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Application of Density Functional Theory for evaluation of standard two-electron reduction potentials in some quinone derivatives

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ABSTRACT

In this research, two-electron reduction potentials are calculated for a set of eight quinones using Density Functional Theory (DFT) at B1B95/6-31G** and B1B95/6-311++G** levels in aqueous solution. Two different mechanisms, direct and indirect, which have been presented before, are employed for these calculations. DPCM and CPCM models of solvation are carried out to include solution phase contribution. The results show that CPCM is properly matched with DFT method at the B1B95 level in both direct and indirect mechanisms. It is found that direct mechanism gives more accurate two-electron reduction potentials in comparison to indirect mechanism. Mean Absolute Deviation (MAD) obtained through indirect mechanism and CPCM model of solvation are about 0.041 and 0.022 V for 6-31G** and 6-311++G**, respectively. The MAD values of direct mechanism are about 0.024 and 0.018 V for 6-31G** and 6-311++G** basis sets, respectively. The calculated MAD for both direct and indirect mechanisms is comparable with MAD previously reported at MP3 level for this set of molecules.

1. Introduction

Electron transfer is one of the important processes in vital cells [1]. An experimental measurement of the ability of the electron transfer is called redox potential. There are different methods for these measurements and absolute value of redox potentials are obtained for a wide range of molecules. Nevertheless, providing experimental condition for these determinations has usually its own difficulties. Theoretical prediction of redox potentials based on quantum mechanical calculations has been of major interest in recent years to avoid experimental difficulties [2].

Quinone is one of the most important compounds in analytical chemistry for determination of redox potentials. A natural example of quinones as oxidizing agents is the spray of bombardier beetles. Hydroquinone (pyrocatecol) reacts with hydrogen peroxide to produce a fiery blast of steam, a strong deterrent in the animal world. Occupational exposure to quinone may occur in the dye, textile, chemical, tanning, and cosmetic industries. Acute (short-term) exposure to high levels of quinone, via inhalation in humans, results in irritation of the eyes, consisting of discoloration of the conjunctiva and cornea, and causes dermatitis from dermal exposure [3]. On the other hand quinone can be used as anti cancer agent because of its redox nature [4].

Several articles have been published on redox potential prediction of quinone derivatives [6–12]. Since many electrochemical reactions occur in liquid solutions, the redox potential predictions have been carried out by considering quinones in either aqueous or non-aqueous solutions using different models of solvation such as Direct Polarized Continuum Model (DPCM) [5]. On the other hand several levels of computational methods were tested in order to obtain more and more reasonable theoretical redox potentials in comparison to experimental values [10]. In the case of aqueous solution, Namazian et al. employed B3LYP [7], and recently Moller–Plesset (MP3) level of theory [10] for a set of eight quinone derivatives. Though the results of B3LYP were far from experimental values, theoretical results of MP3 showed the best agreement. Total average error, which is denoted by Mean Absolute Deviation (MAD), was reported about 0.019 V. Nevertheless computational time using an ordinary computer is more significant than B3LYP.

Refining new functional for DFT has obtained an active research area in theoretical chemistry [13]. Many new functionals have been developed for special levels [13]. According to Zhao and Truhlar assessments [13] some hybrid DFT and hybrid meta-DFT methods such as B3LYP [14], B1B95 [15], MPW1PW91 [16] and B97-2 [17] have been recommended for prediction of thermochemistry quantities, in which refining new functional is based on semiempirical approach.

In this article Becke's first hybrid meta-GGA (B1B95) is assessed for prediction of two-electron reduction potentials of a set of eight quinone derivatives in aqueous solution. This level of DFT method is used in order to save computational time in comparison to MP3

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calculations [10] and to improve accuracy of results in comparison to those reported in literature by B3LYP [7]. Two different mechanisms of oxidation and reduction presented in the recent publications [10] are used here. The results are compared with other theoretical and experimental reported two-electron reduction potentials for the of quinone derivatives.

2. Computational and theoretical background

In this research the calculations of two-electron reduction potentials have been carried out using Density Functional Theory at B1B95 level. It has proven that in this method the incorrect DFT pure exchange part is replaced by exact exchange energy in the local exchange-correlation DFT, and therefore B1B95 properly describes long-range interactions [15].

Choosing an efficient model of solvation is of importance in these types of calculations. Among several approaches suggested for describing the solvent effect, continuum models are quite famous [5]. Another approach is Conductor-like Solvation Model (COSMO) which describes the solvent reaction filed by means of apparent polarization charges distributed on the cavity surface. The COSMO model is physically less founded than continuum models. Nevertheless it is attractive because of its simpler boundary conditions in computation. Using cavity parameters optimized for a well-known polarizable continuum model such as DPCM the COSMO procedure gives hydration energy in very good agreement with experimental results [5]. In this model, which is called an implementation of Conductor-like Polarizable Continuum Model (CPCM), the nonelectrostatic terms are exactly the same as the DPCM. The difference between these two models of solvation comes from the electrostatic term description. In the CPCM, the electrostatic expression is computationally very efficient since it doesn't require the calculation of charge derivatives [5].

