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Registry No. [I] γ (Y = S), 3331-14-4; [I] γ (Y = O), 83416-52-8; [I] α

(Y = S), 83416-50-6; [I] α (Y = O), 59242-30-7; [I] β (Y = S), 83416-51-7; [I] β (Y = O), 83416-53-9; III (Y = S), 12105-68-9; III (Y = O), 83416-54-0; MeCl, 74-87-3; MeF, 593-53-3; CH₃FCH₃⁺, 64710-12-9; CH₃ClCH₃⁺, 24400-15-5; Me⁺, 14531-53-4; NMe₃, 75-50-3; furan, 110-00-9; thiophene, 110-02-1; benzene, 71-43-2.

Time-Resolved Study of the Solvent and Temperature Dependence of Singlet Oxygen (¹ Δ_g) Reactivity toward Enol Ethers: Reactivity Parameters Typical of Rapid Reversible Exciplex Formation

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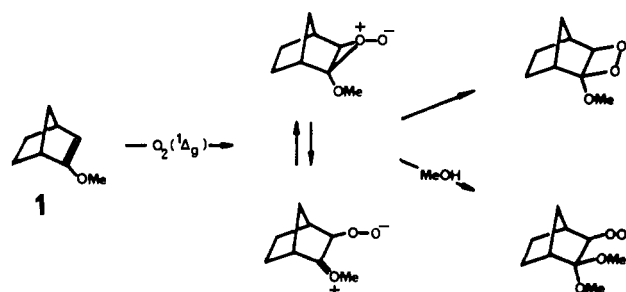
Abstract: Pulsed nitrogen laser excitation has been used to examine and compare the reactivities of four enol ethers toward singlet oxygen (¹ Δ_g) in five solvents. The experimental values of ΔH^\ddagger (0 ± 1.0 kcal mol⁻¹), ΔS^\ddagger (-23 to -34 eu), and the overall reaction rate constants (10^4 – 10^8 L mol⁻¹ s⁻¹) are characteristic of excited-state processes involving rapid reversible exciplex formation. Solvent effects are small but in some cases significant. It is concluded that such effects are the result of solvation entropy requirements at the transition state leading from exciplex to product, particularly in the case of dioxetane formation. The possibility is raised that the reversible exciplex mechanism operates generally for O₂ (¹ Δ_g) reactions.

1. Introduction

The nature of the reaction of singlet oxygen, O₂ (¹ Δ_g), with alkenes and enol ethers to give "ene"-type products continues to be a subject of considerable discussion and argument.¹⁻⁶ The controversy has centered around two mechanisms involving (a) a classical six-center transition state and (b) a perepoxide intermediate. The advent of theoretical calculations in this area has in no way decreased mechanistic controversy. Orbital correlation diagrams³ and CNDO/2 CI⁷ and MINDO/3⁸ calculations favour initial perepoxide formation. On the other hand GVB-CI⁹ calculations are claimed to rule out this intermediate in favor of a 1,4 biradical although a concerted mechanism is not excluded.¹⁰ More recently STO-3G and unrestricted MINDO/3 (UM3) results have been taken to exclude both perepoxide and biradical mechanisms and favor the concerted process.¹²

Experimentally it has been shown that for molecules containing a trisubstituted double bond, both enol ethers, and simple olefins, there exists a pronounced preference for hydrogen migration from the most substituted side of the double bond.¹³ This, together

Scheme I



with small but apparently significant isotope effects,^{11,14} led to the suggestion¹⁵ that the initial reaction between O₂ (¹ Δ_g) and olefin is irreversible formation of a complex, the geometry of which, and subsequently that of the products, is determined by secondary orbital effects. It has, however, been argued that the steric preferences cited are consistent with ground-state conformational effects.¹⁶

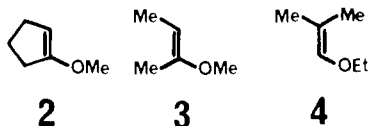
Of particular interest have been reports of methanol trapping of intermediates.^{17,18} In Scheme I are reproduced conclusions reached by Jefford and Rimbault¹⁷ concerning the reaction of 2-methoxynorbornene (1) with O₂ (¹ Δ_g) in methanol. The isolation of the solvent addition product, shown not to be derived from the

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- (6) A. A. Frimer, *Chem. Rev.*, **79**, 359 (1979).
- (7) S. Inagaki and K. Fukui, *J. Am. Chem. Soc.*, **97**, 7480 (1975).
- (8) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975); **99**, 2338 (1977).
- (9) L. B. Harding and W. A. Goddard, *J. Am. Chem. Soc.*, **102**, 439 (1980).
- (10) The biradical mechanism may be rejected on experimental grounds, particularly the proven suprafacial character of allylic hydroperoxide formation¹¹ and the lack of correlation of reactivity with radical stability.¹³
- (11) M. Orfanopoulos and L. M. Stephenson, *J. Am. Chem. Soc.*, **102**, 1417 (1980).
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corresponding dioxetane, was taken as evidence for a zwitterionic intermediate and claimed to support calculations^{8,19} in favor of peroxide intermediacy in general.

In this paper we report the determination of rate and activation parameters for the reaction in five solvents of O₂ (¹Δ_g) with a series of enol ethers (1–4). Compounds 2 and 3 bear an obvious rela-

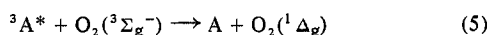
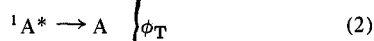


tionship to 2-methoxynorbornene (1) while 4 is typical of compounds shown^{13d} to exhibit a preference for H migration from the most substituted side of the double bond during allylic hydroperoxide formation.

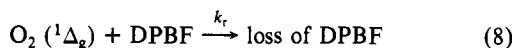
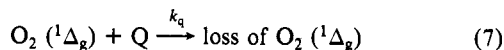
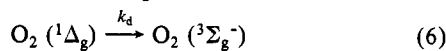
In terms of product distribution compounds 2–4 show behavior typical of enol ethers,^{20,14e} i.e., allylic hydroperoxide formation in the less polar media, cyclohexane and toluene, with increasing proportions of dioxetane derived products on going from acetone to methanol to acetonitrile.²¹ As mentioned, the products of reaction of 1 have been published.¹⁷ It is generally accepted²² that most organic substrates, and certainly those of the class under consideration, react with O₂ (¹Δ_g) exclusively in a chemical as opposed to a physical sense. In this work we therefore assume that rate constants for quenching of O₂ (¹Δ_g) by substrate reflect removal of the transient via chemical reaction.

