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AN ANALYSIS OF HEAVY-ATOM PERTURBATION OF INTERSYSTEM CROSSING AS A MECHANISTIC TOOL IN PHOTOCHEMISTRY

PROBING FOR SINGLET AND TRIPLET DOMINATED REACTIONS[1,2]

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Abstract—A kinetic analysis of heavy-atom enhanced intersystem crossing is presented, with the object of using this perturbation method for determining whether the majority of a photoproduct originates from an excited singlet or an excited triplet precursor. Expressions are derived which relate the quantum efficiencies of product formation (ϕ_r) and $S_1 \rightarrow T_1$ intersystem crossing (ϕ_{isc}) with potential quenching or enhancement by the heavy-atom. These allow limits to be placed on the possible quenching or enhancement that may be observed in particular cases (see Fig. 4 and 6) and thereby make an interpretation of the data less ambiguous than has been suggested in recent discussions. A particularly useful observation is that for those molecules (for example, aromatics) having triplets which are relatively unaffected by heavy-atoms, quenching of a product by more than 50% demonstrates that a majority of this product must be derived from the excited singlet state.

Heavy-atom enhanced $S_1 \rightarrow T_1$ intersystem crossing has proven quite useful in synthetic and mechanistic photochemistry. Molecules having a π,π^* S_1 state are particularly susceptible to such enhancement[3] and xenon, for example, has been used to determine ϕ_{isc}[4,5] and to probe for the involvement of singlet and/or triplet states in photoproduct formation.[6] One approach to the latter application is to determine whether xenon quenches or enhances a photoreaction. Thus, if separate Stern–Volmer analyses of xenon quenching of a reactant's fluorescence and of its product formation give identical slopes, the reaction is entirely derived from the excited singlet state.[7] However, it is commonplace for both singlet and triplet states to participate in a photoreaction, and kinetic analyses by Birks[8] and by Caroll[7] have demonstrated that, under such circumstances, *quenching* unambiguously confirms that a majority of the product is *singlet* derived so long as the unperturbed $\phi_{isc} \leq 0.5$. The observation of xenon induced enhancement likewise indicates a triplet dominated reaction when the unperturbed $\phi_{isc} \geq 0.5$. Unfortunately, ϕ_{isc} is frequently difficult to measure and the above cited restrictions imply large regions of ambiguity even when ϕ_{isc} is known. These limitations have led to a justifiable questioning of the utility of heavy-atom perturbation as a general mechanistic tool.[7]

We have considered the kinetics of xenon perturbation in greater detail, with particular emphasis on the role of the quantum efficiency of product formation (ϕ_R) in the interpretation of the data. We assume that the substrate triplet will be ineffectively quenched by xenon,[7,8] an assumption for which there is ample experimental evidence with aryl triplets[4,5] and which is readily tested[4] (the kinetic implications of a large $T_1 \rightarrow S_0$ effect are discussed later in this paper). Our conclusion is that the regions of ambiguity are smaller than previously suspected and that limits can be placed upon the amount of *quenching* theoretically observable for a predominantly *triplet* derived photoproduct, or the amount of *enhancement* observable for a predominantly *singlet* derived photoproduct. An especially useful observation is that *the quenching of a photoreaction by more than 50% requires that a majority of the product is derived from the singlet state, regardless of the substrate* ϕ_{isc}.

DISCUSSION

A. *Definitions and kinetic scheme*

We will initially consider the following processes[7,8]:

$$A \xrightarrow{h\nu} S_1 \quad \text{excitation} \tag{1}$$

$$S_1 \xrightarrow{k_2} A(+h\nu') \quad \text{singlet decay} \tag{2}$$

$$S_1 \xrightarrow{k_{RS}} P \quad \text{singlet product formation} \tag{3}$$

$$S_1 \xrightarrow{k_{isc}} T_1 \quad \text{intersystem crossing} \tag{4}$$

$$T_1 \xrightarrow{k_4} A(+h\nu'') \quad \text{triplet decay} \tag{5}$$

$$T_1 \xrightarrow{k_{RT}} P \quad \text{triplet product formation} \tag{6}$$

$$S_1 + H \xrightarrow{k_7} T_1 + H \quad \text{enhanced intersystem crossing.} \tag{7}$$

