ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 1, pp. 30–33. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © G.Yu. Vasil'eva, A.S. Yudina, V.N. Perminov, V.I. Porkhun, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 1, pp. 34–38.

Features of Complex Formation between Semiquinone Radicals and Copper Ions

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Received August 18, 2014

Abstract—Complex formation between copper ions and semiquinone radicals stabilizes the radicals, increases their concentration, and promotes their participation in the electron transport. The complex formation changes the system redox potential and facilitates the electron transfer.

Keywords: impulse photolysis, semiquinone radical, charge transfer complex, copper

DOI: 10.1134/S1070363215010053

Semiquinone radicals found in biologically active compounds (vitamin K, steroids, hormones, antibiotics, and plastoquinones, the latter being bound to the cell membrane and accounting for primary electron transfer from chlorophyll in the course of photosynthesis) form an important class of radical species [1].

So far it has been proved that various semiquinone radicals are formed in the course of electron transport in plant and animal tissues as well as in microorganisms. Those biological systems contain metal ions (in particular, copper and iron), and it is thus important to understand the interaction between semiquinone radicals and those ions [2–5]. *p*-Benzosemiquinone radical is a convenient model for such studies [6–9].

In this work semiquinone radicals were prepared via impulse photoexcitation of aqueous-propanolic (5 : 1 v/v) solutions of 2,6-dimethyl-1,4-hydroquinone (QH_2, $c \times 10^{-4}$ mol/L) through an UFS-1 filter (λ 300–390 nm) at room temperature. Under those conditions, reactions (1) and (2) occurred.

$$QH_2 + h\nu \rightarrow QH^{+} H^{\cdot}, \quad (1)$$

$$QH^{\cdot} \rightarrow Q^{-\cdot} H^{+} \text{ at pH 4}. \quad (2)$$

Absorbance spectrum of semiquinone anion-radical contained the bands with maximum at 400 and 425 nm (Fig. 1), $\varepsilon = 7.3 \times 10^3$ mol L^{-1} cm^{-1} at 425 nm. Addition of CuCl or $CuSO_4$ into hydroquinone solution induced slow oxidation of the latter to form quinone; therefore, freshly prepared solutions were used in the experiments. CuCl is among a few Cu(I) compounds relatively stable in aqueous media. A reducing agent is normally added to the mixture in order to maintain constant concentration of Cu(I); in the studied system hydroquinone acted as a reducer. Impulse excitation of the hydroquinone solution containing $CuSO_4$ ($c = 5 \times 10^{-3}$ mol/L) and CuCl ($c = 7.5 \times 10^{-4}$ mol/L) led to disappearance of the band of $Q^{-\cdot}$; simultaneously, the absorbance bands of other intermediates appeared (Fig. 1).

Such spectral changes could be explained by formation of new complex radical species according to reactions (3) and (4).

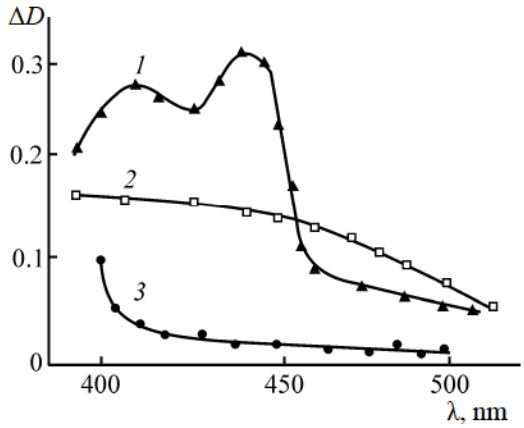


Fig. 1. Absorbance spectra of intermediates formed at time 3×10^{-5} s upon impulse excitation of solutions of (*1*) hydroquinone (c 10^{-4} mol/L) in the presence of (*2*) CuCl ($c = 7.5 \times 10^{-4}$ mol/L) or (*3*) $CuSO_4$ ($c = 5 \times 10^{-3}$ mol/L).

