

CCLXVIII.—*The Polysulphides of the Alkali Metals.*  
*Part IV. Miscellaneous Reactions. Part V.*  
*Discussion of Molecular Structures.*

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AN attempt has been made systematically to investigate the polysulphides of the alkali metals (*J.*, 1930, 1473; this vol., pp. 413, 1304), and certain additional experimental data are here presented, which, although not included in the earlier papers in this series, are necessary before a review of the whole subject (see Part V, p. 1986) can be made.

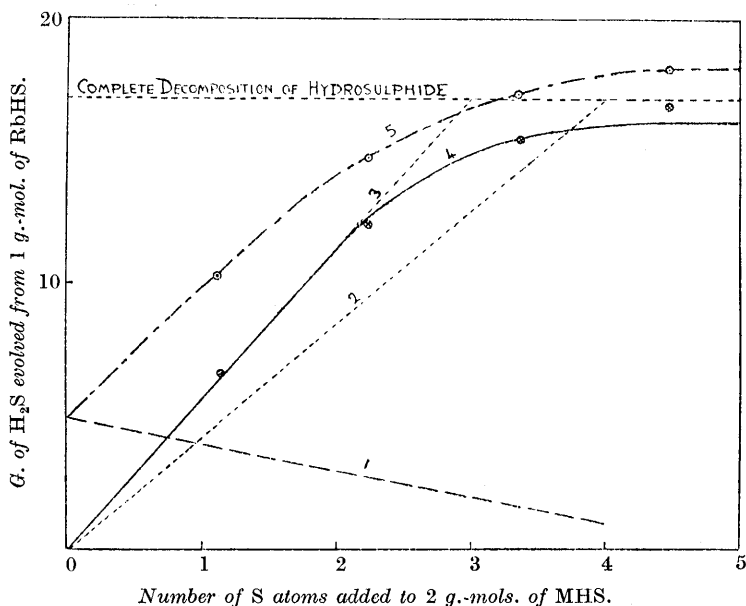
(I) *The Reaction between Rubidium Hydrosulphide and Sulphur.*—This reaction has not previously been examined. The method employed was to measure the amount of hydrogen sulphide evolved when various proportions of sulphur were dissolved in a solution of rubidium hydrosulphide. Table I shows that the hydrosulphide suffered considerable hydrolysis, and in interpreting the results this must receive due consideration. An accurate correction is not obtainable, but an approximate one may be deduced. Free hydrosulphide is strongly hydrolysed during the period of boiling (Table I, Expt. 1). At the same time, when excess of sulphur is added, the amount of hydrogen sulphide evolved is greater than that required for the complete transformation of the hydrosulphide to polysulphide, indicating that the polysulphides also suffer some hydrolysis. Hence, in any given experiment, the amount of hydrogen sulphide evolved is greater than that actually produced by the reaction of sulphur with hydrosulphide to a degree depending upon (a) the quantity of unchanged hydrosulphide, (b) the extent of the hydrolysis of the polysulphide produced. Factor (a) is at a maximum and (b) at a minimum when the hydrosulphide is boiled alone, and the converse obtains when all the hydrosulphide has been converted into polysulphide. Examination of the results in Table I shows that the whole of the hydrosulphide is not decomposed until 3 or 4 atoms of sulphur have been added. By assuming that the whole of the hydrosulphide is decomposed when 4 atoms of sulphur have been added (whether 3, 4, or 5 are taken makes little difference to the correction), a graph can be drawn (No. 1, Fig. 1) from which the necessary adjustment may be obtained.

The corrected curve is remarkably similar to that obtained in the case of potassium hydrosulphide and sulphur, and indicates the formation of only higher sulphides in the solution, doubtless either tetra- or penta- and, by analogy with potassium, most probably penta-sulphide.

(II) *The Action of Rubidium on Sulphur.*—By allowing molten rubidium to react with sulphur under toluene, we have now shown that the product of the reaction is rubidium tetrasulphide, thus bringing out the essential similarity between this element and potassium.

