

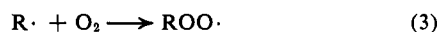
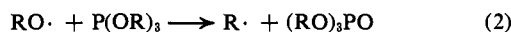
Absolute Rate Constants for the Reaction of *tert*-Butylperoxy Radicals with Trivalent Phosphorus Compounds¹

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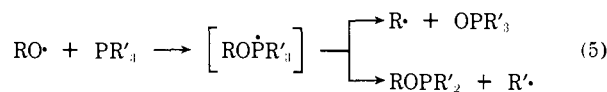
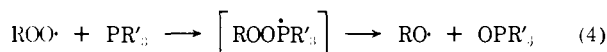
Abstract: Trivalent phosphorus compounds have been shown to react rapidly with *tert*-butylperoxy radicals by a simple bimolecular reaction. Absolute values of the rate constants for this reaction depend on the structure of the phosphorus compound and increase as the electron donating capacity of the α substituent increases.

Trivalent phosphorus compounds are known to react rapidly with molecular oxygen, particularly in the presence of radical sources such as α, α' -azobisisobutyronitrile (AIBN), to give pentavalent oxygenated products.² For example, trialkyl phosphites undergo autoxidation almost quantitatively to give trialkyl phosphates.^{3a-d} The free-radical nature of this reaction was recognized by Walling and Rabinowitz^{3a} who proposed that the reaction involved the following propagation steps



where $\text{ROO}\cdot$, $\text{RO}\cdot$, and $\text{R}\cdot$ represent alkylperoxy, alkoxy, and alkyl radicals, respectively, and $\text{P}(\text{OR})_3$ is a trialkyl phosphite. Reactions 1 and 2 are believed to proceed through the four-coordinate phosphoranyl radicals, $\text{ROOP}(\text{OR})_3$ and $\text{ROP}(\text{OR})_3$, which undergo β scission to give the reaction products. Phosphoranyl radicals of the structure, $\text{ROP}(\text{OR})_3$, have in fact recently been detected during photolysis of di-*tert*-butyl peroxide and trialkyl phosphites directly in the cavity of an esr spectrometer.⁴

The autoxidation of tertiary phosphines⁵ (PR'_3) is a more complex process principally because the intermediate phosphoranyl radical can undergo either β or α scission to give a phosphine oxide or alkyl dialkylphosphinite (ROPR'_2) (eq 4 and 5). Alkyl dialkyl-



phosphinites are also susceptible to autoxidation and react with alkoxy or alkylperoxy radicals to give either

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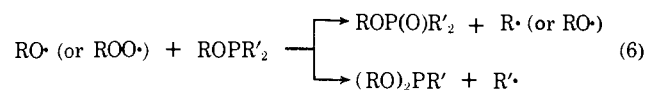
(2) (a) J. I. Cadogan, *Quart. Rev., Chem. Soc.*, **16**, 208 (1962); (b) C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, **3**, 1 (1966); (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, p 158ff.

(3) (a) D. G. Coe, *Nature (London)*, **181**, 1519 (1958); (b) J. I. G. Cadogan, M. Cameron-Wood, and W. R. Foster, *J. Chem. Soc.*, 2549 (1963); (c) J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **28**, 2908 (1963); (d) K. Smeykal, H. Baltz, and H. Fischer, *J. Prakt. Chem.*, **22**, 186 (1963); (e) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1243 (1959).

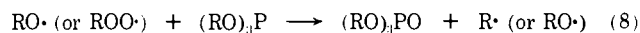
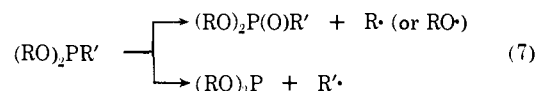
(4) (a) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3944 (1969); *Chem. Soc. Spec. Publ.*, No. 24, 147 (1970); (b) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed., Engl.*, **10**, 738 (1971).

(5) (a) P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Amer. Chem. Soc.*, **83**, 103 (1961); (b) S. A. Buckler, *ibid.*, **84**, 3093 (1962).

alkyl dialkylphosphinites or dialkyl alkylphosphonites (eq 6). Further autoxidation of dialkyl alkylphos-



phinite yields dialkyl alkylphosphonate, trialkyl phosphite, and trialkyl phosphate (eq 7 and 8).



Qualitative kinetic experiments^{5b} suggested that the overall rate of oxidation of tri-*n*-butylphosphine was independent of the phosphine concentration but was dependent on the oxygen pressure. Floyd and Boozer⁶ have subsequently studied the kinetics of the azobisisobutyronitrile-initiated autoxidation of tri-*n*-butylphosphine, tri-*n*-butyl phosphite, and triphenylphosphine in *o*-dichlorobenzene. The order of reactivity was found to be $(n\text{-Bu})_3\text{P} > (n\text{-BuO})_3\text{P} > (\text{Ph})_3\text{P}$. Kinetic data further indicated that the overall rate of oxidation of $(n\text{-Bu})_3\text{P}$ obeyed the kinetic expression

$$\frac{-d[\text{O}_2]}{dt} \propto \frac{[\text{AIBN}][n\text{-Bu}]_3\text{P}}{p_{\text{O}_2}} \quad (I)$$

where p_{O_2} represents the pressure of oxygen, while for $(\text{C}_6\text{H}_5)_3\text{P}$

$$\frac{-d[\text{O}_2]}{dt} \propto [\text{AIBN}][(\text{C}_6\text{H}_5)_3\text{P}] \quad (II)$$

This work also demonstrated that autoxidations of phosphorus(III) compounds have relatively long chain lengths (10^2 – 10^3) and that the chain propagation steps have almost zero activation energy.

