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THE ACTION OF AQUEOUS AMMONIA ON MERCUROUS CHLORIDE.—

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Mercurous chloride is turned grayish black by the action of aqueous ammonia. This is the standard method used in the qualitative analysis of mercury in the mercurous state. Though the test is extremely easy to carry out in the laboratory, theoretically it presents many intricate and scientifically interesting problems.

Before we can assign an equation to the reaction, we must consider the empirical formula for mercurous chloride. The structural formula is necessary for a more thorough consideration of the mechanism of the reaction.

It has long been known that mercurous chloride contains one atom of chlorine for each atom of mercury. The molecular weight of the compound, however, is a point of dispute. Many chemists support the view that the molecule is HgCl , analogous to cuprous chloride; while others consider that there are substantial data in favor of the formula Hg_2Cl_2 .

Since mercurous chloride passes into the vapor phase below 400°C ., it is natural to suppose that vapor density determinations would give a definite answer to support one view or the other. At 518° the vapor density is 235.5 ($\text{O}_2=32$). This seems to indicate that the formula HgCl is correct. But it has been suggested that, if the dimolecular form were to dissociate in the gaseous state into metallic mercury and mercuric chloride, $\text{Hg}_2\text{Cl}_2=\text{Hg}+\text{HgCl}_2$, then the vapor density of the

resulting mixture should be $\frac{1}{2}(200+270.9) = 235.5$, or the same as found by experiment. This possibility led to many experiments designed to prove the presence of free mercury in the vapor². Though these experiments indicated that some dissociation took place, for the most part they failed to give any idea of the extent. A. Smith and A. W. C. Menzies³, however, concluded from their work on the vapor pressure of calomel that neither HgCl nor Hg_2Cl_2 was present in the vapor. The case seems to be analogous to that of ammonium chloride. Ordinarily, ammonium chloride dissociates on volatilization to give a gaseous mixture of ammonia and hydrogen chloride. But if the ammonium chloride be dried with extreme care before heating, then the dissociation does not take place. H. B. Baker⁴ has obtained results with very dry mercurous chloride indicating that the molecules in this condition exist in the gaseous form chiefly as Hg_2Cl_2 but dissociate in the presence of a trace of moisture to Hg and HgCl_2 .

A. Smith and A. W. C. Menzies³ found that mercurous chloride, dissolved in mercury, lowered the vapor pressure of the mercury to an extent equal to the lowering calculated on the assumption that the molecule of calomel is HgCl . On the other hand, E. Beckmann⁵ obtained the molecular weight corresponding to Hg_2Cl_2 by the freezing point method, using either mercuric chloride or anthraquinone as the solvent. Similarly, he obtained the formulae Hg_2Br_2 and Hg_2I_2 by noting the effect of these halides on the freezing points of the corresponding mercuric halides.

From the point of view of the modern theories of atomic structure, it is hard to conceive of the molecule HgCl existing to any extent at ordinary temperatures. According to C. R. Bury⁶, the electron structure for mercury is 2.8.18.32.18.2. It is easy to see that an atom of such a structure would lose two electrons readily to chlorine for instance. But to lose only one electron ought to leave a very unstable and extremely reactive substance. The case is in no wise analogous to that of copper. Here, according to the same hypothesis, the two

forms have different electron structures; -2.8.18 for the cuprous ion and 2.8.17 for the cupric. From the above electron structure for mercury, one would predict, *a priori*, that if mercury could exist with any valence other than two, the trivalent would be more stable than the monovalent form.

The evidence is so much in favor of the formula Hg_2Cl_2 for mercurous chloride, that in this paper it will be used in preference to the simpler form.