(III) *The Reaction of the Alkali-metal Polysulphides with Water.*—It is shown below that polysulphide materials of high sulphur con-

FIG. 1.



1. Correction for hydrolysis.
2. Theoretical evolution of hydrogen sulphide when only pentasulphide is produced.
3. Theoretical evolution of hydrogen sulphide when only tetrasulphide is produced.
4. Curve given by potassium hydrosulphide.
5. Uncorrected curve for rubidium hydrosulphide.
- ⊙ Corrected values for rubidium hydrosulphide.

tent, either in the solid state or in concentrated alcoholic solution, react with excess of water to give penta-sulphide solutions. In the case of lithium, and less so in the case of sodium, the solutions on standing tend to deposit sulphur, leaving solutions with a slightly lower ratio of sulphur to alkali metal than is required for  $M_2S_5$ .

(IV) *The Action of Carbon Disulphide on the Polysulphides.*—In an endeavour to prepare lower sulphides by the extraction of sulphur from higher sulphides, we treated various polysulphides with carbon disulphide, both in the liquid and in the vapour state. The pro-

cesses led to some removal of sulphur, but the issue was confused by the formation of thio- and perthio-carbonates.

(V) *The Action of Alkali-metal Polysulphides on Anhydrous Formic Acid.*—It seemed likely that the polysulphides of the alkali metals would behave precisely as ammonium pentasulphide (Mills and Robinson, J., 1928, 2326) towards formic acid. Our experiments so far indicate that this is not so, and it would appear that these compounds are not convenient sources of pure hydrogen persulphides.

(VI) *The Action of Alkali-metal Polysulphides on Certain Organic Liquids.*—Alkali-metal polysulphides react in the cold with many organic liquids, e.g., nitrobenzene, pyridine, aldehydes, and ketones, to give intensely coloured solutions, which, when filtered from unchanged polysulphide, deposit sulphur on standing, and appear to contain complexes of the polysulphide with the respective liquid. It is proposed to investigate this matter more fully.

#### EXPERIMENTAL.

(I) 1.5 G. of metallic rubidium dissolved in 100 c.c. of absolute alcohol were converted into the hydrosulphide by saturation with hydrogen sulphide, excess of the gas being removed by 45 mins.' boiling in a stream of nitrogen. The solution was made up to 500 c.c. with absolute alcohol, and the hydrogen sulphide evolved when 50 c.c. portions were treated with various amounts of sulphur was measured by the method used in the case of lithium (this vol., p. 415). The results are given in Table I and Fig. 1.

TABLE I.  
G. of H<sub>2</sub>S evolved per g.-mol. of RbHS.

Atoms S added.	G. of H <sub>2</sub> S evolved per g.-mol. of RbHS.					
	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 4.	Expt. 5.	Mean.
0.00	4.90	—	—	—	—	4.90
1.12	10.34	—	—	—	—	10.34
2.24	14.62	14.97	—	—	—	14.80
3.36	16.54	14.28	17.85	19.03	18.27	17.19
4.48	17.88	18.39	—	—	—	18.14
5.60	17.75	18.42	—	—	—	18.09
∞	16.91	—	—	—	—	16.91

(II) Metallic rubidium was melted under about 10 c.c. of toluene, and sulphur was added in small quantities. The reaction was similar to that with sodium and potassium, and the product was prepared for analysis in the same way. The rubidium was estimated by conversion into sulphate, and the sulphur as before (J., 1930, 1475). The results are as follows. :

Wt. of Rb, g.	Sulphur added, g.	atoms.	Product.			S/Rb, atoms.
			Rb, %.	(S), %.	S, %.	
0.1868	large excess		54.0	35.0	44.5	2.20
0.4650	0.5226	6	56.7	31.5	42.9	2.02

(III) 6—7 G. quantities of the required polysulphide (or concentrated alcoholic solution of equivalent content) were added to a litre of freshly-boiled distilled water. When the sulphur had been deposited, it was allowed to coagulate, filtered off, washed, dried, and weighed. The results are summarised in Table II.

