and 6 parts each of mono- and trimethyldiboranes.

TABLE X

CHANGES OF VAPOR TENSION DURING THE DECOMPOSITION OF SYMMETRICAL DIMETHYLDIBORANE

Hours at room temp.	0	1	24	48
<i>p</i> , mm. at $-78.5^{\circ}$	7.0	7.3	7.9	8.1
Hours at room temp.	72	144	168	192
<i>p</i> , mm. at $-78.5^{\circ}$	8.3	10.0	10.8	11.7

### Summary

The methyl derivatives of borine trimethylamine have been prepared and characterized. In these compounds the stability decreases as the number of methyl groups increases; all are less

stable than borine trimethylamine itself. Methylation of borine trimethylamine increases the rate at which hydrogen chloride attacks the remaining B-H links to produce hydrogen. Only in the trimethyl derivative is the B-N link broken by hydrogen chloride.

By treatment of monomethyldiborane with dimethyl ether at  $-80^{\circ}$ , borine dimethyl etherate and the new compound, symmetrical dimethyldiborane, were obtained. The dimethyl etherate of monomethylborine apparently does not exist at  $-80^{\circ}$ .

The structure of symmetrical dimethyldiborane (m. p.  $-124.9^{\circ}$ ; extrapolated b. p.  $4.9^{\circ}$ ) has been established by its reaction with water to produce methylboric acid and hydrogen, and with trimethylamine to produce monomethylborine trimethylamine.

The diammoniate of symmetrical dimethyldiborane has been prepared. On heating at  $200^{\circ}$ , it gives a 60% yield of B-methyl derivatives of triborine triamine (mostly the tri-B-methyl compound).

A study of the stability of symmetrical dimethyldiborane has shown that it changes slowly, but probably almost completely, into the symmetrical isomer; this next disproportionates partially, yielding other methyl derivatives of diborane. The failure of earlier attempts to prepare the compound is thus explained.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY AT SMITH COLLEGE]

## Formation of Aminomonopersulfuric Acid by the Interaction of Fuming Sulfuric Acid and Hydrogen Azide<sup>1</sup>

BY H. E. M. SPECHT, A. W. BROWNE AND K. W. SHERK

It has been found that hydrazine sulfate is formed when anhydrous hydrogen azide is condensed upon concentrated sulfuric acid,<sup>2</sup> and that the sulfates of both hydrazine and ammonia are obtained when hydrogen azide vapor is bubbled either through concentrated sulfuric acid<sup>3</sup> or

through an ethereal solution of 100% sulfuric acid.<sup>4</sup> In the presence of water, Schmidt<sup>5</sup> obtained hydroxylammonium sulfate, but found that hydrogen azide acted as an *aminating agent* toward benzene in hot sulfuric acid, with formation of aniline sulfate as the principal product.

On the assumption that the formation of hydrazine, ammonia, and hydroxylamine from hydrogen azide in these experiments may have been due to the decomposition of an intermediate product

(1) This article is in part based upon the thesis presented to the Faculty of the Graduate School of Cornell University by H. E. M. Specht in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work of K. W. Sherk has been supported through the personal generosity of Mr. Haymo V. Pfister of the Pfister Chemical Company.

(2) A. E. McKinney, Ph.D. Thesis, Cornell University, 1923.

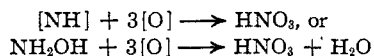
(3) Dennis and Isham, *THIS JOURNAL*, **29**, 218 (1907).

(4) H. S. Bennett, Ph.D. Thesis, Cornell University, 1917.

(5) Schmidt, *Ber.*, **57**, 704 (1924); **58**, 2413 (1925).

in various ways, in some cases at least as the result of hydrolysis, the authors have substituted fuming sulfuric acid that contained from 20 to 30% of sulfur trioxide for the ordinary concentrated acid. It was hoped that the fuming acid would not only prevent or minimize hydrolysis or hydration, but would also serve as a fixative for relatively unstable intermediate products.

Preliminary nitrometric and volumetric experiments with hot fuming sulfuric acid and sodium azide furnished conclusive proof of (1) the quantitative liberation of two-thirds of the azide nitrogen in the form of nitrogen gas, (2) the presence in the residual solution of a reducing agent that required, for complete oxidation by permanganate ion to nitric acid, exactly three atoms of oxygen per molecule of sodium azide originally taken



and (3) the absence, from the liberated nitrogen gas, of hydrogen azide, sulfur dioxide, and oxides of nitrogen.

