J. Phys. Chem. A **2007,** *111,* 7227−7232

Accurate Calculation of Absolute One-Electron Redox Potentials of Some *para*-Quinone Derivatives in Acetonitrile

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Received: April 2, 2007; In Final Form: June 7, 2007

Standard ab initio molecular orbital theory and density functional theory calculations have been used to calculate absolute one-electron reduction potentials of several *para*-quinones in acetonitrile. The high-level composite method of G3(MP2)-RAD is used for the gas-phase calculations and a continuum model of solvation, CPCM, has been employed to calculate solvation energies. To compare the theoretical reduction potentials with experiment, the reduction potentials relative to a standard calomel electrode (SCE) have also been calculated and compared to experimental values. The average error of the calculated reduction potentials using the proposed method is 0.07 V without any additional approximation. An ONIOM method in which the core is studied at G3(MP2)-RAD and the substituent effect of the rest of the molecule is studied at R(O)MP2/6-311+G(3df,2p) provides an accurate low-cost alternative to G3(MP2)-RAD for larger molecules.

1. Introduction

The standard redox potential, which measures the propensity of a molecule to donate or accept an electron in solution, is fundamental to understanding chemical and biological electron-transfer reactions.[1] The accurate theoretical calculation of electrode potentials therefore plays an important role in explaining the nature of these important reactions[2] and is particularly useful when the design of molecules with specific redox properties is of interest or when experimental measurements are difficult due to the participation of complex chemical equilibria.[3] Indeed, it has been suggested that in some problematic cases, where there is a great discrepancy between theory and experiment, a re-examination of the experimental data may be warranted[4] and that theoretical approaches might actually be as reliable as experimental ones for determining redox properties of molecule.[5]

Quinones are important naturally occurring pigments that are widely distributed in nature and are known to demonstrate various physiological activities as antibiotics and anticancer agents due to their electrochemical properties.[6] Quinones, for example, function in cellular respiration, photosynthesis, and blood coagulation.[7] Their biological action is often linked to their electron-transfer rates and redox potentials.[8] Calculations of the electrode potentials of quinone derivatives in aqueous solution have been recently of interest because of the ability of these molecules to inhibit the growth of tumors.[2,5,7,8]

Reduction of quinones is different in aqueous and nonaqueous solutions. Although the process is a two-electron reduction in aqueous solution, in aprotic solvents, the reduction of quinones can be separated by two one-electron steps.[9] The calculation of the redox potential of quinones in *aqueous* solution has been extensively studied (see, for example, recent works by Wass,[9] Liu-Guo,[1] Truhlar-Cramer,[10] and Garza[11]). In aqueous solution, the average error in the calculation of redox potential can be as small as 0.01 V.[10] In contrast, the average errors in *nonaqueous* solutions have been reported to be much higher.[1,2] Improving the theoretical calculation of electrode potentials of quinones in nonaqueous solution is therefore the focus of the present study.

In the present work, which builds on our previous studies of other quinone derivatives,[12] we have calculated the absolute one-electron reduction potentials of thirteen *para*-quinone derivatives using standard high-level ab initio calculations and employing a continuum model of solvation. The focus of this study was to identify an accurate method for calculation of reduction potentials and to assess the validity of solvation energies where radical species are involved. The validity of calculated solvation energies for radical species is of wider importance to the study of radical chemistry in solution phase. We show that the average error of calculated reduction potentials using the proposed methods is less than 0.1 V without any additional approximation.

2. Computational Methods

Standard ab initio molecular orbital theory[13] and density functional theory calculations[14] were carried out using the Gaussian 03[15] and Molpro 2000.6[16] softwares. Geometries of all species were optimized at the B3-LYP/6-31G(d) level of theory,[14] and where necessary, extra care was taken to select the minimum-energy conformation via systematic conformational searching at this level. The nature of each stationary point was established via B3-LYP-6-31G(d) frequency calculations. The Gibbs free energy of each species was calculated using single-point energies obtained at the G3(MP2)-RAD level of theory.[17] This high-level composite procedure, which was designed especially for the prediction of reliable thermochemistry for free radicals, aims to approximate CCSD(T). calculations with a large triple-ζ basis set via additivity approximations. The principal features of the G3(MP2)-RAD procedure include

