

PHOTOCHEMICAL MECHANISMS FOR PHOTO GALVANIC CELLS PART 5: GENERAL TREATMENT FOR PHOTOCHEMICAL MECHANISMS*

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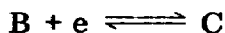
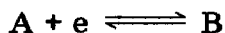
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Summary

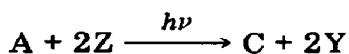
A general treatment is presented for photo-redox systems in which a one-electron redox couple reacts with a two-electron redox couple. It is demonstrated that there are six different mechanisms by which the system can react. Which mechanism is found depends not only on the concentrations of the different species but also on the irradiance of the light. The inter-relation of the different mechanisms and the implications for photogalvanic cells are discussed.

1. Introduction

A common type of photogalvanic cell employs an organic dye redox couple such as thionine (A) and an inorganic couple such as Fe(II), Fe(III) [1]. The organic redox couple involves two electrons and ignoring protonation we shall write such a couple as



In the example we have taken B would be a semi-thionine radical and C the doubly reduced form leucothionine. In the dark the equilibrium between the two redox couples is very much in favour of thionine and Fe(II). However, under illumination a photostationary state is established with significant concentrations of leucothionine and Fe(III):



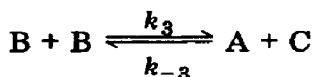
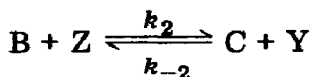
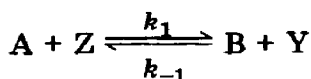
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where following our previous notation [3] we have written Fe(II) as Z and Fe(III) as Y.

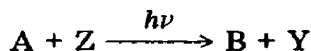
In a photogalvanic cell the products C and Y react on the electrodes to produce power [4]. This paper describes a general treatment and classification of the different mechanisms for the reaction given. An understanding of the different mechanisms and how they are related to each other is essential in order to optimize the performance of such photogalvanic cells for solar energy conversion.

2. The system and notation

We shall consider the following thermal reactions



and we assign a flux g to the photochemical reaction



For monochromatic radiation

$$g = \phi_B I \epsilon [A]$$

where ϕ_B is the quantum efficiency for the production of B from A + Z, I is the irradiance of the light (in moles per square metre per second) and ϵ is the natural molar extinction coefficient of A. We assume that the concentration of A is small enough for the solution to be uniformly illuminated. We further assume that the photochemical flux g is larger than the thermal flux $k_1 [A] [Z]$:

$$g \gg k_1 [A] [Z] \quad (1)$$

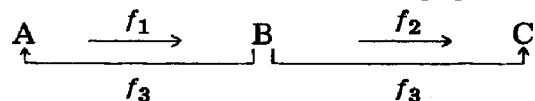
The fluxes f_n for each electron transfer reaction are given by

$$f_1 = g - k_{-1} [B] [Y] \quad (2)$$

$$f_2 = -k_2 [B] [Z] + k_{-2} [C] [Y] \quad (3)$$

$$f_3 = k_3 [B]^2 - k_{-3} [A] [C] \quad (4)$$

The fluxes are linked as follows [5]:



In the photostationary state we then obtain

$$f_1 = f_2 = f_3 \quad (5)$$

From eqns. (3) - (5) we obtain

$$[C](k_{-2}[Y] + k_{-3}[A]) = [B](k_2[Z] + k_3[B]) \quad (6)$$

and from eqns. (2) - (6)

$$g = k_{-1}[B][Y] + \frac{k_{-2}k_3[Y][B]^2}{k_{-2}[Y] + k_{-3}[A]}(1 - R) \quad (7)$$

where

$$\begin{aligned} R &= \frac{k_2k_{-3}[A][Z]}{k_{-2}k_3[Y][B]} \\ &= \frac{[A]}{[A]_D} \frac{[Z]}{[Z]_D} \frac{[Y]_D}{[Y]} \frac{[B]_D}{[B]} \end{aligned}$$

and the subscript D indicates the concentration in the dark. Consideration of the ratios in R shows that, for a significant perturbation in the photostationary state when B and Y are made from A and Z, then

$$R \ll 1 \quad (8)$$

and can be ignored in eqn. (7).

