trans-BuOz when obtained as a cross ozonide from unsymmetrical *cis*- and *trans*-alkenes has also been forwarded.[8b,9] Like the situation for 1-alkenes, these proposals are useful starting points for a stereochemical analysis. Nevertheless, the ozonolyses in $CHClF_2$ are a reminder that the solvent environment may also play a role in determining the ozonide stereochemistry. The neglect of reaction–solvent coupling in present stereochemical Criegee models is a possible origin, at least in part, for some of the limitations that occur in their application.

Experimental Section

^1H NMR were obtained with a Brüker WM-360 spectrometer. Microwave spectra were recorded with a Hewlett-Packard 8460A spectrometer. Conventional vacuum-line techniques on a calibrated manifold were employed for most manipulations of reactants and products. A Welsbach Model T-408 ozonator was employed.

Materials. CP grade propylene (Matheson), *cis*-2-butene (Matheson), *trans*-2-butene (Matheson), *trans*-2-pentene (Aldrich), acetaldehyde (Matheson Coleman and Bell), and solvents (isobutane, $CHClF_2$, and CH_3Cl) were normally dried by passage through cold traps. (*E*)-Propene-*1*-d_1 (67% enriched) was prepared in our lab,[36] and propene-*2*-d_1 (98% enriched) was purchased from Merck Co. Isotopic enrichments were checked by microwave spectroscopy.

Ozonolysis Procedure. Reactions were conducted with flow rates of 0.1–0.2 mmol of O_3/min by standard techniques.[9,15,16] The solutions were ~1.0 M in alkene (usually 2 mmol of alkene in 20 mmol of solvent), and 0.6–1.0 mmol of ozone was used. All the input ozone was consumed in the reaction vessel. After reaction, a fast warm-up procedure was employed.[6a] The reaction mixture was then distilled through traps held at −78 and −196 °C. The ozonides were collected in the −78 °C trap.

The total yields of ozonides were determined manometrically. They were around 60% from propylene, 35% from *cis*- or *trans*-2-butene, and less than 20% from *trans*-2-pentene.

Relative Yields and *cis*-/*trans*-2-Butene Ozonide Stereochemistry. Ozonolysis of propylene produces the normal and cross ozonides (Scheme II). The relative yields of these ozonides were analyzed by 360-MHz proton NMR. Figure 1 shows a part of the NMR spectrum of the ozonide mixture. Peak assignments were obvious from the relative integrations and the splittings. For *cis*- and *trans*-2-butene ozonides, a quartet arises from the methine hydrogen for each stereoisomer. The downfield quartet was assigned to the cis isomer,[8,10,30,31] consistent with the GC/microwave results, which unequivocally determined the stereochemistry.[9] Integration of these peaks and the other resonances in this region gave the relative ozonide yields. Although the methyl groups in the *cis*- and *trans*-2-butene ozonide mixture also produce two doublets at δ 1.40, they were too overlapped to be used for quantitative measurements. ^1H NMR (room temperature, in $CDCl_3$): ethylene ozonide δ 5.082; propylene ozonide, δ 1.424 (d, J = 4.90 Hz, 3 H), 5.038 (d, J = 0.46 Hz, 1 H), 5.178 (s, br, 1 H), 5.256 (q, 1 H); *cis*-2-butene ozonide δ 1.404 (d, J = 4.98 Hz, 3 H), 5.335 (q, 1 H); *trans*-2-butene ozonide δ 1.402 (d, J = 4.88 Hz, 3 H), 5.290 (q, 1 H).

KSIE of $CH_3CH{=}CH_2/CH_3CD{=}CH_2$ and $CH_3CH{=}CH_2/CH_3CH{=}CHD$. A mixture of approximately 50% propylene-d_0 and 50% propylene-d_1 was prepared on a vacuum line and a portion saved for later analysis. The mixture was ozonized to 30% in isobutane at −78 °C followed by distillation through −78, −116, and −196 °C traps. Ozonide was collected at −78 °C, solvent at -116 °C, and unreacted propylene at −196 °C. The recovered and initial propylene as well as the ozonides were analyzed by 360-MHz NMR in $CDCl_3$ at room temperature.

