

OXIDATION OF ORGANOPHOSPHORUS COMPOUNDS—II¹

THE INFLUENCE OF pH UPON THE OXIDATION OF SOME DIARYL PHOSPHINE OXIDES BY PEROXYACIDS

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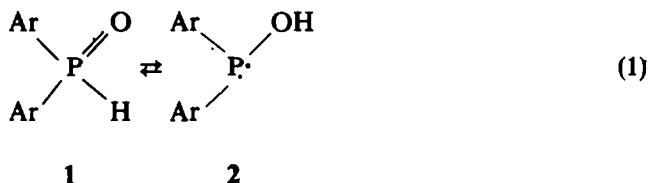
(Received in the UK 24 February 1970; Accepted for publication 7 April 1970)

Abstract—The influence of aqueous OH⁻ concentration in the solvent medium dioxan-water 40:60 upon the oxidation rates of diphenylphosphine oxide by peroxybenzoic acid (PBA) and *p*-nitroperoxybenzoic acid has been studied. In alkaline media, the substituent effects have been investigated by determining the rates of oxidation by PBA for a series of unsymmetrically substituted diarylphosphine oxides (X·C₆H₄)₂PhPHO [with X = *p*-OMe, *p*-Me, H, *p*-Cl] and for two symmetrically substituted terms (Y·C₆H₄)₂PHO [with Y = *p*-Me, *p*-Cl].

On the basis of the kinetic results, a mechanism involving nucleophilic attack by peroxyacid anions RCO₃⁻ on the phosphorus substrate is proposed for the reactions in alkaline media.

In a previous paper the general kinetic features of the oxidation reaction of secondary phosphine oxides by peroxybenzoic acid have been reported.¹

We wish to report here the results of a study upon the influence of the aqueous OH⁻ concentration on the rates and mechanism for the oxidation of some symmetrical and unsymmetrical diarylphosphine oxides **1** by peracids. For these substrates, the prototropic equilibrium (1) can be envisaged;¹ however, little is known about either the thermodynamics of this equilibrium or the rates of its attainment.



Our aim was to establish possible analogies (and/or differences) with our previous studies on the oxidation mechanism of organic sulphoxides by peroxyacids in alkaline and acidic media.²⁻⁴

For the latter compounds we were able to show that, although in acidic or neutral media oxidation of sulphoxides to sulphones occurs by means of nucleophilic attack by the sulphur compound on the peroxidic O—O bond,⁴ in alkaline media an alternative mechanism seems to be operative. This would imply nucleophilic attack by the peroxyacid anion at sulphur in the sulphoxide molecule.

RESULTS

The effect of changing the concentration of aqueous base OH⁻ on the oxidation rate of diphenylphosphine oxide Ph₂P(:O)H by peroxybenzoic acid PhCO₃H was

determined by running kinetic experiments in dioxan-water 40:60 (by volume) at increasing apparent pH (pH_{app}) and H_- values.^{2, 5}

The disappearance of the peroxide was followed by iodometric techniques, as already described.¹ For the experiments performed in the pH_{app} range from 1.30 to 11.60, the apparent pH value—as monitored by a standard glass electrode and a calomel reference electrode—was constant due to the presence of an excess of suitable inorganic buffers.² Owing to the relatively scarce solubility of some of the buffers employed (phthalate, phosphate or borate) in the mixed solvent adopted, initial concentrations of both reagents were usually kept relatively low [i.e., in the range $(0.5-0.9) \times 10^{-2}M$].

For the experiments performed in the H_- range from 13.48 to 14.60, KOH solutions in dioxan-water were made up so that the base was always in large excess over the initial concentration of both reactants (Table 1). Measurements of the H_- function⁵⁻⁷ were made following the spectrophotometric method given by Stewart and O'Donnell.⁷ The following indicators were employed: 4,4'-dinitrodiphenylamine (pK_a 14.08) and 2,4,4'-trinitrodiphenylamine (pK_a 12.35).⁷

Within the range explored it was found that the H_- scale could be anchored to the pH_{app} values as measured in the mixed solvent used (see Table 1 and Fig 1).

