JOC Article
pubs.acs.org/joc

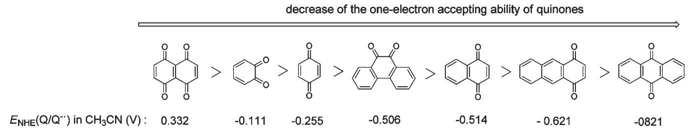
Accurate Estimation of the One-Electron Reduction Potentials of Various Substituted Quinones in DMSO and CH_3CN

Xiao-Qing Zhu* and Chun-Hua Wang

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

xqzhu@nankai.edu.cn

Received April 15, 2010



The one-electron reduction potentials of 116 important *p*- and *o*-quinones in DMSO and CH_3CN were predicted for the first time by using the B3LYP/DZP++ method and the PCM cluster continuum model. The calculated gas-phase electron affinities and one-electron reduction potentials agree well with the available experimental observations, respectively. The study showed the one-electron reduction potentials of the 116 quinones range from -0.949 to 1.128 V in DMSO and from -0.904 to 0.971 V in CH_3CN. The one-electron reduction potentials of *p*-quinones are generally smaller than those of the *o*-quinones by about 0.132 V. For quinones with aromatic properties, 2-substituted-1,4-naphthquinones have the largest one-electron reduction potentials, followed by substituted-1,4-anthraquinones and then by substituted-9,10-anthraquinones. The study also showed that the one-electron reduction potentials of quinones in DMSO are linearly dependent on the sum of the Hammett substituent parameters σ_p: $E_{NHE}(p\text{-}Q/p\text{-}Q^{\bullet -}) = 0.45\Sigma\sigma_p - 0.194$ (V) and $E_{NHE}(o\text{-}Q/o\text{-}Q^{\bullet -}) = 0.45\Sigma\sigma_p - 0.059$ (V). Combined with the hydride affinities of quinones in the former paper [$\Delta G_{H^-A}(p\text{-}Q) = -16.0\Sigma\sigma_p - 70.5$ (kcal/mol) and $\Delta G_{H^-A}(o\text{-}Q) = -16.2\Sigma\sigma_p - 81.5$ (kcal/mol)] and the one-electron reduction potentials of quinones estimated in this work, we obtained the homolytic bond dissociation energies of the hydroquinone anions (QH^-) and found that these thermodynamic parameters also have linear correlations against the sum of the Hammett substituent parameters σ_p if only the substituents have no larger electrostatic inductive force and no large steric hindrance: $BDE(p\text{-}QH^-) = 5.05\Sigma\sigma_p + 63.18$ (kcal/mol) and $BDE(o\text{-}QH^-) = 5.33\Sigma\sigma_p + 71.30$ (kcal/mol). Knowledge about the redox potentials of the quinones should be of great value for the understanding of the nature of chemical reactions of quinones, the designing of new electronic materials of quinones, and the examining of biological activities of quinones.

Introduction

Because of their particular electron-accepting abilities, quinones not only are involved in the redox chemistry of virtually all living organisms and fulfill important biological functions[1] but also have widespread use in organic and industrial synthesis.[2-9] For example, ubiquinone-10, a 1,4-benzoquinone derivative, acts both as an electron carrier between the different components of the electron transport chain in the mitochondrion and as a redox component for the coupling of electron and proton transfer for the generation of pH gradients across the mitochondrial membrane (the Q) cycle.[10,11] In photosynthesis, quinones act as primary and secondary electron acceptors, both in plant and bacterial photosynthesic reaction centers.[12-15] Recent work

---

(1) Ahlberg, E.; Panas, I.; Schiffrin, D. J. *J. Phys. Chem. A* **2006**, *110*, 2005.

(2) *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U. R., 1988; Vol. 2, Parts 1 & 2.

(3) Stryer, L. *Biochemistry*, 3rd ed.;W. H. Freeman & Co.: New York, 1988.

(4) *Function of Quinones in Energy ConserVing Systems*; Trumpower, B. L., Ed.; Academic: New York, 1982.

(5) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225.

(6) Smith, J. G.; Fieser, M. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1990; Vol. 12.

(7) Bayer, O. In *Methoden der Organischen Chemie* (*Houben-Weyl-Müller*), 4th ed.; Georg Thieme Verlag: Stuttgart, 1979; Vol. 7/3c; pp 270ff.

(8) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. D, pp 303ff.

(9) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

(10) Mathews, C. K.; van Holde, K. E.; Ahern, K. G. *Biochemistry*, 3rd ed.; Benjamin, Cummings: San Francisco, CA, 2000.

(11) Mitchell, P.; Moyle, J. *Eur. J. Biochem.* **1969**, *9*, 149.

DOI: 10.1021/jo100735s Published on Web 07/06/2010

have demonstrated that quinones can function precisely as electrocatalysts that can reduce O_2 to stop at the hydrogen peroxide stage.[16−21]

Despite the importance of the electron-accepting abilities played by quinones, the redox potentials of these species have not been systematically studied. Examination of past publications on these subjects shows that the redox potentials of fewer than 20 and 6 quinones, in CH_3CN and DMSO, respectively, have been determined.[22] In fact, these important thermodynamic values can contribute to the understanding of electron-accepting abilities, the comparison of the relative stabilities of the diverse radical anions, the prediction of the reaction mechanism, and the product distribution in the electron-initiated reduction process of quinones. The main experimental difficulty in studying the quinone radical anions could be that these radical anions tend to be extremely short-lived, and it is difficult to determine whether the reduction process is a two-electron process or one-electron process.[23]

However, present-day electronic structure theories, combined with electronic computers technology, have increased the number of theoretical studies aiming at deriving thermochemical properties for chemical compounds difficult or impossible to measure.[24−38] Recently, some attention has been paid to the estimation of the redox potentials of quinones in aqueous solution and nonaqueous solvents.[39−52] Nevertheless, some of these predictions were made only with fairly low-level theoretical methods, and more accurate systematic theoretical estimation of redox potentials of quinones has not been released in the literature. Besides, some of the theoretical results were compared with the experimental data, but interface effects on the electrodes were not considered. Furthermore, most of the theoretical estimations only limit their attention to *p*-quinones; the redox potentials of *o*-quinones remain poorly understood.

Systematical estimation of the redox potentials of quinones in solution requires two critical steps: estimation of electron affinities (EA) and computation of solvation free energies. According to a recent review, the average absolute error for the B3LYP method is 0.14 ev for 91 atomic and molecular systems for which electron affinities have been determined reliably from experiment.[53,54] Given the great difficulty of experimental measurements of EAs, this is an important achievement, indicating that theory can be a valuable guide in situations where meaningful experiments are not currently feasible.[55] Very recently, Guo and co-workers developed a generally applicable protocol that could successfully predict the standard redox potentials of 270 structurally unrelated organic molecules in acetonitrile. The standard deviation of the predictions was 0.17 V.[56] The study demonstrated that computational electrochemistry could become a powerful tool for the organic chemical community.

Armed with the carefully benchmarked theoretical protocol, in this study we report a detailed theoretical examination of the one-electron affinities and one-electron reduction potentials of quinones in DMSO and CH_3CN at the best level of theory reported for this system. The primary objectives of this paper include the following: (1) the theoretical methods that are reliable to predict the electron affinities and reduction potentials of quinones; (2) the scales of the reduction potentials of

---

(12) Michel, H.; Deisenhofer, J. *Biochemistry* **1988**, *27*, 1.

(13) Mattoo, A. K.; Marder, J. B.; Edelman, M. *Cell* **1989**, *56*, 241.

(14) Diner, B. A.; Petrouleas, V.; Wendoloski, J. J. *Physiol. Plant* **1991**, *81*, 423.

(15) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618.

(16) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1997; Chapter 14.

(17) Tammeveski, K.; Kontturi, K.; Nichols, R. J.; Potter, R. J.; Schiffrin, D. J. *J. Electroanal. Chem.* **2001**, *515*, 101.

(18) Sarapuu, A.; Vaik, K.; Schiffrin, D. J.; Tammeveski, K. *J. Electroanal. Chem.* **2003**, *541*, 23.

(19) Vaik, K.; Schiffrin, D. J.; Tammeveski, K. *Electrochem. Commun.* **2004**, *6*, 1.

(20) Mirkhalaf, F.; Tammeveski, K.; Schiffrin, D. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1321.

(21) Vaik, K.; Sarapuu, A.; Tammeveski, K.; Mirkhalaf, F.; Schiffrin *J. Electroanal. Chem.* **2004**, *564*, 159.

(22) (a) Cheng, J. -P.; Handoo, K. L.; Xue, J.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 5050. (b) Frontana, C.; Mayagoitia, A. V.; Garza, J.; Vargas, R.; Gonzalez, I. *J. Phys. Chem. A* **2006**, *110*, 9411 and references therein. (c) Eriksson, L. A.; Himo, F.; Siegbahn, P. E. M.; Babcock, G. T. *J. Phys. Chem. A* **1997**, *101*, 9496 and references therein.

(23) Wass, J. R. T. J.; Ahlberg, E.; Panas, I.; Schiffrin, D. J. *J. Phys. Chem. A* **2006**, *110*, 2005.