$$Q^{\cdot-} + Cu^{+} \rightarrow X_1^{\cdot+}, \quad (3)$$

$$Q^{\cdot-} + Cu^{2+} \rightarrow X_2^{\cdot+}. \quad (4)$$

Molar absorptivities of those complexes were determined assuming that at $[Cu^{n+}] >> [Q^{\cdot-}]_0$ the solution contained only the $X_1^{\cdot+}$ and $X_2^{\cdot+}$ complexes; therefore, $[Q^{\cdot-}]_0 = [X_{1,2}^{\cdot+}]_0$. Validity of the assumption was confirmed by spectral and kinetic observations at varied concentrations of Cu^{+} and Cu^{2+}. Using the known molar absorptivity of $Q^{\cdot-}$ [10], we got ε_1 of 4.1×10^{-3} mol L^{-1} cm^{-1} ($X_1^{\cdot+}$) and ε_2 of 8.3×10^{-2} mol L^{-1} cm^{-1} ($X_2^{\cdot+}$) (λ 425 nm). Equilibrium constant of reactions (3) and (4) is as follows [reaction (5)]:

$$K_{3,4} = \frac{[X_{1,2}^{\cdot+}]}{[Cu^{n+}][Q^{\cdot-}]}. \quad (5)$$

For $[Q^{\cdot-}]$, Eq. (6) is held.

$$[Q^{\cdot-}] = [Q^{\cdot-}]_0 - [X_{1,2}^{\cdot+}]. \quad (6)$$

Then Eqs. (7) and (8) follow:

$$K = \frac{[X_{1,2}^{\cdot+}]}{[Cu^{n+}]([Q^{\cdot-}]_3 - [X_{1,2}^{\cdot+}])}, \quad (7)$$

$$[X_{1,2}^{\cdot+}]^{-1} = (K[Q^{\cdot-}]_3[Cu^{n+}])^{-1} + [Q^{\cdot-}]^{-1}. \quad (8)$$

The equilibrium constants of reactions (3) and (4) were calculated using Eq. (8). The linear plot of $[X_{1,2}^{\cdot+}]^{-1}$ as function of $[Cu^{n+}]^{-1}$ (Fig. 2) confirmed the 1 : 1 complex composition.

Formation of the complexes via reactions (3) and (4) essentially consists in substitution of water molecules forming coordination sphere of Cu^{+} and Cu^{2+} with the radical. The Cu^{2+} in water forms a highly labile six-coordinated aquatic complex $Cu(H_2O)_6^{2+}$. Its lability is due to the distorted octahedral structure of Cu^{2+} complexes leading to weaker bonding of the axial ligands.

Reactions (3) and (4) occur between oppositely charged ions; hence, K_4 should be greater than K_3, other conditions being the same. That was confirmed experimentally: $K_3 = 7 \times 10^3$ mol/L, $K_4 = 1 \times 10^4$ mol/L.

Addition of CuCl and $CuSO_4$ ($c = 5 \times 10^{-3}$ mol/L) into acidic solution (pH 1.0, in that case neutral semiquinone radical $QH^{\cdot}$ was formed), the complex formation with $QH^{\cdot}$ was not observed. Absorption spectra of the intermediates were identical to those of the neutral semiquinone radical, and the ions influence on the $QH^{\cdot}$ radicals decay was not significant [8, 11, 12].