Ogata and Yamashita⁷ have recently reported that overall rates of oxidation of trimethyl phosphite and methyl diphenylphosphinite obey eq II while triphenylphosphine fits a more complex kinetic expression.

Measurements of overall rates of oxidation of phosphorus(III) compounds have demonstrated the free-radical nature of these autoxidations. However, they have not enabled precise kinetic and relative reactivity

(6) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963).

(7) Y. Ogata and M. Yamashita, *J. Chem. Soc., Perkin Trans. 2*, 730 (1972).

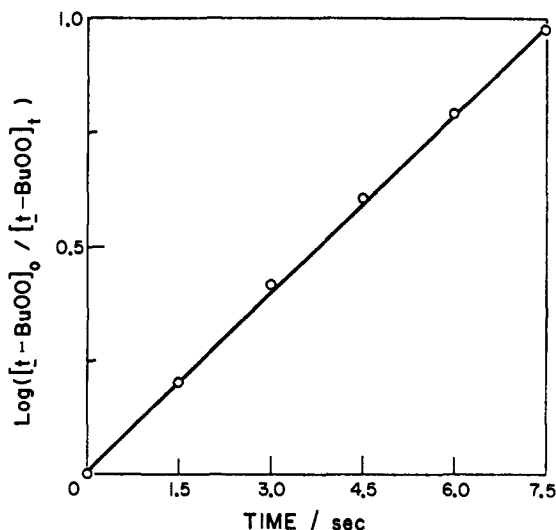
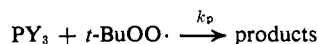


Figure 1. A first-order plot of log (relative radical concentration) vs. time for the disappearance of *tert*-butylperoxy radicals in the presence of trimethyl phosphite ($2.9 \times 10^{-2} M$) in isopentane at -86° .

data for this class of compounds to be determined. We have used kinetic electron spin resonance (esr) spectroscopic techniques⁸ to investigate the reaction of phosphorus(III) compounds (PY_3) with *tert*-butylperoxy radicals (*t*-BuOO·)



This method has enabled us to measure absolute values of k_p for a variety of phosphorus(III) compounds with different α substituents.

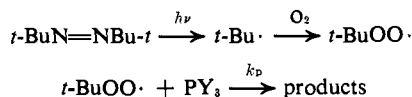
Experimental Section

Materials. Trimethyl, triethyl, triisopropyl, and triphenyl phosphites, triphenyl-, diphenyl-, diphenylmethyl-, and diphenylchlorophosphines, methyl diphenyl phosphinite, phosphorus trichloride, phosphorus tribromide, and phosphorus triiodide were commercial materials which were purified either by distillation or recrystallization. We are indebted to Dr. K. U. Ingold for samples of triallyl phosphite and 2-methoxy-1,3,2-dioxaphosphorinane and to Dr. G. B. Watts for a sample of tri-*tert*-butyl phosphite.⁹

Tris(*p*-methoxyphenyl)phosphine (mp $130\text{--}132^\circ$), tris(*p*-chlorophenyl)phosphine (mp $101\text{--}103^\circ$), tris(*p*-fluorophenyl)phosphine (mp $80\text{--}81.5^\circ$), and tris(*p*-methylphenyl)phosphine (mp $144\text{--}146^\circ$) were prepared from the respective arylmagnesium bromides and phosphorus trichloride.¹⁰

Isopentane (Phillips Research Grade) and Freon 11 (Matheson Coleman and Bell) were generally used as solvents without further purification. Toluene was used as a solvent for the tris(*p*-substituted phenyl)phosphines because these compounds were insoluble in either isopentane or Freon 11. Di-*tert*-butyl peroxide was percolated through alumina and distilled to remove hydroperoxidic impurities. 2,2'-Azobisobutane was obtained from Merck, Sharpe, and Dohme of Canada, Ltd.

Kinetic Procedure. *tert*-Butylperoxy radicals were generated by photolysis (using an Osram 200-W super pressure mercury lamp) of 2,2'-azobisobutane in an air-saturated inert solvent in the presence of a large excess (but known concentration) of the phosphorus(III) compound.



(8) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971).

(9) This compound was prepared by the method of V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964).

