248. *Electrometric Studies of the Precipitation of Hydroxides. Part X. The Action of Ammonia on Solutions of Potassium Mercuri-iodide, and Mercuric Bromide, Nitrate, Sulphate, and Perchlorate.*

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THE study of the reaction between ammonia and mercuric chloride solutions (see Part IX, this vol., p. 601) has been extended to other mercuric halides and to oxy-acid salts, which, unlike the halides, undergo appreciable hydrolysis and ionisation. From solutions of the halides dilute ammonia causes precipitation at lower p_H values than when sodium hydroxide is used, evidently on account of the diminished solubility of the ammoniated precipitate so obtained. The use of concentrated ammoniacal solutions, however, not only causes precipitation but retains a little mercury in solution. In this regard mercury is similar to such metals as silver, copper, cadmium, etc., in forming complex ammine solutions. Precipitation from oxy-acid salt solutions with ammonia occurs under similar conditions of hydrogen-ion concentration to those with alkali, although the precipitates contain much ammonia, apparently in a state of combination. A perusal of the extensive literature on the composition of the various precipitates leads one to the erroneous impression that they are analogues of either fusible white precipitate, infusible white precipitate, or the respective salts of the so-called Millon's base. Usually the composition of precipitates is indefinite and depends largely on the precise conditions under which the precipitations were performed, including the concentration of ammonium salt originally present or formed in the course of the reaction.

EXPERIMENTAL.

I.a. *The Reaction between Ammonia and Mercuric Bromide.*—The crystalline bromide was prepared from its constituents as described by Larine (*J. Pharm. Chim.*, 1904, **20**, 455), Reinders (*Z. physikal. Chem.*, 1900, **32**, 494), and Löwig (*Mag. Pharm.*, 1828, **33**, 7). Owing to its sparing solubility, very dilute solutions had to be employed. Thus 100 c.c. of 0·005*M*-mercuric bromide were titrated with 0·02*N*-ammonium hydroxide at 16° using the glass electrode, and also at 25° by means of conductivity measurements. The curves obtained are given in Fig. 1, where the p_H curve is compared with that obtained by performing a similar titration with sodium hydroxide. Not only did the ammonia cause precipitation at a lower p_H, but, as the inflexion shows, it was complete with approximately 1·75 mols. of ammonia to 1 mol. of the bromide. The conductivity curve, I, also shows that a maximum specific conductivity occurred when 1·75 mols. had been added. Curves II and III give respectively the variations in specific conductivity that would have resulted if mercuric oxide alone or the analogue of infusible white precipitate, *viz.*, $HgO,HgBr_2,2NH_3$, had been precipitated. The precipitate was pale yellow and granular. By adding the ammonia directly, with shaking, slightly less is required for complete precipitation. Thus, analysis of the mother-liquors when 2, 3, and 4 mols. of ammonia had been added, showed that 1·60, 1·60, and 1·65 mols. of ammonia respectively had been required for precipitation, whilst the molecular proportions of ammonium bromide present were 1·12, 1·15, and 1·17 respectively, from which it follows that the precipitate varied from $HgBr_{0{\cdot}88}(OH)_{1{\cdot}12}(NH_3)_{0{\cdot}48}$ to $HgBr_{0{\cdot}83}(OH)_{1{\cdot}17}(NH_3)_{0{\cdot}48}$.

