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Reversible Exciplex Formation between Singlet Oxygen, $^1\Delta_g$, and Vitamin E. Solvent and Temperature Effects

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Abstract: Pulsed nitrogen laser excitation has been used to determine rate and activation parameters for the reaction of singlet oxygen with α-tocopherol (α-T; vitamin E), 6-hydroxy-2,2,5,7,8-pentamethylchroman (HPMC), and 2,4,6-tri-*tert*-butylphenol (TTBP) in five solvents. The experimental activation enthalpies for α-T and HPMC, predominantly physical quenchers, are significantly more negative than values previously determined for chemical quenchers of $^1\Delta_g$, and it is concluded that these reactions proceed via the intermediacy of an exciplex which is formed reversibly. It is concluded that the balance between physical and chemical quenching is a sensitive function of spin-orbit coupling properties and entropy factors which play a dominant role as a consequence of a flat enthalpy profile along the critical portions of the reaction coordinate.

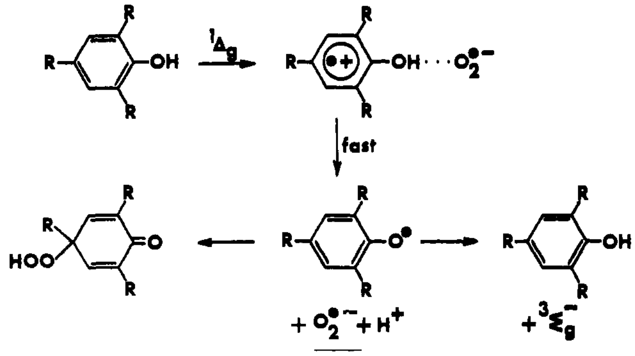
I. Introduction

The mechanism(s) of reaction of singlet oxygen, $^1\Delta_g$, with organic and bioorganic substrates continues to be the subject of intense discussion and research effort.[1-7] Such reactions may be physical or chemical in nature, and clearly, from a biological protection viewpoint, physical quenchers would seem of greatest potential importance. Quenchers of this kind are typified by the naturally occurring β-carotene and α-tocopherol (vitamin E). While it is well established that β-carotene quenches $^1\Delta_g$ by electronic energy transfer[8] (eq 1), the mechanism of the quenching by α-tocopherol is more complicated. Although some chemical

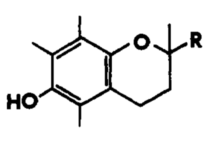
$$O_2(^1\Delta_g) + \beta\text{-C} \rightarrow O_2(^3\Sigma_g^-) + {}^3\beta\text{-C}^* \qquad (1)$$

reaction takes place, and products have been thoroughly examined,[9] the percentage of physical quenching is high, 93-99% depending on solvent.[10] The same is true for a series of trisubstituted phenols;[11] for example, the quenching of $^1\Delta_g$ by 2,4,6-tri-*tert*-butylphenol in methanol is >98% physical in character. The major contribution to mechanistic understanding in this area is due to Foote and co-workers,[11-13] who showed conclusively that, certainly for the trisubstituted phenols, charge donation from the phenol is an important factor. The currently accepted mechanism[13] is summarized in Scheme I and is based on data for the trisubstituted phenols which show (a) a correlation between log k_q and phenol half-wave oxidation potentials, (b) a ρ value of -1.72 for a Hammett plot employing σ^+ values, (c) k_q values significantly greater in methanol, and (d) evidence in the case of 2,4,6-triphenylphenol for the formation of the corresponding phenoxy radical.

Scheme I

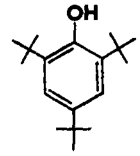


In this work we report the determination of the rate and activation parameters for the reaction of $^1\Delta_g$ with α-tocopherol (α-T, **1**), 6-hydroxy-2,2,5,7,8-pentamethylchroman (HPMC, **2**),[14] and 2,4,6-tri-*tert*-butylphenol (TTBP, **3**), a representative of the trisubstituted phenolic series already referred to. The significance of the experimental results with respect to mechanism will be discussed.



