Full Paper

Computational Electrochemical Oxidation of Some N-Hydroxy Compounds in Aqueous Solution

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Abstract- Density functional theory method at the level of B3LYP/6-31G(d,p) in combination with the polarizeable continuum model have been used to compute one-electron oxidation potentials for eighteen N-hydroxy compounds in aqueous solution. Analysis of correlation between the experimental oxidation potentials and the theoretically calculated values revealed that notable relations existed between the experimental potentials and the eigenvalues of SOMO's of the N-Hydroxy {-N (OH)-} derivatives.

Key words- N-hydroxy Compounds, Redox Potential, Polarizeable Continuum Model, Computational Studies

1. INTRODUCTION

The electron transfer process constitutes the basic feature of chemical, biochemical and, especially, electrochemical reactions. These electron transfers can be either oxidative or reductive. Thus, the assessment of electron transfer in the reactions of N-Hydroxy [-N (OH)-] compounds with electrophiles and oxidants requires values of the standard oxidation potentials. Cyclic voltammetry provides an experimental means for the measurement of redox potentials when the electron-transfer process is reversible. For non-reversible reactions, the experimental situation is more complicated. Thus, the ability to accurately predict redox potentials via using the theoretical methods for a given molecule in a number of different

areas is highly desirable, particularly where the experimental measurements are difficult [1-10]. The analysis of correlations between observable and calculated molecular descriptors has proved to be effective in the study of the electrochemical reaction mechanisms in the case of a variety of organic compounds [11-13]. This is commonly based on the fundamental relations between different important quantities, including the half-wave potential, $E_{1/2}$ (or the voltammetric peak potentials, E^a_p and E^c_p), the standard oxidation potential, E, the electron affinity of the reduced species in the gas phase, EA, the ionization potential for the reverse reaction, IP, the energy of the highest occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO).

This article focuses on predicting the electrode oxidation potentials of a series of eighteen N-hydroxy compounds {-N (OH)-}$_1$ -- {-N(OH)-}$_{18}$ (Fig. 1) in water by quantum chemical density functional level of gas-phase calculations and the polarizable continuum model (PCM) for solvation energies. Traditionally, the metal ion-chelating property of these compounds has made them useful for extractive metallurgy, corrosion prevention, and nuclear fuel processing. The redox property of some -N (OH) - compounds, which is of great interest for the development of laccase-catalyzed pulp delignification, water/soil decontamination, and other biocatalyses in aqueous solution, has already been reported by Feng Xu *et al.* using cyclic and differential pulse voltammetry [14].