We now introduce the following dimensionless variables:

$$b = \frac{[B] k_2}{[A] k_1} \quad (9)$$

$$c = \frac{[C] k_2 k_{-2}}{[A] k_1 k_{-1}} \quad (10)$$

$$y = \frac{[Y] k_{-2}}{[A] k_{-3}} \quad (11)$$

$$z = \frac{[Z] k_2^2}{[A] k_1 k_3} \quad (12)$$

$$\gamma = \frac{g k_2^2}{k_1^2 k_3 [A]^2} \quad (13)$$

Then using the following relation between the rate constants,

$$\frac{k_3}{k_{-3}} = \frac{k_{-1} k_2}{k_1 k_{-2}}$$

eqns. (6) and (7) can be written as

$$c(1 + y) = b(b + z) \quad (14)$$

and

$$\gamma = by \left(1 + \frac{b}{1 + y} \right) \quad (15)$$

Now each bracket in eqns. (14) and (15) consists of the sum of two terms. Depending on which term in each pair is dominant we have six different possible mechanisms. We now proceed to classify and label these different mechanisms.

3. The different mechanisms

We start with eqn. (7) which describes the main route for the regeneration of A. If

$$k_{-1}[B][Y] > \frac{k_{-2}k_3[B]^2[Y]}{k_{-2}[Y] + k_{-3}[A]} \quad (16)$$

then the main route for the regeneration of A is simply the reverse of the photochemical generation, *i.e.* the reaction $B + Y$. We give this the label A1. In contrast, if the inequality in eqn. (16) is reversed then the main route is the disproportionation of B and we allocate the label A2 to this route. The numbers refer to the order of the route with respect to B.

Next we take the pair of terms on the right-hand side of eqn. (6). The terms describe the main route for the conversion of B to C. If

$$k_2[Z] > k_3[B] \quad (17)$$

then the main route is through transition state 2. We give this the label B1. However, if the inequality is reversed then the main route is the disproportionation reaction with label B2. Again the numbers refer to the order with respect to B.

Finally we consider the pair of terms on the left-hand side of eqn. (6). These terms describe the fate of C. If

$$k_{-2}[Y] > k_{-3}[A] \quad (18)$$

then the main route is through transition state 2 and we give this route the label C1. However, if the inequality in eqn. (18) is reversed then the main route is the conproportionation reaction with label C2. Thus all the routes with the number 1 involve inorganic species, while all the routes with the number 2 involve the disproportionation reaction.

The overall mechanism is a combination of one of each of the three pairs, A1 or A2, B1 or B2, and C1 or C2. In Table 1 we list the different possible mechanisms and show schematically the main routes for each mechanism. It will be noticed that out of the eight possible combinations two are missing, namely A1 B1 C2 and A2 B1 C2. This is because the conditions for these mechanisms cannot be met. For C2 we require

$$k_{-3}[A] > k_{-2}[Y]$$

TABLE 1
List of different possible mechanisms

Label	[B]	[C]	Scheme
A1 B1 C1	$\frac{g}{k_{-1}[Y]}$	$\frac{k_2 g [Z]}{k_{-1} k_{-2} [Y]^2}$	A \rightleftharpoons B \rightleftharpoons C
A1 B2 C1	$\frac{g}{k_{-1}[Y]}$	$\frac{k_3 g^2}{k_{-1}^2 k_{-2} [Y]^3}$	A \rightleftharpoons B \rightleftharpoons C ↑-----↑-----↑
A1 B2 C2	$\frac{g}{k_{-1}[Y]}$	$\frac{k_3 g^2}{k_{-1}^2 k_{-3} [Y]^2 [A]}$	A \rightleftharpoons B \rightleftharpoons C ↑-----↑-----↑
A2 B1 C1	$\left(\frac{g}{k_3}\right)^{1/2}$	$\frac{k_2 [Z]}{k_{-2} [Y]} \frac{g}{k_3}^{1/2}$	A \longrightarrow B \rightleftharpoons C ↑-----↑-----↑
A2 B2 C1	$\left(\frac{g}{k_3}\right)^{1/2}$	$\frac{g}{k_{-2} [Y]}$	A \longrightarrow B \longleftarrow C ↑-----↑-----↑
A2 B2 C2	$\left(\frac{g k_{-3} [A]}{k_{-2} k_3 [Y]}\right)^{1/2}$	$\frac{g}{k_{-2} [Y]}$	A \longrightarrow B \longleftarrow C ↑-----↑-----↑

