KINETIC EVALUATIONS OF EXCIPLEX-MEDIATED PHOTOCHEMICAL REACTIONS

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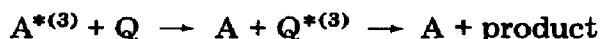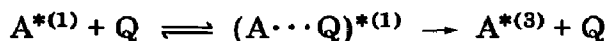(Received January 4, 1982; in revised form February 18, 1982)

Summary

Kinetic expressions are derived for photochemical reactions proceeding through singlet exciplexes. It is shown that approximately linear plots of the inverse of product appearance quantum yield *versus* the inverse of quencher concentration can arise from more than one mechanism. Heavy atom enhancement of intersystem crossing can be used in some cases to study the reaction pathways.

1. Introduction

Excited state complexes are frequently proposed as intermediates in photophysical processes and in photochemical reactions. In some cases emission from exciplexes gives direct evidence for their existence. In other cases kinetic data provide indirect evidence for them. (Ware and coworkers [1, 2] have presented a thorough analysis of exciplex photophysics.) The most interesting cases are those in which exciplexes appear to direct photochemical reactions along unexpected pathways, especially those in which product formation apparently arises directly from a singlet exciplex:

$$A^{*(1)} + Q \rightleftharpoons (A \cdots Q)^{*(1)} \longrightarrow A + \text{product}$$
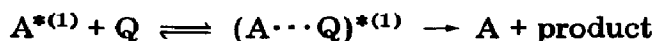
If the product is one which is also formed in triplet-sensitized reactions, however, exciplex-mediated enhancement of intersystem crossing [3, 4] should also be considered:

$$A^{*(1)} + Q \rightleftharpoons (A \cdots Q)^{*(1)} \longrightarrow A^{*(3)} + Q$$
$$A^{*(3)} + Q \longrightarrow A + Q^{*(3)} \longrightarrow A + \text{product}$$
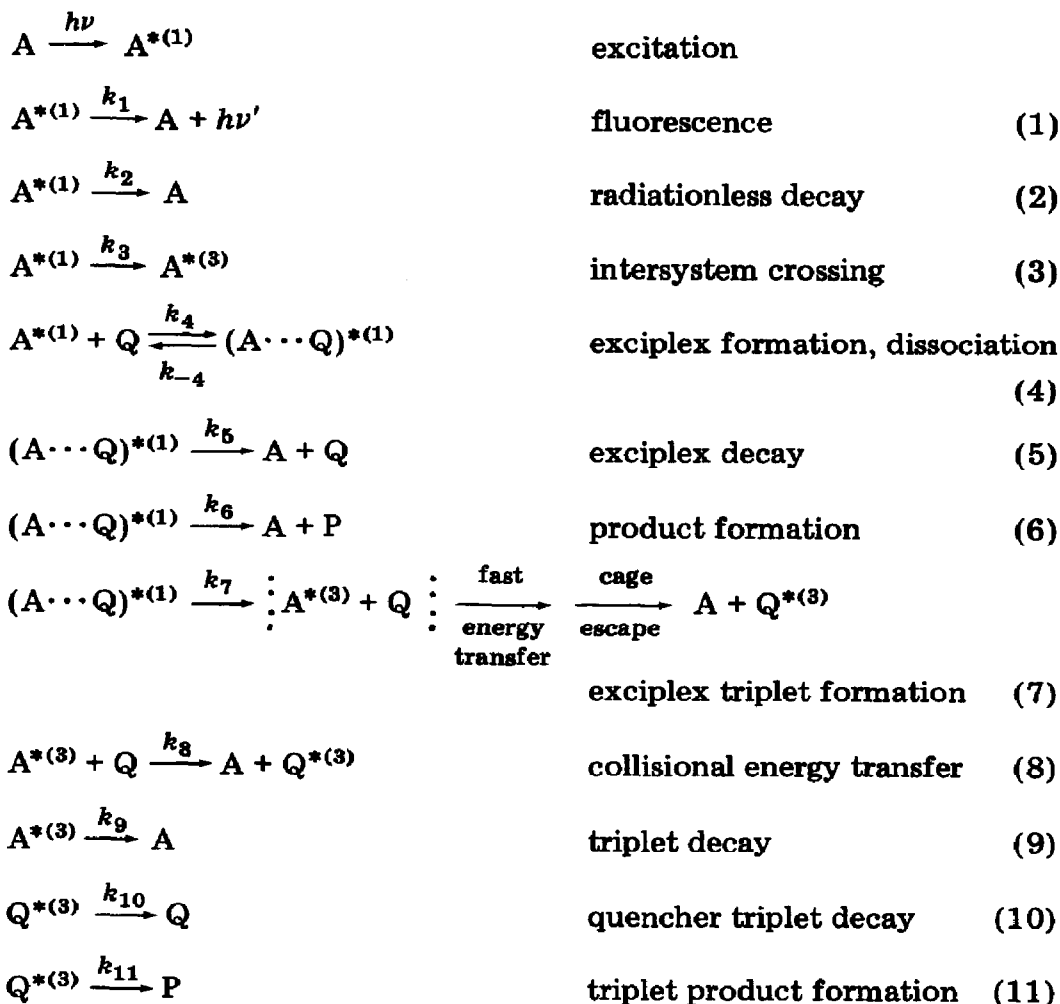
The purpose of this paper is to discuss the kinetics of systems in which either or both of these processes can operate, to offer a cautionary note about basing mechanistic conclusions on simple kinetic data and to illustrate the utility of heavy atom effects in elucidating reaction pathways. The present analysis is formulated for cases in which only product quantum yield

