

CCLXIX.—*The Behaviour of Molybdenum Pentachloride in Organic Solvents.*

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It is generally considered that in the pentahalides of the metals and non-metals five covalencies are present, as in the pentachloride of phosphorus or antimony. Holroyd (*Chem. and Ind.*, 1923, 348;

Holroyd, Chadwick, and Mitchell, J., 1925, **127**, 2492) found that phosphorus pentachloride had a small conductivity in nitrobenzene solution although it had none in benzene or ethylene dibromide, and inferred the presence of an ionised form  $[\text{PCl}_4]\text{Cl}$ . The evidence for such an assumption, however, is inconclusive (Sidgwick, "Electronic Theory of Valency," p. 162). It is interesting to read, therefore, that Lloyd (*J. Physical Chem.*, 1913, **17**, 592) records conductivity measurements of molybdenum pentachloride in various organic solvents which suggest that, in the case of this pentahalide, ionisation can take place. He finds that when the black crystalline pentachloride is dissolved in organic liquids the solutions produced are either green or red-brown. Green solutions are obtained with methyl acetate, benzaldehyde, and acetone, and the molecular conductivities in the first two solvents decrease with dilution; in acetone, a minimum value for the molecular conductivity is recorded. On the other hand, pyridine and glycerol give red-brown solutions with small molecular conductivities which increase on dilution. In carbon tetrachloride, carbon disulphide, and nitrobenzene, dark red solutions result which are practically non-conducting.

Lloyd describes the solution in methyl acetate as being "almost as conductive as standard potassium chloride." Although this investigator does not advance any theoretical explanation of his results, one is justified in deducing that considerable ionisation of the pentachloride takes place in this last solvent, and varying degrees of ionisation in the other solvents mentioned. In the course of some work on molybdenum pentachloride it was apparent that the substance was very reactive, and it appeared remarkable to us that in some of the cases cited above a chemical reaction did not take place between the solvent and the solute. Molybdenum pentachloride is immediately attacked by moisture, for example, and if the water is not present in excess, green solutions are obtained containing molybdenyl trichloride,  $\text{MoOCl}_3$ , and hydrogen chloride. Furthermore, we found that at ordinary temperatures dry alcohol reacts vigorously with the pentachloride, ethyl chloride and hydrogen chloride being evolved and green molybdenyl trichloride produced. Here the pentachloride shows a marked resemblance in behaviour to phosphorus pentachloride. These results are especially significant, for, with one exception (pyridine), the solvents used by Lloyd are difficult to free from traces of moisture or organic substances containing a hydroxyl group. For example, he states that "on account of the difficulty of keeping benzaldehyde free from benzoic acid no great accuracy is claimed for the results obtained from it." As he does not record that rigid precautions were taken in other cases to ensure the purity of the solvents used and to exclude

moisture during the conductivity determinations, his conductivity data, especially for the green solutions, are open to criticism.

It is not improbable that the green colour of his solutions was due to the presence of molybdenyl trichloride formed by the decomposition of the pentachloride. The fact that he obtained oxychlorides on electrolysis of molybdenum pentachloride in his organic solvents substantiates this view. Moreover, we have found that the presence of small amounts of hydrogen chloride greatly accelerates the rate of absorption of oxygen by solutions of the pentachloride in certain organic solvents.

The case of acetone is especially noteworthy. This alone of the solvents used gave a minimum value for the molecular conductivity of the molybdenum pentachloride solution although at every dilution the solution was green. We found that such solutions acquired an increasingly darker green colour as the drying of the solvent became more intense, but even with the most intensively dried acetone an exothermic reaction took place with the pentachloride. It appears that with this solvent there is a specific reaction with the molybdenum pentachloride like that with phosphorus pentachloride. In view of the disadvantages of the solvents used by Lloyd in preparing green solutions, ether was selected as a solvent which can be readily obtained free from moisture and organic hydroxylic compounds and yet is stated in the literature (Lichte and Kempe, *Annalen*, 1873, **169**, 344) to give a green solution with molybdenum pentachloride. When specially dried ether was used, the solution was not green but very dark red (almost black); with traces of water, however, it reverted immediately to green. From the ethereal solution it was possible to isolate the co-ordination *compound*  $\text{MoCl}_5 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , which, in the presence of water, yielded green molybdenyl chloride. These results confirm the suggestion that the formation of green solutions is in all cases due either to a reaction between the solvent and the solute or to the use of an impure solvent.

It may be urged that, even if the conductivity measurements of the green solutions are open to the objection that possibly molybdenyl chloride and other products are present, such a suggestion is not applicable to the red-brown solution in pyridine which conducts and gives increasing molecular conductivity with dilution. Investigation showed that here, also, a reaction occurs between the solute and the solvent, and co-ordination *compounds*,  $\text{MoCl}_4 \cdot x\text{C}_5\text{H}_5\text{N}$ , where  $x = 3, 4, \text{ and } 5$ , may be isolated from the reaction products. The results of this investigation show that molybdenum pentachloride is a most reactive substance, and one cannot accept, therefore, the results of conductivity measurements in the non-

aqueous solvents hitherto employed, as indicating that molybdenum pentachloride is other than a covalent compound.

