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

# The Action of Ethyl Azide and Phenyl Azide on Fuming Sulfuric Acid[1]

BY K. W. SHERK, A. G. HOUPT[2] AND A. W. BROWNE

The action of hydrogen azide on fuming sulfuric acid has been shown[3] to yield aminomonopersulfuric acid which is capable of acting both as an aminating agent and as a strong oxidizing agent. In the attempt to throw more light upon the structure and nature of this compound and its possible derivatives, a study has been made of the action of fuming sulfuric acid on two derivatives of hydrogen azide: phenyl azide and ethyl azide. This work also was undertaken in the attempt to determine the conditions under which the monazene (NH=) radical or its substitution products might polymerize or condense to form compounds of the diazene series of hydronitrogens, as exemplified by the condensation of RN= residues to form azo compounds.[4]

**Phenyl Azide.**—The formation of *p*-aminophenol and its *o*-sulfonic acid, respectively, by the action of phenyl azide on dilute and concentrated sulfuric acid, as noted by Bamberger[5] is in a sense analogous to the formation of hydroxylamine as a product of the action of hydrogen azide on concentrated sulfuric acid. Since no hydroxylamine is formed when the fuming acid is used in place of the ordinary concentrated acid, it seemed likely that the phenyl derivative of aminomonopersulfuric acid, rather than *p*-aminophenol, might be obtainable from the action of phenyl azide on fuming sulfuric acid.

The phenyl azide used in the present work was prepared from nitrosyl chloride and phenylhydrazine.[6] It was separated by steam distillation and dried with anhydrous sodium sulfate. The introduction of this reagent into fuming sulfuric acid, even when the acid was cooled in an ice-salt mixture and thoroughly stirred, resulted in considerable charring. At room temperature, each drop of the phenyl azide, as it struck the acid, detonated with a violet flash and formed a purple-black smoke. To overcome these difficulties the phenyl azide was introduced in the form of vapor by drawing a slow stream of dried air through the azide and then through the fuming acid at room temperature. In this way 12 g. of phenyl azide was drawn into 20 ml. of 20% fuming acid in eighteen hours. Almost from the outset evolution of nitrogen took place, and the acid assumed a maroon color. After the azide had been introduced the acid solution was allowed to stand until gas evolution had ceased.

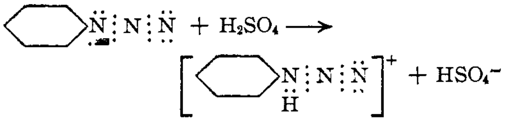
The solution was poured into vigorously agitated, ice-cold, dry ether with the result that a bulky, rose colored precipitate was formed. This was washed with dry ether until the washings were free from sulfate ion. A yield of 11 g. of a very hygroscopic solid was obtained. On exposure to air a sample of this product quickly became blue and sticky.

The solid dissolves in water to yield a solution from which needle-like crystals are at once deposited. These are soluble in dilute sodium hydroxide and reprecipitated by acid. A sample of this product of hydrolysis weighing several grams was prepared, redissolved, reprecipitated, washed with water and alcohol, and dried. Qualitative tests and further analysis proved the compound to be *p*-aminophenol *o*-sulfonic acid monohydrate. *Anal.* Calcd. for *p*-aminophenol *o*-sulfonic acid monohydrate: neut. equiv., 207.1; S, 15.48; N, 6.76; $H_2O$, 8.70. Found: neut. equiv., 207; S, 15.28; N, 6.76, 6.74, 6.77; $H_2O$, 8.53.

The original hygroscopic material, when heated, chars without melting. Its aqueous solution gives a positive phenol test, and fails to liberate iodine from acidified potassium iodide solution. It yields at once, even at room temperature, a heavy precipitate of barium sulfate when treated with barium chloride and hydrochloric acid. Although analysis was hindered by the hygroscopic nature of the substance, the following data were obtained. Found: S, 21.75, 21.90, 21.95; N, 4.90, 4.92; atomic ratio S:N, 1.986/1.

In conjunction with the observed formation of *p*-aminophenol *o*-sulfonic acid and sulfuric acid by hydrolysis, this strongly indicates that the original substance was mainly phenylaminomonopersulfuric acid *m*-sulfonic acid. Unlike aminomonopersulfuric acid, this compound does not liberate iodine from potassium iodide in acid solution but hydrolyzes immediately and rearranges to *p*-aminophenol *o*-sulfonic acid. It shows no tendency to form monopersulfuric acid.

**Mechanism of the Reaction between Phenyl Azide and Fuming Sulfuric Acid.**—The first step may be considered to consist of the coördination of a hydrogen ion to the alpha nitrogen of the azide group.



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[1] This article is based in part upon the thesis submitted to the Faculty of the Graduate School of Cornell University by A. G. Houpt in partial fulfilment of the requirements for the degree of Master of Arts. The work of K. W. Sherk has been supported by the personal generosity of Mr. Haymo V. Pfister of the Pfister Chemical Company.

[2] Present address: American Cyanamide Company, Stamford, Conn.

