CXXIII.—*The Determination of Carbonyl in Aldehydes and Ketones.*

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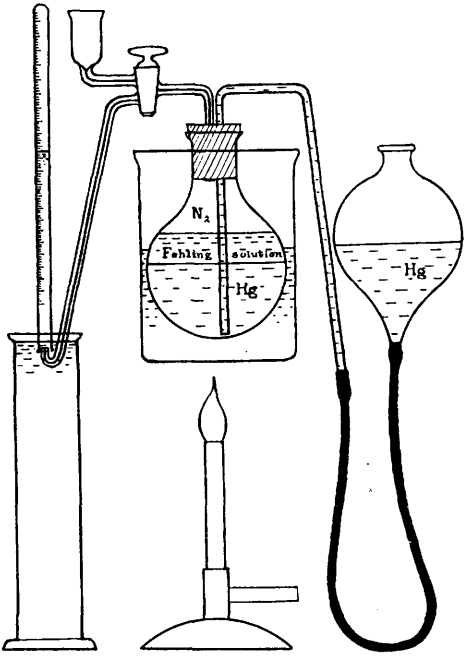
THE present method is a modification of one described by Strache (*Monatsh.*, 1891, **12**, 514; 1892, **13**, 299). It depends essentially upon the formation of phenylhydrazones and estimation of the excess of phenylhydrazine by measuring the nitrogen evolved by the action of Fehling's solution ($C_6H_5 \cdot NH \cdot NH_2 + O = C_6H_6 + N_2 + H_2O$), a control being carried out upon phenylhydrazine alone. Since the hydrazones do not evolve nitrogen, and since few compounds are likely to interfere with the reaction, the method is of wider application than any other that has been proposed.

Strache used steam to drive out the air from his apparatus and, subsequently, to transfer the evolved nitrogen to the eudiometer, where it was measured saturated with water and benzene vapour. Watson Smith (*Chem. News*, 1906, **93**, 83) substituted carbon dioxide for steam and protected the Fehling's solution by means of a layer of paraffin. Also, to avoid the correction for benzene vapour, the small quantity evolved was nitrated and so absorbed. His apparatus was therefore more elaborate than that of Strache. Both workers recorded satisfactory results, but in the author's experience, both methods are unnecessarily tedious and often untrustworthy. Watson Smith appears to have attributed this to Strache's use of steam, which may cause an evolution of air from the generator or from the water under the eudiometer; but carbon dioxide is required in such quantities as to heat the alkaline solution under the eudio-

meter and thus cause a similar error. Since, however, nitrogen is soluble in water at 100° to the extent of nearly 1% by vol. (Winkler), it will be appreciated that the delay in the cessation of the appearance of nitrogen in the eudiometer is almost entirely due to the solubility of this gas in the solutions employed in the reaction mixture. Strache recommended the use of 200 c.c. of Fehling's solution and about 50 c.c. of the phenylhydrazine solution. Further, the experiments were adjusted so as to yield about 20 c.c. of gas both in the actual estimation and in the control. Hence about 15% of the nitrogen may be retained in solution. This is slowly evolved by the passage of steam through the solutions in Strache's method, but it must be indefinitely retained in the paraffin-protected solutions employed by Watson Smith.

FIG. 1.



The method now described almost entirely obviates the above disadvantages, and utilises the well-known fact that dissolved gases can only be rapidly removed from their solutions by vigorous ebullition under reduced pressure. Further, it is not necessary to arrange for the production of the same volume of nitrogen in the two measurements of each estimation, and thus another possible source of error, due to manipulation of aliquot parts, is avoided.

EXPERIMENTAL.

At the bottom of a strong, short-necked, round-bottomed flask of about 300 c.c. capacity (Fig. 1) are placed about 250 c.c. of mercury, connected with a smaller quantity in a reservoir by means of a glass tube of about 3 mm. bore and rubber tubing. Above the mercury in the flask are placed about 50 c.c. of Fehling's solution. The two-way stopcock connects the upper part of the flask either with a cup of 5—10 c.c. capacity or with the eudiometer, both connexions being

of capillary tubing. The flask is almost completely surrounded by a beaker, but only a little boiling water is contained in the latter.

