

Mercury Sulphites, and the Constitution of Oxygenous Salts.

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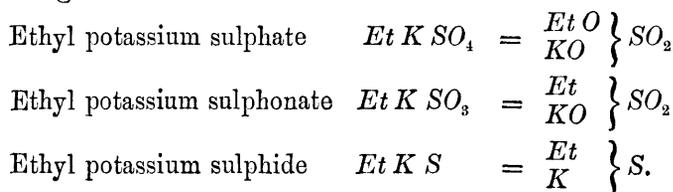
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Much less can be done in the direction of determining the constitution of inorganic compounds than of carbon compounds. One consequence of this is the one-sided development of descriptive chemistry, in which our knowledge of carbo-hydrogen compounds far exceeds that of all the others. Modern views about the constitution of inorganic salts is based almost entirely upon observations of the nature of organic compounds, since it is usually considered that very little can be learned on this point by a study of the salts themselves. In the course of our own studies, the main results of which have been already published, it has seemed, however, to us that in the metals mercury, silver, and to a less extent, copper, we have elements differing sufficiently in their chemical affinity from other well-known metals, to enable us by their means to test at least one important point in the constitution of salts. The metals we have named do not decompose water or set free hydrogen from an acid; their affinities are for nitrogen and for sulphur, rather than for oxygen; and they

form two series of salts in which they are strongly basic. Thus differentiated from most metals, their behaviour ought to throw light upon the relations of oxygen salts to 'haloid' salts; and in order to show that they may thus be used, we shall take sulphates to represent oxygen salts, and sulphides as haloid salts.

A sulphate may be constituted as a sulphide with its sulphur oxidised, or it may be oxidised metal combined with oxidised sulphur, or, again, have other constitutions which we here pass over. An examination of the mercury and, say, the magnesium salts seems at once to settle this point, because mercury sulphide is one of the most stable compounds known, and mercury sulphate is instantly decomposed by water, while magnesium sulphide is decomposed by water, and magnesium sulphate is a most stable salt, quite unaffected. For magnesium here preserves its oxylic union with sulphur, ($Mg=O_2=SO_2$), and drops that with sulphur direct, ($Mg=S$), while mercury behaves in the reverse way, as the result, we may well conclude, of the well-known affinity of mercury for sulphur rather than oxygen, and that of magnesium for oxygen rather than sulphur.

Many elements, and sulphur is one of them, form more than one oxygen acid and corresponding series of salts, and the question suggests itself, whether in the less oxidised salts there will not be a constitution intermediate to those of haloid and fully oxidised salts. In organic chemistry this question has long been answered, and the less oxidised salts, distinguished by the termination, —*onates*, recognised as constituted partly as oxylic salts, partly as haloid salts, as the following names and formulæ will serve to make clear :—



Here it will be seen that in the sulphonate, the ethyl is directly united to the sulphur, and the potassium only by the intervention of an atom of oxygen. Whether these sulphonates are true organic sulphites, and whether, therefore, inorganic sulphites are similarly constituted, or have their base wholly in oxylic union, has long been uncertain, although now the opinion most generally held is that sulphites have half their metal directly united to sulphur, thus, $Mg \overset{O_1}{\text{---}} SO_2$, and not, $Mg=O_2=SO$. This opinion has been based, however, wholly upon evidence afforded by organic bodies, and it seemed to us desirable that evidence from the inorganic sulphites themselves should be sought for, by examining the mercury, silver, and copper sulphites. Hence, the reason of our working upon mercury sulphites. We have also done a little upon silver sulphite, already pretty well known, but have not yet examined copper sulphites.

Mercury sulphites, we found, had been but very imperfectly studied. Several had been described, but we were soon convinced that of these only one really existed. To this, however, we succeeded in adding two new ones in the separate state, besides one which we only got in dilute aqueous solution. Yet after all, most remarkable to state, we could get neither the normal mercuric sulphite, $Hg SO_3$, nor the mercurous sulphite, $Hg_2 SO_3$, but only a basic salt; an acid salt; a mixed salt, partly mercurous, partly mercuric; and another mixed salt, partly hypomercurous, partly mercuric. Besides these, there are double sulphites, one of which, sodium mercuric sulphite, we have examined more fully than had been done before.

The evidence afforded by the mercury sulphites, and by silver sulphite, as to the constitution of sulphites, proved even greater than we had expected. They are not decomposed by dilute nitric or sulphuric acid, and in this they resemble the chlorides and cyanides of these metals, instead of their oxygen, (or rather oxylic), salts, while in

the same point they differ from most sulphites, which, as every chemist knows, are exceedingly easily decomposed by acids. They are not decomposed by water, except when hot, and then they are resolved into metal, whether mercury or silver, and SO_3 , which with the water forms sulphuric acid, and this again, where very little water is present, may react with any unchanged sulphite, and give mercurous or silver sulphate and sulphurous acid. This property of decomposing into metal and a non-metallic element, or group of elements, at once recalls the decomposition of mercury or silver cyanide, or gold chloride, by heat.

