

C.—*Tetramethylammonium Hydroxide.*

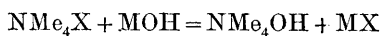
By JAMES WALKER and JOHN JOHNSTON, Carnegie Research Scholar.

It is remarkable that, notwithstanding the interesting properties displayed by the tetralkylammonium hydroxides, the free bases have never been isolated in any definite form, and that nearly all experiments in which they have played a part have been conducted with the crude solutions obtained by the action of moist silver oxide on the

solution of the corresponding iodide. It is, of course, [View Article Online](#) well known that such a solution on evaporation in a vacuum yields a crystalline mass, but no attempt seems to have been made to separate the crystals in a form suitable for analysis. Victor Meyer and Jacobson, in their *Lehrbuch der organischen Chemie*, say on the subject: "Es darf nicht unerwähnt bleiben, dass Analysen der freien Hydroxyde bislang nicht vorliegen, dass demnach die Annahme einer Hydroxylgruppe vorläufig noch eine durch das Verhalten der Basen freilich sehr wahrscheinlich gemachte Hypothese einschliesst." In the present paper, the isolation of several hydrates of tetramethylammonium hydroxide is described, together with a new method for the preparation of this and similar compounds.

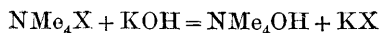
One occasionally finds statements in text-books and in original memoirs drawing attention to the great stability of the salts of tetralkylammonium hydroxides and to the great strength of the bases themselves, and referring the impossibility of separating the hydroxides from their salts by means of caustic alkali to one or other of these causes. That the hydroxides cannot be liberated from their salts in this way has little to do with either the stability of the salts or with the affinity of the bases themselves, but in reality depends on the relative solubility (or volatility) of the reacting substances. It is strange that this erroneous conception should have persisted so long, or even that it should have arisen, for Hofmann is perfectly clear and explicit about the point in his original paper describing the first of these bases (*Annalen*, 1851, **78**, 266).

Practically the preparation of tetramethylammonium hydroxide from its salts resolves itself into a question of solubility as follows. In general, the equation



will represent a real action proceeding nearly to completion if M, X, and the solvent are so chosen that all the substances except MX shall be soluble, or at least that MX shall be much less soluble than either of the original reacting substances. This principle was applied by Hofmann in his preparations with water as solvent. For M and X he chose either the pair Ag, I or Ba, SO₄, in both of which cases MX is practically insoluble in water.

It is clear that if the general application of the above principle is justifiable, tetramethylammonium hydroxide may be prepared from a tetramethylammonium salt by means of potassium hydroxide if we so choose X and the solvent that of the substances represented in the equation



all shall be soluble except KX. The condition is fulfilled if X is Cl

and methyl or ethyl alcohol the solvent, for tetramethylammonium chloride and hydroxide, as well as potassium hydroxide, are all soluble in either solvent, whilst potassium chloride is almost insoluble. [View Article Online](#)

It was found that a cold concentrated solution of tetramethylammonium chloride in methyl alcohol, when mixed with a similar solution of caustic potash in the same solvent, yielded at once a copious precipitate of potassium chloride, the action being accompanied by disengagement of heat. When the precipitate of potassium chloride had been removed by filtration, the solution was found to contain tetramethylammonium hydroxide, with only a trace of chloride or of carbonate when the reacting substances were pure and in equivalent proportions.

The same reaction takes place when ethyl alcohol is used as solvent, and indeed yields a product containing even less chloride, owing to the smaller solubility of potassium chloride in ethyl than in methyl alcohol. This advantage, however, is counterbalanced by the drawback that the alcohol is discoloured by the strongly alkaline solutions, and yields a somewhat coloured hydroxide. It is inadvisable to employ either sodium hydroxide or tetramethylammonium iodide in the reaction, as the sodium salts are more soluble in alcohol than the potassium salts and the alkaline iodides more soluble than the corresponding chlorides.

The isolation of the hydroxide from the alcoholic solution was at first attended with considerable difficulty. When the solution is subjected to distillation under diminished pressure, the alcohol at first evaporates at a low temperature, but as the solution becomes more concentrated, the temperature of the liquid must be raised, until eventually at about 50° the tetramethylammonium hydroxide in the solution begins to decompose into trimethylamine and methyl alcohol. If the operation is stopped at this point, the liquid contains about half its weight of hydroxide, and the syrupy solution on cooling deposits some crystals which, however, are difficult to remove, and are contaminated with chloride. A crop of crystals obtained from such a solution seemed to contain methyl alcohol of crystallisation, the composition being represented approximately by the formula $\text{NMe}_4\text{OH}\cdot 2\text{CH}_3\text{OH}$. It was found that the separation of the tetramethylammonium hydroxide could be most easily effected by the addition of a sufficient quantity of water to permit of the formation of a crystalline hydrate. The mode of operation may be illustrated by the account of a preparation made when the conditions had been determined with some accuracy.

