CCLXIV.—*The Polysulphides of the Alkali Metals.*
Part II. The Polysulphides of Potassium.

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IN a previous paper (Rule and Thomas, this vol., p. 177) were described the results of an investigation of the action of sulphur on alcoholic solutions of pure sodium hydrosulphide. It was shown that the reaction provided a simple and certain means of preparing sodium tetrasulphide in the pure anhydrous state, and further, that the polysulphide product obtained as a result of the reaction under varied conditions consisted almost entirely of the tetrasulphide.

It has been pointed out by several authors that much of the earlier work on the polysulphides of sodium and potassium is quite untrustworthy, but descriptions of series of these compounds based on the results of such work still appear in many text-books. In the case of potassium the highest polysulphide obtainable is generally

accepted to be the pentasulphide, which seems to be fairly well characterised.

Bloxam (*Thesis*, London, 1898; T., 1900, **77**, 753), in criticising the work of previous authors, has shown that by the methods usually adopted it is impossible to obtain pure polysulphides in the solid state. When aqueous solutions of the monosulphides are employed the resulting product always contains thiosulphate, and Bloxam attributed the formation of that compound to the presence of hydroxides in the solution as a result of the hydrolysis of the monosulphides.

Bloxam investigated the action of sulphur on aqueous solutions of potassium hydrosulphide, which is only very slightly hydrolysed (compare Walker, *Zeitsch. physikal. Chem.*, 1900, **32**, 137). Although he does not appear to have succeeded in isolating any compound of undoubted chemical individuality, yet he established the fact that within certain limits the sulphur added to the solution reacted with a portion only of the hydrosulphide, and the resulting polysulphide product was richer in sulphur than a polysulphide corresponding to the amount of sulphur added. It is probable that in aqueous solution there is a tendency for the formation of one predominating polysulphide, and this would account for Bloxam's results, as that author has pointed out. In the case of alcoholic solutions the work described in the present paper proves that the action of sulphur tends undoubtedly to the formation of one polysulphide only, namely, the pentasulphide, which has been isolated in the pure anhydrous condition.

The preparation of anhydrous potassium pentasulphide by the action of sulphur on potassium in liquid ammonia has also been described by Hugot (*Compt. rend.*, 1899, **129**, 388), but no account is given of the properties of the product.

Action of Sulphur on Alcoholic Solutions of Potassium Hydrosulphide.

In a previous paper (T., 1911, **99**, 558) one of us described the preparation of pure potassium hydrosulphide by the action of hydrogen sulphide on an alcoholic solution of potassium ethoxide. In the work now under consideration solutions prepared in that way were used throughout, and the actual experimental details were precisely similar to those already described in the paper on the polysulphides of sodium (*loc. cit.*), to which reference may be made.

A series of experiments was carried out in which quantities of sulphur corresponding with possible polysulphides of potassium from the di- up to the hexa-sulphide were added to alcoholic solu-

tions of the hydrosulphide of the same concentration throughout. Since the only polysulphide product obtained as a result of these experiments was the pentasulphide the preparation and properties of that compound will be dealt with in the first place.

Potassium Pentasulphide.

One gram of potassium was dissolved in 15 c.c. of absolute ethyl alcohol,* and the solution was saturated with dry hydrogen sulphide. 1.64 Grams of finely ground recrystallised rhombic sulphur were added, and the solution was boiled gently on a water-bath for about one hour, a rapid current of dry hydrogen being passed through it. On the addition of the sulphur a vigorous reaction at once took place even in the cold with evolution of hydrogen sulphide, and the solution became deep red. The sulphur dissolved, and after a short time a bright orange-red, crystalline solid separated out. The solution was concentrated to about 5 c.c., the product collected on a filter, sprayed with alcohol, and kept in a vacuum over phosphoric oxide.

The dry product consisted of a mass of glistening crystals, and appeared to be perfectly homogeneous. The yield was 2.5 grams, that is, 82 per cent. of the theoretical amount:

0.3506 gave 0.2560 K_2SO_4 . $K = 32.73$.

0.3475 „ 0.1850 S. $\dagger(S) = 53.23$.

