# Homolytic Organometallic Reactions. Part VII.[1] An Electron Spin Resonance Study of the Reaction of t-Butoxyl Radicals with Trialkyl Phosphites: Kinetics of β-Scission of the t-Butoxytriethoxyphosphoranyl Radical

By **Alwyn G. Davies,* D. Griller, and B. P. Roberts,** Christopher Ingold Laboratories, University College, 20 Gordon Street, London WC1H OAJ

The oxidation in solution of trialkyl phosphites by t-butoxyl radicals has been studied using e.s.r. spectroscopy, and intermediate tetra-alkoxyphosphoranyl radicals [$a(^{31}P)$ *ca.* 900 G] have been detected. Rates of reactions (i) and (ii) were determined using e.s.r. spectroscopy to monitor the radical concentrations.

$$Bu^tO\cdot + P(OEt)_3 \longrightarrow Bu^t\cdot + OP(OEt)_3 \qquad (i)$$

$$Bu^tO\dot{P}(OEt)_3 \longrightarrow Bu^t\cdot + OP(OEt)_3 \qquad (ii)$$

The rate constants are given by the expressions log ($k_i$/l mol$^{-1}$ s$^{-1}$) = 9·83 − 2·24/θ and log ($k_{ii}$/s$^{-1}$) = 12·95 − 10·34/θ where θ = 2·303*RT* kcal mol$^{-1}$.

Tetra-alkoxyphosphoranyl radicals react with oxygen to give tetra-alkoxyphosphoranylperoxyl radicals [$a(^{31}P)$ *ca.* 9 G] which are detected by e.s.r. at low temperatures.

ALTHOUGH the majority of known reactions of phosphorus compounds proceed by heterolytic mechanisms, an increasing number of free-radical processes are being identified (reviewed in references 2—8).

The presence of unoccupied low energy *d*-orbitals makes valence-shell expansion of second-row elements possible. Thus a phosphorus(III) compound can react with a free-radical to increase the co-ordination number to four and give a phosphoranyl radical[9,10] with nine valence electrons [equation (1)].

$$Y\cdot + PX_3 \longrightarrow Y\dot{P}X_3 \qquad (1)$$

Tetra-alkoxyphosphoranyl radicals are proposed as intermediates in the oxidation of trialkyl phosphites by t-butoxyl or cumyloxyl radicals, generated thermally from the dialkyl peroxides [equations (2) and (3); R = Bu$^t$, Ph(Me)$_2$C].[10-12]

$$ROOR \longrightarrow 2RO\cdot \qquad (2)$$

$$RO\cdot + (EtO)_3P \longrightarrow RO\dot{P}(OEt)_3 \longrightarrow R\cdot + OP(OEt)_3 \qquad (3)$$

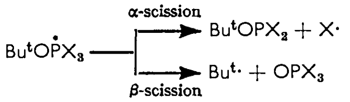
More recently reaction (3) has been studied by e.s.r. spectroscopy. When di-t-butyl peroxide was irradiated with high-intensity u.v. light in the presence of a trialkyl phosphite the e.s.r. spectrum of the t-butyl radical was observed, although the intermediate phosphoranyl radical was not detected.[13,14]†

However, when a solution of trimethylphosphine and di-t-butyl peroxide in cyclopropane was irradiated at low temperature, a phosphoranyl radical was detected[13,16] by e.s.r., although the methyl radical and not the t-butyl radical was observed in addition [equation (4); R = Me].

$$Bu^tO\cdot + PR_3 \longrightarrow Bu^tO\dot{P}R_3 \longrightarrow Bu^tOPR_2 + R\cdot \qquad (4)$$

Similar phosphoranyl species were also observed with phosphine, methylphosphine, and dimethylphosphine.[13,16] With higher trialkylphosphines no intermediate phosphoranyl radical was detected initially ‡ although an intense spectrum of the displaced radical R· [equation (4)] was observed.[13,16,17]

The phosphoranyl radical produced by addition of a t-butoxyl radical to a trivalent phosphorus compound may undergo either α- or β-scission depending on the nature of the groups attached to phosphorus and the conditions of the reaction.[7,8]



$$Bu^tO\dot{P}X_3 \begin{cases} \xrightarrow{\alpha\text{-scission}} Bu^tOPX_2 + X\cdot \\ \xrightarrow[\beta\text{-scission}]{} Bu^t\cdot + OPX_3 \end{cases} \qquad (5)$$

We report here the detection by e.s.r. of phosphoranyl intermediates in the reaction of t-butoxyl radicals with trialkyl phosphites, and the use of this technique in the study of the kinetics of the reaction.