The next point to consider is how these four atoms may be combined in the molecule. The structural formula for Hg_2Cl_2 is universally represented as Cl-Hg-Hg-Cl . This might be written according to the Lewis-Langmuir hypothesis as $:\text{Cl}:\text{Hg}:\text{Hg}:\text{Cl}:$ where each chlorine has completed its octet leaving the two mercury atoms held together by a single electron pair. However a radically different structure explains the properties of mercurous chloride more satisfactorily. It is well known that mercuric compounds easily form complex ions such as HgCl_4^{2-} , HgI_4^{2-} , etc. It seems that the mercuric ion is capable of attracting to itself four groups. By sharing an electron pair with each of these groups, it completes an additional octet about the mercury kernel. When chlorine acts on an excess of metallic mercury, the primary reaction is probably $\text{Hg} + \text{Cl}_2 = \text{HgCl}_2$. Then the mercuric chloride reacts with metallic mercury to give mercurous chloride: $\text{HgCl}_2 + \text{Hg} = \text{Hg}_2\text{Cl}_2$. It is quite possible that the atom of metallic mercury first loses its two valence electrons to the mercuric chloride molecule and then shares an additional pair of electrons from the outer shell of its kernel to give a compound containing a mercury ion surrounded by an additional octet as in $\text{Hg}:\ddot{\text{H}}\text{g}:\text{Cl}$, which can be represented by the non-electronic

$$\text{Cl}$$

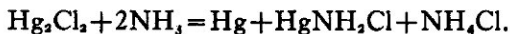
formula $\text{Hg}=\text{HgCl}_2$. This structure is substantiated by the fact that calomel dissociates so easily. If mercurous chloride be exposed to light, it soon turns dark due to the formation of free mercury. It is a common phenomenon for light to loosen

electrons in compounds. Kinetic vibration also tends to break down the molecule. But heat alone is not sufficient; at least a trace of water must be present to catalyze the dissociation. The action of water is possibly that of making the unshared electron pair in the additional octet about one of the mercury atoms more mobile so that it can migrate to the other mercury with the formation of the metal.

This type of structure may be applied to other mercurous compounds than the halides. Mercurous nitrate is $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, which might be represented as mercurio diaquo mercuric nitrate or $[\text{Hg}=\text{Hg}(\text{H}_2\text{O})_2] (\text{NO}_3)_2$. According to this structure, the nitrate ions are not held in the complex, but are free to ionize in solution. The great solubility of mercurous nitrate in contrast to the insolubility of the halides is thus accounted for.

From the isotopic point of view mercurous chloride is very complex. F. W. Aston⁸ has shown that mercury is a mixture of isotopes. By the mass spectrograph method, he obtained a band from mass number 197 to 200 probably including isotopes for each unit within this range, in addition to lines at mass numbers 202 and 204. That is, mercury may consist of a mixture of six isotopes of mass numbers 197, 198, 199, 200, 202 and 204. He also found chlorine to be a mixture of two isotopes with mass numbers 35 and 37. If the structure of mercurous chloride is $\text{Hg}=\text{HgCl}_2$, then 108 isotopic isomers are possible.

We are now in a position to consider the reaction between mercurous chloride and aqueous ammonia. This is best expressed by the equation



The formation of metallic mercury as one of the products of the reaction has not been universally accepted. R. J. Kane⁹ believed that $\text{Hg}_2\text{NH}_2\text{Cl}$ was formed instead of mercury and infusible white precipitate. This view has persisted in many text books to the present day. Therefore the most important question to settle concerning the reaction is whether or not metallic mercury is formed. C. Barfoed¹⁰ exposed the dry

precipitate to the air and found that about half of the mercury volatilized on standing, leaving a residue much lighter in color than the original precipitate. This residue was identical with the infusible white precipitate formed by the reaction between mercuric chloride and aqueous ammonia. H. Saha and K. N. Choudhuri¹¹ found that infusible white precipitate was soluble in concentrated aqueous ammonia. When the precipitate obtained by the action of ammonia on calomel was extracted with this solvent, infusible white precipitate was found to go into solution leaving a residue of metallic mercury. J. G. F. Druce¹² found that the precipitate would not amalgamate metallic copper, and at first announced that this was proof that metallic mercury could not be present, but later he reversed his opinion.

It seemed to me that these proofs, especially the second, were not rigid, because of the possibility of secondary reactions. Therefore a purely physical proof was devised, which depended on the difference in density between mercury and infusible white precipitate. The freshly prepared precipitate was thoroughly mixed with cold glycerine. The mixture was floated on a layer of glycerine in a test tube and whizzed in a centrifuge. The mercury settled out faster than the infusible white precipitate so that the part that was thrown out last was very perceptibly lighter in color, being nearly white. The part that settled out first gave a residue of free mercury on treatment with hydrochloric acid, while the white precipitate was dissolved without residue by the same reagent. The use of cold glycerine as a suspending medium was necessary to prevent too rapid deposition. There does not seem to be any possibility for secondary reactions in this method, so it can be taken as proved that the precipitate formed by the action of aqueous ammonia on mercurous chloride is not a simple substance but a mixture with metallic mercury as one of the components.