Forty grams of pure dry tetramethylammonium chloride, in a sample of which the chlorine had been accurately estimated by titration, were dissolved in 80 c.c. of absolute methyl alcohol; a filtered solution of

potassium hydroxide in methyl alcohol had previously [View Article Online](#) been prepared, and its concentration determined by the titration of a known weight with acid. Of this solution, 83.8 grams containing 20.4 grams of potassium hydroxide were mixed with the solution of tetramethylammonium chloride. A white precipitate at once separated, and was filtered off after the mixture had remained for 1½ hours at the ordinary temperature. The mixing and filtration were carried out in a case with glass top and back, which contained quicklime and was furnished with holes in movable slides for the reception of the hands. By the use of this case, contamination by carbon dioxide was reduced to a minimum. For the filtration, a Buchner filter with very slight suction was employed, and the precipitate was washed with a few c.c. of methyl alcohol. To the clear filtrate were now added 45 c.c. of water, and the liquid was subjected to distillation under reduced pressure from a water-bath at 35°. After 2 hours, the distillation was interrupted, and a sample of the remaining solution removed for analysis. It was found that 0.53 gram of the solution contained 0.19 gram of tetramethylammonium hydroxide, and that 90 grams of distillate contained 30 grams of water. No odour of trimethylamine was perceptible. To the solution, 35 grams of water were added, and the distillation was continued for 1 hour. The solution, which weighed 77 grams, was now practically free from methyl alcohol, and titration of a weighed sample showed that it contained 30 grams of tetramethylammonium hydroxide, the theoretical yield being 32.4 grams. The solution, which had no odour of trimethylamine, was then transferred to a glass crystallising dish with ground overlapping lid. On cooling, it partially crystallised, and 15 grams of a crystalline hydrate were filtered off. After the filtrate had remained for some days in a desiccator, 15 grams more of the same hydrate were deposited. Both the first and second crops of crystals were free from chloride and from carbonate, and left no residue on ignition. The mother liquor, on continued evaporation, deposited further quantities of crystals, but these were not quite so pure.

The crystalline hydrate yielded the following results on titration and combustion :

0.176 gram contained 0.089 gram of anhydrous $\text{NMe}_4\text{OH} = 50.6$.

0.091 " " 0.046 " " $\text{NMe}_4\text{OH} = 50.5$.

NMe_4OH in $\text{NMe}_4\text{OH}, 5\text{H}_2\text{O} = 50.3$ per cent.

0.3570 gave 24.9 c.c. moist nitrogen at 15° and 748 mm. $\text{N} = 8.0$.

0.1860 " 0.1822 CO_2 and 0.2085 H_2O . $\text{C} = 26.7$; $\text{H} = 12.5$.

$\text{NMe}_4\text{OH}, 5\text{H}_2\text{O}$ requires $\text{C} = 26.5$; $\text{H} = 12.7$; $\text{N} = 7.7$ per cent.

The crystals thus consisted of a pentahydrate of tetramethylammonium hydroxide. When slowly deposited, the pentahydrate forms

long, interlacing needles, which are excessively [View Article Online](#) hygroscopic and extremely avid of carbon dioxide. As far as possible, therefore, all operations involving the transference of it or of any other hydrate were carried out over quicklime inside the above-mentioned case. The pentahydrate fuses at 62—63° without the odour of trimethylamine being perceptible. In a desiccator over quicklime or phosphoric oxide, the pentahydrate slowly loses water at the ordinary temperature and pressure, the change being visible by the efflorescence of the crystals; *in vacuo*, the dehydration is much more rapid. Measurements of the vapour pressure of the pentahydrate in a Frowein differential tensiometer resulted as follows :

Temp.	8°	15°	25°	35°	40°	45°	50°	55°	58°
Mm. bromonaphthalene	2	4	6.5	14	21	32	44	65	85
„ mercury	0.21	0.43	0.7	1.5	2.3	3.5	4.8	7.0	9.2

The pentahydrate is very soluble in water, as the following figures show :

Temp.	Parts of pentahydrate dissolved by 100 parts of water.	Parts of tetramethylammonium hydroxide in 100 parts of solution.
0°	151	30
15	220	34.6
63	∞	50.3

The heat of solution of the pentahydrate in 30 parts of water was found in two experiments to be -2120 and -2170 cal. for the gram-molecule.