and fluorescence intensity data are available. Ware and coworkers [2, 5] have demonstrated that fluorescence decay measurements, when available, provide more accurate measures of exciplex behavior.

2. Analysis

We consider the following kinetic scheme:

$$A \xrightarrow{h\nu} A^{*(1)} \qquad\qquad \text{excitation}$$

$$A^{*(1)} \xrightarrow{k_1} A + h\nu' \qquad\qquad \text{fluorescence} \qquad (1)$$

$$A^{*(1)} \xrightarrow{k_2} A \qquad\qquad \text{radiationless decay} \qquad (2)$$

$$A^{*(1)} \xrightarrow{k_3} A^{*(3)} \qquad\qquad \text{intersystem crossing} \qquad (3)$$

$$A^{*(1)} + Q \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} (A \cdots Q)^{*(1)} \qquad \text{exciplex formation, dissociation} \qquad (4)$$

$$(A \cdots Q)^{*(1)} \xrightarrow{k_5} A + Q \qquad\qquad \text{exciplex decay} \qquad (5)$$

$$(A \cdots Q)^{*(1)} \xrightarrow{k_6} A + P \qquad\qquad \text{product formation} \qquad (6)$$

$$(A \cdots Q)^{*(1)} \xrightarrow{k_7} \; \vdots A^{*(3)} + Q \; \vdots \xrightarrow[\substack{\text{energy} \\ \text{transfer}}]{\text{fast}} \xrightarrow[\text{escape}]{\text{cage}} A + Q^{*(3)}$$

$$\text{exciplex triplet formation} \qquad (7)$$

$$A^{*(3)} + Q \xrightarrow{k_8} A + Q^{*(3)} \qquad \text{collisional energy transfer} \qquad (8)$$

$$A^{*(3)} \xrightarrow{k_9} A \qquad\qquad \text{triplet decay} \qquad (9)$$

$$Q^{*(3)} \xrightarrow{k_{10}} Q \qquad\qquad \text{quencher triplet decay} \qquad (10)$$

$$Q^{*(3)} \xrightarrow{k_{11}} P \qquad\qquad \text{triplet product formation} \qquad (11)$$

2.1. Case I

If the reaction under consideration proceeds directly from a singlet exciplex to products, *i.e.* reaction (6) operates but reactions (7) and (8) or (11) do not, then the following results obtain:

$$\tau_s^0 = 1/k_d$$

where $k_d = k_1 + k_2 + k_3$,

$$\tau_s^0/\tau_s' = F^0/F' = 1 + k_q'\tau_s^0[Q]$$

$$k_q' = \frac{k_4(k_5 + k_6)}{k_{dE}}$$

where $k_{dE} = k_{-4} + k_5 + k_6$. In these equations τ_s^0 is the lifetime of A in the absence of quencher and τ_s' is the lifetime of A in the presence of some quencher concentration $[Q]$. The ratio of the unquenched to quenched lifetimes is assumed to be equal to the ratio of unquenched to quenched intensities (for cautions, see refs. 1, 2 and 5). A plot of F^0/F' versus $[Q]$ yields a Stern–Volmer plot with slope $k_q'\tau_s^0$ where the rate constant for quenching k_q' is defined as shown.