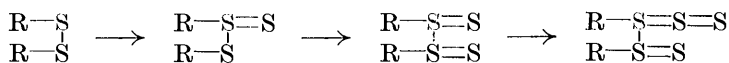
TABLE II.

Sulphide.	Result on treatment with water of polysulphide of		
	lithium.	sodium.	potassium.
Tetra-	Clear solution	Clear solution	Clear solution
Penta-	0.04 Atom S deposited	Faint opalescence	Clear solution
Hexa-	1 Atom S deposited	1 Atom S deposited	1 Atom S deposited

### Part V. Molecular Structures.

The most acceptable of many attempts to ascribe structures according with the physical and chemical properties to the polysulphides of the alkali metals appear to be those of Spring and Demarteau (*Bull. Soc. chim.*, 1889, **1**, 11) and of Küster and Heberlein (*Z. anorg. Chem.*, 1905, **42**, 72). The former authors, after dismissing Dreschel's conception (*Bull. Soc. chim.*, 1871, **16**, 238) of thio-substituted sulphite, thiosulphates, and sulphates, advance the view that these compounds behave with inorganic reagents as though constituted  $R_2S_nS_{n-1}$ , and towards organic reagents as though the metal were attached to two sulphur atoms,  $R_2S_2S_{n-2}$ . Küster and Heberlein (*loc. cit.*) criticise the formula  $R_2S_2S_{n-2}$  as implying that all polysulphides are salts of  $H_2S_2$  and hence should all be hydrolysed to an equal degree in aqueous solution; they therefore advocate the formula  $R_2S_nS_{n-1}$ , by analogy with polyiodides.

Thomas and Rule (*J.*, 1917, **111**, 1085), whilst recognising the criticisms of Küster and Heberlein, maintain that their own experimental results indicate that two of the sulphur atoms behave differently from the rest, and contend that disulphide is the unit from which by direct addition all other polysulphides result :—



These attempts were made in the absence of such detailed information regarding the methods of preparation and the properties of the alkali polysulphides as is provided in the current series of researches, and before the general application of the electronic theory of valency. By taking advantage of the knowledge now available, it has been possible to show that the division into two structural types  $R_2S_2S_{n-2}$  and  $R_2S_nS_{n-1}$  is probably illusory, and to ascribe tentative structures to these compounds, the full interpret-

ation of which leads to a better understanding of their methods of preparation and properties.

TABLE III.

Method of prepn.	Action of S on			M <sub>2</sub> S, giving M <sub>2</sub> S <sub>x</sub> , yH <sub>2</sub> O. x. y.	Sulphide formed by desulphurising highest sulphides in nitrogen.	By melting metal with sulphur.	
	metal under toluene.	MHS.	Compn. of satd. solid soltn.			Highest stable sulphide.	
Li	Li <sub>2</sub> S	Li <sub>2</sub> S <sub>4</sub>				Li <sub>2</sub> S <sub>2</sub>	
Na	Na <sub>2</sub> S <sub>3</sub>	Na <sub>2</sub> S <sub>4</sub>	2 3 4 5	2, 5, 6 3, 8 6, 8 6, 8	Na <sub>2</sub> S <sub>2</sub>	Na <sub>2</sub> S <sub>5</sub>	Na <sub>2</sub> S <sub>5</sub> ·28
K	K <sub>2</sub> S <sub>4</sub>	K <sub>2</sub> S <sub>5</sub>	2 3 4 5	3 0 2, 3 1	K <sub>2</sub> S <sub>2</sub>	K <sub>2</sub> S <sub>6</sub>	K <sub>2</sub> S <sub>6</sub> ·150
Rb	Rb <sub>2</sub> S <sub>4</sub>	Rb <sub>2</sub> S <sub>5</sub>	3 4 5	1 0, 2 0	Rb <sub>2</sub> S <sub>2</sub>	Rb <sub>2</sub> S <sub>6</sub>	Rb <sub>2</sub> S <sub>6</sub> ·266
Cs			3 4 5	1 0, 1 0	Cs <sub>2</sub> S <sub>2</sub>	Cs <sub>2</sub> S <sub>6</sub>	Cs <sub>2</sub> S <sub>6</sub> ·339

Table III epitomises the available information on the preparative methods and their respective products, and Table IV summarises the properties of the compounds.

