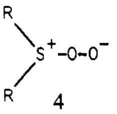

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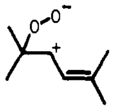

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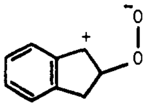

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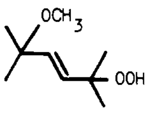

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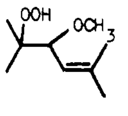

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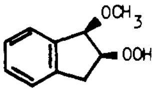

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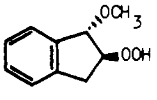

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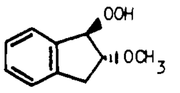

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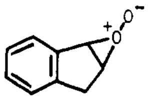
stabilized relative to simple olefins. Zwitterionic intermediates such as **5** and **6** have often been proposed as precursors to dioxetanes in $^{1}\mathrm{O}_2$ reactions,[39-41] and dioxetane formation from $^{1}\mathrm{O}_2$ reactions is important only with compounds that would give stabilized cationic centers, including enol ethers[42] and enamines.[43] Even adamantylideneadamantane, which gives only dioxetane products,[44] would give a more stable cationic center than most simple olefins, and has no other reaction path other than dioxetane formation available to it. That **5** and **6** could be the precursors to dioxetanes is consistent with the fact that, in methanol (where **5** and **6** should be stabilized by hydrgen bonding) both DMHD and indenes give dioxenes much more efficiently than in aprotic solvents.[19,28] (Further discussion is deferred to the accompanying paper.)[32]

It would be anticipated that methanol would attack the zwitterionic intermediates **5** and **6** giving two methanol addition products in each case, **7** and **8** for DMHD and **9** and **10** for indene. It has been reported previously that photooxidation of DMHD under either acidic or basic conditions in methanol yielded both **7** and **8**.[19] We have also found that **7** is formed from the photooxidation of DMHD in methanol under neutral conditions (**7**/**1** = 0.6[32]). However, we did not isolate any **8**. Initially it was reported that photooxidation of indene gave two isomeric methanol addition products **10** and **11**.[45] These two isomers are consistent with nucleophilic attack by methanol on a perepoxide intermediate, **12**, and their appearance was used as evidence in support of **12**.[45]



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Recent investigations have shown that the two methanol addition products are actually **9** and **10**,[46] which are more consistent with the intermediacy of a zwitterion.

The relationship between the interaction leading to the ene product, **1**, for DMHD and that leading to dioxetane and quenching is discussed in the accompanying paper.[32]

Acknowledgment. We thank the National Science Foundation for support through Grant No. CHE80-20140. R.C.K. thanks Dr. P. R. Ogilby for his many hours of invaluable assistance and guidance in this work. Paper 42 in this series is by Ogilby and Foote, see ref 23.

Registry No. DMHD, 764-13-6; MPI, 10425-96-4; $^{1}\mathrm{O}_2$, 7782-44-7.

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Chemistry of Singlet Oxygen. 44. Mechanism of Photooxidation of 2,5-Dimethylhexa-2,4-diene and 2-Methyl-2-pentene

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Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received November 26, 1982*

Abstract: Solvent and temperature effects on the singlet oxygen oxidations of 2,6-dimethyl-2,4-hexadiene (DMHD) and 2-methyl-2-pentene (2M2P) are studied. It is concluded that the initial interaction between 2M2P and $^{1}\mathrm{O}_2$ (which gives only ene products) and that between DMHD and $^{1}\mathrm{O}_2$ (which gives ene products, dioxetane, and nonreactive quenching) are identical. It is also suggested that the quenching path for DMHD could involve formation of an intermediate zwitterion or 1,4-biradical, which undergoes intersystem crossing and decays to ground-state oxygen and DMHD.

In the accompanying paper[1] we show that the interaction of $^{1}\mathrm{O}_2$ with 2,5-dimethyl-2,4-hexadiene (DMHD) and 1-methyl-2-phenylindene (MPI) can lead to both reaction and quenching of $^{1}\mathrm{O}_2$. Although the rate constant for initial interaction with $^{1}\mathrm{O}_2$ is nearly independent of solvent and temperature, the relative amount of quenching depends strongly on solvent in the case of DMHD and on both solvent and temperature in the case of MPI. Arguments were put forth that both dioxetane and methanol adducts are formed from an intermediate zwitterion. It was suggested that the zwitterion can form only with substrates that can stabilize a cationic center at one end of the double bond. For

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(1) Manring, L. E.; Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

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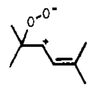
example, DMHD would give the stabilized zwitterion ZI.



ZI

The strongest arguments against the intermediacy of zwitterions and biradicals in $^1O_2$ ene reactions have been based on the lack of solvent polarity effects,[2] the fact that radical scavengers are ineffective, that cis-trans isomerization does not occur, and the lack of Markovnikov-directing effects.[3] However, solvent polarity effects are well documented in several reactions where ene and dioxetane pathways compete, for example, with dihydropyran[4] and 1-(ethylthio)-2-ethyl-1-hexene.[5] In both cases, more polar solvents favor dioxetane formation over ene reaction.

The proposal that zwitterionic intermediates are formed in these $^1O_2$ reactions does not preclude formation of other inermediates as well. As shown in the accompanying manuscript, the reaction of DMHD resembles that of simple olefins in that there are only small solvent effects on the rate constant for the total interaction ($k_r + k_q$) with $^1O_2$, consistent with a transition state of very low polarity. A possible explanation would be that a non-ionic intermediate or transition state such as an exciplex precedes the zwitterion in a pathway of low activation enthalpy. In this paper we address the question of whether the initial interaction between $^1O_2$ and DMHD, which leads to various products (ene, dioxetane, or solvent addition adducts)[6] or quenching, depending on conditions, is the same as the initial interaction between simple olefins and $^1O_2$, which leads only to "ene" products under all conditions.

As a simple olefin for comparison with DMHD, we chose 2-methyl-2-pentene (2M2P), which gives only two ene products with $^1O_2$, **1** and **2**, in approximately a 50:50 mixture.[7] This olefin has been shown not to quench $^1O_2$ by a nonreactive pathway in methanol.[8]

Experimental Section

Chemicals. Pyridine *N*-oxide (Aldrich) was distilled twice, bp 99 °C (1 mm Hg). 2,3-Dimethyl-2-butene (Chemical Samples Co.) (TME) was distilled from sodium and stored under N_2; it was passed through basic alumina immediately before use. All other chemicals have been described.[1]

Photolysis. Variable-temperature kinetic runs were done with use of a vacuum-jacketed pipeline designed by Dr. P. R. Ogilby.[9,10] The sample was placed in a 1-cm × 1-cm cuvette in the vacuum-jacketed pipeline with the temperature controlled ±0.3 °C. The solution was photolyzed through Corning filters 3-68 (to remove light below 520 nm) and 1-58 (to keep IR from heating the sample), with a Norelco 500 Q/CL 500 W tungsten-halogen lamp controlled by a Variac 70-100 V. The absorbance of the sensitizer at λ_{max} was >3. Air was bubbled through the solution. The light intensity was constant since identical photolyses of 2M2P gave identical amounts of products within 1%. No sensitizer degradation occurred during photolysis.

