CCXCII.—*Lithium Sulphite and some Derivatives.*

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PUBLISHED data concerning lithium sulphite are both scanty and unsatisfactory. Danson (J., 1848, **2**, 207) appears to have been the first to prepare the hydrated salt. He passed sulphur dioxide into an aqueous suspension of lithium carbonate until a colourless solution was obtained, and precipitated the hydrated sulphite either by addition of alcohol or by boiling to expel excess of sulphur dioxide. He noticed its ready oxidisability.

Apparently the only other investigator was Röhrig (*J. pr. Chem.*, 1888, **37**, 225), who believed he had isolated both a mono- and di-hydrate, the former by methods similar to those of Danson, the latter by precipitation with alcohol from strongly acid solution. Röhrig's research is the one usually quoted, and there can be no doubt that he obtained a hydrate of lithium sulphite, but the inadequate nature of his analyses appears to have escaped observation. The lithia was correctly estimated as sulphate, but the sulphur dioxide content was calculated after oxidation to sulphate and weighing as barium or lead sulphate. The amount of oxidising agent required was not ascertained, and no tests are recorded to prove the absence of sulphate. In view of the ready oxidation of the salt, this was a singular omission, for it is evident that the ratio $Li_2O : SO_2$, as calculated by the above method, would be the same for the known *sulphates*, Li_2SO_4 and Li_2SO_4,H_2O, as for the supposed *sulphites*. Further, since the water was calculated by difference, the analyses were insufficiently complete to distinguish between

Li_2SO_4 and Li_2SO_3,H_2O, on the one hand, and between Li_2SO_4,H_2O and $Li_2SO_3,2H_2O$, on the other. Moreover, since the higher hydrate was alleged to be formed from the more strongly acid solution, we deemed it desirable to re-investigate the subject.

We have confirmed the existence of the monohydrate, but have obtained no clear evidence of a dihydrate: it is possible that Röhrig's salt was the monohydrate imperfectly freed from water and/or alcohol, for it retains these substances very tenaciously. We have also prepared the pure anhydrous salt for the first time, and, although we have not been able to isolate the hydrogen sulphite, we have prepared its *compounds* with aldehydes and ketones.

EXPERIMENTAL.

The *monohydrate*, Li_2SO_3,H_2O, is readily prepared by making lithium carbonate into a very thin cream with water and passing a mixture of sulphur dioxide and purified hydrogen through it at room temperature with shaking, access of air being prevented with water seals. The object of the hydrogen is to avoid inrush of air during absorption of sulphur dioxide and passage of the liquid up the delivery tube when the supply of the latter gas is cut off. Passage of the sulphur dioxide is continued until the whole of the lithium carbonate has passed into solution and effervescence has ceased, but too great excess should be avoided. The sulphite may be separated in one of the following ways:

1. Evaporation on the water-bath, care being taken to minimise oxidation (see analysis *a*). Unless pure sulphite is required this is a rapid and convenient method of preparation.
2. Evaporation over concentrated sulphuric acid in a vacuum; this is tedious, but yields a very pure, crystalline product (see analyses *b* and *c*).
3. Pouring the solution into excess of alcohol, whereby a white precipitate is obtained which is somewhat difficult to filter, particularly when excess of sulphur dioxide is present. The precipitate is washed with alcohol and ether, and may be dried at 100° or preferably at room temperature in a vacuum desiccator over sulphuric acid: with care, the latter procedure gives a white powder entirely free from sulphate (analysis *d*).

As obtained by the above methods, the monohydrate is readily soluble in water. When exposed to water vapour in the absence of air the salt steadily increases in weight and finally deliquesces to a colourless solution. Exposed to air, it slowly oxidises to sulphate, even in a desiccator. Thus, a specimen of the pure salt after keeping for 8 days contained only 46·20% SO_2, and this fell, after a further 7 days, to 36·76% (Calc. for Li_2SO_3,H_2O, 57·22%).

In dilute solution, the salt oxidises rapidly; an $M/10$-solution exposed to air oxidised somewhat less rapidly than equivalent solutions of the sodium and potassium salts.