TABLE IV.

Property.	Solubility in				Most stable sulphides.	Highest hydrate of					Volatility of anhydrous compound.
	C <sub>2</sub> H <sub>5</sub> O.		H <sub>2</sub> O.			M <sub>2</sub> S.	M <sub>2</sub> S <sub>2</sub> .	M <sub>2</sub> S <sub>3</sub> .	M <sub>2</sub> S <sub>4</sub> .	M <sub>2</sub> S <sub>5</sub> .	
Li	*	*	*	*	Li <sub>2</sub> S <sub>2</sub> , Li <sub>2</sub> S <sub>4</sub>	Too soluble for investigation					*
Na	↑	↑	↑	↑	Na <sub>2</sub> S <sub>2</sub> , Na <sub>2</sub> S <sub>4</sub>	9	6	8	8	8	↓
K			E	E	K <sub>2</sub> S <sub>2</sub> , K <sub>2</sub> S <sub>5</sub>	5	3	0	3	1	
Rb			H	M	Rb <sub>2</sub> S <sub>2</sub> , Rb <sub>2</sub> S <sub>5</sub>	4	3	1	2	0	
Cs			S	N	Cs <sub>2</sub> S <sub>2</sub> , Cs <sub>2</sub> S <sub>5</sub>	4	3	1	1	0	

\* Arrows show direction of increased solubility or volatility.

E = Extraordinarily hygroscopic. H = Highly hygroscopic. M = Moderately hygroscopic. S = Somewhat hygroscopic. N = Not hygroscopic.

The following generalisations may also be made :

(1) The polysulphides of (i) lithium and sodium, and of (ii) potassium, rubidium, and caesium resemble one another fairly closely, but a marked difference exists between the two groups.

(2) There is an increase in the number of sulphur atoms in the highest polysulphide from lithium (Li<sub>2</sub>S<sub>4</sub>) to caesium (Cs<sub>2</sub>S<sub>6</sub>). (This is analogous to the polyoxides and polyiodides.)

(3) From lithium to caesium, there is an increasing tendency to take up sulphur, as exemplified by (a) preparations from mono

sulphides, (b) preparations from hydrosulphides, (c) the action of sulphur on the metals, and (d) the quantity of sulphur in the saturated solid solutions of sulphur in the highest polysulphides.

(4) All the metals form *two* sulphides of relatively outstanding stability; one is invariably the disulphide, and the other, tetrasulphide in the case of lithium or sodium, and pentasulphide in the case of potassium, rubidium, or caesium.

(5) The amount of water of crystallisation and the solubility decrease with increase in atomic weight of the metal, the gradation being most marked between sodium and potassium.

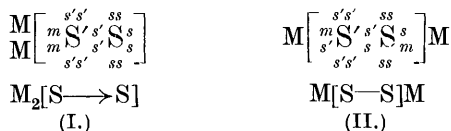
(6) Sulphur reacts with the monosulphides in solution to give a series of polysulphides, but with the hydrosulphides to give only the higher stable compound referred to in (4).

(7) In ionised solution the polysulphides react as if *one* of the sulphur atoms were unique, and under all other conditions, as if *two* were bound differently from the rest.

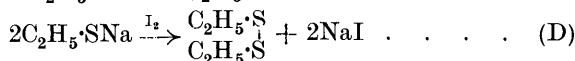
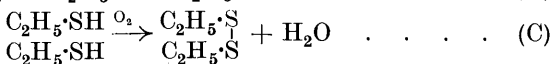
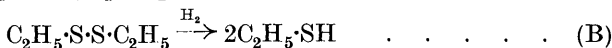
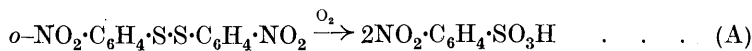
*Mono- and Hydro-sulphides.*—The monosulphide and hydrosulphide are best represented by the formulæ.\*



*Disulphide.*—Here there are two possibilities: the sulphur atoms may be connected by a co-ordinating link (I), or by a covalent one (II).



