CCCVI.—*Ammonium Polysulphides, Hydrogen Pentasulphide, and the Thiocarbonic Acids.*

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POLYSULPHIDES of ammonium may be prepared by passing hydrogen sulphide into a suspension of sulphur in aqueous ammonia, and Bloxam (J., 1895, **67**, 2707) claimed to have obtained the tetra-, penta-, hepta-, and nona-sulphides in this way, but Thomas and Riding (J., 1923, **123**, 1726), using alcoholic in place of aqueous solutions, only obtained the di-, penta-, and hepta-sulphides. We have prepared the pentasulphide, and bring forward evidence that the alleged heptasulphide is a solid solution of sulphur in the pentasulphide, but we have been unable to confirm the existence of the disulphide.

Previous workers (for references see Walton and Parsons, *J. Amer. Chem. Soc.*, 1921, **43**, 2539) obtained yellow oils, which on fractional distillation yielded hydrogen disulphide and trisulphide, by treating cold concentrated hydrochloric acid with a cold solution of sodium polysulphides. Examination of the solubility of sulphur in hydrogen trisulphide led to the inference that the hexasulphide existed below −1·45° (Walton and Whitford, *ibid.*, 1923, **45**, 601). In the present investigation pure anhydrous ammonium pentasulphide has been decomposed by anhydrous formic acid with the formation of *hydrogen pentasulphide*, the properties of which have been investigated.

Red crystals obtained by refluxing ammonium pentasulphide with carbon disulphide in the manner of Thomas and Riding (*loc. cit.*), and believed by them to have been $(NH_4)_2S_2$ although analysing to $(NH_4)_2S_{2\cdot2}$, have been shown to be pure ammonium thiocarbonate, $(NH_4)_2CS_3$, whilst a yellow residue, not mentioned by these authors, consists of ammonium perthiocarbonate, $(NH_4)_2CS_4$. From these salts the corresponding *thiocarbonic acids* have been prepared and their properties investigated.

EXPERIMENTAL.

Ammonium Polysulphides.

Ammonium Pentasulphide.—Sulphur (40 g.) suspended in 100 c.c. of aqueous ammonia (*d* 0·88) and saturated with hydrogen sulphide in the absence of air, gave a deep red solution from which yellow crystals separated slowly on cooling [Found, mean of five closely-agreeing analyses of separate preparations: NH_3, 17·2; H_2S, 17·1; S, 65·3. Calc. for $(NH_4)_2S_5$: NH_3, 17·4; H_2S, 17·4; S, 65·2%]; these had all the properties previously ascribed to ammonium pentasulphide.

Ammonium Heptasulphide (alleged).—When greater proportions of sulphur were used, the hard cake formed on crystallising was obviously non-homogeneous, consisting mainly of yellow pentasulphide together with darker crystals. Hand-picked (*a*) dark red and (*b*) orange-red crystals were repeatedly analysed (Table I) and showed both considerable variation amongst themselves and an increase in the sulphur content with darkening colour. Any of these crystals when extracted with cold carbon disulphide gave a yellow substance having all the properties of the pentasulphide. Such crystals are decomposed by water with liberation of sulphur, and when treated with anhydrous formic acid give a considerable deposit

TABLE I.

Analyses of $(NH_4)_2S_n$.

Type of crystal.	NH_3.		H_2S.		S_{n-1}.	
	Range.	Mean.	Range.	Mean.	Range.	Mean.
Deep red *	10·5—14·3	12·6	11·3—11·8	11·6	70·0—74·0	73·0
Orange red *	14·8—15·2	14·9	14·6—15·0	14·8	68·0—68·3	68·2
$(NH_4)_2S_7$ requires		13·1		13·1		73·8
$(NH_4)_2S_6$ requires		14·9		14·9		70·2

* Number of analyses, four.

of sulphur together with a yellow oil, similar in most respects to that obtained from the pentasulphide. The conclusion reached is that materials of greater sulphur content than the pentasulphide consist of solid solutions of these two substances, and this is borne out by the preparative methods employed by other investigators, *viz.*, (i) allowing saturated alcoholic solutions of pentasulphide to stand in contact with sulphur for 4 months in stoppered bottles, and (ii) slow decomposition of the pentasulphide.

