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# Oxidation of Ferrocenylboric Acid with Hydrogen Peroxide in Organic and Aqueous Media

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**Abstract**—Oxidation of ferrocenylboric acid with hydrogen peroxide in organic solvents and in aqueous solutions in the presence and in the absence of acids and bases has been investigated by electron absorption spectroscopy. Kinetics of $FcB(OH)_2$ oxidation in neutral, acidic, and basic media has been studied; possible mechanisms of the reactions accounting for the substituent acting as the Lewis-type acidic center have been suggested.

**Keywords:** ferrocenylboric acid, peroxide, oxidation, acid, base, dioxane, hydroxyl-containing solvent, kinetics

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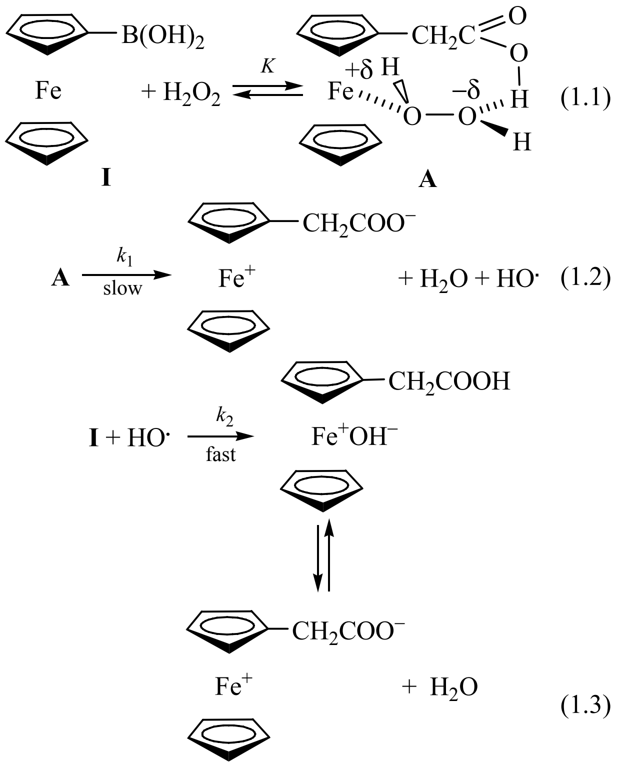
Under certain conditions, some ferrocene derivatives (aldehydes, ketones, and acids) are more reactive towards hydrogen peroxide as oxidizer as compared to parent ferrocene [1, 2], even though their substituents are strong electron acceptors {$\sigma_P$(CHO) 0.42 and $\sigma_P$($COCH_3$) 0.50 [3]} meaning that their standard redox potential should be higher than that of ferrocene. The mentioned derivatives are oxidized with hydrogen peroxide to give the corresponding substituted ferrocenium cations at room temperature in the absence of the Brønsted acids, whereas the presence of the Brønsted acids is essential for oxidation of ferrocene [4, 5]. The observed effect results from participation of the substituents (acting as the Brønsted or the Lewis acid) in the metal complex oxidation (Schemes 1 [1] and 2 [2]).

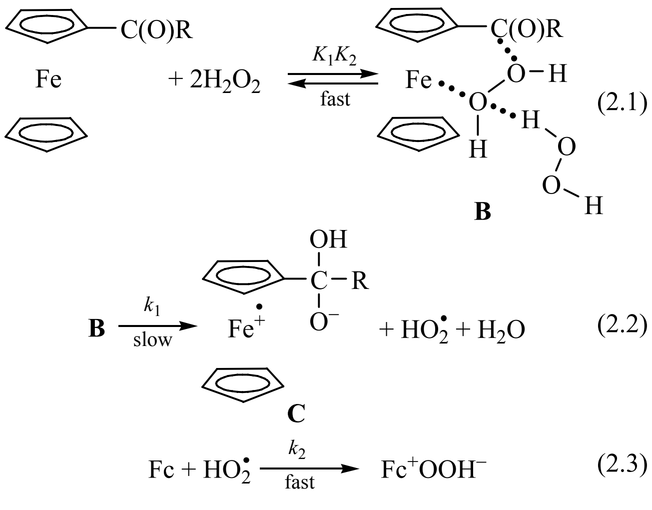
The bifunctional nature of the $C_5H_5FeC_5H_4CH_2\cdot COOH$, $C_5H_5FeC_5H_4C(O)CH_3$, and $C_5H_5FeC_5H_4C(O)H$ complexes in the reaction with $H_2O_2$ results in their higher reactivity as compared to that of ferrocene in the {$Cp_2Fe + PhCOOH + H_2O_2$} and {$Cp_2Fe + CH_3C(O)CH_3 + H_2O_2$} systems, where similar reaction centers (iron atom and carboxy or carbonyl groups) are contained in the different molecules. This obviously demonstrates the effect of approaching and orientation [6] on the reactivity of various ferrocene derivatives with respect to the same oxidizer.