(24) Levine, I. N. *Quantum Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1993.

(25) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(26) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to AdVanced Electronic Structure Theory*, 1st revised ed.; McGraw-Hill: New York, 1989.

(27) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(28) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J., Eds.; Springer-Verlag: New York, 1991.

(29) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(30) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(32) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. w.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN92/DFT*; Gaussian, Inc.: Pittsburgh,1992.

(33) Boesch, S. E.; Wheeler, R. A. *J. Phys. Chem. A* **1997**, *101*, 5799.

(34) Balakrishnan, G.; Mohandas, P.; Umapathy, S. *Spectrochim. Acta, Part A* **1997**, *53*, 1553.

(35) Burie, J.-R.; Boullais, C.; Nonella, M.; Mioskowski, C.; Nabedryk, E.; Breton, J. *J. Phys. Chem. B* **1997**, *101*, 6607.

(36) Grafton, A. K.; Boesch, S. E.; Wheeler, R. A. *J. Mol. Struct.* (*THEOCHEM*) **1997**, *392*, 1.

(37) Razeghifard, M. R.; Kim, S.; Patzlaff, J. S.; Hutchinson, R. S.; Krick, T.; Ayala, I.; Steenhuis, J. J.; Boesch, S. E.; Wheeler, R. A.; Barry, B. A. *J. Phys. Chem. B* **1999**, *103*, 9790.

(38) Kaupp, M.; Remenyi, C.; Vaara, J.; Malkina, O. L.; Malkin, V. G. *J. Am. Chem. Soc.* **2002**, *124*, 2709.

(39) Reynolds, C. A.; King, P. M.; Richards, W. G. *J. Chem. Soc., Chem. Commun.* **1988**, 1434.

(40) Reynolds, C. A.; King, P. M.; Richards, W. G. *Nature* (*London*) **1988**, *334*, 80.

(41) Reynolds, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7545.

(42) Wheeler, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 11048.

(43) Raymond, K. S.; Grafton, A. K.; Wheeler, R. A. *J. Phys. Chem. B* **1997**, *101*, 623.

(44) Rzepa, H. S.; Suñer, G. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1743.

(45) Jalali-Heravi, M.; Namazian, M.; Peacock, T. E. *J. Electroanal. Chem.* **1995**, *385*, 1.

(46) Jalali-Heravi, M.; Namazian, M. *J. Electroanal. Chem.* **1997**, *425*, 139.

(47) Namazian, M.; Almodarresieh, H. A. *J. Mol. Struct.* (*THEOCHEM*) **2004**, *686*, 97.

(48) Namazian, M.; Almodarresieh, H. A.; Noorbala, M. R.; Zare, H. R. *Chem. Phys. Lett.* **2004**, *396*, 424.

(49) Namazian, M.; Norouzi, P. *J. Electroanal. Chem.* **2004**, *573*, 49.

(50) (a) Namazian, M.; Norouzi, P.; Ranjbar, R. *J. Mol. Struct.* (*THEOCHEM*) **2003**, *625*, 235. (b) Namazian, M. *J. Mol. Struct.* (*THEOCHEM*) **2003**, *664−665*, 273.

(51) Namazian, M.; Coote, M. L. *J. Phys. Chem. A* **2007**, *111*, 7227.

(52) Rosso, K. M.; Smith, D. M. A.; Wang, Z.; Ainsworth, C. C.; Fredrickson, J. K. *J. Phys. Chem. A* **2004**, *108*, 3292.

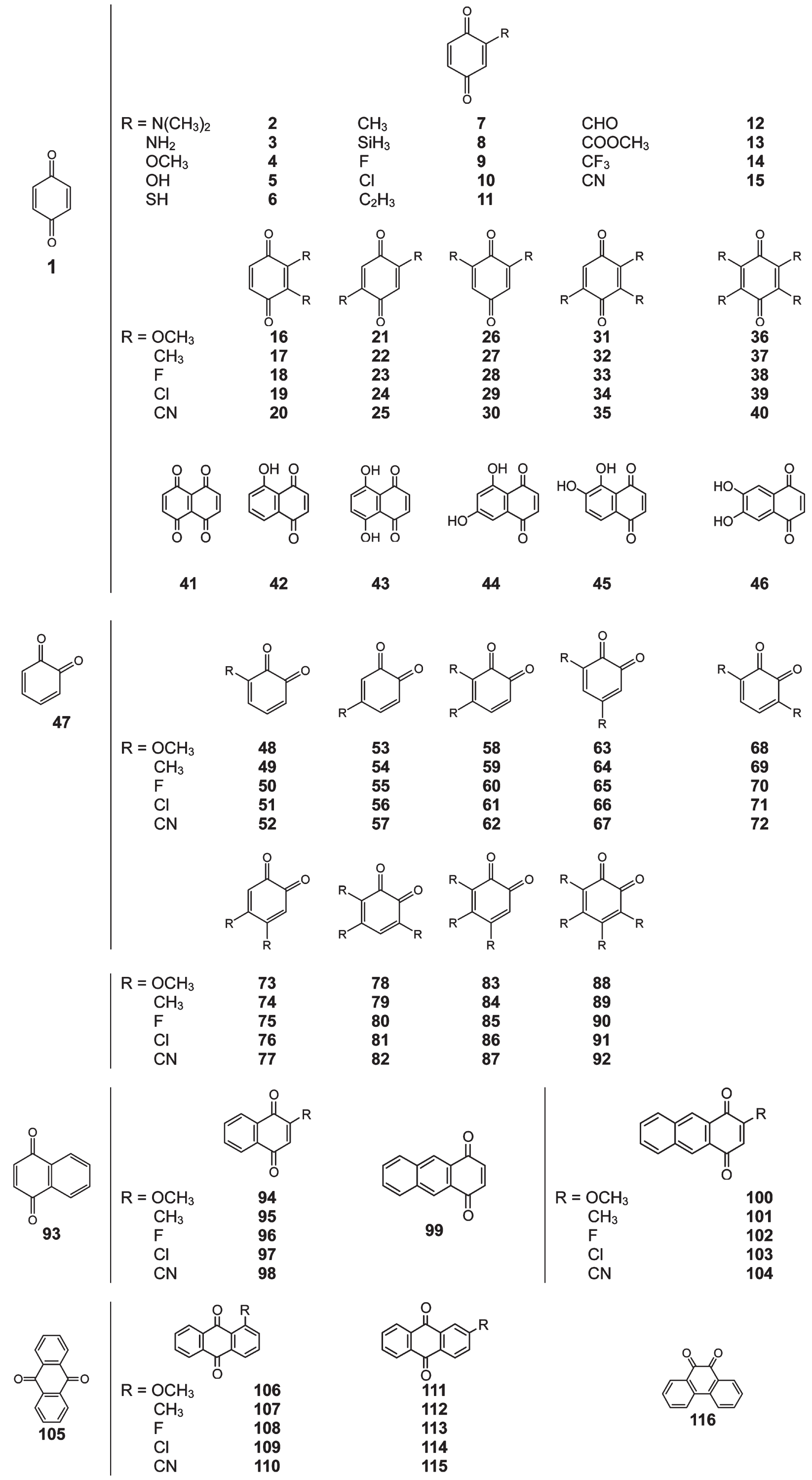
(53) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Sreela, N.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231.

(54) (a) Galbraith, J. M.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 862. (b) Jensen, F. *J. Chem. Phys.* **2002**, *117*, 9234.

(55) Xie, Y. M.; Schaefer, H. F.; Cotton, F. A. *Chem. Commun.* **2003**, 102.

(56) Fu, Y.; Yu, H. Z.; Wang, Y. M.; Guo, Q. X. *J. Am. Chem. Soc.* **2005**, *127*, 7227.

SCHEME 1. Chemical Structures and Numbers of Examined Quinones



R		R		R	
$N(CH_3)_2$	**2**	CH_3	**7**	CHO	**12**
NH_2	**3**	SiH_3	**8**	$COOCH_3$	**13**
OCH_3	**4**	F	**9**	CF_3	**14**
OH	**5**	Cl	**10**	CN	**15**
SH	**6**	C_2H_3	**11**		

R					
OCH_3	**16**	**21**	**26**	**31**	**36**
CH_3	**17**	**22**	**27**	**32**	**37**
F	**18**	**23**	**28**	**33**	**38**
Cl	**19**	**24**	**29**	**34**	**39**
CN	**20**	**25**	**30**	**35**	**40**

R					
OCH_3	**48**	**53**	**58**	**63**	**68**
CH_3	**49**	**54**	**59**	**64**	**69**
F	**50**	**55**	**60**	**65**	**70**
Cl	**51**	**56**	**61**	**66**	**71**
CN	**52**	**57**	**62**	**67**	**72**

R				
OCH_3	**73**	**78**	**83**	**88**
CH_3	**74**	**79**	**84**	**89**
F	**75**	**80**	**85**	**90**
Cl	**76**	**81**	**86**	**91**
CN	**77**	**82**	**87**	**92**

R		R	
OCH_3	**94**	OCH_3	**100**
CH_3	**95**	CH_3	**101**
F	**96**	F	**102**
Cl	**97**	Cl	**103**
CN	**98**	CN	**104**

R		
OCH_3	**106**	**111**
CH_3	**107**	**112**
F	**108**	**113**
Cl	**109**	**114**
CN	**110**	**115**

quinones; (3) the relationship between substituent and the reduction potentials of quinones; (4) the homolytic bond dissociation energies of the hydroquinone anions; (5) the relationship between gas-phase electron affinities and the reduction potentials in the liquid phase of quinones. It is evident that the answer of these questions are of great value in the understanding of the reduction mechanisms of quinones, the designing of new electronic materials and the catching of biological activities about quinones. The quinones examined in this work are shown in Scheme 1.

