JOC Article
pubs.acs.org/joc

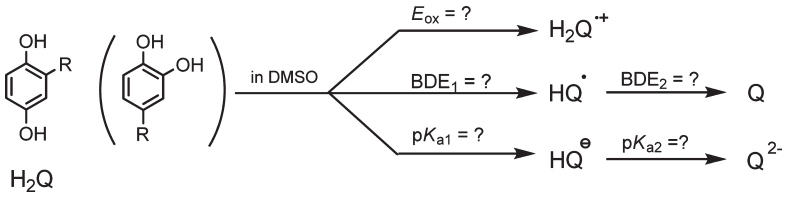
Scales of Oxidation Potentials, pK_a, and BDE of Various Hydroquinones and Catechols in DMSO

Xiao-Qing Zhu,* Chun-Hua Wang, and Hao Liang

State Key Laboratory of Elemento-Organic Chemistry, Department of Chemistry, Nankai University, Tianjin 300071, China

xqzhu@nankai.edu.cn

Received July 25, 2010



The one-electron oxidation potentials [$E^{ox}_{NHE}(H_2Q)$], pK_a (pK_{a1} and pK_{a2}) values, and bond dissociation energies (BDE_1 and BDE_2) of 118 important *p*- and *o*-dihydroquinones in DMSO were systematically predicted for the first time by using DFT method and the PCM cluster continuum model. The calculated results agree well with the available experimental determinations. The study shows that all the five thermodynamic parameters correlate well with the Hammett substituent parameters σ_p (for *p*-H_2Q, $E^{ox}_{NHE}(H_2Q^{\cdot+}/H_2Q) = 1.66\Sigma\sigma_p + 0.54$, $pK_{a1} = -5.69\Sigma\sigma_p + 16.54$, $pK_{a2} = -5.19\Sigma\sigma_p + 23.91$, $BDE_1 = 3.43\Sigma\sigma_p + 82.29$, $BDE_2 = 4.64\Sigma\sigma_p + 67.70$ and for *o*-H_2Q, $E^{ox}_{NHE}(H_2Q^{\cdot+}/H_2Q) = 1.85\Sigma\sigma_p + 0.46$, $pK_{a1} = -5.53\Sigma\sigma_p + 13.28$, $pK_{a2} = -5.24\Sigma\sigma_p + 26.70$, $BDE_1 = 3.54\Sigma\sigma_p + 82.08$, $BDE_2 = 3.82\Sigma\sigma_p + 75.93$), which hints that we can get these thermodynamic parameters as long as the structure of the hydroquinones were known. The comparisons of the calculated five thermodynamic parameters between *p*-hydroquinones and *o*-hydroquinones and the number of the phenyl ring effects on these thermodynamic parameters were also studied. At last, intramolecular hydrogen bond energies in hydroquinones at neutral, radical cation, radical, anion different state were systematically calculated and analyzed. Combined with the papers published in our group before, we will have a systematic thermodynamic picture of the transfer details between different kinds of quinones and corresponding hydroquinones, which strongly promote the fast development of the understanding and applications of quinones.

Introduction

Hydroquinones and catechols are well-known two-electron reductants, which play important roles in chemistry, biology, industries and our environmental science.[1] For example, in organic syntheses, hydroquinones are valuable reagents for the hydrogenation of polycyclic hydroacromatic compounds,[2] cyclic ketones, and nitrogen heterocycles.[3] Quinone/hydroquinone redox couples have been widely used in electrochemical studies because they are readily available and exhibit well behaved electrochemistry.[4] Hydroquinone derivatives are also active in cellular respiration,[5] photosynthesis,[6] and blood

(1) (a) Brodovitch, J. C.; McAuley, A.; Oswald, T. *Inorg. Chem.* **1982**, *21*, 3442. (b) Macartney, D. H.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1984**, 103. (c) Giraudi, G.; Mentasti, E. *Transition Met. Chem.* **1981**, *6*, 230. (d) Herbert, J. W.; Macartney, D. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1931. (e) Castro, C. E.; Hathaway, G. M.; Havlin, R. *J. Am. Chem. Soc.* **1977**, *99*, 8032. (f) Clemmer, J. D.; Hogaboom, G. K.; Holwerda, R. A. *Inorg. Chem.* **1979**, *18*, 2567. (g) Hoddenbagh, J. M. A.; Macartney, D. H. *J. Chem. Soc., Dalton Trans.* **1990**, 615. (h) Kustin, K.; Liu, S.-T.; Nicolini, C.; Toppen, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 7410. (i) Kamau, P.; Jordan, R. B. *Inorg. Chem.* **2002**, *41*, 3076. (j) Binstead, R. A.; McGuire, M. E.; Dovletoglou, A.; Seok, W. K.; Roecker, L. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 173.

(2) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

(3) Becker,H.-D.;Turner, A. B. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, Chapter 23, pp 1351.

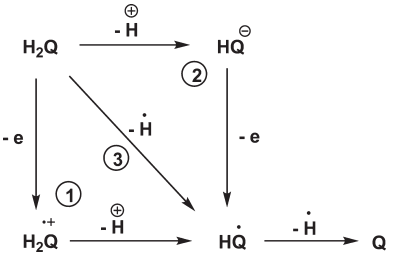
(4) Richard, D. A.; Shaobin, M. *J. Am. Chem. Soc.* **2004**, *126*, 5056.

(5) (a) Larsen, P. L.; Clarke, C. F. *Science* **2002**, *295*, 120123. (b) Do, T. Q.; Hsu, A. Y.; Jonassen, T.; Lee, P. T.; Clarke, C. F. *J. Biol. Chem.* **2001**, *276*, 18161. (c) Reynolds, C. A; King, P. M.; Richards, W. G. *Nature* **1988**, *334*, 80. (d) Lister, S. G.; Reynolds, C. A.; Richards, W. G. *Int. J. Quantum Chem.* **1992**, *41*, 293. (e) Reyolds, C. A.; Richards, W. G.; Goodford, P. J. *Anti-Cancer Drug Des.* **1987**, *1*, 291.

(6) (a) Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S.-C.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature* **1997**, *385*, 239. (b) Diner, B. A.; Babcock, G. T. In *Oxygenic Photosynthesis: The Light Reactions*; Ort, D. R., Yocum, C. F., Eds.; Kluwer: Dordrecht, The Netherlands, 1996; pp 213−247. *Antennas and Reaction Centers of Photosynthetic Bacteria*; Michel-Beyerle, M. E., Ed.; Springer-Verlag: Berlin, 1985. *Functions of Quinones in Energy Conserving Systems*; Trumpower, B. L., Ed.; Academic Press: New York, 1986.

Published on Web 09/28/2010 DOI: 10.1021/jo101455m

SCHEME 1. Chemical Conversion Pathways from H_2Q to Q



coagulation.[7] Propyl gallate and nordihydroguaiaretic acid, the skeleton of which is catechols, are commericial antioxidants which widely used as food additives to prevent oxidation of fats.[8]

The oxidation of hydroquinones and catechols to corresponding quinones has been a subject of great interest and is increasing drawing the attention of researchers. From the chemists' viewpoint, there are three pathways mainly for the oxidation of hydroquinones and catechols. The first is initial electron transfer followed by rapid proton transfer. The net result is the hydrogen atom transfer and this mechanism usually occur between hydroquinones and transition metal complexes.[9] The second mechanism is initial proton transfer followed by electron transfer. This mechanism is not uncommon for ArOH/dpph (2,2-diphenyl-1-picrylhydrazil radical) in solvents that support ionization.[10] The last one is the hydrogen-atom transfer and can be widely seen in biological process since hydroquinones and catecholes are also phenol derivatives.[11] The final step of these three mechanisms of the oxidation process of the hydroquinones is the conversion from semiquinones to quinones (eq 1).[12]

$$2HQ^{\bullet} \rightarrow Q + H_2Q \qquad (1)$$

Although other factors, such as biological context, solubility, transport to specific tissues, the presence of bulky groups near the OH group, hydrogen bonding characteristics of the solvent may play a role in determining which mechanisms of the hydroquinone oxidation process,[13] it is clear, however, that as long as molecular specific properties are concerned, the oxidation potentials, proton dissociation energies and bond dissociation energies are of particular importance. For example, many authors stated that the three mechanisms mentioned above are active and occur in parallel, but this begs a question as to which one is dominant or by how much. As a consequence, experimental chemists paid substantial research activities to the determinations of these three thermodynamic parameters in the past decades. In 1983, L. E. Friedrich obtained the bond dissociation energies of hydroquinones by using half cell reactions in water,[14] and in 1991, Bordwell reported the p*K*a values and oxidation potentials of hydroquinones.[15] Recently, Lucarini and co-workers determined the bond dissociation energies of polyphenols by using EPR equilibration technique.[16] However, experimental determinations of the thermodynamic parameters of the hydroquinones and catechols are relative small. The reason could be that the low stability of some hydroquinones, the difficulty of achieving high purity state, difficulties of handling of harmful compounds and so usually inconsistent with each other.[17] Furthermore, experimental techniques are not adequate to determine bond dissociation energies or proton dissociation energies in compounds containing more than one O−H bond, and provide only either an average of the several O−H bonds or the lowest O−H bonds in the molecule.[18]

Considering the difficulty in obtaining these three important thermodynamic parameters for the O−H bonds in these compounds, it is necessary to develop some theoretical methods to predict these important quantities. These methods would be useful for researchers in a variety of traditional as well as emerging areas. Fox et al. used DFT in an attempt to determine whether a biochemical reaction mechanism proceeds via hydrogen atom transfer or electron transfer,[19] and Wright et al. used the DFT approach to determine accurate BDE and IE values of phenols (including hydroquinone and catechol) in the gas-phase.[18] Recently, Leopoldini et al. studied a series of phenols at the DFT level to specify whether the antioxidant activity of these compounds proceeds via hydrogen atom transfer or sequence electron transfer, in the gas-phase, and for the first time, in two solvents (water and benzene).[20] More recently, E. G. Bakalbassis first reported the theoretical insights of the 2-monosubstituted phenols.[21] All of the previous theoretical predictions have contributed

(7) (a) Cross, J. V.; Deak, J. C.; Rich, E. A.; Qian, Y.; Lewis, M.; Parrott, L. A.; Mochida, K.; Gustafson, D.; VandePol, S.; Templeton, D. J. *J. Biol. Chem.* **1999**, *274*, 31150. (b) Reynolds, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7545.

(8) (a) De Heer, M. I.; Korth, H. G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969. (b) De Heer, M. I.; Mulder, P.; Korth, H. G.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **2000**, *122*, 2355.

(9) Chambers, J. Q. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley and Sons: New York, 1988; Vol. II, p 719. (b) Lemberg, R. Barret, J. *Cytochromes*; Academic Press: London, 1973. (c) Rich, P. R. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 349.

(10) (a) Erik, K.; Vladimir, L. *J. Phys. Chem. A* **2006**, *110*, 12312. (b) Musialik, M.; Litwinienko, G. *Org. Lett.* **2005**, *7*, 4952. (c) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2003**, *68*, 3433. (d) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2004**, *69*, 5888. (e) Foti, M. C.; Daquino, C.; Geraci, C. *J. Org. Chem.* **2004**, *69*, 2309. (f) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2005**, *70*, 8983.

(11) (a) Bakalbassis, E. G.; Lithoxoidou, A. T.; Vafiadis, A. P. *J. Phys. Chem. A* **2003**, *107*, 8594. (b) Vafiadis, A. P.; Bakalbassis, E. G. *Chem. Phys.* **2005**, *316*, 195. (c) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605. (d) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737. (e) de Heer, M. I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969. (f) Pratt, D. A.; DiLabio, G. A.; Mulder, P.; Ingold, K. U. *Acc. Chem. Res.* **2004**, *37*, 334. (g) Johnson, E. R.; Clarkin, O. J.; DiLabio, G. A. *J. Phys. Chem. A* **2003**, *107*, 9953. (h) DiLabio, G. A.; Pratt, D. A.; LoFaro, A. D.; Wright, J. S. *J. Phys. Chem. A* **1999**, *103*, 1653. (i) Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am. Chem. Soc.* **1997**, *119*, 4239. (j) Cabral, B. J. C.; Canuto, S. *Chem. Phys. Lett.* **2005**, *406*, 300. (k) Yao, X.-Q.; Hou, X.-J.; Jiao, H.; Xiang, H.-W.; Li, Y.-W. *J. Phys. Chem. A* **2004**, *108*, 10834. (l) Estácio, S. G.; do Couto, P. C.; Cabral, B. J. C.; da Piedade, M. E. M.; Simões, J. A. M. *J. Phys. Chem. A* **2003**, *107*, 9991.

(12) William, W. Y. L.; Mendy, F. W. L.; Lau, T. C. *Inorg. Chem.* **2006**, *45*, 315.