According to the p_H values set up after 1·75 mols. of ammonia had been added, approximate calculation reveals that the precipitate corresponding to the addition of 2·4 mols. of ammonia was $HgBr_{0{\cdot}86}(OH)_{1{\cdot}14}(NH_3)_{0{\cdot}61}$, but that as the titration proceeded it became $HgBr_{0{\cdot}69}(OH)_{1{\cdot}31}(NH_3)_{0{\cdot}44}$ with 3·6 mols. of ammonia. The conductometric data lead to similar results. Calculations were carried out as in Part IX, in which the specific conductivity at any point in the titration is assumed to be due entirely to the ammonium bromide formed, that of any unattacked mercuric bromide being negligible. During precipitation, the precipitate varied from $HgBr_{0{\cdot}82}(OH)_{1{\cdot}18}(NH_3)_{0{\cdot}57}$ with 0·4 mol. of ammonia to $HgBr_{0{\cdot}71}(OH)_{1{\cdot}29}(NH_3)_{0{\cdot}46}$ with 1·6 mol., whilst after precipitation had ended the composition gradually varied from $HgBr_{0{\cdot}71}(OH)_{1{\cdot}29}(NH_3)_{0{\cdot}46}$ at 2 mols. of ammonia to $HgBr_{0{\cdot}57}(OH)_{0{\cdot}43}(NH_3)_{0{\cdot}32}$ at 4 mols. This titration was carried out very slowly, and thus it would appear that the greater time in which the mother-liquor was in contact with the precipitate before the measurements were made, enabled further decomposition of the precipitate to take place. It is also possible that the ammonia content of the precipitate may have increased somewhat, for the disappearance of ammonia from the solution in the presence of much ammonium bromide is not indicated by the specific conductivity. To ascertain whether an ammoniated bromide of definite composition would result if ample time were allowed for the attainment of equilibrium between the liquid and the solid phase, 0·02*N*-ammonia (in the first three cases) and 0·1*N*-ammonia (in the last three) were added in varying molecular proportions to 100 c.c. of 0·005*M*-mercuric bromide and mechanically shaken for several days. Table I gives the amounts of ammonia and ammonium bromide present in the liquid phase from which the composition of the solid phase was computed.

FIG. 1.

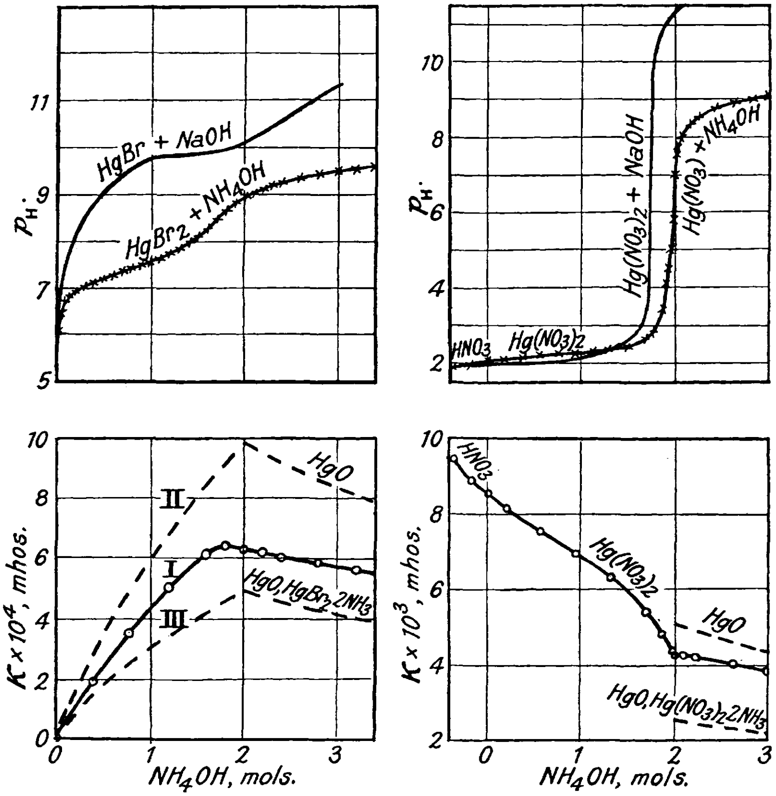

TABLE I.

NH₃ added.	NH₃ found.	NH₄Br found.	NH₃ reacted.	Combined with Hg.	
				Br.	NH₃.
2·07	0·32	1·36	1·75	0·64	0·39
2·99	1·16	1·40	1·83	0·60	0·43
3·99	2·15	1·43	1·84	0·57	0·41
9·97	7·90	1·50	2·07	0·50	0·57
14·96	12·81	1·53	2·15	0·47	0·62
19·94	17·75	1·57	2·19	0·43	0·62

These data show that some little ammonia reacted with the precipitate and that the total ammonia slightly exceeded 2 mols. The precipitate is seen not to correspond exactly with the analogue of either " fusible " or " infusible " white precipitate or with the bromide of Millon's base, except perhaps in a qualitative sense.