Results

Calculation of Gas-Phase Electron Affinities of Quinones. Before we try to estimate the redox potentials of the quinones in DMSO and CH_3CN, the electron affinities (EA) of them should be calculated reliably at first. In this paper, electron affinities of studying quinones were computed according to the difference of the state Gibbs free energies between the neutral quinones and the corresponding radical anions at their respective optimized geometries.

$$\mathrm{EA} = G_{\mathrm{neutral}} - G_{\mathrm{anion}} \quad (1)$$

Throughout this study, a simulated annealing method was used at first for our conformation analysis, and one with minimum energy was selected as our starting structure in our Gaussian optimization. The geometry of each species was optimized using B3LYP method and DZP++, a standard basis set of contracted double-ζ Gaussian functions, was used. This basis set was constructed by augmenting the Huzinaga–Dunning[57,58] set of contracted double-ζ Gaussian functions with one set of *p*-type polarization functions for each H atom and one set of five *d*-type polarization functions for each C, N, and O atom [$\alpha p(\mathrm{H}) = 0.75$, $\alpha d(\mathrm{C}) = 0.75$, $\alpha d(\mathrm{N}) = 0.80$, $\alpha d(\mathrm{O}) = 0.85$]. To complete the DZP++ basis, one diffuse *s* function was added to each H atom while sets of diffuse *s* and *p* functions were centered on each heavy atom. The even tempered orbital exponents were determined according to the prescription of Lee and Schaefer:[59]

$$\alpha_{\mathrm{diffuse}} = \frac{1}{2}\left(\frac{\alpha 1}{\alpha 2} + \frac{\alpha 2}{\alpha 3}\right)\alpha 1 \quad (2)$$

where α_1, α_2, and α_3 are the three smallest Gaussian orbital exponents of the *s*- or *p*-type primitive functions for a given atom ($\alpha_1 < \alpha_2 < \alpha_3$). The final DZP++ set contains 6 functions per H atom and 19 functions per C, N, or O atom.[60] Each optimized structure was checked by frequency calculations to be a real minimum without any imaginary frequency at the same level of theory used in the geometry optimization.

The electron affinities that calculated using the above approach were compiled in Supporting Information (Table S1).

Comparing the experimental[22b] and theoretical electron affinities (Supporting Information, Table S2), we found that the B3LYP/DZP++ method systematically overestimates the EAs. Similar overestimation behaviors were also found by Schaefer and co-workers.[53] In spite of the overestimation problem, it is found that the B3LYP EAs correlate well with the experimental results, that is:

$$\mathrm{EA(exp)} = 0.912\mathrm{EA(B3LYP)} - 0.080 \quad (3)$$

From Figure 1, it is easy to find that the maximum deviation, the standard deviation and correlation coefficient (*r*) are 0.37ev, 0.038 ev, and 0.9941, respectively. Accordingly, it is accurate to estimate the adiabatic EAs of quinones through multiplying the B3LYP/DZP++ calculated results by 0.912. These corrected values are summarized in Supporting Information (Table S1).

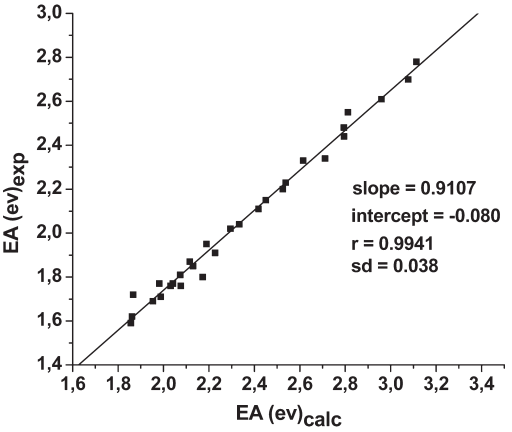


FIGURE 1. Correlation between the theoretical and experimental EAs.

Calculations of One-Electron Reduction Potentials of Quinones in DMSO and CH_3CN. The definition of the standard one-electron reduction potential of quinone is

$$E°\!: \mathrm{Q} + \mathrm{e}^- \rightarrow \mathrm{Q}^{\bullet -} \quad (4)$$

The value of *E*° is usually measured relative to a reference electrode, for instance, the normal hydrogen electrode (NHE). The NHE half reaction is $\mathrm{H}^+(\mathrm{aq}) + \mathrm{e}^- \rightarrow 1/2\,\mathrm{H}_2(\mathrm{g})$. Thus, the *E*° value is connected to the standard free energy change of the reaction:

$$\Delta G°\!: \mathrm{Q} + \frac{1}{2}\mathrm{H}_2(\mathrm{g}) \rightarrow \mathrm{Q}^{\bullet -} + \mathrm{H}^+(\mathrm{aq}) \quad (5)$$

$$E_{\mathrm{NHE}} = \frac{\Delta G°}{F} \quad (6)$$

where *F* is the Faraday constant equal to 23.06 kcal/(mol·V).

In order to estimate the one-electron reduction potentials of quinones in DMSO and CH_3CN, *p*-BQ was chosen as a reference to construct a reaction, i.e., electron interchange reaction (eq 7), since accurate reduction potentials relative to the normal hydrogen electrode in DMSO and CH_3CN is available (−0.319 and −0.314 V) for *p*-BQ.

$$\mathrm{Q} + p\text{-}\mathrm{BQ}^{\bullet -} \rightarrow \mathrm{Q}^{\bullet -} + p\text{-}\mathrm{BQ} \quad \Delta G_{\mathrm{sol}}{}^* \quad (7)$$

The reduction potentials of quinones could be calculated by eq 7

$$E_{\mathrm{NHE}}(\mathrm{Q}/\mathrm{Q}^{\bullet -}) = E_{\mathrm{NHE}}(p\text{-}\mathrm{BQ}/p\text{-}\mathrm{BQ}^{\bullet -}) + \frac{\Delta G_{\mathrm{sol}}{}^*}{F} \quad (8)$$

In order to calculate $\Delta G_{\mathrm{sol}}{}^*$, a thermodynamic cycle (Figure 2) was proposed, from which the term $\Delta G_{\mathrm{sol}}{}^*$ can be expressed with eq 9:

$$\Delta G_{\mathrm{sol}}{}^* = \Delta G_{\mathrm{g}}{}^* + \Delta G_{\mathrm{sol}} \quad (9)$$

where $\Delta G_{\mathrm{g}}{}^*$ is the standard Gibbs energy change of the electron interchange reaction in the gas phase, ΔG_{sol} is solvation energy of the reaction in DMSO and CH_3CN.

$$\Delta G_{\mathrm{g}}{}^* = G_{\mathrm{g}}(\mathrm{Q}^{\bullet -}) + G_{\mathrm{g}}(p\text{-}\mathrm{BQ}) - G_{\mathrm{g}}(\mathrm{Q}) - G_{\mathrm{g}}(p\text{-}\mathrm{BQ}^{\bullet -}) \quad (10)$$

$$\Delta G_{\mathrm{sol}} = \Delta G_{\mathrm{sol}}(\mathrm{Q}^{\bullet -}) + \Delta G_{\mathrm{sol}}(p\text{-}\mathrm{BQ}) - \Delta G_{\mathrm{sol}}(\mathrm{Q}) - \Delta G_{\mathrm{sol}}(p\text{-}\mathrm{BQ}^{\bullet -}) \quad (11)$$

---

(57) Glaus, M. A.; Heijman, C. G.; Schwarzenbach, R. P.; Zeyer, J. *Appl. Environ. Microbiol.* **1992**, *58*, 1945.

(58) Schwarzenbach, R. P.; Stierli, R.; Lanz, K.; Zeyer, J. *Environ. Sci. Technol.* **1990**, *24*, 1566.

(59) Fredrickson, J. K.; Zachara, J. M.; Kennedy, D. W.; Dong, H. L.; Onstott, T. C.; Hinman, N. W.; Li, S. M. *Geochim. Cosmochim. Acta* **1998**, *62*, 3239.

(60) Wesolowski, S. S.; Leininger, M. L.; Pentchev, P. N.; Schaefer, H. F. *J. Am. Chem. Soc.* **2001**, *123*, 4023.

$$\begin{tikzcd}
Q_g \arrow[d, "\Delta G_{sol}(Q)"'] & + & p\text{-BQ}_g^{\bullet-} \arrow[r, "\Delta Gg*"] \arrow[d, "\Delta G_{sol}(p\text{-}\overset{\bullet-}{\text{BQ}})"'] & Q_g^{\bullet-} \arrow[d, "\Delta G_{sol}(\overset{\bullet-}{Q})"'] & + & p\text{-BQ}_g \arrow[d, "\Delta G_{sol}(p\text{-BQ})"] \\
Q_s & + & p\text{-BQ}_s^{\bullet-} \arrow[r, "\Delta Gsol*"] & Q_s^{\bullet-} & + & p\text{-BQ}_s
\end{tikzcd}$$

FIGURE 2. The thermodynamic cycle proposed to convert standard Gibbs energy of the reaction in gas phase to the standard Gibbs free energy of the reaction in the solution phase.

