

AN ANALYSIS OF THE DEPENDENCE OF THE QUANTUM YIELDS OF PHOTOCHEMICAL COUPLING REACTIONS ON THE LIGHT INTENSITY

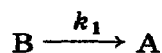
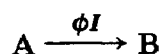
DAVID R. TYLER

Department of Chemistry, Columbia University, New York, NY 10027 (U.S.A.)

(Received January 21, 1982; in revised form March 24, 1982)

Summary

If a product is formed by the coupling of two photochemically generated intermediates then the quantum yield for the appearance of the product may be intensity dependent. The quantum yields of a generalized photochemical coupling reaction were examined with the goal of elucidating the limitations and restrictions that apply in the use of this rule. For the general reaction pathway



it was found that the quantum yield Φ of product formation will be directly proportional to I when k_1^2/k_2 is much greater than ϕI and Φ will be constant (with a value of $\phi/2$) when k_1^2/k_2 is much less than ϕI . Other values of k_1^2/k_2 lead to quantum yields that are intensity dependent but not directly proportional to I . If Φ is to be experimentally determinable then k_1^2/k_2 must be no greater than $10^4\phi^2I$.

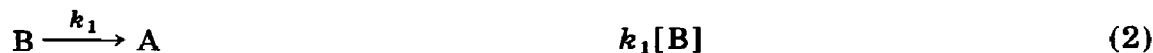
If a product is formed by the coupling of two photochemically generated intermediates (or excited states) then the quantum yield for the appearance of the product may be intensity dependent. This principle is frequently invoked to explain the intensity-dependent quantum yield results obtained in photochemical coupling reactions [1, 2].

Unfortunately, the kinetic derivations underlying the principle have not been reported. Consequently, the limitations and restrictions that apply in the use of this rule have not been formulated. Because we are interested in the mechanisms of the photochemical coupling reactions of organometallic complexes, we found it necessary to know when we could and when we could not expect a quantum yield to be intensity dependent. For that reason

we examined the quantum yield of a generalized photochemical coupling reaction with the goal of determining under what conditions the quantum yield will be intensity dependent.

A generalized coupling reaction in which a binuclear product is formed via the coupling of two photogenerated intermediates (or excited states) is shown in Scheme I in which the rates of the reactions are also included.

Scheme I:



In this scheme ϕ is the quantum yield for formation of B (if B is an intermediate). If B is an excited state of A then ϕ is equal to unity. The variable I represents the intensity of the absorbed radiation. The rate constant k_1 is the first-order rate constant for the decay of B to the ground state A. Reaction (2) may represent a single deactivation process or the summation of many unimolecular processes resulting in deactivation. Because the primary photoprocess of many organometallic complexes is metal–ligand bond dissociation [3] eqn. (2) may also represent the back reaction of the metal with the ligand to re-form the starting material. In this case, k_1 is a pseudo-first-order rate constant that is more precisely written as $k_i[L]$. Reaction (3) is the actual coupling reaction of the two intermediate species yielding the binuclear product. The quantum yield Φ for product formation is given by

$$\Phi = \frac{k_2[B]^2}{I} \quad (4)$$

The concentration of B can be determined from the steady state approximation

$$\frac{d[B]}{dt} = 0 = \phi I - k_1[B] - 2k_2[B]^2 \quad (5)$$

At low light intensities the steady state concentration of B is expected to be extremely small so in all likelihood $2k_2[B]^2$ is much less than $k_1[B]$. Using this simplification in eqn. (5) we find that

$$[B] = \frac{\phi I}{k_1} \quad (6)$$

and hence

$$\Phi = \frac{k_2}{I} \left(\frac{\phi I}{k_1} \right)^2 = \frac{k_2}{k_1^2} \phi^2 I \quad (7)$$

Thus Φ is directly proportional to the intensity for $2k_2[B]^2 \ll k_1[B]$. This expression can be simplified by substituting for $[B]$ the expression found by solving eqn. (5) using the quadratic formula. We then obtain the result that Φ will be directly proportional to I when

$$\frac{k_1^2}{k_2} \gg \phi I \quad (8)$$

When the light intensity is extremely high, it is possible that $2k_2[B]^2$ will be much greater than $k_1[B]$. If this is the case then from eqn. (5) we derive

$$[B]^2 = \frac{\phi I}{2k_2} \quad (9)$$

and hence

$$\Phi = \frac{k_2}{I} \frac{\phi I}{2k_2} = \frac{\phi}{2} \quad (10)$$

Thus Φ is constant when $2k_2[B]^2$ is much greater than $k_1[B]$. Just as above, this expression can be simplified: Φ will be constant (with a value of $\phi/2$) when

$$\frac{k_1^2}{k_2} \ll \phi I \quad (11)$$

The results of the discussion above are summarized pictorially in Fig. 1 where Φ is plotted against I . As the figure shows, at low intensities the values of Φ will asymptotically approach the line defined by $\Phi = (k_2/k_1^2)\phi^2 I$; at high intensities Φ approaches the value $\phi/2$ asymptotically. In between the two limiting regions is a transition region where Φ is neither directly proportional to I nor constant. It is in this region that the quadratic formula must

