

Calculating Reversible Potentials for Elementary Reactions in Acid and Base from Model Reaction Energies

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Reversible potentials, U° , have been calculated based on reaction energies, E_r , for the intermediate steps in the outer-sphere oxygen reduction reaction to water. The working formula is $U^\circ = (-E_r \text{ eV}^{-1} + c) \text{ V}$, where U° is the reversible potential and the reference energy of the electron is -4.6 eV on the physical (vacuum) or 0 V on the hydrogen scale. Results using a 6-31G** basis in the B3LYP hybrid density functional theory are shown to be comparable to ab initio MP2 results obtained previously for acid solution with $c = 0.49$ for the former and 0.50 for the latter. Both methods are shown to work for basic solution but, unlike in acid, the c values are different, 0.58 for B3LYP and 0.76 for MP2, reflecting differences in the two computational methods in treating anions.

Introduction

Several studies^{1–6} in the past have reviewed electron transfer theory. Applications to oxygen reduction are important with a view toward reducing the high over potential. Quantum chemical calculations have addressed some of the electronic and mechanistic aspects of oxygen reducing electrocatalysis.^{7–10} To understand intermediates in electrocatalytic reactions such as O_2 reduction, this lab has developed a theoretical approach for calculating the reversible potentials, U° .⁹ It uses the relationship between the change in free energy, ΔG° , and reversible potential

$$\Delta G^\circ = -nFU^\circ \quad (1)$$

where n is the number of electrons used in the reaction and F is Faraday's constant. When the ion solvation is accurately calculated, enthalpy and entropy contributions at constant temperature (T) and pressure (P) can be added to calculated reaction energies, ΔE , to obtain Gibbs reaction energies

$$\Delta G^\circ = \Delta E + P\Delta V + T\Delta S \quad (2)$$

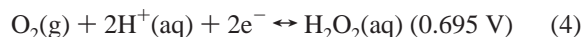
As was shown in ref 9 for five reduction reactions in acid involving H_xO_y reactants and products, U° is well-approximated by the formula

$$U^\circ = (-E_r \text{ eV}^{-1} + c) \text{ V} \quad (3)$$

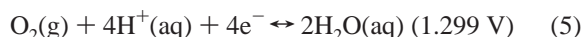
Here E_r is the reaction energy per electron and c is a constant. When ab initio Møller Plesset (MP2) calculations were performed with a 6-31G** basis set to determine E_r , with the electron energy referenced to -4.6 eV on the physical (vacuum) scale or 0 V on the hydrogen scale, c was determined to be 0.49 . This formula was also shown to give reasonable predictions for reductions when the intermediates were bonded to Pt catalysts.¹⁰

In this paper, the five reduction reactions, which were studied in the previous MP2 calculations are reexamined using the B3LYP hybrid density functional theory. The model is also

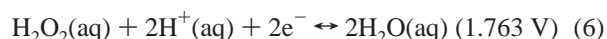
extended to several reactions in base. In practice, there are two important products of oxygen reduction, hydrogen peroxide and water. In acid, some oxygen reduction cathodes^{11–16} generate hydrogen peroxide



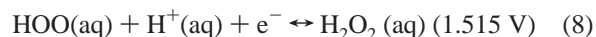
and others^{17–19} carry out the four-electron reduction to water



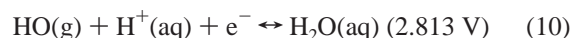
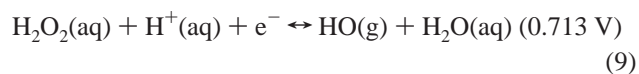
Theoretical work in this lab supports the hypothesis that active sites for hydrogen peroxide formation are 1-fold, allowing only end-on O_2 coordination, whereas active sites for four-electron reduction to water are 2-fold, allowing O–O bond cleavage after $\text{OOH}(\text{ads})$ formation in the first reduction step.²⁰ In eqs 4 and 5 and in subsequent equations, the U° from standard sources²¹ are given in parentheses. Hydrogen peroxide is reduced to H_2O at a high potential, making it an undesirable intermediate at a fuel cell cathode



As mentioned in ref 10, the reversible potentials for the intermediate noncatalyzed solution phase steps in oxygen reduction to hydrogen peroxide



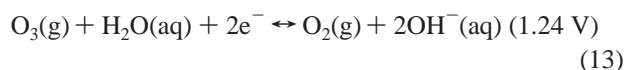
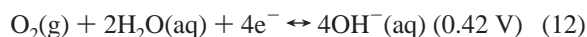
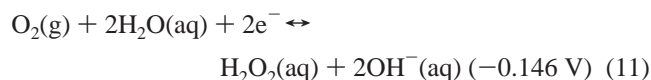
are not as well founded as those for H_2O_2 reduction to water



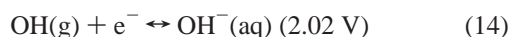
Consequently, eqs 7 and 8 were not used in establishing the 0.49 V constant in ref 9 and are not used in this work either.

