Journal of Photochemistry, 3 (1974/75) 393 - 401

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THE PHOTOPEROXIDATION OF UNSATURATED ORGANIC MOLECULES. XII. DISSOCIATIVE OXCIPLEX RELAXATION*

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(Received October 24, 1974)

Summary

The experimental evidence indicates that the self-sensitized addition of molecular oxygen to a dissolved aromatic hydrocarbon M involves a reaction sequence

$$M(S_1) + O_2\,{}^3\Sigma \xrightarrow{1} M(T_1) + O_2\,{}^3\Sigma \xrightarrow{2} M(S_0) + O_2\,{}^1\Delta \xrightarrow{3} MO_2$$

in which the products of processes (1) and (2) are the reactants in processes (2) and (3), rather than the direct addition of $O_2\,{}^3\Sigma$ to either the excited singlet $M(S_1)$ or triplet $M(T_1)$ states of the acceptor.

An orbital correlation scheme presented for the concerted addition process (3) and based on anthracene as a model acceptor with a "planar peroxide" complex configuration of highest symmetry shows that the complex or oxciplex states ${}^3(S_1\,{}^3\Sigma)$ and ${}^{1,3}(T_1\,{}^3\Sigma)$ must correlate endothermically with electronically excited states of the peroxide MO_2. Arguments are given in support of the exchange mechanism for process (2) in non-polar solvents in which, for a similar oxciplex configuration, the final state correlates with that component of the $O_2\,{}^1\Delta$ state which does not lead to formation of the MO_2 ground state ${}^1A_1$. Direct formation of $MO_2\,{}^1A_1$ in processes (1) or (2) therefore requires electronic relaxation of the initially formed oxciplex states ${}^3(S_1\,{}^3\Sigma)$ and ${}^1(T_1\,{}^3\Sigma)$ which is either spin or orbitally forbidden but is achieved by dissociation and recombination of the molecular components.

Introduction

Certain catacondensed aromatic hydrocarbons M are capable of acting as both sensitizer and $O_2\,{}^1\Delta_g$ acceptor in the overall photoperoxidation process:

$$M \xrightarrow{h\nu/O_2} MO_2$$

*Paper presented at the 11th Informal Conference on Photochemistry, Nashville, Tennessee, June 16 - 19, 1974.

where the product MO_2 is a transannular peroxide [1]. Measurements of the overall quantum yield γ_{MO_2} ([O_2], [M]) as a function of the reaction variables are consistent with the reaction sequence 1 - 3 in the scheme [2, 3]:

$$\begin{array}{ccc} M(S_1) + O_2\,{}^3\Sigma & \xrightarrow{1} & M(T_1) + O_2\,{}^3\Sigma \\ & & \downarrow 2 \\ MO_2 & \xleftarrow[3]{} & M(S_0) + O_2\,{}^1\Delta \end{array}$$

which together with (unimolecular) intersystem crossing $S_1 \rightarrow T_1$ of efficiency γ_{1S} lead to the general expression:

$$\gamma_{MO_2}([O_2], [M]) = \left\{\frac{\gamma_{1S} + k_1\tau_S[O_2]}{1 + k_1\tau_S[O_2]}\right\}\left\{\frac{k_2\tau_T[O_2]}{1 + k_2\tau_T[O_2]}\right\}\left\{\frac{k_3\tau_\Delta[M]}{1 + k_3\tau_\Delta[M]}\right\} \quad (I)$$

Equation (I) affords a quantitative description of the reduction in quantum yield γ_{MO_2} by selective interception (quenching) of the electronically excited singlet (S_1) or triplet (T_1) states of the sensitizer or of $O_2\,{}^1\Delta$ owing to a reduction in the corresponding lifetimes τ_S, τ_T and τ_Δ [3].

The identity of the products of processes (1) and (2) with the reactants of processes (2) and (3) respectively raises a question [4] concerning the preference of this reaction sequence to one in which the peroxide is formed directly by $O_2\,{}^3\Sigma$ addition to $M(S_1)$ or $M(T_1)$, either of which would remove the dependence of quantum yield on acceptor concentration and dispense with $O_2\,{}^1\Delta$ as a reaction intermediate. An explanation is offered below in terms of the properties of the intervening states of the (M . . . O_2) complex, or oxciplex, based on anthracene as a model acceptor.

