Electron Affinities of Substituted *p*-Benzoquinones from Hybrid Hartree−Fock/Density-Functional Calculations

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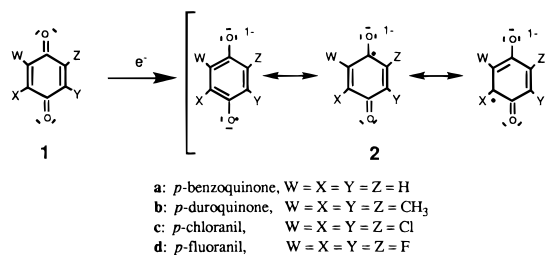
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Electron affinity calculations usually require sophisticated methods to account for electron correlation and large basis sets to model the diffuse electron density of anions. Quantum chemical methods currently used to approximate molecular energies may therefore require prohibitively large amounts of computer time and/or disk storage for large, polyatomic molecules such as the *p*-benzoquinones important in chemical and biochemical electron transfer reactions for energy storage, energy utilization, and catalytic chemistry. This contribution compares the abilities of several molecular orbital, density-functional, and hybrid Hartree−Fock/density-functional methods for calculating the adiabatic electron affinity of *p*-benzoquinone and presents calculated electron affinities for a number of methylated and halogenated *p*-benzoquinones. Of all methods and basis sets tested, the three-parameter hybrid Hartree−Fock/density-functional B3LYP method combined with the 6-311G(3d,p) basis set is most accurate for *p*-benzoquinone and yields an electron affinity of 1.85 eV compared to the experimental value of 1.91 ± 0.06 eV. The same method also gives calculated adiabatic electron affinities within 0.11 eV of experiment for 11 other methyl-, chloro-, and fluoro-*p*-benzoquinones, predicts an electron affinity of 1.74 eV for 2,3-dimethyl-*p*-benzoquinone, and verifies electron affinities for chloro- and 2,3-dichloro-*p*-benzoquinone previously estimated from charge transfer spectra. Thus, the B3LYP method shows promise as an accurate, economical alternative to highly sophisticated MO methods for calculating electron affinities of large, polyatomic molecules.

Introduction

The quantum mechanical calculation of thermodynamic data to chemical accuracy (within several kcal/mol of experiment) is required to model chemical reactions. A number of methods,[1] ranging from semiempirical MO[2−4] to *ab initio* MO[5−11] to Green's function or propagator techniques[12−17] have been developed to calculate atomization energies, ionization energies, proton affinities, and/or electron affinities. Any general procedure developed for thermochemical calculations must account for extensive electron correlation encountered when making and breaking covalent bonds, as well as the diffuse electron density evident for anions. Hence, such methods usually include high-level approximations for electron correlation, employ large basis sets, and consequently require a substantial investment of computational resources. More economical local density-functional methods have also been used to estimate electron detachment energies, but calculated electron detachment energies typically differ from experimental electron affinities by an adiabatic correction as large as 0.5 eV.[18,19]

A continuing interest in electron transfer chemistry and the recent development of thermodynamic cycle methods for calculating one-electron reduction potentials[20,21] has led us to investigate the performance of a number of methods for calculating gas-phase, adiabatic electron affinities for large, polyatomic molecules. Since *p*-benzoquinones[22] are vital electron acceptors in photosynthesis,[23−25] respiration,[23,24] organic synthesis,[26,27] and synthetic electron transfer systems,[28,29] we chose to study the energetics of reducing *p*-benzoquinone and a number of its methylated and halogenated derivatives (including those sketched in **1**) to their *p*-benzosemiquinone radical anions (e.g., **2**) by using several molecular orbital (MO),[30−32] density-functional (DF),[33−36] and hybrid Hartree−Fock/density-

a: *p*-benzoquinone, W = X = Y = Z = H
b: *p*-duroquinone, W = X = Y = Z = CH₃
c: *p*-chloranil,   W = X = Y = Z = Cl
d: *p*-fluoranil,   W = X = Y = Z = F

functional (HF/DF) methods.[37−39] The hybrid HF/DF methods were recently parametrized to reproduce thermodynamic data[37] to better accuracy than that afforded by DF methods and potentially provide economical alternatives to the computationally more expensive methods for calculating thermochemical properties of relatively small molecules.[5−17] HF/DF methods therefore offer the hope of calculating accurate energies for polyatomic molecules too large for more sophisticated methods.