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† We understand from Professor Kochi that he has now been able to detect an intermediate phosphoranyl radical in these reactions.[15]

‡ On prolonged photolysis phosphoranyl species were detected but these are thought to arise from the reaction of t-butoxyl radicals with the $R_2POBu^t$ produced in reaction (4).[15,17]

[1] Part VI, A. G. Davies, T. Maki, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 744.

[2] J. I. G. Cadogan, *Quart. Rev.*, 1962, **16**, 226.

[3] R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, London, 1965, ch. 9.

[4] C. Walling and M. S. Pearson, *Topics Phosphorus Chem.*, 1966, **3**, 1.

[5] A. J. Kirby and S. G. Warren, 'The Organic Chemistry of Phosphorus,' Elsevier, Amsterdam, 1967.

[6] J. I. G. Cadogan, *Adv. Free Radical Chem.*, 1968, **2**, 203.

[7] A. G. Davies and B. P. Roberts, *Nature Phys. Sci.*, 1971, **229**, 221.

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[9] F. Ramirez and N. McKelvie, *J. Amer. Chem. Soc.*, 1957, **79**, 5829.

[10] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, 1957, **79**, 5326.

[11] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, 1958, **81**, 1243.

[12] C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262.

[13] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

[14] A. Hudson and H. A. Hussain, *J. Chem. Soc.* (*B*), 1969, 793.

[15] P. J. Krusic, W. Mahler, and J. K. Kochi, unpublished results.

[16] J. K. Kochi and P. J. Krusic, *Chem. Soc. Spec. Publ.*, No. 24, 1970, 147.

[17] R. W. Dennis, unpublished results from this laboratory.

## EXPERIMENTAL

A Varian E-4 e.s.r. spectrometer was used in conjunction with a Mazda 1 kW ME/D mercury lamp with a lens system as described.[18] The intensity of light incident on the sample was varied by placing metal gauze of different transmittance, measured with a spectrophotometer, in the light path. The heating effect of irradiation at different light intensities was measured with a chromel–alumel thermocouple protected from direct irradiation. The field setting dial of the spectrometer was shown to be linear over a range of ±400 G about 3300 G, by recording the spectrum of oxovanadium(IV) acetylacetonate in benzene.[19] *g*-Factors were measured by comparison with naphthacene in concentrated sulphuric acid (*g* 2·00260) contained in narrow glass capillaries immersed in the samples. Radical concentration measurements were carried out as described previously, employing the first-moments of the signals in derivative presentation.[18]

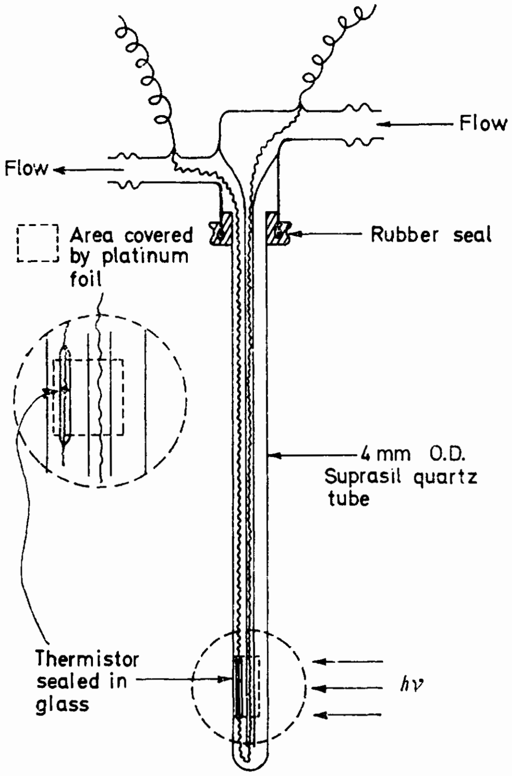


FIGURE 1 E.s.r. flow cell used to measure the kinetics of the competition between triethyl phosphite and cyclopentane for t-butoxyl radicals

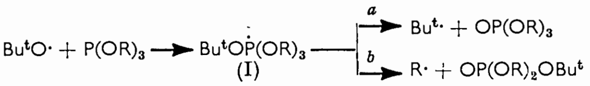
Di-t-butyl peroxide was Koch–Light pure grade and was passed through activity 1 basic alumina (Woelm) before use. 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (II) [20] and 2,8,9-trioxa-1-phospha-adamantane (III) [21] were prepared as previously described. Tricyclopentyl phosphite was prepared from cyclopentanol and tris(dimethylamino)phosphine;[22] b.p. 102—104° at 0·1 mmHg. Trineopentyl phosphite was a gift from Dr. H. R. Hudson and Mr. J. Weekes of the Polytechnic of North London. The remaining trialkyl phosphites were commercial products; the trimethyl and triethyl phosphite were distilled under nitrogen from sodium. Attempts to prepare 2,6,7-trioxa-1-phosphabicyclo[2,2,1]heptane were unsuccessful.[23]