Propylene gives a complex spectrum with multiplets centered at δ 1.71, 4.93, 5.02, and 5.82. The peak at δ 5.82 arises from the methine hydrogen since its multiplicity appeared to be 16 and its intensity decreased with propene-*2*-d_1. The peak at 4.93 could be assigned to the H trans to CH_3 from the intensity change with (*E*)-propene-*1*-d_1. Multiplet regions were integrated and simple relationships were used to extract the d_0/d_1 ratios. For example, with mixtures of propene-d_0 and -*2*-d_1, the resonances at 5.82 arise from the d_0 species while the multiplets at either 4.93 or 5.02 can be used to determine the d_0 and *2*-d_1 sum. For mixtures of propene-d_0 and (*E*)-propene-*1*-d_1, the resonances at 4.93 arise from the d_1 species while either of the other two multiplets downfield determine the d_0 and d_1 sum. The relative intensities of the $1_{01} \rightarrow 2_{02}$ and $1_{10} \rightarrow 2_{11}$ microwave transitions of the normal and both deuterated species of propylene were also used to determine the d_0/d_1 ratios.[36,37] These transitions are split into partially resolved doublets due to methyl tunneling effects so the intensity ratios were evaluated by cutting and weighing. Base-line problems are accentuated by this procedure and contribute to some of the data scatter. The d_0/d_1, NMR analysis of the propylene ozonide was carried out in a manner similar to that of propylene. These data were used in relationships previously discussed to determine k_H/k_D.[15]

Acknowledgment. We are grateful to Frank Parker who was invaluable in obtaining NMR spectra, Dr. Misako Imachi who provided the (*E*)-propene-*1*-d_1, and Dr. Kurt Hillig who advised on ozonolysis techniques. This work was supported by Grant CHE-8005471 from the National Science Foundation.

Registry No. D_2, 7782-39-0; CH_3CHO, 75-07-0; propylene, 115-07-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *trans*-2-pentene, 646-04-8.

---

[34] Fliszár, S.; Renard, J.; Simon, D. Z. *J. Am. Chem. Soc.* **1971**, *93*, 6953.

[35] Rouse, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 5095.

[36] Imachi, M.; Cant, N.; Kuczkowski, R. L. *J. Catal.* submitted for publication.

[37] Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1961**, *35*, 1374.

Chemistry of Singlet Oxygen. 43. Quenching by Conjugated Olefins

Lewis E. Manring, Richard C. Kanner, and Christopher S. Foote*

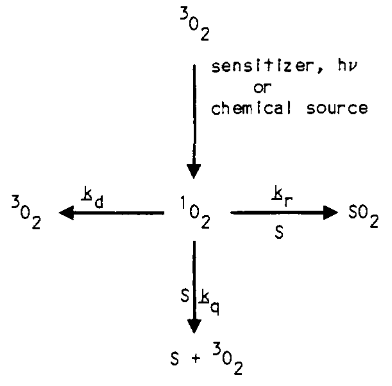
Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received November 26, 1982*

Abstract: The interaction of singlet oxygen with the olefins 2,5-dimethyl-2,4-hexadiene (DMHD) and 1-methyl-2-phenylindene (MPI) leads to both reaction and quenching. Although the initial interaction with singlet oxygen is nearly independent of solvent and temperature, the relative amount of quenching depends on solvent in the case of DMHD and on both solvent and temperature in the case of MPI. The increased reaction rate for indenes at lower temperatures is caused by a decrease in the fraction of the initial interaction which leads to quenching. A similar factor governs the increase in DMHD rates in going from aprotic to protic solvents.