Quantum efficiencies are then defined as follows: ϕ_{RS} for product formation from the singlet state, ϕ_{RT} as the fraction of triplet which goes to the product (the "intrinsic" triplet state quantum efficiency) and ϕ_R as the unperturbed total quantum efficiency for product formation (i.e. eqn 8). A "predominantly singlet derived

$$\phi_R = \phi_{RS} + \phi_{isc}\phi_{RT} \tag{8}$$

product" is one which $\phi_{RS} > \phi_{isc}\phi_{RT}$, and a "predominantly triplet derived product" is one for which $\phi_{RS} < \phi_{isc}\phi_{RT}$. The xenon perturbed efficiency of product formation is represented as $\phi_R{}^P$.

B. *Xenon quenching of product formation*

The concept of limiting quenching. Equation (9) gives the rate of product formation which, upon using the steady-state approximation and incorporating heavy-atom perturbed intersystem crossing, leads to eqn (10).

$$\frac{d[P]}{dt} = k_{RS}[S_1] + k_{RT}[T_1] \tag{9}$$

$$\phi_R{}^P = \frac{1}{k_2 + k_{RS} + k_{isc} + k_7[H]}\left[k_{RS} + \frac{k_{RT}(k_{isc} + k_7[H])}{k_5 + k_{RT}}\right]. \tag{10}$$

Using $\phi_{RT} = k_{RT}(k_5 + k_{RT})$, ${}^1\tau = 1(k_2 + k_{RS} + k_{isc})$, $\phi_{RS} = k_{RS}{}^1\tau$ and $\phi_{isc} = k_{isc}{}^1\tau$, eqn (10) reduces to eqn (11). We may define the

$$\phi_R{}^P = \frac{\phi_R + \phi_{RT}{}^1\tau k_7[H]}{1 + {}^1\tau k_7[H]} \tag{11}$$

fraction of quenching (Q) as in eqn (12), and combining eqn (11) and

$$Q = \frac{\phi_R - \phi_R{}^P}{\phi_R} = 1 - \frac{\phi_R{}^P}{\phi_R} \tag{12}$$

(12), gives eqn (13). Inversion of eqn (13) and expansion

$$Q = \frac{(\phi_R - \phi_{RT}){}^1\tau k_7[H]}{\phi_R(1 + {}^1\tau k_7[H])} \tag{13}$$

then gives eqn (14), the dependence of quenching on xenon concentration. Note

$$\frac{1}{Q} = \frac{\phi_R}{\phi_R - \phi_{RT}}\left[1 + \frac{1}{{}^1\tau k_7[H]}\right] \tag{14}$$

from eqn (14) that (1) when $\phi_{RT} > \phi_R$, Q *is negative and this represents enhancement of reaction*, (2) when $\phi_{RT} < \phi_R$, Q *is positive and this represents quenching of reaction*, (3) *limiting quenching occurs at infinite* [H], at which point eqn (15) becomes valid (note that at $[H]_\infty$, $\phi_R{}^P$ becomes ϕ_{RT} and $\phi_{isc} = 1.0$, see eqn (12)).

$$Q_{lim} = \frac{\phi_R - \phi_{RT}}{\phi_R} = 1 - \frac{\phi_{RT}}{\phi_R}. \tag{15}$$

The dependence of Q_{lim} on ϕ_{RS}, ϕ_{RT} and ϕ_{isc} is obtained by combining eqn (8) and eqn (15), and dividing by ϕ_{isc}, to give eqn (16). It may be seen from this equation that (1) $Q_{lim} \rightarrow 1.0$ (i.e.

$$\frac{\phi_{RS}}{\phi_{RT}\phi_{isc}} = \frac{1}{\phi_{isc}(1 - Q_{lim})} - 1 \tag{16}$$

