tion of Niemann's experiments. By the action of dilute aqueous acids or alkalies, acetanilide is hydrolyzed to aquo acetic acid and aniline.

Acid Chlorides.—Benzotrichloride, $C_6H_5COCl_3$, is hydrolyzed by the action of water at 150° to aquo benzoic acid. It is simultaneously hydrolyzed and ammonolyzed by the action of aqua ammonia at 130° to aquo benzoic acid, aquo-ammono-benzoic acid (benzamide) and benzoic anammonide (benzonitrile). Niemann obtained a 75% yield of benzonitrile by allowing a liquid ammonia solution of benzotrichloride to stand at laboratory temperatures for some time. When he heated such a solution for a time at 100°, good yields of monomolecular and trimolecular benzonitrile were obtained.

Summary

An account is given of the ammonolytic behavior of three dialkylcyanamides, of triphenylguanidine, of two N-esters of urea, of acetic acid and acetamide, of diphenylacetamidine and diphenylbenzamidine, of acetanilide and of benzotrichloride.

It is shown that the dialkylcyanamides unite with alkali metal amides at low temperatures in liquid ammonia solution to form metallic salts of dialkylguanidines.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Metallic Salts of Carboxazylic Acids[1]

BY EDWARD C. FRANKLIN

In this Laboratory we have come to use the general name carbylic acids to include the closely related carboxylic acids, the acid amidines and the acid amides and to speak of the three classes of compounds as carboxylic acids, carbazylic acids and carboxyazylic acids, respectively. Acetic acid, acetamidine and acetamide are examples of the three classes of compounds. Acetic acid and acetamidine we regard as acetic acids belonging, respectively, to an oxygen system and a nitrogen system of compounds.[2] The first acid, as a derivative of water, is an aquo acetic acid, the second, as a derivative of ammonia, is an ammono acetic acid, while acetamide, which may be said to be derived at the same time from water and ammonia, is an aquo-ammono acetic acid.

In many ways the acid amidines and the acid amides closely resemble the carboxylic acids. For example, Franklin and Stafford[3] showed that

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(1) The laboratory work upon which this report is based was done by Ruth V. Fulton, Thesis Stanford University, 1925.

(2) Franklin, *Am. Chem. J.*, **47**, 285 (1912); Fernelius and Johnson, *J. Chem. Educ.*, **5**, 664, 828 (1928); **7**, 1291, 1602, 1850 (1930).

(3) Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902).

certain acid amides in liquid ammonia solution react with the alkali metals and their amides and with metallic magnesium to form salts strictly after the manner of the formation of metallic salts by the action of carboxylic acids in water solution, and Cornell[4] found that metallic salts of the acid amidines may be prepared by using liquid ammonia in which to carry out the necessary reactions.

This paper is written to place on record the preparation of a number of metallic salts of carboxyazylic acids and to give the results of their pyrogenetic decomposition as observed by Miss Fulton. The general methods of manipulation used in preparing these salts are described elsewhere.[5]

The salts listed were obtained by the action of alkali metal amides on the respective acid amides in liquid ammonia solution.

SALTS OF CARBOXAZYLIC ACIDS

Salt	Formula	Analyses, % Metal Calcd.	Metal Found	Nitrogen Calcd.	Nitrogen Found
K-Formate	HCONHK	47.0	46.6 46.9 46.8	16.8	16.1 16.2 16.9
Na-Formate	HCONHNa	34.3	34.4	20.9	21.1
K-Propionate	C_2H_5CONHK	35.2	35.5	12.6	12.1
K-Isobutyrate	C_3H_7CONHK	31.2	30.8	11.2	11.8
K-Valerate	C_4H_9CONHK	28.0	27.7 27.2 27.2	10.0	10.0
K-Caproate	$C_5H_{11}CONHK$	25.5	25.2 24.7	9.1	8.5 9.0
K-Benzoate	C_6H_5CONHK	25.6	25.6	8.8	8.8
K-Palmitate	$C_{15}H_{31}CONHK$	13.2	12.8	4.8	4.5
K-Malonamide	$CHK(CONHK)_2$	54.1	54.8 53.7	13.8	13.5 13.4 12.9

All these salts, excepting potassium palmitamide and tripotassium malonamide which are formed as amorphous precipitates when dilute solutions of the respective acid amides are added to an excess of potassium amide in dilute solution, are soluble in liquid ammonia and were obtained well crystallized. They are all vigorously hydrolyzed by the action of water to the respective alkali metal hydroxides and acid amides.

Pyrogenetic Decomposition of the Potassium Carboxazylates.—Just as the alkali metal carboxylates when heated with soda-lime yield saturated hydrocarbons and alkali metal aquocarbonates, sodium acetate for example in accordance with the equation, $CH_3COONa + NaOH = CH_4 + Na_2CO_3$, and as potassium ammonoacetate, when heated with potassium amide, forms methane and a potassium ammonocarbonate, $CH_3C(NH)NHK + KNH_2 = CH_4 + K_2CN_2$,[4] so, at elevated temperatures, the potassium salts of the acid amides might be expected to decompose in accordance with the equation $RCONHK = RH + KNCO$, to form saturated hydrocarbons and a potassium aquo-ammono-carbonate. As a matter of fact that is what happens except that a portion of the salt simul-

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(4) Cornell, THIS JOURNAL, **50**, 3311 (1928).

(5) Franklin, *ibid.*, **27**, 820 (1905); *J. Phys. Chem.*, **15**, 509 (1911); THIS JOURNAL, **35**, 1453 (1913).

taneously decomposes into a nitrile and potassium hydroxide, $\mathrm{RCONHK} = \mathrm{RCN} + \mathrm{KOH}$.

In accordance with the scheme, $\mathrm{RCONHK}\begin{array}{l}\nearrow \mathrm{RH} + \mathrm{OCNK} \\ \searrow \mathrm{RCN} + \mathrm{KOH}\end{array}$, Miss Fulton found that at temperatures around 250–300° four potassium carboxylates decomposed to yield potassium cyanate and potassium hydroxide in the following molecular ratios; potassium propionamide 33/67, potassium isobutyramide 25/75, potassium valeramide 38/72, potassium capronamide 28/72. At the same time the first salt was found to yield ethane and propionitrile, the second, propane and butyronitrile, the third, normal butane and valeronitrile, the fourth, normal pentane and capronitrile. Neither benzonitrile nor potassium hydroxide was found among the decomposition products of potassium benzamide. Approximately quantitative yields of benzene were obtained. Excepting in the case of the latter salt considerable amounts of dark colored, amorphous residues were formed. Potassium cyanate in liberal quantities, potassium hydroxide in small amounts, and a high boiling liquid which was assumed to be a mixture of pentadecane and palmitic acid nitrile were found among the decomposition products of potassium palmitamide.

Summary

Alkali metal salts of nine acid amides (carboxazylic acids) have been prepared by the action of alkali metal amides on the respective acid amides in liquid ammonia solution.

When heated in the dry state these salts yield saturated hydrocarbons and potassium cyanate (potassium aquo-ammono-carbonate).

Attention is called to the close resemblance between the reactions represented by the equations, (1) $\mathrm{RCOOK} + \mathrm{KOH} = \mathrm{RH} + \mathrm{K_2CO_3}$, (2) $\mathrm{RC(NH)NHK} + \mathrm{KNH_2} = \mathrm{RH} + \mathrm{K_2CN_2}$ and (3) $\mathrm{RCONHK} = \mathrm{RH} + \mathrm{KNCO}$.

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