

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

## Ammonium and Substituted Ammonium Sulfamates

BY M. JOSETTA BUTLER AND L. F. AUDRIETH

The recent commercial development of sulfamic acid<sup>1</sup> has stimulated interest in the properties not only of the acid but of its derivatives as well. The present paper describes the preparation of ammonium sulfamate and a study of its behavior as an acid in liquid ammonia. As a preliminary step in the investigation of the effect of pyrolysis on alkyl substituted ammonium sulfamates<sup>2</sup> a series of 18 alkylamine sulfamates was prepared, and such physical data as melting point, hygroscopicity, and solubilities in common solvents were determined.

### Experimental

**Ammonium Sulfamate as an Ammonio Acid.**—Ammonium sulfamate is prepared readily by the direct addition of sulfamic acid to liquid ammonia. The excess solvent is allowed to evaporate spontaneously and the ammonium sulfamate is obtained as a finely divided white powder. If necessary, it may be purified by recrystallization from hot ethanol.

The modern concept of acidity as well as the generalizations permitted by the nitrogen system of compounds lead to the conclusion that ammonium salts behave as acids in liquid ammonia. It is a well-known fact that many compounds containing the  $-\text{NH}_2$  group, where it replaces an  $-\text{OH}$  radical in such groupings as  $-\text{SO}_2\text{NH}_2$ ,  $-\text{CONH}_2$ , are also acidic in liquid ammonia. Ammonia is a strongly basic solvent and so undoubtedly possesses a higher proton affinity than the corresponding  $(-\text{SO}_2\text{NH})^-$  or  $(-\text{CONH})^-$  residues. It was regarded as highly probable, therefore, that sulfamic acid might function as a dibasic acid in liquid ammonia.

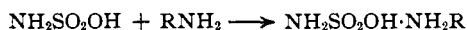
Rapid addition of sulfamic acid to a solution of sodium dissolved in liquid ammonia results in the discharge of the blue color together with the formation of a slight amount of precipitate.<sup>3,4</sup> When treated with an excess of sodium, such a solution shows evidence of further reaction, during which reaction additional quantities of an insoluble precipitate are formed, as the sodium is used up. Both sulfamic acid (converted to ammonium sulfamate in liquid

ammonia) and sodium sulfamate are very soluble in liquid ammonia. These observations were, therefore, interpreted as indicating that the first step, or rapid reaction, involves the formation of sodium sulfamate, followed by a second, but much slower, reaction involving the replacement of an amidic hydrogen with the formation of the insoluble disodium salt. The sulfamate group does not appear to suffer any degradation or disruption in this reaction.

Quantitative studies were carried out to verify the above supposition. Weighed quantities of sulfamic acid and an excess of sodium were dissolved in anhydrous ammonia. The solutions were allowed to stand for three hours to give ample time for complete reaction. The excess sodium was then titrated with solid ammonium chloride to the disappearance of the blue color. The mole ratio of sodium to sulfamic acid was calculated and found to agree fairly well with that required for the formation of the disodium salt.

In a typical experiment 1.153 g. (0.0118 mole) of sulfamic acid and 1.028 g. (0.0447 mole) of sodium were dissolved in 400 cc. of liquid ammonia. The reaction was allowed to proceed for three hours. Ammonium chloride, weighing 1.0965 g. (0.0205 mole), was required to discharge the blue color of the excess sodium still present. These results indicate that 0.0242 mole of sodium was required to react with 0.0118 mole of sulfamic acid corresponding to a molar ratio of 2.05:1. The formation of the disodium salt,  $\text{NaNH}_2\text{SO}_2\text{ONa}$ , requires a mole ratio of 2 Na:1  $\text{NH}_2\text{SO}_2\text{OH}$ .

**Substituted Ammonium Sulfamates.**—These derivatives of sulfamic acid were prepared according to the equation



A calculated amount of finely pulverized sulfamic acid was added slowly to an equivalent quantity of the amine. In several instances where the anhydrous amine was used, the salt began to precipitate from solution just as soon as the acid was added. Water or alcohol had to be added to dissolve the salt so that the addition of acid could be continued. The final solution was always made slightly basic by adding a few drops of the amine. This was done in order to avoid contamination of the product with the free acid. After filtration the salt usually was obtained from the solution by the addition of alcohol followed by cooling, or by the addition of ether to the alcoholic solution. Such procedures were necessary because of the high solubility of these salts in water and in alcohol. None of the compounds was found to be soluble in ether. Calculated and experimentally determined sulfur and nitrogen values as well as melting points are recorded for all compounds in Table I.

Nitrogen was determined by the micro-Dumas method. For the determination of sulfur, weighed samples were treated with nitrite in acid solution, thus effecting conversion of the sulfamate ion into the sulfate ion, followed by precipitation as barium sulfate.

(1) Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

(2) Paal and Jänicke, *Ber.*, **28**, 3160 (1895), obtained N-aryl ammonium sulfamates by heating the corresponding aryl amine sulfamates.

