

The Synthesis and Reactions of Bis(diphenylphosphinic) Peroxide¹

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Bis(diphenylphosphinic) peroxide has been found to be stable at -80°, but at room temperature a rearrangement occurs to an unsymmetrical anhydride. In most solvents the thermal rearrangement is first order with respect to the phosphinic peroxide and has an energy of activation of 22.5 kcal./mole. In the presence of amines the peroxide oxidizes the solvent. This base-catalyzed reaction is first order with respect to both the peroxide and amine concentrations. A base-catalyzed addition to cyclohexene produced trans- α -hydroxycyclohexyl diphenylphosphinate. When the decomposition of the phosphinic peroxide is catalyzed by acids, the first-order dependence on peroxide concentration is maintained. The acid catalysis is complicated however by a concurrent catalysis by the conjugate base. A photochemically induced decomposition of the peroxide is second order with respect to the peroxide and leads to the unsymmetrical anhydride.

Although the inorganic salts of peroxydiphosphoric acid have been known for some time, organic compounds containing a bisphosphorus peroxide linkage have not been reported. These materials would certainly be new oxidizing agents and conceivably might dissociate homolytically to fragments with a radical site on oxygen. The present work was undertaken to synthesize representative peroxides of this type and to make some preliminary studies of their reactions with various organic compounds.

Experimental Section

Solvents. Alcohol-free chloroform and methylene chloride were obtained by washing reagent grade materials successively with concentrated sulfuric acid, sodium bicarbonate solution, and water, then drying over Drierite and fractionally distilling. For all kinetic runs freshly purified solvents were invariably used. Tetrachloroethane (dried over calcium chloride), cyclohexene (dried over phosphorus pentoxide), and reagent grade acetic acid were all fractionated before use.

Dimethylformamide was purified according to the procedure of Thomas and Rochow.²

Phenyl Hydrogen Phenylphosphonate. To a well-stirred solution of phenylphosphonic dichloride (19.5 g., 0.1 mole) and pyridine (7.9 g., 0.1 mole) in benzene (200 ml.) was added phenol (9.4 g., 0.1 mole). After refluxing for 30 min. and standing overnight, pyridine hydrochloride was re-

moved by filtration and the filtrate was refluxed with water (5 ml.) for 30 min. The benzene layer was separated from the water layer and dried with Drierite, the solvent was removed by distillation, and the residue was recrystallized from petroleum ether (b.p. 30-60°) to give phenyl hydrogen phenylphosphonate (12.1 g., 51%), m.p. 82° (lit.³ m.p. 71-72°).

Anal. Calcd. for C₁₂H₁₁O₃P: C, 61.55; H, 4.70. Found: C, 61.25; H, 4.63.

***p*-Nitrophenyl Phenylphosphinic Chloride.** *p*-Nitrophenyl phenylphosphinic acid⁴ (25 g., 0.095 mole) was heated (1 hr.) with freshly distilled thionyl chloride (100 ml.), the excess thionyl chloride was removed under reduced pressure, and the residue was distilled at 225-227° (0.5 mm.) to give 15 g. (56% yield) of *p*-nitrophenyl phenylphosphinic chloride which solidified on standing to a hygroscopic solid, m.p. 83-84°.

Anal. Calcd. for C₁₂H₉ClNO₃P: Cl, 12.6. Found (Volhard): Cl, 12.3.

***p*-Tolyl phenylphosphinic chloride,** m.p. 60°, was prepared from the corresponding acid, m.p. 136-138° (lit.⁵ m.p. 134-136°), in 84% yield by a procedure identical with that just described for the *p*-nitrophenyl analog. The product, b.p. 190-195° (1.0 mm.), had m.p. 60° (described in the literature⁶ as an oil).

Anal. Calcd. for C₁₃H₁₂ClOP: Cl, 14.2. Found (Volhard): Cl, 13.95.

Bis(diphenylphosphinic) Anhydride. To a stirred solution of diphenylphosphinic chloride (11.8 g., 0.05 mole) and triethylamine (5.1 g., 0.05 mole) in 200 ml. of dry benzene was added diphenylphosphinic acid (10.9 g., 0.05 mole) and the mixture was refluxed for 3 hr. After standing overnight the amine hydrochloride was removed by filtration. The filtrate was reduced in volume to 50 ml. and then chilled to precipitate 16 g. (76% yield) of bis(diphenylphosphinic) anhydride which, after recrystallization from benzene, melted at 144-145°.