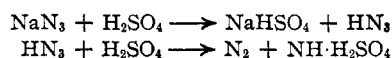
In view of this evidence that the reaction between sodium azide and fuming sulfuric acid leads to the formation of a monazene radical, the authors prepared to study the reaction of anhydrous hydrogen azide vapor upon hot fuming sulfuric acid.

An apparatus was designed for the passing of a continual stream of dry hydrogen azide vapor, mixed with dry air, into fuming sulfuric acid held at a desired temperature. The generator was constructed from an ordinary condenser, and so arranged that water at a regulated temperature could be passed through the outer jacket. The inner tube of the condenser was filled with glass beads over which a solution of sodium azide and concentrated sulfuric acid slowly dripped while a current of air was pulled in a direction counter to the flow of the solutions. The hydrogen azide vapor (approx. 10 to 12%)-air mixture was then drawn through a drying chain and bubbled into the fuming sulfuric acid which was in a specially constructed glass-jointed cell kept in a well-stirred electrically-heated oil-bath. The temperature of the bath was regulated with a thermostat of the mercury-toluene type and the conventional relay system. Tests of the spent solutions from the generator showed only traces of the azide ion. Further experiments with known amounts of sodium azide showed that over 95% of the available hydrogen azide was retained by the fuming acid.

The generator was charged with 37 g. of sodium azide in 200 ml. of water and 250 ml. of concentrated sulfuric acid. These solutions were added continuously and dropwise. The water in the outside jacket was about 75°, while the oil-bath was held at 80 ± 1°. A slow stream of the mixed vapors was allowed to bubble into the acid for about thirty

hours. Continual evolution of gas was observed during this time and, usually, after thirty hours crystals began to appear in the sulfuric acid. The current of hydrogen azide was then stopped and the solution held at 80° until all evidences of gas evolution had disappeared. More crystals were formed during this interval. The liquid was then filtered through a sintered glass filter, and the solid dried in a current of dry air. The crystals were well washed with five successive portions of ether which had been previously distilled over sodium wire. After the ether had been removed in a current of dry air, the crystals were stored in glass-stoppered bottles in a vacuum desiccator containing phosphorus pentoxide.

In later experiments the conditions were altered by lowering the temperature of the oil-bath to 60°, and in other cases by making the addition of hydrogen azide vapor intermittent with subsequent cooling to room temperature. In all cases, however, the crystalline product was the same. The yields were approximately 65% of the theoretical on the basis of the following equations



The crystals were colorless orthorhombic prisms with truncated ends. They were quite deliquescent and easily soluble in water. In an open capillary tube they melted close to 210° (uncorr.) and decomposed a few degrees higher. Their aqueous solution had a strong acid reaction and was an oxidizing agent toward hydriodic acid, titanous chloride, ferrous hydroxide, and ferrous ion. The solution acted as a reducing agent toward permanganate ion, chromate ion, ammoniacal silver nitrate, and hot Fehling's solution. The crystals were slightly soluble in methyl and ethyl alcohols; they reacted with acetone to form a two-liquid layer system, and were insoluble in chloroform and carbon tetrachloride. They were stable toward shock and friction and decomposed without violence when thrown onto a hot iron plate.

#### Analysis of Product

**Sulfur.**—Sulfur was determined as barium sulfate which was precipitated in the ordinary way, from an aqueous solution of the crystals which had been boiled for two hours with 6 *N* hydrochloric acid.

**Iodine Equivalent.**—A weighed sample was placed in a glass-stoppered flask with 150 ml. of water in which was dissolved 2 g. of potassium iodide and 10 ml. of 9 *N* sulfuric acid. One-half gram of sodium bicarbonate was added so that carbon dioxide would sweep any dissolved air out of the solution and the stoppered flask was allowed to stand in ice (usually about one hour) until no more iodine was liberated. The iodine was titrated with standard sodium thiosulfate solution to the conventional starch-iodide end-point.

**Nitrogen.**—The nitrogen content of the substance was determined by the Dumas method. It was found that the residual solutions from the thiosulfate titrations contained all the nitrogen as ammonium sulfate, so in most cases the nitrogen was also determined as ammonia in these solutions by distilling from an alkaline solution into standard acid.

**Hydrogen.**—Hydrogen was determined in two samples by combustion with copper oxide. Since the crystals

were deliquescent it is expected that these results are slightly high.

The analytical data are presented in Table I. Of the several samples prepared, complete analysis was done on only two, after which it was considered sufficient to determine the iodine equivalent and the percentage of nitrogen, and sometimes the percentage of sulfur. The data from 14 other experiments were in similar accord.

