plexes but at values that are 45–75 nm lower.

(3) The λ_2 value for **9D**–TCNE (510 nm) is lower than that of **9C**–TCNE (520 nm), indicating the absence of conjugation through the double bonds in **9D**. This conclusion contrasts with that made for **3F**, which shows evidence of conjugation.

Acknowledgment. We are grateful for financial support from the Peter White Fund, the Faculty Research Grant Fund, and the Development Fund of Northern Michigan University. We thank Dr. David W. Kingston, Dr. Philip I. Pavlik, and Dr. Jerome A. Roth for valuable discussions. We are indebted to Dr. Rolf Gleiter, Dr. Peter Bischof, and their colleagues in the Organisch-Chemisches Institut of Heidelberg University for their hospitality and assistance during the preparation of this paper.

Registry No. **1A**·TCNE, 123884-13-9; **1B**·TCNE, 123884-14-0; **1C**·TCNE, 123884-15-1; **1D**·TCNE, 123884-16-2; **1E**·TCNE, 123884-17-3; **2A**·TCNE, 93245-61-5; **2B**·TCNE, 123884-18-4; **2C**·TCNE, 123884-19-5; **2D**·TCNE, 51930-60-0; **2E**·TCNE, 123884-20-8; **2F**·TCNE, 36880-85-0; **2G**·TCNE, 123884-21-9; **2H**·TCNE, 93758-83-9; **2I**·TCNE, 52515-79-4; **2J**·TCNE, 61822-51-3; **2K**·TCNE, 123884-22-0; **2L**·TCNE, 123884-23-1; **3A**·TCNE, 123884-24-2; **3B**·TCNE, 123884-25-3; **3C**·TCNE, 123884-26-4; **3D**·TCNE, 123884-27-5; **3E**·TCNE, 123884-28-6; **3F**·TCNE, 123884-29-7; **3G**·TCNE, 123884-30-0; **4A**·TCNE, 1446-08-8; **4B**·TCNE, 6165-98-6; **5A**·TCNE, 2590-60-5; **5B**·TCNE, 18852-73-8; **5C**·TCNE, 26515-97-9; **5D**·TCNE, 26819-20-5; **5E**·TCNE, 17557-14-1; **5F**·TCNE, 2590-61-6; **5G**·TCNE, 2590-62-7; **5H**·TCNE, 2590-63-8; **5I**·TCNE, 123884-31-1; **5J**·TCNE, 26034-90-2; **5K**·TCNE, 2590-64-9; **5L**·TCNE, 2590-65-0; **5M**·TCNE, 123884-32-2; **5N**·TCNE, 2590-66-1; **5O**·TCNE, 123884-33-3; **5P**·TCNE, 26034-91-3; **5Q**·TCNE, 2590-68-3; **5R**·TCNE, 2590-69-4; **5S**·TCNE, 1223-67-2; **5T**·TCNE, 962-69-6; **5U**·TCNE, 2605-01-8; **5V**·TCNE, 78717-32-5; **5W**·TCNE, 123884-34-4; **5X**·TCNE, 123884-35-5; **6A**·TCNE, 62371-33-9; **6B**·TCNE, 123884-36-6; **6C**·TCNE, 70239-05-3; **6D**·TCNE, 123884-37-7; **6E**·TCNE, 51644-54-3; **6F**·TCNE, 6140-60-9; **6G**·TCNE, 2987-74-8; **6H**·TCnE, 123884-38-8; **7A**·TCNE, 7431-42-7; **7B**·TCNE, 123884-39-9; **7C**·TCNE, 33429-76-4; **7D**·TCNE, 33429-74-2; **7E**·TCNE, 123884-40-2; **7F**·TCnE, 123884-41-3; **7G**·TCNE, 123884-42-4; **7H**·TCNE, 123884-43-5; **7I**·TCNE, 123884-44-6; **7J**·TCNE, 53039-88-6; **7K**·TCNE, 123884-45-7; **7L**·TCNE, 123884-46-8; **7M**·TCNE, 123884-47-9; **7N**·TCNE, 7378-72-5; **7O**·TCNE, 123884-48-0; **7P**·TCNE, 123884-50-4; **7Q**·TCNE, 123884-51-5; **8A**·TCNE, 60977-89-1; **8B**·TCNE, 7371-39-3; **8C**·TCNE, 7371-38-2; **8D**·TCNE, 108461-13-8; **8E**·TCNE, 123884-52-6; **8F**·TCNE, 123884-53-7; **8G**·TCNE, 123884-54-8; **8H**·TCNE, 60977-90-4; **8I**·TCNE, 60977-91-5; **8J**·TCNE, 19255-32-4; **8K**·TCNE, 123884-55-9; **8L**·TCNE, 123884-56-0; **8M**·TCNE, 123884-57-1; **9A**·TCNE, 29578-48-1; **9B**·TCNE, 29578-50-5; **9C**·TCNE, 62371-37-3; **9D**·TCNE, 123884-58-2.

(Diphenylphosphinoyl)oxyl: An Extremely Reactive Oxygen-Centered Radical[1]

H.-G. Korth*,[2]

Institut für Organische Chemie, Universität-GHS Essen, D-4300 Essen, Federal Republic of Germany

J. Lusztyk and K. U. Ingold

Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6

Received April 27, 1989

The title radical, $Ph_2P(O)O^\bullet$, has been generated by laser flash photolysis (LFP) of the peroxide $[Ph_2P(O)O]_2$ (**1**) in CH_3CN solution. It has a broad, structureless absorption extending from 400 to beyond 800 nm. Absolute bimolecular rate constants k for its reactions with various organic substrates have been measured by LFP. It has been found that $Ph_2P(O)O^\bullet$ is more reactive in hydrogen abstraction (e.g., cyclohexane, $k = 2.4 \times 10^8$ M^{-1} s^{-1}) and addition (e.g., benzene, $k = 9.1 \times 10^8$ M^{-1} s^{-1}) than any other organic oxygen-centered radical. Only $HO^\bullet$ is (generally) more reactive. Although $Ph_2P(O)O^\bullet$ could not be directly detected by EPR spectroscopy, it was successfully spin-trapped with a nitrone and with alkenes and alkynes. The formation of $Ph_2P(O)O^\bullet$ in the photodecomposition but not in the thermal decomposition of **1** is supported by ^{31}P NMR analyses of reaction products. Semiempirical AM1–PM3 calculations on $H_2P(O)O^\bullet$ are also reported.

Absolute rate constants for the reactions of several classes of carbonyloxyl radicals, $XC(O)O^\bullet$, with a variety of organic substrates have recently been measured in this laboratory by using the technique of laser flash photolysis (LFP).[3-6] The magnitude of the second-order rate constant for hydrogen atom abstraction and/or addition reactions of $XC(O)O^\bullet$ with a specific substrate generally increased with an increase in the inductive electron-withdrawing effect of the substituent X.[4-7] Differences in the reactivities of different $XC(O)O^\bullet$ were attributed to variations in the relative contribution that polar, canonical structures (e.g., $[XC(O)O^-,RH^{\bullet+}]^\ddagger$) make to the stabilization of the reaction's transition state.[4-6] It therefore seemed possible that oxyl radicals even more reactive than the $XC(O)O^\bullet$ already examined[7] might be derived from oxy acids having greater intrinsic (i.e., gas phase) acidities[8] than the intrinsic acidities of the XC(O)OH acids. An attractive possibility for a preliminary test of this hypothesis was the (diphenylphosphinoyl)oxyl radical, $Ph_2P(O)O^\bullet$,[9] since the

---

[1] Issued as NRCC No. 30772. This paper is dedicated to the memory of the late Professor A. Mangini, University of Bologna, Italy.

[2] NRCC/Summit Postdoctoral Fellow, 1987–1988.

[3] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877–2885.

[4] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886–2893.

[5] Chateauneuf, J.; Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 6727–6731.

[6] Korth, H.-G.; Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 5929–5931.

[7] X = aryl,[4] alkoxy,[5] alkenyl,[6] and alkynyl.[6]

[8] As measured by ΔG for the gas-phase reaction: $HA \rightarrow H^+ + A^-$.