In view of the above, we studied the reactions of $H_2O_2$ and other peroxides with ferrocenylboric acid $FcB(OH)_2$ (**I**), the substrate substituent acting as a typical Lewis acid due to the unoccupied *p*-orbital of boron atom, similarly to the cases of $BX_3$ compounds (X being halogen OH, alkyl, or phenyl). Similarly to

**Scheme 1.**



**Scheme 2.**



$BX_3$ [7], ferrocenylboric acid can form the $Fc\overline{B}(OH)_2R$ anions via addition of the $R^-$ anion ($Ph^-$ or $OH^-$) as well as the $Fc\overline{B}Ph_3$ anion [8]. Addition of hydroxide ion should significantly affect the reactivity of the anionic metal complex with respect to different oxidizers (including peroxides) as a function of the reaction medium acidity. The mentioned fact along with $FcB(OH)_2$ solubility in water and in organic solvents noticeably extends the area of study of the substrate oxidation with peroxides.

In contrast to ferrocene ($\sigma_P$ 0), ferrocenylboric acid **I** ($\sigma_P$ 0.12 [9]) was capable of oxidation with hydrogen peroxide in organic solvents (dioxane, acetonitrile, and dimethylsulfoxide) at room temperature in the absence of strong acid; as a result, the $Fc^+B(OH)_2$ cation was formed as confirmed by the appearance of the band at $\lambda_{max}$ 620 nm in the electron absorption spectrum of the reaction mixture (Fig. 1). The dilution of the organic solvents with water accelerated the $FcB(OH)_2$ oxidation, the reaction rate being the highest in aqueous medium.

A special feature of compound **I** oxidation with hydrogen peroxide in hydroxyl-containing (ethanol or water) and the mixed (dioxane–water or dioxane–ethanol) solvents is the presence of two long-wavelength maxima in the electron absorption spectra of the reaction mixture: at $\lambda_{max}$ of 620 and 840 nm (water as solvent) or at 620 and 860 nm (ethanol as solvent). The bands could be respectively assigned to the $Fc^+B(OH)_2$ cation (**D**) and likely to the $Fc^+\overline{B}(OH)_3$ cation (**E**). The assignment was confirmed by the fact that on the addition of $HClO_4$ to the reaction mixture containing both cations and the non-oxidized $FcB(OH)_2$ the first band grew stronger and the second one ($\lambda_{max}$ 840–860 nm) completely disappeared (Fig. 1, curve *5*). The addition of KOH to the same mixture led to disappearance of the band at $\lambda_{max}$ 620 nm, and the only

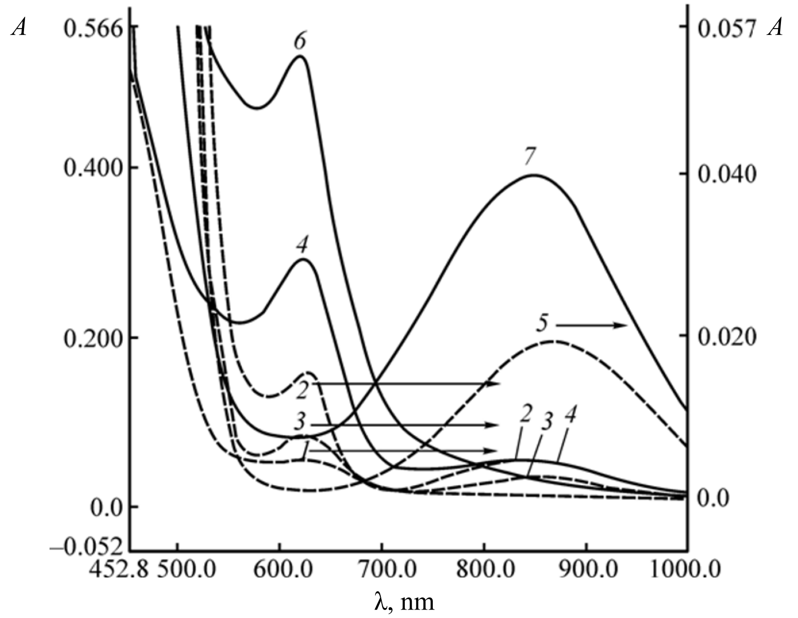
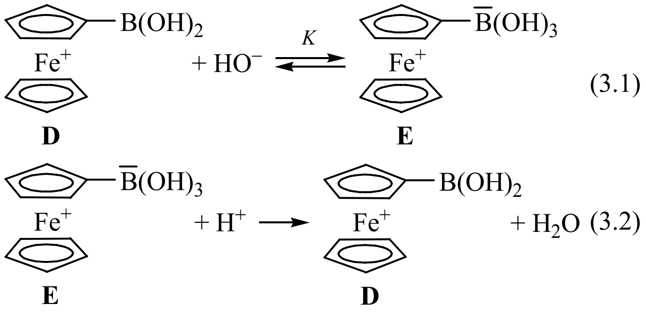


**Fig. 1.** Electron absorption spectra of products of ferrocenylboric acid **I** oxidation during 30 s with hydrogen peroxide in dioxane (*1*), ethanol (*3*, *7*), 1 : 1 dioxane–ethanol mixture (*5*), 1 : 1 ethanol–water mixture (*2*, *6*), and in water (*4*). (*1*–*5*) $c_I^0$ 0.003 mol/L, $c^0(H_2O)$ 0.15 mol/L; (*6*) $c_I^0$ 0.003 mol/L, $c^0(H_2O)$ 0.15 mol/L, $c^0(HClO_4)$ 0.1 mol/L; (*7*) $c_I^0$ 0.003 mol/L, $c^0(H_2O_2)$ 0.05 mol/L, $c^0_{KOH}$ 0.006 mol/L.