0.3027 „ 1.4742 $BaSO_4$. $S = 66.90$.

K_2S_5 requires $K = 32.77$; $(S) = 53.78$; $S = 67.22$ per cent.

Potassium pentasulphide is extremely hygroscopic, and is rapidly oxidised on exposure to the air, with liberation of sulphur. It dissolves readily in water to form a clear, deep orange solution, which becomes dark red on heating. It is only sparingly soluble in alcohol, forming a red solution, which also becomes darker on heating. Both the aqueous and alcoholic solutions soon begin to deposit sulphur when allowed to remain in the air. Biltz and Dorfürst (*Ber.*, 1905, **43**, 53) state that rubidium pentasulphide is at once decomposed on treatment with water, whilst caesium pentasulphide is apparently not affected. It is noteworthy that potassium pentasulphide should be more stable in this respect than the corresponding rubidium compound.

On heating in a capillary tube the substance begins to darken at about 130° , and at 182° becomes quite black, this change being sharply marked; it begins to sinter at 200 – 205° , and melts not very sharply at about 220° . On cooling the substance passes through

* Commercial absolute alcohol was shaken for two days over freshly prepared quicklime, boiled over quicklime and then distilled.

† (S) indicates "polysulphide sulphur."

the same series of colour changes in the reverse order, and finally assumes its original appearance. No deposit of sulphur was noticed on the walls on the tube, and the solidified product dissolved to a perfectly clear solution in cold water. Potassium pentasulphide can therefore be fused without decomposition.

The majority of organic solvents are without action on the pentasulphide, but a very striking behaviour may be noted in the case of pyridine. On treating the substance with pure pyridine the latter is coloured an intense brownish-red, and on heating the mixture the liquid becomes quite opaque. A definite reaction appears to take place, and the observed effect may be due to the formation of an additive compound, but apparently very little of the pentasulphide dissolves in the pyridine. With sodium tetrasulphide the action of pyridine is even more marked, the solvent being at once coloured intensely green and the solid slowly changing in colour to bright yellow. This action is being further investigated.

Nitrobenzene, on treatment with the pentasulphide, is coloured magenta in the cold. On heating the colour fades, and the solid can be fused below the liquid; on cooling again the colour returns, and the pentasulphide remains apparently unchanged. This behaviour with nitrobenzene is similar to that of rubidium pentasulphide, as noted by Biltz and Dörfurt (*loc. cit.*).

When shaken with alcohol at the ordinary temperature the pentasulphide forms a well-defined, bright yellow alcoholate, which crystallises in small, monoclinic prisms.

From a consideration of the results obtained by numerous workers in this field it appears to have been generally assumed that a series of polysulphides from the di- up to the penta-sulphide could be prepared by adding the theoretical amount of sulphur to aqueous solutions of the mono- or hydro-sulphide. The results obtained by the use of alcoholic solutions of sodium hydrosulphide and varying quantities of sulphur have already been dealt with in detail (*loc. cit.*), and it is therefore only necessary to mention briefly the nature of the products of the action of sulphur on alcoholic solutions of potassium hydrosulphide. With the proportions for the disulphide a small quantity of pentasulphide separated from the hot solution, and on cooling a yellow product was obtained, which was obviously not homogeneous, and consisted of a mixture of pentasulphide and unchanged hydrosulphide. A similar result was obtained when proportions for the trisulphide were used, but the yield of pentasulphide was greater.

With the proportions for the tetrasulphide a comparatively good

yield of pure pentasulphide was obtained, separating out from the hot solution. With the proportions for a possible hexasulphide it was found that all the sulphur added dissolved in the first place, and the solid product consisted of the pentasulphide mixed with a little sulphur, which remained undissolved on treating the product with water. The solution from which this product separated gave a copious precipitate of sulphur on treatment with water, whereas in all other cases mentioned the solution remained perfectly clear.