1 R = $C_{16}H_{33}$; α-T

2 R = CH_3; HPMC



3 TTBP

II. Determination of Rate Parameters

The determination of rate parameters for decay and reaction of $^1\Delta_g$ in solution by pulsed laser excitation is well documented.[15] In this work we have employed the 2.5-ns pulse of a nitrogen laser (337 nm), 2-acetonaphthone as sensitizer,[16] and the bleaching of diphenylisobenzofuran (DPBF) as the means of monitoring $^1\Delta_g$ decay. The approach has been described in detail,[17] and it suffices to point out here that, under suitably controlled conditions, the

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Table I. Solvent Dependence of Rate Constants, k_q/L mol^{-1} s^{-1}, for Quenching of Singlet Oxygen

solvent	α-T	HPMC	MCP[a]	TTBP
cyclohexane	$8.4\ (9)^b \times 10^7$	2.4×10^7	2.4×10^6	5.8×10^5
toluene	2.2×10^8	1.5×10^8	1.2×10^7	1.4×10^6
acetone	4.3×10^8	2.6×10^8	1.6×10^7	2.4×10^6
methanol	$3.0\ (6.7)^c \times 10^8$	3.4×10^8	1.3×10^7	$2.8\ (3.4)^d \times 10^6$
acetonitrile	5.9×10^8	5.7×10^8	2.5×10^7	2.5×10^6

[a] 1-Methoxycyclopentene.[17] [b] Reference 10b. [c] Reference 10a. [d] Reference 11.

first-order constant for DPBF bleaching, k', is given by eq 2 where $k_{d\Delta}$ is the rate constant for natural decay of $^1\Delta_g$ in the medium and k_r and k_q are the rate constants for reaction of this species with DPBF and added quencher (Q), respectively. These rate

$$k' = k_{d\Delta} + k_r[\mathrm{DPBF}] + k_q[\mathrm{Q}] \qquad (2)$$

parameters are obtained by plotting k' against (a) [DPBF] in the absence of quencher for $k_{d\Delta}$ and k_r and (b) [Q] at fixed [DPBF] for k_q. The latter rate constant includes both physical and chemical contributions to quenching.

III. Determination of Activation Parameters

In order to determine the effect of temperature on k_q for individual quenchers in a particular solvent it is not necessary to determine separately the temperature effect on $k_{d\Delta}$ and k_r (cf. ref 18–20) but only on their composite contribution to k' (eq 2). Thus, over the required temperature range, $^1\Delta_g$ quenching experiments may be performed on a reaction solution which is identical, apart from the presence of quencher, with the solution for a set of background experiments. The difference in the two thus obtained k' vs. temperature plots gives the variation of k_q[Q] with temperature (cf. eq 2). Correction for changes in quencher concentration with temperature allows construction of Arrhenius plots for k_q.

IV. Experimental Section

Pulsed Laser Excitation. The pulsed laser system and variable-temperature equipment have been described in detail elsewhere.[17] Thermal equilibration of cell contents was to an accuracy of ±0.5 °C; a variable temperature run was carried out on a single stock solution, the cell sample being automatically replenished after each shot at a given equilibrated temperature. Corrections for solvent density variations with temperature were therefore necessary. Samples were aerated, and all data points were from first-shot traces. In all experiments the optical density change at 415 nm during the DPBF bleaching event corresponded to <10% removal of the monitor. In addition, substrate (quencher) concentrations were generally considerably higher than for DPBF. The assumptions upon which eq 2 is based were thus valid.

Materials. The purification of cyclohexane, toluene, acetone, methanol, acetonitrile, 2-acetonaphthone, and DPBF has been described.[17] α-Tocopherol (Fluka) was used as supplied. 6-Hydroxy-2,2,5,7,8-pentamethylchroman was prepared as described.[21] 2,4,6-Tri-*tert*-butylphenol (Fluka) was recrystallized twice from ethanol.

V. Results

In the light of the considerations outlined in sections II and III we have determined the rate constants for quenching of $^1\Delta_g$ by α-T, HPMC, and TTBP in five solvents together in the majority of cases with the corresponding activation parameters.