Computational Methods

A variety of MO, DF, and hybrid HF/DF methods were tested to determine the most accurate way of calculating adiabatic electron affinities for *p*-benzoquinone and several of its substituted derivatives. Methods tested here include the unrestricted Hartree−Fock (UHF) molecular orbital, density-functional, and hybrid Hartree−Fock/density-functional (HF/DF) methods. The density-functional methods explored here involve combinations of different exchange and correlation functionals. The exchange functionals considered include Slater's local density approximation (abbreviated S with the adjustable parameter α equal to 2/3)[40] and Becke's functional (abbreviated B),[41] which includes gradient corrections to Slater's exchange. Correlation functionals used include the local spin density form of Vosko, Wilk, and Nusair (VWN),[42] the gradient-corrected form of Lee, Yang,

TABLE 1: Adiabatic Electron Affinities (EA) for *p*-Benzoquinone Calculated by Using a Variety of Different Computational Methods and Basis Sets

method basis	6-31G(d)	6-311G(d,p)	6-311G(3d,p)	6-311++G(d,p)	6-311++G(3d,p)
UHF	0.73	0.86	0.80	1.10	1.02
SVWN	2.22	2.54	2.54	2.84	2.80
BLYP	1.36	1.68	1.70	2.05	2.02
B3LYP	1.58	1.85	1.85	2.17	2.13
BP86	1.70	1.98	1.98	2.28	2.25
B3P86	2.25	2.49	2.47	2.75	2.70

[a] The EA for *p*-benzoquinone measured by experiment is 1.91 ± 0.06 eV[b,c] and calculated by using the CBS-4 method[d] (this work) is 2.48 eV. For all basis sets tested, the UHF method underestimates the EA, the local DF SVWN method overestimates the EA, whereas the gradient-corrected DF and hybrid HF/DF methods give intermediate values. [b] Chowdhury, S.; Grimsrud, E. P.; Kebarle, P. *J. Phys. Chem.* **1986**, *90*, 2747−2752. [c] Heinis, T.; Chowdhury, S.; Scott, S. L.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 400−407. [d] Ochterski, J. W.; Petersson, G. A.; Montgomery Jr., J. A. *J. Chem. Phys.* **1996**, *104*, 2598−2619.

and Parr (LYP),[43] and Perdew's 1986 gradient-corrected functional (P86).[44] Specific mathematical forms of each functional are provided in references cited above and will not be repeated here. We simply note that acronyms for density-functional methods begin with the approximate form for the exchange functional and follow with the form for the correlation functional. For example, SVWN indicates Slater's exchange functional used in conjunction with the correlation functional of Vosko, Wilk, and Nusair.

Hybrid HF/DF methods use a weighted sum of Hartree−Fock (E_X^{HF}), local DF, and gradient-corrected DF expressions for the exchange and correlation energies according to the general formula

$$E = (1 - a_0)E_X^{Slater} + a_0 E_X^{HF} + a_X E_X^{Becke} + a_C E_C^{LYP} + (1 - a_C)E_C^{VWN} \quad (1)$$

where E_X^{Slater} is Slater's local spin density approximation for the exchange energy,[40] E_X^{Becke} is Becke's gradient-corrected expression for exchange,[41] E_C^{VWN} represents the local correlation functional of Vosko, Wilk, and Nusair,[42] and E_C^{LYP} is Becke's gradient-corrected correlation functional.[43] In this equation, the constants $a_0 = 0.20$, $a_X = 0.72$, and $a_C = 0.81$ were determined empirically to reproduce heats of formation for a number of small molecules[37] for the case where $E_C[\rho]$ is Becke's 1986 correlation functional[44] (the Becke3P86 or B3P86 method[37]). More recently, the method was adapted to use Lee, Yang, and Parr's correlation functional, the same general expression for the energy, and the same values for a_0, a_X, and a_C (the Becke3LYP or B3LYP method).[38,39] To our knowledge, only limited tests of the B3LYP method's ability to reproduce accurate thermochemical data are currently published.[45−47] Electron affinities were estimated by simply calculating the energy difference between the anions and their corresponding neutral molecules. Because this procedure includes no explicit correction for differences in zero-point energies, it may favor the HF/DF methods because their parametrization presumably includes the zero point energy implicitly.