(13) (a) Pedulli, G. F.; Lucarini, M.; Pedrielli, P. *Free Radicals in Biology and Enviroment*; Minisci, F., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; p 169. (b) Burton, G. W.; Ingold, K. U. *Acc. Chem. Res.* **1986**, *19*, 194. (c) Valgimigli, L.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3545. (d) Barclay, L. R. C.; Edwards, C. E.; Vinqvist, M. R. J. *J. Am. Chem. Soc.* **1999**, *121*, 6226.

(14) Friedrich, L. E. *J. Org. Chem.* **1983**, *48*, 3852.

(15) Bordwell, F. G.; Cheng, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

(16) Lucarini, M.; Mugnaini, V.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 928.

(17) Li, M. J.; Liu, L.; Fu, Y.; Guo, Q. X. *J. Molec. Struct. (THEOCHEM)* **2007**, *815*, 1.

(18) Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1997**, *119*, 4252.

(19) Fox, T.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 2950.

(20) Leopoldini, M.; Marino, T.; Russo, N.; Toscano, M. *J. Phys. Chem. A* **2004**, *108*, 4916.

(21) Lithoxoidou, A. T.; Bakalbassis, E. G. *J. Phys. Chem. A* **2005**, *109*, 366.

positively to the understanding of the chemistry of hydroquinones, nevertheless, it is worth mentioning that none of the previous studies have provided systematically ionization potentials in the gas-phase, oxidation potentials, bond dissociation, and proton dissociation energies of the O−H bond of hydroquinones and catechols in the solution phase. Although the bond dissociation energies of some catechols have been estimated, the predictions were made only with fairly low level theoretical methods such as AM1 or only in the gas-phase.[22] Furthermore, the comparisons of the first and second bond dissociation energies or proton dissociation energies of hydroquinones and catechols have not been released in the literatures until now. The structure−activity relationships for the chemical activities also remain to be established.

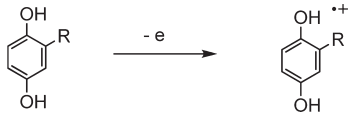
We recently initiated a long-term project to study the fundamental chemistry of quinones and hydroquinones and we successfully developed a theoretical method that could calculate the hydride affinities, the first and second reduction potentials of a variety of quinones. As a continuation of our previous research, this paper will investigates the oxidation potentials, the first and second proton dissociation and bond dissociation energies of various hydroquinones and catechols by accurate DFT-based calculations. The structures of the hydroquinones and catechols of interest in the present paper are shown in Scheme 2. Knowledge of these values was expected to be very valuable to organic chemists and biochemists who want to know the detailed oxidation mechanisms of the hydroquinones and catechols.

Computational Methods

All the calculations were conducted by using Gaussian 03 packages.[23] The geometries of all species were fully optimized at the B3LYP/6-31+G* level of theory without any constraints. The optimized structures were confirmed to be real minima by frequency calculation (no imaginary frequency). For the species having more conformers, all conformers were investigated. The conformer with the lowest electronic energy was used in this work. Considering the large number of molecules and three parameters that will be calculated, in this work, single-point energies were estimated at B3LYP/6-311++G (2df, p) level based on the B3LYP/6-31+G* geometry, corrected with the zero point energies and thermal corrections.

To attain maximum accuracy of the solvation energy calculations, herein we utilized the most recent version of the polarized continuum model, that is IEF-PCM (integral equation formalism PCM), at the B3LYP/6-31+G* level to calculate the solvation free energies.[24] In this work, we choose Bondi's atomic radii, and the solvent here is DMSO.

From the calculated Gibbs free energies in the gas-phase and solution phase, we defined following quantities:

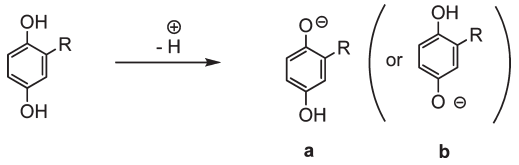


$$\mathrm{IP} = G(\mathrm{H_2Q})_g - G(\mathrm{H_2Q^{\bullet+}})_g$$

(ionization potential in gas phase) (2)

$$E_{ox} = [G(\mathrm{H_2Q})_{sol} - G(\mathrm{H_2Q^{\bullet+}})_{sol}]/F$$

(oxidation potential of hydroquinones in DMSO) (3)

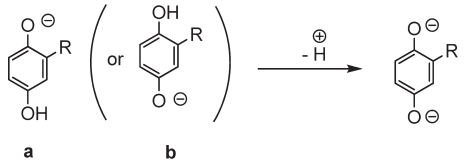


$$\mathrm{PA_{1g}} = G(\mathrm{HQ^-})_g + G(\mathrm{H^+})_g - G(\mathrm{H_2Q})_g$$

(the first proton dissociation energy in gas phase) (4)

$$\mathrm{PA_{1sol}} = G(\mathrm{HQ^-})_{sol} + G(\mathrm{H^+})_{sol} - G(\mathrm{H_2Q})_{sol}$$

(the first proton dissociation energy in DMSO) (5)

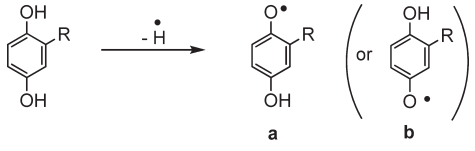


$$\mathrm{PA_{2g}} = G(\mathrm{Q^{2-}})_g + G(\mathrm{H^+})_g - G(\mathrm{HQ^-})_g$$

(the second proton dissociation energy in gas phase) (6)

$$\mathrm{PA_{2sol}} = G(\mathrm{Q^{2-}})_{sol} + G(\mathrm{H^+})_{sol} - G(\mathrm{HQ^-})_{sol}$$

(the second proton dissociation energy in DMSO) (7)



$$\mathrm{BDE_{1g}} = G(\mathrm{HQ^{\bullet}})_g + G(\mathrm{H^{\bullet}})_g - G(\mathrm{H_2Q})_g$$

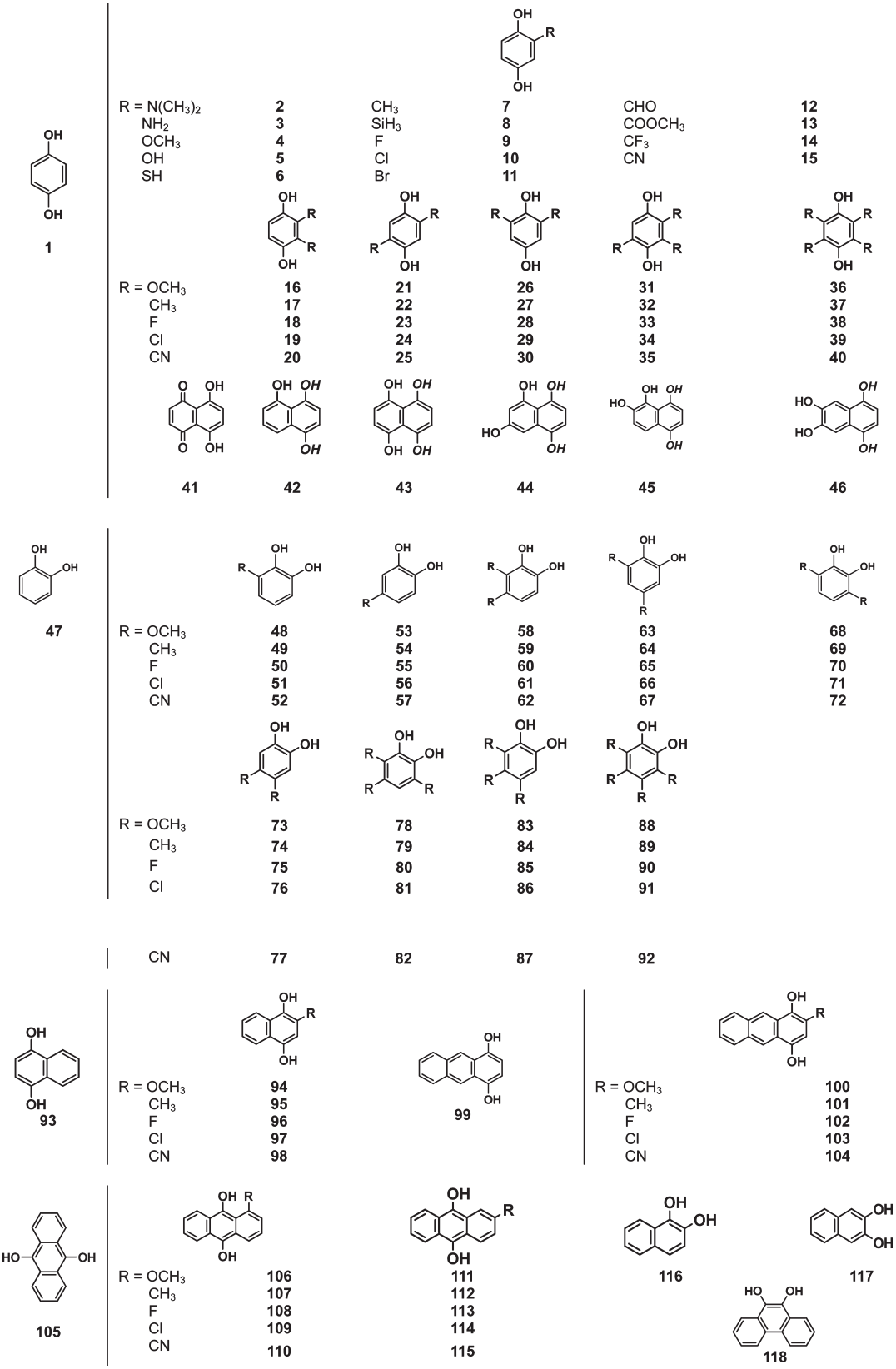
(the first hydrogen dissociation energy in gas phase) (8)

(22) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

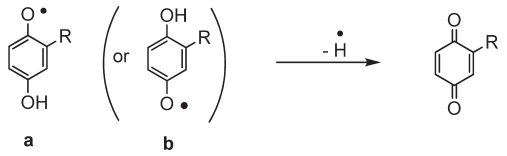
(24) (a) Fu, Y.; Shen, K.; Liu, L.; Guo, Q. X. *J. Am. Chem. Soc.* **2007**, *129*, 13510. (b) Qi, X. J.; Liu, L.; Fu, Y.; Guo, Q. X. *Organometallics* **2006**, *25*, 5879. (c) Fu, Y.; Liu, L.; Yu, H. Z.; Wang, Y. M.; Guo, Q. X. *J. Am. Chem. Soc.* **2005**, *127*, 7227. (d) Fu, Y.; Liu, L.; Li, R. Q.; Liu, R.; Guo, Q. X. *J. Am. Chem. Soc.* **2004**, *126*, 814. (e) Fu, Y.; Wang, H. J.; Chong, S. S.; Guo, Q. X.; Liu, L. *J. Org. Chem.* **2009**, *74*, 810.

SCHEME 2. Chemical Structures and Numbers of the Hydroquinones and Catechols



$$BDE_{1sol} = G(HQ^{\bullet})_{sol} + G(H^{\bullet})_{sol} - G(H_2Q)_{sol}$$

(the first hydrogen dissociation energy in DMSO) (9)



$$BDE_{2g} = G(Q)_g + G(H^{\bullet})_g - G(HQ^{\bullet})_g$$

(the second hydrogen dissociation energy in gas phase) (10)

$$BDE_{2sol} = G(Q)_{sol} + G(H^{\bullet})_{sol} - G(HQ^{\bullet})_{sol}$$

(the second hydrogen dissociation energy in DMSO) (11)

Since it has been shown that DFT methods tend to systematically overestimate or underestimate chemical properties, and the solvation energy of protons remains uncertain, we decided to utilize three isodesmic reaction to improve the accuracy of the calculation of the oxidation potentials, pK_a values and bond dissociation energies of hydroquinones in DMSO, respectively, and phenol was chosen as a reference to construct, that is, electron, proton, and hydrogen atom interchange reaction (Scheme 3).

According to the thermodynamic cycle shown in Scheme 3, the ionization potentials, oxidation potentials, proton dissociation energies and bond dissociation energies can be obtained by eqs 14−19, respectively.

$$IP(H_2Q)_g = IP(phenol)_g - \Delta G_{12} \quad (14)$$

$$E^{ox}{}_{NHE}(H_2Q) = E^{ox}{}_{NEH}(phenol) + \Delta G_{13}/F \quad (15)$$

$$pK_a(H_2Q)_g = pK_a(phenol)_g + \Delta G_{12}/(2.303RT) \quad (16)$$

$$pK_a(H_2Q)_{sol} = pK_a(phenol)_{sol} + \Delta G_{13}/(2.303RT) \quad (17)$$

$$BDE_g = BDE(phenol)_g + \Delta G_{12} \quad (18)$$

$$BDE_{sol} = BDE(phenol)_{sol} + \Delta G_{13} \quad (19)$$

where ΔG_{12} in eqs 14, 16, and 18 denotes the Gibbs free energy changes of the electron, proton and hydrogen atom interchange in the gas-phase, respectively, while ΔG_{13} in eqs 15, 17, and 19 denotes the Gibbs free energy changes of the electron, proton and hydrogen atom interchange in DMSO, respectively. F is the Faraday constant equal to 23.06 kcal/(mol·V).