2. COMPUTATIONAL STUDIES

Gas-phase molecular geometries for all species were optimized at DFT-B3LYP level using 6-31G(d,p) basis set [15-17]. The calculations give internal energies at 0 K. In order to obtain gas phase free energies at 298.15 K, it is necessary to calculate the zero-point energies and thermal corrections together with entropies to convert the internal energies to Gibbs energies at this temperature [18-20]. These corrections for neutral and radical species were carried out using frequency calculations [21]. The ΔG_{solv}^{o} value was computed using the version of polarizable continuum model (PCM) to describe the solvent and its interaction with solutes [22-24]. The salvation calculations were carried out using the B3LYP/6-31G(d,p) method. In the PCM model, the solvation energy is partitioned into four components including electrostatic interaction (ΔG_{elec}), cavity term (ΔG_{cav}), dispersion (ΔG_{dis}) and repulsion energies (ΔG_{rep}), the last three terms indicating the non-electrostatic interactions between solute and solvent ($\Delta G_{non-elec}$). All quantum theoretical calculations were carried out by means of DFT-B3LYP/6-31G(d,p) level of theory, using the Gaussian 98 package of programs [25].
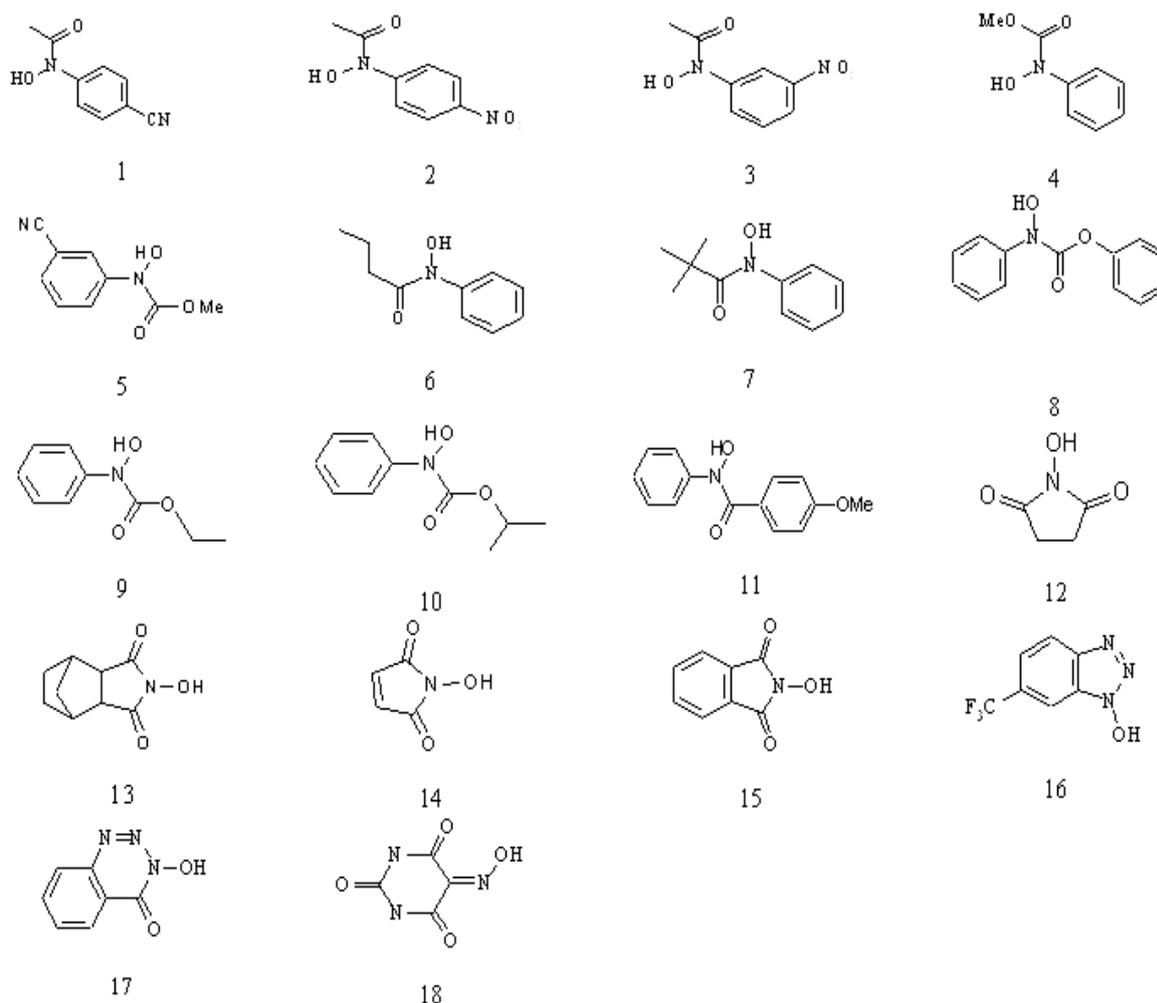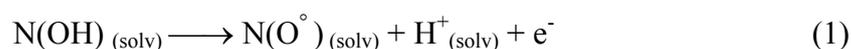
Fig. 1. Structural features of N-hydroxy compounds

3. RESULTS AND DISCUSSION

Formally, the oxidation of a substituted -N (OH)-compound (N (OH)) in solution can be represented by the following equation:

$$N(OH)_{(solv)} \longrightarrow N(O^\circ)_{(solv)} + H^+_{(solv)} + e^- \qquad (1)$$

