

OXIDATION MECHANISM OF FERROCENE WITH MOLECULAR OXYGEN

Kinetic and thermodynamic aspects

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The present work is devoted to the thermodynamic and kinetic analysis of literature data on the oxidation of ferrocene in the presence of Bronsted acids, since up to now the mechanism of this reaction is still not explained.

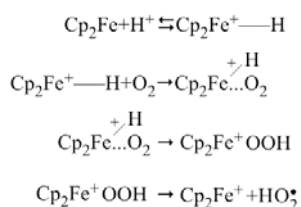
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Introduction

It is known that, in the absence of strong acids ferrocene is remarkable for its extreme resistance to oxygen [1, 2]. The reason for this phenomena lies in the high value of its redox-potential ($\varphi^0(\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe})=0.59\text{ V}$ [3] that is substantially higher than the redox-potential of the oxygen ($\varphi^0(\text{O}_2^-/\text{O}_2)=-0.56\text{ V}$). In an acidic medium the oxidation properties of the latter greatly increase therefore, from the point of view of thermodynamic criteria the oxidation of ferrocene takes place according to the following equation:

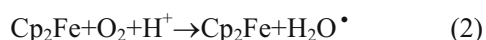


since the standard redox-potential of the oxidation system $\text{O}_2 + 4\text{H}^+$ is equal to 1.23 V. An opportunity of the realization of reaction (1) was demonstrated elsewhere [4] on studying the oxidation of ferrocene in trifluoroacetic acid. In addition, the authors [4] proposed the gathered information up to the present mechanism of this reaction (Scheme 1).



Scheme 1

The resultant equation is written as follows:



Authors [4] suppose that a molecule of O_2 at coordination with $\text{Cp}_2\text{Fe}^+ - \text{H}$ conducts itself as a Lewis acid used for bonding the filled d -orbitals of iron. Besides, the protonation of ferrocene leading to form a structure with inclined Cp-ligands that facilitate the oxygen attack to iron atoms owing to the reduction of steric hindrances.

Discussion

The above scheme of oxidation of ferrocene with molecular oxygen [2, 4] rising certain doubts for the following reasons:

- Although oxygen can generate highly labile adducts with Cp_2Fe fixed at a temperature of liquid nitrogen [5] however, as noted in [6] the protonation of the metallocomplex makes it a weak base of coordination with another molecule of Lewis acid therefore, it does not form $\text{Cp}_2\text{FeH}_2^{2+}$ dication. The coordination of such weak Lewis acid as O_2 molecule with $\text{Cp}_2\text{Fe}^+ - \text{H}$ is still less probable.
- For the introduction of triplet oxygen via a Fe—H link, if it occurs through the molecular mechanism, a spin prohibition exists.
- If one believes that in Scheme 1 the stage of O_2 introduction through the Fe—H link is limited it can be easily shown that the process rate is described by the Eq. (3):

$$V = k_{\text{eff}}[\text{Cp}_2\text{Fe}][\text{O}_2][\text{H}^+] \quad (3)$$

The experimentally derived kinetic equation of the considered reaction is [7]:

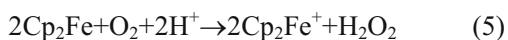
$$V_{\text{exp}} = k_{\text{eff}}[\text{Cp}_2\text{Fe}]^2[\text{O}_2][\text{H}^+]^2 \quad (4)$$

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and consequently, one may talk about its other mechanism.

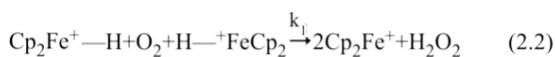
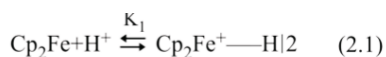
- The change of the standard Gibbs energy for reaction (2) calculated by the known relation $\Delta_r G^0 = -zFE^0$, where E^0 is the difference between the redox-potentials of an oxidant and an oxidisable substance, F is Faraday's number and z is the number of electrons; it is a significant positive value equal to 69.5 kJ mol^{-1} and the formal equilibrium constant corresponding to it, amounts to $6.3 \cdot 10^{-13}$ at 298 K that testifies to a small probability of the reaction to occur.

