

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Action of Liquid Ammonia upon Sulfur Trioxide Addition Compounds

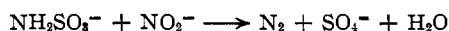
BY H. H. SISLER AND L. F. AUDRIETH

Theoretically, interaction of ammonia with sulfur trioxide should lead to ammonium sulfamate; actually, ammonium imidodisulfonate is obtained almost exclusively. However, when aqueous ammonia acts upon various sulfur trioxide-tertiary amine addition compounds¹ appreciable quantities of ammonium sulfamate are formed. In order to gain a clearer insight into the mechanism of these reactions, and also to prevent the simultaneous action of water (present in aqueous ammonia), the behavior of these sulfur trioxide addition compounds in liquid ammonia was investigated. The addition compounds studied were those with pyridine,² dimethylaniline,³ dioxane,⁴ hydrogen chloride (chlorosulfonic acid), and sodium chloride (sodium chlorosulfonate). The reaction products were analyzed for sulfamate, imidodisulfonate, and sulfate.

Recorded observations that ammonium imidodisulfonate is the sole product of the reaction of sulfur trioxide with liquid ammonia were verified.

Experimental

Method of Analysis.—The reaction products were analyzed by the following procedure. Sulfate and imidodisulfonate were precipitated as the respective barium salts by the addition of barium chloride to an ammoniacal, aqueous solution of the reaction product. The filtrate was next acidified with dilute hydrochloric acid, then treated with potassium nitrite solution for the purpose of converting the sulfamate ion into sulfate, which was then precipitated as barium sulfate.



The joint precipitate of basic barium imidodisulfonate and barium sulfate was extracted with dilute hydrochloric acid, leaving the barium sulfate in the filtering crucible. The imidodisulfonate was estimated as barium sulfate after treatment of the acidified filtrate with nitrite and barium chloride. This procedure gives results which are fairly reproducible, but is not satisfactory for exact work due to the facts, (1) that the precipitate of basic barium imidodisulfonate is slightly soluble in water, and (2) that complete precipitation of sulfate as barium sulfate is difficult in the presence of large amounts of sulfamate ion.⁵

Experimental Results.—Pyridine-sulfur trioxide and dimethylaniline-sulfur trioxide were added directly to liquid ammonia at -33° . These reactions, while vigorous, could

be controlled without difficulty. However, both dioxane-sulfur trioxide and liquid ammonia had to be precooled to the temperature of a solid carbon dioxide-ether bath to moderate the reaction. The chlorosulfonic acid was dissolved in a large excess of chloroform (20 g. in 140 ml. of CHCl_3) and then added slowly to liquid ammonia. Even under these conditions the reaction was found to be a very vigorous one, as was the reaction between sodium chlorosulfonate and ammonia. In every case, the excess of ammonia was allowed to evaporate and the residual product, after treatment to remove amine or solvent, was washed with ether and dried to constant weight. Samples were analyzed by the procedure given above.

Quantities of sulfur trioxide addition compounds used varied from 15 to 40 g. Large excesses of liquid ammonia (between 200 and 400 ml.) were used in all experiments. Typical experimental results are reproduced in Table I. The percentage composition of the reaction products, also the ratio of the percentages of ammonium sulfamate to triammonium imidodisulfonate, are given in each case.

TABLE I

| Addn. cpd. | (NH ₄) ₂ -SO ₄ , % | NH ₄ N-(SO ₂ NH ₄) ₂ , % | NH ₂ SO ₂ -NH ₄ , % | $\frac{\% \text{NH}_2\text{-SO}_2\text{NH}_4}{\% \text{NH}_4\text{N-(SO}_2\text{NH}_4)_2}$ |
|---|--|---|--|--|
| C ₅ H ₅ N·SO ₃ | 13.5 | 2.1 | 83.5 | 39.8 |
| | 15.5 | 3.4 | 80.5 | 23.7 |
| C ₅ H ₅ N(CH ₃) ₂ ·SO ₃ | 13.5 | 8.6 | 72.3 | 8.4 |
| | 30.2 | 9.8 | 56.5 | 5.8 |
| | 36.8 | 6.4 | 55.0 | 8.6 |
| O(CH ₂ CH ₂) ₂ O·SO ₃ | 34.9 | 15.7 | 51.5 | 3.3 |
| | 30.1 | 15.2 | 56.8 | 3.7 |
| HCl·SO ₃ ^a | 7.7 | 7.5 | 53.0 | 7.1 |
| | 11.5 | 8.1 | 51.0 | 6.3 |
| NaCl·SO ₃ ^a | 13.2 | 4.3 | 41.5 | 9.7 |
| | 14.5 | 4.2 | 39.0 | 9.3 |

^a NH₄Cl and NaCl, respectively, make up the rest of the reaction product.