in which case

$$k_3[B] > k_3[B]_D > k_2[Z]$$

However, B1 requires the contradictory condition that

$$k_2[Z] > k_3[B]$$

In Table 1 we have also listed expressions for the concentrations of B and C in the photostationary state for each mechanism. In most photogalvanic cells the concentrations of the inorganic couple Y,Z are larger than the concentrations of the organic dye and hence the concentrations of Y and Z will not be greatly perturbed in the photostationary state. In Table 2 we list how the

TABLE 2
The order of the dependence of [C] on [A], [Y], [Z] and I

Mechanism	[A]	[Y]	[Z]	I
A1 B1 C1	1	-2	1	1
A1 B2 C1	2	-3	0	2
A1 B2 C2	1	-2	0	2
A2 B1 C1	1/2	-1	1	1/2
A2 B2 C1	1	-1	0	1
A2 B2 C2	1	-1	0	1

concentration of C depends upon [A], [Y], [Z] and the irradiance I , where we have assumed that

$$g \propto I[A]$$

It can be seen that apart from A2 B2 C1 and A2 B2 C2 each mechanism has a unique set of dependences which can be used to identify the appropriate mechanism for any particular system.

4. The location of the different mechanisms

We must consider the boundaries between the different mechanisms and how they depend on the concentrations of the different species and the irradiance. In Table 3 we summarize eqns. (16) - (18) and express the equations in the dimensionless notation introduced in eqns. (9) - (13). The A1-A2 and B1-B2 boundaries depend upon the concentration of B which in turn depends on the photo-driven flux g as given in eqns. (7) or (15). Substitution from the equations in Table 3 gives the equations

$$\text{A1-A2} \quad \gamma = 2y(1 + y) \quad (19)$$

$$\text{B1-B2} \quad \gamma = zy \left(1 + \frac{z}{1 + y} \right) \quad (20)$$

We can now construct a three-dimensional figure (Fig. 1) to show the volume of γ, y, z space that is occupied by each mechanism. In most experiments the concentrations of Y and Z are controlled: y and z are plotted across and "into" the diagram. The irradiance and the concentrations of A and Z will control g which is plotted as γ on the vertical axis. The bottom of the figure is bounded by the "thermodynamic plane" OFWGHJ. The condition for this plane is obtained by considering the thermal reaction

$$g_D = k_1[A][Z]$$

TABLE 3

The boundary conditions for the mechanisms

Boundary	Equation number	Equation	Equation ^a
A1-A2	16	$[Y] + \frac{k_{-3}[A]}{k_{-2}} = \frac{k_3[B]}{k_{-1}}$	$y + 1 = b$
B1-B2	17	$k_2[Z] = k_3[B]$	$z = b$
C1-C2	18	$k_{-2}[Y] = k_{-3}[A]$	$y = 1$

^aEach equation is expressed in the dimensionless notations of eqns. (9) - (13).

