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Electron Transfer from Semiquinone Radicals to Copper and Iron Ions

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Abstract—Kinetic and thermodynamic parameters of redox reactions and electron transfer between *o*-benzosemiquinone radicals and iron ions have been determined. The rate constant of the anion-radicals oxidation with Cu^{2+} ions has been calculated.

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Various semiquinone radicals are known to be formed in the biological processes involving electron transport in plant and animal tissues, and also in microorganisms. These biological systems also contain metal ions, thus the interaction of semiquinone radicals with metal ions is of practical importance.

Radical $BH^{\cdot}$ and anion-radical $B^{\dot{-}}$ of *o*-benzosemiquinone provide much opportunities in the formation of complexes with copper ions. They may act as bidentate ligands and thus form chelate complexes. To the best of our knowledge, the information of the spectral and kinetic characteristics of o-semiquinone radicals and their complexes has been absent in the literature. To fill in this gap, in this work we studied the interaction of $BH^{\cdot}$ radical with Cu^{2+}.

The pulsed photoexcitation of catechol BH_2 (1×10^{-3} mol L^{-1}, pH 2) through the UFS-2 filter (λ = 250–380 nm) led to the appearance of absorption bands due to the intermediates formation (Fig. 1).

A very broad band (λ_{max} = 360 nm) was assigned to *o*-hydroxyphenoxide radical.

$$BH_2 + h\nu \rightarrow BH^{\cdot} + H^+ + \bar{e}. \qquad (1)$$

The termination of radicals $BH^{\cdot}$ followed the second order kinetics.

$$BH^{\cdot} + BH^{\cdot} \rightarrow BH_2 + B. \qquad (2)$$

The presence of oxygen in the solution did not influence $BH^{\cdot}$ termination kinetics, however, the radical yield increased 1.5–2 times in the oxygen-free solution. This could possibly point to the participation of the triplet molecule $BH^{\cdot}_{2T}$ in reaction (1) in the absence of oxygen. The $BH^{\cdot}$ yield and the termination kinetics virtually did not changed with pH in the range of 1–7, thus, $pK_{BH^{\cdot}} > 7$. Furthermore, the ionic strength effect on the kinetics of Eq. (2) was studied at pH = 2 and pH = 7. In both cases, k_2 decreased with increasing ionic strength.

The $BH^{\cdot}$ radical yield sharply decreased with addition to the solution of $K_3Co(CN)_6$. The catechol fluorescence ($\lambda_{max} \approx$ 350 nm) was quenched by that salt; thus, the cobalt complex oxidized the singlet excited state of $BH^{\cdot}_{2S}$.

The molar absorptivity of $BH^{\cdot}$ (ε_{380} = 490 mol^{-1} L cm^{-1}) was determined as described in [1]. Thus, at the zero ionic strength, $k_2 = 3.9\times 10^8$ mol^{-1} L s^{-1}.

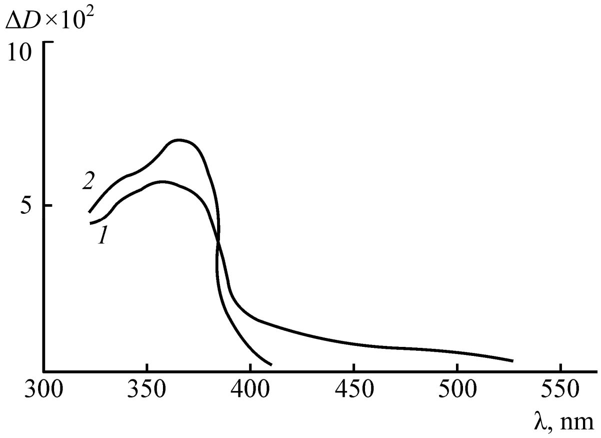


Fig. 1. Absorption spectra of intermediates at time 3×10^{-5} s in the course of pulsed photoexcitation of 10^{-3} mol L^{-1} solutions of catechol (*1*) without $CuCl_2$ and (*2*) with 2×10^{-2} mol L^{-1} of $CuCl_2$ at pH = 2.

