

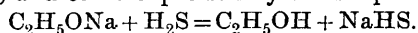
LXVI.—*The Action of Hydrogen Sulphide on the Alkyl-oxides of the Metals. Part I. Sodium and Potassium Ethoxides.*

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THE work described in this paper forms the first portion of an investigation of certain metallic salts, which, owing to hydrolysis, cannot be obtained from aqueous solution, and up to the present have only been prepared in the dry way. The sulphides of chromium, aluminium, and ferric iron are examples of such compounds, and it is doubtful if these substances have ever been obtained in the pure state.

The possibility of preparing these sulphides from alcoholic solution by precipitation with either hydrogen sulphide or an alcoholic solution of sodium sulphide suggested itself to the author, but it was necessary, in the first place, to find derivatives of the metals which were soluble in alcohol, and which, on decomposition according to the method indicated, would not give rise to products likely to react in any way on the sulphides, if the latter were formed.

The alkyloxides of the metals in question appeared to be suitable for trial in this way, but on endeavouring to ascertain if previous work had been done in this direction, the author was unable to find any record of the action of hydrogen sulphide, either on these compounds or on the alkyloxides of sodium or potassium. The action of certain other gases, such as carbon monoxide, on the alkyloxides of sodium and potassium is well known, and has been thoroughly investigated. When sodium is dissolved in absolute alcohol in such amount as to give a solution of sodium ethoxide of moderate concentration, and this solution is then saturated with dry hydrogen sulphide, no precipitate is formed, but on adding sufficient benzene or ether to the solution, a precipitate of practically pure anhydrous sodium hydrosulphide is obtained. A solution of potassium ethoxide, similarly treated, gives a precipitate of pure anhydrous potassium hydrosulphide. There is no indication of the formation of organic sulphur compounds, and from the results obtained under varied conditions, the reaction appears to be quantitative, and to be expressed by the simple equation:



In view of the considerable amount of work already done on the sulphides and hydrosulphides of the alkali metals, and the difficulty experienced in obtaining the anhydrous compounds in the pure

state, the investigation of this apparently simple method of preparation seemed of importance.

Gay Lussac and Thénard made an attempt to obtain the anhydrous hydrosulphides of sodium and potassium by the action of hydrogen sulphide on the heated metals. A brown mass was obtained, and to the sodium compound they ascribed the composition Na_3HS_2 . According to Sabatier, these products always contain polysulphides.

Sabatier (*Ann. Chim. Phys.*, 1881, [v], **22**, 1) states that anhydrous sodium hydrosulphide is obtained by saturating crystals of sodium sulphide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, with hydrogen sulphide, and evaporating the solution obtained in a current of hydrogen sulphide. The product is described as a yellowish-white mass, nearly pure. Bloxam (*Trans.*, 1900, **77**, 763) found, however, that sodium sulphide was only slowly acted on by hydrogen sulphide in the solid state, and failed to obtain sodium hydrosulphide by this method.

From the foregoing evidence it seems practically certain that the pure hydrosulphides are unobtainable by any of the methods mentioned. Bloxam (*loc. cit.*) describes a method suggested by Dr. Scott for the preparation of anhydrous potassium hydrosulphide. Hydrogen sulphide was passed into rectified ether containing metallic potassium, and in this way the hydrosulphide was obtained pure as a pale yellow, crystalline powder.

The use of alcohol as a solvent for sodium hydroxide in the ordinary method for the preparation of sodium monosulphide is described by Böttger (*Annalen*, 1884, **223**, 335), but the resulting product was hydrated, owing to the formation of water by the action of hydrogen sulphide on the sodium hydroxide in solution.

The author of the present paper has also investigated the action of hydrogen sulphide on the pure dry ethoxides of sodium and potassium. In each case reaction takes place in the cold, the sole products being alcohol and the hydrosulphides of the metals. There is no evidence of the formation of the monosulphides, as is the case when hydrogen sulphide is allowed to act on dry sodium hydroxide (Kircher, *Annalen*, 1839, **31**, 339).