The *ab initio* MO, DF, and HF/DF calculations reported here use standard Gaussian basis sets.[31,48] Although conventional wisdom implies that diffuse basis functions are necessary to calculate accurate energies for anions, our goal of finding the most economical way to calculate accurate electron affinities for large polyatomic molecules includes finding the smallest basis set. We therefore began by using the split-valence plus polarization 6-31G(d) basis set, progressed to a triple-zeta valence plus polarization basis (6-311G(d,p) basis), added more polarization functions (the 6-311G(3d,p) basis) and, finally, added diffuse functions to the basis set (6-311++G(3d,p)). In addition, we tested several of Dunning's correlation-consistent basis sets augmented with diffuse functions (aug-cc-pV*x*Z,

where x = D, T, Q, 5, to indicate correlation-consistent polarized valence double, triple, quadruple, and quintuple zeta basis sets, respectively). These correlation-consistent basis sets were designed to display systematic convergence and allow smooth extrapolation to the complete basis-set limit in MO calculations.[49−51]

All calculations were performed by using the GAUSSIAN92/DFT[38] or GAUSSIAN94[39] set of quantum chemistry computer programs and the spin unrestricted formalism. Integrals required to solve the DF Kohn−Sham equations[52,53] were evaluated numerically on a grid of points using standard techniques described elsewhere.[54] Berny's optimization algorithm[55] in internal coordinates was used to optimize all geometries fully in their appropriate symmetries.

Calculated Electron Affinities for *p*-Benzoquinones

Calculating electron affinities as the difference in energy between an anion and the corresponding neutral molecule presents special challenges because (1) the correlation energy of anions is usually large and requires sophisticated methods to reproduce accurately, and (2) diffuse functions must usually be included in the basis set to represent the charge density distribution of the anion correctly. We note that molecular orbital-based methods more complicated than the DF and HF/DF methods used here, such as the Gaussian-1,[5,6] Gaussian-2,[7] and complete basis set (CBS)[8−11] methods, currently require prohibitive amounts of disk storage and/or CPU time for calculating the energies of large polyatomics such as the quinones. At a reviewer's suggestion, however, we tested the new CBS-4 method[56] to calculate the electron affinity of *p*-benzoquinone and found that the method requires 200 CPU min and 972 MB of temporary disk storage using a single processor (with 512 MB of memory) of an IBM SP2 supercomputer. Although the CBS-4 method requires less than the 380 CPU min used by the B3LYP/6-311G(3d,p) method described below, the B3LYP/6-311G(3d,p) method used only 69 MB of disk storage and gave a much more accurate electron affinity (experimental electron affinity: 1.91 ± 0.06 eV;[57,58] B3LYP: 1.85 eV; CBS-4: 2.48 eV). Because of the deficiencies of MO-based methods and the availability of newer DF and HF/DF methods whose thermochemical accuracies are only beginning to emerge,[45−47,54,59] we decided to test the performance of the newer DF and HF/DF methods to calculate electron affinities of *p*-benzoquinones.

Table 1 lists electron affinities for *p*-benzoquinone, **1a**, calculated by using a variety of different techniques and basis sets. The experimental electron affinity is also given in the table footnotes for comparison. For each basis set shown in Table 1, the UHF method gives an electron affinity that is smaller than the experimental value, the local DF SVWN method gives an electron affinity that is too large, whereas the gradient-corrected DF methods (BLYP and BP86) and hybrid HF/DF

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TABLE 2: Geometries of *p*-Benzoquinone Determined by Electron Diffraction[63] and by Using the 6-311G(3d,p) Basis Set (Standard Deviations in Parentheses)

	experimental	B3LYP	BP86
C=O	1.225(2)	1.216	1.230
C=C	1.344(3)	1.337	1.349
C−C	1.481(2)	1.485	1.488
C−H	1.089	1.084	1.094
O=C−C	121.0	121.4	121.4
H−C−C		115.8	115.8

methods (B3LYP and B3P86) give intermediate values. Therefore, the hybrid HF/DF energies usually fall in between the UHF and SVWN energies, as one might expect, because HF/DF energies are a weighted sum of SVWN, gradient-corrected DF, and UHF energies according to eq 1. Although the BLYP method gives an electron affinity within 0.11 eV of experiment for the largest basis set used, calculated electron affinities closest to experiment are obtained by using the BP86 or B3LYP computational methods with the 6-311G(d,p) and 6-311G(3d,p) basis sets.