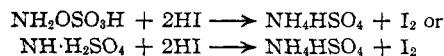
TABLE I  
ANALYTICAL DATA FOR AMINOMONOPERSULFURIC ACID

Expt.	% S	% N	% H	Iodine equiv.
1	27.96	12.35	2.88	56.7
	28.11	12.37	2.82	56.8
2	27.87	12.52	2.72	57.0
	28.06	12.39	2.77	56.9
3		12.55		56.9
		12.42		57.0
4		12.18		56.4
		12.37		57.0
5	28.05	11.95		56.6
	28.14	12.05		
Calcd. for NH·H <sub>2</sub> SO <sub>4</sub>	28.33	12.38	2.66	56.5

#### Evidence Pertaining to the Structure of the Compound

It is evident, from these data, that the composition of the compound is empirically H<sub>3</sub>NSO<sub>4</sub>. That the structure is either that of aminomonopersulfuric acid (NH<sub>2</sub>OSO<sub>3</sub>H)<sup>6</sup> or that of monazenium sulfate ( $\text{HN} \leftarrow \text{OSO}_2\text{OH}$ )<sup>H</sup> is inferred from a study of the reactions of the substance with hydriodic acid, water, ammonia, and ethyl alcohol.

**Reaction with Hydriodic Acid.**—Aminomonopersulfuric acid or monazenium sulfate reacts quantitatively with hydriodic acid to liberate iodine and to form ammonium sulfate. In every experiment the ratio, moles of ammonia to atoms of iodine, was found to be between 0.495 and 0.500. This ratio is in conformity with the equations



**Reaction with Water.**—The compound reacts with water to form hydroxylamine sulfate and sulfuric acid. The hydroxylamine was identified by preparing benzaldoxime from benzaldehyde. This hydrolysis may be followed by either of two methods, *viz.*: titration with standard base, or, better, the determination of the iodine equivalent.

In a freshly prepared aqueous solution, there was one equivalent of acid per molecule of

compound, but on standing, or especially on boiling, the concentration of acid gradually increased to a maximum of two equivalents per molecule of substance. Two 0.1671-g. samples in water were neutralized by 15.42 and 15.44 ml. of 0.0953 *N* sodium hydroxide, respectively; after heating for four hours, duplicate samples required 30.61 and 30.78 ml. of 0.0953 *N* sodium hydroxide.

In the second case, the hydrolysis was followed by the loss in oxidizing power of the solution noted by determining the iodine equivalent from time to time. A standard solution was prepared and the iodine equivalent of an aliquot part was determined at specified time intervals. The hydrolysis was carried out in four different solutions, *viz.*: (1) water, (2) sulfuric acid 0.014 *N*, (3) hydrochloric acid 0.014 *N*, and (4) hydrochloric acid 0.16 *N*. The results of these experiments are shown graphically in Fig. 1.

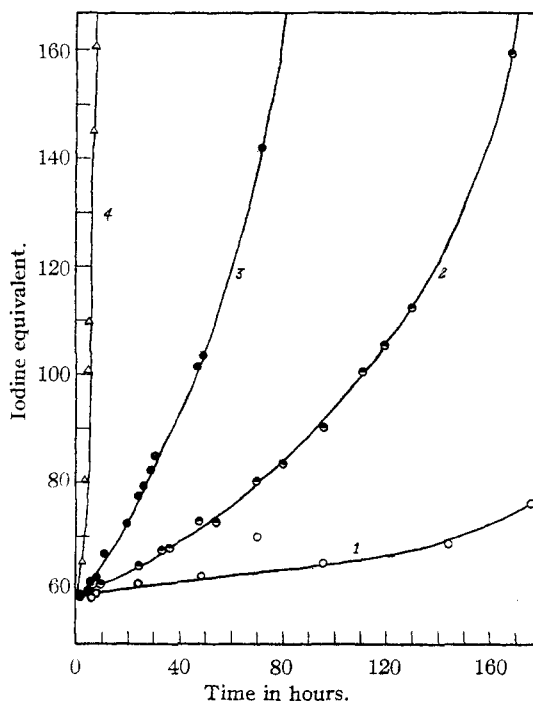
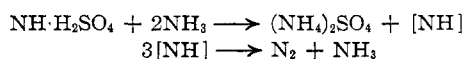


Fig. 1.—Hydrolysis of aminopersulfuric acid.

