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LETTERS TO THE EDITOR

On the Radical Chain Mechanism of Oxidation of a Series of Ferrocene Derivatives with Molecular Oxygen

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It is known that the oxidation of ferrocene with molecular oxygen, occurring only in the presence of strong Brønsted acids (HX), is characterized by formation of the radical-ion salt $Cp_2Fe^{+\cdot}X$ in a quantitative yield at insignificant oxygen consumption (N_{O_2}). Depending on the solvent, it reaches 0.25–0.3 mol per mole of the oxidized complex [1, 2]. This fact suggests the molecular or ion-molecular mechanism possibly involving other active species.

We have studied autooxidation of a series of ferrocene derivatives containing both electron-donating and electron-withdrawing substituents in the Cp ligand: 1,1'-diethylferrocene **I**, hydroxymethylferrocene **II**, formylferrocene **III**, acetylferrocene **IV**, and ferrocenecarboxylic acid **V**. Perchloric, trifluoroacetic, and benzoic acids were used as catalysts. The reaction was studied in toluene, dioxane, and ethanol at 40–50°C. It was found for the first time that the oxidation is a sequence of two macrosteps: molecular oxidation with the generation of free radicals and the radical chain oxidation initiated by them. For all the compounds studied, the radical chain pathway makes the main contribution to the oxidation. The radical chain step of the oxidation of the ferrocene derivatives was confirmed by the inhibiting effect of additives known as inhibitors of the radical chain processes, such as *o*-phenylenediamine and Ionol (C^0/C^0_{In} = 100). Addition of *tert*-butyl hydroperoxide caused the reaction acceleration (C^0/C^0_{ROOH} = 10). The inhibitors and the initiator were added at the beginning as well as in the course of the process. It was shown that the rate of the radical chain oxidation of all the ferrocene derivatives strongly depends on the solvent and decreases in the series dioxane > toluene > water–dioxane > ethanol. The inhibiting effect of water and ethanol, known also for the other processes of the radical chain oxidation [3], is usually attributed to a decrease in the reactivity of the peroxy radicals $RO_2^{\cdot}$ leading the chain, due to the formation of hydrogen-bonded complexes $RO_2^{\cdot}\cdots HOR'$, where R' is H or alkyl.

An important specific feature of the reactions under study is that the effect of acids on the character of oxidation of the ferrocene derivatives specifically depends on the acid strength. This is especially clear from the comparison of oxidation of compounds **I** and **II**. The oxidation of **I** in the presence of strong acids shows no evidence of a radical chain reaction, because the addition of inhibitors does not affect the reaction rate and stoichiometry. Similarly to ferrocene, oxidation of **I** leads to the quantitative formation of the salt $(C_2H_5C_5H_4)_2Fe^{+\cdot}X^-$ at the N_{O_2} value of ~0.3. The oxidation of **I** in the presence of benzoic acid has a pronounced radical chain character. At the same time, the N_{O_2} value can be higher (depending on the reaction time), and the concentration of the forming diethylferrocenium cation, significantly lower than in the case of oxidation of **I** in the presence of strong acids. Such a difference in the character of oxidation of **I** suggests that the mechanisms of its molecular oxidation in the presence of strong and weak acids are essentially different: In the presence of perchloric and trifluoroaceric acids, the oxidation of **I** most probably proceeds via its protonation, which is unlikely in the case of benzoic acid when, apparently, oxygen reacts with the nonprotonated complex.

Solutions of **II** do not take up oxygen in the presence of perchloric acid, though fast transformation of

the complex into the dimeric cation $(C_5H_5Fe^{+\cdot}C_5H_4 \cdot CH_2)_2$ is observed. This results from a series of consecutive reactions caused by protonation of the OH group of the substituent [4]. In the presence of benzoic acid, no such transformations take place for **II**, because it is not protonated with weak acids. Nevertheless, in this case its oxidation with oxygen becomes possible. The main contribution to it is made by the radical chain pathway leading to the formation of compounds **III** and **V**.

Oxidation of the ferrocene derivatives containing strong electron-withdrawing substituents, i.e., of compounds **III**–**V**, takes place only in the presence of strong acids, and the rate of their oxidation exceeds many times that of unsubstituted ferrocene under the same conditions (dioxane or ethanol, 50°C). The N_{O_2} value may reach 2–3. These features result from the decisive contribution of the radical chain pathway to oxidation of the ferrocene derivatives. This conclusion is also confirmed by the effect of inhibitors. It is known that the above-mentioned ferrocene derivatives in the presence of strong acids are protonated at the functional group of the substituent [5–7]. These data, in combination with the above reasonings, indicate that oxygen reacts with the protonated forms of **III**–**V**. Hence, the substituents directly participate in the processes of both molecular and radical chain oxidation of these complexes. The probability of oxidation of **II** in the presence of benzoic acid also suggests direct participation of the CH_2OH group in the process.

The oxidation of ferrocene derivatives was carried out in a vacuum static installation with vigorous stirring of the reaction mixture. The reaction progress was monitored by the oxygen uptake, which was measured manometrically and by GLC. Complex **I** was prepared according to [8] and purified by distillation. Complex **II** was synthesized according to [9], and complex **IV**, according to [10]. Both substances were purified by column chromatography on Al_2O_3 using the Trapp's eluotropic series of solvents [11]. Compound **III** was synthesized according to [12] and was recrystallized from ether. Compound **V** was prepared according to [13] and was recrystallized from ligroin and ethanol. The electronic spectra of diethylferricenium cation were recorded on an SF-2000 spectrophotometer. Formation of compounds **III** and **V** in the course of oxidation of **II** was proved by TLC on Silufol plates, elution with chloroform.

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