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TRIPLET QUANTUM YIELD DETERMINATION BY PHOTOSENSITIZED OXYGENATION IN THE PRESENCE OF HEAVY ATOM ADDITIVES: EOSIN IN METHANOL

Klaus Gollnick* and Mohamed F.R. Fouda

Institut für Organische Chemie der Universität, Karlstr. 23, D-8000 München 2, Germany

Summary Relative rates of heavy-atom-enhanced photosensitized $^1O_2$-reactions and relative quantum efficiencies of heavy-atom-quenched fluorescence yield $\phi_T^o = 0.66 \pm 0.03$ for a $5 \cdot 10^{-5}$ M methanolic solution of Eosin.

In the preceding paper [1] we have described a rather simple procedure to obtain triplet quantum yields, ϕ_T^o, of molecules which are able to sensitize singlet oxygen reactions. The procedure makes use of the fact that heavy atom additives (Q) enhance the rate of oxygen consumption due to an increased production of triplet sensitizer molecules:

$S_1 \xrightarrow[k_q]{+Q} T_1$.

In the present paper further experimental evidence will be offered that the basic assumptions about the mechanism on which the procedure is based are sound.

Under certain (experimentally easily attainable) conditions [1], under which triplet counting by energy transfer from the triplet sensitizer to $^3O_2$ to give singlet oxygen ($^1O_2$) as well as trapping of $^1O_2$ by an acceptor like 2,5-dimethylfuran are both quantitative, the rate of O_2 - consumption in a heavy-atom-free solution is given by

$$v_o = I_a k_t \tau_F^o \qquad \text{(equ. 1)}$$

whereas in the presence of heavy atom additives the rate is

$$v_Q = I_a (k_t + k_q[Q]) \tau_F^Q \qquad \text{(equ. 2)}$$

with I_a = number of light quanta absorbed, $\tau_F^o = 1/(k_f + k_{ic} + k_t)$, $\tau_F^Q = 1/(k_f + k_{ic} + k_t + k_q[Q])$, and k_f, k_{ic}, and k_t = rate constants of fluorescence, internal conversion, and intersystem crossing, respectively.

Only measurements of relative rates v_o / v_Q at various concentrations of the added heavy atom compounds are necessary to determine ϕ_T^o, since

$$(1 - v_o/v_Q)^{-1} = (1 - \phi_T^o)^{-1} (1 + k_t/k_q[Q]) \qquad \text{(equ. 3)}$$