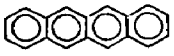
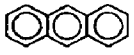
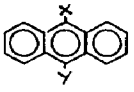
$O_2\,{}^1\Delta_g$–acceptor addition

Estimates of k_3 from the experimental quantity γ_{MO_2}([M]) and independent measurements [5] of τ_Δ are given in Table 1 for representative acceptors [6, 8] in benzene at 25 °C, the activation energies for $O_2\,{}^1\Delta$ addition being given relative to that for pentacene on the assumption of a constant entropy factor. Insofar as the reduction in activation energy by one or two identical substituents at the site of $O_2\,{}^1\Delta$ attack (on anthracene) is additive, these data are consistent with the concerted nature of process (3) and it is therefore appropriate to examine $O_2\,{}^1\Delta$ addition from the standpoint of orbital symmetry conservation [7]. For this purpose the complex configuration shown in Fig. 1 belonging to the C_{2v} point group is adopted; however, orbital correlations are constructed at two levels of symmetry as follows.

Of the fourteen π_c orbitals of anthracene, twelve are converted to π_c orbitals of two benzene ring systems in the final product and do not participate directly in localized bond formation with O_2; if these are treated [8] in the full D_{2h} symmetry of the π_c system, orbitals π_1–π_6 and π_9^*–π_{14}^* of anthracene correlate with the twelve symmetry-adapted linear combinations $\pi_i \pm \pi_i$ (i = 1, 2, 3) and $\pi_j^* \pm \pi_j^*$ (j = 4, 5, 6) respectively of benzene

TABLE 1

Rate constants k_3 and activation energies $E^{\neq}$ for $O_2\,^1\Delta_g$ addition to aromatic hydrocarbons in benzene at 25 °C

Acceptors	$k_3(M^{-1}s^{-1})$[a]	$E^{\neq}$ (kcal/mol)[b]
	4.2 (9)	0
	1.2 (7)	3.5
	1.5 (5)	6.1
		
X = H, Y = CH_3	3.2 (6)	4.3
X = Y = CH_3	2.1 (7)	3.1
X = H, Y = C_6H_5	4.2 (5)	5.5
X = Y = C_6H_5	1.2 (6)	4.9
X = H, Y = OCH_3	2.7 (6)	4.5
X = Y = OCH_3	1.4 (7)	3.4

[a] Estimated from experimental values of $k_3\tau_\Delta$ [8] and τ_Δ = 24 μs in this solvent [5]. X(Y) = X × 10^y.

[b] Relative to $E^{\neq}$ for pentacene.

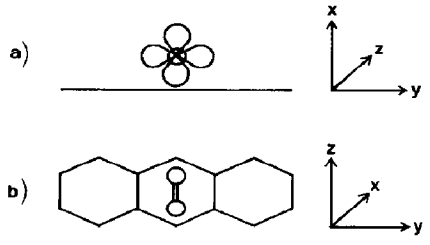


Fig. 1. Planar peroxide complex configuration for anthracene–O_2 system viewed (a) along and (b) normal to the anthracene plane.

orbitals in the peroxide, leaving the HOMO ($\pi_7 = \pi_c$) and LUMO ($\pi_8^\star = \pi_c^\star$) of anthracene available for interaction with O_2.

In constructing the orbital correlation diagram for anthracene–O_2 interaction (Fig. 2), the orbitals of interest (and their transformation properties in C_{2v}) are $\pi_c(b_1)$ and $\pi_c^\star(a_1)$ of anthracene, $\sigma_{00}(a_1)$, $\sigma_{00}^\star(b_1)$, $\pi_x(a_1)$, $\pi_y(b_2)$, $\pi_x^\star(b_1)$ and $\pi_y^\star(a_2)$ orbitals of molecular oxygen, and the symmetry-adapted linear combinations $\sigma_{co} \pm \sigma_{co}(a_1, b_1)$ and $\sigma_{co}^\star \pm \sigma_{co}^\star(a_1, b_1)$ of σ_{co} orbitals in the peroxide. The following points are noted in connection with Fig. 2.