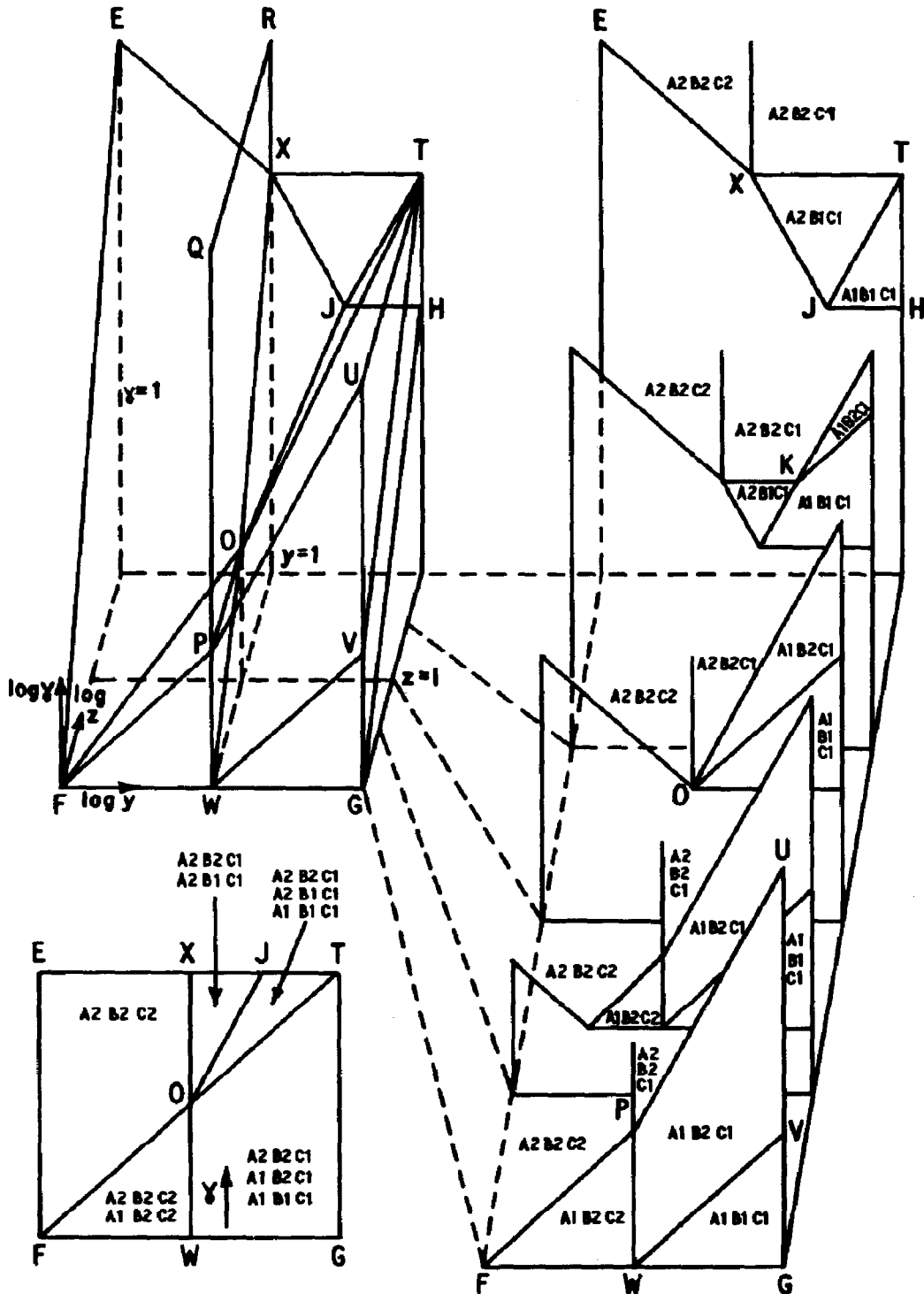


Fig. 1. Block diagram locating the six different mechanisms. The dimensionless variables y , z and γ describing $[Y]$, $[Z]$ and the photo-driven flux g are defined in eqns. (11) - (13). Sections of the block at constant z are shown on the right. Below the block we show a case diagram which is a projection onto a horizontal plane. The line WOX is the line $y = 1$; the line FOT is the line $z = y$.

or in dimensionless notation

$$\gamma = z$$

We also assumed (eqns. (1) and (8)) that g was large enough to cause a significant perturbation to the concentrations of B and C. For these assumptions to hold we require

$$\gamma > \frac{z^2}{y(1+y)}$$

This condition is represented by the plane OFEX for $y < 1$ and the plane OJX for $y > 1$. Of the planes that divide the mechanisms, the easiest one to see is the vertical C1-C2 plane OWPQRX with the condition $y = 1$. The A1-A2 surface given by eqn. (19) is represented by the planes OFP for $y < 1$ and OPUTJ for $y > 1$. To prevent the diagram being too complicated we have ignored the factor of 2 in eqn. (19). Finally the B1-B2 surface given by eqn. (20) is represented by the planes OWVT for $z < y$ and the plane OTX for $z > y$.

