Summary and Conclusions

It has been shown that chlorides may be determined calorimetrically with a fair degree of accuracy when other ions capable of being precipitated by silver nitrate are absent. In cases where mixed halides, or halides and cyanide, are present in the solution, the total amount of standard solution used is indicated by a break in the curve. Breaks indicating the fractional precipitation of the insoluble salts do not appear. The method cannot be applied to the analysis of organic compounds by the decomposition in liquid ammonia when cyanides are likely to be formed, as with chloroform, carbon tetrachloride, etc.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND OF NORTHWESTERN UNIVERSITY]

THE PREPARATION OF FREE HYDROXYLAMINE

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Until recently, the best way to isolate free hydroxylamine was by fractional vacuum distillation of a solution of hydroxylamine in methanol. Two years ago, Lecher and Hofmann[1] showed that hydroxylamine could be made to crystallize from absolute ethyl alcohol in a yield of 40%. This is comparable to the yield obtained by the older method. The great advantage of the crystallization method, however, is that there is no loss of hydroxylamine. The material which remains in solution after the recrystallization is easily recoverable. A few methods of recovery are listed in the work which follows.

It seemed reasonable that with the selection of a better solvent, the yield of free hydroxylamine might be increased. Lobry de Bruyn[2] showed that the solubility of hydroxylamine was much less in methanol than in water, less in ethanol than in methanol, and that it was insoluble in hydrocarbons. It was inferred that the longer the hydrocarbon chain of an alcohol, the lower would be the solubility of the hydroxylamine. Butyl alcohol, because of its longer hydrocarbon chain and because of its commercial availability, was a logical choice.

It was found that with butyl alcohol, a consistent yield of 50% of free hydroxylamine was attainable. In addition, several time-saving factors were introduced. Contrasted with the high purity required for ethyl alcohol, commercial butyl alcohol need be purified only by distillation; the fraction boiling at 115.5–117.5°, was used. Instead of cooling the

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[1] Lecher and Hofmann, *Ber.*, **55B**, 912 (1922). See also, Houben, *J. prakt. Chem.*, [2] **105**, 20 (1922).

[2] De Bruyn, *Rec. trav. chim.*, **11**, 18 (1892).

solution to —18° or lower during the crystallization, it sufficed to lower the temperature to —10°. The increased yield by further cooling (with butyl alcohol) was negligible. Furthermore, as will be apparent in that which follows, the apparatus was considerably simplified. One advantage of the apparatus which is not immediately obvious is that less solvent is required for the preliminary stirring, due to the fact that a round-bottomed flask has replaced a flat-bottomed beaker.

Experimental Part

Preparation of Sodium Butylate.—About 12 to 12.5 g. of sodium was added at once to 150 cc. of butyl alcohol, contained in a 500cc. flask, to which was attached a reflux condenser. A soda-lime drying tube, hanging downwards and attached to the upper end of the condenser by a ∩-tube, served as a hydrogen trap. The contents of the flask were kept in gentle ebullition until solution of the sodium was complete. This step took about two and a half to three hours. It was usually necessary to add 10 to 20 cc. more of alcohol towards the close of the process.

Apparatus and Method.—The reaction vessel consisted of a round-bottomed 1-liter flask equipped with three vertical outlets, each closed with a one-holed cork stopper.[3] Through the center opening was inserted an efficient stirrer. Through a side opening passed the tube from a dropping funnel containing the sodium butylate, bent so as to deliver the solution to that part of the flask which was stirred most efficiently. The stopper in the third hole carried a tube with a capillary outlet.

Hydroxylamine.—A mixture of 0.1 g. of phenolphthalein, 34.8 g. of powdered, dry hydroxylamine hydrochloride and 30 cc. of butyl alcohol was placed in the flask, warmed gently and stirred for ten minutes. Then, to prevent solidification of sodium butylate in the stopcock, 2 cc. of butyl alcohol was poured into the dropping funnel and some of this was allowed to pass into the tube beneath it. The warm sodium butylate solution was transferred rapidly into the funnel. During this process, the air imparted a brown coloration to the solution, but this did not interfere with the reaction. The solution was added as rapidly as the phenolphthalein permitted; usually one to one and a half hours was required. If necessary, the delivery tube was warmed occasionally to prevent solidification within it.

The sodium chloride was filtered off, pressed well and washed first with 8 cc. of butyl alcohol and then with three 8cc. portions of ether. The total filtrate was placed in an ice-salt freezing mixture until the temperature of the former was —10°. Hydroxylamine began to crystallize in large white flakes at 0°. These crystals were then collected quickly upon a filter, washed with ether and placed in a desiccator for 15 minutes to remove the adhering solvent; yield, 8 to 9 g. The crystals were kept in a stoppered tube in an ice chest.

If larger proportionate amounts than the above are desired, time will be

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[3] A one-holed flask with three holes in the stopper might also be used.

saved by dissolving the sodium simultaneously in several flasks, so that in no one flask will there be a larger mass of sodium than is indicated above.

Utilization of the Hydroxylamine Remaining in the Filtrate

1. **Conversion to Hydroxylamine Hydrochloride.**—Between 8 and 9 g. of hydroxylamine was present in the solution. The calculated amount of concd. hydrochloric acid was added. The resulting precipitate was collected upon a filter; yield, 15 g. The filtrate consisted chiefly of butyl alcohol. Treatment with lime and distillation were the only two steps necessary for its recovery.

2. **Conversion to Benzohydroxamic Acid.**—About 35 cc. of ethyl benzoate was added to the solution of hydroxylamine in butyl alcohol. There was no reaction until one equivalent of sodium ethylate was added. Immediately the solution turned pink due to the presence of phenolphthalein, and there followed the precipitation of the sodium salt of benzohydroxamic acid. This was removed by filtration and was washed with a little alcohol. It was then transferred to a beaker. After drying somewhat, the salt was dissolved in the least possible quantity of water. Gradual addition of concd. hydrochloric acid until the pink color was discharged caused the precipitation of benzohydroxamic acid. The small amount which remained in aqueous solution was precipitated as the copper salt, with cupric acetate solution; yield, 22 g.

3. **Conversion to Phenyl-acethydroxamic Acid.**—This conversion is similar to the former, save that the sodium salt did not precipitate when the sodium ethylate was added. Therefore, after some hours, one equivalent of concd. hydrochloric acid was added and the solution freed from sodium chloride by filtration. The solvent was removed by vacuum distillation until crystals of the hydroxamic acid appeared, at which time the solution was cooled in ice and filtered. Further concentration of the filtrate gave an additional quantity of crystals; yield, 23 g.

Summary

Directions are given for the preparation of free hydroxylamine. The principle of the method is to obtain the hydroxylamine in solution in butyl alcohol, from which 50% of it crystallizes at low temperatures.

Methods are suggested by which the unprecipitated hydroxylamine may be recovered.

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