[9] The structure is written as $Ph_2P(O)O^\bullet$ rather than $Ph_2PO_2^\bullet$ in order to distinguish this radical from its (unknown) peroxyl isomer, $Ph_2POO^\bullet$.

0022-3263/90/1955-0624$02.50/0 Published 1990 by the American Chemical Society

Table I. Bimolecular Rate Constants for Reactions of $Ph_2P(O)O^{\bullet}$ and Some Other Oxygen-Centered Radicals with Selected Organic Substrates at 295 ± 2 K

	k, $M^{-1}\ s^{-1}$				
substrate	$Ph_2P(O)O^{\bullet a}$	$PhC(O)O^{\bullet b}$	$n\text{-}C_3H_7OC(O)O^{\bullet c}$	$(CH_3)_3CO^{\bullet d}$	$HO^{\bullet e}$
cyclohexane	$(2.4 \pm 0.6) \times 10^8$	1.4×10^6	1.6×10^7	1.6×10^6	6.1×10^9
triethylsilane	$(1.0 \pm 0.2) \times 10^9$	5.6×10^6	8.9×10^7	5.4×10^6	
benzene	$(9.1 \pm 1.8) \times 10^8$	7.8×10^7	7.4×10^6		7.8×10^9
1,4-cyclohexadiene	$(4.3 \pm 0.4) \times 10^9$	$6.6 \times 10^{7\,b}$	$9.9 \times 10^{8\,f}$	5.4×10^7	7.7×10^9
1,1-diphenylethene	$(4.2 \pm 1.0) \times 10^9$	$3.0 \times 10^{8\,f}$	$1.3 \times 10^{9\,f}$		
chloroform	$(3.8 \pm 1.0) \times 10^7$			4.6×10^5	$\sim 1 \times 10^7$
tert-butylethene	$(2.5 \pm 0.2) \times 10^9$				
acetonitrile	$\leq 7.8 \times 10^4$	$\leq 1 \times 10^{5\,g}$	$\leq 1.9 \times 10^6$		2.2×10^7

[a] This work. Acetonitrile as solvent. Errors correspond to 2σ. [b] Reference 4 unless otherwise noted. CCl_4 as solvent. [c] Reference 5 unless otherwise noted. CCl_4 as solvent. [d] Howard, J. A.; Scaiano, J. C. In *Landolt-Börnstein, New Series*; *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, part d. Benzene as solvent. [e] Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* 1988, *17*, 513–886. Water as solvent. [f] Unpublished results from this laboratory. [g] Reference 4. The reaction is probably decarboxylation. For the $4\text{-}CH_3OC_6H_4C(O)O^{\bullet}$ radical's attack on CH_3CN, $k \leq 1 \times 10^3\ M^{-1}\ s^{-1}$, see ref 3.

corresponding peroxide, $Ph_2P(O)OOP(O)Ph_2$ (1), can be readily prepared,[10,11] and although the intrinsic acidity of $Ph_2P(O)OH$ is unknown, it seems likely to be greater than, for example, the intrinsic acidity of benzoic acid.[12] Our hopes were fulfilled in that $Ph_2P(O)O^{\bullet}$, generated by LFP of the parent peroxide, was found to be extremely reactive. In this paper we report absolute rate constants for reaction of the $Ph_2P(O)O^{\bullet}$ radical with some representative organic substrates, the characterization of this radical by its UV–visible absorption spectrum, some EPR spin-trapping experiments, some ^{31}P NMR product studies, and the results of AM1–PM3 semiempirical calculations.

Results

LFP Measurements. Solutions of the peroxide 1 ($2\text{–}5 \times 10^{-3}$ M) in acetonitrile were subjected to 308-nm LFP at room temperature. A transient absorption in the visible spectrum appeared "instantaneously" (i.e., within 8 ns) following the laser flash. This absorption is broad and structureless, increasing in intensity from ca. 400 to 800 nm (see Figure 1). It has a lifetime of ca. 0.1 μs and decays with (pseudo)-first-order kinetics, a decay that is accompanied by the growth of a longer lived transient absorbing at ca. 320 nm (lifetime ca. 16 μs). Spectra recorded at three different times after the laser flash are shown in Figure 1.

The rates of decay of the visible absorption band were the same in nitrogen- and in oxygen-saturated solutions, which excludes the possibility that this transient is a carbon- or phosphorus-centered radical or some triplet species.[3,4] The spectrum shown in Figure 1 is strikingly similar to the spectra of carbonyloxyl radicals.[4-6] The kinetic behavior of the new transient is generally similar to that of the other $XC(O)O^{\bullet}$ radicals (vide infra). We therefore conclude that this visible absorption is due to the desired (diphenylphosphinoyl)oxyl radical.

$$\underset{1}{[Ph_2P(O)O]_2} \xrightarrow[308\ \text{nm}]{h\nu} 2Ph_2P(O)O^{\bullet} \qquad (1)$$

The 320-nm band which "grows in" after the laser pulse is probably due to cyclohexadienyl radicals formed by the addition of $Ph_2P(O)O^{\bullet}$ to an aromatic ring of the starting peroxide. Similar grow-in absorption bands have been observed during LFP of diaroyl peroxides.[3,4]

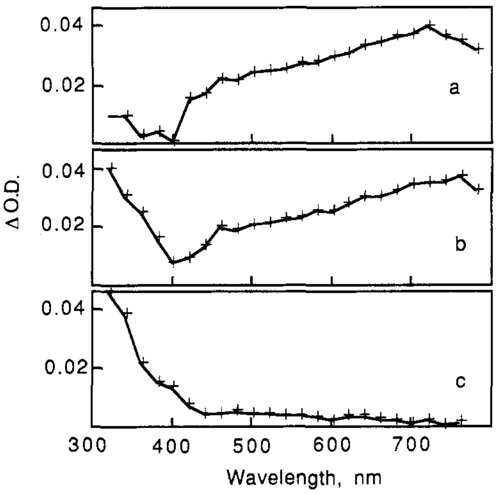


Figure 1. UV–visible spectra observed: (a) 8 ns, (b) 40 ns, and (c) 630 ns after 308-nm LFP of 3.4×10^{-3} M $Ph_2P(O)OOP(O)Ph_2$ in CH_3CN at 18 °C.

The visible absorption was quenched (i.e., decayed more rapidly) in the presence of compounds with which $Ph_2P(O)O^{\bullet}$ might be expected to react. Second-order rate constants k were calculated from the experimental pseudo-first-order decay traces, monitored at 720 nm, and measured at various substrate concentrations (range, $10^{-3}\text{–}10^{-2}$ M) via the relationship

$$k_{\text{exptl}} = k_0 + k[\text{substrate}]$$

In this equation, k_0 stands for all first- and pseudo-first-order processes by which $Ph_2P(O)O^{\bullet}$ might decay at zero substrate concentration, i.e., an intramolecular rearrangement (vide infra) and reaction with the starting peroxide and/or solvent. Bimolecular rate constants k for reaction of $Ph_2P(O)O^{\bullet}$ with some representative substrates are given in Table I.

The rate constant k_2 for reaction of $Ph_2P(O)O^{\bullet}$ with its peroxide precursor, 1, was obtained by varying the peroxide concentration in the absence of any other substrate:

$$k_0 = k_{\text{exptl}} = k_0' + k_2[1]$$

The value found for k_2, viz., $(9.2 \pm 0.8) \times 10^8\ M^{-1}\ s^{-1}$, is essentially equal to the rate constant for reaction of $Ph_2P(O)O^{\bullet}$ with benzene, viz., $9.1 \times 10^8\ M^{-1}\ s^{-1}$ (see Table I). We presume that k_2 corresponds largely or entirely to the addition of the radical to a phenyl ring of the peroxide. The value found for k_0', viz., $(1.5 \pm 0.3) \times 10^6\ s^{-1}$, corresponds to the decay of $Ph_2P(O)O^{\bullet}$ by rearrangement (vide

---

(10) Dannley, R. L.; Kabre, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4805–4810.

(11) This compound would appear to be the only stable peroxide of this class.[10]

(12) The pK_a of $Ph_2P(O)OH$ has been measured in ethanol/water mixtures,[13] and a value of 2.10 is obtained by extrapolation to 100% water. The pK_a of benzoic acid is 4.19.[14]

(13) Mastryukova, T. A.; Melent'eva, T. A.; Shipov, A. E.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1959**, *29*, 2178–2182.

