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XLIX.—*Reactions of Selenious Acid with Hydrogen Sulphide, and of Sulphurous Acid with Hydrogen Selenide.*

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E., Imperial Japanese College of Engineering, Tôkio.

THE nature of the reaction of hydrogen sulphide with selenious acid, and of that of hydrogen selenide with sulphurous acid, is evidently of special interest on account of the close similarity of sulphur and selenium, and many chemists—Berzelius, Rose, Rathke, Bettendorff, Ditté, v. Gerichten—have been led to study it in consequence. We have just completed a simple investigation of these reactions, and have observed some new facts of interest, which not only supplement what is already known concerning them, but also appear to us to place their nature in a clearer light than that in which it has hitherto stood.

Hydrogen Sulphide and Selenious Acid react together in two ways.

A very cold dilute solution of selenious acid yields a precipitate with hydrogen sulphide, composed of two atoms of sulphur to one of selenium, and which is yellow and pulverulent. This is well known, and also that in warmer solutions the precipitate becomes plastic and

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* Since this fact was communicated to the *Chemical News*, we have found that H. Rose had observed the same thing, and mentioned it in his "Quantitative Analysis," but it seems to be one little known, and *tellurocyanates* are treated as having no existence.

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red. But when the solution is warm another reaction also takes place, which appears to have as yet escaped all notice. In this case, namely, *sulphuric acid is formed, and the precipitate does not now contain so much as two atoms of sulphur to one of selenium.*

Selenious acid, therefore, exerts an oxidising action not only on the hydrogen, but also on the sulphur of the hydrogen sulphide. This action always occurs to a sufficient extent to allow of the sulphuric acid being detected, except when the solutions are cold in the cold season of the year, and should, therefore, be taken into consideration in analytical work. In hot solutions, it is very extensive. Thus, in one trial we got nearly one-fourth of the oxygen of the selenium dioxide in the form of sulphuric acid, SO_4H_2. Here we kept the solution boiling, and allowed the gaseous hydrogen sulphide to flow upon its surface only. In another trial, in which we bubbled the gas through a hot solution, we obtained nearly one-sixth of the oxygen as sulphuric acid. The precipitates produced in these trials were analysed and found to contain, in the former case scarcely more than two-fifths of an atom of sulphur to one of selenium, and in the latter case only two-thirds of an atom of sulphur to one of selenium.

These quantities of precipitated sulphur are, however, very far from representing all the unoxidised sulphur, as this escaped in abundance with the steam and excess of gas. By calculation, indeed, more than one atom of sulphur must thus have volatilised to every atom of selenium precipitated from the boiling solution, and just about one atom to one of precipitated selenium from the merely hot solution. Although the evolved vapour was quite clear, the condensed water contained much milky sulphur, and believing that this sulphur might come from a reaction between sulphur dioxide and hydrogen sulphide gases, because the extent of the volatilisation of sulphur so far exceeded that which occurs when sulphur in powder is boiled with water, we tested, first, the steam with no result, and then the action of hydrogen sulphide on a hot concentrated solution of ferric chloride, which we found to give a similarly abundant volatilisation of sulphur. We also tested our mother-liquors from the precipitates for other sulphur acids, but found nothing except sulphuric acid. The presence of hydrochloric acid during precipitation seemed to have no effect beyond that of causing the precipitate to aggregate and settle.

The selenious acid used in our experiments was prepared in our College Laboratory from selenium free from sulphur or tellurium, and almost pure, and was repeatedly evaporated to dryness with hydrochloric acid, and heated to the subliming point.

On consideration, it will be seen that since selenious acid so readily oxidises sulphurous acid, the fact of its completely oxidising hydrogen sulphide under favourable circumstances is only what might have

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been expected. In exerting this action, four times as much selenium is precipitated from it as when only the hydrogen of the same quantity of sulphide is attacked by it, as may be seen from the equations—

$$2SH_2 + 4SeO_3H_2 = 2SO_4H_2 + 4Se + 4OH_2$$
$$2SH_2 + SeO_3H_2 = 2S + Se + 3OH_2.$$

Sulphurous Acid with Hydrogen Selenide in Excess yields Selenium, Water, and Hydrogen Sulphide.

On adding a weak solution of sulphur dioxide to a strong solution of hydrogen selenide, gradually and with agitation, so as to leave some hydrogen selenide undecomposed, *selenium alone is precipitated*, quite free from sulphur, and of a fine deep-red colour from the first and for some time after; it ultimately becomes brown-red, however, if hydrogen selenide is kept in contact with it. *The mother-liquor contains hydrogen sulphide* along with any remaining hydrogen selenide.

When, on the other hand, gaseous hydrogen selenide is passed into sulphur dioxide solution, an orange-red precipitate is produced which contains sulphur. A precipitate thus generated in a mother-liquor in which a little sulphur dioxide was purposely left undecomposed, was analysed and found to contain only one—strictly 0·95—atom of sulphur to two of selenium. In another experiment in which no sulphur dioxide was left unchanged, the mother-liquor contained a very little selenium, even after boiling; this only slowly yielded a black precipitate of silver selenide with silver nitrate. We conclude from this that it contained a seleniothionic acid, perhaps one of those already known.

