ONE-ELECTRON REDOX PROPERTIES OF DNA NUCLEOBASES AND COMMON TAUTOMERS

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Abstract: The redox properties of DNA play an influential role in several important processes such as DNA mutation and the interaction of DNA with drugs. Structural changes in DNA nucleobases from its canonical form to its tautomeric forms can alter these properties and may lead to DNA mutation due to altered base-pairing properties. Experimental results for the standard value of DNA redox properties vary due to choice of methodology and solvent. Theoretical determination of these properties is helpful in pinpointing standard values but still vary depending on methodology and chosen experimental benchmark. However, it is of importance to identify the overall trend of electron mobility within DNA while providing reliable standard values for redox reactions. In this work, we present the results of theoretical calculations for redox properties. All calculations are computed at the M06-2X/6-31++G(d,p) level of theory. Using the thermodynamic cycle, we can approximate reliable values. We report the electron affinities, ionization potentials, and redox potential for the canonical DNA nucleobases and their rare tautomers. All tautomers had a lower adiabatic ionization potential than their canonical counterparts except for guanine. When considering ionization potentials, canonical thymine was the least capable electron donor due to its high ionization potential values. The adenine tautomer had the lowest vertical ionization potential, and canonical guanine had the lowest adiabatic ionization potential. Therefore, they appear to donate electrons more readily than the other constructs. Thymine proved to be the best electron acceptor due to it having the highest adiabatic electron affinity. Guanine was found to have the lowest reduction ($X^-/X$) and oxidation ($X^+/X$) potential. Cytosine was found to have the highest oxidation potential, while thymine had the highest reduction potential. A consolidated table of reduction half-reactions was created to gain a better understanding of electron mobility and electron attachment.

Keywords: DNA mutation, in silico, electron affinity, ionization potential, nucleic acid, enol, keto, imine, reduction potential, oxidation potential, tautomerization

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