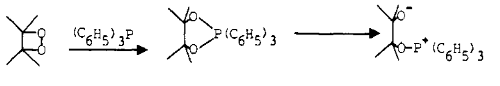
Large-scale photolyses were done with a Sylvania 650 W tungsten-halogen DWY lamp placed next to the sample in a water-cooled immersion well. Oxygen was continuously bubbled through the solutions. The light was filtered through a 0.5-cm, 2-g/1000-mL $H_2O-K_2Cr_2O_7$ solution which cut off all light below 500 nm.

Errors. Errors are 95% confidence intervals in all cases. They are estimated from the slopes of plots of k_{obsd} vs. [S] for ($k_r + k_q$); for k_3 and k_r, they are from slopes of the competition plots with the assumption that the 2M2P rate is correct.

Direct Determination of $k_r + k_q$. Measurements of ($k_r + k_q$) (sum of reaction and quenching of $^1O_2$ by DMHD and 2M2P) were made by monitoring the effect of added substrate on the observed decay rate of $^1O_2$ luminescence at 1270 nm. The germanium photodiode and instrumentation used to measure the $^1O_2$ luminescence decay rate constants have been described previously.[9,10]

Analytical gas chromatograpohy and integration was done on a Hewlett-Packard Model 5880A gas chromatograph. Ultraviolet spectra were taken on a Beckman Model 25 spectrophotometer.

The amount of ene product, **3**, was determined by measurement of alcohol **3a**, produced by $(C_6H_5)_3P$ reduction of **3**. Excess $(C_6H_5)_3P$ was added to an aliquot of the crude reaction mixture and mixed for at least 15 min in the dark before injection (2 ft × $^1/_8$ in. OV-101; injection temperature = 250 °C; oven temperature, initial value = 40 °C, final value = 100 °C; program rate = 15 °C/min; *p*-dimethoxybenzene was added as internal standard after photolysis before reduction). The amount of **3a** formed was determined by comparison to standard solutions (see below). The amount of dioxetane, **4**, formed in methanol, acetonitrile, and methanol/acetonitrile mixtures was determined by a second injection of the crude reaction mixture without reduction (6 ft × $^1/_8$ in. 10% carbowax; injection temperature = 250 °C; oven temperature; initial value = 40 °C, final value = 180 °C; program rate = 15 °C/min; *p*-dimethoxybenzene was added as internal standard after photolysis). The amount of acetone was determined by comparison to standard solutions. It is known that **4** thermally decomposes to **4a** and senecialdehyde **4b** with a half-life of 37 min at 44 °C.[6] We assume that all of **4** decomposes within the injector port (at 250 °C) to **4a** and **4b** and that the amount of **4** in the crude mixture was equal to the amount of **4a** detected. The amount of methanol addition product, **5a**, formed after $(C_6H_5)_3P$ reduction of the crude reaction mixture was determined by comparison to standard solutions of **5a**; however, not all of the **5a** produced came from **5**; that $(C_6H_5)_3P$ also converted 4 to **5** was determined as follows. Injection of an unreduced aliquot of the photolyzed reaction mixture gave the expected amount of acetone. Upon addition of excess $(C_6H_5)_3P$, the acetone disappeared entirely and both **3a** and **5a** appeared. The ratio of **5a**/**3a** was 3.0; however, if the sample was heated to decompose **4** before the addition of $(C_6H_5)_3P$ (15 min, 75 °C, sealed tube), the ratio of **5a**/**3a** was ~0.6, and **4a** was still present after $(C_6H_6)_3P$ addition. Further heating had no effect on the **5a**/**3a** ratio. If the solution was heated for short periods, more **5a** and less **4a** were formed but the ratio (**5a** + **4a**)/**3a** was always ~3. The amount of **3** formed during the reaction was assumed to be equal to the total amount of **3a** detected minus the amount of **4** formed during the reaction. That $(C_6H_5)_3P$ can promote decomposition of **4** to **5a** is not unexpected considering the known reaction of dioxetanes with $(C_6H_5)_3P$ to give a pentacoordinate phosphorus species **7**.[11] Compound 7 decomposes via heterolytic cleavage of a P–O bond to **8** which yields an epoxide.[11] It is not unreasonable that nucleophilic attack by methanol can be faster than epoxide formation. There was no epoxide detected after addition of $(C_6H_5)_3P$ to the dioxetane in methanol, as was determined by injection of an authentic sample. Solvent mixtures of known (±1%) composition by weight were prepared by weighing methanol into a 10-mL volumetric flask, filling to the mark with acetonitrile, and reweighing the flask.



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For the competitive photooxidation experiments with 2M2P and DMHD, products **1a**, **2a**, **3a**, and **5a** were analyzed after addition of excess $(C_6H_5)_3P$ (6 ft × $^1/_8$ in. 3% carbowax column; injection temperature = 250 °C; oven temperature, initial value = 40 °C, final value = 180 °C; program rate = 10 °C/min; $(C_6H_5)_2CH_2$ was added as internal standard before photolysis). Absolute amounts of **1a**, **2a**, **3a**, and **5a** were determined by comparison to standard solutions (see below).

Determination of Relative Rate Constants of Product Formation for DMHD. The rate constants for disappearance of DMHD and the appearance of **3** in all solvents were determined by the method of Higgins et al.[12] relative to 2M2P. In the case of 2M2P, where only two products form (**1** and **2**) and no quenching occurs, the amount of products is equal to the disappearance of starting materials and (1 – [**1a** + **2a**]/[2M2P]$_0$) = ([2M2P]$_f$/[2M2P]$_0$). Relative rate constants for DMHD disappearance were determined by plotting log ([DMHD]$_f$/[DMHD]$_0$) vs. log (1 – [**1a** + **2a**]/[2M2P]$_0$). Relative rate constants of appearance of ene product (**3a**) were determined by plotting log (1 – [**3a**]/DMHD]$_0$) vs. log (1 – [**5a** + **6a**]/[2M2P]$_0$).

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Table I. $(k_r + k_q)$ Values for 2M2P and DMHD Removal of $^1O_2$ in Various Solvents

	$(k_r + k_q)$, M^{-1} s^{-1} × 10^{-6}		$1/k_d$,[a] (μs)	
solvent	2M2P	DMHD	2M2P	DMHD
CH_3OH (ME)	$0.67^{b,c}$	2.6 ± 0.2		
CH_3OD		2.6 ± 0.2		24.6
C_6H_6(BZ)	0.72 ± 0.08	3.6 ± 1.2	29.1	29.9
$(CH_3)_2CO$ (AC)	0.81 ± 0.07	3.9 ± 0.6	45.7	46.7
CH_2Cl_2 (MC)	0.97 ± 0.07	5.2 ± 1.1	54.6	57.7
CH_3CN (AN)	1.2 ± 0.2	6.3 ± 1.1	64.1	65.4

[a] Intercepts from runs using these substrates. [b] β determination by Young et al. (ref 18). [c] See ref 1; assumes k_d for ME is 1.0 × 10^5 s^{-1}.