Anal. Calcd. for C₂₄H₂₀O₃P₂: C, 68.89; H, 4.78; mol. wt., 418. Found: C, 68.85; H, 4.82; mol. wt., 416.

Bisphenylphosphonic Anhydride Diphenyl Ester. To a solution of phenylphosphonic dichloride (19.5 g., 0.1 mole) in 300 ml. of benzene was added triethylamine (10.1 g., 0.1 mole) and phenol (9.4 g., 0.1 mole). The reaction mixture was stirred overnight and then filtered to remove the amine hydrochloride. To the filtrate was added additional triethylamine (10.1 g., 0.1 mole) and phenyl hydrogen phenylphosphonate (23.4 g., 0.1 mole). After 6 hr. the reaction mixture was filtered to remove the amine salt, the filtrate was

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(2) A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

(3) A. Burger and J. J. Anderson, *ibid.*, **79**, 3575 (1957).

(4) L. Freedman and G. O. Doak, *ibid.*, **74**, 2884 (1952).

(5) L. Horner, H. Hoffman, and H. Wippel, German Patent 1,044,813 (1958); *Chem. Abstr.*, **55**, 3521e (1961).

(6) A. Michaelis, *Ann.*, **315**, 43 (1901).

evaporated to dryness, and the residue was recrystallized from anhydrous ether to yield 30 g. (66.6% yield) of the expected anhydride, m.p. 96°.

Anal. Calcd. for $C_{24}H_{20}O_5P_2$: C, 64.0; H, 4.45; P, 13.8; mol. wt., 450. Found: C, 63.94; H, 4.35; P, 13.52; mol. wt., 452.

trans- α -Hydroxycyclohexyl Diphenylphosphinate.

To a solution of *trans*-1,2-cyclohexanediol⁷ (2.32 g., 0.02 mole) in 25 ml. of benzene was added diphenylphosphinic chloride (4.72 g., 0.02 mole) and the mixture was refluxed for 2 hr. The solution was then chilled and filtered to collect 3.5 g. (55% yield) of *trans- α -hydroxycyclohexyl diphenylphosphinate*, which, after recrystallization from benzene, melted at 176°.

Anal. Calcd. for $C_{18}H_{21}O_3P$: C, 68.4; H, 6.65; P, 9.82; mol. wt., 316. Found: C, 68.53; H, 6.69; P, 10.16; mol. wt., 313.

Preparation of Bisdiphenylphosphinic Peroxide. To a cold solution of sodium peroxide (4.8 g., 0.06 mole) in 100 ml. of water was added slowly, over a period of 45 min., a solution of diphenylphosphinic chloride (23.6 g., 0.1 mole) in 50 ml. of toluene. During the addition and for an additional 15 min. stirring time the temperature was not allowed to rise above 3°. The mixture was filtered and the precipitate was washed twice with cold water and finally with acetone to give 12.5 g. (57% yield) of a light yellow solid. The solid was purified by dissolving in alcohol-free chloroform and reprecipitating with petroleum ether. The purification was carried out below 10°. The bisdiphenylphosphinic peroxide had a m.p. of 88–89° and was analyzed by conventional means⁸ for active oxygen content.

Anal. Calcd. for $C_{24}H_{20}O_4P_2$: peroxidic oxygen, 7.37. Found: peroxidic oxygen, 7.35.

The compound could be stored at -80° for extended periods of time without loss of peroxide content. At room temperature an exothermic, but not violent, decomposition occurred.

Other methods of synthesis attempted generally led mainly to hydrolysis of the acid chloride. Application of the procedure used by Green and Kazan⁹ for the preparation of diacyl peroxides led to diphenylphosphinic anhydride in 60% yield.

Substituted Bisdiphenylphosphinic Peroxides. The procedure successful with diphenylphosphinic chloride was applied to *p*-nitrophenyl, *p*-chlorophenyl, and *p*-tolyl phenylphosphinic chlorides but in each case the corresponding phosphinic acid was isolated and no peroxide was found.