(10) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

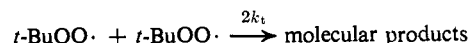
The reactions were performed in an esr tube (Suprasil, 4-mm o.d.) directly in the cavity of a Varian E-3 spectrometer equipped with a V-4557 variable temperature accessory. Reaction temperatures were carefully checked with a thermocouple. During photolysis the spectrometer was set at the magnetic field corresponding to the maximum peak height of the first derivative of the *tert*-butylperoxy radical signal¹¹ and the field sweep was switched off. Decays in the signal intensity were monitored when the initiating light was interrupted. Slow decays ($t_{1/2} > 1.5$ sec) were recorded on the X-Y recorder provided with the spectrometer while faster decays were accumulated in a Fabri-Tek 1072 signal averager. Initial radical concentrations were varied by up to a factor of 50 by inserting screens of known transmission between the light source and the reaction mixture. Absolute values of k_p were calculated from the expression

$$k_p (M^{-1} \text{sec}^{-1}) = \frac{2.303 \log \{ [t\text{-BuOO}\cdot]_0 / [t\text{-BuOO}\cdot]_t \}}{t [PY_3]_0}$$

where t was the time taken for the *tert*-butylperoxy radical concentration to fall from $[t\text{-BuOO}\cdot]_0$ to $[t\text{-BuOO}\cdot]_t$ and $[PY_3]_0$ was the initial concentration of phosphorus(III) compound. The constancy of k_p over a 50-fold change in $[t\text{-BuOO}\cdot]_0$ and a 50-fold change in $[PY_3]_0$ was used to test if the reaction was a simple bimolecular process. In general absolute values of k_p were accurate to about $\pm 50\%$. The principal sources of error were the reaction temperature, which varied by $\pm 2^\circ$ and the preparation of standard solutions of phosphorus(III) compounds.

Results and Discussion

(i) **Tertiary Phosphites.** Rates of decay of *tert*-butylperoxy radicals were determined in the presence of known concentrations of $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(i\text{-C}_3H_7O)_3P$, $(t\text{-C}_4H_9O)_3P$, $(CH_2=CH-CH_2O)_3P$, $(C_6H_5O)_3P$, and 2-methoxy-1,3,2-dioxaphosphorinane from -30 to -100° . In this temperature range, in the absence of added reactant, *tert*-butylperoxy radicals decayed by the self-reaction



with a rate constant, $2k_t$, that is given by the Arrhenius equation

$$2k_t (M^{-1} \text{sec}^{-1}) = 10^{9.2} \exp(-8.5/\theta)$$

with $\theta = RT \text{ kcal mol}^{-1}$.¹⁴ However, at phosphite concentrations $> 10^{-4} M$ radical decays were first order (e.g., Figure 1) which indicated that the self-reaction was completely suppressed.

The half-life of *t*-BuOO·, at a constant temperature, was proportional to the phosphite concentration and therefore the kinetic expression

$$\frac{-d[t\text{-BuOO}\cdot]}{dt} = k_p [t\text{-BuOO}\cdot] [(RO)_3P]$$

was strictly obeyed. Absolute values of k_p for trimethyl phosphite determined at different initial phosphite concentrations, radical concentrations, and temperatures are summarized in Table I and a plot of the

(11) A referee has suggested that phosphoranylperoxy radicals formed during oxidation may influence *tert*-butylperoxy radical decays. We could find no evidence for the production of phosphoranylperoxy radicals $t\text{-BuOO}(Y)_2\text{POO}\cdot$ during continuous irradiation. These radicals would be expected to have g factors similar to those for phosphoranylperoxy radicals of the structure $t\text{-BuO}(\text{MeO})_2\text{POO}\cdot$ ¹² and $t\text{-BuO}(C_6H_5)_2\text{POO}\cdot$ ¹³ which have g factors of 2.02. The large difference in g factors between a phosphoranylperoxy radical and the *tert*-butylperoxy radical ($g = 2.015$) eliminates the possibility that the production of the former radical could influence the decay of the latter radical.

(12) (a) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972); (b) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

(13) J. A. Howard and E. Furimsky, unpublished results.

(14) J. A. Howard, *Advan. Free Radical Chem.*, **4**, 49 (1972).

Table I. Kinetic Data for the Reaction of *tert*-Butylperoxy Radicals with Trimethyl Phosphite

Temp, °C	$10^2[(\text{CH}_3\text{O})_3\text{P}]_0, M$	$k_p, M^{-1} \text{sec}^{-1}$
-47	0.3	83
	0.87	105
	3.0	62
-55	0.3	48
	0.87	64
	3.0	53
-67.5	0.3	39
	0.87	46
	3.0	38
-76	0.3	21.5
	0.87	28
	3.0	27
-86	0.87	20
	3.0	19
	3.0	11
-95.5	0.87	11
	3.0	11

variation of $\log k_p$ with the reciprocal of the absolute temperature is given in Figure 2.

Similar kinetic data were obtained for the other phosphites and activation parameters and absolute values of k_p at -95° are listed in Table II.