In this case, the whole molecule by passing from the neutral to the radical form, becomes slightly planar and achieves the chance to delocalize the negative charge further and so assume a higher energetic stability. The three dimensional mapped isosurface of a sample molecule, like compound 11, between the eighteen N-hydroxy compounds studied is shown in Fig. 2. This means that the purely theoretical approach can give information on the system which is not obtained directly by experiments, but is remarkable when further experimental evidence is investigated [1].
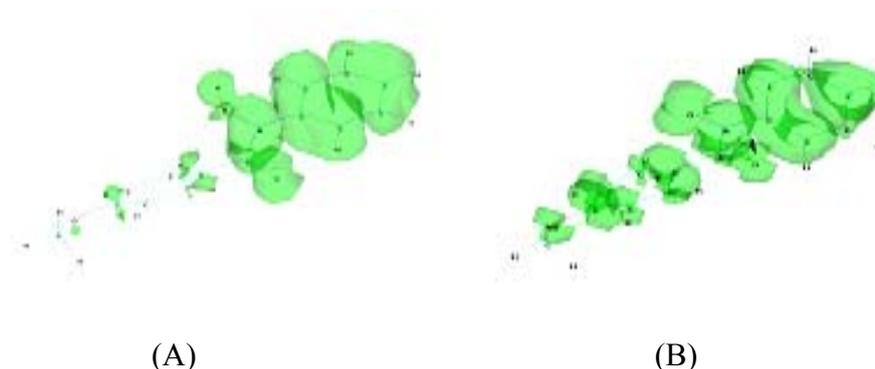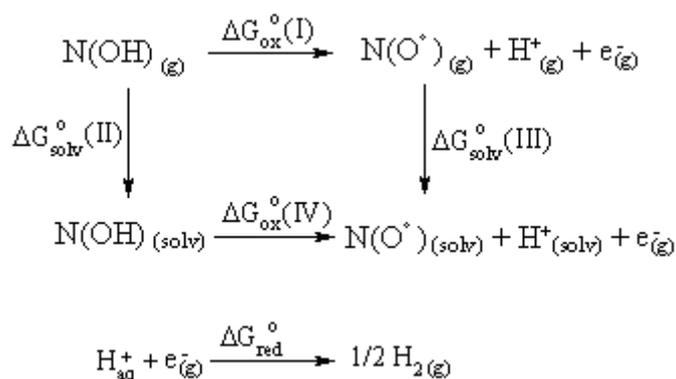
Fig. 2. The three dimensional mapped isosurface of the (A) neutral and (B) radical species of compound 11

The free energy of this reaction corresponds to the absolute redox energy for the above process. Then, it is possible to calculate the redox energy of reaction (1) using a thermodynamic cycle without any experimental data [1,3,5-10,17,26,27]. Scheme 1 is an illustration of such a thermodynamic cycle for the particular example of a molecule N (OH) as a reactant.

$$N(OH)_{(g)} \xrightarrow{\Delta G^{o}_{ox}(I)} N(O^{\bullet})_{(g)} + H^{+}_{(g)} + e^{-}_{(g)}$$

$$\Delta G^{o}_{solv}(II) \downarrow \qquad \qquad \downarrow \Delta G^{o}_{solv}(III)$$

$$N(OH)_{(solv)} \xrightarrow{\Delta G^{o}_{ox}(IV)} N(O^{\bullet})_{(solv)} + H^{+}_{(solv)} + e^{-}_{(g)}$$

$$H^{+}_{aq} + e^{-}_{(g)} \xrightarrow{\Delta G^{o}_{red}} 1/2\ H_{2\,(g)}$$

Scheme 1

where, the absolute redox potential $E^{\circ}_{ox(calc.)}$ can be calculated according to the following expression [26]:

$$\Delta G^{o}_{ox} = n\ F\ E^{\circ}_{ox(calc.)} \qquad\qquad (2)$$

From Scheme 1, the standard oxidation potential of the N(OH)/N(O$^{\bullet}$) couple in water can be determined as ΔG^{o}_{ox}(N(OH)/N(O$^{\bullet}$) *vs.* SHE)= ΔG^{o}_{ox}(IV)+ΔG^{o}_{red}. In fact, by considering the oxidation process in solution, the Gibbs energy variation for the half reaction given in step IV of Scheme 1 can be written as ΔG^{o}_{ox}(IV)= ΔG^{o}_{ox}(I) + ΔG^{o}_{solv}(III) - ΔG^{o}_{solv}(II). The first term of the right hand side of this equation is calculated by using IP(g) and the difference in

thermal contributions to the Gibbs energy of substituted N-hydroxy compound due to changes in electronic, vibrational and rotational partition functions upon oxidation, namely ΔG_{solv}^{o} (III) and ΔG_{solv}^{o} (II), are the Gibbs energies of solvation in solution of the Oxidized N-hydroxy compound(radical) and neutral species, respectively.

