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OPTIMIZATION OF PRODUCT QUANTUM YIELD IN SENSITIZED PHOTOCYCLOADDITIONS

H. Leismann, H.W. Gaidetzka, J. Berix, J. Mattay, H.D. Scharf^x

Institut für Organische Chemie, Lehrstuhl II, der RWTH Aachen, D-5100 Aachen, Prof.-Pirlet-Str.1

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Introduction: Product quantum yields of triplet-sensitized additions - ${}^3A^x + B \rightarrow$ adducts - depend on the yields of intersystem crossing of the sensitizer (Φ_{isc}^{sens}), triplet energy transfer to the molecule A (Φ_{ET}^{A}) and addition of the triplet excited molecule ${}^3A^x$ to ground state molecule B (Φ_{Add}^{B})[1]:

$$\Phi_P = \Phi_{isc}^{sens} \cdot \Phi_{ET}^{A} \cdot \Phi_{Add}^{B} \,. \qquad (1)$$

The determination of Φ_{ET}^{A} and Φ_{Add}^{B} from the measured product quantum yield Φ_P and the kinetic SCHEME 1 gives informations about the efficiency of the sensitizer and the reactivity of the triplet molecule ${}^3A^x$. From these parameters one can furthermore calculate the optimal concentration ratio $[A]/[B]$, since B can also quench the sensitizer triplet and thus hinder the desired reaction.

1.) Sensitizing process:

$$\left.{}^3\text{sens}^x + A \xrightarrow{k_q^A} {}^3A^x + \text{sens}\right\} \text{(sensitization neglecting energy wasting)}^{2)}$$

$$\left.\begin{array}{l} {}^3\text{sens}^x + B \xrightarrow{k_q^B} {}^3B^x \text{ or } B) + \text{sens} \\ {}^3\text{sens}^x \xrightarrow{1/\tau_{sens}} \text{sens} \end{array}\right\} \text{deactiviation}$$

$$\Phi_{ET}^{A} = \frac{k_q^A \cdot [A]}{k_q^A \cdot [A] + k_q^B \cdot [B] + 1/\tau_{sens}} \qquad (2)$$

2.) Addition process for a particular adduct.

$$\left.{}^3A^x + B \xrightarrow{k_{Add}} \text{adduct}\right\} \text{reaction}$$

$$\left.\begin{array}{l} {}^3A^x + B \xrightarrow{k_{DA}} A + (B \text{ or } {}^3B^x) \\ {}^3A^x \xrightarrow{1/\tau_A} A \end{array}\right\} \text{deactivation}$$

$$\Phi_{Add}^{B} = \frac{k_{Add} \cdot [B]}{k_{Add} \cdot [B] + k_{DA} \cdot [B] + 1/\tau_A} \qquad (3)$$

Scheme 1 Kinetic scheme for triplet-sensitized adduct formation (The rate constants k_{DA} and k_{Add} can also describe addition and adduct formation via a common metastable intermediate.)

EQUATIONS (1)-(3) give the expression for the product quantum yield:

$$\frac{\Phi_{isc}^{sens}}{\Phi_P} = \left(\frac{k_{DA}}{k_{Add}} + 1\right) \cdot \left(1 + \frac{1/\tau_{sens}}{k_q^A \cdot [A]}\right) + \frac{1}{\tau_A \cdot k_{Add}} \cdot \frac{k_q^B}{k_q^A \cdot [A]} \qquad (4.1)$$

$$+ \frac{1}{\tau_A \cdot k_{Add}} \cdot \left(1 + \frac{1/\tau_{sens}}{k_q^A \cdot [A]}\right) \cdot [B]^{-1} \qquad (4.2)$$

$$+ \frac{k_q^B}{k_q^A \cdot [A]} \cdot \left(1 + \frac{k_{DA}}{k_{Add}}\right) \cdot [B] \qquad (4.3)$$