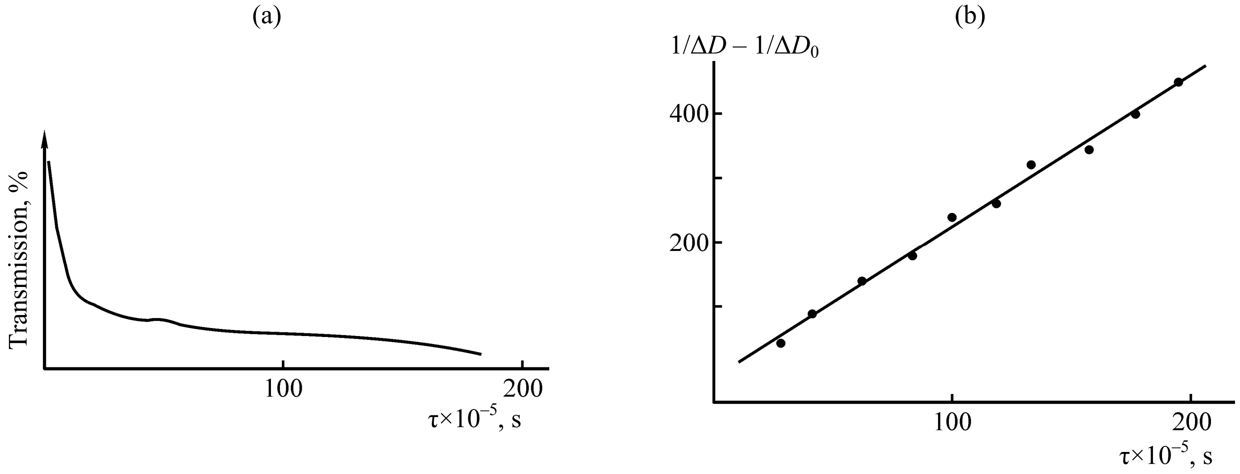
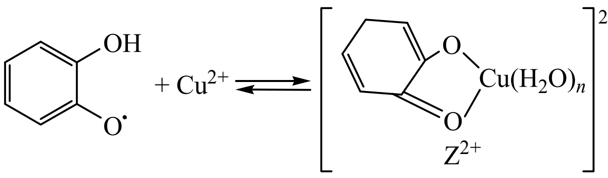


Fig. 2. Oscillogram of the spectral changes at $\lambda = 380$ nm due to termination of complexes of $BH^{\cdot}$ radical and ${}^{\cdot}Z^{2+}$ (a) and the corresponding linear plot in coordinates $1/\Delta D - 1/\Delta D_0$ vs t (b). Conditions: pulsed photoexcitation of the solution containing BH_2 (10^{-3} mol L^{-1}) and $CuCl_2$ (1.4×10^{-2} mol L^{-1}) at 20°C.

The spectral and kinetic characteristics of *p*-semiquinone radicals have been described in detail in the available literature, but the data on *o*-semiquinone radicals, in particular, on $BH^{\cdot}$ and $B^{\dot{-}}$, is not available. The rate constant of $BH^{\cdot}$ disproportionation was about 15 times lower than the diffusional constant calculated according to the Debye equation; the termination constant of the radicals were lower than those theoretically predicted. Thus, the mutual orientation of the radicals in the solvent cage and the spin effects should be accounted for.

Under certain conditions, catechol is known to form complexes of varied composition with many metal ions, including copper ions. At pH 2, the absorption spectrum of the solution containing BH_2 and $CuCl_2$ was a sum of the spectra of individual components and did not change with time. In the course of pulsed photoexcitation of BH_2 solution (1×10^{-3} mol L^{-1}) in the presence of $CuCl_2$ (2×10^{-2} mol L^{-1}), the band assigned to $BH^{\cdot}$ disappeared; simultaneously, the bands of more stable intermediate appeared (Fig. 1, curve *2*). These changes were due to the complex formation between $BH^{\cdot}$ and Cu^{2+}.



(3)

Thus, in the presence of 2×10^{-2} mol L^{-1} of $CuCl_2$ in the solution during a single pulse all the radicals were transformed into the complexes ${}^{\cdot}Z^{2+}$ ($[BH^{\cdot}]_0 = [{}^{\cdot}Z^{2+}]_0$).

The molar absorptivity of ${}^{\cdot}Z^{2+}$ could be derived from the relation (4).

$$\varepsilon_{380} = \varepsilon_{380}\frac{\Delta D_{380}}{\Delta D_{380}} = 4.1\times10^{2}\ \text{mol}^{-1}\ \text{L cm}^{-1}. \tag{4}$$

At lower concentration of $CuCl_2$ (10^{-3} mol L^{-1}) the kinetics of the intermediate termination could be observed (Fig. 2). Two stages of the process were recognized: fast $BH^{\cdot}$ termination following Eq. (5) and slow complex termination according to Eq. (6).

$$BH^{\cdot} + Cu^{2+} \rightarrow {}^{\cdot}Z^{2+}, \tag{5}$$

$$Z^{2+} + {}^{\cdot}Z^{2+} \rightarrow \text{Products}. \tag{6}$$

The value of k_5 was 5×10^{6} mol^{-1} L s^{-1}, k_6 was strongly dependent on the solution ionic strength due to the added salt (Fig. 3); k_6 was 1.6×10^{6} mol^{-1} L s^{-1} at $\mu = 0$.

