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Activation of electron transfer reduction of *p*-benzoquinone derivatives by intermolecular regioselective hydrogen bond formation

Shunichi Fukuzumi,* Hironori Kitaguchi, Tomoyoshi Suenobu and Seiji Ogo
Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Japan Science and Technology Corporation (JST), Suita, Osaka 565-0871, Japan.
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

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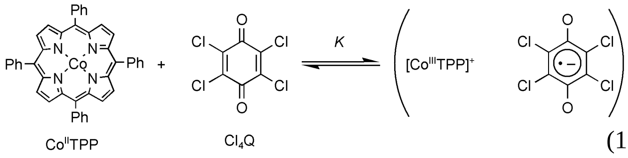
Electron transfer reduction of *p*-benzoquinones by cobalt tetraphenylporphyrin is enhanced significantly by the presence of *o*-bis(phenylcarbamoylmethyl)benzene (*o*-L) due to the regioselective hydrogen bond formation between the corresponding semiquinone radical anions and *o*-L, whereas *m*- and *p*-isomers (*m*-L and *p*-L) have no effect on the electron transfer equilibrium or the rate.

Electron transfer reactions are regulated through non-covalent interactions such as hydrogen bonding which play a crucial role in a variety of biological redox reactions as well as molecular recognition to form higher-order structures of proteins, nucleic acid base pairs and enzyme–substrate complexes.[1] Hydrogen bonding is a specific recognition motif which can selectively stabilize or destabilize different oxidation states of substrates, thus modulating the electron transfer processes.[2] Rotello and coworkers have developed excellent examples of recognition-modulated electron transfer processes in host–guest complexes in which multi-point hydrogen bondings of diacyldiaminopyridine derivatives to flavin modulate the redox potentials of flavin.[3,4] Strong hydrogen bonding is formed by the multi-point recognition of flavin which has two oxygen atoms and nitrogen atom in proximity.[3,4] In contrast, *p*-benzoquinones have two oxygen atoms far from each other and it may be difficult to form strong hydrogen bonds by single point recognition. In photosynthesis, however, two *p*-benzoquinones termed Q_a and Q_b act in concert to enable efficient charge separation to take place.[5,6] Q_a and Q_b are often identical quinones: plastoquinone in higher plants and ubiquinone in bacterial systems.[7] Differences in the nature of the hydrogen-bonding interactions of both quinones have been suggested to result in the differing functions observed; *i.e.*, specific hydrogen bonds to nearby amino acid residues are able to tailor the quinone to perform a specific function.[8] Hydrogen bonding is expected to be more favorable in the one-electron reduced state, semiquinone radical anion, because of the negative charge present in the oxygen atom of the radical anion. However, there is no example for strong hydrogen bond formation of *p*-benzoquinone or semiquinone radical anion with external hydrogen bond donors in solution, which can modulate the electron transfer reduction of *p*-benzoquinone.[9]

We report herein the first example of regiospecific intermolecular hydrogen bond formation between the radical anions of *p*-benzoquinone derivatives and hydrogen bond donors in a polar solvent such as dimethyl sulfoxide (DMSO), which can activate the electron transfer reduction of *p*-benzoquinone derivatives by a one-electron reductant. Three regioisomers of *o*-, *m*-, and *p*-bis(phenylcarbamoylmethyl)benzene (denoted as *o*-**L**, *m*-**L** and *p*-**L**, respectively) are employed as a hydrogen bond donor to demonstrate regioselective hydrogen bond formation. Quite remarkably, only *o*-**L** is effective to activate the electron transfer reduction of *p*-benzoquinone derivatives.

Cobalt tetraphenylporphyrin ($Co^{II}TPP$) is used as an electron donor to reduce *p*-benzoquinone derivatives.[10] Since the one-electron oxidation potential of $Co^{II}TPP$ in DMSO (E^0_{ox} *vs.* SCE $= 0.03$ V) is quite close to the one-electron reduction potentials of *p*-chloranil (Cl_4Q: E^0_{red} *vs.* SCE $= -0.01$ V),[11] the electron transfer between $Co^{II}TPP$ and Cl_4Q is expected to be in equilibrium at 298 K [eqn. (1)].