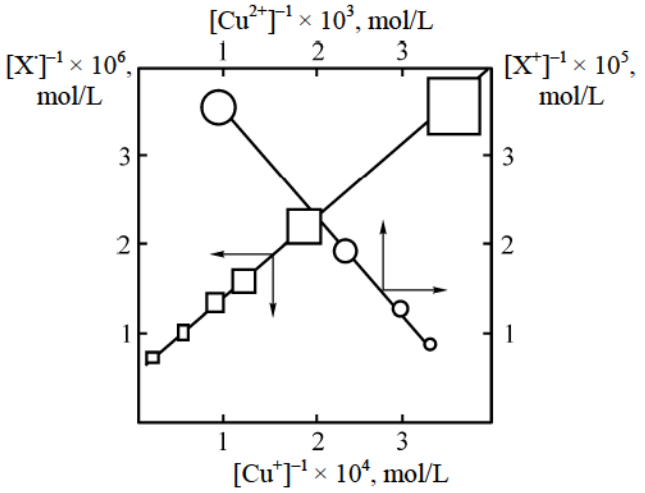
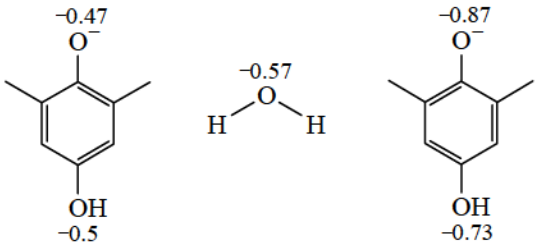


Fig. 2. The complex concentration as function of concentration of the added salt.

The complexes of $Cu(H_2O)_6^{2+}$ with $X_2^{\cdot+}$ were simulated taking advantage of semiempirical PM-3 method. Substitution of the weakly bound H_2O ligand with the $Q^{\cdot-}$ ion-radical was exothermal (heat of reaction of 205 kcal/mol). In the $X_2^{\cdot+}$ complex, the energy of *trans*-ligand H_2O was approximately twice lower than that in the $Cu(H_2O)_6^{2+}$ complex, and the ligand was readily substituted by $Q^{\cdot-}$ ion-radical. The total energy was down by 95 kcal/mol, and the $Q^{\cdot-}Cu(H_2O)_4^{2+}\cdots Q^{\cdot-}$ complex was formed. Heat of H_2O substitution in the starting complex was much lower, of 45 kcal/mol. Furthermore, the relative electronic density in the anion-radical was almost twice higher as compared with the semiquinone radical. The simulation results suggested that water molecules of copper coordination sphere were substituted by the anion-radical via nucleophilic attack. The radical did not form any complexes; that was in line with the spectral observations.

Formation of the $X_{1,2}^{\cdot+}$ complexes via the nucleophilic attack was accompanied with the bond formation between the metal ion and oxygen atom. Hence, the role of the charge at the oxygen atom of the ligand should be crucial. Below the computed charges at oxygen atom of the three studied ligands are given.



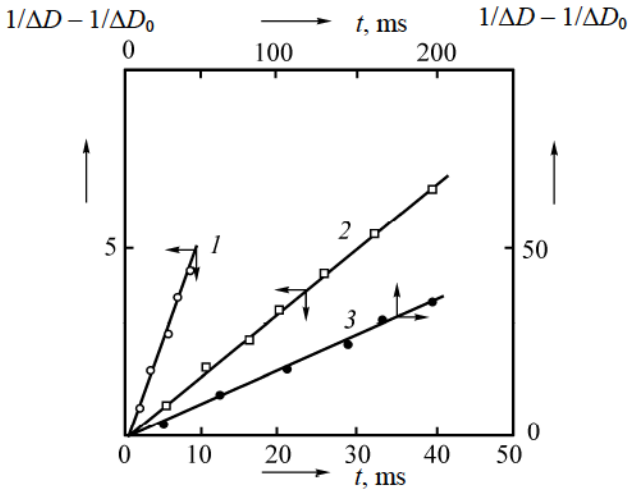


Fig. 3. Linearization of kinetics of spectral changes (λ 425 nm) reflecting the second-order decay of (*1*) semiquinone radical, (*2*) complex $X_1^{\cdot}$, (*3*) and complex $X_2^{\cdot+}$.