Results

The calculated solution phase oxidation potentials, the first and second proton dissociation and hydrogen dissociation energies (O−H) were summarized in Table 1. The corresponding gas-phase energies were summarized in Supporting Information.

Discussion

1. Reliability of the Calculated Results. It is well-known that the electron, proton, and hydrogen atom transfer driving forces of H_2Q are very important thermodynamic parameters for H_2Q, which can be used as indicators of the mechanism analyses of the oxidation processes of H_2Q. Examination of the past publications shows that much attention has been paid to the determinations of these three thermodynamic parameters of phenol series,[15] very little research has hitherto been reported on the corresponding determinations of H_2Q. Thus, it is impossible to evaluate the reliability of the theoretical predictions by comparing some of the predicted values with the corresponding experimental data of H_2Q. To solve this problem, we hypothesized that a theoretical method must be able to reliably handle H_2Q series as long as the same method was known to be successful for handling phenols. The scientific basis of this hypothesis is that H_2Q, actually, are special substituted phenols.

In Supporting Information (Table S1), we collected numbers of experimental and theoretical proton, electron and hydrogen atom transfer driving forces of phenols. From Table S1, it is clear that the theoretical proton, electron and hydrogen atom transfer thermodynamic driving forces of phenols obtained in this work all are very close to the corresponding previously reported experimental observations (MD = 0.29, 0.02, 0.58 and r = 0.98, 0.97, 0.98 for proton, electron, and hydrogen atom transfer driving forces of phenols, respectively), indicating that the theoretical

SCHEME 3. Thermodynamic Conversion from Gas Phase to the Solution Phase

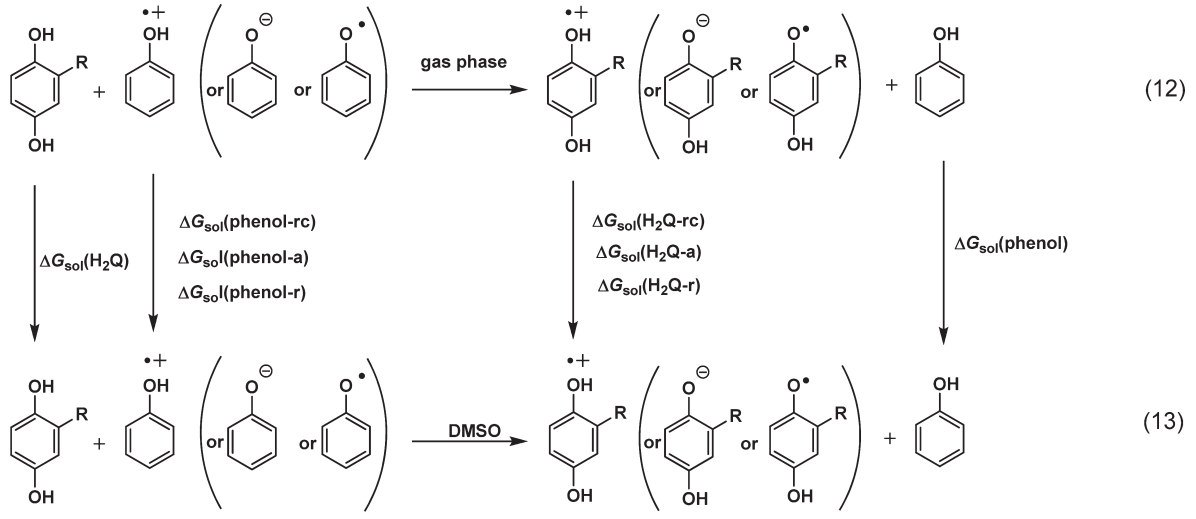


TABLE 1. Solution Phase Oxidation Potentials (V), the First and Second Proton Dissociation (pK_a), and Hydrogen Dissociation Energies (kcal/mol) of the Hydroquinones and Catechols Calculated by IEFPCM//B3LYP/6-311++G(2df,p)//B3LYP/6-31+G(d) Method

		pK_{a1}		pK_{a2}		BDE_1		BDE_2	
compound	E^{ox}_{NHE}	a	b	a	b	a	b	a	b
1	1.607	19.1		25.2		83.4		69.4	
2	1.138	18.1	18.3	24.5	24.3	75.5	81.6	69.0	62.8
3	1.188	16.8	19.7	25.4	22.5	72.4	79.0	69.7	63.1
4	1.400	20.0	18.0	24.2	26.3	84.0	81.7	65.0	67.2
5	1.472	15.5	18.5	24.9	21.9	78.1	82.9	70.3	65.5
6	1.579	16.3	17.5	15.5	14.3	79.8	84.1	70.8	66.5
7	1.543	18.3	18.0	25.4	25.7	81.5	82.3	68.1	67.3
8	1.638	15.4	17.9	25.6	23.1	81.8	83.9	70.7	68.5
9	1.724	15.7	17.2	24.1	22.6	82.9	84.4	70.9	69.4
10	1.730	14.5	18.2	21.4	25.0	84.7	83.1	68.8	70.4
11	1.730	16.5	16.9	22.7	22.3	83.3	84.6	71.2	70.0
12	1.823	15.8	19.2	23.2	19.8	88.6	89.9	73.7	72.3
13	1.780	17.3	17.3	24.4	24.4	87.6	85.7	72.4	74.3
14	1.914	13.7	16.5	23.8	21.0	83.2	86.5	72.5	69.3
15	1.966	11.5	16.0	23.3	18.8	83.7	87.3	74.3	70.8
16	1.850	18.3		24.7		81.8		69.3	
17	1.473	18.1		27.2		80.3		65.9	
18	1.859	15.8		20.5		83.7		70.0	
19	1.820	15.1		21.4		84.0		69.5	
20	2.537	9.3		15.4		87.9		74.7	
21	1.699	17.3		26.3		78.4		65.5	
22	1.431	18.5		26.1		80.8		65.9	
23	1.818	15.8		21.0		83.4		69.8	
24	1.837	14.6		21.4		84.3		69.8	
25	2.504	9.8		17.5		87.0		73.9	
26	1.619	21.5	19.1	24.8	27.2	85.2	84.3	59.0	59.9
27	1.445	19.0	18.4	25.6	26.2	80.0	82.4	66.7	64.3
28	1.551	9.5	11.4	21.9	19.9	74.9	78.5	72.0	68.3
29	1.851	13.0	15.9	20.0	22.8	86.0	82.5	68.0	71.5
30	2.507	6.8	13.7	21.2	14.3	85.3	90.5	77.2	72.0
31	1.663	19.3	19.1	22.7	23.0	82.2	83.6	62.1	60.7
32	1.339	17.8	20.4	28.1	25.5	81.0	79.6	62.7	64.1
33	1.963	12.8	14.3	20.0	18.5	82.7	84.4	70.6	68.9
34	1.923	13.3	12.6	20.0	19.3	85.1	83.1	68.5	70.5
35	2.798	4.4	7.1	14.0	11.4	88.5	90.4	77.1	75.1
36	1.823	16.8		25.7		79.8		64.9	
37	1.294	20.0		27.8		78.9		61.9	
38	2.086	12.1		17.5		83.6		69.9	
39	1.995	11.5		18.1		84.1		69.1	
40	2.897	2.0		9.35		91.2		77.9	
41	2.040	16.1		20.8		92.1		84.9	
42	1.181	11.7	19.0	21.8	14.5	72.5	77.8	72.5	67.1
43	0.970	12.8		15.3		70.8		61.1	
44	1.114	11.7	19.5	22.1	14.3	72.1	77.2	70.2	65.1
45	1.076	10.4	18.9	22.4	13.8	70.0	76.9	71.8	64.9
46	1.148	18.9		24.6		76.7		64.2	
47	1.824	14.6		27.6		83.3		76.5	
48	1.963	15.8	15.9	27.5	27.4	83.1	86.0	73.3	70.5
49	1.995	15.1	14.6	28.5	29.0	81.8	82.7	76.2	75.2
50	1.982	13.3	16.6	24.9	21.5	82.8	86.7	77.7	73.8
51	2.204	12.1	13.1	26.3	25.3	82.9	84.5	77.4	75.8
52	2.124	8.3	10.9	24.8	22.2	82.9	84.4	78.6	77.2
53	1.472	14.3	14.7	26.0	25.6	79.8	77.7	71.7	73.8
54	1.663	14.8	15.0	27.5	27.2	82.1	80.8	74.7	75.9
55	1.816	13.8	15.1	26.8	25.5	82.9	82.0	75.6	76.4
56	1.855	13.0	13.6	26.4	25.9	83.9	83.0	76.2	77.1
57	2.163	11.9	10.3	23.5	25.1	86.8	86.7	79.9	79.9
58	1.454	15.6	16.3	26.9	26.1	83.4	81.8	71.5	73.0
59	1.701	15.9	15.5	27.7	28.1	82.0	81.5	74.5	75.0
60	1.977	11.8	13.8	25.2	23.2	82.8	83.3	76.8	76.3
61	1.952	10.9	12.3	25.5	24.1	83.1	83.9	76.9	76.1
62	2.471	5.1	6.2	19.9	18.8	86.5	87.7	82.4	81.3
63	1.341	17.7	15.7	25.5	27.5	78.8	84.8	70.0	64.0
64	1.605	15.6	14.9	28.5	29.2	81.0	81.9	74.4	73.5
65	1.980	13.2	12.7	24.1	24.6	81.7	84.8	77.8	74.7
66	1.971	11.0	11.4	24.3	23.9	82.3	84.9	78.1	75.5
67	2.444	4.2	8.1	21.9	18.1	86.2	87.6	81.7	80.3
68	1.399	16.9		27.9		85.0		70.4	
69	1.712	14.4		30.2		80.6		75.2	
70	2.151	11.9		23.3		84.0		77.4	

TABLE 1. Continued

compound	E^{ox}_{NHE}	pK_{a1}		pK_{a2}		BDE$_1$		BDE$_2$	
		a	b	a	b	a	b	a	b
71	2.127	10.6		23.7		84.0		76.9	
72	2.423	5.5		18.7		85.5		79.4	
73	1.247	15.6		24.0		82.1		60.1	
74	1.515	15.0		27.0		80.0		74.4	
75	1.844	13.9		25.4		82.1		75.2	
76	1.898	12.1		24.7		83.7		77.4	
77	2.483	7.8		21.0		89.7		82.5	
78	1.300	14.4	14.9	27.8	27.3	83.1	79.5	70.6	74.1
79	1.499	15.0	15.3	30.6	30.4	80.1	78.7	73.3	74.8
80	2.131	10.7	11.9	22.9	21.7	84.6	82.9	76.1	77.7
81	2.086	9.5	9.9	23.0	22.7	84.3	83.3	76.2	77.1
82	2.748	2.4	1.2	14.1	15.3	88.8	88.6	82.7	82.9
83	1.254	15.6	15.6	26.5	26.5	80.9	82.6	65.4	63.7
84	1.455	15.4	14.0	28.5	29.9	78.8	79.3	74.1	73.6
85	2.004	11.8	12.6	25.1	24.4	81.7	83.6	76.8	74.9
86	2.003	10.2	11.1	24.9	24.0	83.1	84.9	78.1	76.3
87	2.769	1.5	3.7	17.5	15.3	89.3	90.4	84.8	83.8
88	1.400	13.2		28.3		78.6		69.3	
89	1.458	15.0		31.9		78.6		73.6	
90	2.168	10.5		24.4		83.2		76.5	
91	2.106	9.0		24.4		83.9		77.1	
92	3.050	−1.7		11.5		91.3		85.9	
93	1.251	16.7		25.3		77.7		62.8	
94	1.051	20.2	17.5	23.0	25.6	74.7	75.3	67.0	66.4
95	1.198	18.9	19.2	23.6	23.3	75.7	77.4	63.8	62.2
96	1.350	16.1	16.6	22.2	21.7	76.9	78.2	64.8	63.4
97	1.373	15.7	16.7	22.3	21.2	77.2	78.8	65.6	64.0
98	1.608	11.0	16.3	21.7	16.4	77.7	81.9	69.3	65.2
99	1.043	17.8		23.4		74.9		63.0	
100	0.856	20.0	17.2	22.7	25.5	75.0	72.5	57.0	59.6
101	0.987	18.4	18.5	23.3	23.3	73.1	74.6	61.8	60.4
102	1.115	17.0	16.0	20.4	21.4	74.4	75.1	62.2	61.6
103	1.144	15.4	16.5	21.8	20.7	74.5	76.3	63.9	62.1
104	1.357	10.4	16.2	21.5	15.7	74.8	79.4	68.0	63.3
105	0.920	14.2		25.2		69.8		54.9	
106	0.824	20.9	19.7	23.9	25.1	74.4	69.5	56.7	61.6
107	0.894	17.2	17.7	24.0	23.5	69.2	69.4	56.6	56.3
108	0.949	17.4	15.7	22.4	24.0	71.2	70.0	57.5	58.7
109	0.952	17.3	15.8	22.6	24.1	71.4	70.1	57.3	58.6
110	1.094	13.7	13.8	21.2	21.1	69.3	70.8	58.4	56.8
111	0.825	17.3	16.3	22.2	23.2	68.6	68.7	56.2	56.1
112	0.879	17.0	16.5	22.9	23.4	69.2	69.3	56.6	56.5
113	1.002	16.9	15.7	22.4	23.6	70.6	70.3	57.2	57.5
114	1.006	16.2	15.9	22.4	22.7	70.4	70.5	57.7	57.6
115	1.104	13.2	15.3	22.2	20.2	70.4	71.4	59.4	58.4
116	1.405	15.0	15.0	26.6	26.5	76.0	78.0	71.2	69.2
117	1.727	13.8		24.9		83.8		86.2	
118	1.298	12.4		29.2		73.5		67.2	

method used in this work can reach the experimental uncertainties and the results from this method are very reliable. On the basis of these data we can discuss, for the first time, some important yet unanswered questions concerning the structure−property relationships behind the proton, electron and hydrogen atom transfer driving forces of H_2Q.