(14) *Handbook of Chemistry and Physics*, 69th ed., 1988–1989; CRC Press Inc.: Boca Raton, FL, 1989; p D-161.

Table II. Selected EPR Parameters[a] for Some Spin-Adducts Produced by the Trapping of Certain Phosphorus-Containing Radicals $X^\bullet$

	$X^\bullet = Ph_2P(O)O^{\bullet}$ [b]			$X^{\bullet}$ [c]	
spin adduct	a^P	a^{other}	g	structure	a^P
$PhC(X)HN\dot{O}C(CH_3)_3$	ND[d]	13.28 (N), 0.93 (1 H)	2.00637 (5)	$(EtO)_2\dot{P}{=}O$	24.75
				$(PhO)_2\dot{P}{=}O$	25.25
$XCH_2\dot{C}HC(CH_3)_3$[e]	0.88	23.75 (2 H), 21.5 (1 H)	2.0034 (1)	$(\overline{OCH_2CH_2O)_2P}P^\bullet$	104.5
				$Et_2\dot{P}{=}O$	77.5
$XCH_2\dot{C}[C(CH_3)_3]_2$[e,f]	4.08	6.68 (2 H), 0.58 (18 H)	2.00258 (3)	$(Et_2O)_2\dot{P}{=}O$	109.4
				$(\overline{OCH_2CH_2O)_2P}^\bullet$	128.9
$XCH{=}\dot{C}C(CH_3)_3$[e]	13.0	34.5 (1 H)	2.0028 (1)		
$(CH_3)_3CC(X){=}\dot{C}C(CH_3)_3$	2.5		2.0038 (1)	$(EtO)_2\dot{P}{=}O$	132.7
				$(\overline{OCH_2CH_2O)_2P}^\bullet$	176.5

[a] Hyperfine splittings are in gauss. Numbers in parentheses indicate the probable error in the last digit. [b] At 292 ± 1 K in CH_3CN unless otherwise noted. [c] Data taken from *Landolt-Börnstein, New Series*; *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1977; Vol. 9, part b, part c1; 1987, Vol. 17, part b. [d] Not detected, therefore $a^P < 0.4$ G, the line width. [e] In $CHCl_3$. [f] At 253 K.

infra) and by reaction with the acetonitrile solvent. This value for k_0' puts a limit of 7.8×10^4 M^{-1} s^{-1} as the maximum possible rate constant for the reaction of $Ph_2P(O)O^\bullet$ with acetonitrile. Thus, acetonitrile is at least 480 times less reactive than chloroform, but it was the latter solvent that was employed in the only detailed investigation of the thermal and photochemical decomposition of **1**.[15,16] We have previously observed that acetonitrile, which is very electron deficient, is rather unreactive toward aroyloxyl radicals[3,4] and (alkoxycarbonyl)oxyl radicals[5] (see also Table I).

EPR Spectroscopic Measurements. Additional proof that $Ph_2P(O)O^\bullet$ was being monitored in the LFP experiments was sought by EPR spectroscopy. Unfortunately, **1** was extremely insoluble in the solvents most suitable for low-temperature (<170 K) EPR such as cyclopropane and the Freons.[19] No EPR signals could be observed on UV photolysis of **1** in chloroform at 210 K nor in acetonitrile at 230 K. We therefore turned to the spin-trapping technique in which the transient $Ph_2P(O)O^\bullet$ radical could add to a reagent to form a persistent and readily identifiable spin-adduct. Continuous UV photolysis of solutions of the peroxide and spin trap in CH_3CN or $CHCl_3$ directly in the cavity of a Varian E-104 EPR spectrometer gave spectra consistent with the adduct radical structures presented in column 1 of Table II. The EPR parameters of these radicals are listed in columns 2–4 of this table. EPR data from the literature yield columns 5 and 6. Column 5 lists some phosphorus-centered radicals that have been spin-trapped by four out of the five traps used in the present work while column 6 lists the phosphorus hyperfine splittings (hfs) of the corresponding spin-adducts. Comparison of the phosphorus hfs listed in column 2 with those listed in column 6 makes it obvious that the radical that is trapped by photolysis of peroxide **1** is *not* phosphorus-centered. We therefore conclude that we are generating and trapping the oxygen-centered radical, $Ph_2P(O)O^\bullet$.

We sought additional EPR evidence for the generation of a reactive oxygen-centered radical without success except for the observation of the extremely persistent radical[20,21] $(Me_3Si)_2CH\dot{C}(SiMe_3)_2$ on photolysis of the peroxide at 291 K in $CHCl_3$ containing $(Me_3Si)_2CHCH(SiMe_3)_2$. Specifically, no EPR signals were observed on photolysis of **1** in the presence of benzene or hexafluorobenzene (both of which have been used to spin-trap aroyloxyl radicals),[4] nor were EPR signals obtained in the presence of styrene or 1,3- or 1,4-cyclohexadiene. We presume that these failures can be attributed to an induced decomposition of the peroxide by sterically unhindered carbon-centered radicals (vide infra).

^{31}P NMR Product Studies. In Dannley et al.'s[10,15] studies of the thermal and photochemical decomposition of peroxide **1** in chloroform, the only product identified (albeit somewhat indirectly) was the unsymmetrical anhydride $Ph_2P(O)OP(O)(Ph)OPh$ (**2**). Using an ^{18}O-labeled peroxide, **1**(^{18}O), they found that in the thermal reaction the ^{18}O label remained in the oxo oxygens, which implied that decomposition involved an intimate ion pair or was a concerted process:

$$\underset{\mathbf{1}(^{18}O)}{Ph_2P(^{18}O)OOP(^{18}O)Ph_2} \xrightarrow{\Delta} \underset{\mathbf{2}(^{18}O)}{Ph_2P(^{18}O)OP(^{18}O)(Ph)OPh} \tag{2}$$

In contrast, photolysis of **1**(^{18}O) yielded the anhydride with the ^{18}O label scrambled, at least to some extent,[22] suggesting a reaction involving free $Ph_2P(O)O^\bullet$ radicals. A reasonable mechanism for the photoreaction would be a radical-chain process in which the $Ph_2P(O)O^\bullet$ radical underwent an intramolecular rearrangement to form a phosphorus-centered radical, reaction 3, this step being followed by an S_H2 reaction with the starting peroxide, probably at one of the peroxidic oxygen atoms, reaction 4.

$$Ph_2P(^{18}O)OOP(^{18}O)Ph_2 \xrightarrow{h\nu} 2Ph_2P(^{18}O)O^\bullet \tag{1}$$

$$Ph_2P(^{18}O)O^\bullet \rightarrow Ph\dot{P}(^{18}O)^{18}OPh \tag{3}$$

$$Ph\dot{P}(^{18}O)^{18}OPh + Ph_2P(^{18}O)OOP(^{18}O)Ph_2 \rightarrow Ph_2P(^{18}O)OP(^{18}O)(Ph)^{18}OPh + Ph_2P(^{18}O)O^\bullet \tag{4}$$

In view of our kinetic data, which show that the $Ph_2P(O)O^\bullet$ radical is extremely reactive, we were surprised that the photoreaction should have yielded the unsymmetrical

---

(15) Dannley, R. L.; Waller, R. L.; Hoffman, R. V.; Hudson, R. F. *J. Org. Chem.* **1972**, *37*, 418–421.

(16) Less detailed studies of the thermal decomposition of **1** in other solvents are reported in ref 10. The amine (base) catalyzed decomposition has also been investigated in chloroform[10,17] and methylene chloride.[18]

(17) Yaouanc, J. J.; Masse, G.; Sturtz, G. *Synthesis* **1985**, 807–810.

(18) Boche, G.; Sommerlade, R. H. *Tetrahedron* **1986**, *42*, 2703–2706.

(19) Even ca. 1 mg of **1** in 2 mL of solvent crystallized at low temperatures, and no resolved EPR spectrum could be obtained.

(20) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6203–6205.

