METHODS OF ESTIMATION OF SEMICARBAZIDE BY ITS INTERACTION WITH HALOGENS AND HALOGEN OXYACIDS.

By Rasik Lal Datta.

Received March 12, 1914.

The action of chlorine, and potassium chlorate and hydrochloric acid on semicarbazide has been taken up for study in order to ascertain the nature of the decomposition of the latter body. It was found that these reagents bring about the complete rupture of the semicarbazide molecule, with liberation of large amounts of nitrogen and carbon dioxide. Following this up, the action of other similar reagents was taken into consideration. These have been, bromine, bromic acid and iodic acid, the latter in the form of salt. It has been found that semicarbazide hydrochloride is decomposed by the above reagents, yielding an amount of nitrogen which always bears a certain invariable proportion to the total nitrogen of semicarbazide. These reactions, as will be shown later, could be used conveniently for the gasometric estimation of semicarbazide, for which no satisfactory method of estimation is as yet known. It is to be noted that the reagents named do not react with urea and, hence, the estimation of semicarbazide could be effected in the presence of this body.

Maselli[1] has given a round-about method for the estimation of semicarbazide. He utilizes the reaction that when semicarbazide is boiled with dilute acids, decomposition occurs with the quantitative separation of ammonia and hydrazine, according to the equation:

$$NH_2CO.NH.NH_2 + 2H_2O = NH_3 + CO_2 + H_2O + N_2H_4.$$

The quantity of semicarbazide can hence be estimated either (1) by determining the amount of hydrazine, by adding an excess of a standard solution of potassium iodate, boiling until all the iodine set free is removed, and titrating the excess of potassium iodate with standard sodium thiosulfate; (2) by determining the amount of ammonia formed, by adding sodium hydroxide and distilling the ammonia set free into a known volume of standard acid.

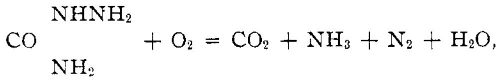
The action of semicarbazide upon the halogen oxyacids is interesting and varies progressively with the atomic weight of the halogens. Like carbamide, semicarbazide hydrochloride is completely decomposed by sodium hypochlorite or sodium hypobromite with the quantitative liberation of nitrogen. The action of potassium chlorate and hydrochloric acid is, however, quite different.

To a solution of semicarbazide hydrochloride in a Crum's nitrometer, a little powdered potassium chlorate and then strong hydrochloric acid is added. A vigorous reaction ensues with copious evolution of a gas consisting of nitrogen, carbon dioxide and chlorine. After washing down the excess of chlorine, the carbon dioxide was completely absorbed by strong

---

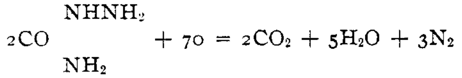
[1] *Gazz. chim. ital.*, **35**, I, 267 (1905).

alkali. The remaining gas was found to bear a constant ratio to the total nitrogen, namely, $^2/_3$ of the total. The reason for washing down the chlorine before the addition of alkali is that the alkali, in the presence of chlorine, acts as hypochlorite and, hence, instead of $^2/_3$, the total amount of nitrogen is liberated. So potassium chlorate and hydrochloric acid liberate only $^2/_3$ of the nitrogen according to the following equation:



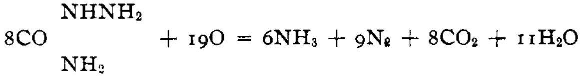
$$CO\begin{matrix}NHNH_2\\ \\ NH_2\end{matrix} + O_2 = CO_2 + NH_3 + N_2 + H_2O,$$

while alkaline hypochlorite decomposes it quantitatively thus:



$$2CO\begin{matrix}NHNH_2\\ \\ NH_2\end{matrix} + 7O = 2CO_2 + 5H_2O + 3N_2$$

The reaction between semicarbazide hydrochloride and potassium bromate is a little more energetic than the reaction with potassium chlorate and hydrochloric acid. When solid potassium bromate is added to solid semicarbazide hydrochloride and the mixture is moistened, a vigorous reaction instantly begins with the copious evolution of gas and bromine vapors. At the same time the mixture becomes intensely hot. But if the semicarbazide hydrochloride be in the form of a tolerably strong solution, a few seconds elapse before any sign of reaction is visible, after which, suddenly, a vigorous reaction ensues with the evolution of gas and liberation of bromine. The time required for the reaction to take its course depends upon the dilution of semicarbazide hydrochloride. In the case of somewhat dilute solutions, as long as 5 to 10 minutes elapses before the sign of any reaction is evident. When the dilution is very great no reaction takes place at all. But a little hydrochloric acid added to such a mixture starts up the reaction at once. If the reaction be carried out in a Crum's nitrometer with the help of a little hydrochloric acid, finally treating the resulting gas with alkali after washing down the excess of free bromine, the percentage of nitrogen comes out nearly $^3/_4$ of the total quantity present in semicarbazide. The reaction evidently takes place according to the equation:



$$8CO\begin{matrix}NHNH_2\\ \\ NH_2\end{matrix} + 19O = 6NH_3 + 9N_2 + 8CO_2 + 11H_2O$$

But if the alkali be added directly in the presence of bromine in the above reaction, it acts as hypobromite and quantitative liberation of nitrogen is the result.

The reaction of semicarbazide hydrochloride with potassium iodate is more energetic than that with potassium bromate. Potassium iodate interacts with semicarbazide hydrochloride in very dilute solutions with copious evolution of gas and liberation of iodine. On carrying through the reaction in a Crum's nitrometer, it is found that the nitrogen given out is $^3/_4$ of the total nitrogen. Hence there is noticeable a beautiful transition in the reactions of the halogen oxyacids towards semicarbazide. Potassium chlorate interacts only in conjunction with hydrochloric acid, setting free $^2/_3$ of the total nitrogen. Potassium bromate interacts without the help of any acid in moderately strong solutions and in the presence of acid in dilute solutions, liberating nearly $^3/_4$ of the total nitrogen. Potassium iodate interacts without the help of any acid at all dilutions, liberating just $^3/_4$ of the total nitrogen.

Chlorine and bromine decompose semicarbazide hydrochloride with the evolution of gas. The decomposition by means of chlorine could not be used as an analytical method since chlorine cannot be obtained in a good concentration suitable for carrying out such reactions.

When bromine water is added to semicarbazide solution in a Crum's nitrometer, copious evolution of gas takes place. On washing down the excess of bromine and absorbing the carbon dioxide generated by strong lye, the resulting nitrogen is found to be $^3/_4$ of the total, and the reaction is expressed by a similar equation given above in the case of potassium bromate and hydrochloride acid. But if, instead of washing down the excess of bromine, caustic alkali be directly added, the action is equivalent to that of alkaline hypobromite with the quantitative liberation of nitrogen.

The actual data of a few of the numerous experiments performed are given below:

I. With potassium chlorate and hydrochloric acid.

(*a*) Using alkali in the presence of chlorine, 0.2368 g. was dissolved in 9.1 cc. of water; 1 cc. of this solution gave: (i) 8.9, (ii) 9.1, (iii) 9.0 cc. N_2 at 30° and 760 mm. Found N = 37.41; calc. for CH_6N_3OCl; N = 37.67.

(*b*) Using alkali after washing down excess of chlorine, 0.6722 g. dissolved in 30.75 cc. of water; 1 cc. of this solution gave: (i) 5.1, (ii) 5.0, (iii) 5.2 (iv) 5.1 cc. N_2 at 33° and 760 mm. Found N = 24.91; calc. for $^2/_3$ N_2 = 25.11.

