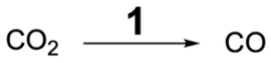
T8. Recycling of Carbon Dioxide

7%										
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	∑
2	16	2	29	5	10	2	4	12	2	84

Removing CO_2 gas from the atmosphere is key to combat climate change. One promising solution is the photocatalytic reduction of CO_2 to CO using molecular catalyst **1**.



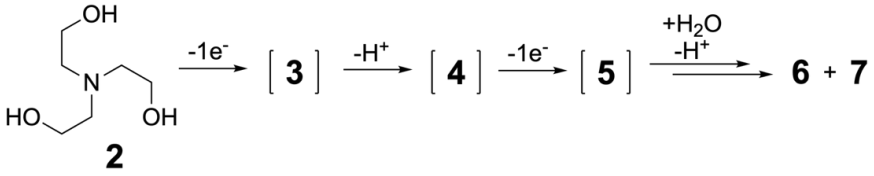
8.1 **Write** the half equation for the reduction of CO_2 to CO in an acidic medium. 2.0 pt

SOLUTION:

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

2 points for a fully correct reaction equation.

The conjugate oxidation reaction occurs with sacrificial reductant **2** in aqueous solution with the following mechanism:

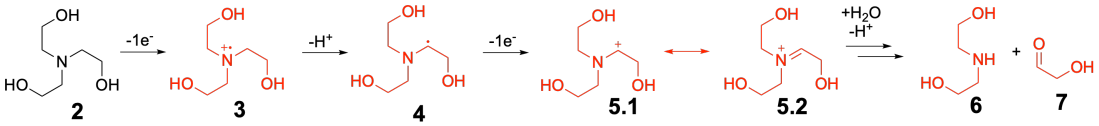


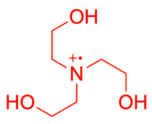
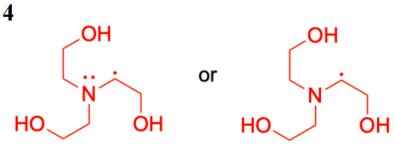
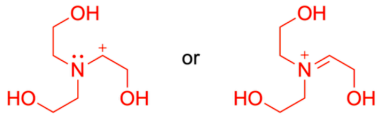
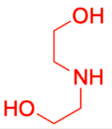
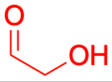
Species **3**, **4**, and **5** are short-lived ionic and/or radical intermediates. **7** yields a silver mirror with the $[Ag(NH_3)_2]OH$ test.

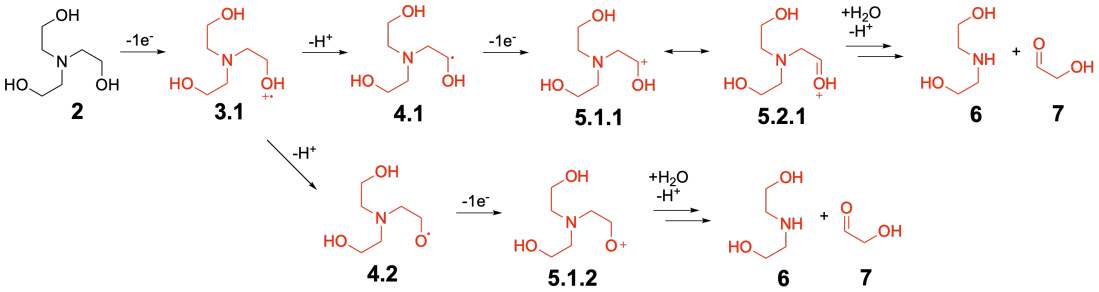
8.2 **Draw** the structures of **3-7**. 16.0 pt

SOLUTION:

Both resonance structures **5.1** and **5.2** are correct answers.

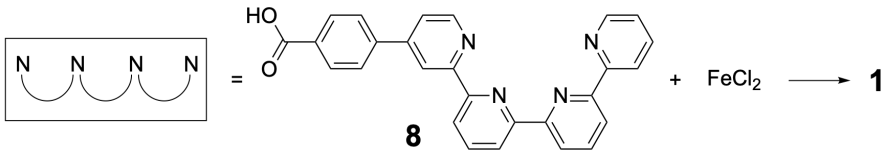


3 	**4** 
5 	**6** 
7 	



4 points for each correctly drawn structure of **3**, **4**, and **5.1** or **5.2**.
2 points for each correctly drawn structure of **6** and **7**.
Half of the marks will be given for the alternative reasonable structures, as shown above.

