structural and magnetic properties and the reactivity of oxo-bridged Mn aggregates are underway.

Acknowledgment. The authors gratefully acknowledge Professors K. Wieghardt, C. Dismukes, and J. Philo for preprints of work prior to publication. This work was supported by Grant No GM 382751-01 from the National Institute of General Medical Sciences.

Registry No. **1**$(CF_3SO_3)_5$, 118831-88-2; **2**$(CF_3SO_3)_4$, 118831-90-6; **3**$(CF_3SO_3)_4$, 118867-65-5; **3**$(ClO_4)_4$, 118867-62-2; **4**$(ClO_4)_5 \cdot 3CH_3CN$, 118867-64-4.

Supplementary Material Available: For each of **1**$(CF_3SO_3)_5$, **4**$(ClO_4)_5$, and **3**$(ClO_4)_4$ a fully labeled ORTEP drawing and tables of interatomic distances, interatomic angles, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and molar susceptibility data (27 pages). Ordering information is given on any current masthead page.

Trimethyl Phosphite Traps Intermediates in the Reaction of $^1O_2$ and Diethyl Sulfide

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Received November 28, 1988

A variety of intermediates in $^1O_2$ reactions (ene reaction, 1,2-dioxetane, and endoperoxide formation) have been proposed as a result of studies of solvent and isotope effects and theoretical calculations.[1] The proposed intermediates have been trapped in a few cases.[2-6] Diphenyl sulfide and diphenyl sulfoxide have been used to trap intermediates in the reaction of $^1O_2$ with diethyl sulfide,[2] and methyl phenyl sulfoxide has been used to trap the intermediate in the reaction of $^1O_2$ with adamantylidene adamantane.[4] We report that trimethyl phosphite is surprisingly unreactive toward $^1O_2$ but very efficient in trapping the intermediate in the photooxidation of Et_2S.

Table I. Rate Constants of $^1O_2$ Quenching by $(MeO)_3P$ and Sulfides[a]

quencher	methanol	acetonitrile	benzene	acetone	C_6H_6/MeOH[b]
$(MeO)_3P$	2.7×10^4 [c]	6.6×10^4	4.7×10^4	6.3×10^4	3.9×10^4 [d]
Et_2S	1.7×10^7	2.1×10^7 [e]	2.0×10^7 [e]		
PhSPh	$\sim 1.0 \times 10^5$ [e]				

[a] $M^{-1}\ s^{-1}$. [b] 4:1 (v/v). [c] Methanol-OD. [d] $1.5 \times 10^7\ M^{-1}\ s^{-1}$ from ref 11. [e] Reference 8c.

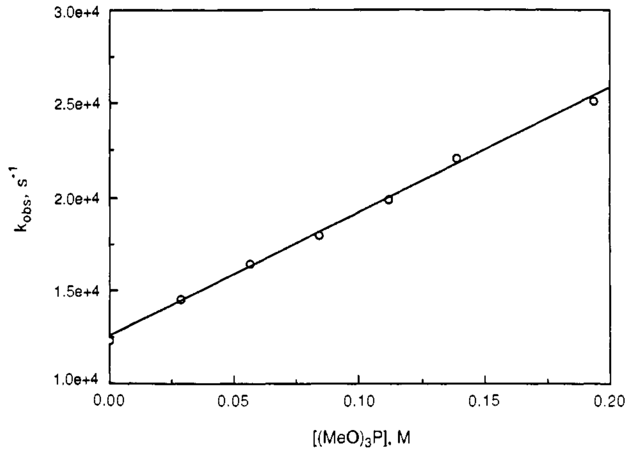


Figure 1. Singlet oxygen quenching by $(MeO)_3P$ in acetonitrile. The plot of k_{obsd} vs $[(MeO)_3P]$ has slope = quenching rate constant and intercept = singlet oxygen decay rate constant in the pure solvent: slope = $6.6 \times 10^4\ M^{-1}\ s^{-1}$, intercept = $1.25 \times 10^4\ s^{-1}$.