In most of the kinetic runs, EDTA disodium salt [$(0.1-0.3) \times 10^{-3}M$] was also added to sequester trace amounts of heavy metal ions (if any present), which might otherwise cause a rapid decomposition of the oxidizing species.^{8, 9}

Under the conditions given, the oxidation reactions were found to obey a second-order kinetic-law (first-order in each of the reagents) up to 80% reaction or more. Furthermore, it was verified that—in the entire pH_{app} (or H_-) range explored—the uncatalyzed self-decomposition^{8, 9} of the peroxyacid employed is too slow to influence appreciably the kinetics of the oxidation reactions.

Kinetic data are reported on Table 1; Fig 1 shows the effect of changing the OH^- concentrations on the log of observed k_2 values for the oxidation reaction. This plot shows (in the range pH_{app} 1 to 11) a characteristic profile, which is typical for specific base catalysis. Furthermore, in the pH_{app} range above, a plot of $\Delta(\log k_2)/\Delta(pH_{app})$ versus pH_{app} would show a maximum near to $pH_{app} \approx 9$, which corresponds to the estimated apparent pK_a value for peroxybenzoic acid in the same mixed solvent.² Therefore, the rate law would appear to be:

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{PBA}]}{dt} = \\ &= k_2'[\text{Ar}_2\text{PHO}][\text{PhCO}_3\text{H}] + k_2''[\text{Ar}_2\text{PHO}][\text{PhCO}_3^-] = \\ &= k_2(\text{obs})[\text{Ar}_2\text{PHO}][\text{PBA}] \end{aligned} \quad (2)$$

where, at all values of pH_{app} , the conditions are:

$$[\text{PBA}] = [\text{PhCO}_3\text{H}] + [\text{PhCO}_3^-] \text{ and } [\text{PhCO}_3^-]/[\text{PhCO}_3\text{H}] = K_a/[\text{H}_3\text{O}^+]$$

Hence:

$$k_2(\text{obs}) = [1/(B + 1)]k_2' + [B/(B + 1)]k_2'' \quad (3)$$

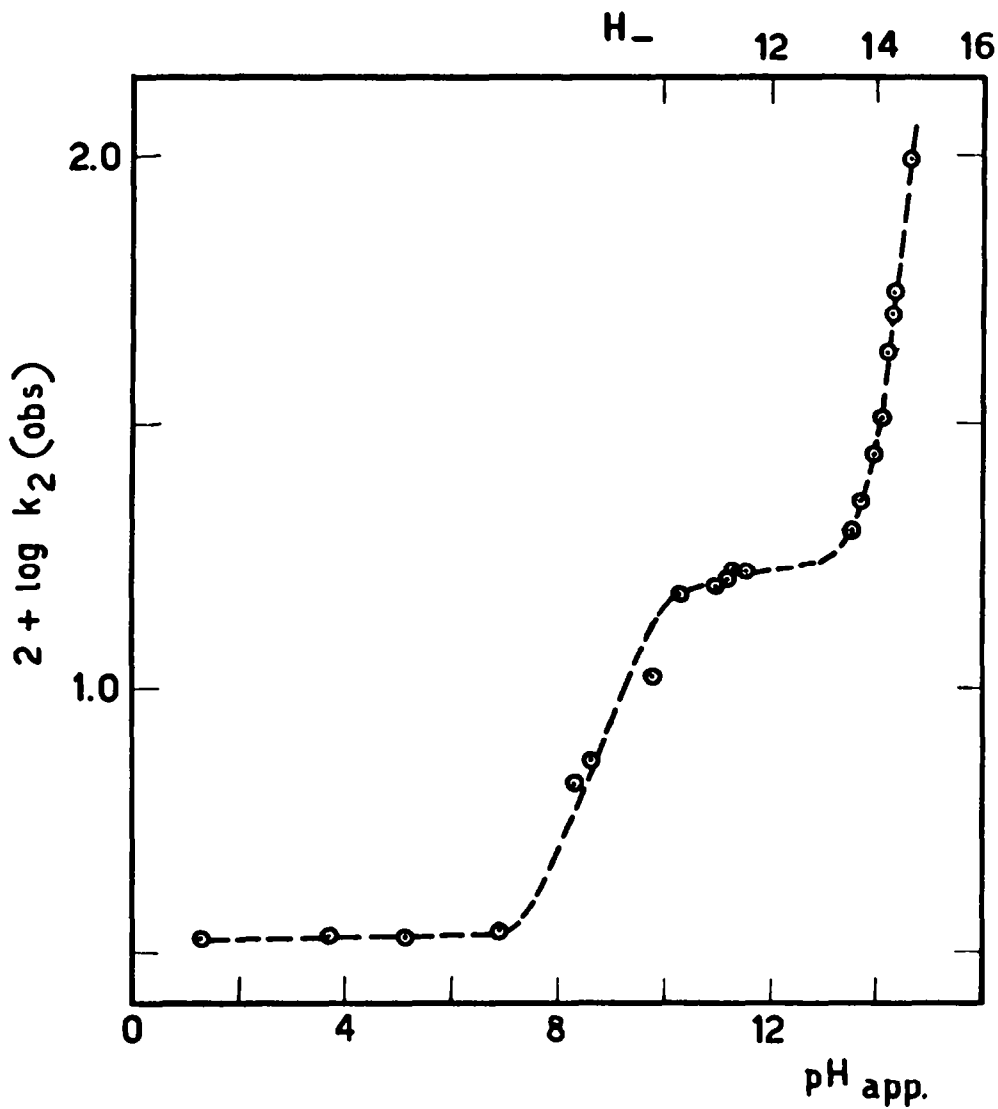


FIG 1. Rate of peroxybenzoic acid oxidation of diphenylphosphine oxide as a function of acidity

TABLE 1. OXIDATION RATES OF DIPHENYLPHOSPHINE OXIDE BY PEROXYBENZOIC ACID IN DIOXAN-WATER 40:60 AT VARIOUS BASICITIES OF THE SOLVENT MEDIUM^c

[OH ⁻], M	H ^d	pH _{app} ^b	10 ² k ₂ (obs) ^f		
			25°	15°	5°
—	—	1.30 ^e	3.37	—	—
—	—	3.6-3.4 ^f	3.30	—	—
—	—	3.70	3.38	—	—
—	—	5.10	3.30	—	—
—	—	6.85	3.42	—	—
—	—	8.30	6.58	—	—
—	—	8.60	7.24	—	—
—	—	9.80	10.40	—	—
—	—	10.30	14.9	—	—
—	—	11.10	15.3	—	—
—	—	11.20	16.1	—	—
—	—	11.30	16.7	—	—
—	—	11.50	16.6	—	—
—	11.50	11.60	16.5	—	—
(0.001)	11.95	12.00	—	—	—
0.005	12.45	12.50	—	—	—
0.030	13.50	—	19.7	9.62	—
0.035	—	—	—	—	6.06
0.050	13.70	—	22.3	—	—
0.055	—	—	—	11.8	—
0.080	—	—	—	15.3	10.1
0.090	13.95	—	27.8	—	—
0.100	14.05	—	32.8	—	—
0.150	14.20	—	43.2	—	—
0.180	—	—	—	30.0	18.2
0.190	14.30	—	50.2	—	—
0.200	14.35	—	55.7	—	—
0.385	14.60	—	97.4	—	—

^a Reactants concentrations were kept in the range $(0.5-1.0) \times 10^{-2}M$; $(0.2-0.4) \times 10^{-3}M$ EDTA disodium salt was present in all kinetic runs.

^b Unless otherwise indicated, in each kinetic run, the pH_{app} value was constant due to the presence of M 0.07 to M 0.09 phthalate, phosphate or borate buffers.

^c In M⁻¹ sec⁻¹; second-order rate constants, from second order integrated plots.

^d H_L acidity function values (at rt), measured by UV spectroscopy following the method given by Stewart and O'Donnell (Ref 7). See also Experimental.

^e M 0.1 HClO₄.

^f Unbuffered medium.