In the experiment to measure the competition between triethyl phosphite and cyclopentane for the t-butoxyl radical the reaction mixture had to be continuously flowed (*ca.* 3 ml min$^{-1}$) through the sample tube in order to avoid selective depletion of the more reactive phosphite. Increasing the flow rate did not affect the radical concentrations observed. The temperature of the flowing solution was continuously monitored using a digital voltmeter connected to a calibrated thermistor positioned in the photolysis region but protected from direct radiation by platinum foil. The sample cell which was contained in the standard Varian variable temperature probe is shown in Figure 1. For the other reactions the sample preparation technique used was that described previously.[18]

The spectra described in the text were observed only in the presence of both phosphite and dialkyl peroxide. When 2,2′-azoisobutane was photolysed in the presence of triethyl phosphite only the t-butyl radical was observed and no phosphoranyl species was detected in the temperature range covered by the kinetic experiments. No phosphoranyl radicals were detected when di-t-butyl peroxide was irradiated in the presence of triethyl phosphate. When methyl or n-butyl radicals were generated in the presence of triethyl phosphate neither phosphoranyl radicals (at −40°) nor ethyl radicals (at +52°) were detected.

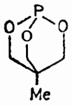
## RESULTS AND DISCUSSION

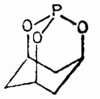
When a solution, usually in cyclopentane, of a trialkyl phosphite (10% v/v) and di-t-butyl peroxide (15% v/v) was irradiated at −70° the e.s.r. spectra of the tetra-alkoxyphosphoranyl radicals (I) listed in Table 1 were observed. The less soluble caged phosphites (II) and (III) were examined in toluene solution.


(6)

$$\mathrm{Bu^tO\cdot + P(OR)_3 \longrightarrow \underset{(I)}{Bu^tO\dot{P}(OR)_3} \longrightarrow \begin{cases} \xrightarrow{a} \mathrm{Bu^t\cdot + OP(OR)_3} \\ \xrightarrow{b} \mathrm{R\cdot + OP(OR)_2OBu^t} \end{cases}} \qquad (6)$$

(II)





(III)

The phosphites listed in Table 1 showed a large doublet splitting from phosphorus, with no further fine structure (see Figure in reference 24). The high-field line was usually broader than the low-field line, especially at low temperature.

In addition to the e.s.r. spectrum of the phosphoranyl radical (I), that of the t-butyl radical formed by β-scission of (I) was detected for the phosphites listed in Table 1 [equation (6*a*)]. The overall oxidation of triethyl

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[18] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[19] R. N. Rogers and G. N. Pake, *J. Chem. Phys.*, 1960, **33**, 1107.

[20] C. W. Heitch and J. G. Verkade, *Inorg. Chem.*, 1962, **1**, 393.

[21] K. D. Berlin, C. Hildebrand, J. G. Verkade, and O. C. Dermer, *Chem. and Ind.*, 1963, 291.

[22] R. Burgada, *Ann. Chim. France*, 1963, **8**, 347.

[23] R. S. Edmundson and E. W. Mitchell, *J. Chem. Soc.* (*C*), 1971, 3179.

[24] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

phosphite by t-butoxyl radicals to give phosphate and t-butyl radicals is *ca.* 62 kcal mol$^{-1}$ exothermic.

Table 1

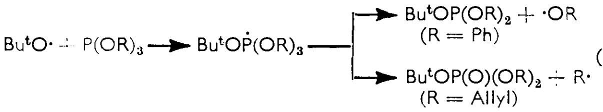
E.s.r. parameters of trialkoxy(t-butoxy)phosphoranyl radicals (I) in solution at −70°

| Trialkyl phosphite | Solvent | $a(^{31}P)$ [a] G | $g$ [a] |
|---|---|---|---|
| $(MeO)_3P$ [b] | C [c] | 891·5 | 2·004 |
| $(EtO)_3P$ | C | 890·3 [d] | 2·003 |
| $(EtO)_3P$ | T [c] | 887·1 | 2·003 |
| $(ClCH_2CH_2O)_3P$ | T | 908·5 | 2·003 |
| $(Bu^nO)_3P$ | C | 891·9 | 2·004 |
| $(Bu^nO)_3P$ | T | 886·7 | 2·004 |
| $(Pr^iO)_3P$ | C | 902·3 | 2·003 |
| $(Bu^tO)_3P$ | C | 920·0 | 2·004 |
| $(c\text{-}C_5H_9O)_3P$ | C | 902·3 | 2·003 |
| $(neo\text{-}PentO)_3P$ | C | 904·2 | 2·003 |
| (II) | T | 973·2 | 2·004 |
| (III) | T | 955·7 | 2·004 |