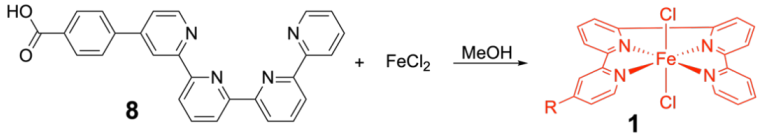
Catalyst **1** can be synthesised with the following reaction.



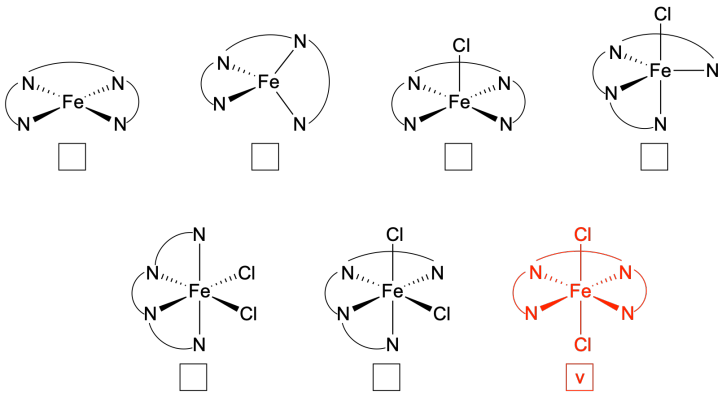
8.3 **Tick** the correct geometry for the structure of **1**. 2.0 pt

SOLUTION:

The pyridine donor groups are planar in ligand **8**, thus, the final configuration of ligand **8** should also be in one plane around the metal in complex **1**.

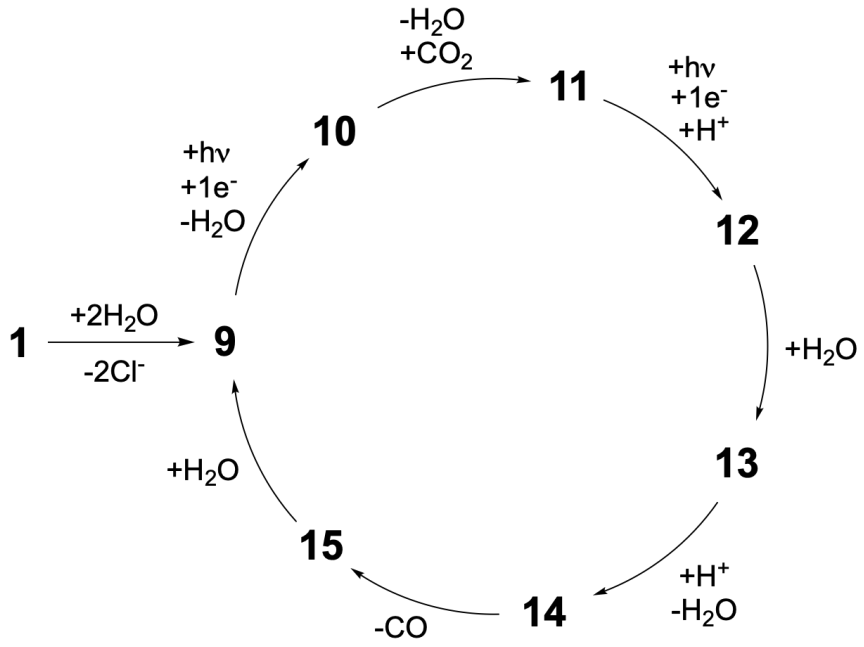


There is only one option that corresponds to this complex.



2 points for the only correct answer.