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF DIPHENYLPHOSPHINE OXIDE BY PEROXYBENZOIC ACID IN ALKALINE MEDIA, IN DIOXAN-WATER 40:60

	t, °C			ΔH [‡] , Kcal mole ⁻¹	ΔS [‡] , cal deg ⁻¹ mole ⁻¹
	25°	15°	5°		
10 ² k ₂ ^g , M ⁻¹ sec ⁻¹	10.6	4.91	2.95	11.1	- 30
10 ² k ₃ , M ⁻² sec ⁻¹	222	134	83.7	8.6	- 32

On the other hand, for the oxidation of diphenylphosphine oxide by PBA at relatively high OH^- concentrations (H_- values from 13.5 to 14.6), the peroxyacid might be considered present almost completely in the anion form PhCO_3^- . In this range, plots of k_2 (obs) values versus $[\text{OH}^-]$ (last thirteen entries on Table 1) gave satisfactory straight lines.

Consequently, the rate law for the reaction in solutions more alkaline than $\text{pH}_{\text{app}} 13$ seems to be:

$$\begin{aligned} \text{Rate} &= -d[\text{PhCO}_3^-]/dt = \\ &= k_2''[\text{Ar}_2\text{PHO}][\text{PhCO}_3^-] + k_3[\text{Ar}_2\text{PHO}][\text{PhCO}_3^-][\text{OH}^-] = \\ &= k_2(\text{obs})[\text{Ar}_2\text{PHO}][\text{PhCO}_3^-] \end{aligned} \quad (4)$$

where:

$$k_2(\text{obs}) = k_2'' + k_3[\text{OH}^-] \quad (5)$$

From the data shown on Table 2, by plotting $k_2(\text{obs})$ versus $[\text{OH}^-]$, the values of k_2 and k_3 could be obtained at each temperature; from these the activation parameters for both the catalyzed and $[\text{OH}^-]$ independent processes could be evaluated by the usual Arrhenius plots. The results are summarized on Table 2.

TABLE 3. SUBSTITUENT EFFECTS ON THE OXIDATION RATES OF SOME DIARYLPHOSPHINE OXIDES ($\text{Y}\cdot\text{C}_6\text{H}_4$) ($\text{X}\cdot\text{C}_6\text{H}_4$) $\text{P}(\text{O})\text{H}$ BY PEROXYBENZOIC ACID IN DIOXAN-WATER 40:60. TEMPERATURE 25.0°

at $\text{pH}_{\text{app}} 11.3$ (borate buffer)						
$\text{X} = \text{Y} =$	$\underline{p\text{-CH}_3}$	$\underline{\text{H}}$	$\underline{p\text{-Cl}}$			
$10^2 k_2(\text{obs})^a$	3.28	16.7	817	}	$\rho \approx 3.0$	
$\Sigma\sigma^b$	-0.340	0.00	+0.454			
at $H_- 14.0$ (0.10 M KOH)						
$\text{X} = \text{H}; \text{Y} =$	$\underline{p\text{-OCH}_3}$	$\underline{p\text{-CH}_3}$	$\underline{\text{H}}$	$\underline{p\text{-Cl}}$	$\underline{m\text{-Cl}}$	
$10^2 k_2(\text{obs})^a$	8.06	10.7	32.8	155.	480.	
σ^b	-0.268	-0.170	0.000	+0.227	+0.375	$\rho = 2.82$

^a $k_2(\text{obs})$ values are in $M^{-1}\text{sec}^{-1}$; ^b σ values are from H. H. Jaffe, *Chem. Revs* 53, 191 (1953)

As shown on Table 3, the substituent effects were studied by measuring the oxidation rates by PhCO_3^- of diphenylphosphine oxide and some symmetrically and unsymmetrically substituted secondary phosphine oxides at $\text{pH}_{\text{app}} 11.3$ and at $H_- 14.0$.

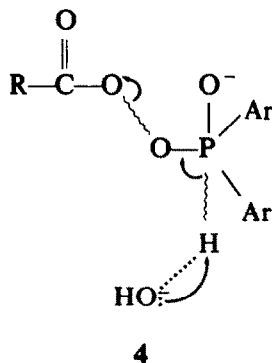
The results of a few experiments aimed to elucidate the effect of introducing an electron-withdrawing group such as $-\text{NO}_2$ in the peroxyacid aromatic ring on the oxidation rates in acidic and alkaline media are reported on Table 4.