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In this present study, the first aim is to calculate the reversible potential for the acid reduction reactions 4–10 using the B3LYP/6-31G** level of theory for comparison with the earlier study with MP2. As in the previous MP2 work,¹⁰ H⁺(aq) is modeled as a hydronium ion with the hydrogen bonded water molecules attached to it, and the other species are isolated unsolvated molecules. This was the source of reaction energies, defined as the total energy of products minus the total energy of reactants in eq 3. Second, electronic and vibrational contributions to $T\Delta S$ are calculated for reactions 4–10 to see if they account for the 0.49 eV term in eq 3. Third, to see if relationships similar to eq 3 apply in base, the reversible potentials for four reduction reactions in base are calculated using a solvation model for OH[−](aq) with E_r , calculated at the MP2/6-31G** and B3LYP/6-31G** levels of theory. The reactions are



and



The OH[−] ion used in this calculation is solvated by three water molecules hydrogen bonded to the O.

Computational Methods

The MP2 and hybrid density functional method B3LYP were employed using the 6-31G** basis set for O and H atoms. All of the calculations were carried out using the Gaussian 94 program.²² Analytical frequency calculations have been carried out to determine the nature of the stationary points and to obtain contributions to the free energy at 298 K.

Results and Discussion

U° for Acid Reduction Reactions in Acid. To calculate the reaction energies for the acid reduction reactions 4–10, the species that are to be reduced, O₂, H₂O₂, H₂O, and HO, were optimized at both MP2/6-31G** and B3LYP/6-31G** levels of theory. The calculated parameters for the other molecules are in Table 1. The hydrogen atoms are well described, with the calculated ionization potentials being 13.558 and 13.613 eV for the MP2 and B3LYP methods, respectively, compared to 13.606 eV, the exact value. The proton used in these reduction reactions was in the form of a hydronium ion coordinated by three hydrogen-bonded water molecules as H₃O⁺(H₂O)₃; see Figure 1. Structural parameters at both levels of theory are given in Table 2. The proton stabilization energies of H₃O⁺(H₂O)₃ calculated with the MP2 and B3LYP methods are 11.636¹⁰ and 11.796 eV, respectively. The calculated reaction energies and the reversible potentials for these reactions are in Table 3 along with the experimental values. Figure 2 shows that eq 3 holds with nearly the same constants, 0.50 for MP2 and 0.49 for B3LYP calculations, because both methods predict the IP of H, the proton stabilization, and the other contributions to the reaction energies to be almost the same. If the Gibbs reaction energies were calculated with MP2 theory using the electronic

TABLE 1: Calculated Equilibrium Intermolecular Distances R_e (Å) and Angles θ_e (deg) for O₂, H₂O₂, H₂O, HO, and O₃ Using MP2/6-31G and B3LYP/6-31G** Levels of Theory^a**

molecule	$R_e(\text{O}-\text{O})$		$R_e(\text{H}-\text{O})$		$\theta_e(\text{HOO})$	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
O ₂ ^b	1.247	1.215 [1.208]				
H ₂ O ₂ ^{c,d}	1.477	1.467 [1.464]	0.968	0.969 [0.965]	97.20	98.33 [99.40]
H ₂ O ^{c,e}			0.961	0.965 [0.957]		
HO ^b			0.972	0.979 [0.970]		
O ₃ ^f	1.313	1.337				

^a Experimental values in brackets. ^b Hrusak, J.; Friedrichs, H.; Schwartz, H.; Razafinjanahary, H.; Chermette, H. *J. Phys. Chem.* **1996**, *100*, 100–110. ^c Landolt-Börnstein. In *Structure Data of Free Polyatomic Molecules*; Kuchitsa, K., Ed.; Springer: Berlin, 1995; Vol. XXIII. ^d The dihedral angles are 120.42° (MP2) and 121.46° (B3LYP) [111.80°], see footnote c of Table 1. ^e The HOH angles are 103.72° (MP2) and 103.74° (B3LYP) [104.51°], see footnote c of Table 1. ^f The OOO angles are 97.46° (MP2) and 98.04° (B3LYP).