When the pentahydrate is dehydrated at temperatures above 40° but below 60°, it partially liquefies after a time, but, as dehydration proceeds, solidification again takes place. In this respect, the dehydration resembles that of the hexahydrate of ferric chloride between 30° and 32°. By careful dehydration at a comparatively low temperature, a trihydrate may be prepared apparently identical with a crystalline hydrate which separated, on cooling, from the mother liquors of a pentahydrate crystallisation which had been concentrated further *in vacuo*. Analysis of the latter preparation yielded the following results :

0.148 required 10.35 c.c. *N*/10 HCl for neutralisation. Anhydrous base = 63.6 ; $\text{NMe}_4\text{OH}, 3\text{H}_2\text{O}$ requires 62.8 per cent.

0.0956 gave 0.1153 CO_2 and 0.1134 H_2O . C = 32.9 ; H = 13.2.

$\text{NMe}_4\text{OH}, 3\text{H}_2\text{O}$ requires C = 33.1 ; H = 13.1 per cent.

The trihydrate melts at 59—60° and has a vapour pressure much lower than that of the pentahydrate, a pressure of 1 mm. of mercury being reached at about 45°.

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Dehydration of the pentahydrate for four days at 55° and under 18 mm. pressure yielded a solid having the composition of the monohydrate, $\text{NMe}_4\text{OH}\cdot\text{H}_2\text{O}$, when determined by titration. This monohydrate lost no water on being heated under the same conditions for five days longer. It decomposed without melting at 130—135° with formation of trimethylamine, and dissolved somewhat slowly in water with evolution of heat. Experiments on dehydration by means of quicklime and phosphoric oxide were conducted in sealed tubes evacuated by means of the mercury pump, but in no case was the anhydrous substance formed. Even if the dehydration were pushed to the point of decomposition, the residue always gave, on titration, numbers which corresponded closely with the formula $\text{NMe}_4\text{OH}\cdot\text{H}_2\text{O}$. Two such tubes, allowed to remain for a year and a half at the ordinary temperature, gave solids which had the composition $\text{NMe}_4\text{OH}\cdot 1\cdot 1\text{H}_2\text{O}$ and $\text{NMe}_4\text{OH}\cdot 1\cdot 3\text{H}_2\text{O}$ respectively. It is thus apparently impossible to obtain tetramethylammonium hydroxide in the anhydrous state, as the monohydrate decomposes with formation of trimethylamine before a temperature is reached at which it has a perceptible vapour pressure of water.

As the amount of water in the hydrates was usually and most conveniently estimated by deducting from the weight of hydrate the amount of anhydrous hydroxide determined by titration with acid, some direct experiments were made to check the indirect method. A weighed quantity of hydrate was placed in the closed end of a long, narrow, glass tube, and was covered with a long layer of quicklime. The tube and its contents were weighed and attached by the open end to a soda-lime tube to protect the quicklime. The hydrate was then gradually heated to the temperature of decomposition of the hydroxide, the trimethylamine and methyl alcohol escaping in the form of vapour. The increase in weight of the tube and quicklime was equal to the weight of the water in the hydroxide. The method gave results in exact accordance with the indirect method by titration. For example, crystals found by titration to contain 46·7 per cent. of water gave 46·5 per cent. by the direct method.

In the proportion of water in its hydrates, tetramethylammonium hydroxide does not correspond with the inorganic alkali hydroxides, at least, as far as the hydrates stable at the ordinary temperature are concerned, except in the case of the monohydrate. Complex quaternary bases (those, for example, derived from some alkaloids) are, however, known to exist as pentahydrates, in this respect resembling tetramethylammonium hydroxide.

An estimation of the strength of the base by means of the velocity of saponification of methyl acetate in *N*/80 solution showed that it was somewhat weaker than sodium hydroxide. The velocity constants

obtained at 25° were 0·0106 and 0·0115 respectively, so that if the strength of sodium hydroxide is represented as 100, that of tetramethylammonium hydroxide, under the above conditions, will be represented by 92. [View Article Online](#)

The method of preparation described in this paper has been applied to other tetralkylammonium hydroxides, of which it is hoped to give an account in the near future. The expenses of the research were defrayed by a grant from the Research Fund of the Society.

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