CCXLI.—*Compounds of Tervalent Molybdenum. Part I. A New Oxysulphate.*

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Molybdenum, tungsten, and uranium, in their highest stage of oxidation, form together with chromium a group of closely related elements, but much yet remains to be discovered concerning their tervalent derivatives. Although complex salts of the types $[MoCl_6]R_3$, $[MoCl_5H_2O]R_2$, $[MoBr_5H_2O]R_2$, $Mo_2F_9R_3$, and $[Mo(CNS)_6]R_3$ have been isolated, the chloride, bromide, and sulphide are the only simple salts of tervalent molybdenum known. Attempts to prepare the alums and oxalates (Foerster and Fricke, *J. angew. Chem.*, 1923, **36**, 62, 458; Chilesotti, *Z. Elektrochem.*, 1906, **12**, 146, 173) have been unsuccessful.

Early investigators endeavoured to isolate tervalent salts of molybdenum by evaporating reduced solutions of the trioxide, and obtained grey or greyish-black residues which were apparently the products of hydrolysis and oxidation of the compounds sought

By taking suitable precautions, we have been able to isolate from a solution of molybdenum trioxide in sulphuric acid reduced to the tervalent state, a well-defined *hydrated molybdenum oxysulphate*, $Mo_2O(SO_4)_2,xH_2O$, where x is 5 or 6.

EXPERIMENTAL.

Preparation of the Oxysulphate.—Molybdenum trioxide (40 gms.) was dissolved in 81 c.c. of boiling sulphuric acid (d 1·84) containing a few drops of concentrated nitric acid; the solution was made up to a litre (concentration of sulphate approximately $3N$), and 500 c.c. were electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969). As the final stage of reduction was approached, shown by the colour change in the cathode chamber from red to dark green, a current of air-free carbon dioxide was passed through the cell. The electrolysis was continued until the colour was vivid green. All subsequent operations were performed in atmospheres of carbon dioxide, air being rigidly excluded. The liquid was distilled under reduced pressure from an all-glass apparatus at an initial temperature of 70°, which was gradually lowered to 55° as the solution became concentrated. The whole success of this operation depends on avoiding air oxidation, and on concentrating the solution, which must be initially vivid green, to a bulk at which the colour is still distinctly green. If the temperature of distillation is too high, the solution becomes brown, and if the solution is too concentrated, the green reverts to red; from such solutions it is impossible to precipitate any solid. The green solution, after concentration and cooling, was poured into air-free acetone, and the *oxysulphate*, which separated as a fine green powder and gradually became granular, was washed with dry acetone and with dry ether and quickly transferred to a desiccator filled with carbon dioxide and containing phosphoric oxide. The substance was free from any product of hydrolysis and formed a green solution in air-free water.

Valency of the Compound.—A solution of the oxysulphate in dilute sulphuric acid was titrated in an inert atmosphere with standard permanganate solution (required: 20·25, 24·70 c.c.). A similar solution was oxidised with hydrogen peroxide, passed through the reductor (*loc. cit.*), and titrated with the permanganate (required: 20·35, 24·80 c.c.). Since the latter titration value represents the oxidation of tervalent molybdenum to the sexavalent state, it is evident that the molybdenum of the oxysulphate is tervalent.

Analysis.—The oxysulphate was oxidised by sodium peroxide and water, the excess of hydrogen peroxide removed by warming, the solution neutralised, and freshly prepared ammonium sulphide added. The molybdenum sulphide, precipitated by hydrochloric acid, was washed with dilute hydrochloric acid (1 : 100) saturated with hydrogen sulphide, and ignited.

The sulphate in the filtrate and washings was estimated in the usual way [Found : Mo = 39·12, 37·60; Mo : SO_4 = 1 : 1, 1 : 0·95. $Mo_2O(SO_4)_2,5H_2O$ requires Mo = 39·18 per cent.; $Mo_2O(SO_4)_2,6H_2O$ requires Mo = 37·80 per cent.].

The oxysulphate was heated in a current of air-free nitrogen, and the moisture estimated by absorption. With careful temperature regulation, the oxysulphate was quantitatively decomposed to molybdenum pentoxide. Further ignition of this oxide in a current of air yielded the trioxide [Found : Mo = 39·11; H_2O = 18·04. $Mo_2O(SO_4)_2,5H_2O$ requires Mo = 39·18; H_2O = 18·37 per cent. 0·1885 gave 0·1043 residue (*b*) and 0·1106 trioxide (*c*). 0·1659 gave 0·0918 residue (*b*) and 0·0971 trioxide (*c*). Ratio b/c : Found 0·943, 0·945. Calc., 0·944].

The above results are in agreement with the decomposition $Mo_2O(SO_4)_2,xH_2O = Mo_2O_5 + 2SO_2 + xH_2O$.

Properties and Reactions of the Oxysulphate.—The freshly precipitated substance is intensely green, but on drying over phosphoric oxide it gradually becomes grey and the sulphate content decreases. The substance is very hygroscopic and readily hydrolysable. It is insoluble in alcohol, ether, or acetone, but dissolves readily in water; the solution loses its green colour immediately on exposure to air, and a rusty-brown precipitate, readily soluble in acids, gradually forms. The oxysulphate immediately precipitates the metals from solutions of copper sulphate and silver nitrate at the ordinary temperature, and reduces mercuric and ferric salts to the "ous" state. On warming with sulphur or sodium sulphite, a solution of the new solid, acidified with dilute sulphuric acid, evolves hydrogen sulphide (see J., 1923, **123**, 975). Barium chloride produces no precipitate in a freshly prepared solution of the oxysulphate, but barium sulphate is thrown down on warming. Lead acetate with acetic acid gives similar results. Sodium and potassium hydroxides give green deposits. Ammonia is without action in the cold, but produces a black precipitate on warming. Potassium ferricyanide gives a deep red coloration; a similar coloration is slowly produced by potassium ferrocyanide.

Conclusion.

No normal sulphate of molybdenum has yet been prepared. A sexavalent oxysulphate, MoO_2SO_4, separates from a solution of molybdenum trioxide in concentrated sulphuric acid (*Ber.*, 1871, **4**, 14), whilst by treatment with hydrogen sulphide this solution yields a dark green quinquevalent oxysulphate (*Compt. rend.*, 1901, **132**, 475). Chilesotti (*loc. cit.*, p. 173) concluded from potential measurements that in the electrolytic reduction of acid solutions of molybdenum trioxide the molybdenum is first completely reduced to the quinquevalent condition and that further reduction produces tervalent molybdenum without the intermediate formation of quadrivalent compounds. If so, a quinquevalent sulphate may yet be isolated from an appropriately reduced molybdenum solution, but the isolation of a quadrivalent compound will probably not be realised. The oxysulphates so far produced form an interesting series in which the ratio of molybdenum to sulphate remains constant whilst the difference in valency involves a progressive elimination of oxygen: $Mo_2O_4(SO_4)_2$, $Mo_2O_3(SO_4)_2$, $Mo_2O(SO_4)_2$.

Double salts of the tervalent oxysulphate are being prepared and investigated.

Summary.

1. A green oxysulphate, $Mo_2O(SO_4)_2,xH_2O$, where x is 5 or 6, has been prepared from a solution of molybdenum trioxide in sulphuric acid, reduced electrolytically to the tervalent state.

2. The oxysulphate is characterised by strong reducing properties.

3. On heating, it decomposes in accordance with the equation $Mo_2O(SO_4)_2,xH_2O = Mo_2O_5 + 2SO_2 + xH_2O$.

4. The sulphate radical is not precipitated by barium chloride in the cold.

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