ORGANIC LETTERS

2001
Vol. 3, No. 23
3719−3722

Reaction of Arylphosphines with Singlet Oxygen: Intra- vs Intermolecular Oxidation

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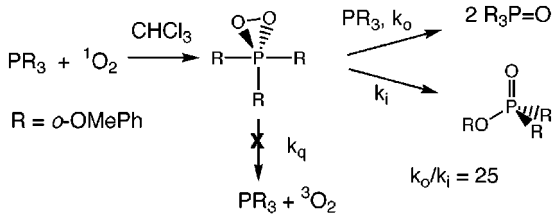
Received August 29, 2001

ABSTRACT



The chemistry of singlet oxygen with all three isomers of tris(methoxyphenyl)phosphine has been studied. For the severely hindered ortho isomer, intramolecular rearrangement to form phenyl diphenyl phosphinate is preferred to formation of phosphine oxide at low concentration in aprotic solvents. In protic solvents, no intramolecular reactivity is observed. A detailed kinetic analyses has been undertaken. There is no physical quenching, regardless of solvent. Mechanistic implications of these findings are discussed.

The affinity of trivalent phosphorus for oxygen is well-known, and the oxidation of phosphines is one of the best known reactions in all of chemistry. The mechanism of autoxidation of phosphines with triplet dioxygen was studied a long time ago.[1] However, there have been remarkably few investigations concerning the reactivity of phosphines with singlet oxygen, which is in stark contrast with the reaction of singlet oxygen with organic sulfides. Trapping studies by Sawaki et al.[2] indicate that the primary intermediate in the photooxidation of triphenylphosphines and tributyl phosphite is electrophilic, in contrast with the nucleophilic behavior of the persulfoxide intermediate in the photooxidation of organic sulfides. Ab initio calculations by Foote, Houk, and co-workers[3] suggest a cyclic phosphadioxirane intermediate which would indeed be expected to behave as an electrophile. No reactions of arylphosphines and singlet oxygen have been studied to date, even though such phosphines are widely used as ligands in organometallic chemistry. Chemical properties of arylphosphines are influenced by the steric bulk of the aryl groups, and the cone angle of a phosphine ligand has long been used as a measure of its bulk.[4] This cone angle is obtained by taking a space-filling model of the MP(R_3) group. The metal is the apex of the cone, and the entire ligand forms the actual cone.[4,5] We reasoned that it would be particularly interesting to study the photooxidation of arylphosphines whose metal complexes have very large cone angles (>180°). For such phosphines, the primary intermediate in the reaction with singlet oxygen—presumably the phosphadioxirane—would be expected to have a much longer lifetime than that of phosphines with small cone angles, as the approach of a second phosphine molecule to react with the intermediate would be severely hindered. This might lead to intramolecular reactivity of the intermediate[2] or even loss of the dioxygen molecule and re-formation of the starting phosphine. The latter pathway would amount to indirect

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(1) Buckler, S. A. *J. Am. Chem. Soc.* **1962**, *84*, 3093−3097.
(2) Tsuji, S.; Kondo, M.; Ishiguro, K.; Sawaki, Y. *J. Org. Chem.* **1993**, *58*, 5055−5058.
(3) Nahm, K.; Li, Y.; Evanseck, J. D.; Houk, K.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 4879−4884.
(4) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(5) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons: New York, 1988; pp 72−74.

10.1021/ol010195v CCC: $20.00
Published on Web 10/20/2001

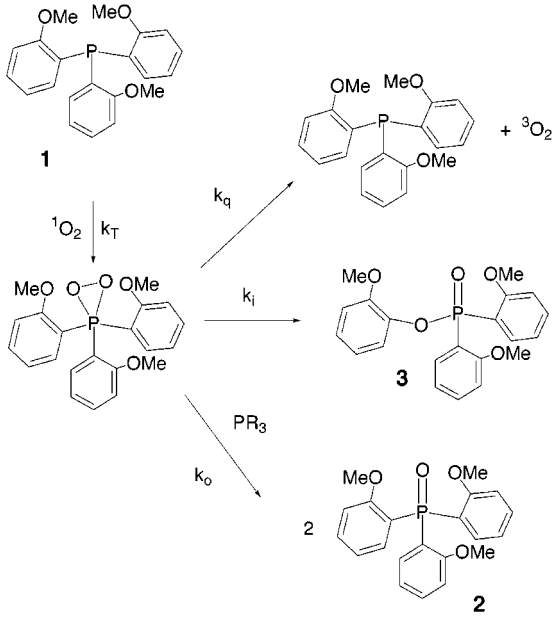
physical quenching of singlet oxygen.[6] Except for triphenylphosphine and several trialkyl phosphites,[7] no kinetic data are known for reactions of phosphines with singlet oxygen, and the possibility of physical quenching has never been examined. We have therefore conducted detailed product and kinetic studies of the reaction of the ortho, meta, and para isomers of tris(orthomethoxyphenyl)phosphine with singlet oxygen. The ortho-isomer has a particularly large cone angle of 205°.[8] All of these arylphosphines are unreactive with triplet oxygen, thus allowing kinetic investigations of their reactions with singlet oxygen.