On the other hand, the $\Delta_r G^0$ value of gross-process (1) equal to $-247.0 \text{ kJ mol}^{-1}$ can not be regarded as a true thermodynamic criterium of the ferrocene oxidation in an acidic medium, since this magnitude characterizes the energetics of all stages of the process including those which proceed after its limiting stage and result in the fission of O_2 molecule and the formation of H_2O . Taking into consideration that the kinetic Eq. (4) and the fact that the maximum quantity of electrons which the oxygen molecule can accept as an oxidant without breaking an oxygen–oxygen bond accounts for two, it is necessary to evaluate the variation of the Gibbs energy for the oxidation reaction with the participation of two ferrocene molecules, i.e. for reaction (5):



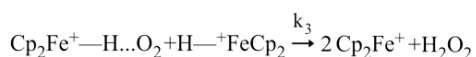
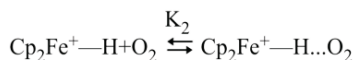
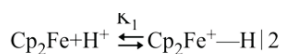
The authors [5] paid attention first just to this reaction, though the analysis of its mechanism was not made by them. The standard redox-potential of the oxidation system $O_2 + 2H^+$ is equal to 0.682 V and it follows that the change of the standard Gibbs energy for reaction (5) is $-17.8 \text{ kJ mol}^{-1}$. This value is smaller by 87.3 kJ mol^{-1} than, that needs for reaction (2). Accordingly, the probability of a proceeding reaction (5) is higher than for reaction (2).

While comparing the stoichiometry of reaction (5) with the results of kinetic studies of the oxidation process of ferrocene, it can be concluded that the mechanism, meeting kinetic Eq. (4) is possible exactly for reaction (5). Two probable mechanisms very close in



$$V_2 = k_2 [Cp_2Fe^+ - H]^2 [O_2]$$

Scheme 2



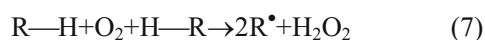
$$V_3 = k_3 [Cp_2Fe^+ - H \dots O_2] [H - ^+FeCp_2]$$

Scheme 3

reality were offered by us for the above reaction (Schemes 2 and 3):

Two facts form the basis of these schemes proposed: 1) the ability of ferrocene for a rapid equilibrium protonation with strong acids as demonstrated in numerous works [6, 8–11] and 2) a low energy of the Fe–H link ($209.2 \text{ kJ mol}^{-1}$) in the protonated ferrocene [10] that allows the consideration of it as an effective donor of atomic hydrogen onto an oxidant molecule.

Similar analogs of reaction (2.2) are widely known stages of the chain origination in the course of autooxidation of hydrocarbons in a liquid phase [11, 12]:



As calculations and studies [12] show, in the case of the oxidation of hydrocarbons having relatively weak C–H links, which energy does not exceed 330 kJ mol^{-1} of reaction (7) is significantly more preferable in comparison with reaction (6) from the standpoint of kinetics and thermodynamics. The energy of the Fe–H link in $Cp_2Fe^+ - H$ is much lower than this threshold value. Reaction (7) should not be necessarily trimolecular, it can proceed via the stage of an intermediate interaction of oxygen with one of RH molecules due to the formation of a hydrogen bond [11, 12]. This circumstance was reflected in Scheme 3 of the ferrocene oxidation. The ability of protonated ferrocene to form complexes with H-donors of electrons, to which O_2 molecule belongs also, means of hydrogen bonds as it is shown in [10].

According to Schemes 2 and 3, one may suggest the same structure of a transition state at the limited process state – $[Cp_2Fe^+ \dots H \dots O - O \dots H \dots ^+FeCp_2]^\ddagger$. Such structure is optimal in terms of steric hindrances for proceeding the reaction and the composition of its products and favors a coordinated fission of old links and the appearance of new links in the reagent molecules that has to lead to decrease in the activation energy of the limit stage.

The validity of the proposed mechanisms from the view of thermodynamic criteria is confirmed with the calculation results of $\Delta_r H^0(298.15)$ and $\Delta_r G^0(298.15)$ for reaction (2.2) in a gaseous phase (Table 1). For comparison the values of the same parameters of reaction (8):



are given in this table.