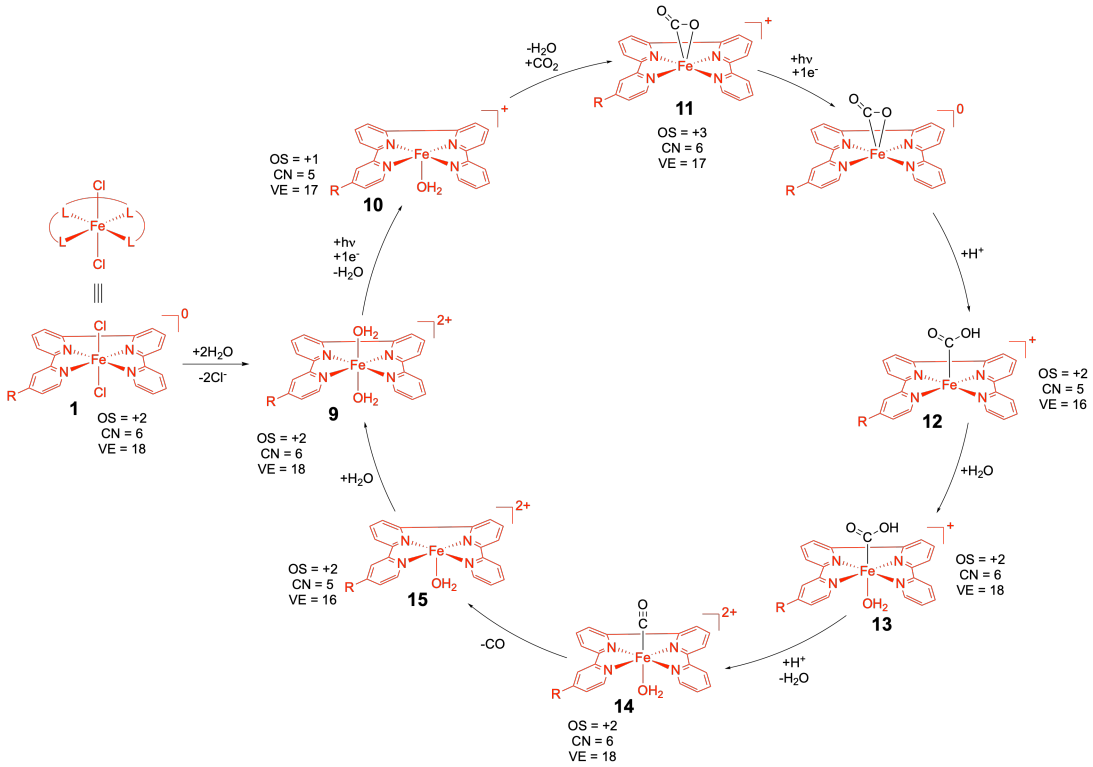
When **1** is loaded on crystalline carbon nitride (C_3N_4) support material, it can reduce CO_2 via the following mechanism.



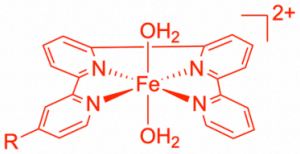
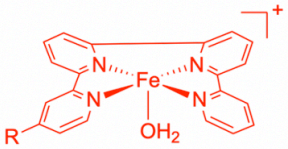
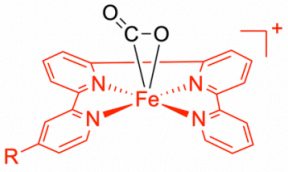
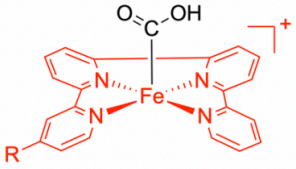
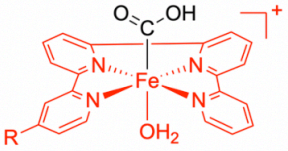
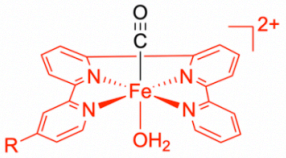
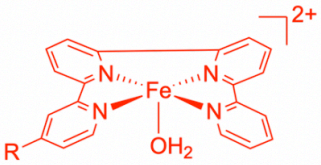
8.4 **Draw** the structures of **9-15**. Use the cartoon structure for ligand **8** shown above. For **9-15**, **specify** the oxidation state, OS, coordination number, CN, and number of valence electrons, VE, of Fe, along with the total charge of corresponding complex structures, Z. Note: Some information is provided on the answer sheet. 29.0 pt

SOLUTION:

The catalytic cycle is presented below. In this part of the task, the arrangement of ligand **8** is not graded as long as it corresponds to the one around the metal complex in the previous part of the task (to avoid double punishment).



