

Preliminary communication

REDUCTION OF FERRICENIUM SALTS WITH ANIONIC NUCLEOPHILES AND THE MECHANISM OF AN OSCILLATORY PROCESS IN FERROCENE-FERRICENIUM CATION SYSTEMS

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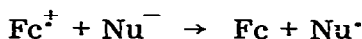
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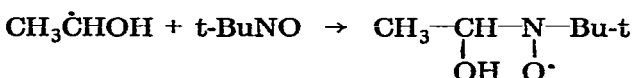
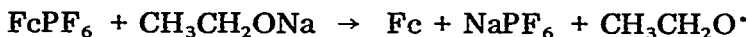
Summary

Ethylate ion reduces ferricenium cation to ferrocene and forms the α -oxyethyl radical identified by means of a spin-trap. The same radical is seen when irradiating ethanol solutions of methylferrocene in an ESR spectrograph cell in the presence of traces of oxygen. Taking into account these results we propose a scheme for the photoinduced oscillatory process in alcohol solutions of methylferrocenes or methylferricenium salts.

Recently, we have shown [1] that azole anions act as one-electron reducing agents towards ferricenium cations: ferrocene (Fc) and azolyl radicals are formed as a result of the reaction. These radicals are identified by means of a spin-trap — tert.-nitrosobutane. We have now extended the series of anionic nucleophiles (Nu^-) to alcoholate anions. The electron transfer process



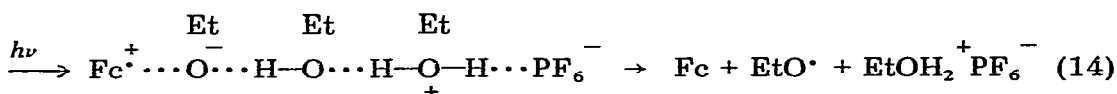
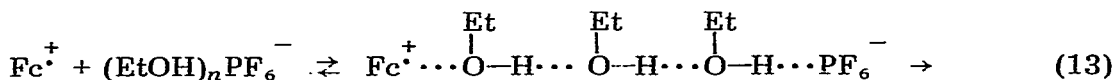
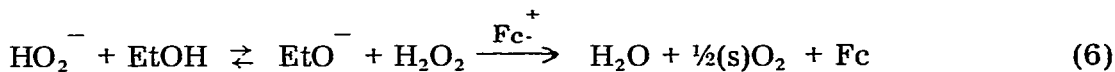
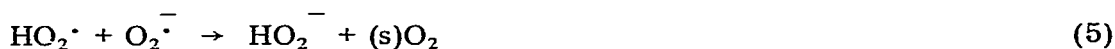
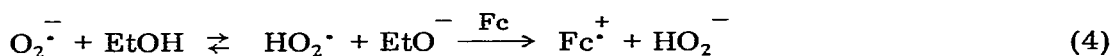
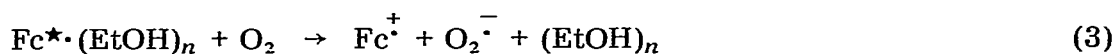
proceeds also for alcoholate ions:



We identified the well known stable α -hydroxyethyl-tert.-butylnitroxide radicals by their ESR spectrum (g 2.0050, a_{N} 14.6 G, a_{H} 2.3 G; cf. lit. [2] a_{N}

14.5 G, a_N 2.3 G [2]). We found the same radicals with the aid of tert.-nitrosobutane when irradiating an undegassed ethanol solution of octamethylferrocene in the ESR spectrometer cell.

We used the results obtained to consider the mechanism of the oscillatory process in ethanol solutions of methylferrocenes or methylferricenium salts photoinduced by irradiation with a normal electric lamp [3,4]. The period of the oscillation is a function of several factors: the number of methyl groups, the concentration of the solution and the quantity of oxygen in the solution. These experimental data indicate that the mechanism of this oscillatory process must include the effects of the solvent, oxygen and the free-radical nature on the transformations. Therefore we proposed the scheme as follows:



Ferrocene acts as a photosensitizer in these processes. The reactions 1–3 transmit the initiation of the oscillatory reaction starting from ferrocene. Oxygen is an initiator of the radical transformations. Reactions 4 and 7 form the cycle necessary for ferrocene–ferricenium interchange and for regenera-

tion of the parent ferrocene. Reactions 8 and 9 provide the final result of the reaction. These reactions account for the open oscillatory process and describe this reaction as a ferrocene- (or ferricenium cation-) photosensitized oxidation of ethanol by atmospheric oxygen. The reactions 4–6 and 10 account for the partial regeneration of oxygen. The macrokinetic oscillatory nature is provided by reactions 11–14 arising due to rapid electron exchange reactions between ferrocene and ferricenium cation ($k \approx 10^5$ – 10^7 l mol⁻¹ sec⁻¹ in the series of systems containing methylferrocene + 1% methylferricenium salt [5]) on the one hand and proton exchange reactions between solvent molecules on the other hand ($k = 1.4 \times 10^6$ l mol⁻¹ sec⁻¹ [6]). Presumably the proton exchange is catalyzed by ferricenium salts, see eq. 13 and 14. These two latter reactions show the initiation of the reaction and the interchange of ferrocene and ferricenium cation if the salt of ferricenium cation is the parent compound. In addition these reactions show the presence of the charged species with the following counterions: EtO⁻ for Fc⁺ and EtOH₂⁺ for PF₆⁻.

Considering reactions 3, 4 and 7 and our investigations of the reduction of Fc⁺ by anionic nucleophiles (particularly by azole anions [1]) in the presence of oxygen and studies on proton transfer in azoles [7], raises the question of the possible role of radical states of histidine imidazole and on the contribution of one-electron reduction of Fe³⁺ by deprotonated imidazolyl residues of systems such as haemoglobin and certain cytochromes. It is very likely that a similar mechanism of concerted electron and proton transfer occurs in the processes of oxygen transport by blood haemoglobin and in related processes of pH conservation in tissues. In these processes proximal and distant imidazolyl residues of histidine and iron atoms of the haemoglobin molecule take part.

As it is stated above, we studied a model of reaction 7 by ESR technique. Ethoxide anion necessary for this stage may arise in reactions 4–6 or in reactions 13 and 14, depending on the nature of the ferrocene compounds. In addition we studied a model of the whole oscillatory process by the same ESR technique under the usual experimental conditions [3,4] and with rigid exclusion of oxygen. No α -ethoxy radicals appeared in the latter case. Irradiation of ethanol under experimental conditions [3,4] also does not generate this radical when ferrocene is absent.

We tried to identify stable final products of ethanol oxidation (acetaldehyde, for example; see eq. 9). For this purpose we saturated ethanol with oxygen and prepared a 10⁻² M solution of octamethylferrocene in this ethanol. This solution was irradiated with a 500 W lamp for 10 hours. We used the GLC method for detection of products of oxidation. Only acetaldehyde was found. No other products of oxidation were detected. Thus, photosensitized oxidation of ethanol with air oxygen catalysed by the ferrocene-ferricenium cation system actually occurs in this case.

Decrease of the period of the oscillation with increase of the number of methyl groups in the parent ferrocene compound is in accordance with IR data on the strength of hydrogen bonds in complexes of methylferrocenes with increasing number of methyl groups in the molecule [8]. The latter factor (i.e. H-bond strengthening) may account for the acceleration of reaction 1–3 and 13–14.

We are proceeding with the investigation of this oscillatory process.

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