THE SULPHOHALIDES OF LEAD.

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WHEN hydrogen sulphide is allowed to come in contact with a solution of lead chloride in hydrochloric acid, a brick-red precipitate appears. This precipitate consists of a combination of lead sulphide with the chloride. Hünefeld[1] prepared and studied this red substance and ascribed to it the formula $3PbS.2PbCl_2$. He treated a dilute lead acetate solution with hydrochloric acid and added hydrogen sulphide to the solution.

Reimsch[2] later studied the same substance. Parmentier[3] considers the formula $PbS.PbCl_2$ more nearly correct as it would be analogous to the oxychloride, $PbO.PbCl_2$.

It is also possible to prepare a yellowish red sulphochloride by digesting freshly precipitated lead sulphide with a solution of lead chloride.

Lead sulphochloride is a rather unstable body. Hot water gradually extracts lead chloride from it, leaving the sulphide. Excess of hydrogen sulphide completely converts it into the pure black sulphide.

Lead bromosulphide, like the chlorosulphide, is brick-red in color. Parmentier, who first obtained it, states that it can be prepared more readily than the chlorosulphide, but it is similar in its properties to the chlorosulphide. It corresponds to the formula $PbS.PbBr_2$.

Various attempts had been made to prepare the analogous iodosulphide of lead, but on account of the insolubility of lead iodide in dilute hydriodic acid, the attempts were fruitless until the author[4] tried the action of a solution of hydrogen sulphide on a solution of lead iodide in potassium iodide. This method of procedure gives the lead iodosulphide brick-red in color, having a more yellow shade than the other sulphohalides but similar in all respects to these derivatives. This brick-red lead iodosulphide corresponds to the formula $PbS.4PbI_2$. It is a very unstable compound.

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[1] *J. prakt. Chem.*, **7**, 27.

[2] *Ibid.*, **13**, 130.

[3] *Compt. rend.*, **114**, 298.

[4] This Journal, **17**, 511.

While lead iodide is almost insoluble in dilute hydriodic acid, it dissolves readily in the stronger acid. When hydrogen sulphide gas is added to a solution of lead iodide in hydriodic acid, neither the sulphide nor the iodosulphide is obtained. If, however, an aqueous solution of hydrogen sulphide is added to the hydriodic acid solution of the iodide, yellow lead iodide is first precipitated by the dilution and appears as a fine crystalline precipitate. Further addition of hydrogen sulphide solution causes the conversion of the yellow iodide into the brick-red iodosulphide. This precipitate on analysis was found to correspond to the formula $PbS.4PbI_2$. We are therefore led to believe that whatever the method of preparation, the red iodosulphide of lead has always the same composition.

Thus far it has been impossible to obtain a lead fluorsulphide. The slight solubility of lead fluoride in water, and in the alkaline fluorides has thus far prevented its preparation. It has likewise been impossible to obtain a fluorsulphide by digesting lead fluoride with lead sulphide in a similar manner to that by which it is possible to prepare the chlorosulphide. Moreover, lead sulphide is insoluble in hydrofluoric acid while the other halogen acids readily dissolve the sulphide. Its preparation would appear improbable.

That these derivatives are possible under certain definite conditions and that these conditions must be adhered to, is evidenced by the fact that a too dilute solution of the lead salt in the halogen acid, or even a slight excess of hydrogen sulphide, causes the formation of pure black lead sulphide, which contains no halogen. On the other hand, since lead sulphide is soluble in the strong aqueous solutions of the halogen acids, it is impossible to prepare these compounds by means of the addition of hydrogen sulphide to the strong acid solutions. It is necessary that certain conditions be observed in order to make the existence of these compounds possible.

That such conditions are necessary can be shown in a very simple manner. Either precipitated lead sulphide or the natural sulphide, galena, dissolves readily in the strong aqueous halogen acids with evolution of hydrogen sulphide gas and the formation of the corresponding halide. With a strong halogen acid, hydrogen sulphide is liberated and when sufficient liquid is present, part of the gas remains in solution. The addition of water to this solution gives, when proper conditions are established, the brick-red compound which might be considered as an intermediate product between the halide and the sulphide.

The three sulphohalides of lead are all readily prepared by this means. The bromosulphide is the most stable of the compounds and it can be prepared in a very striking manner by treating 2 to 3 grams of lead sulphide or galena with 10 to 15 cc. of strong hydrobromic acid, and diluting with a large volume of water. The acid should be allowed to act until hydrogen sulphide is freely evolved. The solution will retain sufficient gas so that when a liter of water is quicky added, the brick-red bromosulphide appears.

Hydrochloric and hydriodic acid solutions of galena, when freshly prepared and quickly diluted, behave in a similar manner. With the hydrochloric acid solution the conditions are better obtained when more acid is present than above noted for hydrobromic. When this solution is diluted with water, the bright red chlorosulphide appears, sometimes preceded by the white chloride. Excess of water invariably causes the chlorosulphide to change to the black lead sulphide, which is the final product. The formation of the bromosulphide by this method makes an extremely beautiful experiment; the simple addition of water to a freshly prepared solution of galena in hydrobromic acid gives bright yellow bromide which almost instantly changes to a bright red. On further diluting and allowing to stand, the black sulphide is obtained. These changes seem to indicate that the formation of these compounds is due to certain definite relations between the halide and hydrogen sulphide in a solution of the corresponding halogen acid.

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A MODIFICATION OF THE SULPHURIC ACID TEST FOR FORMALDEHYDE IN MILK.

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WHILE estimating nitrogen, by the Kjeldahl-Gunning method, in a number of samples of milk which had been preserved by the addition of a small quantity of formaldehyde, a peculiar violet coloration of the potassium sulphate crystals and sulphuric acid, surrounding them, was noticed. Especially was