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Theoretical Prediction of the Hydride Affinities of Various *p*- and *o*-Quinones in DMSO

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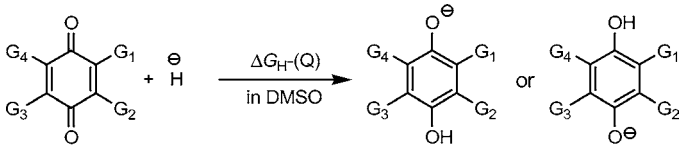
Received October 21, 2006



Quinone (Q)

The hydride affinities of 80 various *p*- and *o*-quinones in DMSO solution were predicted by using B3LYP/6-311++G (2df,p)//B3LYP/6-31+G* and MP2/6-311++G**//B3LYP/6-31+G* methods, combined with the PCM cluster continuum model for the first time. The results show that the hydride affinity scale of the 80 quinones in DMSO ranges from −47.4 kcal/mol for 9,10-anthraquinone to −124.5 kcal/mol for 3,4,5,6-tetracyano-1,2-quinone. Such a long scale of the hydride affinities (−47.4 to −124.5 kcal/mol) indicates that the 80 quinones can form a large and useful library of organic oxidants, which can provide various organic hydride acceptors that the hydride affinities are known for chemists to choose in organic syntheses. By examining the effect of substituent on the hydride affinities of quinones, it is found that the hydride affinities of quinones in DMSO are linearly dependent on the sum of the Hammett substituent parameters σ: $\Delta G_H^-(Q) \approx -16.0\Sigma\sigma_i - 70.5$ (kcal/mol) for *p*-quinones and $\Delta G_H^-(Q) \approx -16.2\Sigma\sigma_i - 81.5$ (kcal/mol) for *o*-quinones only if the substituents have no large electrostatic inductive effect and large ortho-effect. Study of the effect of the aromatic properties of quinone on the hydride affinities showed that the larger the aromatic system of quinone is, the smaller the hydride affinity of the quinone is, and the decrease of the hydride affinities is linearly to take place with the increase of the number of benzene rings in the molecule of quinones, from which the hydride affinities of aromatic quinones with multiple benzene rings can be predicted. By comparing the hydride affinities of *p*-quinones and the corresponding *o*-quinones, it is found that the hydride affinities of *o*-quinones are generally larger than those of the corresponding *p*-quinones by ca. 11 kcal/mol. Analyzing the effect of solvent on the hydride affinities of quinones showed that the effects of solvent (DMSO) on the hydride affinities of quinones are mainly dependent on the electrostatic interaction of the charged hydroquinone anions (QH^-) with solvent (DMSO). All the information disclosed in this work should provide some valuable clues to chemists to choose suitable quinones or hydroquinones as efficient hydride acceptors or donors in organic syntheses and to predict the thermodynamics of hydride exchange between quinones and hydroquinones in DMSO solution.

Introduction

Quinones and their corresponding hydride reduced forms, hydroquinones, are two types of very important organic compounds, the chemistry of which occupies an important place in the fields of chemistry, biological chemistry, and technochemistry.[1−8] Since quinone can become hydroquinone by obtaining a hydride anion, and the hydroquinone can return to quinone by releasing a hydride (eq 1), it is evident that quinones can serve as hydride acceptors. In fact, many well-known quinones, such as *p*-chloranil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and

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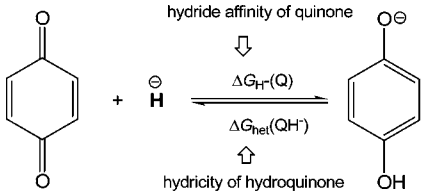
10.1021/jo0621928 CCC: $37.00 © 2007 American Chemical Society
Published on Web 01/09/2007

tetracyano-*p*-benzoquinone all have strong power of oxidation, which have been extensively used as oxidants in organic syntheses.[9] At the same time, it is also evident that hydroquinones serving as hydride donors may be used as reducing agents and many important hydroquinones, such as dihydroquinone, coenzyme Q,[10] catechol,[10] hydronaphthoquinone,[11] as hydride or electron donors play very vital roles in cellular respiration,[12] blood coagulation,[13] and plant and bacterial photosynthesis.[14] Since the family of quinones and the family of hydroquinones are very large, and the abilities of quinones to obtain a hydride and of hydroquinones to release a hydride are generally quite different from each other, respectively, which indicates that it is necessary to develop the hydride affinity scale of various quinones and the hydricity scale of various hydroquinones in gas phase, especially in solution to quantitatively predict the oxidation potential order of quinones and the reduction potential order of hydroquinones. Examination of the past publications on this subject shows that although much attention has been paid to the chemistry of quinones and hydroquinones,[15−25] rather scant attention has been paid to the determination of the hydride affinities of quinones or the hydricity of hydroquinones especially in solution, the main reason is that the reactions of quinones with hydride are quite complex, which could result in large uncertainties of the experimental observations.[26−28]In fact, no hydride affinities of quinones and no hydricities of hydroquinones in solution were reported so far except for five hydride affinities of quinones in DMSO, which were estimated by Parker and co-workers using thermodynamic cycle method in 1993.[29] It is clear that the terrible lack of knowledge about the hydride affinities of quinones and the hydricities of hydroquinones in solution has seriously restricted the development of the chemistry of quinones and hydroquinones.



(1)

$$\Delta G_{H^-}(Q) = -\Delta G_{het}(QH^-) \quad (2)$$

Since Pople was awarded the Nobel Prize in 1994, computational chemistry has achieved great progress. Some important thermodynamic parameters of organic small molecules in gas phase, such as bond dissociation energy (BDE), can be calculated with the accuracy equivalent or better than that obtained from experiments, when the extended basis sets are used and the electron correlation effects are recovered through post-Hartree−Fock or density functional approaches.[30,31] In fact, at present, the hydride affinities of some organic small molecules like the BDE in the gas phase also can be accurately estimated by theoretical methods.[32−35] At the same time, the theoretical

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estimations of solvation effect on the thermodynamic parameters also have achieved great progress. Several efficient approaches to estimate solvation energy including molecular simulations,[36] Langevin dipole models,[37] integral equation techniques,[38] and dielectric continuum methods[39] have been developed. Among these well-known methods, the dielectric continuum method becomes more and more popular.[40] One of the best representatives of this method is the polarized continuum model (PCM), which was developed by Tomasi and co-workers in 1997.[41] By using the PCM method, the mean error of the estimated absolute solvation energies in water can reach as small as about 0.5−2.2 pK_a units for some neutral molecules and ions, respectively.[42] Recently, Guo and co-workers used the PCM method to successfully predict the pK_a's of 105 organic acids in DMSO; the precision is within 1.7−1.8 pK_a units.[43] More recently, Guo and co-workers have developed a generally applicable protocol that could well predict the standard redox potentials of 270 structurally unrelated organic molecules in acetonitrile, and the results all are very well in agreement with the experimental observations.[44] All these great achievements of computational chemistry encourage us to examine the hydride affinity scale of various quinones and the hydricity scale of various hydroquinones in solution by using theoretical method. In this work, the hydride affinities of 80 important *p*- and *o*-quinones (Scheme 1) in dimethyl sulfoxide (DMSO) solution were examined in order to develop the hydride affinity scale of various quinones and the hydricity scale of various hydroquinones in DMSO solution. Since the hydricity of hydroquinone is just equal to the hydride affinity of the corresponding quinone by switching the sign (eq 2), only the hydride affinity scale of the various quinones in DMSO was developed in this paper.

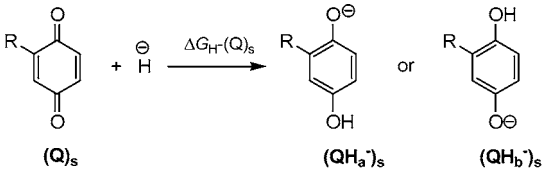
Computational Methods

All the calculations were conducted using Gaussian 98 programs.[45] The geometry of each species was optimized using the B3LYP/6-31+G* method. 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. Single-point electronic energies were derived at the B3LYP/6-311++G (2df,p) and MP2/6-311++G** levels (they are denoted as B3LYP and MP2 in the following discussion, respectively). The free energy change was corrected with ZPE, thermal corrections (0−298 K), and the entropy term obtained at the B3LYP/6-31+G* level. The calculations of gas-phase free energies use a reference state of 1 atm and 298 K.

