

A Laser Flash Photolysis Study of t-Butoxyphosphoranyl Radicals. Optical Spectra and Kinetics of Formation, Fragmentation, and Rearrangement

By Brian P. Roberts,* Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

Juan C. Scaiano,* Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6

Addition of t-butoxyl radicals to a number of phosphorus(III) compounds in solution has been studied using laser flash photolysis techniques. Transient optical spectra ascribed to the phosphoranyl radical adducts have been detected between 300 and 800 nm and the kinetics of their formation and decay examined. Addition of Bu^tO• to (EtO)₃P or PhP(OEt)₂ takes place at close to the diffusion controlled rate at ca. 300 K. Comparison of optical and e.s.r. spectra permits correlation of the former with radical structure and hypervalent and ligand-π phosphoranyl radicals give rise to characteristically different types of optical spectra. Activation parameters for β-scission of the t-butoxyl

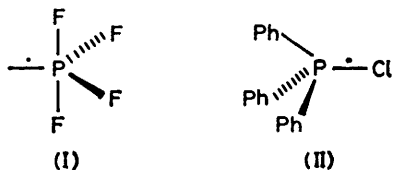
radical adducts of (EtO)₃P, PhP(OEt)₂, Ph₂POMe, and $\overline{\text{OCH}_2\text{CH}_2\text{O}}\text{P}(\text{SiMe}_3)_3$ agree well with those obtained previously by kinetic e.s.r. spectroscopy. α-Scission of Bu^tO $\dot{\text{P}}\text{Bu}^n_3$ (which is too short-lived to be studied by e.s.r. techniques) to give Buⁿ• has been studied and k_α is given by equation (A), in which $\theta = 2.303RT \text{ kJ mol}^{-1}$. The

$$\log(k_\alpha/\text{s}^{-1}) = 12.7 - 24.3/\theta \quad (\text{A})$$

optical spectra of the valence isomers Bu^tO(EtO)₂ $\dot{\text{P}}\text{NCO}$ and Bu^tO(EtO)₂P=N- $\dot{\text{C}}=\text{O}$ are readily distinguishable and a kinetic study of the rearrangement of the former to the latter led to equation (B).

$$\log(k_{\text{rearr.}}/\text{s}^{-1}) = 12.6 - 28.9/\theta \quad (\text{B})$$

THERE have been numerous electron spin resonance studies of phosphoranyl radicals ($\dot{\text{P}}\text{X}_4$), most of which were generated by homolytic addition to phosphorus(III) compounds or electron capture by phosphorus(IV) compounds.^{1,2} The structures and electronic configurations of phosphoranyl radicals are markedly dependent on the nature of the ligands. The tetrafluorophosphoranyl radical adopts the C_{2v} structure (I) and is usually described as being trigonal bipyramidal (TBP) since the unpaired electron may be regarded as the third equatorial ligand.³

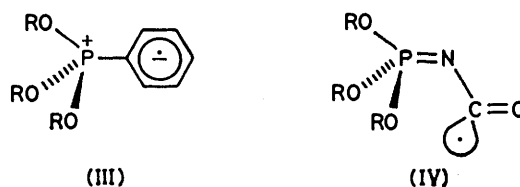


In contrast, the radical $\dot{\text{P}}\text{h}_3\text{PCl}$ adopts the trigonal pyramidal structure (II) with local C_{3v} symmetry at phosphorus and the SOMO † is essentially a $\sigma^*\text{P-Cl}$ orbital.⁴ The SOMOs of both (I) and (II) have significant P-3s character and the isotropic phosphorus hyperfine splitting constants are very large (1 322 and 604 G, respectively). TBP and σ^* species may be described as *hypervalent* phosphoranyl radicals, because in each there are formally nine electrons in the valence shell of phosphorus. The radicals (I) and (II) represent structural extremes and species with intermediate geometry should be common.‡

† Singly occupied molecular orbital.

‡ The radical Ph₃PBr appears to adopt such an intermediate structure.⁵ The energy required to deform a TBP radical to a σ^* structure (or *vice versa*) is probably quite small (<ca. 40 kJ mol⁻¹).¹

Several examples of phosphoranyl radicals are known in which the unpaired electron is centred on one of the ligands, rather than on the central phosphorus, in a π or σ type orbital. For example, phenyl(trialkoxy)phosphoranyl radicals adopt the *ligand-π* structure (III) and are best regarded as benzene radical anions with phosphonium substituents.^{6,7} Vinyl-⁸ and imino-(trialkoxy)phosphoranyl⁹ radicals have similar ligand-π structures.



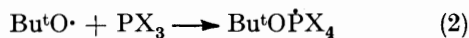
E.s.r. evidence indicates that the most stable electronic configuration of an isocyanato(trialkoxy)phosphoranyl radical is the acyl-type species (IV) (the PN bond may be written P=N ↔ $\dot{\text{P}}-\ddot{\text{N}}$) which provides an example of the *ligand-σ* structure.¹⁰

In the hope of characterising the optical absorption spectra of these different radicals and in order to monitor their chemical transformations using a technique other than e.s.r. spectroscopy, we have investigated the reactions of t-butoxyl radicals with a number of phosphorus(III) compounds in solution by means of laser flash photolysis using a detection system capable of nanosecond response.¹¹

RESULTS AND DISCUSSION

Transient optical absorptions due to phosphoranyl radicals were detected after hydrocarbon solutions containing di-t-butyl peroxide and a phosphorus(III) com-

pound (ca. 2% of v/v) had been irradiated with a pulse from a nitrogen laser (337.1 nm; up to 10 mJ per pulse of ca. 8 ns duration).¹¹ The reagent concentrations were such that only the peroxide absorbed a significant amount of the pulse to give t-butoxyl radicals which are known to add rapidly to trivalent phosphorus [equations (1) and (2)].^{1,12,13}



The spectrum of $\text{Bu}^t\text{OP}(\text{OEt})_3$ (V) (Figure 1a) showed continuously increasing absorption below 350 nm and no maximum above 300 nm (ϵ_{330} ca. $1\ 100\ \text{l mol}^{-1}\ \text{cm}^{-1}$).