Ammonium Disulphide (alleged).—The preparation of this substance would be of considerable importance, because its decomposition by anhydrous formic acid would probably yield hydrogen disulphide directly. Weighed quantities of ammonium pentasulphide were decomposed in evacuated Faraday tubes, one limb being heated to 100° and the other cooled to $-7°$, for a considerable period. A yellow liquid, which subsequently solidified to a white solid, collected in the cooled limb and proved on analysis to be ammonium monosulphide [Found : NH_3, 50·1 ; H_2S, 49·9. Calc. for $(NH_4)_2S$: NH_3, 50·0 ; H_2S, 50·0%]. The residue of sulphur left in the heated limb amounted to 66·0% of the pentasulphide taken, thus indicating the decomposition $(NH_4)_2S_5 \longrightarrow (NH_4)_2S + 4S$: we have been unable to confirm the observations of Thomas and Riding (*loc. cit.*), who claim that the reaction is represented by $(NH_4)_2S_5 \longrightarrow (NH_4)_2S_2 + 3S$. The fact that the pale yellow liquid or the white solid plunged into either dilute or concentrated hydrochloric acid gives neither free sulphur nor any oil confirms the conclusion indicated by the quantitative synthesis from pentasulphide and the analysis of the material. Thus the decomposition here follows the usual course observed on dry distillation in open vessels or on refluxing with organic solvents, in both of which monosulphide is produced.

Hydrogen Pentasulphide.

The production of hydrogen polysulphides by the wet methods previously employed is invariably accompanied by the precipitation of much sulphur. It has been found that dry ammonium polysulphide crystals give hydrogen polysulphides on treatment with concentrated mineral acids (except nitric) at either laboratory or higher temperatures, but sulphur, varying in extent with the excess of sulphur in the crystals over that required for pentasulphide, is always liberated. Even selected pure pentasulphide yields sulphur under these conditions. Formic acid as concentrated as 90% offers no advantage over mineral acids, but commercial anhydrous formic acid, further dried by phosphorus pentoxide, gives excellent results, the formation of the polysulphide being unaccompanied by free sulphur. Probably the presence of water accounts for the formation of the free sulphur in these reactions.

From ammonium pentasulphide crystals, pale yellow oils were repeatedly prepared in this way and analysed; from Table II it will be seen that the persulphide sulphur (S_{n-1} in H_2S_n) falls only twice below the 82·5% required for H_2S_6, but rises as high as 92·6% (Calc. for H_2S_7 85·0; for H_2S_8 86·8; for H_2S_9 88·3%). Observation proved that the more free sulphur liberated in a reaction the higher was the indicated persulphide sulphur of the accompanying oil. It was believed that the differences found in the oils prepared with formic acid were due to differences in the sulphur content of the crystals, and in order to test this, they were ground to a powder and extracted with boiling carbon disulphide. The centrifuged residue gave a reddish-brown oil which had 77% of persulphide sulphur, the low sulphur content and the colour being due to the formation of a certain amount of ammonium perthiocarbonate (see below). If the crystals were extracted with cold carbon disulphide for a short period and centrifuged, the trouble was avoided, and they gave a pale orange-yellow oil, separate specimens of which had persulphide sulphur 79·0, 79·0, 79·3, 79·9, 79·6% respectively, mean 79·3% (H_2S_5 requires 79·0%). The faint orange tint is doubtless due to traces of thiocarbonic acids, and attempts were made to avoid this by extracting the crystals with benzene at various temperatures, but this did not furnish material suitable for the preparation.

TABLE II.

Acid used.	Persulphide sulphur in separately prepared samples, %.
Hot HCl	92·6, 92·0, 90·3, 90·0, 89·3.
Cold HCl	88·0, 85·0.
Cold anhydrous $H·CO_2H$	86·4, 86·1, 85·9, 85·4, 84·9, 84·6, 83·3, 82·3, 81·9.

Pure *hydrogen pentasulphide* is a thin, clear, yellow oil, which on cooling becomes suddenly viscous at −25°, almost solid at −35°, and glassy at −50°, melting to a clear liquid again on warming; *d* 1·67 at 16° (Found : *M*, cryoscopic in benzene, 152·5. H_2S_5 requires

M, 162). It froths badly at 40°/15 mm., but cannot be distilled. The solubility of sulphur in the liquid, expressed for convenience as the percentage of sulphur not evolved as hydrogen sulphide, has been found to be 93 at 15°, 90 at 0°, and 88 at $-18°$. From Walton and Whitford's figures (*loc. cit.*) for the solubility of sulphur in hydrogen trisulphide, similarly expressed, *viz.*, 86·8 at 17·9°, 83·0 at 0·0°, and 71·2 at 15·4°, it is seen to be improbable that the material here considered is a solution of sulphur in a lower sulphide.

Ammonium Thiocarbonates and the Thiocarbonic Acids.

Ammonium thiocarbonates have been described by Yeoman (J., 1921, **119**, 38) and by O'Donoghue and Kahn (J., 1906, **89**, 1812), but they have not been prepared by the methods here used (compare Thomas and Riding, *loc. cit.*).