2. Oxidation Potentials Scale of Various Hydroquinones in DMSO. From the second column in Table 1, it is clear that the oxidation potentials of the H_2Q range from 0.824 V for **106** to 3.050 V for **92**. This large scale of oxidation potentials of H_2Q indicates that these H_2Q can construct a large and useful library of organic reductants, which can provide several of electron donors one needs. Comparison of the one-electron oxidation potentials of H_2Q with those of some well-known organic one-electron donors, such as BNAH, $AcrH_2$ and XnH[25] shows that most of *p*-H_2Q and *o*-H_2Q are poor electron donors and most of 1,4-H_2AQ and 9,10-H_2AQ belong to strong electron donors. 1,4-H_2NQ are due to middle strong electron donors (Figure 1). Detailed examination of the calculated results indicate that the oxidation potential scales of each series of H_2Q are from 0.970 to 2.987 V for *p*-H_2Q, from 1.247 to 3.050 V for *o*-H_2Q, from 1.051 to 1.608 V for1,4-H_2NQ, from 0.856 to 1.357 V for 1,4-H_2AQ, and from 0.824 to 1.104 V for 9,10-H_2AQ, respectively. The one-electron oxidation potentials of *o*-H_2Q are similar to those of corresponding phenols,[15] and both of them are larger by about 0.2 V than those of *p*-H_2Q, which suggest that *p*-H_2Q have largest electron-donating abilities than those of corresponding *o*-H_2Q and phenols, which may be rationalized by noting that the combination results from electron-donating effect of OH group and the intramolecular hydrogen bond (see Scheme 5).

Comparison of the one electron oxidation potentials of *p*-H_2Q, 1,4-H_2NQ, and 1,4-H_2AQ shows that the electron-donating

(25) Cheng, J. P.; Lu, Y.; Zhu, X. Q.; Mu, L. *J. Org. Chem.* **1998**, *63*, 6108.

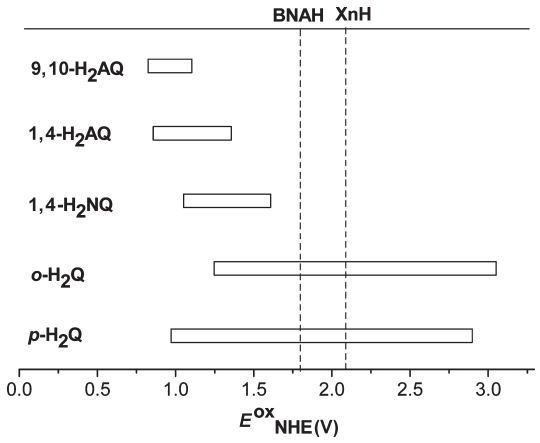


FIGURE 1. Standard oxidation potentials scale of various hydroquinones in DMSO.

abilities of H_2Q with the same substituents decrease in the order *p*-H_2Q > 1,4-H_2NQ > 1,4-H_2AQ, indicating that the larger the aromatic system of the hydroquinone is, the smaller the oxidation potential of the hydroquinone is. The main factor causing this could be that the hydroquinone radical cation with larger aromatic system could have larger stability in thermodynamics, which makes the hydroquinone easier to release the electron. The oxidation potentials of 9,10-H_2AQ are generally smaller than those of corresponding 1,4-H_2AQ by about 0.1 V, the reason for this small difference can be explained by the fact that 9,10-H_2AQ radical cation is more stable than the corresponding 1,4-H_2AQ.

3. pK_a Scale of Various Hydroquinones and Catechols in DMSO. The propensity of a compound to donate or accept a proton, measured by its acidity or basicity, is fundamental to understanding many chemical and biochemical processes.[26] In the past decades, considerable efforts have been devoted to the determination of the pK_a values of phenols by using experimental methods.[27,28] However, since the similarity of the two hydrogen atoms in hydroquinones, the pK_a values of the hydroquinones have not been released in the literature until now. By using theoretical methods developed in this paper, the systematical calculations of these values were done for the first time and the results were summarized in Table 1.

From Table 1, it is clear that the pK_{a1} values of the hydroquinones in DMSO range from 2 to 21.5 for hydroquinones, from −1.7 to 17.7 for catechols, and the pK_{a2} values range from 9.4 to 28.1 for hydroquinone anion and from 11.5 to 31.9 for catechols anions. Since CF_3COOH, CH_3COOH, PhOH, and H_2O are well-known organic strong acid, middle strong acid, weak acid, and very weak acid in DMSO, respectively,[29] the hydroquinones and catechols can be divided into five categories according to the pK_a values of these molecules. The first category is that the pK_a values are less than 5, such as **35**, **82**, **92**, and so on. These hydroquinones are strong organic acid. The second category is that

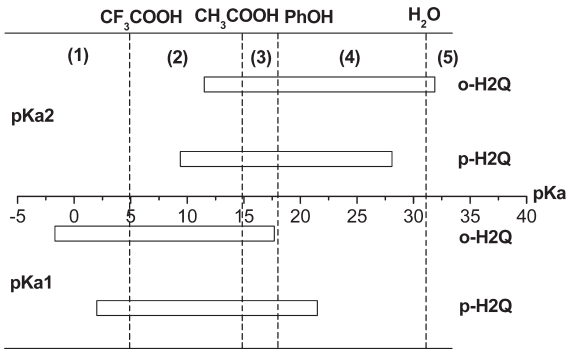


FIGURE 2. pK_a scales of hydroquinones and catechols in DMSO.

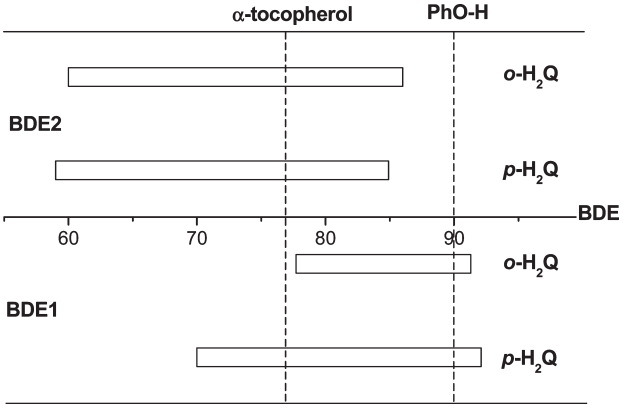


FIGURE 3. Bond dissociation energy scales of the O−H bonds in hydroquinones and catechols in DMSO.

the pK_a values are between 5 and 15, such as **38**, **45**, **52**, and so on. These hydroquinones are due to middle strong organic acid. The third category is that the pK_a values are between 15 and 18, such as **13**, **36**, **93**, and so on, and they are due to normal organic acid. The forth categories is the pK_a values are between 18 and 31, such as **31**, **42** anion, **106**, and so on. In this category, the hydroquinones are due to weak organic acid. The last categories is that the pK_a values are larger than 31, such as **79** anion, **89** anion, and so on. These hydroquinones are due to very weak organic acid. In one world, most of the hydroquinones are strong or middle strong organic acid. However, Figure 2 shows that the pK_{a2} values of HQ^- in DMSO are relatively high, which indicates that the acidities of these anions are very weak.

4. BDE Scales of Various Hydroquinones and Catechols in DMSO. To the best of our knowledge, the calculations of the hydrogen releasing abilities of various hydroquinones and catechols are very important since most of literatures support that the most likely oxidation process from hydroquinone to quinone is direct hydrogen atom transfer and large numbers of hydroquinones are antioxidants and the bond dissociation energy of the O−H bond is an important parameter in determing the antioxidant activity. However, little attention has been paid to the bond dissociation energies of the two O−H bonds in hydroquinones and catechols. In the present study, we bridged this gap and the detailed calculation results were summarized in Table 1.

Our calculated energies changed from 70 to 92.1 kcal/mol for the BDE_1 of hydroquinones, from 77.7 to 91.3 kcal/mol

(26) Bell, R. P. *The Proton in Chemistry*; Chapman and Hall: London, 1973.
(27) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; Chapman and Hall: New York, 1984.
(28) (a) Fu, Y.; Liu, L.; Li, R. Q.; Liu, R.; Guo, Q. X. *J. Am. Chem. Soc.* **2004**, *126*, 814. (b) Fu, Y.; Shen, K.; Liu, L.; Guo, Q. X. *J. Am. Chem. Soc.* **2007**, *129*, 13510.
(29) Fu, Y.; Liu, L.; Li, R. Q.; Liu, R.; Guo, Q. X. *J. Am. Chem. Soc.* **2004**, *126*, 814.

for the BDE_1 of catechols, from 59 to 84.9 kcal/mol for the BDE_2 of hydroquinones, and from 60 to 86 kcal/mol for the BDE_2 of catechols, which suggest that the hydrogen donating abilities of the hydroquinones decrease in the following order: *p*-$HQ^{\bullet} \approx$ *o*-$HQ^{\bullet} >$ *p*-$H_2Q \approx$ *o*-H_2Q. The small difference the hydrogen donor abilities between hydroquinone and catechol will be discussed in the following part. Calculations have shown that in catechol, the two hydroxyl groups afford almost identical to the experiment BDE of 81.83 kcal/mol. We consider here that there is only one BDE value for catechol, regardless of which O−H bond is broken in the parent molecule. This is because the radical is allowed to rearrange, at room temperature, affording the most stable toward conformer.

Most of the BDEs of these hydroquinones and catecholes are lower than that of phenol, suggesting that most of these compounds are good antioxidants. In order to get a detailed knowledge of the antioxidant activity of the hydroquinones and catecholes, we conducted a comparison of the bond dissociation energies of various antioxidants, including coenzyme Q, flavonoids, olives, curcumins, indolinonic hydroxylamines, phenothiazines, edaravones and antioxidants used as food additives which were listed in Table 2.

If the bond dissociation energies of hydroquinones were compared with those of various antioxidants listed in Table 2, the following suggestions can be offered: (1) The hydrogen donating abilities of all the HQ• are not only smaller than those of phenothiazine (N−H) and edaravone (C−H) but also smaller than those of flavonoids, olives, curcumins, indolinonic hydroxylamines, and so on (O−H). They are always very good hydrogen donors. (2) More hydroxyl groups on the ring will significantly decrease the O−H BDEs, which holds consistence with experimental observations, the reason could be that the intramolecular hydrogen bond adds the coplanatity of all the ring, which increase the antioxidant reactivity. (3) Different substituents have little effect on the O−H BDEs in flavonide, olive, and edaravone but have large effect on those of hydroquinones, indicating that various organic reducing hydroquinones agents can be obtained by only change the substituents on the hydroquinone rings. Substituted hydroquinones can construct a large and useful library of dynthetic antioxidants. (4) Electron-donating groups decrease the BDE values, while electron-withdrawing groups make hydrogen abstraction more energetically demanding, which is in accordance with experimental observation of phenols.

