Table I. Spectra of $(C_5H_5)_2M(H)(L)$ Compounds

Compound	Infrared ν_{M-H}	Infrared ν_{CO}	Nmr τ_{M-H}	Nmr J_{P-H}, Hz
$(C_5H_5)_2Nb(H)(CO$	1695	1900	16.39	
$(C_5H_5)_2Ta(H)(CO)$	1750	1885	16.80	
$(C_5H_5)_2Nb(H)(PMe_3)$	1635		17.84	27
$(C_5H_5)_2Nb(H)(PEt_3)$	1650		17.69	29
$(C_5H_5)_2Ta(H)(PEt_3)$	1705		19.54	21
$(C_5H_5)_2Nb(H)(C_2H_4)$	1735		12.95	

a pattern typical of the π-crotyl group. The position of the methyl group in X is syn with respect to the hydrogen on the central atom of the allylic system. The structure of X is thus like that of IX[11,12] and of 1,2-dimethylallyldicyclopentadienyltitanium.[13]

The original expectation that $(C_5H_5)_2NbH_3$, like $(C_5H_5)_2TaH_3$, would catalyze H–D exchange between H_2 and C_6D_6 has been realized. However, the two catalysts produce grossly different relative exchange rates with substituted benzenes.[14] These results will be reported in detail soon.

Acknowledgment. We are indebted to L. J. Guggenberger for initial and continuing crystallographic studies of the niobium dimer.

---

(12) H. J. DeLiefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, 4, 651 (1970).

(13) R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Recl. Trav. Chim. Pays-Bas*, 86, 1263 (1967).

(14) U. Klabunde, manuscript in preparation.

(15) Contribution No. 1809.

F. N. Tebbe, G. W. Parshall*
Central Research Department,[15] Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received April 26, 1971

Chemistry of Singlet Oxygen. XIV. A Reactive Intermediate in Sulfide Photooxidation[1]

Sir:

Dialkyl sulfides undergo sensitized photooxidation to give sulfoxides in a smooth reaction with overall stoichiometry[2,3]

$$2R_2S + O_2 \xrightarrow[\text{sens}]{h\nu} 2R_2\overset{+}{S}\text{—}\overset{-}{O}$$

We have previously reported that the reaction involves singlet oxygen (since it is competitively inhibited by singlet oxygen acceptors and quenchers), and that the reaction proceeds efficiently in methanol but very inefficiently in benzene.[3] In benzene, kinetic analysis shows that over 95% of the reactions of singlet oxygen with diethyl sulfide result in quenching, and only a few per cent lead to sulfoxide.[3] No quenching occurs in methanol. An attractive formulation for the reaction involves the intermediacy of an oxidizing species, which might be the zwitterion ("persulfoxide") **1**,[3,4] the diradical **2**,[2] or, possibly the cyclic peroxide **3**.

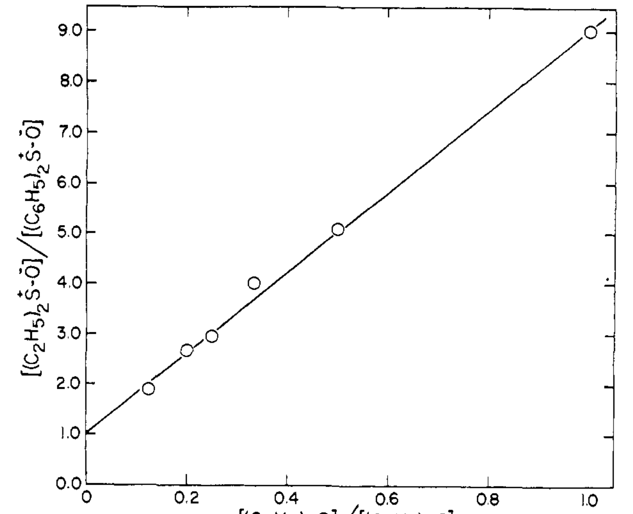
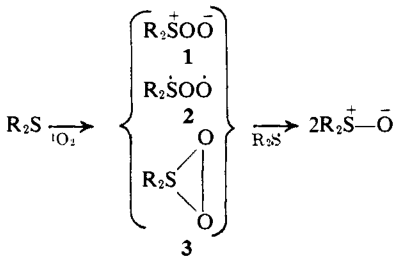
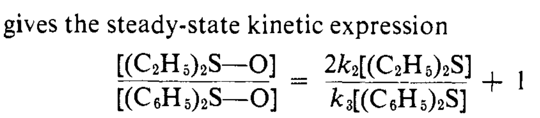


Figure 1. Photooxidation (methanol, rose bengal, 25°) of mixtures of diphenyl and diethyl sulfides: slope = 7.98 ± 0.38; intercept = 1.09 ± 0.17.