Photooxidation of tris(orthomethoxyphenyl)phosphine (**1**) in aprotic solvents leads to a mixture of the corresponding phosphine oxide (**2**) and the orthomethoxyphenyl di(orthomethoxyphenyl) phosphinate (**3**).[9] The product distribution depends on the concentration of the starting phosphine **1**: The higher the starting concentration, the larger the ratio of compound **2**/**3**. When [**1**] > 0.5 M, more than 90% of the total product is the phosphine oxide **2**; conversely, when [**1**] < 0.003 M, phosphinate **3** is more than 90% of the total product formed.[10] In contrast, in protic solvents or solvent mixtures, only phosphine oxide **2** is obtained, regardless of the concentration of **1**. A large excess of protons relative to the starting compound **1** is required to completely suppress formation of the phosphinate **2**. 2-Propanol also suppresses formation of the insertion product but is less efficient than MeOH. For example, in the absence of any protic solvent, photooxidation of a 0.013 M solution of **1** in $CHCl_3$ leads to equal amounts of products **2** and **3** (at 40% conversion of **1**). In contrast, treatment of the same solution of **1** with 2 M MeOH results only in formation of phosphine oxide **2** (again, at 40% conversion of **1**). Conversely, addition of 2 M 2-propanol instead of MeOH results in about 90% formation of **2** and ca. 10% of **3** under otherwise identical conditions.

The other two isomers, tris(metamethoxyphenyl)phosphine (**4**) and para(methoxyphenylphosphine) (**5**), show very different behavior: only the corresponding phosphine oxides are obtained upon reaction with singlet dioxygen, regardless of their concentrations or the nature of the solvent.

Kinetic Studies. Scheme 1 shows the different reaction pathways of the possible peroxidic intermediate. The peroxidic intermediate must be formed upon reaction of a phosphine with singlet dioxygen, as a primary product. In

Scheme 1. Photooxidation of Tris(*o*-methoxyphenyl)phosphine (**1**) and Different Reactivity Pathways for the Peroxidic Intermediate in This Reaction



aprotic solvents, this intermediate may undergo three different reactions: intermolecular oxygen atom transfer to another phosphine molecule; intramolecular rearrangement, leading to the phosphinate observed for the photooxidation of **1**, and loss of dioxygen and regeneration of the starting phosphine (indirect physical quenching). If Scheme 1 holds, the ratio of phosphine oxide **2** vs insertion product **3** should be proportional to the starting phosphine concentration (at low conversion), regardless of whether physical quenching occurs. Using the steady-state approach leads to eq 1:

$$[\mathbf{2}]/[\mathbf{3}] = (2k_o[\mathbf{1}])/k_i \qquad (1)$$

Plots of [**2**]/[**3**] are indeed linear (Figure 1), with a slope of 50 ± 6 in $CHCl_3$. Thus the rate ratio of intermolecular vs intramolecular oxidation k_{ox}/k_i is 25 ± 3.

The total rate constant of singlet oxygen removal by **1** (k_T) has been measured by luminescence quenching experiments in a variety of solvents (Figure 2).[11] The values are considerably smaller than those of arylphosphines without the ortho substituents (see Table 1).