Therefore,

$$\begin{aligned}
E_{\mathrm{NHE}}(\mathrm{Q}/\mathrm{Q}^{\bullet-}) &= E_{\mathrm{NHE}}(p\text{-BQ}/p\text{-BQ}^{\bullet-}) + \frac{\Delta G_{\mathrm{sol}}*}{\mathrm{F}} \\
&= E_{\mathrm{NHE}}(p\text{-BQ}/p\text{-BQ}^{\bullet-}) + [G_{\mathrm{g}}(\mathrm{Q}^{\bullet-}) \\
&\quad + G_{\mathrm{g}}(p\text{-BQ}) - G_{\mathrm{g}}(\mathrm{Q}) - G_{\mathrm{g}}(p\text{-BQ}^{\bullet-}) + \Delta G_{\mathrm{sol}}(\mathrm{Q}^{\bullet-}) \\
&\quad + \Delta G_{\mathrm{sol}}(p\text{-BQ}) - \Delta G_{\mathrm{sol}}(\mathrm{Q}) - G_{\mathrm{sol}}(p\text{-BQ}^{\bullet-})]/F \qquad (12)
\end{aligned}$$

In eq 12, E_{NHE} (p-BQ/p-BQ$^{\bullet-}$) is the reduction potential of p-BQ in DMSO and CH_3CN (−0.319 and −0.314 V, respectively) relative to the normal hydrogen electrode. G_g(Q), G_g(Q$^{\bullet-}$), G$_g$(p-BQ), and G_g(p-BQ$^{\bullet-}$) are the standard state Gibbs free energies of the species Q, Q$^{\bullet-}$, p-BQ, and p-BQ$^{\bullet-}$ in the gas phase, respectively which can be estimated by B3LYP/DZP++ method, and the detailed results are summarized in Supporting Information (Table S1). ΔG_{sol}(Q), ΔG_{sol}(Q$^{\bullet-}$), ΔG_{sol}(p-BQ), and ΔG_{sol}(p-BQ$^{\bullet-}$) are the solvation energies of the species Q, Q$^{\bullet-}$, p-BQ, and p-BQ$^{\bullet-}$ in DMSO and CH_3CN. In order to attain maximum accuracy, herein we utilized the most recent version of the polarized continuum model, that is, IEF-PCM (integral equation formalism PCM),[61] to calculate the solvation free energies (at B3LYP/6-31+G** level and using Bondi'S radii and gas-phase geometries). These results were also listed in Supporting Information (Table S3).

In Table 1, a number of experimental reduction potentials for quinones in DMSO and CH_3CN are collected.

From Table 1, it is clear that in CH_3CN, if uncorrected electron affinities are used directly in our calculation, we will get very large mean deviation and standard deviation in redox potential results (calc 1 in Table 1) if experimental redox potentials (RP) were compared, whereas the mean deviation and standard deviation become smaller (calc 2 in Table 1) if corrected electron affinity results were used, indicating our electron affinity correction is very important. Table 1 also shows that our calculated data (calc 2) are generally smaller than the experimental values.

$$\mathrm{RP(exp)} = 1.01\mathrm{RP(B3LYP, calc\ 2)} + 0.06 \quad \text{in } CH_3CN \qquad (13)$$

$$\mathrm{RP(exp)} = 1.11\mathrm{RP(B3LYP, calc\ 2)} + 0.12 \quad \text{in DMSO} \qquad (14)$$

In order to get more reliable theoretical results, we corrected our results again according to eqs 13 and 14, and all the final results are summarized in Table 1 as calc 3. The results obtained in this way are all very close to the corresponding experimental observations with very small mean deviation and standard deviation, showing that calc 3 results are fairly reliable. In DMSO, similar conclusions can be made. In this part, we should also keep in mind that the positions of the oxygens in o-quinone are nearer to each other than those in p-quinone. It is reasonable to predict that the p-quinone radical anion is much more stable than the o-quinone radical anion, and accordingly, the redox potential of p-quinone should be more negative than the one of o-quinone. So we exclude the experimental data of o-quinone when we do the corrections and suggest some groups to redetermine the redox potential of this compound.

TABLE 1. Comparison of Theoretical Reduction Potentials (V) of Some Quinones in CH_3CN and DMSO with the Corresponding Experimental Data[22]

	$E_{\mathrm{NHE}}(\mathrm{Q}/\mathrm{Q}^{\bullet-})$			
quinones	exp	calc 1[a]	calc 2[b]	calc 3[c]
		CH_3CN		
1	−0.314	−0.314	−0.314	−0.255
7	−0.391	−0.409	−0.399	−0.340
10	−0.065	−0.172	−0.199	−0.139
11	−0.305	−0.358	−0.367	−0.308
22	−0.465	−0.512	−0.492	−0.434
24	0.002	−0.040	−0.093	−0.033
26	−0.513	−0.560	−0.526	−0.468
27	−0.473	−0.497	−0.479	−0.421
29	0.021	−0.036	−0.088	−0.028
32	−0.638	−0.614	−0.587	−0.529
39	0.278	0.131	0.049	0.110
93	−0.492	−0.588	−0.572	−0.514
94	−0.626	−0.661	−0.639	−0.582
95	−0.576	−0.684	−0.659	−0.602
99	−0.722	−0.698	−0.679	−0.622
101	−0.779	−0.795	−0.767	−0.710
103	−0.647	−0.561	−0.565	−0.507
105	−0.670	−0.915	−0.877	−0.820
112	−0.697	−1.005	−0.961	−0.905
DDQ	0.510	0.642	0.483	0.546
MD		0.054	0.058	−0.001
SD		0.101	0.092	0.049
correlation coefficient		0.967	0.965	0.965
		DMSO		
1	−0.319	−0.319	−0.319	−0.235
37	−0.635	−0.738	−0.706	−0.668
39	0.170	0.110	0.032	0.158
47	−0.492	−0.188	−0.190	−0.090
91	0.348	0.222	0.150	0.290
DDQ	0.622	0.630	0.479	0.651
MD[d]		0.056	0.110	−0.002
SD[d]		0.067	0.057	0.064
correlation coefficient[d]		0.994	0.994	0.994

[a] From uncorrected electron affinities calculations. [b] From corrected electron affinities calculation by using eq 3. [c] Corrected according to eqs 13 and 14 in CH_3CN and DMSO, respectively. [d] Compound **47** is not included, because the reported experimental data is evidently unreasonable.

According to the designed strategy described above and with these facts in mind, we performed calculations for 116 important p-quinones and o-quinones in DMSO and CH_3CN, and the detailed results are listed in Table 2. Since the reduction potentials of the quinones in CH_3CN are similar to those in DMSO (in the solvation effect section, we will discuss this issue in detail), the reduction potentials of quinones in DMSO were chosen for discussion.

Discussion

Scale of the One-Electron Reduction Potentials of the 116 Quinones in DMSO. All the above analyses made us

---

[61] Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.

TABLE 2. Theoretical One-Electron Affinities (EA, eV) and One-Electron Reduction Potentials (E_{NHE}, V) of the 116 Quinones in DMSO and CH_3CN