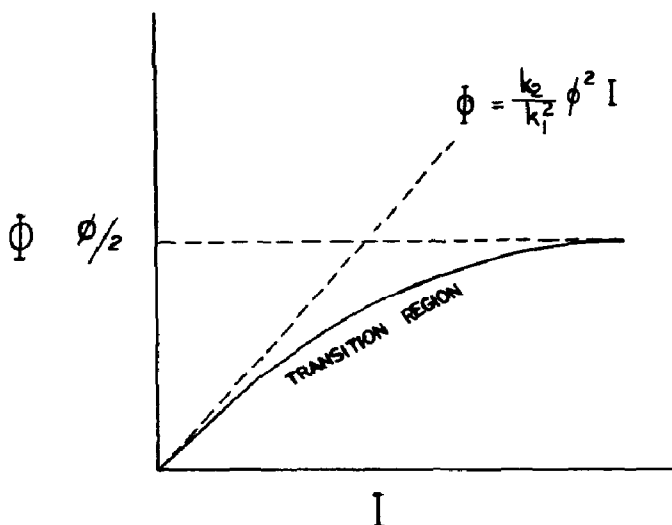


Fig. 1. A plot of Φ vs. I for the coupling reaction in Scheme I.

be applied to eqn. (5) to determine $[B]$ because $2k_2[B]^2$ is neither much greater nor much less than $k_1[B]$.

If a coupling mechanism similar to that in Scheme I is suspected but the quantum yield for the reaction is constant then at least two things can be done to test the mechanism: (1) I can be lowered substantially in order to move Φ into the directly proportional region of Fig. 1, or (2) the viscosity of the solvent can be increased with the aim of decreasing the coupling reaction rate constant k_2 [4]. The increase in viscosity might thus lower Φ so that it will be in the directly proportional region.

We have shown that Φ will be directly proportional to I when $2k_2[B]^2$ is much less than $k_1[B]$. If we assume that this inequality means that $2k_2[B]^2$ is no greater than $0.1k_1[B]$ (this assumption leads to a maximum differential error in Φ of about 20%) then we can derive that Φ is directly proportional to I when

$$\frac{k_1^2}{k_2} \geq 10^2 \phi I \quad (12)$$

Similarly, if we assume that $2k_2[B]^2 \gg k_1[B]$ can be replaced by $2k_2[B]^2 \geq 10k_1[B]$, Φ will be constant when

$$\frac{k_1^2}{k_2} \leq 10^{-2} \phi I \quad (13)$$

Figure 2 is a plot of $\log k_2$ versus $\log k_1$. The shaded area of Fig. 2 is centered about the line $\log k_2 = 2 \log k_1 - \log \phi I$ and it corresponds to the values of k_1 and k_2 for which Φ is neither constant nor directly proportional to I . The boundaries of the shaded region are defined by the lines $\log k_2 = 2 \log k_1 - \log \phi I \pm 2$. Values of $\log k_1$ and $\log k_2$ in the region above the shaded area yield constant values of Φ while values below the shaded area give values of Φ directly proportional to I .

Figure 2 is deceiving because it gives the impression that to check whether a coupling reaction follows the generalized pathway in Scheme I all that need be done is to adjust I such that the point (k_1, k_2) or $(\log k_1, \log k_2)$ falls below the shaded area of the graphs; a plot of I versus Φ will then reveal whether Φ is directly proportional to I . Although this approach is sound in theory, in practice it suffers from two limitations: (1) values of I are restricted to the range 10^{-6} - 10^{-8} einsteins $l^{-1} s^{-1}$ [5] and (2) quantum yields have lower limits of detection. Generally speaking, to be experimentally measurable quantum yields must be greater than 10^{-4} .