Table II. Activation Parameters and Rate Constants at -95° for the Reaction of *tert*-Butylperoxy Radicals with Some Tertiary Phosphites

Phosphite	$\log(A_p/M^{-1} \text{sec}^{-1})$	$E_p, \text{kcal mol}^{-1}$	k_p° at $-95^\circ, M^{-1} \text{sec}^{-1}$
$(\text{CH}_3\text{O})_3\text{P}$	5.7	3.8	11
$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	5.0	3.3	17.5
$(i\text{-C}_3\text{H}_7\text{O})_3\text{P}$	6.2	4.3	14
$(t\text{-C}_4\text{H}_9\text{O})_3\text{P}$	6.3	5.5	0.5
$(\text{CH}_2=\text{CHCH}_2\text{O})_3\text{P}$	5.7	3.7	11
$(\text{C}_6\text{H}_5\text{O})_3\text{P}$	7.3	4.8	26
$\text{CH}_2\text{OP}(\text{OCH}_3)\text{OCH}_3$	6.0	4.6	7.5

^a Experimentally determined values.

The preexponential factors and activation energies for trimethyl, triethyl, triisopropyl, and triallyl phosphites are the same within experimental error and therefore these compounds have approximately the same reactivity to *t*-BuOO \cdot . Tri-*tert*-butyl phosphite is less reactive probably because of steric inhibition to the addition of *t*-BuOO \cdot to phosphorus for this compound. Triphenyl phosphite was consistently more reactive to *t*-BuOO \cdot than the other phosphites. It has been reported^{3b} that triaryl phosphites undergo autoxidation much less readily than trialkyl phosphites and that the addition of small quantities of triphenyl phosphite produces a significant decrease in the rate of autoxidation of trialkyl phosphites. These effects are probably because the intermediate alkylperoxytriphenoxyphosphoranyl radical can undergo α scission to give a phenoxy radical



which would react rapidly with a chain carrying peroxy radical. If this is the case a triaryl phosphite would have the same effect on an autoxidation as a phenol.¹⁴ It would also mean that the absolute values of k_p for

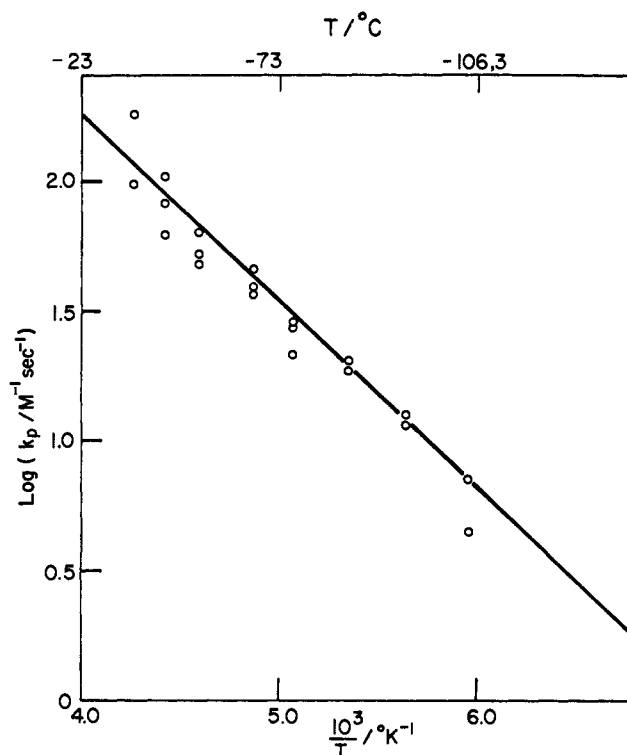
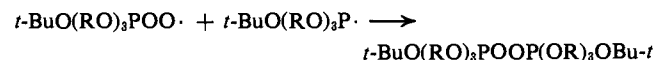


Figure 2. A plot of $\log k_p$ for trimethyl phosphite against the reciprocal of the absolute temperature.

triphenyl phosphite determined in this work are too large by a factor of 2 and a revised value of $k_p = 13 M^{-1} \text{sec}^{-1}$ at -95° implies that this phosphite has about the same reactivity to *t*-BuOO \cdot as most of the other phosphites.

The simple kinetics that we have found for the reaction of *tert*-butylperoxy radicals with trialkyl phosphites contrast with the more complex kinetics that have been determined for the disappearance of the phosphoranylperoxy radicals *t*-BuO(RO) $_3$ POO \cdot , in the presence of the appropriate phosphite (RO) $_3$ P (where R was CH $_3$, C $_2$ H $_5$, *i*-C $_3$ H $_7$, and *t*-C $_4$ H $_9$) by Watts and Ingold.^{12a} It was found that these phosphoranylperoxy radicals decayed by a second-order process below -85° . For example, rate constants for self-reaction ($2k_t$) at -90° were 1 to $6 \times 10^4 M^{-1} \text{sec}^{-1}$, considerably larger than the corresponding rate constant, $2k_t(-90^\circ) = 0.13 M^{-1} \text{sec}^{-1}$, for *tert*-butylperoxy radicals.

Although at temperatures from -45 to -70° the phosphoranylperoxy radicals decayed with first-order kinetics, rates of radical decay were only slightly dependent on the phosphite concentration even at phosphite concentrations as high as $0.3 M$. It was concluded that the radicals disappeared by the cross radical-radical reaction



Since in our case rates of *t*-BuOO \cdot decay were proportional to the phosphite concentration, an analogous radical-radical reaction would appear to be unimportant.