Thermal Decomposition of Bisdiphenylphosphinic Peroxide in Chlorobenzene. A solution of the peroxide (8.7 g., 0.02 mole), 99% pure by peroxide titration, in 750 ml. of chlorobenzene was refluxed for 5 hr. Removal of the chlorobenzene by vacuum distillation left 8.7 g. of a viscous residue. This residue was dissolved in 75 ml. of benzene, 15 ml. of water added, and the mixture was refluxed for 1 hr. The benzene layer was separated and evaporated to dryness. Extraction of the mixture of acids with hot Skelly-B and chilling the extract gave phenyl hydrogen phenylphosphonate

(4.06 g., 0.018 mole) which after recrystallization from Skelly-B melted at 82° and did not depress the melting point of an authentic sample.

The Skelly-B insoluble acid fraction when recrystallized from benzene gave diphenylphosphinic acid (4.06 g., 0.018 mole), m.p. 190°. A mixture melting point with an authentic sample showed no depression.

Thermal decomposition of bisdiphenylphosphinic peroxide in alcohol-free chloroform, tetrachloroethane, dimethylformamide, and acetic acid at 25° in each instance gave the same products as those obtained in chlorobenzene (equimolecular quantities of the two acids).

Thermal Decomposition of Bisdiphenylphosphinic Peroxide in Methylene Chloride. A solution of bisdiphenylphosphinic peroxide (20 g., 0.046 mole) in 500 ml. of methylene chloride was stirred at 25° for 6 hr. and the solvent was then removed by distillation. The residue was extracted with hot ether and the insoluble residue was recrystallized from benzene to give diphenylphosphinic acid (9.5 g. 0.0436 mole), m.p. 190°. The ether extract was chilled and filtered to collect bisphenylphosphonic anhydride diphenyl ester (6 g., 0.0133 mole) which after recrystallization from ether melted at 96° and did not depress the melting point of an authentic sample.

The ether filtrate was evaporated to dryness to yield phenyl hydrogen phenylphosphonate (4 g., 0.017 mole) which after recrystallization from Skelly-B melted at 82° and did not depress the melting point of an authentic sample.

Acid-Catalyzed Decomposition of Bisdiphenylphosphinic Peroxide in Chloroform Solution. To a solution of bisdiphenylphosphinic peroxide (3 g., 0.007 mole) in 100 ml. of alcohol-free chloroform was added 2 ml. of acetic acid and the mixture was stirred at 25° for 24 hr. Conventional treatment as described before in the thermal decomposition in chlorobenzene led to the isolation of phenyl hydrogen phenylphosphonate (1.0 g., 0.0043 mole, 31%) and diphenylphosphinic acid (1.95 g., 0.0089 mole, 65%).

Base-Catalyzed Decomposition of Bisdiphenylphosphinic Peroxide. A solution of the peroxide (8.6 g., 0.02 mole) and anhydrous pyridine (1.6 g., 0.02 mole) in 250 ml. of chloroform was stirred at 25° for 24 hr. During the decomposition no gas was evolved. The solvent was removed under reduced pressure and the residue was placed in a desiccator over phosphorus pentoxide for a few days to produce large crystals of bisdiphenylphosphinic anhydride (8.4 g., 0.02 mole, 100% yield) which melted at 144–145° and showed no depression of melting point with an authentic sample. Pyridine was collected in the distilled solvent and identified as the picrate. Gas chromatographic analysis of the recovered solvent showed no extraneous peaks representing impurities. The substitution of quinoline for pyridine gave identical results.

Photolytic Decomposition of Bisdiphenylphosphinic Peroxide in Chloroform. A solution of the peroxide (2.37 g., 0.005 mole) in alcohol-free chloroform (100 ml.) was irradiated with 2537-Å. light for 4 hr. at a temperature of 21°. A strong odor of phosgene was observed and conventional treatment of the solution led to the isolation of phenyl hydrogen phenylphos-

(7) A. Roebuck and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 217.