I.b. *The Reaction between Ammonia and Potassium Mercuri-iodide.*—As shown in Part VII, sodium hydroxide has no effect on solutions of mercuric chloride in potassium iodide. Unlike the chloride and bromide, the complex mercuric iodide solutions do not react with aqueous ammonia; in fact, not only is no precipitate produced, but p_H measurements with the glass electrode have shown that no reaction ensues whatsoever. Thus in the titration of 100 c.c. of 0·01*M*-potassium mercuri-iodide and 0·006*N*-potassium iodide with 0·1086*N*-ammonia at 17·5° the p_H values on adding 5, 10, and 20 c.c. were 10·57, 10·71, 10·86. Knowing that $p_{K_{NH_4OH}} = 4{\cdot}70$, it follows that if no ammonia had reacted, the p_H values should have been respectively 10·66, 10·79, and 10·92. If any ammonium iodide had been formed as the result of reaction, much lower p_H values would have been obtained.

If, however, sufficient sodium hydroxide is added to raise the p_H through about 1 unit, the characteristic Nessler's reagent coloration will first be produced, which will soon be followed by the separation of a precipitate. Table II gives some figures concerning the amounts of sodium hydroxide necessary to produce a precipitate, and shows that the hydrogen-ion concentration plays an important part in the separation of the ammoniated precipitates which are thereby formed.

TABLE II.

Addition of 0·1046N-*Sodium Hydroxide to* 100 *c.c. of* 0·01M-*Potassium Mercuri-iodide and* 0·006M-*Potassium Iodide* + x *c.c. of* 0·1086N-*Ammonia at* 18°.

	Coloration.		Precipitation.			Coloration.		Precipitation.	
x.	NaOH, c.c.	p_H.	NaOH, c.c.	p_H.	*x*.	NaOH, c.c.	p_H.	NaOH, c.c.	p_H.
2·5	22·5	12·51	35·0	12·54	10·0	5·0	11·71	17·5	12·23
5·0	12·5	12·16	20·0	12·34	20·0	5·0	11·73	17·5	12·25

II.a. *The Reaction of Ammonia with Mercuric Nitrate.*—In order to maintain the nitrate in clear solution it is necessary to include some nitric acid. The diagrams at the right of Fig. 1 represent a glass-electrode titration at 18° and a conductometric titration at 25° of 100 c.c. of 0·02674*M*-mercuric nitrate and 0·00961*N*-nitric acid with 0·1*N*-ammonia. Both titration curves indicate that exactly 2 mols. of ammonia were required to complete the precipitation. The precipitate was white. Analysis of the mother-liquor when 2 mols. of ammonia had been added revealed that the precipitate contained $Hg(NO_3)_{0\cdot54}(OH)_{1\cdot46}(NH_3)_{0\cdot54}$. The p_H values indicate somewhat higher NO_3 and NH_3 contents at first, but on the addition of 110 c.c. of ammonia (*i.e.*, 1·75 mols. in excess) the precipitate had acquired the same composition. Using Jones's (Carnegie Institution of Washington Publications, 1912, 170) conductivities of ammonium nitrate, calculations have been made from the specific conductivities of the liquid phases after precipitation had become complete, the specific conductivity of the excess of ammonia being negligible. They indicate an average composition of $Hg(NO_3)_{0\cdot34}(OH)_{1\cdot66}(NH_3)_{0\cdot34}$, whilst the specific conductivities of mother-liquors that had been shaken with their precipitates for several days lead to $Hg(NO_3)_{0\cdot40}(OH)_{1\cdot60}(NH_3)_{0\cdot40}$.

On comparing this curve with that obtained when sodium hydroxide is substituted for ammonia, it is seen that precipitation with either reagent occurs within a similar p_H range.

Although the curves show that 2 mols. of ammonia react with 1 mol. of mercuric nitrate, some little absorption of ammonia by the precipitate takes place on adding excess, *e.g.*, with 2 mols. in excess the ammonia which had reacted was 0·16 mol. per mol. of the nitrate.