**Scheme 3.**



band observed in the spectrum was a very strong band at $\lambda_{\max}$ 840–860 nm (Fig. 1, curve *6*).

The described changes in the electron absorption spectra of the reaction mixture could be explained, firstly, by the ability of cations **D** and **E** to interact with $OH^-$ and $H^+$, respectively, to form cations **E** and **D** [Scheme 3, reactions (3.1) and (3.2)]; and, secondly, by the probability of oxidation of the unreacted $\mathrm{FcB(OH)_2}$ in the presence of acid or base to yield cations **D** and **E**, respectively, as confirmed by the direct experiments. Hence, in the alkaline medium the oxidation of $\mathrm{FcB(OH)_2}$ should proceed via the stage of the $\mathrm{Fc\bar{B}(OH)_3}$ anion formation.

If oxidation of $\mathrm{FcB(OH)_2}$ was performed in the presence of acid at the concentrations ratio of $c(H_2O_2)/c[\mathrm{FcB(OH)_2}] > 10–15$, the absorption band of ferrocenium cation ($\lambda_{\max}$ 620 nm) was shifted towards longer wavelength due to the hydroxylation of the metal complex under the reaction conditions [10]. The band shift ($\Delta\lambda_{\max}$) depended on the solvent nature decreasing in the dioxane > ethanol >> water series. The oxidation in alkaline medium (water or ethanol as solvent) was not accompanied with shifting of the band at $\lambda_{\max}$ 840–860 nm.

The cations **D** and **E** were formed also when benzoyl peroxide was used as oxidizer instead of hydrogen peroxide (Fig. 2). Moreover, the formation of the cation **E** was observed in the case of $\mathrm{FcB(OH)_2}$ oxidation with *tert*-butylhydroperoxide and oxygen in the alkaline medium (Fig. 2) due to formation of the $\mathrm{Fc\bar{B}(OH)_3}$ complex further interacting with $O_2$. Oxygen did not oxidize ferrocenylboric acid **I** in neutral or acidic medium. Noteworthily, $\mathrm{Fc\bar{B}(OH)_3}$ anion was close to the triphenylferrocenylborate $\mathrm{Fc\bar{B}Ph_3}$ with respect to the oxidation ability, the latter being oxidized with air oxygen in the aqueous-ethereal solution [8].

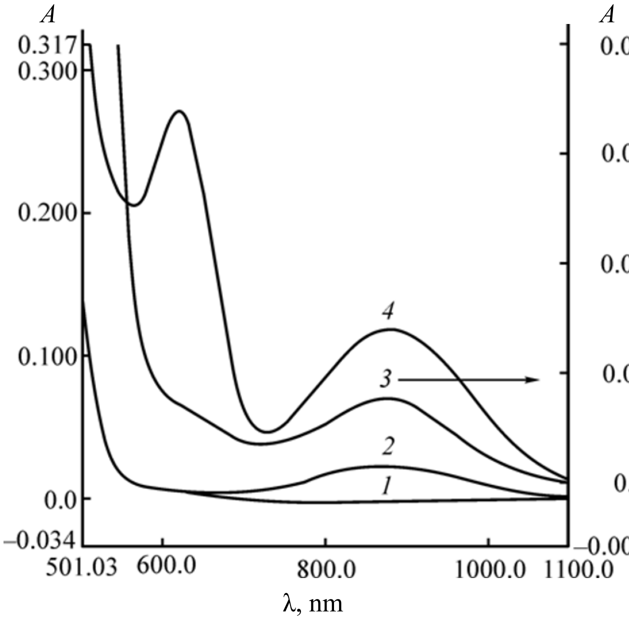


**Fig. 2.** Electron absorption spectra of (*1*) compound **I** and products of its oxidation with (*2*) oxygen, (*3*) *tert*-butylhydroperoxide, and (*4*) benzoyl peroxide in 2 : 1 dioxane–water mixture in the presence of KOH at 20°C. $c_{\mathrm{I}}^0$ 0.003 mol/L, $c^0_{t\text{-BuOOH}}$ 0.1 mol/L, $c^0_{\mathrm{BzOOH}}$ 0.01 mol/L, $c^0_{\mathrm{KOH}}$ (*2*) 0.01 mol/L, $c^0_{\mathrm{KOH}}$ (*3*, *4*) 0.006 mol/L; oxidation duration (*2*) 5 min and (*3*, *4*) 48 s.

The significant shift of absorption band of cation **E** with respect to that of cation **D** was due to the fact that the negatively charged substituent $\{-\bar{B}(OH)_3\}$ was an extremely strong electron donor. Similar red shift of the absorption band was earlier observed as a result of ferrocenium cation substitution with electron-donating groups [11], clearly seen from comparison of $\lambda_{\max}$ of the absorption bands of $\mathrm{Cp_2Fe^+}$ and $\mathrm{[C_5(CH_3)_5]_2Fe^+}$ (618 and 780 nm, respectively) [12].

