An excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Since secondary alcohols of the type studied are easily prepared it is believed that the process will be of importance in synthetic organic chemistry.

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[Contribution from the Department of Chemistry, University of Wisconsin.]

# ON THE PREPARATION OF FORMAMIDE.[1]

By Albert Brann.

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In order to carry out a series of experiments on the linear velocity of the crystallization of formamide, it was necessary to use a product that had a definite melting point. Such a product apparently has not heretofore been prepared. Freer and Sherman,[2] who did a great deal of work on the preparation of formamide, determined its freezing point to be —1.0°. Davis and Putnam,[3] in their work on the conductivities of formamide and its solutions, very carefully distilled formamide that gave a minimum conductivity. However, they seem not to have determined the melting point of the formamide used by them, but quoted Walden,[4] who at different times obtained products with melting points varying between 1.5° and 2.1°. English and Turner[5] prepared formamide by fractional distillation that froze between 2.0° and 2.2°, a small sample freezing at the last named temperature. To show that the true melting point of formamide has been found, that it is a very definite thing, and to emphasize a few details regarding the preparation of formamide, are the objects of this paper.

Hoffman[6] discovered the fact that formamide is formed when ammonium formate is decomposed by heat. Freer and Sherman,[2] utilizing this reaction, worked out a very favorable method for its formation. However, the product with a freezing point of —1.0° produced by them was far from pure, probably due to the fact that they failed to distill off all the products of decomposition.

For the sake of clearness, the detailed operations in the preparation of formamide are given here. The operations are not new, but have been carried out and studied to a finality not hitherto accomplished.

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[1] A portion of a thesis to be submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] *Am. Chem. J.*, **20**, 223 (1898).

[3] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* **230**.

[4] *Z. phys. Chem.*, **46**, 145 (1903); *Ibid.*, **55**, 230 (1906); *Ibid.*, **75**, 575 (1910).

[5] *Trans. Chem. Soc. J.*, **105**, 1656 (1914).

[6] *Ber.*, **15**, 980 (1882).

A dry 3-liter round-bottomed flask was half filled with pure formic acid. The flask was connected directly to a Liebig's condenser which emptied into a filter flask, which, in turn, was attached to a tube through which excess ammonia vapors escaped. Dry ammonia gas was led into the formic acid through a glass tube reaching to the bottom of the flask, the gas first passing through two separate towers of stick caustic soda and soda lime. Considerable heat is evolved during the reaction. It is desirable to keep the contents of the flask at as low a temperature as possible, otherwise formic acid distills over, which combines with the ammonia in the condenser tube, forming crystals of ammonium formate. The flask was therefore immersed in cold running water. Fifteen to twenty minutes was sufficient time in which to neutralize all the formic acid. An inside coating, consisting of crystals of ammonium formate, collected on the cool parts of the flask while the rest of the salt remained melted. A bath of melted paraffin was now substituted for the water bath, and the ammonium formate gradually heated. The flow of ammonia gas was not interrupted during the whole process, except the rate of flow was somewhat diminished after the neutralization of the acid. At about 150° water of decomposition began to distill. The temperature was increased gradually to 180° at which temperature no more water distilled over. This operation usually took from 4 to 5 hours when starting with 1.5 liters of formic acid, but it is necessary to distill off all the water. It is desirable to do this at as low a temperature as possible in order to give the minimum decomposition of formamide. The resulting liquid should be brown in color. If the heating is continued too long or the temperature becomes too high, the liquid will be very dark brown or even black in color, a disadvantageous condition. The liquid was allowed to cool in the stream of ammonia gas.

This liquid was distilled under diminished pressure. The apparatus used was similar to that described so completely by Davis and Putnam.[1] The different distillates were colorless and had freezing points ranging from —2.0° to 0°. The combined distillates which froze at —1.1°, were allowed to stand over anhydrous sodium sulfate for 3 months. This was done because it was believed that the varying freezing points were due to the presence of water. This was probably not the case, however, but the impurities responsible for the variation, in all likelihood, were decomposition products; for at the end of the 3 months the formamide was again distilled under diminished pressure, and it was found that the freezing point of the resulting product had not materially changed. It was noticed, however, that during the first part of the distillation a few crystals of ammonium formate collected in the condenser tube. Accordingly, the middle portion of the first distillate was redistilled, whereupon the second product

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[1] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* 230.

of distillation gave a freezing point considerably higher than that of the first. Repeated fractional distillations brought up the freezing point higher and higher, till the fifth and sixth distillates gave identical freezing points, *i. e.*, 2.25°. New portions of the original formamide which had stood over sodium sulfate were fractionally distilled in the same manner and the same final highest freezing point, 2.25°, was reached. From these results it was concluded that the important thing to do in order to obtain a pure product is to get rid of the volatile decomposition products, particularly the products of hydrolysis, by fractional distillation.