The interaction of $^1O_2$ with organic substrates has been studied extensively.[1-3] It is known that three major paths are available to $^1O_2$ in solution, as shown in Scheme I.[4]

Two of the three paths in Scheme I are dependent on the

Scheme I



presence of substrate (S): k_q (nonreactive quenching) and k_r (oxidation of substrate by $^1O_2$). The third path, k_d, is the rate of radiationless decay and is solvent dependent.[1-3,5]

With the assumption that $[S](k_r + k_q) > k_d$, i.e., the substrate interacts with a majority of the $^1O_2$ formed, a number of possible situations arise. First, when $k_r \gg k_q$, product SO_2 is formed on every collision with $^1O_2$ which results in its removal. If $k_r \sim k_q$, S is still oxidized to SO_2, but the rate of SO_2 appearance is less than the total rate of removal of $^1O_2$ because path k_q leads to starting material and ground-state oxygen, causing no loss of substrate. Finally, if $k_q \gg k_r$, SO_2 is not formed appreciably, although $^1O_2$ may be removed at a very high rate. All of the above situations are known to occur in singlet oxygen chemistry.[4,6-8]

Quenching of singlet oxygen was first reported by Schenck and Gollnick for nicotine.[9] Two mechanisms of quenching are known. An energy-transfer process occurs with carotenes and certain other compounds with very low triplet energies.[10] A second process involves formation of a charge-transfer complex between the electron-rich substrate and $^1O_2$ in which intersystem crossing restrictions are relaxed, leading to $^3O_2$ and S. This process occurs with substrates such as amines,[7] sulfides,[8] and phenols.[11] Quenching of $^1O_2$ by simple olefins is believed to be unimportant,[12] although this has been firmly established for only a few cases.[6]

Because olefins are not commonly expected to quench $^1O_2$, both $(k_r + k_q)$[13-15] and k_r[16-19]values are often used as measures of relative olefin reactivities. Previously, relative $(k_r + k_q)$ values have usually been derived from measurements of β, where $\beta = k_d/(k_r + k_q)$ and is calculated from the dependence of product formation on substrate concentration,[13] or from a similar analysis based on competitive inhibition of a reactive substrate.[14,15] Most k_r values are determined by the amount of product formed[17] or starting material consumed[16,18] in competition with a substrate whose reaction rate is well characterized.[20] The use of both k_r and $(k_r + k_q)$ values as reactivity measurements can obviously lead to confusion unless $k_r \gg k_q$. The problem is compounded if k_q is solvent and/or temperature dependent, as has been shown to be the case for dialkyl sulfide–$^1O_2$ reactions.[8,21,22] The availability of direct time-resolved 1.27 μ luminescence detection from $^1O_2$ provides a new and more precise method of measuring $(k_r + k_q)$.[5,23-26] In this paper we report that two substrates with conjugated olefinic double bonds do quench $^1O_2$ significantly and that the relative amount of quenching depends on solvent and temperature.

Table I. Rates of Interaction and Reaction of DMHD with $^1O_2$

solvent	$k_r + k_q$ (M^{-1} s^{-1}) × 10^{-6}	k_r[c] (M^{-1} s^{-1}) × 10^{-6}	k_r[d] (M^{-1} s^{-1}) × 10^{-6}
CH_3OH	2.6 ± 0.2[a]	3.4	2.5 ± 0.6
C_6H_6	3.6 ± 1.2[b]		<0.25
CH_3COCH_3	3.9 ± 0.6[b]	0.38	0.74 ± 0.08
CH_2Cl_2	5.2 ± 1.1	0.60	1.4 ± 0.3
CH_3CN	5.2 ± 0.43,[a] 6.3 ± 1.1[b]	0.76	1.6 ± 0.2

[a] Calculated from β, measured by Young's technique.[29] See experimental for k_d. [b] Determined directly, see ref 5. [c] Reference 34. Determined by competition with methylcyclohexene. [d] This work. Determined by competition with 2M2P, adjusted for solvent effects on 2M2P rates.[32]