100% quenching) as $\phi_{RS}/\phi_{isc}\phi_{RT} \rightarrow \infty$ (i.e. pure singlet derived product), (2) for a particular ϕ_{isc}, the equation defines ϕ_{RS}/ϕ_{RT} ratios for which $Q_{lim} = 0$, with further decreases in $\phi_{RS}/\phi_{RT}\phi_{isc}$ leading to negative Q_{lim} values (i.e. enhancement). Heavy atom enhancement is treated later, and eqn (16) is plotted in Fig. 1 to show positive values of Q_{lim} for several values of ϕ_{isc}. Note, in this figure, that $\phi_{isc} = 0.5$ is an important cross-over point; any quenching observed for $\phi_{isc} \le 0.5$ requires that $\phi_{RS} > \phi_{isc}\phi_{RT}$ (i.e. that a majority of the reaction is singlet derived) but when $\phi_{isc} > 0.5$, quenching may also be observed for triplet dominated reactions.[7,8]

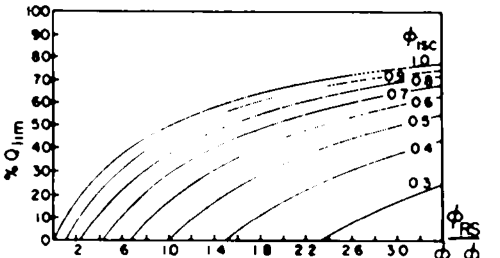

Fig. 1. % Q_{lim} vs $\phi_{RS}/\phi_{isc}\phi_{RT}$ using $\frac{\phi_{RS}}{\phi_{isc}\phi_{RT}} = \frac{1}{\phi_{isc}(1 - Q_{lim})} - 1$ with only positive values of Q shown.

Limiting triplet quenching. For any ϕ_{isc} value >0.5, there is a maximum Q_{lim} that a triplet dominated reaction can attain, and this limit is reached as $\phi_{RS}/\phi_{isc}\phi_{RT} \rightarrow 1.0$. Using this fact, one can insert $\phi_{RS} = \phi_{isc}\phi_{RT}$ into eqn (16) to obtain a limiting Q value for a triplet dominated reaction (Q^T_{lim}); see eqn (17). Equation (17) is plotted in Fig. 2 and it is obvious that the maximum possible quenching that can be observed for a photoproduct

$$Q^T_{lim} = 1 - \frac{1}{2\phi_{isc}} \tag{17}$$

which is predominantly triplet derived is approached at $\phi_{isc} \rightarrow 1.0$, and equals 50% quenching. Thus, *if greater than 50% quenching is observed for a photoproduct, it must be predominantly singlet derived, regardless of the values of ϕ_R, ϕ_{RS}, ϕ_{isc}, ϕ_{RT} or the fraction of singlet states intercepted by xenon.*[9]

Obviously, experimentally attainable Q values will depend on the xenon concentration and substrate singlet lifetime (*cf* eqn (14)). Using previously described techniques,[5] we have readily observed as much as 79% quenching of the photosolvolytic rearrangement of exo-

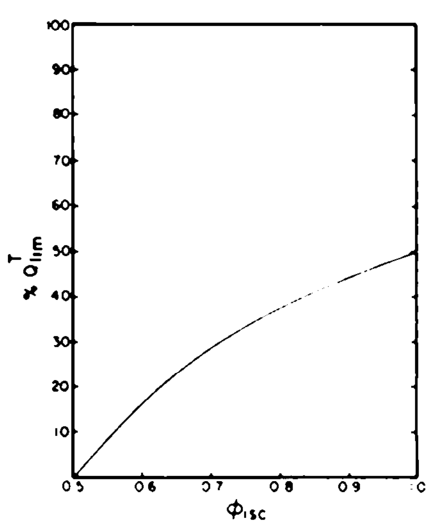

Fig. 2. % Q^T_{lim} vs ϕ_{isc} using $Q^T_{lim} = 1 - \frac{1}{2\phi_{isc}}$.

benznorbornen-2-yl methanesulfonate (${}^1\tau \sim 7$ nsec).[10] and 61% quenching of the photoinduced anti-Markovnikov addition of methanol to 2-isopropylidenebenznorbornene (${}^1\tau = 4$ nsec).[11] Measurements of Q exceeding 50% should therefore be experimentally feasible for many singlet dominated reactions.