II. With potassium bromate and hydrochloric acid.

(*a*) Using alkali in the presence of bromine, 0.1907 g. was dissolved in 9.6 cc. of water; 1 cc. gave: (i) 7.00, (ii) 6.8, (iii) 6.9 cc. N_2 at 30° and 760 mm. Found N = 37.57; calc. for CH_6N_3OCl; N = 37.67.

(*b*) Using alkali after washing down excess of bromine, 0.6722 dissolved in 30.75 cc. of water; 1 cc. of this solution gave: (i) 5.6, (ii) 5.6, (iii) 5.6 cc. N_2 at 33° and 760 mm. Found N = 27.35; calc. for $^3/_4$ N_2 = 28.25.

III. With potassium iodate solution.

0.1680 g. dissolved in 9.65 cc. of water; 1 cc. of this solution gave: (i) 4.5, (ii) 4.6, (iii) 4.55 N_2 at 32° and 760 mm. Found N = 28.07; calc. for $^3/_4$ N_2 = 28.25.

IV. Bromine water.

0.1680 dissolved in 9.6 cc. of water; 1 cc. of this solution gave: (i) 4.5, (ii) 4.45, (iii) 4.6 N_2 at 32° and 760 mm. Found N = 27.89; calc. for $^3/_4$ N_2 = 28.25.

I am at present engaged in studying the behavior of thiosemicarbazide and carbohydrazide towards the above reagents, and the possibility of estimating chloric, bromic and iodic acids by means of semicarbazide.

CHEMICAL LABORATORY, PRESIDENCY COLLEGE,
CALCUTTA.

INDIRECT FORMATION OF DOUBLE SALTS.[1] V. THE DOUBLE PLATINIC, CUPRIC AND SILVER IODIDES OF SUBSTITUTED AMMONIUM BASES.

BY RASIK LAL DATTA AND TARAPADA GHOSH.

Received March 12, 1914.

In continuation of the researches on the indirect formation of double salts, it was thought desirable to test the further applicability of the indirect method used in the preparations of the double salts already described. It was found that this method was applicable not only to the formation of double salts which cannot be obtained by direct means, but also to the preparation of other salts which can be obtained by the direct method, *viz.*, the solution of the insoluble metallic component in the other soluble constituent and crystallization of the double salt from the solution. The preparation of double cupric iodides is not possible directly, since cupric iodide is not stable by itself and decomposes into cuprous iodide and iodine as soon as it is precipitated, or rather, liberated in chemical reactions. It is only when the indirect method is applied that the salt formation is successful. This, as has been pointed out before, is due to the fact that, when the cupric iodide is liberated in the presence of a large excess of ammonium iodide, it at once combines to form the double salt before it has time to decompose into its constituents. This behavior brings the conception of nascent molecules into prominence. The same reason applies to the formation of double carbonates of the alkaline earth metals and lead with potassium carbonate. These could not be prepared by the direct method, *viz.*, the solution of the carbonates of the alkaline earth metals and lead in potassium carbonate. For the preparation of these double salts, the indirect method was employed. This consisted in the precipitation of the carbonates of the alkaline earth metals and lead in the presence of a large excess of a strong solution of potassium carbonate; so that reaction took place between substances in the nascent state, and hence proceeded more readily. In addition to serving for the

---

[1] Previous communications on the subject:

I. "The Double Platinic and Cupric Iodides of Substituted Ammonium Bases," Datta, *J. Chem. Soc.*, **103**, 426 (1913).

II. "Double Carbonates of the Alkaline Earth Metals and Lead with Potassium Carbonate," Datta and Mukherjea, *Proc. Chem. Soc.*, **29**, 185 (1913).

III. "The Double Cadmic and Mercuric Iodides of Substituted Ammonium Bases," Datta, THIS JOURNAL, **35**, 949 (1913).

IV. "Iodoplatinates of Substituted Ammonium and Sulfonium Bases," Datta, THIS JOURNAL, **35**, 1185 (1913).