The simple reaction whereby anhydrous sodium hydrosulphide is obtained in alcoholic solution will doubtless prove of considerable value in the preparation of organic sulphur compounds, where, ordinarily, crystalline sodium hydrosulphide is employed. In these cases the presence of water of hydration, and often of free sodium hydroxide in the salt, occasions loss through hydrolysis.

EXPERIMENTAL.

For analysis of the hydrosulphides dealt with in this section, gravimetric methods were employed in every case. Owing to the extremely hygroscopic character of these substances, it was found necessary to carry out weighing operations with special care and rapidity. Sulphur was estimated by oxidation with concentrated bromine water, and precipitation as barium sulphate. Sodium and potassium were estimated as sulphates, but before the addition of sulphuric acid to the substances they were treated with bromine water. Otherwise, the violent evolution of hydrogen sulphide on adding acid is liable to cause loss.

The action of hydrogen sulphide on sodium ethoxide in alcoholic solution can be illustrated very rapidly on a small scale by dissolving 0.5 gram of metallic sodium in about 10 c.c. of ethyl alcohol in a test-tube, adding an equal volume of dry benzene, and then passing in the gas. The solution becomes warm, and after a short time a precipitate begins to separate out, becoming thicker as the passage of the gas is continued. When the solution is saturated with the gas, the product is rapidly collected, washed with a little ether, and then placed immediately in a desiccator and allowed to remain in a vacuum. The substance obtained by this method possesses a light buff tint, is extremely deliquescent, and when freshly prepared dissolves in hydrochloric acid to a clear solution with violent evolution of hydrogen sulphide.

A similar experiment with potassium ethoxide gives a product quite analogous to the sodium compound, but only very faintly buff-coloured.

If the solution, after collecting the precipitate, is treated with a further quantity of benzene, or, better, with dry ether, a considerable precipitate is obtained, which is identical in properties and composition to the first product. It was obvious that in order to obtain a maximum yield, careful regulation of the relative amounts of alcohol and precipitant would be necessary.

Action of Hydrogen Sulphide on a Saturated Solution of Sodium Ethoxide.

Two grams of sodium were added to 20 c.c. of absolute ethyl alcohol (freshly distilled over lime) in a small flask fitted to a reflux condenser. When sodium ethoxide began to separate out, more alcohol was added, until just sufficient was present to retain the product in solution at room temperature. Forty c.c. of alcohol were required. The flask was then furnished with a tightly-fitting

cork, through which passed a delivery tube and an exit tube with calcium chloride bulb attached. Hydrogen sulphide, washed by passing through water, and then dried over a long column of calcium chloride, was passed into the solution in a rapid stream, and after a few minutes a fine crystalline precipitate began to form in the solution, and increased with continued passage of the gas.

When the solution was saturated with hydrogen sulphide, the precipitate was collected as rapidly as possible, sprayed with absolute alcohol, and kept in a vacuum over calcium chloride. The substance thus obtained was buff-coloured. It weighed 0.25 gram. For analysis a larger quantity was prepared under precisely similar conditions:

0.2514 gave 0.3142 Na_2SO_4 . Na=40.48.

0.2641 ,, 1.0721 BaSO_4 . S=55.84.

NaHS requires Na=41.07; S=57.14 per cent.

The product is slightly impure sodium hydrosulphide, and there is no indication that double compounds of sodium ethoxide and monosulphide are formed in the course of the reaction, as the precipitate does not dissolve on continued passage of the gas, but increases in amount (compare Bloxam, *loc. cit.* Preparation of sodium monosulphide). This substance was found to contain a trace of iron, which appears to be an impurity of metallic sodium, and probably causes the coloration of the substance.

The filtrate from the above product was quickly transferred to a dry flask, and 50 c.c. of pure dry ether were added. A pure white, crystalline precipitate was immediately formed. The flask was corked and kept in a desiccator until the precipitate had settled, and a further quantity of ether was added, this operation being repeated until the addition of ether produced only a slight turbidity in the supernatant liquid: 110 c.c. of ether were used. The product was collected, washed with dry ether, and kept in a vacuum for several hours. Further addition of ether to the filtrate only produced a faint cloud.

The substance was a pure white, granular powder:

0.1598 gave 0.2010 Na_2SO_4 . Na=40.74.