Isolation and Characterization of Products 1a, 2a, 3a, 5a, 6, and 12a. Preparation of 2M2P ene products **1a** and **2a** followed previous procedures.[7] The compounds were isolated by preparative GC (3 ft × 0.21 in. silicone DC-200/500 on Chromosorb WHP 60–80; injection temperature = 150 °C; detection temperature = 150 °C, column temperature = 60 °C). The GC trace showed three peaks with retention time (RT) = 0.9, 4.5 (**1a**), and 6.5 min (**2a**). NMR analysis of the isolated compounds was consistent with that of the previously reported structures.

Preparation and Isolation of 2,5-Dimethyl-1,4-hexadienol (3a). A solution of 4 mL of DMHD in 300 mL of acetone containing 50 mg of rose bengal (RB) was photolyzed for 8 h, after which time 90% of the starting material was gone (by GC). The solution gave a positive starch-iodide test and $(C_6H_5)_3P$ was added until a negative test was obtained. The solvent was evaporated and the residue washed with hexane. The $(C_6H_5)_3PO$ and excess $(C_6H_5)_3P$ were filtered off by a quick pass through cellulose. The hexane was evaporated and the crude mixture vacuum distilled. The major component, **3a**, distilled at 35 °C (0.7 mmHg); NMR ($CDCl_3$) δ 1.55 [broad s, 1 H, OH], 1.73–1.75 [mult, 9 H, $C(CH_3)_2$ and CH_3], 4.78 [d, 1 H, OCH, $J_{CHCHO} = 8.8$ Hz], 4.82 and 5.02 [two s, 2 H, CCH_2], 5.20 [d of d, 1 H, C=CH, $J_{CHCHO} = 8.8$ Hz, $J_{(CH_3)_2CCH} = 1.5$ Hz]; IR (neat) 3620, 1650, 1670, 1390, 900 cm^{-1}.

Preparation and Isolation of 2,5-Dimethyl-5-methoxy-3-hexen-2-ol (5a). A solution of 1.5 g of DMHD in 100 mL of CH_3OH containing 1 mg of methylene blue and 1 drop of concentrated HCl was photolyzed for 4 h, after which time 90% of the starting material was gone. $(C_6H_5)_3P$ (3.5 g) was added to reduce the hydroperoxides and the solvent evaporated. The residue was taken up in hexane and cooled to 0 °C to remove most of the $(C_6H_5)_3PO$ and excess $(C_6H_5)_3P$. The solution was filtered and the solvent evaporated. The products were separated from residual $(C_6H_5)_3PO$ by flash distillation under vacuum and the individual products isolated by preparative GC (6 ft × $^1/_4$ in. 10% carbowax column, injection temperature = 150 °C, column temperature = 90 °C). Three major peaks were collected: **12a** (conjugated alcohol) 3%, **3a** (ene product) 10%, and **5a** (methanol addition product) 83%. **5a**: NMR ($CDCl_3$) δ 1.27, 1.34 [two s, 12 H, $MeOC(CH_3)_2$ and $HO(CH_3)_2$], 1.63 [broad s, 1 H, OH], 5.67, 5.76 [two d, 2 H, CHCH, $J_{CHCH} = 15.9$ Hz]; IR (neat) 3620, 1385, 1370, 1180, 1140, 1080, 970, 920, 870, 750 cm^{-1}.

Preparation and Isolation of 3,3,6,6-Tetramethyl-1,2-diox-4-ene (Endoperoxide 6). A solution of 1 mL of DMHD in 10 mL of CH_3OH containing 5 × 10^{-5} M RB was photolyzed at 0 °C for 70 min. A white precipitate was collected and recrystallized twice from CH_3OH: mp 57–58 °C; NMR ($CDCl_3$) δ 1.27 [s, 12 H, 2 $(CH_3)_2CO$], 5.67 [s, 2 H, CH=CH]; IR (CCl_4) 1363, 1380, 1132, 880 cm^{-1}; MS (16 eV) m/e (rel intensity) 142 (M^+, 0.1), 127 ($M^+ - CH_3$, 18), 113 (2.1), 112 (7.7), 111 (27), 110 (6.0), 109 (9.1), 95 (3), 87 (4), 85 (63), 84 ($M^+ - CH_3COCH_3$, 100), 83 (88), 69 (9), 67 (6), 59 (20), 43 (40).

2,5-Dimethyl-1,3-hexadien-5-ol (12a). This compound was isolated by preparative GC from the crude mixture from preparation of **5a**; it was also formed when **3a** was passed over acidic silica (eluted with diethyl ether and ethyl acetate): NMR ($CDCl_3$) δ 1.36 [s, 6 H, $OC(CH_3)_2$], 1.61 [broad s, 1 H, OH], 1.84 [s, 3 H, CH_3], 4.98 [s, 2 H, CCH_2], 5.79, 6.32 [two d, 2 H, CH=CH, $J_{CH=CH} = 16.1$ Hz]; IR (neat) 3500, 1730, 1615, 1370, 1360, 1150, 970, 885 cm^{-1}.

Results

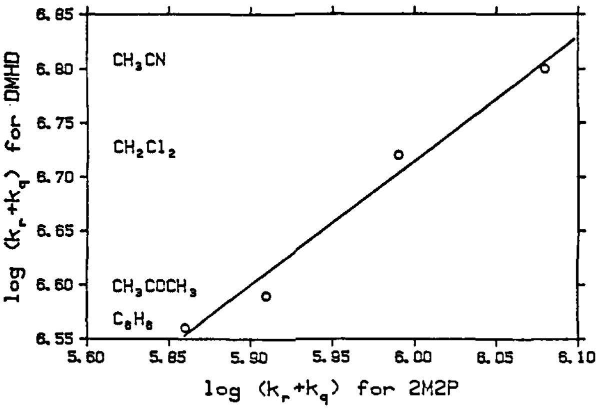

Figure 1. Plot of log $(k_r + k_q)$ for DMHD vs. log $(k_r + k_q)$ for 2M2P in various solvents.

Table II. Effect of Solvent and Temperature on Ene Product Ratios from 2M2P-$^1O_2$ Reaction

solvent	temp, °C	2a/1a
CH_3OH (ME)	22	1.11 ± 0.02
CH_3OH	−32	0.96 ± 0.04
CH_3OH	−78	0.83 ± 0.04
C_6H_6 (BZ)	22	1.17 ± 0.04
$(CH_3)_2CO$ (AC)	22	1.10 ± 0.04
$(CH_3)_2CO$	−32	0.92 ± 0.04
$(CH_3)_2CO$	−78	0.75 ± 0.04
CH_2Cl_2 (MC)	22	1.29 ± 0.04
CH_3CN (AN)	22	1.39 ± 0.04

Direct Determination of $(k_r + k_q)$ Values for 2M2P and DMHD Quenching of $^1O_2$. Since time-resolved detection of the luminescence of $^1O_2$ is now possible,[14-16] $(k_r + k_q)$ values for the quenching of $^1O_2$ can be determined with increased reliability. Therefore, values for 2M2P, a kinetic standard,[17] were carefully redetermined (for a general kinetic scheme see accompanying paper). The rate constant of $^1O_2$ luminescence decay, k_{obsd}, is described by eq 1, where $(k_r + k_q)$ is the total rate constant for

$$k_{obsd} = (k_r + k_q)[S] + k_d \qquad (1)$$

$^1O_2$ removal by substrate (S) and k_d is the rate constant for radiationless decay for $^1O_2$. Plots of k_{obsd} vs. [S] are linear with slope $(k_r + k_q)$ and intercept k_d. The $(k_r + k_q)$ values for quenching of $^1O_2$ luminescence by 2M2P and DMHD in acetonitrile (AN), methylene chloride (MC), acetone (AC), and benzene (BZ) measured by this technique are shown in Table I.