TABLE I.—TYPICAL RISE IN FREEZING POINT THROUGH FRACTIONAL DISTILLATION.

| Fractional distillate. | Temperature of freezing point. ° C. |
|---|---|
| Original | —1.1 |
| 1 | —0.2 |
| 2 | +0.75 |
| 3 | +1.45 |
| 4 | +2.0 |
| 5 | +2.25 |
| 6 | +2.25 |

It should be stated regarding the yield of formamide that with so many distillations necessary to obtain a pure product, considerable loss in material was occasioned. The combined products from the first distillation of the brown liquid having a freezing point of —1.1° was 82% of the theoretical yield. By fractional distillation the final product freezing at 2.25° was 55% of the material freezing at —1.1°. The first and last portions of each distillate were combined and redistilled as before and an additional 25% of the material freezing at —1.1° was obtained pure. As a final pure product then approximately 66% of the theoretical yield was obtained.

The pure product is viscous, sticky to the touch, and neutral to litmus. A small sample of it was sealed off in a glass bottle, and has stood in a cupboard exposed to daylight and ordinary room temperatures for seven months. So far no discoloration or apparent change has taken place.

Formamide is hygroscopic, and workers with it have laid great stress upon this fact, being careful not to expose it to the air any more than necessary while using it. That the amount of error due to the taking up of moisture by short periods of exposure to the air is very slight, if any error is occasioned at all, is shown by the following facts: A given sample of formamide was exposed to the air by being poured from one flask to another during the distillation process 6 times. It was again exposed to the air in making up solutions; again in filling tubes from the flask containing the solutions; and again in transferring the used solutions to the distilling flask. On distilling off the formamide from such solutions, the first product of distillation gave the highest freezing point, 2.25°, showing that the exposures to the air had not interfered with the purity of the solvent. These facts do not belittle the care which should be taken to keep away moisture, for slow hydrolysis takes place when formamide is exposed to water, the products of hydrolysis being ammonia and formic acid, substances which do materially lower the freezing point, as pointed out by Freer and Sherman.[1]

## Summary.

The important facts upon which this paper wishes to lay emphasis are the following:

1. The freezing point of formamide has been found to be 2.25°, which is the highest freezing point so far obtained for it, and which is probably the true freezing point of the pure substance.
2. Formamide can be obtained pure and is best freed from its products of decomposition and hydrolysis by fractional distillation.
3. Although formamide is hygroscopic in nature, when reasonable care is exercized regarding its exposure to the air, moisture is not taken up in quantities great enough to interfere with its purity as determined by its freezing point.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE LABORATORIES OF THE OFFICE OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

# THE ACTION OF NEUTRAL SALTS ON HUMUS AND OTHER EXPERIMENTS ON SOIL ACIDITY.

BY LOUIS J. GILLESPIE AND LOUIS E. WISE.

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## Introduction.

The action of neutral salts on soils is an interesting one, and has been the subject of numerous investigations, the aim of which in many cases was to measure the quantity of acid substance in soils and to determine the nature of soil acidity. There are undoubtedly many soils of so-called acid character, from which very little acid can be extracted with water, in many cases so little that the water extracts are not observed to turn litmus paper. The acidic nature is manifested, however, in other ways. The soil may (1) affect vegetation in certain characteristic ways, (2) give a water extract which does not react alkaline to phenolphthalein when the carbon dioxide is removed by boiling, even after small quantities of lime have been added to the soil, (3) act on neutral salts with the development of appreciable quantities of acid, and (4) act readily on litmus paper if the paper is brought into intimate contact with the moist soil. These manifestations are not always perfectly correlated, but whenever evident, they may be caused to disappear by adding sufficient lime or other basic material.

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[1] *Am. Chem. J.*, 20, 223 (1898).