The next point for examination is the mechanism for the formation of the mercury. It has already been pointed out that there is an equilibrium between mercurous chloride on the one hand and metallic mercury plus mercuric chloride on the

other. $\text{Hg}=\text{HgCl}_2 \rightleftharpoons \text{Hg} + \text{HgCl}_2$. This equilibrium may be expressed according to the law of mass action as

$$\frac{[\text{Hg}][\text{HgCl}_2]}{[\text{Hg}=\text{HgCl}_2]} = K.$$

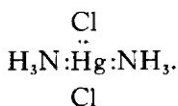
Any secondary reaction that will lower the concentration of mercuric chloride will cause further dissociation of the mercurous chloride until a new point of equilibrium will have been reached. The addition of soluble chlorides such as NH_4Cl or NaCl with the formation of $\text{M}_2[\text{HgCl}_4]$ has this effect to some extent¹³. Ammonia reacts very completely with mercuric chloride to form infusible white precipitate, which is very insoluble. Therefore when aqua ammonia is added to calomel, it reacts with the small concentration of mercuric chloride in equilibrium with the calomel. More of the calomel then dissociates, and, if there is sufficient ammonia present, the reaction proceeds to completion. When the materials are thoroughly dried, the reaction with ammonia is slowed down very considerably if not prevented entirely¹⁴. This is probably due to the fact that the presence of water is necessary for the formation of mercuric chloride which, evidently, must be present before the reaction with ammonia takes place.

Another fact pointing to the dissociation of mercurous chloride preliminary to the reaction with ammonia is that one product formed, namely infusible white precipitate, is identical with that produced by the action of ammonia on mercuric chloride. This last reaction may be expressed by the equation $\text{HgCl}_2 + 2\text{NH}_3 = \text{HgNH}_2\text{Cl} + \text{NH}_4\text{Cl}$, but it probably takes place with a number of intermediate steps.

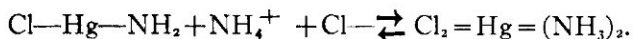
An attempt to determine the structural formula of infusible white precipitate is rather futile so long as its molecular weight is not known. Nevertheless, many such attempts have been made. A provisional formula is often an aid to further work and, for this purpose, that of R. J. Kane¹⁵ and E. C. Franklin¹⁶ is most suitable. Franklin has been able to assign structures in agreement with the empirical formulae

to a very large number of ammonia mercury compounds by assuming that they are more or less complex derivatives of the hypothetical HO-Hg-NH_2 . In this system, infusible white precipitate is the chloride of the above base, i. e., Cl-Hg-NH_2 . This formula has the advantage of fitting into a scheme consistent with a large group otherwise difficult to account for.

Franklin's formula expresses the chemical properties of the compound sufficiently well. For instance it is readily acted upon by hydrochloric acid with the formation of mercuric and ammonium chlorides. Moreover all its nitrogen is liberated as ammonia when treated with potassium hydroxide. Amido-mercuric chloride, as we may now call it, reacts with ammonium chloride to give fusible white precipitate. This substance is generally considered as being $\text{HgCl}_2 \cdot 2\text{NH}_3$, that is, mercuric chloride with two molecules of ammonia of crystallization. It would be better to represent the two ammonia molecules as sharing their free electron pairs with the mercury to give

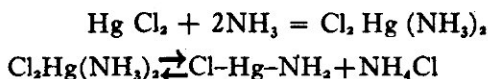


Here we have an additional octet formed about the mercury as in HgCl_4^- or $\text{Hg}=\text{HgCl}_2$. The reaction is reversible because in the presence of aqua ammonia, fusible white precipitate or dichloro diammine mercury, loses ammonium chloride with the formation of amido-mercuric chloride:

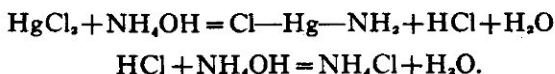


This reaction therefore supports the view that the mercury in amido-mercuric chloride is not surrounded by an additional octet, at least not by a stable one. Actually the molecule may be some polymerization product, because the simple formula does not account for the infusibility of the compound.

