XLI.—*On Tellurium Sulphoxide.*

By EDWARD DIVERS and M. SHIMOSÉ.

IN connection with a reaction which we had observed between sulphuric acid and tellurium compounds, we made experiments, some time ago, upon the action of sulphur trioxide upon tellurium. These resulted in the discovery of the sulphoxide of tellurium, of which, at that date, no account had then reached us. But, soon afterwards, we found in the number of the *Berichte* for June, and that of the Journal of this Society for August, abstracts of Rudolph Weber's paper announcing the prior discovery of this substance. On reading these accounts, however, we noticed that our results were not quite in accordance with his, and we therefore proceeded to complete our own experiments.

The Tellurium used.—We obtained tellurium free from the mud of the lead chambers of the Imperial Japanese Sulphuric Acid Works in Osaka. The greater part of the tellurium existed in the weak acid supernatant liquor of the mud. This mud had been exposed to the air for a long time, and the tellurium had become oxidised and dissolved during the exposure. From this liquor the tellurium, mixed with a little selenium, was precipitated by hydrogen sulphide. The washed precipitate was dissolved in nitrohydrochloric acid, and the solution precipitated by sulphur dioxide. The washed precipitate was dissolved in melting potassium cyanide, and the product, after cooling, treated with water. After leaving the mixture at rest, the clear solution was decanted from insoluble matters, and precipitated by a

current of air. The precipitate was washed and dried, and distilled in a hard glass tube in a current of carefully purified hydrogen.

The Sulphur Trioxide used.—This was prepared, and rectified, and combined with the tellurium in a piece of glass apparatus, consisting of a piece of combustion-tube drawn out as shown in the figure.

The tellurium, finely powdered, and dried in a water-oven was introduced, in weighed quantity, into the seventh receptacle, through the drawn-out end of the tube. The tellurium did not adhere to the sides of the tube. Dried air having been passed through the apparatus for a considerable time, both before and after the introduction of the tellurium, the drawn-out end was sealed. Through the other end a considerable charge of sulphuric acid and phosphorus pentoxide was then introduced into the first receptacle, and the funnel-like end sealed off in the lamp. Ice having been applied to the second receptacle, the mixture in the first was gently heated until enough sulphur trioxide had distilled into the second. The first receptacle was then sealed off. The sulphur trioxide was next successively distilled into the third, fourth, fifth, and sixth receptacles. Only in the second was there any sensible residue after very gentle heating. The other receptacles having been sealed off, one after the other, there remained only two in connection, one holding the sulphur trioxide, the other the tellurium. The sulphur trioxide thus prepared was a mobile liquid, crystallising in transparent prisms, and having for some time, at least, a melting point of about 15° C.

Preparation of the Tellurium Sulphoxide.—Sometimes we distilled the sulphur trioxide over into the tellurium, but we found it preferable to pour the oxide on to the metal, because in this way we could ensure contact of all the particles of the latter with the former. The two substances remain in contact for a short time without reaction, and for a longer time if the mixture is cold enough. The reaction takes place with distinct evolution of heat, and becomes visible by conversion of the loose grey tellurium into the more bulky, deep red, coherent sulphoxide. The supernatant trioxide in excess remains quite colourless, as observed by Weber. The reaction appears to be complete in a few moments after it has set in. The new solid having

been digested in the liquid oxide for some time at a temperature of 30—40°, the latter was drained off into the other receptacle and this was sealed off. The other sealed end was connected with a Sprengel pump, and its point broken off within the caoutchouc tube. The sulphur trioxide adhering to the tellurium compound was then removed, as completely as possible, by letting the mercury fall for an hour, while the tube holding the sulphoxide was immersed in water at about 35°. A long tube packed with borax and drawn out at each end, and interposed between the pump and the preparation-tube, served very effectively to arrest any sulphur trioxide. Potassium hydroxide, used at first instead of borax, was acted upon so violently as to melt and sometimes choke the tube. The preparation-tube was finally detached momentarily from the pump, so as to admit air, and its open end was then sealed.