compd	EA[a]	E_{NHE}(DMSO)[b]	E_{NHE}(CH_3CN)[c]	compd	EA	E_{NHE}(DMSO)	E_{NHE}(CH_3CN)
1	1.95	−0.235	−0.255	**59**	1.79	−0.292	−0.306
2	1.67	−0.573	−0.557	**60**	2.35	0.109	0.056
3	1.71	−0.524	−0.515	**61**	2.43	0.097	0.044
4	1.78	−0.363	−0.373	**62**	3.25	0.558	0.460
5	2.05	−0.269	−0.285	**63**	1.61	−0.386	−0.395
6	2.12	−0.257	−0.272	**64**	1.79	−0.273	−0.294
7	1.86	−0.327	−0.341	**65**	2.36	0.105	0.056
8	2.12	−0.227	−0.245	**66**	2.49	0.122	0.044
9	2.16	−0.115	−0.139	**67**	3.29	0.510	0.461
10	2.22	−0.107	−0.139	**68**	1.74	−0.182	−0.208
11	2.04	−0.290	−0.307	**69**	1.82	−0.270	−0.272
12	2.48	−0.045	−0.068	**70**	2.43	0.222	0.157
13	2.25	−0.050	0.022	**71**	2.52	0.182	0.120
14	2.44	0.002	−0.039	**72**	3.28	0.492	0.401
15	2.61	0.092	0.042	**73**	1.53	−0.547	−0.540
16	1.83	−0.400	−0.404	**74**	1.78	−0.275	−0.291
17	1.76	−0.486	−0.478	**75**	2.48	0.136	0.082
18	2.35	0.006	−0.036	**76**	2.46	0.081	0.031
19	2.39	−0.025	−0.064	**77**	3.26	0.497	0.411
20	3.17	0.465	0.381	**78**	1.85	−0.308	−0.324
21	1.69	−0.499	−0.492	**79**	1.73	−0.377	−0.377
22	1.77	−0.428	−0.434	**80**	2.58	0.256	0.188
23	2.34	−0.012	−0.053	**81**	2.67	0.220	0.154
24	2.46	−0.011	0.033	**82**	3.81	0.827	0.705
25	3.17	0.346	0.273	**83**	1.65	−0.501	−0.491
26	1.62	−0.475	−0.467	**84**	1.71	−0.370	−0.471
27	1.77	−0.436	−0.420	**85**	2.48	0.136	0.080
28	2.36	0.022	−0.045	**86**	2.63	0.180	0.119
29	2.46	−0.015	0.028	**87**	3.77	0.822	0.697
30	3.20	0.357	0.239	**88**	1.67	−0.452	−0.443
31	1.72	−0.483	−0.475	**88**	1.77	−0.453	−0.451
32	1.70	−0.548	−0.529	**90**	2.70	0.290	0.219
33	2.55	0.117	0.064	**91**	2.80	0.290	0.208
34	2.62	0.093	0.041	**92**	4.23	1.128	0.971
35	3.69	0.701	0.593	**93**	1.81	−0.516	−0.514
36	1.81	−0.535	−0.520	**94**	1.75	−0.607	−0.581
37	1.62	−0.668	−0.646	**95**	1.72	−0.624	−0.601
38	2.72	0.221	0.156	**96**	1.98	−0.419	−0.422
39	2.75	0.158	0.110	**97**	2.05	−0.394	−0.397
40	4.11	0.974	0.837	**98**	2.44	−0.153	−0.183
41	2.85	0.367	0.332	**99**	1.79	−0.641	−0.621
42	2.04	−0.440	−0.431	**100**	1.60	−0.794	−0.757
43	2.16	−0.429	−0.424	**101**	1.70	−0.740	−0.710
44	2.05	−0.471	−0.464	**102**	1.94	−0.547	−0.533
45	2.06	−0.489	−0.481	**103**	2.01	−0.519	−0.507
46	1.77	−0.588	−0.582	**104**	2.38	−0.265	−0.283
47	1.97	−0.090	−0.111	**105**	1.61	−0.872	−0.821
48	1.82	−0.147	−0.160	**106**	1.48	−0.942	−0.883
49	1.89	−0.179	−0.187	**107**	1.56	−0.949	−0.905
50	2.20	0.065	0.020	**108**	1.71	−0.825	−0.781
51	2.26	0.051	0.008	**109**	1.73	−0.838	−0.803
52	2.65	0.204	0.138	**110**	1.98	−0.718	−0.689
53	1.75	−0.333	−0.318	**111**	1.52	−0.928	−0.874
54	1.87	−0.186	−0.193	**112**	1.56	−0.904	−0.903
55	2.13	−0.046	−0.074	**113**	1.75	−0.822	−0.778
56	2.24	−0.009	−0.043	**114**	1.81	−0.806	−0.763
57	2.68	0.228	0.157	**115**	2.08	−0.705	−0.677
58	1.87	−0.227	−0.228	**116**	1.79	−0.512	−0.506

[a] Corrected by using eq 3 in the paper. [b] Corrected according to eq 14. [c] Corrected according to eq 13.

confident that we had constructed the first scale of reliable reduction potentials for diverse quinones in DMSO. On the basis of the scale of data, it was found among the 116 quinones, 1-MeO-9,10-anthraquinone (**1**) ($E_{\mathrm{NHE}} = -0.949$ V) is the weakest oxidant and the most difficult to be reduced, whereas 3,4,5,6-tetra-CN-*o*-quinone (**92**) ($E_{\mathrm{NHE}} =$ 1.128 V) is the strongest oxidant and the easiest to be reduced. Such a long scale of the reduction potentials (from −0.949 to 1.128 V) evidently shows that the 116 quinones can construct a large and useful library of organic oxidants, which can provide various electron acceptors that may be needed.

From Table 2 and Figure 3, it is clear that the reduction potentials of quinones in DMSO ranged from about −0.535 (**39**) to 0.974 (**127**) V for *p*-benzquinones and from −0.547 (**3**) to 1.128 (**128**) V for *o*-benzquinones. Examining *p*-BQ and *o*-BQ, it was found that *p*-BQ has electron affinities similar to those of *o*-BQ, indicating *p*-BQ has a similar ability to capture an electron compared with *o*-BQ in the gas phase. The reason for this could be that *o*-BQ and *o*-BQ radical

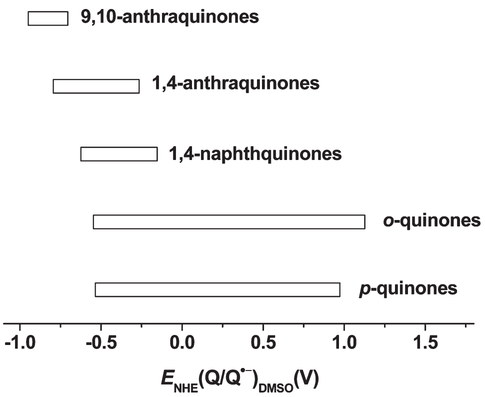


FIGURE 3. Value scale of the standard one-electron reduction potentials of the various types of quinones in DMSO.

anion have smaller state free energies than *p*-BQ and *p*-BQ radical anion, respectively. However, the reduction potential of *p*-BQ is smaller than that of *o*-BQ by about 0.135 V, showing that in the liquid phase the reducing ability of *p*-BQ is smaller than that of *o*-BQ. The reason could be that the solvation energies of *o*-BQ and *o*-BQ radical anion are larger than those of *p*-BQ and *p*-BQ radical anion by about 1.5 and 4.2 kcal/mol, respectively. In fact, from eqs 13 and 14 (next section), it is easy to find that the reduction potentials of *o*-quinones are larger than those of the corresponding *p*-quinones by about 0.13 V.

Table 2 and Figure 3 also show that the reduction potentials range from −0.624 (**21**) to −0.153 (**93**) V for 1,4-naphthquinones, from −0.794 (**6**) to −0.265 (**87**) V for 1,4-anthraquinones, and from −0.949 (**5**) to −0.705 (**67**) V for 9,10-anthraquinones. The reduction potentials of quinones decrease in the order substituted 1,4-benzquinones > 2-substituted-1,4-naphthquinones > 2-substituted-1,4-anthraquinones, indicating that the larger the aromatic system of the quinone is, the smaller the reduction potential is. The main factor to cause this could be that the quinone with a larger aromatic system could have larger stability in thermodynamics, which makes it more difficult for the quinone to capture an electron.

As we know, in the hydride transfer reduction reaction, if the energy required for an initial electron transfer is well below the empirical energy limit (1.0 V, i.e., 23.06 kcal/mol), a multistep reaction (e − $H^{\bullet}$ or e − H^{+}− e) will possibly take place. If the barrier for an initial electron transfer is well above the line, the one-step process would then most likely be the one for the reaction to follow, provided that it is energetically feasible. Cases between may proceed by a merged ("hybrid") mechanism. According to this viewpoint and the reduction potentials of various quinones, the detailed hydride transfer mechanism between quinones and some other hydride donors can be easily distinguished. For example, the driving forces of the first electron transfer of the reactions of DDQ with BNAH and *p*-BQ with $AcrH_2$ are 2.2 and 31.2 kcal/mol,[22,62] respectively. On the basis of the above thermodynamic analysis, it is reasonable to conclude that the reaction of DDQ with BNAH proceeded by an electron transfer initiated multistep mechanism, whereas the reaction of *p*-BQ with $AcrH_2$ is a one-step hydride transfer mechanism. These conclusions are surely in good accordance with our earlier observations and some other experimental results.[63−66]

Effect of Substituent on the One-Electron Reduction Potentials of Quinones. It is known to all that although the reactivity of an organic molecule is mainly determined by the functional group participating in the reaction in question, it is also affected by the substituents of the molecule. Knowledge of substituent effects is of great importance in selecting new compounds as possible candidates for the synthesis of new electron acceptors. From Table 2, it is clear that the reduction potentials are strongly depended on the nature of the substituents. In this work, the effects from substituents and their positions on the reduction potentials were systematically examined.

The plot lines of the reduction potentials of these *p*-quinones and *o*-quinones against the Hammett substituent parameter $\Sigma\sigma_p$ are depicted in Figure 4. Good linear correlations in the plots were observed (r = 0.9615 and 0.9640 for *p*-quinones and *o*-quinones, respectively), which indicate the reduction potentials of the quinones can be safely estimated from the plot lines or their extensions. According to the line slopes and line intercepts, the reduction potentials of any substituted quinones can be easily estimated.

$$E_{\mathrm{NHE}}(p\text{-Q}/p\text{-Q}^{\bullet-}) \approx 0.45\Sigma\sigma_p - 0.194 \quad (\mathrm{V}) \tag{15}$$

$$E_{\mathrm{NHE}}(o\text{-Q}/o\text{-Q}^{\bullet-}) \approx 0.45\Sigma\sigma_p - 0.059 \quad (\mathrm{V}) \tag{16}$$

Since the line slope in the plot of the reduction potentials against σ_p is positive, e.g., electron-withdrawing groups increase the reduction potentials whereas the electron-donating groups show the opposite effect, the reduction potentials of quinones should be mainly controlled by the stabilities of the quinone radical anions. The reason is that electron-withdrawing groups increase the relative stabilities of the quinone radical anions. The more stable the quinone radical anion is, the larger reduction potential the quinone has.

