Cyclooctatetraene Iron Tricarbonyl

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Recently Hallam and Pauson[1]) investigated butadiene iron tricarbonyl and its derivatives and concluded that the conjugation of the double bonds was essential for the formation of such compounds. However, Pettit[2]) reported the preparation of analogous compounds with non-conjugated bicyclo [2.2.1] heptadiene. He considered that a suitable spatial arrangement of the double bonds, not their conjugation was necessary for their effective overlap with the atomic orbitals of the metal which was an essential factor leading to the bond formation.

Since cyclooctatetraene (COT), in its tub form, seems to have such a suitable spatial arrangement of the double bonds, we have tried to prepare cyclooctatetraene iron tricarbonyl, $(C_8H_8)Fe(CO)_3$ (I), and its successful preparation is reported here*.

After irradiation of an equimolar mixture of COT and iron pentacarbonyl with sunlight for 8 hr. and subsequent removal of the unreacted starting materials under reduced pressure, dark red crystals were obtained in 10% yield. These crystals were purified by sublimation under reduced pressure (5 mmHg) at 80°C or by recrystallization from light petroleum.

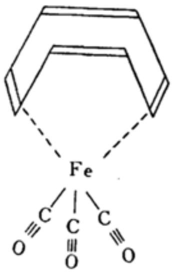
Anal. Found: C, 54.31; H, 3.35; mol. wt. (Rast), 243. Calcd. for $C_{11}H_8FeO_3$: C, 54.14; H, 3.31%; mol. wt., 244.

The combustion analysis apparently conformed to the composition, $(CO)_3Fe.(C_8H_8)$ (I). The purified compound I was beautiful dark red needles, melting at 94°C without decomposition and was stable in air and readily soluble in most organic solvents including pyridine and glacial acetic acid. I dissolved in cold concentrated sulfuric acid and could be recovered unchanged on neutralization, but it decomposed when its solution in concentrated sulfuric acid was heated to 110°C. The solution of I in carbon tetrachloride reacted readily with bromine at room temperature to give ferric bromide and brominated products of COT. I could also be prepared by heating the both components under nitrogen at 120°C for 18 hr.

The infrared spectrum of I (in KBr disk) showed bands at 1961 and 2050 cm^{-1} and at 699, 716 and 720 cm^{-1}. The former group of bands is similar to those of butadiene iron tricarbonyl and the latter group of bands indicates the presence of *cis*-type double bonds.

In the visible region of the spectrum no distinct absorption maxima were observed. In the ultraviolet region it showed a weak absorption maximum at 300 mμ (log ε: 3.99 in 95% alcohol) similar to that of COT. On treatment with aqueous potassium iodide-iodine solution at 50°C, the solution of I in benzene evolved 3 mol. of carbon monoxide indicating the presence of three —C≡O groups in one molecule of I. For further proof of the structure of I, I was decomposed by iodine in toluene. COT was detected in the decomposition products by its reaction with mercuric sulfate to give phenyl acetaldehyde. COT formed was further identified and determined by gas chromatography (the yield of COT was 76%).

From the above results it may be concluded that COT is π-bonded to iron without change in its skeletal structure. It is a well established fact that the molecule of COT is not planar. Therefore, it may be reasonable to assume that COT molecule in I would not be planar, too; and the following structure of I is proposed:



(I)

Fig. 1

When iron pentacarbonyl was used in excess in the photosynthesis of I, yellow crystals were obtained in addtion to I in 3% yield from COT. These crystals were purified by fractional sublimation at 120°C (5 mmHg) followed by recrystallization

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1) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, **1958**, 642.

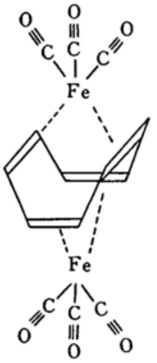
2) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

* After completion of our work, it has become known to us that T. A. Manuel and F. G. A Stone, (*Proc. Chem. Soc.*, **1959**, 90), also reported the preparation of cyclooctatetraene iron tricarbonyl and the related compounds. They suggested a planar structure to COT which was attached to the iron atom of cyclooctatetraene iron tricarbonyl. In their report, however, no practical description of the preparation of these compounds are given.

from benzene to give orange-yellow needles which decomposed at 185°C.

Anal. Found: C, 43.72; H, 2.35. Calcd. for $C_{14}H_8FeO_6$: C, 43.80; H, 2.11%.

The combustion analysis conformed to the composition, $(CO)_3Fe(C_8H_8)Fe(CO)_3$ (II). This compound II was slightly soluble in light petroleum and methanol, soluble in pyridine, glacial acetic acid and benzene, insoluble in hydrochloric acid and aqueous sodium hydroxide solution. It decomposed in concentrated sulfuric acid at room temperature.



(II)

Fig. 2

The infrared spectrum of II (in KBr disk) showed bands at 1972 and 2035 cm^{-1} for CO stretching region. The characterictic bands indicating the presence of *cis*-type double bonds which were shown in the infrared spectrum of I did not appeared and the whole spectrum was relatively simple compared with that of I, suggesting the higher symmetry of the molecule of II. The ultraviolet absorption spectrum of II had a shoulder at 258 mμ (log ε : 3.15, in 95% ethanol) and no distinct absorption bands appeared in the visible region. Compared with the absorption band of I the shift of the band toward shorter wavelength and the decrease in intensity are apparent. These spectral changes in the ultraviolet region may be considered to indicate the immobility of the π-electrons of COT in II. From the above results the structure shown in Fig. 2 is proposed.

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