#### EXPERIMENTAL.

*Preparation of Molybdenum Pentachloride.*—The method adopted was a modification of that recommended by Biltz (*Z. anorg. Chem.*, 1924, **172**, 385). The molybdenum, purchased in the form of sheet metal from Messrs. Johnson Matthey and Co., was cut into small pieces and introduced into a combustion tube. Air was displaced by the passage of chlorine through the apparatus for at least 3 hours. When using sheet metal, it was found unnecessary to displace the air by carbon dioxide and then remove traces of oxygen as molybdenum oxychloride by the passage of hydrogen chloride as advocated by Biltz. At low red heat, chlorination begins. Too high a temperature causes the production of lower chlorides. It is not advisable to chlorinate more than 6 g. of metal at one time when using the standard combustion tube, for otherwise, stoppages are likely to occur in the tube. The dark green, almost black solid gave Mo, 35.20 (Calc. : Mo, 35.10%).

*Reaction with Alcohol.*—Dry alcohol reacts vigorously with molybdenum pentachloride. If the quantity of alcohol is small, the solution is dark, becoming dark green and finally brown on the addition of further quantities of alcohol. The presence of molybdenyl trichloride in this solution was proved by the isolation of the derivative  $[\text{NMe}_2\text{H}]_2[\text{MoOCl}_5]$  (Found : Mo, 24.9; Cl, 46.65. Calc. : Mo, 25.16; Cl, 46.53%) with dimethylamine hydrochloride. The analogy with the reaction of alcohol and phosphorus pentachloride is very clearly seen.

Other alcohols (*e.g.*, methyl and benzyl) gave a similar reaction, but phenols did not.

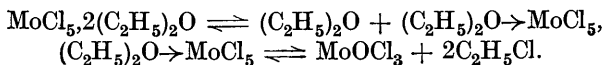
*Reaction with Ether.*—Dry ether (100 c.c.) was added to powdered molybdenum pentachloride (5 g.) out of contact with air, and the dark solution decanted and evaporated in a vacuum. Black hygroscopic leaflets, insoluble in chloroform and in benzene and decomposed by alcohol, were obtained [Found : Mo, 22.34; Cl, 42.39.  $\text{MoCl}_5 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  requires Mo, 22.77; Cl, 42.11%]. Ethyl chloride was obtained by heating the compound to 80° and condensing the product.

If slightly moist ether is used, a green oil is formed; if this is washed with ether it forms green needle-shaped crystals, melting a little above room temperature [Found : Mo, 24.90; Cl, 30.71.  $\text{MoOCl}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  requires Mo, 26.18; Cl, 29.06%]. The product is very unstable and has not yet been obtained pure. By saturating the green oil with hydrogen chloride, a second green crystalline

*compound* was obtained in flat plates, difficult to purify [Found: Mo, 31.42; Cl, 37.00.  $\text{MoOCl}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  requires Mo, 32.82; Cl, 36.41%]. In view of the difficulty in purifying the preceding compounds, confirmation of the presence of molybdenyl trichloride in the green oil was obtained by adding dimethylamine hydrochloride in chloroform and forming the co-ordination compound of the type  $\text{R}_2[\text{MoOCl}_5]$ . The green salt thus obtained was recrystallised from a solution of alcoholic hydrogen chloride (Found: Mo, 25.16; Cl, 46.81. Calc.: Mo, 25.17; Cl, 46.53%).

The pyridinium compound  $(\text{C}_5\text{H}_6\text{N})_2[\text{MoOCl}_5]$  was also isolated by a similar procedure and confirms the formation of molybdenyl trichloride in the original reaction.

The reaction between molybdenum pentachloride and ether is remarkable in that a trace of moisture appears to convert the black addition product (*q.v.*) into the green molybdenyl chloride. This suggests that the following cycle of changes takes place:



Compounds of the type  $\text{R}_2[\text{MoOCl}_5]$  are known to be green, but hitherto these have been obtained in a stable form only when  $\text{RCl}$  is an ionised substance. This may explain the instability of the intermediate product.

*Determination of Molybdenum.*—This was done by boiling the substance with ammonia (5*N*), oxidising the molybdenum to the sexavalent state with "hyperol," adding colourless ammonium sulphide, and precipitating the sulphide of molybdenum by addition of dilute sulphuric acid. The chlorine was determined as silver chloride in the filtrate and washings.

*Reaction with Pyridine.*—Molybdenum pentachloride (12 g.) and dry pyridine (250 c.c.) were allowed to react in a sealed vessel for ten days. The brown amorphous suspension was then filtered off, and washed free from pyridine and soluble salts with dry chloroform. Pyridinium chloride was present in the filtrate. The light brown amorphous powder (13 g.) thus obtained (Found: Mo, 20.27; Cl, 30.01; N, 8.95.  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  requires Mo, 20.21; Cl, 29.87; N, 8.84%) was insoluble in the usual organic solvents. It was slowly decomposed by heating with water, dilute acids, or ammonia.