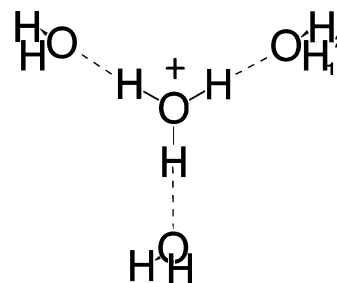


Figure 1. Structure of the hydronium ion model used in the calculations.

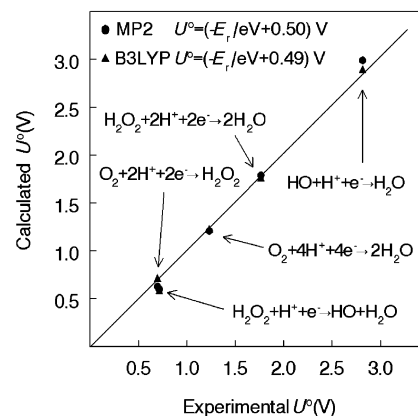


Figure 2. Calculated reversible potentials for acid solution, U° (V), vs experimental values indicated by the line.

and vibrational entropy contributions, they would be about 0.48 eV greater than the E_r in Table 3, mainly because of the 0.48 eV vibrational entropy contribution from H₃O⁺(H₂O)₃. The next largest contributions are the electronic entropy contributions for O₂, a triplet, OH, and OOH, both doublets, and are 0.03 and 0.018 eV, respectively; the singlet state species have zero contributions. The vibrational entropy contributions for O₂, H₂O₂, and H₂O are negligible. This 0.48 would have to be added to 0.50 to give a c value 0.98 in eq 3. Thus, the extra-molecular contributions to the free energy are important, as shown in ref 9, and there is no point in calculating ΔG° based on entropy contributions for the isolated molecules for use in eq 1.

U° for Reduction Reactions in Base. To calculate the reaction energies for the reduction reactions in base, reactions

TABLE 2: Calculated Equilibrium Intermolecular Distances R_e (Å), Angles θ_e (deg), and Dihedral Angles D (deg) for C_{3v} $H_3O^+(H_2O)_3$ from MP2/6-31G** and B3LYP/6-31G** Calculations Subject to Constraining the Projection of the O–H⁺–O Axis on the H_3O^+ Plane to Be Linear

method	R_e (O–H ⁺)	R_e (OH ⁺ ...H)	R_e (O–H ₁)	R_e (O–H ₂)	θ_e (HOH ⁺)	θ_e (OH ⁺ O)	θ_e (H ⁺ OH ₁)	θ_e (H ⁺ OH ₂)	D (OH ⁺ OH ₁)	D (OH ⁺ OH ₂)
MP2	1.012	1.539	0.964	0.964	112.61	178.53	120.01	123.78	–4.50	136.46
B3LYP	1.021	1.527	0.967	0.967	112.99	178.60	118.88	122.23	–1.92	135.28

TABLE 3: Calculated Reaction Energies Per Electron, E_r (eV), from the MP2/6-31G** and B3LYP/6-31G** Methods and the Reversible Potential, U° (V), from Equation 3 for the Reduction Reactions 4–10 in Acid^a

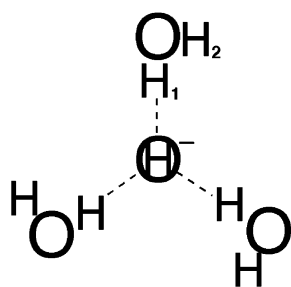
reaction	E_r		U°		
	MP2	B3LYP	MP2	B3LYP	
$O_2(g) + 2H^+(aq) + 2e^- \leftrightarrow H_2O_2(aq)$	–4.74	–4.83	0.63 ^b	0.72	[0.695]
$O_2(g) + 4H^+(aq) + 4e^- \leftrightarrow 2H_2O(aq)$	–5.32	–5.34	1.21 ^b	1.23	[1.229]
$H_2O_2(aq) + 2H^+(aq) + 2e^- \leftrightarrow 2H_2O(aq)$	–5.90	–5.88	1.79 ^b	1.77	[1.763]
$O_2(g) + H^+(aq) + e^- \leftrightarrow HOO(aq)$	–3.59	–4.09	–0.52 ^c	–0.01	[–0.125]
$HOO(aq) + H^+(aq) + e^- \leftrightarrow HO(g) + H_2O(aq)$	–5.90	–5.57	1.79 ^c	1.46	[1.515]
$H_2O_2(aq) + H^+(aq) + e^- \leftrightarrow HO(g) + H_2O(aq)$	–4.71	–4.70	0.60 ^b	0.59	[0.713]
$HO(g) + H^+(aq) + e^- \leftrightarrow H_2O(aq)$	–7.10	–7.01	2.99 ^b	2.90	[2.813]

