THE PHOTOPEROXIDATION OF UNSATURATED ORGANIC MOLECULES
VIII. THE EFFECT OF BIACETYL*

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SUMMARY

The increased rate of diphenylanthracene consumption in the presence of biacetyl in air-saturated benzene far exceeds that computed on the basis of a catalyzed intersystem-crossing process, and appears to lead to the production of a 9,10-dihydroanthracene derivative which is not the endoperoxide normally formed.

The effect is interpreted in terms of a biacetyl–oxygen complex or biacetyl oxciplex intermediate formed by oxygen quenching of the biacetyl triplet state and which has an estimated lifetime of at least 6 μsec.

INTRODUCTION

Measured quantum yields of photoperoxidation γ_{MO_2} of an unsaturated organic molecule M in solution, as a function of concentration of dissolved oxygen[1,2] and of the inhibitor azulene[3] are quantitatively consistent with the reaction sequence shown in Fig. 1. Essentially the accepted[4] reaction intermediate $O_2{}^1\Delta_g$ is generated by oxygen quenching of a sensitizer triplet state $^3S^*$ which is in turn produced both by intersystem crossing from, and oxygen quenching of, the sensitizer singlet state $^1S^*$. The overall quantum yield is given by:

$$\gamma_{MO_2}([M], [O_2]) = \Phi_T([O_2])\Phi_\Delta([O_2])\Phi_M([M])$$

$$= \left\{\frac{k_2 + k_4[O_2]}{k_1 + k_2 + k_3 + k_4[O_2]}\right\}\left\{\frac{k_6[O_2]}{k_5 + k_6[O_2]}\right\}\left\{\frac{k_7[M]}{k_8 + k_7[M]}\right\} \quad (1)$$

and eqn. (II) describes the oxygen quenching of sensitizer fluorescence, F:

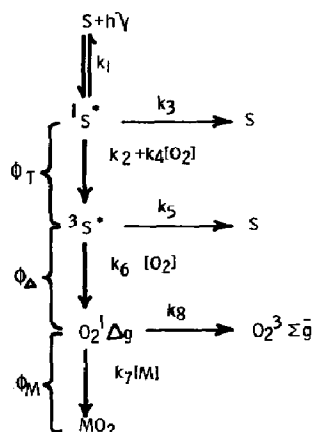$$F_0/F = 1 + k_4[O_2]/(k_1 + k_2 + k_3) = 1 + K_{O_2}[O_2] \quad (II)$$

Fig. 1. Sensitized photoperoxidation sequence.

At oxygen concentrations $[O_2] \gg k_5/k_6$, the sensitizer triplet state essentially produces $O_2{}^1\Delta_g$ with 100% yield ($\Phi_\Delta = 1$) and eqns. (I) and (II) rearrange to:

$$\gamma_{MO_2} F_0/F = \left\{ \gamma_{ISC} + \frac{F_0}{F} - 1 \right\} \left\{ \frac{[M]}{\beta + [M]} \right\} \tag{III}$$

which affords values for the sensitizer intersystem crossing yield $\gamma_{ISC} = k_2/(k_1 + k_2 + k_3)$ and the substrate $O_2{}^1\Delta_g$ reactivity parameter $\beta = k_8/k_7$ from experimental measurements of γ_{MO_2} and F_0/F as a function of dissolved oxygen concentration. In this way values of $\gamma_{ISC} = 0.13 \pm 0.05$ and $\beta = 0.040 \pm 0.004$ M have been determined[5] for 9,10-diphenylanthracene (DPA) in benzene at $25 \pm 1°C$.

For sensitizers of low intersystem crossing efficiency ($k_2 \ll k_1 + k_3$) the photoperoxidation quantum yield is limited by the rate of triplet state production in the oxygen quenching process (4), and should be substantially increased by the addition of a singlet energy acceptor B with a high intersystem crossing yield to a triplet state ^3B which may act directly as a source of $O_2{}^1\Delta_g$ or indirectly by energy transfer to produce $^3S^*$. These additional processes shown in Fig. 2 for autoperoxidation ($S \equiv M$) effectively increase Φ_T and hence γ_{MO_2} by the factor:

$$\frac{\gamma_{MO_2}^B}{\gamma_{MO_2}} = \frac{\Phi_T^B}{\Phi_T} = \left\{ 1 + \frac{k_9[B]}{k_2 + k_4[O_2]} \right\} \left\{ 1 + \frac{k_9[B]}{k_1 + k_2 + k_3 + k_4[O_2]} \right\}^{-1} \tag{IV}$$

which has the limiting value of:

$$\left\{ \frac{\gamma_{MO_2}^B}{\gamma_{MO_2}} \right\}_{[B] \to \infty} \to \frac{1 + K_{O_2}[O_2]}{\gamma_{ISC} + K_{O_2}[O_2]} \tag{V}$$

