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Research paper

One-electron oxidation and redox potential of nucleobases and deoxyribonucleosides computed by QM/MM simulations

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ABSTRACT

Our work provides a simple method in QM/MM simulations to estimate one-electron oxidation and redox potential of DNA components using linear response approximation. The standard one-electron oxidation and redox potential of four deoxyribonucleosides (dRNs) and their nucleobases are computed using the referenced quantities from present and previous QM/MM computations. The computational oxidation potentials of dA and dG agree with experimental values. The orders of dRN oxidation and reduction potential are dG < dA < dC ≈ dT and dA ≈ dG < dC ≈ dT separately. Our results suggest that ribose produces large effect on reduction potential and has a small contribution to oxidation potential of dA, dG, and dC.

1. Introduction

The redox properties including reduction potential, oxidation potential, electron affinity, and ionization potential of DNA greatly affect DNA functionality as replication, mutation, and degradation [1]. The ionization of and excess electron attachment to DNA components are important processes in radiation interaction with living cells. They could cause DNA damage and cell degradation [2]. The ionization properties can be illustrated with vertical ionization energy (VIE) and adiabatic ionization energy (AIE) [3]. The vertical electron affinity (VEA), adiabatic electron affinity (AEA), and vertical detachment energy (VDE) could be used to describe the capabilities of electron affinity for DNA components [4]. The ionization of and excess electron attachment to nucleobases and DNA deoxyribonucleosides (dRNs) in aqueous environment have been thoroughly studied in our previous works [5,6]. The results indicate that the bulk water molecules could have the evident effect on ionization and electron attachment to aqueous nucleobases as well as obviously stabilizes the dRN anions.

Moreover, the redox potential and free energy measurement would help to get better understanding of the driving force for electron-transfer reactions as well as radiation damages to DNA [7,8]. Experiments of one-electron oxidants [8], pulse radiation [9] and cyclic voltammetry [10] were used to determine the redox potential of nucleosides. Guanine was found to be most readily oxidized and served as positive charge center for DNA [8,11,12]. The different experiments present the similar redox potential variation [13–15]. The theoretical calculation revealed that the redox potential values largely affected by the choice of functional and basis set [16,17]. In order to obtain exact standard redox potential values and identify the electron selectivity trend of DNA base, Kristen L. and co-workers calculated the redox properties of DNA nucleobase using the DFT/M06-2X hybrid meta functional [18]. Their work reported that the oxidation potential of four DNA nucleobases are G (1.40 eV) < A (1.75 eV) < T (2.00 eV) < C (2.18 eV). The oxidation potential of guanine is smallest and the result is consistent with the experimental and other computational values. The reduction potential follows the sequence of G (−3.31 eV) < A (−2.86 eV) < C (−2.41 eV) < T (−2.32 eV).

The investigations of the nucleobases standard redox potential suggests that inclusion of specific waters would leads to significant reduction of the calculation error [19]. Our recent works have illustrated the significant impact of bulk water on DNA redox properties [5]. Thus, it could be important to use explicit water model to calculate the redox potential of nucleobases and dRNs. Further, the values can be employed to examine the ribose impact on DNA redox properties.

Here, we applied the combined quantum mechanical/mechanical molecular (QM/MM) simulation to compute the DNA standard one-electron oxidation and redox potential. It has been verified that the simulations with B3LYP functionalcan give better redox properties [20]. Instead of using thermos-dynamical reaction cycle, we applied linear response approximation (LRA) for the DNA one-electron redox potential estimation. LRA had been successfully used to determine one-electron redox processes [21–23]. The LRA derived from the Marcus

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theory of electron transfer rates in solution assumes that the polarization of the solvent is a linear function of the charge of solute [24–26]. Thus, the solute's free energy of solvation is also a linear function of the solute charge at the solvent-accessible surface [27,28]. In such simplification way, the computational cost of DNA redox potential calculation would be decreased.

2. Computational details

In this work, we used the QM/MM simulations to compute the standard one-electron oxidation and redox potential of four nucleobases (A, G, C and T) and their corresponding dRNs (dA, dG, dC, and dT). The computational procedure follows the previous investigations [29,30]. Here we give the important formulas to compute the oxidation and redox potential.