^a Experimental values in brackets from ref 21. ^b Reference 9. ^c Reference 10.**TABLE 4:** Calculated Equilibrium Intermolecular Distances R_e (Å) and Angles θ_e (deg) for $HO^-(H_2O)_3$ (Figure 3) Using MP2/6-31G** and B3LYP/6-31G** Levels of Theory^a

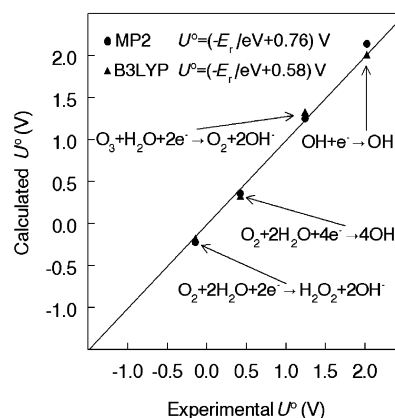
method	R_e (O–H [–])	R_e (HO [–] ...H ₁)	R_e (O–H ₁)	R_e (O–H ₂)	θ_e (H [–] OH ₁)	θ_e (O–H ₁ O)	θ_e (H ₁ OH ₂)	D (HO [–] H ₁ O)	D (O–H ₁ OH ₂)
MP2	0.965	1.656	0.982	0.982	102.34	171.34	99.83	102.45	12.22
B3LYP	0.967	1.653	0.987	0.987	101.47	171.31	99.83	94.81	18.31

^a The OH[–] axis is constrained to be perpendicular to the plane defined by H₂O.**TABLE 5:** Calculated Reaction Energies Per Electron, E_r (eV), from the MP2/6-31G** and B3LYP/6-31G** Methods and the Reversible Potential, U° (V), from Equation 3 for the Reduction Reactions 11–14 in Base^a

reaction	E_r		U°		
	MP2	B3LYP	MP2	B3LYP	
$O_2(g) + 2H_2O(aq) + 2e^- \leftrightarrow H_2O_2(aq) + 2OH^-(aq)$	–0.98	–0.76	–0.22	–0.18	[–0.15]
$O_2(g) + 2H_2O(aq) + 4e^- \leftrightarrow 4HO^-(aq)$	–0.40	–0.25	0.36	0.33	[0.42]
$O_3(g) + H_2O(aq) + 2e^- \leftrightarrow O_2(g) + 4HO^-(aq)$	0.49	0.75	1.25	1.33	[1.24]
$HO(g) + e^- \leftrightarrow OH^-(aq)$	1.38	1.43	2.14	2.01	[2.02]

^a Experimental values are in brackets from ref 20.**Figure 3.** Structure of hydroxyl anion used in the calculations.

11–14, the species that are to be reduced, O_2 , H_2O , O_3 , H_2O_2 , and OH , were optimized at both MP2/6-31G** and B3LYP/6-31G** levels of theory. These structures are given in Table 1. The OH^- ion used in these reactions has three water molecules hydrogen bonded to it as $HO^-(H_2O)_3$; see Figure 3. The structure parameters are given in Table 4. Coordination of OH^- by $3H_2O$ has been computationally explored by others.^{23–26} The calculated reaction energies and the reversible potentials for reactions 11–14 are given in Table 5 along with the experimental values. The electron affinity EA of OH^- by experiment is 1.825 eV,²⁷ but the calculated EAs of OH^- are –0.165 and +0.060 eV, respectively by MP2 and DFT methods. These predictions are low by 1.988 and 1.766 eV for MP2 and B3LYP methods, respectively, and these correction factors are included in E_r calculations. For hydrogen atom ionization, no

**Figure 4.** As in Figure 2, but for base solution.

such corrections were used because the calculated values were more accurate. When they are used, the c value decreases by 0.04 for the MP2 calculation and increases by 0.01 for B3LYP. The EA of OH^- could be made more accurate if the basis set were enhanced by adding diffuse functions and additional polarization functions. However, because bond strengths are well calculated with the present basis set, there is no need to extend the basis set for this work. Figure 4 shows the predicted values of U° based on E_r and adding 0.76 and 0.58 V for MP2 and B3LYP methods, respectively. It is noted that the OH^- anion stabilization energies were calculated to be 4.154 and 4.317 eV by the MP2

and B3LYP methods, respectively. The difference between OH⁻ anion stabilization energies of the MP2 and B3LYP methods is 0.163 eV, and this is responsible for the different constants added to E_r . The two methods do not treat hydrogen bonding for H₂O to OH⁻ equally.