[a] These parameters were determined using the measured line positions and the microwave frequency in conjunction with the Breit–Rabi formula.[25] [b] Other phosphoranyl species were present especially at higher temperatures, and the origin of these radicals is currently being investigated. [c] C ≡ Cyclopentane; T ≡ Toluene. [d] The temperature dependence of the phosphorus hyperfine splitting was measured in this case. [$a(^{31}P)$/G, T/°C]: 893·1, −20; 891·9, −40; 890·5, −60; 889·1, −80; 888·1, −90.

As the temperature was increased, the concentration of t-butyl radicals increased at the expense of the phosphoranyl radical. With a tri-primary-alkyl phosphite and the caged phosphite, the t-butyl radical was the only alkyl radical detected. With tricyclopentyl phosphite, although the t-butyl radical predominated at 20° in di-t-butyl peroxide solvent, a small concentration of cyclopentyl radicals was also detected ($[Bu^t\cdot]/[c\text{-}C_5H_9\cdot]$ *ca.* 11). Thus even though loss of a cyclopentyl radical [equation (6*b*)] is statistically favoured, loss of the more stable t-butyl radical is still the dominant β-scission process. With tri-isopropyl phosphite, overlap of the spectra of the t-butyl and isopropyl radicals prevented an accurate estimate of the concentration of the latter, although they were probably present ($[Bu^t\cdot]/[Pr^i\cdot]$ *ca.* 20 at 20°).

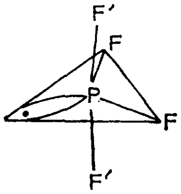
No phosphoranyl radicals were detected with triphenyl phosphite or triallyl phosphite at −90° in toluene



$$Bu^tO\cdot + P(OR)_3 \longrightarrow Bu^tO\dot{P}(OR)_3 \longrightarrow \begin{cases} Bu^tOP(OR)_2 + \cdot OR \quad (R = Ph) \\ Bu^tOP(O)(OR)_2 + R\cdot \quad (R = Allyl) \end{cases} \tag{7}$$

or iso-octane respectively. This is apparently due to rapid scission of the phosphoranyl radical in both cases.[13]

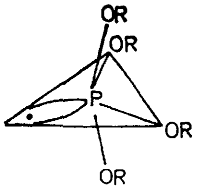
*Stereochemistry of Tetra-alkoxyphosphoranyl Radicals.*—Higuchi's[26] calculations predict a slightly distorted trigonal bipyramidal structure for the tetrafluorophosphoranyl radical, (IV), with $\widehat{F'PF'}$ 174 ± 5° and $\widehat{FPF}$ 109 ± 9°, and the orbital of the unpaired electron occupying a position in the equatorial plane.



(IV)

The isotropic phosphorus hyperfine splitting constant in $\dot{P}F_4$ is 1330 G,[27] and the value of $a(^{31}P)$ decreases in the series $\dot{P}F_4 > \dot{P}Cl_4 > Me\dot{P}Cl_3$.[28] It is not unreasonable to associate this change with the relative electronegativities of the groups attached to phosphorus and a greater distortion of the trigonal bipyramid towards a square pyramidal structure, giving rise to a decreased proportion of *s*-character in the orbital of the unpaired electron.[28] On this basis, tetra-alkoxyphosphoranyl radicals are expected to have a smaller value of $a(^{31}P)$ than $\dot{P}F_4$ and $\dot{P}Cl_4$, as observed, and to be more distorted from the trigonal bipyramid than either. Substitution of alkyl groups for alkoxy should further decrease the phosphorus hyperfine splitting and the value of $a(^{31}P)$ in $Me_3\dot{P}OBu^t$ is reported to be only 618 G.[13,16] Reference to Table 1 shows that there is an increase in the value of $a(^{31}P)$ of 21·4 G on going from $(EtO)_3\dot{P}OBu^t$ to $(ClCH_2CH_2O)_3\dot{P}OBu^t$, which is again consistent with the increased electronegativity of the 2-chloroethyl groups compared with ethyl.

