Summary.

Acid amides may be decomposed very largely into the cyanides and water by heating in a flask with various substances—aluminium oxide, pumice stone, sand—the flask being provided with an outlet sufficiently far above the contact substance to permit the more volatile cyanide and water to escape while causing the amides to condense and drop back upon the hot contact material.

Syracuse, N. Y.

[Contribution from the Chemical Laboratory of Syracuse University.]

THE PYROGENETIC DECOMPOSITION OF AMIDES. II.

By R. S. Boehner and A. L. Ward.

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In the previous paper[1] it has been shown that the acid amides may be decomposed into the cyanides and water by heating with various contact materials but the method used did not permit of an accurate determination of the temperature at which the most complete decomposition could be effected. In order to determine this the amides were passed through hot tubes filled with these contact substances, the temperature being determined by a Hoskins' pyrometer. Using this method a temperature of about 425° was found to give the best results when passing acetamide through a tube filled with aluminium oxide and this temperature was employed in working with the other contact materials. It has thus been possible to effect practically a complete decomposition of the amides into cyanide and water, allowance being made for the lack of quantitative methods for the determination of the cyanides under the conditions obtaining in this work.

Experimental.

Combustion tubing wrapped in asbestos paper was wound with "Nichrome" ribbon, this covered with several layers of asbestos paper, and the whole placed in an iron pipe which was also covered with asbestos paper. The current from a 110 volt lighting circuit served to give the required temperature. The pyrometer couple was enclosed in a hard glass tube before being placed in the combustion tubing. A. Mailhe,[2] endeavoring to reduce the amides by passing their vapors mixed with hydrogen over reduced nickel and copper, obtained unsatisfactory results because of the lack of volatility of the amides. In order to overcome this difficulty air was passed through the slightly boiling amide contained in a flask and thence passed by means of a glass tube into the furnace. In this way 20 g. of amide were completely and satisfactorily volatilized and carried over the contact material in the course of about five hours. In the case

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[1] This Journal, **38**, 2503 (1916).

[2] *Chem. Ztg.*, **31**, 1146 (1907).

of benzamide, however, it was found that the tube connecting the flask and furnace became clogged with the solid amide. Benzamide, contained in a porcelain boat, was therefore placed directly in the end of the inner tube of the furnace, and air passing over this when heated serving to carry it forward over the contact material. The pyrometer in this case measured the temperature between the two tubes of the furnace. The products of decomposition in all cases passed into a condenser and were collected and determined by the method mentioned in the previous paper.[1]

To determine what effect, if any, the air would have on the reaction below the point at which oxidation might take place, nitrogen was substituted for air and determinations were also made in which the amide vapors were made to pass over the contact material without the aid of gases. The amounts of methyl cyanide obtained from 20 g. of acetamide using aluminium oxide and pumice stone, respectively, as contact substances at a temperature of 425°, were as follows:

Aluminium oxide and with acetamide.

In presence of air gave	11.4 g. CH_3CN.	82% of theory
In presence of nitrogen gave	9.3 g. CH_3CN.	66.2% of theory
Without gases gave	7.2 g. CH_3CN.	53.2% of theory

Pumice stone and acetamide.

	12.7 g. CH_3CN.	91.5% of theory
	8.0 g. CH_3CN.	57.5% of theory
	2.5 g. CH_3CN.	18.0% of theory

Acetamide and propamide vapors along with air were passed through empty tubes, 10.8% and 10% of the theoretical yield being respectively obtained.

The general results are given in the following table, air being used in each case with 20 g. of amide at a temperature of about 425°:

TABLE I.

	Aluminium oxide.		Pumice stone.		Sand.		Graphite.	
Substance.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.
Acetamide	11.4	82.0	12.7	91.5	12.0	86.3	10.5	75.5
Propamide	13.0	86.1	13.5	89.4	13.5	89.4	..	..
Normal-butyramide	13.2	83.0	14.0	88.0	14.0	88.0	..	..
Iso-butyramide	..	..	14.5	91.2	..	..	..	..
Iso-valeramide	..	..	14.7	89.1	..	..	..	..
Caproamide	13.9	80.9	15.0	89.3	..	..	..	..
Benzamide	..	..	..	..	13.6	90.6	..	..

The contact materials here used may be arranged in order of efficiency in promoting the decomposition of the amides as follows: Pumice stone, sand, aluminium oxide, and graphite. The variations in extent of decomposition with the different contact materials are but small and we are of the opinion that they may be explained by the differences in the state of division of the particles of the contact substances, the more finely divided providing a larger surface and being the more effective.

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[1] THIS JOURNAL, **38**, 2503 (1916).

A. Mailhe's[1] reduction of the amides to amines by passing the vapors of the former along with hydrogen over finely divided nickel and copper may be explained by assuming that the amides decompose into the cyanide and water and that the cyanides were then reduced to the amines. On passing acetamide over finely divided nickel at 180° to 200° without hydrogen it was found that a slight decomposition into cyanide and water had taken place.

Summary.

The acid amides may be completely decomposed into the cyanides and water by passing their vapors along with air over various contact material at a temperature of about 425°.

SYRACUSE, N. Y.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES. VI. THE UTILIZATION OF HYPOCHLORITE COLOR REACTIONS IN ESTABLISHING THE MECHANISM OF THE ACTION OF DIMETHYLSULFATE ON ANILINE.

BY NORMAN A. SHEPARD.

Received August 19, 1916.

The method of alkylating amines recently proposed by Werner,[2] by means of which monomethylated amines can be obtained by alkylation with dimethylsulfate in benzene solution, gave promise of important practical applications. According to this investigator a primary amine like aniline and this ester interact in molecular proportions, under such conditions, giving practically a quantitative yield of the methylsulfuric acid salt of the monomethylated derivative. The transformation was expressed by him in the following manner:

$$C_6H_5NH_2 + (CH_3)_2SO_4 = C_6H_5.NH_2CH_3.CH_3SO_4 \qquad (1)$$

Having occasion to apply this method for the production of methyl β-phenylethylamine, $C_6H_5CH_2CH_2NHCH_3$, the writer was surprised to find that the crystalline addition product formed by interaction of dimethylsulfate and β-phenylethylamine did not give the desired alkyl derivative when decomposed with alkali. On the contrary, the greater portion of the original amine was recovered unaltered. In order to determine the cause of the failure to obtain alkylation in this case, attention was naturally turned to a study of Werner's reaction. This work has now been completed and the purpose of this paper is to record new data that have been obtained, which are not in accord with his interpretation.

Previous to the work of Werner, Ullmann[3] had investigated the be-

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[1] *Chem. Ztg.*, **31**, 1146 (1907).

[2] *J. Chem. Soc.*, **105**, 2762 (1914).

[3] *Ann.*, **327**, 104 (1903).