2. Determination of Rate Parameters by Pulsed Laser Photolysis

The extraction of rate parameters for decay and reaction of O₂ (¹Δ_g) in solution by pulsed laser photolysis is well documented,²⁴ in this work we have employed the 2.5-ns pulse of a nitrogen laser emitting at 337 nm. Absorption of such a pulse by an aerated solution of anthracene (A) as sensitizer (1–3 × 10⁻⁴ mol L⁻¹) results in O₂ (¹Δ_g) formation via channels 1–5. In the presence



of the monitor diphenylisobenzofuran (DPBF) and an additional quencher (Q) the decay of O₂ (¹Δ_g) is governed by channels 6–8,



the rate parameters for which may depend to a lesser or greater extent on the medium. When the initial concentration of O₂ (¹Δ_g)

is small compared to the initial concentrations of DPBF and Q the rate of loss of DPBF is given by eq 9, where Q may act via

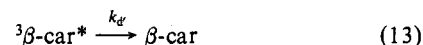
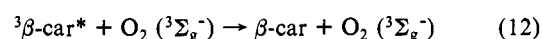
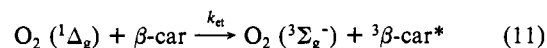
$$\frac{d(-[\text{DPBF}])}{dt} = k_r[\text{DPBF}][O_2({}^1\Delta_g)]_0 \exp[-(k_d + k_r[\text{DPBF}] + k_q[Q])t] \quad (9)$$

chemical or physical action and [O₂ (¹Δ_g)]₀ is the concentration of O₂ (¹Δ_g) at the end of the laser pulse. It is readily shown that a plot of ln(D_t - D_∞) against time will be linear with a slope, k', given by eq 10, where D_t and D_∞ are respectively the DPBF optical

$$k' = k_d + k_r[\text{DPBF}] + k_q[Q] \quad (10)$$

densities at time t and at completion of the bleaching event. The rate parameters, k_d, k_r, and k_q can be evaluated from plots of k' against (1) DPBF concentration (in the absence of quencher) for k_d and k_r, and (2) quencher concentration (at fixed DPBF concentration) for k_q.

An alternative O₂ (¹Δ_g) monitor is the triplet state of β-carotene.²⁵ The carotenoid quenches O₂ (¹Δ_g) via collisional energy transfer according to eq 11 and the subsequent triplet decay is



via channels 12 and 13. At sufficiently high carotene concentrations its triplet formation is rate limiting and therefore the rate constant for decay of ³β-car*, k', follows the decay of O₂ (¹Δ_g) and eq 10 is replaced by eq 14. Extraction of individual rate constants is as for DPBF bleaching.

$$k' = k_d + k_{et}[\beta\text{-car}] + k_q[Q] \quad (14)$$

3. Determination of Activation Parameters by Pulsed Laser Photolysis

We have already demonstrated the temperature dependence of k_d and k_r using the pulse radiolysis technique²⁶ and compared these results with those previously reported.²⁷ In order to determine the effect of temperature on k_q for individual substrates in a particular solvent, it is not necessary to determine separately the temperature effect on k_d and k_r but only the effect on their composite contribution to k'. Thus, over the required temperature range, O₂ (¹Δ_g) quenching experiments (section 2) 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' v. temperature plots gives the variation in k_q[Q] with temperature. Correction for changes in quencher concentration with temperature thus allows construction of the Arrhenius plot for k_q. Either the DPBF or β-carotene methods may be used. The former method has been employed to show that the quenching of O₂ (¹Δ_g) by furans and indoles is entropy controlled.²⁶

4. Experimental Section

4.1. Pulsed Laser Photolysis. Experiments were carried out with the 2.5-ns pulse (337 nm) of a Lambda Physik 1-MW nitrogen laser, at right angles to a pulsed 250-W xenon analyzing lamp and Hilger-Watt monochromator. Back-off circuitry, built in house, allowed small deviations from the initial high pulsed lamp intensity to be displayed. The period of exposure of reactants to the analyzing light was confined to <10 ms by use of a Compur programmable electronic shutter, the operational control of which was built into the master trigger generating circuitry. Signal time dependencies were displayed, via a Tektronix 7912 Digitizer, as CRO traces of voltage waveforms at (a) the anode of an RCA IP28 photomultiplier coupled to a 10-kΩ load resistance, detection rise time <100 ns, for DPBF bleaching and (b) the anode of an EMI 9781 photomultiplier coupled to a 50-Ω load resistance, detection rise time 1 ns, for β-carotene triplet decay. In all DPBF bleaching experiments the

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Table I. Solvent Dependence of Singlet Oxygen Lifetimes (τ_{Δ})^a and Rate Constants for Reaction with Diphenylisobenzofuran (k_r)

solvent	$\tau_{\Delta}/\mu\text{s}$ (lit.)	$k_r/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (lit.)
cyclohexane	20 (17 ^b)	4.5×10^8
toluene	26, 25 ^c (25 ^d)	6.7×10^8 (6.6×10^8 e)
acetone	36 (26, ^b 42, ^f 51, ^g 50 ^h)	6.4×10^8 (1.02×10^9 h)
methanol	10 (7, ^b 5, ⁱ 11 ^j)	8.1×10^8 (8×10^8 b, 1.3×10^9 k)
acetonitrile	35 (30, ^b 33, ^l 57, ^f 77 ^h)	1.1×10^9 (1.28×10^9 h)

^a DPBF bleaching method unless otherwise stated. ^b Reference 24a. ^c β -Carotene triplet method. ^d Reference 30. ^e Reference 31. ^f Reference 22e. ^g Reference 33. ^h Reference 34. ⁱ Reference 24b. ^j Reference 35. ^k Reference 24c. ^l Reference 36.

optical density change at 415 nm during the bleaching event corresponded to <10% removal of the monitor. In addition, substrate (quencher) concentrations were generally considerably higher than for DPBF. Corresponding restrictions applied to the experiments with β -carotene triplet as monitor (520–550 nm). The assumptions upon which eq 10 and 14 are based were thus valid.