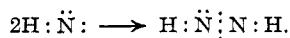
**Reaction with Ammonia.**—Sommer<sup>6</sup> has reported that aminomonopersulfuric acid reacts with ammonium hydroxide to form hydrazine in amounts varying with the concentration of the ammonia. This was verified. The reaction with gaseous ammonia was also investigated. The substance reacts with ammonia with evolution of heat and subsequent decomposition which is accompanied by a mild explosion. However, by

(6) (a) Sommer and Templin, *Ber.*, **47**, 1221 (1914); (b) Sommer, Schulz and Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

carefully and slowly passing dry ammonia over the substance it was possible to prevent such a decomposition. A weighed sample was placed in a U-tube and dry ammonia was passed slowly over it until it had come to constant weight. In one case liquid ammonia was condensed upon the residue and allowed to evaporate but no further increase in weight was found. Two samples of 0.1009 and 0.1153 g. were found to gain 0.0167 and 0.0193 g., respectively, when subjected to the treatment described above. This increase is in the ratio of 18.8 units for 113 units of the original substance. The residue was ammonium sulfate, probably formed according to the equations



Aminomonopersulfuric acid was put into liquid ammonia and flocculent ammonium sulfate triammonate precipitated. The decanted solution possessed oxidizing and reducing properties. If such liquid ammonia solutions were allowed to evaporate, there was always a violent decomposition with evolution of heat and nitrogen when the ammonia was almost all evaporated. This decomposition may be ascribed to the breakdown of free NH groups, or possibly to the breakdown of the much sought diazene or diimide which might have been formed by the condensation of two NH groups

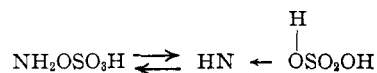


**Reaction with Ethyl Alcohol.**—When aminomonopersulfuric acid was refluxed with absolute ethyl alcohol for forty-eight hours, and the solution treated with dry ether, a white crystalline product was obtained. This substance was very soluble both in water and alcohol but insoluble in chloroform and in ether. The crystals melted sharply at 102.5° (uncorr.) in an open capillary tube. An aqueous solution gave no precipitate with barium chloride until boiled with hydrochloric acid, when barium sulfate was precipitated. The material had a neutral equivalent of 158 and was found to contain 19.81% of sulfur and 8.55% of nitrogen. The crystals showed no oxidizing properties toward hydriodic acid but were capable of reducing potassium permanganate. The analytical data correspond to the compound  $\text{NH}_2\text{OH}\cdot\text{HOSO}_2\text{OC}_2\text{H}_5$ . The composition of this compound was further established

by identifying hydroxylamine and ethyl alcohol as products of hydrolysis when the compound was boiled with dilute hydrochloric acid.

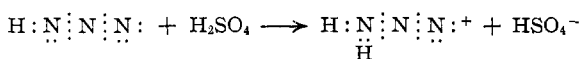
### Discussion

It seems to the authors that the structures

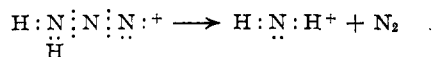


in equilibrium satisfactorily explain all of the reactions studied. A possible mechanism for the formation of these compounds is outlined below.

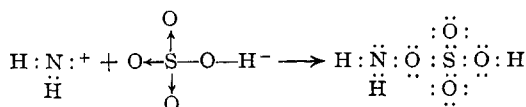
First, hydrogen azide accepts a proton from the sulfuric acid



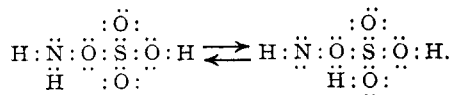
Second, two atoms of nitrogen split off and leave an unsaturated and unstable residue



Third, this residue combines with a  $\text{HSO}_4^-$



A shift of a proton from the nitrogen to the adjacent oxygen would account for all of the reactions observed



### Summary

1. The reaction of hydrogen azide with fuming sulfuric acid has been studied.
2. Aminomonopersulfuric acid, or monazenium sulfate, has been prepared by a hitherto undescribed method.
3. A quantitative study of the reactions of aminomonopersulfuric acid with water, hydriodic acid, ammonia, and ethyl alcohol has been made.
4. A possible mechanism for the formation of aminomonopersulfuric acid from hydrogen azide and fuming sulfuric acid has been suggested.
5. The possibility of the formation of the unknown diazene from aminomonopersulfuric acid and liquid ammonia has been pointed out.

SMITH COLLEGE  
NORTHAMPTON, MASS.

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