V.—*Researches on the Metallic Carbonyls.*

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MOND, HIRTZ, and COWAP (T., 1910, **97**, 798) describe the methods of preparation and some of the properties of the metallic carbonyls. We have continued these researches, but owing to the great difficulty with which these compounds are prepared, our knowledge of their chemical and physical properties is still very incomplete. We desired, for instance, to study the compound $\text{Mo}(\text{CO})_6$, but it required two years to prepare 170 milligrams of this carbonyl, using the apparatus and methods described in the above paper.

The Composition of Molybdenum Carbonyl.

The analysis of this compound, as given by Mond, Hirtz, and Cowap, is "Found, CO = 0.0432 gram. Mo = 0.0279 gram. The formula is therefore $\text{Mo}(\text{CO})_6$."

The actual ratio Mo:CO given by the above analysis is 1:5.3. Reference to the authors' notebook showed that they found 0.0249 gram of Mo, and not 0.0279 as published. This gives a molecular ratio of 1:6.01.

It seemed desirable, however, to repeat the analysis of this carbonyl, and this we did by two different methods.

In the first analysis 40 mg. of the carbonyl were heated in a sealed tube for ten hours at 240° , whereby the compound was completely decomposed. The resulting gases were measured and analysed, and the molybdenum remaining in the tube was dissolved out and estimated as lead molybdate (Found: Mo:CO = 1:5.20).

In the second analysis, 103 mg. of the resublimed carbonyl were decomposed by bromine water. The evolved carbon monoxide was collected, measured, and analysed, and the molybdenum in solution estimated as lead molybdate (Found: 62.0 mg. CO and 41.3 mg. Mo). This gives a molecular ratio Mo:CO = 1:5.18.

These analyses suggest that the composition of molybdenum carbonyl is not represented by the formula $\text{Mo}(\text{CO})_6$, and that the molecule is very large, the constitution of which is probably $\text{Mo}_5(\text{CO})_{26}$. Molybdenum carbonyl is almost insoluble in benzene, alcohol, or other common solvents, so that its molecular weight cannot be determined by the cryoscopic method.

Ruthenium Carbonyls.

The existence of a volatile compound of ruthenium and carbon monoxide was mentioned by Mond, Hirtz, and Cowap. It is obtained by heating the metal at 300° with carbon monoxide at 400 atmospheres. We have not obtained sufficient to determine its composition. This carbonyl is crystalline, and is soluble in benzene, but is insoluble in alcohol and in water.

Non-volatile Ruthenium Carbonyl.—Upon examining the contents of the retort after treating ruthenium with carbon monoxide for fifty hours at 250° and 350 atms., we found a quantity of chocolate-brown powder, which was insoluble in benzene and readily soluble in alcohol or water. The bulk of the powder was dissolved in alcohol, filtered from the unattacked ruthenium, and the solution evaporated in a current of hydrogen at 85°. The residue was then dried in a vacuum at 40°. The resulting brown, amorphous powder possessed all the characteristic properties of a metallic carbonyl.

The powder was analysed by heating it in a sealed tube at 400° for several hours, after which the gases in the tube were measured and analysed, and the deposited ruthenium metal was estimated : 64.8 mg. of the powder contained 42.1 mg. of Ru and 24.8 mg. of CO. This gives a molecular ratio $\text{Ru} : \text{CO} = 1 : 2.14$. The compound is therefore $\text{Ru}(\text{CO})_2$.

This new metallic carbonyl differs from all others by being soluble in water and completely insoluble in benzene.

Iron Pentacarbonyl.

This compound was described in a paper by the late Drs. Ludwig Mond and Quincke (T., 1891, 59, 604). It has been comparatively easy to prepare it in small quantities up to a few cubic centimetres, but, in spite of continuous efforts, it was found nearly impossible to obtain a reasonable yield, although we have undertaken a careful examination of the yield at different temperatures and pressures so as to obtain the best conditions for the preparation of this compound. The following pressure-temperature experiments were carried out in the high-pressure apparatus previously described (Mond, Hirtz, and Cowap, *loc. cit.*).

The retort used had a total capacity of 49.2 c.c., and into this were placed 30 grams of finely divided (pyrophoric) iron, which had been prepared by the reduction of ferric oxide by hydrogen at 450°. The iron was then allowed to react with carbon monoxide at the desired temperature and at constant pressure for two hours. The gases in

the retort were then rapidly passed through tubes cooled to -20° , and the condensed iron pentacarbonyl was measured.

This process was repeated for each of the determinations given below :

100 atms.		150 atms.		200 atms.		300 atms.	
Temp.	C.c. of $\text{Fe}(\text{CO})_5$.	Temp.	C.c. of $\text{Fe}(\text{CO})_5$.	Temp.	C.c. of $\text{Fe}(\text{CO})_5$.	Temp.	C.c. of $\text{Fe}(\text{CO})_5$.
150°	0.20	150°	2.70	130°	0.70 (1.00)	120°	2.60
160	1.30	175	6.10	140	3.90	140	8.00
200	2.90	200	7.00	150	6.00	150	10.00
220	1.50	225	4.70	180	9.20	160	11.60
230	0.30	250	0.60	200	9.75	222	14.30
				225	7.50	235	12.20
				250	2.80	250	7.60
				260	1.60	275	3.30

We have plotted these results, and the curves show how rapidly the formation of the carbonyl diminishes above 200° . Up to this temperature, there is practically no conversion of carbon monoxide into carbon dioxide and carbon, but above it the rate of the reaction $2\text{CO} = \text{CO}_2 + \text{C}$ increases as the yield of carbonyl decreases.

Nickel Carbonyl and Oxygen.

Some attention has been directed to the varnish-like solid which Mond, Hirtz, and Cowap state to be a colloidal oxide of nickel

obtained by heating at 200° a mixture of nickel carbonyl vapour, air, and carbon monoxide. If moist carbon monoxide containing about 5 per cent. of nickel carbonyl vapour and sufficient air to oxidise the latter is passed through a tube at 200° , a golden-yellow deposit is obtained. As the deposit thickens, it becomes opaque and metallic in appearance. Repeated analysis of this substance showed that it is a colloidal basic carbonate of nickel of varying composition.

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