

TABLE III. Absolute Rates for Electron Transfer Reactions in Photosynthetic Reaction Centers

Reaction ^a	ΔG° ^b [kcal mol ⁻¹]	τ_{obsd}	τ_{calcd}
cyt c ^{II} \rightsquigarrow BChl ₂ ⁺	-3.9	0.2 μ s	0.02 μ s
*BChl ₂ \rightsquigarrow BChl \rightsquigarrow BPh	-5(?)	- 1 to 4 ps ^c	>0.3 μ s ^d
BPh ⁻ \rightsquigarrow Q	-12	100 to 200 μ s ^e	140 μ s
BPh ⁻ \rightsquigarrow Q _A , Q _B ⁻ present	- 0.2 eV ^f	increases factor of 2	increases factor of 2
BPh ⁻ \rightsquigarrow Q, Q varied	- 0.2 eV ^g	changes factor of 2	changes factor of 2
*Porphyrin \rightsquigarrow Q	- λ	$\tau_{\text{min}} \sim 4$ μ s	$\tau_{\text{min}} \sim 9$ μ s

^a Asterisks indicate electronically excited states.

^b The ΔG° values are approximate.

^c Assignment of time constants is uncertain.

^d The value of τ_{calcd} is larger than this value if smaller λ 's are used, i.e., τ_{calcd} is about 1 ps when $\lambda = 1.2$ kcal mol⁻¹. (See also Appendix II of Ref. [1].)

^e Value depends on temperature.

^f This is the approximate decrease in $|\Delta G^\circ|$ due to the presence of Q_B⁻.

^g This is the approximate variation in $|\Delta G^\circ|$ as Q is varied.

the change in C-O bond length accompanying the Q + Q⁻ reaction and partly because of the smaller size of the Q molecule. (Cf Ref. [1] for factors influencing reaction rates, e.g., (2)-(6) there.) Calculated rates are given in Table III.

Variation of the Q caused ΔG° to vary by ~ 0.2 eV [17] and caused experimentally a variation in the lifetime for the BPh⁻ + Q reaction of a factor of two, with some randomness due to the somewhat different positions, shapes, or orientations of the different Q's. Again, when a second quinone was present (presumably as Q⁻), creating a coulombic repulsion with the other Q⁻ newly formed in the BPh⁻ + Q reaction, the rate constant for the latter reaction was smaller by almost a factor of two [18]. Theoretical calculations for this effect, taken from [1], are included in Table III.

The lifetime for the reduction of the (BChl)₂⁺ by ferricytochrome c-558 is about 0.2 μ s at room temperature [19]. The reduction of this (BChl)₂⁺ is presumably by the closest ferrocycytochrome c molecule. In the calculations in Table III, an estimated edge-to-edge separation distance of (BChl)₂⁺ to the closest heme ring of about 11 Å was used, estimated