Solvation energies were estimated with the most recent PCM version called integral equation formalism (IEFPCM).[46] This model has been shown to have a significantly extended range of applications with dramatically improved accuracy. The solvation effects were calculated at the level of HF/6-31+G** ($\alpha = 1.35$, radii = bondi).[47] It is worth noting that in this work the geometries of the molecules in gas phase were used in DMSO solution for energy calculations according to the following two reasons: (i) the effect of solvent DMSO on the molecular geometry is usually not significant;[48] (ii) the energy of molecular geometry change from one phase to another phase can be ignored in an isodesmic reaction.[49]

Definition and Results

Hydride affinity of quinone in solution is defined in this work as the free energy change in the reaction of quinone with free hydride ion to form the corresponding hydroquinone anion at 25 °C in solution (eqs 3 and 4).[50]



(3)

$$\Delta G_H^-(Q)_s = G(QH^-)_s - [G(Q)_s + G(H^-)_s] \quad (4)$$

In the eqs 3 and 4, the subscript **s** is a symbol of solution phase. Since asymmetrically substituted quinones, such as **2**−**15**,

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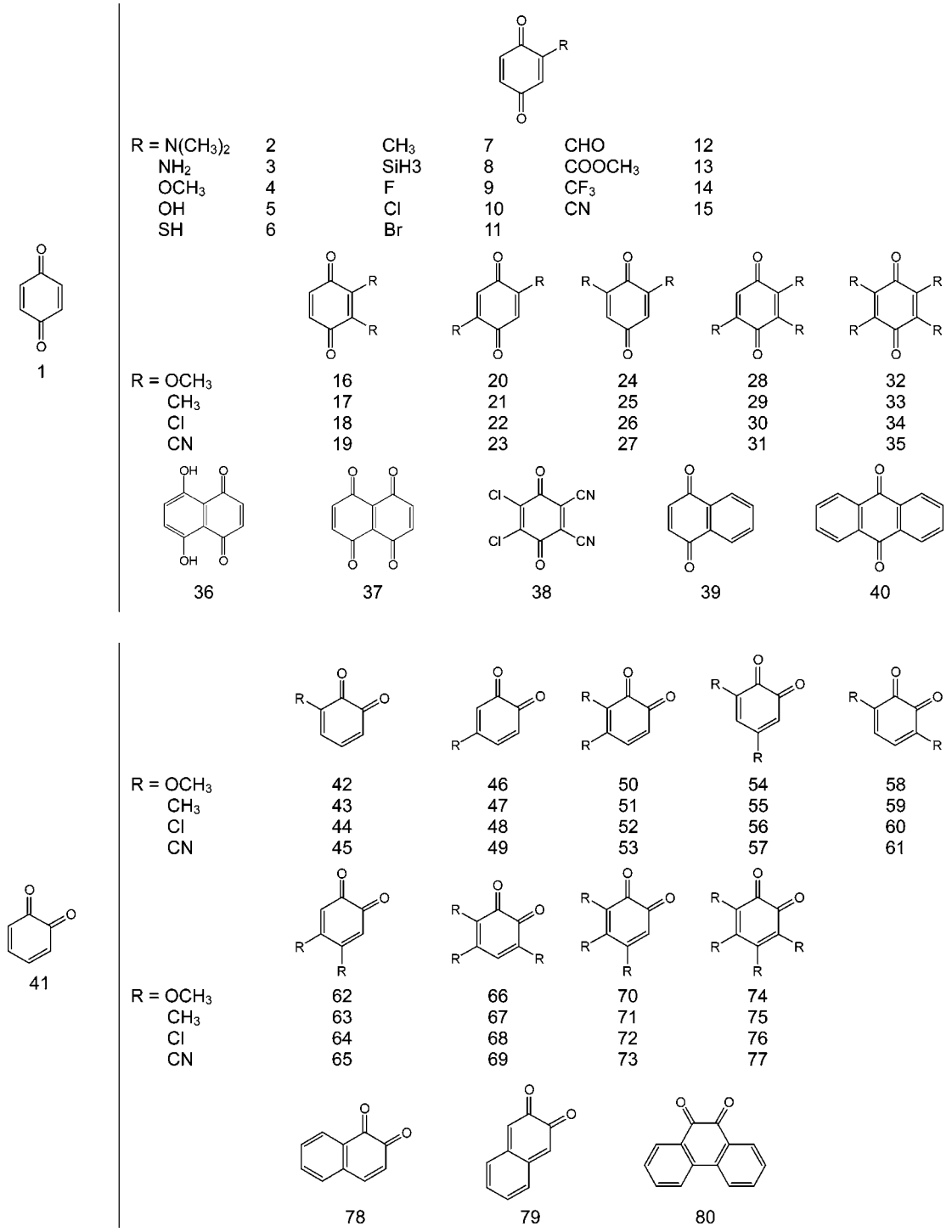
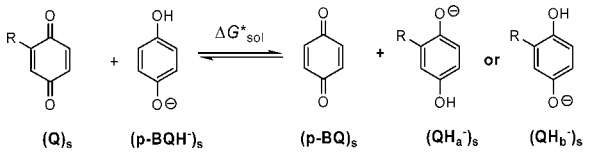
SCHEME 1. Chemical Structures of 80 Examined Quinones



24−**31**, **42**−**57**, **66**−**73**, and **78** can yield two different hydroquinone anions QH_a^- and QH_b^- in the reductions, the asymmetrically substituted quinones should have two different hydride affinities $\Delta G_H^-(QH_a^-)_s$ and $\Delta G_H^-(QH_b^-)_s$ for the formation of QH_a^- with more substituents close to the negatively charged oxygen and for the formation of QH_b^- with less substituents close to the negatively charged oxygen, respectively.

In order to safely estimate the hydride affinities of quinones in DMSO $[\Delta G_H^-(Q)_s]$, *p*-BQ was chosen as a reference to construct an isodesmic reaction, i.e., hydride interchange reaction (eq 5), since the accurate hydride affinity of *p*-BQ in DMSO is available (−70.0 kcal/mol).[29]

In eq 5, ΔG_{sol}* is the Gibbs energy change of the isodesmic reaction in DMSO, which is equal to the difference of hydride affinities between Q and the reference *p*-BQ in DMSO (eq 6). It is clear that the hydride affinity of Q in DMSO $[\Delta G_H^-(Q)_s]$ should be equal to the summation of the Gibbs energy change of the isodesmic reaction in DMSO (ΔG_{sol}*) and the hydride affinity of the reference *p*-BQ in DMSO $[\Delta G_H^-(p\text{-BQ})_s]$ (eq 7). Since the hydride affinity of *p*-BQ in DMSO is well-known,



(5)

$$\Delta G_{sol}^{*} = \Delta G_{H^-}(Q)_s - \Delta G_{H^-}(p\text{-BQ})_s \quad (6)$$

$$\Delta G_{H^-}(Q)_s = \Delta G_{H^-}(p\text{-BQ})_s + \Delta G_{sol}^{*} \quad (7)$$

the hydride affinities of the specimen quinones in DMSO can be easily obtained from the eq 7 only if ΔG_{sol}^{*} is available.

In order to calculate the ΔG_{sol}^{*}, a thermodynamic cycle was constructed as shown in Scheme 2, from which ΔG_{sol}^{*} can be expressed with ΔG_g^{*} and ΔG_{sol} (eq 8)

$$\Delta G_{sol}^{*} = \Delta G_g^{*} + \Delta G_{sol} \quad (8)$$

where ΔG_g^{*} is the standard Gibbs energy change of the isodesmic reaction in gas phase and ΔG_{sol} is solvation energy of the isodesmic reaction in DMSO, which can further be expressed with eqs 9 and 10, respectively:

$$\Delta G_g^{*} = G_g(QH^-) + G_g(p\text{-BQ}) - G_g(Q) - G_g(p\text{-BQH}^-) \quad (9)$$

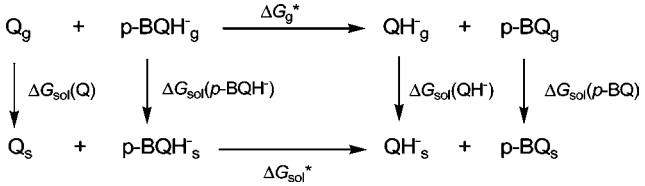
$$\Delta G_{sol} = \Delta G_{sol}(QH^-) + \Delta G_{sol}(p\text{-BQ}) - \Delta G_{sol}(Q) - \Delta G_{sol}(p\text{-BQH}^-) \quad (10)$$

Therefore, considering eqs 8−10, eq 7 becomes eq 11:

$$\Delta G_{H^-}(Q_s) = \Delta G_{H^-}(p\text{-BQ}) + \Delta G_{sol}^{*} = \Delta G_{H^-}(p\text{-BQ}) + \Delta G_g^{*} + \Delta G_{sol} = \Delta G_{H^-}(p\text{-BQ}) + \{[G_g(QH^-) + \Delta G_{sol}(QH^-)] - [G_g(Q) + \Delta G_{sol}(Q)]\} + \{[G_g(p\text{-BQ}) + \Delta G_{sol}(p\text{-BQ})] - [G_g(p\text{-BQH}^-) + \Delta G_{sol}(p\text{-BQH}^-)]\} \quad (11)$$

In eq 11, $\Delta G_{H^-}(p\text{-BQ})$ is the hydride affinity of the reference *p*-BQ in DMSO available from literature (−70.0 kcal/mol).[29] $G_g(Q)$, $G_g(QH^-)$, $G_g(p\text{-BQ})$, and $G_g(p\text{-BQH}^-)$ are the standard state Gibbs free energies of the species Q, QH^-, *p*-BQ, and *p*-BQH^- in the gas phase, which can be estimated by using B3LYP and MP2 methods; the detailed results are listed in Table S1 (Supporting Information). $\Delta G_{sol}(Q)$, $\Delta G_{sol}(QH^-)$, $\Delta G_{sol}(p\text{-BQ})$, and $\Delta G_{sol}(p\text{-BQH}^-)$ are the solvation energies of species Q, QH^-, *p*-BQ, and *p*-BQH^- in DMSO. Since the solution−solvent interactions consist of an electrostatic interaction, a cavity interaction, a dispersion interaction, and a repulsion interaction, all four contributions were considered in the estimation of solvation energies according to IEFPCM models.[51] The detailed results are listed in Table S2 (Supporting Information). According to the results in Tables S1 and S2, the hydride affinities of the 80 examined quinones in DMSO can be obtained from eq 11; the detailed results are summarized in Table 1.