4.2. Variable-Temperature System. The flow-through quartz reaction cell was housed in a variable-temperature box.²⁸ The cell was in good thermal contact with an aluminum heat sink which was warmed and cooled by means of cartridge heaters and precooled nitrogen gas, respectively. The temperature of the cell contents was measured by means of a Comark electronic thermometer utilizing a copper-Constantan thermocouple sunk into the cell shoulder. This allowed equilibration of the cell contents between -50 and 90 °C 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. Thus concentration changes due to solvent density variations had to be corrected for.

4.3. Materials. Cyclohexane (reagent grade) was subjected to sulfuric acid-water-bicarbonate-water treatment, passed down a column of activated silica gel, and then distilled through a 4-ft steel wool packed column. Toluene (Analar, B.D.H.) was refluxed over lithium aluminum hydride for 48 h and fractionally distilled. Acetone (Proanalysis, May and Baker) was refluxed with potassium permanganate overnight and distilled through a 4-ft steel wool packed column. Methanol (Analar, Hopkin and Williams) was stood over sodium, refluxed overnight with sodium borohydride, and fractionally distilled. Acetonitrile (Hopkin and Williams) was passed down a column of freshly activated alumina, refluxed over potassium borohydride for 4 days and fractionally distilled.

Anthracene (Scintillation Grade, B.D.H.) was used as supplied. 2-Acetonaphthone (Aldrich) was recrystallized twice from absolute ethanol. DPBF (Aldrich) was recrystallized from methanol/water. β -Carotene (Fluka) was recrystallized from benzene/methanol before use. (E)-2-Methoxy-2-butene²⁹ and 2-methoxynorbornene¹⁷ were prepared as described.

1-Ethoxy-2-methylpropene (4). A mixture of triethyl orthoformate (65 g), isobutyraldehyde (50 g), absolute ethanol (190 g) and absolute ethanol (2 g) saturated with dry HCl gas was left to stand at room temperature overnight. Aqueous sodium carbonate (10%, 10 mL) hydrogen peroxide (30 vol, 3 mL), and water (50 mL) were added in that order, and the dried organic phase was fractionally distilled to give pure acetal (50 g, bp 136–138 °C). This product was fractionally distilled under nitrogen from toluenesulfonic acid (2 g). The material collected below 100 °C was washed with water, dried, and refractionated under nitrogen to give 1-ethoxy-2-methylpropene (10 g, bp 93.5 °C) which was homogenous by GLC (6 ft, 3% Dexil 410 on Supelcoport 100–120, 80 °C, 20 psi): IR ν_{max} (film) 1693; ¹H NMR τ (CDCl₃) 4.21 (1 H, m), 6.29 (2 H, q, 7 Hz), 8.42 (6 H, m), 8.77 (3 H, t, 7 Hz).

1-Methoxycyclopentene (2). A mixture of cyclopentanone (47 g), trimethyl orthoformate (80 g), and methanol (100 g) containing toluenesulfonic acid (0.5 g) was refluxed under nitrogen for 1 h. Fractionation yielded the ketal (50 g, bp 138–140 °C) which was slowly fractionated under nitrogen from toluenesulfonic acid (2 g). A second fractionation was necessary to give pure 1-methoxycyclopentene (5.7 g, bp 110 °C), homogenous by GLC (conditions as in preceding preparation): IR ν_{max} (film) 1644; ¹H NMR τ (CDCl₃) 5.59 (1 H, br s), 6.46 (3 H, s), 7.4–8.5 (6 H, m).

5. Results

In the light of the considerations outlined in sections 2 and 3, we have been able to determine O₂ (¹ Δ_g) lifetimes ($\tau_{\Delta} = k_d^{-1}$),

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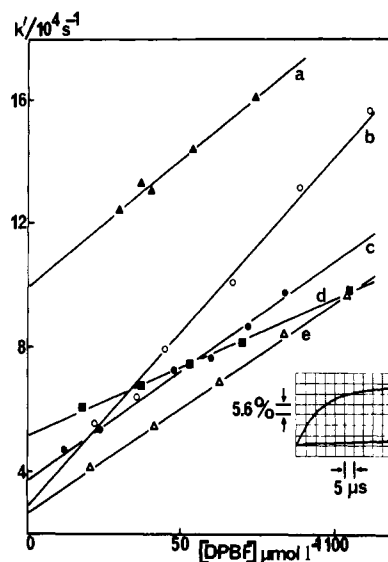


Figure 1. Dependence of the first-order constant for DPBF bleaching, k' , on DPBF concentration for aerated solutions containing anthracene (3.1×10^{-4} mol L⁻¹) in (a) methanol, (b) acetonitrile, (c) toluene, (d) cyclohexane, and (e) acetone. Inset: Time dependence of DPBF bleaching at 415 nm after absorption of a 2.5-ns laser pulse by anthracene (3.1×10^{-4} mol L⁻¹) in aerated acetone containing DPBF (8.4×10^{-5} mol L⁻¹); lower trace is for an identical experiment with the laser shutter closed.

rate constants for its reaction with DPBF (k_r), and rate constants (k_q) and activation parameters for its reaction with the enol ethers 1–4 in five solvents. These results are summarized in Table I and II.

5.1. O₂ (¹ Δ_g) Lifetimes and Rate Constants for Reaction with DPBF. Pulsed nitrogen laser photolysis (337 nm) of aerated solutions of anthracene (3×10^{-4} mol L⁻¹) containing varying concentrations of DPBF ($(2-10) \times 10^{-5}$ mol L⁻¹) resulted in first-order bleaching of DPBF. Plots of the first-order bleaching constant, k' , vs. [DPBF] according to eq 10 yielded slopes k_r and intercepts k_d (Figure 1). These values are reproduced in Table I together with published data. In the case of toluene, a check with the β -carotene method gave the same τ_{Δ} . These data confirm the viability of our system.³⁷ It is of interest that the values of k_r vary over the range $(4-11) \times 10^8$ L mol⁻¹ s⁻¹ according to solvent. On the basis of repeated determinations giving reproducibility better than $\pm 5\%$, there is no doubt that these differences are real and represent a distinct but small solvent effect characterized by an increase in k_r with increasing solvent polarizability (cf. ref 39).

