

## THE PREPARATION OF MOLYBDENUM OXIDETETRACHLORIDE\*

By R. COLTON,† I. B. TOMKINS,† and P. W. WILSON†

There have been previous claims to the preparation of molybdenum oxide-tetrachloride,  $\text{MoOCl}_4$ , but until recently the compound has not been well established.<sup>1</sup> Puttbach<sup>2</sup> claimed to have isolated green molybdenum oxidetetrachloride by reacting molybdenum pentachloride with molybdenum dioxidedichloride, but these results were refuted by Klason<sup>3</sup> and Nordenskjold<sup>4</sup> who considered the product to be a mixture. However, the compound has been recently prepared by this same reaction and also by the interaction of molybdenum pentachloride and molybdenum trioxide,<sup>5,6</sup> but the method is inconvenient, requiring preliminary preparation of the pentachloride and separation of the required compound from other reaction products.

Thionyl chloride has been shown to be a useful reagent in the preparation of rhenium chloride compounds, for example rhenium tetrachloride<sup>7</sup> and ammonium dioxotetrachlororhenate(VI)<sup>8</sup> and we now report a very rapid and convenient preparation of molybdenum oxidetetrachloride by the action of thionyl chloride on molybdenum trioxide.

Thionyl chloride reacts rapidly with molybdenum trioxide on refluxing to give an intensely coloured red solution. Evaporation of this solution under vacuum gave a crystalline product which could be purified by sublimation at 50–60° to give large green crystals.

Molybdenum oxidetetrachloride is thermally stable, melting at about 100° to a dark brown liquid and giving a reddish brown vapour at about 120°. The thermal stability is far greater than that of technetium oxidetetrachloride which readily decomposes to technetium oxidetrichloride on gentle heating<sup>9</sup> (60–70°).

Molybdenum oxidetetrachloride hydrolyses in alkali solution to give a strong blue colouration at first, but this rapidly disappears, especially on warming the solution, to give a clear colourless solution containing all the molybdenum as molybdate ion.

Molybdenum oxidetetrachloride is very sensitive to moisture and all manipulations must be performed in a dry box or in a vacuum system.

\* Manuscript received November 28, 1963.

† Department of Inorganic Chemistry, University of Melbourne.

<sup>1</sup> Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." (Interscience: New York 1962.)

<sup>2</sup> Puttbach, W., *Liebigs Ann.*, 1880, **201**, 125.

<sup>3</sup> Klason, P., *Ber. dtsh. chem. Ges.*, 1901, **34**, 1572.

<sup>4</sup> Nordenskjold, I., *Ber. dtsh. chem. Ges.*, 1901, **34**, 148.

<sup>5</sup> Glukov, I. A., and Eliseev, S. S., *Izvest. Akad. Nauk Tadzhik SSR*, 1959, 79.

<sup>6</sup> Glukov, I. A., and Eliseev, S. S., *Zhur. Neorg. Khim.*, 1962, **7**, 81.

<sup>7</sup> Brown, D., and Colton, R., *Nature*, 1963, **198**, 1300.

<sup>8</sup> Brown, D., and Colton, R., *J. Chem. Soc.* (in press).

<sup>9</sup> Colton, R., unpublished data, 1963.

*Experimental*

Molybdenum trioxide (2 g) was placed in a small quickfit round-bottom flask equipped with a reflux condenser and thionyl chloride (25 ml) (redistilled laboratory reagent) was added. No precautions against moisture are necessary at this stage. After refluxing for 30 min, the deep red solution was transferred to a dried subliming tube and the solvent pumped off under vacuum. For the sublimation stage it was found convenient to place the tube in a horizontal position and under these conditions the compound sublimed at 50–60° at  $10^{-3}$  mm. In a vertical tube the sublimation is very slow, presumably owing to the very dense nature of the vapour. The yield is 85–90% based on the weight of molybdenum trioxide taken.

Samples were analysed by weighing them in sealed tubes and later weighing the empty tube. The sample was hydrolysed in alkali solution, diluted to standard volume, and aliquots taken for the determination of molybdenum gravimetrically as its 8-hydroxyquinolate<sup>10</sup> and as chloride potentiometrically using silver nitrate (Found: Mo, 38.0; Cl, 55.5%. Calc. for  $\text{MoOCl}_4$ : Mo, 37.8; Cl, 55.9%).

<sup>10</sup> Hollingshead, R. G. W., "Oxine and its Derivatives." (Butterworths: London 1954.)