SCHEME 2. Thermodynamic Cycle Proposed To Convert Standard Gibbs Energy of the Isodesmic Reaction in the Gas Phase to the Standard Gibbs Free Energy of the Reaction in the Solution Phase



Discussion

Reliability of the Calculated Values. Since this is the first estimation of the hydride affinities of quinones in DMSO by using theoretical methods, the reliability of the estimated results need to be examined.

At first, the examination was carried out in the estimations of gas-phase values. As is well-known, considerable evidence has shown that the geometry optimization of molecular structure is reliable by using the B3LYP method.[47] Although the methods of B3LYP and MP2 could usually underestimate the absolute bond energies of molecules, the calculated results about the absolute bond energies of molecules are very reliable if suitable isodesmic reactions are used.[52,53] In the present study, *p*-BQ was chosen as a reference to construct isodesmic reactions, and the state free energies of the relative species in gas phase were calculated at B3LYP/6-311++G (2df,p)//B3LYP/6-31+G* and MP2/6-311++G**//B3LYP/6-31+G* level of theories. The relative hydride affinities of quinones in gas phase (ΔG_g^{*}) are summarized in Table S1 (Supporting Information). Since the

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(49) (a) Namazian, M.; Almodarresieh, H. A. *J. Mol. Struct.* **2004**, *686*, 97. (b) Heravi, M. J.; Namazian, M.; Peacock, T. E. *J. Electroanal. Chem.* **1995**, *385*, 1. (c) Heravi, M. J.; Namazian, M. *J. Electroanal. Chem.* **1997**, *425*, 139.

(50) In fact, the reaction of quinone with hydride in DMSO could be initiated by the hydride transfer to the carbon atom rather than to the oxygen atom in the carbonyl groups of quinones to form a nonaromatic hydroquinone anion, the formed nonaromatic hydroquinone anion then automatically become stabler aromatic hydroquinone anion as the final product: QH_a^- or QH_b^- by [1,5] proton transfer. In this paper, the hydride affinity of quinone denotes the free energy change of the reaction from quinone to the final aromatic hydroquinone anion rather than to the nonaromatic hydroquinone anion, the free energy change of the latter does not belong to the hydride affinities of quinones, merely belongs to the hydride affinities of carbonyl compounds. The investigations on the hydride affinity of carbonyl group in quinone are in progress in our laboratory.

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TABLE 1. Theoretical Hydride Affinities of the 80 Quinones Shown in Scheme 1 in DMSO (kcal/mol)

	$-\Delta G_H^-$(*p*-quinone)					$-\Delta G_H^-$(*o*-quinone)			
	B3LYP		MP2			B3LYP		MP2	
Q	QH_a^-	QH_b^-	QH_a^-	QH_b^-	Q	QH_a^-	QH_b^-	QH_a^-	QH_b^-
1	70		70		**41**	82.8		82.3	
2	60.9	58.0	65.5	60.8	**42**	95.7	97.2	97.1	98.2
3	60.0	58.8	63.7	61.8	**43**	79.3	78.6	79.6	78.5
4	63.6	60.4	65.4	60.7	**44**	86.7	86.0	85.5	85.6
5	68.3	63.2	70.2	64.3	**45**	95.5	91.9	93.1	90.4
6	70.3	67.9	71.4	69.3	**46**	73.2	74.5	72.9	75.3
7	64.3	66.7	65.3	67.2	**47**	76.8	75.1	76.5	75.0
8	70.8	71.1	71.4	71.3	**48**	86.9	85.2	85.7	83.7
9	74.6	72.5	74.6	71.9	**49**	93.8	97.5	91.8	93.8
10	73.4	70.4	72.8	69.2	**50**	76.8	73.7	80.3	76.7
11	75.7	70.9	75.2	70.1	**51**	74.9	76.5	75.3	76.9
12	83.6	76.4	80.6	75.5	**52**	90.5	88.6	88.9	86.9
13	76.2	79.7	72.9	78.8	**53**	109.7	107.8	106.2	103.6
14	80.3	81.6	79.6	81.8	**54**	67.8	63.5	70.4	64.4
15	85.8	78.5	83.6	77.5	**55**	74.8	72.7	75.6	72.9
16	67.0		71.2		**56**	90.4	89.2	88.5	87.6
17	63.5		64.7		**57**	109.9	103.9	105.0	101.1
18	77.7		76.2		**58**	74.0		76.1	
19	96.3		93.3		**59**	75.5		76.0	
20	59.5		63.3		**60**	91.8		90.2	
21	63.2		64.7		**61**	104.0		100.9	
22	78.2		76.6		**62**	63.0		65.9	
23	93.6		91.3		**63**	73.7		74.0	
24	56.5	52.4	59.8	54.0	**64**	90.4		88.6	
25	62.6	62.9	64.4	64.0	**65**	109.0		105.2	
26	76.7	74.0	75.7	72.6	**66**	73.3	72.3	77.0	76.3
27	98.2	89.2	94.3	87.5	**67**	75.0	71.4	75.8	72.4
28	58.3	57.9	63.8	63.1	**68**	92.8	93.5	90.8	91.3
29	59.4	58.8	61.7	61.1	**69**	117.7	119.3	113.5	113.8
30	82.8	80.3	81.2	78.8	**70**	60.6	57.9	64.7	61.3
31	107.4	103.3	103.8	100.2	**71**	72.6	72.3	72.9	72.4
32	68.1		73.9		**72**	89.8	89.1	87.9	87.3
33	54.5		57.3		**73**	119.2	117.1	114.5	112.9
34	83.4		81.8		**74**	69.8		74.5	
35	115.9		112.7		**75**	73.1		73.9	
36	59.5		63.1		**76**	96.2		93.9	
37	100.8		94.8		**77**	129.8		124.5	
38	101.0		98.2		**78**	72.5	70.5	71.3	69.4
39	61.6		61.1		**79**	97.5		99.6	
40	49.6		47.4		**80**	64.3		62.3	

relative hydride affinities derived from MP2 are very close to the results derived from B3LYP, and the linear relationship of the two results is quite good (see Figure 1, the line slope is 0.92 and the *r* value of the line is 0.997), the constructed isodesmic reactions should be very suitable, which indicates that the estimated relative hydride affinities of quinones in gas phase should be quite reliable according to the statements above.

For the hydride affinities of quinones in DMSO, the reliability of the estimation can be supported by the four available experimental values of quinones in DMSO (see Table 2).

From Table 2, it is clear that the four hydride affinities of quinones **33**, **34**, **38**, and **76** in DMSO obtained in this work all are very close to the corresponding previously reported experimental observations, respectively, which indicates that the calculated results in this work should be reliable. Since the results estimated by using MP2 method are much closer to the experimental determinations than the results estimated by using B3LYP method, the results from MP2 were chosen in the following discussion for convenience.

Hydride Affinity Scale of the 80 Quinones in DMSO. From Table 1, it is clear that the hydride affinity scale of the 80 quinones in DMSO ranges from −47.4 kcal/mol for quinone **40** (9,10-anthraquinone) to −124.5 kcal/mol for quinone **77** (3,4,5,6-tetracyano-1,2-quinone). Such a long scale of the hydride affinities of the quinones (−47.4 to −124.5 kcal/mol) evidently shows that the 80 quinones could construct a large and useful library of organic hydride acceptors, which can provide various organic oxidants that the hydride affinities are known for chemists to choose in organic syntheses. Evidently, in the library, quinone **77** is the strongest hydride acceptor [ΔG_H^-(**77**)$_{DMSO}$ = −124.5 kcal/mol], the ability of **77** to accept hydride is not only far larger than that of the well-known strong hydride acceptor, triphenylcarbenium, in DMSO (ΔG_H^- = −96.5 kcal/mol),[54] but also larger than that of 9-methyl-10-nitroanthracene carbenium (ΔG_H- = −120 kcal/mol) by 4.5 kcal/mol,[55] the latter has the largest hydride affinity known so far. This result indicates that quinone **77** can capture hydride from all of the known organic hydride donors so far. But as to quinone **40**, the hydride affinity is −47.4 kcal/mol, quite smaller than NAD^+ coenzyme model BNA^+ [$\Delta G_H^-(BNA^+)_{DMSO}$ = −59.0 kcal/mol],[56] which indicates that quinone **40** cannot be reduced by NADH and its models in DMSO under general experimental conditions; in fact, this suggestion is also in line with experimental results. Since *p*-BQ (**1**) is a well-known weak organic hydride acceptor (ΔG_H^- = −70.0 kcal/mol in DMSO), chloranil (**34**) is a well-known middle-strong organic hydride acceptor (ΔG_H^- = −82 kcal/mol in DMSO), tetracyano-*p*-benzoquinone (**35**) and DDQ (**38**) are well-known strong organic hydride acceptors (ΔG_H^- = −112.7 kcal/mol for **35** and 98.2 kcal/mol for **38** in DMSO), the hydride affinity scale of the 80 quinones can be grouped into three categories. The first category is that the hydride affinities are less negative than −70 kcal/mol, in

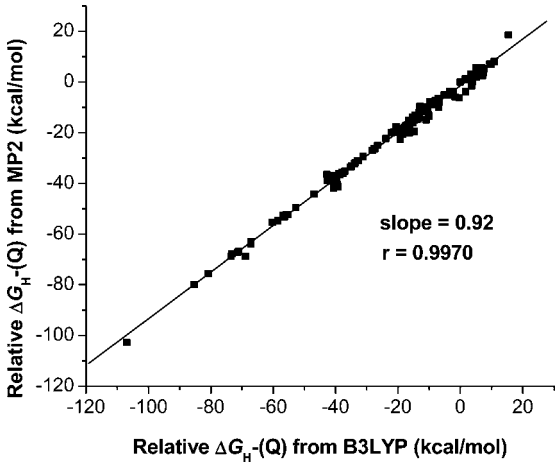


FIGURE 1. Relationship between the two results from MP2 and B3LYP about the relative hydride affinities of the quinones in gas phase.