The derivative of Φ_P with respect to B gives the concentration B_{max} for the largest possible product quantum yield for a particular concentration of A and a particular sensitizer:

$$[B]_{max} = \left(\frac{1/(\tau_A \cdot k_{Add}) \cdot (k_q^A [A] + 1/\tau_{sens})}{k_q^B \cdot (1 + k_{DA}/k_{Add})}\right)^{1/2} \qquad (5)$$

for sufficiently small concentrations of B the third term in EQU. (4) is negligible and a plot of $1/\Phi_P$ versus $1/[B]$ is linear and yields the values of k_{DA}/k_{Add} and $1/(\tau_A \cdot k_{Add})$ from its slope and intercept (FIGURE 2).

Results and discussion: The four sensitized (2+2)-photocycloadditions in TABLE 1 serve as a test for the applicability of equations (1)-(5) to mechanistic evaluation and optimization of the considered reactions. Provide that either of the two partners alternatively can initiate the reaction by quenching the triplet sensitizer, those processes indicated by $\Phi_{Add} > 1$ have to be excluded. So it can be decided, that reactions 2 and 4 proceed via triplet of I, while reactions 1 and 3 proceed via triplet of II.

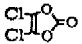
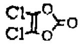
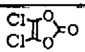
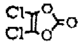
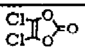
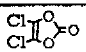
reaction No.	Lit.	triplet-sensitized partner A[8]	ground state partner B[8]	$\frac{k_q^A \cdot \tau_{Bu}}{M^{-1}}$	Φ_P[9]	Φ_{Add}^B
1	5	 I		12.4	.30	(3.9)
		 II		149.		.33
2	4	 I		12.4	.72	.85
		 III		1.9		(5.5)
3		 II		149.	.019	.02
		 III		1.9		(1.5)
4	3	 I		12.4	.12	.13
		 IV		13.4		(5.7)

TABLE 1: Overall yields of product-formation (Φp) and of addition of the triplet-sensitized partner $^3A^\times$ to ground state partner B (Φ_{Add}^B). Solvent: dioxane, 20°C; Sensitizer: acetophenone, $\Phi_{isc}^{sens} = 1$. Φ_{Add}^B is calculated by EQUs. (1) and (2), where the needed k_q-values are replaced by the Stern-Vollmer quenching constants $k_q \cdot \tau_{Bu}$ of the type-II-cleavage of butyrophenone.

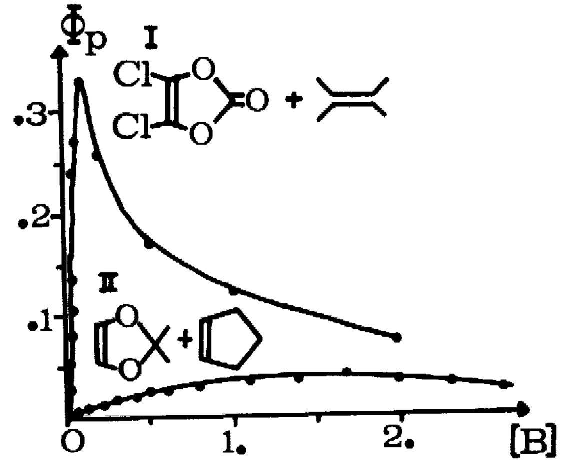


FIGURE 1:
Variation of product quantum yield of reactions 3 and 4 with concentration of ground state partner B (tetramethylethylene or cyclopentene).

[I] = .5 M [II] = .06 M

sensitizer: .08 M acetophenone

solvent: dioxane, 20 ^{o}C

FIGURE 1 shows as an example the behaviour of product quantum yield in reactions 3 and 4 with increasing concentration of ground state partner B (III or IV) in accordance to EQU. 4: For small concentrations of B Φ_p increases with the reciprocal of term (4.2), in the range of high concentrations Φ_p decreases with the reciprocal of term (4.3), so that a maximum obtainable value Φ_p^{max} exists. This maximum is broad for of $k_q^A \gg k_q^B$, and it is narrow for $k_q^A \approx k_q^B$.

