CLXVIII.—*Hydrates of Some Quaternary Bases.*

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WALKER AND JOHNSTON (Trans., 1905, **87**, 955) have described a method for preparing tetramethylammonium hydroxide by the interaction of potassium hydroxide and tetramethylammonium chloride in a alcoholic solution, and have shown how definite hydrates of the quaternary base may be separated from the solution obtained. At Prof. Walker's suggestion I have prepared by the same method solutions of tetraethylammonium and tetrapropylammonium hydroxides and of trimethylsulphine hydroxide, and in this paper hydrates of the first two bases are described.

Tetraethylammonium Hydroxide.

The preparation of this base was conducted as follows: 11.5 grams of potassium hydroxide, dissolved in eight times its weight of methyl alcohol, were mixed with 33.9 grams, the equivalent quantity, of tetraethylammonium chloride dissolved in its own weight of methyl alcohol. A bulky precipitate of potassium chloride at once separated and was removed after an hour's interval by filtration through an asbestos filter, the operation being carried out as rapidly as possible by the aid of the pump in an atmosphere free from carbon dioxide. The filtrate was transferred to a large distilling flask and to it were added 100 c.c. of water. The methyl alcohol and a portion of the water were then removed under diminished pressure at a temperature not exceeding 50°. When the distillation had continued for three hours, the liquid, which then contained 44 per cent. of anhydrous base, was placed in a vacuum desiccator charged with phosphorus pentoxide. In the course of a few days, the liquid partly set to a mass of fine needles, which were separated by filtration on an asbestos filter, and preserved in a closed glass-box in a desiccator. A second quantity of the hydrate was prepared in a similar way, 47.5 grams of crystalline base in all being obtained from 70 grams of the chloride.

The crystals were proved to be free from potassium and from chlorine, and titration showed them to contain four molecules of water of crystallisation.

I.	0.2442	required 44.1 c.c. of $N/40$ HCl.	Equiv. = 221.
II.	0.1563	„ 27.3 „ „ „	229.
III.	0.1050	„ 19.4 „ „ „	221.

$N(C_2H_5)_4OH, 4H_2O$ has the equivalent 219.

Analysis of the crystals dried in a vacuum resulted as follows:

I.	0.1472	gave 7.76 c.c. of nitrogen at N.T.P.	N = 6.60.
II.	0.2014	„ 10.84 „ „ „	N = 6.73.
III.	0.3957	„ 0.5823 CO_2 and 0.4343 H_2O .	C = 44.14; H = 13.41.
IV.	0.1612	„ 0.2612 CO_2 „ 0.1915 H_2O .	C = 44.19; H = 13.20.

$N(C_2H_5)_4OH, 4H_2O$ requires C = 43.84; H = 13.25; N = 6.39 per cent.

A *tetrahydrate* of tetraethylammonium hydroxide thus separates from aqueous solution instead of a pentahydrate as is the case with tetramethylammonium hydroxide under the same conditions.

Tubes containing small weighed quantities of the tetrahydrate were preserved over phosphorus pentoxide at various temperatures and pressures in order to ascertain if it were possible to dehydrate the hydrate wholly or partly. At the ordinary temperature and pressure, the loss of weight is very slow, but in an evacuated space decomposition proceeds with considerable rapidity. Thus 0.2276 gram at 25°

in a vacuum desiccator was found to have lost 0.046 gram in three days. The loss, however, was not due to dehydration alone, for the residual solid on titration was found to possess the equivalent 217, that is, practically the equivalent of the tetrahydrate. Another portion, weighing 0.1169 gram, lost 0.0224 gram in two days at 15° in a tube evacuated by means of a mercury pump. The residue on titration showed the equivalent weight of 220. It is apparent from these experiments that the tetrahydrate when it loses water also decomposes even at the ordinary temperature, as the hydroxide is not in itself volatile. As the decomposition observed by Hofmann at 100° was in the sense of the equation (*Annalen*, 1851, **78**, 268):

the gaseous contents of one of the tubes (originally evacuated by means of a Krafft mercury pump) were collected by the aid of a Sprengel pump, and were found on analysis to consist of practically pure ethylene. It is thus impossible directly to dehydrate the tetrahydrate of tetraethylammonium hydroxide at or above the ordinary temperature without the base itself undergoing decomposition. This behaviour is in sharp contrast to that of tetramethylammonium hydroxide, which can be dehydrated to the stage of monohydrate before decomposition sets in (Walker and Johnston, *loc. cit.*, p. 960).