Conclusions

The reversible potentials calculated for five reduction reactions in acid with the B3LYP hybrid density functional theory using eq 3 are essentially the same as with the MP2 method in ref 9. For four reduction reactions in base, the working formula for MP2 calculations is

$$U^\circ = (-E_r/\text{eV} + 0.76) \text{ V} \quad (15)$$

and for B3LYP calculations the working formula is

$$U^\circ = (-E_r/\text{eV} + 0.58) \text{ V} \quad (16)$$

The different constants in eqs 15 and 16, 0.76 and 0.58 V, respectively, stem from the two methods not treating the solvation of the negative OH⁻ anion equally.

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References and Notes

- (1) For a review up to 1995, see: Miller, R. J. D.; McLendon, G. L.; Nozik, A. J.; Schmickler, W.; Willig, F. *Surface Electron-Transfer process*; VCH: New York, 1995; Section 3.3.
- (2) Hush, N. S. *J. Electroanal. Chem.* **1999**, 460, 5–29.
- (3) Koper, T. M.; Schmickler, W. In *Electrocatalysis*; Lipkowski, J., Ross, P. N., Eds.; Wiley: New York, 1998; pp 291–322.
- (4) Koper, M. T. M.; Voth, G. A. *J. Chem. Phys.* **1998**, 109, 1991–2001.
- (5) Anderson, A. B.; Kang, D. B. *J. Phys. Chem.* **1998**, A102, 5993–5996.
- (6) Anderson, A. B.; Albu, T. V. *Electrochem. Commun.* **1999**, 1, 203–206.
- (7) Goodenough, J. B.; Manoharan, R. *Proc. Electrochem. Soc.* **1992**, 92–11, 523–539.
- (8) Anderson, A. B. *Proc. Electrochem. Soc.* **1992**, 92–11, 434–439.
- (9) Anderson, A. B.; Albu, T. V. *J. Am. Chem. Soc.* **1999**, Vol. 121, No. 50, 11855–11863.
- (10) Anderson, A. B.; Albu, T. V. *J. Electrochem. Soc.* **2000**, 147 (11), 4229–4238.
- (11) Adzic, R. In *Electrocatalysis*; Lipkowski, J., Ross, P. N., Eds.; Wiley: New York, 1998; pp 197–242.
- (12) Markovic, N. M.; Gasteiger, H. A.; Ross, P. N., Jr. *J. Phys. Chem.* **1995**, 99, 3411–3415.
- (13) Yeager, E. *Electrochim. Acta* **1984**, 29, 1527–1537.
- (14) Tarasevich, M.; Sadkowsky, A.; Yeager, E. In *Comprehensive Treatise of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Yeager, E., Khan, S. U. M., White, R. E., Eds.; Plenum: New York, 1983; Vol. 7, p 301.
- (15) Mehandru, S. P.; Anderson, A. B. *Surf. Sci.* **1989**, 216, 105–124.
- (16) Vasudevan, P.; Santosh; Mann, N.; Tyagi, S. *Transition Met. Chem.* **1990**, 15, 81–90.
- (17) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; McBreen, J. *J. Phys. Chem.* **1995**, 99, 4577–4589. Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; McBreen, J. *J. Electrochem. Soc.* **1995**, 142, 1409–1422.
- (18) Coutanceau, C.; Crouigneau, P.; Leger, J. M.; Lamy, C. *J. Electroanal. Chem.* **1994**, 379, 389–397.
- (19) Shi, C.; Anson, F. C. *Inorg. Chem.* **1996**, 35, 7928–7931.
- (20) Anderson, A. B.; Sidik, R. A. *J. Electroanal. Chem.* **2002**, 528, 69–76.
- (21) Hoare, J. P. In *Standard potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985. *Handbook of Chemistry and Physics*, 67th ed.; Weast, C. R., Ed.; CRC Press: Boca Raton, FL, 1986.
- (22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (23) Xantheas, S. X. *J. Am. Chem. Soc.* **1995**, 117, 10373–10380.
- (24) Tuñón, I.; Rinaldi, D.; Ruiz-López, M. F.; Rivail, J. L. *J. Phys. Chem.* **1995**, 99, 3798–3805.
- (25) Pilego, J. R., Jr.; Riveros, J. M. *J. Chem. Phys.* **2000**, 112, 4045–4052.
- (26) Brodskaya, E.; Lyubartsev, A. P.; Laaksonen, A. *J. Phys. Chem. B.* **2002**, 106, 6479–6487.
- (27) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. Vol. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; p 516.