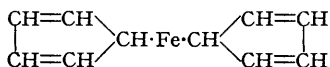


114. *Dicyclopentadienyliron.*

By SAMUEL A. MILLER, JOHN A. TEBBOTH, and JOHN F. TREMAINE.

Reduced iron (in presence of alumina and potassium oxide, and preferably also molybdenum oxide) reacts with *cyclopentadiene* in nitrogen at 300° to give a yellow compound $C_{10}H_{10}Fe$, m. p. 172·5—173°, believed to be *dicyclopentadienyliron*. It sublimes above 100° without decomposition, is volatile in steam, and soluble in organic solvents. The formation of this compound proceeds only for 10—15 minutes, after which further reaction is only effected after careful oxidation and re-reduction of the iron. After being heated in a glass tube at 250° in nitrogen, and frequently as first prepared, the iron compound contains small amounts of adsorbed nitrogen which is sufficiently firmly held to give positive sodium-fusion tests for nitrogen. It has not been possible to use this property to make the material behave as a catalyst for ammonia formation.

COMPOUNDS containing only carbon, hydrogen, and iron have not hitherto been described, and the direct replacement of hydrogen attached to carbon by iron would not be expected to be feasible. It has now been found that reduced iron, in the form of the well-known "doubly-promoted synthetic ammonia catalyst," can be made to react with *cyclopentadiene* in nitrogen at 300° and at atmospheric pressure, to give a yellow crystalline compound, of composition $C_{10}H_{10}Fe$. The iron is in its bivalent form, since treatment of a carbon tetrachloride solution of the material with bromine in the same solvent gave a dark green precipitate, which dissolved in water to give a blue solution containing ferrous and bromide ions. The structure of the compound has not been further elucidated, but by analogy with the well-known *cyclopentadienylpotassium*, it is believed that substitution has occurred in the methylene group, and that the compound has the structure inset.



The compound melts without decomposition at 172·5—173° and sublimes readily, still without decomposition. It is soluble in alcohol, ether, and benzene, but not in water. On concentration of an alcoholic solution on the water-bath, the compound distils in the alcohol vapour; it is also steam-volatile. It is charred by and reduces sulphuric acid, and decolorises acid potassium permanganate.

The conversion of the reduced iron into *dicyclopentadienyliron*, when a stream of nitrogen containing *cyclopentadiene* vapour is passed over it, proceeds only for 10—15 minutes. The residual reduced iron is then unchanged in regard to its activity as a catalyst with respect to the synthesis of ammonia at 550°, and the reason for the inhibition of further formation of the iron derivative has not been elucidated. It is possible to revivify the iron by oxidation at 450° in an atmosphere of nitrogen containing steadily increasing proportions of oxygen, and finally in air, and then reduction at 450°. The revived product can then again be made to produce *dicyclopentadienyliron* for 10—15 minutes only.

The initial rate of production of iron *dicyclopentadienyl*, and the total period of reaction before inhibition sets in, can both be increased, resulting in about a 3-fold increase in output, by the addition of 1% of molybdenum oxide to the doubly-promoted catalyst.

A curious feature of several of the preparations of *dicyclopentadienyliron* was that the crude products contained nitrogen and gave positive results in the Lassaigne test. Purification always resulted in a product free from nitrogen. In view of this capacity to adsorb nitrogen at comparatively low temperatures, some experiments were carried out with 3 : 1 mixtures of hydrogen and nitrogen under a variety of conditions, but the compound was not capable of acting as a vapour-phase catalyst for ammonia synthesis.