TABLE 2. Comparison between the Theoretical and Experimental Hydride Affinities of Quinones in DMSO (kcal/mol)

			theoretical[b]	
quinone	no.	experimental[a]	B3LYP	MP2
p-BQ	**1**	−70	−70	−70
tetramethyl-*p*-BQ	**33**	−58	−55	−57
tetrachloro-*p*-BQ	**34**	−83	−83	−82
DDQ	**38**	−101	−101	−98
tetrachloro-*o*-BQ	**76**	−91	−96	−94

[a] From the literature: Cheng, J.-P.; Handoo, K. L.; Xue, J.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 5050. [b] From Table 1.

(54) Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655.

(55) Unless specified, the magnitude of the hydride affinity in this paper indicates the absolute value rather than the pure mathematical values (negative values) for the sake of convention.

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

this category, the quinones are due to the weak organic hydride acceptors. The second category is that the hydride affinities are within −70 to −90 kcal/mol, in the second category, the quinones are due to the middle-strong organic hydride acceptors. The third category is that the hydride affinities are more negative than −90 kcal/mol; in this category, the quinones are due to the strong organic hydride acceptors. According to this simple classification, quinones **19**, **23**, **27**, **31**, **35**, **36**, **38**, **42**, **45**, **49**, **53**, **57**, **60**, **61**, **65**, **68**, **69**, **73**, **76**, **77**, and **79** all are due to the strong organic hydride acceptors; generally, these quinones can be chosen as good organic oxidants in organic syntheses. By contrast, quinones **2**−**4**, **7**, **17**, **20**, **21**, **24**, **25**, **28**, **29**, **33**, **36**, **39**, **40**, **62**, **70**, and **80** all are due to weak organic hydride acceptors; generally, these quinones cannot be chosen as efficient organic oxidants in organic syntheses. But, according to the well-known relationship that if quinone (Q) is a weak hydride acceptor, the corresponding hydroquinone anion (QH^-) should be a strong hydride donor, it is certain that the corresponding hydroquinone anions (QH^-) of **2**−**4**, **7**, **17**, **20**, **21**, **24**, **25**, **28**, **29**, **33**, **37**, **39**, **40**, **62**, **70**, and **80** should be strong hydride donors, which can be used as good organic reducing agents in organic syntheses. In fact, many important dihydroquinones (QH_2), such as 1,4-dihydroquinone, 1,4-dihydroxynaphthalene, 1,2-dihydroxynaphthalene, 1,4-dihydroxy-2-naphthoic acid phenyl ester, and 5,8-dihydroxy-1,4-naphthoquinone, have been extensively used as good organic hydride donors in basic solution in organic syntheses. As to the quinones **5**, **6**, **8**−**16**, **18**, **22**, **26**, **30**, **32**, **34**, **41**, **43**, **44**, **46**−**48**, **50**, **51**, **52, 54**−**56**, **58**, **59**, **63**, **64**, **66**, **67**, **71**, **72**, **74**, **75**, and **78**, they are all due to the middle-strong organic hydride acceptors. Some of them can be easily reduced by well-known organic hydride donors, such as NADH models: BNAH, Hantzsch 1,4-dihydropyridine, and 9,10-dihydroacridine to form the corresponding reduced forms. But the reduced forms of the quinones also can be used as an organic hydride donor to reduce the stronger hydride acceptors, such as DDQ. Quinone 5,8-dihydroxy-1,4-naphthoquinone (**36**) has an interesting structure, one side is *p*-benzenquinone, which can accept a hydride, but the other side is dihydro-p-benzenquinone, which can provide a hydride, so, **36** is a zwitter-redox. Since **36** can form intramolecular hydrogen bond to make the molecule more stable, the ability of the molecule to accept a hydride or to donate a hydride should be smaller than that of the free *p*-benzenquinone to accept a hydride and that of the free dihydro-*p*-benzoquinone to donate a hydride.

In order to make the systematical comparison and convenient application of organic hydride acceptors for organic syntheses, the available hydride affinities of hydride acceptors in DMSO from literature and this work are listed together in Table 3, listing the order of hydride affinities from small to large. From Table 3, it is clear that if you choose an organic hydride donor to reduce quinone **40** (no. 19 in Table 3), the weakest hydride acceptor among the 80 quinones in Scheme 1, only the stronger hydride donors, such as the reduced forms of nos. 1−18 in Table 3, can be chosen to efficiently reduce **40** under general thermal reaction conditions.

Effect of Substituent on the Hydride Affinities. From Table 1, it is clear that the hydride affinities of quinones are strongly dependent on the nature of the substituent. In order to elucidate the reason that the substituents affect the hydride affinities, three plots of the hydride affinities of quinones **1**−**15** [$\Delta G_H^-(QH_a^-)$] against Hammett substituent parameters σ, Hammett substituent resonance parameters σ_R and Hammett substituent inductive parameters σ_F are shown in Figures S1−S3, respectively (Supporting Information). From Figures S1−S3, it is found that the linear dependences of hydride affinities on the Hammett substituent parameters σ ($r = 0.914$) and on σ_R ($r = 0.891$) are much better than on σ_F ($r = 0.452$), and the slope of the plot line of hydride affinities against Hammett substituent parameters σ (13.5) in Figure S1 is close to that of the plot line of hydride affinities against Hammett substituent resonance parameters σ_R (15.7) in Figure S2. These results indicate that the hydride affinities of quinones could have a linear relationship with the "resonance factor" rather than "inductive factor" of the substituents; i.e., the linear free energy relationship should hold in this system except for the subtituents with large inductive effect (such as, OCH_3, CF_3). Since the line slope in the plot of hydride affinities against Hammett substituent parameter σ is positive (+13.5), i.e., electron-withdrawing groups (EWG) make the hydride affinities increase, electron-donating groups (EDG) make the hydride affinities decrease, and the hydride affinities of quinones in DMSO should be mainly controlled by the stabilities of the formed hydroquinone anions (QH^-) (eq 5).

In order to examine the concerted effects of multiple substituents attached to the quinone ring on the hydride affinities, methoxy-substituted quinones (**4**, **16**, **28**, and **32**), methyl-substituted quinones (**7**, **17**, **29**, and **33**), chloro-substituted quinones (**10**, **18**, **30**, and **34**), and cyano-substituted quinones (**15**, **19**, **31**, and **35**) were examined. Figures S4−S7 (Supporting Information) gave Hammett-type plots of hydride affinities against the sum of the Hammett substituent parameters σ of cyano, chloro, methyl, and methoxy, respectively. From Figures S4−S7, it is interesting to find that when the substituent is CN, Cl, and CH_3, the linear correlation is very good ($r = 0.997$, 0.982, and 0.915 for cyano, chloro, and methyl, respectively), but when the substituent is OCH_3, which has large inductive effect, a saw-shaped curve was found (Figure S7); these results indicate that the concerted effects of multiple substituents except for the substituents with large inductive effect have good linear additivity on the hydride affinities of quinones. Figures 2 and 3 give the plot lines of hydride affinities versus the sum of the Hammett substituent parameters σ for various substituted *p*-quinones and *o*-quinones in Scheme 1 except for the substituents with large inductive effect (OCH_3, CF_3, NH_3, NMe_2, and OH). From Figure 2, it is clear that a good linear correlation in the plot was observed ($r = 0.981$), which means that the hydride affinities of mono- or multi-substituted *p*-quinones can be safely estimated from the plot line or its extension according to the sum of Hammett substituent parameters σ. From the line slope (16.0) and line intercept (70.5), a general formula of the plot line can be easily written (eq 12) to estimate the hydride affinities of various substituted *p*-quinones. Similarly, eq 13 can also be obtained to estimate the hydride affinities of various substituted *o*-quinones only if the substituents have no strong electrostatic inductive effect.

$$\Delta G_H^-(p\text{-Q}) \approx -16.0\Sigma\sigma_i - 70.5 \text{ (kcal/mol)} \quad (12)$$

$$\Delta G_H^-(o\text{-Q}) \approx -16.2\Sigma\sigma_i - 81.5 \text{ (kcal/mol)} \quad (13)$$

Relative Stability of Monohydroquinone Anions QH_a^- and QH_b^- and Relative Acidity of the Corresponding Two Different OH Groups in the Dihydroquinones. From eq 5, it is clear that asymmetrically substituted quinones, such as **2**−**15**, **24**−**31**, **42**−**57**, **66**−**73**, and **78** can yield two different mono-