The monohydrate retains its water over sulphuric acid at room temperature, but becomes anhydrous at 180°, undergoing slight oxidation to sulphate if exposed to air during heating. Numerous analyses of the different batches of salts have been made, the lithium being estimated as sulphate, and the sulphur dioxide iodometrically. The water is usually calculated by difference. Typical analyses are as follows:

	a.	*b.*	*c.*	*d.*	Theory.
Li_2O (%) …………………	27·42	25·37	26·28	27·29	26·69
SO_2 (%) …………………	56·85	54·39	56·35	57·66	57·22
H_2O (by diff.) (%) ………	15·73	20·24	17·37	14·90	16·09
Ratio Li_2O/SO_2 …………	0·4823	0·4664	0·4664	0·4733	0·4664

Salt *b* was quite free from sulphate, but retained some adsorbed moisture. Salt *c* contained a trace of sulphate but less adsorbed water, having been kept in a vacuum desiccator for a longer period than the preceding salt. Salt *d* was prepared by the third method, sulphur dioxide being present in only very slight excess. While in the vacuum desiccator, it was repeatedly " rinsed " with air until it ceased to smell of ether. It was entirely free from sulphate but contained 0·15% of iron, calculated as Fe_2O_3.

Following Röhrig's procedure for the preparation of the supposed dihydrate, sulphur dioxide and hydrogen were passed into an aqueous suspension of lithium carbonate until a yellow, acid solution was obtained, the yellow colour indicating the presence of acid sulphite in solution. This was poured into excess of alcohol, and the precipitated salt filtered off (with difficulty) at the pump. A portion was analysed immediately and contained 72·02% of alcohol plus water. Had it not contained alcohol, this would have corresponded to $Li_2SO_3,14H_2O$, which requires H_2O, 72·86%. It was not a definite compound and lost weight rapidly in the balance case. The remainder, when placed on a clock glass in a vacuum desiccator over sulphuric acid, continuously lost weight for 24 hours, but then remained practically constant and was analysed. All the alcohol had evaporated, and the salt consisted of lithium sulphate monohydrate with a trace of sulphate (Found: H_2O, 15·71. Calc.: 16·09%).

Anhydrous lithium sulphite, Li_2SO_3, is conveniently prepared in a pure state by passing a mixture of sulphur dioxide and purified hydrogen into a cream of lithium carbonate and water until effervescence ceases. The flask is then heated to 180—200° in an oil-bath, dry hydrogen being passed through until the salt is anhydrous.

Thus obtained, lithium sulphite is a dull white powder, more stable than the monohydrate. A sample kept in a desiccator for a month was free from all but a trace of sulphate (Found: Li_2O, 31·84; SO_2, 67·72; H_2O, 0·38; total, 99·94; $Li_2O:SO_2$, 0·4702. Li_2SO_3 requires Li_2O, 31·81; SO_2, 68·19%; $Li_2O:SO_2$, 0·4664).

The salt melts at approximately 455° and undergoes partial decomposition, yielding a brown, green, or blue mass according to circumstances. If air is excluded, some lithium sulphide appears to be formed, for the product smells of hydrogen sulphide. This was observed by Röhrig, who suggested the reaction: $4Li_2SO_3 = 3Li_2SO_4 + Li_2S$. An analogous reaction has since been shown to take place on heating sodium sulphite at 700° in a vacuum (Picon, *Compt. rend.*, 1924, **178**, 1548).

Organic Derivatives of Lithium Hydrogen Sulphite.

Acetone. A thin cream of lithium carbonate and water was covered with acetone in a flask, and sulphur dioxide diluted with hydrogen passed through. The temperature rose slightly and after all the carbonate had decomposed a white, crystalline derivative formed. This was washed with acetone and ether. The lithium content was determined by heating with concentrated sulphuric acid and weighing as sulphate (Found: Li_2O, 9·03. $LiHSO_3,C_3H_6O$ requires Li_2O, 9·11%). The acetone was estimated iodometrically; the method did not appear to be very accurate, but sufficed to show that at least 93% of the theoretical quantity of acetone was present. After two months in a stoppered bottle, analysis gave Li_2O, 9·12%; but in another sample that had been less securely stoppered, the percentage of Li_2O rose in a few weeks to 13·57, and the residue smelt of sulphur dioxide, indicating appreciable decomposition.

Benzaldehyde. This derivative was obtained in a similar manner as a beautifully white product; it smelled strongly of benzaldehyde, which was rapidly evolved on warming (Found, for two specimens: Li_2O, 7·14, 8·61. Li_2HSO_3,C_7H_6O requires Li_2O, 7·70%).

Acetaldehyde gave a white product, not analysed. Acetophenone did not react.

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