Since the lifetime of $^1O_2$ in methanol (ME) is too short for direct determination with our apparatus, $(k_r + k_q)$ values in methanol (ME) were calculated from β values, where $\beta = k_d/(k_r + k_q)$; $(k_r + k_q)$ could be determined directly for DMHD in methanol-*O-d*. The data in Table I indicate that the total rate constant for interaction with $^1O_2$ varies only slightly and increases in the order ME < BZ < AC < MC < AN. Figure 1 is a plot of log $(k_r + k_q)$ for DMHD vs. log $(k_r + k_q)$ for 2M2P of the data in Table I which were determined by the direct technique (C_6H_6, CH_3COCH_3, CH_2Cl_2, and CH_3CN).

The plot has slope 1.18 ± 0.53 ($r = 0.99$), showing that the effect of solvent polarity on the two substrates is very similar. The variation in rate is outside the experimental error in the different solvents and in the opposite direction to the effect previously reported;[19] this problem will be addressed in the discussion section.

Also shown in Table I are $^1O_2$ lifetimes (1/intercept from eq 1) for each solvent. As expected, values of $1/k_d$ for the two different substrates in the same solvent are the same within experimental error.[20]

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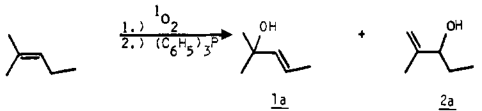
Table III. Effect of Temperature on the Rate of 2M2P Oxidation by $^1O_2$

solvent	temp, °C	k_r, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
CH_3OH (ME)	22	6.7×10^5		
CH_3OH	−32	4.0×10^5	0.93 ± 0.83	−28.9 ± 3.5
CH_3OH	−78	2.0×10^5		
$(CH_3)_2CO$ (AC)	22	8.1×10^5		
$(CH_3)_2CO$	−32	4.0×10^5	0.75 ± 0.32	−29.2 ± 1.2
$(CH_3)_2CO$	−78	2.8×10^5		

Photooxidation of 2M2P. Solvent and Temperature Effects on Products. As reported previously,[7] the $^1O_2$ oxidation of 2M2P gave only two products after $(C_6H_5)_3P$ reduction, **1a** and **2a**. The



1a 2a

ratio of **2a**/**1a** was found to be slighly dependent on both solvent and temperature, Table II. The ratios of **2a**/**1a** were independent of photolysis time. As reported previously,[4] the relative amounts of **1a** and **2a** are almost constant in ME, BZ, and AC; however, the product distribution shifts noticeably in MC and AC. Variation of ene product ratios with solvents or temperature has not, to our knowledge, been previously observed. The order in which product ratios vary is the same as the order in which the rates vary, allowing for the relatively large errors. The significance of this observation is not obvious at this time.

Determination of 2M2P Quenching of $^1O_2$. We reported in the accompanying paper[1] that DMHD quenches $^1O_2$ by a nonreactive pathway in BZ, AC, MC, and AN but not in methanol. It has also been shown that 2M2P does not quench $^1O_2$ in ME;[8] however, data are not available to show that $k_q \ll k_r$ for 2M2P in any of the other solvents. To determine whether the interaction of 2M2P does give quenching in AC or AN, we photolyzed 2M2P–rose bengal (RB) solutions under identical conditions in ME, AC, and AN. It can be tentatively assumed that equal amounts of RB absorb nearly equal amounts of light in all three solvents; the λ_{max} and extinction coefficient for RB in methanol, acetonitrile, and acetone are (λ_{max} (nm)/ϵ (cm^{-1} M^{-1})) 556/8.0 × 10^4, 556/9.3 × 10^4, and 561/1.0 × 10^5, respectively. Then eq 2 describes the relative rate constant for 2M2P photooxidation, k_{rel}, for each solvent:

$$k_{rel} = \Phi_T k_r[2M2P]/(k_r[2M2P] + k_q[2M2P] + k_d) = \Phi_T Z \tag{2}$$

where Φ_T = the quantum yield of ^{3}RB formation. If $k_q \ll k_r$ for 2M2P in AN and AC (as it is for 2M2P in ME), then k_r is equal to the $(k + k_q)$ values in Table I. The concentration of 2M2P is known, as is k_d (from Table I); therefore, the value of Z can be determined for each solvent. Equalities 3 and 3a should hold

$$\frac{k_{rel}^{AN}/Z^{AN}}{k_{rel}^{ME}/Z^{ME}} = \frac{\Phi_T^{AN}}{\Phi_T^{ME}} \tag{3}$$

$$\frac{k_{rel}^{AC}/Z^{AC}}{k_{rel}^{ME}/Z^{ME}} = \frac{\Phi_T^{AC}}{\Phi_T^{ME}} \tag{3a}$$

if the assumption that $k_q \ll k_r$ is true. The values for Φ_T/Φ_T^{ME} determined from our data were 0.72 and 0.77, close to the values calculated from data in ref 21 and 22, 0.72 and 0.68 for AN and AC, respectively. The consistency between the known values and those calculated from our data indicates that the assumptions made are correct within the error limitations. If 2M2P had a significant k_q component in either AN or AC, the calculated Φ_T/Φ_T^{ME} would have been considerably less than the known values.[23]

Scheme I

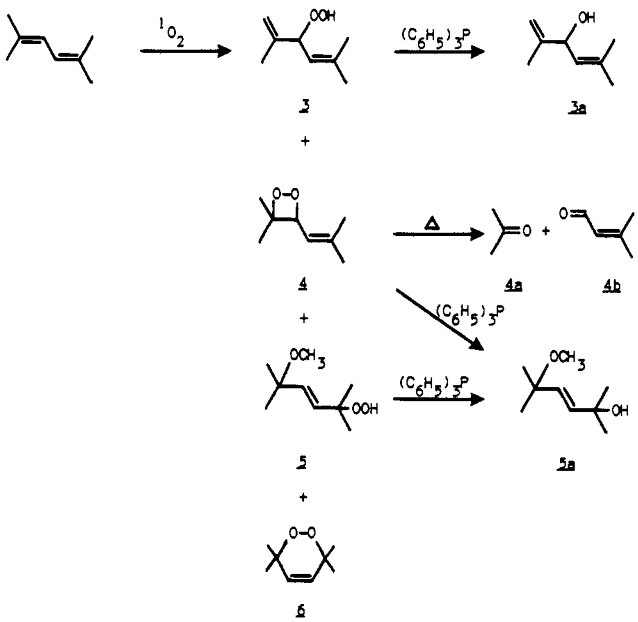


Table IV. Temperature Effect on Relative Amounts of Product from DMHD Photooxidation in Methanol

temp, °C	3	4	5	6
22	1.00	2.45	0.59	<0.1[a]
−32	1.00	3.90	1.60	
−78	1.00	8.21	6.79	

[a] Increases as temperature is lowered.