The rate constant of (3) was calculated from the linear dependence. The linear dependence of $({}^{\cdot}Z^{2+})^{-1}$ and $(Cu^{2+})^{-1}$ (Fig. 4) confirmed the 1:1 complex composition, k_3 was of 5.4×10^{2} mol^{-1} L s^{-1}, and the complex decay rate constant k_5 was of 10^{4} s^{-1}.

The studies of *o*-benzosemiquinone anion-radical complexes by means of ESR were carried out with radicals containing bulky substituents (which increased the radical stability); unsubstituted radical $B^{\dot{-}}$ was studied in the alkaline medium, where it became relatively stable. Cu^{2+} complexes were the most stable as compared with the complexes of other double-charged cations and the same ligands, however, copper(II) *o*-benzoseniquinolate could not be isolated [2]. In this

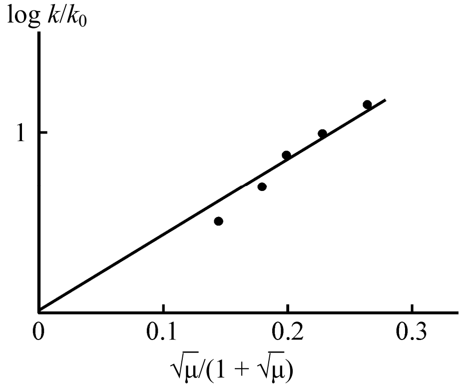


Fig. 3. Ionic strength effect on the rate constant of reaction (6).

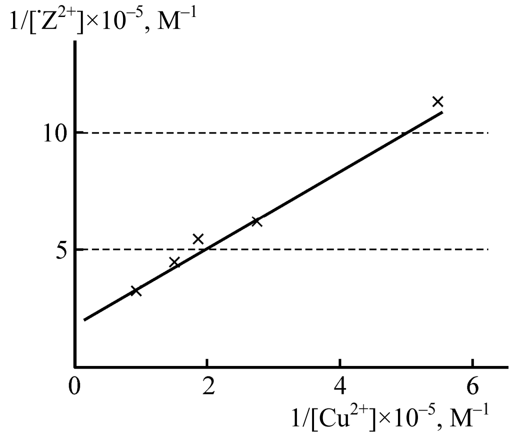


Fig. 4. The complex concentration as a function of concentration of $CuCl_2$.

work we obtained the inner-sphere complex with a short-lived neutral radical $BH^{\cdot}$. The suggested complex structure is shown in Eq. (3), likely, $n \le 4$.

The Coulomb attraction was important in the complex formation between semiquinone radicals and copper ions. The rate constants of complex formation with Cu^{2+} were higher in the case of *p*-benzoquinone anion-radical than in the case of $BH^{\cdot}$ under similar conditions.

The semiquinone complex with metal ions seemingly preserved its π-radical nature, being heavier and larger than the initial radical. Usually it is assumed that the radical termination constant does not depend on the size of the reagent (the Debye equation). This is true if the probability of the radicals to interact does not depend on their orientation. However, the low value of k_2 as determined in this work showed that the mutual orientation of the radicals in the cage affected the course of reaction (2). With increasing radical volume, its termination rate decreased. The termination rate of $^{\cdot}Z^{2+}$ was by two orders of magnitude lower than that of $BH^{\cdot}$. The enhanced stability of $^{\cdot}Z^{2+}$, connected with the diffusion characteristics, could be caused by the Coulomb repulsion, steric hindrance preventing the reaction of $^{\cdot}Z^{2+}$ in the cage, as well as by additional delocalization of the unpaired electron on the copper electronic shell.

The data obtained in this work allow attribution of the stabilization of *o*-benzosemiquinone radical to its complex formation with copper ions.

Redox reactions between transition metals compounds and quinoid compounds are important models for the investigation of certain biological processes. Kinetic studies of the simplest model systems (hydroquinone or quinone – transition metal compounds) demonstrated that they involved semiquinone radicals formed upon single-electron reduction of quinone or oxidation of hydroquinone. These radicals participated in disproportionation and redox reactions with iron ions. Thermodynamic parameters of semiquinone radical disproportionation and kinetics of their interaction with iron compounds have remained unknown to date. In this work we studied the kinetics of *p*-benzosemiquinone radicals termination in the presence of Fe^{II} and Fe^{III} salts.