The one-electron oxidation potential of aqueous DNA components ($O_{aqu} \rightarrow O^{+}_{aqu} + e^{-}_{g}$) can be described by [31,32]

$$E^{0}_{ox} = \frac{\Delta G_O}{nF} - SHE. \tag{1}$$

ΔG_O is the Gibbs free energy change of oxidation according to Faraday's law. n is the number of electrons (here n = 1) and F is Faraday's constant (1.0 eV/V). *SHE* is the absolute potential of the standard hydrogen electrode (4.44 eV used in this work) [19,33]. The free energy change of oxidation (ΔG_O) is given by

$$\Delta G_O = G_{aqu}\left(O^{+}\right) + G_g\left(e^{-}\right) - G_{aqu}\left(O\right). \tag{2}$$

$G_g(e^{-})$ is the free energy of the gas phase electron and its value is –0.867 kcal/mol. In the LRA, the oxidation free energy change ΔG_O can thus be written by [29,30]

$$\Delta G_O = \frac{\left(VIE + \Delta E_{CN}\right)}{2}. \tag{3}$$

VIE is vertical ionization energy of QM/MM computations and ΔE_{CN} is given by

$$\begin{aligned}&\Delta E_{CN}\\ &= E\left(optimized\ \ cation\right)\\ &\quad - E\left(neutrals\ \ at\ \ optimized\ \ cationic\ \ structure\right).\end{aligned} \tag{4}$$

The one-electron reduction potential ($R_{aqu} + e^{-}_{g} \rightarrow R^{-}_{aqu}$) can be given by [19,34]

$$E^{0}_{red} = \frac{-\Delta G_{red}}{nF} - SHE. \tag{5}$$

The Gibbs free energy change of reduction can be written by

$$\Delta G_{red} = G_{aqu}\left(R^{-}\right) - G_{aqu}\left(R\right) - G_g\left(e^{-}\right). \tag{6}$$

LRA ΔG_{red} can be computed by

$$\Delta G_{red} = -\frac{\left(VDE + VEA\right)}{2}, \tag{7}$$

where VDE is vertical detachment energy and VEA is vertical electron affinity. In the QM/MM computations, the equations to compute the two quantities are presented in our previous studies [5,6].

Three quantities (VIE, VEA and VDE) reported in our investigation of aqueous nucleobases were used to compute the one-electron standard oxidation and redox potential for four bases [5]. Here we only calculated ΔE_{CN} of nucleobases oxidation and computational parameters followed the VIE simulations. The VEA and VDE which are used to calculate the dRN standard redox potential are obtained from the computations of the excess electron attachment to dRNs [6]. In order to calculate the oxidation potential of dRNs, we computed the VIEs and ΔE_{CN} of aqueous dRNs. The computational procedure is similar to the investigation of aqueous nucleobases.

In the QM/MM VIEs and ΔE_{CN} calculations of aqueous dRNs, four dRNs (dA, dG, dC, and dT) were firstly dissolved in water sphere with 30.0 Å radius (~11,800 atoms). Freezing dRNs, we optimized initial water geometries at MM level and carried out NVT molecule dynamics (MD) simulations at 300 for 20 ps to relax water molecules. The pre-equilibrated configurations were as the initial structures. The systems of four aqueous dRNs were heated to 300 K in 20 ps and equilibrated at 300 K for 2 ns. The CHARMM package was used to dissolve dRNs in water and perform MD simulations [35]. The water molecules were computed by TIP3P force field [36]. We calculated the root-mean-square deviation (RMSD) of 2 ns MD simulations. All the systems would reach the equilibrations after about 0.6 ns (See Fig. S1 of the Supporting Information). In the MD simulations of last 1 ns, the structures were extracted at the intervals of 0.05 ns to get initial geometries of the QM/MM calculations. Total 20 snapshots are used in corresponding physical quantities. Our previous investigation indicated that QM/MM computation using 20 snapshots can give converged VIE, VEA and VDE [5,6].