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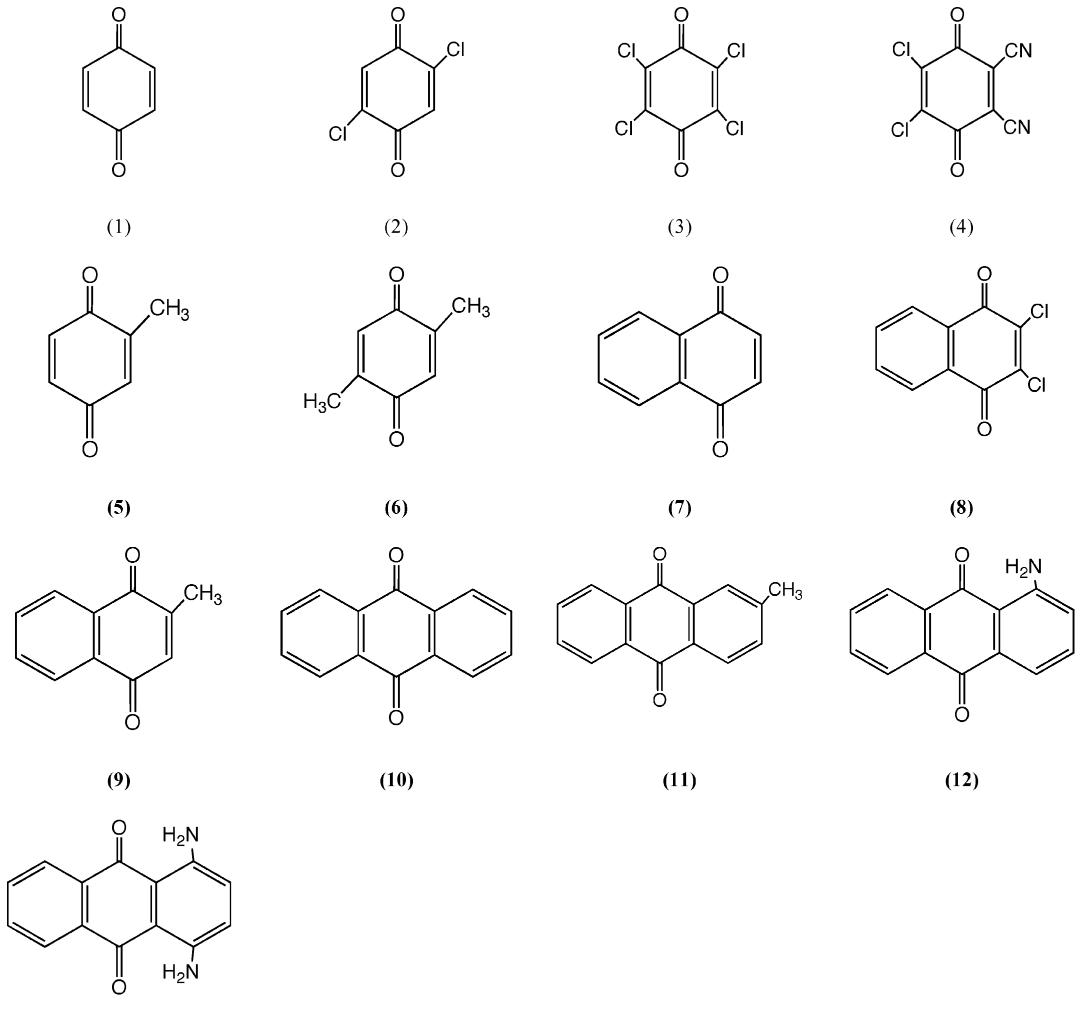
10.1021/jp0725883 CCC: $37.00



(1) (2) (3) (4)

(5) **(6)** **(7)** **(8)**

(9) **(10)** **(11)** **(12)**

(13)

Figure 1. Studied *para*-quinones.