where $K_{O_2} = k_4/(k_1 + k_2 + k_3)$. The necessary conditions for the observation of this catalytic effect are: (a) the acceptor B neither absorbs the actinic radiation nor reacts with $O_2{}^1\Delta_g$; (b) the singlet and triplet states of the acceptor lie between those
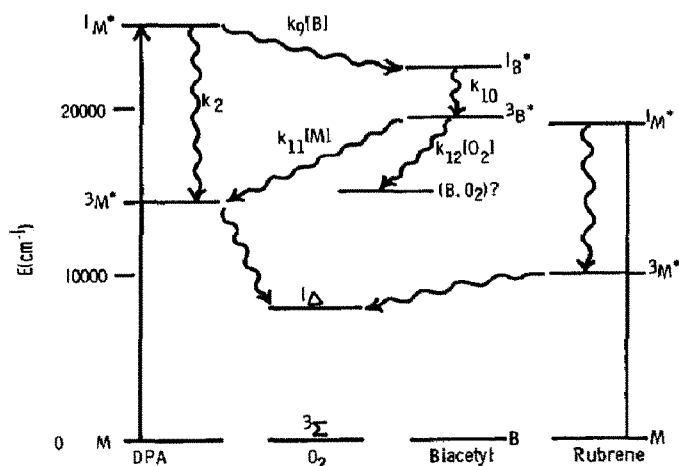
Fig. 2. Energy level diagram.

of the sensitizer (Fig. 2); (c) the acceptor and sensitizer have high and low inter-system crossing yields respectively.

This contribution reports an examination of the effect of biacetyl ($\varepsilon_{365} = 3.4$ M^{-1} cm^{-1}, $E_{1B*} \approx 22,000$ cm^{-1}, $E_{3B} \approx 19,700$ cm^{-1}, $\gamma_{ISC} \approx 1.0$) on the autoperoxidation quantum yield of DPA ($\varepsilon_{365} = 10^4\ M^{-1}$cm^{-1}, $E_{1M*} = 25,000$ cm^{-1}, $E_{3M} \approx$ 14,300 cm^{-1}, $\gamma_{ISC} = 0.13$) excited at 365 nm in air-saturated benzene at 25°C. With $K_{O_2} = 250 \pm 20\ M^{-1}$ for DPA[6], the limiting catalytic effect defined by condition (V) should be 2.7.

EXPERIMENTAL

Quantum yields of autoperoxidation and the biacetyl quenching constant of DPA fluorescence were measured as previously described[1]. Biacetyl (MCB 99% by chromotography) was used without further treatment and DPA and rubrene (Aldrich) were subjected to fractional microsublimation. All measurements were made using benzene ('Baker Analysed' Reagent) as solvent at 25 $\pm$ 1°C.

RESULTS AND DISCUSSION

The absence of any discernable effect of biacetyl on the quantum yield of rubrene autoperoxidation at 546 mm, where energy transfer to biacetyl is energetically prohibited (Fig. 2), confirms the very low reactivity of biacetyl towards $O_2{}^1\Delta_g$ required for a purely catalytic effect of this additive. However, the quantum yield of DPA consumption at 365 nm was found to increase markedly with biacetyl concentration as shown in Table 1, far exceeding the limiting effect of 2.7 computed on the basis of catalyzed intersystem crossing at biacetyl concentrations ($\leqslant 10^{-2}M$) responsible for $<3.5\%$ of the total absorption of actinic radiation. Control

TABLE 1

EFFECT OF BIACETYL B ON QUANTUM YIELD γ_M OF DPA CONSUMPTION AT 365 NM IN BENZENE AT 25°C
[DPA] = $10^{-4}M$, [O_2] = $1.46 \times 10^{-3}M$

[B] $\times 10^3$ (M)	0.00	0.67	1.33	2.00	2.67	3.33	6.67	10.0
γ_M (expt.)	0.0009	0.030	0.045	0.064	0.071	0.10	0.14	0.17
γ_M (calc.)[a]		0.025	0.047	0.069	0.089	0.11	0.18	0.25

[a] From eqn. (VI) using quoted values for K'_B, β' and k_{11}/k_{12}

experiments showed that oxygen is consumed during the photochemical reaction and that in the absence of dissolved oxygen the quantum yield of DPA removal is less than 10^{-6} in the presence of $10^{-2}M$ biacetyl.