Properties and Composition of Sulphoxide.—The sulphoxide, thus prepared, is an amorphous solid, which softens without melting at about 30°. It is of a beautiful red colour, and transparent in very thin layers. So far, it is just as Weber has described it. It is finely vesiculated, in consequence of the vaporisation within its substance of the excess of sulphur trioxide at first mixed with it. This vesicular state lightens the shade of the redness of the substance, and the walls of the vesicles are so thin as to make the surface of the mass iridescent.

Weber (*loc. cit.*) describes it as being very unstable, decomposing even in sealed tubes at ordinary temperatures, and yielding sulphur dioxide.* But, according to our experience, it appears to be quite stable at ordinary temperatures in the closed tube when pure, neither changing colour nor evolving sulphur dioxide.† During its preparation and purification, also, no sulphur dioxide was produced, when the sulphur trioxide was quite anhydrous. The sulphoxide does, indeed, sometimes slowly decompose when left in the crude state, its red colour assuming a brown shade, and then, too, sulphur dioxide is formed. We have not succeeded in determining the conditions of the occurrence of this change. Possibly it depends upon the sulphur trioxide used not being quite anhydrous. At one time we thought that it might be due to this action of light, but experiment has not confirmed our supposition.

* And tellurium also, according to the abstract in this Journal, but if so it must yield either tellurium dioxide or sulphur trioxide as well.

† A specimen of it, prepared on or about January 18th, will be laid before the meeting at which this paper is read, and it will be interesting to see whether it has remained unchanged during an interval of some months and a journey half round the world. [The specimens received from the authors, judging from their description, are unaltered.—HENRY E. ARMSTRONG.]

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We have several times analysed the red sulphoxide, but only in one case have we found it to contain exactly the quantity of sulphur trioxide indicated by the formula SO_3Te , all the analyses giving an excess of SO_3 . This one case, however, assuming the absence of error in our analysis, must be regarded as establishing its composition. The excess of sulphur trioxide in the other cases was most probably due to a retention of some of this substance within cavities in the viscid mass. Weber assigns to the sulphoxide the composition as we indicated by the above formula, having obtained in one case the calculated quantity of tellurium, in another a very little less than this. He purified his preparations from sulphur trioxide by pressing the warm viscid masses with a glass rod. This method of purification proved impracticable in our hands.

The details of our analyses are as follows:—The weight of tellurium used was taken before converting it into the sulphoxide; one point of the sealed tube containing the purified sulphoxide having been scratched with a file, the tube was weighed, its point cracked off, and the open end immersed in a dilute solution of bromine and hydrochloric acid. Very gradually this solution was allowed to act on the sulphoxide, so as to avoid loss by violent action. The tube, having been washed out and dried was weighed; the difference between the two weighings gave the weight of the sulphoxide, and the difference between this and the weight of the tellurium, gave the weight of the sulphur trioxide; but to make certain of the absence of water or any other foreign matter, the telluric acid in solution was reduced to tellurous acid by boiling with hydrochloric acid, and the sulphuric acid precipitated by barium chloride and weighed. These were the results:—

	I.	II.
Tellurium	0·6510	0·4862
Sulphur trioxide	0·4608	0·3020
Sum	1·1118	0·7882
Tellurium sulphoxide ..	1·1113	0·7885
Difference	−0·0005	+0·0003

The following are the percentage quantities calculated:—

	I.	II.	SO_3Te .
Tellurium	58·58	61·66	61·54
Sulphur trioxide	41·46	38·30	38·46
			100·00

β-Tellurium Sulphoxide.

When red tellurium sulphoxide is heated sufficiently, its colour changes to a bright fawn-brown. Prolonged heating in a vacuum even at 35° effects this change, but so very slowly that no change can be perceived, even after the lapse of an hour. At higher temperatures the transformation is more rapid, and at 90° almost instantaneous. No gas is evolved, and besides the striking change of colour, nothing else is observable. The vesicular condition remains just as it was, even to the iridescence of the superficial vesicles.* Heated to 130°, it softens and shrinks, its vesicular structure collapsing. Its brown colour is now of a deeper shade, owing to the absence of the vesicles. Heated to 180°, it again changes colour, and again becomes vesiculated, this time from evolution of sulphur dioxide. The mass becomes eventually black and solid on further heating, and now consists of the tellurium monoxide, described by us in another paper, the decomposition being almost complete at about 230°. The earlier effects of heating the red sulphoxide under atmospheric pressure do not appear to differ essentially from those of heating in a vacuum.