Table V. Rate of DMHD Disappearance (k_r) and Ene Product Appearance (k_3) in Various Solvents

solvent	k_r, M^{-1} s^{-1} × 10^{-6}	k_3, M^{-1} s^{-1} × 10^{-6}
CH_3OH (ME)	2.5 ± 0.6	0.29 ± 0.02
C_6H_6 (BZ)	<0.25[a]	0.14 ± 0.03
$(CH_3)_2CO$ (AC)	0.74 ± 0.08	0.34 ± 0.01
CH_2Cl_2 (MC)	1.4 ± 0.3	1.3 ± 0.1
CH_3CN (AN)	1.6 ± 0.2	1.7 ± 0.1

[a] This value is an upper limit, estimated when <5% of the DMHD has reacted.[26]

Temperature Effect on the 2M2P–$^1O_2$ Reaction Rate Constant in ME and AC. The relative rate constants of 2M2P photooxidation were determined at 22, −32, and −78 °C in both ME and AC. The rate constants at 22 °C were assumed equal to the $(k_r + k_q)$ values from Table I and relative rate constants were determined under identical conditions at −32 and −78 °C from the product (**1a** + **2a**) appearance.[24] The temperature effect on

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(20) the $1/k_d$ values obtained for BZ and AC are slightly larger than those reported previously.[16] It is known that the excitation power,[15] dye concentration,[16] and solvent history[15] can all affect k_d; these effects probably cause the variations of k_d. This variation does not affect our results because the $(k_r + k_q)$ values determined according to eq 1 are independent of k_d.

(21) Fleming, G. R.; Knight, A. E. W.; Morris, J. M.; Morrison, R. J. S.; Robinson, G. W. *J. Am. Chem. Soc.* **1977**, *99*, 4306.

(22) Cramer, L. E.; Spears, K. G. *J. Am. Chem. Soc.* **1978**, *100*, 221.

(23) The results indicate that slightly more $^1O_2$ is produced in AC than would be predicted from the RB intersystem crossing value alone; however, since the RB absorption in AC is red-shifted relative to both ME and AN, RB probably absorbs more light from the tungsten–halogen lamp in AC than it does in either AN or ME, because the intensity of these lamps drops off with decreasing wavelength. In comparing the rate constant of 2M2P–$^1O_2$ oxidation to that of the DMHD–$^1O_2$ oxidation, we assume that $k_q \ll k_r$ for the 2M2P reaction in BZ and MC also.

(24) Possible effects due to changes in the quantum yield of $^1O_2$ formation with temperature (for example, because of temperature effects on Φ_T for RB) were checked by photolyzing high enough concentrations (0.50 M) of tetramethylethylene (TME) that 100% of the $^1O_2$ would be trapped at all three temperatures and comparing the amount oxidized at each temperature. It was found that 30% less $^1O_2$ was formed at −78 °C than at 22 °C in both acetone and methanol. This effect is comparatively small compared to the threefold rate change observed, and inaccuracies in its determination therefore have only a minor effect on the relative rate constants measured.

Table VI. Effect of Temperature on DMHD-$^1O_2$ Reaction Rates in Methanol and Acetone

			rates, M^{-1} s^{-1} × 10^{-6}			
solvent	temp, °C	$(k_r + k_q)$	k_r	k_3	k_4	k_5
CH_3OH	22		2.5 ± 0.6	0.29	0.71	0.17
CH_3OH	−32		1.5 ± 0.3	0.10	0.39	0.16
CH_3OH	−78		0.82 ± 0.11	0.028	0.23	0.19
$\Delta H^{\ddagger}$, kcal			0.64 ± 0.32	2.2 ± 2.0	0.8 ± 1.6	0.6 ± 2.0
$\Delta S^{\ddagger}$, eu			−27.4 ± 1.4	−27 ± 8	−29 ± 7	−37 ± 9
$(CH_3)_2CO$	22	3.9 ± 0.6	0.74 ± 0.08	0.34		
$(CH_3)_2CO$	−32	3.9 ± 1.0[a]	0.59 ± 0.26	0.25		
$(CH_3)_2CO$	−78	3.1 ± 0.30[b]	0.64 ± 0.10	0.32		
$\Delta H^{\ddagger}$, kcal		0.3 ± 3.2	−0.23 ± 1.9	0.4 ± 5		
$\Delta S^{\ddagger}$, eu		30 ± 14	−33 ± 8	−35 ± 22		

[a] Determined at −55 °C. [b] Determined at −68 °C.

the 2M2P photooxidation is shown in Table III. It is apparent that the reaction has comparable enthalpies, $\Delta H^{\ddagger}$, and entropies, $\Delta S^{\ddagger}$, of activation in the two solvents. These large negative entropies of activation are consistent with previously reported values for simple olefins: Koch[25] has determined a $\Delta S^{\ddagger}$ for the 2M2P-$^1O_2$ oxidation in ME of −28.2 eu, very close to our value of −28.9 eu. Very similar values have recently been reported for other simple olefins.[44b] Our value for $\Delta H^{\ddagger}$ of 0.93 kcal corresponds to an E_a of 1.5 kcal, probably within experimental error of Koch's E_a, 2 kcal.

Photooxidation of DMHD. Photooxidation of **DMHD** in ME at the three temperatures studied (22, −32, and −78 °C) gave four major products, **3**, **4**, **5**, and **6** (Scheme I). Products were determined by GC (see Experimental Section) and are listed in Table IV.

Rates of DMHD Product Formation. The rate constants of disappearance of DMHD and the appearance of **3** in ME, AC, BZ, MC, and AN were determined at 22 °C relative to 2M2P by the method of Higgins et al.[12,26] The value of k_r (total rate constant for product formation) and of formation of ene products (k_3) for DMHD in each solvent was calculated relative to 2M2P by using the data in Table I for the 2M2P rate constants. The results are listed in Table V.

It can be seen by comparing k_r to k_3 that formation of ene product accounts for all of the DMHD disappearance in AN and MC, ~50% in AC and BZ and only 11% in ME. Comparison of the $(k_r + k_q)$ values for DMHD from Table I with k_3 indicates that in all solvents, less than 30% of the total interaction leads to ene product **3**. Thus in solvents in which quenching occurs, a greater fraction of the reactive pathway produces ene product than in methanol, where no quenching occurs. In other words, quenching occurs largely at the expense of "non-ene" products **4** and **5**.

Temperature Effect on the DMHD-$^1O_2$ Reaction in AC and ME. Values for k_r, and the partial rate constants of formation of **3**, **4**, and **5** (k_3, k_4, and k_5 respectively), were also determined in ME at 22, −32, and −78 °C. Values of k_r and k_3 were determined in AC at the same temperatures. The results are shown in Table VI.