Experimental Section

Chemicals. Solvents were Mallinkrodt spectrograde CH_3COCH_3, CH_3CN (distilled from P_2O_5), C_6H_6, and CH_3OH and AR CH_2Cl_2. CD_3COCD_3 and DMHD were obtained from Aldrich. In early experiments, the DMHD was purified by spinning band column distillation, and in later experiments by preparative GC. 2-Methyl-2-pentene (Aldrich) was passed through basic alumina immediately prior to use. 1,3-Diphenylisobenzofuran (Aldrich) (DPBF) was recrystallized several times under dim lighting from benzene-ethanol, mp, 130–131 °C.[27] The synthesis of 1-methyl-2-phenylindene (MPI) has been described previously.[28] Rose bengal (Eastman) was chromatographed on silica gel plates with 2-butanone/H_2O 20:1; tetraphenylporphine (Aldrich) (TPP) and mesoporphyrin IX–dimethyl ester (Sigma) were used without further purification.

Rate Determinations. Values of $(k_r + k_q)$ were determined either from β ($k_d/(k_r + k_q)$) or directly from the effect of added substrate on the $^1O_2$ luminescence decay rate k_{obsd} ($(k_r + k_q)[S] + k_d$). β values were determined by Young's technique[29] (inhibition of the photooxygenation of DPBF followed by DPBF fluorescence) as described previously;[30] 10^{-5} M rose bengal and 5×10^{-7} to 1×10^{-6} M DPBF were used. Values of $(k_r + k_q)$ were calculated by assumming $k_d^{MeOH} = 1.05 \times 10^5$ s^{-1},[24] $k_d^{acetone} = 2.17 \times 10^4$ s^{-1},[5] and $k_d^{MeCN} = 1.54 \times 10^4$ s^{-1}.[31] The methods for direct determination of $(k_r + k_q)$ by $^1O_2$ luminescence are described elsewhere.[5,32] Mesoporphyrin IX–dimethyl ester, 5×10^{-5} M, was used as a sensitizer in MeCN, acetone, CH_2Cl_2, and benzene.

Olefin k_r values were determined by the method of Higgins et al.[20] by competition with 2-methyl-2-pentene (2M2P) (Aldrich). Values of k_r for 2M2P in all solvents were determined by the direct technique,[5] assuming[6] $k_q^{2M2P} \ll k_r^{2M2P}$ (see accompanying paper[32]). Rose bengal, 5×10^{-5} M, was used as a sensitizer in actone, methanol, and acetonitrile, and TPP (2×10^{-4} M) was used in C_6H_6 and CH_2Cl_2. The disappearance of DMHD and the appearance of the 2M2P products were monitored (after $(C_6H_5)_3P$ reduction) by GLC.[32] The disappearance of MPI

---

(1) Schaap, A. P. "Singlet Molecular Oxygen"; Dowden, Hutchinson and Ross, Inc.: Stroudsburg, Pennsylvania, 1976.

(2) Ranby, B.; Rabek, J. F. "Singlet Oxygen-Reactions with Organic Compounds and Polymers"; Wiley: New York, 1978.

(3) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979.

(4) For review see: Foote, C. S., ref 3, Chapter 5, p. 139.

(5) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 2069.

(6) Foote, C. S.; Ching, T.-Y., *J. Am. Chem. Soc.* **1975**, *97*, 6209.

(7) Young, R. H.; Martin, R. L.; Feriozi, D.; Brewer, D.; Kayser, R. *Photochem. Photobiol* **1973**, *17*, 233.

(8) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

(9) Schenck, G. O.; Gollnick, K. *J. Chim. Phys.* **1958**, *55*, 892.

(10) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 6233.

(11) Thomas, M.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683.

(12) Gormann, A. A.; Rodgers, M. A. J. *Chem. Soc. Rev.* **1981**, *10*, 205.

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

(14) Monroe, B M. *J. Phys. Chem.* **1978**, *82*, 15.

(15) Monroe, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 7253.

(16) Matsuura, T.; Horinaka, R.; Nakashima, R. *Chem. Lett.* **1973**, 887.

(17) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5168.

(18) Frimer, A. A.; Roth, D. *J. Org. Chem.* **1979**, *44*, 3882.

(19) Hasty, N. M.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380.

(20) Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *77*, 102.