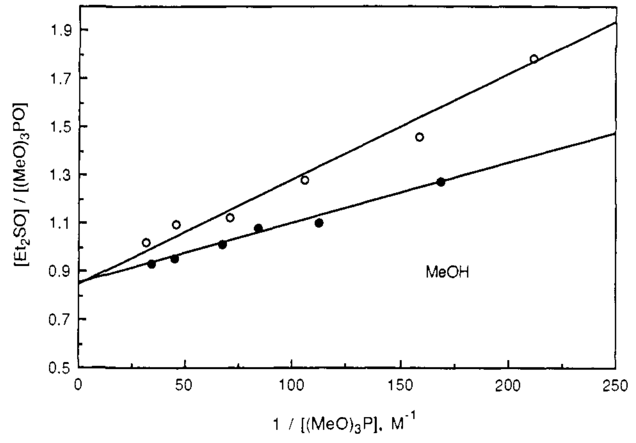
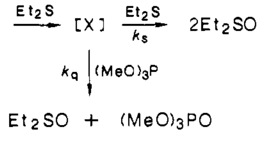
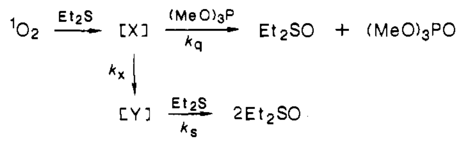


Figure 2. $(MeO)_3P$ trapping of Et_2S intermediate in MeOH: (○) 0.10 M Et_2S, slope = 0.0025(●), 0.20 M Et_2S, slope = 0.0044.

Scheme I



Scheme II



Trimethyl phosphite has been used as a powerful reducing agent for peroxides,[7] but to our knowledge there has been no report of its use as to trap intermediates in photooxidation. We chose the reaction of Et_2S with $^1O_2$ because it is relatively well understood.[2,3,8] The rate constants for $^1O_2$ quenching by $(MeO)_3P$ and Et_2S were measured by $^1O_2$ emission (1270 nm) in various solvents (see Table I);[9] Figure 1 shows a typical plot from the $^1O_2$ emission study. The slope is equal to the bimolecular quenching rate constant. The rates of quenching by Et_2S are at least 300 times faster than those by $(MeO)_3P$. A trap for intermediates must be relatively inert toward $^1O_2$ but reactive to the intermediates; from Table I, $(MeO)_3P$ satisfies the first condition. The rate constants for $(MeO)_3P$ (2.7–$6.6 \times 10^4\ M^{-1}\ s^{-1}$) are far lower than those reported by Goe et al. ($1.5 \times 10^7\ M^{-1}\ s^{-1}$) from β-carotene

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(9) An acridine solution was pulsed at 355 nm with a Nd/YAG laser, and the data were analyzed by the Guggenheim method.[10] For experimental details, see: Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.

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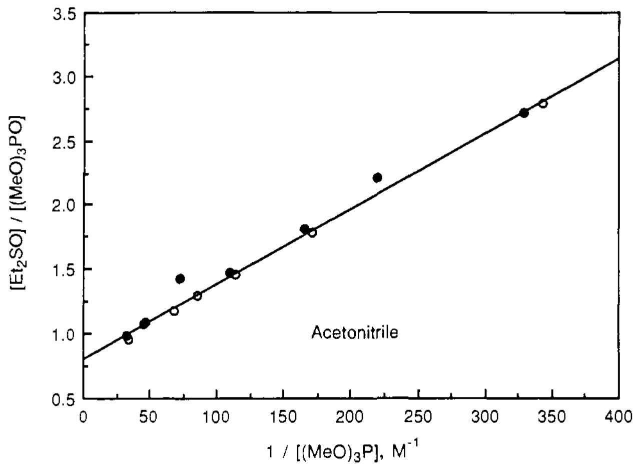

Figure 3. $(MeO)_3P$ trapping of Et_2S intermediate in CH_3CN: (○) 0.10 M Et_2S, slope = 0.0058 M, (●), 0.20 M Et_2S, slope = 0.0058 M.

quenching of the photooxidation of trimethyl phosphite.[11]

When Et_2S in methanol or acetonitrile was oxidized with $^1O_2$ in the presence of various amounts of $(MeO)_3P$, diethyl sulfoxide and trimethyl phosphate were formed.[12] The concentration of $(MeO)_3P$ was kept lower than that of Et_2S,[13] ensuring that Et_2S was the primary reactant with $^1O_2$. Figures 2 and 3 show plots of $[Et_2SO]/[(MeO)_3PO]$ vs $1/[(MeO)_3P]$ in methanol and acetonitrile, respectively.

In methanol, the slopes depend on the concentration of Et_2S, but not in acetonitrile. These observations are very similar to those in the Et_2S–Ph_2SO system.[2] If the mechanism of trapping by $(MeO)_3P$ in methanol is similar to that reported for Ph_2SO, Scheme I can be derived which gives eq 1 by steady-state kinetics. This equation predicts a sulfide dependence of the slope, as observed with diphenyl sulfide trapping in methanol and as observed in Figure 2.

$$[Et_2SO]/[(MeO)_3PO] = 1 + (2k_s[Et_2S]/k_q)(1/[(MeO)_3P]) \tag{1}$$

Scheme II was derived for sulfide trapping of the intermediate in aprotic solvents, and leads to eq 2, which has no dependence

$$[Et_2SO]/[(MeO)_3PO] = 1 + (2k_x/k_q)(1/[(MeO)_3P]) \tag{2}$$

of the slope on sulfide concentration, as observed with diphenyl sulfide.[2] This scheme is consistent with the results in acetonitrile (Figure 3).