(1)

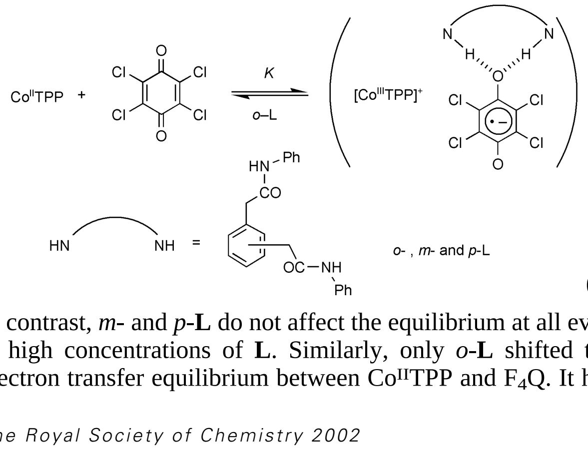
In fact, addition of an excess amount of Cl_4Q to a deaerated DMSO solution of $Co^{II}TPP$ results in partial conversion of $Co^{II}TPP$ to $Co^{III}TPP^+$ as indicated by the appearance of the absorption band due to $Co^{III}TPP^+$ at 434 nm.[12] Further addition of Cl_4Q causes further increase of the absorption band due to $Co^{III}TPP^+$ to approach a constant value. Formation of $Cl_4Q^{\cdot -}$ is confirmed by a clear isotropic ESR signal with no hyperfine splitting at $g = 2.0058$ in deaerated DMSO.[13]

According to eqn. (1), the equilibrium constant (K) is obtained from the plot of $(A - A_0)^{-1}$ *vs.* $[Cl_4Q]^{-1}$ where A_0 is the absorbance of $Co^{II}TPP$ at 434 nm. From the slope and intercept the electron transfer equilibrium constant ($K = 3.7 \times 10^4$ M^{-1}) is determined. Similarly the K value for *p*-fluoranil (F_4Q) was determined as 2.2×10^4 M^{-1}. The rate of formation of $Co^{III}TPP^+$ obeys pseudo-first-order kinetics in the presence of a large excess Cl_4Q and the pseudo-first-order rate constant (k_{obs}) increases linearly with increasing Cl_4Q concentration. According to eqn. (1), k_{obs} is expressed by eqn. (2),

$$k_{obs} = k_{-et} + k_{et}\,[Cl_4Q] \tag{2}$$

where k_{et} and k_{-et} are the forward and back electron transfer rate constants, respectively. From the slope and intercept are determined the k_{et} and k_{-et} values from which the K ($= k_{et}/k_{-et}$) value was obtained as 4.1×10^4 M^{-1}. This value agrees with the K value (3.7×10^4 M^{-1}) determined independently from the spectral titration.

When a hydrogen bond donor (*o*-**L**) is added to the solution, the electron transfer equilibrium is shifted to the product side due to the stabilization of semiquinone radical anion ($Cl_4Q^{\cdot -}$) by hydrogen bonding with *o*-**L**. The K value increases linearly with increasing *o*-**L** concentration as shown in Fig. 1, indicating that $Cl_4Q^{\cdot -}$ forms a 1 : 1 complex with *o*-**L** as expressed by eqn. (3).



(3)

In contrast, *m*- and *p*-**L** do not affect the equilibrium at all even at high concentrations of **L**. Similarly, only *o*-**L** shifted the electron transfer equilibrium between $Co^{II}TPP$ and F_4Q. It has

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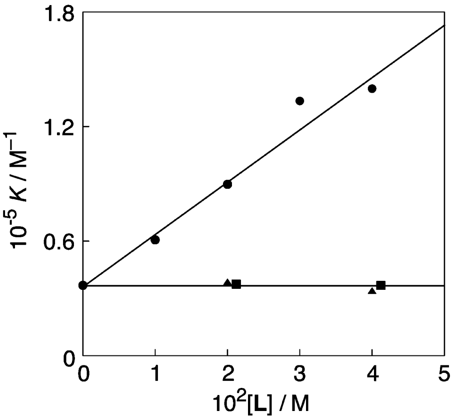

Fig. 1 Plots of K *vs.* [**L**] for electron transfer from $Co^{II}TPP$ to Cl_4Q, in the presence of *o*- (●), *m*- (▲) and, *p*-**L** (■) in deaerated DMSO at 298 K.

been confirmed that a mono-chelating compound (benzanilide) has no effect as the hydrogen bond donor in the present system. This indicates that the hydrogen bond formation is quite sensitive to the geometry of interaction between the dichelating hydrogen bond donor and the semiquinone radical anion.

When Cl_4Q is replaced by a weaker electron acceptor, 2,6-dichloro-*p*-benzoquinone (Cl_2Q: E^0_{red} *vs.* SCE = −0.19 V), electron transfer from $Co^{II}TPP$ to Cl_2Q becomes endergonic, and the electron transfer equilibrium is shifted to the reactants side.[14] When *o*-**L** is added to the $Co^{II}TPP–Cl_2Q$ system, the equilibrium is drastically shifted to the product side and the observed first-order rate constant of electron transfer (k_{obs}) increases linearly with increasing *o*-**L** concentration as shown in Fig. 2.[15] No such enhancement of electron transfer was observed with *m*-**L** or *p*-**L**.