In the absence of direct physical quenching, the value of k_T is the rate of formation of the peroxidic intermediate. To determine whether all of the intermediate leads to formation of either product **2** or **3** or whether loss of dioxygen from the intermediate (indirect physical quenching) is a major process, competition experiments have been carried out. 9,10-Dimethylanthracene (DMA) was used as a singlet oxygen

(6) We use the term *indirect* physical quenching to describe deactivation of singlet oxygen via formation of an unstable intermediate which then loses a dioxygen molecule. *Direct* physical quenching refers to physical deactivation without formation of any unstable adduct. This terminology has been used for the reaction of singlet oxygen with organic sulfides. Foote, C. S.; Peters, J. W. *IUPAC Congr., 23rd, Spec. Lec.* **1971**, *4*, 129.

(7) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 909.

(8) Hirsivaara, L.; Guerricabeitia, L.; Haukka, M.; Suomalainen, P.; Laitinen, R. H.; Pakkanen, T. A.; Pursiainen, J. *Inorg. Chim. Acta* **2000**, *307*, 47. Ab initio calculations by these authors indicate that smaller cone angles which would make the phosphorous atom more exposed to intermolecular attack correspond to higher energy conformers. Several X-ray strucures described in this paper of Cr and W complexes containing the ortho isomer do not indicate any unusual flattening of the phosphine ligand.

(9) Sawaki et al. observed trace amounts of a similar insertion product, phenyl diphenyl phosinate, during the photooxidation of triphenylphosphine.[2]

(10) Sawaki et al. also noted that for triphenylphosphine a decrease in the starting concentration leads to in increase in the amount of insertion product. However, the maximum yield of insertion product that was obtained from triphenylphosphine was only 1.2%. See ref 2.

(11) Time-resolved singlet oxygen luminescence quenching experiments are conducted by exciting a solution containing the sensitizer and varying amounts of substrate (quencher) with a short (a few ns) laser pulse and monitoring the singlet oxygen decay at right angle.

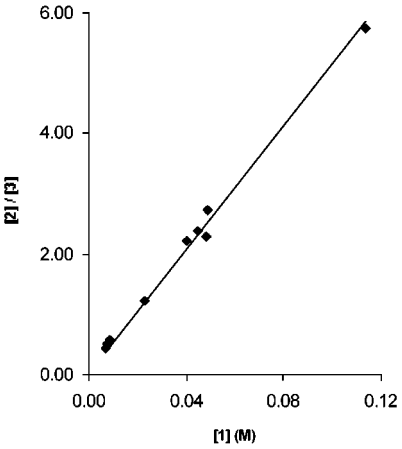


Figure 1. Plot of product distribution for the photooxidation of **1** vs starting concentration of **1**.

acceptor in these experiments. DMA is known to interact with singlet oxygen by chemical reaction only, and we have remeasured its reaction rates with singlet oxygen to be 2.5 $\pm$ 0.1 $\times$ 10^7 M^{-1} s^{-1} in $CHCl_3$, 2.9 $\pm$ 0.2 $\times$ 10^7 M^{-1} s^{-1} in benzene, and 4.7 $\pm$ 0.6 $\times$ 10^7 M^{-1} s^{-1} in 75% CH_2Cl_2/25% MeOH, in excellent agreement with the literature.[12] Loss of DMA and compound **1** was monitored by NMR, and conversion of **1** was kept at 20% or less. Relative reaction rates were obtained from the equation of Higgins et al.[13,14]

$$\frac{\log\{[\mathbf{1}]^f/[\mathbf{1}]^0]}{\log\{[\mathrm{DMA}]^f/[\mathrm{DMA}]^0\}} = \frac{k_r(\mathbf{1})}{k_r(\mathrm{DMA})} \qquad (2)$$

The relative reaction rate k_r thus obtained is related to the rates of insertion product formation (k_i), phosphine oxide formation (k_o), and indirect physical quenching (k_q) as follows (at low conversion of **1**):

$$k_r = \frac{k_T(2k_o[\mathbf{1}] + k_i)}{k_q + k_i + k_o[\mathbf{1}]} \qquad (3)$$

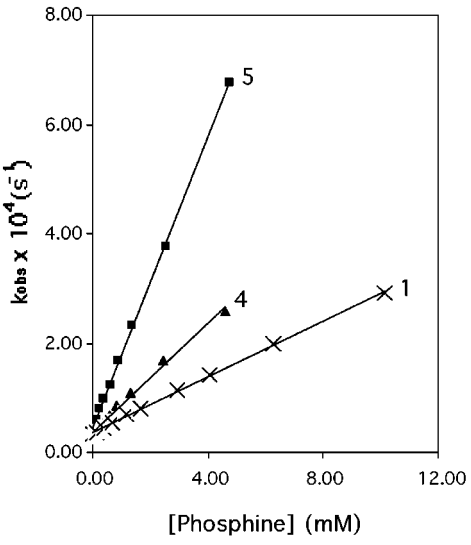


Figure 2. Singlet oxygen luminescence quenching by phosphines **1**, **4**, and **5**.