Due to use of different standard states in quantum chemistry and electrochemistry, the oxidation potentials are usually reported relative to a reference potential, typically taken as the normal hydrogen electrode (NHE); this convention then refers to the free energy change for the net reaction resulting from addition of the NHE half-reaction to the half-reaction given at the bottom of the free energy cycle (Scheme 1). It should be noted that, by definition, the NHE and N-hydroxy molecule half-reactions involve a gas-phase electron, so that the solvation free energy of the electron is not a relevant quantity in the free energy cycle. The free energy change for the reference electrode process $e^{-}(g)+H^{+}(aq) \longrightarrow 1/2\ H_2(g)$ is -4.36 eV. This is an experimental value, which again was not adjusted for the purposes of this study [19,27,28].

The calculations of Gibbs energy for eighteen N-hydroxy compounds for radical and neutral forms in the gas phase were carried out and the results are summarized in Table 1. In order to evaluate the Gibbs energy of substituted -N(OH)- derivatives for the redox reaction, the corresponding solvation energies consisting of electrostatic and non-electrostatic terms were also computed using the PCM method and the resulting values are also included in Table 1. The calculated ΔG_{ox}^{o} (IV) values with considering $G_{H^{+},gas}$ and $\Delta G_{H^{+},solv}$ are also presented in Table 1. The values for $G(H^{+}_{gas})$ and $\Delta G_{solv}(H^{+})$ are derived from experiment. We have used the values $G(H^{+}_{gas})$= -6.28 kcal/mol and $\Delta G_{solv}(H^{+})$= -260 kcal/mol [29].

The calculated $E^{\circ}_{ox(calc.)}$ values together with the corresponding experimental oxidation potentials, $E^{\circ}_{ox(exp.)}$ are given in Table 2. In addition, in Table 2 are also listed the negative energies of the single occupied molecular orbitals for open-shell radical species (SOMOs) for the eighteen N-hydroxy derivatives in the presence of solvent at the B3LYP/6-31G(d,p) level of theory.

Table 1. Calculated Gibbs energies for one-electron oxidation potentials of eighteen N-hydroxy derivatives in the gas and solution phases obtained from B3LYP/6-31G(d,p)

$-(HO)N-\}$	ΔG_{gas} (a.u.) [a]		ΔG_{sol} (kJ.mol^{-1})		ΔG_{ox}^{o} (kJ.mol^{-1})
	-N(OH)-	-N(O$^{\circ}$)-	-N(OH)-	-N(O$^{\circ}$)-	
1	-607.544622	-606.941201	-38.660160	-10.836560	497.989765
2	-719.800587	-719.196422	-37.195760	-9.162960	500.152336
3	-719.798411	-719.195251	-39.915360	-10.376320	499.019949
4	-590.514042	-589.902956	-21.966000	-22.886480	489.370140
5	-682.762369	-682.149091	-19.330080	-21.505760	493.870036
6	-593.869505	-593.254606	-19.664800	-25.438720	494.527731
7	-633.150732	-632.549613	-30.877920	-6.359680	488.640504
8	-782.197851	-781.585869	-22.844640	-22.844640	492.643068
9	-629.807264	-629.196054	-21.338400	-22.677280	489.277302
10	-669.098709	-668.492721	-30.877920	-13.054080	494.729663
11	-821.476113	-820.874901	-43.722800	-17.238080	490.851156
12	-435.756479	-435.134718	-44.475920	-38.325440	524.468310
13	-629.586301	-628.96422	-30.752400	-24.518240	525.392150
14	-434.535581	-433.921609	-32.718880	-25.564240	505.022453
15	-588.158991	-587.543336	-38.702000	-28.116480	512.872049
16	-807.983999	-807.373279	-36.024240	-10.920240	514.433687
17	-584.269547	-583.653843	-40.542960	-27.865440	515.092698
18	-619.297671	-618.693482	-65.981680	-40.668480	497.495748