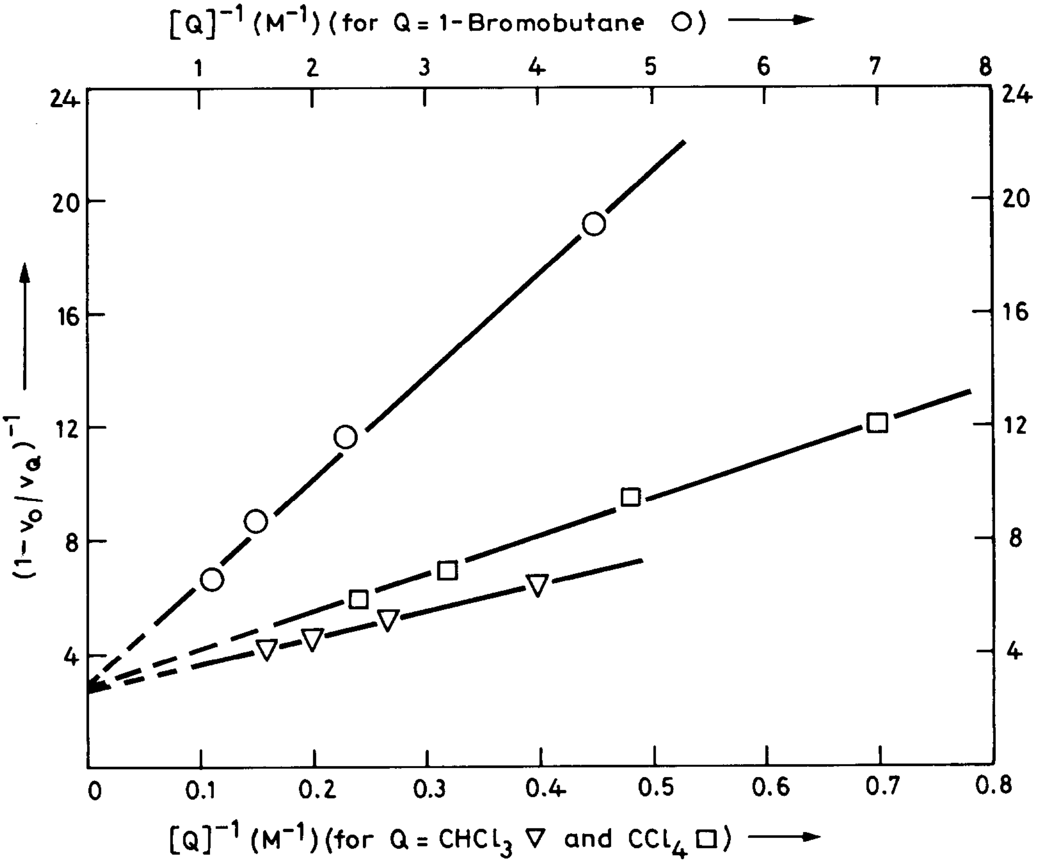

Figure 1 Plots of $(1-v_o/v_Q)^{-1}$ vs. $1/[Q]$ for alkyl halide-enhanced photosensitized oxygenations of 2,5-dimethylfuran ($[A]_{start}$ = 10^{-1} M) in methanol at 13°C

Sensitizer: Eosin, $5 \cdot 10^{-5}$ M; Light Source: Hg-high pressure lamp HPK 125 W, Philips; Filter: yellowish-colored glass (Glashütte Wertheim, Germany), cut-off at 373 nm.

ϕ_T^o is therefore easily determined from the intercept of a plot of $(1-v_o/v_Q)^{-1}$ vs. $1/[Q]$ with the ordinate.

Figure 1 shows the results obtained for a $5 \cdot 10^{-5}$ M methanolic solution of eosin at 13°C. Each point in the figure represents an average value of at least five runs; the accuracy is better than ± 10%. The regression lines, and thus the intercepts (int_1) and slopes (sl_1) of Table 1, were obtained by the method of least squares. The average value determined from the intercepts is $\phi_T^o = 0.65 \pm 0.02$.

Since $k_t = \phi_T^o/\tau_F^o$, we may rewrite equ. 3 into

$$(1-v_o/v_Q)^{-1} = (1-\phi_T^o)^{-1} + \phi_T^o/k_q\tau_F^o(1-\phi_T^o)[Q] \qquad \text{(equ. 4)}$$

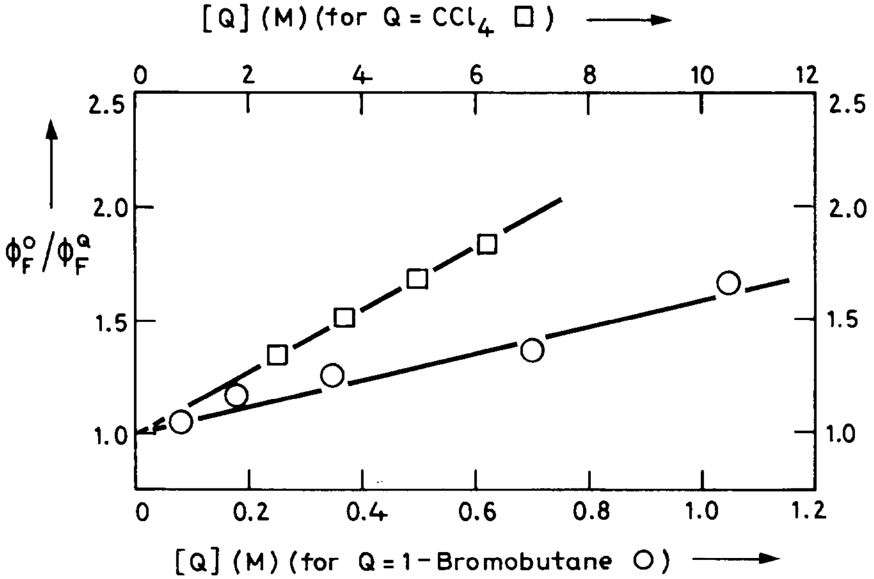

Figure 2 Stern-Volmer plots of relative fluorescence quantum yields of $5 \cdot 10^{-5}$ M eosin in methanol

Equ. 4 enables us to determine ϕ_T^o not only from the intercept but also from the slope (sl_1) of a plot of $(1 - v_o/v_Q)^{-1}$ vs. $1/[Q]$, if $k_q\tau_F^o$ is known. This entity, however, is the slope of the well-known Stern-Volmer plot of relative fluorescence quantum yields, ϕ_F^o/ϕ_F^Q, vs. $[Q]$, since

$$\phi_F^o/\phi_F^Q = 1 + k_q\tau_F^o[Q] \qquad \text{(equ. 5)}$$

in which ϕ_F^o and ϕ_F^Q are the fluorescence quantum yields in the absence and in the presence of heavy atom quenchers Q, respectively.