II.b. *The Reaction of Ammonia with Mercuric Perchlorate.*—Glass-electrode and conductometric titration curves of solutions of mercuric perchlorate and free perchloric acid were very similar to those obtained with the nitrate solutions. Also, the end-points again occurred when exactly 2 mols. of ammonia had been added. The hydrogen-ion concentration prevailing during precipitation was almost identical with that established when sodium hydroxide was used. With 100 c.c. of 0·02578*M*-mercuric perchlorate and 0·01337*N*-perchloric acid and 0·1*N*-ammonia a very pale yellow precipitate was obtained which, however, did not coagulate until a considerable excess of ammonia had been added; owing to the colloidal nature of the precipitate, analysis did not yield entirely satisfactory results. The p_H data indicated that the precipitate ranged in composition from $Hg(ClO_4)_{0\cdot52}(OH)_{1\cdot48}(NH_3)_{0\cdot52}$ to $Hg(ClO_4)_{0\cdot59}(OH)_{1\cdot41}(NH_3)_{0\cdot59}$ during the addition of 2 mols. of ammonia in excess, whereas the corresponding conductivity measurements pointed to $Hg(ClO_4)_{0\cdot41}(OH)_{1\cdot59}(NH_3)_{0\cdot41}$.

II.c. *The Reaction of Ammonia with Mercuric Sulphate.*—The sulphate hydrolyses so readily that a large amount of sulphuric acid is necessary to keep it in solution. Hence, on addition of ammonia there results a large concentration of ammonium sulphate which eventually reduces the accuracy of the calculations based on either p_H or conductivity data. The electrometric curves, however, gave well-defined end-points when the stoicheiometric amounts of ammonia had been added, and the p_H values during precipitation were comparable with those which would have prevailed had sodium hydroxide been the precipitant. An analysis was made of the precipitate obtained by the interaction of 132·8 c.c. of 0·3*N*-ammonia and 200 c.c. of a solution 0·02415*M* with regard to mercuric sulphate and 0·1438*N* with regard to sulphuric acid. The precipitate was dissolved in potassium iodide solution and the free ammonia and potassium hydroxide were estimated [see Part VIII (this vol., p. 9) and Part IX (*loc. cit.*)]. The molecular composition of the precipitate may be expressed as $\mathrm{Hg(SO_4)_{0\cdot29}(OH)_{1\cdot42}(NH_3)_{0\cdot58}}$.

DISCUSSION.

It will be seen that ammonia causes the precipitation of ammoniated basic salts from solutions of mercuric salts of nitric, perchloric, and sulphuric acids within the same range of hydrogen-ion concentration as when sodium hydroxide is employed. Since the solubility product of mercuric hydroxide, $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$, is 1×10^{-26}, and because these salts are ionised to an extent of about 40% (cf. Morse, *Z. physikal. Chem.*, 1902, **41**, 709), it follows that mercuric oxide should be precipitated from fairly acid solutions, p_{H} 2—3. This happens to be the range within which the ammoniated nitrate, perchlorate, and sulphate precipitates are formed, and thus it appears that as far as their precipitation is concerned, they are intimately connected with the mercuric oxide they contain. This is in harmony with the view expressed in Part IX that ammonia gives precipitates of ammoniated basic salts. On the contrary, approximate calculation showed that the ionic product, $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$, corresponding to the conditions under which ammoniated mercuric chlorides were precipitated was equal to *ca.* 10^{-29}. Table III shows that similar conditions prevail during the precipitation of ammoniated bromides. The mercuric-ion concentrations at different stages of the process of precipitation were computed by means of the relationship $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{Br}']^2/[\mathrm{HgBr_2}] = 2\cdot0 \times 10^{-18}$ governing the equilibria $\mathrm{HgBr_2} \rightleftharpoons \mathrm{Hg}^{\cdot\cdot} + 2\mathrm{Br}'$ as found by Morse (*loc. cit.*). The ammonium bromide concentration, and therefore that of the bromide ion, was estimated from the conductometric titration curve, and the concentration of mercuric bromide was based on the assumption that the precipitation proceeded uniformly, requiring 1·75 mols. of ammonia per mol. of mercuric bromide.

TABLE III.

Ionic Product, $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$, *during Titration of* 100 *c.c. of* 0·005*M*-$\mathrm{HgBr_2}$ *with* 0·02*N*-$\mathrm{NH_4OH}$.

