

# The photophysics of photosensitization: A brief overview

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## ABSTRACT

The concept of photosensitization had its origins in the serendipitous discovery in the 19th century that dye molecules could enhance the spectral range of photographic emulsions. In the latter half of the 20th century, photosensitization reached maturity as a mechanistic photochemical tool for the identification and quantification of the role of triplet states as intermediates in organic photoreactions in solution. The photophysical properties desirable in a photosensitizer and the kinetic aspects of the diffusional encounter of sensitizer and energy acceptor are outlined, together with the role of spin selection rules in photosensitization processes, with emphasis on the photosensitized formation of singlet oxygen, the key photophysical step in Type II photosensitization.

## Photosensitization becomes a science

A significant limitation of early photography arose from the fact that silver bromide is most sensitive to UV and blue light, which made blue objects lighter and yellow and red objects much darker in photographs. In 1873, however, the German photochemist and photographer Hermann Wilhelm Vogel in Berlin serendipitously discovered that the addition of certain colored optical sensitizer dyes to the AgBr-containing photographic emulsion extended the range of sensitivity to light of wavelengths longer than those absorbed by AgBr alone [1]. This led to the commercial development of black-and-white films that responded to light across the visible spectrum and, somewhat later, to color photography by employing a sandwich of layers, each of which was sensitive to a different region of the visible spectrum [2]. Despite the near disappearance of silver halide-based photography in the 21st century with the advent of digital photography, the use of photosensitizer dyes to absorb light of longer wavelengths and inject electrons into semiconductors continues to be fundamental to the development of dye-sensitized solar cells [3].

## Triplet sensitization and quenching as mechanistic tools in organic photochemistry

In the 1940s through the 1950s and even into the 1990s, the excited triplet state of atomic mercury, responsible for the 254 nm emission line of low-pressure mercury lamps, was employed for the sensitization of photochemical reactions [4] such as olefin isomerization [5] and the spectroscopic detection of the triplet states of organic molecules in the gas phase [6]. The 1960s saw the development of a more widely applicable methodological approach (Fig. 1) that permitted the identification and quantification of the role of triplet states as intermediates in

photoreactions in solution [7,8]. Employing as the donor a photosensitizer that absorbs at longer wavelength and whose excited triplet state is higher in energy than that of the acceptor, it is possible to populate the triplet manifold of the acceptor molecule indirectly via triplet-triplet energy transfer. Thus, by circumventing the excited singlet state of the acceptor molecule, the triplet photoreactivity of the acceptor molecule can be investigated in the absence of its singlet photoreactivity. Conversely, if the molecule of interest plays the role of the photosensitizer or donor, its triplet state can be selectively quenched by an acceptor molecule with a triplet state of lower energy, providing additional discrimination between singlet and triplet photoreactivity.

## Desirable photophysical properties for a photosensitizer

As indicated in Fig. 1, to avoid competitive excitation of the acceptor molecule of interest, the lowest excited singlet state of the sensitizer should lie energetically below that of the acceptor. The excited singlet lifetime of the sensitizer should be relatively short due to fast and efficient intersystem crossing to the triplet manifold at the expense of fluorescence, internal conversion or competing intra- or intermolecular photoreactions or quenching processes, resulting in a near quantitative quantum yield of intersystem crossing. The excited triplet state lifetime should be relatively long, e.g., typically tens of microseconds in the absence of molecular oxygen. Furthermore, in order to act as an irreversible energy donor [7,8], the triplet energy of the photosensitizer should be at least 12 kJ/mol (3 kcal/mol) above that of the acceptor molecule of interest. Intrinsic photostability and inefficient reactivity with singlet oxygen are also requisite properties of a good photosensitizer.