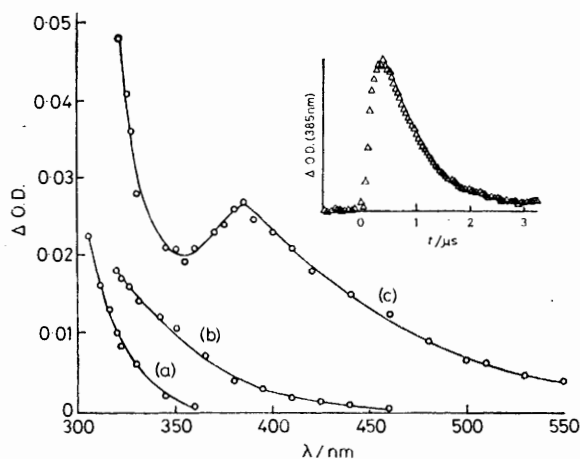
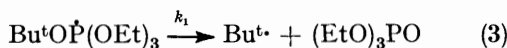


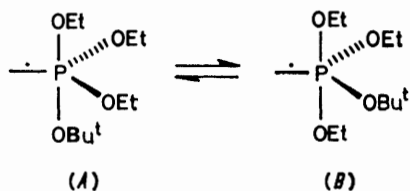
FIGURE 1 Transient optical spectra of (a) $\text{Bu}^t\text{OP}(\text{OEt})_3$ (V) at 296 K, (b) $\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}\text{Cl}_2$ (VI) at 298 K, (c) $\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}(\text{OEt})_2$ (VII) at 299 K, all in Bu^tOOBu^t -iso-octane (7:3 v/v). Optical densities have been normalised to the same radical concentration. The inset shows the time dependence of the absorption due to (VII) after irradiating with a laser pulse a solution of $\text{PhP}(\text{OEt})_2$ ($1.89 \times 10^{-3}\text{M}$) in Bu^tOOBu^t -iso-octane (7:3 v/v) at 303 K

This phosphoranyl radical has been studied extensively by e.s.r. spectroscopy^{1,2} and is a hypervalent species, almost certainly TBP.* The phosphoranyl radical (V) undergoes β -scission to give triethyl phosphate and t-butyl radicals [equation (3)] and kinetic e.s.r. studies¹⁴⁻¹⁶



have shown that the temperature dependence of k_1 can

* Two TBP isomers [(A) and (B)] are possible and the value of the equilibrium constant K is probably close to 0.5 at 233 K.¹⁴



The optical spectra of (A) and (B) are assumed to be indistinguishable. It is probable that (A) is formed initially in reaction (2; X = EtO), but equilibration probably takes place on the nano-second time scale at room temperature.¹⁵

be expressed by equation (4), in which $\theta = 2.303RT$ kJ mol⁻¹.

$$\log(k_1^{\text{e.s.r.}}/\text{s}^{-1}) = 10.6 - 32.1/\theta \quad (4)$$

The assignment of the optical spectrum to (V) was confirmed by monitoring the first-order decay of the absorption at 322–345 nm over a wide range of temperature (237–350 K). The rate constants were independent of phosphite and peroxide concentrations and of the intensity and wavelength distribution of the monitoring beam. An Arrhenius plot of the results, shown in Figure 2a,

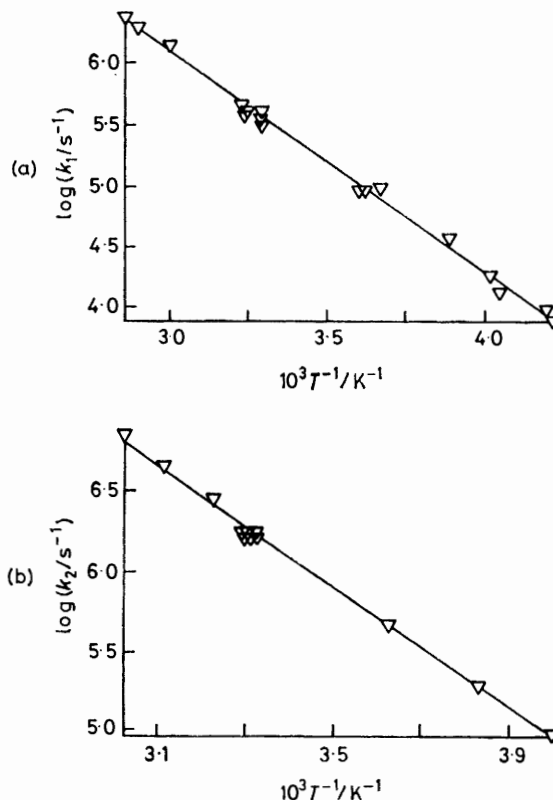
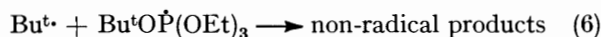


FIGURE 2 Arrhenius plots for the decay by β -scission of (a) $\text{Bu}^t\text{OP}(\text{OEt})_3$ (V) and (b) $\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}(\text{OEt})_2$ (VII)

leads to equation (5). The good agreement between the activation parameters obtained from decay of the e.s.r.

$$\log(k_1/\text{s}^{-1}) = 11.5 - 34.3/\theta \quad (5)$$

and optical spectra provides strong support for the assignment of the latter to the hypervalent phosphoranyl radical (V). In fact the rate constants and activation parameters determined by laser flash photolysis are probably more accurate than those obtained using kinetic e.s.r. spectroscopy, because the extent to which the cross-combination reaction (6) contributes to the decay of the e.s.r. spectrum of (V) cannot be assessed



with certainty. In the laser flash experiments, which are carried out at higher temperatures than the e.s.r.

studies, the pre-fragmentation lifetime of the phosphoranyl radical is much shorter (*ca.* 3 μ s at 300 K) and radical-radical reactions of the type (6) make an insignificant contribution to the decay. Furthermore, decay may be monitored over a much wider range of temperature using optical spectroscopy and magnetic polarisation and relaxation effects, which may complicate interpretation of an e.s.r. signal decay, are absent.

