XXVII.—*On Sulphine Salts containing the Ethylene Radical.*
Part II. *Dehn's Reaction between Ethylene Bromide and Ethyl Sulphide.*

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IN 1865 Dehn published (*Annalen*, Suppl. **4**, 83) an account of the action which occurs when ethylene bromide and ethyl sulphide are heated together with water in sealed tubes. In the same year,

Cahours (*Annalen*, **136**, 151; and *Compt. rend*, **60**, 1147) described the action of methyl sulphide on ethylene bromide. They arrived, however, at very different conclusions; for, whilst Cahours stated that a disulphine salt of the constitution $(\text{CH}_3)_4(\text{C}_2\text{H}_4)\text{S}_2\text{Br}_2$ is produced, Dehn observed no such product of direct union. According to him, the main reaction consists in double decomposition by which ethyl bromide and diethylene disulphide are formed—

and this is accompanied by the union of part of the ethyl bromide with ethyl sulphide to form triethylsulphine bromide—

Returning to the subject in 1869 (*Ber.*, **2**, 479), Dehn stated that he had repeated his experiments with similar results, using methyl sulphide in place of ethyl sulphide; and he accordingly asserted that Cahours' supposed disulphine salt was in reality only trimethylsulphine bromide. This was afterwards, in 1875, acknowledged by Cahours to be the case (*Compt. rend.*, **80**, 1317; also *Ann. Chim. Phys.* [5], **10**, 13), and he fully confirmed Dehn's statement as to the formation of diethylene disulphide and triethyl(or methyl)sulphine bromide as the main products of the reaction. It is necessary to mention these facts, as descriptions of the purely imaginary salt, $(\text{CH}_3)_4(\text{C}_2\text{H}_4)\text{S}_2\text{Br}_2$, occur in some of our dictionaries of chemistry.

According to Dehn, the two equations given above do not represent the whole reaction; for in addition to the triethylsulphine bromide there are formed the bromides of two other sulphine bases, but in much smaller quantity than the former. His complete scheme for the reaction includes the equations—

That is to say, there are formed side by side three distinct sulphine salts, one of which is of the ordinary kind containing tetrad sulphur, whilst the others are of a different character and contain hexad sulphur. In his second paper (*Ber.*, **2**, 479), Dehn states that he regards the formation of the salt, $(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{SBr}_2$, as proved by his experiments, and that of $(\text{C}_2\text{H}_4)_2\text{SBr}_2$ as not absolutely proved, but shown to be very probable. Cahours, in his later papers, corroborated Dehn as to the formation in small quantity of at least one other sulphine compound besides triethylsulphine bromide. He did not himself investigate this product, but he expressed a doubt as to the

* Dehn wrote the formula $\text{C}_2\text{H}_4\text{S}$, but his description of the substance shows it to have been the disulphide.

accuracy of Dehn's view of its constitution, a view, however, which he most strangely misrepresented.

As regards equation IV, one thing is at once obvious, that it involves a neglect of the fact that it is diethylene disulphide, $(C_2H_4)_2S_2$, and not a substance of the formula C_2H_4S , that, according to Dehn's own showing, results from the primary reaction. Other considerations, however, combine to make it difficult to accept Dehn's theory concerning these secondary products. It is based upon the idea that a class of sulphinic salts can exist, resembling the sulphinous salts in their general characters, and standing to them in a relation similar to that of sulphuric anhydride to sulphurous anhydride. This view, though plausible enough in 1865, is considerably weakened by the fact that no additional evidence of its truth has been published since that date. Indeed, if his theory be really a correct one, Dehn's salts stand alone, and occupy a position of very considerable importance to the student of sulphur compounds. This was recognised by Divers, who, in a recent paper bearing on the atomicity of sulphur (*Trans.*, 1885, 213), referred to Dehn's salts, and to the halogen addition products of trimethylsulphine (described by Dobbin and myself) as exceptions—and apparently the only ones—to his rule that sulphur is never more than tetrad. The latter exception is, as yet, at any rate, a somewhat doubtful one; and I believe that the sequel will show that Dehn's salts need form no exception at all.

Dehn was unable to isolate and examine the bromides themselves; and a perusal of his paper shows that his theory of their constitution rests entirely on the properties and partial analyses of their platinochlorides. The question to be answered therefore resolves itself into this:—Is there sufficient reason for believing that these salts were respectively $(C_2H_4)(C_2H_5)_2S^{VI}Cl_2$, $PtCl_4$ and $(C_2H_4)_2S^{VI}Cl_2$, $PtCl_4$, as he represented them, or is it possible to substitute for these formulæ others more in keeping with the experimental evidence and with general probability?

His method of procedure was as follows:—The cold dilute aqueous solution of the mixed sulphine bromides, freed from diethylene disulphide and ethyl bromide, was shaken with recently prepared silver oxide, and the resulting mixture of hydroxides was treated with excess of hydrochloric acid, warmed, and fractionally precipitated with solution of platinic chloride. The triethylsulphine salt, being soluble in hot water, was the last to form. The first salts precipitated were yellow powders, apparently crystalline, practically insoluble in cold or hot water and in dilute acids, but somewhat soluble in strong aqueous ammonia. They were not acted on by hydrogen sulphide in the cold, but were decomposed by a stream of the gas when suspended in hot water.