The high intensity of the absorption band of the cation **E** ($\lambda_{\max}$ 840–860 nm) was also a noticeable feature; such strong absorption is typical of decamethylferrocenium cation [12] due to the single-electron transition assigned to the charge transfer **L** → **M** ($e_{1u}^4 a_{1g}^2 e_{2g}^3 > e_{1u}^3 e_{1g}^2 e_{2g}^4$) [13]. The presence of strong electron donor in the Cp-ligand should have enhanced the probability of the transition.

The above-discussed reversible transformation of the cations **D** and **E** due to the change in the solution acidity was also observed in the neutral media, for instance, in ethanol, as well as in the mixed solvents (dioxane–water) due to the change of the co-solvents ratio. That evidently follows from the experimental

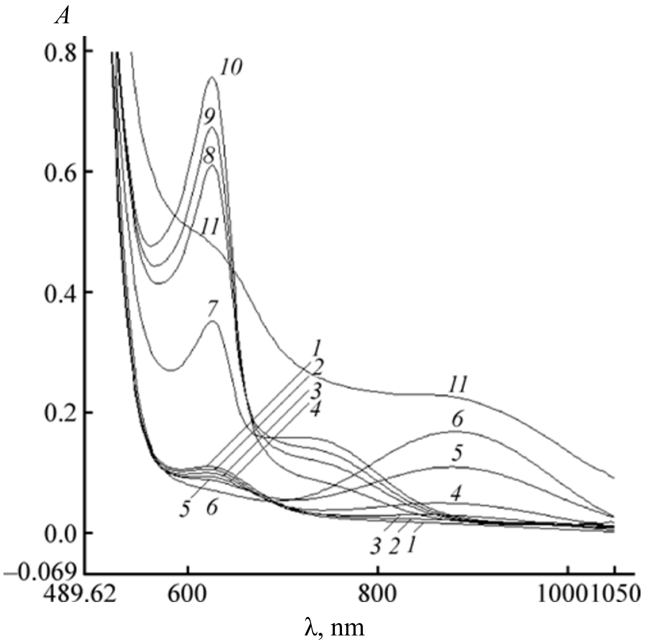
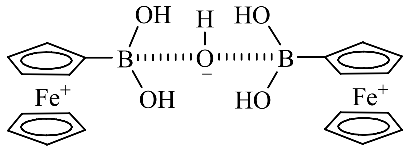


**Fig. 3.** Electron absorption spectra of products of oxidation of compound **I** with hydrogen peroxide (*1–6*) in ethanol and (*7–10*) after introduction of $HClO_4$ or (*11*) KOH to the reaction mixture. $c_{\mathrm{I}}^0$ 0.03 mol/L, $c^0(H_2O_2)$ 0.003 mol/L, $c^0(HClO_4)$ 0.05 mol/L, $c^0_{\mathrm{KOH}}$ 0.06 mol/L; reaction duration (*1*) 17 s, (*2*, *8*) 1.5 min, (*3*, *11*) 5 min, (*4*) 10 min, (*5*) 27 min, (*6*) 57 min, (*7*) 0.5 min, (*9*) 3.5 min, and (*10*) 9.5 min; temperature 20°C.

results (Fig. 3) of the oxidation of $FcB(OH)_2$ in ethanol, the substrate being taken in significant excess with respect to hydrogen peroxide. In particular, the band at $\lambda_{max}$ 620 nm initially appeared in the absorption spectrum of the reaction mixture; in the course of the reaction the band weakened, and simultaneously a band at $\lambda_{max}$ 840 nm appeared and grew stronger. The effect was not observed in the case of excess of the oxidizer (hydrogen peroxide) with respect to compound **I**.

The curves plotted in Fig. 3 evidenced a complete transformation of cation **D** into cation **E** in the course of oxidation of compound **I** in the absence of acid (Fig. 3, curve *6*). If perchloric acid was added to the reaction mixture, the band at $\lambda_{max}$ 860 nm disappeared whereas the stronger band at $\lambda_{max}$ 620 nm re-appeared, the process occurring via the formation of an intermediate ($\lambda_{max}$ 732 nm). The intermediate might be an adduct of cations **D** and **E**. The formation of that adduct (**F**) might occur via coordination of one of OH groups of cation **E** with boron atom of cation **D** when the cations concentrations were comparable (Scheme 4).

**Scheme 4.**



**F**

In the adduct **F** the negative charge is uniformly distributed between the components resulting in the absorption band position in between these for the cations **D** and **E**. Upon addition of acid, the absorption band of cation $Fc^+\overline{B}(OH)_3$ (**E**) disappears immediately, whereas that of adduct **F** vanishes within about 10 min, likely due to the steric factors and the difference in the energy parameters of the interaction of cation **E** and adduct **F** with protons.

Upon addition of KOH (to pH > 7) to the reaction mixture containing cation $Fc^+B(OH)_2$ (**D**) in acidic medium, the band at $\lambda_{max}$ 620 nm disappeared and the band at $\lambda_{max}$ 840 nm appeared, assigned to cation $Fc^+\overline{B}(OH)_3$ (**E**) (Fig. 3, curve *11*).

