

The Reaction Between Silver Amidosulfonate and the Alkyl Iodides

W. W. BINKLEY¹ with ED. F. DEGERING, Purdue University

Methyl amidosulfonate was prepared from methyl iodide and silver amidosulfonate in 1911 by Ephraim and Lasocky (1). The purpose of the present work is to show that the procedure used by these workers is unsuitable for the preparation of the higher alkyl esters of amidosulfonic acid, what products are formed, and what course the reactions between the higher alkyl iodides and silver amidosulfonate follows. The procedure used in the experimental part of this work is essentially the same as that used by Ephraim and Lasocky.

Experimental

The Reaction Between Methyl Iodide and Silver Amidosulfonate. Ten grams of silver amidosulfonate (ground to pass a 100 mesh screen), 25 ml. of absolute ethyl ether, and 6.5 g. of methyl iodide were added to a flask equipped for stirring. After 24 hours of agitation at room temperature, the reaction products were transferred to a weighed extraction thimble and extracted for 6 hours in a Soxhlet with ethyl ether and then for 6 hours with absolute methanol. The contents of the thimble were washed with 200 ml. of hot distilled water. This final residue was dried and weighed as AgI. The results are included in Table I.

The Reaction Between Ethyl Iodide and Silver Amidosulfonate. Ten grams of silver amidosulfonate (ground to pass a 100 mesh screen), 25 ml. of absolute ethyl ether, and 7.2 g. of ethyl iodide were agitated at room temperature for 24 hours. The reaction products were transferred to a weighed thimble and extracted for 24 hours in a Soxhlet with ethyl ether. The contents of the thimble was then washed with 200 ml. of hot distilled water. This final residue was dried and weighed as AgI. The results are listed in Table I.

TABLE I.—Analytical Results

Experi- ment	Alkyl Iodide†	AgI	Amount of	Ether	Alcohol	HOSO ₂ NH ₂
		Formed	Reacted Iodide	Extract	Extract	Found
1.	Methyl	7.2	4.3	0.3	3.2	0.0
2.	Methyl	7.0	4.2	0.3	2.8	0.0
3.	Ethyl	9.5	6.2	1.8	3.7	0.0
4.	Ethyl	9.4	6.2	1.8	1.8	1.0
5.	Ethyl	9.5	6.2	2.0	0.8	1.4
6.	Ethyl	9.5	6.2	2.4	..	1.9
7.	Ethyl	9.4	6.2	2.3	..	1.8
8.	<i>n</i> -propyl	3.9	2.8	1.1	..	0.7
9.	<i>n</i> -propyl	3.9	2.8	1.2	..	0.8

† Slightly less than 1/20 mole of alkyl iodide was used.

‡ The amount of reacted alkyl iodide was calculated from the amount of AgI formed.

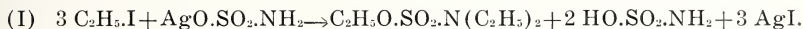
¹ Present address, Ohio State University, Columbus, Ohio.

The Reaction Between n-Propyl Iodide and Silver Amidosulfonate.

This reaction was conducted in the same manner as the reaction between ethyl iodide and silver amidosulfonate. The 7.2 g. of ethyl iodide were replaced by 7.8 g. *n*-propyl iodide. The extraction with ethyl ether required only 8 hours and 400 ml. of hot distilled water were used in the subsequent washing. The results are given in Table I.

Discussion

Good yields of methyl amidosulfonate (based on the amount of AgI formed) can be obtained from methyl iodide and silver amidosulfonate by the procedure of Ephraim and Lasocky (Expts. 1 and 2). When the reaction products of ethyl iodide and silver amidosulfonate were extracted 8 to 12 hours with ethyl ether, ethyl *N,N*-diethylamidosulfonate was isolated (cf. Expts. 3, 4, 5). If the products of this reaction were extracted 24 hours with ethyl ether, the theoretical amount of ethyl *N,N*-diethylamidosulfonate (based on the amount of ethyl iodide that reacted) was formed to satisfy Equation I (cf. Expts. 6 and 7).



When the ethyl ether extraction was followed by 6 hours extraction with absolute ethyl alcohol, all the amidosulfonic acid formed in the reaction was converted to ethyl ammonium sulfate (cf. Expt. 3 and Equation II):

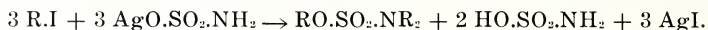


If the ether extraction was followed by washing the residue with two 25 ml. portions of hot absolute ethyl alcohol, a mixture of ethyl ammonium sulfate and amidosulfonic acid was obtained with a composition approximating ethyl amidosulfonate (2) (cf. Expt. 4). When 50 ml. of cold absolute ethyl alcohol was used for the washing instead of the two 25 ml. portions, a mixture containing amidosulfonic acid was obtained (cf. Expt. 5). When extraction with ethyl alcohol was replaced by washing with hot distilled water, the amount of amidosulfonic acid found approached the theoretical value required by Equation I (cf. Expts. 6 and 7). The reaction between *n*-propyl iodide and silver amidosulfonate followed the same course as the reaction between ethyl iodide and silver amidosulfonate (cf. Equation I). The amount of amidosulfonic acid was equal to the expected theoretical value (based on the amount of *n*-propyl iodide that reacted). The weight of the residue from the ether extraction was equal to the theoretical value for *n*-propyl *N,N*-di-*n*-propylamidosulfonate (cf. Expts. 8 and 9).

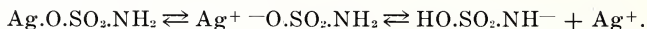
Summary

Good yields of methyl amidosulfonate were obtained from methyl iodide and silver amidosulfonate by the procedure of Ephraim and Lasocky. The reactions between ethyl and *n*-propyl iodides and silver amidosulfonates do not give the corresponding esters of amidosulfonic

acid. The corresponding esters of *N,N*-dialkylamidosulfonic acid and amidosulfonic acid were formed according to the following equation:



This appears to be another interesting case of preferential alkylation of the nitrogen atom over that of the oxygen atom, which may be explained by the following postulated system:



in which the alkyl iodide reacts with either of the postulated ions. The salt may exist, moreover, according to Hennion, as a chelate complex in which the bond on either side of the silver atom might become activated.

Bibliography

1. Ephraim and Lasocky: Ber. **44**:395. 1911.
2. Binkley and Degering: Ind. Acad. of Sc. **47**:122. 1938.