The crystals of tetrahydrate are extremely soluble in water, dissolving with considerable absorption of heat. They melt at 49–50° without perceptible decomposition.

The comparative strength of the base as against sodium hydroxide was determined in *N*/100 solution by the rate of saponification of ethyl acetate, using Walker's conductivity method (*Proc. Roy. Soc.*, 1906, **78**, 4, 152). It was found that if the strength of sodium hydroxide in centinormal solution is represented by 100, that of tetraethylammonium hydroxide in equivalent solution is represented by 95.

Hexahydrate.—The filtrate from the original preparation of tetrahydrate was found, when it had stood for some days in a desiccator, to have deposited a further quantity of crystals, larger in size than those of the original crop. These were dried on porous porcelain and titrated with the following result:

0.0933 required 14.35 c.c. *N*/40 HCl. Equiv. = 260.

0.1873 " 29.4 " " 255.

$\text{N}(\text{C}_2\text{H}_5)_4\text{OH} \cdot 6\text{H}_2\text{O}$ has the equivalent 255.

The composition is that of a hexahydrate. When heated, the hexahydrate melts at 50°. A portion which had been melted and allowed to resolidify gave the following result on titration:

0.2217 required 35.0 c.c. *N*/40 HCl. Equiv. = 255.

The hexahydrate can thus be melted without fundamental change. At 55° , however, the liquid obtained by fusion of the hydrate begins to decompose, the odour of triethylamine being distinctly perceptible. When the liquid which has been heated for some time at 55° is cooled, the solid obtained has the composition of the tetrahydrate. The tetrahydrate may also be formed from the hexahydrate by dehydration in a vacuum over phosphorus pentoxide. Thus 0.1090 gram of hexahydrate lost 0.0154 gram in two days, and the equivalent of the residue was found to be 220, the equivalent of the tetrahydrate being 219. That the hexahydrate is converted at 55° into a lower hydrate is made evident by the progressive lowering of the melting point of the solid which results on cooling. Thus a specimen which originally melted at 49.5° was found after being heated for five minutes to melt at 47° , and after thirty minutes' heating to melt at 43° .

The hexahydrate, like the tetrahydrate, dissolves in water with notable absorption of heat.

Tetrapropylammonium Hydroxide.

Tetrapropylammonium chloride was dissolved in methyl alcohol and mixed with the equivalent quantity of potassium hydroxide dissolved in the same solvent. An abundant precipitate of potassium chloride at once separated. The subsequent treatment was identical with that described under the preparation of tetraethylammonium hydroxide. The aqueous solution finally obtained did not crystallise after standing for a week in a vacuum desiccator over phosphorus pentoxide, and even on prolonged exposure to a temperature of -20° showed no sign of solidification. A portion of this liquid, which had approximately the composition of a heptahydrate, was sealed in an evacuated tube with phosphorus pentoxide, and gently warmed for some time. On cooling in a freezing mixture, the liquid now partly crystallised, but the crystals disappeared when the temperature rose to that of the room. However, by rapid filtration through an asbestos filter surrounded by a good freezing mixture, it was found possible to separate the crystals from the mother-liquor. The crystals melted at the room temperature, and the liquid formed by their fusion was found to contain 2 per cent. of potassium chloride. Making allowance for this impurity, it was ascertained that 0.315 gram of the hydroxide required 38.5 c.c. of $N/40$ HCl for neutralisation, corresponding to an equivalent of 327. The heptahydrate of tetrapropylammonium hydroxide has the equivalent 329, so that in all probability the crystals consisted of the heptahydrate. The liquid from which the crystals separated had

practically the same composition. Attempts to prepare a lower hydrate by dehydration were unsuccessful.

Trimethylsulphine Hydroxide.

An aqueous solution of trimethylsulphine hydroxide was prepared from trimethylsulphine chloride and potassium hydroxide according to the method already described, except that the temperature at which the distillation was conducted did not exceed 40°. The solution obtained, which had approximately the composition of an octahydrate, could not be made to crystallise in a freezing mixture, and even after slight warming in a vacuum tube over phosphorus pentoxide showed no signs of crystallisation at -20° , although it then had a composition intermediate between that of a pentahydrate and a tetrahydrate. Further attempts at dehydration and crystallisation were unsuccessful, owing to the ease with which the base decomposed.

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