(ii) **Triarylphosphines.** *tert*-Butylperoxy radicals reacted rapidly with triphenylphosphine at low temperatures. Rates of radical decay were first order in

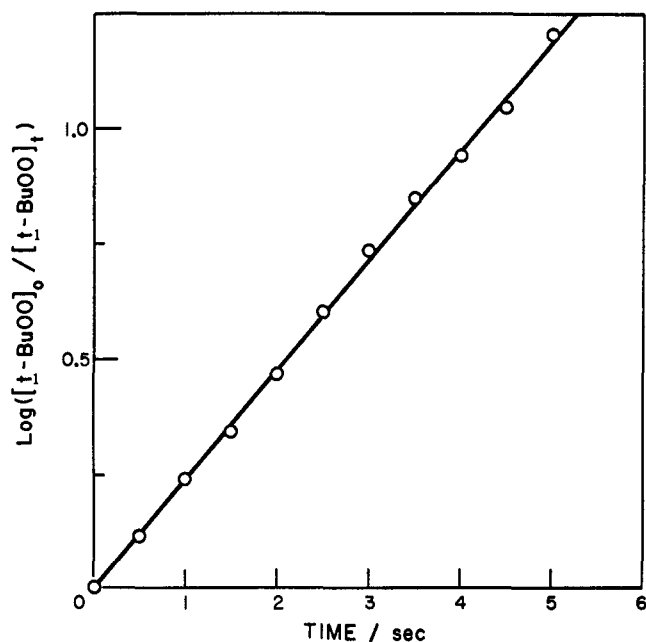


Figure 3. A first-order plot of log (relative radical concentration) vs. time for the disappearance of *tert*-butylperoxy radicals in the presence of triphenylphosphine ($9 \times 10^{-4} M$) in isopentane at -80° .

both the radical concentration (e.g., Figure 3) and the triphenylphosphine concentration, i.e.

$$\frac{-d[t\text{-BuOO}\cdot]}{dt} = k_p[t\text{-BuOO}\cdot][(C_6H_5)_3P]$$

Absolute values of k_p determined under different experimental conditions are listed in Table III and a plot

Table III. Kinetic Data for the Reaction of *tert*-Butylperoxy Radicals with Triphenylphosphine

Temp, $^\circ C$	$10^3[(C_6H_5)_3P]_0, M$	$k_p, M^{-1} \text{sec}^{-1}$
-60	0.4	770
-70	0.4	557
-70	0.9	570
-80	0.4	445
-80	0.9	340
-80	4.0	450
-90	0.4	305
-90	0.90	214
-90	4.0	330
-95	2.0 ^a	200
-95	2.0 ^b	190
-95	2.0 ^c	210
-100	0.4	175
-100	0.9	130
-100	4.0	150
-110	0.9	66
-120	0.9	32.5

^a $[t\text{-BuOO}\cdot]_0 = 4.0 \times 10^{-6} M$. ^b $[t\text{-BuOO}\cdot]_0 = 1 \times 10^{-6} M$. ^c $[t\text{-BuOO}\cdot]_0 = 4 \times 10^{-7} M$.

of the variation of $\log k_p$ with the reciprocal of the absolute temperature is shown in Figure 4. The Arrhenius equation for this compound is given by

$$k_p (M^{-1} \text{sec}^{-1}) = 10^6 \exp(-3.0/\theta)$$

with $\theta = RT \text{ kcal mol}^{-1}$. At -95° $k_p = 200 M^{-1} \text{sec}^{-1}$ and at this temperature triphenylphosphine is at

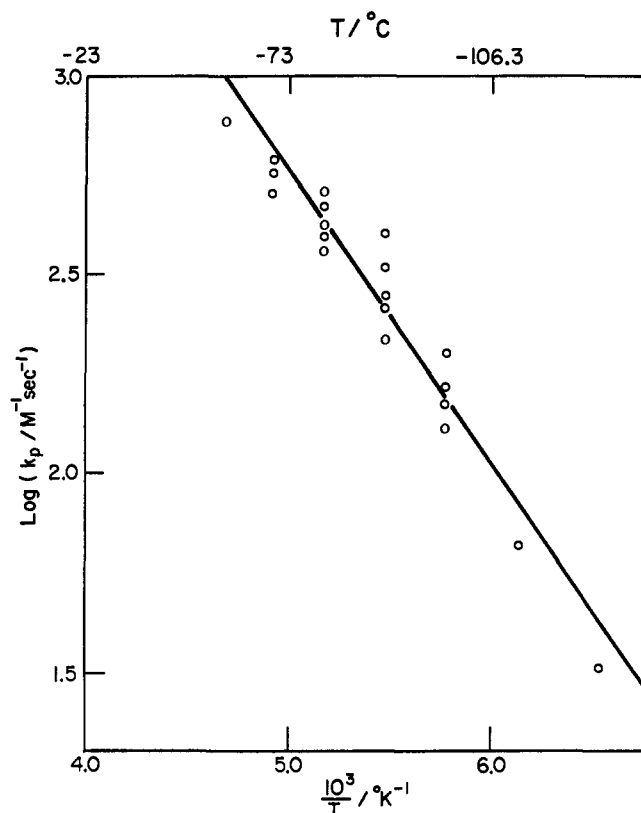


Figure 4. A plot of $\log k_p$ for triphenylphosphine against the reciprocal of the absolute temperature.

least 14 times as reactive as a trialkylphosphite to *t*-BuOO \cdot . The preexponential factors, A_p , for triphenylphosphine and trialkyl phosphites are very similar which implies that the differences in k_p are due principally to differences in the activation energy E_p .