Table 1 also shows that there is an increase in the value of $a(^{31}P)$ with increasing bulk of the alkyl groups in the trialkyl phosphite, especially on α-branching of the alkyl group. Steric repulsion would be expected to increase both the axial and equatorial OPO angles in (V), but reference to Higuchi's[26] calculations on $\dot{P}F_4$ leads us to expect these deformations to have opposing effects on $a(^{31}P)$: an increase in $\widehat{OPO}$ (axial) should increase the value of $a(^{31}P)$, whereas an increase in $\widehat{OPO}$ (equatorial) should decrease it.



(V)

A distorted trigonal bipyramidal structure (VI) is also likely for the phosphoranyl radicals derived from the caged phosphites (II) and (III).

In (VI) the t-butoxy-group is assumed to take up the

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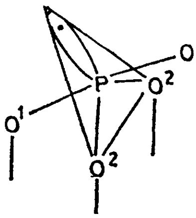
[25] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 238.

[26] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[27] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.

[28] G. F. Kokoszka and F. Brinckman, *Chem. Comm.*, 1968, 349; *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

axial position using the rule of Muetterties *et al.*[29] in which the more electronegative groups prefer to take



(VI)

up the axial positions in five-co-ordinate trigonal bipyramidal phosphoranes. In the parent phosphites[30] (II) and (III) $O^2\widehat{P}O^2$ is *ca.* 104°, and the angle between $O^1P$ and the plane $O^2PO^2$ can be calculated as 95°. These angles could remain similar in a trigonal bipyramidal phosphoranyl radical. The increased value of $a(^{31}P)$ compared with that of the radicals derived from the acyclic phosphites could be due to $O^1\widehat{P}OBu^t$ being greater, and $O^2\widehat{P}O^2$ being less, than the corresponding preferred angles in the acyclic radicals.

*Tetra-alkoxyphosphoranylperoxyl Radicals.*[31]—When a solution containing a dialkyl peroxide in a trialkyl phosphite was irradiated with u.v. light at low temperature (−70°) in the presence of oxygen, the spectrum of the tetra-alkoxyphosphoranyl radical was quenched and replaced by a strong doublet spectrum with a much smaller phosphorus hyperfine splitting (see Table 2). The low value of $a(^{31}P)$ and the *g*-value are consistent with the assignment of these spectra to the tetra-alkoxyphosphoranylperoxyl radicals.

$$\mathrm{RO\dot{P}(OR')_3 + O_2 \longrightarrow RO(R'O)_3POO\cdot} \qquad (8)$$

When the photolysis was conducted at higher temperature (−40°) the spectrum of the tetra-alkoxyphosphoranylperoxyl radical persisted for only a short time (*ca.* 1 min) before being replaced by that of the phosphoranyl radical. This is consistent with rapid removal of oxygen by a chain process [equations (9)—(11)].

$$\mathrm{(RO)_4PO_2\cdot + (RO)_3P \longrightarrow (RO)_4PO\cdot + (RO)_3PO} \qquad (9)$$

$$\mathrm{(RO)_4PO\cdot + (RO)_3P \longrightarrow (RO)_4P\cdot + (RO)_3PO} \qquad (10)$$

$$\mathrm{(RO)_4P\cdot + O_2 \longrightarrow (RO)_4PO_2\cdot} \qquad (11)$$

Reactions (9) and (10) probably take place through intermediate phosphoranyl radicals[8] and the radical $(RO)_4PO\cdot$ may undergo β-scission [equation (12)] faster than it is reduced [equation (10)]. Reactions of the type (9)—(12)

$$\mathrm{(RO)_4PO\cdot \longrightarrow (RO)_3PO + RO\cdot} \qquad (12)$$

probably participate in the free-radical chain autoxidation of trialkyl phosphites,[11,12,32] especially at low temperatures when β-scission of a tetra-alkoxyphosphoranyl radical [equation (13*a*)] will be retarded relative to its reaction with oxygen [equation (13*b*)].

$$\mathrm{(RO)_4P\cdot} \begin{cases} \xrightarrow[a]{\beta\text{-scisson}} \mathrm{(RO)_3PO + R\cdot} \\ \xrightarrow[b]{\mathrm{O_2}} \mathrm{(RO)_4PO_2\cdot} \end{cases} \qquad (13)$$

Phosphoranylperoxyl radicals have been suggested previously as reactive intermediates although they have not been detected by e.s.r. spectroscopy. It has been proposed[33] that $RO(EtO)_3PO_2\cdot$ is the hydroxylating species when aromatic compounds react with mixtures of triethyl phosphite and oxygen [*e.g.* equation (14)].