Although the ultra-violet absorption spectrum of the product (in hexane solution) closely resembles that of DPA endoperoxide, it did not regenerate the original hydrocarbon on heating, contrary to the behavior of the endoperoxide[7]. It is suggested that the product has structure A

(A)

formed in the presence of biacetyl by the reaction sequence:

$$^3B + O_2{}^3\Sigma \rightarrow (B.O_2) \tag{12}$$

$$(B.O_2) + M \rightarrow A \tag{13}$$

$$(B.O_2) \rightarrow B + O_2{}^3\Sigma \tag{14}$$

where (B.O_2) denotes a biacetyl–oxygen complex or oxciplex. A detailed product analysis has been prevented by the necessary use of low DPA concentrations ($\sim 10^{-4}M$) to avoid process (11) (Fig. 2) which would restore the normal auto-peroxidation sequence.

Under the conditions of observation the quantum yield of DPA consumption should be given by:

$$\gamma_M = \left\{ \frac{K_B[B]}{1 + K_{O_2}[O_2] + K_B[B]} \right\} \left\{ \frac{k_{12}[O_2]}{k_{12}[O_2] + k_{11}[M]} \right\} \left\{ \frac{[M]}{\beta' + [M]} \right\} \tag{VI}$$

where $K_B = k_9/(k_1 + k_2 + k_3)$, $K_{O_2} = k_4/(k_1 + k_2 + k_3)$ and $\beta' = k_{14}/k_{13}$. The effect of the experimental variables [B], [O_2] and [M] on the quantum yield γ_M are examined in terms of eqn. (VI).

Dependence of yield on DPA concentration

This was investigated for the biacetyl-sensitized reaction at 436 nm, under which conditions the quantum yield expression becomes:

$$\gamma'_{M} = \left\{ \frac{k_{12}[O_2]}{k_{12}[O_2] + k_{11}[M]} \right\} \left\{ \frac{[M]}{\beta' + [M]} \right\} \tag{VII}$$

At low concentrations of DPA ($< 3 \times 10^{-5}M$) in air-saturated benzene ($[O_2] = 1.5 \times 10^{-3}M$) it is assumed that $k_{12}[O_2] \gg k_{11}[M]$ to obtain a value for $\beta' = 1.5 \pm 0.5 \times 10^{-5}M$ as the slope/intercept ratio of $1/\gamma'_M$ plotted as a function of $[M]^{-1}$.

Dependence of quantum yield on dissolved oxygen concentration

As in the case of the normal photoperoxidation reaction, the quantum yield of DPA consumption at 365 nm in the presence of biacetyl was found to increase with concentration of dissolved oxygen to a limiting value. Under the experimental conditions:

$$K_{O_2}[O_2] \leqslant 0.17 \ll K_B[B] = 3.5$$

the first term in eqn. (VI) is relatively insensitive to oxygen concentration and for a constant substrate concentration of $[M] = 10^{-4}M$ the reciprocal yield is found to vary linearly with $[O_2]^{-1}$ to provide a slope/intercept ratio of:

$$k_{11}[M]/k_{12} = 3 \pm 1 \times 10^{-4}M$$

This is consistent with a value for k_{12} of 3.3×10^9 M^{-1} s^{-1} which is an order of magnitude lower than reported values for oxygen quenching of singlet states in this solvent; this may be rationalized on a spin-statistical basis[8] if the biacetyl oxciplex formed in process (12) is the singlet state necessary for the spin-allowed process (13).

The biacetyl concentration dependence of quantum yield

At 365 nm (Table 1) this may be described in terms of eqn. (VI) which requires only the independent measurement of the biacetyl quenching constant of DPA fluorescence $K'_B = K_B/(1 + K_{O_2}[O_2]) = 53 \pm 6$ M^{-1} in air-saturated benzene. The values of γ_M(calc) given in Table 1 computed from eqn. (VI) using the data quoted for K'_B, k_{11}/k_{12} and β', adequately describe the experimental data at lower biacetyl concentrations but the agreement is less satisfactory in the higher concentration region where perhaps biacetyl quenches an electronically excited intermediate in a yet unspecified process.

The biacetyl oxciplex

This may be regarded as an example of the sensitizer–oxygen complex (formed from the sensitizer triplet state and $O_2{}^3\Sigma$) at one time believed to be the

reactive intermediate in photosensitized peroxidation[9]. If the rate constant for process (13) has a diffusion-limited upper value, the oxciplex lifetime computed as $1/k_{14}$ from β' is at least 6 μsec consistent with the spin-forbidden nature of process (14). This is on the order of recently reported[10] values for the lifetime of $O_2{}^1\Delta_g$ in solution, however, the oxciplex substrate reactivity far exceeds that of $O_2{}^1\Delta_g$ in this system at least as indicated by the values $\beta' = 1.5 \times 10^{-5}$ M and $\beta = 0.04$ M estimated for the corresponding reactivity parameters for DPA. The formation of a benzil oxciplex has recently been proposed by Saltiel and Curtis[11].

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