

A Study of the Reaction of Iron Dichloride with the Pyridine Activated Cyclopentadiene in Anhydrous 2-Propanol

Z. G. Kurbanov

*Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaijan,
ul. Dzhavida 29, Baku, AZ 1143 Azerbaijan
e-mail: itpcht@itpcht.ab.az*

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Abstract—A reaction was studied between iron dichloride solvate and pyridine activated cyclopentadiene in anhydrous 2-propanol. We showed that pyridine hydrochloride formed in the course of this reaction can be easily separated from the target product (ferrocene) and recycled after neutralization with sodium isopropoxide, which imparts the preparative value to the studied reaction.

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As known, there are numerous ways of obtaining ferrocene and related compounds. A few of them are of preparative value by the reasons of fire safety and accessibility of starting reagents. An important and necessary requirement to the ferrocene technology is preventing environmental releases of hazardous substances and recycling auxiliary chemicals and compounds after appropriate transformations or a possibility of using them in other chemical processes [1]. This is only possible at the use of the exchange reactions resulting in the formation of neutral non-polluting chemical compounds. These reactions include the interaction of anhydrous iron dihalide with an alkali metal (Li, Na, K) cyclopentadienate resulting in the formation of the neutral ferrocene and the metal halide [2].

Another method for the synthesis of ferrocene is based on the reaction between FeO and C₅H₆ at 500°C. The water and ferrocene formed do not pose environmental problems. Other industrial methods for the synthesis of ferrocene that include polycondensation or pyrolysis and other reactions of cyclopentadiene result, besides the main substance, in a number of side products, requiring additional resources for their utilization [3, 4].

In the one-step synthesis of ferrocene there is an important experimental problem of the choice of reaction conditions providing neutralization of hydro-

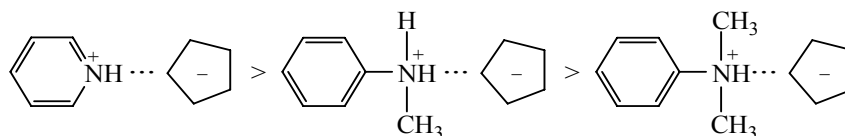
rogen chloride liberated in the reaction of FeCl₂ with cyclopentadiene, to direct the process toward the formation of ferrocene. To this end, we chose for the study the reaction of anhydrous iron dichloride with the cyclopentadiene activated with pyridine, in the medium of anhydrous 2-propanol.

Note that cyclopentadiene itself being a weak CH-acid (pK_a 15.5) does not react with FeCl₂ to form ferrocene. According to [5], for the realization of this reaction the cyclopentadiene pK_a should be equal to 22 at least.

In order to synthesize ferrocene in the reaction (1) between cyclopentadiene and iron dichloride, we investigated a possibility of activation of cyclopentadiene with some amines. In the literature the interaction of cyclopentadiene with the amines like (CH₃)₃N, C₆H₅CH₂NH₂, and C₆H₅NH₂ is described leading to the formation of the active intermediate bipolar imido complexes [3]. According to [4], the chemical stability of the resulting cyclopentadienyl anion depends on the electron-withdrawing characteristics of the substituents at the nitrogen atom and decreases in the series: C₆H₅NH₂ > C₆H₅CH₂NH₂ > (CH₃)₃N. Taking in the consideration this property of the substituted amines, we investigated the possibility of activating cyclopentadiene with industrially accessible amines. To this end, we tested diethylamine, triethylamine, methylaniline, dimethylaniline, and pyridine.

^1H NMR study of a mixture of pyridine with cyclopentadiene showed the presence of two signals only, belonging to the protons of the pyridine–cyclopentadiene complex. One signal is shifted upfield to the position with chemical shift $\delta = 0.75$ ppm, while the proton signal of cyclopentadienyl anion is shifted downfield to $\delta = 16.57$ ppm.

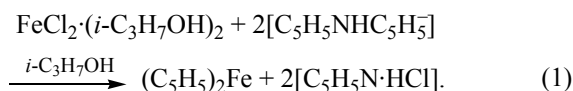
We found that at equimolar ratio of cyclopentadiene, amine, and FeCl_2 in 2-propanol at 20°C , 2 h after mixing a mixture is formed, which in the case of dimethylaniline consists of ferrocene (22–26%), cyclo-



The higher activating ability of pyridine compared to other aromatic amines is due apparently to its structural features: the nitrogen atom in the aromatic ring exhibits a sufficiently basicity and forms with cyclopentadiene a stronger complex than other amines.

On the other hand, the above experimental data support the hypothesis that, in the exothermic reaction (1) the less stable imide complexes easily decompose into the initial compounds, and the formed cyclopentadiene immediately transforms in dimer, trimer and polymer, impeding the isolation of ferrocene from the reaction mixture. Therefore, pyridine is a more effective activator of cyclopentadiene.

The intermediate imido complex of cyclopentadiene and pyridine thus obtained was subsequently used for the synthesis of ferrocene in the reaction with anhydrous iron dichloride solvated by anhydrous 2-propanol, at 30 – 40°C . After processing the reaction mixture, the pure ferrocene yield was over 70%.



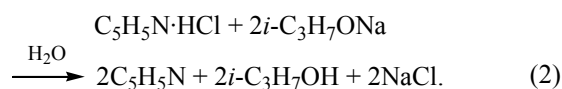
Ferrocene was isolated from the reaction mixture by extraction with a light fraction of petroleum ether (bp 40 – 70°C).

We found that after extraction of the product obtained in reaction (1) the residue consisted mainly of pyridine hydrochloride $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$, a small amount of ferrocene, isopropyl alcohol, 1.2% of pyridine, and some other compounds which were not unidentified [5].

pentadiene dimer (22–24%) and trimer (11–13%), and the remaining cyclopentadiene is converted into a polymer. In the case of monomethylaniline the ferrocene yield reaches 37–43%, and the reaction mixture contains only 10–15% of the cyclopentadiene dimer. When the intermediate complex was prepared with pyridine, the yield of ferrocene was over 70%.

Thus, using the data on the complexing ability of cyclopentadiene with the tested amines we found the following series of decrease in activity depending on the nature of the organic groups:

Of particular interest here is the neutralization of the pyridine hydrochloride, its treatment and re-use of pyridine as an activator in the reaction (1) with cyclopentadiene. To this end, it was necessary to find an appropriate neutralizing agent to carry out this reaction effectively. As the neutralizing agent might be used NaOH , the most common and cost-effective reagent. However, NaOH is unacceptable for the $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ decomposition since it reacts simultaneously with the admixtures of $i\text{-C}_3\text{H}_7\text{OH}$, $(\text{C}_5\text{H}_5)_2\text{Fe}$, and others complicating further purification of $\text{C}_5\text{H}_5\text{N}$. Therefore, for the neutralization we used $i\text{-C}_3\text{H}_7\text{ONa}$ [reaction (2)]. This allowed the return of the neutralizing agent into the reaction (2) as 2-propanol, and excluded decomposition of the present ferrocene and other compounds. The by-product in the reaction (2) is only NaCl .



Thus, we investigated the reaction between the anhydrous iron dichloride in the form of solvated salt $\text{FeCl}_2 \cdot (i\text{-C}_3\text{H}_7\text{OH})_2$, and cyclopentadiene activated with pyridine, in anhydrous 2-propanol, as well as a possibility of obtaining ferrocene in a high yield. We found that the ferrocene formed in this reaction can be easily separated from the pyridine hydrochloride, and the latter after neutralization with sodium isopropoxide can be returned as an activator to the reaction with cyclopentadiene, providing effective and waste-free method of producing ferrocene.

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