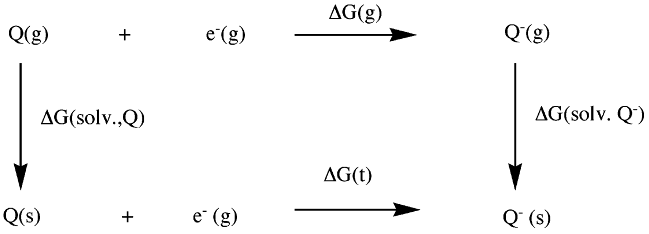
the use of B3-LYP geometries and its scaled frequencies,[18] the use of URCCSD(T)/6-31G(d) as the highest-level correlation method, and the use of ROMP2 to approximate basis-set-extension effects. This level of theory has been demonstrated to provide an accuracy of 1 kcal/mol when assessed against large test sets of thermochemical data.[17] The lower-cost (RO)-MP2/6-311+G(3df,2p) method was also used to calculate the gas-phase Gibbs energy of species. Previous studies showed this method could be used to get reasonable energies that were relatively compatible with G3(MP2)-RAD calculations.[19] We also examine whether calculations using the popular DFT method, B3-LYP, recently recommended for studying redox potentials,[1a] offers a cost-effective alternative to G3(MP2)-RAD for larger systems.

To calculate solvation energies, a continuum model of solvation, the conductor-like polarizable continuum model (CPCM),[20] has been used at the recommended levels of theory, HF/6-31+G(d) and B3-LYP/6-31+G(d).[21] The radii of the united atom topological model applied on radii optimized for the Hartree−Fock level of theory (UAHF), have been chosen for solvation energies as recommended.[22] The rest of the parameters in the solvation models, such as *f* (Alpha), have been kept as default values.[22] All geometries of the studied species have been optimized fully in the presence of solvent using their respective levels of theory. In the case of the HF/6-31+G(d) solvation calculations on the open-shell molecules, the geometries were optimized fully at the UHF/6-31+G(d) level of theory; however, the solvation energy calculation itself was then performed on the optimized geometries at the ROHF/6-31+G(d) level.

3. Experimental Test Set of Reduction Potentials of *para*-Quinone Derivatives

In the present work we benchmark our theoretical calculations against the experimental data of Sasaki and co-workers.[23] They reported the reduction of thirteen *para*-quinones in several aprotic solvents using cyclic voltammetry. The studied *para*-quinones, which are shown in Figure 1, consist of six *para*-benzoquinone, three *para*-naphthoquinones and four *para*-anthraquinones. Two one-electron reduction steps were studied in nonaqueous solutions and the reduction potential for each step was reported using standard calomel electrode (SCE) as the reference electrode. The first one-electron reduction of the studied para-quinones, E°_1, covers a wide range of values, from −1.200 V for molecule **13** to +0.502 V for molecule **4**, relative to SCE. The study was carried out in six different aprotic solvents including acetonitrile, benzonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, dimethylacetamide, and propylene carbonate, and the results revealed that change of solvent did not affect E°_1 significantly. For our calculations, we selected acetonitrile as the solvent because it is one of the most popular organic solvents for the measurement of redox potentials.[1]

SCHEME 1: Thermodynamic Cycle Used To Calculate $\Delta G°$(t) of Reaction 1 from Its Components[a]



[a] $\Delta G°$(g) is the change of Gibbs free of reaction 1 in the gas phase, and $\Delta G°$(solv,Q^-) and $\Delta G°$(solv,Q) are solvation energies of Q and Q^- in acetonitrile, respectively.

4. Calculation of Standard Reduction Potentials

The following reaction presents the one-electron reduction potential of a *para*-quinone (Q) in the aprotic solvent, acetonitrile:

$$\mathrm{Q(s)} + \mathrm{e^-(g)} \rightarrow \mathrm{Q^-(s)} \tag{1}$$

where s and g denote solution phase and gas phase, respectively. The total change of Gibbs free energy of reaction 1 is related to $E°_1$ according to

$$E°_1 = -\Delta G°(\mathrm{t})/-nF \tag{2}$$

where n is the number of electrons transferred ($n = 1$ in this case) and F is the Faraday constant (96485.338 C mol^{-1}).[24a]

As Scheme 1 shows, $\Delta G°$(t) of reaction 1 can be calculated from its components by introducing a thermodynamic cycle:

$$\Delta G°(\mathrm{t}) = \Delta G°(\mathrm{g}) + \Delta G°(\mathrm{solv,Q^-}) - \Delta G°(\mathrm{solv,Q}) \tag{3}$$

where $\Delta G°$(g) is the change of Gibbs free of reaction 1 in the gas phase, and $\Delta G°$(solv,Q^-) and $\Delta G°$(solv,Q) are solvation energies of Q and Q^- in acetonitrile, respectively.