(Row label B3LYP/6-31G(d,p) spans rows 14–18)

[a] Energies are in atomic units, Hartree (1 Hartree = 2625.49975 kJ mol^{-1})

Table 2. $E^\circ_{ox(calc.)}$ and $E^\circ_{ox(exp.)}$ for one-electron oxidation potentials of eighteen N-hydroxy derivatives at the B3LYP/6-31G(d,p) level of theory and the SOMO energies for their oxidized forms

{-N(OH)-}	$E^\circ_{ox(calc.)}$ (mV) B3LYP/6-31G(d,p)	$E^\circ_{ox(exp.)}$ (mV) [a]	SOMO(oxidized) (eV) [b]
1{-N(OH)-}	801.318	753	-6.396
2 {-N(OH)-}	823.732	759	-6.501
3 {-N(OH)-}	811.995	748	-6.431
4 {-N(OH)-}	711.982	687	-6.089
5 {-N(OH)-}	758.62	743	-6.391
6 {-N(OH)-}	765.436	709	-6.223
7 {-N(OH)-}	704.419	720	-6.087
8 {-N(OH)-}	745.903	740	-6.074
9 {-N(OH)-}	711.019	679	-6.076
10 {-N(OH)-}	767.529	676	-6.051
11 {-N(OH)-}	727.331	700	-5.904
12 {-N(OH)-}	1075.75	1180	-7.388
13 {-N(OH)-}	1085.32	1190	-7.118
14 {-N(OH)-}	874.207	950	-6.641
15 {-N(OH)-}	955.563	1001	-7.001
16 {-N(OH)-}	971.748	1170	-7.406
17 {-N(OH)-}	978.578	1220	-7.506
18 {-N(OH)-}	796.198	870	-6.384

[a] Experimental $E^\circ_{ox(exp.)}$ *vs*. NHE taken from [14].   [b] SOMO energies for the oxidized forms were obtained from B3LYP/6-31G(d,p)

It is well known that the theoretical descriptor SOMO is physically correlated with the oxidation potential [6-10,19,26,30], since molecule in oxidized form has already lost electron. The correlation between the calculated negative energies of this descriptor and the experimental oxidatin potentials $E^\circ_{ox(exp.)}$ for the eighteen N-hydroxy derivatives was also examined. Based on the data given in Table 2, there is a linear relationship between the $E^\circ_{ox(exp.)}$ values of the related -N(OH)- compounds and the corresponding SOMO (eV) energies, with a regression equations of:

$$E^{\circ}_{ox(exp.)} (mV) = -372.01\ SOMO_{oxidized} (eV) - 1571 \qquad (R^2=0.93) \qquad (3)$$

The resulting graph is depicted in Fig. 3. Also a comparison between experimental $E^{\circ}_{ox(exp.)}$) and calculated ($E^{\circ}_{ox(calc.)}$) oxidation potentials revealed a very good agreement (Fig. 4), with a linear correlation equation of:

$$E^{\circ}_{ox(exp.)} (mV) = 1.541\ E^{\circ}_{ox(calc.)} (mV) - 428.7 \qquad (R^2=0.90) \qquad (4)$$

From the predicted values of the electrochemical property (oxidation potential) a statistical quantity, root mean square errors of prediction (rms) was calculated. The value of rms(93.6 mv) indicates the good prediction ability of the resulted method.
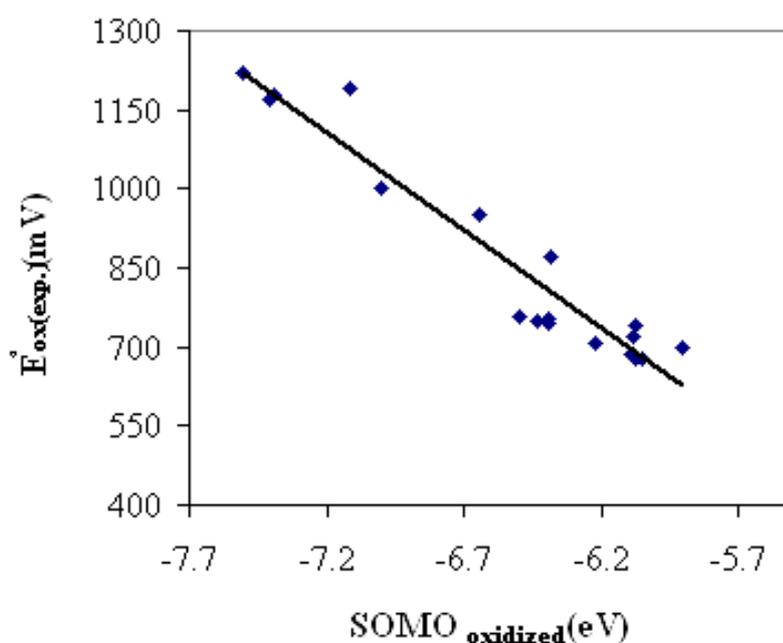