5.2. Rate Constants for Quenching of O₂ (¹ Δ_g) by Enol Ethers. Typically five aerated solutions containing identical concentrations of anthracene ($(2-3) \times 10^{-4}$ mol L⁻¹) and DPBF ($(3-4) \times 10^{-5}$ mol L⁻¹) but varying amounts of enol ether were subjected to pulsed laser photolysis. First-order bleaching of DPBF took place in all cases and plots of k' vs. [enol ether] according to eq 10 yielded rate constants, k_q , for reaction at ambient temperature between O₂ (¹ Δ_g) and enol ether (Figure 2). Three main points arise from these rate constant data (Table II): (1) rate constants,

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(37) Identical results were obtained when anthracene was replaced by 2-acetonaphthone as sensitizer.³⁸

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(39) B. A. Lindig and M. A. J. Rodgers, *Photochem. Photobiol.*, **33**, 627 (1981).

Table II. Solvent Dependence of Rate Constants, $k_q/L \cdot mol^{-1} \cdot s^{-1}$, and Activation Parameters $\Delta H^\ddagger/kcal \cdot mol^{-1}$; $\Delta S^\ddagger/cal \cdot mol^{-1} \cdot deg^{-1}$ for Quenching of Singlet Oxygen by Enol Ethers 1-4^a

solvent	1	2	3	4
cyclohexane	$<1.0 \times 10^4$ ^b	2.4×10^6 , (-0.7; -32.0)	2.5×10^6 , (0.9; -24.7)	1.6×10^7 , (-0.5; -28.6)
toluene	1.1×10^4 ^b	1.2×10^7 , (-1.0; -29.8)	1.2×10^7 , (-0.3; -27.5)	3.1×10^7 , (0.2; -23.4)
acetone	2.5×10^5 ^b	1.6×10^7 , (-0.8; -28.3)	1.1×10^7 , (-0.6; -28.3)	4.2×10^7 , (-0.6; -25.7)
methanol	6.2×10^5 , (-0.2; -31.0)	1.3×10^7 , (-0.3; -27.1)	1.3×10^7 , (-0.5; -27.6)	2.3×10^7 , (0.2; -23.0)
acetonitrile	6.2×10^5 , (-0.3; -33.7)	2.5×10^7 , (-0.5; -26.7)	2.4×10^7 , (-0.8; -27.3)	3.9×10^7 , (-0.3; -24.0)

^a Error in $\Delta H^\ddagger = \pm 0.5 kcal \cdot mol^{-1}$. ^b Rate constants too low to allow determination of activation parameters.

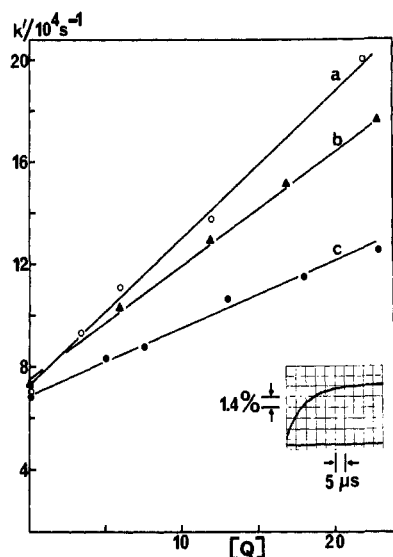


Figure 2. Dependence of the first-order constant for DPBF bleaching, k' , on quencher concentration: (a) 2-methoxynorbornene (1) in aerated acetonitrile, [anthracene] = $2.4 \times 10^{-4} mol L^{-1}$, [DPBF] = $3.8 \times 10^{-5} mol L^{-1}$, [Q] in units of $10^{-2} mol L^{-1}$; (b) 1-ethoxy-2-methylpropene (4) in aerated acetonitrile, [anthracene] = $2.2 \times 10^{-4} mol L^{-1}$, [DPBF] = $3.2 \times 10^{-5} mol L^{-1}$, [Q] in units of $10^{-4} mol L^{-1}$; (c) (*E*)-2-methoxy-2-butene (3) in cyclohexane, [anthracene] = $1.0 \times 10^{-4} mol L^{-1}$, [DPBF] = $4.1 \times 10^{-5} mol L^{-1}$, [Q] in units of $10^{-3} mol L^{-1}$. Inset: Time dependence of DPBF bleaching at 415 nm after absorption of a 2.5-ns laser pulse by anthracene ($2.4 \times 10^{-4} mol L^{-1}$) in aerated acetonitrile containing DPBF ($3.8 \times 10^{-5} mol L^{-1}$) and 2-methoxynorbornene ($5.9 \times 10^{-2} mol L^{-1}$); lower trace is for an identical experiment with the laser shutter closed.

as for DPBF, generally increase slightly with solvent polarizability and are particularly slow for cyclohexane; (2) rate constants for reaction of O₂ (¹Δ_g) with 2, 3, and 4 are significantly greater, by a factor of 10²-10³ depending on solvent, than for 2-methoxynorbornene (1); (3) rate constants for the latter show a much larger variation with solvent (a factor of 56 from toluene to acetonitrile) than do those for 2, 3, and 4 (2.1-1.3). Quite clearly 2-methoxynorbornene (1) shows behavior toward O₂ (¹Δ_g) which is significantly different from that of compounds 2-4.

As discussed in section 5.4, 1 also reacts with ground-state oxygen, O₂ (³Σ_g⁻). In determination of the rate constants for quenching of O₂ (¹Δ_g) by 1, the pulsed laser experiments were performed immediately after introduction of quencher to the aerated reaction solution. The ground-state reaction was totally insignificant on the resulting experimental time scales.