(21) Foote, C. S.; Peters, J. W. *IUPAC Congr., Special Lect. 23rd.* **1971**, *4*, 129.

(22) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949.

(23) (a) Ogilby, P. R. Ph.D. Dissertation, 1979, UCLA. (b) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.*, 1983, *105*, 3423.

(24) Krasnovsky, A. A. *Chem. Phys. Lett.* **1981**, 443.

(25) Hurst, J. R.; Macdonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065.

(26) Parker, J. G.; Stanbro, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 2067.

(27) Provided by Dr. P. R. Ogilby.

(28) Burns, P. A.; Foote, C. S.; Mazur, S. *J. Org. Chem.* **1976**, *41*, 899.

(29) Young, R. H.; Wehrly, K.; Martin, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5774.

(30) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1219.

(31) Values of k_d for CH_3CN in the literature range from 1.85×10^4 s^{-1}[5] to 1.54×10^4s^{-1}.[25] Under our conditions we obtain a value of 1.54×10^4 s^{-1} for CH_3CN dried over P_2O_5.

(32) Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.*, following paper in this issue.

Table II. Effect of Temperature on $^1O_2$ Interaction with MPI, DPI, and DMHD in Acetone

temp, °C	substrate	$(k_r + k_q)^a$ $(M^{-1}\ s^{-1}) \times 10^{-6}$	$k_r{}^b$ $(M^{-1}\ s^{-1}) \times 10^{-6}$
25	MPI	1.5 ± 1.0	0.17 ± 0.05
−50	MPI	1.0 ± 0.04	0.98 ± 0.49[d]
25	DPI	0.84 ± 0.06[c]	
−25	DPI	0.82 ± 0.05	
25	DMHD	3.9 ± 0.6	0.69 ± 0.08
−78	DMHD	3.1 ± 0.3[e]	0.64 ± 0.10[f]

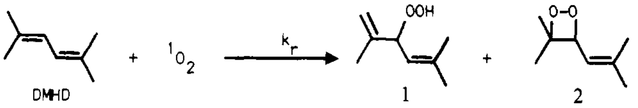
[a] Determined from either β or directly, see accompanying paper.[32] [b] Determined relative to 2M2P, see accompanying paper.[32] [c-f] Determined at (*c*) −49 °C, (*d*) −78 °C, (*e*) −68 °C, (*f*) −78 °C.

and 2M2P in CD_3COCD_3 was monitored by NMR (JEOL-FX 90Q, CH_3NO_2 added as internal standard).

Product Ratios. The isolation of the dioxetane from DMHD and its spectral properties has been described previously by Hasty and Kearns.[19] The isolation and characterization of the products from DMHD–$^1O_2$ reactions are described in the accompanying paper.[32]

Results and Discussion

The reaction of 2,5-dimethyl-2,4-hexadiene (DMHD) with $^1O_2$ was reported by Hasty and Kearns[19] and reinterpreted by Gollnick and Kuhn.[33]



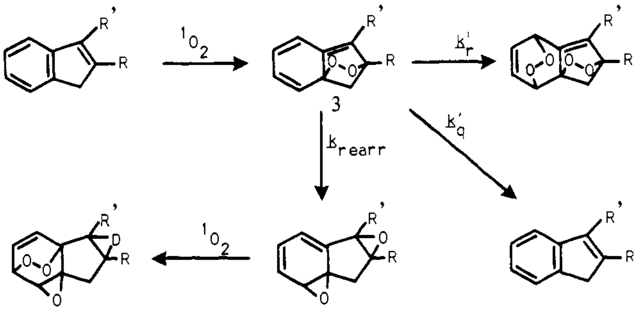
These workers showed that the major products were the ene reaction product **1** and dioxetane **2**. The ratio of **2**/**1** was shown to be extremely solvent dependent, being 2.6, 0.2, and 0.01 in methanol, acetone, and acetonitrile, respectively. We confirmed the product ratios for methanol and acetonitrile, obtaining 2.4 and 0.03, respectively. (The products obtained from this reaction are described in detail in the following paper.) The rate constant for reaction, k_r, determined by competition experiments with methylcyclohexene, was also shown to be solvent dependent, being ~10 times larger in methanol than in acetone.[34] The rate constant for methylcyclohexene was assumed to be constant in all the solvents studied; however, rates for other olefins are now known to be solvent dependent.[32] We redetermined k_r by competition with 2M2P, whose reaction rate is known in all the solvents;[32] the values are shown in Table I. Although the values show a slightly smaller range of variation than those reported previously,[33] the value of k_r varies over a factor of 4 between acetone and methanol. Such large variations in k_r are not seen with simple olefins in these solvents.[32,35]