$\mathrm{NH_4OH}$, mols.	$p_{\mathrm{Hg}^{\cdot\cdot}}$.	$p_{\mathrm{OH}'}$.	$p_{\mathrm{Hg}^{\cdot\cdot}} + 2p_{\mathrm{OH}'}$.	$\mathrm{NH_4OH}$, mols.	$p_{\mathrm{Hg}^{\cdot\cdot}}$.	$p_{\mathrm{OH}'}$.	$p_{\mathrm{Hg}^{\cdot\cdot}} + 2p_{\mathrm{OH}'}$.
0·4	14·33	7·08	28·5	1·2	15·68	6·45	28·6
0·8	15·14	6·77	28·7	1·6	16·45	5·94	28·4

The inability of ammonia to produce a precipitate from a solution of potassium mercuri-iodide, 0·01*M*-$\mathrm{K_2HgI_4}$ + 0·006*M*-KI, appears to be due to the non-attainment of 10^{-29} for $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$. This is evident from the last column of Table IV. The mercuric-ion concentration was calculated from Sherrill's value (*Z. physikal. Chem.*, 1903, **43**, 721), $5\cdot3 \times 10^{-31}$, for $K = [\mathrm{Hg}^{\cdot\cdot}][\mathrm{I}']^4/[\mathrm{HgI_4}'']$ governing the ionisation of the complex ion $\mathrm{HgI_4}''$.

TABLE IV.

Ionic Product, $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$, *during Addition of* 0·1086*N*-$\mathrm{NH_4OH}$ *to* 100 *c.c. of* 0·01*M*-$\mathrm{K_2HgI_4}$ *and* 0·006*M*-KI.

No.	$\mathrm{NH_4OH}$, c.c.	$\mathrm{NH_4OH}$, mols.	$p_{\mathrm{Hg}^{\cdot\cdot}}$.	$p_{\mathrm{OH}'}$.	$p_{\mathrm{Hg}^{\cdot\cdot}} + 2p_{\mathrm{OH}'}$.	No.	$\mathrm{NH_4OH}$, c.c.	$\mathrm{NH_4OH}$, mols.	$p_{\mathrm{Hg}^{\cdot\cdot}}$.	$p_{\mathrm{OH}'}$.	$p_{\mathrm{Hg}^{\cdot\cdot}} + 2p_{\mathrm{OH}'}$.
1	3·0	0·33	23·34	3·65	30·69	3	10·0	1·09	23·38	3·44	30·27
2	5·0	0·54	23·32	3·59	30·57	4	20·0	2·17	23·16	3·29	29·97

In order to increase the ionic product, $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$, it is necessary to increase the hydroxyl-ion concentration, which may be done by the addition of sodium hydroxide. Although this alkali alone does not cause precipitation from potassium mercuri-iodide solutions, it does so in the presence of ammonia, on account of the diminished solubility of the ammoniated mercuric iodide. Thus it has been calculated that, on the addition of 10 c.c. of 0·1046*N*-sodium hydroxide to solutions 2 and 4 (Table IV), the product $[\mathrm{Hg}^{\cdot\cdot}][\mathrm{OH}']^2$ had reached $10^{-27\cdot4}$ and $10^{-27\cdot2}$ respectively.

