

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 (H_{AB}) between the reactants and products at the transition state, the reaction driving force (ΔG^0), and the reorganization energy (λ) 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 β . Small β 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

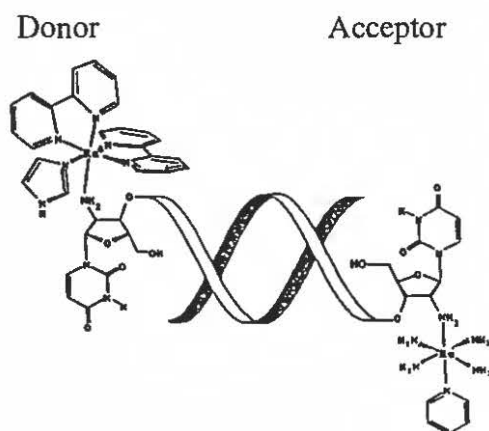


Figure 1

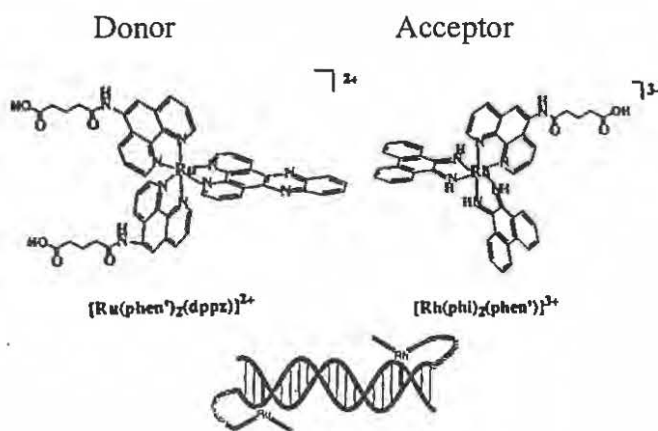


Figure 2

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 $1.6 \times 10^6 \text{ s}^{-1}$ ($r = 21 \text{ \AA}$) 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.¹² Furthermore, experiments using organic donors and acceptors yield protein-like ($\beta = 1.0 \text{ \AA}^{-1}$) β values.¹ Barton's group is using covalently attached, intercalating metal complexes.^{3-5,7} (Figure 2)⁷ The rates of electron transfer from time resolved luminescence data are fast ($\geq 10^9 \text{ s}^{-1}$, $r = 40 \text{ \AA}$).⁷ Electron transfer is shown to proceed over large distances (30 – 40 \AA).^{3-5,7} This result indicates that DNA is a very efficient ET medium, with $\beta \cong 0.1 \text{ \AA}^{-1}$.⁵

Inconsistent β values^{1,5-7} arise from the use of different donor/acceptor systems and the use of different methods for determining k_{ET} . Different donor/acceptor systems are coupled differently to the DNA base stack and might yield different β 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 k_{ET} , fluorescence quenching, absorption spectroscopy, and the product distribution of a reduction step, must be proven reliable. Before conclusions about the β values for ET in DNA can be made, the donor/acceptor systems and methods used on these systems must be further studied.

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