We do not at once discuss the nature of the reaction between hydrogen selenide and sulphurous acid, and of the secondary reactions which may accompany it, because we have yet to describe, in a later section of this paper, experiments which throw further light on what happens when the two substances come together.

Iron Monoselenide, and the Preparation of Hydrogen Selenide from it.

In preparing the hydrogen selenide required we imitated the common process of preparing hydrogen sulphide. An iron selenide was first made by projecting into a black-lead pot, heated in a wind-furnace, a mixture of wrought-iron filings and selenium. In this operation most of the selenium was dissipated in vapour. When the iron had grown hot more selenium was added which combined with the iron with very little loss, causing vivid ignition and complete liquefaction of the whole. The fluid compound was run into a mould

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and cooled. The solid mass thus obtained was indistinguishable in appearance from iron sulphide similarly prepared.

Not being very sensitive to the action of acids, it was powdered before being put in the apparatus for generating the gas, and then warmed with dilute hydrochloric acid. This gave a steady stream of gas.

The iron selenide proved on analysis to be a compound of almost exactly one atom of selenium with one of iron. It was, therefore, iron monoselenide. Like artificial iron sulphide it was, nevertheless, impure, although only slightly so. For, on the one hand, the gas evolved on treating it with hydrochloric acid contained a very small fraction of its volume of free hydrogen, and, on the other, a very small but voluminous black residue was left insoluble in the acid; this contained selenium, and was doubtless iron biselenide. Our preparation, consequently, contained both a little free iron and a little biselenide intermixed with the monoselenide. This is the first time iron monoselenide has been obtained.

Sulphur Decomposes Hydrogen Selenide.

A solution of hydrogen selenide is very much more sensitive to the action of air than one of hydrogen sulphide, and quickly becomes red on the surface after a very short exposure. As oxygen precipitates selenium so readily from its hydride, sulphur may be expected to do the same, although less actively, and our experiments have shown us that sulphur has this action, and even appears to exert it as freely as oxygen. As flowers of sulphur usually contain some sulphurous acid, we employed only roll-sulphur in our experiments. On adding this to a solution of hydrogen selenide, or on bubbling hydrogen selenide through water containing it in lumps or in powder, it instantly becomes coloured by precipitated selenium, at first orange-red, then deep red, and, lastly, but only by the prolonged action of the gas, dark brown-red. The action of the hydrogen selenide on the sulphur is, however, quite superficial; so that much of it is required to decompose completely a little hydrogen selenide. Simultaneously with the deposition of the selenium, *hydrogen sulphide is formed.* This being so readily carried away by the current of hydrogen selenide gas, it is better, in order to detect it, to digest the sulphur in a closed bottle with hydrogen selenide solution, add some hydrochloric acid to aggregate and separate suspended selenium, and then quickly filter with but little exposure to the air. The mother-liquor thus obtained and deprived of all hydrogen selenide will furnish ample evidence of the formation of hydrogen sulphide.*

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* Hydrogen selenide quickly permeates black vulcanised rubber tubing, turning it red and, no doubt, by the above reaction with the sulphur in it.

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The sulphur with its deposited selenium, dried and heated in a vacuum, gave off no gas, so that the deposit contains no hydrogen persulphide or perselenide. The cause of the brown-red instead of bright red colour of the deposit remained unexplained. It can be produced in pure bright red selenium by digesting it in hydrogen selenide solution.

Having established the occurrence of a reaction between sulphur and hydrogen selenide, we tried whether we could not get selenium free from sulphur by treating the orange-red precipitate which is produced when sulphurous acid is first acted on by hydrogen selenide with an excess of the last-named substance. By this treatment the colour of the precipitate changed to deep red, ultimately to brown-red, and on examination it was found to contain only traces of sulphur. In performing this experiment, we took the precaution, in order to avoid any consolidation of the precipitate, to work with it freshly prepared and suspended in very cold water. We are now in a better position than we were to consider the nature of the reaction between hydrogen selenide and sulphurous acid.

Hydrogen selenide in excess yielding with sulphurous acid both hydrogen sulphide and a precipitate wholly selenium, the presence of sulphur in the precipitate, when the sulphurous acid has been kept in excess, might be attributed to the interaction of hydrogen sulphide and sulphurous acid, thus :—

$$\begin{aligned} 6SeH_2 + 2SO_3H_2 &= 6Se + 2SH_2 + 6OH_2 \\ 2SH_2 + SO_3H_2 &= 3S + 3OH_2. \end{aligned}$$

These reactions combined give the 2Se to 1S found by us, and recognised in books as sulphur biselenide. But if they represent the true order of events, some pentathionic acid should be formed, whereas, in the mother-liquor we found none ; but, instead, a little seleniothionic acid. It is, besides, certain that in the reduction of sulphur dioxide the oxygen will be before the sulphur in taking hydrogen, and that thus nascent sulphur will be in presence of hydrogen selenide, with which it must react. The order of the changes will therefore be represented more correctly by the following equations than by those above set out :—

$$\begin{aligned} 2SeH_2 + SO_3H_2 &= 2Se + S + 3OH_2 \\ SeH_2 + S &= Se + SH_2. \end{aligned}$$

Our finding a little less than one atom of sulphur to two of selenium is thus accounted for by some action under the circumstances between the sulphur precipitated and the hydrogen selenide ; whilst the absence of pentathionic acid no longer remains a difficulty, and the presence of a little seleniothionic acid becomes an occurrence to be expected.