(a) The $\pi_{x,y}^\star$ orbital degeneracy is lifted in the encounter complex [7] by construction of complex orbitals as linear combinations of π_c and $\pi_c^\star$ with π_x and $\pi_x^\star$ of the form:

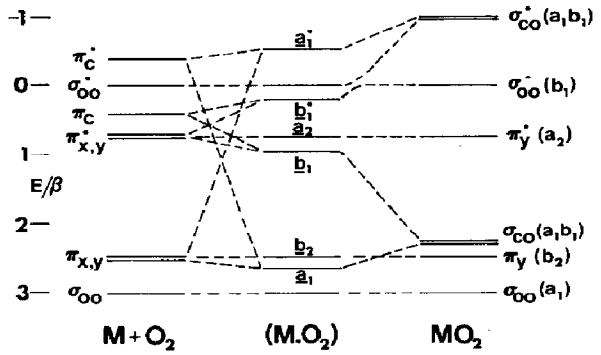


Fig. 2. Orbital correlation diagram for O_2 addition to anthracene where $\pi_c = \pi_7$ (HOMO) and $\pi_c^* = \pi_8^*$ (LUMO). Orbitals π_1–π_6 and π_8^*–π_{14}^* are omitted (see text).

$$
\begin{aligned}
a_1 &= (1+\lambda^2)^{-1/2}(\lambda\pi_c^* + \pi_x)\\
b_2 &= \pi_y\\
b_1 &= (1+\mu^2)^{-1/2}(\mu\pi_c + \pi_x^*)\\
a_2 &= \pi_y^*\\
b_1^* &= (1+\mu^2)^{-1/2}(\pi_c - \mu\pi_x^*)\\
a_1^* &= (1+\lambda^2)^{-1/2}(\pi_c^* - \lambda\pi_x)
\end{aligned}
\qquad \text{(A)}
$$

where λ and μ are coefficients.

(b) Except for those of the complex which are assigned on a qualitative basis, orbital energies given in units of the resonance integral β are estimated from previously adopted values [7, 9] of the Huckel parameters.

(c) Application of the non-crossing rule leads to the ultimate correlation of $b_1^*(\pi_c, \pi_x^*)$ with $\sigma_{oo}^*(b_1)$ rather than $\sigma_{co}^*(b_1)$.

If the behaviour of the O_2 electronic states of interest is differentiated in terms of non-degenerate $\pi_{x,y}^*(a_2, b_1^*)$ orbital occupancy in the encounter complex [7], *viz.*

$$
\begin{aligned}
{}^3\Sigma_g^- \ (m_s = 0) &= \sqrt{1/2}\{|\pi_x^*\bar{\pi}_y^*| + |\bar{\pi}_x^*\pi_y^*|\} \rightarrow a_2b_1^*\\
{}^1\Delta_g &= \sqrt{1/2}\{|\pi_x^*\bar{\pi}_x^*| - |\pi_y\bar{\pi}_y^*|\} \rightarrow a_2^2\\
{}^1\Delta_g^* &= \sqrt{1/2}\{|\pi_x^*\bar{\pi}_y^*| - |\bar{\pi}_x^*\pi_y^*|\} \rightarrow a_2b_1^*\\
{}^1\Sigma_g^+ &= \sqrt{1/2}\{|\pi_x^*\bar{\pi}_x^*| + |\pi_y^*\bar{\pi}_y^*|\} \rightarrow b_1^{*2}
\end{aligned}
\qquad \text{(B)}
$$

an examination of Fig. 2 leads to the state correlations:

