

TRIPLET QUANTUM YIELD DETERMINATION BY PHOTSENSITIZED OXYGENATION IN
 THE PRESENCE OF HEAVY ATOM ADDITIVES: RHODAMINE B IN METHANOL

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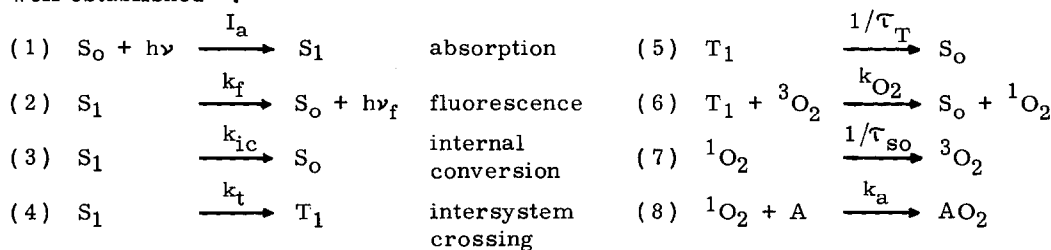
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Summary Relative rates of heavy-atom-enhanced photosensitized 1O_2 -reactions may be used to determine Φ_T^O of sensitizers in heavy-atom-free solutions. $\Phi_T^O = 0.12 \pm 0.02$ is obtained for a $5 \cdot 10^{-5}$ M methanolic solution of Rhodamine B.

Procedures to determine triplet quantum yields, Φ_T^O , have been reviewed recently by F. Wilkinson¹, who has developed a rather elegant method which utilizes heavy atom additives to increase Φ_T^O at the expense of the fluorescence quantum yield. Photosensitized singlet oxygen (1O_2) reactions may be used to obtain Φ_T^O directly from the product quantum yield².

We now wish to report on a simple procedure which appears to be especially well suited to determine Φ_T^O of dyes which sensitize singlet oxygen reactions with quantum yields above about 0.05. The method makes use of the fact that heavy atom additives enhance the rate of O_2 -consumption due to an increased production of dye triplet states³.

The sequence of reactions involved in photosensitized singlet oxygen reactions is well established⁴:



with S_0 , S_1 , and T_1 being the sensitizer (dye) in its ground-state, lowest excited singlet state, and lowest triplet state, respectively.

In the absence of any other excited sensitizer quenching or singlet oxygen quenching, and with $\tau_F^O = 1/(k_f + k_{ic} + k_t)$ = fluorescence lifetime, the rate of oxygen consumption is given by

$$v_o = I_a k_t \tau_F^O = I_a \cdot \Phi_T^O \quad (\text{equ. 1})$$

under the conditions that (a) $k_a[A] \gg 1/\tau_{so}$ (which is the case with 2,5-dimethylfuran as A at $[A] \geq 5 \cdot 10^{-3} M$ in methanol, since $k_a \geq 10^8 M^{-1} sec^{-1}$ ⁴ and $\tau_{so} = 5 \cdot 10^{-6} sec$ ⁵), and (b) $k_{O_2}[O_2] \gg 1/\tau_T$. Generally, interaction of 3O_2 is negligible with S_1 but quantitative with T_1 if τ_F^O is shorter than about $10^{-8} sec$ and if τ_T is longer than about $10^{-6} sec$, since in oxygen-saturated common solvents $[O_2]$ varies between about 10^{-2} and $10^{-3} M$, whereas the rate constant varies between about 10^{10} (fluorescence quenching) and $10^9 M^{-1} sec^{-1}$ (triplet quenching)^{4,6,7}. Xanthene dyes meet these requirements⁴.

In solution, internal conversion among excited singlet states occurs generally so fast that processes (2), (3), and (4) arise from the thermally relaxed lowest excited singlet state and thus proceed with quantum yields which are independent of the exciting wavelengths. Since xanthene dyes fulfil these conditions⁸, the number of oxygen molecules consumed is proportional to the integral of the photon distribution absorbed by these sensitizers ($= I_a$); the proportionality constant is ϕ_T^O .

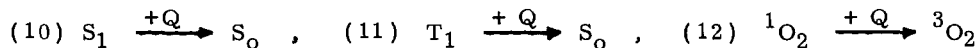
With Rhodamine B in methanol, we find that addition of chloro-, bromo-, and iodoalkanes ($=Q$) up to rather high concentrations enhances the O_2 -consumption rate. If process

(9) $S_1 \xrightarrow[k_q]{+Q} T_1$ is responsible for the increased rate of O_2 -uptake, the rate expression is given by

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

with $\tau_F^Q = 1/(k_f + k_{ic} + k_t + k_q[Q])$.

Compared with its lifetime in methanol, 1O_2 lives about 10-times longer in chloroform and 100-times longer in carbon tetrachloride⁹. Heavy atom interaction with S_1 results in T_1 -formation rather than in S_0 -production and is many orders of magnitude more effective than with T_1 ¹⁰. Processes (10), (11), and (12) are therefore considered as negligible:



Provided that the heavy atom additives do not alter appreciably the absorption spectrum of the sensitizer, ϕ_T^O may be determined from the intercept of a plot of $(1 - v_o/v_Q)^{-1}$ vs. $1/[Q]$ with the ordinate, since

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

Figures 1 and 2 show the results. Each experimental point represents an average value from at least five experiments; the accuracy is generally better than $\pm 10\%$. The regression lines, and thus the intercepts and slopes given in Table 1, were obtained by the method of least squares.