The results are therefore very similar to those obtained in the case of sodium, except that here there is not the slightest indication of the formation of higher polysulphides when larger quantities of sulphur than that corresponding with the pentasulphide are used. The moderate solubility of potassium pentasulphide in alcohol has already been mentioned, and it might therefore be assumed that this compound is the saturation product, and that in the solution itself a series of polysulphides might exist in equilibrium according to the conditions of experiment. In order to test the accuracy of this assumption and to gain some idea as to the nature of the substances in solution after the action of sulphur on the hydrosulphide, a series of measurements similar to those described in connexion with the polysulphides of sodium was carried out.

It will be seen that according to the equation:

the amount of hydrogen sulphide formed is strictly proportional to the amount of hydrosulphide involved in the reaction. By determining the amounts of hydrogen sulphide evolved in the course of a series of reactions with different amounts of sulphur it is possible to decide whether (1) a series of polysulphides is formed according to the amount of sulphur added, (2) only one polysulphide is formed independent of the amount of sulphur present, or whether (3) an equilibrium mixture of several polysulphides is formed.

The apparatus used and the method adopted were exactly similar to those employed in the case of sodium (*loc. cit.*), except that ammoniacal hydrogen peroxide was used throughout as the absorbent for hydrogen sulphide instead of bromine. Owing to the sparing solubility of potassium pentasulphide in alcohol, and the necessity of preventing any solid product from separating out during the experiment, it was necessary to work with fairly dilute solutions of the hydrosulphide, and an error is thereby introduced owing to the fact that the hydrosulphide undergoes slight alcoholysis with the formation of hydrogen sulphide. Since it was necessary to carry out the determination in a stream of hydrogen the equilibrium was constantly disturbed, and in consequence a

certain amount of hydrogen sulphide derived from this alcoholysis was driven over into the absorbent. In consequence the results obtained are too high. For the purpose of ascertaining the magnitude of this error, blank experiments, in which the conditions approximated as nearly as possible to those employed in the actual determinations, were performed first of all with solutions of potassium hydrosulphide of varying concentration. Using a normal solution it was found that after boiling in a current of hydrogen for forty-five minutes the amount of hydrogen sulphide evolved and calculated for 72 grams of potassium hydrosulphide was 0.54 gram; a 0.5*N*-solution under similar conditions gave 1.2 grams.

It will be seen that the amount of unchanged hydrosulphide remaining in solution decreases progressively with addition of sulphur, and therefore the error decreases as the amount of sulphur increases. In order to overcome this error as far as possible the concentration of the hydrosulphide solutions used was varied from *N* to 0.25*N*, the effect of this being to keep the solutions nearly saturated with respect to the pentasulphide formed, assuming that to be the chief product of the reaction, throughout the series of determinations.

The results are expressed graphically in the diagram; the numbers in brackets at the various points on the curve indicate the concentrations of the hydrosulphide solutions in terms of normality.

The results show that there is a gradual increase in the amount of hydrogen sulphide evolved with increase in the amount of sulphur added. In the diagram the theoretical straight lines are shown which would indicate the values for the tetrasulphide and pentasulphide if these were the only polysulphides respectively formed in the course of the reaction.

The curve at first approximates very closely to the values for the tetrasulphide, but then bends away and eventually crosses the pentasulphide line not far away from the maximum, after which the values become practically constant. Taking into consideration the effect of alcoholysis it may be stated that all the values on the left-hand branch of the curve lie below the tetrasulphide line. Although the lower values possibly indicate the presence of polysulphides lower than the pentasulphide in the solution, and more especially of the tetrasulphide, it must be noted that unchanged hydrosulphide still remains in solution below the pentasulphide stage, and it is not until the amount of sulphur corresponding with the pentasulphide is present that the amount of hydrogen sulphide evolved is approximately equal to the maximum obtained in the series of determinations.

It is clear that when quantities of sulphur less than those corre-

sponding with the tetrasulphide are used, very little di- or trisulphide, if any, can be formed, otherwise the values for hydrogen sulphide at these stages would be much higher. On the other hand, since the value at the pentasulphide stage is very near the theoretical maximum for hydrogen sulphide there is no indication of the presence of any higher polysulphides in solution (compare the curve for sodium hydrosulphide, *loc. cit.*). As a result of this investigation, therefore, as well as from the results of experiments in which the solid was allowed to separate out, it is fair to conclude that the chief product of the action of sulphur on potassium hydrosulphide under the conditions described is the pentasulphide, and at the same time it is obvious that it is impossible to obtain

the lower polysulphides simply by adding the equivalent quantity of sulphur to solutions of the hydrosulphide.