$$
\begin{aligned}
&{}^3\Gamma_1(S_0\,{}^3\Sigma)\,(\ldots a_1^2b_2^2b_1^2a_2b_1^*) \rightarrow MO_2\,{}^3B_2(\ldots \pi_y^2\sigma_{co}^4\pi_y^*\sigma_{oo}^*)\\
&{}^1\Gamma_0(S_0\,{}^1\Delta)\,(\ldots a_1^2b_2^2b_1^2a_2^2) \rightarrow MO_2\,{}^1A_1(\ldots \pi_y^2\sigma_{co}^4\pi_y^{*2})\\
&{}^1\Gamma_1(S_0\,{}^1\Delta^*)\,(\ldots a_1^2b_2^2b_1^2a_2b_1^*) \rightarrow MO_2\,{}^1B_2(\ldots \pi_y^2\sigma_{co}^4\pi_y^*\sigma_{oo}^*)\\
&{}^1\Gamma_2(S_0\,{}^1\Sigma)\,(\ldots a_1^2b_2^2b_1^2b_1^{*2}) \rightarrow MO_2\,{}^1A_1^*(\ldots \pi_y^2\sigma_{co}^4\sigma_{oo}^{*2})\\
&{}^1\Gamma_i(T_1\,{}^3\Sigma)\,(\ldots a_1^2b_2^2b_1a_2b_1^*a_1^*) \rightarrow MO_2\,{}^1A_2(\ldots \pi_y^2\sigma_{co}^3\pi_y^*\sigma_{oo}^*\sigma_{co}^*)\\
&{}^3\Gamma_j(S_1\,{}^3\Sigma)\,(\ldots a_1^2b_2^2b_1a_2b_1^*a_1^*) \rightarrow MO_2\,{}^3A_2(\ldots \pi_y^2\sigma_{co}^3\pi_y^*\sigma_{oo}^4\sigma_{co}^*)
\end{aligned}
\qquad \text{(C)}
$$

where electronic configurations are given parenthetically. As in the case of non-aromatic acceptors only $^1\Gamma_0(S_0{}^1\Delta)$ correlates (exothermically) with the peroxide $^1A_1$ ground state.

Since the components $O_2{}^1\Delta$ and $O_2{}^1\Delta^*$ of the oxygen delta state are distinguishable only in complex formation it is expected that k_3 will include an orbital statistical factor of ½, and the transition state formulation of k_3 becomes:

$$k_3 = (ekT/2h)\exp(\Delta S^{\neq}/R)\exp(-E^{\neq}/RT)$$

or for the most reactive aromatic acceptor, pentacene, where $k_3 = 4 \times 10^9$ M^{-1} s^{-1}; $\Delta S \simeq -15.3$ e.u. for an activation energy of zero; this is in the range of values $\Delta S = -15.6 \pm 1.0$ e.u. reported by Koch [26] for a series of 5 peroxide forming acceptors and since $-\Delta S$ is unlikely to be less than the value calculated for pentacene we conclude that the energy barrier to $O_2{}^1\Delta$ addition to this acceptor is small or zero.

$O_2{}^3\Sigma_g^-$ quenching of the triplet state

The available kinetic [2, 3] and spectroscopic [11] evidence supports the conclusions of Kearns and co-workers [12] reached on theoretical grounds that the energy transfer sequence:

$$M(T_1) + O_2(^3\Sigma) \underset{k_r}{\overset{k_d/9}{\rightleftharpoons}} {}^1\Gamma_i(T_1{}^3\Sigma) \xrightarrow{k_{if}} {}^1\Gamma_f(S_0{}^1O_2) \rightarrow M(S_0) + {}^1O_2$$

is responsible for oxygen quenching of aromatic hydrocarbon triplet states; the quenching product designated $^1O_2$ is either one of the degenerate $^1\Delta$ states at 8000 cm^{-1} above the $O_2{}^3\Sigma$ ground state or $O_2{}^1\Sigma$ (at 13,000 cm^{-1}) which must undergo rapid quantitative relaxation to $O_2{}^1\Delta$ in solution [13].

Porter *et al.* [14] have shown that the overall rate constant $k_2 = k_d k_{if}/9(k_r + k_{if})$ increases with a reduction in triplet state energy E_T to a spin-limited value of $k_d/9$ when $E_T \leqslant 15{,}000$ cm^{-1} consistent with the singlet nature of the quenching products and the absence of intersystem crossing between the $^{5,3,1}\Gamma_i$ complex states during their (dissociative) lifetimes. Insofar as the dissociation frequency k_r is independent of E_T, these observations also suggest that internal conversion $^1\Gamma_{i\rightarrow f}$ in the singlet oxciplex manifold is the rate-determining quenching process [15] when $E_T >$ 15,000 cm^{-1}.