Theories of non-radiative transitions provide insight into the requisite molecular structural features and the types and ordering of excited states of organic molecules that are most consistent with this set of desirable photophysical properties. The rate constant for intersystem cross-

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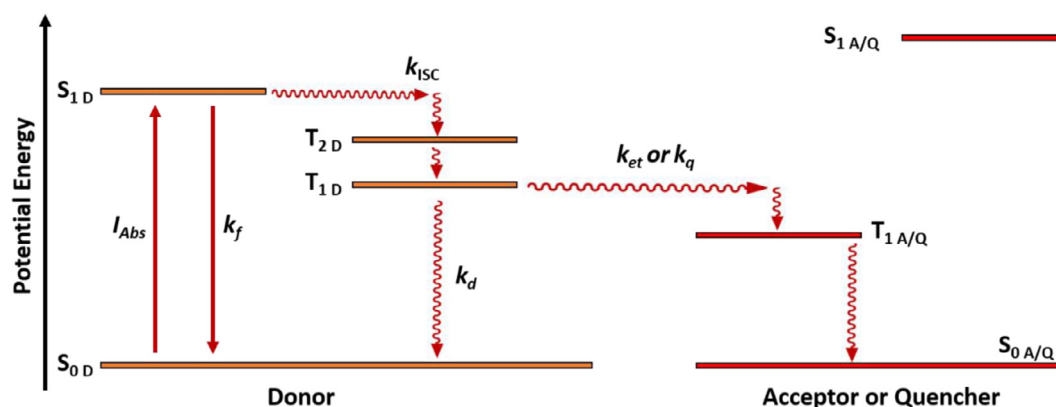


Fig. 1. Jablonski diagram illustrating the connection between the mechanistic photochemical tools of triplet sensitization and triplet quenching. In triplet sensitization, the selective population of the triplet state of the acceptor by energy transfer from a triplet donor is of interest, while in triplet quenching it is the selective deactivation of the triplet state of the donor by energy transfer to the quencher that is of interest.

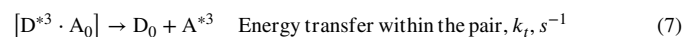
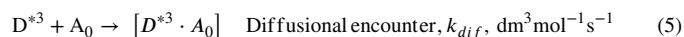
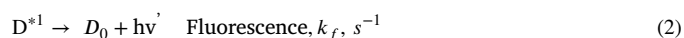
ing of the sensitizer depends on the square of the electronic coupling between the excited singlet and triplet states and on the Frank–Condon factors controlling the conversion of electronic into vibrational energy during the transition [9,10]. According to El-Sayed's rules [11], the electronic coupling is much larger between states of different electronic origins, i.e.,  $n, \pi^* \leftrightarrow \pi, \pi^*$  or  $\pi, \pi^* \leftrightarrow n, \pi^*$ , than between states of the same electronic origin, i.e.,  $\pi, \pi^* \leftrightarrow \pi, \pi^*$  or  $n, \pi^* \leftrightarrow n, \pi^*$ . The energy-gap law [9] reflects the fact that the Franck-Condon factors, and hence the intersystem crossing rate constant, decrease approximately exponentially with the increase in the energy gap between the singlet and triplet states involved in the intersystem crossing. The splitting or energetic separation between  $n, \pi^*$  singlet and triplet states is much smaller than that between  $\pi, \pi^*$  singlet and triplet states [8]. A lowest energy  $n, \pi^*$  singlet state with a small energy gap to a  $\pi, \pi^*$  triplet state or vice-versa will thus facilitate fast intersystem crossing. Lowest energy  $\pi, \pi^*$  singlet and triplet states with intersystem crossing via an intermediate upper  $n, \pi^*$  triplet state is preferable over the opposite situation due to the electrophilic character of  $n, \pi^*$  states, which can result in deactivation of  $n, \pi^*$  singlet and triplet states via hydrogen atom abstraction reactions. Molecular rigidity is desirable in order to reduce rates of internal conversion of the excited singlet state or decay of the triplet state. Although beyond the scope of the current mini-review, tuning of the redox properties of the sensitizer excited states can be used to control or prevent electron transfer quenching by other molecules present in the medium of interest.

In addition to these desirable photophysical properties, successful application of a photosensitizer in living systems, as in photodynamic therapy (PDT), imposes additional restrictions that must also be met by the photosensitizer and/or its delivery system. These include solubility, transport to and selectivity for the target site, as well as an adequate absorbance permitting one- or two-photon excitation of the sensitizer in an appropriate therapeutic window, i.e., a spectral region where competitive absorption by intervening tissues of the living system exhibits minimal interference. The sensitizer should have minimal toxicity in the absence of light and be neither carcinogenic nor mutagenic. This automatically eliminates the use of intersystem crossing-inducing substituents such as nitro groups that are known to be toxicologically problematic [12]. If the photosensitizer is to be used internally rather than topically, the residence time in the living system and mechanisms of clearance are additional obvious considerations since the photosensitizer should be eliminated after carrying out its photodynamic effect.