In contrast, the total rate of interaction between DMHD and $^1O_2$ ($k_r + k_q$), determined either from the β value (see experimental) or measured directly (see ref 30), is almost constant in methanol, acetone, and acetonitrile (Table I). The rate of disappearance (k_r) of DMHD in methanol is close to ($k_r + k_q$). This indicates that DMHD does not quench $^1O_2$ by a nonreactive pathway in methanol, consistent with the results for simple olefins.[6] In contrast, k_r for DMHD in both acetonitrile and acetone is much less than the total interaction rate between $^1O_2$ and DMHD. The major interaction between DMHD and $^1O_2$ leads to nonreactive quenching in these two solvents, e.g., close to 75% in CH_3CN.

We reported previously that the reaction of $^1O_2$ with indenes is faster at −78 °C than at room temperature.[28,36] We have now found that the rates of total interaction ($k_r + k_q$) for $^1O_2$ with 1-methyl-2-phenylindene (MPI) and 1,2-diphenylindene (DPI) in acetone are almost constant at 25 and −49 °C, (Table II), but that nonreactive quenching of $^1O_2$ by MPI occurs at room temperature and disappears at low temperature. (The temperature dependence of k_r for DPI could not be readily determined because of the lack of solubility of DPI at low temperatures.) The rate of MPI disappearance increases roughly 5-fold in going from 25 to −78 °C. The apparent increased reaction rate of indenes at low temperature is caused by a decrease in the fraction of quenching for indenes as the temperature is lowered; $k_q/(k_r + k_q)$ drops from 0.89 at 25 °C to nearly zero at −50 °C.

Also shown in Table II are rate constants for DMHD at different temperatures. The total rate of interaction ($k_r + k_q$) of $^1O_2$ with DMHD is almost independent of temperature; in contrast to the situation with MPI, however, the rate of reaction k_r does *not* increase as the temperature is lowered.

The reason for this difference between MPI and DMHD is not clear; it could be related to the fact that the indenes can undergo [2 + 4] addition of $^1O_2$ whereas DMHD cannot readily do so because of the difficulty of reaching an s-cis arrangement. The indenes give increased amounts of [2 + 4] addition product as temperature is lowered.[28] (At low temperatures DMHD also starts to give a small amount of the stable [2 + 4] addition product in methanol, but not in acetone.[32]) The initially formed [2 + 4] addition products from $^1O_2$ and indenes seem either to react with a second $^1O_2$, k_r', to give the final products, or revert to starting indene[37a,b] with rate k_q', if the third process (k_{rearr}, which is a photosensitized reaction[38]) is suppressed. The results suggest that k_q' is more sensitive to temperature than $k_r'[^1O_2]$. (The addition of a second mole of singlet oxygen does not affect the kinetics since the concentration of the monoadduct is always very much smaller than that of the indene.)