According to the Robinson–Frosch treatment [16] of radiationless transitions, the internal conversion frequency given by:

$$k_{if} \sim \rho_f(\Delta E_{if})\beta_{if}^2 F(\Delta E_{if})/h$$

is sensitive to the energy separation ΔE_{if} of initial and final states $^1\Gamma_i$ and $^1\Gamma_f$ which determines the magnitude of the vibrational overlap integral $F(\Delta E_{if})$ summed over final states of density $\rho_f(\Delta E_{if})$; for a weak interaction ΔE_{if} should be close to $E_T - 8000$ cm^{-1} for the production of $O_2{}^1\Delta$ or to $E_T - 13{,}000$ cm^{-1} if $O_2{}^1\Sigma$ is the primary quenching product. On the other hand, the magnitude of the electronic matrix element β_{if} depends on the

nature of the interaction which may involve direct exchange with

$$\beta_{if} = \langle \Gamma_f | \mathcal{H} | \Gamma_i \rangle$$

or indirect mixing via a change-transfer state Γ_k of energy E_k; in the latter case application of second-order perturbation theory leads to the approximation [12]:

$$\beta'_{if} \sim \langle \Gamma_f | \mathcal{H} | \Gamma_k \rangle \langle \Gamma_k | \mathcal{H} | \Gamma_i \rangle / (E_i - E_k)$$

Proceeding on the assumption that the quenching process must be allowed (or forbidden) in a complex configuration of highest symmetry (shown in Fig. 1 for the model anthracene–O_2 system), the initial state has the electronic configuration ${}^1\Gamma_i(T_1\,{}^3\Sigma)$ (. . . . $a_1^2 b_2^2 b_1 a_1 b_1^* a_1^*$) whereas the electronic configurations of possible singlet final states ${}^1\Gamma_0(S_0\,{}^1\Delta)$, ${}^1\Gamma_1(S_0\,{}^1\Delta^*)$ and ${}^1\Gamma_2(S_0\,{}^1\Sigma)$ are described in scheme (C) above. For a purely exchange interaction in the assumed complex geometry (Fig. 1) the electronic matrix elements reduce to [12]:

$$\beta_{i0} = \beta_{i2} = 0$$

$$\beta_{i1} = (3/2)^{1/2} \langle a_1^*(\mu) b_1^*(\mu) | r_{\mu\nu}^{-1} | b_1(\nu) b_1^*(\nu) \rangle$$

whereas indirect mixing of initial and final oxciplex states via a charge transfer state leads to the relation:

$$\beta'_{i0} \sim \beta'_{i1} \sim \beta'_{i2}$$

regardless of the relative orientation of π_x^* and π_c orbitals in the complex. The recognition that ${}^1\Gamma_0(S_0\,{}^1\Delta)$ correlates (exothermically) with the peroxide ground state which is not a primary quenching product in benzene even in the absence of an energy barrier to addition (pentacene) eliminates ${}^1\Gamma_0(S_0\,{}^1\Delta)$ as a final state consistent with an exchange quenching mechanism ($\beta_{i0} = 0$) for this solvent. Accordingly, $O_2\,{}^1\Sigma$ is not expected [17] to be a primary quenching product ($\beta_{i0} = 0$) and ${}^1\Gamma_1(S_0\,{}^1\Delta^*)$ is identified as the final state ${}^1\Gamma_f$; this is a consequence of the symmetric isolation of the $a_2(\pi_y^*)$ spectator orbital in this complex configuration which restricts the weak exchange interaction to O_2 states of the same orbital and spin assignments *viz.* $O_2\,{}^3\Sigma_g^-$ ($m_s = 0$) and $O_2\,{}^1\Delta^*$ (scheme B). Since $O_2\,{}^1\Sigma$ and $O_2\,{}^1\Delta$ also have identical orbital and spin assignments, triplet state quenching via exchange interaction might also be expected to lead directly to peroxide formation in the sequence:

$${}^1\Gamma_2(S_0\,{}^1\Sigma) \rightarrow {}^1\Gamma_0(S_0\,{}^1\Delta) \rightarrow MO_2\,{}^1A_1$$

if ${}^1\Gamma_2(S_0\,{}^1\Sigma)$ were the "final" state, contrary to observation.