Absolute reactivities of several tris(*p*-substituted phenyl)phosphines to *t*-BuOO \cdot were determined (Table IV) and they were found (with the exception of *p*-F)

Table IV. Activation Parameters and Rate Constants at -95° for the Reaction of *tert*-Butylperoxy Radicals with Some Triphenylphosphines

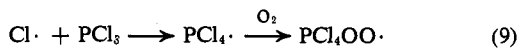
Phosphine	$\text{Log } (A / M^{-1} \text{sec}^{-1})$	$E, \text{ kcal mol}^{-1}$	$k_p^a \text{ at } -95^\circ, M^{-1} \text{sec}^{-1}$
$(C_6H_5)_3P$	6.0	3.0	200
$(p\text{-CH}_3\text{OC}_6\text{H}_4)_3P$	5.9	3.2	130
$(p\text{-ClC}_6\text{H}_4)_3P$	6.8	4.1	110
$(p\text{-FC}_6\text{H}_4)_3P$	5.9	3.1	200
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3P$	6.3	3.8	70

^a Experimentally determined values.

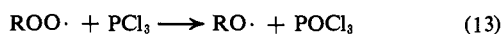
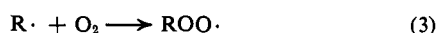
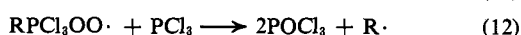
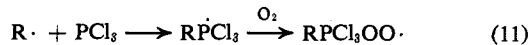
to be slightly less reactive than $(C_6H_5)_3P$. A *p*-methoxy substituent usually activates the benzylic hydrogens of an alkylaromatic compound to abstraction by a peroxy radical.¹⁴ This is because peroxy radicals are electrophilic and the *p*-methoxy group is a powerful electron donating group. Tris(*p*-methoxyphenyl)phosphine is, however, less reactive than triphenylphosphine to *t*-BuOO \cdot which implies that electron donation by conjugation is not important in this class of compounds. The difference in reactivity between the tris(*p*-substituted phenyl)phosphines and triphenylphosphine is

therefore most probably due to inductive withdrawal of electrons from the phosphorus.

(iii) **Phosphorus Trihalides.** The reaction of phosphorus trichloride with molecular oxygen to give phosphorus oxychloride occurs readily and competes with chlorophosphonation of hydrocarbons in the presence of PCl_3 .^{2,15} In the absence of added hydrocarbon the reaction is believed to involve the following propagation steps



while in the presence of a hydrocarbon the following additional reactions have to be considered



These three free-radical chain processes involve peroxy radicals as transient intermediates and their subsequent reaction with PCl_3 , *i.e.*, reactions 10, 12, and 13. To obtain some quantitative kinetic data for this reaction we have investigated the reaction of *t*-BuOO \cdot with PCl_3 and also with PBr_3 and PI_3 , *i.e.*, under conditions when reactions other than (13) were irrelevant. We were not able to obtain reproducible rate constants from decays of *t*-BuOO \cdot after interruption of the photolysis of azoisobutane, oxygen, and the phosphorus trihalide directly in the cavity of the spectrometer. This was probably because the facile photolysis of the phosphorus halide interfered with their reaction with *t*-BuOO \cdot . However, it was possible to generate *t*-BuOO \cdot at -95° and then add a known concentration of the phosphorus compound in the dark. Radical decays could then be followed after the reaction mixture had reached equilibrium. This technique was much less precise than the one described above for the determination of values of k_p for other organophosphorus compounds. However, because the values of k_p for the trihalides were relatively small we were able to demonstrate that k_p was independent of $[\text{t-BuOO}\cdot]_0$ and $[\text{PX}_3]_0$. Absolute values of k_p at -95° for PCl_3 and PBr_3 were 5.0 and $4.0 \text{ M}^{-1} \text{ sec}^{-1}$, respectively. Absolute values of k_p for PI_3 could not be estimated because *t*-BuOO \cdot was destroyed immediately when a $7.5 \times 10^{-3} \text{ M}$ solution of PI_3 was added. PI_3 would, therefore, appear to be more reactive than PBr_3 or PCl_3 to *t*-BuOO

(iv) **α -Substituted Diphenylphosphines.** Activation parameters and absolute values of k_p for diphenylphosphine, diphenylmethylphosphine, diphenyl methyl phosphinite, and diphenylchlorophosphine were determined and are summarized in Table V. The reactivity of these compounds at -95° to *t*-BuOO \cdot increases in the order $(\text{C}_6\text{H}_5)_2\text{P} < (\text{C}_6\text{H}_5)_2\text{POCH}_3 < (\text{C}_6\text{H}_5)_2\text{PH} < (\text{C}_6\text{H}_5)_3\text{P} < (\text{C}_6\text{H}_5)_2\text{PCH}_3$. This implies that the reactivity increases as the inductive electron donating capacity of the α substituent increases. When the values of $\log k_p$ were plotted against Taft's σ^* substituent con-

(15) F. R. Mayo, L. Durham, and K. Griggs, *J. Amer. Chem. Soc.*, **85**, 3156 (1963).