The quantum yield for product formation Φ_{A-P}' and its inverse $(\Phi_{A-P}')^{-1}$ are given by the equations

$$\Phi_{A-P}' = \frac{k_4 k_6 [Q]/k_{dE}}{k_q'[Q] + k_d}$$

$$(\Phi_{A-P}')^{-1} = \frac{k_q' k_{dE}}{k_4 k_6} + \frac{k_d k_{dE}}{k_4 k_6}[Q]^{-1}$$

A plot of $(\Phi_{A-P}')^{-1}$ versus $[Q]^{-1}$ should yield a straight line with intercept-to-slope ratio i/s equal to the slope for the Stern–Volmer plot of fluorescence quenching by Q ($i/s = k_q'/k_d = k_q'\tau_s^0$). This is the expected result for a reaction proceeding from a singlet excited state, and an observation of such a result has been reported as evidence for product formation arising directly from a singlet exciplex (specific references to conclusions based on this type of correlation will not be given here). Such a conclusion should be supported by additional evidence, as shown below.

2.2. Case II

We consider a mechanism in which the singlet exciplex-mediated reaction is accompanied by a triplet mechanism arising from unimolecular intersystem crossing and bimolecular energy transfer (i.e. process (7) does not occur but processes (8) - (11) do). The following results obtain:

$$\Phi_{A-P}' = \frac{k_4 k_6 [Q]/k_{dE} + \beta k_3 \tau_T k_8 [Q]}{k_q'[Q] + k_d}$$

where

$$\beta = \frac{k_{11}}{k_{10} + k_{11}}$$

$$\tau_T = \frac{1}{k_9 + k_8 [Q]}$$

$$\tau_s' = \frac{1}{k_q'[Q] + k_d}$$

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and

$$(\Phi_{A-P}')^{-1} = (k_q' + k_d [Q]^{-1}) \left(\frac{k_4 k_6}{k_{dE}} + \frac{\beta k_3 k_8}{k_9 + k_8 [Q]} \right)^{-1}$$

In this case $(\Phi_{A-P}')^{-1}$ is a complex function of $[Q]^{-1}$ and a plot of $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ will not necessarily be linear. However, for those situations in which $[Q]$ is very small and either k_8 is small or k_9 is large (perhaps because of an inherently short triplet lifetime or efficient impurity quenching), $k_9 + k_8[Q] \approx k_9$ and an approximately linear correlation of $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ will result. Similarly, an approximately linear correlation may result at larger $[Q]$ if the rate constants are such that $k_4 k_6 / k_{dE}$ is much greater than $\beta k_3 k_8 / (k_9 + k_8[Q])$. A very low intersystem crossing rate constant (low k_3) or efficient triplet decay processes (large k_9) could produce such a result. In the higher $[Q]$ concentration range the greater is $[Q]$ the more singlets are intercepted and the fewer triplets are available for triplet-sensitized product formation. A plot of $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ will be linear because negligible triplet product formation occurs, and the intercept-to-slope ratio of that plot will equal $k_q' \tau_s^0$ as expected for a predominantly singlet reaction. Note that if a linear correlation of $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ is not observed over a particular $[Q]$ range, some triplet participation in product formation is evident. However, singlet exciplex-mediated product formation (process (6)) may still be occurring.

2.3. Case III

Now let us consider the mechanism in which exciplex-mediated intersystem crossing does occur (*i.e.* process (7) occurs in lieu of process (6)). The following discussion will assume that energy transfer from $A^{*(3)}$ to Q occurs rapidly in comparison with diffusion from the solvent cage in which the $A^{*(3)} Q$ pair is formed. For situations in which that assumption is valid (*vide infra*), the following results obtain:

$$(\Phi_{A-P}')^{-1} = (k_q' + k_d [Q]^{-1}) \left(\frac{\beta k_4 k_7}{k_{dE}} + \frac{\beta k_3 k_8}{k_9 + k_8 [Q]} \right)^{-1}$$

$$k_q' = \frac{k_4 (k_5 + k_7)}{k_{dE}}$$

where $k_{dE} = k_{-4} + k_5 + k_7$.