Table 1. Kinetic Parameters for the Reaction of Arylphosphines with Singlet Oxygen

	k_T (M^{-1} s^{-1} $\times$ 10^{-6})[a]			k_o/k_i
compound	in $CHCl_3$	in C_6H_6	in CH_2Cl_2/MeOH	in $CHCl_3$
tris(*o*-methoxyphenyl)-phosphine (**1**)	2.8 $\pm$ 0.4	5.0 $\pm$ 0.2	3.1 $\pm$ 0.2	25 $\pm$ 3
tris(*m*-methoxyphenyl)-phosphine (**4**)	5.3 $\pm$ 0.5	9.2 $\pm$ 0.3	6.4 $\pm$ 0.2	
tris(*p*-methoxyphenyl)-phosphine (**5**)	14.9 $\pm$ 1.6	33.1 $\pm$ 4.3	27.4 $\pm$ 3.9	

[a] Average of four experiments; error is 1 standard deviation.

Equation 3 can be used to determine whether there is significant physical quenching at various concentrations of **1**: if $k_q = 0$, then the ratio $k_r/k_T = 1$ at very low concentrations of **1** where formation of phospine oxide **2** is insignificant. The ratio k_r/k_T will rise to a value of two at high concentration of **1** where formation of the insertion product **3** is insignificant. Competition experiments were carried out at various starting concentrations of [**1**] in $CDCl_3$, and a plot of the ratios k_r/k_T against the corresponding starting concentrations of **1** is shown in Figure 3. Comparison with the curve that is predicted by eq 3 if $k_q = 0$ (based on a k_o/k_i ratio of 25) shows that within limits of error there is no significant physical quenching regardless of the phosphine concentration employed.[15] Thus, loss of dioxygen from the peroxidic intermediate is not a significant process. Competition experiments carried out under protic conditions (75% CD_2Cl_2/25% CD_3OD) resulted in values of k_r twice the rate of k_T (data not shown), demonstrating that there is no physical quenching under protic conditions. Kinetic parameters for the reaction of compound **1** with singlet oxygen are summarized in Table 1.

Kinetic parameters for meta and para isomers **4** and **5** have also been obtained. These values are summarized in Table 1. The values for singlet oxygen removal (k_T) are considerably larger than those for **1**, undoubtedly because of the smaller steric bulk of these molecules. In all cases the relative

(12) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663, and references therein.

(13) Control experiments demonstrated that within 60 min no oxidation (within 1%) of the phosphines by the 9,10-dimethylanthracene endoperoxide product occurs. Since the irradiation times during the competition experiments were only 5−15 min, oxidation of the phosphine by DMA endoperoxide did not interfere with the kinetic measurements. Compounds **2** and **3** are oxidized substantially over longer time periods by DMA endoperoxide (20% during 36 h) while compound **1** is unreactive with DMA endoperixe even over a 36 h time period, probably because of its steric bulk.

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

(15) This also rules out direct physical quenching prior to formation of the peroxidic intermediate.

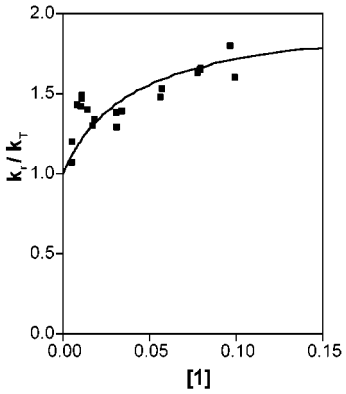
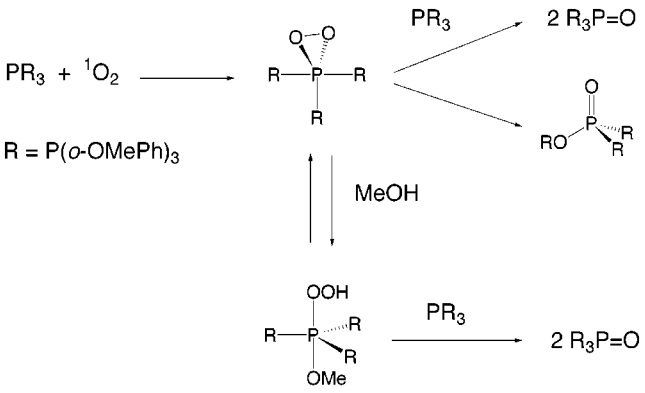