The *t*-butoxyl adducts of the chlorophosphines (EtO)_{*n*}-PCl_{3-*n*} (*n* = 0–2) also showed structureless absorption below 400 nm, but the spectra were more intense (peak maximum red-shifted?) and ϵ was *ca.* twice the value for (V) (see Table 1). E.s.r. studies¹⁷ have shown that the

TABLE 1

Optical absorption spectra of phosphoranyl radicals in solution

Radical ^a	<i>T</i> /K	$\lambda_{\max.}$ / nm	$\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1} \text{ }^b$		
			$\lambda_{\max.}$ nm	330 nm	770 nm
Bu ^t O \dot{P} (OEt) ₃	296			1 100	
Bu ^t O(Cl) \dot{P} (OEt) ₂	301			2 050	
Bu ^t O(Cl) ₂ \dot{P} OEt	301			1 850	
Bu ^t O \dot{P} Cl ₃	301			2 750	
Bu ^t O(Ph) \dot{P} (OEt) ₂	299	385	5 250	5 100	
Bu ^t O(Ph) \dot{P} (Ph)OMe ^c	298	390	2 500	8 500	1 350
Bu ^t O(Ph) \dot{P} (Ph)Me	300	410	3 280	8 900	16 800
Bu ^t O(Ph) \dot{P} Ph ₂	298	395	2 400	12 100	2 700
Bu ^t O(Cl) \dot{P} Ph ₂	298			9 050	
Bu ^t O(Cl) ₂ \dot{P} Ph	298			2 600	
Bu ^t O($\text{OCH}_2\text{CH}_2\text{O}$) \dot{P} OSiMe ₃	301			450	
(Bu ^t O) ₂ \dot{P} -OCH ₂ CH ₂ O	303			250	
Bu ^t O \dot{P} Bu ₃ ^d	212			1 000	
Bu ^t O(EtO) ₂ \dot{P} NCO ^e	208			900	
Bu ^t O(EtO) ₂ P=N-C=O ^f	301	415	125		
Bu ^t O $\dot{A}s$ Ph ₃	301			11 700	

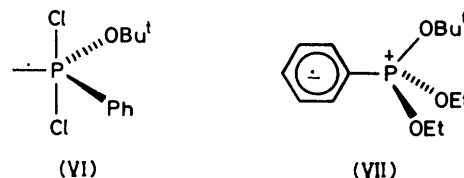
^a In Bu^tOOAu^t-*iso*-octane (7 : 3 v/v) unless otherwise noted.
^b Calculated assuming ϵ for Ph₂COH at 545 nm is 5 000 l mol⁻¹ cm⁻¹. ^c In neat Bu^tOOBu^t. ^d In Bu^tOOBu^t-*iso*-octane (4 : 6 v/v). ^e In Bu^tOOBu^t-*iso*-octane (1 : 1 v/v). ^f The spectrum was unchanged, apart from a reduction in intensity, at 208 K in Bu^tOOBu^t-*iso*-octane (1 : 1 v/v).

chlorophosphoranyl radicals Bu^tO(EtO) \dot{P} Cl₂ and Bu^tO-(EtO)₂ \dot{P} Cl are hypervalent, the former (and probably Bu^tO \dot{P} Cl₃, although its e.s.r. spectrum has not been reported) is close to regular TBP¹⁸ with two apical chlorines, whilst the latter may be distorted towards $\sigma^*(\text{P}-\text{Cl})$ but, if so, this distortion is not reflected in a marked difference in its optical spectrum.

The radical Bu^tO(Ph) \dot{P} Cl₂ shows an e.s.r. spectrum characteristic of a TBP radical with apical chlorine ligands (VI)⁶ and its optical spectrum (Figure 1b) is similar to that of Bu^tO(EtO) \dot{P} Cl₂ (ϵ_{330} 2 600 l mol⁻¹ cm⁻¹). In sharp contrast, optical absorption by the *ligand- π* radical Bu^tO(Ph) \dot{P} (OEt)₂ (VII) (Figure 1c) is significantly more intense and the spectrum shows a clear maximum at 385 nm. Figure 1 also shows the growth and subsequent decay of the absorption at 385

nm after laser excitation of a solution of PhP(OEt)₂ (1.89×10^{-3} M) in Bu^tOOBu^t-*iso*-octane (7 : 3 v/v).

The *ligand- π* radicals 6,7 (VIII)–(X) (formed by addition of Bu^tO \cdot to Ph₂POMe, Ph₂PMe, and Ph₃P, respectively) show spectra similar to that of (VII)



below 550 nm, but, whereas (VII) shows no absorption between 620 and 800 nm, the radicals (VIII)–(X) show continuously increasing absorption in this region (see Figure 3a).^{*} The long wavelength absorption thus