DISCUSSION

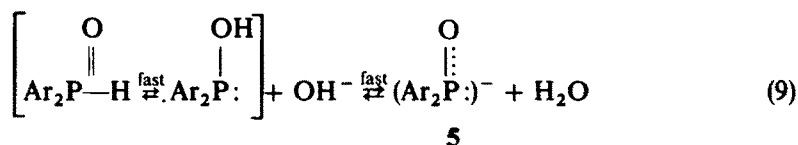
Two main mechanisms have been offered for the oxidation of diarylphosphine oxides in acidic media.¹

In alkaline media, taking into account the rate law found as well as the substituent

envisaged as in the scheme below.



The observed rate law, however, could also be consistent with a reaction path involving the preequilibrium formation of a diarylphosphine oxide (or diarylphosphinous acid) anion **5**, followed by reaction with the peroxyanion, i.e.:



However, it is difficult for us to envisage a simple mechanism to account for the oxygen transfer among $(\text{Ar}_2\text{PO})^-$ and the peroxyacid anion required by Eq (10). It could be expected, instead, that ionization of $\text{Ar}_2\text{P}(\text{:O})\text{H}$ to the corresponding anion, when becoming significant, should lead to a *decrease* in the oxidation rate.

Streuli *et al.* reported an apparent $\text{p}K_a$ value of 28.0 for diphenylphosphine oxide in *t*-BuOH;¹⁴ these authors have also shown that only those diarylphosphine oxides bearing relatively strong electron-withdrawing groups in the aromatic nucleus [i.e., bis(*m*-trifluoromethylphenyl)-, and bis(*p*-bromophenyl)phosphine oxide] are acidic enough to allow their apparent $\text{p}K_a$ values (12.5 and 12.7 respectively) to be measured in 95% EtOH.

The results seem to suggest it is unlikely that diphenylphosphine oxide has (in the mixed solvent adopted in this study) an apparent $\text{p}K_a$ value such as to allow its ionization reaction (9) to affect the kinetics significantly.

Nucleophilic attack by the peroxyacid on the substrate is supported by the faster rates in alkaline media found for both the peracids employed. Furthermore, some preliminary results indicate that oxidations of diphenylphosphine oxide in the same mixed solvent by H_2O_2 and *t*-BuOOH are extremely slow in acidic media whereas the oxidation proceeds in alkaline media at rates comparable with those observed for PhCO_3^- . This agrees with the mechanism outlined above and it is expected, since ROO^- is, of course, a better nucleophile than ROOH . The data collected so far seem to indicate that, in the reaction scheme (7), the breakdown of intermediate **3** to the products should be slow.

On this basis the effect of the substituents in the peroxyacid nucleus may be rationalized. The electronwithdrawing substituent $-\text{NO}_2$ would lower the nucleophilicity of the peroxyanion thus affecting the preequilibrium leading to the intermediate; however, the resultant intermediate will be less stable since the heterolysis of the O—O bond should proceed more easily. As a result one would expect the effect on k_1 and k_{11} to balance leading to a relatively small substituent effect as observed (estimated ρ value is roughly + 0.5).

On the other hand, electron-withdrawing substituents in the aromatic nucleus of $\text{Ph}_2\text{P}(\text{:O})\text{H}$ should have the effect of increasing k_1 by rendering the phosphorus reaction center more electropositive hence favoring nucleophilic attack by PhCO_3^- . The effect on k_{11} instead, is more difficult to predict. Indeed, while electron-withdrawing groups are expected to increase the stability of intermediate 3, they should also promote an easier cleavage of P—H bond (and perhaps of the O—O bond) in the t.s. of the rate determining step leading to the observed products. The relatively high and positive overall ρ values observed (+ 3.0 and + 2.8) in alkaline media seem to indicate that the latter effect is likely to prevail.