In the QM/MM computations, B3LYP theories [37,38] with 6-31 + G* [39–41] basis set were used to treat the QM region. The computations at the level gave the reliable redox potential [42]. The QM calculations were done by TURBOMOLE 6.4 program [43], and the ChemShell 3.5 package were used to carry out all QM/MM computations [44]. The high-efficient double-optimizations-of-buffer-region (DOBR) micro-iterative scheme was employed in the QM/MM optimizations of the calculations for several quantities (VIE, ΔE_{CN}, VEA, and VDE) to reduce the expensive computational cost [45]. We tested the convergence of QM-region sizes. The minimal distance (R_{QM}) between O atom of the water molecule and each atom of the dRN was employed to assign the QM-region sizes. The converged R_{QM} values are 3.6, 3.4, 3.4, 3.4 Å for dA, dG, dC, and dT respectively (see Fig. S2). The very large QM regions including several water molecules are applied in the following QM/MM calculations.

3. Results and discussions

We calculated the QM/MM VIEs and AIEs of four dRNs in water. The formulas and process to compute the two quantities are similar to the simulations in Ref. [5]. Table 1 displays QM/MM VIEs and AIEs for four dRNs. We compare the present results with the previous investigations. The QM/MM VIEs of dC (8.34 eV) and dT (8.38 eV) are in well agreement with the experimental values of cytidine and dT in water (both 8.3 eV) [46]. The order of QM/MM VIEs follows dG (7.67 eV) < dA (7.99 eV) < dC (8.34 eV) ≈ dT (8.38 eV). VIE of dG is the smallest and the feature is consistent with the computation using the non-equilibrium polarizable continuum model [3]. The values of VIEs for four dRNs are close to those of corresponding nucelobases [5]. QM/MM VIEs of dG and guanine both are 7.67 eV. The differences of the pyrimidines (dC and dT) between RNs and nucleobases VIEs are slight larger and still less than 0.09 eV.

Table 1
Vertical ionization energies (VIEs) and adiabatic ionization energies (AIEs) of four aqueous dRNs in comparison with their corresponding nucleobases computed by QM/MM calculations and experimental values (in eV).

	VIE			AIE	
	dRNs		Nucleobases	dRNs	Nucleobases
	QM/MM	Exp. [a]	QM/MM [b]	QM/MM	QM/MM [b]
dA	7.99	N/A	7.97	5.97	5.85
dG	7.67	N/A	7.67	5.32	5.29
dC	8.34	8.3	8.39	6.00	5.83
dT	8.38	8.3	8.29	6.29	5.96

[a] Ref. [46].
[b] Ref. [5].

QM/MM AIEs follow the order dG (5.32 eV) < dA (5.97 eV) ≈ dC (6.00 eV) < dT (6.29 eV). We compared the AIEs with the previous computations of nucleobases in water [5]. The sequence of the AIEs for four dRNs is same with that of the nucleobases. Due to the screening effect of the water, the differences (~0.16 eV) of QM/MM AIEs between the dRNs and nucleobases are much smaller than gas ones (~0.45 eV). The ribose obviously has the small effect on the ionizations of aqueous dRNs. We can calculate the deviations between the QM/MM VIEs and AIEs. It describes the energy changes in cationic structural relaxations after vertical ionization. The values of four dRNs (~2.2 eV) suggest that the cationic structural relaxations after the ionizations of aqueous dRNs are strong exothermic processes.

We also computed electrostatic-potential (ESP) charges on QM atom by Merz-Kollman parameters [47]. The differences of the charges on dRNs and nucleobases were used to explore the hole distributions in the vertical and adiabatic ionizations. Fig. 1 shows the holes on dRNs and nucleobases in vertical and adiabatic ionizations for four dRNs. The vertical distributions indicate that the main holes (~0.73 *e*) of four systems localize on the dRNs. The majority (~0.64 *e*) of the hole is on the nucleobases. In the adiabatic ionization, the holes on the dRNs and nucleobases are respectively ~0.85 *e* and ~0.71 *e*. The results suggest that electron on the bases is excited in the ionization of aqueous dRNs.