Again, a plot of $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ will be a complex function, but it may appear to be linear over some $[Q]$ ranges for the same reasons as discussed in case II if k_7 is similar in magnitude to k_6 (see ref. 3). We note that such a linear correlation for this case will have a slope-to-intercept ratio of $k_q'/k_d = k_q' \tau_s^0$, the same as the Stern–Volmer slope for fluorescence quenching, even though all the product is derived through the triplet state.
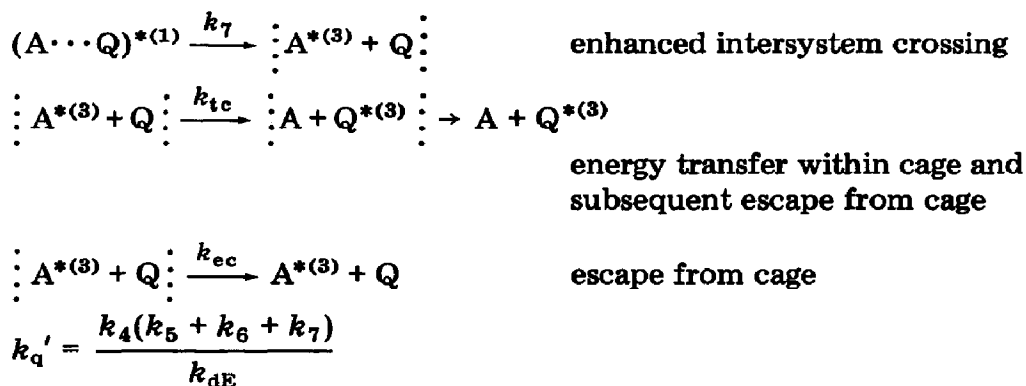
Comparison of the results for cases II and III indicates that a non-linear $(\Phi_{A-P}')^{-1}$ *versus* $[Q]^{-1}$ plot indicates some triplet involvement in product formation but does not rule out some singlet exciplex-mediated product

formation. Similarly, observation of an approximately linear $(\Phi_{A-P}')^{-1}$ versus $[Q]^{-1}$ plot indicates that quenching of singlet states is the dominant route to product formation, even if only over a particular range of $[Q]$. However, such a plot alone does not indicate whether the quenched singlets produce the product directly or via exciplex-mediated triplet states.

The validity of the discussion of case III is strongly dependent on the validity of the assumption that energy transfer from $A^{*(3)}$ to Q occurs before escape from the solvent cage. This assumption would seem to be reasonable for energy transfer reactions that are exothermic by a few kilocalories per mole. For those cases in which energy transfer is not efficient, the kinetics become more complex.

2.4. Case IV

We consider the most general mechanism in which both process (6) and process (7) are considered possible and in which process (7) is rewritten as shown below with two new processes added:

$$(A \cdots Q)^{*(1)} \xrightarrow{k_7} {:}A^{*(3)} + Q: \qquad \text{enhanced intersystem crossing}$$

$$:A^{*(3)} + Q: \xrightarrow{k_{tc}} :A + Q^{*(3)}: \rightarrow A + Q^{*(3)}$$

$$\text{energy transfer within cage and subsequent escape from cage}$$

$$:A^{*(3)} + Q: \xrightarrow{k_{ec}} A^{*(3)} + Q \qquad \text{escape from cage}$$

$$k_q' = \frac{k_4(k_5 + k_6 + k_7)}{k_{dE}}$$

where $k_{dE} = k_{-4} + k_5 + k_6 + k_7$. If ϵ is the fraction of triplets that transfer energy before cage escape ($\epsilon = k_{tc}/(k_{tc} + k_{ec})$), the equation for product formation is composed of four terms:

$$\Phi_{A-P}' = k_3 \beta k_8 \tau_T [Q] \tau_s' + \frac{k_4 k_6 \tau_s'[Q]}{k_{dE}} + \frac{k_4 k_7 [Q] \beta \epsilon \tau_s'}{k_{dE}} +$$

$$+ \frac{(1 - \epsilon)\beta \tau_s' k_8 \tau_T [Q]^2 k_4 k_7}{k_{dE}}$$

The first term represents the product formed by unimolecular intersystem crossing and bimolecular energy transfer, the second term represents the product formed directly from a singlet exciplex, the third term represents the product formed by enhanced intersystem crossing and energy transfer within the solvent cage, and the fourth term represents the product formed by exciplex-enhanced intersystem crossing, escape of $A^{*(3)}$ from the solvent cage and subsequent energy transfer. Now $(\Phi_{A-P}')^{-1}$ is the following:

$$(\Phi_{A-P}')^{-1} = (k_q' + k_d[Q]^{-1}) \left\{ \frac{\beta k_3 k_8}{k_9 + k_8[Q]} + \frac{k_4 k_6}{k_{dE}} + \frac{\epsilon \beta k_4 k_7}{k_{dE}} + \right.$$

$$\left. + \frac{(1 - \epsilon)\beta k_8 k_4 k_7}{k_{dE}(k_9 + k_8[Q])} \right\}^{-1}$$