EXPERIMENTAL

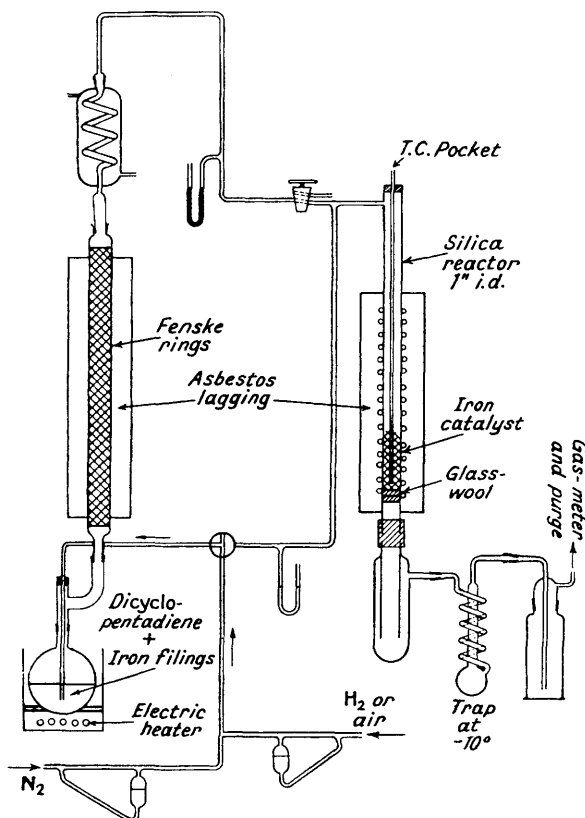
Preparation of Dicyclopentadienyliron.—The following series of preparations with one specimen of catalyst was carried out after preliminary experiments establishing the formation

of the product and its nature, the rapid failing of reactivity of the reduced iron, and the practicability of revivification.

Ferric nitrate (3 kg.) and a aluminium nitrate (300 g.) were dissolved in distilled water (4 l.), and treated with the equivalent of potassium hydroxide as a 40% solution. The precipitate was separated on the centrifuge, and washed *in situ* with distilled water (5 l.). It was dried at 100° for 4 hours, and then ignited at 600° in a muffle furnace for 10 hours. As it still contained 10.7% of water-soluble material (calculated as K_2CO_3), it was washed with 2-l. portions of distilled water, dried again, and then converted into $\frac{3}{8}$ "-diameter pellets. Analysis then showed: Fe_2O_3 , 90.1; FeO , 1.4; Al_2O_3 , 6.9; water-solubles (as K_2CO_3), 1.3; moisture, 0.3%.

40 ml. of the unreduced pellets were charged into the 1"-diameter silica reactor tube of the apparatus shown in the accompanying diagram, and reduced during 10 hours at 450° in a

Apparatus for the preparation of iron dicyclopentadienyl.



50 l./hour stream of dry hydrogen. A short test was then carried out, by passing a 1 : 3 mixture of nitrogen and hydrogen through the reactor at 550°, to confirm the activity of the reduced iron as a catalyst for the synthesis of ammonia.

It was found to be most convenient to prepare *cyclopentadiene* as required from its dimer. This was boiled with a little iron filings, and a stream of nitrogen passed through it, and the issuing mixture of monomer and dimer passed up through the fractionating column (see figure) surmounted by a reflux condenser. The nitrogen issuing from the top of the reflux condenser was regarded as being saturated with *cyclopentadiene* at the temperature of the cooling water. For the present series of experiments, the nitrogen was fed at 25 l./hour, the condenser kept at 15°, and the reactor at 300°.

After the first reaction with *cyclopentadiene*, the reactor was purged with nitrogen, and then mixtures of nitrogen and air were passed through it at 25 l./hour. In order to avoid developing high temperatures on the catalyst surface, the air content of the mixture was increased slowly, in 5 half-hourly steps as 5, 10, 20, 40, and 100% of air, and the temperature was gradually

raised, but never allowed to reach 450°. Oxidation was considered complete when the measured temperature kept quite steady with 100% air passing. The reactor was then flushed out with nitrogen, and hydrogen passed through at 50 l./hour for 12 hours at 450°. A further experiment with nitrogen and *cyclopentadiene* was then carried out.

The product in each case was washed out of the receiver with ether, and the ether evaporated off under reduced pressure. Some of the *cyclopentadiene* was recovered in the cold trap. Conversion of *cyclopentadiene* into its iron compound could only be estimated approximately, but during the 15-minute periods of activity, the conversion amounted to 40–50%.

The following amounts of product were isolated in 15 successive experiments with the same charge of iron pellets: 0.93, 0.88, 1.01, 1.10, 1.08, 0.96, 0.53, 1.04, 0.35, 0.98, 0.61, 0.31, 0.97, 0.41, 0.75 g., giving in all 11.91 g. In the ninth cycle the oxidation had been omitted, the pellets being only treated with hydrogen for 2 hours. Although on three other occasions the full revivification procedure also only gave small amounts of product (0.31–0.53 g.), and no explanation for these low amounts can be offered, it is considered that revivification without oxidation was less efficient.