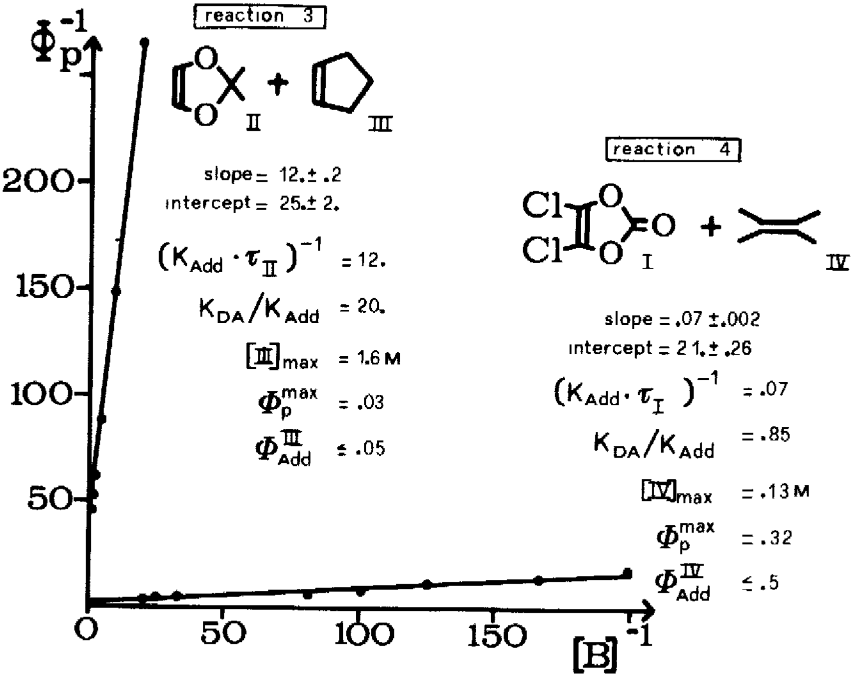


FIGURE 2:

Dilution plots corresponding to FIGURE 1 for "small" concentrations of B.

FIGURE 2 shows the corresponding linear plots with respect to small concentrations of B. From these plots the indicated reaction parameters can be calculated:

i) Lifetime of reactive triplet state $^3A^x$

In reaction 3 the rate constant of intramolecular deactivation of the reactive triplet molecule is 12 times faster than the rate constant of the reaction, whereas in reaction 4 this ratio is reverse.

ii) Chemical deactivation of the reactive triplet state

In reaction 3 the rate constant for the chemical deactivation k_{DA} is 20 times the constant for adduct-formation, whereas in reaction 4 these constants are of the same order of magnitude.

i and ii) explain the relative small product quantum yield of reaction 3.

iii) The calculated values of $[B]_{max}$ and Φ_P^{max} fit the experimental facts (FIGURE 1).

iv) For $[B] \rightarrow \infty$ in EQU. (3) one can calculate the maximum possible yield of addition:

$$\Phi^{B}_{Add} \leqslant (1 + k_{DA}/k_{Add})^{-1}$$

The corresponding values of .05 and .5 for reaction 3 and 4 respectively indicate, that the reactivity of triplet I to IV is 10 times the reactivity of triplet II to III.

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in: Creation and detection of the excited state, A.A. Lamola ed.
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2) Because of the rigidity of the molecules considered, the energy wasting process during energy transfer observed by Gupta and Hammond (JACS 98, 1218 (1976)) on sterically hindred acyclic olefines is assumed to be negligible.

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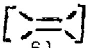
8) Concentrations of substrates = .5 M with the exception of


= .01 M

Dimerization of I[6] and III[7] are very inefficient.
Dimerization of III is about 10 % in reaction 3.

9) Measured by potassium-ferri-oxalate actinometry at 312 nm