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THE TRIPLET SENSITIZED REACTION OF SINGLET OXYGEN WITH 2,5-DITERTIARYBUTYLFURAN: YIELD EVIDENCE FOR INEFFICIENT TRIPLET ENERGY TRANSFER FROM BENZOPHENONE TO OXYGEN

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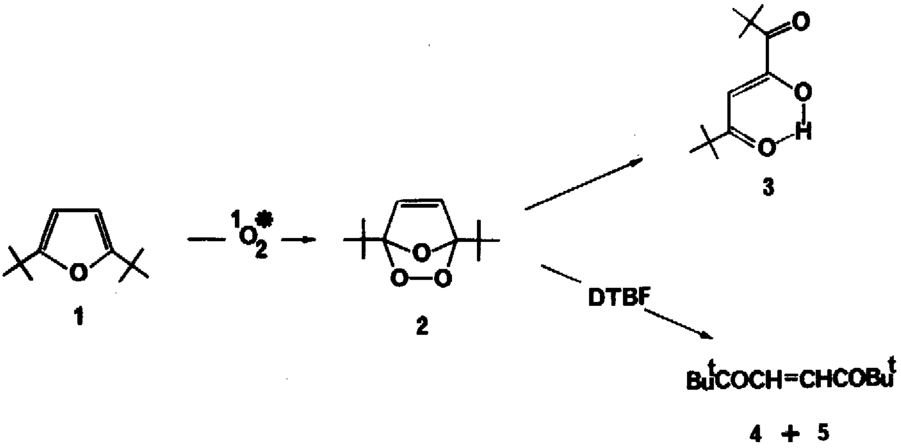
The reaction of 2,5-ditertiarybutylfuran with singlet oxygen has been used as a monitor to show that the quenching of triplet benzophenone by oxygen gives singlet oxygen with considerably less than unit efficiency.

Singlet oxygen, $^1O_2^*$, is now accepted as an important participant in the process termed photodynamic action.[1,2] It is probable that the major process by which it is formed in biological systems involves energy transfer from a triplet sensitizer, $^3S^*$, and indeed this process is the most common means of its production in the laboratory. It has been generally assumed,[3] and in fact concluded,[4] that the sensitization process occurs with unit efficiency, i.e. for each quenching of a sensitizer triplet by oxygen one molecule of $^1O_2^*$ is produced. Recently we[5] and Garner and Wilkinson[6] have provided evidence based on time-resolved studies that this is not the case and that benzophenone, in particular, is an inefficient sensitizer of $^1O_2^*$ production. To date, despite the vast amount of published work on triplet sensitized oxidations, no steady-state yield data have been used in an attempt to establish the efficiency of the energy transfer process. To be meaningful such an exercise requires a complete analysis of all possible yield affecting processes within the particular system. We have done this for the reaction of 2,5-ditertiarybutylfuran (DTBF, 1) with $^1O_2^*$ produced by triplet energy transfer from acridine, anthracene and benzophenone. Our results show conclusively that the triplet state of benzophenone is a significantly poorer sensitizer of $^1O_2^*$ production than are the corresponding states of acridine and anthracene.

The isolated product of reaction of $^1O_2^*$ at the low DTBF concentration (5.6×10^{-3} mol l^{-1}) used in this work was the enol 3 but at higher DTBF concentrations the *cis* and *trans* enediones 4 and 5 begin to predominate. We assume that, as indicated in Scheme 1, these products arise *via* the intermediacy of the endoperoxide 2.

Our choice of DTBF as substrate resulted from work on the effect of substituents on rate constants for reaction with $^1O_2^*$.[7]

Details concerning the characterisation and concentration dependence of oxidation products will be the subject of a separate paper.



Scheme 1

Aerated benzene solutions of DTBF and sensitizer which absorbed all of the incident light throughout the reaction[†] were irradiated at 313 nm[8] on a conventional merry-go-round. The loss of DTBF, monitored by GLC, was very much less in the case of benzophenone (1.5%) than for anthracene (8.8%) and acridine (9.2%). These values are reproduced in Table 1 as relative quantum yields, ϕ_{rel}, normalised for comparative purposes to the theoretical value, ϕ_{-DTBF}, for acridine (see below).