Ammonium Thiocarbonate.—This is most conveniently obtained by digesting ammonium pentasulphide with carbon disulphide in a wide-necked flask fitted with a cork carrying a wide tube, in which cold water is rapidly circulated, and a reflux condenser. A deposit of white, crystalline ammonium monosulphide first forms on the cold surface, and this is later converted into the pale orange-yellow thiocarbonate by the carbon disulphide vapour. On exposure to moisture or air these orange-yellow crystals turn red. The material obtained from this sublimation process is remarkably pure if washed with carbon disulphide and ether, and centrifuged [Found : NH_3, 23·68; H_2S, 23·40; total S, 65·70. Calc. for $(NH_4)_2CS_3$: NH_3, 23·61; H_2S, 23·61; total S, 66·66%].

Ammonium Perthiocarbonate, $(NH_4)_2CS_4$.—The yellow, crystalline residue from the incomplete refluxing of ammonium pentasulphide in carbon disulphide was shown to be ammonium perthiocarbonate. A better product was obtained by extracting the pentasulphide with carbon disulphide in a Soxhlet apparatus, washing with hot fresh carbon disulphide followed by ether, and then centrifuging [Found : NH_3, 19·10; H_2S, 19·10; total S, 73·88; persulphide S, 19·8. $(NH_4)_2CS_4$ requires NH_3, 19·32; H_2S, 19·32; total S, 72·73; persulphide S, 18·18%].

Earlier workers have been unable to decide satisfactorily whether the acid obtained from thiocarbonates is tri- or tetra-thiocarbonic. Yeoman (*loc. cit.*) considers it to be tetra-, whilst O'Donoghue and Kahn (*loc. cit.*), although believing it to be tri-thiocarbonic, were unable to demonstrate this with certainty.

Trithiocarbonic Acid.—This was prepared by dropping pure solid ammonium thiocarbonate into a large excess of concentrated hydrochloric acid, and the bright red liquid which separated was dried with phosphorus pentoxide [Found : Total S (by Carius), 87·28 (mean of 8 concordant determinations on independent specimens); *M*, cryoscopic in bromoform, 107·2. H_2CS_3 requires total S, 87·28%; *M*, 110]. The liquid has $d_{4^\circ}^{17\cdot0^\circ}$ 1·47 and freezes sharply to an orange-yellow solid at −30·5°. The surface tension by capillary rise = 48·3 dynes/cm. at 12·5°, giving a parachor of 197·3 (H_2CS_3 requires 201·1, if the parachor of sulphur is taken as 46·2, the mean from the data for carbon disulphide).

The acid decomposes on standing, rapidly at first but more slowly later, evidently forming a red solution of itself in the carbon disulphide produced; distillation of the fresh material leads to its dissociation to carbon disulphide and hydrogen sulphide without residue of sulphur. It is slightly soluble in water, organic solvents, or acids, giving yellow solutions which rapidly decompose with loss of colour. Its behaviour with acetone, in which it dissolves without liberation of sulphur even on long standing, deserves special note because of the marked difference shown by the tetrathiocarbonic acid with this reagent.

Yeoman (*loc. cit.*) has stated that aqueous solutions of pure thiocarbonates do not give the red liquid when acted upon by concentrated hydrochloric acid in the complete absence of oxygen. This statement has been examined by conducting the reaction with the ammonium salt at −5° both in a vacuum and in an atmosphere of hydrogen sulphide, and, provided the concentration of the thiocarbonate is more than sufficient to saturate the hydrochloric acid with thiocarbonic acid, the red liquid separates.

Tetrathiocarbonic (*Perthiocarbonic*) *Acid*, H_2CS_4.—This is a dark brown liquid obtained by the action of 98% formic acid upon ammonium perthiocarbonate, but the total and persulphide sulphur and the estimated molecular weight show considerable variation from sample to sample. The following properties, however, indicate that the liquid is largely composed of this acid. It is decomposed vigorously, with *crackling*, by acetone, giving a colourless solution with deposition of sulphur ($H_2CS_4 \longrightarrow CS_2 + H_2S_2 \longrightarrow H_2S + S$); on distillation under reduced pressure with a small bead-column two fractions are obtained—first carbon disulphide, and subsequently a small quantity of a pale yellow oil distilling at 70° and having all the properties of hydrogen disulphide. A large residue of sulphur is left.

It is interesting that concentrated hydrochloric acid used in place of formic acid gives a red liquid which proves to be a solution of sulphur in trithiocarbonic acid. This liquid is soluble in acetone to a yellow solution, without the violence or crackling associated with the hydrogen polysulphides; from this solution the sulphur previously dissolved in the trithiocarbonic acid is slowly precipitated.

On distillation this liquid gives no evidence of a polysulphide, the distillate being colourless carbon disulphide, and the residue sulphur.

It has been observed that ammonium polysulphides and thiocarbonates are only very slowly decomposed by anhydrous formic acid below −7°.

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