TABLE 2

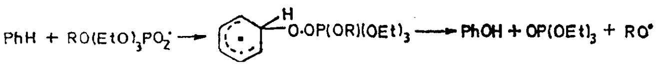
E.s.r. parameters for tetra-alkoxyphosphoranylperoxyl radicals in cyclopentane at −70°

| $RO(EtO)_3POO\cdot$ | $a(^{31}P)$ G | *g* |
|---|---|---|
| R = Bu$^t$ | 9·45 | 2·021 |
| R = Et * | 9·25 | 2·022 |

* Produced by photolysis of diethyl peroxide in the presence of triethyl phosphite and oxygen. Phosphoranyl radicals derived from photolysis of diethyl peroxide in the presence of phosphorus(III) compounds are being studied.

A similar phosphoranylperoxyl species is probably responsible for the deoxygenation of pyridine *N*-oxide by triethyl phosphite in the presence of oxygen.[34] The radicals $Cl_3(R)PO_2\cdot$ and $Cl_4PO_2\cdot$ are thought to be involved in the chlorophosphonation of hydrocarbons by mixtures of phosphorus trichloride and oxygen.[35]

*Kinetic Studies.*—The overall rate of production of t-butyl radicals from t-butoxyl radicals and triethyl phosphite was measured using kinetic e.s.r. spectroscopy by causing the phosphite to compete with cyclopentane for reaction with the alkoxyl radicals.[18] Because of the large reactivity difference it was found necessary to flow the sample through the reaction cell to avoid a rapid change in the reactant ratio. The kinetics of the β-scission of the t-butoxytriethoxyphosphoranyl radical to give a t-butyl radical and triethyl phosphate were also investigated.



(14)

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[29] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613; E. L. Muetterties, W. Mahler, J. K. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298; see also P. Gillespie, P. Hoffman, H. Khusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew Chem. Intern. Edn.*, 1971, **10**, 687.

[30] J. G. Verkade and R. W. King, *Inorg. Chem.*, 1962, **1**, 948.

[31] An independent study of these radicals will be reported: G. B. Watts and K. U. Ingold, unpublished.

[32] K. Smeykal, H. Baltz, and H. Fischer, *J. prakt. Chem.*, 1963, **22**, 186; T. B. Plumb and C. E. Griffin, *J. Org. Chem.*, 1963, **28**, 2908; J. I. G. Cadogan, M. Cameron-Wood, and W. R. Foster, *J. Chem. Soc.*, 1963, 2549.

[33] R. Higgins, K. M. Kitson, and J. R. Lindsay Smith, *J. Chem. Soc.* (*B*), 1971, 430.

[34] T. R. Emmerson and C. W. Rees, *J. Chem. Soc.*, 1962, 1917.

[35] F. R. Mayo, L. Y. Durham, and K. S. Griggs, *J. Amer. Chem. Soc.*, 1963, **85**, 3156.

All experiments were carried out in cyclopentane solvent but the cyclopentyl radical only became apparent when the concentration of triethyl phosphite was reduced to $10^{-1}$—$10^{-2}$M. In the measurements of the rate of β-scission of the phosphoranyl radical the concentration of triethyl phosphite was *ca.* 1M and the concentration of cyclopentyl radicals was sufficiently small to be neglected in deriving the kinetic equations.

The system is described by equations (15)—(25). Combination of equations (15) and (17) gives equation (18).

$$\mathrm{Bu^tO\cdot + P(OEt)_3 \rightleftharpoons \underset{(P)}{Bu^tO\dot{P}(OEt)_3}} \tag{15}$$

$$\mathrm{P \longrightarrow Bu^tOP(OEt)_2 + \cdot OEt} \tag{16}$$

$$\mathrm{P \longrightarrow Bu^t\cdot + OP(OEt)_3} \tag{17}$$

$$\mathrm{Bu^tO\cdot + P(OEt)_3 \longrightarrow \underset{(B)}{Bu^t\cdot} + OP(OEt)_3} \tag{18}$$

$$\mathrm{Bu^tO\cdot + C_5H_{10} \longrightarrow \underset{(C)}{C_5H_9\cdot} + Bu^tOH} \tag{19}$$

$$\left.\begin{array}{ll} \mathrm{B + B \longrightarrow} & (20) \\ \mathrm{B + P \longrightarrow} & (21) \\ \mathrm{B + C \longrightarrow} & (22) \\ \mathrm{P + P \longrightarrow} & (23) \\ \mathrm{P + C \longrightarrow} & (24) \\ \mathrm{C + C \longrightarrow} & (25) \end{array}\right\} \text{Non-radical products}$$

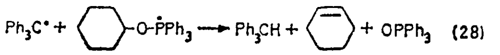
Radical–radical reactions involving t-butoxyl radicals can be neglected because of the high rates of reactions (18) and (19).