The concept of maximum quenching. Discussion so far has centered on the influence of ϕ_{isc} on Q_{lim}. The relationship of Q_{lim} to ϕ_R is also instructive and it is clear from eqn (15) that Q_{lim} increases as ϕ_R increases. Since ϕ_R depends on ϕ_{RS} and $\phi_{isc}\phi_{RT}$ (eqn 8), this is equivalent to stating that S_1 internal conversion to S_0 reduces the potential ϕ_R, and we can define a maximum Q_{lim} ("Q_{max}") as the Q_{lim} when $S_1 \rightarrow S_0$ decay is absent (eqn 18).

$$Q_{max} = Q_{lim} \text{ when } \phi_{RS} = 1 - \phi_{isc}. \tag{18}$$

Substituting eqn (18) into eqn (8), solving for ϕ_{RT} and inserting the resulting expression into eqn (15) provides an expression for Q_{max} in terms of ϕ_R and ϕ_{isc} (eqn 19).

$$Q_{max} = \frac{(\phi_{isc} - 1)(\phi_R - 1)}{\phi_R \phi_{isc}} \tag{19}$$

A further restriction results from the requirement that $\phi_{RS} \leq \phi_R$, so that at Q_{max} (where $\phi_{RS} = 1 - \phi_{isc}$), $\phi_{isc} \geq 1 - \phi_R$. With this boundary condition, eqn (19) is plotted in Fig. 3 for $\phi_R = 0.4$; the plot defines theoretically attainable quenching values for a photoproduct of such ϕ_R, as a function of ϕ_{isc} and regardless of the degree of singlet or triplet involvement. Were such a plot to be drawn for other ϕ_R's, it would be evident that the "impossible Q" region increases as ϕ_R increases.

Quenching plots. One can now combine eqn (17) [which defines the limiting quenching of a predominantly triplet derived photoproduct (see Fig. 2)] with eqn (19) [which defines maximum quenching regardless of origin (see Fig. 3)] to produce "quenching plots" for any value of ϕ_R (see Fig. 4 for $\phi_R = 0.4$). Point H in Fig. 4 corresponds to eqn (20), and therefore, to eqn (21).

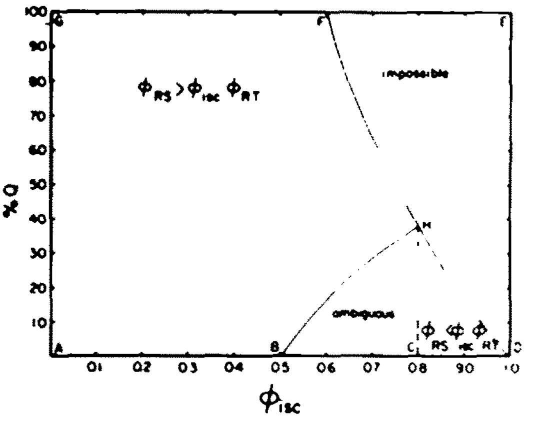

Fig. 4. "Quenching plot" for $\phi_R = 0.40$ using eqn (17) and eqn (19).

$$1 - \frac{1}{2\phi_{isc}} = \frac{(\phi_{isc} - 1)(\phi_R - 1)}{\phi_R \phi_{isc}} \tag{20}$$

$$\phi_{isc} = 1 - \frac{\phi_R}{2}. \tag{21}$$

Such quenching plots may be conveniently subdivided into several well defined regions.

(1) FED. Defined by arc FD (eqn 11), this region corresponds to theoretically impossible quenching.

(2) AGFHB. Any quenching observed in this region requires that the photoproduct be predominantly singlet derived. Since the maximum possible quenching observable for a predominantly triplet derived photoproduct is point H, for $\phi_R = 0.40$ any quenching greater than 37.5% indicates a majority of the product is of singlet origin, regardless of ϕ_{isc} or the percentage of singlet states intercepted by xenon.

