Evidence for a Duality of Mechanism in the Oxidation Reactions of Triphenyl Phosphite Ozonide

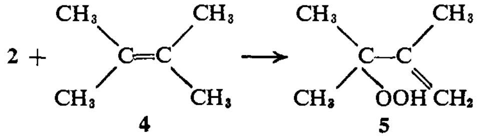
Sir:

The triphenyl phosphite ozonide (**2**) of Thompson,[1] formed at −78° by eq 1, has been shown[2] upon decomposition at −15° (eq 2) to yield singlet oxygen, which rapidly undergoes peroxide-forming conjugate addition to dienes and anthracenes, and an ene-type reaction to yield hydroperoxides from olefins with allylic hydrogens.[3]

$$\underset{\mathbf{1}}{(C_6H_5O)_3P} + O_3 \xrightarrow{-78^\circ} \underset{\mathbf{2}}{(C_6H_5O)_3PO_3} \qquad (1)$$

$$\mathbf{2} \xrightarrow{-15^\circ} \underset{\mathbf{3}}{(C_6H_5O)_3PO} + {}^1O_2 \qquad (2)$$

The reaction with tetramethylethylene (**4**) to yield the hydroperoxide **5** at low temperatures (eq 3) has been



(3)

regarded as quite characteristic of singlet oxygen. However, we have observed that this hydroperoxide, unlike the transannular peroxides from substituted anthracenes or dienes, can be produced directly from triphenyl phosphite ozonide (**2**)[4] at temperatures far below those at which **2** yields free oxygen at an appreciable rate. At −60° the nmr signal of **4** at δ 1.6 gave way to the spectrum of **5** (δ 1.2, singlet, 6 H; δ 1.7, poorly resolved doublet, 3 H; δ 4.8, multiplet, 2 H). A solution 0.20 *M* in both **2** and **4** in methylene chloride was prepared in an nmr tube below −70° and warmed to −70°; the disappearance of the signal at δ 1.6 was followed for 90 min. The results are shown in Figure 1. The reaction is 85% complete in this time, and the hydroperoxide **5** could be isolated in 81% yield on distillation. The ozonide itself, in the absence of tetramethylethylene, is less than 1% decomposed under the same conditions. Its half-life at this temperature in chlorobenzene, obtained by an extrapolation of an Arrhenius plot, is over 1 year.

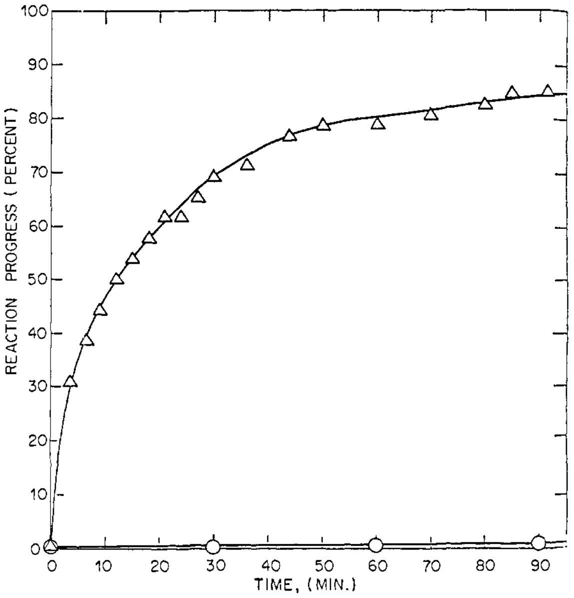


Figure 1. Reaction of triphenyl phosphite ozonide with tetramethylethylene (−70°, methylene chloride): △, consumption of TME; ○, oxygen evolution from ozonide in absence of TME.