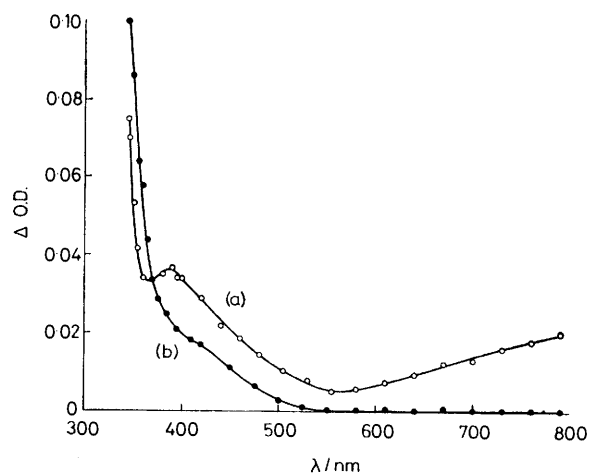


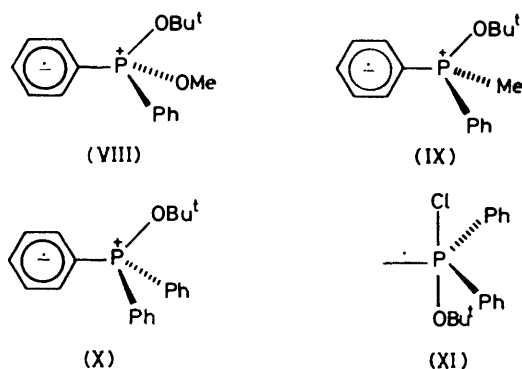
FIGURE 3 Transient optical spectra of (a) Bu^tO(MeO)Ph \dot{P} Ph (VIII) and (b) Bu^tO(Cl) \dot{P} Ph₂ (XI), both at 298 K in neat Bu^tOOBu^t. Optical densities have been normalised to the same radical concentration.

appears to be characteristic of *ligand- π* radicals with more than one *P*-phenyl substituent. In this context, it is noteworthy that a recent e.s.r. study¹⁹ of (X) has revealed that the unpaired electron is centred on one ring rather than delocalised over all three.

The e.s.r. spectrum of Bu^tOPh₂ \dot{P} Cl is indicative of a hypervalent species,⁶ possibly somewhat distorted from the TBP structure (XI) towards a $\sigma^*(\text{P}-\text{Cl})$ structure.¹⁹ The difference between (XI) and (VIII)–(X) is reflected in the optical spectrum of (XI) (Figure 3b) which shows no clear maximum in the 400 nm region and no long wavelength absorption. However, the magnitude of ϵ_{330} appears to be indicative of the number of *P*-phenyl

^{*} The spectrum of (X) obtained in the present work differs somewhat from that reported previously.¹³ The spectrum was essentially the same in Bu^tOOBu^t-*iso*-octane or Bu^tOOBu^t-benzene (both 2 : 1 v/v); in the latter solvent $\lambda_{\max.}$ was 405 nm (ϵ *ca.* 2 500 l mol⁻¹ cm⁻¹) and ϵ_{800} was also *ca.* 2 500 l mol⁻¹ cm⁻¹. In the earlier report¹³ the short wavelength maximum was given as 430 nm and was stronger (ϵ 6 200 l mol⁻¹ cm⁻¹) than the long wavelength absorption (ϵ_{800} *ca.* 2 100 l mol⁻¹ cm⁻¹). The reasons for these differences are not clear.

substituents and to be independent of the electronic structure of the phosphoranyl radical. The e.s.r. spectrum of $\text{Bu}^t\text{OAsPh}_3$ shows that, in contrast to (X), this



species is hypervalent²⁰ and the optical spectrum of the arsoranyl radical is also consistent with this structure, showing no maxima and no long wavelength absorption below 850 nm (see Table 1).

The ligand- π phosphoranyls (VII) and (VIII) are known^{6,8} to undergo β -scission to give t-butyl radicals

the rate constant for decay of absorption due to (VII) at 380 nm was independent of the intensity of the monitoring beam and was unchanged when a 370 nm cut-off filter was positioned in this beam. Hence, photolysis of (VII) by the monitoring light was not contributing to the decay of the phosphoranyl radical. At 300 K (VII) undergoes β -scission about four times more rapidly than (V) (see Table 2).

Decay of the optical absorption due to (VIII) was monitored at 331, 385, and 770 nm between 260 and 338 K ($4.4\text{--}8.8 \times 10^{-2}\text{M}$ -phosphine in neat Bu^tOOBu^t). The first-order rate constants were wavelength-independent and an Arrhenius plot led to equation (11).

$$\log(k_3/s^{-1}) = 12.0 - 36.1/\theta \quad (11)$$

At 770 nm the absorption decayed to the pre-pulse baseline at all temperatures, but at 331 and 385 nm some residual absorption remained after the first-order decay, especially at low temperatures. Thus, at 260 K the absorption decayed to 14 (331) and 22% (385 nm) of its intensity immediately after the laser pulse, whereas at 334 K these figures were 6 and 7%, respectively.* The reason for this residual absorbance is not clear at present. It is possible that a small amount of a product other

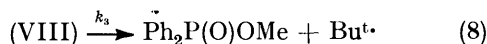
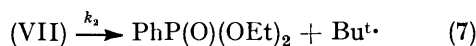
TABLE 2

Activation parameters for unimolecular decay of phosphoranyl radicals generated by laser flash photolysis

Radical ^a	Decay process	Temp. range (K)	$\log(A/s^{-1})^b$	$E_a/kJ\text{ mol}^{-1}^b$	$k(300\text{ K})/s^{-1}$
$\text{Bu}^t\text{O}\dot{\text{P}}(\text{OEt})_3$	β -Scission ^c	237—350	11.5	34.3	3.4×10^6
$\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}(\text{OEt})_2$	β -Scission ^c	250—330	12.4	35.7	1.5×10^6
$\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}(\text{Ph})\text{OMe}^d$	β -Scission ^c	260—338	12.0	36.1	5.2×10^5
$\text{Bu}^t\text{O}(\text{Ph})\dot{\text{P}}\text{Ph}_2^e$	β -Scission ^c		11.7 ^f	50.6 ^f	7.8×10^2 ^f
$\text{Bu}^t\text{O}(\text{OCH}_2\text{CH}_2\text{O})\dot{\text{P}}\text{OSiMe}_3$	β -Scission ^g	301—344	10.8 ^h	35.6 ^h	4.0×10^4 ^h
$[\text{Bu}^t\text{O}]_2\dot{\text{P}}\text{—OCH}_2\text{CH}_2\text{O}$	β -Scission ^c	303			5.5×10^5 ⁱ
$\text{Bu}^t\text{O}\dot{\text{P}}\text{Bu}^t_3$ ^j	α -Scission ^k	194—229	12.7	24.3	2.9×10^8
$\text{Bu}^t\text{O}(\text{EtO})_2\dot{\text{P}}\text{NCO}^l$	Rearrangement ^m	207—265	12.6	28.9	3.7×10^7