0.1795 ,, 0.7398 BaSO_4 . S=56.71.

NaHS requires Na=41.07; S=57.14 per cent.

4.31 Grams were obtained; thus the total yield of sodium hydrosulphide from 2 grams of sodium = 4.31 + 0.25 = 4.56. Theory requires 4.86 grams. (A slight loss occurred through a little of the substance sticking to the sides of the flask; owing to its hygroscopic nature it was neglected.) The reaction, therefore, appears

to be quantitative, but the amount of ether required to precipitate the product completely is considerable. The ether is, however, very easily recoverable in the pure state.

The freshly prepared compound dissolved to a clear solution in hydrochloric acid, with vigorous evolution of hydrogen sulphide. After the substance had been kept for a few days, a solution so obtained was faintly opalescent, owing to separation of a trace of sulphur derived from products of slight oxidation. The substance is extremely soluble in water, and moderately so in alcohol. On allowing it to remain in the air for a few moments, a faint odour of hydrogen sulphide is noticeable. It deliquesces very rapidly, forming an almost colourless solution, from which colourless crystals separate out after a few days (compare Bloxam, *loc. cit.*).

Action of Hydrogen Sulphide on Sodium Ethoxide Suspended in Benzene.

For the preparation of larger quantities of sodium hydrosulphide, it was found more convenient to carry out the reaction in presence of the precipitant. Ether is unsuitable for this purpose on account of its volatility, but good results were obtained with benzene.

One hundred c.c. of pure dry benzene were mixed with 10 grams of absolute alcohol in a flask fitted with a reflux condenser, the inner tube of which was ground to fit the mouth of the flask. Five grams of metallic sodium in small pieces were introduced into the mixture, which was then heated to boiling on the water-bath. As the reaction slowed, further quantities of alcohol were added, until the sodium was completely dissolved. On allowing to cool, sodium ethoxide separated out as a gelatinous mass. Dry hydrogen sulphide was passed in, and reaction took place immediately with considerable evolution of heat and the formation of a fine crystalline precipitate of sodium hydrosulphide. The passage of the gas was continued until the precipitate had settled, and no further turbidity was produced in the supernatant liquid. The product was collected, washed with dry benzene, and finally with dry ether, which caused a slight precipitation in the filtrate. After remaining for one day in a vacuum, it weighed 11.92 grams. Theory requires 12.15 grams. Yield = 98.1 per cent.:

0.2720 gave 0.3386 Na_2SO_4 . Na = 40.32.

0.2429 ,, 0.9992 BaSO_4 . S = 56.49.

NaHS requires Na = 41.07; S = 57.14 per cent.

The substance was slightly buff-coloured, but in all other respects identical with that obtained by precipitation with ether. It was found somewhat difficult to remove the last traces of benzene from

the product, which still possessed a faint odour of the hydrocarbon after remaining in a vacuum for a week. It was finally expelled by heating the substance to 110° in a slow current of hydrogen.

Action of Hydrogen Sulphide on Solid Sodium Ethoxide.

One gram of metallic sodium was dissolved in absolute alcohol contained in a small distillation flask of known weight fitted to a condenser. Excess of alcohol was distilled off, and the product then heated gradually to 180° in an oil-bath, in a current of dry hydrogen, until no more alcohol passed over. Sodium ethoxide was obtained in this way as a perfectly homogeneous, white mass. The contents of the flask were then allowed to cool in hydrogen, and when quite cold, dry hydrogen sulphide was passed into the flask. The ethoxide immediately began to assume a light buff tint, which quickly spread over its surface. The mass became hot, alcohol was evolved, and condensed on the walls of the flask. After passage of the gas had continued for about twenty minutes, it was possible to detach a considerable portion of the substance from the glass by tapping the flask. The product was very light pink, and appeared homogeneous, except where it had been in contact with the glass; these portions were dirty white on the surface.