TABLE 3. Comparison of Available Hydride Affinities of Some Organic Compounds in DMSO (kcal/mol)

no.	hydride acceptors	$-\Delta G_H^-$	no.	hydride acceptors	$-\Delta G_H^-$
1	9-*c*-C_4H_8N-fluorene-9-carbon radical[a]	31	92	2,6-dichloro-*p*-quinone (**26**)[b]	75.7
2	9-$C(Me)_2(CH_2)_3C(Me)_2N$-9-carbon fluorene radical[a]	32.5	93	3,4,6-trimethyl-*o*-quinone (**67**)[b]	75.8
3	9-mesityl-fluorene-9-carbon radical[a]	33.5	94	3,6-dimethyl-*o*-quinone (**59**)[b]	76.0
4	9-Ph-fluorene-9-carbon radical[a]	34	95	$(4\text{-}Me_3NC_6H_4)_3C$ cation[e]	76
5	9-(*i*-$Pr)_2N$-fluorene-9-carbon radical[a]	35	96	4-nitro-$C_6H_4CPh_2$ radical[a]	76
6	9-NMe_2-fluorene-9-carbon radical[a]	35	97	3,4-dimethoxy-*o*-quinone (**58**)[b]	76.1
7	9-C(Me)(H)$(CH_2)_3$C(Me)(H)N-fluorene-9-carbon radical[a]	35.5	98	2,3-dichloro-*p*-quinone (**18**)[b]	76.2
8	9-*c*-$C_5H_{10}N$-fluorene-9-carbon radical[a]	36	99	4-methyl-*o*-quinone (**47**)[b]	76.5
9	9-PhCH(Me)N-fluorene 9-carbon radical[a]	37.5	100	$AcrH^+$[f]	76.5
10	2-NMe_2-fluorene-9-carbon radical[a]	38	101	cis-p-nitro-$C_6H_4CH{=}NO$ radical[d]	76.6
11	fluorene-9-carbon radical[a]	40	102	2,5-dichloro-*p*-quinone (**22**) [b]	76.6
12	9-MeOCO-fluorene-9-carbon radical[a]	40.5	103	3,5-dimethyl-*o*-quinone (**51**)[b]	76.9
13	3-trifluoro-$CF_3C_6H_4CPh_2$ radical[a]	43	104	$(4\text{-nitro-}C_6H_4)_3CH$ radical[a]	77
14	9-EtO-fluorene-9-carbon radical[a]	43	105	3,4,6-trimethoxy-*o*-quinone (**66**)[b]	77.0
15	4-$PhC_6H_4CPh_2$ radical[a]	44	106	10-nitro-9-methyl-An 9-carbon radical[a]	78.5
16	4-$PhSC_6H_4CPh_2$ radical[a]	46	107	2-COOMe-*p*-quinone (**13**)[b]	78.8
17	9-(*p*-OCH_3-C_6H_4NH)arylcluorenimine[f]	46.8	108	3-methyl-*o*-quinone (**43**)[b]	79.6
18	9-EtS-fluorene-9-carbon radical[a]	47	109	*m*-nitro-C_6H_4O radical[d]	80.2
19	anthraquinone (**40**)[b]	47.4	110	3,4-dimethoxy-*o*-quinone (**50**)[b]	80.3
20	9-CH_2CN-anthracene radical[c]	49	111	2-CHO-*p*-quinone (**12**)[b]	80.6
21	9-(C_6H_4NH)arylcluorenimine[f]	49.1	112	2,3,6-trichloro-*p*-quinone (**30**)[b]	81.2
22	9-(*p*-Cl-C_6H_4NH)arylcluorenimine[f]	50.3	113	3,5-dinitro-C_6H_3COO radical[d]	81.3
23	carbazole-nitrogen radical[a]	52	114	2,3,5,6-tetrachloro-*p*-quinone (**34**)[b]	81.8
24	*p*-cyano-C_6H_4NH radical[a]	53.5	115	2-trifluoromethyl-*p*-quinone (**14**)[b]	81.8
25	4-$PhSO_2C_6H_4CPh_2$ radical[a]	54	116	*p*-nitro-C_6H_4O radical[d]	81.8
26	9-MeOCHAn radical[a]	54.5	117	4-nitro-$C_6H_4CH_2$ radical[a]	82
27	9,10-dimethyl-An-9-carbon radical[a]	55	118	*o*-quinone (**41**)[b]	82.3
28	9-methyl-An-9-carbon radical[a]	55.5	119	cycloheptatriene cation[e]	83
29	1,3H-dibenzo[*a*,*i*]carbazole-nitrogen radical[a]	55.5	120	2,4-dinitro-C_6H_3NH radical[d]	83.2
30	2-cyanofluorene-9-carbon radical[a]	56	121	2-cyano-*p*-quinone (**15**)[b]	83.6
31	10-methoxy-9-methyl-An-9-carbon radical[a]	56	122	*p*-nitro-C_6H_4NPh radical[a]	85
32	iminostilbene-nitrogen radical[a]	57	123	3-chloro-*o*-quinone (**44**)[b]	85.5
33	tetramethyl-*p*-quinone (**33**)[b]	57.3	124	4-chloro-*o*-quinone (**48**)[b]	85.7
34	10-phenyl-9-methyl-An-9-carbon radical[a]	58	125	3,4,5-trichloro-*o*-quinone (**72**)[b]	87.9
35	*m*-cyano-C_6H_4NH radical[a]	58	126	*p*-nitro-C_6H_4NH radical[a]	88
36	2-$PhSO_2$-fluorene-9-carbon radical[a]	58	127	9-NMe_2-fluorene-9-carbon cation[e]	88
37	9-cyano-CHAn radical[a]	58	128	3,5-dichloro-*o*-quinone (**56**)[b]	88.5
38	BNA^+[f]	59.0	129	4,5-dichloro-*o*-quinone (**64**)[b]	88.6
39	2,6-dimethoxy-*p*-quinone (**24**)[b]	59.8	130	3,4-dichloro-*o*-quinone (**52**)[b]	88.9
40	9-$PhOCH_2$An-9-carbon radical[a]	60	131	9-phenylxanthene-9-carbon cation[e]	89
41	10-chloro-9-methyl-An-9-carbon radical[a]	60	132	9-methoxy-fluorene-9-carbon cation[e]	89
42	4-$PhCOC_6H_4CPh_2$ radical[a]	60	133	9-phenylxanthylium ion[f]	89.3
43	2,3-dihydro-1,4-nathphoquinone (**39**)[b]	61.1	134	9-phenylthioxanthene-9-carbon cation[e]	90
44	2,3,6-trimethyl-*p*-quinone (**29**)[b]	61.7	135	1,2,3-triphenylcyclopropene cation[e]	90
45	9-PhCOCHAn radical[a]	62	136	3,6-dichloro-*o*-quinone (**60**)[b]	90.2
46	phenanthrene-9,10-dione (**80**)[b]	62.3	137	xanthylium[f]	90.3
47	10-PhS-9-MeAn-9-carbon radical[a]	62.5	138	9-methyl-10-methoxyanthracene cation[e]	91
48	9-$PhSO_2$-fluorene-9-carbon radical[a]	63	139	2,5-dicyano-*p*-quinone (**23**)[b]	91.3
49	9-PhSMeAn-9-carbon radical[a]	63	140	3,4,6-trichloro-*o*-quinone (**68**)[b]	91.3
50	5,8-dihydroxy-1,4-naphthoquinone (**36**)[b]	63.1	141	2,4-dinitronaphthol radical[d]	92.8
51	2,5-dimethoxy-*p*-quinone (**20**)[b]	63.3	142	3-cyano-*o*-quinone (**45**)[b]	93.1
52	2-NH_2-*p*-quinone (**3**)[b]	63.7	143	2,3-dicyano-*p*-quinone (**19**)[b]	93.3
53	2,3,6-trimethoxy-*p*-quinone (**28**)[b]	63.8	144	4-cyano-*o*-quinone (**49**)[b]	93.8
54	3,6-dibromocarbazole-nitrogen radical[a]	64	145	3,4,5,6-tretrachloro-*o*-quinone (**76**)[b]	93.9
55	2,6-dimethyl-*p*-quinone (**25**)[b]	64.4	146	2,6-dicyano-*p*-quinone (**27**)[b]	94.3
56	10-PhCO-9-MeAn-9-carbon radical[a]	64.5	147	*o*-nitro-*p*-chloro-$C_6H_3NH_2$ radical[a]	94.5
57	2,4,6-trichloro-C_6H_2NH radical[a]	64.5	148	naphthalene-1,2,5,8-tetraone (**37**)[b]	94.8
58	3,4,5-trimethoxy-*o*-quinone (**70**)[b]	64.7	149	9,10-dimethylanthracene radical anion[e]	95
59	2,3-dimethyl-*p*-quinone (**17**)[b]	64.7	150	4-phenyl-$C_6H_4CPh_2$ cation[e]	96
60	2,5-dimethyl-*p*-quinone (**21**)[b]	64.7	151	triphenylmethane (TPM) cation[e]	96
61	2-methoxy-*p*-quinone (**4**)[b]	65.4	152	trityl ion[f]	96.5
62	2-NMe_2-*p*-quinone (**2**)[b]	65.5	153	9-PhS-fluorene-9-carbon radical[e]	97
63	4,5-dimethoxy-*o*-quinone (**62**)[b]	65.9	154	9-phenyl-fluorene-9-carbon radical[e]	97
64	10-cyano-9-methyl-An 9-carbon radical[a]	66.5	155	$(4\text{-chloro-}C_6H_4)_3C$ cation[e]	98
65	2-methyl-*p*-quinone (**7**)[b]	67.2	156	9-methylanthracene cation[e]	98
66	2,7-dinitro-fluorene-9-carbon radical[a]	67.8	157	*p*-chloro-2,6-dinitro-C_6H_2O radical[d]	98.2
67	*p*-quinone (**1**)[b]	70	158	3-methoxy-*o*-quinone (**42**)[b]	98.2
68	9-$PhSO_2CH_2$An radical[a]	70	159	2,3-dichloro-5,6-dicyano-*p*-quinone (**38**)[b]	98.2
69	9-methyl-10-nitromethlanthracene radical[c]	70	160	naphthalene-2,3-dione (**79**)[b]	99.6
70	2-HO-*p*-quinone (**5**)[b]	70.2	161	3,4-dicyano-*o*-quinone (**61**)[b]	100.9