^a In Bu^tOOBu^t -iso-octane (7 : 3 v/v) unless otherwise stated. ^b Errors in activation parameters are difficult to estimate; these might typically be ± 0.5 and ± 2 kJ mol⁻¹ for $\log A$ and E_a , respectively. ^c To give Bu^t . ^d In neat Bu^tOOBu^t . ^e In Bu^tOOBu^t -benzene or Bu^tOOBu^t -toluene. ^f Determined by flash photolytic and e.s.r. techniques; taken from ref. 13. ^g To give $\text{Bu}^t + \cdot\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OBu}^t)\text{OSiMe}_3$, see ref. 15. ^h Relatively inaccurate because of the low extinction coefficient and long lifetime. ⁱ At 303 K. ^j In Bu^tOOBu^t -iso-octane (2 : 3 v/v). ^k To give Bu^t . ^l In Bu^tOOBu^t -iso-octane (1 : 1 v/v). ^m To give $\text{Bu}^t\text{O}(\text{EtO})_2\text{P}=\text{N}-\dot{\text{C}}=\text{O}$.

[equations (7) and (8)] and equation (9) was obtained from a kinetic e.s.r. study of (VII).⁸



$$\log(k_2^{\text{e.s.r.}}/s^{-1}) = 12.0 - 36.7/\theta \quad (9)$$

The first-order decay of the optical absorption due to (VII) at 380 nm was monitored at 250—330 K for phosphine concentrations in the range $5.1\text{--}10.2 \times 10^{-2}\text{M}$ in Bu^tOOBu^t -iso-octane (7 : 3 v/v). The Arrhenius plot shown in Figure 2b led to equation (10) and the activation parameters are seen to be in good agreement with those determined by e.s.r. At room temperature

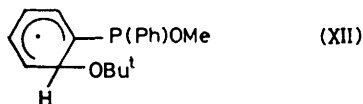
$$\log(k_2/s^{-1}) = 12.4 - 35.7/\theta \quad (10)$$

than $\text{Ph}_2\text{P}(\text{O})\text{OMe}$ and hydrocarbons derived from Bu^t is formed during decomposition of (VIII) and that this minor product absorbs very strongly ($\epsilon > 10^4$ l mol⁻¹ cm⁻¹) at 395 nm and below. It is unlikely to be a cyclohexadienyl radical formed by addition of Bu^t to Ph_2POMe , since the fraction of residual absorption did not increase with the phosphine concentration. Alternatively, formation of (VIII) may be accompanied by formation of another species, possibly the cyclo-

* In a previous flash photolytic study of $\text{Bu}^t\text{O}\dot{\text{P}}\text{Ph}_3$ (X) at 295 K a residual absorbance was detected when decay of the radical by t-butyl forming β -scission was monitored in the 400 nm region, but not in the 700 nm region.¹³ Triphenylphosphine oxide (which shows insignificant absorption above 290 nm; $\epsilon_{330} < 0.3$ l mol⁻¹ cm⁻¹) was isolated in almost quantitative yield from the reaction of t-butoxyl radicals with triphenylphosphine²¹ and a ³¹P n.m.r. study of thermolysis of di-t-butyl hyponitrite in the presence of Ph_3P confirms this result.¹⁹

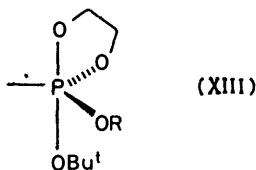
hexadienyl adduct (XII) (or positional isomers), which decays much more slowly than (VIII).*

β -Scission of (VIII) [equation (8)] is somewhat slower than that of (VII), but introduction of a third phenyl group has a more dramatic effect and (X) undergoes cleavage to $\text{Ph}_3\text{P}=\text{O}$ and Bu^\cdot too slowly to be measured



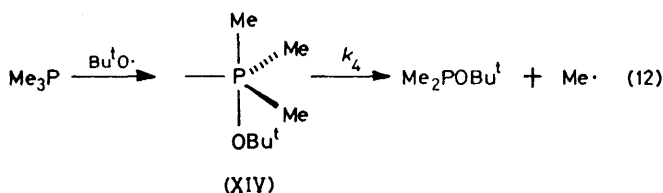
using the present experimental arrangement. The activation parameters for β -scission of (X), determined previously¹³ by a combination of e.s.r. and conventional flash photolysis studies, are included in Table 2.

The optical spectra of the cyclic hypervalent phosphoranyls (XIII; $\text{R} = \text{Bu}^\cdot$ or Me_3Si) were weaker than, but otherwise similar to, that of $\text{Bu}^\cdot\text{O}\dot{\text{P}}(\text{OEt})_3$. Decay of (XIII; $\text{R} = \text{Me}_3\text{Si}$) was monitored at 320 nm between 301 and 344 K and the activation parameters (see Table 2) are in good agreement with those determined using kinetic e.s.r. spectroscopy.¹⁵ Decay of (XIII; $\text{R} = \text{Bu}^\cdot$)



was monitored between 320 and 330 nm at 303 K and the rate constant for β -scission ($5.5 \times 10^5 \text{ s}^{-1}$) is consistent with an earlier kinetic e.s.r. result for a similar radical.^{15,22,†}

α -Scission of Phosphoranyl Radicals.—The hypervalent phosphoranyl radical (XIV) is detectable by e.s.r.

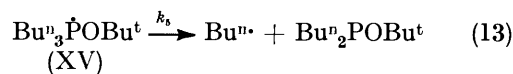


spectroscopy and its decay by loss of a methyl radical (α -scission) has been studied.²³ At 173 K in cyclopropane the measured value of k_4 was 32.3 s^{-1} . The t-butoxyl adducts of higher trialkylphosphines are much less stable towards α -scission and only for Et_3P has an e.s.r.