Fig. 3. Correlation diagram between the experimental $E^{\circ}_{ox(exp.)}$ values and the corresponding calculated SOMO energies (for oxidized forms) of the eighteen N-hydroxy compounds using the B3LYP/6-31G(d,p) method together with the linear regression line according to equation 3
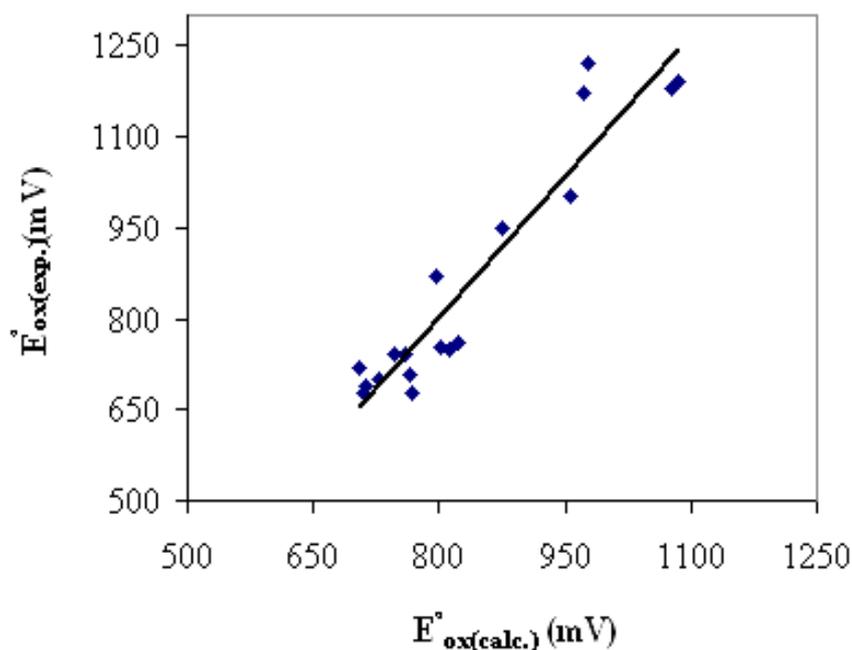
Fig. 4. Correlation diagram between the experimental $E^{\circ}_{ox(exp.)}$ and calculated $E^{\circ}_{ox(calc.)}$ values of the eighteen N-hydroxy compounds using the B3LYP/6-31G(d,p) method together with the linear regression line according to equation 4

4. CONCLUSION

The electrochemical oxidation potentials have been calculated, with the inclusion of the solvent effect, for some of -N(OH)- derivatives whose experimental electrode oxidation potentials in aqueous solution were available to us [14]. The B3LYP/6-31G(d,p) method was used to calculate the gas-phase free energy differences, and the polarizable continuum model (PCM) was applied to calculate the free energy differences of solvation for the N-hydroxy derivatives and their corresponding radical species. Acceptable linear correlations were found between the experimental oxidation potentials, $E^{\circ}_{ox(exp.)}$ and the eigen values of SOMO, as well as the calculated electrode oxidation potentials, $E^{\circ}_{ox(calc.)}$ of the studied N-hydroxy molecules. The values of regression analyses were found to be 0.93 and 0.90, respectively (Fig. 3, 4). Such linear relationships may be used as a tool to predict the physical properties of N-hydroxy compounds without having to synthesize them.

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