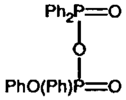
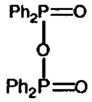
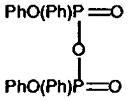
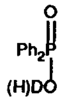
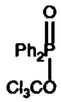
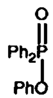
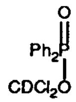
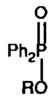
(21) Brownstein, S.; Dunogues, J.; Lindsay, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 2073–2078.

(22) Dannley et al.[15] reported that "the phenoxy group contains essentially one-half the enrichment...of oxygen-18 compared to the original oxo oxygen enrichment". However, the structure of the photogenerated ^{18}O-labeled unsymmetrical anhydride was shown as having every oxygen labeled though no evidence was presented that would support such complete scrambling of the label.

anhydride **2** as the only product. We therefore decided to reinvestigate very briefly the thermal and, in slightly more detail, the photochemical decomposition of peroxide 1 by using ^{31}P NMR to examine the products. Preliminary assignments of ^{31}P resonances were based on literature data[23] and were confirmed, whenever possible, by independent synthesis of the compound in question, which was then used to "spike" the product mixture.

A 4.6×10^{-2} M solution of 1 in $CDCl_3$ decayed completely within 2 days at ambient temperatures. This thermal decomposition, which was monitored by UV at 308 nm, followed clean first-order kinetics with a rate constant, k_d, for decay of 1 equal to $(2.26 \pm 0.05) \times 10^{-5}$ s^1 at 294 K, a value in excellent agreement with the literature.[10] In CD_3CN, decay was rather more rapid ($k_d^{296} = (5.6 \pm 0.2) \times 10^{-5}$ s^{-1}).[24] After the decomposition in $CDCl_3$ of 1 (δ = 43.2 ppm),[17,25,26] *five* new ^{31}P resonances appeared (see Table III), two of which (δ = 7.4 and 29.1 ppm) were split into a doublet (J = 34 Hz), indicating a compound that contained two nonequivalent phosphorus atoms. These signals were assigned to the unsymmetrical anhydride **2** (area % = 41), and this assignment was confirmed by independent synthesis of **2**. The symmetrical anhydride, diphenylphosphinic anhydride (**3**) (δ = 28.9 ppm),[25-27] is also formed (area % = 11). Literature data[23] suggested that the resonance at 17.6 ppm (area % = 30) might be phenylphosphonic acid, $PhP(O)(OH)_2$, or its phenyl ester, PhO(Ph)P(O)OH, but following independent syntheses of these two compounds, they were found to give ^{31}P resonances at 20.2 ppm (broad, in CD_3CN because of very low solubility in $CDCl_3$) and 12.3 ppm, respectively. The ^{31}P resonance at 17.6 ppm was eventually assigned to diphenyldiphosphonic acid diphenyl diester, (**4**) by independent synthesis.[26] Diphenylphosphinic acid (**5a**) (**5**, R = D(H)) is responsible for the signal at 34.0 ppm[25,26,28] (area % = 18); it was isolated from a reaction mixture[29] and was identified by comparison of its physical properties with those of independently synthesized material.

Table III. Area Percent of Peaks in the ^{31}P NMR Spectra of Products Formed by Thermal Decomposition and Photodecomposition of Peroxide 1 at 295 K[a]

		product[b]							
		 $Ph_2P(=O)OP(=O)(Ph)OPh$ **2**	 $Ph_2P(=O)OP(=O)Ph_2$ **3**	 $PhO(Ph)P(=O)OP(=O)(Ph)OPh$ **4**	 $Ph_2P(=O)O(H)D$ **5a** (5, R = D(H))	 $Ph_2P(=O)OCCl_3$ **T5b** (5, R = CCl_3)	 $Ph_2P(=O)OPh$ **5c** (5, R = Ph)	 $Ph_2P(=O)OCDCl_2$ **T5d** (5, R = $CDCl_2$)	 $Ph_2P(=O)OR$ **5e** (5, R = Et_3Si) **T5f** (5, R = CD_2CN)
chemial shift, ppm		7.4/29.1 (J = 34 Hz)	28.9	17.6	34.0	33.5	30.9	31.8	22.6 (Et_2Si) 31.6 (CD_2CN)
conditions[c]	1 conv[d]								
Δ, 2 days, $CDCl_3$	100	41	11	30	18				
hν, 5 min, $CDCl_3$	39	46			---40[e]---		5	9	
hν, 10 min, $CDCl_3$	66	41			~32[e]	~12[e]	6	9	
hν, 60 min, $CDCl_3$	100	33	10	7	---38[e]---		5	7	
hν, 20 min, $CDCl_3/C_6H_6$ (7/3)	95	47	11	11	24		7		
hν, 20 min, $CDCl_3/Et_3SiH$ (7/3)	100	26	8		39			5	22 (Et_3Si)
Δ, 3 days, CD_3CN	100	32	20	26	22				
hν, 20 min, CD_3CN	100	23	18	6	36		11		6 (CD_2CN)

[a] Area % values are given relative to the amount of peroxide converted, i.e., they always add up to 100%. The area % values for the $CDCl_3$ solutions have been corrected for the initial composition, but area % values for CD_3CN solutions have not been corrected (see Experimental Section). [b] If the identification of the product is only tentative, the letter T appears before the product number. [c] Thermal = Δ; photo = hν. [d] Percentage of 1 converted to products. [e] Broad line which is, at best, only poorly resolved into two peaks.

---

(23) (a) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 231–457. (b) Gorenstein, D. G.; Shaik, D. O. In *Phosphorus-31 NMR*; Gorenstein, D. G., Ed.; Academic: Orlando, 1984; Chapter 18, pp 549–604. (c) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quinn, L. D., Eds.; VCH: Deerfield Beach, 1987; pp 1–60.

(24) Dannley, et al.[10] have given k_d^{298} = 3.77, 9.6, 18.5, and 157.5 × 10^{-5} s^{-1} in $CHCl_3$, dimethylformamide, tetrachloroethane, and acetic acid, respectively.

(25) Chemical shifts are given relative to 85% H_3PO_4.

(26) Note that the ^{31}P chemical shifts of some of the products were strongly dependent (±0.8 ppm) on the solution in which the product was formed (perhaps because of acidic products or traces of H_2O and even, perhaps, because of small variations in the temperature at which the NMR spectra were recorded). As an example, the ^{31}P resonance assigned to diphenyldiphosphonic acid diphenyl diester (**4**) generally appeared at 17.6 ppm (as indicated in Table III), but in some experiments this resonance appeared at 17.2 ppm. Pure **4** gave a resonance at 16.7 ppm in pure $CDCl_3$ and at 16.8 ppm in pure CD_3CN, but when added to $CDCl_3$ solutions containing products and/or other compounds gave a resonance that varied in position from 16.1 to 17.6 ppm. Since structural identification of the products was based wherever possible on "spiking" raw product mixtures with authentic materials, this chemical shift variability caused only minor difficulties.

(27) Literature,[17] δ = 28 ppm; authentic pure material in $CDCl_3$, δ = 29.5 ppm.

(28) (a) Kasler, F.; Tierney, M. *Anal. Chem.* **1979**, *51*, 1070–1074. (b) Authentic pure material in $CDCl_3$, δ = 33.2–33.6 ppm.

(29) This compound slowly crystallized from the products obtained in the $CDCl_3/Et_3SiH$ (7/3, v/v) experiment (Table III) after partial removal of this solvent mixture under vacuum and addition of CH_3CN. Crude mp: 188–189 °C; lit. mp 190 °C,[10] 196–198 °C.[30] The infrared (KBr disk)[30,31] and ^1H NMR[30] spectra were in agreement with the literature[30,31] and with independently synthesized material (mp 190–191 °C).

(30) Rainville, D. P.; Zingaro, R. A. *J. Organomet. Chem.* **1980**, *190*, 277–288.

(31) *The Aldrich Library of Infrared Spectra*; 2nd ed.; Pouchert, C. P., Ed.; Aldrich Chemical Co.: St. Paul, 1975; p 1037.