(8) V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

(9) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

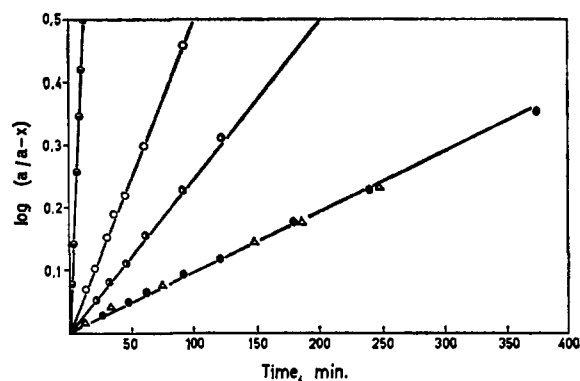


Figure 1. First-order plots of disappearance of bisdiphenylphosphinic peroxide for its thermal decomposition in the initial concentrations indicated at 25° in: ●, chloroform (0.0875 *M*); Δ, chloroform (0.124 *M*); ⊙, dimethylformamide (0.044 *M*); ○, tetrachloroethane (0.0272 *M*); and ⊖, acetic acid (0.0785 *M*).

phonate (1.05 g., 0.0045 mole, 82%) and diphenylphosphinic acid (1.25 g., 0.0057 mole, 105%).

Alkali-Catalyzed Decomposition of Bisdiphenylphosphinic Peroxide in Cyclohexene. A heterogeneous mixture of the peroxide (8.7 g., 0.02 mole), chloroform (40 ml.), cyclohexene (250 ml.), and 10 ml. of aqueous sodium hydroxide (1.8 g., 0.045 mole) was stirred at 25° for 8 hr. The organic layer was separated, evaporated to dryness, and the residue was recrystallized from ether to give *trans*- α -hydroxycyclohexyl diphenylphosphinate (1 g., 0.003 mole, 16%). The melting point was 176° and a mixture melting point with an authentic sample showed no depression.

Kinetic Experiments. To a weighed sample of the peroxide was added 100 ml. of solvent equilibrated to the proper temperature and 5-ml. aliquots were regularly removed and titrated.⁸ The initial concentration of peroxide was obtained by extrapolation.

Results

Thermal Decomposition of Bisdiphenylphosphinic Peroxide in Chloroform, Tetrachloroethane, Dimethylformamide, and Acetic Acid. A kinetic study of the reaction in chloroform at 25° in 0.0875 and 0.0124 *M* concentrations gave first-order rate constants (with respect to peroxide) independent of the peroxide concentration, $k = 3.77 \times 10^{-5} \text{ sec.}^{-1}$ in each case (Figure 1). Therefore no induced decomposition occurs. Similar first-order rate dependencies were observed in tetrachloroethane, dimethylformamide, and acetic acid (Figure 1). Additional measurements were made at 15 and 35° with chloroform, dimethylformamide, and tetrachloroethane. The speed of decomposition was so rapid in acetic acid that a 35° study was not feasible and an additional run was made at 18° only. The results are listed in Table I. From these data the energy of activation for the thermal decomposition in all four solvents was calculated to be 21.5 kcal./mole.

In methylene chloride, the decomposition was zero order with respect to the peroxide (Figure 2), and from the rate constants at 15 and 25° (0.560×10^{-5} and $1.33 \times 10^{-5} \text{ mole l.}^{-1} \text{ sec.}^{-1}$, respectively) an activation energy of 14.9 kcal./mole was calculated. The products of the decomposition in methylene chloride dif-

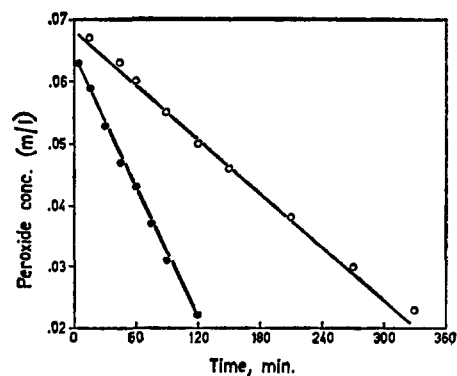


Figure 2. Zero-order plots of disappearance of diphenylphosphinic peroxide for its thermal decomposition at the temperatures and initial concentrations indicated in methylene chloride: ○, 15° (0.0705 *M*); and ●, 25° (0.0690 *M*).

fered upon superficial examination from those in the other solvents in that the symmetrical anhydride of phenyl hydrogen phenylphosphonate (0.6 mole/mole of peroxide) was isolated. However if this is discounted as an isolation possible because of its insolubility only in this particular solvent, the products are again equimolecular quantities of diphenylphosphinic acid and phenyl hydrogen phenylphosphonate.

