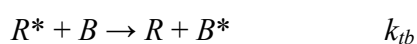
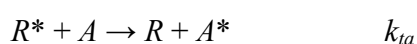


Supplementary Information

Part I. Derivation of the relationship the equations to those of Wagner's

Wagner's reaction scheme **36-41** (reference 3) can be developed as follows to show the mathematical correspondence between Wagner's equations for photosensitization and equations (1) and (2) for direct photoisomerization. This is done below where R is the photosensitizer and A and B are the two isomers.



In a photosensitization reaction, the two fundamental equations for the ground states of the isomers A and B are

$$\frac{d[A]}{dt} = k_{da}[A^*] + k_{ba}[B^*] - k_{ta}[R^*][A] \quad (S1)$$

$$\frac{d[B]}{dt} = k_{ab}[A^*] + k_{db}[B^*] - k_{tb}[R^*][B] \quad (S2)$$

The three equations for the intermediates, R^* , A^* , and B^* are

$$\frac{d[R^*]}{dt} = \phi_{ES}I - k_{ta}[R^*][A] - k_{tb}[R^*][B] \quad (S3)$$

$$\frac{d[A^*]}{dt} = k_{ta}[R^*][A] - k_{da}[A^*] - k_{ab}[A^*] \quad (S4)$$

$$\frac{d[B^*]}{dt} = k_{tb}[R^*][B] - k_{db}[B^*] - k_{ba}[B^*] \quad (S5)$$

ϕ_{ES} is the probability that R^* is produced from R absorbing a photon. Making the steady state approximation for R^* , A^* , and B^* :

$$[R^*]_{ss} = \frac{\phi_{ES} I}{k_{ta}[A] + k_{tb}[B]} \quad (S6)$$

$$[A^*]_{ss} = k_{ta}[A][R^*] \frac{1}{k_{da} + k_{ab}} = \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \frac{1}{k_{da} + k_{ab}} \quad (S7)$$

$$[B^*]_{ss} = k_{tb}[B][R^*] \frac{1}{k_{db} + k_{ba}} = \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \frac{1}{k_{db} + k_{ba}} \quad (S8)$$

Putting these last three equations into the two basic equations (S1) and (S2):

$$\frac{d[A]}{dt} = \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \frac{k_{da}}{k_{da} + k_{ab}} + \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \frac{k_{ba}}{k_{db} + k_{ba}} - \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \quad (S9)$$

$$\frac{d[B]}{dt} = \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \frac{k_{ab}}{k_{da} + k_{ab}} + \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \frac{k_{db}}{k_{db} + k_{ba}} - \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \quad (S10)$$

Finally rearranging these last two equations (S9) and (S10)

$$\frac{d[A]}{dt} = \frac{k_{ba}}{k_{db} + k_{ba}} \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} - \frac{k_{ab}}{k_{da} + k_{ab}} \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \quad (S11)$$

$$\frac{d[B]}{dt} = \frac{k_{ab}}{k_{da} + k_{ab}} \phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} - \frac{k_{ba}}{k_{db} + k_{ba}} \phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \quad (S12)$$

Then the correspondence with equations (1) and (2)

$$\frac{d[A]}{dt} = \Phi_{B \rightarrow A} I_{tot}^{abs} \frac{\varepsilon_B(\lambda)[B]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} - \Phi_{A \rightarrow B} I_{tot}^{abs} \frac{\varepsilon_A(\lambda)[A]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} \quad (1)$$

$$\frac{d[B]}{dt} = \Phi_{A \rightarrow B} I_{tot}^{abs} \frac{\varepsilon_A(\lambda)[A]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} - \Phi_{B \rightarrow A} I_{tot}^{abs} \frac{\varepsilon_B(\lambda)[B]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} \quad (2)$$

can be made for

$$\Phi_{B \rightarrow A} \Rightarrow \frac{k_{ba}}{k_{db} + k_{ba}}$$

$$\Phi_{A \rightarrow B} \Rightarrow \frac{k_{ab}}{k_{da} + k_{ab}}$$

$$I_{tot}^{abs} \Rightarrow \phi_{ES} I$$

$$\varepsilon_A(\lambda) \Rightarrow k_{ta}$$

$$\varepsilon_B(\lambda) \Rightarrow k_{tb}$$

But this is purely a mathematical correspondence.