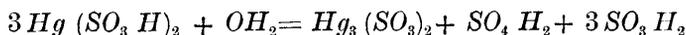
One more point of relationship with haloid salts is the particular readiness with which mercury and silver sulphites form double sulphites with very oxidisable metals, such as potassium and sodium, and the comparative stability of these salts. Thus, while a mercury or silver sulphite is decomposed by hot water, and sodium sulphite even by cold water, (if we may judge from the strongly alkaline character of its solution), yet the mercuric (or silver) sodium sulphite is neutral to litmus, and may be boiled with water, or with alkali, without decomposition. Having now discussed some of the points in chemical doctrine, which these bodies serve to throw light upon, we proceed to notice the several mercury sulphites, which in other respects are not without interest.

Mercuric oxysulphite, $(OHg_2 SO_3)_2, H_2O$, first prepared by Péan de St. Gilles, is best prepared by adding a solution of sodium sulphite to an excess of somewhat concentrated solution of mercuric nitrate, as free as possible from nitric acid. Some mercuric nitrate remaining undecomposed, the oxysulphite almost at once makes its appearance as a flocculent precipitate, rapidly becoming granular and dense. It is of a pale yellow colour, and very unstable. When dry, it is explosive; sudden and complete, though very gentle, detonation being caused by

the touch of a hot wire at any point of a mass of it, or a rise of temperature to about 73° C., or percussion. Another of the properties of the sulphite, calling for notice, is its indifference to sufficiently dilute nitric acid, although it is a basic or oxysalt. Another is that, when dissolved by stronger acid, it rapidly changes into the metameric substance, mercurous sulphate. The same change takes place in the oxysulphite, under any circumstances, upon keeping it for a day. The metamerism shown by mercurous sulphate and mercuric oxysulphite, is of very rare occurrence in inorganic chemistry, though so common in organic chemistry. Treated with potassim hydroxide, three-fourths only of its mercury are left as oxide, the rest dissolving as double sulphite. Sodium chloride leaves half the mercury as oxide, and dissolves the other as double salts.

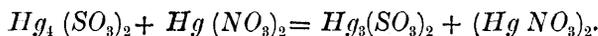
Mercury hydrogen sulphite, $Hg(SO_3H)_2$. This salt we can get only in dilute solution, by cautiously adding precipitated mercuric oxide suspended in water to excess of sulphurous acid. Mercuric oxide rashly added precipitates the sulphite next described. So, too, strange to state, does a little sulphuric or nitric acid added to the sulphurous solution of the mercuric oxide. The solution is unstable, slowly decomposing into metallic mercury and sulphuric acid. Potassium hydroxide does not precipitate the mercury.

Mercurous sulphite, $Hg(SO_3)_2$ Hg'_2 , $4H_2O$, can be prepared in two sets of ways, either by hydrolysis of mercuric hydrogen sulphite, or by some form of double decomposition. When sulphurous acid is treated with precipitated mercuric oxide, mercuric hydrogen sulphite is first formed, as already described, but the attempt to make much of it in the same solution is at once followed by the precipitation of mercurous sulphite, and the generation of sulphuric acid, thus:—

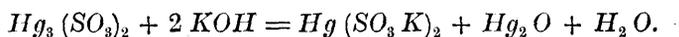


Mercuric oxide, in a thin paste with water, is treated with a stream of

sulphur-dioxide gas, at first slowly, as else some black hypomercurosic sulphite may be formed. Or, to the paste of mercuric oxide strong sulphurous-acid solution containing a little sulphuric acid is added until in excess. The presence of the sulphuric acid prevents any formation of hypomercurosic sulphite. Mercurosic sulphite, thus prepared, is a splendent-white, distinctly crystalline, voluminous precipitate, insoluble in water and in dilute sulphuric or nitric acid, and when dry comparatively stable, except in being efflorescent. It can also be prepared from hypomercurosic sulphite and mercuric nitrate, but it is then of a pale buff colour, and amorphous :—



In thus existing in two forms, white and buff coloured, this sulphite resembles mercurous chloride. Like the white, the buff-coloured variety is insoluble in dilute sulphuric or nitric acid. By hydrochloric acid mercurosic sulphite is decomposed giving both chlorides of mercury. In other respects, too, it behaves as a compound half-mercurous, half-mercuric ; thus potassium hydroxide yields with it mercuric potassium sulphite and mercurous oxide :—



Heated with water, it suddenly decomposes into metallic mercury and sulphuric acid ; while when little or no water is present, mercury, sulphur dioxide, and mercurous sulphate are the products.

Hypomercurosic sulphite, $Hg_4(SO_3)_2$, H_2O , is best prepared by treating precipitated mercurous sulphate with sulphurous acid, in presence of a little sulphuric acid, this acid having the property of preventing decomposition of the hypomercurosic sulphite by the sulphurous acid, just as it prevents that of mercurosic sulphite. Hypomercurosic sulphite can also be prepared by the addition of sodium sulphite, not in excess, to mercurous nitrate, and in other ways. It is a flocculent, voluminous, greyish-black precipitate, insoluble in dilute nitric or sul-

phuric acid, but slowly decomposed by hydrochloric acid into the two chlorides of mercury, metallic mercury, and sulphurous acid. It is similarly decomposed by sodium chloride, and by potassium hydroxide. Sulphurous acid, or sodium sulphite, rapidly converts it into mercury, sulphuric acid, and mercuric hydrogen sulphite, or mercuric sodium sulphite. Heated alone, or with very little water, it yields the same products as mercurous sulphite; and heated with much water it is wholly and suddenly converted into mercury and sulphuric acid.