* If (XII) were to rearrange slowly to (VIII) which then undergoes rapid β -scission this would be consistent with the almost quantitative yields of phosphine oxides obtained by oxidation of phenylphosphines with t-butoxyl radicals. Addition of Bu^\cdotO to benzene rings carrying electron-donating, radical-stabilising substituents could be more rapid and common than hitherto believed. We note that the e.s.r. spectra ascribed to ligand- π phenylphosphoranyls are very unlikely to be due to cyclohexadienyls of the type (XII).

† The rate constant for β -scission of $\text{OCH}_2\text{CH}_2\text{O}\dot{\text{P}}(\text{OPe}^\cdot)\text{OBu}^\cdot$ to form t-butyl and t-pentyl radicals is given¹⁵ by $\log(k_\beta/\text{s}^{-1}) = 10.8 - 31.7/\theta$ and $k_\beta = 2.2 \times 10^5 \text{ s}^{-1}$ at 303 K.

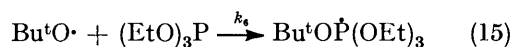
spectrum tentatively assigned to the adduct been detected.²⁴ The shorter timescale of our laser flash experiments has allowed detection of an optical spectrum which we ascribe to $\text{Bu}^\cdot\text{O}\dot{\text{P}}\text{Bu}^\cdot_3$ (XV) and, by monitoring its decay at 321–325 nm in the temperature range 194–229 K, the Arrhenius equation (14) was obtained for the α -scission process (13). At 173 K the extrapolated



$$\log(k_5/\text{s}^{-1}) = 12.7 - 24.3/\theta \quad (14)$$

value of k_5 is $2.3 \times 10^5 \text{ s}^{-1}$. The A -factors for α -scission of (XIV) and (XV) are probably similar and the difference in rates of fragmentation is presumably the result of a smaller activation energy for cleavage of the weaker P– Bu^\cdot bond.

Rates of Formation of Phosphoranyl Radicals.—The rate constants for addition of t-butoxyl radicals to triethyl phosphite and to phenyldiethoxyphosphine were measured using laser flash photolysis. The first-order growth of absorption due to $\text{Bu}^\cdot\text{O}\dot{\text{P}}(\text{OEt})_3$ (V) was monitored at 328 nm after irradiating solutions of $(\text{EtO})_3\text{P}$ in $\text{Bu}^\cdot\text{OOBu}^\cdot$ -iso-octane (7:3 v/v) with the laser pulse. The rate constant (k_{growth}) was measured as a function of phosphite concentration (2.3 – $11.7 \times 10^{-3}\text{M}$). Assuming that equation (16) holds,¹³ in which k_0 is the sum of first- and pseudo-first-order rate constants for removal of Bu^\cdotO by reactions other than with phosphite, k_6 was obtained as the slope of the straight-line plot of k_{growth} against $[(\text{EtO})_3\text{P}]$. At 301 K, k_6 was $1.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

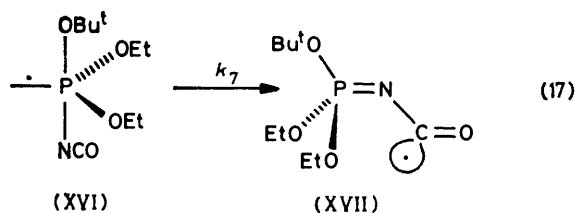


$$k_{\text{growth}} = k_0 + k_6[(\text{EtO})_3\text{P}] \quad (16)$$

Similar experiments with $\text{PhP}(\text{OEt})_2$ [1.9 – $21.9 \times 10^{-3}\text{M}$ in $\text{Bu}^\cdot\text{OOBu}^\cdot$ -iso-octane (7:3 v/v)] in which the growth of absorption was monitored at wavelengths between 385 and 430 nm gave the rate constant for t-butoxyl radical addition as $1.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at 303 K. Both these rate constants are approaching the diffusion controlled values and are in accord with a previous indirect estimate^{12,13} of the rate constant for addition to $(\text{EtO})_3\text{P}$ ($8.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$) and with a direct measurement¹³ of that for addition to Ph_3P ($1.9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) obtained by laser flash photolysis. The transition states for these additions must occur very early along the reaction co-ordinate and must involve very little distortion of the reagents from their ground state structures.

Ligand- σ Phosphoranyl Radicals.—On the basis of e.s.r. evidence, it has been proposed that addition of t-butoxyl radicals to $(\text{EtO})_2\text{PNC O}$ gives initially the hypervalent phosphoranyl radical (XVI) and that this subsequently undergoes electronic rearrangement to give (XVII), in which the unpaired electron occupies a σ -type orbital centred on the carbon of the NCO group.¹⁰ The species (XVII) had been referred to as a ligand- σ phosphoranyl radical.

In the hope of observing this rearrangement by optical spectroscopy, we examined the reaction of *t*-butoxyl radicals with $(\text{EtO})_2\text{PNCO}$ using laser flash photolysis. During the first *ca.* 100 ns after the laser



pulse, a solution of $(\text{EtO})_2\text{PNCO}$ in Bu^tOOBu^t -iso-octane (1:1 v/v) at 208 K gave rise to the optical spectrum, shown in Figure 4a, expected for the hypervalent adduct (XVI). However, this initial spectrum evolved rapidly with time and *ca.* 12 μs after the laser pulse the spectrum shown in Figure 4b was recorded. The latter spectrum decayed much more slowly, at a rate

(XVI) to (XVII). The Arrhenius plot, shown in Figure 4, of the results obtained between 207 and 265 K leads to equation (18).[†]

$$\log(k_7/\text{s}^{-1}) = 12.6 - 28.9/\theta \quad (18)$$

The absorption spectrum of (XVII), λ_{max} 410 nm (ϵ 125 l mol⁻¹ cm⁻¹), is quite similar to those reported for the related acyl radicals $\text{Ph}\dot{\text{C}}=\text{O}$, λ_{max} 368 nm (ϵ 200 l mol⁻¹ cm⁻¹)²⁷ and $\text{PhCH}=\text{CH}\dot{\text{C}}=\text{O}$, λ_{max} 400 nm.²⁸

In conclusion, it is clear that e.s.r. and kinetic optical absorption spectroscopy constitute complimentary techniques for the study of transient free radicals in solution. E.s.r. spectroscopy is the more powerful tool for identification of radical intermediates but, provided that assignment of the optical spectrum is not in doubt, flash photolysis is the more versatile technique for kinetic studies.

