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ELECTROCHEMICAL ALKYLATION OF FERROCENE

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Summary

The conditions for the electrochemical alkylation of ferrocene and its derivatives are discussed.

Numerous examples of electrophilic substitution of hydrogen atoms into the ferrocene molecule are well known [1]. The possibility of hydrogen substitution in the ferricinium cation by its reaction with radicals generated in preceding chemical reactions has been also shown [2—4]. We found that hydrogen substitution by alkyl radicals in the ferricinium cation, occurs at the platinum electrode surface under anodic decarboxylation of carboxylic acid anions (conditions of the Kolbe reaction).

Ferrocene electrolysis was carried out in a cylindrical vessel with a cooling jacket, dropping funnel, reflux condenser, gaseous products outlet, and inert gas inlet. The 15.8 cm^2 platinum net electrodes were placed perpendicular to the cylinder axis over its entire cross-section. Anhydrous methanol was used as solvent and potassium or sodium acetate served as electrolytes.

The first experiments were performed by passing the previously prepared methanolic electrolyte solution and respective carboxylic acid through the electrolyzer. Ferrocene was placed in a special pocket in the vicinity of the anode and the electrolysis was conducted with a current density of 5.0—7.7 ampere/dm^2, the flow rate was usually about 5.5 ml/min.

After completion of the electrolysis the solution was reduced with $SnCl_2/HCl$ solution and extracted with petroleum ether. The products were analyzed by GLC, mass-spectrometric and IR spectroscopic methods. Fig. 1 shows a typical chromatogram of the electrolysis products. It can be seen that monomethylferrocene (30%) and small quantities of isomeric dimethyl- and trimethylferrocenes are present in the mixture along with unreacted ferrocene (60%). Experiment shows that this method may yield 53% of methyiferrocene per mol of reacted ferrocene. Variation in flow rate, replacement of electrolyte and change of electrolysis temperature do not alter essentially the qualitative and quantitative composition of the reaction products.

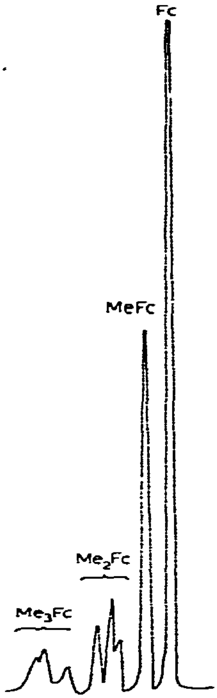


Fig. 1. Chromatogram of the electrolysis products of a methanolic solution of potassium acetate and acetic acid in the presence of ferrocene (in flow).

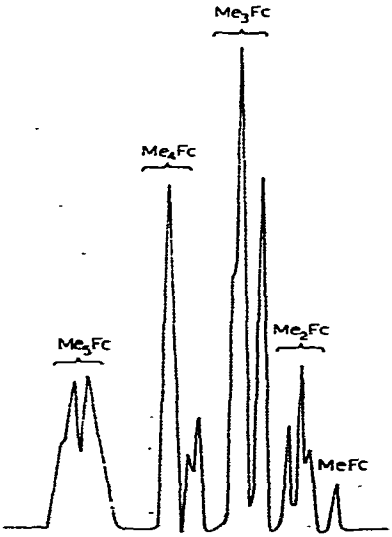


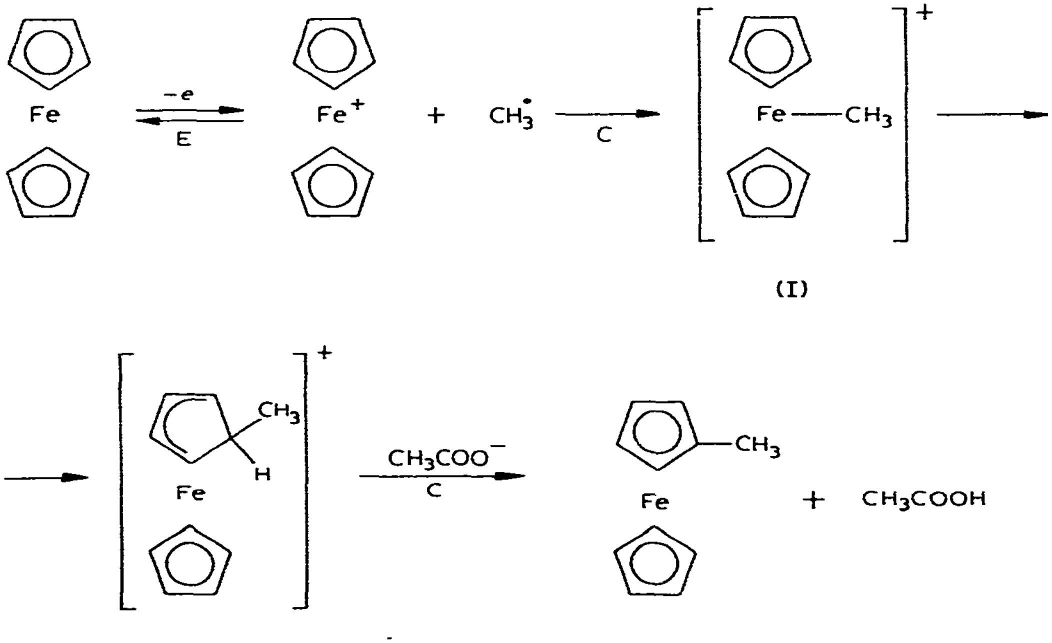
Fig. 2. Chromatogram of the electrolysis products of a methanolic solution of potassium acetate, acetic acid and ferrocene.

This method afforded not only a mixture of methylferrocene homologs but also a mixture of propylferrocenes (7% of monopropylferrocene in the reaction mixture). A major application was shown: the synthesis of alkylferrocenes by decarboxylation of stearic and myristic acids and the methylation of cyclopentadienylmanganese tricarbonyl was also performed.

It is known that the alkyl radicals generated in the Kolbe reaction strongly absorb onto the platinum electrode surface [5]. Thus one may assume that the reaction of alkyl radicals with the ferricinium cation is heterogenic. Hence the following transformations occur at the anode, this is the first example of E(E'C')CC type reactions with respect to the ferrocene substrate.

$$CH_3COO^- \xrightarrow{-e} CH_3COO^\bullet \qquad E'$$

$$CH_3COO^\bullet \longrightarrow CH_3^\bullet + CO_2 \qquad C'$$



(I)

(II)

The formation of intermediates, I and II has previously been suggested in the mechanism of hydrogen substitution in the ferricinium cation [4].

Since oxidation of alkylferrocenes proceeds more easily than that of unsubstituted ferrocene [6], the alkylferrocene cations also react with the alkyl radicals generated at the anode. The reaction mixture contains the products of further alkylation: di- and polyalkylferrocenes. Variation of the electrolysis conditions may provide predominant formation of polyalkylferrocenes. This was achieved by performing the reaction in the same electrolyzer but without flow. Thus the reaction mixture giving the chromatogram of Fig. 2 was obtained after passing a current of 0.22 F into the solution. It is seen from the chromatograms that tri-, tetra- and pentamethylferrocenes are the main products. An increase in the quantity of electricity caused an increase in polyalkylated products. Under these conditions ferrocene may enter completely into reaction.

Thus the conditions for the electrochemical alkylation of ferrocene and its derivatives have been found. The reaction could also be employed using other transition metal complexes capable of electrochemical oxidation. These experiments are under way.

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