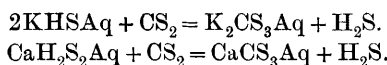


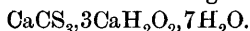
CLXXIV.—*Thiocarbonic Acid and some of its Salts.*

By IDA GUINEVERE O'DONOGHUE, B.Sc., and ZELDA KAHAN, B.Sc.

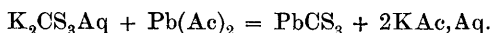
By the interaction of aqueous solutions of hydrosulphides and carbon disulphide, Berzelius (*Trans. Acad. Roy. Stockholm*, 1826, *Ann. Phys. Chem.*, 1826, **6**, 425) obtained unstable solutions of a number of metallic derivatives of thiocarbonic acid which yielded unstable crystalline salts. These on distillation evolved carbon disulphide, and left a residue of sulphide, their constitution being deduced from the method of formation according to the equations :



By the action of hydrochloric or sulphuric acids on the dry salts, a red oil was obtained which rapidly decomposed, and was similar to the one discovered and described by Zeise in 1824, who found it to be equally unstable. In 1862, Berzelius' experiments were repeated by Huseman (*Annalen*, **123**, 67), who also prepared complex salts of the thiocarbonates, isocyanates, &c., which were more stable. Sestini (*Gazzetta*, 1871, **1**, 473), during some experiments on the solubility of carbon disulphide in water, exposed calcium hydroxide, carbon disulphide, and water to sunlight for some time. The mixture reacted slowly, and the red solution gave crystals to which he assigned the formula



Similarly, Walker (*Chem. News*, 1874, **30**, 28) obtained a basic thiocarbonate to which he gave the formula $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 6\text{H}_2\text{O}$. A salt similar to this, but containing $10\text{H}_2\text{O}$, was obtained by a different method by Veley (*Trans.*, 1885, **47**, 478), who also repeated Berzelius' and Zeise's experiments with very similar results. Amongst other basic thiocarbonates, he also obtained deliquescent, red crystals which corresponded to the formula $\text{CaH}_2\text{O}_2, \text{CaCS}_3, 7\text{H}_2\text{O}$. It will be seen, therefore, that, although much work has been done on the thiocarbonates, the solid normal salts have been but little investigated, if indeed they have been obtained at all, and owing to their instability their constitution has been inferred merely from their methods of formation, namely :



The experiments to be described below were undertaken at the suggestion of Sir William Ramsay, and had for their aim the formation

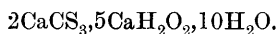
of the pure normal thiocarbonates and the elucidation of their constitution. It is extremely difficult to deal quantitatively with the normal salts owing to their instability, but the ratios of their elements have been determined.

Thiocarbonic acid has been prepared in considerable quantities. It has been analysed and its properties investigated, and very nearly pure metallic thiocarbonates have been prepared from it. Their analyses prove the acid to have the constitution H_2CS_3 .

Preparation of Calcium Thiocarbonate in Solution.—This substance was prepared by shaking together calcium hydrosulphide, carbon disulphide, and air-free water in a well-stoppered bottle as nearly full as possible. An orange solution was obtained which always contained polysulphides. Various attempts were made to free the solution from the latter, the most successful being the addition of carbon disulphide and calcium hydroxide in small quantities, and shaking (often for several days), until the solution no longer gave a black precipitate with lead acetate. Such a solution was red and quite stable when kept out of contact with air, but when exposed to the atmosphere it at first slowly deposited red or orange, needle-shaped crystals, then gradually became paler in colour, giving rise to a variety of products, amongst which were identified sulphur, carbonates and sulphides. The solution had a peculiar odour, and with solutions of the salts of the heavy metals yielded characteristic coloured precipitates, which decomposed in air and could not be dried.

By complete evaporation in a vacuum, a crystalline mass was obtained which was only partially soluble in water and was mixed with some white and green substance. The soluble portion consisted of either basic or normal calcium thiocarbonate, since it gave with lead acetate the characteristic bright red lead thiocarbonate. On attempting to obtain crystals again by re-evaporating in a vacuum, there only resulted a mixture of white and green substances.