To calculate $\Delta G°$(g), the Gibbs free energies of Q and Q^- have been calculated in the gas phase using the G3(MP2)-RAD level of theory as described before. For the free electron, we have followed electron convention (EC) in which the electron is considered to be equivalent to an element and its thermal energy is considered as an ideal monatomic gas, $^5/_2RT$.[25] This value is used to convert the energy of the electron from 0 to 298 K considering the integrated heat capacity for the free electron.[25]

$$\Delta G°(\mathrm{g}) = G°(\mathrm{g,298\ K,Q^-}) - G°(\mathrm{g,298\ K,Q}) - {}^5/_2RT \tag{4}$$

Following this convention, it is necessary to include a correction (RT ln 24.46) for the change in standard state from 1 atm to 1 mol L^{-1}.[26]

To this point, one can calculate the absolute values for $E°_1$ based on $\Delta G°$(t) of reaction 1 using eq 2. To calculate reduction potentials relative to SCE, the reduction potential of standard hydrogen electrode (SHE) and standard calomel electrode (SCE) should be taken into account. It should be noted that the values of these standard electrodes themselves differ between aqueous and nonaqueous solution. In the present work we have therefore selected a value of 4.52 V for SHE, which was recently suggested by Cramer and Truhlar for nonaqueous solution of acetonitrile, based on Boltzmann statistics.[10f] For SCE, we used a value of 0.15 V, which was obtained by taking the literature value of the reduction potential of aqueous SCE relative to SHE at 298 K (0.24 V[24a]), and correcting it to its corresponding value in acetonitrile solution using the literature value of the liquid junction potential (ljp) of acetonitrile−water (93 mV[24b,c]). Therefore, $E°_1$ relative to nonaqueous SCE (without ljp) was obtained using

$$E°_1(\mathrm{V}) = \Delta G°(\mathrm{t})\ (\mathrm{J\ mol^{-1}})/(-1 \times F) - 4.67\ (\mathrm{V}) \tag{5}$$

It is worth noting that the combination of 4.52 V for nonaqueous SHE and 0.15 V for nonaqueous SCE (4.67 V) is approximately equal to the combination of the corresponding aqueous values, 4.36 V for SHE[10d,e] and 0.24 V for SCE[24a] (4.60 V).

5. Results and Discussion

Benchmark Calculations of Reduction Potentials. As shown in Scheme 1, the calculation of change of Gibbs free energy of reaction 1, $\Delta G°$, comprises two different components: the calculation of the gas-phase values, $\Delta G°$ (g), and the calculation of the solvation energies. In the present work, gas-phase energies are calculated using the high-level composite method G3(MP2)-RAD. This method has been already tested for the calculation of electron affinities, ionization energies, proton affinities, and heats of formation of the species in the G2/97 test set and found to provide chemical accuracy.[17] For the specific case of electron affinities, the mean absolute deviation of G3(MP2)-RAD results from experiment was reported to be 5.81 kJ mol^{-1}.[17] Of the molecules included in the present study, we had only access to the experimental values for the electron affinities of molecules **1**, **2**, **6**, **7**, and **10**, which are 1.86, 2.44, 1.76, 1.81, and 1.59 eV, respectively.[27] Using the G3(MP2)-RAD method, the electron affinities of these molecules have been calculated as 1.93, 2.47, 1.80, 1.84, and 1.69 eV, respectively, resulting in a mean absolute deviation of 0.05 eV or 5.21 kJ mol^{-1}. Therefore, the gas-phase energies calculated using the high-level composite method of G3(MP2)-RAD are reliable and valid.

Solvation energies are too demanding to be calculated accurately by atomistic methods for molecules of this size. Instead, in the present work we use a continuum model of solvation, CPCM.[20] This method, applied at either the HF/6-31+G(d) or B3-LYP/6-31+G(d) levels of theory, has been widely used for the calculation of solvation energies of other species.[21] Ideally, one would assess its validity for calculating the solvation energies of quinones and their corresponding radical anions through direct comparison of the calculated and experimental solvation energies. Unfortunately, however, such experimental data are not available for the present systems (indeed, experimental solvation energies for radicals in general do not appear to be readily available in the literature). Instead, an indirect approach will be adopted whereby we compare the calculated and experimental reduction potentials, having first benchmarked the gas-phase calculations against experimental electron affinities. Because the gas-phase energies were shown to be reliable to within 0.05 eV (see above), one can assume that the remaining error arises in the treatment of solvation effects.