(3) CHD. This is a region where the photoproduct must be primarily triplet derived (i.e. if $\phi_{isc} > 0.8$ and $\phi_R = 0.40$, $\phi_{RS} < 0.2$ and $\phi_{isc}\phi_{RT} > \phi_{RS}$).

(4) BHC. This is the only region which is ambiguous; quenching in this region could indicate a majority of the product is triplet derived or could correspond to incomplete quenching of a singlet dominated product. By plotting 1/Q vs 1/[H] (see eqn 14), one can obtain Q_{lim} from the intercept (see eqn 15) and eliminate the remaining ambiguity.

Although a knowledge of ϕ_{isc} is useful to interpret Q values below point H, the regions of ambiguity are not large and, for example, 30% quenching when $\phi_R = 0.40$ is only ill-defined for ϕ_{isc} between 0.73 and 0.80. Though the exact ϕ_{isc} may not be known, a comparison with a model system may well permit one to say that ϕ_{isc} is less than 0.7. Finally, if ϕ_{isc} can be measured, a plot of 1/Q vs 1/[H] (eqn 14) will give Q_{lim} and the use of eqn (16) and eqn (8) will provide ϕ_{RS} and ϕ_{RT}.

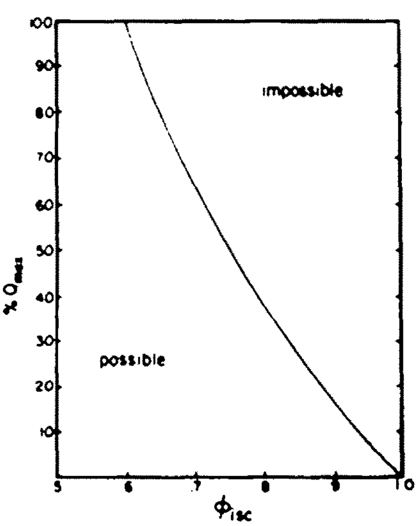

Fig. 3. % Q_{max} vs ϕ_{isc} for $\phi_R = 0.40$ using $Q_{max} = \frac{(\phi_{isc} - 1)(\phi_R - 1)}{\phi_R \phi_{isc}}$.

C. *Xenon enhancement of product formation*

It was noted earlier that $-Q$ represents enhancement, i.e. compare eqns (12) and (22). We can thus expand our

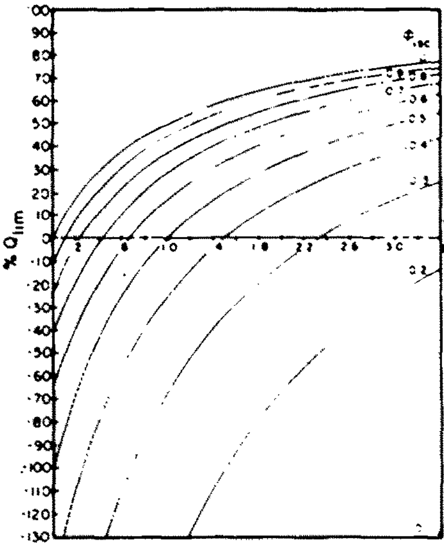

Fig. 5. % Q_{lim} vs $\phi_{RS}/\phi_{isc}\phi_{RT}$ using $\frac{\phi_{RS}}{\phi_{isc}\phi_{RT}} = \frac{1}{\phi_{isc}(1-Q_{lim})} - 1$ with negative values of Q ("enhancement") included (compare Fig. 1).

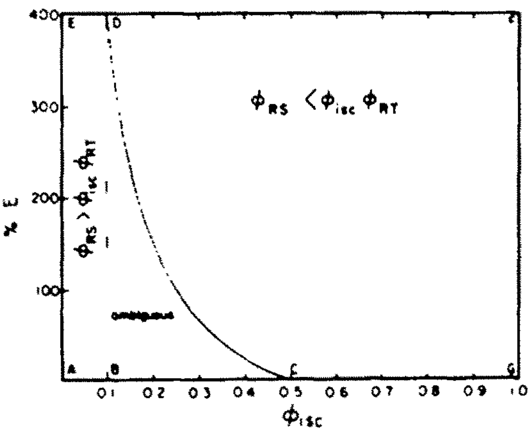

Fig. 6. "Enhancement plot" for $\phi_R = 0.20$ using eqn (24) and eqn (25).