We have analysed this brown substance in the same way as the red, and find that it has the same composition. The results were:—

	I.	II.	III.
Tellurium.....	0·5829	0·1709	—
Sulphur trioxide.....	0·3715	0·1070	0·3178
Sum	0·9544	0·2779	
Tellurium sulphoxide..	0·9548	0·2780	
Difference ..	+0·0004	+0·0001	

In III we had not weighed the tellurium before making the sulphoxide. Calculating from the above numbers we get—

	I.	II.	III.	Mean.	SO ₃ Te.
Tellurium	61·04	61·47	—	61·26	61·54
Sulphur trioxide ..	38·91	38·53	37·90	38·45	38·46
					100·00

The brown sulphoxide now described remains unaffected when digested with liquid sulphur trioxide. But like the red sulphoxide, it dissolves readily in sulphuric acid, without evolution of sulphur dioxide, and yields the usual deep amethyst-red solution. In its behaviour with water, no difference from the red sulphoxide has been

* A specimen of the brown sulphoxide accompanies this paper.

observed, if we except a somewhat more violent action in the case of the red, perhaps due to the presence of a little sulphur trioxide in the preparation so tested.

As remarked in our paper on tellurium monoxide, the sulphoxide of tellurium yields with water free tellurium, the monoxide, tellurous acid, sulphurous acid, and sulphuric acid. A quantitative examination of this reaction has shown us that much more than half the tellurium is reduced to the elemental state.

The equations—

and secondarily—

under the influence of the sulphuric acid formed, may serve to show how the products can be derived from the sulphoxide, and the elemental tellurium be in excess. But a satisfactory theory of the change has not presented itself to us. Even if the occurrence of the monoxide among the products be disregarded, and the equation

be adopted, the production of excess of tellurium, and of the sulphuric acid remains inexplicable, since sulphurous acid has no reducing action upon tellurous acid either alone or in presence of sulphuric acid, hydrochloric acid being required. We are strongly inclined to hold that the decomposition, $\text{SO}_3\text{Te} + \text{H}_2\text{O} = \text{TeO} + \text{SO}_3\text{H}_2$, is the primary one, although this assumption does not remove all the difficulties.

We do not think that the problem of the constitution of the sulphoxide receives any solution from the existence of its two modifications and their conversion into the monoxide. The monoxide does appear to be a base, and does not enter into chemical combination with other substances, while the modifications of the sulphoxide do not exhibit any differences in their few known reactions. If the sulphoxide is a sulphite, it is strange that it should dissolve in sulphuric acid without giving off sulphurous acid. Further, if it is a sulphite, it should be in the same series of tellurium compounds as tellurium monoxide, and there should be a corresponding hypotellurous sulphate, SO_4Te , formed from tellurium monoxide and sulphuric acid, which is not the case. As described elsewhere, the monoxide does dissolve in sulphuric acid, but it is at the same time converted into dioxide and—in solution in the acid—the red compound, which we must now regard with more certainty than before as the sulphoxide itself, and not a sulphuric compound corresponding with it.

We think that, for the present, the most probable formulæ of the sulphoxide in its two modifications, are—

which represent the red modification as a sulphonate of tellurium in the unstable condition of bivalency, and the brown modification as a better balanced combination of oxides of the two elements, in which both are quadrivalent, and the combination, therefore, more stable under rise of temperature than the red modification, and yet a combination out of which the tellurium cannot be expected to separate from the sulphur without reduction at the same time to a state of lower valency. If we had not Weber's evidence of the non-existence of two modifications of sulphur trioxide, we might connect these with the two modifications of tellurium sulphoxide.

Two quite distinct modifications of selenium sulphoxide appear to exist. We are at present examining them.