EXPERIMENTAL

Materials.—Di-*t*-butyl peroxide was freed from traces of *t*-butyl hydroperoxide by passage through activated basic alumina and was stored over molecular sieves. Iso-octane and benzene (spectroscopic grades) were dried over molecular sieves. Diphenylmethanol was sublimed twice. Diethoxyisocyanatophosphine,²⁹ 2-*t*-butoxy-1,3,2-dioxaphospholan,^{14,30} and 2-trimethylsiloxy-1,3,2-dioxaphospholan¹⁶ were prepared by published methods. The remaining phosphorus(III) compounds were obtained commercially and redistilled or recrystallised from ethanol (Ph_3P) before use.

Laser Flash Photolysis.—Samples were contained in 3 mm path length rectangular Suprasil cells and irradiated with pulses from a Moletron UV-24 nitrogen laser. The experiment was controlled by a PDP 11/03L computer which receives and processes the data and provides visual display and hardcopy facilities. Full details of the experimental arrangement have been given elsewhere.¹¹

Oxygenated reagents and solvent (total volume 1—3 ml) were introduced using hypodermic syringes into the dry, nitrogen-filled sample cell which was closed by a self-sealing rubber cap. Traces of oxygen were removed by purging the solution in the cell with a fine stream of dry nitrogen. The optical absorption spectra of the samples were recorded (Cary 219) before and after the experiment. For the experiments with triphenylphosphine the sample solution was flowed slowly through the cell under nitrogen to overcome interference from yellow-brown reaction products which build up rapidly in static samples.¹³ No transient absorptions were detected if the peroxide was omitted from the samples.

Extinction Coefficients.—The extinction coefficients of the phosphoranyl radicals were measured relative to that of the diphenylhydroxymethyl radical (taken³¹ as 5 000 l mol⁻¹ cm⁻¹ at 545 nm) in Bu^tOOBu^t -benzene (7:3 v/v) at room temperature. Benzene was used as solvent because of the low solubility of diphenylmethanol in iso-octane and it was

[†] An explanation for the existence of a barrier to the exothermic rearrangement of (XVI) to (XVII) may be seen if we begin by considering correlation of electronic states with a linear PNCO grouping and local C_{3v} symmetry at phosphorus. Baird²⁶ has given an analogous explanation for the relatively large barrier for exothermic decomposition of $\text{HN}=\text{N}\cdot$ to give $\text{H}\cdot$ and N_2 .

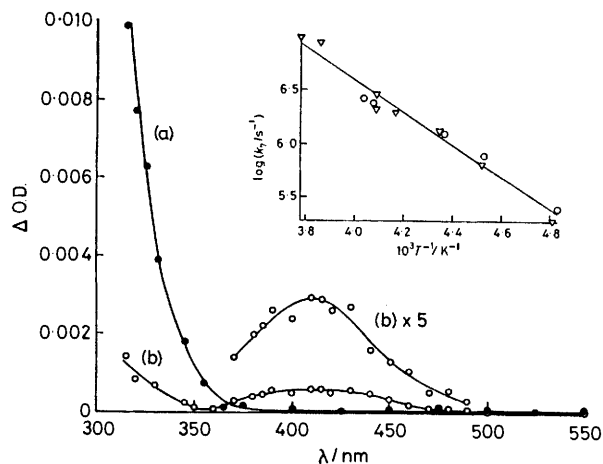
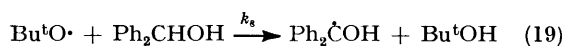


FIGURE 4 Transient optical spectra of (a) $\text{Bu}^t\text{O}(\text{EtO})_2\dot{\text{P}}\text{NCO}$ (XVI) at 208 K in Bu^tOOBu^t -iso-octane (1:1 v/v) and (b) $\text{Bu}^t\text{O}(\text{EtO})_2\text{P}=\text{N}-\dot{\text{C}}=\text{O}$ (XVII) at 301 K in Bu^tOOBu^t -iso-octane (7:3 v/v). Optical densities have been normalised to the same radical concentration. The inset shows the Arrhenius plot for the rearrangement of (XVI) to (XVII); ∇ obtained from the decay of absorption at 322 nm, \circ obtained from the growth of absorption at 435 nm

consistent with removal of the absorbing species by bimolecular self-reaction, and we assign it to the acyl-type ligand- σ radical (XVII). The spectrum of (XVII) was unchanged at 301 K. Absorption by (XVI) is insignificant at 435 nm and absorption by (XVII) at 322 is much smaller than that of (XVI). First-order decay of the initial absorption at 322 nm and first-order growth at 435 nm were monitored and, at a given temperature, the two rate constants were equal within experimental error.* The rate constant was independent of the isocyanate concentration (9.2 — $27.6 \times 10^{-2}\text{M}$) and is thus identified as k_7 , the rate constant for rearrangement of

* The time dependence of the absorption at 322 nm is the resultant of the decay of absorption due to (XVI) and the growth of that due to (XVII). The rate constant obtained from the resultant decay curve is equal to that for decay of (XVI).²⁶

assumed that the quantum yield of $\text{Bu}^t\text{O}\cdot$ from photolysis of Bu^tOOBu^t at 337 nm was the same in these two solvents.