$Ph_2P(O)OP(O)Ph_2$
3
$PhOP(O)(Ph)OP(O)(Ph)OPh$ $Ph_2P(O)OR$
4 **5**

Our ^{31}P NMR data do serve to confirm that the unsymmetrical anhydride **2** is an important product formed during the thermal decomposition of peroxide **1**. However, the overall pattern of products proves that the decomposition is very much more complex than originally suggested.[10,15,32]

Photolysis of a 4.6×10^{-2} M solution of peroxide **1** in $CDCl_3$ gave a decay which again obeyed first-order kinetics ($k_d^{298} = 1.8 \times 10^{-3}$ s^{-1}). The unsymmetrical anhydride **2** was formed in an amount comparable to that produced by thermolysis. Several new ^{31}P resonances in the δ = 30–35 ppm region were also produced (see Table III). The most intense peak (δ = 34.0 ppm) was resolved from a weaker resonance (δ = 33.5 ppm) only in the experiment in which the sample was irradiated for 10 min. The 34.0 ppm resonance can again be assigned to diphenylphosphinic acid, and since there was no O*H* signal in the ^1H NMR spectrum of the reaction mixture, it would appear that the $Ph_2P(O)O^\bullet$ radical has been generated and has abstracted a deuterium atom from the solvent, i.e., **5a** (**5**, R = D) has been produced as a major product by reaction 5.

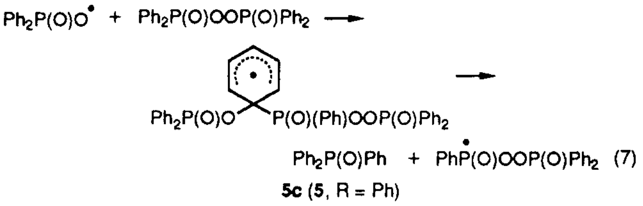
$$Ph_2P(O)OOP(O)Ph_2 \xrightarrow{h\nu} 2Ph_2P(O)O^\bullet \quad (1)$$

$$Ph_2P(O)O^\bullet + CDCl_3 \rightarrow \underset{\mathbf{5a}\ (\mathbf{5},\ R\ =\ D)}{Ph_2P(O)OD} + \dot{C}Cl_3 \quad (5)$$

The poorly resolved, weaker resonance at 33.5 ppm was absent when the photolysis was carried out in $CDCl_3/C_6H_6$ (7/3, v/v), in $CDCl_3$/triethylsilane (7/3, v/v), or in neat CD_3CN (see Table III). These results imply that the 33.5 ppm resonance is due to the trichloromethyl ester of diphenylphosphinic acid formed in an S_H2 reaction of the $\dot{C}Cl_3$ radical with the peroxide, reaction 6. Reactions 5

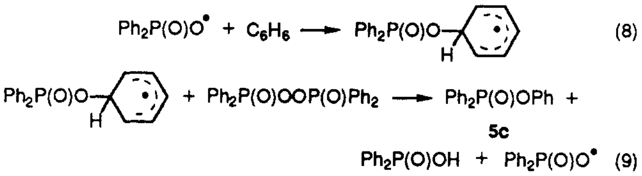
$$\dot{C}Cl_3 + Ph_2P(O)OOP(O)Ph_2 \rightarrow \underset{\mathbf{T5b}\ (\mathbf{5},\ R\ =\ CCl_3)}{Ph_2P(O)OCCl_3} + Ph_2P(O)O^\bullet \quad (6)$$

and 6 together constitute a free-radical-induced, chain decomposition of the peroxide. Unfortunately, the trichloromethyl ester of diphenylphosphinic acid is unknown and we were not able to synthesize it; for this reason, the assignment must remain tentative, i.e., **T5b**.[33]



(7)
5c (**5**, R = Ph)

Literature data[34] suggested that the resonance at 30.9 ppm was due to the phenyl ester of diphenylphosphinic acid, **5c** (**5**, R = Ph). This assignment was confirmed by "spiking" with independently synthesized material. Since this compound is formed in the photolysis but not in the thermolysis of the peroxide in $CDCl_3$ and in CD_3CN (see Table III), it seems probable that the $Ph_2P(O)O^\bullet$ radical is involved in its formation. The most likely reaction would appear to be a homolytic substitution on a phenyl group of the peroxide, reaction 7. Consistent with this mechanism is our observation that **5c** was not produced on photolysis of the peroxide in the $CDCl_3/Et_3SiH$ solvent mixture. The highly reactive triethylsilane (see Table I) would be expected to trap all the $Ph_2P(O)O^\bullet$ radicals and thus prevent reaction 7 from occurring. However, replacement of the Et_3SiH by an equal volume of benzene does, if anything, enhance the yield of **5c**, probably by a direct attack on the benzene, i.e.,



(8)
5c
(9)

We tentatively identify the resonance at 31.8 ppm as being due to the dichloromethyl ester of diphenylphosphinic acid, **T5d** (**5**, R = $CDCl_2$).[33] This resonance is presumably due to a product formed via the $Ph_2P(O)O^\bullet$ radical since it is not formed during the thermal decomposition in $CDCl_3$. Its absence in the photodecomposition in CD_3CN implicates a $CDCl_3$-derived moiety, which could only be $CDCl_2$. Although the identification of this ester must remain tentative since it was not synthesized, we believe it to be a perfectly "reasonable" product which requires only that the $Ph_2P(O)O^\bullet$ radical should undergo the intramolecular rearrangement postulated earlier to account for the results of Dannley et al.'s[15] photodecomposition of ^{18}O-labeled peroxide, reaction 3, followed by a chlorine atom abstraction from the solvent, reaction 10, and an S_H2 reaction of the $\dot{C}DCl_2$ radical on the peroxide, reaction 11.

$$Ph_2P(O)O^\bullet \rightarrow Ph\dot{P}(O)OPh \quad (3)$$

$$Ph\dot{P}(O)OPh + CDCl_3 \rightarrow PhP(O)(Cl)OPh + \dot{C}DCl_2 \quad (10)$$

$$\dot{C}DCl_2 + Ph_2P(O)OOP(O)Ph_2 \rightarrow \underset{\mathbf{T5d}}{Ph_2P(O)OCDCl_2} + Ph_2P(O)O^\bullet \quad (11)$$

Further support for the foregoing reaction scheme is provided by two observations. First, photolysis of the peroxide in $CDCl_3/C_6H_6$ does not yield a 31.8 ppm resonance, presumably because the $Ph_2P(O)O^\bullet$ radicals are trapped by the benzene, reaction 8, more rapidly (cf. Table I) than they rearrange via reaction 3. Second, the 31.8 ppm resonance is produced by photolysis of **1** in $CDCl_3/Et_3SiH$ together with a new resonance at 22.6 ppm, and we have firmly identified the latter resonance (by independent synthesis)[35] as being due to the triethylsilyl ester of diphenylphosphinic acid, **5e** (**5**, R = Et_3Si). The triethylsilane traps $Ph_2P(O)O^\bullet$ radicals just as efficiently as benzene (see Table I), but this reaction is expected to yield mainly the triethylsilyl radical, which will rapidly abstract chlorine from the solvent, reaction 13, as well as attacking the peroxide in a S_H2 process, reaction 14, to produce **5e**, i.e.,

$$Ph_2P(O)O^\bullet + Et_3SiH \rightarrow Ph_2P(O)OH + Et_3Si^\bullet \quad (12)$$

---

[32] Dannley et al.[10] hydrolyzed their product(s) and obtained $Ph_2P(O)OH$ and $PhO(Ph)P(O)OH$, both in yields of ca. 90%, i.e., ca. 1:1. These two acids were presumed to arise solely from the unsymmetrical anhydride **2**. However, our thermolysis products (see Table III) would yield the same ca. 1:1 ratio of these two acids after hydrolysis, viz., $Ph_2P(O)OH$ = 18% (directly) + 11% (from **3**) + 20.5% (from **2**) = 49.5%; $PhO(Ph)P(O)OH$ = 30% (from **4**) + 20.5% (from **2**) = 50.5%.

[33] For products that could only be tentatively identified, the letter **T** is placed before the product number.

[34] Hoz, S.; Dunn, E. J.; Buncel, E.; Bannard, R. A. B.; Purdon, J. G. *Phosphorus Sulfur* **1985**, *24*, 321–326.