Rate Constants for Quenching of $^1\Delta_g$ by Phenols. Typically five aerated solutions containing identical concentrations of 2-acetonaphthone (3–5 × 10^{-4} mol L^{-1}) and DPBF (4–10 × 10^{-5} mol L^{-1}) but varying amounts of phenol were subjected to pulsed laser excitation. First-order bleaching of DPBF took place in each case, and plots of k' vs. [phenol] according to eq 2 yielded rate constants, k_q, for quenching of $^1\Delta_g$ by phenol (Figure 1). These data are summarized in Table I together with available literature data and, for comparative purposes, the corresponding rate constants for reaction of $^1\Delta_g$ with a typical chemical quencher, 1-methoxycyclopentene. The two main points which arise from these data are (a) that rate constants only increase slightly with solvent polarizability and (b) that this solvent dependence is no greater than for chemical quenchers as typified by 1-methoxycyclopentene.

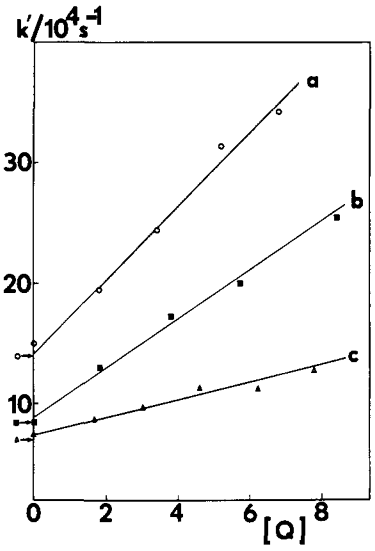

Figure 1. Dependence of first-order constant for DPBF bleaching, k', on quencher concentration: (a) α-T in aerated acetonitrile, [2-acetonaphthone] = 5 × 10^{-4} mol L^{-1}, [DPBF] = 1 × 10^{-4} mol L^{-1}, [Q] in units of 5 × 10^{-5} mol L^{-1}; (b) HPMC in cyclohexane, [2-acetonaphthone] = 4.7 × 10^{-4} mol L^{-1}, [DPBF] = 6.8 × 10^{-5} mol L^{-1}, [Q] in units of 10^{-4} mol L^{-1}; (c) TTBP in toluene, [2-acetonaphthone] = 4.3 × 10^{-4} mol L^{-1}, [DPBF] = 4.7 × 10^{-5} mol L^{-1}, [Q] in units of 5 × 10^{-3} mol L^{-1}. Arrows indicate anticipated intercepts based on $k_{d\Delta}$ and k_r values previously determined by using the same experimentation.[17]

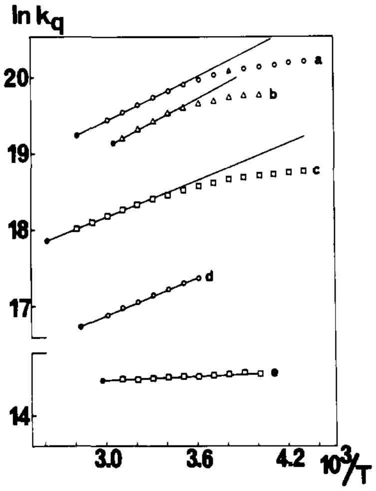

Figure 2. Arrhenius plots of the rate constants for quenching of $^1\Delta_g$, k_q, by (a) α-T in acetonitrile, (b) α-T in acetone, (c) HPMC in toluene, (d) HPMC in cyclohexane, and (e) TTBP in methanol. Solid circles represent solvent boiling points.