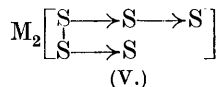
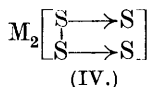
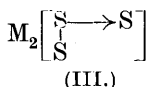
The behaviour of the organic disulphides supports (II), for oxidation gives quantitatively only one acid (A), and reduction gives two molecules of the mercaptan (B), gentle oxidation reconverting this into the disulphide (C). Again, the action of iodine on sodium mercaptide gives disulphide (D). All these reactions are concerned entirely with the making or breaking of the sulphur bond.



\* In these formulæ the small letters indicate the element from which the corresponding electron is derived.

The stability of the inorganic disulphides and their behaviour under all conditions in which ionisation is prevented suggest the covalent linking, and are certainly in favour of structure (II).

*Trisulphide.*—From the disulphide (II) it is suggested that trisulphide is produced by co-ordination with one of the sulphur atoms as represented by (III), co-ordination to both being excluded by the strain inherent in such a structure. This formula implies no



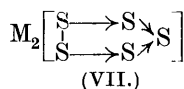
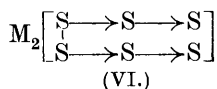
particular difficulty of formation, but a great readiness to acquire another acceptor, *e.g.*, water or sulphur. This accounts for the ready formation and great stability of trisulphide monohydrate, and offers an explanation of the preferential formation of higher sulphides in preparative methods involving the addition of sulphur to hydro- and mono-sulphide.

It seems also reasonable to suppose that the inherent instability of the trisulphide unit towards heat is accounted for by this unbalanced structure.

In the case of ammonium, where no disulphide unit is found, the absence of any polysulphide below pentasulphide is significant (see below).

*Tetrasulphide.*—The tetrasulphide may be presumed to consist of the disulphide unit, to each sulphur atom of which another is co-ordinated, giving the balanced arrangement (IV). The mode and ease of formation and the stability of tetrasulphides bear out this conception.

*Penta- and Hexa-sulphides.*—The formation of these by further co-ordination, giving (V) and (VI), fails to account either for the superior stability of the pentasulphides or for the frequent absence of a hexasulphide. With the pentasulphide, however, the closing of the sulphur chain becomes a possibility, giving (VII), since if the angle between the valencies of an atom whose valency is less than four remains the same as it would be if the full covalency were exerted (compare Sidgwick, "The Electronic Theory of Valency," p. 238) then such a ring would be almost without strain (see Table V). In such a configuration, the two co-ordinate links holding



the fifth sulphur atom must be of the single-electron type if the octet is to be maintained and each atom to be neutral. Closure

TABLE V.

Number of atoms in ring .....	3	4	5	6
Strain per atom .....	+49° 28'	+19° 28'	+1° 28'	-10° 32'

in the case of hexasulphides appears unlikely, and their instability is at once explicable in view of the length of the sulphur chain.

The structures suggested accord very well with the properties of the compounds under consideration. Thus, a general increase would be looked for in the sulphur/metal ratio as the alkali-metal series is ascended, successive members of which, by losing an electron more and more easily, tend to increase the length of the chain of co-ordinated sulphur atoms. Without some modification of this chain, however, such as the ring formula here suggested, the peculiar stability of the pentasulphide would remain unexplained. In this connexion the stability of ammonium and certain organic pentasulphides is significant.

These structures indicate that, in the degradation of any higher polysulphide, fission should occur at the co-ordinate linkings, and actually disulphides are formed when the alkali polysulphides are heated or the organic pentasulphides are even kept in solution.

The authors wish to thank Mr. J. H. Smith for his valuable assistance in the experimental work.

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[Received, June 5th, 1931.]

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