basic properties, dissolving in alkalies with a *blue* color and forming *colorless* hydrochlorides.

5. Monobromo- and dibromodinitrophenoltetrachlorophthalein have been prepared and the action of ammonia on these compounds has been studied.

6. The effect of introducing acid groups into the phenoltetrachlorophthalein molecule has been studied. Tetranitrophenoltetrachlorophthalein has the strongest acid properties; dinitrophenoltetrachlorophthalein the weakest, while the monobromo- and dibromodinitrophenoltetrachlorophthalein stand intermediate.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SYRACUSE UNIVERSITY.]

THE PYROGENETIC DECOMPOSITION OF AMIDES. I.

BY R. S. BOEHNER AND C. E. ANDREWS.

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It is a well-known fact that, on distillation, the acid amides of both the aliphatic and aromatic series decompose to a very slight degree into the corresponding cyanides and water. Wöhler and Liebig[1] passed the vapor of benzamide through a red hot glass tube obtaining a small quantity of an oily liquid which was later identified as phenyl cyanide. In view of the decomposition of alcohols into ethylene hydrocarbons, or ethers, and water, on being passed through hot tubes filled with various materials,[2] it was thought possible that a more complete decomposition of the amides into cyanides and water might be effected by a similar method. Since the products of decomposition of amides, namely the cyanides and water, have a much lower boiling point than the amides, it was thought that the method referred to above might be modified by heating the amides with the contact material in a flask whose outlet was high enough to permit the cyanides and water to distill off, but would cause the amides to condense in the flask and drop back upon the hot contact material. The contact substances used were aluminium oxide, pumice stone, glass, sand, and graphite. By the above method and using the substances mentioned a much more complete decomposition of the amides into the cyanides and water was effected.

Experimental.

A round-bottomed flask of 100 cc. capacity, containing the contact substance and amide, and provided with a ground-glass stopper with the outlet tube about 25 cm. above the bottom of the glass, was heated in an asbestos air bath. The heating was in each case regulated so that the

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[1] *Ann.*, 3, 249 (1832).

[2] Ipatiew, *Ber.*, 34, 596, 3579 (1901); *Ibid.*, 35, 1047, 1057 (1902); *Ibid.*, 36, 1990 (1903); Sabatier and Mailhe, *Compt. rend.*, 146, 1376 (1908); *Ibid.*, 147, 106 (1908); *Ibid.*, 148, 1734 (1909).

cyanide and water formed would distil off but so that at the same time the amide would condense and return to the flask before the outlet was reached. The temperature, measured by a thermometer placed in the bath and outside the flask, naturally varied with the amide used and was probably not accurately observed. It was generally at 250° to 260°. The operation required about four hours for completion. The escaping water and cyanide vapors were condensed in an ordinary condenser and caught in a receiver cooled and closed as completely as possible in order to avoid loss by evaporation. The amount of cyanide obtained was determined according to the method of Gatterman,[1] a method which is not quantitative but gives low values.

The relative proportions in which to use the amides and contact substance were determined by repeated trials with acetamide and aluminium oxide. The best results were obtained using 50 g. of the oxide to 10 g. of the amide. In all the experiments thereafter 10 g. of any amide were employed and a volume of the finely ground contact substance equal to the volume of 50 g. of aluminium oxide.

In all the experiments the odor of ammonia was noticeable and there was a slight blackening of the contact material due to some slight carbonization.

In the case of formamide it was found that the amide distilled off practically unchanged. The procedure was therefore modified by heating the contact substance alone to 250° to 300° and then allowing the amide very slowly to drop upon the hot material in the flask. The hydrocyanic acid formed was passed into a solution of caustic potash and the amount of potassium cyanide formed was then determined by precipitation with standard silver nitrate solution and titration of the excess silver by Volhard's process.

Because of the high boiling point of phenylacetamide and its ready sublimation this method was found unsatisfactory, the greater part subliming over before decomposing into the cyanide and water.

	Aluminium oxide.		Pumice stone.		Glass.		Sand.		Graphite.	
Substance.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.
Formamide	0.47	7.8	...	..	...	..	...	..	...	..
Acetamide	4.7	68.0	4.5	65.0	4.5	65.0	3.6	52.0	4.6	66.0
Propamide	4.2	56.0	4.6	61.0	5.5	73.0	...	..	4.7	62.0
Normal-butyramide	4.6	58.0	...	..	4.0	51.0	4.6	58.0	4.9	62.0
Iso-butyramide	5.3	67.0	...	..	4.9	62.0	...	..	5.7	72.0
Normal-valeramide	5.2	63.0	...	..	...	..	...	..	6.0	73.0
Iso-valeramide	4.7	57.0	...	..	6.1	74.0	...	..	5.8	71.0
Caproamide	6.1	72.0	...	..	...	..	...	..	6.1	72.0
Benzamide	4.6	54.0	4.7	55.0	5.5	64.0	...	..	5.8	68.0
Phenylacetamide	..	..	...	..	...	..	...	..	2.0	..

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[1] "Practical Methods of Organic Chemistry," Third Edition, p. 155.

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.

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THE PYROGENETIC DECOMPOSITION OF AMIDES. II.

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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).