Intuitively, if ϵ is small, then k_8 is probably small as well. However, it would be difficult to predict the relative magnitudes of the four terms in braces and thus difficult to predict the relative linearity of the plot of $(\Phi_{A-P}')^{-1}$ versus $[Q]^{-1}$. To the extent that such a plot does appear to be linear, however, the intercept-to-slope ratio remains $k_q' \tau_s^0$.

As the previous discussion has indicated, the observation of an apparently linear $(\Phi_{A-P}')^{-1}$ versus $[Q]^{-1}$ plot may be consistent with several mechanistic schemes. If sufficient rate constant and lifetime data are available to show that any triplet product formation should cause curvature of $(\Phi_{A-P}')^{-1}$ versus $[Q]^{-1}$ or if normal bimolecular triplet sensitization does not produce the product proposed in eqn. (6), then the argument for case I will be strengthened. The molecular systems most likely to provide ambiguous results are those with low rates of intersystem crossing from $A^{*(1)}$ (low k_3), and in these cases the products of $A^{*(3)}$ sensitization of Q may not be known. If so it may be useful to explore heavy atom enhancement of intersystem crossing, a method used by a number of groups to elucidate photochemical and photophysical processes [6 - 9] (a related application of heavy atom effects to the determination of the multiplicity of reacting states is given in ref. 10). Although heavy atoms may be incorporated into charge transfer quenchers that may quench with multiple decay pathways, heavy atom quenchers such as xenon have been shown to quench singlets to triplets efficiently [8].

2.5. Case V

We consider the mechanism assumed in case III. In a study carried out with a fixed concentration of Q and with varying concentrations of a heavy atom additive H, the following additional step occurs [6, 8]:

$$A^{*(1)} + H \xrightarrow{k_{12}} A^{*(3)} + H \qquad \text{enhanced intersystem crossing} \qquad (12)$$

In the equations below, the primes indicate values measured in the presence of Q but in the absence of H. (Throughout this paper zero superscripts refer to values measured in the absence of both Q and H.) Symbols without superscripts are for parameters measured in the presence of both Q and H. At constant $[Q]$, τ_T is presumed constant:

$$\tau_s = \frac{1}{k_d + k_q'[Q] + k_{12}[H]} \qquad \tau_s' = \frac{1}{k_d + k_q'[Q]}$$

$$\tau_s'/\tau_s = F'/F = 1 + k_{12}\tau_s'[H]$$

$$\frac{\Phi_{A-P}}{\Phi_{A-P}'} = \frac{(k_3 + k_{12}[H])\tau_s k_8 [Q]\beta\tau_T + k_4\tau_s\beta k_7 [Q]/k_{dE}}{k_3 k_8 \tau_s' [Q]\beta\tau_T + k_4\tau_s'\beta k_7 [Q]/k_{dE}}$$

$$\frac{\Phi_{A-P}}{\Phi_{A-P}'}\frac{F'}{F} = 1 + \frac{k_{12}k_8\tau_T}{k_3 k_8 \tau_T + k_4 k_7/k_{dE}}[H]$$

A plot of $(\Phi_{A-P}/\Phi_{A-P}')(F'/F)$ *versus* [H] should yield a linear correlation if triplets can sensitize the reaction. Observation of a zero slope will suggest exclusively singlet responsibility for the reaction [10] (this conclusion is correct, of course, only if [Q] is great enough for quenching of $A^{*(3)}$ by Q to be significant).

3. Conclusion

In summary, kinetic studies of product formation arising from singlet quenching interactions can give useful information about the nature of the excited state interactions[†]. However, such data must be interpreted with the knowledge that more than one type of process can appear to give the same kinetic result. Other information about the photochemistry and photophysics of the system should be available to reinforce conclusions based on the kinetic studies.

Acknowledgments

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[†]Some other publications relating the kinetics of excited state reactions to multiplicities have appeared. In particular, Dalton and Snyder [11] have presented a kinetic analysis for bimolecular reactions involving more than one excited state but not involving exciplexes. Farid *et al.* [12] have considered a more complicated situation involving product formation from both a singlet exciplex and from a triplet exciplex formed from it.

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