TABLE 3. Continued

no.	hydride acceptors	$-\Delta G_H^-$	no.	hydride acceptors	$-\Delta G_H^-$
71	3,5-dimethoxy-*o*-quinone (**54**)[b]	70.4	162	9-CH_2OMe-anthracene-9-carbon cation[e]	102
72	10-CHO−9-MeAn−9-carbon radical[a]	70.5	163	9-(3-chloro-C_6H_4)-fluorene cation[e]	102
73	2,3-dimethoxy-*p*-quinone (**16**)[b]	71.2	164	protonated *p*-benzoquinone[f]	102.9
74	1,2-naphtho-quinone (**78**)[b]	71.3	165	*p*-nitro-C_6H_4COO radical[d]	103.2
75	2-HS-*p*-quinone (**6**)[b]	71.4	166	2,3,6-tricyano-*p*-quinone (**31**)[b]	103.8
76	2-SiH_3-*p*-quinone (**8**)[b]	71.4	167	Ph_2CH cation[e]	105
77	*p*-nitro−2,6-(t-Bu)$_2C_6H_3$O radical[d]	71.8	168	9-methyl-10-chloroanthracene cation[e]	105
78	*p*-nitro-C_6H_4S radical[d]	72.7	169	3,5-dicyano-*o*-quinone (**57**)[b]	105.0
79	2-chloro-*p*-quinone (**10**)[b]	72.8	170	4,5-dicyano-*o*-quinone (**65**)[b]	105.2
80	3,4,5-trimethyl-*o*-quinone (**71**)[b]	72.9	171	3,4-dicyano-*o*-quinone (**53**)[b]	106.2
81	9-nitro-CHAn radical[a]	73	172	9-*tert*-butylfluorene-9-carbon cation[e]	108
82	3,4,5,6-tetramethyl-*o*-quinone (**75**)[b]	73.9	173	9-CH_2SPh-anthracene-9-carbon cation[e]	109
83	2,3,5,6-tetramethoxy-*p*-quinone (**32**)[b]	73.9	174	fluorene−9-carbon cation[e]	109
84	4,5-dimethyl-*o*-quinone (**63**)[b]	74.0	175	9-CH_2OPhanthracenen cation[e]	111
85	3,4,5,6-tetramethoxy-*o*-quinone (**74**)[b]	74.5	176	2,3,5,6-tetracyano-*p*-quinone (**35**)[b]	112.7
86	trans-m-nitro-C_6H_4CH═NO radical[d]	74.6	177	3,4,6-tricyano-*o*-quinone (**69**)[b]	113.8
87	cis-*m*-nitro-C_6H_4CH═NO radical[d]	74.6	178	9-CO_2Me-fluorene-9-carbon cation[e]	114
88	2-fluoro-*p*-quinone (**9**)[b]	74.6	179	3,4,5-tricyano-*o*-quinone (**73**)[b]	114.5
89	2-bromo-*p*-quinone (**11**)[b]	75.2	180	9-methyl-10-nitro-anthracene-9-carbon cation[e]	120
90	4-methoxy-*o*-quinone (**46**)[b]	75.3	181	3,4,5,6-tetracyano-*o*-quinone (**77**)[b]	124.5
91	3,4-dimethyl-*o*-quinone (**55**)[b]	75.6			

[a] Zhang, X. M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 904. [b] This work, calculated by MP2 method. It is worth pointing out herein that when the quinone is an asymmetrically substituted quinone such as **2**−**15**, **24**−**31**, **42**−**57**, **66**−**73**, and **78**, the larger hydride affinity (more negative) was chosen. [c] Handoo, K. L.; Cheng, J. P.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 5067. [d] Zhao, Y.; Bordwell F. G. *J. Org. Chem.* **1996**, *61*, 6623. [e] Cheng, J.P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655. [f] Cheng, J.-P.; Lu, Y.; Zhu, X.-Q.; Mu, L. *J. Org. Chem.* **1998**, *63*, 6108.

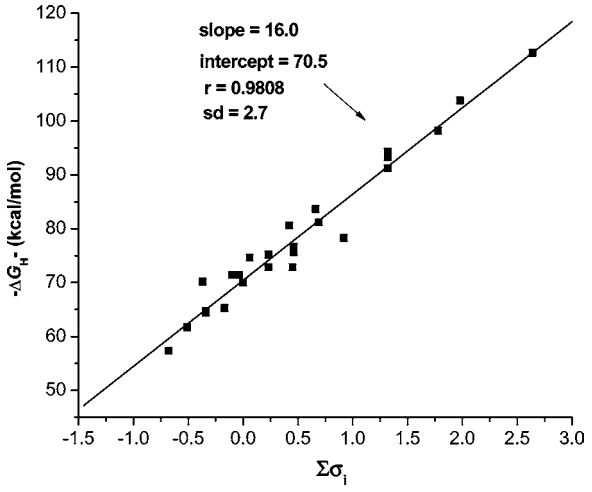


FIGURE 2. Plot of $-\Delta G_H^-(QH^-)$ against the sum of Hammett substituent parameter σ.

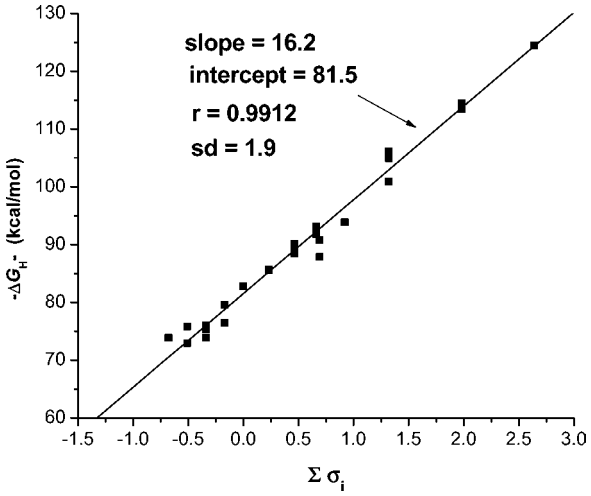


FIGURE 3. Relationship between theoretical negative hydride affinities of *o*-quinones and sum of Hammett substituent parameters σ (except the OCH_3 group).

hydroquinone anions QH_a^- and QH_b^- in the reductions, the asymmetrically substituted quinones have two hydride affinities $\Delta G_H^-(QH_a^-)$ and $\Delta G_H^-(QH_b^-)$. By examining Table 1, it is found that $\Delta G_H^-(QH_a^-)$ are generally larger than $\Delta G_H^-(QH_b^-)$, which means that QH_a^- with the substituents closer to the negatively charged oxygen should have larger thermodynamic stability than the corresponding QH_b^-, which could mainly result from the ortho-static and steric effect of the substituents. But if the $\Delta G_H^-(QH_a^-)$ and $\Delta G_H^-(QH_b^-)$ in Table 1 were examined in detail, it is found that when the substituents have no strong inductive effect or large ortho-steric effect, $\Delta G_H^-(QH_a^-)$ is generally close to $\Delta G_H^-(QH_b^-)$. However, in the other cases, the differences between them all are remarkable. Since the differences between $\Delta G_H^-(QH_a^-)$ and $\Delta G_H^-(QH_b^-)$ are directly dependent on the relative stabilities of the two corresponding hydroquinone anions QH_a^- and QH_b^-, it is conceivable that the relative acidities of the corresponding two different OH groups in the dihydroquinones (QH_2) can be estimated from the difference of the two different hydride affinities $\Delta G_H^-(QH_a^-)$ and $\Delta G_H^-(QH_b^-)$. Table 4 gave the difference of state free energies between QH_a^- and QH_b^- and the difference of pK_a between the two different OH groups in the dihydroquinones in DMSO solution. It is evident that according to the difference of pK_a, the relative acidities of the two OH groups in the asymmetrically substituted dihydroquinones can be efficiently estimated and differentiated. By examining Table 4, it is found that for the asymmetrically substituted dihydroquinones, the acidity of the OH group nearer to the substituents is generally larger than that of the one far from the substituents. The main reason could be that the ortho-steric and/or ortho-electrostatic effects of the substituents prefer the nearer OH group to the other one to release a proton. Taking 2-(dimethylamino)-*p*-dihydroquinone (the neutral reduced form of quinone **2**) as an example, the pK_a of OH group at the1-position is smaller than

TABLE 4. Difference of the State Free Energy between QH_a^- and QH_b^- and the Difference of pK_a between the Two Different OH Groups in Dihydroquinone in DMSO Solution