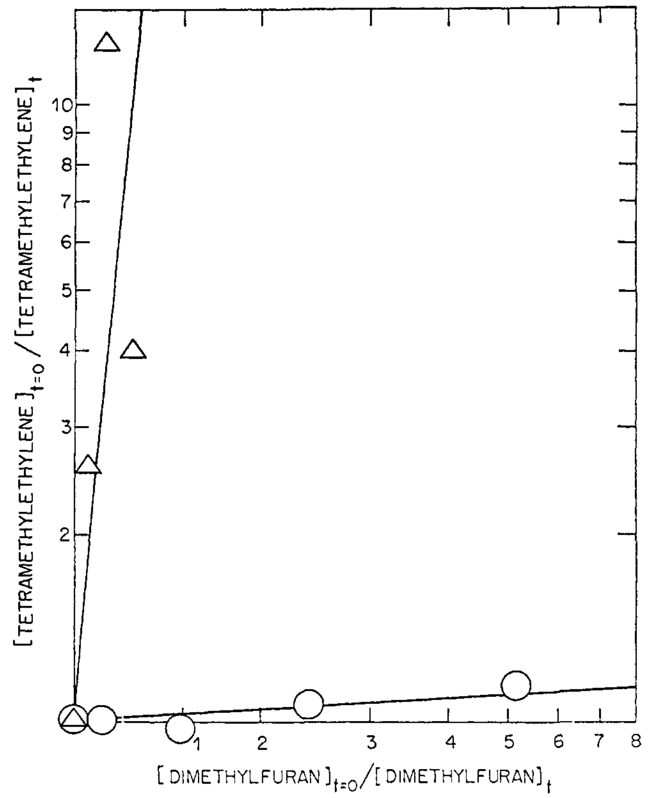


Figure 2. Competition study of 2,5-dimethylfuran *vs.* tetramethylethylene (−78°, methylene chloride): △, triphenyl phosphite ozonide; ○, photooxidation, methylene blue sensitizer.

This result might be consistent with formation of the hydroperoxide **5** exclusively by way of free singlet oxygen only under one condition: that the dissociation of **2** be rapid and reversible.[5] In such a case oxygen would bubble off only when its equilibrium concentration exceeded its solubility, but it could be consumed at lower temperatures by a rate-determining reaction with **4**. In such a case two different acceptors of singlet oxygen would always show the same competitive reactivity ratio toward **2** as toward singlet oxygen generated in any other way. In such a case the unique ability of **4** to react at low temperatures would mean that **4** was much more reactive toward free singlet oxygen than any diene or substituted anthracene investigated. We have ruled out this explanation on two counts.

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(1) Q. E. Thompson, *J. Amer. Chem. Soc.*, **83**, 845 (1961).

(2) (a) R. W. Murray and M. L. Kaplan, *ibid.*, 90, 537 (1968); (b) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *ibid.*, 90, 4160 (1968).

(3) C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

(4) **2** was prepared by the slow addition of triphenyl phosphite to methylene chloride at −78° continuously saturated with a stream of ozone. This procedure avoids secondary reactions between **1** and **2** and maximizes the yield.

(5) A referee has suggested a second way in which free singlet oxygen might intervene: that **4** catalyzes the decomposition of **2** and then, being present in the same solvent cage with the oxygen, competes for it despite the greater reactivity of **6** in the competition experiments. For this to occur, the reaction of $^1O_2$ and **4** would have to be in the range of diffusion-controlled rates, ~10^9 l./mol sec, and that of $^1O_2$ with **6** even faster.

First, the dissociation of **2** to singlet oxygen and triphenyl phosphate is not reversible. At −78° no **2** was formed on a 3-hr irradiation of a mixture of triphenyl phosphate, rose bengal, and oxygen in methylene chloride–methanol with a 500-W incandescent lamp. The absence of **2** was established by the sensitive test of warming slowly with 0.20 equiv of rubrene. The rubrene color remained unchanged, and thin layer chromatography showed no transannular peroxide. Under the same conditions **2**, prepared from triphenyl phosphite and ozone, reacted completely with rubrene on warming.

Second, competitive reactions in methylene chloride at −78° between tetramethylethylene and 2,5-dimethylfuran (**6**) show that the former is far more reactive toward **2**, but the latter is much the stronger competitor under conditions of photosensitization where the evidence strongly favors free singlet oxygen as the reagent.[3,6–8] At −78° methylene blue photooxidation (lower curve of Figure 2) shows a ratio k_4/k_6 of 0.090 ± 0.017,[9] whereas in thermal reaction with **2**, k_4/k_6 is of the order of 10 (upper curve of Figure 2).

Sensitized oxidation of **6** alone gave a solution with a simple nmr spectrum consistent with the 2,5-endoperoxide (singlets at δ 1.7 and 6.3). Triphenylphosphine yielded 3-hexene-2,5-dione, isolated as its bis-2,4-dinitrophenylhydrazone, mp 287.5–289° (lit.[10] 289.0–289.5°), in 61% yield. The nmr spectrum of the reaction product from **2** and **6** showed more complex, unresolved signals indicative of a mixture of products, and the bis-DNP was isolated in only 25% yield.