The Fehling's solution must first be freed from dissolved gases. The water in the beaker is kept rapidly boiling, the stopcock is closed, and the mercury reservoir is lowered as far as possible so as to reduce the pressure in the flask. When most of the mercury in the flask has been forced into the reservoir by the vapour formed, the rubber tubing is pinched by a clip and a fine jet of cold water is directed upon the upper surface of the flask. The reduced pressure in the flask causes a vigorous ebullition, and by maintaining as great a difference of temperature as possible between the upper and lower parts of the flask, the greater part of the dissolved gases is removed from solution. After about 5 minutes' constant attention to these conditions, the reservoir is raised, the clip is removed, and the gases are forced out of the apparatus. The process is repeated until only a small break, or a slight froth, passes through the capillary tubing. This operation takes about 15 minutes if only 50 c.c. of Fehling's solution are used. A similar treatment is applied at the end of the actual estimations of nitrogen.

A pipette of about 2 c.c. capacity was constructed from tubing of 5—6 mm. bore by drawing it to a fine orifice at one end and melting to a fine, short constriction in the middle. When this pipette is filled with fluid just above the constriction and held with the outlet touching the wall of a container, the liquid automatically stops at the constriction. The quantity so retained, after being blown and washed out, varies to only a fraction of a mg.

About 0·43 g. of phenylhydrazine hydrochloride, with a similar quantity of anhydrous sodium acetate, was dissolved in 3 measures of water from the pipette, and the solution filtered. Of this, 2 measures were conveyed to separate tubes, the third being employed for rinsing the pipette. In one tube, having a thickened bottom, was broken a small bulb containing 0·0619 g. of salicylaldehyde. Both tubes were placed in a water-bath for a few minutes.

The contents of the tube which held the reagent only were placed in the cup of the apparatus and drawn into the flask by careful lowering of the reservoir. The tube and cup were washed several times, and the washings drawn in, the whole of the phenylhydrazine being thus brought to the top of the Fehling's solution. The reservoir was then lowered until vapour formed at the top of the flask, thereby causing a mixing of the reagents and an evolution of nitrogen and benzene vapour. It may be noted here that an alcoholic solution of the hydrazine base may be employed and that some care must be exercised at this stage, for an injudicious lowering of the reservoir may produce so much vapour as to force the Fehling's

solution out of the flask. In the actual experiment described, the greater part of the mercury was allowed to pass into the reservoir, and the water in the beaker was kept boiling for 3 or 4 minutes, after which most of the nitrogen was transferred to the eudiometer. The remainder of the nitrogen, which was chiefly in solution in the reaction mixture, was removed as described above for the preliminary operation; 20·0 c.c. at 16° and 773·7 mm. were obtained, measured saturated with aqueous and benzene vapours as recommended by Strache.

The excess of phenylhydrazine remaining in the other tube was then estimated. It was necessary to filter off the hydrazone so as to prevent clogging of the capillary; this was effected by means of a small drawn-out tube, plugged with cotton wool and leading into another tube placed in a vacuum filtering-flask. It was thus possible to filter and wash the hydrazone so that the total bulk of liquid was no more than that used in the first estimation. The excess of the reagent, under exactly the same conditions, yielded 9·3 c.c. (Found: CO, 22·2. Calc.: CO, 22·9%).

The results of various estimations by the new method are given below. For those in which more than 0·1 g. of material was taken, 200 c.c. of Fehling's solution were employed, as used by Strache; but the author's method of using smaller quantities was found to be more rapid and even more accurate. The substances taken were carefully purified for the purpose, but their degree of purity was not ascertained.

Results.—Salicylaldehyde; found: CO, 22·2, 24·8, 23·2; calc., 22·9%. Acetone; found: CO, 47·3; calc., 48·2%. Phenylhydrazine; found, 102, 100·1%. Phenylhydrazine hydrochloride; found, 99, 102%.

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