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LETTERS TO THE EDITOR

Features of Reaction of *p*-Benzosemiquinone Radicals with Iron Salts

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We have earlier examined some intracellular mechanisms of photoreactions of semiquinone radicals with various reagents by means of chemical nuclear polarization [1–3].

In the present work we studied the reactions of *para*-benzosemiquinone radicals with $Fe_2(SO_4)_3$ and Mohr's salts at the flash-photolysis. These reactions were carried out in the aqueous-alcoholic solutions (the water–propanol ratio 9:1 by volume) with neutral and acidic (pH = 4.6) media. To avoid the influence of the changing ionic strength we used solutions containing sodium sulfate (0.1 M). To prevent the occurrence of additional dark reactions of oxidation and reduction at the use of $Fe_2(SO_4)_3$ we used *p*-benzoquinone as a source of the semiquinone radicals, and with Mohr's salt, hydroquinone. The pulse photoexcitation of hydroquinone or *p*-benzoquinone using a UFS-2 (280–350 nm) filter in the presence of the hydrogen donor (alcohol) leads to the formation of *p*-semiquinone radicals. At pH = 4.6 the semiquinone anion-radical $Q^{\dot{-}}$ forms. These radicals are terminated not only as a result of the disproportionation, but they react with the bivalent iron to give hydroquinone and trivalent iron:

$$QH^{\cdot} + QH^{\cdot} \rightarrow Q + QH_2, \tag{1}$$

$$Q^{\dot{-}} + Fe^{2+} \xrightarrow{+2H^+} QH_2 + Fe^{3+}. \tag{2}$$

At high concentrations of Mohr's salt the kinetics of $Q^{\dot{-}}$ disappearance adheres to the first order equation. The value $K_2 = 4.3\times10^5\ m^{-1}\ s^{-1}$ was calculated from the linear dependence between the effective constant and Mohr's salt concentration. The semiquinone radicals $QH^{\cdot}$ are generated in the neutral medium. They disproportionate by themselves and also react with the bi- and trivalent iron:

$$QH^{\cdot} + Fe^{2+} \xrightarrow{+H^+} QH_2 + Fe^{3+}, \tag{3}$$

$$QH^{\cdot} + Fe^{3+} \xrightarrow{+2H^+} Q + Fe^{2+}. \tag{4}$$

The reactions (3) and (4) are the pseudofirst order reactions at the salt concentrations 10^{-4} M and above with the constants $K_3 = 10^5\ m^{-1}\ s^{-1}$ and $K_4 = 7\times10^5\ m^{-1}\ s^{-1}$.

The oxidation-reduction reactions between the iron salts and radicals $QH^{\cdot}$ proceed through complexes formation. The latter are destroyed by the reaction with the hydrogen ions.

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