In order to assess the significance of these differences we have calculated the theoretical quantum yield for loss of DTBF, ϕ_{-DTBF}, for each sensitizer by considering the processes summarised in equations (1)-(11). We would make the following comments concerning the required quantitative data reproduced in Table 1:

(a) The sensitizer triplet yields in aerated benzene were the same within experimental error as in degassed experiments,[‡] i.e. $\phi_t^o = \phi_t$.

(b) Only the triplet state of benzophenone is significantly quenched by DTBF, equation (7).

(c) Of the sensitizer ground states, only that of benzophenone quenches $^1O_2^*$ significantly.

(d) All rate constants in Table 1 have been determined by us either previously or as part of this work using pulsed laser photolysis or the previously described pulse radiolysis method.[9]

[†] Sensitizer concentrations were 1.2×10^{-3}, 4.4×10^{-3} and 3.2×10^{-2} mol l^{-1} for acridine, anthracene and benzophenone respectively.

[‡] Shown by pulsed nitrogen laser experiments.

Table 1 Rate Constant and Yield Data for Reaction of 2,5-Ditertiarybutylfuran with Singlet Oxygen

Rate Constants*	Acridine	Anthracene	Benzophenone
k_d/s^{-1}	4.5×10^4	2.2×10^4	1.5×10^5 [a]
$k_o/l\ mol^{-1}\ s^{-1}$	1.8×10^9 [b]	2.5×10^9 [b]	1.8×10^9 [b]
$k_q/l\ mol^{-1}\ s^{-1}$	-	-	2.2×10^8
$k_{sq}/l\ mol^{-1}\ s^{-1}$	1.6×10^6	-	4.0×10^5 [a]
$k_s/l\ mol^{-1}\ s^{-1}$	-	-	1.8×10^7
	$k'_d = 3.8 \times 10^4\ s^{-1}$ [b]	$k_r = 1.8 \times 10^8\ l\ mol^{-1} s^{-1}$ [c]	

Yields	Acridine	Anthracene	Benzophenone
$\phi_t^o = \phi_t$	0.76 [d]	0.75 [e]	1.0 [e]
ϕ_{rel}	0.72	0.69	0.12
ϕ_{-DTBF}	0.72	0.72	0.45

[a] Ref. 9 [b] Ref. 5 [c] Ref. 7 [d] Ref. 10 [e] Ref. 11

* Rate constants not specified were too small to be measured.

$$\left.\begin{array}{rcl} S & \xrightarrow{h\nu} & {}^1S^* \\ {}^1S^* & \longrightarrow & S \\ {}^1S^* & \longrightarrow & {}^3S^* \\ {}^1S^* + O_2 & \longrightarrow & {}^3S^* + O_2 \end{array}\right\} \phi_t^o \qquad \begin{array}{r} (1) \\ (2) \\ (3) \\ (4) \end{array}$$

$$\begin{array}{rcll} {}^3S^* & \xrightarrow{k_d} & S & (5) \\ {}^3S^* + O_2 & \xrightarrow{k_o} & S + {}^1O_2^* & (6) \\ {}^3S^* + DTBF & \xrightarrow{k_q} & S + DTBF\ (\text{or products}) & (7) \\ {}^3S^* + S & \xrightarrow{k_{sq}} & S + S & (8) \\ {}^1O_2^* & \xrightarrow{k'_d} & O_2 & (9) \\ {}^1O_2^* + DTBF & \xrightarrow{k_r} & \text{loss of DTBF} & (10) \\ {}^1O_2^* + S & \xrightarrow{k_s} & ? & (11) \end{array}$$

The theoretical quantum yield for loss of DTBF is then given by:

$$\phi_{\text{-DTBF}} = \phi_t^o \left[\frac{k_o[O_2]}{k_d + k_o[O_2] + k_q[\text{DTBF}] + k_{sq}[S]} \right] \left[\frac{k_r[\text{DTBF}]}{k'_d + k_r[\text{DTBF}] + k_s[S]} \right]$$

and the calculated values are shown in Table 1. Comparison with the ϕ_{rel} values clearly shows that triplet benzophenone produces $^1O_2^*$ several times less efficiently than is to be anticipated on the basis of an oxygen quenching process which gives this species with unit efficiency. Work with other sensitizers is in progress.

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