From Hydride Affinities and Reduction Potentials of Quinones to Bond Dissociation Energies of QH^{-}. To the best of our knowledge, the reduction of quinones (Q) to hydro-quinone anions (QH^{-}) can be initiated by direct hydride transfer or some other multistep hydride transfer mechanism, such as e − $H^{\bullet}$, e − H^{+} − e and so on. According to the hydride affinities reported in the former paper and the reduction potentials estimated in this work, the bond dissociation energies of the hydroquinone anions (the hydrogen atom affinities of the quinone radical anions are just equal to the bond dissociation energies of the hydroquinone anions by switching the sign), which are very difficult to be obtained only by using experimental methods, can be easily evaluated using a thermodynamic cycle (Scheme 2) and eq 17. The detailed bond dissociation energies of the hydroquinone anions were summarized in Table 3.

$$\begin{aligned}\mathrm{BDE}(\mathrm{QH}^-) &= -\Delta G_{\mathrm{HA}}(\mathrm{Q}^-)\\ &= F[E_{\mathrm{NHE}}(\mathrm{H}/\mathrm{H}^-) - E_{\mathrm{NHE}}(\mathrm{Q}/\mathrm{Q}^-)]\\ &\quad - \Delta G_{\mathrm{H}^-\mathrm{A}}(\mathrm{Q})\end{aligned} \tag{17}$$

From Table 3, it is clear that the homolytic bond dissociation energy scales of the hydroquinone anions in DMSO

---

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

(63) Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *J. Org. Chem.* **1984**, *49*, 3571.

(64) Miller, L. L.; Valentine, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 3982.

(65) Bunting, J. W.; Sindhuatmadji, S. *J. Org. Chem.* **1981**, *46*, 4211.

(66) Bunting, J. W.; Chew, V, S. F.; Chu, G. *J. Org. Chem.* **1982**, *47*, 2303.

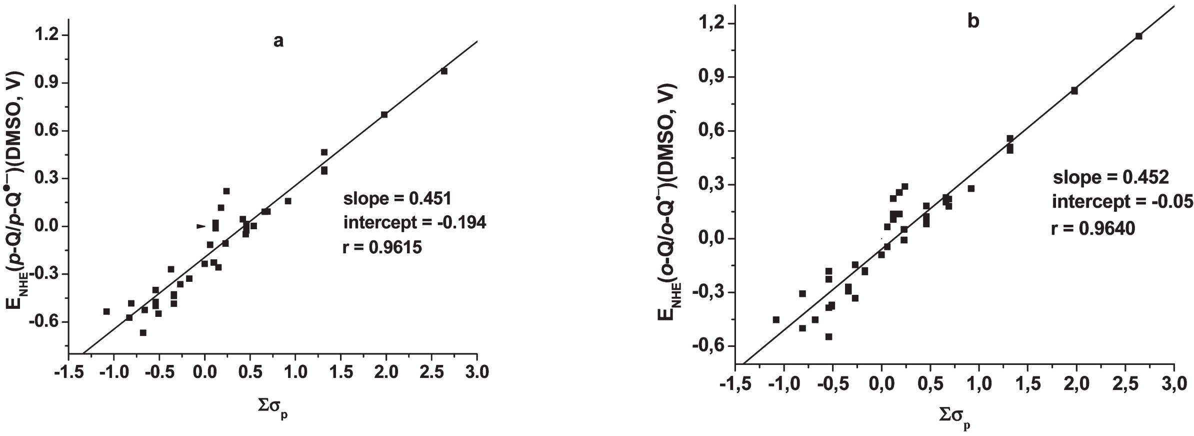
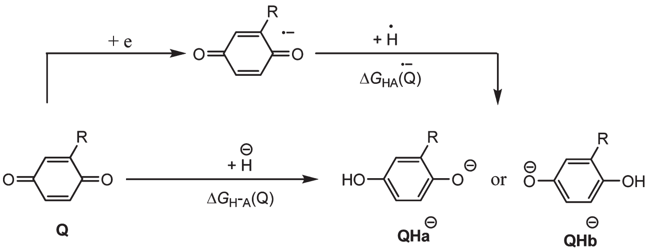


FIGURE 4. Plot of $E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}})$ in DMSO against the sum of Hammett subsituent parameter σ_p: (a) *p*-quinones, (b) *o*-quinones.

SCHEME 2. Possible Pathways of the Reduction of Quinones by Hydride



range from 56.0 kcal/mol for 9,10-anthraquinone to 85.7 kcal/mol for 3,4,5,6-tetra-CN-*o*-BQ. Such large bond dissociation energies evidently show that the hydrogen atom transfer could be extremely fast and possibly diffusion-controlled. The reactions observed clean and rapid in the literature do in fact support this expection.[62] By comparing the energies of the electron capture of the quinones and the hydrogen atom transfer of the corresponding radical anions (the four and the last column of Table 3), it is clear that when the quinones are reduced by hydride donors initiated by single electron transfer, the driving forces of the initial electron transfer are smaller than those of the hydrogen atom transfer, suggesting that the electron transfer in the first step could be the rate-determining step. This conclusion is in accord with many experimental observations. The long scale of the bond dissociation energies also indicates that these hydroquinone anions can construct a large and useful library of hydrogen atom donors.

Since $\mathrm{Q^{\bullet-}}$ and $\mathrm{QH^-}$ are isoelectronic species (both afford Q by electron or hydride releasing), it is reasonable to predict that substituents affect the reduction potentials of quinones (Q) and the hydricities of $\mathrm{QH^-}$ (the hydricity of $\mathrm{QH^-}$ is just equal to the hydride affinity of the corresponding Q by switching the sign) in a related way.

$$\Delta G_{\mathrm{H^-D}}(\mathrm{QH^-}) = \alpha E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}}) + \beta \qquad (18)$$

$$\Delta G_{\mathrm{H^-D}}(\mathrm{QH^-}): \quad \mathrm{QH^-} \rightarrow \mathrm{Q} + \mathrm{H^-} \qquad (19)$$

$$E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}}): \quad \mathrm{Q^{\bullet-}} \rightarrow \mathrm{Q} + \mathrm{e} \qquad (20)$$

In fact, the linear dependence of hydricities of $\mathrm{QH^-}$ on the reduction potentials of quinones is very good ($\alpha = 33.86$, $\beta = 78.53$, and $r = 0.9875$ for *p*-benzquinones, $\alpha = 34.39$, $\beta = 85.45$, and $r = 0.9841$ for *o*-benzquinones).

Since

$$\mathrm{BDE(QH^-)} = F[E_{\mathrm{NHE}}(\mathrm{H/H^-}) - E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}})] - \Delta G_{\mathrm{H^-A}}(\mathrm{Q}) \qquad (17)$$

then

$$\mathrm{BDE(QH^-)} = mE_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}}) + n \qquad (21)$$

where $m = \alpha - 23.06$ and $n = \beta - FE_{\mathrm{NHE}}(\mathrm{H/H^-}) = \beta - 12.68$ ($m = 10.64$, $n = 65.78$ for *p*-quinones and $m = 11.23$, $n = 72.64$ for *o*-quinones, see Table 3)

In another aspect,

$$E_{\mathrm{NHE}}(p\text{-Q}/p\text{-Q}^{\bullet-}) \approx 0.45\sum\sigma_{\mathrm{p}} - 0.194 \quad (\mathrm{V}) \qquad (15)$$

$$E_{\mathrm{NHE}}(o\text{-Q}/o\text{-Q}^{\bullet}) \approx 0.45\sum\sigma_{\mathrm{p}} - 0.059 \quad (\mathrm{V}) \qquad (16)$$

combining eqs 15 and 16, we can get for *p*-quinones:

$$\Delta G_{\mathrm{H^-A}}(p\text{-Q}) \approx 16.00\sum\sigma_{\mathrm{p}} + 70.50 \quad (\mathrm{kcal/mol}) \qquad (22)$$

$$\mathrm{BDE}(p\text{-QH}^-) \approx 5.05\sum\sigma_{\mathrm{p}} + 63.18 \quad (\mathrm{kcal/mol}) \qquad (23)$$

and for *o*-quinones:

$$\Delta G_{\mathrm{H^-A}}(o\text{-Q}) \approx 16.20\sum\sigma_{\mathrm{p}} + 81.50 \quad (\mathrm{kcal/mol}) \qquad (24)$$

$$\mathrm{BDE}(o\text{-QH}^-) \approx 5.33\sum\sigma_{\mathrm{p}} + 71.30 \quad (\mathrm{kcal/mol}) \qquad (25)$$

The relationships between the electron affinities of quinones, the reduction potentials of quinones, the hydricities of hydroquinone anions, and the Hammett substituent σ_p are summarized in Table 4.

