

XCIII.—*On Iron Carbonyls.*

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THE existence of a volatile compound of iron and carbon monoxide was made known to the Society last session in a communication by one of us and Dr. F. Quincke (Trans., 1891, 59, 604). In a paper read before Section B of the British Association in August last,* it was announced that we had succeeded in obtaining this compound in the form of an amber-coloured liquid, which boils at 102° , solidifies below -21° , and deposits tabular crystals of a darker colour on standing. We have since found that these crystals are only obtained when the liquid is exposed to light, and that their formation is accompanied by the evolution of carbon monoxide.

This liquid compound of iron with carbon monoxide is prepared in the following manner:—Ferrous oxalate, precipitated from a hot solution of ferrous sulphate by adding to it a slight excess of potassic oxalate, is washed by repeated decantation with water and dried at 120° . The dry powder is introduced into a combustion tube, and heated in a gentle current of hydrogen, the temperature being gradually raised until the oxalate has turned black, and is then kept stationary until, on arresting the current of hydrogen, no more gas escapes. The finely-divided iron thus obtained is allowed to cool to the ordinary temperature, and is then put into water without allowing it to come into contact with the air, boiled several times with water until all sulphate is removed, dried quickly on plates of gypsum, and then returned to the combustion tube and slowly heated in a current of hydrogen to about 300° to drive off all the water. After allowing it to cool again, the hydrogen is displaced by carbon monoxide and the tube is then closed at one end, the other remaining connected with the gasholder containing carbon monoxide, which is slowly absorbed by the iron. After the lapse of 24 hours, the tube is heated to about 120° , when the iron carbonyl formed distils over. The yield is somewhat increased when this distillation takes place in a slow current of carbon monoxide and the issuing gases are passed through a tube cooled to -20° . When no more iron carbonyl comes over, the tube is allowed to cool, and put into communication again with the gasholder containing the carbon monoxide, which is absorbed as before. This operation can be repeated during several weeks; the daily yield, however, is always small, and rarely exceeds 1 gram from

* "On Nickel Carbon Oxide and its Application in Arts and Manufactures," by Ludwig Mond.

100 grams of iron. We have tried to increase this yield by exposing the iron to carbon monoxide under a pressure of 10 atmospheres, but have obtained no material augmentation.

The iron carbonyl thus obtained is a somewhat viscous liquid of a pale-yellow colour. Its sp. gr. at 18° is 1.4664 compared with water at 18° . It distils completely without decomposition at 102.8° under a pressure of 749 mm. It solidifies below -21° into a mass of yellowish, needle-shaped crystals. It is soluble in many organic liquids such as alcohol, ether, benzene, mineral oils, &c. On exposure to the air, it is slowly decomposed with formation of a brown precipitate consisting mainly of hydrated ferric oxide. On heating the vapour to 180° , the compound is completely decomposed into iron and carbon monoxide. The vapour density has been determined in a Victor Meyer apparatus filled with hydrogen and heated in a bath of xylene. We obtained the following figures:—

0.1912 gram substance displaced 25.0 c.c. hydrogen at 17.7° ; air pressure, 751 mm.; density, 6.5.

0.1249 gram substance displaced 16.4 c.c. hydrogen at 17.7° ; air pressure, 759 mm.; density, 6.4.

This corresponds very nearly to the calculated density of $\text{Fe}(\text{CO})_5$, = 6.7, whilst $\text{Fe}(\text{CO})_4$ would require 5.7, and $\text{Fe}(\text{CO})_6$ 7.25. The formula $\text{Fe}(\text{CO})_5$ is also corroborated by analysis of the substance.

We determined the iron by heating a weighed quantity with chlorine-water in a sealed tube and subsequently precipitating and weighing the ferric oxide; and the carbon monoxide by burning a weighed quantity in a current of air in a combustion tube partly filled with copper oxide, and weighing the carbon dioxide formed. The following figures were obtained:—

- I. 0.3014 gram substance yielded 0.1265 gram Fe_2O_3 = 0.08855 gram Fe.
- II. 0.1318 gram substance yielded 0.05523 gram Fe_2O_3 = 0.03867 gram Fe.
- III. 0.2463 gram substance yielded 0.2702 gram CO_2 = 0.17195 gram CO.
- IV. 0.2838 gram substance yielded 0.3172 gram CO_2 = 0.2022 gram CO.

	Found.				Theory.
	I.	II.	III.	IV.	$\text{Fe}(\text{CO})_5$.
Fe	29.37	29.34	—	—	29.08
CO	—	—	69.88	71.14	70.92

We propose to call this compound ferropentacarbonyl. It is isomeric with ferrous croconate, C_5FeO_5 .

Ferropentacarbonyl is not acted upon by dilute sulphuric, hydrochloric, or nitric acid at the ordinary temperature. Concentrated nitric acid, chlorine-water, and bromine-water, however, act readily, forming ferric nitrate, chloride, or bromide respectively.

Alcoholic solutions of sodium and potassium hydroxide absorb the vapour rapidly, and also dissolve the liquid without evolution of gas. After a while, a greenish precipitate is formed, which contains chiefly hydrated ferrous oxide, and the solution becomes brown. On exposing it to the air, it takes up oxygen, and the colour changes to a dark-red, whilst hydrated ferric oxide separates out. On account of this rapid change of the solution in contact with air, and the small quantity at our disposal, we have not yet been able to isolate any well-defined compound suitable for analysis from it.

On mixing alcoholic solutions of ferropentacarbonyl and mercury chloride, a slight evolution of carbon monoxide is observed, and a yellowish, crystalline precipitate is formed containing iron, mercury, chlorine, and carbon monoxide. The analyses, however, did not give figures from which a definite formula could be deduced. The liquid ferropentacarbonyl undergoes no change when kept in the dark, but when it is exposed to the light for several hours in a sealed tube, gold-coloured, tabular crystals are formed, and the pressure in the tube rises very high. When dry, these crystals have a metallic lustre, and resemble flakes of gold. On exposure to the air, they are gradually decomposed and coloured brown. We have prepared this substance for analysis by collecting it on a filter, washing with ether, and drying over sulphuric acid for about 30 minutes. A weighed quantity was treated with bromine-water, which dissolves the substance with evolution of gas. The iron was precipitated from the solution and weighed as ferric oxide.

0.0800 gram substance yielded 0.0412 gram $\text{Fe}_2\text{O}_3 = 0.02884 \text{ Fe}$,
or 36.05 per cent. Fe.

0.0742 gram substance yielded 0.0381 gram $\text{Fe}_2\text{O}_3 = 0.02662 \text{ Fe}$,
or 35.90 per cent. Fe.

These figures agree sufficiently with the formula $\text{Fe}_2(\text{CO})_7$ (diferroheptacarbonyl), which requires 36.36 Fe. We have, so far, not succeeded in obtaining a sufficient quantity of this substance to control its composition by determining the carbon monoxide, nor has it been possible to ascertain its molecular weight either by the vapour density or by Raoult's method, as the substance is neither volatile without decomposition nor sufficiently soluble in suitable solvents.

Chlorine, bromine, and nitric acid decompose the crystals; sulphuric acid and hydrochloric acid do not act upon them at the ordinary temperature. Alcoholic potash dissolves them, forming a solution

similar in appearance and behaviour to that obtained with the liquid iron carbonyl.

The solution of iron carbonyl in heavy mineral oil investigated by Mond and Quincke, which gave figures for the proportion of iron to carbon monoxide varying from 1 : 4.03 to 1 : 4.26 undoubtedly contained mixtures of the two substances we have described.

We are continuing the investigation of these compounds, and hope shortly to make a further communication to the Society.