Activation Parameters for Quenching of $^1\Delta_g$ by Phenols. Two aerated solutions containing identical 2-acetonaphthone (3–5 × 10^{-4} mol L^{-1}) and DPBF (7–12 × 10^{-5} mol L^{-1}) concentrations, one containing phenol sufficient to increase k' by a factor of 2 (cf. eq 2), were subjected to laser excitation over a temperature range defined primarily by the atmospheric liquid range of the solvent but no less than 55 °C (cyclohexane). The difference between the two thus constructed k' vs. temperature plots gave a k_q[phenol] vs. temperature relationship (cf. eq 2). Correction for concentration changes due to solvent density variations with temperature allowed construction of Arrhenius plots. As exem-

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Table II. Solvent Dependence of Activation Parameters, $\Delta H^{\ddagger}_{\mathrm{exptl}}$/kcal mol^{-1},[a] $\Delta S^{\ddagger}_{\mathrm{exptl}}$/cal mol^{-1} K^{-1}, for Quenching of Singlet Oxygen

solvent	α-T	HPMC	MCP[b]	TTBP
cyclohexane		−2.1; −31	−0.7; −32	−0.2; −35
toluene	−3.4; −33	−3.5; −33	−1.0; −30	
acetone	−2.8; −29	−2.0; −26	−0.8; −28	
methanol	−1.8; −26	−1.4; −24	−0.3; −27	−0.8; −32
acetonitrile	−2.7; −33	−3.5; −31	−0.5; −27	

[a] ±0.5 kcal mol^{-1}.[17] [b] 1-Methoxycyclopentene.[17]

plified in Figure 2 all plots (except for TTBP in cyclohexane) had positive slopes, implying negative activation energies. However, for the faster quenchers, curvature was apparent. Over the experimental temperature range the plots became less positive with a decrease in temperature. In these cases the $\Delta H^{\ddagger}_{\mathrm{exptl}}$ and $\Delta S^{\ddagger}_{\mathrm{exptl}}$ values listed in Table II were extracted[22] from the essentially linear portion of the curves at higher temperature (Figure 2).

VI. Discussion

It is of course well documented that many bimolecular reactions of electronically excited states, both singlets and triplets, proceed via the intermediacy of an exciplex which may revert to reactants, yield products, or collapse to ground states with or without emission of a photon (eq 3). At one kinetic extreme the exciplex is formed

$$\begin{tikzcd} A^{*} + B \arrow[r, shift left, "k_D"] & \left[A^{*}\text{---}B\right] \arrow[l, shift left, "k_{-D}"] \arrow[r, "k_P"] \arrow[d, "k_d"] & \text{product} \\ & A + B & \end{tikzcd} \qquad (3)$$

essentially irreversibly; $(k_P + k_d) \gg k_{-D}$. The overall quenching rate constant is then given by eq 4, and experimental activation parameters are those for diffusion. At the other extreme where

$$k_q = k_D \qquad (4)$$

the overall quenching rate constant is small, say 2–3 orders of magnitude down on that for diffusion, $k_{-D} \gg (k_P + k_d)$, eq 5 holds where K_e is the equilibrium constant for exciplex formation.

$$k_q = K_e(k_P + k_d) \qquad (5)$$

Equations 4 and 5 represent the diffusion limit and preequilibrium limit, respectively. Experimentally reactions of the latter type exhibit highly negative entropies of activation and small or even negative enthalpies of activation. This is a consequence of the "balancing" of the negative heat of formation of the exciplex and the positive enthalpy of activation of the subsequent step(s). Only a negative enthalpy of activation is considered as definitive evidence of exciplex intermediacy,[23] and three or four examples have been reported.[24] The largest negative value published is an activation energy of −2.4 kcal mol^{-1} ($\Delta H^{\ddagger}_{\mathrm{exptl}}$ = −3.0 kcal mol^{-1}) for the quenching of benzaldehyde phosphorescence by toluene in acetonitrile.[24a] In other cases $\Delta H^{\ddagger}_{\mathrm{exptl}}$ values close to zero and below that for diffusion are consistent with but not proof of exciplex intermediacy.[25] We have previously shown that, experimentally at least, the chemical quenchings of $^1\Delta_g$ by furans,[19] indoles,[19] and enol ethers[17] fall into this category, and the same has been shown to be true for simple olefins.[26] We have therefore concluded[17] that the aforementioned chemical quenching proceeds via a $^1\Delta_g$–substrate exciplex which is formed rapidly and reversibly. As discussed in the following section we feel that the corresponding data for phenols **1**–**3**, predominantly physical quenchers of $^1\Delta_g$, strongly support these conclusions.