The quenching of $^1O_2$ by DMHD must involve intersystem crossing after the initial interaction between $^1O_2$ and substrate. The nature of this process is not certain. In the quenching of $^1O_2$ by amines, sulfides, and phenols it has been suggested that a charge-transfer process causes intersystem crossing restrictions to be relaxed leading to $^1O_2$ quenching.[4]

It is interesting to compare these olefin–$^1O_2$ reactions to dialkyl sulfide–$^1O_2$ interactions. Both diethyl sulfide and 1,4-dithiane are oxidized only very slowly in aprotic solvents (acetonitrile, benzene).[8] In benzene, over 95% of the reaction of singlet oxygen with diethyl sulfide results in quenching. In contrast, 100% of the diethyl sulfide–$^1O_2$ interaction leads to product in protic solvents (methanol, H_2O/acetonitrile).[8] This solvent proticity effect is analogous to the effect found with DMHD and indenes. DMHD gives >90% quenching of $^1O_2$ in benzene and 75% quenching in acetonitrile (Table I); however, as in the case of diethyl sulfide, 100% of the DMHD–$^1O_2$ interaction in methanol leads to product. The reaction also occurs much more efficiently in aqueous acetone than in pure acetone.[19] The indenes behave similarly, also reacting faster in protic than in aprotic solvents.[28] For the dialkyl sulfides it has been suggested that protic solvents stabilize a persulfoxide intermediate **4** by hydrogen bonding. Intermediates analogous to **4** for DMHD and indenes would be compounds **5** and **6**. In both **5** and **6**, the cationic center is

---

(33) Gollnick, K.; Kuhn, H. J., in ref 3, Chapter 8, p. 296.

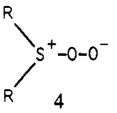
(34) The rates relative to methylcyclohexene were determined by Hasty and Kearns.[19] The absolutes rates were calculated by Gollnick and Kuhn[33] assuming k_r for methylcyclohexene is $1.2 \times 10^5\ M^{-1}\ s^{-1}$.

(35) Gollnick, K.; Hartman, H.; Paur, H. In "Oxygen and Oxy-Radicals in Chemistry and Biology"; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; pp 371–395.

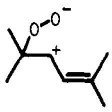
(36) Boyd, J. D.; Foote, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 6758.

(37) (a) Boyd, J. D.; Foote, C. S., unpublished results. (b) Ryang, H.-S.; Kramer, M. K.; Foote, C. S., unpublished results. Small amounts of endoperoxide 3 are detectable at −80 °C by NMR and disappear on warming.

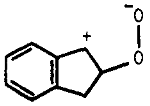
(38) Boyd, J. D.; Foote, C. S., Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641.



4



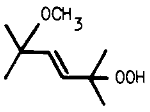
5



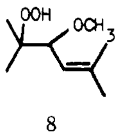
6

stabilized relative to simple olefins. Zwitterionic intermediates such as **5** and **6** have often been proposed as precursors to dioxetanes in $^1O_2$ reactions,[39-41] and dioxetane formation from $^1O_2$ 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]

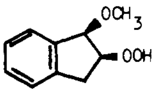
It would be anticipated that methanol would attack the zwitterionic intermediates **5** and **6** giving two methanol addition products in each case, **7** and **8** for DMHD and **9** and **10** for indene. It has been reported previously that photooxidation of DMHD under either acidic or basic conditions 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]



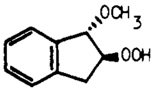
7



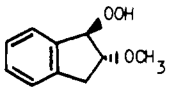
8



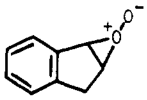
9



10



11



12

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; $^1O_2$, 7782-44-7.

---

(39) Saito, I.; Matsuura, T. *Acc. Chem. Res.* **1977**, *10*, 346.
(40) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437.
(41) Dewar, M. J. S.; Thiel, M. *J. Am. Chem. Soc.* **1975**, *97*, 3978.
(42) Schaap, A. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6055.
(43) Foote, C. S.; Lin, J. W.-P. *Tetrahedron Lett.* **1968**, 3267.
(44) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169.
(45) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 3396.
(46) Hatsui, T.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2655.

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

Lewis E. Manring and Christopher S. Foote*

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 $^1O_2$ (which gives only ene products) and that between DMHD and $^1O_2$ (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 $^1O_2$ with 2,5-dimethyl-2,4-hexadiene (DMHD) and 1-methyl-2-phenylindene (MPI) can lead to both reaction and quenching of $^1O_2$. Although the rate constant for initial interaction with $^1O_2$ 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

---

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