5.3. Activation Parameters for Quenching of O₂ (¹Δ_g) by Enol Ethers 2-4. Two aerated solutions containing identical anthracene ((1-3) × 10⁻⁴ mol L⁻¹) and DPBF ((3.5-4.5) × 10⁻⁵ mol L⁻¹) concentrations, one containing enol ether sufficient to increase k' by a factor of 2 (cf. eq 10) were subjected to laser photolysis over a temperature range defined by the atmospheric liquid range of the solvent (section 4.2). The difference between the two thus constructed k' vs. temperature plots gave a k_q [enol ether] vs. temperature relationship (cf. eq 10). Correction for concentration changes due to solvent density variations with temperature allowed construction of Arrhenius plots which were linear over the experimental temperature ranges (Figure 3); activation energies were very low, 1.4 to -0.5 kcal mol⁻¹ (experimental error = ±0.5 kcal

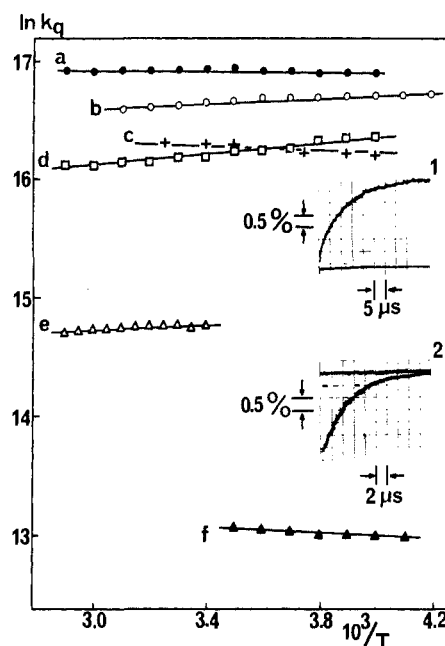


Figure 3. Arrhenius plots of the rate constant for quenching of O₂ (¹Δ_g), k_q , by 1-methoxycyclopentene (2) in (a) acetonitrile, (b) acetone, (c) methanol, (d) toluene, (e) cyclohexane, and by (f) 2-methoxynorbornene (1) in aerated acetonitrile containing β-carotene ($2.8 \times 10^{-5} mol L^{-1}$) and 2-methoxynorbornene ($1.0 \times 10^{-1} mol L^{-1}$), temperature -30.0 °C; upper trace is for an identical experiment with the laser shutter closed. (2) Time dependence of β-carotene triplet decay at 540 nm after absorption of a 2.5-ns laser pulse by 2-acetonaphthone ($3.1 \times 10^{-4} mol L^{-1}$) in aerated acetonitrile containing β-carotene ($2.8 \times 10^{-5} mol L^{-1}$) and 2-methoxynorbornene ($1.0 \times 10^{-1} mol L^{-1}$), temperature 54.0 °C; lower trace is for an identical experiment with the laser shutter closed.

mol⁻¹). Extraction of ΔH^\ddagger and ΔS^\ddagger from these data⁴⁰ gave the values recorded in Table II.

5.4. Activation Parameters for Quenching of O₂ (¹Δ_g) by 2-Methoxynorbornene. In contrast to the experiments described for 2-4 in the preceding section, it was found that aerated solutions prepared for laser photolysis that contained anthracene, DPBF, and 1 became colorless; i.e., DPBF was destroyed, within 2-5 h on standing *in the dark* at room temperature. This was true for all solvents employed in this work; the more polar the solvent, the faster the DPBF bleaching. We have carried out some preliminary work on this effect and our results are summarized as follows:⁴¹ (1) At room temperature *in the dark* aerated solutions of DPBF ($\sim 7 \times 10^{-5} mol L^{-1}$) containing 1 ($10^{-1} mol L^{-1}$) lose DPBF via a zero-order process over 2-5 hours depending on solvent. In the absence of 1 or oxygen DPBF decay is not observed. (2) If a sealed aerated toluene solution of anthracene ($3 \times 10^{-4} mol L^{-1}$) and 1 ($10^{-1} mol L^{-1}$) is maintained at 45 °C *in the dark* for 15 min, subsequent pulsed laser excitation of anthracene leads to the formation of anthracene triplet which decays with a half-life (13 μs) typical of an oxygen-free system.⁴² (3) Corresponding ex-

(40) K. J. Laidler, "Reaction Kinetics", Vol. 2, Pergamon Press, 1963.

(41) Preliminary work carried out by M. Standen of this department is gratefully acknowledged.

periments with enol ethers 2–4 did not show these effects.

To avoid problems associated with this ground-state reaction, we have found it necessary to restrict the determination of activation parameters for **1** to temperatures below 0 °C and have employed the β -carotene monitoring technique (section 2). Due to the very low reactivity of **1** in cyclohexane, toluene, and acetone, variable-temperature experiments were restricted to methanol and acetonitrile. Again ΔH^\ddagger values of essentially zero and highly negative ΔS^\ddagger values were observed (Figure 3 and Table II).

6. Discussion

Our experimental results will be discussed in terms of processes which involve (a) no complex other than the encounter complex and (b) an exciplex which is significantly long-lived relative to the encounter complex and stabilized by electron donor/acceptor interaction.

6.1. Product Formation Direct from the Encounter Complex.

The highly negative ΔS^\ddagger values associated with the reaction of O_2 ($^1\Delta_g$) with the enol ethers 1–4 (Table II) are typical of processes involving a highly ordered transition state. However, it is well documented⁴³ that the ΔS^\ddagger values associated with such transition states containing six, four, and three centers are not significantly different from each other. Thus differentiation between ene-, dioxetane (${}_2a + {}_2b$), or perepoxide-like transition states is not possible on these grounds.

Reactions of the above type generally exhibit significant ΔH^\ddagger values.⁴³ The values close to zero for the reaction of O_2 ($^1\Delta_g$) with enol ether would be attributed to the electronic excitation energy²⁶ and possibly the singlet character of O_2 ($^1\Delta_g$). One is bound to draw the analogy with the reactions of the singlet state of the carbene fluorenylidine with olefins. These exhibit ΔH^\ddagger values "statistically indistinguishable from zero" and ΔS^\ddagger values of -17 to -23 eu in acetonitrile solution.⁴⁴

Of particular mechanistic significance are the relative values of the rate constants for reaction of O_2 ($^1\Delta_g$) with enol ethers 1–4 (Table II). It is well documented that the double bonds in norbornenes exhibit higher rate constants for addition reactions, including many cycloadditions, than do the corresponding bonds in cyclopentenes and acyclic olefins,^{43,45} and this is certainly true for electrophilic additions proceeding via three-center transition states.⁴³ It is, however, quite clear from Table II that O_2 ($^1\Delta_g$) reacts with 2-methoxynorbornene (**1**) with a rate constant which is a factor of 10^2 – 10^3 smaller, depending on solvent, than those for the less rigid systems 2–4. This is in complete contrast to accepted reactivity modes, and on these grounds we reject direct perepoxidation as the mechanism for reaction of O_2 ($^1\Delta_g$) with enol ethers *in general*, although not necessarily for 2-methoxynorbornene (**1**).