[35] The presence of a triethylsilyl group in the nonvolatile products was also confirmed by ^1H NMR.

$$Et_3Si^{\bullet} + CDCl_3 \rightarrow Et_3SiCl + \dot{C}DCl_2 \quad (13)$$

$$Et_3Si^{\bullet} + Ph_2P(O)OOP(O)Ph_2 \rightarrow \underset{\textbf{5e}}{Ph_2P(O)OSiEt_3} + Ph_2P(O)O^{\bullet} \quad (14)$$

In the photolysis of the peroxide in $CDCl_3$, it should be noted that diphenylphosphinic anhydride (**3**) and diphenyldiphosphonic acid diphenyl diester (**4**) are produced only upon prolonged irradiation after all the peroxide has been consumed. The product balance suggests that both of these compounds are formed from the unsymmetrical anhydride **2** and that they are formed in approximately equal amounts. We are grateful to an anonymous referee for suggesting the following two-step, ionic chain mechanism:

$$Ph_2P(O)O^- + \underset{\textbf{2}}{Ph_2P(O)OP(O)(Ph)OPh} \rightarrow \underset{\textbf{3}}{Ph_2P(O)OP(O)Ph_2} + PhO(Ph)P(O)O^- \quad (15)$$

$$PhO(Ph)P(O)O^- + \underset{\textbf{2}}{Ph_2P(O)OP(O)(Ph)OPh} \rightarrow \underset{\textbf{4}}{PhO(Ph)P(O)OP(O)(Ph)OPh} + Ph_2P(O)O^- \quad (16)$$

In the photoreactions in $CDCl_3$, it also seems likely that **2** will be formed both via the S_H2 reaction of $Ph\dot{P}(O)OPh$ on the peroxide, reaction 4, and via a reaction of diphenylphosphinic acid with the PhP(O)(Cl)OPh formed via reaction 10, i.e.,

$$Ph_2P(O)OH + PhP(O)(Cl)OPh \rightarrow \underset{\textbf{2}}{Ph_2P(O)OP(O)(Ph)OPh} + HCl \quad (17)$$

Independent experiments showed that reaction 17 was slow and did not go to completion. After 30 min at room temperature, the products and area % of their ^{31}P NMR resonances were as follows: **2**, 6%; **3**, 10%; **4**, 9%; **5** (R = Ph), 3%; $Ph_2P(O)Cl$, 7%; and the two starting reagents both at 28%. If Et_3N was added to neutralize the HCl, the yield of **2** reached 52% in 10 min.

It is clear that even under photolytic conditions some rather complex ionic chemistry can occur in parallel with the free-radical chemistry.

Unfortunately, the area % of ^{31}P NMR peaks cannot be related in any simple way to the relative concentrations of the different products.[36] Indeed, the only thing that the products demonstrate is that photolysis of the peroxide in $CDCl_3$ yields $Ph_2P(O)O^{\bullet}$ radicals. In addition, the products suggest that the $Ph_2P(O)O^{\bullet}$ radicals undergo a neophyl-type of rearrangement to form a phosphorus-centered radical and that this reaction is fast enough in $CDCl_3$ to compete to some extent with the trapping of the $Ph_2P(O)O^{\bullet}$ radical by the $CDCl_3$.

Finally, the peroxide was also thermolyzed and photolyzed in CD_3CN. Thermolysis gave the same four products (**2**–**4** and **5a**) and with a similar distribution to the products formed by thermolysis in $CDCl_3$ (see Table III). Photolysis of the peroxide in CD_3CN also yields these four products together with **5c** and a new ^{31}P resonance at δ = 31.6 ppm. We tentatively identify the compound responsible for the 31.6 ppm resonance as **T5f** (**5**, R = CD_2CN) formed by reactions 18 and 19.

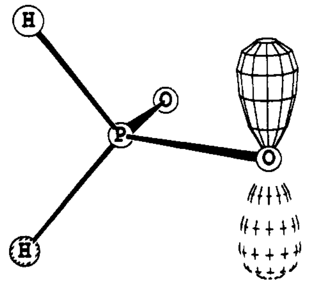


Figure 2. Structure and SOMO of the phosphinoyloxyl radical $H_2P(O)O^{\bullet}$ as calculated by the AM1–PM3 method.

$$Ph_2P(O)O^{\bullet} + CD_3CN \rightarrow Ph_2P(O)OD + \dot{C}D_2CN \quad (18)$$

$$\dot{C}D_2CN + Ph_2P(O)OOP(O)Ph_2 \rightarrow \underset{\textbf{T5f}}{Ph_2P(O)OCD_2CN} + Ph_2P(O)O^{\bullet} \quad (19)$$

Semiempirical Calculations. In order to gain some insight into the reasons for the extraordinarily high reactivity of the $Ph_2P(O)O^{\bullet}$ radical, we carried out an AM1[37] calculation on the simplest phosphinoyloxyl radical, $H_2P(O)O^{\bullet}$, using the new PM3 parameters,[38] which are said to provide more reliable results for phosphorus-containing compounds than the original AM1 (or MNDO) parameters. Full-geometry optimization gives $H_2P(O)O^{\bullet}$ a tetrahedral structure with $\Delta H_f = -78.9$ kcal/mol, unequal P–O bond lengths of 147.2 and 169.9 pm, and an OPO angle of 110.8°. These P–O bond lengths are very close to the standard values for P=O double and P—O single bonds.[39] The singly occupied molecular orbital (SOMO) is largely an oxygen 2p-type orbital located almost exclusively at one oxygen atom and oriented perpendicularly to the OPO plane (see Figure 2).[40] These calculations indicate that $H_2P(O)O^{\bullet}$ is a localized π-type radical. This structure contrasts dramatically with the structures deduced for carbonyloxyl radicals both by experiment[41,42] and by theory,[43] which have led to the conclusion that $PhC(O)O^{\bullet\,41-43}$ and $HC(O)O^{\bullet\,43}$ are delocalized σ radicals with C_{2v} geometry and a $^2B_2$ electronic ground state. Even more astonishing is the fact that our calculations indicate that the SOMO is located on the oxygen atom with the *shorter* P–O bond length. This suggests that $H_2P(O)O^{\bullet}$ is a highly

---

(36) Quantitative ^{31}P NMR measurements would be difficult to carry out because the relaxation times for the peroxide and its products are unknown and might be such as to interfere with the normal setting of the pulse timing; in addition, there may be power saturation effects;[23c] (see also: Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; p 359). These problems cannot be overcome by preparing a standard solution because some products could not be prepared, others cannot be isolated without decomposition, and the parent peroxide is itself unstable.

(37) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(38) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 109–220, 221–264. We thank Dr. T. Clark (University of Erlangen, FRG) for making this parameter set available to us.

(39) Rademacher, P. *Strukturen organischer Moleküle*; VCH: Weinheim, FRG, 1987; p 56. Sutton, L. E. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1965.

(40) The three highest occupied MOs were found to be close in energy, so configuration interaction should play an important role in calculations on $H_2P(O)O^{\bullet}$. We also note that we have previously interpreted the visible absorption band of carbonyloxyl radicals as being due to a transition from the $^2B_2$ ground state to the $^2A_1$ potential energy surface.[4,5] The similarity in the absorption spectra of $Ph_2P(O)O^{\bullet}$ and the carbonyloxyl radicals[3–6,41] suggests that they may have more similar structures than is indicated by the present calculations.

(41) Korth, H.-G.; Müller, W.; Lusztyk, J.; Ingold, K. U. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 183–185. See also ref 6.

(42) McBride, J. M.; Merrill, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1723–1725.

(43) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4515–4520. Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *Ibid.* **1980**, *105*, 1459–1466. McLean, A. D.; Lengsfield, B. H., III; Pacansky, J.; Ellinger, Y. *J. Chem. Phys.* **1985**, *83*, 3567–3576.

electrophilic radical, a result that is consistent with our kinetic data on the $Ph_2P(O)O^{\bullet}$ radical. More definitive structural information will have to await high-level ab initio calculations.

Discussion

All our separate studies (LFP, EPR, and product) demonstrate that the $Ph_2P(O)O^{\bullet}$ radical can be generated in solution by UV photolysis of the corresponding peroxide, 1.