For each correct OS, CN, and VE: 0.5 points.
For each correctly drawn structure of **9-15**: 3 points.
–0.5 points for each structure (**9–15**) in which the total charge is not correct.

9  OS = +2 CN = 6 VE = 18 Z = +2	**10**  OS = +1 CN = 5 VE = 17 Z = +1
11  OS = +3 CN = 6 VE = 17 Z = +1	**12**  OS = +2 CN = 5 VE = 16 Z = +1
13  OS = +2 CN = 6 VE = 18 Z = +1	**14**  OS = +2 CN = 6 VE = 18 Z = +2
15  OS = +2 CN = 5 VE = 16 Z = +2	

8.5 **Calculate** the number of catalytic molecules per nm^2, N_{cat}, of C_3N_4 loaded with **1**, when the mass fraction of catalyst, ω_{cat}= 3.8%, if the specific surface area of C_3N_4 is 17.8 $m^2\ g^{-1}$. M_{cat} = 557.21 g mol^{-1}. 5.0 pt

SOLUTION:

In 1 nm^2 there is $\frac{1}{17.8\times10^{18}} = 5.618 \times 10^{-20}$ g C_3N_4. The catalytic loading formula is $\frac{m_{cat}}{m_{cat}+m_{C_3N_4}} \times 100\% = 3.8\%$. If we find m_{cat} from here it will be $m_{cat} = 2.219 \times 10^{-21}$ g.

The molar mass of catalyst is 557.21 g $mol^{-1} \rightarrow N = \frac{2.219\times10^{-21}}{557.21}\times6.02\times10^{23} = 2.4.$

3 points for using the specific surface area of 17.8 m^2g^{-1} for the C_3N_4/**1** mixture and, calculating N_{cat} as 2.3.
5 points for the correct N_{cat} value.

The Turnover Frequency of a catalyst (TOF) is the number of product molecules formed per active catalyst molecule per hour. Under LED illumination (λ = 390 nm) with power of 50 mW, there was a TOF of 8 h^{-1} for 10 mg of C_3N_4, loaded with **1** with ω_{cat} = 3.8%

The formula for calculating the quantum yield is given below:

$$\varphi = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \cdot 100\%$$

8.6 **Calculate** the quantum yield, $\varphi(\%)$, for CO formation. 10.0 pt

SOLUTION:

$\frac{m_{1,cat}}{m_{1,cat}+0.01} \times 100\% = 3.8\% \rightarrow m_{cat} = 3.95 \times 10^{-4}$ g.

$n = \frac{3.95\times10^{-4}}{557.21} = 7.089 \times 10^{-7}$ mol.

$r_{CO} = \frac{7.089\times10^{-7}\times8\times6.02\times10^{23}}{3600} = 9.48 \times 10^{14}\ s^{-1}$

$E_{photon} = \frac{hc}{\lambda} = 5.1 \times 10^{-19}$ J

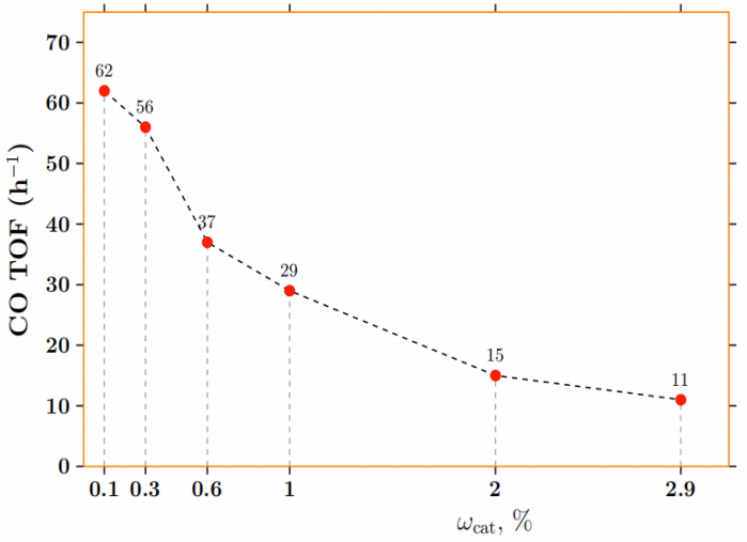
$r_{photon} = \frac{50\times10^{-3}}{5.1\times10^{-19}} = 9.8 \times 10^{16}\ s^{-1}$

