

XXXVIII.—*Note on the Sulphur-compound formed by the action of Sulphuretted Hydrogen on Formate of Lead at a high temperature.*

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IN the year 1856, Limpricht* published an account of some analyses of a crystalline body, obtained together with formic acid

* Ann. Ch. Pharm., xcvii. 361.

by acting upon formate of lead heated to 200° — 300°C with a current of sulphuretted hydrogen. As the result of his sulphur determinations he assigns to this body the formula $\left. \begin{smallmatrix} \text{C} & \text{H} & \text{O} \\ & & \text{H} \end{smallmatrix} \right\} \text{S}$, naming it thioformic acid, and supposing it to be analogous to the thiacetic acid $\left. \begin{smallmatrix} \text{C}_2 & \text{H}_3 & \text{O} \\ & & \text{H} \end{smallmatrix} \right\} \text{S}$ of Kekulé.*

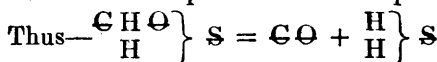
Seeing that the character of this interesting body has been but slightly investigated, I undertook, at the suggestion of Professor Roscoe, a further examination of its properties and the mode of its formation, the results of which, although mainly negative, I think it may be well to place on record.

When dry formic acid is acted on by pentasulphide of phosphorus, no trace of a sulphur acid is produced; the mixture distilled upwards continuously for several hours, slowly evolving sulphuretted hydrogen, the whole distillate boiling exactly at 101°C , and containing no sulphur in combination.

Heated in closed tubes to 106°C , the mixture underwent decomposition, but no thioformic acid was produced. So, likewise, when formic acid and pentasulphide of phosphorus were heated together under a total pressure of 3 atmospheres, torrents of sulphuretted hydrogen and carbonic oxide gases escaped, and the residual liquid all distilled over at 101°C , and contained no sulphur.

Formate of lead and pentasulphide of phosphorus distilled together, both in the dry and moist state, also yielded no thioformic acid.

From these experiments it is evident that thioformic acid cannot be produced by the method which Kekulé employed for the preparation of thiacetic acid. The elimination of sulphuretted hydrogen and carbonic oxide seems to point to a decomposition of the thioformic acid at the temperature of the experiments:



By Limpricht's method of decomposing formate of lead at a high temperature with a current of sulphuretted hydrogen, a solid crystalline body was obtained; but it was produced in much smaller quantities than Limpricht states; 15 kilos. of formate yielding only about 3 grammes of the purified substance.

The body, which crystallizes in beautiful long white needles, was purified by repeated crystallizations from hot formic acid, and

* Ann. Ch. Pharm., xc, 309. Phil. Mag., [4] vii, 518.

dried completely in vacuo over sulphuric acid. The combustion of the substance was effected with chromate of lead in a long tube, the anterior part of which was not heated above low redness, according to the method lately described by Carius*, so that no peroxide of lead was required; and the water in the chloride-of-calcium-tube was found to be quite free from sulphurous acid. The sulphur was determined by oxidation with warm nitric acid; the sulphate of barium, being carefully rewashed with hydrochloric acid, and reweighed after incineration, to remove traces of nitrate of barium carried down.

The results were as follows—

Calculated for the formula

Found.

$\left. \begin{array}{c} \text{C H O} \\ \text{H} \end{array} \right\} \text{S}$		(I.)	(II.)	(III.)	(IV.)
Carbon	19.3	27.93	29.25	28.21	
Hydrogen	3.2	4.70	4.83	5.23	
Sulphur	51.6	58.11	52.87	56.7	55.15
Oxygen	25.9				
	100.0				

Limpricht's numbers were—

Carbon	26.1	25.7	23.4
Hydrogen	5.6	4.7	6.3
Sulphur	51.2	52.5	
Oxygen			

From the foregoing analyses no definite formula can be deduced, in the absence of a vapour-density or accurate atomic weight determination, which the small quantity of the substance at my disposal unfortunately did not allow me to make. The analyses, however, show clearly that the body cannot be thioformic acid, as supposed by Limpricht, the excess of carbon over the theoretical quantity being too large to be explained by experimental error.

The purified substance, which showed under the microscope no trace of foreign bodies, but a perfectly homogeneous structure, crystallizes in white shining needles from solution in alcohol, ether, and acetic or formic acids, the alcoholic solution being neutral to litmus paper. The crystals melt at 120°C., and sublime unchanged at higher temperatures, depositing in long silky needles. The dry substance has a very slight odour, but its solution in formic acid has a strong penetrating sulphur smell.

* Ann. Ch. Pharm., cxvi, 1.

It is not acted on either by hot or cold hydrochloric acid, but is easily decomposed by nitric and sulphuric acids; it is also unacted on by solutions of carbonate or hydrate of potassium, and by sulphide of ammonium. The alcoholic solution gives no precipitate with chloride of barium, but with nitrate of silver a heavy white precipitate soluble in ammonia and boiling alcohol, is produced. I did not succeed in obtaining from this silver-salt any atomic weight from which a satisfactory formula for the body could be calculated.