According to the data summarized in Table 4, $E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}})$, $\Delta G_{\mathrm{H^-A}}(\mathrm{Q})$, and $\mathrm{BDE(QH^-)}$ of various substituted quinones can be easily estimated if we only know the structures of the quinones (*p*-benzquinones or *o*-benzquinones and the substituents attached on them).

Correlation between Electron Affinities and Reduction Potentials. To the best of our knowledge, the correlation between gas-phase electron affinities and reduction potentials has been proposed and used by many authors in either explaining the experimental data or predicting unknown

TABLE 3. Hydride Affinities of Quinones and Homolytic O−H Bond Dissociation Free Energies of Hydroquinone Anions (QH^-) in DMSO

				$\Delta G_{H^-A}(Q)$ (kcal/mol)		BDE(QH^-) (kcal/mol)	
compd		E_{NHE} (V)	FE_{NHE}	to QH_a^-	to QH_b^-	QH_a^-	QH_b^-
105	9-10-AQ	−0.872	−20.1	−47.4		54.8	
37	2,3,5,6-tetra-Me-*p*-BQ	−0.501	−11.6	−57.3		56.2	
26	2,6-di-MeO-*p*-BQ	−0.475	−11.0	−59.8	−54.0	58.1	52.3
7	Me-*p*-BQ	−0.327	−7.5	−65.3	−67.2	60.2	62.1
43	5,8-di-HO-1,4-NQ	−0.429	−9.9	−63.1		60.3	
93	1,4-NQ	−0.516	−11.9	−61.1		60.3	
13	CH_3COO-*p*-BQ	−0.050	−1.2	−72.9	−78.8	61.4	67.3
116	9,10-FQ	−0.512	−11.8	−62.3		61.4	
32	2,3,5-tri-Me-*p*-BQ	−0.548	−12.6	−61.7	−61.1	61.6	61.1
27	2,6-di-Me-*p*-BQ	−0.436	−10.1	−64.4	−64.0	61.7	61.3
4	MeO-*p*-BQ	−0.363	−8.4	−65.4	−60.7	61.8	56.4
22	2,5-di-Me-*p*-BQ	−0.428	−9.9	−64.7		61.9	
21	2,5-di-MeO-*p*-BQ	−0.499	−11.5	−63.3		62.1	
31	2,3,5-tri-MeO-*p*-BQ	−0.483	−11.1	−63.8	−63.1	62.3	61.6
10	Cl-*p*-BQ	−0.107	−2.5	−72.8	−69.2	62.6	59.0
1	*p*-BQ	−0.235	−5.4	−70.0		62.7	
3	NH_2-*p*-BQ	−0.524	−12.1	−63.7	−61.8	63.1	61.2
17	2,3-di-Me-*p*-BQ	−0.486	−11.2	−64.7		63.2	
29	2,6-di-Cl-*p*-BQ	−0.015	−0.3	−75.7	−72.6	63.4	60.3
5	HO-*p*-BQ	−0.269	−6.2	−70.2	−64.3	63.7	57.8
8	H_3Si-*p*-BQ	−0.227	−5.2	−71.4	−71.3	64.0	63.9
19	2,3-di-Cl-*p*-BQ	−0.025	−0.6	−76.2		64.1	
24	2,5-di-Cl-*p*-BQ	−0.011	−0.3	−76.6		64.2	
6	HS-*p*-BQ	−0.257	−5.9	−71.4	−69.3	64.6	62.5
9	*F*-*p*-BQ	−0.115	−2.7	−74.6	−71.9	64.6	61.9
39	2,3,5,6-tetra-Cl-*p*-BQ	0.158	3.6	−81.8		65.5	
73	4,5-di-MeO-*o*-BQ	−0.547	−12.6	−65.9		65.8	
2	$(Me)_2$ N-*p*-BQ	−0.573	−13.2	−65.5	−60.8	66.0	61.3
34	2,3,5-tri-Cl-*p*-BQ	0.093	2.1	−81.2	−78.8	66.4	64.0
63	3,5-di-MeO-*o*-BQ	−0.386	−8.9	−70.4	−64.4	66.6	60.6
14	CF_3-*p*-BQ	0.002	0.0	−79.6	−81.8	66.9	69.1
83	3,4,5-tri-MeO-*o*-BQ	−0.668	−15.4	−64.7	−61.3	67.4	64.0
68	3,6-di-MeO-*o*-BQ	−0.182	−4.2	−76.1		67.6	
16	2,3-di-MeO-*p*-BQ	−0.400	−9.2	−71.2		67.7	
74	4,5-di-Me-*o*-BQ	−0.275	−6.3	−74.0		67.7	
53	4-MeO-*o*-BQ	−0.333	−7.7	−72.9	−75.3	67.9	70.3
95	4-Me-*o*-BQ	−0.186	−4.3	−76.5	−75.0	68.1	66.6
84	3,4,5-tri-Me-*o*-BQ	−0.370	−8.5	−72.9	−72.4	68.7	68.2
15	CN-*p*-BQ	0.092	2.1	−83.6	−77.5	68.8	62.7
12	CHO-*p*-BQ	−0.045	−1.0	−80.6	−75.5	69.0	63.9
64	3,5-di-Me-*o*-BQ	−0.273	−6.3	−75.6	−72.9	69.2	66.5
59	3,4-di-Me-*o*-BQ	−0.292	−6.7	−75.3	−76.9	69.3	70.9
69	3,6-di-Me-*o*-BQ	−0.270	−6.2	−76.0		69.5	
20	2,3-di-CN-*p*-BQ	0.465	10.7	−93.3		69.9	
25	2,5-di-CN-*p*-BQ	0.346	8.0	−91.3		70.6	
49	3-Me-*o*-BQ	−0.179	−4.1	−79.6	−78.5	71.0	69.9
86	3,4,5-tri-Cl-*o*-BQ	0.180	4.2	−87.9	−87.3	71.1	70.5
30	2,6-di-CN-*p*-BQ	0.357	8.2	−94.3	−87.5	71.3	66.6
78	3,4,6-tri-MeO-*o*-BQ	−0.308	−7.1	−77.0	−76.3	71.4	70.7
51	3-Cl-*o*-BQ	0.051	1.2	−85.5	−85.6	71.6	71.7
89	3,4,5,6-tetra-Me-*o*-BQ	−0.452	−10.4	−73.9		71.6	
47	*o*-BQ	−0.090	−2.1	−82.3		71.6	
79	3,4,6-tri-Me-*o*-BQ	−0.377	−8.7	−75.8	−72.4	71.8	68.4
88	3,4,5,6-tetra-MeO-*o*-BQ	−0.453	−10.4	−74.5		72.3	
58	3,4-di-MeO-*o*-BQ	−0.227	−5.2	−80.3	−76.7	72.9	69.3
81	3,4,6-tri-Cl-*o*-BQ	0.220	5.1	−90.8	−91.3	73.0	73.5
66	3,5-di-Cl-*o*-BQ	0.122	2.8	−88.5	−87.6	73.0	72.1
56	4-Cl-*o*-BQ	−0.009	−0.2	−85.7	−83.7	73.2	71.2
71	3,6-di-Cl-*o*-BQ	0.182	4.2	−90.2		73.3	
36	2,3,5,6-tetra-MeO-*p*-BQ	−0.535	−12.3	−73.9		73.6	
41	1,4,5,8-tetra-BQ	0.367	8.5	−94.8		73.7	
57	4-CN-*o*-BQ	0.228	5.3	−91.8	−93.8	73.9	75.9
76	4,5-di-Cl-*o*-BQ	0.081	1.9	−88.6		74.0	
61	3,4-di-Cl-*o*-BQ	0.097	2.2	−88.9	−86.9	74.0	71.9
91	3,4,5,6-tetra-Cl-*o*-BQ	0.280	6.5	−93.9		74.8	
35	2,3,5-tri-CN-*p*-BQ	0.701	16.2	−103.8	−100.2	75.0	71.3
52	3-CN-*o*-BQ	0.204	4.7	−93.1	−90.4	75.7	73.0
72	3,6-di-CN-*o*-BQ	0.492	11.3	−100.9		76.9	
40	2,3,5,6-tetra-CN-*p*-BQ	0.974	22.5	−112.7		77.6	
62	3,4-di-CN-*o*-BQ	0.558	12.9	−106.2	−103.6	80.6	78.0

TABLE 3. Continued

compd		E_{NHE} (V)	FE_{NHE}	$\Delta G_{\mathrm{H}^-\mathrm{A}}$(Q) (kcal/mol)		BDE(QH^-) (kcal/mol)	
				to $\mathrm{QH_a}^-$	to $\mathrm{QH_b}^-$	$\mathrm{QH_a}^-$	$\mathrm{QH_b}^-$
67	3,5-di-CN-*o*-BQ	0.510	11.8	−105.0	−101.1	80.6	76.7
77	4,5-di-CN-*o*-BQ	0.497	11.5	−105.2		81.1	
82	3,4,6-tri-CN-*o*-BQ	0.827	19.1	−113.5	−113.8	81.7	82.0
87	3,4,5-tri-CN-*o*-BQ	0.822	19.0	−114.5	−112.9	82.9	81.3
92	3,4,5,6-tetra-CN-*o*-BQ	1.128	26.0	−124.5		85.8	