5. Substituent Effects. From Table 1, it is clear that the oxidation potentials, the Gibbs free energies of H_2Q and HQ to release proton and hydrogen atoms are strongly dependent on the nature of the substituents. To elucidate the relations of the nature of the substituents with the oxidation potentials and the proton and hydrogen atom releasing Gibbs free energies, the effects of the remote substituents were examined on the $E^{ox}{}_{NHE}(H_2Q^{\bullet+}/H_2Q)$, pK_{a1}, pK_{a2}, BDE_1, and BDE_2, and the results show that the $E^{ox}{}_{NHE}(H_2Q^{\bullet+}/H_2Q)$, pK_{a1}, pK_{a2}, BDE_1, and BDE_2 of the ten chemical and electrochemical processes (five for hydroquinones and five for catechols) all are linearly dependent on the sum of Hammett substituent parameters σ_p with very good correlation coefficients, which not only indicating that the Hammett linear free energy relationship all holds in the ten electrochemical and chemical processes but also suggesting that the concerted effects of the multiple substituents have good linear additivity on the oxidation potentials and proton and hydrogen atom releasing Gibbs free energy changes. From the slopes and the intercepts of the ten straight lines, the corresponding ten mathematical formulas can be easily derived, respectively. Evidently, for any one- or multisubstituted hydroquinones or catechols, it is not difficult to safely estimate the values of the corresponding oxidation potentials, proton, and hydrogen dissociation energies, as long as the corresponding Hammett substituent parameters σ_p are available. Since the family of the hydroquinones and catechols are very large and most of the Hammett substituent parameters are easily obtained from literature, it is evidently that the ten formulas should have very extensive applications in the prediction of the related thermodynamic driving forces of various hydroquinones to provide electron, proton and hydrogen atom.

p-H_2Q

$$E^{ox}{}_{NHE}(H_2Q^{\bullet+}/H_2Q) = 1.66\sum\sigma_p + 0.54 \quad (20)$$

$$pK_{a1} = -5.69\sum\sigma_p + 16.54 \quad (21)$$

$$pK_{a2} = -5.19\sum\sigma_p + 23.91 \quad (22)$$

$$BDE_1 = 3.43\sum\sigma_p + 82.29 \quad (23)$$

$$BDE_2 = 4.64\sum\sigma_p + 67.70 \quad (24)$$

o-H_2Q

$$E^{ox}{}_{NHE}(H_2Q^{\bullet+}/H_2Q) = 1.85\sum\sigma_p + 0.46 \quad (25)$$

$$pK_{a1} = -5.53\sum\sigma_p + 13.28 \quad (26)$$

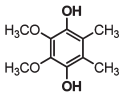
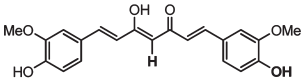
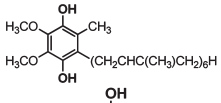
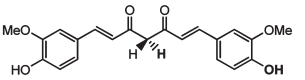
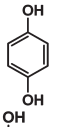
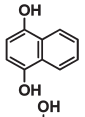
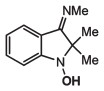
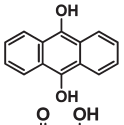
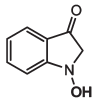
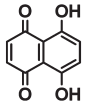
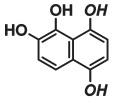
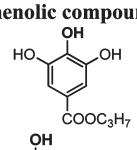
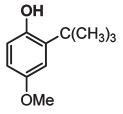
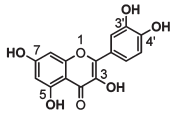
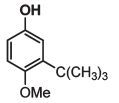
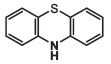
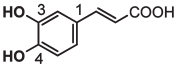
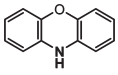
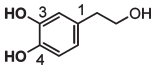
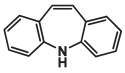
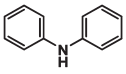
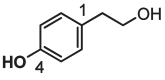
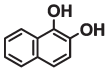
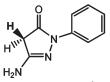
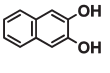
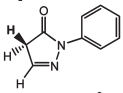
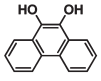
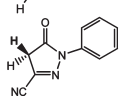
$$pK_{a2} = -5.24\sum\sigma_p + 26.70 \quad (27)$$

$$BDE_1 = 3.54\sum\sigma_p + 82.08 \quad (28)$$

$$BDE_2 = 3.82\sum\sigma_p + 75.93 \quad (29)$$

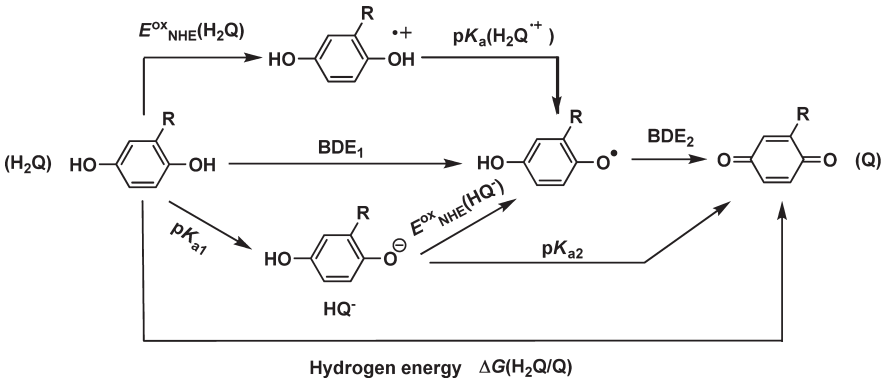
Equations 23, 24, 28, and 29 show that all the correlation slopes are positive, suggesting electron-donating groups decrease the hydrogen atom releasing energies and increase the hydrogen atom donating abilities. However, electron-withdrawing groups show the opposite effect. This is in accordance with the former experimental observation of the substituent effects on the bond dissociation energies of the O−H bonds in phenols. These positive slopes also indicate that electron-donating groups decrease the bond dissociation energies and electron-withdrawing groups decrease the proton dissociation energies, which suggest that more electron-donating groups should be added if we need an antioxidant and more electron-withdrawing groups should be added if we need a strong acid. Concerning the hydroquinone reduction mechanism, we can predict that the hydroquinones with more electron-donating groups may proceed direct hydrogen atom transfer and those with more

TABLE 2. O−H Bond Dissociation Energies of Various Antioxidants (kcal/mol)

compound	BDE	Ref.	compound	BDE	Ref.
Ubiquinol			**Curcuminoids**		
	82.1, 79.7, 81.2±2.0, 78.5±1.5	30		O-H[a] 86.1, 86.6, 80.2, 80.1, 80.4 C-H 115.9, 116.1	34,35
	81.6, 82.0	31		O-H 87.0, 82.5 C-H 91.1, 90.3	34,35
	83.4				
			Indolinonic hydroxylanmine		
	77.7			61.4	36
	69.8			65.6	36
	92.1				
			Phenolic compounds		
	70.0			77.1,75.9	37
				80.7, 78.2	37
Flavonoid					
	3 85.5 5 99.9 7 93.2 3' 81.8 4' 78.7	31,32		84.0, 81.0	37
			Phenothiazine		
				79.3±0.3,76.6, 82.3, 76.8, 78.6	38-42
Olive					
	3 81.8 4 78.9, 77.7, 73.6 1	33,20		77.2±0.3, 79.7	38,40
	3 80.1 4 79.4, 78.4, 73.4 9	33,20		82.4±0.5, 84.6,	38,40
	83.3			85.8±0.7,84.7, 87.5, 85.1, 86.2	38-42
	87.8, 85.4, 81.96				
			Edaravone		
	76.0			77.3, 77.9	43
	83.8			76.8, 79.0	43
	73.5			77.2, 79.6	43

[a]86.1 for weaker phenolic OH group (left side on drawing), 86.6 for the stronger.

SCHEME 4. Possible Pathways of the Conversion of Hydroquinones to Hydroquinone Radicals



electron-withdrawing groups may proceed proton dissociation and then electron transfer mechanisms.

Equations 23, 24, 28, and 29 also show that the correlation intercept between BDE and σp are similar for hydroquinoes and catechols, indicating that with the same groups, hydroquinoes have similar hydrogen atom donating abilities to the corresponding catechols. Because of the electronic repulsion effect, hydroquinone radicals have larger hydrogen atom donating abilities than those of corresponding catechol radicals. Furthermore, hydroquinone radicals or catechol radicals have smaller hydrogen atom releasing energies than those of corresponding hydroquinone or catechol, not only indicating radicals have samller hydrogen atom donating abilities than those of corresponding hydroquinones, but also suggesting that the reactions of hydroquinone radicals would usually associate with the releasion of the hydrogen atoms.

As stated in the Introduction section, the hydrogen atom transfer from the H_2Q generally were initiated by single electron transfer, an incipient radical cation intermediate $H_2Q^{\bullet+}$ should be formed, from which proton transfer is believed to follow in the second reaction step, or initiated by proton transfer from which electron transfer is believed to follow in the second reaction step. The proton dissociation energies of hydroquinone radical cations or the oxidation potentials of hydroquinone anions can be obtained according to the following thermodynamic cycle. Combined with some other thermodynamic cycles (see Supporting Information), eqs 30−32 were derived.

$$E^{ox}{}_{NHE}(HQ^-/HQ^{\bullet}) = (BDE_1 - 2.303RT_pK_{a1})/F + E^{ox}{}_{NHE}(H^+/H^{\bullet}) \quad (30)$$

$$pK_a(H_2Q^{\bullet+}) = \{BDE_1 - F[E^{ox}{}_{NHE}(H_2Q/H_2Q^{\bullet+}) - E^{ox}{}_{NHE}(H^+/H^{\bullet})]\}/(2.303RT) \quad (31)$$

$$\Delta G(H_2Q/Q) = BDE_1 + BDE_2 - 2\Delta G^0{}_f(H^{\bullet}) \quad (32)$$

According to these three equations, linear correlations between oxidation potentials of hydroquinone anions, pK_a values of hydroquinone radical caitons, and the hydrogen energies of quinines against the Hammett substituent σ_p were summarized in eqs 33−38.

p-H_2Q

$$E^{ox}{}_{NHE}(HQ^-/HQ^{\bullet}) = 0.49\sum\sigma_p + 0.11 \quad (33)$$

$$pK_a(H2Q^{\bullet+}) = -25.58\sum\sigma_p + 9.27 \quad (34)$$

$$\Delta G(H_2Q/Q) = 8.07\sum\sigma_p + 44.79 \quad (35)$$

o-H_2Q

$$E^{ox}{}_{NHE}(HQ^-/HQ^{\bullet}) = 0.48\sum\sigma_p + 0.29 \quad (36)$$

$$pK_a(H_2Q^{\bullet+}) = -28.72\sum\sigma_p + 10.48 \quad (37)$$

$$\Delta G(H_2Q/Q) = 7.36\sum\sigma_p + 52.81 \quad (38)$$

According to these equations, $E^{ox}{}_{NHE}(HQ^-/HQ^{\bullet})$, $pK_a(H_2Q^{\bullet+})$, and $\Delta G(H_2Q/Q)$ can be easily estimated by only knowing the structures of the hydroquinones (hydroquinones, catechols, and the substituents attached on them).

6. Difference between Hydroquinones and Catechols. According to our earlier discussion, we know that hydroquinone is a stronger electron donor than catechol. The main reason could be that the state free energies of hydroquinone and catechol, as well as hydroquinone radical cation and catechol radical cation could be different from each other (Figure 4). From Figure 4, it is clear that the state free energy

(30) (a) Espinosa-Garcia, J. *J. Am. Chem. Soc.* **2004**, *126*, 920. (b) Espinosa-Garcia, J. *J. Phys. Chem. A.* **2004**, *108*, 2508. (c) Aberg, F.; Appelkvist, E. L.; Dallner, G.; Ernter, L. *Arch. Biochem. Biophys.* **1992**, *295*, 230.
(31) Li, M. J.; Liu, L.; Fu, Y.; Guo, Q. X. *J. Mol. Struct.(THEOCHEM)* **2007**, *815*, 1.
(32) Leopoldini, M.; Marino, T.; Russo, N.; Toscano, M. *J. Phys. Chem. A* **2004**, *108*, 92.
(33) Menadis, N.; Wang, L. F.; Tsimidou, M. Z.; Zhang, H. Y. *J. Agric. Food. Chem.* **2005**, *53*, 295.
(34) Sun, Y. M.; Zhang, H. Y.; Chen, D. Z.; Liu, C. B. *Org. Lett.* **2002**, *4*, 2909.
(35) Wright, J. S. *J. Mol. Struct.(THEOCHEM)* **2002**, *591*, 207.
(36) Zhang, H. Y.; Wang, L. F. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 225.
(37) Wright, J. S.; Johnson, E. R.; Di Labio, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 1173.
(38) Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Valgimili, L.; Gigmes, D.; Tordo, P. *J. Am. Chem. Soc.* **1999**, *121*, 11546.
(39) Pratt, D. A.; Dilabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085.
(40) Bordwell, F. G.; Zhang, X. M.; Cheng, J. P. *J. Org. Chem.* **1993**, *58*, 6410.
(41) Gomes, J. R. B.; Ribeiro da Silva, M. D. M. C.; Ribeiro da Silva, M. A. V. *J. Phem. Chem. A* **2004**, *108*, 2119.
(42) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1993**, *58*, 6410.
(43) Wang, L. F.; Zhang, H. Y. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3789.

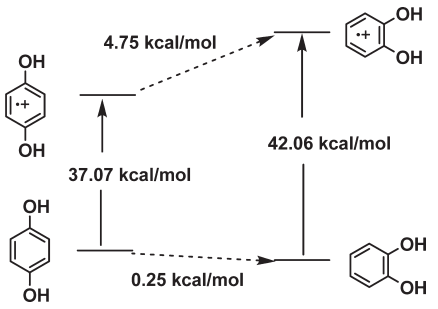


FIGURE 4. Difference of oxidation potentials between hydroquinone and catechol calculated by theoretical methods.