$\varphi = \frac{number\ of\ reacted\ electrones}{number\ of\ incident\ photons} \cdot 100\% = \frac{r_{CO}\cdot2}{r_{photon}} \cdot 100\%$ (eq.8.6.1)

$\varphi = \frac{9.48\times10^{14}\times2}{9.8\times10^{16}} \cdot 100\% = 1.94\%$

2 points for r_{CO} value.
2 point for E_{photon} value.
2 point for the correct photon flux r_{photon}.
2 points for eq.8.6.1.
2 point for the correct φ value.

The diagram below shows the change in the TOF of CO as ω_{cat} is varied.



8.7 **How does** the overall rate of CO formation per gram of C_3N_4 loaded with **1** change with increasing ω_{cat}, within the range $0.1 \leq \omega_{cat} \leq 2.9$? **Tick** the correct box. 2.0 pt

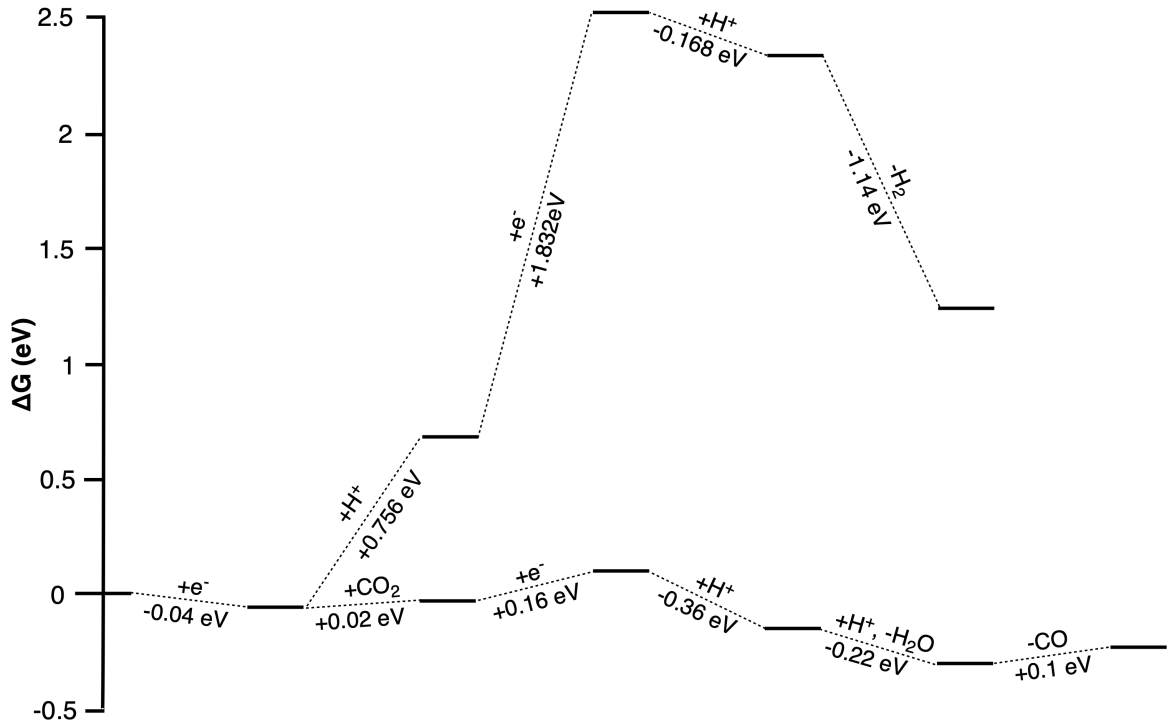
a) increases
b) decreases
c) doesn't change