All calculations are performed using GAUSSIAN 03 program [24]. The geometries of all reduced and oxidized form of quinone derivatives are optimized at B1B95/6-31G** and B1B95/6-311++G** levels of theory in gas phase. DPCM and CPCM are employed for considering the solvent contribution. Vibrational frequencies are carried out at these levels to consider thermal corrections.

3. Methods and theoretical considerations

Eight quinone derivatives which selected by Namazian et al. are used here to calculate two-electron reduction potentials [10]. There are two possibilities to predict two-electron reduction potentials of quinone derivatives in the literature which will be discussed in the following.

3.1. Indirect mechanism

The general theory for this type of reaction is to calculate two-electron reduction potentials of compounds which belong to one family using an isodesmic reaction by choosing one of them as a reference compound [8]. Eq. (1) is selected to calculate two-electron reduction potentials.

$$QH_2(\mathrm{sol}) + Q'(\mathrm{sol}) \rightarrow Q(\mathrm{sol}) + Q'H_2(\mathrm{sol}) \quad \Delta G^0_{\mathrm{rxn}} \tag{1}$$

where in this equation, the reference is molecule number 1 in Fig. 1., which is an unsubstituted quinone (QH_2). This molecule is oxidized and other quinones (Q') of this group are reduced. The change of Gibbs free energy for reaction (1) is obtained by

$$\Delta G^0_{\mathrm{rxn}} = -|Z|F(E_{Q'} - E_Q) \tag{2}$$

where $|Z|$ is the number of electrons transferred (here equals two) and F is the Faraday constant (96485.338 C mol^{-1}) [18]. Solution effects are concerned through a thermodynamic cycle like Scheme 1.

3.2. Direct mechanism

Another way to calculate two-electron reduction potentials is to reduce each quinone with hydrogen molecule in a direct reaction [10]:

$$\mathrm{Q(sol)} + \mathrm{H_2(gas)} \rightarrow \mathrm{QH_2(sol)} \quad \Delta G^0_{(\mathrm{rxn})} \tag{3}$$

This reaction is consisting of two half reactions:

$$\mathrm{Q(sol)} + 2\mathrm{H^+(sol)} + 2\mathrm{e^-(gas)} \rightarrow \mathrm{QH_2(sol)} \quad \Delta G^0_{(1)} \tag{4}$$

$$1/2\mathrm{H_2(gas)} \rightarrow H^+(\mathrm{sol}) + \mathrm{e^-(gas)} \quad \Delta G^0_{(2)} \tag{5}$$

Gibbs free energy change of reaction (5) ($\Delta G^0_{(2)}$) is multiplied by factor 2 and added to $\Delta G^0_{(1)}$ of reaction (4) to obtain the standard Gibbs free energy change of the reaction (3). $\Delta G^0_{(2)}$ has been reported as much as 4.36 eV [1,20].

$$\Delta G^0_{(\mathrm{rxn})} = \Delta G^0_{(1)} + 2\Delta G^0_{(2)} \tag{6}$$

On the other hand, $\Delta G^0_{(1)}$ is obtained by the following equation

$$\Delta G^0_{(1)} = \sum_i v_i \Delta G^0_i \tag{7}$$

in this equation ΔG^0_i is the change of Gibbs free energy for each component of the reaction (4) and is calculated through a thermodynamic cycle like Scheme 2.

The value of $\Delta G^0_{\mathrm{H^+,gas}}$ is reported about -6.28 kcal/mol and $\Delta G^0_{\mathrm{H^+,sol}}$ has a range of -254 to -261 kcal/mol [21]. Thermal electron convention which relates $\Delta G^0_{\mathrm{electron}}$ equals zero in all temperatures is also concerned in this part of calculation [20]. Using Scheme 2 and the following equation ΔG^0_i can be calculated,

$$\Delta G^0_i = \Delta G^0_{(i,\mathrm{gas})} + \Delta G^0_{(i,\mathrm{sol})} \tag{8}$$

Finally $\Delta G^0_{(\mathrm{rxn})}$ can be inserted in the following equation to calculate standard two-electron reduction potentials:

$$\Delta G^\circ_{\mathrm{rxn}} = -|Z|FE^0. \tag{9}$$

4. Results and discussion

Two-electron reduction potentials have been calculated for eight quinone derivatives which were selected by Namazian et al. [10]. Fig. 1 shows the oxidized form of the studied molecules. The results have been compared with available experimental [19,22] and theoretical works.

Table 1 shows the total change of Gibbs free energies in gas and solution phases for studied molecules using Eq. (2) (Section 3.1). Solvation energies have been computed employing DPCM. Calculated two-electron reduction potentials in comparison to experimental data have been shown in this table too. The value of MAD was obtained about 0.071 V at B1B95/6-31G** level.

The required CPU time for B1B95 calculations is significantly less than MP3s, but the calculated MAD using indirect mechanism, is 0.052 V more than MP3s. A detailed study shows that using only change of Gibbs free energies in gas phase to calculate two-electron reduction potentials, causes a significant decrease in total average error. This observation predicts that original source of error arises from solution phase calculations. In other words, calculation of $\Delta G^0_{\mathrm{sol}}$ using DPCM decreases the accuracies of predicted two-electron reduction potentials. There are two options to avoid