In support of the exchange quenching mechanism in non-polar solvents it is noted [14] that the experimental quantity log k_2 is essentially independent of E_T in the region 10,000 - 15,000 cm^{-1} whereas a discontinuity in the region of $E_T \geqslant 13{,}000$ cm^{-1} might be expected for a charge transfer mechanism leading to preferential formation of $O_2\,{}^1\Sigma$, nor does k_2 increase with E_T when this exceeds 15,000 cm^{-1} due to a reduced energy separation

ΔE_{ik} of the perturbing state as observed in the nitric oxide quenching of higher energy triplet states in hexane [18]. It is also of interest that the exchange mechanism accomodates the reverse energy transfer [19] sequence:

$$M(S_0) + O_2{}^1\Delta \rightarrow {}^1\Gamma_1(S_0{}^1\Delta^*) \rightarrow {}^1\Gamma_i(T_1{}^3\Sigma) \rightarrow M(T_1) + O_2{}^3\Sigma$$

where $E_T \leqslant 8000\ cm^{-1}$; in this case the spin statistical factor is unity but with ${}^1\Gamma_1(S_0{}^1\Delta^*)$ functioning as the initial state, the rate constant should again include an orbital statistical factor of ½ consistent with the reported value of $\sim k_d/2$ when M ≡ β-carotene [20]. Reversible energy transfer to low-lying triplet states affords a qualitative interpretation of the low value of k_2 measured for pentacene [14], and may provide a basis for the indirect determination of τ_Δ in solution.

$O_2{}^3\Sigma_g^-$ quenching of singlet states

Oxygen quenching of the fluorescent state $M(S_1)$ of aromatic hydrocarbons is essentially diffusion-limited [10]; possible quenching sequences are:

$$M(S_1) + O_2{}^3\Delta \rightarrow {}^3\Gamma_j(S_1{}^3\Sigma) \begin{cases} \rightarrow {}^3\Gamma_i(T_1{}^3\Sigma) \rightarrow M(T_1) + O_2{}^3\Sigma & (1) \\ \rightarrow {}^3\Gamma_h(T_1{}^1\Delta) \rightarrow M(T_1) + O_2{}^1\Delta & (4) \\ \rightarrow {}^3\Gamma_1^{\cdot}(S_0{}^3\Sigma) \rightarrow M(S_0) + O_2{}^3\Sigma & (5) \\ \rightarrow {}^1\Gamma_0(S_0{}^1\Delta) \rightarrow M(S_0) + O_2{}^1\Delta & (6) \end{cases}$$

Potashnik *et al.* [21] have shown that the quenching yield of $M(T_1)$ is 1.0 ± 0.2 for a series of 8 hydrocarbons in toluene, consistent with the observation that the photoperoxidation sequence is inhibited by azulene quenching of the triplet state of a sensitizer (9,10-dimethylanthracene) with a negligible intersystem crossing yield [3]; this eliminates process (5) which is presumably restricted by the low vibrational overlap integral F_{j1} ($\Delta E_{j1} \sim E_{S1}$) and process (6) which involves intersystem crossing in the oxciplex.

Use of the photoperoxidation reaction as an $O_2{}^1\Delta$ counting technique [22] has shown that the overall yield of $O_2{}^1\Delta$ following $M(S_1)$ excitation does not exceed the $O_2{}^1\Delta$ yield from oxygen quenching of $M(T_1)$ even when process (4) is exothermic ($\Delta E_{ST} > 8000\ cm^{-1}$); moreover, Parmenter and Rau [23] have shown that the rate constant for oxygen quenching of $M(S_1)$ is independent of ΔE_{ST} in the range of 4700 - 12,000 cm^{-1} consistent with a common quenching mechanism which cannot involve $O_2{}^1\Delta$ production. Accordingly, process (1) is preferred to process (4) on experimental grounds despite the indication that both are exchange allowed and the energy separation of initial and final states ($\Delta E_{ji} \sim \Delta E_{jh} + 8000\ cm^{-1}$) favors process (4). The simplest interpretation of this preference is based on a strong coupling of ${}^3\Gamma_j(S_1{}^3\Sigma)$ with an intermediate complex state of charge-transfer character ${}^3\Gamma_k(D^2\pi)$ or of higher triplet state origin ${}^3\Gamma_m(T_2{}^3\Sigma)$ which lies within 8000 cm^{-1} of the final state ${}^3\Gamma_i(T_1{}^3\Sigma)$. Insofar as T_2 lies above S_1 for 9,10-diphenylanthracene ($\Delta E_{S_1T_1} > 8000\ cm^{-1}$) ${}^3\Gamma_m(T_2{}^3\Sigma)$ is