Experiment in Presence of Molybdenum.—A solution was prepared of ferric nitrate (650 g.), aluminium nitrate (29 g.), ammonium molybdate (13 g.), and distilled water (500 ml.), and potassium hydroxide (0.6 g.) in a small quantity of water was then added. The solution was stirred, and concentrated aqueous ammonia was added slowly until the mixture was alkaline to litmus. The excess of ammonia and most of the water were then evaporated off to leave a pasty mass, which was gently heated on a sand-bath to complete the decomposition of ammonium salts; copious nitrous fumes were evolved at this stage. The resulting black residue was ignited in a muffle furnace at 600° for 6 hours. It was then formed into pellets ($\frac{3}{8}$ "') and reduced at 450° in hydrogen. Analysis of the material before reduction showed that after reduction the composition was: Fe, 90; Al₂O₃, 8; Mo₂O₃, 1; K₂O, 1%.

The apparatus used in this experiment was the same as that shown in the above diagram except that the reactor was a silica tube of 0.6" diameter. On passage of nitrogen saturated with *cyclopentadiene* at 15° over the iron at 300°, there was considerable formation of yellow crystals in the receiver, but after 15 minutes the rate of production dropped rapidly. The total solid obtained in 25 minutes was 3.0 g., compared with the average of 1 g. obtained in absence of the molybdenum. Reduced iron prepared in the way just described but with omission of the molybdenum gave only a trace of dicyclopentadienyliron.

Attempted Preparation at High Pressures.—A number of attempts were made to prepare larger amounts of material by reaction in a heated rotating 1-l. autoclave. These included starting with *cyclopentadiene* or *dicyclopentadiene*, and the reduced doubly-promoted iron catalyst, iron filings, "Raney" iron (obtained by dissolving out the aluminium from an iron-aluminium alloy) with and without ethanol, and the material containing molybdenum as described above, and heating in nitrogen at 12–150 atm. and 200–300° for $\frac{1}{2}$ –2 hours. Small quantities of yellow or brown oils containing iron were obtained which were soluble in alcohol and volatile in its vapour, but in no case could dicyclopentadienyliron be isolated.

Analyses.—*Dicyclopentadienyliron*, recrystallised from aqueous ethanol, had m. p. 172.5–173° (Found: C, 64.4, 65.2; H, 5.5, 5.8; Fe, 29.9. C₁₀H₁₀Fe requires C, 64.5; H, 5.4; Fe, 30.1%). The molecular weight as determined by the Rast method gave high and erratic results, but ebullioscopically in benzene values of 210 and 175 were obtained (C₁₀H₁₀Fe requires *M*, 186).

Reaction for Nitrogen.—Several of the specimens of crude product gave positive tests for nitrogen by the sodium-fusion method, but quantitative determination by micro-Kjeldahl or micro-Dumas methods was not possible. Purified specimens usually did not contain nitrogen even by the Lasaigne test. A specimen of this nitrogen-free, purified dicyclopentadienyliron was heated in a Carius tube for one hour at 250–300° in an atmosphere of nitrogen; the resulting material gave a positive test for nitrogen. Another specimen was similarly heated in an atmosphere of ammonia, but the resulting material did not give a positive test for nitrogen. Another specimen was heated in a glass bulb in an atmosphere of nitrogen attached to a manometer; at 100° there was a reduction of pressure corresponding to absorption of 1.0 ml. of nitrogen per g. of dicyclopentadienyliron, but at higher temperatures the material sublimed out of the hot zone into the manometer.

Dicyclopentadienyliron was heated to 100–150° in nitrogen at 10 atm. in a small steel bomb (7-ml. capacity; 40 g. tare weight). There was no detectable adsorption of nitrogen. It is possible that this adsorption occurs in glass but not in steel apparatus.

Tests as an Ammonia Catalyst.—Mixtures of hydrogen and nitrogen (3 : 1) were heated in

an autoclave with dicyclopentadienyliron at 20—50 atm. and 100—250°, but no ammonia was obtained. A similar negative result was found when dicyclopentadienyliron vapour at various concentrations in a stream of nitrogen and hydrogen was passed through Pyrex tubes at 300° and 400°.

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