Photoinduced Electron Transfer Between DNA-Bridged Ruthenium and Rhodium Complexes

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The rate of electron transfer (ET) through duplex deoxyribonucleic acid (DNA) has been studied using a variety of covalent or noncovalent and intercalating or non-intercalating photoreductants and photooxidants.\(^1\)\(^-\)\(^7\) Of particular interest are the coordination compounds of ruthenium and rhodium. This is due to their distinct spectroscopic properties,\(^6\)\(^,\)\(^8\) their reduction potential tunability,\(^3\)\(^,\)\(^9\) their DNA intercalation properties,\(^7\)\(^,\)\(^10\) and their proven utility in probing protein electron transfer rates.\(^11\)\(^,\)\(^12\)

A theory for DNA ET describes the electron transfer rate, \(k_{ET}\), as depending on factors such as the electronic coupling \(\langle H_{AB} \rangle\) between the reactants and products at the transition state, the reaction driving force \(\Delta G^0\), and the reorganization energy \(\lambda\) of the ligand and solvent spheres.\(^11\)\(^,\)\(^13\) In particular, \(H_{AB}\) depends on the intervening medium, the donor/acceptor orientation, and the distance \(r\). Thus, \(k_{ET}\) has a distance dependence often reported as the parameter \(\beta\). Small \(\beta\) values imply a small rate dependence on distance. Another theory for DNA ET is from the recent work by B. Giese.\(^14\) A hole hopping mechanism using guanine residues, is proposed.

Ruthenium and rhodium complexes are known to rigidly intercalate into the major groove of duplex DNA.\(^7\)\(^,\)\(^10\) Using only intercalation to couple donor and acceptor groups, many ET reactions have been performed on DNA.\(^2\)\(^,\)\(^5\)\(^,\)\(^10\)\(^,\)\(^15\)\(^,\)\(^16\) However, controversy surrounds the exact donor/acceptor distance \(r\) due to the possibility of cooperative binding and DNA sequence specific binding of the metal complexes.\(^17\)

The research groups of T.J. Meade and J.K. Barton are using covalently attached ruthenium and rhodium complexes to study ET in DNA. The Meade group is studying a covalently attached, non-intercalating donor/acceptor system.\(^6\) (Figure 1)\(^6\) A \(k_{ET}\) of \(1.6 \times 10^6\) s\(^{-1}\) \((r = 21 \text{ Å})\) is obtained by transient absorption measurements.\(^6\) Although no distance
dependent studies have yet been reported, this rate is similar to the ET rate through protein bridges. Furthermore, experiments using organic donors and acceptors yield protein-like CP values. Barton's group is using covalently attached, intercalating metal complexes. The rates of electron transfer from time resolved luminescence data are fast \( (> 10^9 \text{s}^{-1}, r = 40 \text{ Å}) \). Electron transfer is shown to proceed over large distances \( (30 - 40 \text{ Å}) \). This result indicates that DNA is a very efficient ET medium, with \( \beta \approx 0.1 \text{ Å}^{-1} \).

Inconsistent \( \beta \) values arise from the use of different donor/acceptor systems and the use of different methods for determining \( \kappa_{ET} \). Different donor/acceptor systems are coupled differently to the DNA base stack and might yield different \( \beta \) values. In addition, the different systems used are in some cases not well characterized structurally. This can result in, for example, an uncertain donor/acceptor separation. Finally, the different methods of measuring \( \kappa_{ET} \), fluorescence quenching, absorption spectroscopy, and the product distribution of a reduction step, must be proven reliable. Before conclusions about the \( \beta \) values for ET in DNA can be made, the donor/acceptor systems and methods used on these systems must be further studied.

References