SOLUTION:

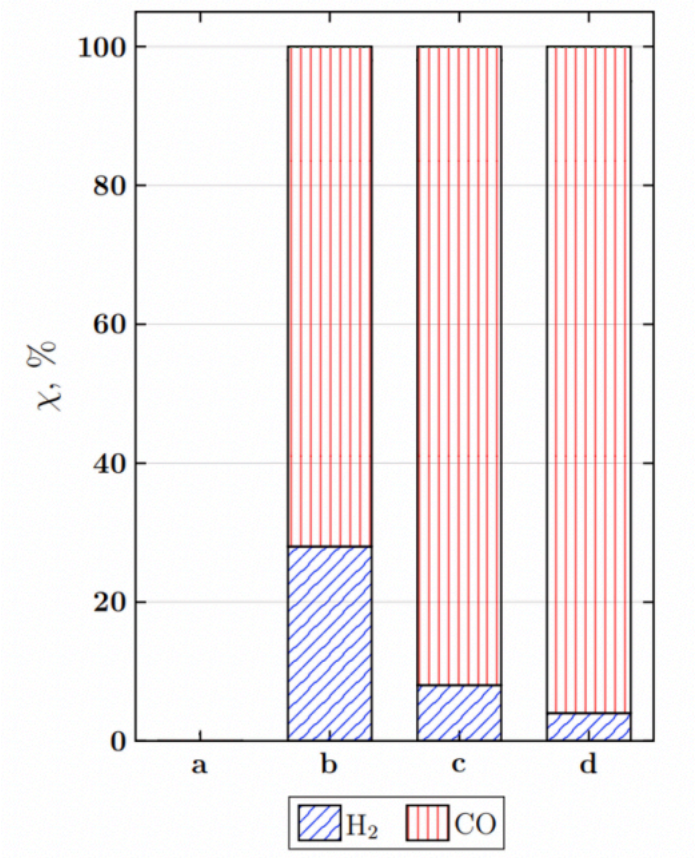
a	b	c
×		

2 point for the only correct ticking

The reduction of CO_2 can be accompanied by the reduction of additional protons. The changes in Gibbs energy during these two reactions are shown in the diagram.



The system was irradiated using different LEDs. The diagram below shows the mole percentages, χ, of H_2 and CO produced during the reduction of CO_2 under four different conditions: no irradiation (N) and irradiation with red (R), green (G), and blue (B) light.



8.8 **Tick** which of the four conditions, mentioned above, corresponds to **a**, **b**, **c** and **d** in the diagram. 4.0 pt

SOLUTION:

	N	R	G	B
a	×			
b				×
c			×	
d		×		

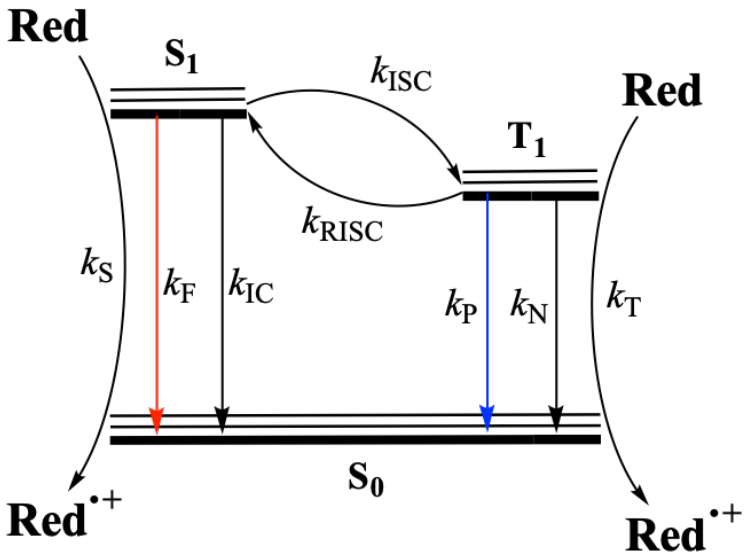
1 point for each correct tick
-1 point for each incorrect tick
The overall score for this part will not be negative.