By evaporating a solution of calcium thiocarbonate to a small bulk in a vacuum, long, red, and sometimes orange, needles were obtained, the colour of which gradually faded in air. They were completely insoluble in water, and became colourless on heating on a platinum foil in a dry test-tube or in water. Although these crystals seem to resemble in some respects those obtained by Berzelius, Sestini, Walker and Veley, analysis shows them to correspond to the formula



	$2\text{CaCS}_3, 5\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$		Walker. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2,$ $6\text{H}_2\text{O}$	Veley. $\text{CaCS}_3, \text{CaH}_2\text{O}_2,$ $7\text{H}_2\text{O}$	Sestini. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2,$ $7\text{H}_2\text{O}$
	Found (per cent.).	Calculated (per cent.).	Found (per cent.).	Found (per cent.).	Found (per cent.).
Ca ...	33.57	33.82	29.70	22.99	32.2
S ...	23.34	23.18	23.76	27.77	19.3
C	2.65	2.8	2.96	3.65	2.4
H.....	3.57	3.38	3.96	—	4.0

By adding alcohol to the red solution and shaking, minute, crystalline, yellow plates were slowly precipitated. When freshly prepared, they were soluble in water, but on standing they gradually turned white, at the same time becoming more and more insoluble. Analysis gave :

Ca = 29.00 ; S = 17.92 ; C = 2.7 ; H = 4.5. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 9\text{H}_2\text{O}$ requires Ca = 30.00 ; S = 18.04 ; C = 2.30 ; H = 4.50 per cent.

Water of crystallisation = 25.5. The above salt containing $9\text{H}_2\text{O}$ requires 30 per cent., or with $7\text{H}_2\text{O}$, 25.4 per cent. Probably the last 2 molecules of water are difficult to remove.

The dry yellow salt was washed with liquid ammonia in order to remove as much water as possible. The substance obtained gave on analysis :

Ca = 23.0 ; S = 36.9. $\text{CaCS}_3, 3\text{Ca}(\text{OH})_2, 3\text{H}_2\text{O}$ requires Ca = 22.6 ; S = 37.7 per cent.

On several occasions, as already mentioned, a green salt was obtained which gave on analysis :

Ca = 32.50 ; S = 21.1 per cent.

Enough of it has never since been prepared pure to enable the determination of carbon and hydrogen to be made. This salt has also been found repeatedly in bottles containing a solution of calcium thiocarbonate.

General Methods of Analysis.—The ordinary Carius method for determining sulphur was found to be the most satisfactory, the metal being estimated in the same solution. In this way, the ratio of metal to sulphur was obtained in those cases in which the salt could not be weighed. A large excess of nitric acid, a high temperature, and prolonged heating were required to decompose the oily drops which were often formed and which resembled carbon disulphide, or possibly thiocarbonic acid, in appearance. In the determination of carbon and hydrogen, the substance was well mixed with freshly-fused potassium dichromate, lead chromate replacing copper oxide in the combustion tube.

It is evident that calcium thiocarbonate is able to form a large number of basic salts, the composition of which depends largely on the

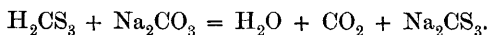
exact conditions of the experiment. The following have been obtained up to the present :

1. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 6\text{H}_2\text{O}$ (Walker).
2. $\text{CaCS}_3, \text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$ (Veley).
3. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$ (Veley).
4. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$ (Sestini).
5. $2\text{CaCS}_3, 5\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$ (red needles).
6. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 9\text{H}_2\text{O}$ (yellow plates).
7. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 3\text{H}_2\text{O}$.
8. Green crystals containing $\text{Ca} = 32.5$ and $\text{S} = 21.1$ per cent.