The reactions were performed in aqueous alcohol solution (water – propanol, 1 9:1 v/v) at pH = 0 and pH = 4.6. To eliminate the effects of ionic strength changes, sodium sulfate (0.1 mol L^{-1}) was introduced.

In order to prevent the dark redox reactions, *p*-benzoquinone was used as source of semiquinone radicals in the experiments with $Fe_2(SO_4)_3$, whereas

Parameters of radical termination reactions at 300 K

Reaction no.	k, $mol^{-1}\ L\ s^{-1}$	ΔS, cal deg^{-1} mol^{-1}	ΔH, kcal mol^{-1}
7	1.8×10^9	–12	1.3
8	1.2×10^8	–1	6.1
9	4.3×10^5	–21	3.6
10	$(1\pm 0.5)\times 10^5$	–	–
11	$(7\pm 3)\times 10^5$	–	–

hydroquinone was used in the similar experiments with $FeSO_4$.

The pulsed photoexcitation (UFS-2 filter, $\lambda = 250$–380 nm) of hydroquinone and *p*-benzoquinone in the presence of hydrogen donor (propanol) led to the formation of semiquinone radicals. At pH = 0 the neutral radical $QH^{\cdot}$ was formed, whereas the anion-radical $Q^{\dot{-}}$ was produced at pH 4.6. The radicals termination was described by the following disproportionation reactions (8), (9).

$$QH^{\cdot} + QH^{\cdot} \rightarrow Q + QH_2, \qquad (7)$$

$$Q^{\dot{-}} + Q^{\dot{-}} \xrightarrow{+2H^+} Q + QH_2. \qquad (8)$$

The termination kinetics of radicals $QH^{\cdot}$ and $Q^{\dot{-}}$ were studied at 415 and 425 nm, respectively. Molar absorbtivities values were taken from [3]. The results are given in the table.

Reaction (7) was controlled by diffusion, as evidenced by the high rate constant and the low activation energy. The value of k_8 was in good agreement with [4]. Reaction (8) was not diffusion-controlled, as followed from a lower by an order of magnitude rate constant and high ΔH^{+}. Fe^{2+} strongly affected the termination kinetics of $Q^{\dot{-}}$ reacting with the latter according to Eq. (9).

$$Q^{\dot{-}} + Fe^{2+} \xrightarrow{+2H^+} QH_2 + Fe^{3+}. \qquad (9)$$

At high concentration of the Fe^{2+} salt ($[Fe^{2+}] >> [Q^{\dot{-}}]$), the termination kinetics of $Q^{\dot{-}}$ followed the pseudo-first order law and was determined solely by Eq. (9), as in that case $k_{10}[Fe^{2+}] >> k_9[Q^{\dot{-}}]$. From the linear dependence of the effective constant on Fe^{2+} salt concentration k_{10} was estimated.

Iron salts accelerated the termination of $QH^{\cdot}$ radicals as well. However, in the studied range of the salts concentrations ($[Fe^{2+}] \leq 1.6\times10^{-2}$ mol L^{-1}, $[Fe^{3+}] \leq 3.5\times10^{-3}$ mol L^{-1}) the termination of $QH^{\cdot}$ occurred according to Eq. (7) and Eq. (10) or Eq. (11).

$$QH^{\cdot} + Fe^{2+} \xrightarrow{+H^+} QH_2 + Fe^{3+}, \qquad (10)$$

$$QH^{\cdot} + Fe^{3+} \xrightarrow{-H^+} Q + Fe^{2+}. \qquad (11)$$

Further increase in the iron ions concentration was accompanied by the radical yield decrease due to quenching of their predecessors (excited states), and thus was not probed.

Reactions (10) and (11) were of the pseudo-first order at the salt concentration of around ~10^{-4} mol L^{-1} or higher. By the linearization of the oscillograms of spectral changes in the appropriate coordinates the values of $k[Fe^{n+}]$ were determined, and thus k_{11} and k_{12} were estimated (see table, on the average 5–6 repeated measurements were performed).

It is supposed that the redox reactions between transition metal compounds and organic radicals occur via the complex formation of the radical with the metal ion. The complex decays upon interaction with protons to give products of the metal oxidation and the radical reduction. Probably, reactions (9), (10) occurred via the same mechanism, and the observed rate constants were effective values corresponding to the two-staged process.

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