For each computational method used, increasing the basis set size increases the calculated electron affinity by lowering the energy of the anion more than that of the neutral. Adding diffuse functions to the basis set causes a particularly large increase in the calculated electron affinities and results in poorer agreement between calculated and experimental electron affinities for the more accurate methods—BP86 and B3LYP. A possible reason for the increased error when adding diffuse functions to the 6-311G(d,p) and 6-311G(3d,p) basis sets comes immediately to mind: computations may not have converged with respect to basis set size, yet errors due to basis set truncation at the 6-311G(d,p) or 6-311G(3d,p) levels cancel other errors (such as those due to omitting nondynamical correlation,[60,61] important for calculating the electronic transition energies of *p*-benzosemiquinone radical anion[62]). To further test convergence with respect to the size of the basis set, two of Dunning's correlation consistent basis sets[49−51] larger than those shown in Table 1 were used with the B3LYP method. These tests gave calculated electron affinities of 2.15 eV (aug-cc-pVDZ basis set) and 2.13 eV (aug-cc-pVTZ), and thus showed little change from the electron affinity calculated with the smaller basis sets. Taken together, these tests raise the intriguing question whether or not the apparent cancellation of errors to give accurate electron affinities using the B3LYP or gradient-corrected BP86 methods with 6-311G(d,p) and 6-311-(3d,p) basis sets is observed for molecules other than *p*-benzoquinone.

Before presenting the results of further electron affinity calculations, we compare bond distances and bond angles for *p*-benzoquinone calculated by using the gradient-corrected BP86 and HF/DF B3LYP methods (with a 6-311G(3d,p) basis set) with those determined by electron diffraction[63] in Table 2. Structures derived from calculations and from the electron diffraction experiment all display D_{2h} symmetry. For the B3LYP method, all calculated carbon−carbon bond distances are within 3 standard deviations of experimentally determined bond lengths, the conventional criterion for determining whether or not two experimentally determined bond distances are the same. Even the least accurate calculated B3LYP bond distance, for the carbon−oxygen bond, is only 0.009 Å shorter than the experimental distance. For the BP86 method, all bond distances except the C−C distance (0.007 Å too long) are within 3 standard deviations of experiment. Bond angles calculated by using both the B3LYP and BP86 methods are also very accurate and differ from bond angles reported from electron diffraction measurements by an absolute magnitude of only 0.4°. Table 2

TABLE 3: Calculated and Experimental[57,58,64−69] Adiabatic Electron Affinities (EA) for a Number of Methylated and Halogenated *p*-Benzoquinones[a]

molecule	calculated EA (eV)	experimental EA(eV ± 0.1)[57,58,64]
p-duroquinone (tetramethyl-*p*-benzoquinone)	1.63	1.62
trimethyl-*p*-benzoquinone	1.66	1.63[b]
2,5-dimethyl-*p*-benzoquinone	1.69	1.76
2,6-dimethyl-*p*-benzoquinone	1.70	1.77
2,3-dimethyl-*p*-benzoquinone	1.74	
methyl-*p*-benzoquinone	1.77	1.79[b]
p-benzoquinone	1.85	1.91
chloro-*p*-benzoquinone	2.19	2.05 ± 0.15[c]
2,3-dichloro-*p*-benzoquinone	2.40	2.19 ± 0.15[c]
2,5-dichloro-*p*-benzoquinone	2.48	2.44
2,6-dichloro-*p*-benzoquinone	2.48	2.48
trichloro-*p*-benzoquinone	2.67	2.56[b]
p-fluoranil (tetrafluoro-*p*-benzoquinone)	2.62	2.70
p-chloranil (tetrachloro-*p*-benzoquinone)	2.83	2.78
average absolute error[d]	0.05	

[a] Calculations employed the B3LYP method and the 6-311G(3d,p) basis set. [b] Electron affinities for these molecules were taken from ref 65. [c] Electron affinities for chloro- and 2,3-dichloro-*p*-benzoquinone were estimated from measured charge transfer spectra.[66] [d] Average absolute error is calculated neglecting electron affinities estimated from charge transfer spectra.

thus emphasizes that the B3LYP and BP86 methods not only give accurate electron affinities but also yield extremely accurate geometries for *p*-benzoquinone, geometries so accurate that neither method is clearly favored over the other for reproducing the structure or electron affinity of *p*-benzoquinone.

