XCVI.—*The Occurrence of Iron Pentacarbonyl in Coal Gas stored under Pressure for* 30 *Years.*

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In the course of a lecture at King Edward's High School, Birmingham, in 1899, at which one of the authors was present, Dr. T. J. Baker used a cylinder of compressed coal gas. Upon ignition, the flame was normal for coal gas of that period and could not be differentiated from that supplied from the mains. The cylinder was then placed aside and apparently overlooked until the spring of 1929, and the gas was then found to give a luminous and very smoky flame. As this clearly indicated that some material change had taken place in the gas during its prolonged storage, Dr. Baker very kindly handed the cylinder to us for further examination. The gas proved to be heavily charged with the vapour of iron pentacarbonyl, as proved by the following experiments, in which the term " dried " gas refers to the gas after filtration through a plug of cotton wool and passage through a drying tube containing calcium chloride.

Experiment 1. The dried gas was ignited at the orifice of a small glass jet, whereby a luminous, smoky flame was obtained. When a cold glass plate was held well into the luminous portion, a black deposit resulted, which consisted partly of carbon; but after treatment with dilute hydrochloric acid, the presence of iron was detected in the solution on addition of the usual reagents. If, however, the cold plate was held a short distance above the flame, a yellow to reddish-brown deposit of ferric oxide was obtained.

The cotton wool was almost imperceptibly darkened on the surface facing the exit from the cylinder, and the solution resulting from its treatment with acid responded to the tests for ferric iron, but not for ferrous. The deposit was therefore probably ferric oxide from the cylinder.

Experiment 2. The previous experiment was varied by interposing a wash bottle of concentrated sulphuric acid between the drying tube and the jet. The flame was now less luminous and entirely free from smoke. It yielded no ferric oxide or other deposit, save water, to a cold plate held above the luminous zone, and only faintly blackened the plate when the latter was held lower down, probably because the acid had not completely absorbed the unsaturated hydrocarbons.

The sulphuric acid turned dark brown and, after dilution, was tested for metals. Iron alone was found, and was present in appreciable quantity.

Experiment 3. The dried gas was passed through a glass tube gently heated with a spirit lamp. A brilliant black mirror resulted, which almost completely dissolved in concentrated hydrochloric acid, a few black specks of carbon alone remaining. A white precipitate of ferrous chloride was obtained, which completely dissolved on dilution. Iron was the only metal present in the solution. Upon repeating the experiment with gas that had been passed through concentrated sulphuric acid, no mirror was obtained.

Experiment 4. The dried gas was passed through a narrow delivery tube into a wider tube suspended vertically in a glass boiling-tube and immersed in liquid air in a Dewar flask. The uncondensed gas was burned at a platinum jet. The flame was pale blue, and yielded no deposit other than water on a cold plate held either within or above the flame. Carbon dioxide was detected as a product of combustion, but, as this would result from the combustion of methane in any case, the gas was analysed to ascertain whether or not carbon monoxide was present. The analyses are given below, unsaturated hydrocarbons being determined by the bromine method, and carbon monoxide by ammoniacal cuprous chloride; the residual gas consisted of hydrogen, nitrogen, and methane.

	Dried gas from cylinder.	Uncondensed gas from Expt. 4.
CO_2, %	0·00	0·00
Unsaturated hydrocarbons, %	5·75	0·00
O_2, %	0·00	0·00
CO, %	7·25	8·55
Residual gas, %	87·00	91·45
Ratio CO : Residual gas	0·0833	0·0935

The higher proportion of carbon monoxide in the uncondensed gas was due to partial retention of methane in the boiling tube along with liquid ethylene (see below). The whole of the methane, however, was not condensed, since, on combustion, the residual gas yielded some carbon dioxide.

A solid deposit, pale lemon in colour, collected in the vertical tube. It melted at approximately — 20°, yielding a viscous liquid which became amber-coloured and increased in mobility as the temperature rose to that of the room. A drop introduced into concentrated sulphuric acid decomposed with evolution of gas, and the solution, diluted with water, showed an abundance of ferrous iron but only the merest trace of ferric iron. Upon exposure to air, the liquid slowly decomposed with the formation of brown hydrated ferric oxide. These properties correspond to those of iron pentacarbonyl (Mond and Langer, J., 1891, **59**, 1090; Dewar and Jones, *Proc. Roy. Soc.*, 1905, *A*, **76**, 558). Approximately 1·25 g. of the carbonyl collected (Found: Fe, 26·5. Calc. for FeC_5O_5: Fe, 28·5%), and this was probably about half the amount contained in the cylinder at the time we received it. It was slightly contaminated with organic matter of tarry odour.

A colourless liquid had collected in the boiling tube. On removal from the Dewar flask, it boiled vigorously, its temperature as registered by a pentane thermometer being about $-160°$. The liquid thus contained appreciable quantities of methane. The remainder was probably ethylene more or less admixed with acetylene, of which it smelled strongly. It was not further investigated.

Discussion.—This research is of special interest, inasmuch as it is known that the cylinder gas was, in 1899, free from carbonyl except in such traces as would not be easily detected. Hence the compound must have been produced by the prolonged influence of compressed carbon monoxide on compact iron (*i.e.*, steel) at the ordinary temperature. From the analysis of the uncondensed gas in Expt. 4, it is evident that free carbon monoxide was still present in considerable amount, and this possibly explains the absence of the lower carbonyls of iron. When freshly filled, the pressure of the gas would, in 1899, have approximated to 120 atm. As some of the gas had been used prior to storage, the pressure leading to the formation of carbonyl would probably lie between 50 and 80 atm.

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