To the right of the block we have shown various sections through the block at different values of z . These sections show how for a given value of y the mechanism changes as γ is increased. For instance on the right-hand side at the front of the block at low irradiance, the system will be reacting without any dismutation of B by the mechanism A1 B1 C1. On increasing the irradiance the mechanism changes to A1 B2 C1 and finally to A2 B2 C1 as the dismutation reaction becomes progressively more important. On the right-hand side at the back of the block we find the same change from A1 B1 C1 to A2 B2 C1 but at these larger concentrations of Z the intermediate mechanism is now A2 B1 C1 rather than A1 B2 C1. The B1 process requires Z to react with B and hence is favoured by large concentrations of Z. These different sequences are summarized in the case diagram obtained by projecting the lines FOT and WOX onto a horizontal plane, as shown in the bottom left-hand corner of Fig. 1. This projection is similar to a phase diagram; the point O (with coordinates 0,0,0) is analogous to the triple point, where in our case the three dividing surfaces intersect. The line WOX at $y = 1$ divides C1 from C2 and describes the fate of C; when $y = 1$

$$k_{-2}[Y] = k_{-3}[A] \quad (21)$$

The line FOT or $z = y$ describes the relative rates for the reaction of B with either Z or Y; when $z = y$

$$k_2[Z] = k_{-1}[Y] \quad (22)$$

The whole diagram allows us to see which mechanisms are adjacent to each other and the effect of changing the concentrations of Y, or Z or the irradiance on the different reaction paths followed by the system.

5. The concentration of B and C

We can now combine the results of Table 1 and of Fig. 1 to describe the concentration of B and C as a function of the concentrations of Y and Z and the intensity of illumination. The results are displayed in Fig. 2. The conditions for the size of γ at the boundaries between the different mechanisms are given. It can be seen that at each boundary we obtain the same value of either b or c on substituting the critical value of γ into the expressions for b and c on either side of that boundary. This shows that there is a good join between the expressions for b and c as the mechanisms change. Even on the mechanistic borderlines our treatment will be correct to within a factor of 2. The joins are equally good on crossing the $y = 1$ or the $z = y$ boundaries.

The boundary OT is particularly interesting. When $z = y$ it can be seen that both the A1-A2 and the B1-B2 boundaries are crossed at the same value of g where

$$\gamma = y^2 = z^2 = yz$$

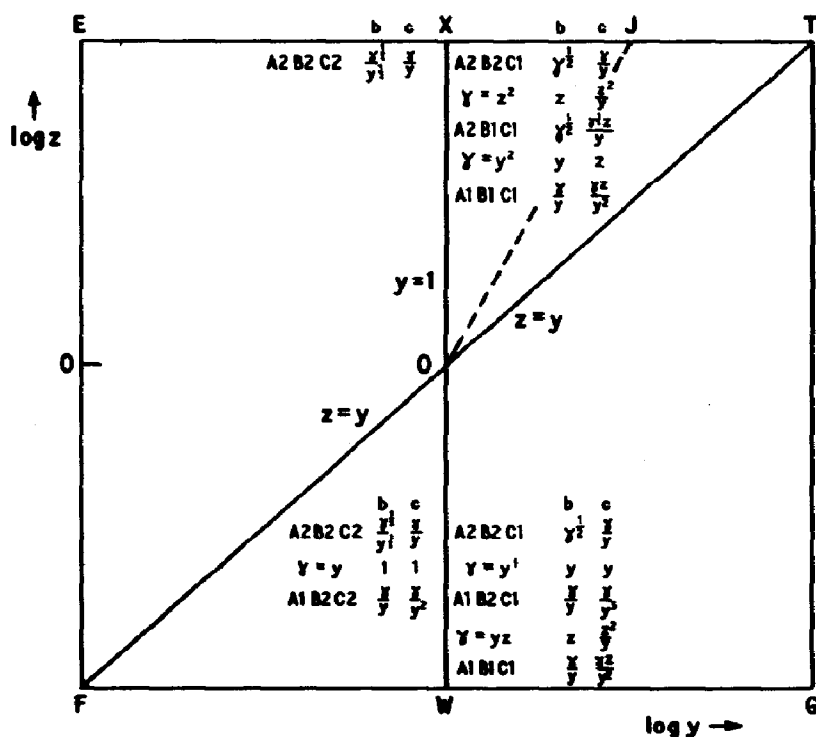


Fig. 2. The different mechanisms with their concentrations of B and C on the case diagram derived from Fig. 1. The values of γ at the mechanistic borderlines are given. Note the good joins for the values of b and c at all the borderlines. The dimensionless variables b and c which describe concentrations of B and C are defined in eqns. (9) and (10). The mechanism A1 B1 C1 is not found in the area OXJ.

