The Effects of Dilution and the Presence of Sodium Salts and Carbonic Acid upon the Titration of Hydroxyamine by Iodine.

By

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Although hydroxyamine is readily oxidisable in solution by many reagents, its estimation volumetrically is more or less interfered with by the fact that the products of its oxidation may vary. Meyeringh and others have shown that cupric hydroxide, permanganic acid, and other oxidising agents give irregular results. Titration with free iodine in non-acid solutions is the only method which has yet been proved to be fairly reliable. With this method I have become very familiar in connection with researches carried out, not only by myself, but by my former colleagues, Mr. KAWAKITA and Mr. SHIMIDZU, in conjunction with Dr. DIVERS, under whom we had studied, and I have long become aware that it is accurate only when some degree of uniformity is maintained in its practice. In order to learn what deviations in the process, as ordinarily carried out, might cause such irregularities as I have at times observed in the results, I made, last winter, a series of estimations of a known quantity of hydroxyammonium chloride, under definitely varied conditions, the results of which furnish the matter for this communication.

The volumetric estimation of hydroxyamine is performed by adding a decinormal solution of iodine in potassium iodide to the hydroxyamine solution in presence of alkali bicarbonate, so long as it is bleached, generally using starch as an indicator. In order to get the best results, I find, firstly, that the solution for titration should not be excessively dilute, and, secondly, that it should contain very little alkali salts, and accordingly, neither contain, to begin with, much acid,—for this needs to be neutralised,—nor receive during titration more sodium bicarbonate than is necessary to take up the hydrogen iodide formed. The hydroxyammonium chloride used in all my experiments had been prepared from mercury fulminate.

Influence of the strength of the solution:—Very concentrated solutions of hydroxyammonium chloride give results too low. For example, 5 ccs. of a solution of which the true titer was 10 ccs. of decinormal iodine solution, required, after evaporation to dryness and addition of a few drops of sodium bicarbonate solution, 9.3 ccs. only of iodine; 5 ccs. of another solution with a titer of 9.9 ccs. iodine solution, required after evaporation only 9.4 ccs., and 5 ccs. of a third solution with a titer of 9.55 ccs. iodine required after evaporation only 9.25 ccs., the differences being not due to loss during evaporation, but to irregular reaction with the iodine. Moderately concentrated solutions give good results, but when the dilution reaches about 1000 to 1 the results become too high, and more and more so with increase of the dilution. With a dilution of 3000 to 1 the results of titration are very markedly too high, as may be seen from the first of the tables which follow.

With an iodine solution approximately decinormal and containing 0.1256 gram in 10 cub. centims., a solution of hydroxyammonium chloride was used containing 0.0330 gram in 10 ccs., and requiring by calculation 9.6 ccs. of iodine solution. Of this 10 ccs. were taken for each experiment.

Dilution.	Cub. cents. of iodine solution required.			
	(1)	(2)	(3)	(4)
Undiluted	9.55	9.65	9.55	9.55
Diluted to 100 ccs. ...	10.1	10.3	10.0	10.0
„ „ 200 ccs. ...	10.15	10.25	10.2	10.2
„ „ 500 ccs. ...	10.9	10.95	10.7	10.7

A single drop of the iodine solution, added to 500 ccs. of water containing a little sodium bicarbonate, gave in the absence of hydroxyamine a strong colour-reaction with starch, so that dilution of the reagent was not the cause of the greater quantity of it required by the attenuated hydroxyammonium chloride solutions.

But by the large dilution of the hydroxyammonium chloride some dissociation of the salt appears to take place, for the iodine solution is consumed by the diluted solutions, while it is not at all attacked by the stronger ones, in the absence of sodium bicarbonate. The following results show this. The solutions used were the same as before, but no addition of sodium bicarbonate was made.

Dilution.	Ccs. of iodine solution required.
Undiluted	0.0
Diluted to 100 ccs. ...	0.4
„ „ 200 ccs. ...	0.8
„ „ 500 ccs. ...	1.4

Probably dependent upon this dissociation is the partial decomposition on standing for some hours of hydroxyamine in very dilute solutions of its hydrochloride. Dilution of 10 ccs. of the hydroxyammonium chloride solution to 500 ccs., and of another 10 ccs. to 1000 ccs., was made, and the solutions left all night and then titrated by iodine, with the usual addition of sodium bicarbonate. The 500 ccs. required then only 10.1 ccs. of iodine solution instead of about the 10.8 ccs. which would have been wanted with that dilution if the titration had been proceeded with at once, as may be seen from the first of the preceding tabular statements. The effect of time upon the dilution to 1000 ccs. was still more marked, for this required only 8.8 ccs.

Influence of sodium chloride, sulphate, or carbonate present in the solutions:— Large excess of sodium bicarbonate gives high results, but I have not made any systematic series of measurements of its effects, since the use of unnecessary quantities can always be avoided. But in many cases, which occur during investigations, the solution of hydroxyamine to be titrated is very acid, and to neutralise this acid with the bicarbonate is to charge the solution with sodium chloride or sulphate, and carbonic acid. Now either of these salts, when present in rather large proportions, affects the titration of the hydroxyamine, while the carbonic acid is also active in this way in presence of one of these salts, although by itself it appears to be without action. Free acid should therefore be nearly all removed—hydrochloric acid by evaporation, sulphuric acid by addition of baryta,—before the sodium bicarbonate is added. The effect of sodium chloride was measured in a series of experiments which are tabulated below. The solutions employed were:—

Hydroxyammonium chloride	6.9772	grams per liter.
Iodine....	12.6238	,, ,, ,,
Sodium chloride	100.0	,, ,, ,,

The same, charged with carbonic acid.