If A is the absorbance at 545 nm (corrected for any radical decay) due to $\text{Ph}_2\dot{\text{C}}\text{OH}$ produced by reaction (19), then it may be shown that equation (20) holds, in which A° is the absorbance that would be produced if all the t-butoxyl radicals react to give $\text{Ph}_2\dot{\text{C}}\text{OH}$ and k_0 is the sum of all other first- and pseudo-first-order rate constants for removal of $\text{Bu}^t\text{O}\cdot$.

$$(1/A) = (1/A^\circ)\{1 + k_0/k_8[\text{Ph}_2\text{CHOH}]\} \quad (20)$$

The incident intensity of the laser pulse was reduced using neutral density filters to a point where the lifetime of $\text{Bu}^t\text{O}\cdot$ (measured from the rate of growth of absorption due to $\text{Ph}_2\dot{\text{C}}\text{OH}$) was independent of light intensity. Under these conditions second-order removal of $\text{Bu}^t\text{O}\cdot$ by self-reaction could be neglected. For diphenylmethanol concentrations between 0.03 and 0.27M a plot of $(1/A)$ against $(1/[\text{Ph}_2\text{CHOH}])$ gave a straight line and A° was obtained from the intercept. After correcting, where necessary, for the different fractions of the laser pulse absorbed by the Bu^tOOBu^t in this actinometer and in the samples, it was possible to calculate the ratio $(\epsilon_{\text{X}}^{\text{Ph}_2\dot{\text{C}}\text{OH}}/\epsilon_{545}^{\text{Ph}_2\dot{\text{C}}\text{OH}})$, since all the t-butoxyl radicals were trapped by the phosphorus(III) compounds at the concentrations employed.

The actinometer also served to calibrate the absorption from triplet 1-methylnaphthalene produced, by energy transfer from excited ketone, when a methanol solution containing *p*-methoxyacetophenone and 1-methylnaphthalene was irradiated with the laser. This secondary standard was used subsequently to monitor the day-to-day performance of the apparatus.

In order to obtain extinction coefficients for radicals detected at temperatures other than ca. 300 K, the temperature dependence of the absorption due to Bu^tOOBu^t at 337 nm was investigated. Between 353 and 283 K the optical density of a solution of Bu^tOOBu^t in iso-octane (1:1 v/v) decreased linearly from 0.90 to 0.67. In the calculation of extinction coefficients it was assumed that linearity would be maintained down to 208 K and that the quantum yield of $\text{Bu}^t\text{O}\cdot$ at 337 nm was independent of temperature.

We are grateful to Mr. S. E. Sugamori for his technical assistance. This work was carried out between July and September 1980 when one of us (B. P. R.) was a Visiting Research Officer at the NRCC and special thanks are due to Dr. K. U. Ingold for making this visit possible.

[0/1758 Received, 17th November, 1980]

REFERENCES

- B. P. Roberts in 'Advances in Free Radical Chemistry,' ed. G. H. Williams, Heyden, London, 1980, vol. 6, ch. 5.
- J. R. Morton and K. F. Preston in 'Landolt-Börnstein, New Series,' eds. H. Fischer and K. H. Hellwege, Springer-Verlag, Berlin, 1977, vol. II/9a; A. G. Davies and B. P. Roberts, *ibid.*, 1979, vol. II/9c; P. Schipper, E. H. J. M. Jansen, and H. M. Buck, *Top. Phosphorus Chem.*, 1977, **9**, 407.
- A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, 1975, **79**, 1855; A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Mol. Phys.*, 1975, **30**, 1367.
- T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Lett.*, 1975, **36**, 677.
- T. Berclaz, M. Geoffroy, L. Ginet, and E. A. C. Lucken, *Chem. Phys. Lett.*, 1979, **62**, 515.
- A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1974, 973 and unpublished results.
- G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 1974, 118.
- J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 781.
- R. S. Hay, B. P. Roberts, K. Singh, and J. P. T. Wilkinson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 756.
- J. A. Baban and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1979, 537.
- J. C. Scaiano, *J. Am. Chem. Soc.*, 1980, **102**, 7747.
- A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Int. Ed. Engl.*, 1971, **10**, 738; *J. Chem. Soc., Perkin Trans. 2*, 1972, 993.
- D. Griller, K. U. Ingold, L. K. Patterson, J. C. Scaiano, and R. D. Small, jun., *J. Am. Chem. Soc.*, 1979, **101**, 3780.
- B. P. Roberts and K. Singh, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1549.
- R. S. Hay and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 770.
- G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 1972, **94**, 8784.
- D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1339.
- D. J. Nelson and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1975, 1164.
- J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, in the press.
- E. Furimsky, J. A. Howard, and J. R. Morton, *J. Am. Chem. Soc.*, 1973, **95**, 6574.
- C. Walling, O. H. Basedow, and E. S. Savas, *J. Am. Chem. Soc.*, 1960, **82**, 2181.
- M. J. Parrott and B. P. Roberts, *J. Organomet. Chem.*, 1975, **99**, C49.
- J. W. Cooper and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1976, 808.
- A. G. Davies, R. W. Dennis, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1101.
- M. V. Encinas, P. J. Wagner, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1980, **102**, 1357.
- N. C. Baird, *J. Chem. Phys.*, 1975, **62**, 300; *J. Chem. Educ.*, 1977, **54**, 291.
- C. Huggenberger, J. Lipscher, and H. Fischer, *J. Phys. Chem.*, 1980, **84**, 3467.
- S. Noda, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, 1968, **49**, 3287.
- E. S. Gubnitskaya and G. I. Derkach, *Zh. Obsch. Khim.*, 1968, **38**, 1530.
- R. Burgada, H. Germa, M. Willson, and F. Mathis, *Tetrahedron*, 1971, **27**, 5833.
- E. J. Land, *Proc. R. Soc. London Ser. A*, 1968, **305**, 457.