

## THE ADDITION COMPOUND OF N,N-DIMETHYLFORMAMIDE AND HYDROGEN CHLORIDE

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A hydrogen chloride addition compound of N,N-dimethylformamide has been prepared, and showed to be the monohydrochloride. The compound can be distilled without decomposition, other properties being similar to those of like known products.

It is known that carboxylic acid amides are neutral compounds, or in any case, the basic character of their amino group is very weak. A few addition compounds of amides with mineral acids, reported in the literature, are rather unstable materials, and suffer an instantaneous hydrolysis when exposed to water. The crystalline adduct of formamide with hydrogen chloride is stable only at lower temperatures, otherwise it undergoes violent decomposition to give carbon monoxide and ammonia [1]. There have been several studies [2, 3] on the preparation of the hydrogen chloride adduct of acetamide; a crystalline product is, in general, obtained when gaseous hydrogen chloride is introduced into a cooled ethereal solution of the acid amide. In some cases, mineral acid adducts of amides may be prepared also by treating the corresponding nitriles with mineral acids, as it was found in the case of propionitrile by HEULE and SCHUPP [4]. WERNER [5] surveyed the methods of preparing hydrogen bromide and hydrogen iodide adducts of various acid amides and discussed their composition, since this group includes addition compounds not only of the molar ratio of 1:1, but also of different compositions. WERNER was the first to describe a hydrogen bromide adduct of formamide having the composition  $(\text{HCONH}_2)_3 \cdot (\text{HBr})_2$ .

In the series of acid-amides alkylated on the nitrogen atom, N-methylacetamide semi-hydrochloride was described by BLICKE (6); this compound could be recrystallized from acetone. A systematic study of N-methyl amides was made by D'ALELIO and REID (7). They observed the formation of two types of hydrogen chloride addition compounds, namely  $\text{R} \cdot \text{CONHCH}_3 \cdot \text{HCl}$  and  $(\text{R} \cdot \text{CONHCH}_3)_2 \cdot \text{HCl}$ . The first type is formed in nonpolar solvents, the second in the absence of solvents.

In the course of the present work we succeeded in preparing the hydrogen chloride addition compound of N,N-dimethylformamide which has not been described in the literature so far. There is but one reference concerning

this compound published by DAWSON *et al.* (8); these authors carried out conductivity measurements in the dimethylformamide — hydrogen chloride system and found diversions both from the ONSAGER equation and the OSTWALD dilution rule. These findings have been interpreted by assuming a strong interaction between the components even at low hydrogen chloride concentrations.

In our experiments, the hydrogen chloride adduct was prepared in the usual way, by introducing hydrogen chloride into dimethylformamide. The reaction gave a crystalline compound. Analysis showed the product to consist of monohydrochloride, at variance with the assumption of D'ALELIO, according to which the semi-hydrochloride was to be expected in the absence of solvents. The hydrogen chloride adduct had a surprisingly high stability; it could be distilled under reduced pressure without decomposition. The boiling point is apparently identical with that of dimethylformamide. When the adduct is treated with water or alkali, the amide can be recovered. The acid content of the adduct is very slowly lost, even when the compound is stored in an exsiccator over sodium hydroxide.

Further investigations are intended to study the basic dissociation constants of non-substituted and substituted amides also in non-aqueous solvents, and to establish the composition and properties of their addition compounds formed with various acids.

### *Experimental*

#### *N, N-Dimethyl-formamide monohydrochloride*

Dry hydrogen chloride was passed for several hours into a solution of 94,84 g freshly distilled N,N-dimethyl-formamide cooled in ice-water. 47,17 g hydrogen chloride was absorbed. (Theory requires 47,42 g HCl for the monohydrochloride.) At the end of the reaction the solution solidified to a crystalline mass. The crystals were washed on a filter with a small amount of anhydrous ether, and the material was distilled, b. p. 76° at 40 mm. The product was a colourless syrupy liquid which soon solidified. Yield 102,5 g (72 %).

For analysis, 6,25 g was dissolved in water in a 10 ml volumetric flask, and an aliquot part titrated. The solution contained 2,07 % calculated as free hydrochloric acid, which gave a hydrogen chloride content of 33,20 % for the compound. The formula of monohydrochloride requires 33,34 % HCl.

#### *Recovery of the amide*

19,53 g of crystalline N,N-dimethylformamide monohydrochloride was ground with 18,9 g anhydrous Na<sub>2</sub>CO<sub>3</sub> in a mortar. The material was filtered from the salt. The filtrate was distilled to give a main fraction boiling at 152—154° (760 mm), yield 6,8 g,  $n_D^{25} = 1,4270$ . The literature (9) records for N,N-dimethyl formamide b. p. 153°,  $n_D^{25} = 1,4269$ .

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#### СОЛЯНО-КИСЛОТНОЕ АДДИЦИОННОЕ СОЕДИНЕНИЕ ДИМЕТИЛФОРМАМИДА

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Было изготовлено соляно-кислотное аддиционное соединение N,N-диметилформамида оказавшееся моногидрохлоридом. Соединение можно перегонять без разложения, другие его свойства являются тождественными со свойствами подобных известных соединений.