To test the general ability of the B3LYP and BP86 methods to yield accurate electron affinities, we are continuing to calculate electron affinities for a variety of different molecules. Because the BP86 method gives a less accurate electron affinity than B3LYP for *p*-chloranil (2.89 eV versus 2.83 eV for B3LYP and 2.78 eV by experiment), the remainder of this paper focuses on the B3LYP method. Table 3 therefore compares experimental electron affinities for a number of methylated and halogenated *p*-benzoquinones[57,58,64−69] with electron affinities calculated by using the B3LYP method. Although the 6-311G-(d,p) and 6-311G(3d,p) basis sets give nearly identical electron affinities for most molecules listed in the table, the 6-311G-(3d,p) basis gives a significantly more accurate electron affinity for *p*-chloranil (2.83 eV vs 2.93 eV for the 6-311G(d,p) basis) and results calculated using only the larger basis are shown in the table. The average absolute difference between calculated and experimental electron affinities is smaller than experimental error and, with the exception of 2,3-dichloro-*p*-benzoquinone and trichloro-*p*-benzoquinone, each individual calculated electron affinity is within experimental error of its measured value. With the exception of *p*-fluoranil, calculated electron affinities for all *p*-benzoquinones tested also fall in the correct relative order and therefore follow trends noted for experimentally measured values. Calculations even imply the small difference in electron affinities between 2,5- and 2,6-dimethyl-*p*-benzoquinone. We note, however, that calculated electron affinities for 2,5-dichloro- and 2,6-dichloro-*p*-benzoquinone are virtually identical, whereas their experimental electron affinities differ by 0.04 eV. To our knowledge an experimental electron affinity for 2,3-dimethyl-*p*-benzoquinone is unknown and the value shown in the table represents a prediction. For in-depth comparisons of experimental structures, energies, and vibrational frequencies of substituted *p*-benzoquinones and their radical anions with those calculated by using MO, DF, and HF/DF

methods, the reader is referred to our other work.[70−72] We note here that calculated bond distances agree well with those determined by gas-phase electron diffraction for *p*-duroquinone,[73] *p*-chloranil,[74] and *p*-fluoranil[73] (average absolute differences between calculated and experimental bond distances are C=O 0.009 Å, C=C 0.004 Å, and C−C 0.003 Å, including C-methyl distances in *p*-duroquinone; C−F 0.002 Å; C−Cl 0.012 Å).

Conclusions

A variety of molecular orbital, density-functional, and hybrid Hartree−Fock/density-functional methods were tested to determine the most accurate way of calculating adiabatic electron affinities for *p*-benzoquinone and a number of methyl- and halogen-substituted *p*-benzoquinones. Results indicate that the B3LYP/6-311G(3d,p) method can yield electron affinities within experimental error for most quinones tested and within an average absolute magnitude of 0.05 eV of experimentally measured electron affinities[57,58,64−69] for the molecules considered. With only one exception, *p*-fluoranil, calculations give the correct relative magnitudes of electron affinities, although our calculations imply essentially equal electron affinities for the extremely similar molecules 2,5- and 2,6-dichloro-*p*-benzoquinone (experimentally measured electron affinities differ by only 0.04 eV). Our calculations also predict an electron affinity of approximately 1.74 eV for 2,3-dimethyl-*p*-benzoquinone and give electron affinities of 2.19 and 2.40 eV for chloro-*p*-benzoquinone and 2,3-dichloro-*p*-benzoquinone, respectively. For the latter two molecules, experimental electron affinities were estimated from charge transfer spectra[66] and are therefore subject to larger experimental error. Although we fully expect these results may be improved upon by using more sophisticated, post-Hartree−Fock MO methods and different, perhaps larger basis sets, the hybrid HF/DF B3LYP method accomplishes remarkable accuracy for the approximate cost of a Hartree−Fock calculation. The B3LYP method also yields calculated bond distances for *p*-benzoquinone with a maximum difference of 0.009 Å from bond distances measured by electron diffraction.[63] Initial results therefore indicate that the B3LYP method presents an economical alternative to more expensive MO-based methods for calculating electron affinities and geometries of *p*-benzoquinones. Because we have tested the methods for a relatively small but very important class of molecules, we are currently testing the B3LYP method's ability to calculate accurate electron affinities for other types of large polyatomic molecules. For information concerning the method's ability to reproduce experimentally determined structures and vibrational frequencies for *p*-benzoquinones, as well as structures, vibrational frequencies, and spin densities for *p*-benzosemiquinone radical anions, the reader is referred to other work.[70−72]

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