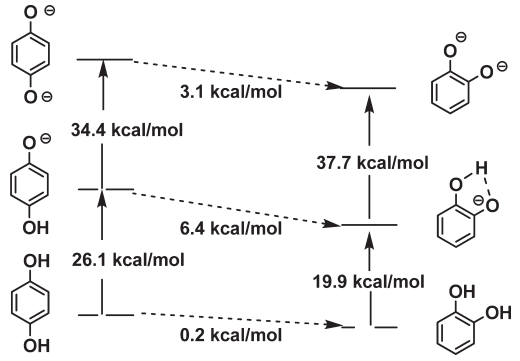


FIGURE 5. Difference of proton dissociation energies between hydroquinone and catechol in DMSO.

of hydroquinone is very similar to that of catechol. However, the state free energy of catechol radical cation is much larger than that of hydroquinone radical cation, the reason could be that the intramolecular hydrogen bond is very weak in catechol radical cation, whereas the electronic repulsion effect is similar to that of catechol. Evidently, combination of the two factors mentioned above makes the oxidation potential of hydroquinone is much smaller than that of catechol.

Equations 20 and 25 show catecholes have larger oxidation potentials (more positive) than hydroquinones when the same substituents attached on them. The line slopes of E^{ox}_{NHE} against σ_p are 1.66 and 1.85 for hydroquinones and catechols, respectively. The positive slopes of the two regressions indicate that the oxidation of the hydroquinones would be mainly dependent on the stabilities of the corresponding radical cations. By comparing the magnitude of the line slopes for hydroquinones and catechols, it is found that the effect of the substituents in the case of catechols is slightly larger than that in the case of hydroquinones, the reason could be that the delocalization of the positive charge on hydroquinones is much delocalized than those of catechols.

Table 1 also indicates that the proton dissociation energy of catechol is smaller by about 6.2 kcal/mol than that of hydroquinone, the reason could be the existence of the intramolecular hydrogen bond in catechol anion. However, hydroquinone anion has smaller proton releasing energy than that of catechol anion by about 3.3 kcal/mol, which indicates that catechol dianion is more stable than that of hydroquinone dianion by about 3.1 kcal/mol. In fact, because of the electrostatic repulsion effect occurs between the two oxygen anions in catechol, catechol dianion is more unstable than hydroquinone dianion in the gas phase. However, the case is reversed in DMSO since the solvation effects on the catechol dianion is much larger than that on the corresponds hydroquinone dianion, which makes the catechol dianion more stable than hydroquinone dianion in DMSO (Figure 5).

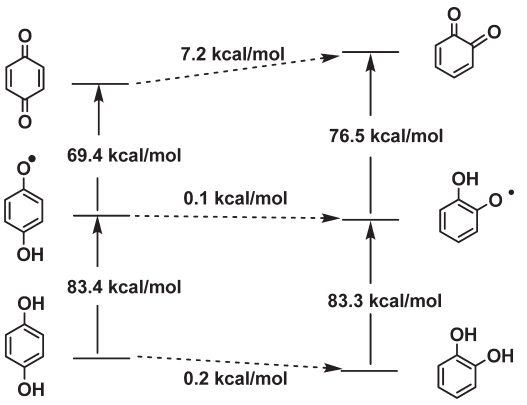


FIGURE 6. Difference of hydrogen dissociation energies between hydroquinone and catechol calculated by theoretical methods.

Equations 21, 22, 26, and 27 show that the four linear correlations have similar slopes (−5.2 to −5.7), suggesting that the substituents have similar effects on the proton releasing energies of hydroquinoes, catecholes as well as corresponding anions. Electron-donating groups increase the proton dissociation energies and decrease the proton donating abilities, whereas electron-withdrawing groups show the reverse effect. However, the correlation intercepts are different from each other. The intercepts of the correlation between pK_{a1} values against σ_p of hydroquinones are generally smaller than that of the correlation between pK_{a2} values against σ_p of correspond anions by about 7.4, suggesting hydroquinone anions are more difficult to release the protons than corresponding hydroquinones, the reason could be that oxygen anion is, in fact, an strong electron-donating groups. The difference of the intercept of the correlations, pK_{a1} vs σ_p and pK_{a2} vs σ_p, for catechols follows the similar trends. Because of the intramolecular hydrogen bond, the pK_{a1} values of hydroquinones are generally larger than those of catechols and the cases are reversed in the order of the pK_{a2} values of hydroquinone anions and catechol anions.

Concerning the bond dissociation energies, Table 1 indicates that hydroquinone and catechol have very similar bond dissociation energies. The reason could be that the state free energies of hydroquinone and catechol as well as corresponding neutral radicals are similar to each other, respectively. However, the hydrogen atom releasing ability of hydroquinone radical is much larger than that of catechol radical, suggesting that hydroquinone radical is a better hydrogen atom donor than catechol radical. This can be attributed to the fact that the state free energy of *o*-quinone is higher than that of *p*-quinone (Figure 6).

7. Hydrogen Bond Effects. From the above discussion, it is not difficult to conclude that the oxidation potentials between hydroquinones and catechols with the same substituents are similar to each other, whereas the pK_a values and hydrogen dissociation energies are different from each other. The main reason could be the existence of the intramolecular hydrogen bonds in catechols. In fact, the cooperativity of hydrogen bond plays an important role in controlling and

SCHEME 5. Hydrogen Bonds of the Interesting Compounds

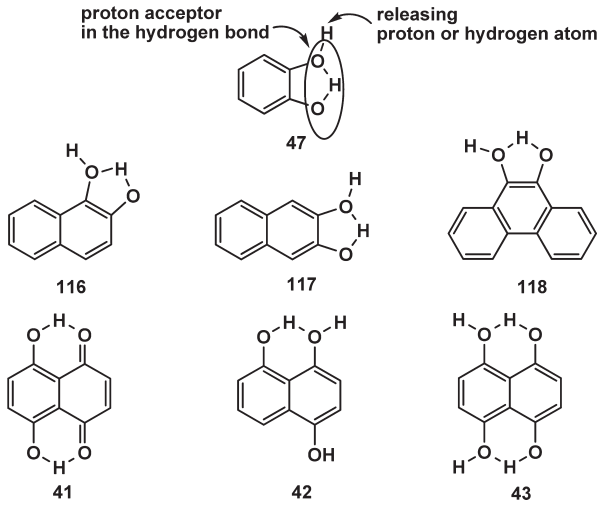


TABLE 3. Intramolecular Hydrogen Bond Energies (Gibbs Free Energies) of Neutral, Radical Cation, Radical, and Anion Species

	hydrogen bond energies in DMSO (kcal/mol)			
compounds	neutral	radical cation	radical	anion
47	−0.68	−0.29	−2.37	−4.94
116	−0.71	−1.46	a: −2.65	a: −3.45
			b: −4.93	b: −3.70
117	−0.95	−0.53	−2.25	−4.44
118	−1.51	−1.57	−3.90	
42	−6.17	−5.61	−7.91	−8.14
41 (first)	−6.57	−5.97		
41 (second)	−3.52	−2.45	−8.01	−13.21
43 (first)	−3.67	−3.08	−8.64	−12.72
43 (second)	−4.03	−3.20	−2.94	−2.84

regulating the processes occurring in living organisms. Many physical and chemical properties of materials are determined by hydrogen bonding cooperativity.[44] However, despite the great importance of the intramolecular hydrogen bonds, only a few experimental and theoretical studies dealing with the estimation of their intramolecular hydrogen bond enthalpies.[45] Furthermore, although the vast majority of the computed intramolecular hydrogen bond energies determined in the literature refer to gas-phase reactions, most of the chemistry to which they are applied occurs in solution. In the present study, we have a unique opportunity to bridge the gap to reliably investigate the intramolecular hydrogen bond in neutral, radical cation, radical and anion species in DMSO. Undoubtedly, these results would be very useful in material chemistry and physical chemistry.

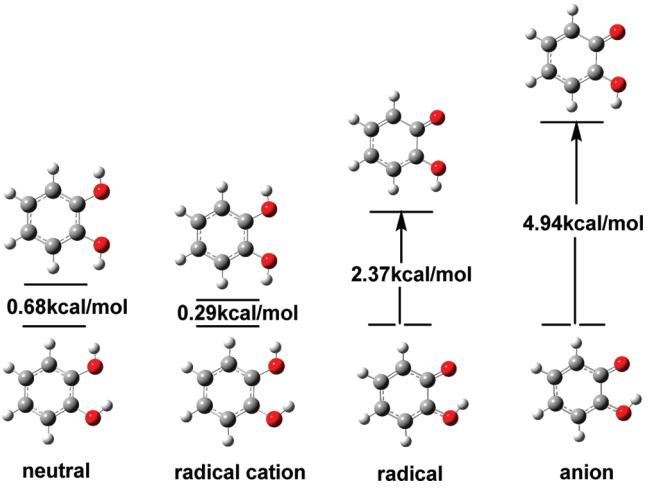


FIGURE 7. Relative hydrogen bond energies (Gibbs free energies), with respect to the most stable neutral, radical cation, radical, and anion conformers of **47** in DMSO.

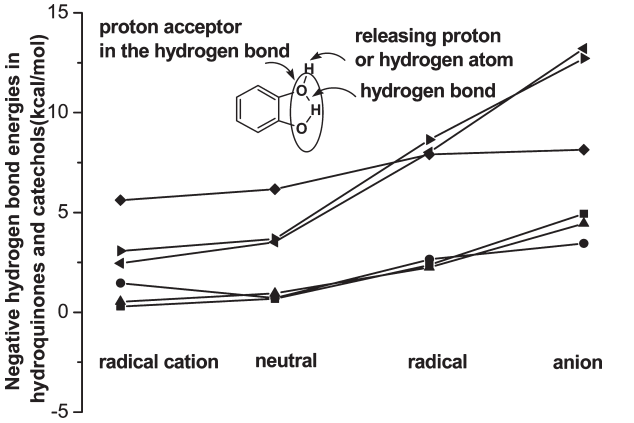


FIGURE 8. Hydrogen bond energies (Gibbs free energies) of hydrquinones and catechols with different charge and spin densities in DMSO.

In this connection, we take some compounds, **47**, **116**, **117**, **118**, **41**, **42**, and **43**, which have classical intramolecular hydrogen bonds, as examples (Scheme 5). Intramolecular hydrogen bond energies of these species in neutral, radical cation, radical, and anion conformers, which were calculated by comparing the Gibbs free energies at 298 K for the intramolecular hydrogen conformer and the lowest energy, fully optimized conformer, in which the hydroxyl group is pointing away from the other hydroxyl, were summarized in Table 3.[46] To illustrate the intramolecular hydrogen bond more clearly, the detailed conformations of neutral, radical cation, radical and anion of compound **47** were listed in Figure 7.

Examination of the calculated results summarized in Table 3, the following conclusions can be made:

(1) The strongest intramolecular hydrogen bond is in anion state of compound **41** (32.7 kcal/mol in the

(44) Steiner, T. *Angrew. Chem. Int. Ed.* **2002**, *41*, 48 and references therein.

(45) (a) Lampert, H.; Mikenda, W.; Karpfen, A. *J. Phys. Chem.* **1996**, *100*, 7418. (b) Catalán, J.; Palomar, J.; De Paz, J. L. G. *J. Phys. Chem. A* **1997**, *101*, 7914. (c) Chung, G.; Kwon, O.; Kwon, Y. *J. Phys. Chem. A* **1997**, *101*, 9415. (d) Levy, J. B.; Martin, N. H.; Hargittai, I.; Hargittai, M. *J. Phys. Chem. A* **1998**, *102*, 274. (e) Kovács, A.; Hargittai, M. *J. Phys. Chem. A* **1998**, *102*, 3415. (f) Simperler, A.; Lampert, H.; Mikenda, W. *J. Mol. Struct.* **1998**, *448*, 191. (g) Kovács, A.; Macsári, I.; Hargittai, M. *J. Phys. Chem. A* **1999**, *103*, 3110. (h) Cuma, M.; Scheiner, S.; Kar, T. *J. Mol. Struct. (THEOCHEM)* **1999**, *467*, 37. (i) Palomar, J.; De Paz, J. L. G.; Catalán, J. *J. Phys. Chem. A* **2000**, *104*, 6453. (j) Broquier, M.; Lahmani, F.; Zehnacker-Rentien, A.; Brenner, V.; Millié, Ph.; Peremans, A. *J. Phys. Chem. A* **2001**, *105*, 6841. (k) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2001**, *105*, 10462. (l) Korth, H.-G.; de Heer, M. I.; Mulder, P. J. *J. Phys. Chem. A* **2002**, *106*, 8779. (m) de Heer, M. I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969.

(46) Lithoxoidou, A. T.; Bakalbassis, E. G. *J. Phys. Chem. A.* **2005**, *109*, 366.