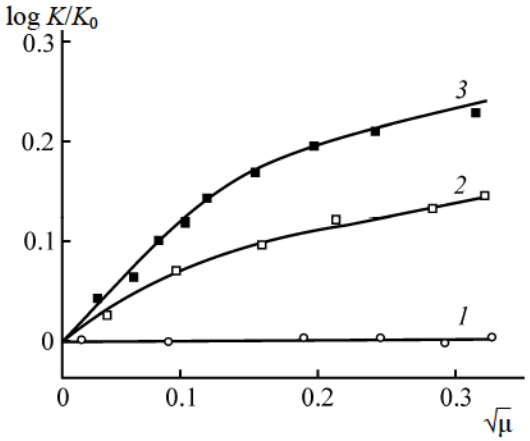


Fig. 4. Ionic strength influence on kinetics of formation of (*1*) the semiquinone radical and (*2*) complexes $X_2^{\cdot+}$ and (*3*) $X_1^{\cdot}$.

Hence, the highest charge at the oxygen atom was revealed in the $Q^{\cdot-}$ anion-radical substituting water molecule in copper coordination sphere. The $QH^{\cdot}$ radical, not capable of the complex formation, showed the lowest charge at the oxygen atom.

Relative electronic density in the anion-radical was higher than that in the semiquinone radical. Therefore, we suggested that nucleophilic attack resulted in the coordinated water substitution with the anion-radical.

Even though the spectral studies revealed no complexes formation by the radical, it was possible to calculate the equilibrium constant of reaction (9).

$$QH^{\cdot} + Cu^{2+} \rightleftarrows X_2^{\cdot+} + H^+, \quad (9)$$

$$QH^{\cdot} \rightleftarrows Q^{\cdot-} + H^+, \quad (10)$$

$$K_{10} = \frac{[Q^{\cdot-}][H^+]}{[QH^{\cdot}]} = 10^{-4} \text{ mol/L},$$

$$Q^{\cdot-} + Cu^{2+} \rightleftarrows X_2^{\cdot+},$$

$$K_4 = \frac{[X_2^{\cdot+}]}{[Q^{\cdot-}][Cu^{2+}]} = 10^{-4} \text{ L/mol},$$

$$K_9 = \frac{[X_2^{\cdot+}][H^+]}{[QH^{\cdot}][Cu^{2+}]} = K_4K_{10} \approx 1.$$

At pH = 1:

$$K_9 = \frac{[X_2^{\cdot+}]}{[QH^{\cdot}][Cu^{2+}]} = 10 \text{ L/mol}.$$

Kinetics of the radical species decay in the studied systems followed the second-order reaction rate law (Fig. 3).

$$Q^{\cdot-} + Q^{\cdot-} + 2H^+ \rightarrow Q + QH_2, \quad (11)$$

$$X_1^{\cdot} + X_1^{\cdot} \rightarrow \text{Products}, \quad (12)$$

$$X_2^{\cdot+} + X_2^{\cdot+} \rightarrow \text{Products}. \quad (13)$$

The rate constants of the intermediates decay in aqueous-propanolic medium at room temperature were determined using the previously found molar absorptivities (λ = 425 nm): $k_{11} = 1.3 \times 10^8$, k_{12} 1.6×10^7, and $k_{13} = 3.8 \times 10^6$ mol L^{-1} s^{-1}.

At low salt concentration, reaction (14) could be observed.

$$Q^{\cdot-} + Cu^{n+} \rightarrow X_{1,2}^{\cdot}. \quad (14)$$

The indexes 1 and 2 stand for the complex with one and two covalent bonds, respectively.

At even lower salt concentration, reaction (15) could seemingly accompany the intermediates decay via reactions (11)–(13).

$$Q^{\cdot-} + X_{1,2}^{\cdot} \rightarrow \text{Products}. \quad (15)$$

We investigated the influence of ionic strength on kinetics of the complex radicals decay (Fig. 4). Rate constant of reaction (13) increased with growing ionic strength, as the reaction occurred via interaction of the likely charged ions. Ionic strength had practically no effect on the reaction (12) course, as the $X_1^{\cdot}$ complex is uncharged. The plots shown in Fig. 4 further

confirmed the complex composition of 1 : 1. From the given values of k_{12} and k_{13} it followed that interaction of the semiquinone radical with copper ions yielded more stable radical species. Recombination of the X_2^{+} complexes required withstanding the Coulombic repultion; indeed, $k_{13} < k_{12}$.