### Kinetics of photosensitization

As first described theoretically by Dexter [13], triplet energy transfer occurs via an electron exchange mechanism, a short range interaction dependent on donor-acceptor orbital overlap. In fluid solution, this re-

quires intimate molecular contact during sensitizer donor (D)-energy acceptor (A) collisions. A minimalist kinetic scheme for photosensitization is the following:



Based on this mechanistic scheme, the quantum yield for net energy transfer ( $\Phi_{et}$ ) is given by Eq. (8):

$$\Phi_{et} = \Phi_{isc} \frac{k_{et}[A_0]}{k_{et}[A_0] + k_d} \quad (8)$$

where  $[A_0]$  is the acceptor concentration,  $\tau_T^0 = 1/k_d$  is the sensitizer triplet lifetime in the absence of the acceptor and  $\Phi_{isc} = k_{isc}/(k_f + k_{isc}) = k_{isc}\tau_f$  is the quantum yield of intersystem crossing with  $\tau_f$  the fluorescence lifetime. The bimolecular rate constant for net triplet energy transfer ( $k_{et}$ ) from  $D^{*3}$  to  $A_0$  is given by Eq. (9):

$$k_{et} = k_{dif} \frac{k_t}{k_t + k_{-dif}} \quad (9)$$

The rate constant  $k_t$  for simple triplet energy transfer within the encounter pair is a Boltzmann function of the difference in the triplet energies of the sensitizer ( $E_{TS}$ ) and acceptor ( $E_{TA}$ ), such that  $k_t = k_0 \exp[(E_{TS} - E_{TA})/RT]$  [7,8]. Eq. (9) thus exhibits two limiting behaviors of the net energy transfer rate constant: (a) when the energy transfer is endothermic, i.e., if  $E_{TS} \ll E_{TA}$ , then  $k_{et} \rightarrow (k_{dif}/k_{-dif})k_t = (k_{dif}/k_{-dif})k_0 \exp[(E_{TS} - E_{TA})/RT]$  and the rate of energy transfer decreases exponentially with the increase in the triplet energy difference; (b) at the other limit, when the energy transfer is exothermic, i.e., when  $E_{TS} \gg E_{TA}$ , then  $k_{et} \rightarrow k_{dif}$  and the energy transfer is controlled exclusively by the

rate of molecular diffusion in the medium, a process briefly considered in the following paragraph.

The average distance  $x$  travelled by a randomly diffusing molecule in a time  $t$  is given by Eq. (10) [14–16]:

$$x = \sqrt{2Dt} \quad (10)$$

where  $D$  is the diffusion coefficient of the molecule in the medium. Since typical diffusion coefficients in water at 298 K are about  $2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , an excited state with a lifetime  $\tau = 1 \text{ ns}$  will migrate ca. 2 nm,  $\tau = 10 \text{ ns}$  just over 6 nm,  $\tau = 100 \text{ ns}$  about 20 nm,  $\tau = 1 \mu\text{s}$  about 63 nm and  $\tau = 10 \mu\text{s}$  about 200 nm during one lifetime (and only twice these average distances during four lifetimes). A rather good approximation [14] for the rate constant of a diffusion-controlled reaction, obtained from a consideration of the mutual diffusion of the excited donor and the acceptor and an assumed encounter radius, is given by Eq. (11):

$$k_{dif} = 6 \times 10^9 \frac{298}{T\eta} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (11)$$

where  $T$  is the absolute temperature and  $\eta$  the solvent viscosity in centipoise (1 cP = 0.001 Pa s). Thus, for water with unit viscosity in cP at 298 K, the limiting diffusion-controlled rate constant is indeed usually found to be close to  $6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and for acetonitrile (viscosity 0.34 cP) about 3-fold higher or  $1.8 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . For a collision with no binding interaction between the sensitizer and the acceptor, the molar volume of the encounter complex provides a simplistic but useful approximation for the ratio  $k_{dif}/k_{dif}$ :

$$\frac{k_{dif}}{k_{-dif}} = \frac{4000}{3} \pi \rho^3 N_{Av} = \left( \frac{\rho}{0.735} \right)^3 \text{ dm}^3 \text{ mol}^{-1} \quad (12)$$

where  $N_{Av}$  is Avogadro's number and  $\rho$  the encounter radius in nm. Thus, for 0.5 nm radius of encounter, the magnitude of  $k_{dif}$ , in  $\text{s}^{-1}$ , would be expected to be ca.  $3 \times k_{dif}$ .

