TABLE I. Comparison of Observed and Calculated Rate Constants for Protein-Protein Reactions

Oxidant	Reductant	k_{12},obsd [M^{-1} s^{-1}]	k_{12},calcd[a] [M^{-1} s^{-1}]
Cytochrome c	Azurin	1.6×10^3	3×10^4
Plastocyanin	Cytochrome c	1.0×10^6	5×10^5[b]
Stellacyanin	Cytochrome c	3.5×10^2	4×10^3
Azurin	Cytochrome c-551	6.0×10^6	8×10^5[c]
Plastocyanin	Cytochrome c-551	7.5×10^5	5×10^5[c]
Cytochrome c	Cytochrome c-551	6.7×10^4	1×10^5[c]

[a] Unless otherwise indicated, the calculated rate constants do not contain the W_{12} correction. References for the results are given in [1].

[b] The W_{12} correction is considerably larger for this reaction than for the other systems considered and was included in the calculation of k_{12}.

[c] Calculated using 1.2×10^7 M^{-1} s^{-1} for the self-exchange rate constant and +0.28 V for the reduction potential of the cytochrome c-551 couple using data cited in [1], where it is also noted that the net charge on the protein is -2/-3.

comes from several sources: (i) the unusual time-dependence of reaction rates when there is a distribution of separation distances of the reactants in frozen or other solid or highly viscous media, e.g., [4,5], (ii) the conductivity of fatty acid salt layers of varying chain length between two electrodes, e.g. [6,7], (iii) intramolecular electron-transfer rates in model compounds containing a pair of fixed sites separated by more or less rigid organic bridges, e.g., [8-11], and (iv) intramolecular transfers between the metal center of a metalloprotein and an inorganic redox complex attached to various sites in the protein [12,13]. Of these sources, there are fairly extensive published data on (i) and (ii), while data are beginning to appear on (iii) and (iv). The published data for the latter two are too few to estimate a distance dependence, although this situation will undoubtedly be remedied soon.

Experimental data for the rate constant or, in the case of method (ii), for the conductivity are usually represented by an exponential dependence on the separation distance r, e.g., [4-7],

$$k(r) \propto \exp[-\beta(r-r_0)] \tag{5}$$

Values of β are given in Table II. A typical value is seen to be in the range 1.0 to 1.2 $Å^{-1}$, and we shall use a value of 1.2 $Å^{-1}$ when, as in Table I, the intervening material between the two redox sites is "saturated", i.e., nonconjugated. When a portion of the intervening material is conjugated (e.g., aromatic) the value of β for that part of the separation distance is expected to be lower.

A functional form for k(r) which takes into account the various nodal properties of the electronic wave functions, as well as the three-dimensional geometry, is expected to be somewhat more complicated