LETTERS TO THE EDITOR

Complexing of Benzo-semiquinone Radicals with Bivalent Copper Ions

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Electron-excited states of phenoxyl radicals, their properties and reactions with metal ions are well studied [1–4].

We examined complexing of benzo-semiquinone radicals with ions of bivalent copper. Radicals were generated from pyrochatechol **I** BH₂ at flash-photolysis in the presence of copper dichloride **II**. Under the experiment condition (pH = 2) the absorption spectrum without flash represented the sum of the starting materials spectra. However, at pulse photoexcitation of solution **I** BH₂ (10^{−3} M) in the presence of CuCl₂ (2 × 10^{−2} M) we observed the disappearance of absorption bands characteristic for BH[•] and the simultaneous appearance of the spectrum of intermediate product with the substantially long lifetime. This change is caused by the formation of complexes BH[•] and Cu²⁺ according to the reaction:

For the formed complexes $\cdot Z^{2+}$ we obtained extinction coefficients from the relationships:

$$\epsilon_{380}^{\cdot Z^{2+}} = \epsilon_{380}^{BH\cdot} (\Delta D_{380}^{\cdot Z^{2+}} / \Delta D_{380}^{BH\cdot}) = 4.1 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}.$$

At the lower concentrations of **II** (10^{−3} M) the quenching of intermediate compounds proceeds by two directions:

The linear dependence between $\cdot Z^{2+}$ and Cu²⁺ at determining the process equilibrium constant shows that the components ratio in the complex is equimolar. The value of the complex decomposition constant is equal to 10⁴ s^{−1}. Complexes of ion Cu²⁺ possess the highest stability in comparison with similar complexes of bivalent transition metals [2].

Hence, in this case intrasphere complex of Cu²⁺ with neutral short-lived radical BH was synthesized.

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