	$-\Delta G_H^-$(MP2)					$-\Delta G_H^-$(MP2)			
quinone	QH_a^-	QH_b^-	ΔG^a	$\Delta pK_a{}^b$	quinone	QH_a^-	QH_b^-	ΔG^a	$\Delta pK_a{}^b$
2	65.5	60.8	4.7	−3.5	**44**	85.5	85.6	−0.1	−0.0
3	63.7	61.8	1.9	−1.4	**45**	93.1	90.4	2.7	2.0
4	65.4	60.7	4.7	−3.4	**46**	72.8	75.3	−2.5	−1.8
5	70.2	64.3	5.8	−4.3	**47**	76.5	75.0	1.5	1.1
6	71.4	69.3	2.1	−1.6	**48**	85.7	83.7	1.9	1.4
7	65.3	67.2	−1.9	1.4	**49**	91.8	93.8	−2.0	−1.4
8	71.4	71.3	0.1	−0.1	**50**	80.3	76.7	3.6	2.6
9	74.6	71.9	2.7	−2.0	**51**	75.3	76.9	−1.6	−1.2
10	72.8	69.2	3.6	−2.7	**52**	88.9	86.7	2.0	1.9
11	75.2	70.1	5.1	−3.8	**53**	106.2	103.6	2.6	1.9
12	80.6	75.5	5.1	−3.8	**54**	70.4	64.4	6.0	4.4
13	72.9	78.8	−5.9	4.3	**55**	75.6	72.9	2.7	2.0
14	79.6	81.8	−2.2	1.7	**56**	88.5	87.6	0.9	0.7
15	83.6	77.5	6.1	−4.5	**57**	105.0	101.1	3.9	2.9
24	59.8	54.0	5.8	−4.3	**66**	77.0	76.3	0.6	0.5
25	64.4	64.0	0.4	−0.3	**67**	75.8	72.4	3.4	2.5
26	75.7	72.6	3.1	−2.3	**68**	90.8	91.3	−0.5	−0.4
27	94.3	87.5	6.8	−5.0	**69**	113.5	113.8	−0.3	−0.3
28	63.8	63.1	0.9	−0.6	**70**	64.7	61.3	3.4	2.5
29	61.7	61.1	0.6	−0.5	**71**	72.9	72.4	0.6	0.4
30	81.2	78.8	2.4	−1.8	**72**	87.9	87.3	0.6	0.4
31	103.8	100.2	3.6	−2.6	**73**	114.5	112.9	1.6	1.2
42	97.1	98.2	−1.1	0.8	**78**	71.3	69.4	1.9	1.4
43	79.6	78.5	1.1	−0.8					

[a] $\Delta G = \Delta G_H^-(QH_a^-) - \Delta G_H^-(QH_b^-)$. [b] $\Delta pK_a = pK_a(QH_2 \rightarrow QH_a^- + H^+) - pK_a(QH_2 \rightarrow QH_b^- + H^+)$, $\Delta G = 1.36 pK_a$.

that of OH group at the 4-position by 3.49 pK_a unit, which means that acidity of the OH at 1-position is much larger than that of the OH at 4-position. In fact, it still is very difficult to safely distinguish the relative acidities between the two OH groups in such asymmetrically substituted dihydroquinones only using the conventional experimental methods so far.

Comparison of Hydride Affinities between *p*-Quinones and *o*-Quinones. Similar to *p*-quinones, *o*-quinones are also one class of very important quinones and have many important roles in chemistry and biology. Since *o*-quinone is an isomer of the corresponding *p*-quinone due to the different position of the two C═O groups, the difference of oxidizability between the two types of quinones has been an interesting question for a long time. Examining *o*-BQ (**41**) and *p*-BQ (**1**), it is found that the hydride affinity of **41** (−82.3 kcal/mol) is larger than that of **1** (−70.0 kcal/mol) by 12.3 kcal/mol,[55] which means that *o*-BQ is a stronger hydride acceptor than *p*-BQ. The main reason could be that the state free energies of *o*-BQ and *p*-BQ as well as monohydro-*o*-quinone anion (*o*-BQH$^-$) and monohydro-*p*-quinone anion (*p*-BQH$^-$) could be different from each other, respectively. By comparing the state free energies of *o*-BQ and *p*-BQ, it is found that the state free energy of *o*-BQ is higher than that of *p*-BQ by 5.5 kcal/mol, which indicates that *o*-BQ has larger chemical potential to capture a hydride anion than *p*-BQ, the reason could be that in *o*-BQ a large electronic repulsion effect occurs between the two oxygen atoms, however, in *p*-BQ, no such electronic repulsion effect exists between the two oxygen atoms. In addition, by examining the state free energy of the reduced form of quinones (BQH$^-$), it is clear that the state free energy of *o*-BQH$^-$ is lower than that of *p*-BQH$^-$ by 7.3 kcal/mol (see Figure 4), which means that *o*-BQH$^-$ is much more difficult to release hydride than *p*-BQH$^-$, the reason is that *o*-BQH$^-$ can form intramolecular hydrogen bond, but *p*-BQH$^-$ cannot (Scheme 3). Evidently, combination of the two factors mentioned above makes the hydride affinity of *o*-BQ quite larger than that of *p*-BQ. In general, from eqs 12 and 13

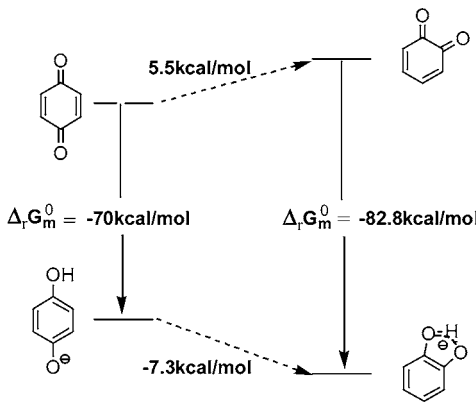
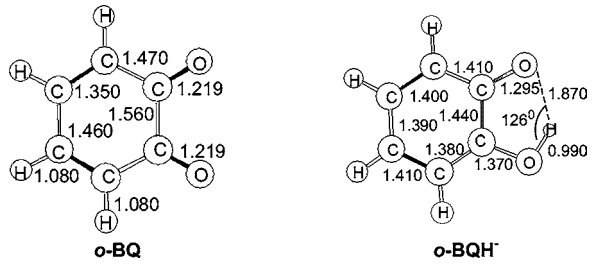


FIGURE 4. Difference of hydride affinities between *p*-quinone and *o*-quinone calculated by the MP2 method.

SCHEME 3



o-BQ *o*-BQH$^-$

it is easy to find that the hydride affinities of *o*-quinones are larger than those of the corresponding *p*-quinones by about 11.0 kcal/mol.

Effect of Aromatic Properties of Quinone on the Hydride Affinity. By examining the hydride affinities of quinones with aromatic structure (*p*-quinones **1**, **39**, **40** and *o*-quinones **41**, **78**, **80**) in Table 1, it is found that the hydride affinities of the *p*-quinones decreased in the order of **1** (−70 kcal/mol) > **39** (−61 kcal/mol) > **40** (−40.0 kcal/mol);[55] the hydride affinities of the *o*-quinones decreased in the order of **41** (−82.3 kcal/mol) > **78** (−71.3 kcal/mol) > **80** (−62.3 kcal/mol), which indicates that the larger the aromatic system of the quinone is, the smaller the hydride affinity of the quinones is. The main factor causing this could be that the quinone with larger aromatic system could have larger stability in thermodynamics, which makes the quinone more difficult to capture a hydride anion. When the hydride affinities of *p*-quinones (**1**, **39**, **40**) and *o*-quinones (**41**, **78**, **80**) were plotted against the number of benzene rings of the quinones, respectively, it was unexpectedly found that the hydride affinities of *p*-quinones and *o*-quinones have good linear relationships to decrease with the increase of the number of benzene rings in the quinones (Figure 5). According to this relationship, the hydride affinities of aromatic quinones containing three or more benzene rings can be predicted. But, it is worth noting herein that although quinone **79** is an isomer of **78** and the molecular structure of **79** is also similar to that of **78**, the hydride affinity of **79** (−99.6 kcal/mol) is much larger than that of the corresponding isomer **78** (−71.3 kcal/mol), even more, much larger than that of quinone **41** (−82.3 kcal/mol). The main reason is that the attached benzene ring in quinone **79** is not due to aromatic system.

Effect of Solvent (DMSO) on the Hydride Affinity. As is well-known, unlike the hydride affinities of quinones in gas phase, the hydride affinities of quinones in solution is not only dependent on the structure of quinones, but also dependent on

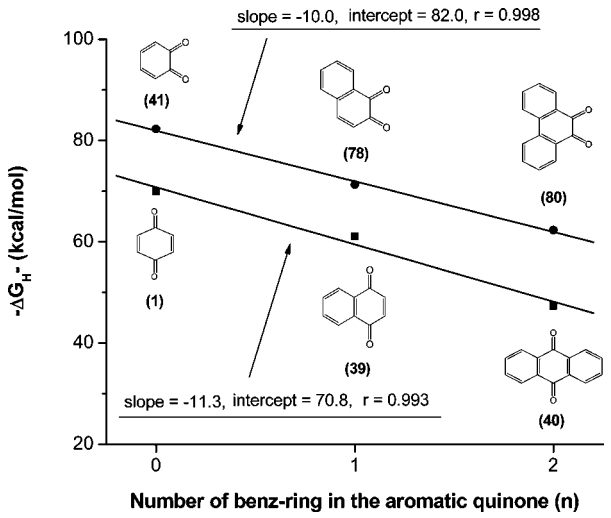


FIGURE 5. Relationship of hydride affinities of aromatic quinones in DMSO with the number of benzene rings in the aromatic quinones.