plot of eqn (16) (see

$$Q = \frac{\phi_R - \phi_R^{P}}{\phi_R} \tag{12}$$

$$E = \frac{\phi_R^{P} - \phi_R}{\phi_R} \tag{22}$$

$$E = -Q \tag{23}$$

Fig. 1) to include $-Q$ values (Fig. 5). As before, $\phi_{isc} = 0.5$ is the critical cross-over point; any enhancement observed for $\phi_{isc} \geq 0.5$ requires that $\phi_{isc}\phi_{RT} > \phi_{RS}$, but when $\phi_{isc} < 0.5$ enhancement may also be observed for singlet dominated reactions.[7,8] In fact, one can see from the Figure that the latter effect may be quite large.

The concepts of limiting singlet enhancement (E^S_{lim}) and maximum enhancement (E_{max}) are analogous to those used for Q^T_{lim} and Q_{max}. E^S_{lim} is defined by eqn (24) (see eqn (17)) and E_{max} is eqn (22) with $\phi_R^{P} = 1.0$, i.e. eqn (25). These equations allow the construction

$$E^S_{lim} = \frac{1}{2\phi_{isc}} - 1 \tag{24}$$

$$E_{max} = \frac{1-\phi_R}{\phi_R} \tag{25}$$

of "enhancement plots", an example of which is given in Fig. 6 for $\phi_R = 0.2$.

The Figure may be subdivided as follows:

(1) DFGC. Since arc DC represents eqn (24), any enhancement observed in this region requires that the photoproduct be predominantly triplet derived. Note that line ED is defined by eqn (25).

(2) AEDB. This is the region where the photoproduct must be primarily singlet derived (i.e. if $\phi_{isc} < 1.0$ and $\phi_R = 0.20$, $\phi_{RS} > \phi_{isc}\phi_{RT}$).

(3) BDC. This is the ambiguous region where enhancement could indicate a majority of the product is singlet derived or there is incomplete quenching of a triplet dominated reaction. A plot of 1/Q vs 1/[H] could resolve the ambiguity by providing E_{lim} and, as with quenching, an additional measurement of ϕ_{isc} would then furnish ϕ_{RS} and ϕ_{RT}.

D. *Xenon perturbation with triplet quenching*

The kinetic scheme presented at the beginning of this paper presumes no effect by [H] on T_1 (eqn 26). Inclusion of this reaction changes ϕ_R^{P} (eqn 11) to eqn (27) and eqn (13) to eqn (28).

$$T_1 + H \rightarrow S_0 + H \tag{26}$$

$$Q_R^{P} = \frac{\phi_R + [\phi_{RS}{}^3\tau k_{26} + \phi_{RT}{}^1\tau k_7[H]}{(1 + {}^3\tau k_{26}[H])(1 + {}^1\tau k_7[H])} \tag{27}$$

$$Q = 1 - \frac{\phi_R + [\phi_{RS}{}^3\tau k_{26} + \phi_{RT}{}^1\tau k_7][H]}{\phi_R(1 + {}^3\tau k_{26}[H])(1 + {}^1\tau k_7[H])}. \tag{28}$$

Expansion and inversion gives eqn (29).[12] Only in rare circumstances

$$\frac{1}{Q} = \frac{1 + [{}^1\tau k_7 + {}^3\tau k_{26}][H] + {}^1\tau k_7{}^3\tau k_{26}[H]^2}{[{}^1\tau k_7(\phi_R - \phi_{RT}) + {}^3\tau k_{26}(\phi_R - \phi_{RS})]\frac{[H]}{\phi_R} + {}^1\tau k_7{}^3\tau k_{26}[H]^2} \tag{29}$$

would eqn (29) give rise to a linear dependence of [Q] on [H]; curvature of a 1/Q vs 1/[H] plot would be the more general observation and an indication that triplet quenching was setting in.

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