5 ccs. of hydroxyammonium chloride, equivalent to 10.1 ccs. of iodine solution, were used in each trial, after dilution to the volume shown in the table by addition of either water, salt solution, or salt solution carbonated.

Diluent.	**Vols. of the dil^d 5 ccs. hydroxyammonium chloride.**					
	15	25	35	45	55	65
	Ccs. of iodine solution required.					
Water...	10.2	10.25	10.4	10.45	10.55	10.65
Salt solution ...	—	10.45	10.7	11.0	11.25	10.85
S. s. carbonated...	10.4	10.8	10.8	10.9	11.5	12.10

Other results confirming those in the above table were obtained with different solutions. Blank tests showed that the diluents of themselves consumed no iodine.

The influence of carbonic acid becomes more marked with lower degrees of dilution of the hydroxyamine solution, when instead of employing sodium-chloride solutions charged with the gas by sending a stream of it through them for an hour, solutions were prepared, in imitation of what happens when an acid solution of hydroxyamine is neutralised preliminary to titration, by mixing equivalent volumes of hydrochloric acid and sodium carbonate. The strength of the solutions employed were:—

Hydroxyammonium chloride	6.8220	grams per liter.
Iodine (as in last series)	12.6238	,, ,, ,,
Sodium carbonate (anhydrous)	96.3075	,, ,, ,,
Hydrochloric acid....	64.5079	,, ,, ,,

The acid was of equivalent strength to the carbonate.

5 ccs. of the hydroxyammonium chloride solution, equivalent to 9.9 ccs. of the iodine solution, were used in each case, and diluted, to the extent stated in the table, by addition, after the water when this was also used, first of the acid and then of the same volume of the carbonate. A little bicarbonate was added as usual during titration.

Acid and carbonate, ccs. of each.	Total vols. of the dil^{d} 5 ccs. of hydroxy^{m} chlor.							
	15	25	35	45	55	65	75	85
	Ccs. of iodine solution required.							
0	9.95	10.1	10.2	10.3	10.25	10.45	10.5	10.6
5	10.7	10.7	10.6	—	11.2	—	11.2	—
10		11.2	—	11.4	—	11.7	—	—
15			11.0	—	11.2	—	11.7	—
20				11.7	—	12.0	—	—
25					11.35	—	12.0	—
30						12.0	12.3	—

Blank tests showed that the diluents alone decolourised no iodine.

A corresponding series of trials were made with sulphuric acid in place of hydrochloric acid. The solutions used were:—

Hydroxyammonium chloride	6.6492	grams per liter.
Iodine (as before)	12.6238	,, ,, ,,
Sodium carbonate (as befors)	96.3075	,, ,, ,,
Sulphuric acid	89.0409	,, ,, ,,

5 ccs. of the hydroxyammonium chloride, equivalent to 9.65 ccs. of iodine solution, were used in each case, and diluted on the same plan as before to the extent shown in the table.

Acid and carbonate, ccs. of each.	**Total vols. of the dil^{d} 5 ccs. hydroxy^{m} chlor.**						
	15	25	35	45	55	65	75
	Ccs. of iodine solution required.						
0	9.7	10.0	9.95	10.0	10.0	10.0	10.2
5	10.3	10.35	10.55	—	10.45	—	10.6
10		10.7	—	10.65	—	10.6	11.0
15			10.8	—	10.4	—	—
20				11.0	—	10.85	11.3
25					11.2	—	—

The experiments here recorded show that high dilution with water causes hydroxyamine to give a higher titer with iodine than that calculated; that this effect of dilution is increased when sodium salts are present in large amount; and that it is still more increased when carbonic acid is also present. They also show that with very high strengths of the solution the titer may be too low. It would seem, therefore, that there must be some deviations from the reaction which is expressed by the equation:—

$$2\,NH_3O + 2\,I_2 = N_2O + 4\,HI + H_2O$$

Should the action of the iodine not go so far, nitrite would be formed, and the low results obtained with very concentrated solutions be accounted for. The production of nitrite from hydroxyamine by various oxidising agents has been noticed by Bertoni, so that its formation through the action of iodine should not be improbable. On testing the point I have found that a distinct formation of nitrite does take place, and that, too, not only where concentrated solutions of hydroxyamine are acted upon, but in all cases, even in those where the iodine titer is higher than that indicated by the above equation.* This fact makes greater the need already present of assuming that the hydroxyamine in decomposing must yield a very little deoxidised nitrogen, either in the free state or in union with iodine. Evidence of the correctness of this assumption seems to be afforded by a remarkable phenomenon to be observed in titrating hydroxyamine with iodine. A very weak solution being mixed with very little sodium bicarbonate, insufficient for the complete titration by iodine, the solution of the latter is added just beyond the point when it is no longer bleached. If now to this solution a little more sodium bicarbonate is added, a milkiness soon appears, strikingly resembling that of iodoform appearing under similar conditions when in place of hydroxyamine a trace of alcohol is present. It disappears on adding more iodine, but may be reproduced several times in succession before the hydroxyamine is exhausted. The substance causing this turbidity may perhaps be in reality an iodamine, related to nitrogen as iodoform is related to carbon.

I am much indebted to Dr. DIVERS for suggestions in carrying out this investigation.

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* The solution after titration always yields a little free iodine when acidified, and this in absence of any iodate in the potassium iodide used, is one proof of the presence of nitrite. The solution also, when freed first from all iodide, and then tested with acidified ferrous sulphate, always gives the brown colour caused by a nitrite.

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