XXI.—*On Baudrimont's Protosulphide of Carbon.*

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Baudrimont has given various processes for the preparation of protosulphide of carbon, a body long expected by chemists and necessary to complete the analogy between sulphur and oxygen. Protosulphide of carbon bears the same analogy to carbonic oxide that bisulphide of carbon does to carbonic acid. The discovery of the body surprised no one, but it was a matter of astonishment that the numerous and simple processes for its preparation had remained so long unknown to chemists.

The description given by Baudrimont* for the preparation and properties of this interesting body is short, further details being promised in a future paper. Meanwhile, the new compound has received admission into systematic works on Chemistry.

Being desirous of making some experiments with protosulphide of carbon, I have repeated without success the processes described by Baudrimont; I have been equally unsuccessful with others which appeared equally promising. It is therefore desirable to obtain further evidence of this existence of the compound; for the products of the processes described are in most cases only carbonic oxide with the vapours of bisulphide of carbon, and, in other cases, mixtures of carbonic oxide, hydrogen, carburetted hydrogen and the vapours of bisulphide of carbon.

Baudrimont, in the memoir above referred to, gives nine processes for the preparation of protosulphide of carbon, but admits that only the first process yielded it in a state of tolerable purity. To this process it will therefore be sufficient to direct special attention. The vapours of bisulphide of carbon are to be passed over red hot pumice-stone or spongy platinum, which have the effect, according to Baudrimont, of doubling the compound, (so much sulphur being at the same time deposited as to choke the exit tubes), while the gaseous protosulphide of carbon passes on, and may be collected, after transmission through solutions of acetate of lead and dichloride of copper.

In repeating this and subsequent experiments, it became obvious that the presence of organic matter and moisture was a frequent source of error, and it was necessary to operate so as to exclude these; accordingly the following arrangement was adopted:—

A long tube of difficultly fusible glass was filled with fragments of pumice-stone to the extent of three feet in length, and then the posterior end was drawn out into a U shape, and the anterior end into a delivery tube for gaseous products. The capacity of the whole tube was about 95 cubic centimeters. The body of the tube containing the pumice stone was placed in Hofmann's gas furnace and heated, a stream of carbonic acid, dried by sulphuric acid, being passed over it until all moisture was expelled. When the desiccation of the tube and pumice-stone had been effected, 8 grammes of dry bisulphide of carbon were sucked into the U portion of the tube, which was then sealed by a lamp and placed in a water-bath.

* Comptes rendus, xliv, 1000.

The whole of the bisulphide of carbon was now slowly passed over the red hot pumice and the products were collected over mercury by the delivery portion of the tube. The heat employed was sufficient to alter the shape of the tube, although it was protected as is usual in combustion, by metallic gauze.

During the experiment gas came over, and with it liquid bisulphide which condensed in the eudiometer. After the 8 grammes of bisulphide had been slowly passed over the red hot pumice-stone, the products were as follows :—

Gas at 730mm. press. 12°C. temp. . . .	155 cub. cent.
Liquid bisulphide of carbon	5 cub. cent.

The gas corrected for temp. and pressure, and for the tension of CS_2 with which it was saturated (200mm. at 12°C. Brezelius) gave

Corrected vol. of gas and 0°C. and 760mm. press. 103·5 cub. cent.

Caustic potash was now passed up to absorb carbonic acid and sulphuretted hydrogen, and the gas now measured 59 cub. cent. at 12°C. and 610mm. pressure, still saturated with bisulphide of carbon. Corrected for this and brought to the normal temperature and pressure there was only 30·49 cub. cent. of gas left.

Hence of the 8 grammes of bisulphide, at least 6·4 grammes were found condensed in the eudiometer; the remaining 1·6 gramme was chiefly in the long delivery tube, which had a column of condensed bisulphide in it, but this was not measured. If we neglect this and assume that 1·3 gramme was decomposed into protosulphide of carbon (0·3 gramme in vapour being allowed for the capacity of the tube), 383 cub. cent. of this gas should have been produced. But after correcting for the pressure, temperature, and for the tension of CS_2 , only 30·49 cub. cent. were obtained. This small quantity of residual gas consisted of carbonic oxide and nitrogen, resulting from the traces of air and moisture still left in the pumice-stone, or introduced when the bisulphide of carbon was drawn into the apparatus. But if we assumed the whole residual gas to be protosulphide of carbon, it would have

weighed only 0·060 gramme, and would have been produced from 0·09 gramme of the bisulphide. Hence in any case not more than 1·4 per cent. of the bisulphide employed could have been decomposed in its passage through the red-hot pumice. But this gas was chiefly carbonic oxide produced by the action of moisture—($\text{CS}_2 + \text{HO} = \text{CO} + \text{S} + \text{HS}$), and required only 0·027 HO to produce it, a quantity which can easily have escaped the drying process.

A careful examination of the tube and pumice-stone showed that no sulphur whatever was deposited, except one or two specks which could not have been weighed, the whole operation having been one of simple distillation without decomposition. When the pumice-stone is not completely dry, then sulphuretted hydrogen and carbonic oxide appear, while sulphur is deposited.

Having failed in obtaining protosulphide of carbon by the only process which Baudrimont describes as giving it pure, it was scarcely necessary to repeat the other methods; but those described as yielding the best results were examined. The chief of these is to pass the vapours of bisulphide of carbon over red-hot charcoal, animal charcoal being recommended.

On repeating these experiments, large quantities of gas were obtained at first; but the gas ceased abruptly, although the tube still contained abundance of animal charcoal, and now bisulphide of carbon distilled over unchanged. The gas collected in the first part of the experiment was washed with solution of acetate of lead and dichloride of copper, but continually decreased in bulk, until only a small quantity remained. This was analysed with the following results:—20·295 cub. cent. gave

Carbonic oxide	.	.	.	.	11·79
Bisulphide of carbon	.	.	.	.	4·66
Nitrogen	.	.	.	.	3·83
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					20·28

The analysis was however only approximate, as some sulphuric acid was formed in the combustion of the gas.

A like experiment made with wood-charcoal gave precisely similar results.

Both these experiments proved that the gas at first obtained was due to the organic matter and moisture acting on the bisulphide of carbon and that the latter distilled over unchanged, as soon as the former were removed.

It is unnecessary to describe the other experiments made in the hope of procuring protosulphide of carbon, as they all gave negative results.

Baudrimont gives as evidence of the composition of the gas obtained by him (1) that lime-water decomposed it into sulphide of calcium and its own volume of carbonic oxide. It is clear that this experiment was not a quantitative one, as no allowance is made for the solubility of the protosulphide of carbon, which is stated to dissolve in its own bulk of water. Hence the result may have been due to a mere mixture of carbonic oxide containing the vapour of bisulphide of carbon and a little sulphuretted hydrogen. (2) Baudrimont states that eudiometric analysis gave equal volumes of CO_2 and SO_2 ; but this result would be equally attained by the combustion of a gas containing equal volumes of CS_2 and CO ; and, at the ordinary temperature, with the diminished pressure in the eudiometer, the tension of CS_2 is more than sufficient to double the volume of gas in the tube. It may further be remarked that Baudrimont does not give any process for removing bisulphide of carbon from the gases obtained by him.

In conclusion, it must be admitted that there is no sufficient evidence of the existence of protosulphide of carbon, all the processes described for its preparation having failed to yield it. Buff and Hofmann* seem to have been equally unsuccessful in their endeavours to obtain it from bisulphide of carbon by electric incandescence.