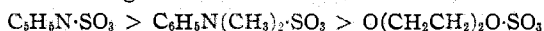
Discussion

The reactions of ammonia with chlorosulfonic acid and sodium chlorosulfonate obviously are ammonolytic in character, involving replacement of a negative constituent by the amido group and leading to the formation of the sulfamate. The same mechanism also characterizes the reaction of ammonia with sulfur trioxide addition compounds. In fact, the tertiary amine complexes have been shown to be esters of N,N-disubstituted sulfamic acids, existing in the betaine form.²

If the three addition compounds of sulfur trioxide with pyridine, dimethylaniline, and dioxane are arranged in the order of the relative predominance of the sulfamate over the imidodisul-

(1) Baumgarten, *Ber.*, **59**, 1976 (1926).(2) Baumgarten, *Ber.*, **59**, 1166 (1926).(3) Willcox, *Am. Chem. J.*, **32**, 446 (1904).(4) Suter, Evans and Kiefer, *THIS JOURNAL*, **60**, 538 (1938).(5) Divers and Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

fonate in their respective ammonolytic products, the following series is obtained



This is also the order of their decreasing stability toward water.^{1,4} In view of the fact that imido-disulfonate only is formed when ammonia and sulfur trioxide react, it is logical to conclude that the presence of this product is due to the ammonation of sulfur trioxide held but loosely by the donor molecule. Consequently, the less stable the sulfur trioxide complex, that is, the weaker the co-

ordinate bond holding the sulfur trioxide molecule, the greater will be the proportion of imido-disulfonate in the ammonolytic product.

Summary

Reactions of liquid ammonia with sulfur trioxide addition compounds result primarily in the formation of ammonium sulfamate. These reactions are considered to be ammonolytic in character.

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The Photochemical Decomposition of Solid Hydrogen Compounds at Low Temperatures

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Very little has been known previously of the photochemical decomposition of solids at low temperatures.^{1,2} It seemed, therefore, worth while to investigate reactions involving the liberation of hydrogen, since the ortho-para concentration of the hydrogen may reveal interesting features of the decomposition mechanism. It is well known that below 200°K. the ortho-para ratio of equilibrium hydrogen is dependent on the temperature and thus this ratio may indicate at which effective temperature the photochemical formation of the hydrogen has taken place.

In the following some experiments on the photochemical decomposition of hydrogen iodide, formaldehyde and methyl alcohol at temperatures between 65° and 85°K. are reported. All these substances give off hydrogen (besides other reaction products) when decomposed photochemically.^{1,3,4}

Experimental

Hydrogen iodide was prepared in the usual way by catalytic combination of hydrogen with iodine and repeated fractional distillation at low temperatures.⁵ It was kept in a glass bulb and was perfectly white in the solid state. Apiezon grease was used for the taps, which was only slowly attacked by hydrogen iodide.

The methyl alcohol was the purest obtainable product. As a source of formaldehyde, the vapor of 40% aqueous solution was used.

- (1) Bonhoeffer and L. Farkas, *Z. physik. Chem.*, **132**, 235 (1928).
- (2) Hilsch and Pohl, *Ann. Physik*, [5] **32**, 155 (1938).
- (3) Cf. Loecker and Patat, *Z. physik. Chem.*, **B27**, 431 (1934).
- (4) Patat, *Z. Elektrochem.*, **41**, 494 (1935).
- (5) Cf. Farkas and Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, 1939, p. 180.

The experimental arrangement is shown in Fig. 1. The hydrogen iodide, formaldehyde or methyl alcohol was condensed on spot S of tube V, which contained liquid air. The glass tube was specially thin at S, in order to improve the heat exchange between the condensed substance and the liquid air. The amount of substance on S was adjusted by a lock system between the tap T and the storage bulb so as to form a white circle of about 5 mm. diameter and of about 10,000–100,000 molecular layers. A mercury arc served as a light source and the ultraviolet light entered through the quartz window Q opposite the spot S.

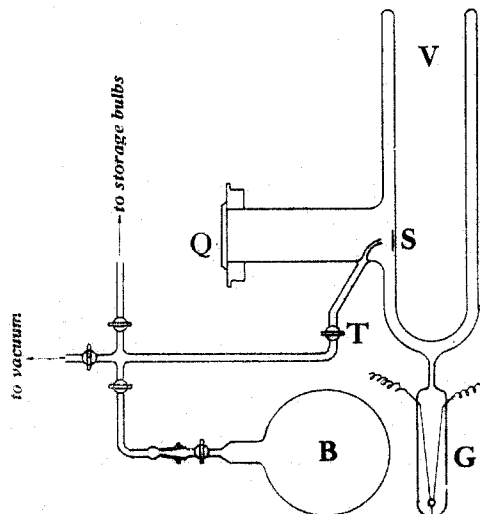


Fig. 1.

Occasionally the temperature of the tube was lowered to 65° K. by pumping off the liquid air. After the substance was condensed into the reaction vessel, the tap T was closed and the evolution of hydrogen during the illumination followed up by the Pirani gage (G). The illumination was continued until 30–40 cu. mm. of gas at S. T. P. was