In order to elucidate the environment effect on the mechanism of ferrocenylboric acid $FcB(OH)_2$ interaction with hydrogen peroxide, we studied its kinetics in acidic, neutral, and alkaline media. The oxidation of compound **I** with hydrogen peroxide in neutral aqueous medium (monitored by accumulation of cation **D** under conditions when accumulation of cation **E** could be neglected) was in line with the first-order kinetic law with respect to both reactants [Eq. (1)].

$$w_{\mathrm{exp}} = k_{\mathrm{eff}}[FcB(OH)_2]^0[H_2O_2]^0. \qquad (1)$$

This followed from the linear increase of the initial reaction rate with growing concentrations of the metal complex **I** and of hydrogen peroxide (Fig. 4, curves *1*, *2*).

The data may be understood through the following presumable mechanism of the studied reaction (Scheme 5).

Scheme 5 accounts for the ability of the $HO^{\bullet}$ radical to act as efficient single-electron oxidizer in neutral and alkaline ($\varphi^0$ 2.0 V) as well as in acidic ($\varphi^0$ 2.8 V) environment [14].

According to the presented scheme, the high reactivity of ferrocenylboric acid as compared to that of ferrocene was due to the participation of the $B(OH)_2$ substituent in the oxidation of compound **I** as the Lewis acid. The substituent favors coordination of hydrogen peroxide with compound **I** and subsequent

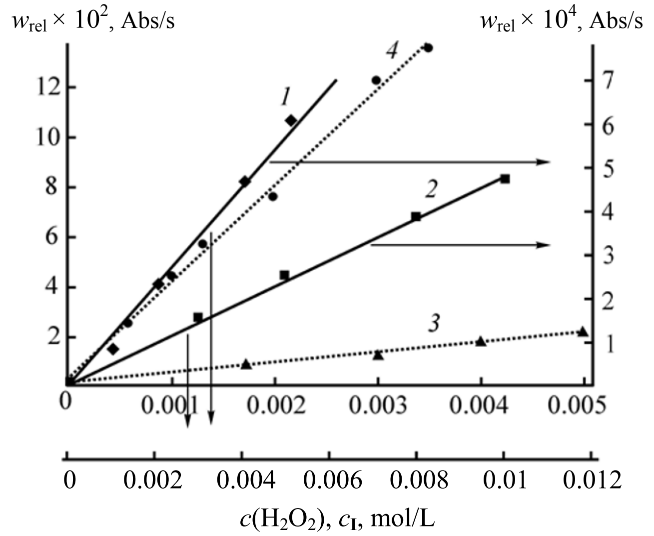
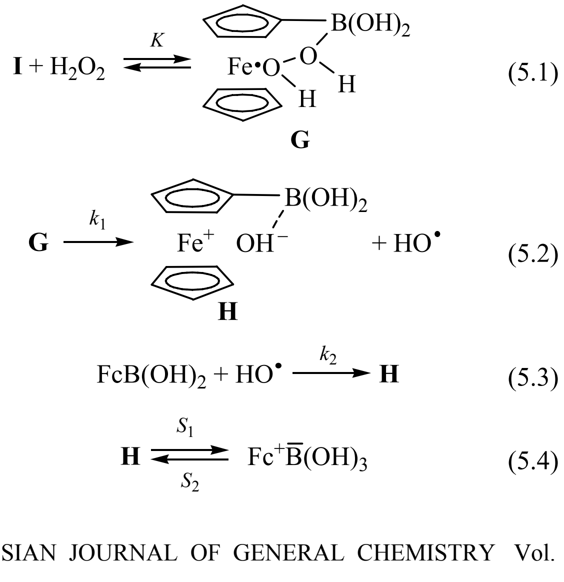


**Fig. 4.** Effect of initial concentrations of (*1*) compound **I** and (*2*) $H_2O_2$ on the rate of metal complex **I** in water; and effect of initial concentrations of (*3*) $HClO_4$ and (*4*) KOH on the rate of oxidation of compound **I** at 20°C. (*1*) $c^0(H_2O_2)$ 0.1 mol/L; (*2*) $c_I^0$ 0.01 mol/L; (*3*) $c_I^0$ 0.006 mol/L, $c^0(H_2O_2)$ 0.1 mol/L; (*4*) $c_I^0$ 0.01 mol/L, $c^0(H_2O_2)$ 0.1 mol/L.

electron transfer from iron atom to hydrogen peroxide as well as stabilization of the formed $OH^-$ anion.