The restriction imposed by limitation (2) above can be derived as follows. When Φ is directly proportional to I the relationship in eqn. (7) holds. By adding to eqn. (7) the restriction that Φ must be greater than 10^{-4} , the following expression is obtained:

$$\Phi = \frac{k_2}{k_1^2} \phi^2 I \geq 10^{-4} \quad (14)$$

By rewriting eqn. (14) we see that Φ will be detectable when

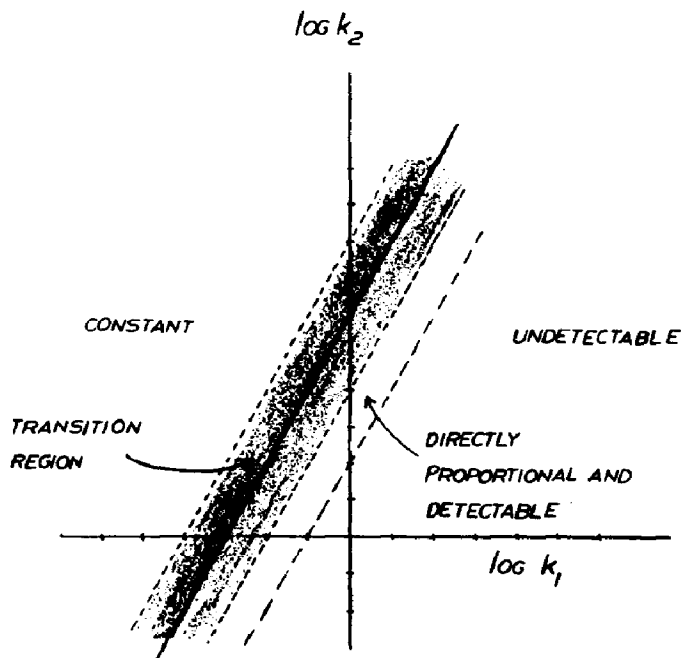


Fig. 2. A plot of $\log k_2$ vs. $\log k_1$ where $\log k_2 = 2 \log k_1 - \log \phi I$. The upper and lower bounds of the shaded area are defined by the equations $\log k_2 = 2 \log k_1 - \log \phi I \pm 2$. Points above the shaded region give constant Φ values while below the shaded region Φ is directly proportional to I . The lower limit of detectability for Φ is indicated by the broken line defined by $\log k_2 = 2 \log k_1 - \log \phi^2 I - 4$. The various regions in which Φ is constant, non-constant, directly proportional to I and undetectable are indicated. The plot shown is for $\phi = 1$ and $I = 1 \times 10^{-6}$ einsteins $l^{-1} s^{-1}$.

$$\frac{k_1^2}{k_2} \leq 10^4 \phi^2 I \quad (15)$$

By combining eqn. (15) with eqn. (12) we find that Φ will be detectable and directly proportional to I when

$$10^2 \phi I \leq \frac{k_1^2}{k_2} \leq 10^4 \phi^2 I \quad (16)$$

This expression is a key result and it shows the rather strict relationship between k_1 , k_2 and I that is necessary if mechanistic data are to be obtained from measurements of Φ versus I . The narrow range of acceptable k_1 and k_2 values (for a given I) is best seen by reference to Fig. 2. The difference between the upper limit of direct proportionality and the limit of detectability is given by $\log \phi + 2$. Obviously, ϕ must be larger than 10^{-2} if there is to be any region in which Φ is detectable and directly proportional to I .

In conclusion, the quantum yield of a coupling reaction is detectable and directly proportional to I if the relationship in eqn. (16) holds and if ϕ is at least 0.01. Given this rather narrow set of conditions it seems likely that much of the time Φ will not be directly proportional to I . However, if we allow for the fact that in the transition region Φ is not constant then a

much wider range of conditions is allowable from which mechanistic information is obtainable (although the information obtained from the transition region is not as definitive for mechanistic purposes as is the information obtained from the directly proportional region of the graph). With due caution, it is safe to conclude that any coupling reaction for which the quantum yield is intensity dependent (*i.e.* non-constant but not necessarily directly proportional) probably proceeds by the coupling of two photo-generated intermediates. When Φ shows no dependence on I and k_1 and k_2 are unknown, then the coupling mechanism is indeterminate.

Acknowledgment

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

References

- 1 D. R. Tyler, *Inorg. Chem.*, 20 (1981) 2257.
- 2 M. S. Wrighton, D. L. Morse, H. B. Gray and D. K. Ottesen, *J. Am. Chem. Soc.*, 98 (1976) 1111.
- 3 G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979.
- 4 G. B. Porter, in A. W. Adamson and P. D. Fleischauer (eds.), *Concepts of Inorganic Photochemistry*, Wiley-Interscience, New York, 1975.
- 5 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966, p. 20.