According to Eqs. (3) and (7), free energy change of one-electron oxidation (ΔG_O) and reduction (ΔG_{red}) for nucleobases and dRNs were computed by using the referenced quantities (VIE, ΔE_{CN}, VDE, VEA) from our previous studies and present calculation [5,6]. Table 2 lists the oxidation and redox free energy change of nucleobases and dRNs. For nucleobases, all oxidation free energy changes are positive, while all reduction free energy changes are negative. The ΔG_O order is G < A < T < C, and reduction free energy changes follow the sequence of T < C < A < G. The guanine ΔG_O is the lowest, and ΔG_O of purine nucleobases are lower than those of pyrimidine. The same trend has been observed in results of one-electron redox free energy change of dRNs. The sequence of dRN ΔG_O is dG < dA < dC ≈ dT. It is obvious that dG has the lowest oxidation free energy change. The reduction free energy changes of four dRNs follow the order of dT ≈ dC < dG ≈ dA. The ΔG_{red} absolute value of pyrimidine dRNs is larger than that of purine dRNs. The ΔG_{red} sequence of dRNs implies that pyrimidine dRNs are the most favorable electron accept center.

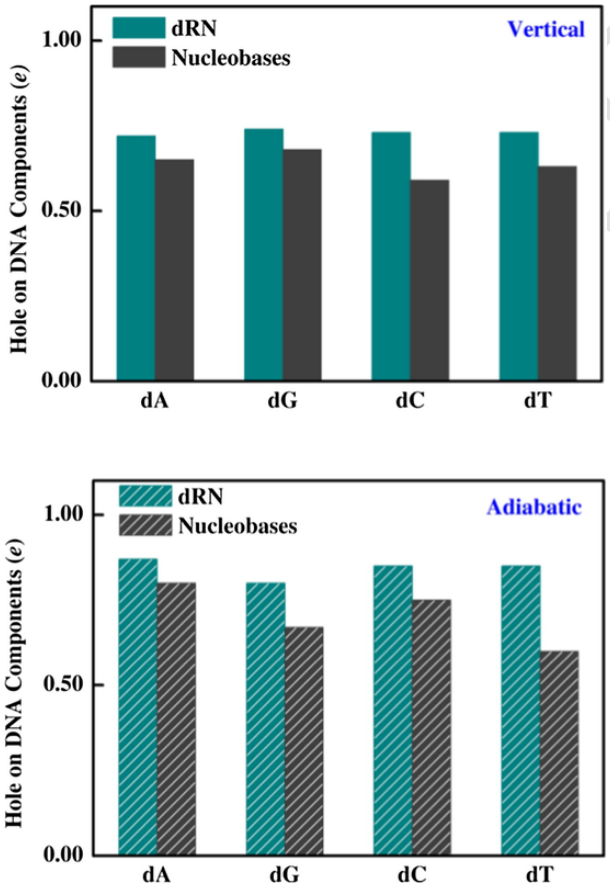

Fig. 1. Hole distribution on dRN and nucleobases in vertical and adiabatic ionizations of aqueous dRNs.

Table 2
Free energy change of one-electron oxidation (ΔG_O) and reduction (ΔG_{red}) for nucleobases and dRNs (in eV).

	ΔG_O	ΔG_{red}		ΔG_O	ΔG_{red}
A	6.66	−1.08	dA	6.72	−1.16
G	6.31	−1.00	dG	6.36	−1.18
C	7.00	−1.27	dC	7.05	−1.50
T	6.85	−1.31	dT	7.06	−1.52

We compare the oxidation free energy changes of nucleobases and dRNs. It can be found that ΔG_O of dA, dG, and dC are higher than their corresponding nuclobases by 0.05 eV. The ΔG_O difference between dT and T is 0.19 eV. It indicates that the ribose causes the large effect on oxidation free energy change of dT. In contrast, the impact of ribose on reduction free energy change is more notable. ΔG_{red} of dG, dC, and dT are lower than their corresponding nucleobases by ~0.2 eV. Adenine redox free energy change is higher than dA by 0.08 eV. The results suggest that the ribose would reduce the reduction free energy change of dRNs.

After the oxidation and redox free energy changes are obtained, we can directly compute the standard one-electron oxidation and redox potential by employing the Eqs. (1) and (5). Table 3 shows the standard one-electron oxidation and redox potential of nucleobases. The values obtained by the calculations of polarizable continuum model (PCM) come from the previous investigation [48]. After explicit water shell was included in QM region of QM/MM calculation, the hole (excess electron) would be delocalized over water molecules in the ionization (excess electron attachment). This would result in deviation of simulation results (VIE, VDE and VEA) between QM/MM and PCM computations. Because the quantities have such differences, the present standard one-electron oxidation and redox potential are different from the PCM calculation [48]. However, the standard one-electron oxidation potential of four nucleobases follow the order of G < A < T < C. The oxidation potential of guanine is the lowest, while cytosine has the largest oxidation potential. The result is in good agreement with others experimental and theoretical studies of nucleobases [8,10,48]. The sequence of standard one-electron reduction potential for four nucleobases is G < A < C ≈ T. Cytosine and thymine have the close reduction potential. The feature consists with PCM computations. The order of present reduction potential for four nucleobases also agrees with those of previous experimental and computational studies [10,48].