Table I. Rate Constants. First Order with Respect to Bisdiphenylphosphinic Peroxide for Its Thermal Decomposition in Chloroform, Dimethylformamide, Tetrachloroethane, and Acetic Acid

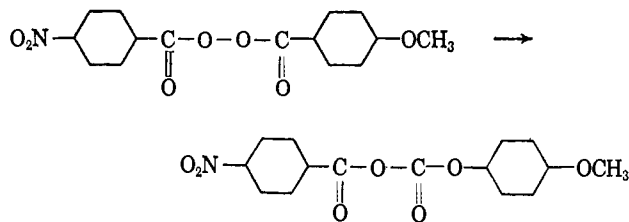
Solvent	Temp., °C.	Initial peroxide concn., mole l. ⁻¹	10 ⁵ k, sec. ⁻¹
Chloroform	15	0.0767	1.20
	25	0.0875	3.77
	25	0.0124	3.77
	35	0.0655	13.7
Dimethylformamide	15	0.0358	2.64
	25	0.044	9.6
	35	0.087	26.4
Tetrachloroethane	15	0.0138	4.80
	25	0.0272	18.5
	35	0.081	44.8
Acetic acid	18	0.073	64
	25	0.079	157.5

The decomposition of the peroxide in chloroform was further studied with respect to base and acid catalysis. With the addition of various concentrations of pyridine an increase in the first-order rate constants for peroxide disappearance was observed (Table II). A plot of these rate constants against the concentration of pyridine yielded a good straight line as proof that the reaction is first order with respect to base.

The effect of acid catalysis was more complex. With acetic, monochloroacetic, dichloroacetic, and trichloroacetic acids the first-order rate constants (Table III) for disappearance of peroxide were obtained at 25° for the concentrations of acids indicated. Plotting these rate constants disclosed that there is a fractional-order rate dependence on acid concentration. This fractional order varies from acid to acid.

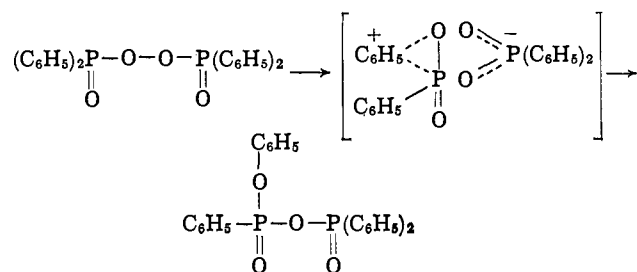
chloride) it may precipitate and shift the equilibrium to yield symmetrical products only.

Mechanism of the Thermal Rearrangement of the Peroxide. Several mechanisms are possible for the thermal decomposition. The first which will be presented arises from the similarity in structural change of the phosphinic peroxide rearrangement to the carboxy inversion of *p*-methoxy-*p'*-nitrobenzoyl peroxide.¹¹ The mechanism proposed for the car-



boxy inversion process (consistent with O¹⁸-labeling experiments¹²) involves an ion-pair intermediate (discussed in some detail by Denney^{12b}).

Applying this mechanism to the phosphinic peroxide yields the following sequence of steps. The phosphinic peroxide however gives high yields (86%) of rearrangement products while the unsymmetrical benzoyl peroxide gives only a 38% yield of carboxy inversion compound. There is a second difference in



that the rate of the phosphinic peroxide decomposition shows no dependence on the dielectric constant of the solvent (Table I) while the carboxy inversion process is markedly affected. This second difference may not be real however for the few solvents suitable for the phosphinic peroxide vary so widely in other properties, *e.g.*, hydrogen-bonding ability, that the effect of dielectric constant may be obscured.