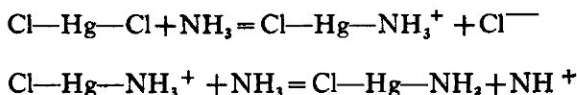
It has been suggested that the formation of infusible white precipitate proceeds through the intermediate formation of dichloro diammine mercury



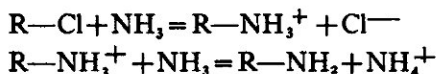
J. G. F. Druce¹² has proved that one molecule of ammonium chloride is formed in the reaction, but he gives the intermediate steps as follows:—



The best mechanism probably is that the reaction proceeds as with organic chlorine derivatives:

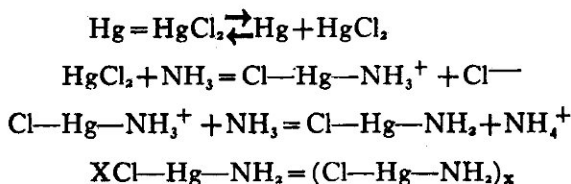


according to the analogy



In both these reactions, before substitution takes place, there may be some feeble addition compound formed between the chlorine and the ammonia.

The action of aqueous ammonia on mercurous chloride may be summarized by the following series of equations which represent what seem to be the most probable steps in the reaction.

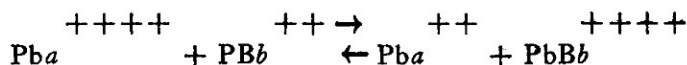


This analysis of the reaction between aqueous ammonia and mercurous chloride was carried out as a part of a general investigation into the possibility of separating isotopes chemically. The point of interest was that mercurous chloride gave two different mercury derivatives in the reaction, namely metallic mercury and infusible white precipitate. If the old

formula Cl—Hg—Hg—Cl for mercurous chloride were the true one, then on dissociation one of the mercury atoms would drop out of the molecule, presumably by thermal agitation, carrying the electron pair with it. On the assumption that the two mercury atoms differed in mass, one having the mass number 197 and the other 204, to take an extreme instance, a separation of isotopes would be accomplished, if there were any selective action. It was thought that by gravitational attraction the electron pair between the two mercury atoms would be somewhat more firmly held by the heavier mercury atom. In this case it would necessarily be the heavier mercury that formed the metal found as a product of the reaction. The effect of mass on the position or orbit of an outer electron has been proved by L. Aronberg, T. R. Merton and others¹⁷ in the case of lead. Though it is very small, it is conceivable that it might exert a deciding factor in the dissociation, provided all other effects were equally balanced.

However we have arrived at the conclusion that mercurous chloride is not symmetrical in structure. If mercurous chloride is formed when chlorine acts on an excess of mercury to give as the primary product mercuric chloride which then adds an atom of mercury to form the compound Hg=HgCl_2 , there seems to be no possibility of separating isotopes by this method. Such a separation would imply that the mercury had been added selectively, which is inconceivable. Moreover there is very little possibility of separating isotopes by this reaction even if the old form of structure for calomel be true. G. Hevesy and L. Zechmeister¹⁸ have proved that in the case of lead there is a dynamic equilibrium existing between ions and electrons when the acetates of divalent and tetravalent lead are mixed. They dissolved the tetraacetate of radioactive lead in a solution of the diacetate of ordinary lead. After separating the two forms of lead, they found that the divalent had become radioactive while the tetravalent form had lost an equivalent part of its activity. In other words there must exist an

equilibrium in which electrons migrate freely from one kind of lead ion to the other.



If this is a typical example of a general principle, we should expect an analogous freedom of movement of electrons between metallic mercury and mercuric compounds. Therefore in the equilibrium $\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg} + \text{HgCl}_2$, no separation of isotopic forms would be expected.

In conclusion I wish to acknowledge my indebtedness to P. D. McLarren, M. D., C. M., for the loan of the centrifuge used in this investigation.

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