Using the average value of $\phi_T^O = 0.12 \pm 0.02$ and the slopes obtained with the n-butyl halides, $k_q(\text{Br})/k_q(\text{I}) = 0.12$, $k_q(\text{Cl})/k_q(\text{Br}) = 0.09$, and $k_q(\text{Cl})/k_q(\text{I}) = 0.01$

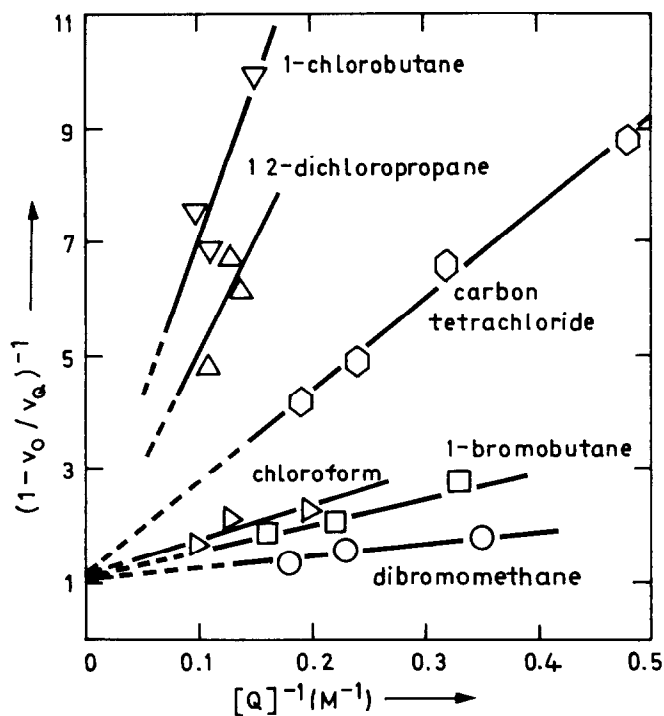


Figure 1

Figures 1 and 2:

Plots of $(1 - v_0/v_Q)^{-1}$ vs. $[Q]^{-1}$ for alkyl halide-enhanced photo-sensitized oxygenations of 2,5-dimethylfuran ($[A]_{\text{start}} = 1.0 \cdot 10^{-1}$ M) in methanol at 13°C
 Sensitizer: Rhodamine B, $5 \cdot 10^{-5}$ M;
 Light Source: Hg - High pressure lamp HPK 125 W, Philips;
 Filter: yellowish-colored glass (Glashütte Wertheim, Germany), cut-off at 373 nm.

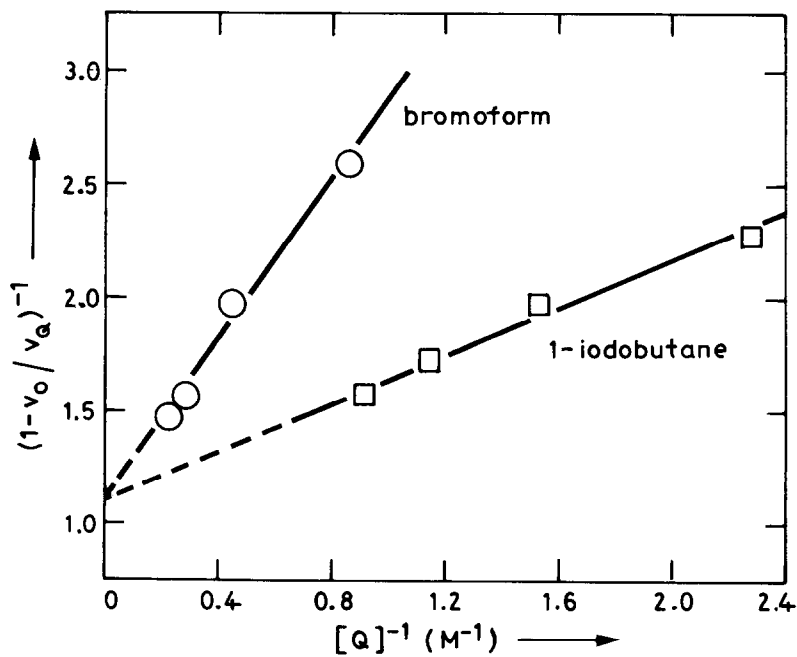


Figure 2

agree fairly well with the ratios of the squares of the atomic spin-orbit coupling factors, $\zeta_{\text{Br}}^2/\zeta_{\text{I}}^2 = 0.24$, $\zeta_{\text{Cl}}^2/\zeta_{\text{Br}}^2 = 0.06$, and $\zeta_{\text{Cl}}^2/\zeta_{\text{I}}^2 = 0.01$, respectively. This result is taken as a support for the mechanism on which the method of Φ_{T}° -determination is based.

A detailed discussion on the value of Φ_{T}° obtained for Rhodamine B will appear elsewhere ¹¹.

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

Q	Intercept	Φ_{T}°	Slope
1-chlorobutane	+))		49.3
1,2-dichloropropane	+))		40.9
chloroform	1.20	0.16	5.92
carbon tetrachloride	1.17	0.14	16.22
1-bromobutane	1.14	0.12	4.55
dibromomethane	1.14	0.12	1.84
bromoform	1.11	0.10	1.76
1-iodobutane	1.11	0.10	0.52
+) heavy atom effect too small to give reliable intercept		$\Phi_{\text{T}}^{\circ} = 0.12 \pm 0.02$	

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