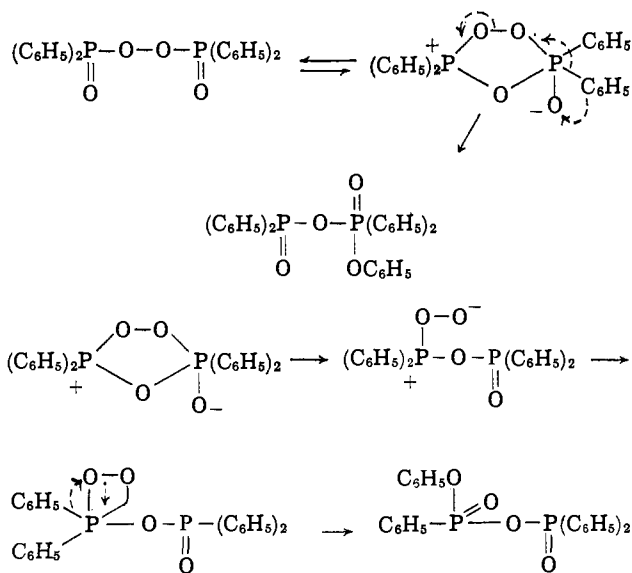
These differences coupled with the smaller probability of a heterolytic cleavage of the symmetrical phosphinic peroxide suggest that an entirely different mechanism is operative in the present case. The highly polar nature of the P=O bond also supports this thesis and leads to the following alternative mechanisms.

One of these mechanisms involves a migration of a carbonium ion represented by the following sequence of steps and predicts that the phenolic oxygen arises exclusively from phosphoryl (P=O) oxygen (proven not to be true of the carbonyl oxygen in the carboxy inversion reaction).

Another alternative mechanism involves the migration of a carbanion similar to those accepted for the Stevens and Wittig reactions.

(11) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950).

(12) (a) D. B. Denney, *ibid.*, **78**, 590 (1956); (b) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).



This sequence of steps is logical in that the $(\text{C}_6\text{H}_5)_2\text{P}^+(\text{=O})\text{OO}^-$ would be a good leaving group, the cyclization would occur because of the known affinity of P^+ for O^- , and the rearrangement involves the established ability of O^- to displace C_6H_5^- from phosphorus.¹³ This mechanism requires that the phenolic oxygen arise exclusively from the peroxidic oxygens. Experiments with O¹⁸-labeled phosphinic peroxide would therefore differentiate between the proposed carbanion and carbonium ion migrations. Such experiments are planned but have not yet been performed.

These mechanisms are based upon an ionic dissociation in the thermal rearrangement. The reactions must be ionic because a different kinetic behavior is observed when an obviously homolytic decomposition is obtained by irradiation of a solution of the peroxide with ultraviolet light (Figure 3). The photolytically accelerated reaction is second order with respect to the peroxide in contrast to the first-order behavior obtained thermally.

The thermal rearrangement must proceed by the same mechanism in chloroform, tetrachloroethane, dimethylformamide, and acetic acid because the products, order of reaction, and activation energy are the same in each case.

The behavior of the phosphinic peroxide in methylene chloride was anomalous. The products were those corresponding to a simple rearrangement but a zero-order rate dependence on peroxide concentration was observed. Methylene chloride differs from the other solvents in that it is less capable of hydrogen bonding and is more likely to contain impurities. Either of these differences may be used to provide a hypothetical explanation for the apparent zero-order kinetics but not enough data are available to reach any conclusions.

Base-Catalyzed Decomposition of the Peroxide. The decomposition of the peroxide is catalyzed by base and is first order with respect to both the peroxide and the amine (Table II). As the peroxide is reduced to diphenylphosphinic acid and the amine is recovered unchanged, the solvent must undergo oxidation. These products of oxidation of the solvent have not