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The only Compound of Sulphur and Selenium known as yet is Selenium Monosulphide.

In so far as it is possible to prepare by definite reactions precipitates having, in one case, the composition of selenium bisulphide and, in the other case, of sulphur biselenide, such precipitates may be these respective compounds. Chemists are not agreed that they are, but in systematic treatises on chemistry it is not uncommon to find them so represented. We ourselves consider, irrespectively of any facts bearing upon the point which our work adds to those already known, that there is no evidence that they are; and that it is theoretically improbable that sulphur biselenide should exist at all.

The precipitate at first obtained from selenious acid is lemon-yellow, and that from sulphurous acid orange-red, and Ditté has shown that, on leaving the former for some time moistened with carbon bisulphide, it becomes converted into transparent, orange-yellow scales, having very accurately the composition of selenium monosulphide. The excess of sulphur in the original precipitate goes into solution in the carbon bisulphide. By taking, in place of selenious acid, a neutral selenite solution for precipitation, this sulphide can be more readily obtained in the subsequent treatment with carbon bisulphide, but it is then of a dark brown-red colour.*

This substance, as prepared by Ditté in apparently two forms, one approaching sulphur in colour, and the other selenium, is not only of constant and simple atomic composition, but it has a density markedly less than that calculated for it from the densities and proportions of its components, and disengages during oxidation much more heat than its components would if uncombined. Ditté places it, therefore, among "explosive" compounds. It is an exceedingly unstable body.

The existence of seleniun monosulphide, SeS, has, therefore, long been incontestably proved (unless Ditté's facts are disputed), although it has not received that general recognition which it deserves.

Precipitates of sulphur with selenium have no other properties than those of mixtures of these simple substances.†

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* This colour Ditté attributes to some action of alkali hydrosulphide that becomes formed during the precipitation, and it has already been mentioned by us, in a previous section of this paper, that the same colour is produced in selenium precipitated by sulphur, when this is long digested with hydrogen selenide solution, and, further, that pure selenium, precipitated from hydrogen selenide by sulphurous acid not in excess, ultimately takes this colour, provided it is kept in hydrogen selenide solution for some time, although otherwise it preserves its brilliant, deep red colour.

† The deep red colour of unmixed precipitated selenium and the orange-red colour of some of its precipitates with sulphur, are well matched by the deep red of ordinary amorphous phosphorus, and the orange-red of this substance when formed during the partial combustion of ordinary crystalline phosphorus.

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We have already described in this paper the copious volatilisation of sulphur which takes place when precipitation takes place in hot solutions, and wish now to point out that, since in precipitating any true metal sulphide from a hot solution, no such volatilisation of sulphur occurs, even in the case of tellurium sulphide, it affords proof that the nascent sulphur is uncombined with the selenium when precipitated along with it.

It is usual to regard the reactions of which we are now treating, as cases of double decomposition, but considering how very similar sulphur and selenium are, the propriety of doing so may well be doubted. The reactions will be sufficiently determined solely by the property possessed by the hydrogen and oxygen of combining together, and the atoms of sulphur and selenium will then be left to unite, each kind together, or in part with the other kind to form selenium monosulphide.

Moreover, it seems like a reversal of the well-established electrochemical order of the elements to admit that selenium can be at one time basylous and at another chlorous to sulphur under very similar conditions. Yet this would be the case if we admit the formation of a sulphur selenide by double decomposition. Were there indeed facts to prove this formation, the force of the objection to it that it is improbable, would not count for much, and it is brought forward here merely to combat the accepted notions of what ought to be the nature of the reactions by showing that analogy gives no support to these views any more than do the facts known concerning the reactions.

Conclusions.

Hydrogen sulphide and selenious acid, and also hydrogen selenide and sulphurous acid, yield a precipitate of sulphur and selenium, which consists of two atoms of sulphur to one of selenium in the former case, and of one atom of sulphur to two atoms of selenium in the latter, for the most part uncombined in both cases.

Hydrogen sulphide and selenious acid also react freely in hot solutions in another way, and then form sulphuric acid and selenium.

Hydrogen selenide and sulphur in contact change at once into hydrogen sulphide and selenium. Accordingly, hydrogen selenide in excess gives with sulphurous acid a precipitate of pure selenium.

What is known concerning the precipitation of sulphur along with selenium furnishes no grounds for admitting the existence of any compound of the two elements other than the very unstable selenium monosulphide described by Ditté in 1871.