Study of the Cu^{2+} ions effect on kinetics of decay of chloranil $CQ^{\cdot}$ anion-radical revealed the reaction of oxidation of the anion-radical with Cu(II) (14).

$$CQ^{\cdot} + Cu^{2+} \rightarrow CQ + Cu^{+}. \quad (16)$$

Absorbance spectrum of the $CQ^{\cdot}$ radical (λ_{max} = 425 nm) was observed in the course of impulse photolysis of chloranil in aqueous-propanolic solution (5 : 1 v/v) at 20°C. Kinetics of the $CQ^{\cdot}$ radicals decay followed the second-order reaction rate law.

$$CQ^{\cdot} + CQ^{\cdot} \rightarrow CQ + CQ^{2-}. \quad (17)$$

Under the experiment conditions, k_{15} was of 4.6×10^8 mol/s, $\varepsilon = 9.1 \times 10^3$ mol L^{-1} cm^{-1} at λ = 420 nm. Addition of $CuCl_2$ to the solution sharply decreased the $CQ^{\cdot}$ radical lifetime. Linear dependence of the effective rate constant on $CuCl_2$ concentration gave $k_{14} \approx 10^9$ mol^{-1} s^{-1}. The data explained stabilization of semiquinone radical via complexation with copper ion.

Oxidation of hydroquinones into quinones with metal ions is a complicated process including several stages. Study of such interactions is important in view of elucidation of details of mechanism of enzymatic processes involving electron transfer. In particular, the data obtained in this work added to explanation of semiquinone radicals stabilization in copper-containing proteins.

Formation of the complex between copper ions and semiquinone radicals stabilized the latter and decreased the rate constant of their decay by two orders of magnitude, thus significantly increasing their equilibrium concentration. Thus, semiquinone radicals can be involved into the electron transfer in biological systems. Additionally, the complex formation changed the system redox potential, facilitating the single-electron transfer to cytochrome system.

The complexes similar to studied in this work are interesting in view of development of new radical labels binding to the metal ion of the enzyme, as they should induce transfer of the spin to the rest of the ligand surrounding via the metal. Benzosemiquinone radical can be used as a model compound to study electron transfer in other complicated systems.

REFERENCES

1. Porkhun, V.I., *Kinetika i mekhanizmy khimicheskikh i fotokhimicheskikh reaktsii khinonov* (Kinetics and Mechanisms of Chemical and Photochemical Reactions of Quinones), Volgograd: VolgGTU, 2009, p. 234.
2. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Gen. Chem.*, 2011, vol. 81, no. 5, p. 890. DOI: 10.1134/S1070363211050112.
3. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Phys. Chem. A,* 2012, vol. 86, no. 12, p. 1915. DOI: 10.1134/S0036024412120242.
4. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Phys. Chem. A,* 2012, vol. 86, no. 11, p. 1751. DOI: 10.1134/S0036024412110222.
5. Porkhun, V.I. and Rakhimov, A.I., *Khim. Fiz.*, 2012, no. 12, p. 15.
6. Blyumenfel'd L.A., *Problemy biologicheskoi fiziki* (Problems of Biological Physics), Moscow: Nauka, 1974, p. 234.
7. Sviridov, B.D., Serdobov, M.V., and Porkhun, V.I., *Russ. Chem. Bull.*, 1983, no. 1. p. 88.
8. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 4, p. 872. DOI: 10.1134/S107036321004033X.
9. Porkhun, V.I. and Rakhimov, A.I., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol.*, 2007, vol. 50, p. 117.
10. Levin, P.P., Khudyakov, I.V., Kokrashvili, T.A., Darmanyan, A.P., and Kuz'min, V.A., *Dokl. Akad. Nauk SSSR*, 1982, vol. 262, no. 5, p. 1180.
11. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 1, p. 150. DOI: 10.1134/S1070363210010238.
12. Porkhun, V.I. and Rakhimov, A.I., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 1, p. 149. DOI: 10.1134/S1070363210010226.