The fact that radical-initiated autoxidation of tetramethylethylene gives exclusively[11] the hydroperoxide **5**, and not the isomeric 2,3-dimethyl-1-hydroperoxy-2-butene, suggests that **2** might be serving in the present case as a chain initiator. However, the inhibitors diphenylamine and 2,6-di-*t*-butylphenol have no effect on the preference of **2** for attacking **4** rather than **6** (Figure 2). Also a reaction between **2** and **4** carried out in the presence of dissolved oxygen gave no greater amount of hydroperoxide than a reaction purged of oxygen by a stream of nitrogen. Thus triphenyl phosphite ozonide donates O_2 at low temperatures by a mechanism which neither involves a chain reaction nor starts one incidentally.

Direct peroxidation by way of free singlet oxygen, though now a widely accepted mechanism for photooxidation, is a relatively recent one. Donation of O_2 by way of a peroxy radical[12] or biradical[13] was proposed many years ago and has not been excluded in any completely general way.

Our present evidence indicates that there is a mechanism of direct O_2 donation from triphenyl phosphite ozonide which yields the same products as free singlet oxygen but has very different selectivities toward different substrates. The Ziegler and Schenck mechanisms both involve the concept of activation of oxygen by the formation of a peroxy radical with an exceptionally weak C–O bond; it has been demonstrated that triphenylmethylperoxy[12] is such a radical.[14] However, unlike the present case, Ziegler's autoxidation catalyzed by the triphenylmethyl radical was a chain reaction with very long chains.[12] Consideration is being given to the possibility of a bimolecular simultaneous donation of two oxygen atoms by **2**; however, any mechanism must take account of the dissymmetry indicated by the fact that the hydroperoxide-forming reactions of singlet oxygen are imitated by the direct process so much more effectively than is the conjugate 1,4 addition.

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[6] C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879, 3880 (1964).

[7] E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

[8] T. Wilson, *ibid.*, **88**, 2898 (1966).

[9] Other determinations of this ratio have been of the order of 0.3: R. Higgins, C. S. Foote, and H. Cheng, Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D. C., 1968, p 102; C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968). These determinations were carried out at room temperature, however.

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[11] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 798 (1967).

[12] K. Ziegler, *Ann.*, **504**, 162 (1933).

[13] G. O. Schenck, *Naturwissenschaften*, **35**, 28 (1948); for reviews see K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

[14] E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Amer. Chem. Soc.*, **89**, 1176 (1967).

Paul D. Bartlett, G. David Mendenhall
Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138

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Triplet Yield Determinations at High Concentrations of *cis*-Piperylene

Sir:

Piperylene has been commonly used in triplet counting experiments.[1,2] Usually a concentration of ~0.1 *M* is sufficient to quench available photoexcited triplets and to determine the triplet yield of an organic molecule. In the course of investigating the triplet yields of molecules as a function of piperylene concentration, it was observed that the isomerization quantum yield increased unexpectedly at high concentrations of piperylene (>1.0 *M*). In order to remove any uncertainties that may arise from the molecular system under study we have reinvestigated the triplet yield of benzophenone determined from the sensitized *cis–trans* isomerization of *cis*-piperylene. The concentration of *cis*-piperylene was varied over the range 0.08–10 *M* and all photolyses were performed at 366 nm. Benzophenone has been commonly used as a standard with a triplet yield of unity.[1] The analysis of our data for concentrations of <1.0 *M* piperylene was satisfactorily described by the following equation[3]

$$1/\Phi' = (1/\phi_{\mathrm{T}})[1 + k_{\mathrm{dt}}/k_{\mathrm{et}}(cis\text{-P})] \qquad (1)$$

where Φ' is the isomerization quantum yield or apparent triplet yield, defined as $\Phi_{c\to t}/f$, $\Phi_{c\to t}$ is the experimentally measured *cis–trans* isomerization yield, $f = 0.55$ is the fraction of triplets which decays to *trans*-piperylene,[1] ϕ_{T} is the triplet yield of the sensitizer, k_{dt} is the rate constant for deactivation of the sensitizer triplet, and k_{et} is the rate constant for triplet–triplet energy transfer between sensitizer and piperylene. When the concentration of *cis*-piperylene was >1.0 *M*, however, the isomerization yield, Φ', increased to values larger than unity. This result suggests that some new process may be occurring. It has been reported that there is no concentration effect on the triplet yield of benzophenone in the concentration range 0.005–0.2 *M* *cis*-piperylene.[1]

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[1] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

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[3] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, 90, 1949 (1968).