For this particular condition there is no region of intermediate mechanism and the system will pass directly from A1 B1 C1 to A2 B2 C1. This can be seen as the point K in Fig. 1.

6. Quantum efficiency for production of C

For a successful photogalvanic device we require that the product C should be produced with as high an efficiency as possible. The concentration of C in the photostationary state may not be a good guide to the quantum efficiency. For instance a large concentration of C may build up because of a slow back reaction of C with Y. A better guide is to imagine that C is removed so rapidly on an electrode that there is no thermal back reaction which destroys C. We can then define a quantum efficiency ϕ_C for the system considered in this paper:

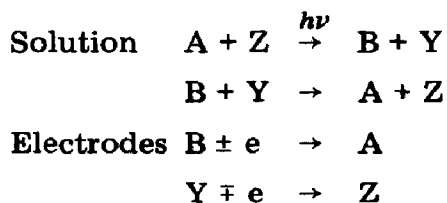
$$\phi_C = f_C/g \quad (23)$$

The overall quantum efficiency will be the product of ϕ_C and the quantum efficiency ϕ_B for the production of B in the primary photochemical steps. In eqn. (23) f_C describes the flux producing C through either transition state 2 or 3. In Table 4 we report the values of ϕ_C for the different mechanisms and the critical values for the mechanistic changes. When $z > y$ ($k_2[Z] > k_{-1}[Y]$) B when formed will react with Z to form C rather than with Y to return to A. Hence for low values of g , when the disproportionation of B is unimportant, the quantum efficiency ϕ_C will be unity. At high irradiance when the disproportionation reaction is important then ϕ_C falls to $\frac{1}{2}$ since it requires two molecules of B to make one molecule of C. Taking the other case when $z < y$, at low irradiance the quantum efficiency is low because now most of the B that is formed returns to A by reacting with Y. As the irradiance increases and the disproportionation mechanism takes over the quantum efficiency rises to the limiting value of $\frac{1}{2}$. (The boundary $\gamma = \frac{1}{2}y^2$ is different from the boundary in Fig. 2 because C is not now reacting with Y to form B.)

TABLE 4
Values of ϕ_C

Mechanism	$z > y$	$z = y$	Mechanism	$z < y$
A2 B2 $\gamma = z^2$	$\frac{1}{2}$	$\frac{1}{2}$	A2 B2 $\gamma = \frac{1}{2}y^2$	$\frac{1}{2}$
A2 B1 $\gamma = \frac{1}{2}y^2$	1	—	A1 B2 $\gamma = zy$	γ/y^2
A1 B1	$\frac{z}{z+y} \approx 1$	$\frac{1}{2}$	A1 B1	$\frac{z}{z+y} \approx \frac{z}{y}$

In characterizing photogalvanic systems it is important to be able to place them in the correct segment of the mechanistic case diagram. For $z > y$ ($k_2[Z] > k_{-1}[Y]$) the quantum efficiency ϕ_C will have its maximum value of unity at low irradiance. The disproportionation mechanism reduces the efficiency to $\frac{1}{2}$. However, for $z < y$ ($k_2[Z] < k_{-1}[Y]$) the low irradiance mechanisms have such low efficiencies that the device could not be successful. Here it is important to drive the system hard enough so that the A2 B2 mechanism is operative. The maximum value of ϕ that can be obtained under these conditions is $\frac{1}{2}$. This is an obvious disadvantage of the mixed one-electron-two-electron system discussed in this paper compared with the simple one-electron system:



For the one-electron system $\phi_B = 1$. However, in practice the back reaction of $B + Y$ is often so rapid that B and Y do not reach the electrodes. Although $\phi_C = \frac{1}{2}$ for the mixed system the species C formed from the disproportionation reaction may not react so rapidly with Y and hence can survive the journey to reach the electrode. It may be better to sacrifice half the photons in order to trap all the photo-product on the electrode.

The mechanistic analysis presented in this paper will be applied in the succeeding paper to the iron-thionine system.

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