Listed below each set of rate constants in Table VI are the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. In ME, k_r, k_3, and k_4 all decrease as the temperature is lowered, indicating a positive activation barrier for these products; k_5 seems to be almost temperature independent. In ME, where no quenching occurs, k_r is a good measure of the total interaction, $(k_r + k_q)$, between $^1O_2$ and DMHD. Because k_r is not a good measure of $(k_r + k_q)$ in AC (where $k_q > k_r$), we measured the temperature effect on $(k_r + k_q)$ by the direct technique (effect of DMHD on $^1O_2$ luminescence lifetime) at 22, −55, and −68 °C in AC. These results, also shown in Table VI, indicate that $(k_r + k_q)$ is almost independent of temperature in AC. The values of k_r and k_3 are also independent of temperature in AC. The intercepts of plots of k_{obsd} vs. [S], eq 1, were independent of temperature, consistent with a previous report that temperature does not affect the $^1O_2$ lifetime $(1/k_d)$ in acetone down to −78 °C.[10]

Table VII. Fraction of DMHD-$^1O_2$ Interaction Which Leads to **3**, (**4** + **5**), DMHD Disappearance, and Quenching

	fraction of total interaction leading to:			
solvent	ene (3)[a]	(4 + 5)	quenching[d]	DMHD disappearance[a]
CH_3OH	0.11	0.34[b]	0.04	0.96
C_6H_6	0.04	0	0.93	<0.07
$(CH_3)_2CO$	0.09		0.81	0.19
CH_2Cl_2	0.27		0.73	0.25
CH_3CN	0.27	0.01[c]	0.72	0.25

[a] From Tables V and I. [b] From Tables VI and I. [c] Diox/ene = 0.03, see text. [d] The fraction of $^1O_2$-DMHD interaction which does not lead to product.

Table VII shows the fraction of the total interaction between $^1O_2$ and DMHD which leads to ene product (**3**), the sum of dioxetane and methanol addition product (**4** + **5**), quenching, and DMHD disappearance, in each solvent (calculated from data in Tables I, V, and VI).

The data in Table VII indicate that the sum of the individual product fractions (**3** + **4** + **5**) does not always equal the total DMHD disappearance. This discrepancy is especially pronounced in ME where (**3** + **4** + **5**)/(total DMHD disappearance) = 0.49; half of the DMHD disappearance is not accounted for. The source of this discrepancy is not certain; it could be caused by an error in k_r. For example, a non-singlet oxygen path might contribute to DMHD disappearance; this would mean a larger fraction of $^1O_2$ quenching by DMHD is occurring in ME than the data indicate. Products attributable to a non-singlet oxygen path were not observed; however, any polymers formed would not have been detected by GC analysis.

Discussion

The initial interaction between 2M2P and $^1O_2$, which gives only ene products, and the initial interaction between DMHD and $^1O_2$, where a variety of reactions occur, seem to be very similar except for differences in absolute rates. The similarities are indicated by two pieces of evidence. First, the sensitivity to solvent effect of the total interaction rate constants $(k_r + k_q)$ is the same for the two substrates (Figure 1). This indicates that the olefin-$^1O_2$ interaction for both olefins is affected similarly by changes in environment. Second, the activation entropies for the interaction of $^1O_2$ with 2M2P in ME and AC, −29.2 and −28.9 eu, respectively, are very similar to the corresponding values for DMHD, −27.1 and −27.4 eu, respectively. The similarity in behavior of the two olefins suggests that they must go through a similar initial intermediate or transition state, X. X should meet the following requirements. It must be highly organized, to account for the large negative $\Delta S^{\ddagger}$, as has been suggested in the past for olefin-$^1O_2$

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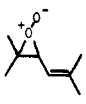
(25) Koch, E. *Tetrahedron* **1968**, *24*, 6295.

(26) The plots were linear for all cases except in BZ, where curvature was seen at long photolysis times. Upon extended photolysis, the rate constant of DMHD disappearance (k_r relative to 2M2P) became $>(k_r + k_q)$ for DMHD in BZ, indicating a nonsinglet oxygen path was occurring.

reactions.[27] It cannot be very polar, because the observed solvent effects on ($k_r + k_q$) values do not correlate at all with solvent polarity. An intermediate commonly proposed for $^1O_2$–olefin reactions which meets these requirements is a perepoxide **9**[28] or a highly organized charge-transfer complex **10**. The difference between these two intermediates is not obvious and they may not even be different. Furthermore, our results cannot distinguish whether X is an intermediate or transition state.



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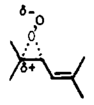

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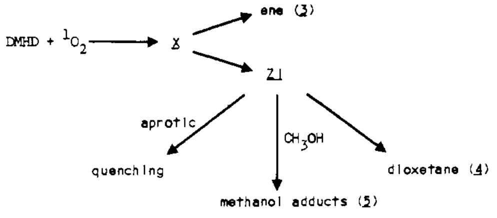
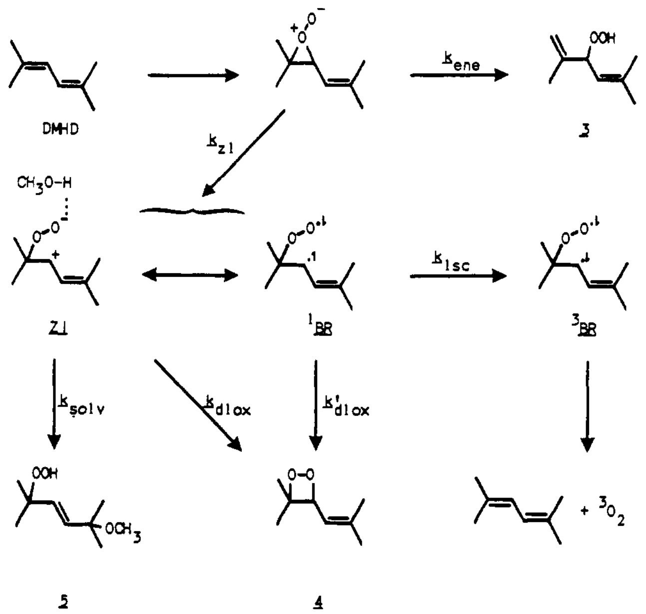
The variations in product ratios **2**/**1** from 2M2P show that after formation of X, the removal of an α-hydrogen leading to ene reaction is affected slightly by both temperature and solvent. The temperature effects on **2**/**1** in both methanol and acetone indicate that the transition state leading from X to **1** is favored by ΔH^* by about 0.4 kcal but has a more negative ΔS^*. From the values in Table II $\Delta\Delta S^*$ (the difference in entropy between the transition states leading to **1** and **2**) are 1.4 and 1.8 eu in methanol and acetone, respectively. The difference in ΔS^* for formation of **1** and **2** from X is consistent with the fact that removal of six α-hydrogens will lead to **2**, whereas the removal of only two α-hydrogens can lead to **1**. The calculated effect would be $\Delta\Delta S^* = (R \ln (6/2)) = 2.2$ eu,[29] close to the observed effect. The difference in ΔH^* leading to **1** and **2** is not so easily rationalized. Houk et al.[30] have attributed such differences to the energy required for the α-hydrogen being abstracted to become nearly perpendicular to the alkene plane. Gollnick and Kuhn have made a similar suggestion.[27] Whether or not the α-hydrogens on the ethyl group in 2M2P can more easily become perpendicular to the alkene plane than those on the methyl groups is not known; however, our results are not inconsistent with these proposals. The fact that **2** is further favored over **1** in MC and AN is also not easily rationalized. It is difficult to see how a change in solvent can affect the enthalpy or entropy barrier to rotation of the α-methyl and α-ethyl groups; however, the changes in product ratios due to solvent are small; the difference in ΔG^* between **1** and **2** varies less than 0.15 kcal in different solvents.