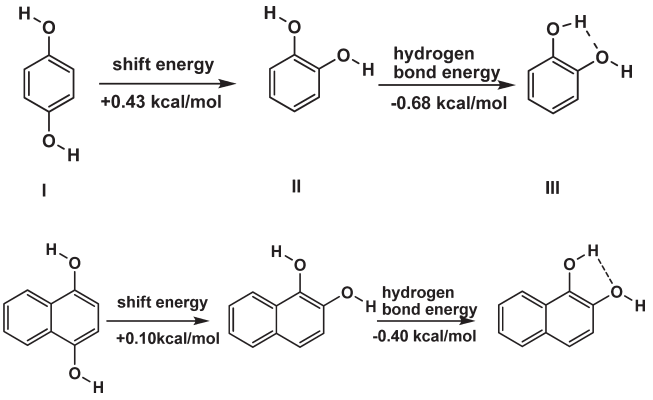
(47) Del Bene, J. E.; Frisch, M. J.; Pople, J. A. *J. Phys. Chem.* **1988**, *89*, 3669.

gas-phase and 13.2 kcal/mol in DMSO), similar to the intermolecular hydrogen bond $[H_2O-H-OH_2]^+$ (33 kcal/mol in the gas-phase).[47] The weakest intramolecular hydrogen bond is in neutral state of compound **117** (4.0 kcal/mol in the gas-phase and 0.40 kcal/mol in DMSO). Such a large scale of hydrogen bond energies shows that the strength of the intramolecular hodrogen bonds are different so much between hydroquinones and catechols. In this sense, we should also be cautious with the gas-phase hydrogen bond energies since hydrogen bonds are always influenced by their environment.

(2) Concerning the same molecule, one may conclude that the hydrogen bond energies in different charge and spin states are in the order of anion > radical > radical cation ≈ neutral, not only indicates that the hydrogen bonds in anion and radical state are all red-shifting hydrogen bonds[48] but also suggests that larger polarity of the molecule corresponding to larger intramolecular hydrogen bond. Because of the opposite orientation of the electronic properties of the molecules and the solvation effects in determining the solution phase molecular properties, we can expect that intramolecular hydrogen bond will be smaller in more polar/protic solvent. This prediction agrees well with the experimental observations. The hydrogen bond energies in anions are larger than those in corresponding radicals, and much larger than that in neutral species, which can be traced by examining the charge densities of the proton acceptor oxygen atom (O−H···**O**) from natural population analysis. For instance, the charge densities of the proton acceptor oxygen atom is −0.8157, −0.5609, and −0.221 for anion, radical, and neutral catechol, respectively. The more negative charge densities the proton acceptor oxygen atom has, the larger the hydrogen bond is. Interestingly, the intramolecular hydrogen bonds in radical cation are similar to those of corresponding neutral state species. For example, the intramolecular hydrogen bonds for radical cation and neutral state catechol are 1.42 and 0.68 kcal/mol, respectively. This result should be attributed to the large solvation energies of the radical cation species. In fact, due to the more negative charge densities of the proton acceptors (−0.221 vs −0.0846) and smaller bond length of the O−H···O in neutral species than those in radical cation state(2.15 vs 2.17 Å), the intramolecular hydrogen bonds in neutral state are larger than those in corresponding radical cation state in the gas-phase.

(3) In view of the intramolecular hydrogen bond in **47**, **117**, **118**, **119** and **41**, **42**, **43**, it is not difficult to find that the hydrogen bond energies in the former series are smaller than those in the latter series, indicating the intramolecular hydrogen bond in five membered rings are weaker than those in the six-membered rings, the reason could be that the O−H···O bond lengths in six membered rings are smaller than those in five membered rings. For example, the O−H···O bond lengths in **41**, **42**, **43** radicals are1.63, 1.68, 1.63 Å, respectively, smaller by about 0.3−0.4 Å than those in **116**, **117**, **118** radicals (they are 2.02, 2.06, 2.00 Å, respectively). The stronger intramolecular hydrogen bonds also result in the more stability of the compound. Based on this fact, it is reasonable to predict that the proton and hydrogen atom releasing process from the proton acceptor oxygen atom will be more easily from the six membered rings than those from the five member rings, in both of which there are intramolecular hydrogen bonds. From Table 1, it is clear that the bond dissociation energies of the O−H bonds are 72.5 and 70.8 kcal/mol in **42** and **43**, respectively, whereas those in **116** and **117** are 76.0 and 83.3 kcal/mol, respectively. These calculated results agree well with our predictions.

SCHEME 6. Shift Energy and Hydrogen Bond Energy



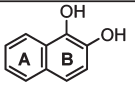
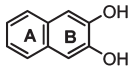
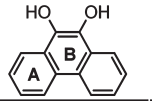
(4) The intramolecular hydrogen bond Gibbs free energies of catechol and of corresponding radical are 0.7 and 1.4 kcal/mol, respectively, whereas corresponding intramolecular hydrogen bond enthalpies are 2.5 and 3.5 kcal/mol, respectively,[49] suggesting the entropic contribution to the hydrogen bond Gibbs free energies are very small. This is easily understandable by considering that there is only one hydrogen atom changed from one place to another. However, intermolecular hydrogen bond usually associated with large entropic changes.

(5) From the above discussion, it is clear that the catechol is more stable than hydroquinone by about 0.25 kcal/mol, while the intramolecular hydrogen bond in catechol is 0.68 kcal/mol, it is conceived to estimate the shift energy of the hydroxyl bond from position 4 to the position 2 is 0.43 kcal/mol. The shift of the hydroxyl bond is an endothermic process since the repulsion of the σ-electron-donating group. If the reaction is the isomeric conversion from hydroquinone to catechol (Scheme 6), we can estimate that isomer II may be one of the intermediates. The hydroxyl group first departs from position 4 to form intermediates II (endothermic), which then produce the final product catechol because of the intramolecular hydrogen bond (exothermic).By using similar process, it is not difficult to predict the shift energies

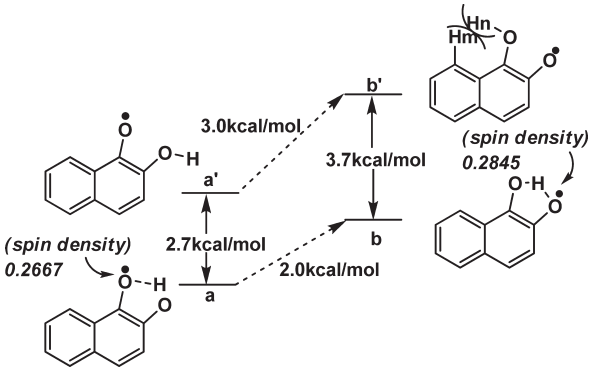
(48) (a) Li, Q.; An, X.; Gong, B.; Cheng, J. *J. Phys. Chem. A* **2007**, *111*, 10166. (b) Klein, R. A. *Chem. Phys. Lett.* **2006**, *433*, 165. (c) Ziokowski, M.; Grabowski, S. J.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 6514.

(49) (a) Schaefer, T. *J. Phys. Chem.* **1975**, *79*, 1888. (b) Kollman, P.; Allen, L. C. *J. Am. Chem. Soc.* **1971**, *93*, 4991.

TABLE 4. NICS(1) Values of Compound 116, 117, and 118

compound			NICS(1)				
			H_2Q	$H_2Q^{\bullet+}$	$HQ^{\bullet}$	HQ^{-}	Q
116		A	-9.97	-5.09	-9.09	-8.59	-8.58
		B	-10.37	-0.93	-2.86	-9.85	3.55
117		A	-10.37	4.06	-4.90	-8.79	2.99
		B	-10.64	4.99	-1.12	-8.93	7.24
118		A	-10.38	-4.65	-9.01	-9.97	-7.93
		B	-7.71	0.74	-1.44	-8.13	4.11

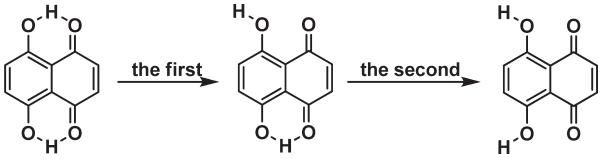
SCHEME 7. Intramolecular Hydrogen Bonds in 116 Radical



of the hydroxyl bond in **93** is 0.1 kcal/mol. According to these results, we can rationalize that the shift energies of **99** and the hydrogen bond energies of the corresponding isomers of **99** will be smaller. In other words, with the increasing of the aromaticity of the system, the isomer energies between hydroquinones and corresponding catechols will become smaller and smaller. On the basis of this conclusion, it is rationale to predict that anthracene-1,4-diol and corresponding anthracene-1,2-diol could not be separated by conventional experimental methods.

(6) For radical and anion species of compound **116**, there are two possible isomers **a** and **b** (Scheme 7). According to our calculated results (take the radical state as an example), the intramolecular hydrogen bond in isomer **a** is 2.7 kcal/mol, smaller by about 1.0 kcal/mol than that in **b**, the reason could be that the state free energies of radical isomers **a** and **b**, as well as isomers **a**′ and **b**′, in which the hydroxyl group is pointing away from the oxygen atom are different from each other. Isomer **a** is more stable than isomer **b** by about 2.0 kcal/mol because of the lower spin densities of the proton acceptor oxygen radical (0.2667 and 0.2845 for **a** and **b**, respectively). In addition, because of the large repulsion effect between the hydrogen atoms ($\mathbf{H}_m$ and $\mathbf{H}_n$) exist in **b**′, which does not exist in **a**′, isomer **a**′ is more stable than **b**′ by about 3.0 kcal/mol. Evidently, combination of the two factors mentioned above makes the hydrogen bond energies in **a** is smaller by 1.0 kcal/mol than that in **b**. However, the difference of the intramolecular hydrogen bond between **a** and **b** is only a theoretical estimation result, we may not separate these two isomers and their corresponding intramolecular hydrogen bonds by experimental methods at present.

SCHEME 8. First and the Second Hydrogen Bond of Compound 41



(7) Examination of Table 3 also shows that there are two intramolecular hydrogen bonds for compound **41** and **43** (Scheme 8). Contrary to the observation that the first hydrogen bond becomes stronger with the increasing of the polarity of the molecule, the second hydrogen bond follows the opposite trend. For example, the second hydrogen bond is 4.16 kcal/mol in neutral **43**, larger than that in radical cation **43** by about 0.8 kcal/mol and much larger than that in radical **43** by about 0.95 kcal/mol. However, the differences of the hydrogen bond energies are very small between the radical cation state and radical state, as well as in anion state of compound **43**, indicating that the charge densities and spin densities of the molecule have little effect on the second hydrogen bond energies. Based on this conclusion, it is not difficult to estimate that solvation will have little effect on the second hydrogen bond energies. If there are three or more hydrogen bonds in the same molecule, the third hydrogen bond energies in radical cation, radical, as well as anion, state of the molecule will be closer to each other and smaller than 4 kcal/mol.

8. Phenyl Ring Effect. To the best of our knowledge, hydroquinones and their phenyl ring substituted series occupy a central place in electron transfer chemistry and biological energy conversion. For example, menaquinone, or vitamin K2, is made up of a 1,4-naphthoquinone headgroup with a methyl substituent at the 2 position and an isoprenoid chain of varying length at the 3 position. Some forms of vitamin K are known to be critical in the blood-clotting cascade and in calcium momeostasis, and the Rieske FeS center in certain baceria uses a menaquinone pool, rather than plastoquinone or ubiquinone. Various properties of these molecules, such as their fundamental vibrational frequencies and their hyperfine interactions, are used to infer information such as binding sites and protein interaction in the photosynthetic reaction center. However, a knowledge of thermodynamic

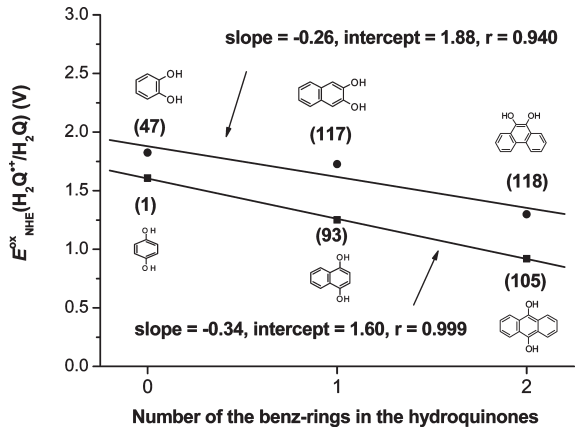


FIGURE 9. Relationship of oxidation potentials of aromatic hydroquinones in DMSO with the number of benzene rings in the aromatic hydroquinones.

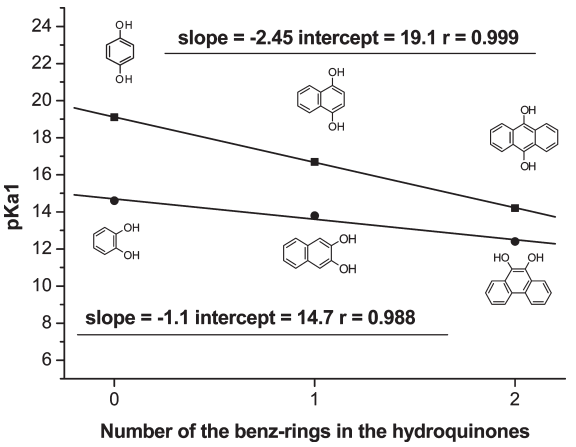


FIGURE 10. Relationship of proton dissociation energies of aromatic hydroquinones in DMSO with the number of benzene rings in the aromatic hydroquinones.