Under conditions when [C] is negligibly small,

$$\mathrm{d[B]/d}t = k_{17}[\mathrm{P}] - 2k_{20}[\mathrm{B}]^2 - k_{21}[\mathrm{B}][\mathrm{P}] \tag{26}$$

Experimentally d[B]/d$t$ is small with respect to terms on the right-hand side of equation (26), and equation (27) holds. At a given temperature the radical concentrations were varied by progressively reducing the incident light intensity to 10% of its maximum value. Plots of 1/[B] against [B]/[P] gave straight lines from which the values of $2k_{20}/k_{17}$ and $k_{21}/k_{17}$ could be determined. The process was repeated at different temperatures. In fact in the temperature range −28 to −69° all the plots passed through the origin within experimental error and thus reaction (21) may be neglected in comparison with reaction (20). This conclusion also follows from the result that [B] was proportional to the square-root of the incident light intensity implying that the reaction removing t-butyl radicals is second order in this radical concentration at these temperatures. In our earlier communication [24] the *assumption* was made that the rate of reaction (21) was much less than that of reaction (20); this has now been justified. Reaction (21) need not be a very slow process, indeed $k_{21}$ could be as high as $10^8$ l $\mathrm{mol^{-1}\ s^{-1}}$ and still be within our experimental error. A disproportionation reaction between triphenylmethyl radicals and cyclohexyloxytriphenylphosphoranyl radicals has been proposed to account for the triphenylmethane formed from the decomposition of phenylazotriphenylmethane in the presence of cyclohexyl diphenylphosphinite.[36]

$$1/[\mathrm{B}] = 2k_{20}[\mathrm{B}]/k_{17}[\mathrm{P}] + k_{21}/k_{17} \tag{27}$$


(28)

A combination reaction to form a tetra-alkoxy(alkyl)-phosphorane is also possible since alkoxyalkylphosphoranes [*e.g.* $\mathrm{Me_3P(OEt)_2}$] are known compounds.[37]

$$\mathrm{R\cdot + \dot{P}(OR)_4 \longrightarrow RP(OR)_4} \tag{29}$$

Reliable measurements at ambient temperatures give $2k_{20}$ as $2 \times 10^9$ l $\mathrm{mol^{-1}\ s^{-1}}$ in similar solvents to those used in this work. The variation of rate constant with temperature for such a diffusion-controlled reaction in solution may be estimated from the activation energy, $E_\mathrm{d}$, for diffusion in the medium.[38] Taking the value of $2k_{20}$ to be $2 \times 10^9$ l $\mathrm{mol^{-1}\ s^{-1}}$ at 30° and raeasonable estimate of $E_\mathrm{d}$ of 2 ± 1 kcal $\mathrm{mol^{-1}}$, the value of $k_{17}$ was obtained as a function of temperature from the slope of plots made according to equation (27). An Arrhenius plot of the data obtained in the temperature range −28 to −69° is shown in Figure 2.

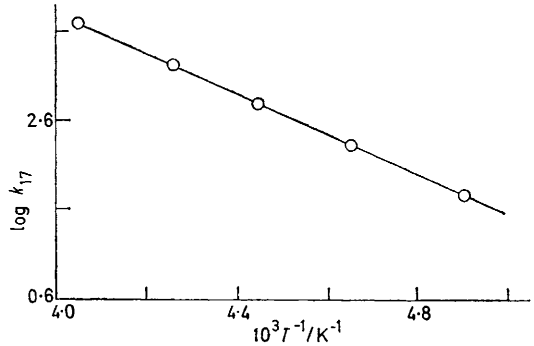


FIGURE 2 Arrhenius plot of kinetic data for the β-scission of the t-butoxy-triethoxyphosphoranyl radical

Least-squares fitting of the data gives,*

$$\log(k_{17}/\mathrm{s^{-1}}) = (12{\cdot}95 \pm 0{\cdot}01) - (10{\cdot}34 \pm 0{\cdot}14)/\theta \tag{30}$$
$$\text{and } k_{17}\,(30°) = 5{\cdot}0 \times 10^5\ \mathrm{s^{-1}}$$

The $A$-factor ($10^{13\cdot0}$ $\mathrm{s^{-1}}$) falls within the range expected for a unimolecular reaction of this complexity.[40]

When the concentration of triethyl phosphite is sufficiently low to enable the e.s.r. spectrum of the

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* In our earlier communication [24] $2k_{20}$ was obtained from the expression $\log(2k_{20}/\mathrm{l\ mol^{-1}\ s^{-1}}) = 10{\cdot}415 - 0{\cdot}830/\theta$ which is the rate constant for the self-reaction of ethyl radicals in liquid ethane.[39] We feel that the treatment given in the present paper is somewhat better, but the ratio $2k_{20}$: $k_{17}$ found in the present work is the same, within experimental error, as that found earlier.