Further work is currently in progress to elucidate the kinetic aspects of the oxidation of diarylphosphine oxides by H_2O_2 and alkyl hydroperoxides at high aqueous base concentrations.

EXPERIMENTAL

Materials and solvents. Diphenylphosphine oxide, phenyl (*p*-methoxyphenyl)phosphine oxide, phenyl (*p*-chlorophenyl)phosphine oxide, phenyl (*m*-chlorophenyl)phosphine oxide, phenyl(*p*-tolyl)phosphine oxide, bis(*p*-chlorophenyl)phosphine oxide, bis(*p*-tolylphosphine oxide and peroxybenzoic acid samples employed in this study have been described.¹ *p*-Nitroperoxybenzoic acid, m.p. 136–137° (lit.¹⁵ m.p. 137°), was prepared and purified as reported by Vilkas.¹⁵ 70% HClO_4 , KH_2PO_4 , H_3BO_3 , NaOH and KOH used to make buffer and alkali standard solns were commercial AnalaR grade reagents (Merck or C. Erba). EDTA disodium salt, AnalaR grade (C. Erba), was employed without further purification. Dioxan and water solvents were purified by standard procedures, as already reported.¹

Kinetics. Kinetic measurements were performed in a thermostatic bath at $25.00 \pm 0.05^\circ$, $15.00 \pm 0.05^\circ$ and $5.00 \pm 0.10^\circ$.

Known volumes of standard solns of each reagent in the mixed solvent were added to a soln of the buffer and the EDTA in the mixed solvent dioxan-water 40:60 (by volume), which had been previously prepared at 25° , 15° or 5° .

At time intervals suitable aliquots of the reaction soln were withdrawn and the change in the peroxide concentration determined by following the iodometric technique already described.¹ The rate constant values reported on the Tables are usually average values from two or more independent runs, the estimated error being better than $\pm 3\%$ in the majority of the cases.

pH_{app} Measurements were made using standard glass electrodes by a W.T.W. (mod. 390) or Radiometer (mod. TTT 1) potentiometers.

H. Values for several KOH concentrations in the mixed solvent employed were obtained following the method described by Stewart and O'Donnell.⁷ Spectrophotometric estimation of the indicator ratios $[\text{BH}]/[\text{B}^-]$ were made through the equation $[\text{BH}]/[\text{B}^-] = (D_{\text{B}^-} - D)/(D - D_{\text{BH}})$ by measuring, for each solution, always containing the same stoichiometric amount of the indicator, the optical density D , after D_{B^-} and D_{BH} had been determined. D values were determined at the wavelength of maximum absorption of B^- , the completely ionized indicator, where D_{BH} was usually negligible or very small.^{5,7} 4,4'-Dinitrodiphenylamine, m.p. 216–217° [lit.¹⁶ m.p. 216–216.5°], $\text{p}K_{\text{a}}$ 14.08,⁷ U.V. (dioxane-water) λ_{max} 415 μm (ϵ_{BH} 30,700) and 575 μm (ϵ_{B^-} 45,800) and 2,4,4'-trinitrodiphenylamine, m.p. 192–192.5° [lit.¹⁷ m.p. 188–189°], $\text{p}K_{\text{a}}$ 12.35, UV λ_{max} 380 μm (ϵ_{BH} 14,800) and 515 μm (ϵ_{B^-} 43,800), were used as indicators in dioxane-water 40:60 solutions containing from 1.020 down to M 0.0005 KOH .

For KOH concentrations ranging from M 0.400 to M 0.005 or lower it was found that a plot of the H.

values determined versus $\log[\text{OH}^-]$ was linear with slope 1.01 ($r = 0.96$) which indicates that, in this range, the various ion activities coefficients ratios remained close to unity.

For both indicators, plots of $\log\left(\frac{[\text{B}^-]}{[\text{BH}]}\right)$ versus H_+ values as well as of H_+ versus pH_{app} (limitedly to the short range of overlapping) were also linear with slope 1.0.

Acknowledgements—Thanks are due to Prof. J. O. Edwards (Brown University, Providence, R.I., USA) for kind interest as well as many helpful discussions on the subject of this work.

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