

XL.—*On a New Oxide of Tellurium.*

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By heating in a vacuum the compound of sulphur trioxide and tellurium until it decomposes, we have obtained sulphur dioxide and a new oxide of tellurium. This oxide is in the solid state, and if sufficiently heated, suffers decomposition into tellurium dioxide and elemental tellurium, the latter volatilising before the former. Decomposition of the sulphoxide begins—according to our observations, which differ from R. Weber's—at about  $180^{\circ}$  C., but is not quite complete even at about  $230^{\circ}$ , above which temperature we have feared to pass, lest we might cause some of the new oxide to decompose.

The operation was carried on in a tube-retort, immersed in a paraffin-bath, and connected with a Sprengel pump. In this vessel

the required sulphoxide had itself been prepared and purified, ready for the experiment, and out of contact with the air.

The solid sulphoxide softens by the heat to a pasty mass before decomposition sets in, and when this happens, intumescs very much in giving off the resulting sulphur dioxide. At the same time its own lustrous brown colour gives place to the black colour, also lustrous, of the new oxide. The oxide now exhibits a marked resemblance to charred cork.

It is not yet quite pure. Even prolonged heating in a vacuum failed to yield it altogether free from a sulphur-compound, which can hardly be other than unchanged sulphoxide of tellurium. We have, therefore, with the view of purifying it, rubbed the vesicular mass to powder, and washed it with water holding in solution a small quantity of sodium carbonate. This treatment effectually removes oxide (or oxides) of sulphur, together with any tellurous acid that may have resulted from the decomposition of the sulphoxide, this acid being readily soluble in sodium carbonate. Washing with hot water to remove soda, and with alcohol to remove water, and then rapid drying in the water-oven, complete the preparation of the new compound.

As thus prepared, however, it may still contain free tellurium resulting from the action of water on the sulphoxide, insignificant indeed in quantity if the heating in the vacuum has been strong and protracted, or perhaps entirely absent. For, as we shall describe further on, the new oxide appears to be one of the products of the decomposition of the sulphoxide by water, and is undoubtedly the first tellurium-product of the reaction, the free tellurium being only a secondary product. The sulphoxide being here present in very small quantity only, and spread through a mass of the new oxide, is probably in the condition most favourable to the permanence of the products of its primary decomposition. Be this, however, as it may, experience and practice have enabled us so to improve our working as at last to prepare the oxide unmixed with any quantity of free tellurium sufficient to betray its presence on analysis, whereas at an earlier stage of our work, we obtained evidence of the presence of small quantities of tellurium diminishing in successive preparations.

The new oxide seems also to be obtained in small quantity by the action of water on the sulphoxide. This action, as Weber has pointed out,\* results in the production of tellurium, tellurous oxide, and sulphurous acid. But besides these substances, there are also formed sulphuric acid and, apparently, the oxide of tellurium here described. For we find the black matter precipitated by this action, not only to

\* Abstracts in this Journal, **42**, 804, and in the *Berichte*, **15**, 1336, of the paper in *J. pr. Chem.*, **24**, 218.

differ somewhat in aspect from tellurium reduced by sulphurous acid, in being brownish rather than bluish-black, but also to yield some tellurium dichloride when acted upon by dry hydrochloric acid. The greater part of the precipitate is undoubtedly free tellurium, and this part remains unaffected by the hydrochloric acid. If the oxide here present were the dioxide, it too would, in contact with the free tellurium, give the dichloride with hydrochloric acid, the tetrachloride being an intermediate product. But the fact of the previous washing with sodium carbonate should preclude the supposition of its presence.

The well-known purple-red solution of tellurium in sulphuric acid, when poured gradually into a very large volume of water, also yields the new oxide, apparently together with the other products obtained from the sulphoxide. But tellurium dichloride, decomposed by water, gives no monoxide even where the water used contains alkali, the sole products being hydrochloric acid, tellurous acid, and free tellurium.

The new oxide of tellurium is quite stable in dry air at common temperatures. It is black in colour with a slight brown shade, and shows, when pressed with a hard body, a graphitic lustre quite distinct from that of powdered tellurium itself, which, when the tellurium is pressed, is light-grey and much brighter.