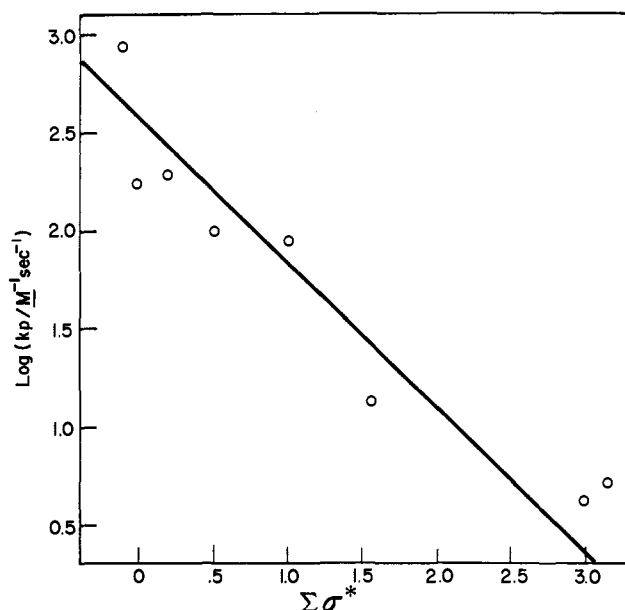


Figure 5. A plot of $\log k_p$ for the reaction of phosphorus(III) compounds with *tert*-butylperoxy radicals against Taft's $\Sigma\sigma^*$ values.

Table V. Activation Parameters and Rate Constants at -95° for the Reaction of *tert*-Butylperoxy Radicals with Some α -Substituted Diphenylphosphines

Phosphine	Log (A/M^{-1} sec^{-1})	E , kcal mol^{-1}	k_p^a at -95° , $M^{-1} \text{ sec}^{-1}$
$(\text{C}_6\text{H}_5)_3\text{P}$	6.0	3.0	200
$(\text{C}_6\text{H}_5)_2\text{PH}$	5.0	2.5	180
$(\text{C}_6\text{H}_5)_2\text{PCH}_3$	5.1	1.5	900
$(\text{C}_6\text{H}_5)_2\text{POCH}_3$	3.7	1.3	120
$(\text{C}_6\text{H}_5)_2\text{PCI}$	3.7	1.3	100

^a Experimentally determined values.

stants, a reasonably linear free-energy correlation was obtained. This correlation is shown in Figure 5 and the values of k_p fit the equation

$$\log(k_p/M^{-1} \text{ sec}^{-1}) = 2.6 - 0.75\Sigma\sigma^*$$

Included in this correlation are the values of $\log k_p$ for the tertiary alkyl phosphites (with the exception of $(\text{t-C}_4\text{H}_9\text{O})_3\text{P}$), PCl_3 , and PBr_3 plotted against $\Sigma\sigma^*$ (*e.g.*, $\Sigma\sigma^*$ for Cl was taken as 3×1.05). The σ^* values were taken from Bunnett's compilation¹⁶ and are the values obtained from the hydrolysis of esters of the structure $\text{XCH}_2\text{C}(=\text{O})\text{OR}$, *e.g.*, σ^* for $\text{C}_6\text{H}_5 = +0.22$, σ^* for $\text{CH}_3\text{O} = +0.52$, and σ^* for Cl = $+1.05$.

It would therefore appear from the relative reactivities of α -substituted phosphines and *para*-substituted phenylphosphines that the differences in k_p are due principally to polar effects.

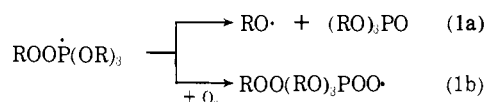
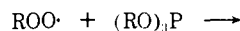
Henderson and Streuli¹⁷ have shown that the basicity of a tertiary phosphine is largely determined by the inductive effect of the substituents attached to phosphorus and $\text{p}K_a = 7.85 - 2.67\Sigma\sigma^*$. We would, therefore, anticipate that there should be a linear correlation between the basicity of phosphorus(III) compounds and their

(16) J. F. Bunnett, "Technique of Organic Chemistry," Vol. VIII, Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Eds., Interscience, New York, N. Y., 1961, Chapter VI.

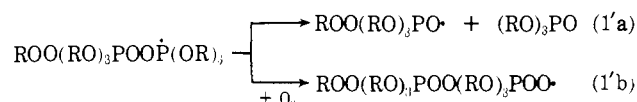
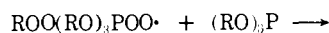
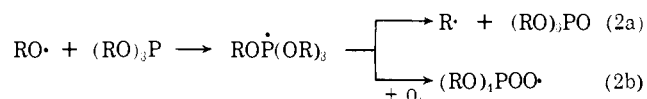
(17) N. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

reactivity to peroxy radicals. That is, the more basic the phosphorus compound the more reactive it would be to an electrophilic radical.