[36] R. S. Davidson, *Tetrahedron*, 1969, **25**, 3383.

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[38] H. Hefter and H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 633.

[39] R. W. Fessenden, *J. Phys. Chem.*, 1964, **68**, 1508.

[40] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968.

cyclopentyl radical to be observed, it can be readily shown that,[18]

$$\frac{k_{18}[P(OEt)_3]}{k_{19}[C_5H_{10}]} = \frac{2k_{20}[B]^2 + k_{21}[B][P] + k_{22}[B][C]}{2k_{25}[C]^2 + k_{24}[C][P] + k_{22}[B][C]} \qquad (31)$$

With the radical concentrations obtained in this work the terms representing reaction of t-butyl and cyclopentyl radicals with phosphoranyl radicals may be neglected, as shown by the experiments at variable light intensity (see above), assuming that both alkyl radicals react at the same rate.* If $2k_{20} = k_{22} = 2k_{25}$ at ambient temperatures [18,42,43] and the temperature coefficients of these rate constants are similar in the same solvent,[38] equation (32) may be derived.

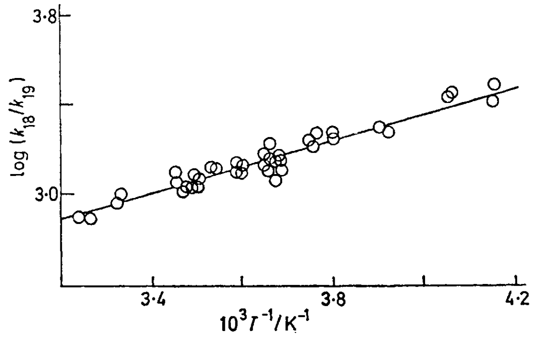

FIGURE 3 Arrhenius plot of kinetic data for the competition triethyl phosphite and cyclopentane for t-butoxyl radicals

$$k_{18}[P(OEt)_3]k_{19}[C_5H_{10}] = [B]/[C] \qquad (32)$$

The ratio $k_{18} : k_{19}$ was determined as a function of temperature for a solution containing triethyl phosphite (0·07M) and di-t-butyl peroxide (1·1M) in cyclopentane and an Arrhenius plot is shown in Figure 3.

Least-squares fitting of the data obtained between +35 and −17° gives,

$$\log (k_{18}/k_{19}) = (0{\cdot}83 \pm 0{\cdot}01) + (2{\cdot}96 \pm 0{\cdot}18)/\theta$$

Taking [18] $\log (k_{19}/\text{l mol}^{-1}\ \text{s}^{-1}) = 9{\cdot}0 - 5{\cdot}2/\theta$ we obtain,

$$\log(k_{18}/\text{l mol}^{-1}\ \text{s}^{-1}) = 9{\cdot}83 - 2{\cdot}24/\theta \qquad (34)$$

and

$$k_{18}\,(30°) = 1{\cdot}6 \times 10^8\ \text{l mol}^{-1}\ \text{s}^{-1}$$

The available evidence suggests that formation of [P] in reaction (15) is essentially irreversible.[44,45] Loss of an ethoxyl radical from [P] [equation (16)] is also not thought to occur in competition with β-scission [equation (17)],[45] although there are indications that with trimethyl phosphite the tetra-alkoxyphosphoranyl intermediate may lose a methoxyl radical.[46]

If loss of an alkoxyl radical from the phosphoranyl intermediate [reactions (−15)] and (16)] is slow in comparison with β-scission [reaction (17)], it can be shown that $k_{18} = k_{15}$, that is the overall rate of oxidation of triethyl phosphite by t-butoxyl radicals is equal to the rate of formation of the intermediate phosphoranyl radical.

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* In experiments at higher phosphite concentration, [P] was approximately proportional to the light intensity indicating that the unimolecular β-scission process is responsible for its removal. The rate of self-reaction of tetra-alkoxyphosphoranyl radicals at lower temperatures is being studied.[41]

[41] G. B. Watts and K. U. Ingold, unpublished.

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[44] W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, 1969, **91**, 2406.

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