TABLE 4. Linear Relationship ($y = kx + b$) between the Electron Affinities of Quinones, the Reduction Potentials of Quinones, the Hydricities of Hydroquinone Anions, the Hydrogen Affinities of Quinone Radical Anions, and the Hammett Substituent σ_{p}[a]

y	x	k	b	r
		p-benzquinones		
ΔG_{H^-}A(Q)	E_{NHE}	33.86	78.53	0.9875
BDE(QH^-)	E_{NHE}	10.64	65.78	0.9006
BDE(QH^-)	ΔG_{H^-}A(Q)	0.33	39.91	0.9569
EA	E_{NHE}	1.58	2.46	0.9866
E_{NHE}	$\Sigma\sigma_{\mathrm{p}}$	0.45	−0.19	0.9615
ΔG_{H^-}A(Q)	$\Sigma\sigma_{\mathrm{p}}$	16.00	70.50	0.9808
BDE(QH^-)	$\Sigma\sigma_{\mathrm{p}}$	5.05	63.18	0.9025
EA	$\Sigma\sigma_{\mathrm{p}}$	0.77	2.13	0.9740
		o-benzquinones		
ΔG_{H^-}A(Q)	E_{NHE}	34.39	85.45	0.9841
BDE(QH^-)	E_{NHE}	11.23	72.64	0.9324
BDE(QH^-)	ΔG_{H^-}A(Q)	0.34	43.69	0.9706
EA	E_{NHE}	1.69	2.28	0.9838
E_{NHE}	$\Sigma\sigma_{\mathrm{p}}$	0.45	−0.06	0.9640
ΔG_{H^-}A(Q)	$\Sigma\sigma_{\mathrm{p}}$	16.20	81.50	0.9912
BDE(QH^-)	$\Sigma\sigma_{\mathrm{p}}$	5.33	71.30	0.9330
EA	$\Sigma\sigma_{\mathrm{p}}$	0.82	2.15	0.9819

[a] Substituents with strong electrostatic inductive effect, such as MeO, were excluded in these correlations.

redox potentials.[67,68] In this work, we have a unique opportunity to reliably reinvestigate this important correlation, since no one has compiled as many standard redox potentials of quinones in DMSO and $\mathrm{CH_3CN}$ previously. In order to systematically reveal some important information about the solvation effect on reduction potentials, two plots of the electron affinities against reduction potentials of *p*-benzquinone and *o*-benzquinone in DMSO are given in Supporting Information (Figures S3 and S4); from these figures, it is found that there are good linear correlations between electron affinities and reduction potentials:

$$\mathrm{EA}(p\text{-Q}) \approx 1.58E_{\mathrm{NHE}}(p\text{-Q}/p\text{-Q}^{\bullet-}) + 2.46 \quad (\mathrm{V}) \qquad (26)$$

$$\mathrm{EA}(o\text{-Q}) \approx 1.69E_{\mathrm{NHE}}(o\text{-Q}/o\text{-Q}^{\bullet-}) + 2.28 \quad (\mathrm{V}) \qquad (27)$$

Since

$$E_{\mathrm{NHE}}(p\text{-Q}/p\text{-Q}^{\bullet-}) \approx 0.45\sum\sigma_{\mathrm{p}} - 0.194 \quad (\mathrm{V}) \qquad (15)$$

$$E_{\mathrm{NHE}}(o\text{-Q}/o\text{-Q}^{\bullet-}) \approx 0.45\sum\sigma_{\mathrm{p}} - 0.059 \quad (\mathrm{V}) \qquad (16)$$

it will be straightforward to derive the following equations:

$$\mathrm{EA}(p\text{-Q}) \approx 0.73\sum\sigma_{\mathrm{p}} - 2.15 \quad (\mathrm{V}) \qquad (28)$$

$$\mathrm{EA}(o\text{-Q}) \approx 0.76\sum\sigma_{\mathrm{p}} - 2.18 \quad (\mathrm{V}) \qquad (29)$$

In general, using only Hammett parameter σ_{p}, four important thermodynamic parameters of quinones, that is, EA(Q), $E_{\mathrm{NHE}}(\mathrm{Q/Q^{\bullet-}})$, BDE($\mathrm{QH}^-$), and $\Delta G_{\mathrm{H}^-\mathrm{A}}$(Q) can be estimated at the same time. The detailed correlations between these five parameters are shown in Supporting Information and summarized in Table 4.

Conclusions

In the present study, we have performed a high level computation (B3LYP/DZP++ for gas-phase electron affinities estimations and PCM method for the solvation energies calculations, respectively) and obtained reliable, accurate electron affinities and reduction potentials of quinones in DMSO and $\mathrm{CH_3CN}$. The primary value of the study is that it provides the scale of the reduction potentials of quinones, ranging from −0.949 to 1.128 V in DMSO and from −1.005 to 1.284 V in $\mathrm{CH_3CN}$. Such a wide scale of the reduction potentials evidently shows that the 116 quinones can construct a large and useful library of organic oxidants, which can provide various electron acceptors that may be needed. The reduction potentials range from −0.535 (**39**) to 0.974 (**127**) V for *p*-benzquinones and from −0.547 (**3**) to 1.128 (**128**) V for *o*-benzquinones. The reduction potentials of *p*-quinones are generally smaller than those of *o*-quinones by about 0.13 V. The reduction potentials of quinones with aromatic benzene rings range from −0.624 (**21**) to −0.153 (**93**) V for 1,4-naphthquinones, from −0.794(**6**) to −0.265 (**87**) V for 1,4-anthraquinones, and from −0.949 (**1**) to −0.705 (**67**) V for 9,10-anthraquinones. Second, the study demonstrated that the reduction potentials of *p*-quinones and *o*-quinones have linear correlations with the Hammett substituent parameter $\Sigma\sigma_{\mathrm{p}}$ (r = 0.9679 and 0.9674 for *p*-quinones and *o*-quinones, respectively): $E_{\mathrm{NHE}}(p\text{-Q}/p\text{-Q}^{\bullet-}) \approx 0.45\Sigma\sigma_{\mathrm{p}} - 0.194$ (V) and $E_{\mathrm{NHE}}(o\text{-Q}/o\text{-Q}^{\bullet-}) \approx 0.45\Sigma\sigma_{\mathrm{p}} - 0.059$ (V). According to the line slopes and line intercepts, the reduction potentials of any substituted quinones can be easily estimated. Combined with the hydride affinities reported in the former paper ($\Delta G_{\mathrm{H}\text{-}}(p\text{-Q}) \approx -16.0\Sigma\sigma_{\mathrm{p}}$ — 70.5 (kcal/mol) and $\Delta G_{\mathrm{H}\text{-}}(o\text{-Q}) \approx -16.2\Sigma\sigma_{\mathrm{p}}$ — 81.5 (kcal/mol)) and the reduction potentials estimated in this work, the homolytic bond dissociation energies of the hydroquinone anions in DMSO were calculated. We determined that BDE-(p-QH-) $\approx 5.05\Sigma\sigma_{\mathrm{p}} + 63.18$ (kcal/mol) and BDE(o-QH-) $\approx 5.33\Sigma\sigma_{\mathrm{p}} + 71.30$ (kcal/mol) only if the substituents have no large electrostatic inductive force and no large steric hindrance. Third, the study also suggested that gas-phase electron affinities have a good linear correlation with the

---

(67) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

(68) Recent examples: (a) Dhiman, A.; Becker, J. Y.; Minge, O.; Schmidbaur, H.; Muller, T. *Organometallics* **2004**, *23*, 1636. (b) Ue, M.; Murakami, A.; Nakamura, S. *J. Am. Chem. Soc.* **2002**, *149*, 1572.

reduction potentials of quinones in DMSO. From the correlation slope and intercept, we obtained that EA(p-Q) $\approx$ $0.77\Sigma\sigma_p - 2.13$ (V) and EA(o-Q) $\approx$ $0.82\Sigma\sigma_p - 2.15$ (V). Knowledge of these important and hard-to-obtain electron affinities in the gas phase and reduction potentials in solution and the conclusions on the effects of substituent, structure of quinone, and solvent on the reduction potentials of quinones are of great value for providing important clues to use quinones as oxidants as well as predicting the thermodynamic mechanisms of the reductions of the quinones.

Acknowledgment. Financial support from the National Natural Science Foundation of China (Grant Nos. 20921120403, 20832004, 20721062 and 20672060), 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: Experimental gas-phase electron affinities and liquid-phase (DMSO and CH_3CN) reduction potentials of quinones. The calculated gas-phase electron affinities, solvation energies, the correlationship between gas-phase electron affinities, reduction potentials in DMSO and CH_3CN, bond dissociation energies of hydroquinone anions, hydride affinities of quinones and the Hammett substituent parameter σ_p. This material is available free of charge via the Internet at http://pubs.acs.org.