We wish to report experimental verification of an unstable reactive intermediate and tentatively assign it the persulfoxide structure **1**. The evidence for the intermediate is of three types.



1. Trapping. Diphenyl sulfide is virtually inert to photooxidation, producing diphenyl sulfoxide at a rate 2800 times slower than diethyl sulfide reacts to form diethyl sulfoxide under similar conditions (in methanol).[5] However, when mixtures of diphenyl and diethyl sulfides are irradiated, considerable amounts of diphenyl sulfoxide are formed. For instance, a solution of 0.02 *M* $(C_2H_5)_2S$ and 0.1 *M* $(C_6H_5)_2S$ in methanol (8×10^{-5} *M* in rose bengal) was irradiated for 1.25 min to produce a solution containing 3.64×10^{-3} *M* $(C_2H_5)_2S^+\text{–}O^-$ and 1.40×10^{-3} *M* $(C_6H_5)_2S^+\text{–}O^-$, a ratio of 2.6:1. The reaction scheme



gives the steady-state kinetic expression

$$\frac{[(C_2H_5)_2S\text{—}O]}{[(C_6H_5)_2S\text{—}O]} = \frac{2k_2[(C_2H_5)_2S]}{k_3[(C_6H_5)_2S]} + 1$$

Figure 1 is a plot of the kinetic data at 25°, which are well fit by this expression with $k_2/k_3 = 4.0$. The relative reactivities are the same at −78°. Thus the reactive intermediate is 700 times less selective toward the two sulfides than is singlet oxygen.

2. Intramolecular Reaction. 1,4-Dithiane, like di-

---

(1) Paper XIII: C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, in press. Supported by National Science Foundation Grants GP-8293 and GP-25,790.

(2) C. H. Krauch, D. Hess, and G. O. Schenck, unpublished; quoted by K. Gollnick, *Advan. Photochem.*, 6, 1 (1968).

(3) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, 171, 139 (1970).

(4) Also discussed as a possible intermediate in thiophene photooxidation: H. H. Wasserman and W. Strehlow, *Tetrahedron Lett.*, 795 (1970); G. N. Skold and R. H. Schlessinger, *ibid.*, 791 (1970).

(5) Product amounts were determined gas chromatographically using an internal standard and a detector calibrated by weighed amounts of knowns. Rose bengal was used as sensitizer in methanol and acetonitrile and zinc tetraphenylporphine in ether and benzene.

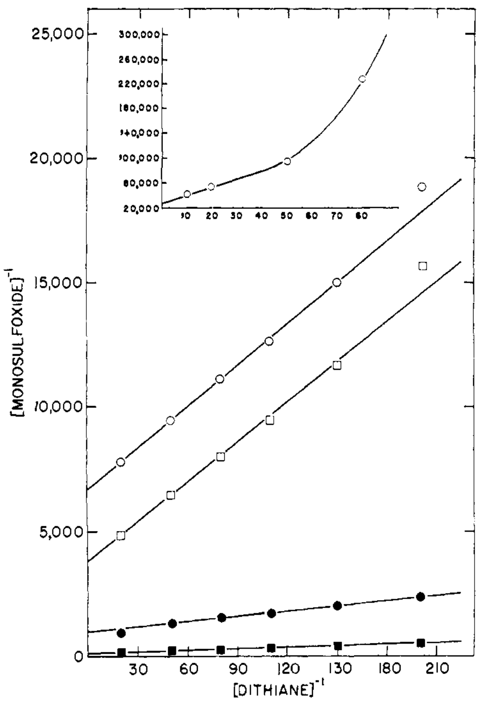
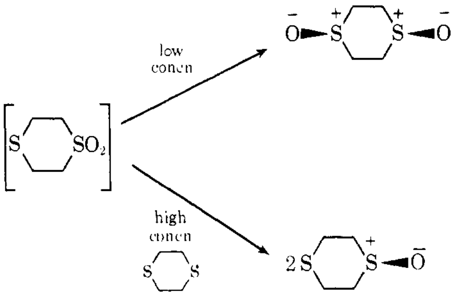
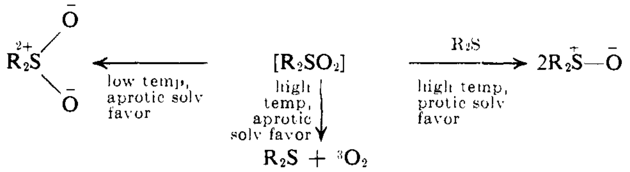


Figure 2. Kinetic behavior of 1,4-dithiane in acetonitrile with varying amounts of water: inset, dry; ○, 10^{-2} *M*; □, 10^{-1} *M*; ●, 1 *M*; ■, 10 *M*.