6.2. Product Formation via an Exciplex. It is clearly a possibility that the reactions under discussion proceed via initial formation of a complex, longer-lived than the encounter complex and stabilized by some degree of charge transfer from substrate to O_2 ($^1\Delta_g$). The possibility of such an intermediate in the case of enol ethers has been raised by Bartlett et al.,^{14c} and on the basis of stereochemical and isotope effect data Stephenson¹⁵ has argued that such complex formation is *irreversible*, i.e., rate limiting. The techniques described in this paper measure the rate constant for removal of O_2 ($^1\Delta_g$), k_q , which in the irreversible situation described would be equal to the rate constant for complex formation. These rate constants are factors of between 10^2 and 10^5 down on diffusion control (Table II) and are not compatible with irreversible complex formation.

A complex between the electronically excited O_2 ($^1\Delta_g$) and an enol ether is an exciplex. Such species, whether involving singlet⁴⁶

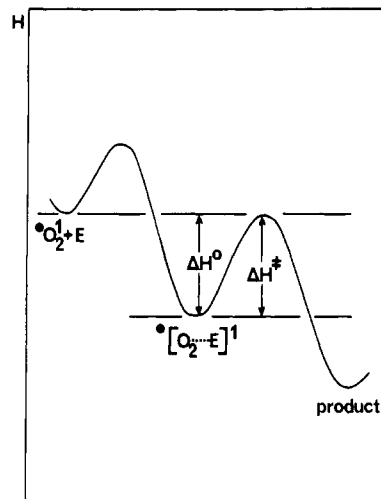
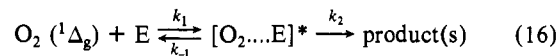


Figure 4. Reaction enthalpy profile leading to an *experimental* activation enthalpy of zero for loss of O_2 ($^1\Delta_g$) when entropy restrictions create a situation in which eq 15 holds.

or triplet⁴⁷ excited states, are formed via essentially diffusion-controlled processes, even when ΔS° values indicate a "tight" exciplex geometry.^{46a,c} In such cases overall rate constants for reaction which are much less than that of diffusion are associated with rate-determining decay and/or reaction from the exciplex which is formed *reversibly*. The rate constants determined for O_2 ($^1\Delta_g$)–enol ether reactivity (Table II) clearly would fit into this category. In addition, the ΔH^\ddagger values close to zero are in excellent agreement with rapid reversible exciplex formation followed by rate-determining reaction, i.e., eq 15 should hold where

$$k_q = Kk_2 \quad (15)$$

$K = k_1/k_{-1}$ (cf. eq 16, E = enol ether). In this situation the



balance between the enthalpy of formation of the exciplex and the activation enthalpy of the subsequent product-forming step can result in a small positive, zero, or small negative experimental activation enthalpy (cf. Figure 4). Only a negative value, however, is definitive evidence for exciplex intermediacy,^{46,48} and one or two such examples have been reported.⁴⁹ In other cases⁵⁰ where reaction via an exciplex is thought likely, ΔH^\ddagger values close to zero and below that for diffusion are consistent with but not conclusive proof of exciplex intermediacy.^{47,50} Although the values of ΔH^\ddagger determined in this work are mostly negative, none is negative enough to rigidly define exciplex involvement. It is to be noted that the arguments put forward against general perepoxide intermediacy in section 6.1 are equally applicable to the situation in which eq 15 and 16 are valid.

In a previous paper²⁶ we showed that the ΔH^\ddagger values for reaction of a series of furans and a series of indoles with O_2 ($^1\Delta_g$) in toluene are zero within experimental error. We at that time discussed, but did not favor, the possibility of rapid reversible complex formation. This was on the grounds that the spread of rate constants observed, 7.0×10^5 to 8.0×10^8 L mol⁻¹ s⁻¹, together

(46) (a) D. V. O'Connor and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4706 (1976); (b) M.-H. Hui and W. R. Ware, *ibid.*, **98**, 4712 (1976); (c) *ibid.*, **98**, 4718 (1976).

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(50) R. O. Loutfy and P. DeMayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977); "Handbook of Chemistry and Physics", 55th ed., CRC Press, Cleveland, OH, 1973, p F51.

(42) In the control experiment carried out in the absence of **1** the anthracene triplet half-life was 130 ns.

(43) F. Freeman, *Chem. Rev.*, **75**, 439 (1975).

(44) J. J. Zupancic, and G. B. Schuster, *J. Am. Chem. Soc.*, **103**, 944 (1981).

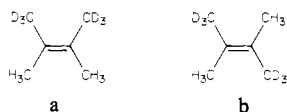
(45) R. Huisgen, P. H. J. Ooms, M. Mingin, and N. L. Allinger, *J. Am. Chem. Soc.*, **102**, 3951 (1980); R. Huisgen, *Proc. Chem. Soc., London* 357 (1961); *Angew. Chem.*, **75**, 604, 742 (1963); S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4054 (1976).

with the existence of two distinct mechanisms, one for furans and one for indoles, made it unlikely that for all 13 substrates investigated the ΔH^\ddagger values of zero were due to a fortuitous matching of enthalpy contributions in a complex process. The present data on a third substrate group, namely enol ethers, would appear to do nothing but reinforce this argument. However, we cannot fail to be impressed by the reactivity parameter similarities between the O₂ (¹Δ_g) processes under discussion and other electronically excited-state processes involving exciplex intermediacy, particularly since we feel that other published O₂ (¹Δ_g) data can be accommodated within such a framework. The experimental ΔH^\ddagger values close to zero would not be dependent on exciplex stability, only on the fact that the heat content of the starting materials be about the same as that of the transition state of the product-forming step (Figure 4). The observed product selectivities, e.g., the *cis* reactivity preference¹³ and small isotope effects,^{11,14} represent small ΔH^\ddagger differences, assuming enthalpy control,^{16b} which are within the experimental error in ΔH^\ddagger .⁵¹

In a situation where ΔH^\ddagger values are consistently close to zero, large variations in k_q from substrate to substrate and/or from solvent to solvent must be largely entropy dependent. Where eq 15 and 16 operate, the experimental ΔS^\ddagger measures the entropy change between reactants and the product-forming transition state, and the factors which influence this parameter may be formally separated into two categories, those due to substrate structural features and those due to solvent reorganization requirements.