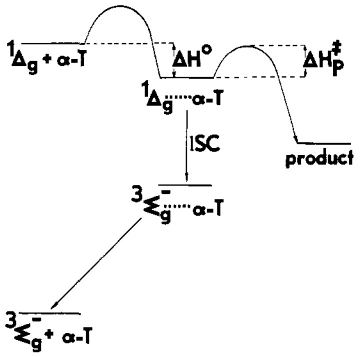
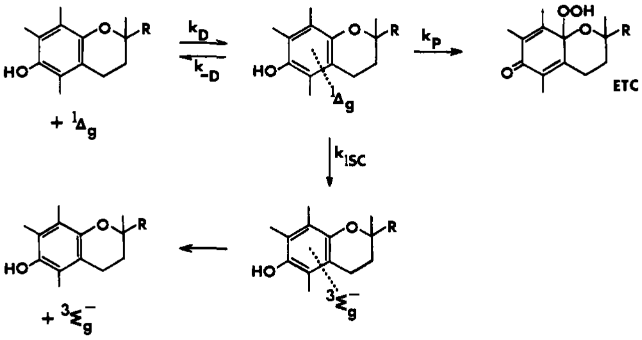


Figure 3. Schematic *enthalpy* profile for the reaction of $^1\Delta_g$ with α-T. The ISC process as drawn is the *result* of two processes, the horizontal nonradiative transition and subsequent relaxation.

Scheme II



Mechanism of Reaction of $^1\Delta_g$ with Phenols. We propose that the reactions of $^1\Delta_g$ with α-T, HPMC, and TTBP take place via a general mechanism which is adequately summarized and exemplified for α-T or HPMC in Scheme II. The reasoning behind this proposal is outlined below.

It is apparent from Figure 2 that for the phenols with relatively high quenching rate constants (α-T and HPMC) the Arrhenius plots show curvature with decreasing slope at lower temperature. This is to be anticipated in a situation in which lowering the temperature destroys the preequilibrium requirement that $k_{-D} \gg k_P + k_d$ (eq 3) or $k_{-D} \gg k_P + k_{ISC}$ (Scheme II). This result in itself is support for exciplex intermediacy. For the low overall quenching rate constants (e.g., TTBP in methanol, Figure 2) the preequilibrium limit still holds at low temperature because k_{ISC}[27] is still much lower than k_{-D}. As has already been emphasised, the appreciably positive slopes at high temperature provide convincing evidence of exciplex involvement.[28]

The consummation of the physical quenching process is envisaged as a spin–orbit coupling-induced intersystem crossing within the exciplex which must possess some degree of charge-transfer character. This would yield a ground-state complex which would

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[27] We refer here to k_{ISC} and not k_P simply because published evidence[10,11] indicates that the latter rate constant is kinetically unimportant for these particular phenols. Ideally one would like to know the temperature dependence of the chemical to physical quenching ratio.

[28] In a much earlier piece of steady-state work[29] the temperature dependence of oxygen uptake was determined for the triplet sensitized photooxidation of a large number of substrates, none of them phenols. Although assumptions made in data analysis led to gross errors in the determination of rate constants, both for the chemical reaction of $^1\Delta_g$ with individual substrates and for its natural decay, the determined β values ($k_{d\Delta}/k_q$; k_q = rate constant for chemical quenching) were reasonably accurate in the light of current data.[30] Arrhenius plots were not constructed, but in some cases plots of ln β vs. 1/T showed curvature at low temperature which almost certainly had its origins in the destruction of the preequilibrium requirement.

be unstable with respect to dissociation (Figure 3).[31] The excellent correlation with phenol half-wave oxidation potentials and the Hammett plot based on σ^+ values are of course consonant with such a mechanism.