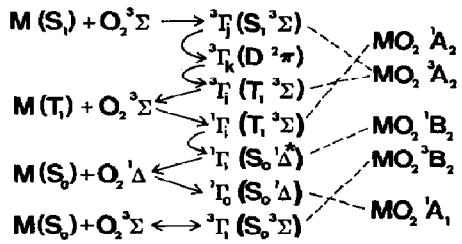


Fig. 3. State correlation diagram for O_2 addition to anthracene in terms of relevant oxciplex states $^{1,3}\Gamma$ of planar peroxide configuration. Energies are relative on a vertical scale and correlations indicated by broken lines do not include transition states assumed to lie at higher energies than corresponding peroxide states.

energetically inaccessible as an intermediate state and the sequential operation of processes (4) and (2) should lead to an upper limit of 2 for quantum yield of $O_2{}^1\Delta$ production; since the extrapolated yield (at infinite oxygen concentration) does not exceed unity is it concluded that process (4) is inoperative [24] and $^3\Gamma_k(D^2\pi)$ is the intermediate complex state [25]. This is supported by the spectroscopic detection of D^+ and the reduced limiting yield of triplet state in oxygen saturated solutions of pyrene in acetonitrile [21], and is consistent with the much larger matrix elements β_{jk}, β_{ki} coupling the initial, final and charge transfer states in the triplet oxciplex manifold [25].

Dissociative intersystem crossing and internal conversion in the oxciplex

The experimental photoperoxidation sequence is illustrated with reference to the state correlation diagram shown in Fig. 3 on a relative energy scale for the relevant complex states assumed to have a planar peroxide configuration.

It is concluded that direct addition of $O_2{}^3\Sigma$ to excited states $M(S_1)$ and $M(T_1)$ is energetically prohibited by the ultimate correlation of complex states $^3\Gamma_j(S_1{}^3\Sigma)$ and $^{1,3}\Gamma_i(T_1{}^3\Sigma)$ with electronically excited states $^{1,3}A_2$ of the peroxide through transition states of even higher energy. On the other hand, formation of the peroxide ground state from oxygen quenching of $M(S_1)$ and $M(T_1)$ requires that electronic relaxation takes place in the singlet and triplet oxciplex manifolds as follows.

The relaxation of $^1\Gamma_i(T_1{}^3\Sigma)$ to $^1\Gamma_0(S_0{}^1\Delta)$ and thence to $MO_2{}^1A_1$ requires an internal conversion $^1\Gamma_1(S_0{}^1\Delta^*) \rightarrow {}^1\Gamma_0(S_0{}^1\Delta)$ which is exchange forbidden in the chosen configuration but is accomplished by the reversible dissociation sequence;

$$^1\Gamma_1(S_0{}^1\Delta^*) \rightarrow M(S_0) + O_2{}^1\Delta \rightarrow {}^1\Gamma_0(S_0{}^1\Delta)$$

This allows the independent relaxation of $O_2{}^1\Delta$ and introduces the dependence of overall quantum yield γ_{MO_2} on acceptor concentration $M(S_0)$. Indirect formation of the peroxide ground state from oxygen quenching of

the singlet state $M(S_1)$ is further subject to the requirement that the intersystem crossing process ${}^3\Gamma_i \rightarrow {}^1\Gamma_i$ occurs within the (dissociative) lifetime of ${}^3\Gamma_i$; the experimentally observed spin-statistical limitation attending process (2) indicates that crossing between triplet and singlet manifolds of the oxciplex is slow compared with the oxciplex dissociation but when this is followed by association in the sequence:

$$ {}^3\Gamma_i(T_1{}^3\Sigma) \rightarrow M(T_1) + O_2{}^3\Sigma \rightarrow {}^1\Gamma_i(T_1{}^3\Sigma) $$

the same result is achieved.

Acknowledgement

This work is supported by the National Science Foundation under Grant No. GP28331X.

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