One can make a chemical/physical correspondence if one correlates the probability of excitation of A with

$$\phi_{ES} I \frac{k_{ta}[A]}{k_{ta}[A] + k_{tb}[B]} \Rightarrow I_{tot}^{abs} \frac{\varepsilon_A(\lambda)[A]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} \quad (\text{S13})$$

and the probability of excitation of B with

$$\phi_{ES} I \frac{k_{tb}[B]}{k_{ta}[A] + k_{tb}[B]} \Rightarrow I_{tot}^{abs} \frac{\varepsilon_B(\lambda)[B]}{\varepsilon_A(\lambda)[A] + \varepsilon_B(\lambda)[B]} \quad (\text{S14})$$

Making this correlation the Wagner equations can be converted to equations for direct excitation and are equivalent to the approach in the main text.

Part II. Derivation of Lamola/Hammond equation from Wagner's solutions

The following is a derivation of Lamola/Hammond's equation (rewritten as eq (28) in the text) showing the approximations that can be used to reach it from the exact solutions of Wagner. In the following the reaction numbers, equations numbers, and notation (including calling the second isomer C rather than B as in the text) are from Wagner's article.





In addition, the decay of R^* in the absence of quenchers has a lifetime of τ_{R^*} .

Wagner gives the exact solution of the kinetics scheme in the absence of a back reaction (41) as

$$(1 - \beta)[C]' + \frac{1/\tau_{R^*} + k_{ic}[A]_0}{k_{ia}} \ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) = \kappa I t \phi_{ES(R^*)} \quad (84)$$

where the prime on the concentration of C means that this is the concentration of C in the absence of the back reaction (41). The idea of the back-reaction correction is to find a formula for the fraction converted ($[C]'/[A]_0$) in the absence of back reaction (41). This fraction $[C]'/[A]_0$ is beta in Lamola-Hammond (reference 2) and gamma on the left-hand side of eq (1) of Saltiel et al., reference 4. In eq. (84) κ is defined as

$$\kappa \equiv \frac{k_{ac}}{k_{ac} + k_{da}} \quad (85)$$

κ is the branching ratio for the excited state A^* to photoisomerize in competition with its decay back to the ground state of A . Also in eq (84), β is the ratio of rate constants for sensitized excitation of C compared to A .

$$\beta \equiv \frac{k_{ic}}{k_{ia}} \quad (86)$$

When the back reaction (41) is included into the scheme, Wagner gives the exact solution as

$$\frac{(\beta - 1)[C]}{Y} + \left[\frac{1}{Yk_{ia}\tau_{R^*}[A]_0} - \frac{\beta(\kappa - \gamma + 1)}{Y^2} \right] [A]_0 \ln\left(\frac{\kappa[A]_0}{\kappa[A]_0 + Y[C]}\right) = I t \phi_{ES(R^*)} \quad (96)$$

where Y is a convenient definition of Wagner's

$$Y \equiv -\kappa + \beta\gamma - \beta \quad (97)$$

and

$$\gamma \equiv \frac{k_{dc}}{k_{ca} + k_{dc}} \quad (95)$$

where γ is the branching ratio for the excited state C^* to decay back to the ground state of C in competition with its photoisomerization to A .

The steady state fraction converted (gamma sub e in the notation of Saltiel et al. (ref. 4) or alpha in Lamola/Hammond's notation (ref. 2)) can be shown to be

$$\frac{[C]_{pss}}{[A]_0} = -\frac{\kappa}{Y}$$

Dividing the numerator and denominator in the argument of the logarithm in eq (96) by $Y[A]_0$ converts the logarithm to

$$\ln\left(\frac{\kappa[A]_0}{\kappa[A]_0 + Y[C]}\right) = \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]}{[A]_0}}\right)$$

This logarithm is the main factor on the right hand side of eq (28) which is a rewrite of eq (4) of Lamola and Hammond. The other factor on the right-hand side of eq (28) can be obtained by multiplying eq (96) by κ and factoring out Y from the denominators in the square brackets in eq (96). This gives a factor of κ/Y or $-[C]_{pss}/[A]_0$ multiplying the logarithm. This gives (within a minus sign) the entire right-hand side of eq (28) with no approximations so far.

However, we want to relate this term to $[C]'/[A]_0$. To do this, we have to bring in eq (84) of Wagner. This can be done substituting the left-hand side of equation (96) for $It\phi_{ES(R^*)}$ in eq (84).