(3) These observations have also been verified by Dr. M. Cupery of the Experimental Station of E. I. du Pont de Nemours and Company. The authors gratefully acknowledge their indebtedness to Dr. Cupery for his interest in the present investigation.

(4) A private communication from Professor F. W. Bergstrom (Stanford University) states that "the dipotassium salt of sulfamic acid can be prepared by the interaction of excess potassium amide with sulfamic acid in liquid ammonia. The product is obtained first as a gelatinous precipitate which becomes finer and presumably micro-crystalline on standing."

TABLE I  
 SUBSTITUTED AMMONIUM SALTS OF SULFAMIC ACID

Amine used	Formula	M. p. (uncorr.) °C.	Sulfur, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found
1 Methylamine <sup>a</sup>	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH <sub>3</sub>	91-92	25.00	25.59	21.9	21.9
2 Dimethylamine <sup>a</sup>	NH <sub>2</sub> SO <sub>2</sub> OH·NH(CH <sub>3</sub> ) <sub>2</sub>	86-87	22.53	24.15	19.7	19.2
3 Trimethylamine <sup>a</sup>	NH <sub>2</sub> SO <sub>2</sub> OH·N(CH <sub>3</sub> ) <sub>3</sub>	147.5-149	20.51	20.60	17.9	17.8
4 Ethylamine <sup>a</sup>	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	65-70	22.53	23.21	19.7	19.3
5 Propylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	67-69	20.51	20.60	18.0	17.6
6 Isopropylamine <sup>a</sup>	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	74-75	20.51	21.54	18.0	18.3
7 <i>n</i> -Butylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	107-108	18.82	18.83	16.5	16.1
8 Isobutylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	138-139	18.82	18.81	16.5	17.1
9 <i>n</i> -Amylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	128-129	17.39	17.65	15.2	15.0
10 Isoamylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	185	17.39	17.65	15.2	15.1
11 <i>n</i> -Hexylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	109-111	16.16	16.25	14.1	14.3
12 2-Ethylbutylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	89-90	16.16	16.18	14.1	14.3
13 Ethylenediamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ·HOSO <sub>2</sub> NH <sub>2</sub>	156-158	25.19	25.22	22.1	22.0
14 Propylenediamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> NH <sub>2</sub> ·HOSO <sub>2</sub> NH <sub>2</sub>	155-156	23.88	24.03	20.9	21.5
15 Cyclohexylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> C <sub>6</sub> H <sub>11</sub>	157-158	16.33	16.40	14.3	14.3
16 Dicyclohexylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	160-162	11.51	11.61	10.1	10.0
17 $\beta$ -Phenylethylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	183-184	14.68	14.63	12.8	12.4
18 $\gamma$ -Phenylpropylamine	NH <sub>2</sub> SO <sub>2</sub> OH·NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	104-105	13.79	14.06	12.1	11.8

<sup>a</sup> These sulfamates were found to be extremely hygroscopic.

### Summary

1. Experimental evidence has been presented to demonstrate that sulfamic acid behaves as a dibasic acid in liquid ammonia.

2. A series of eighteen substituted ammonium

sulfamates has been prepared. Various properties of these compounds, such as melting point, solubilities in common solvents, and hygroscopicity have been determined.

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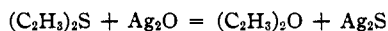
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## The Reaction of Divinyl Sulfide with Silver Oxide

BY WM. L. RUGH<sup>1</sup> AND A. E. ERICKSON

The first reference to the preparation of divinyl ether may be found in a paper by Semmler<sup>2</sup> on the essential oil of the leek, *Allium ursinum* L. When divinyl sulfide derived from this source was treated with dry silver oxide, Semmler obtained a colorless sulfur-free liquid which boiled at 39° and with a molecular weight of 71 as indicated by two vapor density measurements. Without analysis or further characterization he claimed to have prepared divinyl ether (molecular weight 70) for the first time, giving the following equation for the reaction



Recently pure divinyl ether has been synthesized,<sup>3</sup> fully characterized, and its boiling point found to be 28.3°, a value confirmed by Miles

and Menzies<sup>4</sup> and over 10° lower than that reported by Semmler. On theoretical grounds we can find little support for the reaction as formulated by Semmler. It was therefore decided to reinvestigate this reaction.

The repetition of Semmler's work on the natural sulfide was not possible due to the difficulty of obtaining the oil of *A. ursinum*. Synthetic divinyl sulfide, when treated with dry silver oxide at 30° according to Semmler's procedure, failed to give divinyl ether. In one experiment, when the reaction mixture was heated to reflux the divinyl sulfide, a violent explosion occurred. Moist silver oxide and divinyl sulfide likewise failed to give acetaldehyde and silver as stated by Semmler.

We are indebted to Prof. E. Emmet Reid for suggesting the use of  $\beta, \beta'$ -dibromodiethyl sulfide

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(2) Semmler, *Ann.*, **241**, 92 (1887).

(3) Rugh and Major, *This Journal*, **53**, 2662 (1931).

(4) Miles and Menzies, *J. Phys. Chem.*, **37**, 425 (1933).