Supporting Information for BI026327P

Nitric Oxide induced formation of the S_{-2} state in the oxygen evolving complex of photosystem II from *Synechococcus elongatus*

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Extentions to the Kok model to account for a possible direct electron donation of Y_D-NO to $P680^+$

To simulate the effects of direct Y_D-NO oxidation by $P680^+$ on flash-induced oxygen yield patterns, the initial Y_D-NO population, $[Y_D\text{-NO}]_0$, and the miss probability for its oxidation by $P680^+$, $\alpha_{YD\text{-}NO}$, were introduced as additional free parameters. The miss probability results from the relative rates by which Y_Z and Y_D-NO are able to reduce $P680^+$ after single flash excitation at room temperature and from the Q_A^- concentration prior to flash excitation. For simplicity it is assumed that $\alpha_{YD\text{-}NO}$ is S-state independent (see main text). Because in a given PSII center Y_D-NO can be oxidized only once within a flash train, the absolute Y_D-NO fraction that is oxidized per flash, $\gamma_{YD\text{-}NO}(n)$, declines with flash number, n, during the flash train according to:

$$\gamma_{YD\text{-}NO}(n) = (1 - \alpha_{YD\text{-}NO}) \cdot [Y_D\text{-NO}]_{n-1}$$

where $[Y_D\text{-NO}]_{n-1} = [Y_D\text{-NO}]_{n-2} - \gamma_{YD\text{-}NO}(n-1)$ is the fraction of Y_D-NO present in PSII before the n-th flash. It is furthermore assumed that in the fraction of centers $(1 - \gamma_{YD\text{-}NO}(n))$ in which the OEC is oxidized the miss and double hit probabilities are the same as in the control. Since the oxidation of Y_D-NO leads to a miss for the OEC, the now flash number dependent miss parameter can be calculated to be:

$$\alpha(n) = \alpha\,(1 - \gamma_{YD\text{-}NO}(n)) + \gamma_{YD\text{-}NO}(n).$$

Similarly it follows that the double hit, β, and single hit, γ, probabilities of the OEC are:

$$\beta(n) = \beta\,(1 - \gamma_{YD\text{-}NO}(n))$$

$$\gamma(n) = (1 - \alpha - \beta)\,(1 - \gamma_{YD\text{-}NO}(n)).$$

Extentions to the Kok model to account for possible reductions of the S_2 and S_3 states by Y_D-NO during the flash train

Fast reductions of the S_2 and S_3 states by Y_D-NO were implemented into the extended Kok model described in Materials and Methods by splitting the initial S-state populations into a fraction A, where the nitroso tyrosine had been formed, and a fraction B = 1-A, in which back reactions do not take place during the flash train. Once the Y_D-NO centers of fraction A reach the S_2 or S_3 state they were allowed to convert from fraction A into fraction B according to:

$$d[S_2(A)]/dt = - k_{21} \bullet [S_2(A)]$$

$$d[S_3(A)]/dt = - k_{32} \bullet [S_3(A)]$$

$$d[S_1(B)]/dt = k_{21} \bullet [S_2(A)]$$

$$d[S_2(B)]/dt = k_{32} \bullet [S_3(A)].$$