The $Ph_2P(O)O^{\bullet}$ radical has an absorption in the visible that is similar to that of numerous carbonyloxyl radicals.[3-6,41] It is a very electrophilic radical and is extremely reactive in addition to and hydrogen abstraction from organic compounds, other than those that are very electron deficient such as CH_3CN and $CHCl_3$. Indeed, $Ph_2P(O)O^{\bullet}$ is more reactive toward organic substrates than any other organic oxyl radical (see Table I), and it reacts at or very close to the diffusion-controlled limit ($k_{diff}^{298} = 4.8 \times 10^9$ M^{-1} s^{-1})[44] with several of the substrates examined. Only the hydroxyl radical is slightly more reactive than $Ph_2P(O)O^{\bullet}$ toward some (but not all, witness $CHCl_3$) substrates.

Although our failure to observe the EPR spectrum of $Ph_2P(O)O^{\bullet}$ is disappointing, it is hardly surprising in view of the extreme reactivity of this radical. The spin-trapping experiments (see Table II) leave no doubt that photolysis of peroxide 1 yields an oxygen-centered radical, viz., $Ph_2P(O)O^{\bullet}$, rather than a phosphorus-centered radical, such as $Ph_2\dot{P}{=}O$,[45] or the rearranged radical, $Ph\dot{P}(O)OPh$. The lack of any observable EPR signals when 1 was photolyzed in the presence of compounds that would yield sterically unhindered carbon-centered radicals can probably be attributed to a rapid induced decomposition of the peroxide by these radicals.

The products identified by ^{31}P NMR spectroscopy are listed in Table III. They are fully consistent with Dannley et al.'s[10,15] conclusions, based on ^{18}O-labeling experiments, that the $Ph_2P(O)O^{\bullet}$ radical is probably not formed to any significant extent during the thermal decomposition of peroxide 1 at ambient temperatures but that this radical is produced during UV photolysis of the peroxide.

Of course, our products demonstrate that the thermal decomposition of 1 is very much more complex than was originally suggested.[10,15,32] This thermolysis is, unfortunately, fairly rapid at room temperature and for this reason the "thermal products" constitute an unknown but probably not insignificant fraction of the "photoproducts".[36,46] For this reason, a discussion of ^{31}P NMR area % values for the products from the different experiments (Table III) is unwarranted.

The postulated intramolecular rearrangement of $Ph_2P(O)O^{\bullet}$ to form the $Ph\dot{P}(O)OPh$ radical, reaction 3, which can be regarded as a phosphorus to oxygen neophyl-type rearrangement, appears to be required to explain at least some of the products formed during photolysis of the peroxide,[47] as well as the results of Dannley et al.'s[15] photolysis of 1 (^{18}O).[22] This 1,2-phenyl migration appears to be fairly rapid since, if we have correctly identified **T5b** and **T5d**, this rearrangement is able to compete to some extent with deuterium abstraction from $CDCl_3$ by the $Ph_2P(O)O^{\bullet}$ radical, reaction 5, which is a fairly fast process. (For hydrogen abstraction from $CHCl_3$, $k = 3.8 \times 10^7$ M^{-1} s^{-1}; see Table I.) However, only in relatively unreactive organic solvents (like $CDCl_3$ and CD_3CN) is the rearrangement likely to compete with the attack of the $Ph_2P(O)O^{\bullet}$ radical upon the solvent. In CD_3CN our LFP results show that $k_3 \ll 1.5 \times 10^6$ s^{-1} at ambient temperatures. In principle, k_3 could be measured by LFP experiments in an inert solvent such as CCl_4 or Freon 113. Unfortunately, the solubility of 1 in fully halogenated solvents was too low to achieve sufficient UV absorption for such experiments.

The results of our AM1 semiempirical calculations on $H_2P(O)O^{\bullet}$ are intriguing, but until ab initio calculations can be carried out, the electronic structure of this interesting and reactive family of radicals must be considered to remain somewhat uncertain.

Experimental Section

Materials. Dioxybis(diphenylphosphine oxide) (1) was prepared by Dannley's method[10] and was purified by precipitation twice from $CHCl_3$ by the addition of hexane. It was dried under vacuum and stored at −80 °C. Various freshly prepared solutions of 1 in $CDCl_3$ had ^{31}P NMR spectra area % = 63–68% also present were 2, 3, and 5 with area % = 9–17, 5–14, and 9–15, respectively. The area % for the products formed in $CDCl_3$ and listed in Table III have been corrected for these initial impurities. However, the area % for the products formed in CD_3CN and listed in Table III have not been corrected for these same initial impurities since the 1 was very largely decomposed during the time it took to dissolve in CD_3CN and record its spectrum.[46]

The following potential (or actual) products of the thermolysis and photolysis of 1 were prepared (though little effort was expended in their purification) by standard procedures.[48] The phenyl ester of phenylphosphonic diphenylphosphinic anhydride, $Ph_2P(O)OP(O)(Ph)OPh$ (**2**), was prepared by reaction of $Ph_2P(O)OH$ (**5a** (**5**, R = H)) (vide infra) and $PhO(Ph)P(O)Cl$ (vide infra) in an NMR tube in $CDCl_3/Et_3N$ as solvent (see Results, reaction 15): ^{31}P NMR ($CDCl_3/Et_3N$, 85% H_3PO_4) doublet of doublets, $\delta = 7.4$ and 29.3 ppm, $J = 34$ Hz. Attempts to isolate pure **2** were unsuccessful (see also ref 10). Diphenylphosphinic anhydride, $Ph_2P(O)OP(O)Ph_2$ (**3**), was prepared by reaction of $Ph_2P(O)Cl$ (Aldrich) with H_2O in Et_3N/Et_2O: mp 140 °C (lit.[10] mp 144–145 °C); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 29.5$ ppm. Diphenyldiphosphonic acid diphenyl diester, $PhO(Ph)P(O)OP(O)(Ph)OPh$ (**4**), was prepared by reaction of $PhP(O)Cl_2$ (Aldrich) with PhOH in Et_3N/Et_2O to produce $PhO(Ph)P(O)Cl$ [bp 122 °C/0.03 Torr (lit.[49] bp 121–125 °C/0.025 Torr); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 26.4$ ppm], which was treated with H_2O in Et_3N/Et_2O to produce **4**: mp 80–82 °C (lit.[10] mp 96 °C); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 16.7$ ppm. Diphenylphosphinic acid, $Ph_2P(O)OH$ (**5a** (**5**, R = H)), was prepared by refluxing $Ph_2P(O)Cl$ in H_2O/C_6H_6: mp 190–191 °C (lit.[50] mp 193–195 °C); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 33.2$–33.6 ppm for various solutions. Diphenylphosphinic acid phenyl ester, $Ph_2P(O)OPh$ (**5c**), was prepared by reaction of $Ph_2P(O)Cl$ with PhOH in Et_3N/Et_2O: mp 132 °C (lit.[34] mp 137–138 °C); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 31.5$ ppm. Diphenylphosphinic acid triethylsilyl ester, $Ph_2P(O)OSiEt_3$ (**5e**), was prepared by reaction of $Ph_2P(O)OH$ with Et_3SiCl in $CDCl_3/Et_3N$ (in an NMR tube): ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) $\delta = 22.3$ ppm. (Note: In the absence of Et_3N, this resonance is broad and occurs at $\delta = 26.7$ ppm together with a resonance at 37.6 ppm due to unreacted $Ph_2P(O)OH$.) Phenylphosphonic acid, $PhP(O)(OH)_2$, was prepared by reflux of PhP-

---

(44) Calculated via the Stokes–Einstein/von Smoluchowski relationship using the dynamic viscosity of CH_3CN, $\eta^{298} = 0.345$ cP.

(45) Roberts, B. P.; Singh, K. *J. Organomet. Chem.* **1978**, *159*, 31–35.

(46) In addition to the time required to irradiate the sample, time is required to dissolve the peroxide and record its ^{31}P NMR spectrum (only ca. 15 min in $CDCl_3$, but ca. 90 min in CD_3CN). Furthermore, the absorption of ^1H decoupling power by the sample during the recording of the ^{31}P NMR spectrum increased the temperature of the solution to ca. 35–40 °C, which will accelerate the thermal decomposition of 1 by a factor of 4–5 (as estimated from the Arrhenius parameters for this reaction, which were obtained by combining our measurement of the rate constant k_2 at 21 °C in chloroform with the rate constants given by Dannley et al.[10] in this solvent at 15, 25, and 35 °C, viz., $\log (A_2/s^{-1}) = 11.5 \pm 0.8$, $E_2 = 21.7 \pm 1.1$ kcal/mol).