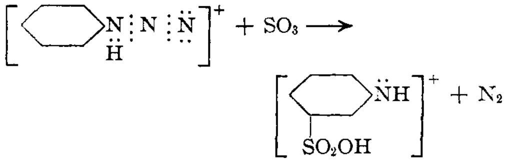
[3] Specht, Browne and Sherk, THIS JOURNAL, **61**, 1083 (1939).

[4] Bertho, *Ber.*, **57B**, 1138 (1924).

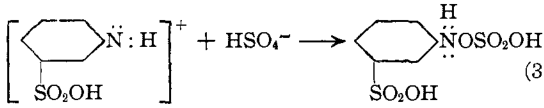
[5] Bamberger, *Ann.*, **424**, 233–296 (1921); **443**, 192–210 (1925).

[6] Tilden and Miller, *J. Chem. Soc.*, **63**, 256 (1893).

The coördination link reduces the stability of the azide group with the result that two atoms of nitrogen split off as nitrogen gas. Sulfonation occurs subsequently to the coördination as indicated by the meta position of the sulfonate group.


(2)

The unstable residue unites with a bisulfate ion to form phenylaminomonopersulfuric acid *m*-sulfonic acid.


(3)

This product probably exists in the isomeric form obtained by a shift of the hydrogen from the nitrogen to the adjacent oxygen as seems likely in the case of aminomonopersulfuric acid.[3]

**Ethyl Azide.**—This reagent was prepared by the action of diethyl sulfate on sodium azide.[7] It was washed with water to remove ethanol, and was dried with anhydrous sodium sulfate. About 8 g. of the azide in the form of vapor was introduced by means of a current of dry air into 15 ml. of 20% fuming sulfuric acid at 80° in eighteen hours. After the evolution of nitrogen had ceased, the clear, slightly yellow solution was slowly poured into vigorously agitated, ice-cold, dry ether. The heavy yellowish precipitate was washed with dry ether until it was free from sulfuric acid. During this operation the solid gradually assumed an orange color and became sticky. *In vacuo*, over phosphorus pentoxide, it soon changed to a deep-orange paste, and finally, after several days, to a brittle orange-colored glass.

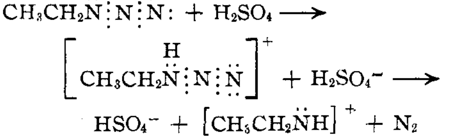
This material was very soluble in water, yielding a yellow solution which slowly became turbid with oily droplets having a strong odor of aldehyde which also was manifested by the glassy solid itself. The solution was strongly acidic and contained sulfate ions. Distillation yielded a clear, colorless, aqueous solution which contained formaldehyde and another aldehyde, assumed under the circumstances to be acetaldehyde. To separate the formaldehyde from the other, a sample of the distillate was treated with an excess of concentrated ammonium hydroxide solution. This converted the formaldehyde to hexamethylenetetramine and the acetaldehyde to aldehyde-ammonia. The solution was made barely acid to methyl red and distilled until no more aldehyde came over. There was no formaldehyde in the distillate. Acetaldehyde was present, however, and was confirmed by the preparation of the *p*-nitrophenylhydrazine derivative.

The residue in the flask was made strongly acid with 1:1 sulfuric acid and distillation resumed. The new distillate gave strong tests for formaldehyde, which was confirmed by the *p*-nitrophenylhydrazine derivative.

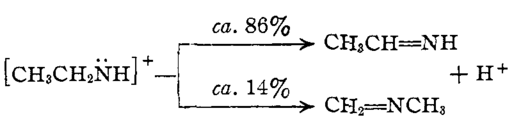
The residue from the distillation of the aldehydes was made alkaline with sodium hydroxide, and distilled into cold water. This distillate contained ammonia and methylamine, which were identified by conversion to benzamide and dinitromethylaniline, respectively. The distillate would not reduce ammoniacal silver nitrate nor Fehling's solution, and therefore contained no hydroxylamine derivatives.

From these results it seems that the unstable yellow solid formed by the action of fuming sulfuric acid on ethyl azide yields, upon hydrolysis, sulfuric acid and a mixture of acetaldehyde, formaldehyde, ammonia and methylamine. No other products such as N-ethylhydroxylamine, ethylidene imine, or ethylene imide could have been present as final products since the volatile bases did not reduce potassium permanganate or ammoniacal silver nitrate solution. The estimation of ammonia and methylamine was accomplished by the method of François[8] in which a solution of the weighed hydrochlorides was used. The mixture was found to contain 0.86 mole of ammonia to 0.14 mole of methylamine. The relative strength of the tests given for acetaldehyde and formaldehyde indicated that these substances were present in a similar ratio.