In order to obtain relative fluorescence quantum yields, we employed equ. 6 [2]

$$\phi_F^o/\phi_F^Q = (F_\lambda^o/F_\lambda^Q)(A_\lambda^Q/A_\lambda^o)(n_o^2/n_Q^2) \qquad \text{(equ. 6)}$$

by measuring 1) the absorption A_λ^o and A_λ^Q of eosin ($5 \cdot 10^{-5}$ M) in pure methanol and in the presence of heavy atom additives at concentrations $[Q]$, respectively, every 5 nm from $\lambda = 380$ nm to the end of the strong visible band, 2) the fluorescence intensity at the fluorescence maximum at 555 nm in the absence (F_λ^o) and in the presence (F_λ^Q) of Q by varying the excitation wavelength every 5 nm from $\lambda = 380$ to $\lambda = 515$ nm, and 3) the refractive indices n_o and n_Q in the absence and in the presence of Q, respectively. The absorption spectrum of eosin in methanol remained practically unaltered; the absorption maximum is slightly shifted from 521 nm (pure methanol) to 525 nm at the highest Q-concentrations of CCl_4 and 1-bromobutane employed. By the procedure described, ϕ_F^o/ϕ_F^Q was found to be independent of the exciting wavelength, i.e. the value did not change by more than ± 10%. The values of relative fluorescence quantum yields in Figure 2 thus represent mean values from 28 single determinations at a given concentration of Q. The regression values were obtained by the method of least squares.

The resulting slopes (sl_2) from Figure 2 are given in Table 1. ϕ_T^o may now be

Table 1 Intercepts, Slopes, and Triplet Quantum Yields Obtained for Eosin ($5 \cdot 10^{-5}$ M) in Methanol at 13° C

Q	Intercept int_1 a)	Slope sl_1 a)	ϕ_T^o b)	Slope sl_2 c)	ϕ_T^o d)	ϕ_T^o e)
chloroform	2.65	9.43	0.62			
carbon tetrachloride	2.93	13.03	0.66	0.14	0.65	0.62
1-bromobutane	2.98	3.62	0.66	0.60	0.69	0.73

a) from Fig. 1 b) calc. from int_1 c) from Fig. 2 d) calc. with equ. 7
e) calc. with equ. 8

calculated either from the two slopes sl_1 and sl_2 since $\phi_T^o = sl_1 \cdot sl_2/(1 + sl_1 \cdot sl_2)$ (equ. 7) or from the two slopes and the intercept int_1 since $\phi_T^o = sl_1 \cdot sl_2/int_1$ (equ. 8) $\phi_T^o = 0.67 \pm 0.03$ and $\phi_T^o = 0.68 \pm 0.08$, respectively, are obtained.

Another possibility to demonstrate the results is to plot ϕ_F^o/ϕ_F^Q vs. $\phi_F^o v_Q/\phi_F^Q v_o$ since

$$\phi_F^o/\phi_F^Q = \phi_T^o \left[\phi_F^o v_Q/\phi_F^Q v_o - 1\right] + 1 \qquad \text{(equ. 9)}^3$$

The slope of such a plot yields $\phi_T^o = 0.66 \pm 0.01$.

The agreement between the values of ϕ_T^o determined solely from the relative rates of O_2-consumptions and those obtained by the additional determination of relative fluorescence quantum yields is taken as further evidence that the method described is based on sound assumptions about the mechanism of photosensitized oxygenation reactions as well as about the mode of action of heavy atom additives.

A detailed discussion on the value of ϕ_T^o of eosin in methanol will appear elsewhere [4]. It should be mentioned that the mean value of $\phi_T^o = 0.66 \pm 0.03$ for eosin obtained here does not agree with our earlier value of 0.3 [5] which, however, was determined at higher eosin concentrations ($3.3 \cdot 10^{-4}$ M) in methanol at 20° C where concentration quenching [6] may come into play.

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