Equilibrium (5.4) states that depending on the solvent nature cation **D** (dioxane, acetonitrile, and dimethylsulfoxide), cation **E** (dioxane–water 1 : 1), or the both cations (water, ethanol, acetonitrile–water 1 : 1, dioxane–water 2 : 1, etc.) may be the reaction products. This is due to the following reasons: (a) non-specific solvation of the reaction products changing the energy of binding of $OH^-$ with the cations resulting from difference in the solvent dielectric constant ε and (b) the difference in specific solvation affecting stabilization of the cation and the anions $OH^-$ and $-\bar{B}(OH)_3$. In the case of dioxane (ε 2.4), the free energy of binding of cation **D** and $OH^-$ in the contact ion pair $\Delta G_{el}$ is up to 100 kJ/mol [15] favoring stabilization of both ions. Evidently, the covalent part of the $Fe^+–OH^-$ bond should be taken into account as well. Moreover, $OH^-$ anion is stabilized due to the interaction with the substituent in the intermediate **H**. Its stabilization via solvation with dioxane could be neglected because of the very low acidity of $OH^-$ [16]. Hence, the addition of $OH^-$ to the substituent to firm $Fc^+\bar{B}(OH)_3$ cation is in general unfavorable by energy, even accounting for the energy of binding of $OH^-$ with $B(OH)_2$ in the $-\bar{B}(OH)_3$ anion. Therefore, in dioxane the cation $Fc^+B(OH)_2$ (**D**) is formed exclusively. In the cases of hydroxyl-containing solvents (ε > 24), the energy of electrostatic interaction between $OH^-$ and ferrocenium cation is significantly lower than that in the case of dioxane, ~15 kJ/mol, and $OH^-$ can be added to the substituent, especially since the $-\bar{B}(OH)_3$ can be specifically solvated by hydroxyl-containing solvents, though less efficiently than the $OH^-$ anion. This favors the establishment of a dynamic equilibrium of cations **D** and **E** observed in the experiment. The difference in $-\bar{B}(OH)_3$ solvation with water and with ethanol is confirmed by the different positions of the absorption band of cation $Fc^+\bar{B}(OH)_3$ (840 nm in water and 860 nm in ethanol). Possibility of the exclusive formation of cation **E** in the mixed solvent (1 : 1 dioxane–water) can be regarded as an anomaly of the system physical properties due to the specific cooperative action of the solvent components with ionic intermediates of the reaction. Such anomaly can hardly be predicted; however, the mixed media can pliably stabilize both hydrophilic and hydrophobic solutes [16]. Cations **D** and **E** are unstable and are quite rapidly transformed into products of oxidative degradation, as indicated by thedisappearance of the cations absorption bands in the course of the reaction.

**Scheme 5.**



The kinetic analysis of Scheme 5 based on the quasi-equilibrium approximation for concentration of the complex **G** and quasi-stationary approximation for concentration of $HO^\bullet$ radical leads to Eq. (2) for the reaction rate; it is identical to Eq. (1) at $t \rightarrow 0$ ($k_{eff} = 2k_1K$).

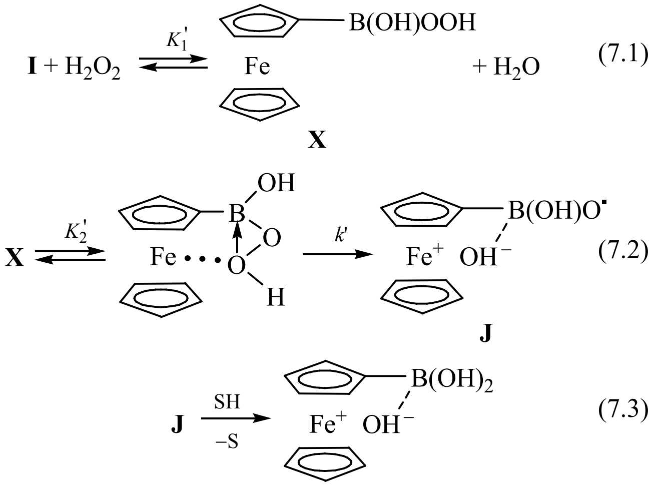
$$w = 2k_1K[FcB(OH)_2][H_2O_2]. \qquad (2)$$

The presented scheme does not account for the possibility of direct reaction of the substituent with

**Scheme 6.**

$$PhB(OH)_2 + H_2O_2 \rightarrow PhB(OH)OOH + H_2O$$

**Scheme 7.**



$H_2O_2$. However, phenylboric acid, analog of compound **I**, is known to react with hydrogen peroxide according to Scheme 6 [17].

If a similar reaction was possible in the case of $FcB(OH)_2$, an alternative mechanism of oxidation of complex **I** into ferrocenium cation could be suggested (Scheme 7), the corresponding kinetic equation being the same as in the case of the mechanism shown in Scheme 5.

The investigation of kinetic features of $FcB(OH)_2$ oxidation in acidic and alkaline media revealed the same reaction rate orders with respect to compound **I** and to $H_2O_2$, namely, equal to unity. The reaction rate orders with respect to initial concentrations of $HClO_4$ and KOH were equal to unity as well (Fig. 4, curves *3*, *4*).

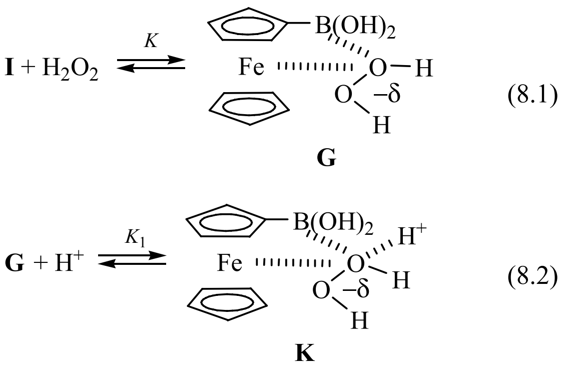
From Fig. 4 it is seen that the plots of the reaction rate as functions of the acid and the alkali concentration showed a nonzero *Y*-intercept corresponding to the rate of compound **I** oxidation in the absence of any additive; that was noticeable if both *Y* axis were plotted in the same scale. That allowed writing the equation for the reaction rate at constant concentrations of the metal complex and of hydrogen peroxide as follows [Eqs. (3) and (4)].

$$w_{HX} = w'^0 + k'_{eff}[H^+], \quad (3)$$

$$w_{KOH} = w''^0 + k''_{eff}[OH^-], \quad (4)$$

where $w'^0$ being the initial rate of cation **D** accumulation in the absence of acid, and $w''^0$ being the initial rate of cation **E** accumulation in the absence of alkali.