The solvation energies of the first 10 studied *para*-quinones $\Delta G°$(solv,i), the total change of Gibbs free energy of reaction 1, $\Delta G°$, and the resulting calculated electrode potentials versus SCE are shown in Tables 1 and 2, together with the corresponding experimental values. In Table 1 the solvation energies were calculated using CPCM at the HF/6-31+G(d) level of theory, and in Table 2 the CPCM solvation energies were calculated using B3-LYP/6-31+G(d). In both cases, the gas-phase energies were calculated using G3(MP2)-RAD and are therefore shown only once (in Table 1). Further details, such

TABLE 1: Gas-Phase Gibbs Free Energies, G°(g), and CPCM Solvation Energies of Studied *para*-Quinones, ΔG°(solv), for Both Neutral (Q) and Reduced (Q$^-$) Forms Calculated at the Level of HF/6-31+G(d), Together with Total Change of Gibbs Energy of Reaction 1, ΔG°(t), and One-Electron Reduction Potentials for the First Ten Studied *para*-Quinones

	G°(g)[b]/kJ mol^{-1}		ΔG°(solv)[c]/kJ mol^{-1}			E°_1[e]/V		
no.[a]	Q	Q$^-$	Q	Q$^-$	ΔG°(t)[d]/kJ mol^{-1}	abs[f]	vs SCE[g]	exp[h]
1	−1000149.7	−1000336.1	−9.0	−204.3	−395.8	4.10	−0.57	−0.522
2	−3411210.9	−3411451.4	3.1	−167.1	−424.7	4.40	−0.27	−0.197
3	−5822258.9	−5822528.8	13.1	−143.9	−441.0	4.57	−0.10	−0.005
4	−3894997.0	−3895342.5	0.7	−138.4	−498.6	5.17	0.50	0.502
5	−1103038.9	−1103212.4	−5.2	−198.1	−380.4	3.94	−0.73	−0.609
6	−1206217.2	−1206391.4	−0.6	−191.2	−378.8	3.93	−0.75	−0.684
7	−1402912.8	−1403091.1	−1.8	−186.0	−376.5	3.90	−0.77	−0.706
8	−3813972.1	−3814191.1	8.4	−158.4	−399.8	4.14	−0.53	−0.448
9	−1505949.9	−1506125.7	2.2	−179.4	−371.4	3.85	−0.82	−0.801
10	−1805674.2	−1805837.9	5.6	−166.9	−350.3	3.63	−1.04	−0.952
MAD[i]							0.07	

[a] For the list of studied molecules, see Figure 1. [b] Gas-phase Gibbs energies of studied *para*-quinones for both neutral (Q) and reduced (Q$^-$) forms using the G3(MP2)-RAD level of theory. [c] Solvation energies calculated at the HF/6-31+G(d) level. [d] Total change of Gibbs free energy of reaction 1. [e] One-electron reduction potentials of studied quinines. [f] Absolute values. [g] Relative to SCE. [h] Experimental values taken from ref 23. [i] Mean absolute deviations of calculated values from the experiment.

TABLE 2: CPCM Solvation Energies of Studied *para*-Quinones, ΔG°(solv,i) Calculated at the B3-LYP/6-31+G(d) Level, Together with the Total Change of Gibbs Free Energy of Reaction 1, ΔG°, and One-Electron Reduction Potentials of the First Ten Studied *para*-Quinones

	ΔG°(solv)[b]/kJ mol^{-1}			E°_1[d]/V		
no.[a]	Q	Q$^-$	ΔG°(t)[c]/kJ mol^{-1}	abs[e]	vs SCE[f]	exp[g]
1	−6.1	−195.3	−389.7	4.04	−0.63	−0.522
2	6.7	−160.0	−421.3	4.37	−0.30	−0.197
3	17.4	−138.1	−439.4	4.55	−0.12	−0.005
4	7.5	−131.5	−498.6	5.17	0.50	+0.502
5	−2.6	−189.5	−374.5	3.88	−0.79	−0.609
6	1.5	−182.8	−372.5	3.86	−0.81	−0.684
7	0.9	−176.1	−369.3	3.83	−0.84	−0.706
8	11.7	−149.7	−394.4	4.09	−0.58	−0.448
9	4.6	−169.9	−364.3	3.78	−0.90	−0.801
10	8.4	−157.6	−343.7	3.56	−1.11	−0.952
MAD[h]					0.12	

[a] For the list of studied molecules, see Figure 1. [b] Solvation energies calculated at the B3-LYP/6-31+G(d) level. [c] Total change of Gibbs free energy of reaction 1. [d] One-electron reduction potentials of studied quinones. [e] Absolute values. [f] Relative to SCE. [g] Experimental values taken from ref 23. [h] Mean absolute deviations of calculated values from the experiment.

as the G3(MP2)-RAD energies and thermochemical data, are provided in the Supporting Information.

