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

# LABORATORY PREPARATION OF ACETALDEHYDE.[1]

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None of the laboratory methods for the preparation of acetaldehyde by the oxidation of alcohol is highly satisfactory, as the yields are low and uncertain. Gattermann's method[2] is recommended by Beilstein but the yield of aldehyde-ammonia at best is only about 23% of the calculated. In ordinary practice the yields are considerably lower than this. Noyes[3] predicts a yield of about 15% for the method outlined.

Preliminary work proved the unsatisfactoriness of the methods. If the oxidizing mixture used oxidizes the aldehyde more readily than alcohol (found by experiment to be true) then the production of aldehyde even in small amounts must be due to its low boiling point and its ability to escape from the mixture before oxidation takes place.

With this idea as a working basis several methods were used to increase the volatilization of the aldehyde, and the use of a mechanical stirrer was the only method found practicable. By this means yields were obtained more than double any obtained previously. That the stirring was responsible for the increase was proved by using the same procedure and apparatus except that the stirring was omitted, in which case the yield was very low.

Working with essentially the same apparatus and method, different concentrations of oxidizing agent were then tried to determine whether under these conditions better results could be obtained with some other concentration than that recommended by Gattermann.

The figures show that the amount of sodium dichromate recommended by Gattermann (200 g. per 100 g. of alcohol) could not be materially im-

TABLE I.

EXPERIMENTAL RESULTS.

| | Alcohol used (95%). G. | Sodium dichromate used per 100 g. alcohol. G. | Additional dichromate on reaction flask at the start. G. | Aldehyde ammonia obtained. G. | Yield. % |
|---|---|---|---|---|---|
| 1 | 50 | 200 | 0 | 27 | 43 |
| 2 | 37 | 200 | 0 | 21 | 45 |
| 3 | 45 | 190 | 0 | 23 | 40 |
| 4 | 47 | 190 | 0 | 25 | 42 |
| 5 | 33 | 170 | 0 | 17 | 41 |
| 6 | 58 | 170 | 0 | 30 | 41 |
| 7 | 37 | 200 | 25 | 14 | 30 |
| 8 | 38 | 200 | 100 | 9 | 19 |

[1] The material of this paper was submitted by Chester E. Adams in partial fulfilment of the requirements for the degree of Master of Science at the University of Oregon.

[2] Gattermann, "Practical Methods of Organic Chemistry," 1915, p. 167.

[3] Noyes, "Organic Chemistry for the Laboratory," 1911, p. 89.

proved upon. Not only are the yields much better than those obtainable formerly, but practically the same results can be obtained repeatedly by using the method. The amounts of alcohol varied in the different experiments because it was forced into the reaction flask by air pressure through a capillary tube and the amount used was determined by difference. The capillary tube was found a convenient means of introducing the alcohol in a steady stream, but a dropping funnel can be used successfully. The method which proved most successful is outlined below.

## Method.

A 1-liter flask is fitted with a 3-holed stopper carrying a reflux condenser tube of good length and placed at an angle for refluxing, a dropping funnel (or capillary tube through which liquid can be forced), and an electrically-driven stirrer provided with a mercury seal. The mercury seal is used to prevent loss of aldehyde through the opening, and in our experiments was of the same type as the water seal recommended by Fischer for a similar purpose.[4] Through the condenser is passed a current of water at about 25°. The upper end of the condenser is fitted with a delivery tube of good size dipping into a small wide-mouthed flask containing about 80 cc. of well-dried ether. This flask is in turn connected with a second similar flask containing about 30 cc. of ether to absorb any aldehyde passing over. One hundred and ten g. of conc. sulfuric acid in 200 cc. of water is put into the flask and the stirrer adjusted. The solution is then heated to about the boiling point. A mixture of 50 g. of alcohol (95%) 100 g. of sodium dichromate and 100 cc. of water is then introduced slowly through the capillary or the dropping funnel, with mechanical stirring. With a small flame under the flask the alcohol is admitted as fast as allowed by complete absorption in the ether and sufficient cooling in the condenser. When the alcohol is all admitted the reaction mixture is stirred for a few minutes as long as aldehyde appears to come over. The ether solution is then saturated with dry ammonia in the usual way and allowed to stand overnight when the crystals of aldehyde-ammonia are filtered off, pressed dry, freed from remaining ether and weighed. For the preparation of purer aldehyde-ammonia probably a preliminary distillation such as recommended by Gattermann should be made before the aldehyde is collected in the ether.

## Summary.

A study of the oxidation of alcohol to aldehyde by sodium dichromate showed that the introduction of a mechanical stirrer to disengage the aldehyde as fast as it is formed, increases the yield of aldehyde-ammonia at least 100% and gives consistent results. The method used is outlined.

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[4] Fischer, "Preparation of Organic Compounds," 1917, p. 41.