Its composition may be expressed by the name and formula *Tellurium monoxide*,  $\text{TeO}$ , but its constitution is probably more complex than such a name and formula indicate. Its composition has been ascertained by oxidising it with bromine in hydrochloric acid water, precipitating the tellurium with sulphurous acid, washing the precipitate on a tared filter, and weighing. Using 0.3179 gram of one preparation, and 0.3378 gram of another, we obtained quantities of tellurium corresponding to 90.0 and 88.8 per cent. respectively. Taking  $\text{Te}$  as 128 and calculating for  $\text{TeO}$ , the tellurium comes out 88.9 per cent.

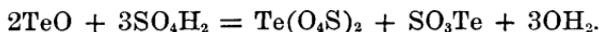
Heated strongly in a vacuum, tellurium monoxide decomposes, as already stated, into tellurium dioxide and tellurium. Heated in the air, it slowly oxidises to dioxide. In the moist state, it slowly cakes together, apparently by formation of dioxide; but whether by oxidation, or by a decomposition with water in which tellurium is liberated, or in both these ways, we have not yet determined.

Potassium hydroxide in cold solution acts but slightly upon it; but when boiled with it gradually decomposes it, leaving elemental tellurium undissolved. It is much more unstable in presence of acids. Even cold dilute solutions of hydrochloric or sulphuric acid act markedly upon it, while hot fuming hydrochloric acid at once decomposes it into tellurium and its dioxide, the latter, of course, dissolving.

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It is readily oxidised by nitric acid and by acid oxidising solutions, less easily by neutral or alkaline solutions. Potassium permanganate is reduced by it to manganate. It is but little acted upon by sulphur dioxide solution in absence of acids, but is slowly reduced by it to the elemental state.

Liquid sulphur trioxide appears to be without any action upon tellurium monoxide, even when boiled upon it. The monoxide becomes, indeed, slightly reddened, but remains otherwise unchanged, and when heated, does not exhibit the least intumescence, as it would do if converted into sulphoxide. The slight reddening observed may with certainty be attributed to the action of a trace of sulphuric acid, partly in the sulphur trioxide, partly formed by hygroscopic moisture in the tellurium monoxide. Sulphuric acid is immediately and strongly coloured red by the monoxide, which dissolves completely in it, but rapidly deposits a considerable quantity of crystalline tellurous sulphate—



Hydrochloric acid gas is absorbed by it, but without much apparent change until a gentle heat is applied, when it partly melts to a brownish-black liquid, and then sublimes as a dark-greenish powdery solid, which is decomposed by water into hydrochloric acid, tellurous acid, and tellurium, and is therefore the already known dichloride of tellurium.

No compound of tellurium monoxide has been obtained by us, and we are unable to assign to it either acid or basic properties. Analogy would make it basic, since the dioxide can act as a feeble base. The monoxide is, however, very probably of complex constitution, more complex than the dioxide can be.

The existence of this new substance only in the solid and amorphous state, and its inability to form compounds, unless we regard the sulphoxide as one, may, perhaps, suggest to others, as such facts did at first to us, doubts of its individuality. We will, therefore, state the results of an examination we made for comparison of the properties of a mixture of free tellurium with an equal weight of tellurium oxidised to dioxide. The tellurium used was in the reguline state rubbed to fine powder. Precipitated tellurium, not easily obtained so pure, was found to be scarcely more sensitive to reagents than the monoxide obtained as above.

This mixture is whitish-grey, and remains so after it has been heated, like the monoxide, to  $230^\circ$  in a vacuum. It is at once resolved by a solution of potassium hydroxide into its ingredients. In cold hydrochloric acid gas it becomes wet, in consequence of formation of the liquid tetrachloride from the dioxide. When heated,

the mixture of tetrachloride and free tellurium behaves, of course, like the monoxide, in yielding the dichloride.

The behaviour of the mixture in liquid sulphur trioxide is strikingly unlike that of the monoxide. It assumes a light-pink colour, and is changed into a mixture of unaltered tellurium dioxide and tellurium sulphoxide, and when the mixture is heated, causes it to swell up enormously. It is, perhaps, necessary to mention here that tellurium dioxide and sulphur trioxide do not combine together. Lastly, in sulphuric acid, the mixture becomes mechanically separated into its ingredients, the dioxide rendering it milky, while the free tellurium is deposited, and dissolves very slowly and slightly, forming a pink colour.

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