Including the algebraic substitutions mention above this gives

$$\begin{aligned}
& (1 - \beta)[C]' + \frac{1/\tau_{R^*} + k_{tc}[A]_0}{k_{ta}} \ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) \\
&= \frac{[C]_{pss}}{[A]_0} (1 - \beta)[C] + \left[\frac{1}{k_{ta}\tau_{R^*}} - \frac{\beta(\kappa - \gamma + 1)[A]_0}{Y} \right] \frac{[C]_{pss}}{[A]_0} \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]}{[A]_0}}\right)
\end{aligned}$$

Or using the definitions for β in eq (86) and for Y in eq (97)

$$\begin{aligned}
& (1 - \beta)[C]' + \left[\frac{1}{k_{ta}\tau_{R^*}} + \beta[A]_0 \right] \ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) \\
&= \frac{[C]_{pss}}{[A]_0} (1 - \beta)[C] + \left[\frac{1}{k_{ta}\tau_{R^*}} - \frac{\beta(\kappa - \gamma + 1)[A]_0}{-\kappa + \beta\gamma - \beta} \right] \frac{[C]_{pss}}{[A]_0} \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]}{[A]_0}}\right) \tag{S15}
\end{aligned}$$

This is a transcendental equation which has no analytical solution, likewise for eqs (84) and (96).

However, for $\beta = 1$, namely the photosensitized excitation rate constants are the same, this equation simplifies to

$$\left[\frac{1}{k_{ta}\tau_{R^*}} + [A]_0 \right] \ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) = \left[\frac{1}{k_{ta}\tau_{R^*}} + [A]_0 \right] \frac{[C]_{pss}}{[A]_0} \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]}{[A]_0}}\right)$$

and

$$\ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) = \frac{[C]_{pss}}{[A]_0} \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]}{[A]_0}}\right)$$

This is almost eq (28). The right-hand side is that of eq (28), but the left-hand side of the equation has to be $[C]'/[A]_0$, the fraction converted without back-reaction **(41)**.

We can get this by a final approximation, namely to assume a small conversion. Then the logarithm on the left-hand side can be expanded in a series. Or rather

$$\ln\left(\frac{[A]_0}{[A]_0 - [C]'}\right) = \ln\left(\frac{1}{1 - \frac{[C]'}{[A]_0}}\right) = \ln\left(\frac{1}{1-x}\right) \approx x \quad (\text{S16})$$

can be expanded, giving

$$\frac{[C]'}{[A]_0} = \frac{[C]_{pss}}{[A]_0} \ln\left(\frac{\frac{[C]_{pss}}{[A]_0}}{\frac{[C]_{pss}}{[A]_0} - \frac{[C]'}{[A]_0}}\right)$$

This is exactly eq (28) aside from calling the second isomer C instead of B . It is not an exact expression. Two approximations were made. First was that β was equal to one. For direct excitation this would be equivalent to assuming that the molecular absorption coefficients are equal at the exciting wavelength. This is not a bad approximation for sensitization experiments where both rate constants are normally close to diffusion controlled. The second approximation was that the equation holds only for small conversion fractions $x = \frac{[C]'}{[A]_0}$.

Another way to derive the Lamola-Hammond equation is to expand the left-hand side of eq (S15) instead of making the approximation $\beta = 1$. The terms containing the factor β then cancel out on the left-hand side leaving only $\left(\frac{1}{k_{ia}\tau_{R^*}} + 1\right)[C]'$. On the right-hand side of eq (S15), the term

$$-\frac{\beta(\kappa - \gamma + 1)[A]_0}{Y} \text{ can be shown to be } 1 - (1 - \beta)\frac{[C]_{pss}}{[A]_0}.$$

If the logarithm on the right-hand side of eq (S15) is expanded about $\frac{[C]}{[C]_{pss}} = 0$, then the terms with containing the factor β again vanish. However, to get the desired equation on the right-hand side of eq (S15), the logarithm multiplying the remaining factor $\left(\frac{1}{k_{ta}\tau_{R^*}} + 1\right) [A]_0 \frac{[C]_{pss}}{[A]_0}$ cannot not be so expanded. This factor $\left(\frac{1}{k_{ta}\tau_{R^*}} + 1\right)$ cancels the other one from the expanded left-hand side of eq (S15), and the Lamola-Hammond equation follows. This version of the derivation avoids the assumption that the excitation functions are equal, i.e. $\beta = 1$.