### Spin selection rules for photosensitization

The spin selection criteria for photosensitization are governed by the Wigner spin rule, which requires that overall spin ( $S$ ), but not multiplicity ( $=2S+1$ ), be conserved in an electron exchange-mediated interaction [7]. Thus, the general reaction:



is spin allowed by the exchange interaction if and only if the following series for the reagents:

$$|S_{D^*} + S_A| \geq |S_{D^*} + S_A - 1| \geq \dots \geq |S_{D^*} - S_A| \quad (14)$$

And the corresponding series for the products:

$$|S_D + S_{A^*}| \geq |S_D + S_{A^*} - 1| \geq \dots \geq |S_D - S_{A^*}| \quad (15)$$

contain at least one common element. The range of possible values for each series is delimited by the sum and difference of the absolute values of the spins of the reagents or the products, respectively. Thus, for example, if the reagents are a singlet ( $S = 0$ ) and a triplet ( $S = 1$ ), the series in Eq. (14) contains the single element 1 (three spin sublevels) and the product series in Eq. (15) must contain this element. Examples of spin-allowed processes in this case (subject to energy conservation restraints) include: (a) conventional triplet sensitization:



(b) triplet ( $S = 1$ ) molecular oxygen-induced intersystem crossing of an excited singlet state, producing singlet oxygen [17–20]:



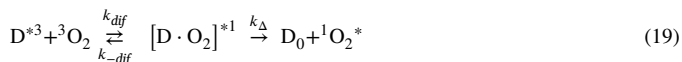
and (c) single electron transfer (SET) to form a triplet radical ion pair:



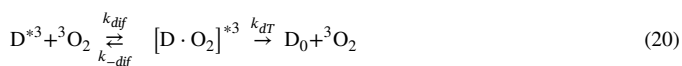
The SET processes in Eq. (18) are responsible for initiating Type I photosensitization in PDT [21] and the radical anions formed can interact with molecular oxygen to produce other reactive oxygen species such as the superoxide anion. The preferred direction of the electron transfer and the corresponding rate constant for SET can be estimated using the Rehm-Weller formulation [22,23] if the excitation energy of  $D^{*3}$  and the one-electron redox potentials of  $D_0$  and  $A_0$  can be measured experimentally [24] or predicted from theoretical calculations [25].

The other major photosensitization mechanism in PDT, known as Type II, is singlet oxygen ( ${}^1\text{O}_2^*$ ) formation resulting from the quenching of the excited triplet state of the quencher by triplet molecular oxygen [21]. The two lowest-lying singlet states of oxygen are the  ${}^1\Delta_g$  state at 0.98 eV ( $\sim 1270 \text{ nm}$ ;  $94 \text{ kJ mol}^{-1}$ ) and the  ${}^1\Sigma_g^+$  state at 1.62 eV ( $\sim 765 \text{ nm}$ ;  $156 \text{ kJ mol}^{-1}$ ) above the triplet ground state [17–20]. The  ${}^1\Sigma_g^+$  state is very short-lived ( $< 1 \text{ ns}$ ) and typically undergoes quantitative internal conversion to the much longer-lived  ${}^1\Delta_g$  state ( $\tau_\Delta = 3.5 \mu\text{s}$  in water), hereafter referred to generically as  ${}^1\text{O}_2^*$  [26]. Photosensitizers with triplet energies above ca. 1 eV can excite oxygen to the  ${}^1\Delta_g$  state, while those with triplet energies above ca. 1.65 eV can also excite oxygen to the  ${}^1\Sigma_g^+$  state as well. Conversely, molecules with triplet energies below 0.95 eV, such as long-chain conjugated carotenoids, are efficient quenchers of singlet oxygen.