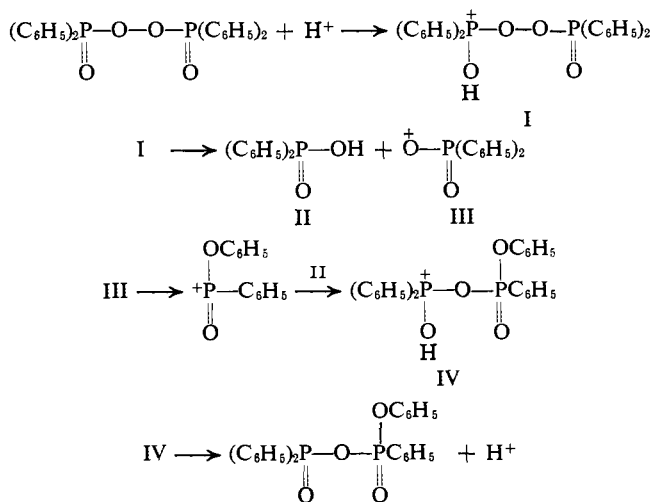
(13) G. Wittig and M. Schlosser, *Ber.*, **94**, 1373 (1961).

been identified and so a discussion of mechanism is useless. This knowledge, although limited, of the behavior of the peroxide as an oxidizing agent in basic solution is essential to a later discussion of the acid-catalyzed reaction.

A sodium hydroxide catalyzed reaction of the peroxide with cyclohexene was investigated as a useful oxidation process. The formation of *trans*- α -hydroxycyclohexyl diphenylphosphinate probably proceeds through an epoxide intermediate but not enough data are available to justify presentation of a mechanism.

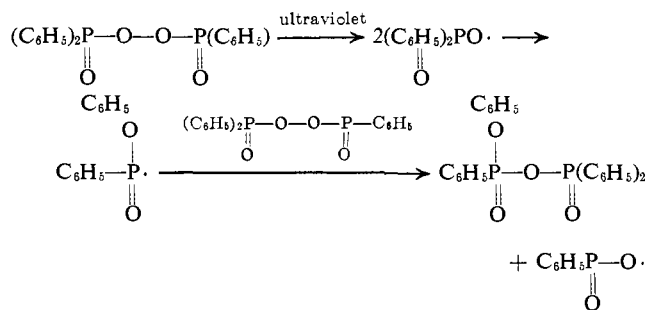
Acid-Catalyzed Decomposition of the Peroxide. The peroxide decomposition is also acid catalyzed. A pronounced rate enhancement is obtained by use of acids with greater ionization constants or by increasing the concentration of the acid (Table III). The order of the reaction with respect to different acid catalysts varies so that a Brønsted plot has no significance. The reaction in the aprotic solvent chloroform is undoubtedly complicated by dimerization of the acid catalyst as well as by concurrent catalysis by the conjugate base. The ratio of phosphorus acids produced (2 moles of diphenylphosphinic acid per mole of phenyl hydrogen phenylphosphonate) is that expected for a concurrent acid-catalyzed simple rearrangement and a base-catalyzed solvent oxidation. There were slight deviations in the ratios of phosphorus acids produced indicating that, as expected, with the stronger carboxylic acid catalysts (weaker conjugate bases), less solvent oxidation occurred. The analytical method (fractional crystallization of the products) was not precise enough to allow definite conclusions to be drawn.

By analogy to the acid-catalyzed carbon peroxide decompositions, the following mechanistic steps seem



reasonable. The data available pertaining to the acid-catalyzed rearrangement are not sufficient to clarify it completely. For example, the decomposition of the peroxide in glacial acetic acid has been classified as a thermal rearrangement, primarily because the energy of activation is identical with that in the aprotic solvents (*e.g.*, chloroform). The agreement is too close to be fortuitous. The alternative conclusion that all of the designated thermal decompositions are really acid catalyzed (by phosphorus acids produced during the decomposition) is unlikely because the reactions are not autocatalytic. The rate in glacial acetic acid (roughly 20 *M* but a very weak acid) is only four times as great as the rate in a chloroform solution 0.3 *M* in acetic acid. Obviously more data, including activation energies for the acid-catalyzed reactions, are needed.

Photochemically Induced Decomposition. The photolytic decomposition of the peroxide has been briefly studied. It is of importance to the present work because it clearly established the kinetics resulting from homolytic dissociation of the peroxide. Although the products were the same as those obtained from a thermal decomposition, the free-radical decomposition was unique in that the rate exhibited a second-order dependence on peroxide concentration (Figure 3). This rate dependence and product relationship are consistent with the following mechanism. Although



a free-radical site on phosphorus has often been proposed,¹⁴ the formation of such a radical site by a rearrangement process seems unusual.

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(14) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).