If the mechanism summarized in Scheme II and Figure 3 is correct, >95% of quenchings proceed via the intersystem crossing process.[10,11] The $\Delta H^{\ddagger}_{\text{exptl}}$ values as negative as -3.5 kcal mol^{-1} which correspond to the high temperature end of the Arrhenius plots (Figure 2), where eq 5 holds, can thus be approximated to the expression of eq 6 (cf. Figure 3). With respect to $\Delta H^{\ddagger}_{\text{ISC}}$

$$\Delta H^{\ddagger}_{\text{exptl}} \sim \Delta H^{\circ} - \Delta H^{\ddagger}_{\text{ISC}} \tag{6}$$

we are unaware of data which would allow a definitive decision concerning its magnitude, although intuitively we feel it would be close to zero. If this is the case, the approximation of eq 7 should hold, and this makes sense to the extent that the $\Delta H^{\ddagger}_{\text{exptl}}$

$$\Delta H^{\ddagger}_{\text{exptl}} \sim \Delta H^{\circ} \tag{7}$$

values for α-T and HPMC (Table II) are significantly more negative than previously determined values for chemical quenchers[17,19,26] of $^1\Delta_g$ which result from the difference between ΔH° and $\Delta H^{\ddagger}_{\text{P}}$ (cf. Figure 3 and data in Table II for 1-methoxycyclopentene). Nevertheless the $\Delta H^{\ddagger}_{\text{exptl}}$ values for α-T and HPMC are still small in real terms (-1.4 to -3.5 kcal mol^{-1}). Thus, the important indication from this analysis is that the reaction enthalpy profiles for $^1\Delta_g$ reactions with organic substrates in general are "flat" between reactants and the transition state of the product-forming step (if there is a chemical contribution to quenching). This readily explains the generality of $\Delta H^{\ddagger}_{\text{exptl}}$ values close to zero for chemical quenchers. They are simply the consequence of the difference between two small numbers, ΔH° and $\Delta H^{\ddagger}_{\text{P}}$, a point that we at least had not appreciated. An obvious corollary to this conclusion is that the apparently general entropy-controlled nature of $^1\Delta_g$ reactions with organic substrates[17,19,26] is readily understood.

We have not included radical intermediates in the mechanism outlined in Scheme II. This contrasts with that proposed earlier by Foote,[13] principally as a result of careful identification of the 2,4,6-triphenylphenoxy radical as a transient in methanol.[11] In a related piece of work[34] we have carried out pulse radiolysis experiments with the aim of initiating the sequence summarized in eq 8 for α-T, HPMC, and TTBP. No transient was observed

$$^3\text{acridine}^* \xrightarrow{^3\Sigma_g^-} {}^1\Delta_g \xrightarrow{\text{phenol}} \text{phenoxy radical} \tag{8}$$

that could be assigned to a phenoxy radical.[35] It is, however, to be emphasised that our and Foote's experiments were performed with different phenols in different media. We cannot in any case exclude the possibility that, subsequent to exciplex formation, a radical pathway to products and/or indeed to reactant ground states exists, although we see no current need to invoke such a possibility in the cases of α-T, HPMC, and TTBP.

VII. Conclusions

We believe that the mechanism outlined in Scheme II and Figure 3 operates generally for $^1\Delta_g$ reactions with organic substrates[36] within the limits $k_{\text{P}} \gg k_{\text{ISC}}$ (chemical) and $k_{\text{ISC}} \gg k_{\text{P}}$ (physical). The balance between these rate constants is a sensitive function of spin-orbit coupling factors and entropy factors which play a dominant role as a consequence of a flat enthalpy profile along the critical portions of the reaction coordinate. Of course, the proposed mechanism is by no means novel from a photochemical point of view. To quote but one example, the quenchings of aromatic carbonyl triplets by amines[37] involve both physical and chemical processes and exhibit a range of rate constants and solvent sensitivities[38] which are quite comparable with those listed in Table I.

Acknowledgment. We thank the Science and Engineering Research Council and the Royal Society for financial support.

Registry No. 1, 59-02-9; **1** (hydroperoxy derivative), 67353-73-5; **2**, 950-99-2; **2** (hydroperoxy derivative), 92014-26-1; **3**, 732-26-3; **3** (hydroperoxy derivative), 33919-05-0; O_2, 7782-44-7.

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[31] This is essentially identical with the mechanism proposed by Ogryzlo and Tang[32] for the gas-phase quenching of $^1\Delta_g$ by amines and subsequently by Young et al.[33] for corresponding reactions in solution.

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