**Scheme 8.**



$$\mathbf{G} \xrightarrow{k_1} \mathbf{H} + OH^{\bullet} \quad (8.3)$$

$$\mathbf{K} \xrightarrow{k'_1} Fc^+B(OH)_2 + HO^{\bullet} + H_2O \quad (8.4)$$

$$FcB(OH)_2 + HO^{\bullet} \xrightarrow{k_2} \mathbf{H} \quad (8.5)$$

$$OH^- + H^+ \rightarrow H_2O \quad (8.6)$$

Assuming that the presence of acid did not influence coordination of compound **I** with $H_2O_2$, the mechanism of its action in the oxidation process could be represented by Scheme 8.

According to the scheme, the rate of ferrocenium ions accumulation should follow Eq. (5) that could be rewritten in the form of Eq. (6).

$$w_{HX} = d[Fc^+B(OH)_2]/dt$$
$$= k_1[\mathbf{G}] + k'_1[K] + k_2[FcB(OH)_2][OH^{\bullet}], \quad (5)$$

$$w_{HX} = 2k_1K[FcB(OH)_2][H_2O_2]$$
$$+ 2k'_1KK_1[FcB(OH)_2][H_2O_2][HX]. \quad (6)$$

At constant concentrations of compound **I** and $H_2O_2$ that linear equation was identical to Eq. (3).

$$w_{HX} = w'^0 + b[HX]. \quad (6')$$

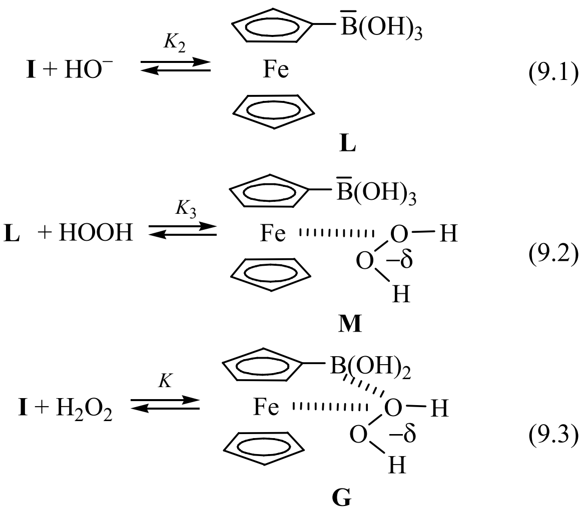
where $b = 2k'_1KK_1[FcB(OH)_2][H_2O_2]$.

The participation of OH– in the oxidation process could be represented by Scheme 9.

From Scheme 9 it is seen that hydroxide ions are regenerated in the course of the reaction and should therefore be regarded as a special catalyst of the process.

Comparison of Schemes 8 and 9 allowed explanation of the reversible transformation of cations **D** and **E** in the course of oxidation of compound **I** in ethanol

**Scheme 9.**



$$\mathbf{M} \rightarrow \mathrm{Fc^{+}\bar{B}(OH)_3 + OH^{-} + HO^{\bullet}} \qquad (9.4)$$

$$\mathbf{G} \xrightarrow{k_3} \mathrm{Fc^{+}\bar{B}(OH)_3 + HO^{\bullet}} \qquad (9.5)$$

$$\mathrm{FcB(OH)_2 + HO^{\bullet} \rightarrow Fc^{+}\bar{B}(OH)_3} \qquad (9.6)$$

**Scheme 10.**

$$\mathrm{Fc^{+}B(OH)_2 + Fc\bar{B}(OH)_3 \rightarrow Fc^{+}\bar{B}(OH)_3 + FcB(OH)_2}$$

when the substrate concentration was significantly higher than that of hydrogen peroxide (Fig. 3) and the absence of such transformation when the oxidizer was taken in excess. In particular, Scheme 8 shows that oxidation of $\mathrm{FcB(OH)_2}$ in neutral medium yields $\mathrm{OH^-}$ as counter-ion of ferrocenium cation **D**. In the excess of non-oxidized metal complex **I** the latter can bind $\mathrm{OH^-}$ to form $\mathrm{Fc\bar{B}(OH)_3}$ that is further oxidized with cation **D** into cation **E** according to Scheme 10.

Possibility of such reaction was confirmed using the example of the reaction between ferrocenium cation with decamethylferrocene resulting in neutral ferrocene and decamethylferrocenium cation.[1]

Increase of hydrogen peroxide concentration up to the significant excess with respect to the $\mathrm{FcB(OH)_2}$ substrate in alkaline medium led to destabilization of cation **E**, reflected in the maximum at the $W = f[c(\mathrm{H_2O_2})]$ plot (Fig. 5).

The possible reaction between the $\mathrm{Fc\bar{B}(OH)_3}$ complex or its cation with $\mathrm{H_2O_2}$ results likely in formation of labile peroxide intermediates further transformed with the destruction of the sandwich structure of the complex.