Photosensitisers (PS) offer some advantages over C_3N_4 for the reduction of CO_2. Mn(I)-containing complexes combined with PS can achieve ~23% quantum yield. In this system, reductive quenching of the *singlet* (**S_1**) and *triplet* (**T_1**) excited states of a PS by reductant (Red) forms $PS^{\bullet-}$, which donates electrons to CO_2 through the Mn(I)-containing complex.

$$PS_{(S_1)} + Red \xrightarrow{k_S} PS^{\bullet-} + Red^{\bullet+} \quad k_S = 2.7 \times 10^9 \ M^{-1} \ s^{-1}$$

$$PS_{(T_1)} + Red \xrightarrow{k_T} PS^{\bullet-} + Red^{\bullet+} \quad k_T = 1.5 \times 10^8 \ M^{-1} \ s^{-1}$$

The following Jablonski diagram describes the processes occurring in the PS:



$\tau_0(\mathbf{S_1}) = 2.9$ ns and $\tau_0(\mathbf{T_1}) = 84$ μs, where τ_0 is the emission lifetime in the absence of the quencher.

8.9 **Calculate** the percentage of quenching, η_q, (in %) of **S_1** and **T_1** states, when [Red] = 0.1 M. Note: here the values of k_{ISC} and k_{RISC} are negligible. 12.0 pt

SOLUTION:

The decay process of the S1 excited state can be represented by the following equation:

$$-\frac{d[S_1]}{dt} = (k_F + k_{IC} + k_{ISC}) \times [S_1] \approx (k_F + k_{IC}) \times [S_1] \qquad \text{(eq.8.10.1)}$$

According to the formula for the lifetime of the reagent in a 1st order reaction

$$\Rightarrow \tau_0 = \frac{1}{k_F + k_{IC}}$$

The decay process of the T1 excited state can be represented by the following equation:

$$-\frac{d[T_1]}{dt} = (k_P + k_N + k_{RISC}) \times [T_1] \approx (k_P + k_N) \times [T_1] \Rightarrow \tau_0 = \frac{1}{k_P + k_N} \qquad \text{(eq.8.10.2)}$$

In the presence of the Red, S_1 is reductively quenched by Red, and the fraction of quenched molecules is as follows:

$$\eta_q = \frac{k_s[S_1][Red]}{(k_F + k_{IC})[S_1] + k_s[S_1][Red]} = \frac{k_s \tau_0 [Red]}{1 + k_s \tau_0 [Red]} \qquad \text{(eq.8.10.3)}$$

$$\eta_q = \frac{2.7 \times 10^9 \times 2.9 \times 10^{-9} \times 0.1}{1 + 2.7 \times 10^9 \times 2.9 \times 10^{-9} \times 0.1} = 0.44 \ (or\ 44\%)$$

In the presence of the Red, T_1 is reductively quenched by it and fraction of quenched molecules as follows:

$$\eta_q = \frac{k_T[T_1][Red]}{(k_P + k_N)[T_1] + k_T[T_1][Red]} = \frac{k_T \tau_0 [Red]}{1 + k_T \tau_0 [Red]} \qquad \text{(eq.8.10.4)}$$

$$\eta_q = \frac{1.5 \times 10^8 \times 84 \times 10^{-6} \times 0.1}{1 + 1.5 \times 10^8 \times 84 \times 10^{-6} \times 0.1} = 0.999 \ (or\ 99.9\%)$$

2 points for each correctly derived equations 8.10.1-8.10.4.

2 points for each correct η_q value.

8.10 **How** do the emission lifetimes of **S_1** and **T_1** states change when [Red] increases? 2.0 pt

Tick the correct box.

a) increases

b) decreases

c) doesn't change

SOLUTION:

After quenching of the PS, the following equation is derived:

$$-\frac{d[S_1]}{dt} = (k_F + k_{IC} + k_S \times [Red]) \times [S_1] \Rightarrow \tau = \frac{1}{k_F + k_{IC} + k_S \times [Red]}$$

As the concentration of [Red] increases, τ decreases accordingly.

a	b	c
	×	

2 points for the only correct ticking