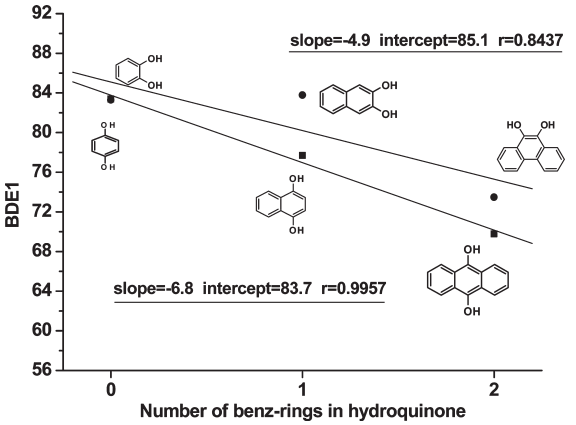


FIGURE 11. Relationship of hydrogen atom releasing energies of aromatic hydroquinones in DMSO with the number of benzene rings in the aromatic hydroquinones.

properties, such as oxidation potentials, proton and hydrogen atom releasing energies are still unreleased in the literature until now.

Detailed thermodynamic parameters of substituted hydroquinone-naphthoquinones and hydro-anthraquinones were listed in Table 1, and their scales and substituent effects have been discussed in detail in the former part. In this connection, we mainly examine the phenyl ring effects on the oxidation potential, proton and hydrogen atom releasing energies of hydroquinone, hydro-naphthoquinone and hydro-anthraquinone.

By examining the oxidation potentials of hydroquinones with aromatic structures (hydroquinones **1**, **93**, and **105** and catechols **47**, **117**, and **118**) in Table 1, it is found that the oxidation potentials of the hydroquinones decrease in the order of **1** > **93** > **105**, and the oxidation potentials of catechols decreased in the order **47** > **117** > **118**, which indicates that the larger the aromatic system of the hydroquinone is, the smaller the oxidation potential of the hydroquinone is. The main reason causing this could be that the odd electron can delocalized in the three phenyl rings in hydro-anthraquinone radical cation whereas it only delocalized in one phenyl ring in hydroquinone. When the oxidation potentials of hydroquinones (**1**, **93**, and **105**) and catecholes (**47**, **117**, and **118**) were plotted against the number of benzene rings of the hydroquinones and catechols, respectively, it was unexpected to found that the oxidation potentials of hydroquinones and catechols have good linear relationships to decrease with the increase of the number of benzene rings in the hydroquinones and catechols (Figure 9). According to this relationship, the oxidation potentials of aromatic hydroquinones and catechols containing three or more benzene rings can be predicted. Furthermore, it is clear that aromatic hydroquinones will be very effective electron donors and may thus be useful in the invention of new materials and new reactions.

From Table 1, we can also find that the proton releasing energies of the hydroquinones decrease in the order of **1** > **93** > **105**, and those of catechols decreased in the order **47** > **117** > **118**. It is worth noting that there are also two linear correlations between pK_{a1} values of hydroquinones or catechols and the numbers of the benzene rings, respectively (Figure 10), which shows the existence of the phenyl ring effects on the proton releasing process, the main reason causing this could be that the hydroquinones with larger aromatic system could have larger ability to delocalize the anion, which ultimately stabilize the corresponding proton releasing product.

Concerning the hydrogen atom releasing process, Table 1 and Figure 11 indicate that bond dissociation energies of the O−H bond in hydroquinones have a good linear correlation with the numbers of the phenyl ring. However, the O−H bond dissociation energy in **117** is larger than that in **47**, suggesting the linear relation between the BDE and the numbers of the phenyls do not exist in hydrocatechol series, the reason could be that the releasing of the hydrogen atom from **117** makes the large change of the molecular structure, which can be shown from the structure parameters and the calculated NICS (1) values. From Table 4 it can be found the NICS(1) values of the **B** ring in **117** is only 1.12, much smaller than those of **116** and **118**. The smaller the NICS(1) value is, the unstability the compound is. So the O−H bond dissociation energy of **117** is larger than those of **116** and **118**. This also tells us that we should be cautious when we make the correlation between the oxidation potentials, proton and

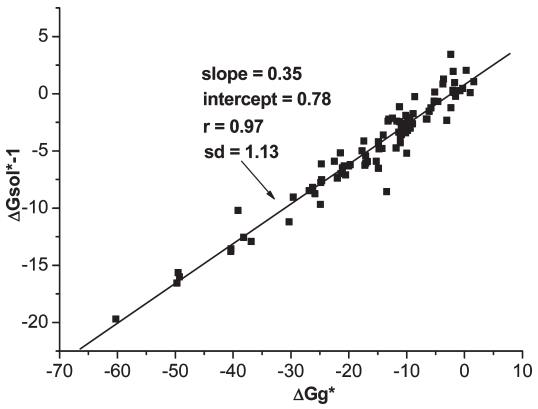


FIGURE 12. Dependence of the relative oxidation potentials of the various hydroquinones and catechols in DMSO on the corresponding ionization potentials in the gas phase.

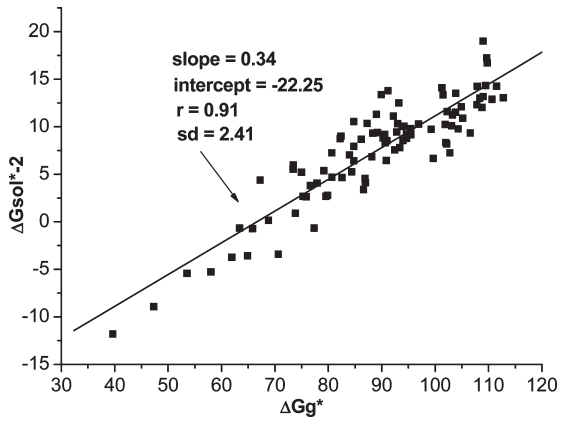


FIGURE 13. Dependence of the relative proton dissociation energies of the various hydroquinones and catechols in DMSO on the corresponding proton dissociation energies in the gas phase.

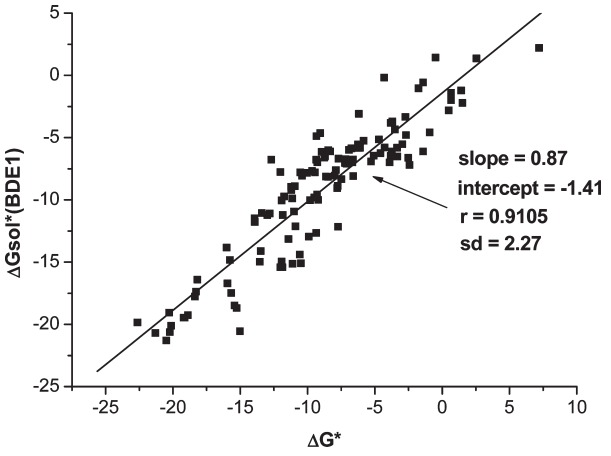


FIGURE 14. Dependence of the relative bond dissociation energies of the various hydroquinones and catechols in DMSO on the corresponding bond dissociation energies in the gas phase.

hydrogen dissociation energies of hydroquinones or catechols, and the numbers of the benzene rings, respectively.

9. Solvation Effects. As well-known, unlike the electron transfer, hydrogen atom and proton transfer in gas-phase, these processes in solution for hydroquinones and catechols are not only dependent on the structures of hydroquinones and catechols but also dependent on the nature of solvent. To quantitatively estimate the relative contribution of the solvation effect to the thermodynamic driving forces of these three processes, the plots of the relative ionization potentials, proton dissociation, and hydrogen dissociation energies in the gas-phase against the relative oxidation potentials, proton dissociation and hydrogen dissociation energies in DMSO were made, respectively (Figures 12−14).

From eqs 10−12, we know that

$$\Delta G^*_{sol} = \Delta G^*_g + G_{sol} \quad (39)$$

From Figure 12−14, it is clear that

$$\Delta G^*_{sol} = 0.35\Delta G^*_g + 0.78 \text{ for electron transfer process} \quad (40)$$

$$\Delta G^*_{sol} = 0.34\Delta G^*_g - 22.25 \text{ for proton transfer process} \quad (41)$$

$$\Delta G^*_{sol} = 0.87\Delta G^*_g - 1.41 \text{ for hydrogen atom transfer process} \quad (42)$$

According to eq 39, we obtained that

$$\Delta G_{sol} = -0.65\Delta G^*_g - 0.78 \text{ for electron transfer process} \quad (43)$$

$$\Delta G_{sol} = -0.66\Delta G^*_g + 22.25 \text{ for proton transfer process} \quad (44)$$

$$\Delta G_{sol} = -0.13\Delta G^*_g + 1.41 \text{ for hydrogen atom transfer process} \quad (45)$$

From the slopes of the plot lines and eqs 40−45, it is clear that 65%, 66%, and 13% of the gas-phase ionization potentials, proton dissociation energies and hydrogen atom transfer energies are offset by the solvation in the liquid phase oxidation potentials and proton and hydrogen atom transfer energies, respectively; the reason could be that no charge separation was made in the hydrogen atom transfer process whereas they were made in ionization and proton dissociation processes, which not only indicate that bond dissociation energies of the O−H bonds in hydroquinones and catechols are similar in the gas-phase and in DMSO but also show that gas-phase thermodynamic driving forces and solvation energies are tracking the same physical parameter: the appropriate physical property seems to be charge densities of the molecules.

Conclusions

Hydroquinones and catechols are well-known two-electron reductants which play important roles in chemistry, biology, industries, and our environmental science. In this work, the oxidation potentials, pK_a (pK_{a1} and pK_{a2}) values and bond dissociation energies (BDE_1 and BDE_2) of 118 important *p*- and *o*-hydroquinones in DMSO were predicted for the first time by using DFT method and the PCM cluster continuum model. The calculated results agree well with the available experimental determinations, respectively. From this paper, we get

(1) The oxidation potential scales of each series of H_2Q are 0.970−2.987 V for *p*-H_2Q, 1.247−3.050 V for *o*-H_2Q, 1.051−1.608 V for 1,4-H_2NQ, 0.856−1.357 V for 1,4-H_2AQ, and 0.824−1.104 V for 9,10-H_2AQ.

(2) The pK_{a1} scale of the hydroquinones in DMSO ranges from 2 to 21.5 for hydroquinones and from −1.7 to 17.7 for catechols, and the pK_{a2} scale ranges from 9.4 to 28.1 for hydroquinone anion and from 11.5 to 31.9 for catechol anions.

(3) BDE_1 scale of H_2Q in DMSO ranges from 70 to 92.1 kcal/mol for hydroquinones and from 77.7 to 91.3 kcal/mol for catechols. BDE_2 scale of H_2Q in DMSO ranges from 59 to 84.9 kcal/mol for hydroquinones and from 60 to 86 kcal/mol for catechols.

(4) All the five parameters correlate well with the Hammett substituent parameters (for *p*-H_2Q, $E^{ox}_{NHE}(H_2Q^{\bullet+}/H_2Q) = 1.66\Sigma\sigma_p + 0.54$, $pK_{a1} = -5.69\Sigma\sigma_p + 16.54$, $pK_{a2} = -5.19\Sigma\sigma_p + 23.91$, $BDE_1 = 3.43\Sigma\sigma_p + 82.29$, $BDE_2 = 4.64\Sigma\sigma_p + 67.70$; for *o*-$H_2Q$, $E^{ox}_{NHE}(H_2Q^{\bullet+}/H_2Q) = 1.85\Sigma\sigma_p + 0.46$, $pK_{a1} = -5.53\Sigma\sigma_p + 13.28$, $pK_{a2} = -5.24\Sigma\sigma_p + 26.70$, $BDE_1 = 3.54\Sigma\sigma_p + 82.08$, $BDE_2 = 3.82\Sigma\sigma_p + 75.93$), which hints we can get these parameters as long as the structures of the hydroquinones were known.

(5) Concerning the same molecule, the hydrogen bond energies in different charge and spin states are in the order of anion > radical > radical cation ≈ neutral. The intramolecular hydrogen bonds in five-membered rings are weaker than those in the six-membered rings. The entropic contribution to the hydrogen bond Gibbs free energies are very small.

(6) Solvation effects on oxidation, proton release, and hydrogen atom release process were systematically studied.

Acknowledgment. Financial support from the National Natural Science Foundation of cChina (Grant Nos. 21072104, 20921120403 and 20832004), the Ministry of Science and Technology of China (Grant No. 2004CB719905) and the 111 Project (B06005) is gratefully acknowledged. The calculations were performed on a Nankai Stars supercomputer at Nankai University.

Supporting Information Available: Comparison of theoretical proton, electron and hydrogen atom transfer driving forces of phenols in DMSO with the corresponding some available experimental data. The calculated gas phase Gibbs free energies and solution phase solvation energies in DMSO for hydroquinones at neutral, radical cation, radical and anion states. This material is available free of charge via the Internet at http://pubs.acs.org.