(v) **Mechanism of the Reaction of *t*-BuOO· with Phosphorus(III) Compounds.** The mechanism of the reaction of peroxy radicals (ROO·) with trialkyl phosphites has been generally represented by (1a). This

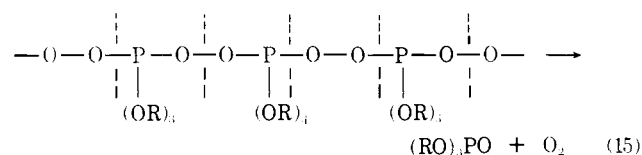


assumes that the rate of (1a) is faster than the rate of the reaction of the phosphoranyl radical with oxygen (1b). *tert*-Butoxytrialkoxyposphoranylperoxy radicals have, however, been detected by esr spectroscopy during photolysis of di-*tert*-butyl peroxide in an oxygen-saturated trialkyl phosphite.¹² Reactions 1a and 1b are therefore in competition and their relative importance must depend on the oxygen pressure as well as on R. The radicals formed in (1a) and (1b) would propagate the chain further by reacting with the phosphite (eq 2a,b). Thus at oxygen pressures at which all



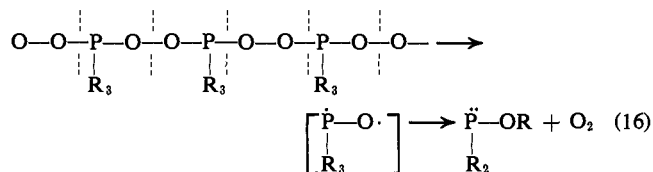
the phosphoranyl radicals react with oxygen the mechanism of autoxidation may be analogous to the one used to describe the copolymerization of an olefin with oxygen.¹⁸

Polyperoxides of the structures (O(RO)₃POOP(RO)₃O)_n are unknown but they could conceivably decompose to the identified reaction products



The production of several reaction products from tertiary phosphines could be because (1a) is more important than (1b) or because the peroxide can decompose by a route alternative to (15) (see eq 16). At the present time (15) and (16) are purely speculation but in view of the affinity of phosphoranyl radicals for oxygen they cannot be ruled out.

(18) F. R. Mayo, *Accounts Chem. Res.*, 1, 193 (1968).



(vi) **A Comparison of the Reactivities of Phosphorus(III) Compounds to *t*-BuOO· with Their Overall Rates of Oxidation.** Table VI summarizes the overall rates

Table VI. A Comparison of the Overall Rates of Oxidation of Some Phosphorus(III) Compounds with Their Absolute Reactivity to *t*-BuOO·.

Organo-phosphorus compd	Concn, M	[AIBN] ₀ , M	10 ⁴ (-d[O ₂]/dt) ₀ , M sec ⁻¹	k _p at -95°, M ⁻¹ sec ⁻¹
(C ₆ H ₅ O) ₃ P	0.4		<i>a</i>	13.0
(C ₆ H ₅ O) ₃ P	0.4	0.1	0.5	
(<i>t</i> -C ₄ H ₇ O) ₃ P	0.42		<i>a</i>	0.5
(<i>t</i> -C ₄ H ₇ O) ₃ P	0.42	0.1	6.3	
(C ₆ H ₅) ₃ P	0.45		2.0	200
(C ₆ H ₅) ₃ P	0.45	0.02	2.0	
(C ₆ H ₅) ₃ P	0.45	0.1	13.5	
(CH ₃ CH ₂ O) ₃ P	0.47		1.3	17.5
(CH ₃ CH ₂ O) ₃ P	0.47	0.02	4.4	
(CH ₃ CH ₂ O) ₃ P	0.47	0.1	16	
Cl ₃ P	0.49		<i>a</i>	5.0
Cl ₃ P	0.49	0.02	460	
Cl ₃ P	0.49	0.1	710	

^a No detectable rate of oxygen absorption. *o*-Dichlorobenzene was used as solvent.

of oxidation of the uninitiated and the AIBN initiated autoxidations of some phosphorus(III) compounds at 50° and at an oxygen pressure of 760 mm. The kinetic data in this table are very meager but they serve to illustrate the complex nature of these autoxidations. Thus tri-*tert*-butyl phosphite, triphenyl phosphite, and phosphorus trichloride do not absorb oxygen in the absence of AIBN while triethyl phosphite and triphenylphosphine absorb oxygen at an appreciable rate. The dependence of the rate of oxidation on the concentration of AIBN depends on the nature of the substrate. It is quite clear from a comparison of [-d[O₂]/dt]₀ and k_p that the relative reactivities to *t*-BuOO· do not follow the same order as the relative overall rates of oxidation. This is not surprising since the rate controlling chain propagating and terminating radicals are probably quite different in the various substrates.

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