The first two fractions of this insoluble precipitate contained 39.13 and 38.39 per cent. of platinum. Dehn's formula, $(C_2H_4)_2S_2Cl_2, PtCl_4$, requires 39.31 per cent. (taking Pt as 195). There was not sufficient material for further analysis. The subsequent fractions had a constant composition, which, as tested by determination of the carbon, hydrogen, and platinum, agreed fairly well with that calculated from the formula $(C_2H_4)(C_2H_5)_2S_2Cl_2, PtCl_4$.

As this is all the actual evidence brought forward by Dehn in proof of his theory of the existence of the sulphinic salts, that theory must fall if it can be shown that there is *a priori* ground for believing that these platinum salts had altogether different formulæ, and also that Dehn's own analyses agree as well, or better, with these formulæ than they do with his own.

As regards the first point. The properties of Dehn's platinum salts are strikingly unlike those of most platinichlorides, but are identical with those of the salt $(C_2H_4)_2S_2(C_2H_5)Cl, PtCl_4$, described in the last paper (p. 245) except in so far as "apparently crystalline" differs from "amorphous." This salt, like Dehn's, is an insoluble yellow powder thrown down when a hot solution containing the parent sulphine chloride is precipitated with platinic chloride. The iodide corresponding to it is formed by the union of diethylene disulphide $(C_2H_4)_2S_2$ with methyl iodide. It is not unnatural to suppose that the same sulphide will unite, though less energetically and completely, with ethyl bromide and even with ethylene dibromide. If these analogous reactions can occur, they will give rise to sulphine salts of the formulæ—

In Dehn's reaction, as we have seen, diethylene disulphide is formed as a product of the first change: it is formed together with ethyl bromide and in the presence of ethylene bromide, and amidst conditions of temperature, &c., specially devised to favour such combinations. If, therefore, the salts whose formulæ are given above are capable of being produced, they would certainly be formed in Dehn's experiment. The platinum salts would then have the formulæ $(C_2H_4)_2S_2(C_2H_5)Cl, PtCl_4$ and $[(C_2H_4)_2S_2]_2(C_2H_4)Cl_2, 2PtCl_4$. The following table gives a comparison of the percentage composition required by the first of these with that required by Dehn's theory and with the numbers deduced from his analysis:—

	Calculated for (C ₂ H ₄) ₂ S ₂ (C ₂ H ₅)Cl ₂ PtCl ₄ .	Found by Dehn.	Calculated for (C ₂ H ₄)(C ₂ H ₅) ₂ SCl ₂ PtCl ₄ .
C	13·81	14·17	13·69
H	2·49	2·66	2·66
S	12·27	—	6·08
Pt	37·39	37·29 and 37·24	37·07
Cl	34·04	—	40·50
	<hr/> 100·00		<hr/> 100·00

Though the differences are comparatively small, they are significant; and they do not favour Dehn's formula. Had he estimated either sulphur or chlorine, it is obvious that he would have come to a different conclusion.

The evidence as to the constitution of the other sulphine salt, or indeed of its existence, is so slight that it seems almost superfluous to suggest that it was most probably $\{(C_2H_4)_2S_2\}_2(C_2H_4)Cl_2, 2PtCl_4$. This requires 38·50 per cent. of platinum: Dehn found in his first fractions 39·13 and 38·39 per cent. But there is reason to believe, from the following experiment, that the corresponding bromide, as well as the salt $(C_2H_4)_2S_2(C_2H_5)Br$, must have been produced in Dehn's reaction, though in small quantity.

Two sealed tubes were prepared, the one containing diethylene disulphide with excess of ethyl bromide and the other diethylene disulphide with excess of ethylene bromide. After being heated for several hours at a temperature of 125—150°, they were cooled and opened. In each case, free hydrobromic acid and disagreeable volatile sulphur compounds were found to have been formed, but the bulk of the disulphide was unaffected. By extraction with warm water, however, small quantities of a sulphine bromide were obtained from each tube; and these possessed the following characteristic properties, a comparison of which with those of the salts of diethylenesulphide-methyl-sulphine removes any possible doubt as to their true nature.

(1.) They both undergo partial decomposition when their solutions are evaporated to dryness, a white insoluble substance being produced. The decomposition occurs to a greater extent than in the case of the corresponding methyl salts.

(2.) They are both decomposed by heating with alkalis: a sudden turbidity occurs, due to the separation of a white flocculent solid, and a volatile sulphur compound is evolved having a strong and peculiar odour. This odour is different in the two cases; for, whilst that derived from the ethylsulphine exactly resembles the smell of the oil C₁₂H₂₄S₅ (p. 247), that from the ethylene compound is of a more pleasant character.

(3.) With recently precipitated silver oxide, they give alkaline solutions, which, on the addition of hydrochloric acid, and, after warming, of platinic chloride, yield insoluble yellow amorphous precipitates.

These facts and the considerations already adduced seem to justify the following equations, III and IV, being written in lieu of Dehn's. The whole scheme for the reaction becomes—

It is probable that the iodides of ethyl and ethylene would combine with diethylene disulphide much more readily and completely than the bromides. If this be so, the products may repay an investigation, more particularly the ethylene one. I propose therefore to continue my experiments.