Thiocarbonic Acid.—The above-mentioned oil could scarcely be detected by dropping acid on to the solid salts, but if a test-tube shaped vessel is partially filled with concentrated hydrochloric acid, and a solution of calcium thiocarbonate slowly dropped in, small drops of oil speedily appear and fall to the bottom. It was found best, however, to cool both solutions previously in a freezing mixture, and to allow the vessel to stand for some time after all the calcium thiocarbonate solution had been added. After an hour or two, the liquid was decanted, the last drops being separated with a separating funnel. The oil was sometimes washed rapidly with ice-cold water, but usually it was found best to dispense with this operation. It was then placed in a small flask surrounded by a freezing mixture, calcium chloride added, and the flask attached to a good pump until bubbles no longer appeared to arise from the oil. In this way hydrochloric acid and water were removed, and the oil was finally dried over phosphorus pentoxide.

The free acid is red in colour and appears darker in some preparations than in others. It has a peculiar, pungent odour, and is soluble in alcohol, giving a yellow solution which decomposes rapidly with deposition of sulphur and formation of carbon disulphide and hydrogen sulphide. It is also soluble in liquid ammonia, turpentine, toluene, ether, or chloroform, in all of which solvents it very soon decomposes, but is most stable in the two latter. In liquid air or solid carbon dioxide it forms a pink solid which melts again to a red liquid on removing the refrigerator. The acid is insoluble in water, but is at once decomposed by it, with evolution of hydrogen sulphide and formation of carbon disulphide and sulphur. This also occurs in a solution of common salt. It is much more stable towards strong acids, especially hydrochloric acid, under which it can be kept for several days if cool. The colour, however, gradually fades, and finally only carbon disulphide is left. In air, it gradually evaporates, often leaving a brownish-black residue consisting largely of sulphur. Sometimes it has been kept for a few days in a loosely-stoppered flask without any considerable loss. The oil dissolves flowers of sulphur readily with

a slight darkening in colour, and it is possible, therefore, that the colour of the oil is due to dissolved sulphur. It does not burn on water like carbon disulphide. Calcium and sodium carbonates produce effervescence with production of the corresponding thiocarbonate,



Sodium and potassium act on the dry oil or on its ethereal solution. Potassium decomposes it very violently, giving an immediate yellow, crystalline precipitate of potassium thiocarbonate, whilst in the former case sodium thiocarbonate gradually separates. Hydrogen sulphide and probably hydrogen are evolved in both cases. Magnesium powder has apparently little action on the oil, and on trituration with mercury a red solid is obtained.

The oil, purified as described above, was analysed :

S = (I) 90.16; (II) 89.41. H_2CS_3 requires S = 87.3, H_2CS_4 requires S = 90.14 per cent.

The salts formed by the oil, however, do not seem to correspond to derivatives of H_2CS_4 . It is therefore more probable that it consists of H_2CS_3 , containing sulphur in solution. An attempt was therefore made to distil the acid under diminished pressure from a flask connected with two receivers surrounded by liquid air.

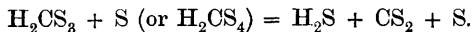
The first distillate was freed from hydrogen sulphide by partly withdrawing the liquid air and allowing the gas which escaped to condense in the second vessel. After standing in a mixture of ice and salt for a quarter of an hour, there was no longer an odour of hydrogen sulphide, and an analysis gave :

S = 84.0. CS_2 requires S = 84.2 per cent.

The distillate had all the properties of pure carbon disulphide.

The second receiver contained hydrogen sulphide and only a few drops of oil. In the distilling flask there remained a brownish-red solid which was chiefly sulphur. The temperature of distillation was 20—30°.

The acid had thus decomposed in accordance with the equation :



At the ordinary pressure, the oil distils at about 50° with decomposition.

With salts of the heavy metals the oil gives the corresponding thiocarbonates. The precipitations were usually carried out at the temperature of solid carbon dioxide. The oil was used either alone or in alcoholic or ethereal solution, and the salt of the weakest acid obtainable was usually employed. The salts thus prepared were

identical with those obtained from a solution of calcium thiocarbonate, but were purer and darkened more slowly.

The *lead* salt, PbCS_3 , is precipitated as a bright red, amorphous solid which, when pure, only darkens slowly in air. This change, according to the equation $\text{PbCS}_3 = \text{PbS} + \text{CS}_2$, takes place more rapidly in an evacuated desiccator, and is quantitative when the salt is distilled in hydrogen.