The structures of the intermediates in Schemes I and II are not certain, although intermediate X has been suggested to be a persulfoxide.[2,3,8] However, Schemes I and II are fit reasonably well by the data.[2] The fact that the intercepts of the plots in both Figures 2 and 3 are less than 1 suggests that some process other than intermediate trapping also contributes a small amount (~ 15%) to the production of trimethyl phosphate.[14] This cannot be direct reaction with singlet oxygen, which is negligible under the conditions.

From the slopes of the plots in Figure 2, values for k_s/k_q (Scheme I) were determined (Table II); the rate constant for trapping of the sulfide reaction intermediate by $(MeO)_3P$ in methanol is 420 times that of Ph_2S, 240 times that of Ph_2SO, and 87 times that of Et_2S. Thus trimethyl phosphite also satisfies the second criterion for a trap, reactivity toward the intermediate.

Table II. Relative Quenching Efficiencies

quencher	k_s/k_q	k_x/k_q	k_q (relative)
Ph_2S[a]	4.81[c]		1.0
Ph_2SO[a]	2.77[c]		1.7 (1)
$(MeO)_3P$[a]	0.0115		420 (240)
Et_2S[a]	1.0		4.8[d]
Ph_2SO[b]		0.082[c]	1
$(MeO)_3P$[b]		0.0029	28

[a] Methanol. [b] CH_3CN. [c] Reference 2 (b). [d] k_s.

In the same manner, k_x/k_q (Scheme II) was calculated. If k_x is the same in both cases, $(MeO)_3P$ is 28 times more reactive than Ph_2SO in acetonitrile. It is not yet possible to estimate the absolute trapping rate of $(MeO)_3P$, but the high rate and relative unreactivity with $^1O_2$ recommends it as a potential trapping agent for short-lived intermediates formed from other substrates.

The properties of other phosphites are being studied to better understand the trapping process. The application of $(MeO)_3P$ to the trapping of other substrates is also under investigation.

Acknowledgment. This work was supported by NIH Grant GM-20080. We are indebted to Richard Kanner for assistance in the singlet oxygen emission measurement.

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[12] Methylene blue was used as a sensitizer with a filter solution of 0.1 M $K_2Cr_2O_7$ (cut-off < 460 nm). Control experiments gave no formation of $(MeO)_3PO$ under the same conditions without sensitizer or light.

[13] For example, 0.10 M Et_2S in oxygen-saturated acetonitrile with various amounts of $(MeO)_3P$ was irradiated on a "merry-go-round" for 4–5 min, and then the products were analyzed by GC. $[(MeO)_3P]$, $[Et_2SO]$, and $[(MeO)_3PO]$, mM; 0.0, 5.07, 0.0; 2.9, 3.97, 1.39; 5.8, 3.34, 1.89; 8.8, 3.39, 2.32; 11.7, 3.35, 2.57; 14.6, 3.40, 2.87; 21.9, 3.54, 3.29.

[14] A control experiment with 2,6-di-*tert*-butylphenol (5.8×10^{-3} M) also had an intercept less than 1.

N–H Bond Length Determinations and Implications for the Gramicidin Channel Conformation and Dynamics from ^{15}N–^1H Dipolar Interactions

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Received August 10, 1988

An atomic resolution structure of the transmembrane channel gramicidin A is still undetermined. This pentadecapeptide dimerizes to form monovalent cation selective channels in lipid bilayers and biological membranes and has been the subject of extensive study over the past two decades. Although two crystal structures of dimerized forms of gramicidin A have been recently reported,[1,2] these crystals do not contain lipid and are double-stranded dimers rather than the N-terminal-to-N-terminal single-stranded dimer generally believed to be the channel form. In this report a direct approach for determining structure that avoids the need for crystallization is utilized, and atomic resolution solid-state NMR data of the channel state is presented. It has been shown previously that observations of dipolar interactions of uniformly aligned samples can be interpreted to determine not only the orientation of specific bonds[3,4] but also the orientation of peptide linkage planes in the molecule with respect to a unique axis.[5] Such orientational data can be used to determine three-dimensional structures with atomic resolution[6,7] in a manner analogous to the use of distance constraints in solution NMR and diffraction techniques.

Recent solid-state NMR spectra of gramicidin provide considerable evidence that either the backbone structure or dynamics is variable along the length of the channel,[8-11] although one recent

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