It might be considered that another way to increase the value of the product,

$[Hg^{\cdot\cdot}][OH']^2$, would be to avoid any excess of potassium iodide in the complex-ion solution and so enable the ion HgI_4'' to yield its maximum concentration of mercuric ions. This actually is done in the preparation of Nessler's solution, which is approximately $0{\cdot}09M$-K_2HgI_4 and $2{\cdot}5N$-KOH and is, moreover, saturated with respect to mercuric iodide. It happens, however, that the mercuric-ion concentration is also determined by $L = [Hg^{\cdot\cdot}][I']^4$ and by eliminating $[I']$ from this expression and from $K = [Hg^{\cdot\cdot}][I']^4/[HgI_4'']$ we get $[Hg^{\cdot\cdot}] = L^2/K[HgI_4'']$. According to Bourgoin (*Bull. Soc. chim.*, 1884, **42**, 620; *Ann. Chim. Phys.*, 1884, **3**, 429), Rohland (*Z. anorg. Chem.*, 1898, **18**, 328), and Morse (*Z. physikal. Chem.*, 1902, **41**, 731), the solubility of mercuric iodide in water at 17·5° is approximately $0{\cdot}000088M$. For $HgI_2 \rightleftharpoons Hg^{\cdot\cdot} + 2I'$, Morse finds $[Hg^{\cdot\cdot}][I']^2/[HgI_2] = 10^{-25}$, whence we find the solubility product $[Hg^{\cdot\cdot}][I']^2 = 8{\cdot}8 \times 10^{-5} \times 10^{-25} = 8{\cdot}8 \times 10^{-30}$. Hence, the mercuric-ion concentration of Nessler's solution, $[HgI_4'']$ being 0·09, is equal to $10^{-26{\cdot}7}$. As the $p_{OH'}$ of the solution is almost 0, the product $[Hg^{\cdot\cdot}][OH']^2$ is approximately 10^{-27}, and therefore the solution is on the verge of precipitating mercuric oxide. Owing to the diminished solubility of the ammoniated mercuric iodide, ammonia will thus be able to cause precipitation.

The presence of iodide ions in a mercuri-iodide solution has an appreciable effect in depressing the mercuric-ion concentration and this, in turn, affects the behaviour of ammonia towards strongly alkaline solutions. It is possible by this means to reduce the mercuric-ion concentration so that ammonia has no visible effect. Thus a solution comprising 10 c.c. of $0{\cdot}1M$-mercuric chloride and 8 c.c. of $2N$-potassium iodide, made up to 25 c.c., and 20 c.c. of $3N$-sodium hydroxide did not begin to undergo precipitation until 20 c.c. of $3N$-ammonia had been added. Calculation shows that $[Hg^{\cdot\cdot}]$ then was $10^{-28{\cdot}6}$ and $[OH']$ *ca.* $10^{-0{\cdot}5}$, whence $[Hg^{\cdot\cdot}][OH']^2 = 10^{-29{\cdot}6}$. The fact that precipitation was incipient shows that it depends on the attainment of an ionic product of similar magnitude to that necessary for the separation of ammoniated chloride and bromide precipitates.

Regarding the composition of the various precipitates, as a rule, the mercuric salt and the ammonia were present in equivalent amounts, suggesting, as in the case of the ammoniated basic chloride, that the constitution of the precipitate might be expressed as $x\mathrm{HgO},(1-x)[\mathrm{HgCl_2,2NH_3}]$. This is in accord with the titrations of the nitrate, perchlorate, and sulphate, in which exactly 2 mols. of ammonia were necessary for complete precipitation. On subjecting the precipitates to an excess of ammonia, a little further absorption of ammonia by the nitrate precipitate occurred, which might have been due to a little ammoniation of the mercuric oxide in the precipitate. It does not take place readily, however. Thus in order to form Millon's base, $2HgO,NH_3,H_2O$, Hofmann and Marburg (*Annalen*, 1899, **305**, 191) digested mercuric oxide with aqueous ammonia for 12 hours.

To reduce the mercuric oxide contents of the precipitates, it is necessary to carry out the precipitation with ammonia from mercuric salt solutions containing much of the same ammonium salt. Mercuric oxide possesses an appreciable solubility in solutions of the various ammonium salts. It dissolves in ammonium bromide with the liberation of free ammonia, which can be titrated with nitric acid to methyl orange. In contrast with this, it dissolves very readily in ammonium sulphate and nitrate solutions, but very little of the resulting ammonia is titratable. It is probable that complex salts are formed probably of the type $Hg(NH_3)_2SO_4$ in which the ammonia is bound. The ease with which ammonia is liberated from the bromide solutions might possibly account for the fact that the ammoniated mercuric bromide precipitate usually obtained [see also Gaudechon (*Compt. rend.*, 1909, **148**, 1763; 1910, **150**, 467), whose precipitate contained $HgBr_{0{\cdot}67}(OH)_{1{\cdot}33}(NH_3)_{0{\cdot}44}$] contains less ammonia than is represented by the general formula.

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