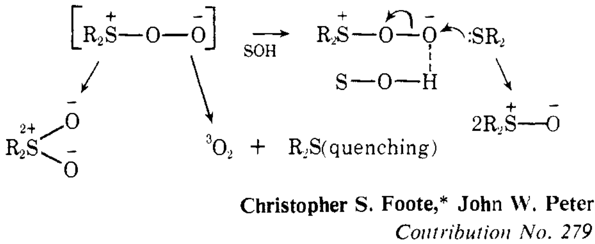
ethyl sulfide, reacts efficiently to give the monosulfoxide in methanol when the reaction is carried to partial conversion. In benzene, the reaction is far less efficient; at concentrations over 10^{-2} *M*, the product at low conversions is the monosulfoxide, but at lower concentrations the principal product becomes the cis disulfoxide; none of the trans isomer is produced.[6,7] Thus the intermediate is trapped intramolecularly when the intermolecular reaction becomes inefficient. Other 1,2- and 1,3-disulfides show similar behavior.



At low temperature or at very low concentration, sulfides give appreciable amounts of sulfone along with sulfoxide. (The sulfoxides are not oxidized to sulfone under the conditions.) In methanol at −78°, at 20% conversion, 0.1 *M* diethyl sulfide gives 93% sulfoxide and 7% sulfone (the amounts are >99 and <1%, respectively, at 25° under the conditions). In dry diethyl ether, 0.02 *M* diethyl sulfide gives equal amounts of sulfoxide and sulfone at −78° (25% conversion in 2 min) but at 25° gives 98% sulfoxide and only 2% sulfone; the reaction is only 5% complete in 2 min under the same conditions. Thus *the reaction is considerably more efficient at low temperature* in ether than at room temperature, and sulfone is a major product. However, even at room temperature in methanol, at low enough concentrations, sulfone becomes the major product: at 10^{-3} *M* diethyl sulfide, equal amounts of sulfone and sulfoxide are produced. Very similar effects are observed with 1,4-dithiane: at −78° in diethyl ether (0.02 *M*), the monosulfone (mp 202.5–203.5° (lit.[7] 203°); ir 1120, 1150, 1285, 1325 cm^{-1}) was produced along with monosulfoxide (1:4, total 20% reaction in 2 min); at room temperature under these conditions no reaction occurred in 20 min; addition of 2% CH_3OH to the solution caused 5% reaction in 2 min; the sole product was monosulfoxide. Low temperatures or aprotic solvents appear to retard intermolecular reaction of the intermediate and favor rearrangement to sulfone. Low temperatures also appear to prevent quenching of singlet oxygen in ether. (The overall rate of oxygen uptake at −78° in ether is comparable to that in methanol, which is the same at −78° and 25°.) These observations are interpreted by the following scheme.



3. Solvent Effect. As mentioned above, the photooxidation is very inefficient in ether and benzene at room temperature. Both diethyl sulfide and 1,4-dithiane are also oxidized only very slowly in dry acetonitrile; addition of only small amounts of water markedly increases the efficiency of the reaction. The amount of singlet oxygen quenching by 1,4-dithiane is decreased by a factor of 4.0 by the addition of 10^{-2} *M* H_2O. The behavior of 1,4-dithiane is shown in the plot of Figure 2; the curvature of the plot in dry acetonitrile is due to the formation of monosulfone and cis disulfoxide at low dithiane concentrations. In all cases, the effect of protic solvents is to favor intermolecular reaction, and is best explained if the intermediate has persulfoxide structure **1**. Protic solvent may act by decreasing the negative charge density on oxygen by hydrogen bonding, thus promoting nucleophilic attack by the second sulfide. In aprotic solvents, intermolecular reaction is less efficient and the intermediate either decomposes, giving ground-state oxygen (favored at room temperature), or rearranges to sulfone (at low temperatures). The evidence does not rule out the possibility that quenching is an entirely separate pathway such as an electron-transfer process.



Christopher S. Foote,* John W. Peters
Contribution No. 2797
Department of Chemistry, University of California
Los Angeles, California 90024

Received March 25, 1971

---

[6] Similar observations have been made by Dr. C. H. Krauch (private communication). Other products accompany the disulfoxide.

[7] Authentic samples were prepared by the method of E. V. Bell and G. M. Bennett, *J. Amer. Chem. Soc.*, **49**, 1798 (1927); **50**, 86 (1928).