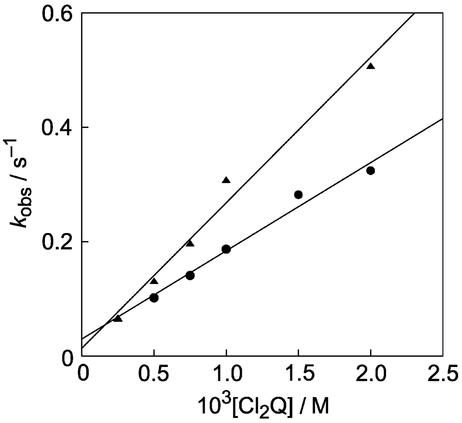

Fig. 2 Plots of k_{obs} *vs.* [Cl_2Q] for electron transfer from $Co^{II}TPP$ (5.0×10^{-6} M) to Cl_2Q in the presence of *o*-**L** (0.10 (●), 0.30 (▲) M) in DMSO at 298 K.

The *ortho*-selective activation of electron transfer from $Co^{II}TPP$ to *p*-benzoquinone derivatives by **L** described above is rationalized by the computed structure of the $Cl_2Q^{\cdot-}$–*o*-**L** complex in which two hydrogens of *o*-**L** interact with the carbonyl oxygen of $Cl_2Q^{\cdot-}$ as shown in Fig. 3, where the hydrogen bond distance is 1.64 Å.[16,17] A similar structure was obtained for the $Cl_2Q^{\cdot-}$–*m*-**L** complex, but the hydrogen bond distance (1.82 Å) is significantly longer than the distance in the $Cl_2Q^{\cdot-}$–*o*-**L** complex. In the case of the $Cl_2Q^{\cdot-}$–*p*-**L** complex, only one hydrogen interacts with the carbonyl oxygen of $Cl_2Q^{\cdot-}$ because of the geometrical restriction. In such a case, only *o*-**L** is effective in accelerating the electron transfer reduction of Cl_2Q by regioselective hydrogen bond formation in DMSO.[17]

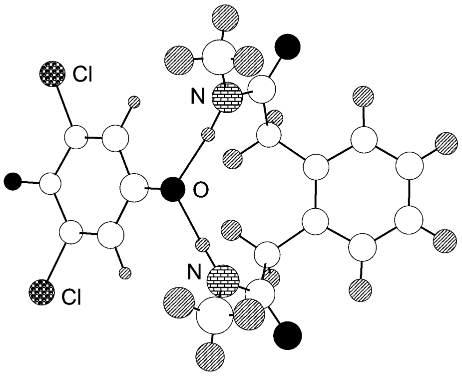

Fig. 3 Optimized structure of the $Cl_2Q^{\cdot-}$–*o*-**L** complex.[16]

The ESR spectrum of the $Cl_2Q^{\cdot-}$–*o*-**L** complex produced in the electron transfer reduction of Cl_2Q by $Co^{II}TPP$ in the presence of *o*-**L** (0.10 M) was observed at 298 K. The g value (2.0056) and the proton hyperfine coupling constants (a_H = 0.268 mT) are virtually the same as observed in the absence of *o*-**L** (g = 2.0056, a_H = 0.268 mT). This indicates the interaction between $Cl_2Q^{\cdot-}$ and *o*-**L** is largely electrostatic.

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11 Electrochemical measurements were performed on a BAS 100B electrochemical analyzer in deaerated DMSO containing 0.01 M $Ph_4As^+ClO_4^-$ as a supporting electrolyte at 298 K. A three-electrode system was used with a platinum working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ (0.01 M) reference electrode.

12 Observation of the $Cl_4Q^{\cdot-}$ absorption band is obscured due to the overlap with the absorption band of $Co^{III}TPP^+$ which has a much larger absorption coefficient than $Cl_4Q^{\cdot-}$.

13 No superhyperfine due to the Co nucleus was observed, indicating no covalent interaction in the $Co^{III}TPP^+–Cl_4Q^{\cdot-}$ complex.

14 The K value of Cl_2Q obtained is 78 M^{-1} which is more than 400 times smaller than that of Cl_4Q.

15 From the plot of k_{obs} *vs.* [Cl_2Q], the K (= k_{et}/k_{-et}) value obtained at [Cl_2Q] = 0.3 M is 1.9×10^4 M^{-1} which is *ca.* 240 times larger than the value of the *o*-**L** free system.

16 Theoretical calculations were performed on a COMPAQ DS20E computer using the Amsterdam Density Functional (ADF) program version 1999.02 developed by Baerends *et al.*[17] The two phenyl groups in **L** were replaced by methyl groups in the calculation.

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