On analysis :

$\text{PbS} = 75.5$. PbCS_3 requires $\text{PbS} = 75.8$ per cent.

The distillation was carried on in a current of hydrogen. The freshly-prepared salt was placed in a small flask and heated by means of an oil-bath in a current of hydrogen. The moisture was absorbed in a tube containing sulphuric acid, and the carbon disulphide in a vessel immersed in liquid air, lead sulphide being left in the receiver.

In general, the lead salt turned black in about half an hour, but occasionally a very small quantity adhering to a glass rod or at the bottom of a beaker would retain its colour for days, and sometimes weeks.

Cadmium salt.—This was obtained as a deep yellow precipitate, which on shaking changed to a reddish-yellow and then to a reddish-brown substance. The latter was identified as cadmium sulphide.

On analysis :

$\text{Cd} : \text{S} = 1.10$. CdCS_3 requires a ratio of $\text{Cd} : \text{S} = 1.16$; CdCS_4 a ratio of $\text{Cd} : \text{S} = 0.87$.

After drying over calcium chloride :

$\text{Cd} : \text{S} = 3.03$. CdS requires a ratio of $\text{Cd} : \text{S} = 3.50$.

Zinc salt.—This is a pale yellow, insoluble, crystalline powder. When freshly prepared, it corresponds to ZnCS_3 , but rapidly decomposes with formation of zinc sulphide.

Sodium salt, Na_2CS_3 .—This was precipitated by adding a dry, freshly-prepared solution of sodium ethoxide to the oil. A yellow, crystalline precipitate gradually formed, which was washed with cold alcohol. It is deliquescent and very easily soluble in water, giving a yellow solution, which, with lead acetate, gives the pure characteristic lead thiocarbonate with no trace of black colour.

On analysis :

$\text{Na} : \text{S} = 0.48$. Na_2CS_3 requires the ratio $\text{Na} : \text{S} = 0.479$.

On drying, the salt decomposed and a mixture of several substances was formed.

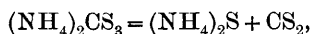
Potassium salt, K_2CS_3 .—This was precipitated by adding alcoholic

1818 THIOCARBONIC ACID AND SOME OF ITS SALTS.

potassium hydroxide to the oil. It resembles the sodium salt, being yellow and crystalline, but is more deliquescent. The aqueous solution also gave a precipitate of pure lead thiocarbonate with lead acetate. The salt is very soluble in liquid ammonia, and when washed with small quantities of this solvent the colour seemed to become lighter, but darkened again on drying. On evaporating the ammoniacal solution, pure potassium thiocarbonate was obtained.

Ammonium salt.—(1) Liquid ammonia and alcoholic thiocarbonic acid, cooled in liquid ammonia, gave a yellowish-pink solution, which, on spontaneous evaporation, yielded a yellow precipitate which soon turned pink. When allowed to remain overnight on a porcelain plate in a desiccator, it decomposed. White, micaceous crystals were obtained on standing for a short time, and were identified as ammonium sulphide. The ammoniacal mother liquor also yielded white needles of sulphur, probably from excess of sulphur in the oil. The yellowish-pink salt was not analysed, but gave pure lead thiocarbonate with lead acetate, and was most probably ammonium thiocarbonate.

Its decomposition is represented by the equations :



and



(2) By shaking dry redistilled carbon disulphide with a saturated solution of ammonia in alcohol, a pale yellow, crystalline precipitate was obtained in about five minutes. It has a peculiar odour, rather different from that of the thiocarbonates. Lead acetate does not give a characteristic precipitate, nor could thiocarbonic acid be obtained from it. When heated, it melts and partially sublimes, at the same time decomposing and evolving hydrogen sulphide and ammonia. It decomposes very gradually in air, becoming moist in appearance. Analysis showed that it is not ammonium thiocarbonate, but its investigation is not yet completed.

In conclusion, we wish to express our thanks to Sir William Ramsay for the encouragement and help he has given us during the progress of this work.

UNIVERSITY COLLEGE,
LONDON.