Comparing first the solvation energies in Tables 1 and 2 we note that both the HF/CPCM B3-LYP/CPCM methods produce very similar solvation energies, and hence very similar reduction potentials. In each case, the calculated reduction potentials show reasonable agreement with experiment. When the solvation energies are calculated using HF/CPCM (Table 1), the best compatibility is for molecule **4**, for which the deviation between the calculated and experimental values is less than 0.01 V (exact calculated and experimental values, are 0.497 and 0.502 V, respectively, with a deviation of 0.005 V). The worst is for molecule **5**, with a deviation of 0.12 V. The overall MAD is 0.07 V, which is slightly smaller than that obtained when the solvation energies are calculated using B3-LYP/CPCM (MAD = 0.12 V), and hence the HF/CPCM method has been adopted for the calculation of the solvation energies in the present work. Because the MAD of the gas-phase electron affinities was 0.05 V, this would imply that the HF/CPCM solvation model is introducing a further error of only approximately 0.02 V to the results. Overall, it appears that the combination of G3(MP2)-RAD energies with HF/CPCM solvation energies can provide one reduction potentials of quinones in nonaqueous solution to within approximately 0.07 V (6.8 kJ mol^{-1}).

ONIOM Calculations of Reduction Potentials. Calculations of URCCSD(T) energies as a part of G3(MP2)-RAD calculation are very time consuming and are not practical for large molecules. Therefore, an alternative method for the gas-phase energies should be considered. Typically, electrode potentials for larger molecules are calculated using DFT methods such as B3-LYP[1a] or lower-cost ab initio methods such as (RO)MP2.[12f] To test the accuracy of this and other low-cost methods for the calculation of the one electron reduction potentials of the quinones, the reduction potentials (Table 3) were calculated using B3-LYP/6-311++G(2df,2p) corrected by a constant offset of 0.28 eV, as recently recommended by Liu−Guo,[1a] as well as using straight B3-LYP/6-311+G(3df,2p) and ROMP2/6-311+G(3df,2p) single point calculations. The results were compared with the corresponding G3(MP2)-RAD values and, where possible, also with experiment.

Of the lower-cost levels of theory examined, the DFT method B3-LYP/6-311+G(3df,2p) shows large deviations from the G3-(MP2)-RAD benchmark values (MAD = 0.21 V). Some of this error cancels with errors in the solvation energy calculations, resulting in smaller deviations when compared with experimental reduction potentials (MAD = 0.13 V). But, nonetheless, the errors remain high and the method is not suitable as an accurate low-cost method for studying larger systems. The use of the

TABLE 3: Calculated Reduction Potentials, $E°_1$ (V), Using G3(MP2)-RAD, ROMP2/6-311+G(3df,2p), B3-LYP/6-311+G(3df,2p), or B3-LYP/6-311++G(2df,2p) Gas-Phase Energies with Solvation Energies Obtained via CPCM Models, at the ROHF/6-31+G(d) Level

no.	B3-LYP[a]	B3-LYP[b]	ROMP2[b]	ONIOM[c]	G3(MP2)-RAD	exp
1	−0.59	−0.32	−0.42	−0.57	−0.57	−0.522
2	−0.15	0.12	−0.10	−0.21	−0.27	−0.197
3	−0.16	0.10	0.04	−0.11	−0.10	−0.005
4	0.49	0.75	0.58	0.42	0.50	+0.502
5	−0.77	−0.50	−0.60	−0.79	−0.73	−0.609
6	−0.82	−0.55	−0.60	−0.75	−0.75	−0.684
7	−0.86	−0.58	−0.68	−0.83	−0.77	−0.706
8	−0.64	−0.37	−0.48	−0.56	−0.53	−0.448
9	−0.97	−0.70	−0.77	−0.84	−0.82	−0.801
10	−1.19	−0.91	−0.97	−1.05	−1.04	−0.952
11	−1.24	−0.97	−1.02	−1.07		−0.981
12	−1.41	−1.13	−1.16	−1.30		−1.042
13	−1.54	−1.27	−1.21	−1.28		−1.200
MAD vs exp	0.18	0.13	0.05	0.10	0.07	
MAD vs G3(MP2)-RAD	0.08	0.21	0.11	0.03		