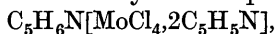
This *compound* was also formed when a solution of pyridine in chloroform was kept in contact with molybdenum pentachloride. Pyridine (30 g.) was dissolved in chloroform (100 c.c.; free from alcohol and acetone, and carefully dried) and shaken at regular intervals during 3 weeks with molybdenum chloride (2 g.). The

light brown solid obtained by filtration and treatment as described above (Found : Mo, 20·68; Cl, 31·02%) had the same properties as that just described.

The mother-liquor from the first preparation of this compound deposits on longer standing an almost colourless crystalline substance which is difficult to separate from other products except by flotation of the amorphous substances and separation of remaining crystals by hand. This *substance* (Found : Mo, 17·07; Cl, 25·0.  $\text{MoCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$  requires Mo, 17·32; Cl, 25·63%) was similar in properties to the previous derivative.

The *compound*  $\text{MoCl}_4 \cdot 5\text{C}_5\text{H}_5\text{N}$  was obtained in the form of dark red orthorhombic crystals on prolonged standing of the mother-liquor from the above preparation. It was more readily obtained by boiling the compound  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  with pyridine for some hours until solution was complete, and concentrating the solution over sulphuric acid (Found : Mo, 15·43; Cl, 22·64.  $\text{MoCl}_4 \cdot 5\text{C}_5\text{H}_5\text{N}$  requires Mo, 15·16; Cl, 22·43%). This compound is unstable in air, the crystals efflorescing with loss of pyridine. Like the other derivatives, it is very insoluble. It passes rapidly into an amorphous light yellow powder (Found : Mo, 17·00; Cl, 25·97%) when kept over sulphuric acid in a vacuum, and this changes slowly with further loss of pyridine into a substance approximating to the composition of the tripyridine salt, but even after 3 months the change is still incomplete.

To decide whether these compounds were derivatives of quadrivalent or of trivalent molybdenum, a valency determination was carried out. It seemed not improbable that the compound  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  might be in reality the complex salt

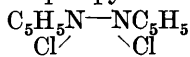


although salts of this type are as yet unknown. Such a configuration assigns a covalency of six to the molybdenum atom, and a valency of three. That such a formula was incorrect and that the compounds contained quadrivalent molybdenum was evident from the following results :  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  (1·4 g.) was dissolved in dilute sulphuric acid (200 c.c.); 50 c.c. of this solution required 14·6 c.c. of *N*/10-potassium permanganate, and after passage through the reductor (*J.*, 1923, **123**, 973) 22·2 c.c. were required; hence valency =  $6 - 14·6/7·4 = 4$ . It will be seen that the percentage of molybdenum present in the compound, as calculated from this titration, *viz.*, 20·2%, is almost that demanded by theory.

A blank determination with pyridinium sulphate indicated that no perceptible reduction of the salt to a piperidine derivative had taken place.

*Discussion.*

The mechanism of the action of molybdenum pentachloride on pyridine is not clear. Sell and Dootson (*J.*, 1898, **73**, 432) state that with phosphorus pentachloride no chlorination of pyridine takes place in the cold, and that even when pyridine had been boiled with a saturated solution of phosphorus pentachloride in phosphorus oxychloride for 14 days, the amount of pentachloride had diminished only very slightly. They conclude, however, (*loc. cit.*, p. 432), that in the reaction of dry chlorine with dry pyridine "there is without doubt an additive compound of pyridine and chlorine formed," and this idea is confirmed by the observations of Reitzenstein and Bruning (*Zentr.*, 1911, i, 819) on the action of chlorine upon pyridine in ethereal solution. They suggest the constitution



for the substance formed, without offering any conclusive evidence in support of this. It is now suggested that possibly the reaction between molybdenum pentachloride and pyridine is preceded by the formation of an addition product,  $\text{C}_5\text{H}_5\text{N} \left\langle \begin{array}{c} \text{Cl} \\ \text{MoCl}_4 \end{array} \right.$ , which then breaks up into molybdenum tetrachloride and the additive compound of pyridine and chlorine constituted as above. The improbability of any appreciable amount of direct chlorination is shown, in our opinion, by the fact that  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  is formed in chloroform solution and also that only a minute amount of a chloropyridine, m. p. 90—92°, can be isolated. In the new compounds of molybdenum tetrachloride now isolated, it appears that the molybdenum can have a covalency of seven in  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$  and eight in  $\text{MoCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$ .

Owing to the insolubility of the material, molecular-weight determinations could not be made, and the possibility of polymerisation cannot therefore be excluded. An alternative configuration for the compound  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ , which obviates the necessity of postulating a covalency of seven for the molybdenum, is



With this structure the covalency of molybdenum is six and the valency four, whilst in the pentapyridine compound the covalency would be eight. A similar structure has been proposed for the platinum compound  $\text{Pt} \left\langle \begin{array}{c} \text{C}_5\text{H}_5\text{N} - \text{Cl} \\ \text{C}_5\text{H}_5\text{N} - \text{Cl} \end{array} \right.$