Solubility of Sulphur in Alcoholic Solutions of Potassium Hydrosulphide.

It has already been shown by Küster and Heberlein (*Zeitsch. anorg. Chem.*, 1905, **43**, 53) that aqueous solutions of sodium monosulphide are able to dissolve considerably more sulphur than is represented by any polysulphide hitherto isolated. The present authors have also shown (*loc. cit.*) that alcoholic solutions of sodium hydrosulphide under certain conditions dissolve sulphur to an extent represented by the formula $Na_2S_{8.9}$. A similar determination was made in the case of potassium hydrosulphide. It has been pointed out above that the solution is capable of dissolving at least

a proportion of sulphur corresponding with a possible hexasulphide, although such a product does not separate out.

A 0.25*N*-solution of the hydrosulphide was shaken with excess of sulphur in a flask in a thermostat at 25° for forty-eight hours, a continuous current of dry hydrogen being passed through the solution. The solution was then allowed to settle, and a portion was removed by means of a pipette, introduced into bromine water, made up to 1 litre, and the potassium and sulphur determined in aliquot portions:

250 c.c. gave 0.1247 K_2SO_4 . $K=0.0559$.

250 „ „ 1.0774 $BaSO_4$. $S=0.148$.

Atomic ratio, $K=1:S=3.23$, corresponding with $K_2:S_{6.46}$.

In the case of sodium hydrosulphide, using a 2*N*-solution at 25°, the ratio found was 2 : 6.36, and at 81° it was 2 : 6.9, but the figure for the higher temperature is rather difficult to determine with accuracy.

The addition of water to these solutions resulted in a copious precipitation of sulphur, and the same holds good for all solutions containing sulphur in proportions higher than that corresponding with the pentasulphide. It must be noted that in these experiments the solubility of sulphur in alcohol is not taken into account, but in any case it is so small as to have very little effect on the results.

Action of Metallic Potassium on Alcoholic Solutions of the Pentasulphide.

When alcoholic solutions of sodium tetrasulphide are treated with metallic sodium, reduction of the polysulphide takes place, and practically pure sodium disulphide separates out. A series of experiments was performed in order to determine if metallic potassium had a similar action on the pentasulphide. Reduction certainly takes place, but in no case were the products obtained individual compounds, but rather mixtures of lower polysulphides with unchanged pentasulphide. When excess of potassium was used the solution became paler in colour, and a yellow product separated out, which on analysis approximated to the trisulphide, but the figure for polysulphide sulphur was too high.

In other experiments with more dilute solutions and varying amounts of potassium the products always contained unchanged pentasulphide, which appears to be "salted out" from the solution by the potassium ethoxide formed. In all cases the figure for polysulphide sulphur was higher than that required for the trisulphide. The method therefore does not provide a means of arriving at a definite lower polysulphide as in the case of sodium, and consider-

ing the sensitive nature of the products separation of the constituent compounds would be a difficult operation.

General Conclusions.

Although it cannot be claimed that the results of this investigation throw any further light on the actual constitution of the polysulphides, yet it may afford some evidence as to the extent to which sulphur can be taken up by any one member of the series of alkali metals to form a stable polysulphide. Biltz and Dorfürt (*loc. cit.*; *Zeitsch. anorg. Chem.*, 1906, **48**, 297; **50**, 67) were successful in obtaining both the tetra- and penta-sulphides of rubidium and caesium by the action of sulphur on aqueous solutions of the monosulphides. These compounds are perfectly well defined, and, moreover, the authors mentioned were able to show the existence of hexasulphides which were characterised thermo-analytically in the course of a freezing-point-curve determination. It is hoped later to give the results of a similar determination for potassium-sulphur and sodium-sulphur, but in the meantime it may be noted that no evidence has been obtained in the course of the authors' experiments of the existence of potassium hexasulphide.