**Mechanism of the Reaction between Ethyl Azide and Fuming Sulfuric Acid.**—From the behavior of hydrogen azide and phenyl azide toward fuming sulfuric acid, it was expected that ethyl azide would react with the fuming acid to form ethylaminomonopersulfuric acid, which would hydrolyze to yield N-ethylhydroxylamine. The first step of the reaction is probably the union of a hydrogen ion with the ethyl azide and the subsequent loss of two nitrogen atoms.


$$CH_3CH_2\ddot{N}\vdots N\vdots\ddot{N}: + H_2SO_4 \longrightarrow$$
$$\left[CH_3CH_2\overset{H}{\underset{\cdot\cdot}{N}}\vdots N\vdots\underset{\cdot\cdot}{N}\right]^+ + H_2SO_4^- \longrightarrow$$
$$HSO_4^- + [CH_3CH_2\ddot{N}H]^+ + N_2 \qquad (4)$$

The unsaturation of the nitrogen is relieved by a shift of a hydrogen or of a methyl group from the alpha carbon to the adjacent nitrogen, rather than by combination with a bisulfate ion to form a derivative of aminomonopersulfuric acid.


$$[CH_3CH_2\ddot{N}H]^+ \begin{cases} \xrightarrow{ca.\ 86\%} CH_3CH{=}NH \\ \xrightarrow{ca.\ 14\%} CH_2{=}NCH_3 \end{cases} + H^+ \qquad (5)$$

The fact that the solution of the glassy yellow product contained sulfate ions indicates that it was probably a mixture of the sulfates of the bases

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[7] Staudinger and Hauser, *Helv. Chim. Acta*, **4**, 872 (1921).

[8] François, *Compt. rend.*, **144** 857 (1907); from "Allen, Commercial Organic Analysis," 5th ed., Vol. V, P. Blakiston's Son and Co., Phila., 1927, p. 287.

shown in equation 5. The hydrolysis of these compounds would account for all of the observed products.

Since no products containing nitrogen linked to nitrogen have been obtained by the interaction of either phenyl or ethyl azide and fuming sulfuric acid, the possibility that diazene or its homologs might be formed by the interaction of hydrogen azide and the fuming acid seems rather remote under the prevailing conditions. The mechanism already suggested for this reaction[3] is confirmed by the behavior of phenyl azide toward the fuming acid.

## Summary

1. The action of fuming sulfuric acid upon phenyl azide apparently results in the formation of phenylaminomonopersulfuric acid *m*-sulfonic acid, which on hydrolysis yields *p*-aminophenol *o*-sulfonic acid.

2. The action of fuming sulfuric acid upon ethyl azide results in the formation of products which on hydrolysis yield sulfuric acid and a mixture of acetaldehyde, formaldehyde, ammonia and methylamine.

3. A useful method for the separation of formaldehyde and acetaldehyde has been described.

4. No compounds containing nitrogen linked to nitrogen were obtained as products of either reaction. The analogy between these reactions, particularly that of the phenyl azide, and that of hydrogen azide and fuming sulfuric acid has been noted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# The Heat Capacities, Heats of Transition and Fusion, and Entropies of Ethylene Dichloride and Ethylene Dibromide

BY KENNETH S. PITZER

Internal rotation in ethylene dichloride and ethylene dibromide has been studied by dielectric constant[1] measurements, electron diffraction,[2] and Raman spectra.[3] Although it has been proved that the rotation is considerably restricted, many aspects are yet to be worked out. With this in mind, the low temperature heat capacities, heats of fusion, and heats of transition for both substances have been measured, leading of course to entropy values. Work is in progress on the heat capacities of these substances in the gas phase.

These substances are also interesting because of the transitions they undergo as solids. Ethylene dibromide shows a sharp transition at 249.54° K., while ethylene dichloride has a large peak in its heat capacity curve near 177°K.

**Apparatus and Materials.**—The vacuum calorimeter used in this investigation already has been described.[4] The value 273.10°K. was taken for the ice point, and the defined calorie, 4.1833 International joules, was used throughout.

The calorimetric samples were purified by washing with water, drying, and repeatedly fractionating. The impurity in each case was estimated from the rise in heat capacity below the melting point, and found to be 0.058% in the case of ethylene dichloride and 0.26% in ethylene dibromide. Although impurities of this magnitude make the true heat capacity below the melting point uncertain, they do not appreciably affect the final entropy values.

**Melting and Transition Temperatures.**—The melting points were observed for different fractions melted and were corrected for impurities. The transition temperature in ethylene dibromide was similarly measured. The results are presented in Table I together with the values obtained by other observers.

**Heat Capacities.**—The heat capacities were measured by the usual method and are listed in Tables II and III shown graphically in Fig. 1. The temperature increments employed can be judged by the spacing of the reported results. In the anomaly in ethylene dichloride small increments were necessary to show that the true curve is rounded at the peak. This special series of measurements is included at the end of Table II. The results of other special measure-

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[1] Beach and Stevenson, *J. Chem. Phys.*, **6**, 635 (1939); Zahn, *Phys. Rev.*, **40**, 291 (1932); **38**, 521 (1931).

[2] Beach and Turkevich, THIS JOURNAL, **61**, 303 (1939); Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

[3] Ta-You Wu, *ibid.*, **7**, 965 (1939), who gives additional references.

[4] Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928); Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).