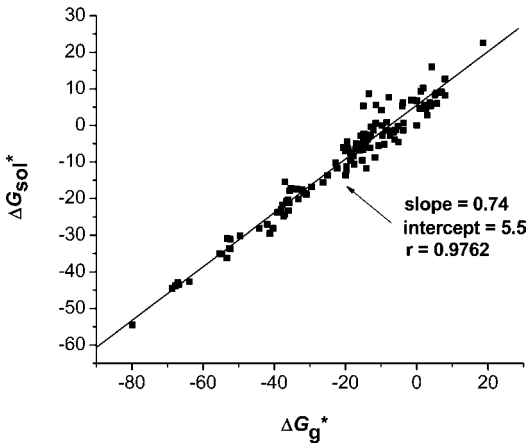


FIGURE 6. Dependence of the relative hydride affinities of the various substituted *p*- and *o*-quinones in DMSO on the corresponding hydride affinities in gas phase.

the nature of solvent. In order to quantitatively estimate the relative contribution of the solvation effect to the hydride affinities of quinones in DMSO, the plot of the relative hydride affinities of quinones in gas phase (ΔG_g*) against the relative hydride affinities of quinones in DMSO (ΔG_{sol}*) were made (Figure 6). From Figure 6, a good linear plot between ΔG_g* and ΔG_{sol}* was observed and a formula linking ΔG_g* and ΔG_{sol}* can be formed (eq 14). From the slope of the plot line (0.74) and eq 14, it is clear that 26% of the gas-phase hydride affinities are offset by the solvation in the liquid-phase hydride addition process.

$$\Delta G_{sol}^* = 0.74\Delta G_g^* + 5.5 \qquad (14)$$

In order to elucidate the efficient nature of DMSO in the solvation effect, various interactions between solute and solvent were examined. According to the calculation model of solvation used in this work, we know that the solvation energies of quinones in DMSO are not only formed from electrostatic interaction between solute and solvent (electrostatic interaction energy), but also from nonelectrostatic interactions between solute and solvent (nonelectrostatic interaction energy). Since nonelectrostatic interactions between solute and solvent have three different types, the formation of cavity in the continuum medium, dispersion of solute in solvent, and repulsion between solute and solvent, the solvation energy of quinones in DMSO is made up of four types of interaction energies: electrostatic energies, the energy of cavity formation in the continuum medium, dispersion energy, and repulsion energy.[57] The data of the four interaction energies of quinones (Q) and their corresponding monohyhroquinone anion (QH^-) in DMSO are summarized in Table S2, respectively (Supporting Information).

By examining the electrostatic and nonelectrostatic interaction energies of Q and QH^- in Table S2, it is found that the electrostatic energies and dispersion energies all are negative, but the cavity energies and repulsion energies all are positive, which indicates that the electrostatic interaction between solutes (Q, QH^-) and solvent (DMSO) and the dispersion of the solutes in the solvent all are exothermic processes, but the cavity formation and the repulsion between solute (Q, QH^-) and solvent (DMSO) all are endothermic processes. Since the nonelectrostatic energies of QH^- are very close to the corresponding nonelectrostatic energies of Q and the dependences of the nonelectrostatic energies (cavity energies, dispersion energies, and repulsion energies of Q and QH^-) all are not strong on the hydride affinities of quinones in gas phase (see Figure S8, Supporting Information), the effects of nonelectrostatic interactions between solute (Q, QH^-) and solvent (DMSO) on the hydride affinities of quinones in DMSO may be ignored. The effect of solvent (DMSO) on the hydride affinities of quinones are mainly dependent on the electrostatic interaction between solute (Q and QH^-) and solvent (DMSO). According to the calculated results in Table S2 that the electrostatic interaction energies of QH^- with solvent (from −41.78 kcal/mol for **73b** to −62.83 kcal/mol for **3b**) is much larger than those of the corresponding Q with solvent (−4.38 kcal/mol for **33** to −14.96 kcal/mol for **61**) and the observation in Figure 6 that the line slope for the electrostatic interaction energies of QH^- with solvent (−0.17) is much larger than that for the electrostatic interaction energies of Q with solvent (0.09),[58] it is believable that the effect of solvent on the hydride affinities of quinones in DMSO mainly come from the electrostatic interaction of charged solutes (QH^- and H^-) with DMSO. Since the electrostatic interaction of solutes and solvent is directly dependent on the polarities of solutes (H^- and QH^-) and solvent (DMSO) and the polarity of H^- is much larger than that of QH^-, it is reasonable to predict that the hydride affinities of quinones in aqueous solution ($\epsilon = 78.4$),[59] which has received more attention from biochemists, should be smaller than that of the corresponding quinones in DMSO ($\epsilon = 46.7$).[59] In fact, this prediction can be supported by the hydride affinities of NAD^+ or its model (BNA^+)[60] in the solvents with different polarity: −53.6 kcal/mol[61] for NAD^+ in H_2O ($\epsilon = 78.4$), −59.0

(57) Namazian, M.; Norouzi, P.; Ranjbar, R. *THEOCHEM* **2003**, *625*, 235.

(58) The magnitude of the line slopes in this paper indicates the absolute value rather than the pure mathematical values (negative values) for the sake of convention.

(59) Isaacs, N. S. *Physical Organic Chemistry*; John Wiley & Sons: New York, 1987; p 180, Table 5.4.

(60) Although NAD^+ is quite different from BNA^+ in the molecular structure, the reaction center structures of NAD^+ and BNA^+ are the same, the hydride affinities of NAD^+ and BNA^+ should be close to each other in the same solvent according to the definition of hydride affinity.

(61) Zhu, X.-Q.; Yang, Y.; Zhang, M.; Cheng, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 15298.

kcal/mol[55] for BNA^+ in DMSO ($\epsilon = 46.7$)[59] and −64.1 kcal/mol[62] for BNA^+ in acetonitrile ($\epsilon = 27.5$).[59]

Conclusions

In this work, the hydride affinities of 80 various derivatives of *p*- and *o*-quinones in DMSO solvent were estimated by using B3LYP/6-311++G (2df,p)//B3LYP/6-31+G* and MP2/6-311++G**//B3LYP/6-31+G* methods, combined with the PCM cluster continuum solvation model. After analyses on the hydride affinity scale of the quinones in DMSO and the detailed examination of the effects of substituent, aromatic property of quinone ring and solvent on the hydride affinities of the quinones, the following conclusions can be made: (i) The hydride affinity scale of the 80 quinones in DMSO is quite large (from −47.4 kcal/mol for 9,10-anthraquinone to −124.5 kcal/mol for 3,4,5,6-tetracyano-1,2-quinone), which indicates that the 80 quinones can form a useful library of organic oxidants to provide various organic hydride acceptors for chemists to choose. (ii) The hydride affinity of *o*-quinone in DMSO is generally larger than that of the corresponding *p*-quinone by 11 kcal/mol in DMSO, which means that the oxidizability of *o*-quinones should be much larger than that of the corresponding *p*-quinones. (iii) The effects of substituents on the hydride affinities of quinones have good additive properties; the total effect of the various substituents on the hydride affinities is equal to the addition of the effect of individual substituent on the hydride affinities, when the substituents have no large electrostatic inductive force and no large steric hindrance. This finding suggests that the hydride affinities of any substituted quinones can all be directly estimated from the Hammett substituent parameter σ. (iv) As to aromatic quinones, the larger the aromatic system of quinone is, the smaller the hydride affinity of quinone is, and the decrease of the hydride affinities is linearly to take place with the increase of the number of benzene rings in the molecule of quinones, from which the hydride affinity of aromatic quinones with multiple benzene rings can be predicted. (v) The effects of solvent (DMSO) on the hydride affinities of quinones are mainly dependent on the electrostatic interaction of the charged monohydroquinone anion (QH^-) with solvent (DMSO). It is evident that these important and hard-to-get hydride affinities of quinones in solution and the conclusions on the effects of substitute, structure of quinone, and solvent on the hydride affinities of quinones could provide very important clues to use quinones as oxidant and use dihydroquinone as reductant as well as predict the thermodynamics of hydride exchange between quinone and hydroquinone.

Acknowledgment. Financial support from the Ministry of Science and Technology of China (Grant No. 2004CB719905), the National Natural Science Foundation of China (Grant Nos. 20272027, 20332020, 20472038, 20421202, and 20672060), the 111 Project (B06005), and the Natural Science Fund of Tianjin (Grant No. 033804311) is gratefully acknowledged.

Supporting Information Available: The relative hydride affinities of the 80 quinones in the gas phase, the detailed solvation energies of quinones and hydroquinone anions in DMSO, the relationships of quinones **1**−**15** with Hammett substituent parameter (σ, σ_R, and σ_F), the relationships of $\Delta G_H^-(QH_b^-)$ with the sum of Hammett parameter σ of substituents (CN, Cl, CH_3, and CH_3O), dependencies of electrostatic energies, cavity energies, dispersion energies and repulsion energies of quinones and hydroquinone anions on the hydride affinities of quinones in gas phase (ΔGg*) (Part 1), as well as the Cartesian coordinates of molecules discussed in the test (Part 2). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0621928

(62) Zhu, X.-Q.; Li, H.-R.; Li, Q.; Ai, T.; Lu, J.-Y.; Yang, Y.; Cheng, J.-P. *Chem. Eur. J.* **2003**, *4*, 871−880.