On calculating $\Delta_r S^0(298.15)$ of the reactions the absolute entropy of a ferrocenium ion was regarded to be equal to the absolute entropy of ferrocene ($365.3 \text{ kJ mol}^{-1}$ [13] because the transition

Table 1 Thermodynamic characteristics of oxidation reactions of ferrocene with various oxidants

Reaction	$-\Delta_r H^0(298.15)/\text{kJ mol}^{-1}$	$\Delta_r S^0(298.15)/\text{J K}^{-1} \text{mol}^{-1}$	$-\Delta_r G^0(298.15)/\text{kJ mol}^{-1}$
(2.2) $2\text{Cp}_2\text{Fe}^+ - \text{H} + \text{O}_2 \rightarrow \text{P}^*$	168.1	-29.5	159.3
(8) $\text{Cp}_2\text{Fe}^+ - \text{H} + \text{O}_2 \rightarrow \text{P}^*$	13.9	-4.2	12.6
(11) $\text{Cp}_2\text{Fe}^+ - \text{H} + \text{H}_2\text{O}_2 \rightarrow \text{P}^*$	82.4	112.3	115.9
(13) $\text{Cp}_2\text{Fe}^+ - \text{H} + \text{HO}^\bullet \rightarrow \text{P}^*$	297.2	-23.0	290.3

*P – reaction products

$\text{Cp}_2\text{Fe} \rightarrow \text{Cp}_2\text{Fe}^+$ is not accompanied with the change in the symmetry number of the metallocene complex and the number of chemical bonds in it.

The data in the table are evidence of the fact that reaction (2.2) is thermodynamically more appreciably favorable than reaction (8) that allows to describe the kinetics of ferrocene oxidation by Eq. (4).

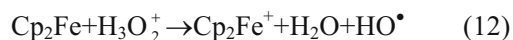
The kinetic analysis of Schemes 2 and 3 leads to expressions for the reaction rate V_2 and V_3 identical to those experimentally found:

$$V_2 = \frac{k_2 K_1^2 [\text{Cp}_2\text{Fe}]_0^2 [\text{O}_2] [\text{H}^+]_0^2}{(1 + K_1 [\text{H}^+]_0)^2} \quad (9)$$

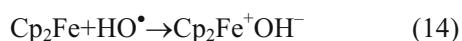
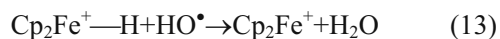
$$V_3 = \frac{k_3 K_1^2 K_2 [\text{Cp}_2\text{Fe}]_0^2 [\text{O}_2] [\text{H}^+]_0^2}{(1 + K_1 [\text{H}^+]_0)^2} \quad (10)$$

With $K_1 [\text{H}^+]_0 \ll 1$ Eqs (9) and (10) are transformed in Eq. (4).

According to Eq. (5), hydrogen hydroperoxide is suggested to be formed as one of the reaction products although, the former was not discovered in the reaction mixture [7]. The reason for its absence can be explained by that in the acidic medium it is a strong oxidant and easily oxidizes ferrocene till ferrocenium ion [5]. The oxidation can result from the following reactions:



A radical HO^\bullet is simultaneously a strong 1-electron oxidant ($\varphi^0 = 2.8$ V in the acidic medium) and an active radical capable of tearing off a hydrogen atom from a molecule of the protonated ferrocene. Thus, it can oxidise ferrocene in accordance with Eqs (13)–(15):



The calculated thermodynamic characteristics of reactions (11) and (15) in the table confirm the foregoing. A total combination of the reactions included in Schemes 2 and 3 and reactions (11–15) lead to the final stoichiometric equation of ferrocene oxidation (1).

Conclusions

- The kinetic and thermodynamic analysis of literature data for oxidation of the ferrocene by molecular oxygen in the presence of the strong Bronsted acids was carried out.
- The probable reaction mechanism, that includes the formation of the protonated ferrocene complex and its interaction as the donor of hydrogen atom with oxygen molecule was suggested.

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