In the case of DMHD, the intermediate X has pathways available to it besides α-hydrogen abstraction. The two main paths lead to quenching (in aprotic solvents) and dioxetane (in protic solvents). We have suggested previously that dioxetane is formed via an intermediate zwitterion, ZI, which can also be trapped by nucleophilic solvents to give **5**.[1] The ZI is formed from X with olefins that can stabilize a cationic center. We will now make the argument that quenching occurs from the ZI as well.

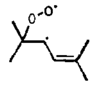


The data for 2M2P indicate that the ene reaction is similar in all solvents studied. With this in mind and the insensitivity of the DMHD ene pathway to conditions, we feel it is safe to assume that the ene path for DMHD also is similar in all the solvents studied; all pathways leading from X compete with the ene path but the total fraction of X going to ene is not much affected by conditions. In AN, where quenching of $^1O_2$ is the predominant reaction, the transition state leading from X to quenching must be lower in energy than the transition state leading to ene product (since ene/quenching = 0.37, $\Delta\Delta G^* \sim 0.6$ kcal). The same is true for AC, BZ, and MC. In ME, however, the path leading to dioxetane and methanol adducts (also via ZI) predominates ($3/(4 + 5) = 0.33$, $\Delta\Delta G^* \sim 0.7$ kcal), and the path leading to quenching disappears. A suggested explanation is that the path leading to quenching in the aprotic solvent leads to formation of products (**4** + **5**) in the protic solvent.

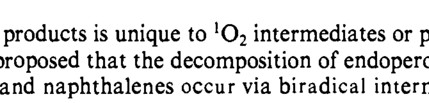
Scheme II



This conclusion suggests that quenching occurs via an intermediate similar to ZI from which intersystem crossing can easily occur. A reasonable candidate is the biradical, BR, Theoretical calculations indicate that 1,4-biradicals, BR, and zwitterions, ZI, are not fundamentally different but that substituents at the terminal centers dictate the electron density at each center.[31-33] If BR and ZI are just two extremes on a continuum,[33] then solvent polarity should also affect the electron density at each center. One major difference between ZI and BR, in the limiting case, is that ^1BR could easily undergo intersystem crossing to ^3BR whereas ZI cannot.[34] After intersystem crossing the diradical can fall apart to starting material and ground-state oxygen in a facile spin-allowed process. This possibility of creating triplet ground-state products is unique to $^1O_2$ intermediates or products. Turro[35] has proposed that the decomposition of endoperoxides of anthracenes and naphthalenes occur via biradical intermediates



BR



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[27] Gollnick, K.; Kuhn, H. J. "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 287.

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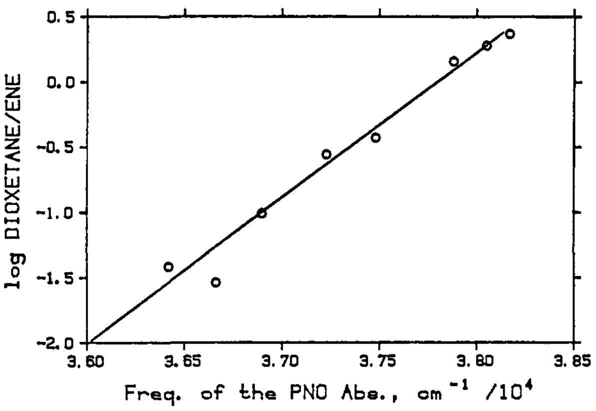
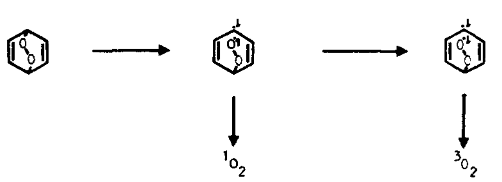


Figure 2. Plot of log dioxetane/ene product ratio for $^1O_2$ oxidation of DMHD in methanol-acetonitrile mixtures vs. the frequency of the PNO absorbance in the same solvent mixtures.

similar to BR which can yield both $^1O_2$ and $^3O_2$, the ratios of which are dependent on the intersystem crossing rate of the biradical.

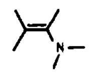


A suggested pathway which rationalizes the observations with DMHD is shown in Scheme II. In the particular case of DMHD, ZI and BR must be of similar energy and the external effect of hydrogen bonding might be enough to favor ZI over BR in ME.

We decided to see if the **4**/**3** ratio could be related to proticity in a more quantitative fashion by studying its variation in methanol-acetonitrile mixtures. The UV absorbance of pyridine *N*-oxide (PNO) was used as a measure of solvent proticity. It is known that both solvent polarity and hydrogen bonding can shift the maximum frequency of the lowest-energy electronic transition (~260 nm) of PNO.[36,37] Hydrogen bonding to the polar ground state, $^1A_1$, stabilizes it relative to the less-polar excited state, $^1B_2$, causing a blue shift in the electronic transition.[38] The extent of the blue shift is a measure of the hydrogen bonding ability of the solvent mixture, assuming the two solvents are of similar polarity (for AC and ME, the dielectric constants are $\epsilon = 36.2$ and $\epsilon = 32.6$, respectively[39]). The difference between ZI and BR is similar to the difference between the $^1A_1$ and the $^1B_2$ state of PNO. The ratio $[{\rm ZI}]k_{\rm diox}/[{\rm BR}]k_{\rm isc}$ should be dependent on the relative stabilization of ZI due to solvent hydrogen bonding. If we assume the ratio $k_{\rm ene}/k_{\rm ZI}$ is constant for the two solvents (they are not exactly constant but similar: 0.11 for ME and 0.27 for AN) and that $k_{\rm solv} < k_{\rm diox}$ in all solvent mixtures ($k_{\rm solv}/k_{\rm diox} = 0.25$ at 22 °C for pure ME, and should be smaller when the mole fraction of ME is less than 1), then a plot of log (**4**/**3**) vs. the frequency of the PNO absorbance should be linear. Figure 2 shows that this is indeed the case.

The absence of solvent polarity effects on the overall reaction rate has been explained by initial formation of a less polar intermediate (or transition state) X, perhaps an exciplex. A fraction of this is then converted to ZI (or its equivalent BR). Since BR is nonpolar, the path with $k_{\rm ZI}$ can occur even in nonpolar solvents; however, we would anticipate increased nonreactive quenching in this case. That radical scavengers are ineffective and cis-trans isomerization of olefins does not occur during ene reaction or dioxetane formation does not rule out the intermediacy of BR or ZI if $k_{\rm diox}$ and $k_{\rm isc}$ are fast relative to the time required for cis-trans isomerization or bimolecular reaction with a scavenger. Some [2 + 2] cycloadditions which are believed to go through a singlet biradical similar to ^{1}BR show little cis-trans isomerization.[40] The lack of Markovnikov directing effects have been noted in $^1O_2$-olefin ene reactions,[27] and this has been used as an argument against a zwitterion intermediate in the ene reaction. The insensitivity of the 2M2P product distribution to solvent is in accord with previous observations.