The substance was heated gradually to 90° in a current of hydrogen. Alcohol commenced to distil over, and continued up to 120° . At this temperature the escaping gas was tested, and found to contain traces of hydrogen sulphide, and in order to prevent possible decomposition of sodium hydrosulphide at higher temperatures, the heating was continued in a slow stream of hydrogen sulphide to 180° , during which the last traces of alcohol were driven over. The flask was then allowed to cool, tightly stoppered, and weighed. Weight of product = 2.41 grams. Theory requires 2.43 grams for 1 gram of sodium:

0.2866 gave 0.3751 Na_2SO_4 . Na = 42.43.

0.1656 ,, 0.2170 Na_2SO_4 . Na = 42.44.

0.3506 ,, 1.4205 BaSO_4 . S = 55.64.

NaHS requires Na = 41.07; S = 57.14 per cent.

The substance dissolved in water, giving a faintly yellow and slightly cloudy solution. The small amount of impurity present appeared to be derived partly from the glass of the distillation flask, but the high figure obtained for sodium suggests that the reaction was not quite complete. The ease with which sodium ethoxide is acted on by moisture and carbon dioxide rendered it necessary to carry out all the operations in one vessel without admitting air, but it is then difficult to bring the substance into

thorough contact with the current of gas, as it adheres closely to the walls of the flask.

The results obtained with potassium ethoxide agree with those for the sodium compound, the product being in every case anhydrous potassium hydrosulphide. The slight coloration present in some of the sodium hydrosulphide preparations was either much fainter or absent altogether in the case of the corresponding products obtained from metallic potassium. The figures obtained on analysis of these products suggest a rather higher degree of purity for ordinary commercial metallic potassium than for metallic sodium.

Action of Hydrogen Sulphide on a Saturated Solution of Potassium Ethoxide.

2.2 Grams of metallic potassium were dissolved in 15 c.c. of absolute ethyl alcohol, and dry hydrogen sulphide was passed in until the solution was saturated. The crystalline product which separated was collected, sprayed with absolute alcohol, and dried in a vacuum. Unlike the corresponding product obtained from sodium, it was pure white. When examined microscopically it was seen to consist of very minute, but well defined, cubes. Weight of product = 1.93 grams:

0.2382 gave 0.2872 K_2SO_4 . K = 54.04.

KHS requires K = 54.16 per cent.

The filtrate was treated with 75 c.c. anhydrous ether, and the white, crystalline precipitate collected, washed, and dried in a vacuum:

0.3763 gave 0.4534 K_2SO_4 . K = 54.01.

0.2969 „ 0.9561 $BaSO_4$. S = 44.22.

KHS requires K = 54.17; S = 44.44 per cent.

Total yield of potassium hydrosulphide = 3.91 grams. Theory requires 4.04 grams. The properties of the substance are similar to those of the sodium compound, but it appears to be even more hygroscopic.

Action of Hydrogen Sulphide on Solid Potassium Ethoxide.

This reaction was carried out exactly as in the case of the sodium compound. Reaction took place immediately in the cold, and was more vigorous than with sodium ethoxide. The flask became hot, and a considerable quantity of alcohol distilled over. The product remaining after all the alcohol had been driven off possessed a very faint buff tint, and appeared more homogeneous

than the corresponding sodium compound. It dissolved in water and hydrochloric acid, giving clear solutions:

0.2122 gave 0.2535 K_2SO_4 . $K=53.55$.

0.1955 „ 0.6196 $BaSO_4$. $S=43.62$.

KHS requires $K=54.17$; $S=44.44$ per cent.

When the hydrosulphides are heated in the air they become yellow, and finally fuse to a dark red liquid. On cooling, a deep yellow solid is formed, which is soluble in water, giving a yellow solution, and is at once decomposed by hydrochloric acid, with vigorous evolution of hydrogen sulphide and precipitation of sulphur. Bloxam (*loc. cit.*) investigated the action of heat on potassium hydrosulphide, and determined its melting point, but there appear to be several matters in connexion with this action which require explanation, and further investigation is at present being carried out by the author.

The possibility of preparing the anhydrous monosulphides of sodium and potassium by the action of the hydrosulphides on the ethoxides in alcoholic solution, analogous to the ordinary preparation in aqueous solution, is obvious, and it is hoped to deal with this portion of the subject in a later paper.

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