(47) Specifically, all of **T5d** and possibly a portion of **2**.

(48) *Methoden der Organischen Chemie (Houben-Weyl)*; Thieme: Stuttgart, 1963, 1982; Vol. XII/1, Vol. E2.

(49) Hersman, M. F.; Audrieth, L. F. *J. Org. Chem.* **1958**, *23*, 1889–1893.

(50) Kosolapoff, G. M.; Struck, R. F. *J. Chem. Soc.* **1959**, 3950–3952. Hunt, B. B.; Saunders, B. C. *Ibid.* **1957**, 2413–2414.

(O)Cl_2 in H_2O/C_6H_6: mp 164 °C (lit.[51] mp 164-166 °C); too insoluble in $CDCl_3$ to record the ^{31}P NMR signal; ^{31}P NMR (CD_3CN, 85% H_3PO_4) δ = 20.2 ppm, broad (lit.,[52] acetone, 85% H_3PO_4, δ = 17.5 ± 1). Phenylphosphonic acid phenyl ester, PhO(Ph)P(O)OH, was prepared by reflux of PhO(Ph)P(O)Cl in H_2O/C_6H_6: mp 70 °C (lit.[53] mp 70-72 °C); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ = 12.3 ppm.

Acetonitrile and $CHCl_3$ (Aldrich, gold label)[3] were passed over neutral alumina and deoxygenated by flushing with dry nitrogen prior to use. The substrates used in the LFP and EPR experiments were purified by standard methods.

LFP Measurements. The experimental procedure has been described.[3]

EPR Spectroscopic Measurements. Degassed samples in 4-mm quartz tubes were placed in the cavity of a Varian E 104 EPR spectrometer and irradiated with the light from a 1-kW Hg/Xe lamp. In a typical spin-trapping experiment, we would employ 1 mL of a ca. 2 × 10^{-2} M solution of **1** in $CHCl_3$ or CH_3CN and 0.1 mL (or 0.1 g) of the trapping agent.

Product Studies. The thermal and photochemical decompositions of 4.6 × 10^{-2} M solutions of **1** in $CDCl_3$ and 2.0 × 10^{-3} M solutions of **1** in CD_3CN were performed in quartz tubes under nitrogen. The kinetics of the thermal decomposition was followed by monitoring the peroxide's UV absorption at 308 nm. For the photolytic decomposition, a 1-kW Hg/Xe lamp with a 260-nm filter was employed. The ^{31}P NMR spectra were recorded on a Varian XL-200 instrument using 85% phosphoric acid as an external standard. ^1H NMR spectra were recorded on a Varian EM-60 spectrometer with TMS as an internal standard.

Acknowledgment. We thank Miss P. Lommes for experimental assistance, H. Bandmann for recording the ^{31}P NMR spectra, Professor T. T. Tidwell (Toronto) for the sample of 1,1-di-*tert*-butylethene, Dr. J. C. Scaiano for a generous allotment of time on his LFP instrument, and an anonymous referee for several very helpful suggestions.

---

(51) Lecher, H. Z.; Greenwood, R. A.; Whitehouse, K. C.; Chao, T. H. *J. Am. Chem. Soc.* **1956**, *78*, 5018-5022.

(52) Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715-5726.

(53) Burger, A.; Anderson, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3575-3579.

NMR and Ultraviolet Spectral Characterization of Dihydrobenzene Intermediates in the Displacement of Hydrogen by Intramolecular Nucleophilic Aromatic Photosubstitution

Gene G. Wubbels,* Simeon Winitz, and Craig Whitaker

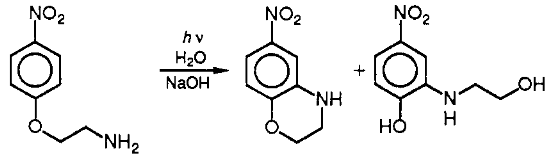
Department of Chemistry, Grinnell College, Grinnell, Iowa 50112

Received May 30, 1989

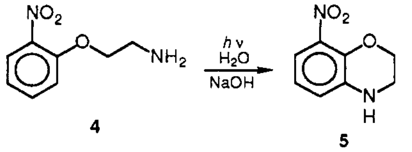
Direct ^1H NMR observation of reaction mixtures reveals that photolysis of $4\text{-}O_2NC_6H_4OCH_2CH_2ND_2$ in $NaOD/D_2O$ generates a long-lived, oxygen-stable dihydrobenzene intermediate (**11**) resulting from formal intramolecular addition of an N-D bond across the C_2–C_1 double bond of the nitrophenyl ether. This species (UV λ_{max} at 321 and 260 nm) is proposed to rearrange thermally by a 1,5-sigmatropic hydrogen shift to a dihydrobenzene (**9**) that adds ^-OD (to give **16**) and further rearranges to an open-chain structure (**17**). These intermediates exist in equilibrium in solution, are not oxidized by oxygen or 1,4-benzoquinone, but are oxidized thermally by 3,5-dinitrobenzoate ion. The aromatized photoproducts (**2** and **3**) reported earlier (ref 11) are generated from the array of intermediates by thermal reaction with 3,5-dinitrobenzoate ion or by prolonged photolysis.

Nucleophilic aromatic photosubstitution involving displacement of hydrogen has been observed in photoreactions of nitrobenzene derivatives with ammonia,[1] cyanide ion,[2] and cyanate ion,[3] imidazoles with cyanide ion,[4] methoxyaromatics with cyanide ion,[5] aromatic hydrocarbons with cyanide ion,[6] and aminoanthraquinones with amines.[7,8] In several of these cases, rather stable UV-absorbing intermediates of unclear structure are observed,[1,2,7] and the presence of oxygen or another oxidant increases the photochemical efficiency or product yield.[1-3,5-8] Lack of knowledge of the structures and stabilities of these intermediates has hindered understanding of which photoproducts are formed and, in flash photolysis studies,[5,9,10] which transient absorptions are to be expected for the several possible σ-complexes.

We reported recently[11] that the intramolecular formal photodisplacements of hydride ion in β-(nitrophenoxy)ethylamines in aqueous alkali—giving **2** and **3** from the para isomer **1** (eq 1), and **5** from the ortho isomer **4** (eq 2)—were accompanied by long-lived UV absorptions at 323



1 **2** **3** (1)



4 **5** (2)

---

(1) van Vliet, A.; Kronenberg, M. E.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1970**, *26*, 1061-67.

(2) Letsinger, R. L.; McCain, J. H. *J. Am. Chem. Soc.* **1966**, *88*, 2884-5; **1969**, *91*, 6425-31.

(3) Hartsuiker, J.; deVries, S.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 611-13.

(4) Oldenhof, C.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 35-38.

(5) Cornelisse, J.; Lodder, G.; Havinga, E. *Rev. Chem. Intermed.* **1979**, *2*, 231-65.

(6) Vink, J. A. J.; Verheydt, P. L.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1972**, *28*, 5081.

(7) Griffiths, J.; Hawkins, C. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2283-87.

(8) (a) Yoshida, K.; Okugawa, T.; Nagamatsu, E.; Yamashita, Y.; Matsuoka, M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 529-33. (b) Yoshida, K.; Hikasa, M.; Ishii, K.; Kadota, H.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 758.

(9) van Eijk, A. M. J.; Huizer, A. H.; Varma, C. A. G. O.; Marquet, J. *J. Am. Chem. Soc.* **1989**, *111*, 88-95.

(10) Wubbels, G. G.; van Zeyl, P. H. M.; Varma, C. A. G. O. *Abstracts of Papers*; 185th National ACS Meeting, Seattle, March 1983; ORGN-50.

(11) Wubbels, G. G.; Halverson, A. M.; Oxman, J. D.; DeBruyn, V. H. *J. Org. Chem.* **1985**, *50*, 4499-4504.

0022-3263/90/1955-0631$02.50/0