[a] Using the 6-311++G(2df,2p) basis set and the correction of 0.28 eV for the gas-phase energies, as recommended by Liu-Guo.[1a] [b] Using the 6-311+G(3df,2p) basis set. [c] For the details of ONIOM calculations, see the text.

B3-LYP/6-311++G(2df,2p) together with a 0.28 eV correction term, as suggested by Liu−Guo,[1a] certainly reduces the error in the B3-LYP calculations with respect to G3(MP2)-RAD (MAD = 0.08 V), but the overall deviations from experiment remain high (MAD = 0.18 V). The MP2 method shows similar performance to the corrected B3-LYP calculations with respect to G3(MP2)-RAD, giving reduction potentials that are systematically higher (i.e., less negative) than those obtained using G3(MP2)-RAD by an average of 0.11 V. Interestingly, when compared with experiment, the net errors in the reduction potentials calculated at this level (MAD = 0.05 V) are actually slightly smaller than those at the G3(MP2)-RAD level as the errors in gas-phase calculations tend to cancel those in the solvation energy calculations. However, because the gas-phase and solvation energy calculations are not related to one another, it would be dangerous to rely upon this error cancellation for other systems and it would appear that (RO)MP2/6-311+G-(3df,2p) is also unsuitable as an accurate lower-cost method for these systems.

Nonetheless, the relatively systematic nature of the errors in the ROMP2/6-311+G(3df,2p) energies when compared with the G3(MP2)-RAD energies suggests an alternative low-cost method for accurate calculations on larger systems based on ONIOM. In the ONIOM method of Morokuma and co-workers,[28] a chemical reaction is divided into a core section that includes the reaction center and principal substituents, and an outer section, which is the rest of the chemical system. The core system is calculated at a high level of theory and also at a lower level of theory, and the full chemical system is calculated only at the lower level. In forming the core section, deleted substituents are replaced with link atoms, typically hydrogens, so that the correct valency is maintained and the core provides a good model of the chemical reaction under study. The energy of the whole chemical system is then obtained as the sum of the high-level energy for the core system, and the substituent effect of the outer section calculated at the lower level. This approximation is exact if the low level of theory measures the substituent effect accurately. Table 3 shows the electrode potentials calculated using an ONIOM procedure in which the core (modeled as the parent compound **1** in all cases) was calculated at G3(MP2)-RAD and the substituent effect of the rest of the molecule was studied at ROMP2/6-311+G(3df,2p). From Table 3, it is seen that the ONIOM method provides excellent agreement with the considerably more expensive G3(MP2)-RAD calculations (MAD = 0.03 V), and very good agreement with experiment (MAD = 0.10 V), particularly considering the size of molecules studied.

6. Conclusions

Calculation of accurate reduction potentials of organic compounds in nonaqueous solutions is practical if standard high-level ab initio calculations are used for the gas-phase energies and solvation energies are obtained by the CPCM continuum model of solvation. Using this procedure, the mean absolute deviations of calculated one-electron reduction potentials of studied *para*-quinones in aprotic solvent of acetonitrile is only 0.07 V, only slightly higher than the errors in the corresponding gas-phase electron affinities (MAD = 0.05 V). The lower-cost computational procedures such as B3-LYP and RMP2 showed large deviations from the G3(MP2)-RAD benchmark values; however, the G3(MP2)-RAD energies could be approximated (to within 0.03 V) using an ONIOM based procedure in which the core is modeled at G3(MP2)-RAD and the substituent effect of the rest of the molecule is studied using ROMP2/6-311+G-(3df,2p).

Acknowledgment. We gratefully acknowledge generous allocations of computing from the Australian Partnership for Advanced Computing and the Australian National University Supercomputing Facility, financial support from the Australian Research Council under their Centres of Excellence program and provision of a Research Fellowship (to M.N.).

Supporting Information Available: B3-LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries, and corresponding total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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