In general the rate constant for reaction of O₂ (¹Δ_g) with π systems of a particular type increases with increasing alkyl substitution, and this has naturally been attributed to the resulting increase in the π -donating ability of the substrate. In a situation where experimental ΔH^\ddagger values are zero such an explanation is at best a gross oversimplification. We have raised the possibility²⁶ that the increase in k_q with substitution is due to a release, at the transition state for product formation, of entropy restrictions due to eclipsed interactions of substituents in a 1,2 relationship on a π bond, and this explanation is equally applicable to a situation in which eq 15 and 16 are valid since the critical entropy difference is still that between initial reactants and the transition state of the product-forming step. The above explanation was originally put forward to rationalize substituted furan and indole reactivity toward O₂ (¹Δ_g) in toluene.^{26,52} An alternative possibility raised in that work was that the highly negative ΔS^\ddagger values and their variation from substrate to substrate were a result of solvent reorganization requirements. This is now excluded since solvent effects on k_q are minimal while ΔH^\ddagger values remain 0 ± 0.5 kcal mol⁻¹. For instance the k_q values for O₂ (¹Δ_g) and 2,5-di-*tert*-butylfuran determined by pulsed laser photolysis are 1.1, 1.8, 2.4, and 2.9×10^8 L mol⁻¹ s⁻¹ for cyclohexane, toluene, acetone, and acetonitrile, respectively.²¹ Tetramethylethylene which reacts

(51) Stephenson's isotope data on deuterated tetramethylethylenes^{14d} have led to the conclusion that reaction involves irreversible formation of an intermediate which is operationally equivalent to a perepoxide which cannot invert at the "oxonium" oxygen.^{14d,15} This appears incompatible with the reversible exciplex mechanism, and as pointed out by the referees, an alternative explanation of the admittedly small differences between the k_{11}/k_D ratios for a (1.05–1.09) and b (1.38–1.41) would appear necessary. While we presently have no detailed rationale of these differences, we would point out that the product-forming transition states for a and b may well be dif-



ferently affected with respect to D or H abstraction by factors such as (a) conformational effects related to those discussed by Houk et al.,^{16b} and (b) differences in C–D as opposed to C–H hyperconjugative effects (cf. section 6.3) which could manifest themselves due to the symmetry differences of a and b. To date isotope data^{11,14} have only been obtained from steady-state experiments and are based on product analysis of intramolecular competition between H and D. No rate constant data are available and we are at present carrying out time-resolved experiments to change this situation.

(52) It is possible that such entropy factors contribute to the *cis* reactivity preference which has been analyzed solely in terms of enthalpy by Houk et al.^{16b}

exclusively to give allylic hydroperoxide exhibits parallel behavior.⁵³

Thus, in general solvent effects do not appear to play a significant role in O₂ (¹Δ_g) reactivity. However, prior to this work, the one notable published exception to this rule did in fact concern an enol ether, namely 2,3-dihydropyran, for which the ratio of allylic hydroperoxide to dioxetane-derived products varies by a factor of 59 (10.15–0.18) on changing from benzene to acetonitrile as solvent.^{14e,20c,54} The fact that k_q for **1** (Table II) varies by an almost identical factor of 56 from toluene to acetonitrile must be fortuitous, but these results, together with product data,^{20,14e} do indicate the relative importance of solvent effects in the case of at least some enol ethers relative to other types of substrate.

6.3. Nature of the Product-Forming Steps for Enol Ethers 1–4.

We have pointed out that the rate and activation parameters for reaction of O₂ (¹Δ_g) with substrates 1–4 are indicative of rapid reversible formation of an exciplex which then decays via rate-determining formation of oxidation products. The overall constants for reaction are principally entropy controlled, and the highly negative experimental ΔS^\ddagger values will be a summation of the ΔS° value for exciplex formation and ΔS^\ddagger for conversion of exciplex to product(s). Exciplexes formed reversibly and at diffusion-controlled rates may exhibit ΔS° values as highly negative as –25 eu,^{46a,c} and thus a significant amount of the order required to consummate product formation may already be present in a relatively "tight" exciplex.

Whatever the detailed nature of the transition states leading to allylic hydroperoxide and dioxetane, the tendency for the latter to be favored with increasing solvent polarizability must reflect a higher polarity of the corresponding transition state. This property will presumably, on symmetry grounds, be more important in the case of enol ethers as opposed to 1,2-dialkoxyethylenes which exhibit no solvent effect for dioxetane formation.⁵⁵ Results by Bartlett et al.^{14e} indicate that allylic C–H interaction can be important at the transition state for dioxetane formation, and one is led to enquire whether hyperconjugative interaction of allylic C–H attached to the β -carbon of an enol ether will lower the polarity and hence the solvent reorganization requirement of such a transition state. In this regard the enol ethers 1–4 split into two categories.

2-Methoxynorbornene (1). As mentioned, the rate constant for reaction of this compound increases by a factor of 56 from toluene to acetonitrile, a small change in general mechanistic terms but a large change by O₂ (¹Δ_g) standards. The observation of this effect is presumably facilitated by the absence of the "masking effect" of a contribution from the "ene" reaction which is relatively insensitive to solvent. The ΔH^\ddagger values of zero in acetonitrile and methanol indicate that the solvent effect for **1** reflects a solvent reorganization requirement on ΔS^\ddagger , in agreement with the fact that allylic C–H hyperconjugation cannot lower the transition-state polarity in this case.

Jefford and Rimbault¹⁷ have reported the isolation of products incorporating solvent on irradiation of oxygen-saturated solutions of methylene blue and **1** in methanol or deuteriomethanol together with the corresponding dioxetane or products derived therefrom (Scheme I).⁵⁶ It was concluded that these results could only be explained in terms of a perepoxide or zwitterionic intermediate (Scheme I) which is either intercepted by solvent or rearranges to dioxetane, the sole product in aprotic media. It was further claimed that these results support the calculations of Dewar,⁸ Fukui,^{19a} and Fueno^{19b} which indicate that a perepoxide lies on the pathway to both allylic hydroperoxide and dioxetane. With regard to these conclusions, we would make the following com-

(53) Values of k_q for tetramethylethylene determined by pulsed laser photolysis are 1.5, 4.0, 4.0, and 7.2×10^7 L mol⁻¹ s⁻¹ for cyclohexane, toluene, acetone, and acetonitrile, respectively.²¹

(54) There are no published rate constant data for this substrate. The solvent dependence of rate and activation parameters is currently under investigation.