Figure 3. Plot of the rate ratio k_r/k_T vs concentration of phosphine **1**. The solid line represents the curve predicted from eq 3 if $k_q = 0$ and $k_o/k_i = 25$. The data points are based on the k_r values obtained from the competition experiments at different starting concentrations of **1**.

reaction rates obtained from competition experiments with DMA are twice the values of k_T, indicating that there is no physical quenching. In dramatic contrast with the reaction of organic sulfides with singlet oxygen,[16] there is very little variation of these numbers with solvent.

The reactivity patterns of compound **1** in protic and aprotic solvents and the kinetic results are consistent with the mechanism outlined in Scheme 2. The observation that protic

Scheme 2. Reactivity of Compound **1** with Singlet Oxygen under Protic and Aprotic Conditions



solvents inhibit formation of the insertion product **3** indicates that under protic conditions protonation of the phosphadioxirane to a hydroperoxy species is taking place.

Foote, Houk, and co-workers[3] have performed ab initio calculations for the protonation of the phosphdioxirane formed by reaction of PH_3 with $^1O_2$. They have found that the pentacoordinate species formed by reaction of the phosphadioxirane with water does indeed have an energy minimum that is considerably lower (by 29.6 kcal/mol at the RHF STO-G(*) level and by 19.9 kcal/mol at the RHF 6-31G* level)[3] than that calculated for the corresponding phosphadioxirane. However, thus far, there has been no experimental evidence for this reaction pathway. The inhibition of intramolecular oxidation observed during the photooxidation of **1** under protic conditions demonstrates that addition of protons and an alkoxide anion does indeed lead to a change in mechanism during the photooxidation of phosphines and that a hydroperoxy phosphorane may be the second intermediate under such conditions. Formation of a pentacoordinate species is supported by the observation that the bulkier 2-propanol is much less efficient in suppressing formation of product **3** than MeOH. Protonation of the phosphadioxirane may be reversible, as a large excess of protons is required to completely suppress formation of the insertion product. This result is in contrast with the observation by Sawaki et al. that addition of 10% MeOH does not affect trapping of the intermediate in the photooxidation of tri-*n*-butyl phosphite.[2] The intermediate in the photooxidation of the phosphite may be much less susceptible to protonation due to an electronic effect, i.e., because of the more electron-poor character of the phosphite.

While an extensive amount of kinetic data has been gathered for the reaction of singlet oxygen with organic sulfides, this paper represents the first detailed kinetic study of the reaction of $^1O_2$ with phosphines. In contrast to organic sulfides, protic solvents only slightly accelerate the reaction rate of phosphines with singlet oxygen, but they do lead to a different product distribution (see above). Furthermore, there is no significant amount of physical quenching of singlet oxygen; instead of losing dioxygen, the peroxidic intermediate undergoes intramolecular rearrangement when intermolecular reactions are severely hindered. These results, together with the trapping experiments by Sawaki et al.[2] that demonstrated the electrophilic nature of the peroxidic intermediate in the photooxidation of phosphines, lend strong support to the formulation of this intermediate as a cyclic phosphadioxirane. The absence of physical quenching and the intramolecular rearrangement of the phosphadioxirane derived from the ortho-substituted arylphosphine **1** suggests that such phosphadioxiranes may have a lifetime sufficiently long enough to be detected at very low temperatures or by transient absorption spectroscopy. Experiments in this direction are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support by the Camille and Henry Dreyfus Foundation (Award number SU-98-021) and the NIH-NIGMS MBRS program (Award number GM 08101) is also gratefully acknowledged.

Supporting Information Available: Detailed kinetic analyses of the reaction of compound **1** with singlet oxygen, including derivation of eqs 1 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

OL010195V

(16) (a) Jensen, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* **1998**, *120*, 4439. (b) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S *J. Am. Chem. Soc.* **1983**, *105*, 4717. (c) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949.