Taking into consideration the results of the work on potassium, rubidium, and caesium, we are able to recognise three definite and stable pentasulphides exhibiting a gradation in respect of certain properties, for example, solubility. The solubility in alcohol decreases with increase in atomic weight of the alkali metal, and it is fair to assume that the solubility in water would vary in the same direction, thus bringing these compounds into line with other series of salts of the same metals, such as the alums, platini-chlorides, etc.

In the case of sodium we find that the highest stable polysulphide is the tetrasulphide, and although under certain conditions there is a tendency to form higher polysulphides, yet there is no definite evidence of the existence of a pentasulphide in the solid state, although the $S_5^{=}$ anion may be present in solution.

Practically nothing is known concerning polysulphides of lithium, although a disulphide is supposed to exist.

It would be interesting to determine if, by working with alcoholic solutions of rubidium and caesium hydrosulphides, the hexasulphides of these metals would separate out as stable compounds in the solid state, and the authors hope to carry out this investigation very shortly.

The fact that alcoholic solutions of sodium tetrasulphide and potassium pentasulphides are still able up to a certain point to dissolve further quantities of sulphur demonstrates the tendency of

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the sulphur complex in each case to combine with more sulphur. At the same time, however, this additional sulphur is apparently in a looser state of combination than that in the stable complex itself, since it is precipitated on the addition of water to the solution. It is possible that the tetrasulphide complex in the case of sodium, and the pentasulphide complex in the case of potassium represent the limits within which ordinary valency considerations apply, and that the sulphur which dissolves over and above these stages may be loosely associated to the complex as a result of the residual affinity exerted by the latter.

These facts taken in conjunction with the work on rubidium and caesium point to the distinct influence of the metal itself on the number of atoms in the stable sulphur complex, and this view is also taken by Biltz and Dörfurt, who apply the well-known electro-affinity theory of Abegg and Bodländer (*Zeitsch. anorg. Chem.*, 1899, **20**, 457) to account for the formation of higher polysulphides of the alkali metals of higher atomic weight.

Abegg and Bodländer show that where the ionising tendency (Ionisierungstendenz) of the metal is considerable that tendency is imparted to the anion which may normally show a weak ionising tendency. The anion, in order to "strengthen" itself, then tends to combine with other atoms or groups to form a complex. The ionising tendency of the alkali metals is shown to increase with increase of atomic weight, and Biltz and Dörfurt apparently consider that, in the case of the polysulphides, as the atomic weight of the metal increases there will be an increase in the number of sulphur atoms which go to make up the highest stable complex.

On the other hand, Hamburger and Abegg (*Zeitsch. anorg. Chem.*, 1906, **50**, 437) in discussing the results of an investigation of the polyiodides of the alkali metals consider that in solution ions of different degrees of complexity are present, and that the particular polyiodide which separates out depends entirely on the particular ionic combination the solubility product of which is first exceeded. Moreover, it does not follow that the compound which separates out will represent a combination of the cation with the anion present in greatest concentration. The fact that the higher polyiodides are more readily formed as we pass up the series of alkali metals from lithium to caesium is explained on the ground that the solubilities of the higher polyiodides decrease in the same order, like the platinichlorides, etc.

Abegg and Bodländer have shown that this inverse order of solubility is frequently exhibited in the case of strong anions in combination with increasingly strong cations, and a normally weak anion becomes stronger owing to addition resulting in the formation

of complexes, a fact which is in agreement with the electro-affinity theory.

It will be seen that Hamburger and Abegg (*loc. cit.*), in dealing with the polyiodides, and in referring also to the work of Biltz and Dörfurt, do not consider that the cation has a definite influence on the particular number of atoms taken up by the anion to form a complex, but only on the formation of complexes in general, the degree of the substance separating out depending on solubility conditions.

So far as the polysulphides are concerned, the work of the present authors does undoubtedly show the tendency for the formation of one particular polysulphide ion in greatly predominating amount, in the case of sodium the tetrasulphide ion, and in that of potassium the pentasulphide ion. At present, however, further considerations must be withheld until data are collected sufficient to test these conclusions.

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