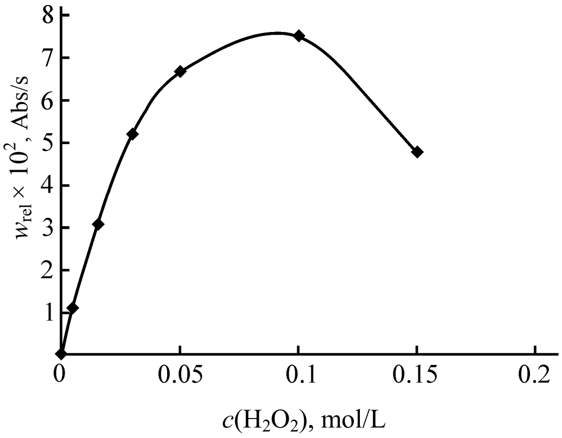


**Fig. 5.** Effect of $\mathrm{H_2O_2}$ concentration on the rate of accumulation of cation **E** during oxidation of compound **I** with hydrogen peroxide in water in the presence of KOH at 20°C. $c_{\mathrm{I}}^{0}$ 0.003 mol/L, $c_{\mathrm{KOH}}^{0}$ 0.003 mol/L.

Hence, the acceleration of compound **I** oxidation in acidic medium was due to the higher standard redox potential of the ($\mathrm{H_2O_2 + H^+}$) system (0.72 V [14]) as compared with that of $\mathrm{H_2O_2}$. The accelerating effect of alkali was due to formation of $\mathrm{Fc\bar{B}(OH)_3}$ (**L**) according to reaction (9.1), the formed species being highly reactive towards various oxidizers due to the pronounced ability of the $\mathrm{-\bar{B}(OH)_3}$ substituent to donate electrons to the Cp-ligand and the resulting significant decrease of the standard redox potential of the metal complex **L**.

The higher rate of $\mathrm{FcB(OH)_2}$ oxidation in water as compared to that in aprotic solvents could be attributed to (a) high dielectric constant of water favoring reactions accompanied with electron transfer and (b) direct participation of water in oxidation of compound **I** according to Scheme 11 resulting in acidification of the reaction mixture and the formation of reactive intermediate **L**. Scheme 11 is analogous to reaction of water with boric acid [reaction (12)] responsible for acid properties of the latter [7].

**Scheme 11.**

$$\mathrm{FcB(OH)_2 + HOH} \overset{K_{11}}{\rightleftharpoons} \mathrm{Fc\bar{B}(OH)_3 + H^{+}}.$$

**Scheme 12.**

$$\mathrm{B(OH)_3 + HOH} \overset{K_{12}}{\rightleftharpoons} \mathrm{B(OH)_4^{-} + H^{+}},\ \mathrm{p}K_{\mathrm{a}\,12}\ 9.$$

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[1] Unpublished data.

**Scheme 13.**

$$\mathrm{HOH} \xrightleftharpoons{K_{13}} \mathrm{H^+ + OH^-},\ \mathrm{p}K_{\mathrm{a}\,13}\ 15.7.$$

**Scheme 14.**

$$\mathrm{B(OH)_3 + OH^-} \xrightleftharpoons{K_{14}} \mathrm{B(OH)_4^-},\ \Delta_\mathrm{r}G^\mathrm{o}_{14}$$

Scheme 12 allowed estimation of the energy of interaction between $FcB(OH)_2$ and $OH^-$ suggesting that it was not much lower than that at the addition of the anion to $B(OH)_3$. To do so, let us combine Schemes 12 and 13.

Subtraction of Scheme 13 from Scheme 12 leads to Scheme 14 for the overall process.

$$\Delta_\mathrm{r}G^0_{14} = \Delta_\mathrm{r}G^0_{12} - \Delta_\mathrm{r}G^0_{13} = 2.3RT\,(\mathrm{p}K_{\mathrm{a}\,12} - \mathrm{p}K_{\mathrm{a}\,13})$$
$$= -38.16\ \mathrm{kJ/mol}\ (T\ 298\ \mathrm{K}).$$

The free energy of $OH^-$ addition to $FcB(OH)_2$ should be lower than $\Delta_\mathrm{r}G^0_{14}$ in the absolute value since the complex is a weaker Lewis acid than boric acid (indeed, the ferrocenyl group is an electron donor, whereas hydroxy group acts as electron acceptor). The result is in agreement with the above-discussed effect of the solvent nature on equilibrium (3.4) at the $FcB(OH)_2$ oxidation (Scheme 3).

To conclude, the example of $FcB(OH)_2$ revealed a unique feature of oxidation of a metal complex with peroxides by both acid and alkali. Both cases were operative to some extent during oxidation of $FcB(OH)_2$ with participation of water.

## EXPERIMENTAL

Commercially available hydrogen peroxide, *tert*-butylhydroperoxide (>99%), and benzoyl peroxide (>99%) (all of “analytically pure” grade) were purified via standard procedures.

Electron absorption spectra were recorded using a SHIMADZU UV-1800 spectrophotometer. The solutions were prepared and studied under argon atmosphere. The reaction course was monitored following the appearance of absorption bands at 620 and 840–860 nm.

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