For an encounter complex formed between an excited triplet sensitizer and triplet molecular oxygen, the series in Eq. (14) contains the elements 2, 1 and 0, corresponding to 9 possible spin states for the encounter complex [17,27]. One of these nine is a singlet encounter complex ( $S = 0$ ) that leads to singlet oxygen as product:



On the other hand, neither the triplet ( $S = 1$ , three spin sublevels) nor the quintet ( $S = 2$ , five spin sublevels) encounter complexes can give rise to singlet oxygen:



On the basis of these spin considerations, the rate constant for triplet quenching can be expressed as [27]:

$$k_{qT} = \left[ \frac{1}{9} \frac{k_\Delta}{k_{-dif} + k_\Delta} + \frac{3}{9} \frac{k_{dT}}{k_{-dif} + k_{dT}} \right] k_{dif} \quad (22)$$

where  $k_\Delta$  and  $k_{dT}$  are the first-order rate constants for  ${}^1\text{O}_2^*$  formation from the singlet encounter or for other quenching pathways via the triplet encounter complex, respectively. Thus, a maximum of 1/9th of the triplet sensitizer/molecular oxygen collisions would be expected to produce  ${}^1\text{O}_2$ . Indeed, rate constants for oxygen quenching of triplet excited states are commonly found to be lower than the diffusion-controlled rate constant [17,26,28], though not necessarily 1/9th due to the reversibility of the encounters and the possibility of other pathways indicated in Eq. (20).

The reactions of triplet molecular oxygen with ground-state molecules (closed-shell singlets) are forbidden by spin and energy conservation, though its reactions with spin  $\frac{1}{2}$  carbon-centered free radicals to form peroxy radicals are spin allowed. In contrast, singlet oxygen is a highly reactive species [19,29,30] due to both its higher potential energy and the spin-allowed nature of its reactions with ground-state molecules to give singlet products (as in the ene reaction or oxygen cycloaddition) or singlet radical pairs (as in hydrogen atom abstraction). Singlet oxygen phosphorescence at 1270 nm permits convenient direct determination of singlet oxygen yields, lifetimes and, with the advent of singlet-oxygen microscopy [31], of its spatiotemporal distribution in

cells. The lifetime of singlet oxygen is dependent on both temperature and the nature of the medium [18,26,32,33]. The ca. 20-fold increase in the lifetime of singlet oxygen upon going from water ( $\tau = 3.5 \mu\text{s}$ ) to deuterium oxide ( $\tau = 69 \mu\text{s}$ ) is indicative of the importance of the Franck-Condon factors associated with the O-H stretching mode of water (much larger than those of the O-D stretching mode of  $\text{D}_2\text{O}$ ) in mediating the rate of nonradiative decay of singlet oxygen in aqueous solution [33].

Although  $^1\text{O}_2$  migrates rapidly in and out of detergent micelles and liposomes [34], the distance that singlet oxygen can migrate is relatively limited in water and most organic solvents. Thus, according to Eq. (10),  $^1\text{O}_2^*$  can be expected to migrate about 100–120 nm during its first lifetime in water, but probably less than that in living cells [15,31] and membranes [35], restricting cellular damage to a limited spatial region around the photosensitizer. The other extreme is represented by perfluorocarbon solvents [33], in which the singlet oxygen lifetime can exceed 50 ms (equivalent to a diffusion length of 14  $\mu\text{M}$ ).

## Concluding remarks

This mini-review provides a brief historical introduction to the origin and development of the concept of photosensitization, followed by an outline of the fundamental aspects of the photophysics involved in photosensitization. These include a consideration of the kinetics and energetics of photosensitization, together with the applicable spin selection rules that govern the photosensitized formation of singlet oxygen, the key reactive intermediate in the Type II mechanism of photodynamic therapy (PDT). Photophysics thus provides guidelines for the *in vitro* selection and evaluation of candidates for potential use as singlet oxygen photosensitizers. However, photophysics alone is insufficient to predict efficacy in practical applications of photosensitizers *in vivo*, such as PDT, where additional factors may govern the preconditions for photosensitization. These include selective transport of the sensitizer to the desired target tissue, adequate access of light to permit the excitation of the sensitizer and the presence of oxygen (in Type II PDT) or an appropriate redox partner (in Type I PDT). The sensitizer should also be non-toxic in the dark and have a relatively short residence time in the biological system of interest. Thus, technologically successful applications of PDT require a compromise or, even better, a symbiosis, between the prerequisites of photophysics and the requirements of photobiology.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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