Table 3
Standard one-electron oxidation (E^0_{ox}) and redox (E^0_{red}) potential of four nucleobases (in V).

	E^0_{ox}		E^0_{red}	
	Present	PCM [a]	Present	PCM [a]
A	2.22	1.78	−3.37	−2.77
G	1.87	1.41	−3.45	−2.97
C	2.52	2.11	−3.17	−2.36
T	2.41	2.01	−3.13	−2.31

[a] Ref. [48].

Table 4 gives the standard one-electron oxidation and redox potential of four dRNs. The adenosine and guanosine oxidation potential obtained by the experimental measurements are also listed in the table [9]. The sequence of standard one-electron oxidation potential of four dRNs is dG < dA < dC ≈ dT. dG has the lowest value of one-electron oxidation potential. The oxidation potentials of pyrimidine dRNs (dC and dT) are very close and higher than ones of purine dRNs by over 0.30 V. Present oxidation potential of dA and dG are reasonably consistent with the experimental values. The reduction potential of four dRNs follow the order of dA ≈ dG < dC ≈ dT. The redox potentials of purine dRNs (dA and dG) are lower than those of pyrimidine dRNs (dC and dT) by ~0.30 V. The redox potentials of two purine dRNs are close and pyrimidine dRNs have the same feature.

We compare the oxidation potential of nucleobases and dRNs (see Tables 3 and 4). dRN standard one-electron oxidation potential are close to the corresponding bases except for dT and T. The E^0_{ox} differences between nucleobases and dRNs are lower than 0.10 V. In contrast, dT oxidation potential is higher than T by 0.21 V. It reveals that ribose would significantly increase the oxidation potential of T in DNA. Thus, it is difficult to oxidize dT in DNA and dT becomes negative charge center for DNA. The difference of redox potential between dA and A is 0.09 V. The redox potential of others three dRNs (dG, dC, and dT) are higher than corresponding bases by ~0.20 V. In comparison with oxidation potential, ribose produces the larger influence on reduction potential and increase the redox potential of DNA components.

4. Conclusion

Here we present a simple model to calculate one-electron oxidation and redox potential in QM/MM simulations. The linear response approximation is used to estimate the oxidation and redox free energy change in the method. VIEs and AIEs of four aqueous dRNs (dA, dG, dC and dT) were computed by QM/MM simulations and the results suggest that cationic relaxation after vertical ionization is a strong process. Ionization hole localizes on the bases of dRNs. We collect the referenced quantities (VIE, ΔE_{CN}, VDE, and VEA) from present and previous QM/MM computations. The standard one-electron oxidation and redox potential of four dRNs and their corresponding nucleobases are computed by using the quantities. The oxidation potential of dA and dG are reasonable agreement with experimental measurements. The oxidation potential of nucleobases follow the order of G < A < T < C, and the sequence of reduction potential is G < A < C ≈ T. For dRNs, the order of oxidation potential is dG < dA < dC ≈ dT, and the sequence of redox potential is dA ≈ dG < dC ≈ dT. Comparing the standard one-electron oxidation and redox potential of nucleobases and dRNs, we can find that ribose has the large effect on redox potential and induces its increase. In contrast, sugar ring has negligible influence on one-electron oxidation potential of dA, dG, and dC. It increases dT oxidation potential by 0.21 V.

Uncited reference

.

Table 4
Standard one-electron oxidation (E^0_{ox}) and redox (E^0_{red}) potential of four dRNs (in V).

	E^0_{ox}		E^0_{red}
	Present	Exp. [a]	Present
dA	2.28	2.03	−3.28
dG	1.92	1.58	−3.26
dC	2.61	N/A	−2.94
dT	2.62	N/A	−2.92

[a] Experimental values of adenosine and guanosine in Ref. [9].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

MD RMSD; QM-region convergence.

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