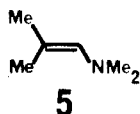
(55) A. P. Schaap and K. A. Zaklika, in ref 5, Chapter 6.

(56) In contrast to a statement by Jefford and Rimbault,¹⁷ **1** reacts with ground-state oxygen in the dark (section 5.4). However, the temperature (–20 °C) and controls described appear consistent with the involvement of O₂ (¹Δ_g) in their work.

ments: (a) Since **1** cannot undergo the 'ene' reaction, peroxide intermediacy (if a fact) in this case does not allow conclusions to be drawn concerning the mechanism of the "ene" reaction unless it is known that **1** reacts with $O_2 (^1\Delta_g)$ at a rate which is typical of enol ethers which undergo the "ene" reaction. As it happens we have shown that this is not the case. (b) There is *no evidence* to show that the peroxide (if it exists) lies on the pathway to dioxetane. Although we do not suggest it to be the case, a perfectly reasonable explanation of the published facts is that formation of the peroxide in protic solvents is due to H-bonding stabilization which allows its production to compete with what is, in this particular case, a slow dioxetane-forming reaction.

Exciplex intermediacy raises a mechanistic option which has not to date been considered. That is that solvent-incorporated products arise via direct attack upon the exciplex. Such a bimolecular process would be favored where dioxetane formation was particularly slow and possibly where the exciplex polarity is greater, as perhaps in the case of enol ethers, particularly of type **1**.

Enol Ethers 2-4. We have argued that the observed solvent effect on the reaction of $O_2 (^1\Delta_g)$ with **1** could be a consequence of the lack of β -allylic C-H hyperconjugation at the transition state for product formation. If this is the case, enol ethers **2-4** should display much smaller solvent effects, although a hindrance to data interpretation is the fact that such enol ethers also participate in the "ene" reaction to an extent which is also solvent dependent. In addition, although the "ene" reaction is not very sensitive to solvent in the case of simple olefins such as tetramethylethylene,³³ it could be more so, albeit less than is dioxetane formation, for enol ethers. Thus β -allylic C-H hyperconjugation, where possible, may have some effect upon this reaction. Although the differences are small, a consideration of Table II shows that k_f increases from cyclohexane to acetonitrile as solvent by factors of 10, 10, and 2.5 for **2**, **3**, and **4**, respectively, in agreement with the involvement of less polar transition state(s) in the case of **4** relative to **2** and **3**. The close similarity of substitution in the cases of **2** and **3** appears to be reflected in almost identical rate constant characteristics; the lower solvent sensitivity for **4** is in agreement with the presence of two β -methyl substituents and is to be compared with the lack of solvent effect on the dioxetane-forming reaction of the enamine **5**.⁵⁷



"Ene" and $\pi 2_a + \pi 2_s$ Transition States. We visualize transition states for conversion of exciplex to allylic hydroperoxide and/or dioxetane which are akin to the concerted "ene" and $\pi 2_a + \pi 2_s$ types, respectively. Peroxide formation was excluded (sections 6.1 and 6.2) as a *general* process because a reaction involving electrophilic attack on a double bond via a three-center transition state is incompatible with the fact that 2-methoxynorbornene

reacts more *slowly* with $O_2 (^1\Delta_g)$ by a factor of 10^2 - 10^3 than do enol ethers **2-4**. In contrast the available evidence concerning the reactivity of norbornenes and cyclopentenes would appear consistent with a $\pi 2_a + \pi 2_s$ cycloaddition mechanism for dioxetane formation. The addition of ketenes to double bonds is thought to proceed via a $\pi 2_a + \pi 2_s$ transition state in which the antarafacial partner is the ketene,⁵⁸ as would be $O_2 (^1\Delta_g)$ in the corresponding dioxetane-forming process.⁵⁹ Although rate and activation parameter data do not exist, it is at least clear that norbornenes are much *less* reactive than cyclopentenes toward, for instance, dichloroketene.⁶⁰ One manifestation of this fact is the exclusive addition of this ketene to the "cyclopentene" double bond of cyclopentadiene dimer.⁶⁰

7. Conclusions

The reactivity parameters determined in this work have led us to raise the possibility that the reaction of $O_2 (^1\Delta_g)$ with enol ethers proceeds via rapid reversible formation of an exciplex. Given exciplex intermediacy we see no necessity, based on published data, to invoke further intermediates on the potential energy surface leading to products. Indeed, the relative values of rate constants for reaction of $O_2 (^1\Delta_g)$ with the substrates **1-4** appear incompatible with general peroxide intermediacy.

For the "normal" enol ethers **2-4**, we visualize competitive reaction from the exciplex via "ene"- and $\pi 2_a + \pi 2_s$ -like transition states, the latter of which has the more polar character. In the case of 2-methoxynorbornene (**1**) which cannot take part in the "ene" reaction, the dioxetane-forming process is relatively sensitive to solvent. This is attributed to a solvation entropy requirement resulting from enhanced polarity of the transition state in this case, possibly due to the lack of β -allylic C-H hyperconjugation. The reported isolation of a solvent incorporation product on reaction of $O_2 (^1\Delta_g)$ with **1** in methanol¹⁷ could reflect peroxide formation in this particular instance. However, assuming that such a product is derived from $O_2 (^1\Delta_g)$ its formation could be the result of direct attack by methanol on the exciplex. Such a process could be significant, in this case because of the enhanced polar character of this particular enol ether- $O_2 (^1\Delta_g)$ exciplex and its relatively inefficient conversion to dioxetane.

It is becoming increasingly clear that many apparently different $O_2 (^1\Delta_g)$ oxidation processes exhibit the same basic characteristics, namely ΔH^\ddagger values close to zero, highly negative ΔS^\ddagger values and rate constants well below that for diffusion.²⁶ The possibility clearly exists that the mechanism outlined here for enol ethers operates generally.

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

Registry No. **1**, 17190-90-8; **2**, 1072-59-9; **3**, 6380-95-6; **4**, 927-61-7; O_2 , 7782-44-7.

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