The proposed general mechanism, Scheme II, would predict that three categories of reaction should exist for olefins with α-hydrogens. (1) When a stabilized zwitterion (or biradical) cannot form, only ene reaction will occur and there will be no quenching. An example is the case of 2M2P. (2) When a stabilized zwitterion can form, dioxetane formation will compete with ene product. If the zwitterion and biradical are of similar energy and $k_{\rm isc} \sim k'_{\rm diox}$, nonreactive quenching will also occur, for example, the case of DMHD. (3) If a zwitterion can form that is very stable, only dioxetane formation will occur and there will be no quenching; *N*,*N*-dimethylisobutenylamine (**11**) provides an example of this case. It has previously been suggested that a zwitterion is the precursor to dioxetane formation from the reaction of **11** with $^1O_2$,[38,39] and theoretical calculations have indicated that the zwitterion is much more stable than either the diradical or perepoxide for the interaction of $^1O_2$ with 1,1-diaminoethylene.[43] In the case of enamines and other compounds which give very stable cations, it is likely that an intermediate (transition state) analogous to X never forms.



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These effects are subtle, and the system is obviously complex. The proposed mechanism is only a first attempt at rationalization, and it is possible that a simpler mechanism can be developed which will explain the observations. The recent intense interest in exciplex intermediates in singlet oxygen reactions[44] has focused attention on their role; they are reasonable candidates for intermediate X.

The effect of solvent on the total interaction rate constants with $^1O_2$, ($k_r + k_q$), for DMHD and 2M2P deserves some attention. Our data for these two olefins, Table I, are consistent with previous reports that solvent has only small effects on ($k_r + k_q$).[45] However, our results are very inconsistent with the solvent effects that have been reported. Gollnick et al.[19] have recently reported that rate constants of tetramethylethylene and cyclohexene photooxidation by $^1O_2$ increase in the order MC < AN < BZ < AC < ME by roughly an order of magnitude. This is almost opposite to our order of ME < BZ < AC < MC < AN (factor of less than 2.5). Gollnick used data from these five solvents and some others to calculate a dipole moment for the transition state of 5.6 ± 0.2 D; he used the Kirkwood-Laidler-Eyring model for changes in k_r with the dielectric constant of the surrounding medium. A plot of log k_r vs. $(\epsilon - 1)/(2\epsilon + 1)$ (where ϵ = dielectric constant of the solvent) gives the dipole moment of the transition state as the slope. When the same analysis is used, our results indicate that the transition state has a dipole moment of <0.4 D (for comparison, nitrobenzene has a dipole moment of 4.19 D and toluene 0.37 D).[46] The reason for this large discrepancy between Gollnick's and our data is probably that Gollnick obtained his (k_r

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(45) Reference 26, p 290.

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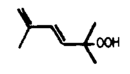
+ k_q) data from β values. These values depend on singlet oxygen lifetimes that were obtained by indirect methods;[47-49] reported values for the same solvent vary widely. Recent $^1O_2$ luminescence decay measurements provide more accurate and consistent $^1O_2$ lifetimes.[14-16] However, for solvents where $^1O_2$ is very long lived, consistent values are still difficult to obtain (for CCl_4 $^1O_2$ lifetimes of 26 000[14] and 900 μs[15] have been reported). Because of this problem and the fact that the data from CCl_4 and CS_2 (where $^1O_2$ is also long lived) are heavily weighted in Gollnick's plots, his transition-state dipole moment is likely to be seriously affected by these errors.

Finally, DMHD has also been reported to yield 2,5-dimethylhexa-1,3-diene 5-hydroperoxide, **12**, upon reaction with $^1O_2$ in a number of solvents.[49] The ratio **12**/**3** was reported to be as high as 9 in CCl_4 and 0.6 in BZ. We found that reaction of DMHD with $^1O_2$ in a C_6H_6:CCl_4 mixture (20% C_6D_6, 80% CCl_4 TPP = sensitizer) carried to low conversions (<10%) showed no sign of **12** by NMR; only **3** was detected. The NMR of **12** would show a distinctive doublet of doublets similar to its $(C_6H_5)_3P$ reduction product **12a** (isolated by preparative GC from photooxidation of DMHD run under acidic conditions, see Experimental Section). Also GC analysis after $(C_6H_5)_3P$ reduction showed only **3a**, and no **12a** (which had a shorter retention time). We believe the reported **12a** is probably formed by rearrangement of either the initial ene product **3** or the $(C_6H_5)P$ reduction product **3a** on TLC.



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Registry No. **3a**, 85939-83-9; **5a**, 85939-84-0; **6**, 85939-85-1; **12a**, 70254-39-6; 2M2P, 625-27-4; DMHD, 764-13-6; $^1O_2$, 7782-44-7.

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Chemistry of Singlet Oxygen. 45. Mechanism of the Photooxidation of Sulfides

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Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received December 6, 1982*

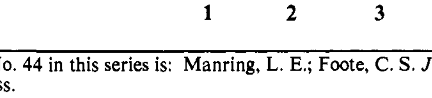
Abstract: The kinetics of the singlet oxygen oxidation of diethyl sulfide in the presence of diphenyl sulfoxide and diphenyl sulfide in various solvents (methanol, benzene, and acetonitrile) have been investigated. The results show that competitive trapping of a single intermediate species by diethyl sulfide, diphenyl sulfide, and diphenyl sulfoxide occurs in protic solvent (methanol), while in aprotic solvents (benzene, acetonitrile) only diphenyl sulfide competes with diethyl sulfide. Diphenyl sulfoxide traps an earlier intermediate; the same intermediate also leads to quenching. A mechanism is proposed in which an initial nucleophilic intermediate **2** can be trapped by electrophiles (diphenyl sulfoxide), lose singlet oxygen, or collapse to an electrophilic intermediate **3** that can be trapped by sulfide nucleophiles.

In the past two decades, there has been considerable interest in and intensive investigation of the photooxidation of sulfides.[1-12] The photosensitized deactivation of several enzymes such as phosphoglucomutase and chymotrypsin has been correlated with the photooxidation of methionine to the corresponding sulfoxide.[6,13-16]

The photooxidation of sulfides was first described by Schenck et al.[1,17,18] They reported that dialkyl sulfides undergo sensitized photooxidation to give 2 mol of sulfoxide per mol of absorbed oxygen.[1]

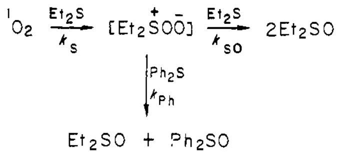
$$2R_2S + O_2 \xrightarrow[\text{sens}]{h\nu} 2R_2SO$$

A stepwise mechanism involving a reactive diradical intermediate, **1**, that reacts with a second sulfide to give the sulfoxide was proposed originally by Gollnick[1] in 1968. Foote et al.[5,6] suggested later that the intermediate might also be a persulfoxide, **2**, or a cyclic sulfurane, **3**, as shown.

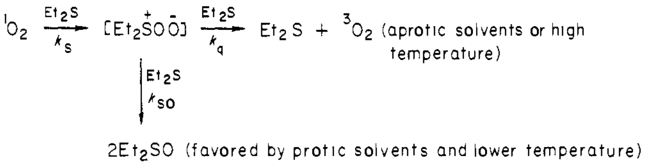


1 **2** **3**

Scheme I



Scheme II



A few years ago, Foote and Peters[2,5,6] reported that considerable diphenyl sulfoxide was produced along with diethyl sullfoxide when

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[†] Paper No. 44 in this series is: Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.*, in press.

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